August 15, 1973

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PHYSICO-CHEMICAL INVESTIGATIONS OF HEXADECYLTRIMETHYLAMMONIUM BROMIDE AND RELATED SURFACTANTS

A Dissertation

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

---

by

Linda Jenny Magid

December 1973

To Ron

1118743

ACKNOWLEDGMENTS

The author wishes to extend her most heartfelt thanks to Dr. John Larsen for his guidance and encouragement in the capacity of research director. His ingenuity in being able to rationalize experimental results is truly without equal.

Appreciation is extended to the National Science Foundation, Rice University and the University of Tennessee for financial assistance during four years of graduate study.

The author also wishes to express gratitude to her husband Ron for his invaluable help with chemical problems and his love, understanding and patience on the domestic scene.

The author's parents have provided invaluable financial assistance and encouragement throughout her academic career. They always believed a career in chemistry was accessible to females as well as males; the author is very grateful for their rejection of stereotypes.

Special thanks are due to Mrs. Joyce Wallace for her diligence in typing this dissertation.

Crane Crest

ABSTRACT

Viscometry was used to investigate micelle sizes in hexadecyltrimethylammonium bromide solutions containing both inorganic salts and organic solutes. Increasing concentrations of sodium bromide produced rod-shaped micelles of increasing size. The electroviscous effect for hexadecyltrimethylammonium bromide micelles in aqueous solution was estimated to be 2.37. The solutes n-hexane and n-octane decreased micelle size in 0.1 M hexadecyltrimethylammonium bromide-0.1 M sodium bromide; the solutes benzene and 1-hexanol increased micelle size in the same system. The viscosity of 0.1 M hexadecyltrimethylammonium bromide was increased by electrolytes in the following order (a lyotropic series): sodium fluoride < sodium bromide < hydrogen bromide < sodium nitrate < potassium chlorate.

Counterion binding to micelles was investigated using ion-specific electrodes and calorimetry. At the critical micelle concentration the degree of dissociation of the micelles of decyltrimethylammonium bromide, dodecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide was found to be independent of the concentration of added sodium bromide. The same behavior was observed for the first two surfactants at concentrations above the critical micelle concentration. For 0.005 M and 0.01 M hexadecyltrimethylammonium bromide the degree of dissociation of the micelles increased with increasing sodium bromide concentration; at 0.1 M surfactant the opposite behavior was observed.

A lyotropic series was found to exist for displacement of bromide

ions from hexadecyltrimethylammonium bromide micelles by other ions: chloride ≈ hydroxide < nitrate < tosylate. In the presence of increasing concentrations of hydroxide and nitrate ions the degree of dissociation (including all ions) of hexadecyltrimethylammonium bromide micelles decreased or stayed roughly constant. A lyotropic series for the enthalpy of binding of anions to these micelles was also observed: hydroxide < nitrate < tosylate (most exothermic).

Observed enthalpies of transfer for anions from water to 0.1 M hexadecyltrimethylammonium bromide or 0.075 M dodecyltrimethylammonium bromide could be arranged in a lyotropic series: carbonate < sulfate < acetate < formate < nitrate < bromide < tosylate (most exothermic). The observed enthalpies of transfer gave straight lines when plotted against the Stokes' Law hydrated radii for the anions. Lyotropic effects with cations were also observed for these surfactants. Observed enthalpies of transfer from water to 0.04 M sodium dodecylsulfate for cations also showed a lyotropic series: lithium < sodium < ammonium < potassium < tetramethylammonium < calcium.

Interactions of organic solutes with hexadecyltrimethylammonium bromide micelles were studied by calorimetry as well as viscometry. London dispersion interactions of solutes with surfactant N-methyl groups were found to be important. Compounds containing aromatic rings were found to have especially favorable enthalpies of transfer from water to 0.1 M hexadecyltrimethylammonium bromide. Observed enthalpies of solution for phenols in 0.1 M hexadecyltrimethylammonium bromide supported surface solubilization for these compounds. Ultraviolet spectroscopy also supported this type of solubilization.

Benzene and benzoic acid were found to displace bromide ions from the micelles in 0.1 M hexadecyltrimethylammonium bromide-0.1 M sodium bromide. Benzene caused line-broadening in the nuclear magnetic resonance spectrum of the methylene and N-methyl protons of the surfactant.

Alkaline hydrolysis of alkyl salicylates was not catalyzed by hexadecyltrimethylammonium bromide. This lack of catalysis was proposed to be due to a difficult proton transfer prior to decomposition of the tetrahedral intermediate for the hydrolysis. Rate versus concentration profiles for bimolecular reactions on micellar surfaces when one reagent is hydroxide ion were rationalized in terms of decreasing hydroxide ion concentration in the micellar phase. Hydroxide ion binding data for hexadecyltrimethylammonium bromide micelles supported this explanation.

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CHAPTER I

GENERAL INTRODUCTION

The formation of molecular aggregates called micelles by surfactant molecules in solution has been known for many years. The surfactant or detergent molecules are amphiphilic, that is they possess regions of hydrophobic and hydrophilic character. The hydrophobic portion of the molecules consists of a hydrocarbon chain, frequently unbranched and unsubstituted; the hydrophilic portion may possess polar, uncharged groups such as ether oxygens, or it may be a charged group, e.g., sulfate, carboxylate, or ammonium ions. Surfactants are accordingly divided into nonionic and ionic types. We will be concerned exclusively with the latter in the course of this work.

Micelles first appear in surfactant solutions over a small range of concentration which is operationally defined as the CMC, the critical micelle concentration. More formally, the CMC is the concentration of surfactant at which the concentration of micelles would become zero if it were to decrease as it does at concentrations above the CMC.[1] The CMC is the saturation concentration of singly dispersed species.[2] The latter definition ignores the possibility of so-called premicellar aggregation, for example dimerization of surfactant occurring at concentrations below the CMC.[3] Frequently it is assumed that at the experimentally determined CMC 2% of the surfactant is present in micellar form.[3] CMC values of 10^{-4} M to 10^{-2} M are commonly found for ionic surfactants; the CMCs are much lower in nonionic systems.[1] At the CMC, the dependence

of a number of physical and chemical properties on concentration changes sharply. This phenomenon can be used to determine the CMC experimentally.[4] Figure 1 illustrates this change for the viscosity of surfactant solutions. Conductivity, surface tension, partial molal volume, solubilization (which will be discussed below) and several other physical properties have also been used.[2] The CMC is determined from the intersection of extensions of the two linear branches of the experimental curve.

At the CMC micelles are generally considered to be spherical. They may contain from 20 to approximately 100 monomers. For ionic micelles three general structural regions can be distinguished:[5,6] (1) the hydrocarbon core, (2) the Stern layer and (3) the Guoy-Chapman double layer. These are shown in a cross-sectional view in Figure 2. The hydrocarbon core is liquid in nature, which is demonstrated by the formation of mixed micelles (micelles containing more than one kind of surfactant molecules) and by the phenomenon of solubilization as well as various spectral techniques.[2] In particular, solids which are sparingly soluble in water may be very effectively dissolved in solutions containing micelles; without the liquid core postulate the formation of mixed crystals would have to be envisaged. ESR measurements on solubilized nitroxide radicals show considerable mobility for the solubilizate and confirm the liquid nature of most micelles.[7-10] There is evidence that the outer portions of the core contain some water.[11] The Stern layer consists of the ionic head groups and a fraction of the associated counterions. The thickness of the layer is within 1 Å of

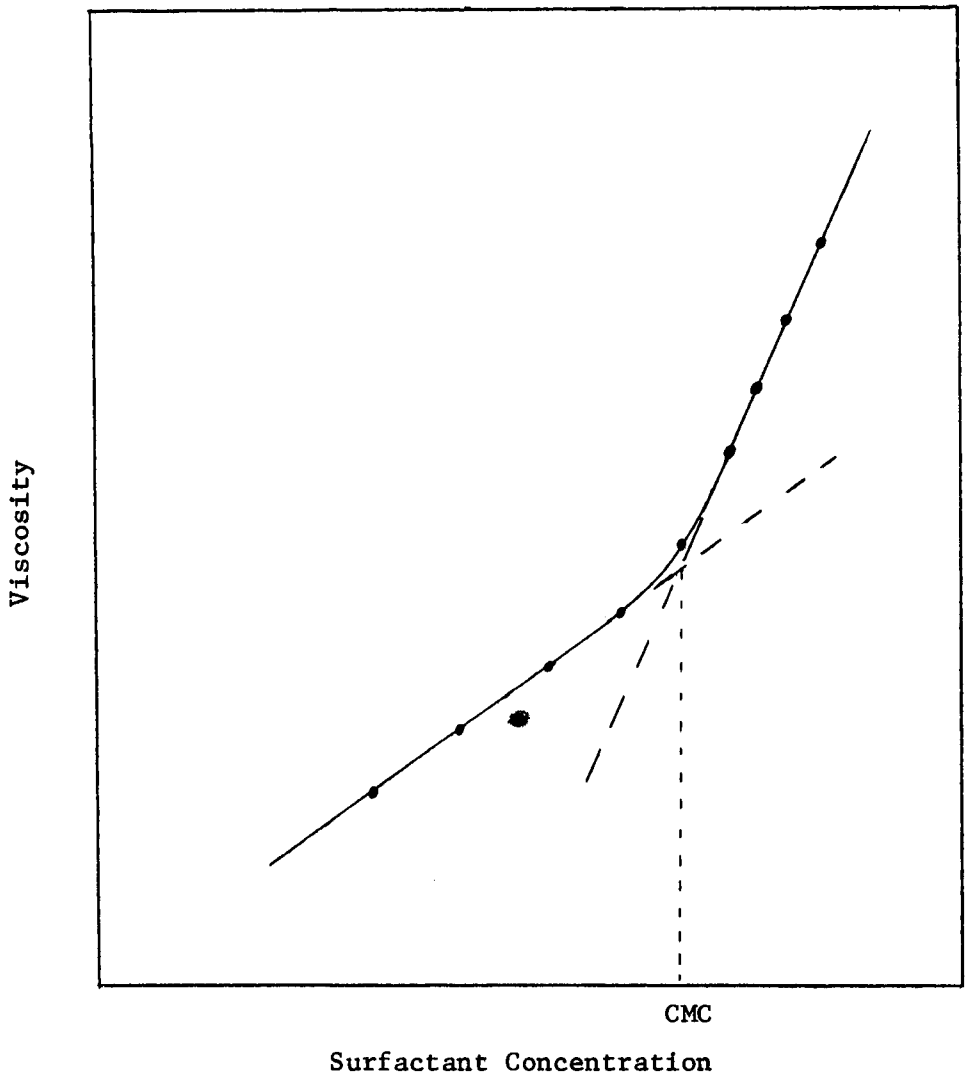


Figure 1. Dependence of the viscosity of a surfactant solution on the surfactant concentration.

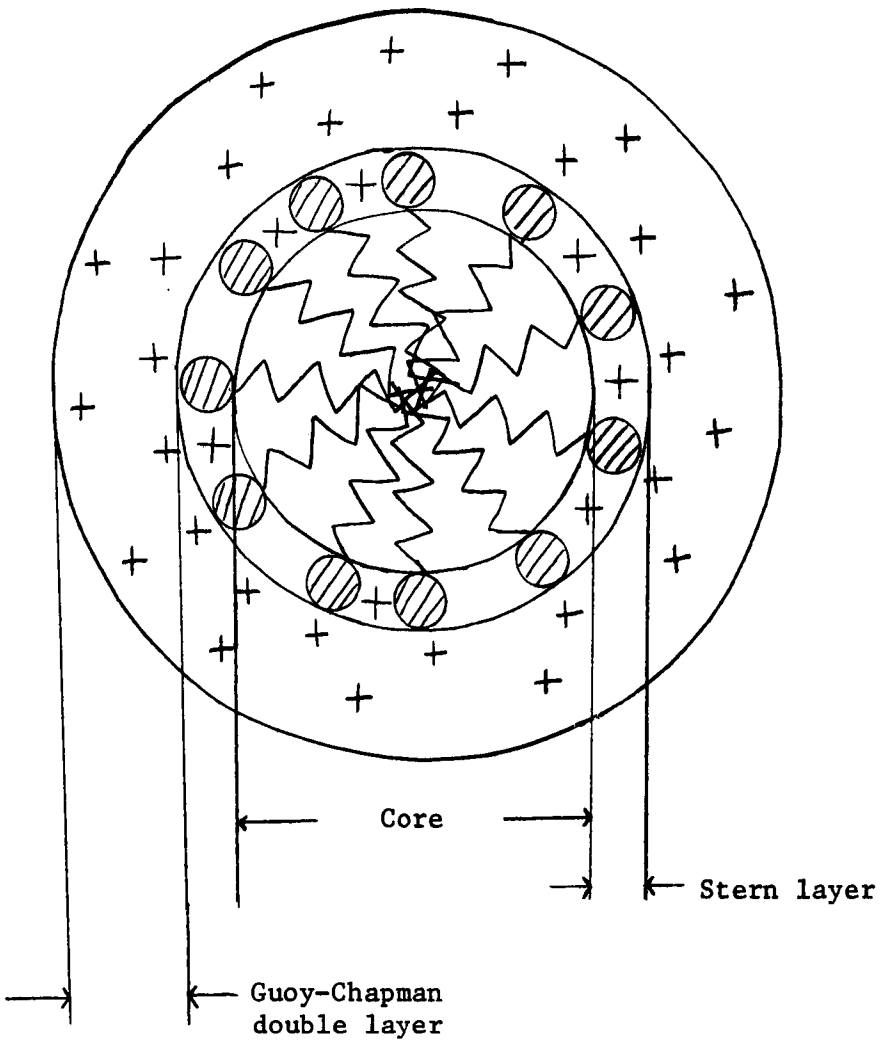


Figure 2. Schematic representation of a typical ionic micelle.

Shaded circles: surfactant head groups, crosses: counterions, zigzag lines: surfactant hydrocarbon chains.

the radius of the hydrated head group; the counterions are also considered to be completely hydrated.[5] The Stern layer therefore contains considerable water, but the dielectric constant is lower than in the bulk solution.[12] One reason for this is undoubtedly the "roughness" of the micellar surface:[13] part of the hydrocarbon chain is considered to be sticking up through the Stern layer. This view arose from the discrepancy between observed and calculated electrophoretic mobilities for certain micelles. Calculations on the amount of micellar surface area per head group[14] and on the free energy of transfer for a methylene[15-17] group from water to micelles further substantiate this. Values for the free energy of transfer are less than for a methylene group going into a pure hydrocarbon environment. The Guoy-Chapman double layer contains the remaining counterions, their concentration obeying the Boltzmann distribution law.[18] The double layer may extend up to several hundred Angstroms into the solution, depending on the total concentration of electrolyte in the solution and the surface potential of the micelle.

For nonionic surfactants the micelles obviously have no associated double layer. They are composed of a hydrocarbon core and an outer capsule or mantle composed of the hydrophilic groups.[1] Commonly these are polyoxyetheylene groups; the ether oxygens are extensively hydrogen-bonded to water. Nonionic surfactants have much lower CMCs than ionic surfactants because the driving force for micellization, transfer of the surfactant hydrocarbon chains from water to a hydrocarbon environment, is not opposed by Coulombic repulsion of ionic head groups. With

ionic surfactants micelle formation is observed only when the gain in free energy from the hydrophobic interactions in the micelle core is sufficient to overcome this Coulombic repulsion.[19] The decrease of the CMC with increasing chain length[2] for a homologous series of detergents can be explained in the following way: for a given head group, the repulsive term is approximately constant; with increasing chain length the hydrophobic interaction term increases, making micellization possible at progressively lower concentrations. This simple explanation ignores the variation in surface area per head group with the radius of the micelle. This variation is not large.[14] The micellar radius may be satisfactorily estimated by assuming that the hydrocarbon chains of the surfactant are fully extended when in micellar form.[1]

The postulate of spherical micelles as the only micellar species at the CMC is not completely general. For some surfactants the micelles are rod-shaped, even in very dilute solutions; sodium oleate is one example.[20] These micelles are referred to as Debye micelles, after Debye,[2] who first proposed them; the rod ends are considered to be hemispherical. Recently Tanford[21] has reexamined and extended the work of Tartar on certain surfactants; he finds that the length of the hydrocarbon chain and the number of surfactant molecules per micelle (the aggregation number) necessitates the existence of ellipsoidal micelles for many detergents. It is also important to keep in mind that even in the spherical micelle, the hydrocarbon chains cannot be arranged radially, as schematically indicated in Figure 2 (p 4). To assume this requires assuming a variation of density with distance within the hydrocarbon core;[2] the core is thought to be analogous to a drop of liquid

hydrocarbon and therefore of constant density throughout. Finally, the size of the micelles at the CMC almost certainly varies over a small range, i.e., the aggregation number is not the same for each micelle. The micellar system is then said to be polydisperse.[22,23] The variation in aggregation number is greater for larger micelles.[22]

As the concentration of surfactant increases beyond the CMC, larger micelles may be formed in certain cases. Small angle X-ray scattering[20] and light scattering techniques have shown this; molecular weights have been calculated. According to some workers, formation of rods decreases the micellar surface area available per head group;[14] this should increase the degree of counterion binding. Others see the rod as the micellar shape with the maximum surface to volume ratio, and hence the minimum electrical free energy.

Micelle formation and dissociation is rapid, with rate constants for the dissociation of one monomer from the micelle in the 10^5-10^6 sec^{-1} range. Common methods used to determine these rate constants include temperature-jump techniques[24] (micelles observed by light scattering), EPR measurements on paramagnetic surfactants[25] (nitroxide free radical head group) and NMR studies. There is a large discrepancy between the temperature-jump results and the other techniques; an example has been reported for dissociation of a nonionic micelle.[26] It is not certain that the same processes are being measured. At this time, it seems that the EPR and NMR techniques are more reliable.[27]

The energetics of micellization may be approached in a number of different ways: (1) by considering micelle formation as the separation

of a second phase from a previously homogeneous system, (2) by using a mass-action model and (3) for the case of ionic surfactants, a modification of (2) which takes into account the electrical free energy necessary to assemble the charged head groups in close proximity to one another. Shinoda[2] has emphasized that (1) can strictly be applied only to micelles with large aggregation numbers; accordingly one speaks of the treatment as the pseudophase model for micelle formation. Several objections have been raised to its use:[3] it predicts that the change occurring at the CMC will be infinitely sharp, it gives differing results for ionic and nonionic surfactants for the chain length dependence of the free energy of micellization, and it predicts enthalpies of micellization which are contrary to experimental results for certain surfactants. The pseudophase model also has its defenders.[28,29]

In the pseudophase model the CMC is considered as a saturation concentration (the solvent is saturated with surfactant monomers and a second phase forms). This is one of the formal definitions of the CMC given earlier. For the pseudophase model the free energy of micellization, ΔG_{mic}, is equal to RTln CMC, where the CMC is expressed in mole fraction units.[3] This takes into account the loss of translational entropy experienced by the monomers upon entering the micelles. The same expression is frequently used for both ionic and nonionic surfactants; in the former case the effect of the counterions is neglected. Shinoda and Hutchinson have modified this treatment to take charge of effects into account.[30] However, Tanford[31] considers that the entropy of mixing of the micellar "phase" with the solvent has been neglected.

The mass-action model, Equation 1, involves the aggregation number, n, and the degree of counterion binding to the micelle (illustrated for a cationic micelle):

$$nS^+ + mX^- \rightleftarrows M^{(n-m)+}; \quad K_M = \frac{f_M[M]}{f_{S+}^n[S^+]^n f_{X-}^m[X^-]^m} \quad . \qquad (1)$$

For anionic surfactants appropriate sign changes need to be made; nonionic surfactants of course have no associated counterions. The symbol f denotes an activity coefficient. The free energy of micellization per monomer is $(-kT/n)(\ln K_M)$. This is expanded in Equation 2. This expression frequently appears as Equation 3. Note that this is not the

$$\Delta G_{mic} = (-kT/n)\{\ln f_M + \ln[M] - n \ln f_{S+} - n \ln[S^+] - m \ln f_{X-} - m \ln[X^-]\} \qquad (2)$$

$$\frac{\Delta G_{mic}}{kT} = (-\ln f_M)/n - (\ln[M])/n + \ln f_{S+} + \ln[S^+] + (m \ln f_{X-})/n + (m \ln[X^-])/n \qquad (3)$$

free energy for addition of one surfactant molecule to a micelle already containing n-1 such molecules. For nonionic surfactants the terms involving the counterions are omitted. In practice, activity coefficient effects are often neglected, since CMC values may be quite low. In addition, $\ln f_M$ is divided by n, which makes it quite small. The term $[S^+]$ should be taken as the CMC; to determine [M], the assumption that 2% of the surfactant is present as micelles at the CMC may be used. Note that for a nonionic surfactant with a large aggregation number (and activity coefficient assumed to be equal to unity) $\Delta G_{mic}/kT$ reduces to ln CMC, which is equivalent to the pseudophase model. For ionic surfactants,

m/n represents the fraction of counterions bound to the micelles and may be determined by a number of experimental techniques. Unfortunately, these techniques may give differing values for the same surfactant; some of these will be presented in a later section on counterion binding.

A more physical approach to the binding of counterions than is found in the mass-action model involves calculation of the electrical free energy of the micelles.[3] The terms in Equation 3 (p 9) involving $[X^-]$ and f_{X^-} are replaced by F_{el}/kT, nF_{el} being the change in electrical free energy on the formation of the micelle. The result is Equation 4.

$$\Delta G_{mic}/kT = -(\ln f_M)/n - (\ln[M])/n + \ln f_{S^+} + \ln[S^+] - F_{el}/kT \qquad (4)$$

The value F_{el} can be evaluated using the tabulated functions provided by Loeb, Overbeek and Wiersema[18] for spherical charged particles of varying radius and surface potential. It is important to note that for micelles of most surfactants, the Poisson-Boltzmann equation cannot be linearized, due to the high surface potentials involved.

Mukerjee[3] has used both the mass-action and the electrical free energy approach for NaLS (sodium dodecylsulfate) and he finds that the two give different results. He prefers the mass-action approach because ΔG_{mic} calculated in that manner agrees with an estimate obtained from a C_{12} nonionic surfactant. One reason for the discrepancy is thought to be the fact that F_{el} calculations do not take the bound counterions' loss of entropy into account. In the mass-action approach this is included in the $\ln[X^-]$ term, where $[X^-]$ is expressed in mole fraction units.

Finally, it must be noted that many surfactant monomers almost certainly undergo some sort of self-association, probably dimerization, below the CMC. Corrections for pre-CMC dimerization[3] will affect the calculated values of ΔG_{mic}.

The most widely used and best technique for determining the aggregation numbers for micelles is light scattering,[1,2,19] which gives the weight-average micellar molecular weight from a graph of $H(C - CMC)/(\tau-\tau_o)$ versus C - CMC. H is a constant involving geometrical and refractive index factors of light scattering, τ is the turbidity of the system under consideration, and τ_o is the turbidity of the system at the CMC. Micellar size is dependent on the temperature, decreasing as the temperature increases for ionic surfactants.[32] For nonionic surfactants the micellar size increases with increasing temperature.[33]

The CMC of any surfactant is dependent on the temperature at which it is measured. For ionic surfactants, the CMC generally has a minimum at around 25°, indicating that the micelles are the most stable at this temperature. The existence of a minimum indicates that contributions to the free energy of micellization from hydrophobic bonding and electrical effects have opposite temperature dependences.[34] Scheraga claims the minimum should be at 60°, if one considers only the hydrocarbon portion of the micelles. Poland and Scheraga[35] feel the discrepancy is explained by a negative enthalpy change associated with a charged head group's solvation changing upon entering the micelle. For at least one surfactant, NaLS, there is considered to be no such

change in solvation, however,[36] or the solvation change is considered to be endothermic.[37]

Both the CMC and micellar size for a given surfactant are affected by added salt. The CMC is lowered and the micellar size increases. The nature of the head group for ionic surfactants[38] also influences the micellar size, when the hydrocarbon portion of the surfactant remains constant. The factors influencing the aggregation number are the distance of closest approach of the counterions to the site of charge of the head group and the hydrophobic bonding between adjacent alkyl groups in the micelles. The dependence of the CMC on electrolyte concentration may be expressed by the empirical Equation 5[17,39]

$$\log \text{CMC} = -(m/n) \log (\text{CMC} + C_a) + \text{constant} \qquad (5)$$

where m/n represents the fraction of counterions bound to the micelle and C_a equals the concentration of counterions contributed by added salt. Determination of the CMC for a surfactant at varying concentrations of counterions thus represents an experimental method of determining m/n. The CMC is independent of the concentration of co-ions because the micelle's surface potential depends only on the charge density due to the head groups and the effect of the counterions in reducing the potential.[2,17] This will be explored in more detail later. An increase in micellar size with addition of added electrolyte is also the result of a decrease in surface potential. This means that the electrical free energy contribution to micelle formation is diminished.[40] At sufficiently high concentrations of electrolyte or surfactant

spherical micelles may change into rod-shaped micelles, containing many more monomers than the spherical micelles from which they were formed. The area per head group is less for a rod-shaped micelle than for a spherical one, provided the micellar partial specific volume remains constant.[41] This would result in a higher surface potential and hence electrical free energy of micelle formation, were it not for the presence of sufficient counterions to reduce them. A decrease in area per head group implies increased interaction between the hydrocarbon chains of the surfactant monomers in the micelle, and hence an increased favorable hydrophobic interaction term when considering the free energy of micellization.[42]

For nonionic surfactants a decrease in CMC with the addition of electrolytes is also observed. This has recently been explained in terms of the salting-out of the hydrocarbon chains in these surfactants;[43] using Equation 6, where C_s is the molar concentration of

$$\log CMC = -k_s C_s + \text{constant} \qquad (6)$$

added salt and k_s is the salt-effect constant for the particular hydrocarbon chain and salt involved. The appropriate k_s may be calculated according to the treatment of Long and McDevit.[44]

It is known that for a homologous series of surfactants, the alkyltrimethylammonium bromides for example, the CMC decreases with an increase in the length of the alkyl chain.[2] The empirical Equation 7 expresses this dependence where m is the number of carbon atoms in

$$\log CMC = A - Bm \qquad (7)$$

the alkyl chain. The quantity A depends on the kind and number of head groups in the surfactant; B depends on the energy change involved in the transfer of a methylene group from water to the hydrocarbon environment and the fraction of bound counterions for ionic micelles. Lin and Somasundaran[45] feel that B contains a hydrophobic and an electrostatic interaction term.

For ionic micelles, a variation in the counterion can affect the CMC and micellar size,[46-49] even when studied at constant counterion concentration. The magnitude and direction of effects are consistent with the lyotropic series for ions;[50-52] for a series such as the alkali metals cations or the halide anions the effects appear explicable in terms of the ions' hydrated radii.[40,48,53] The smaller these radii the closer the distance of approach between head group and counterion; this affects the surface potential of the micelle. For alkylammonium cations interacting with anionic micelles, hydrophobic effects are important; the same is almost certainly true for large organic anions, e.g., benzoate, interacting with cationic micelles.

The addition of various nonelectrolytes also affects the CMC of surfactants; this occurs as the result of solubilization, dissolution of the additive in the micellar "phase." Historically, solubilization referred to the increase in solubility for organic substances in water when a surfactant is added.[1,54] The micelles are known to be involved in the process because solubilization is slight or nonexistent at surfactant concentrations below the CMC; this phenomenon was discovered by Hartley.[49] This is somewhat confusing, since the additives

themselves will lower the CMC. Solubilized material may be located in the micelle's hydrocarbon core, adsorbed on the surface, or oriented radially with polar groups (if any) near the micelle surface (i.e., in the Stern layer). The position of solubilizates has been studied by a variety of physical techniques,[1] including NMR,[55-58] ESR,[7-9] UV [59-61] and potentiometric[62,63] measurements. In general, hydrocarbons are located in the micellar core, but compounds like benzene are adsorbed on the surface.[54] Polar and ionic compounds are usually solubilized in the Stern layer of the micelle. The lifetime of a solubilized molecule in the micelle is quite short, say 10^{-4} to 10^{-6} sec.[57] Strictly speaking solubilization refers to the transfer of a solute from the pure state to the micelles. Micellar binding should be used to describe the transfer from aqueous solution to the micelles.[64]

The partition coefficients for additives between the aqueous and micellar phases can be determined by gel filtration chromatography[65] or potentiometric studies,[62,63] if the solubilizate has a dissociable group. The values obtained depend on the hydrophobic character of the solubilizate, as well as on its charge relative to the surfactant involved. Partition coefficients determined by saturation solubilization are somewhat less satisfactory because of the uncertainty in the activity coefficients for the solubilized material. This method assumes that all of a solubilizate which dissolves in a surfactant solution, above the solubilizate's solubility in water, is due to solubilization by the micelles present in the solution. The solubilizate may also be present in different regions of the micelle. For example, a nonpolar

solute may go first into the core of the micelle and only after this is "saturated" will it associate with the micellar surface. The opposite situation may also occur. A free energy associated with solubilization in each region will of course exist. Also, the presence of large amounts of the solubilizate will affect the structure of the micelle. Thus a different process is measured by saturation solubilization than that using techniques which operate with very low solubilizate concentrations.

Micelles contain considerable water; the first several methylene groups of a typical surfactant chain may be in a partially aqueous environment.[27] Solubilization at the micellar surface has been interpreted as causing displacement of some of these water molecules.[56]

A surfactant's effectiveness in solubilization depends on its chain length, its charge type[1] (cationic surfactants are usually[66] better than anionic, at constant chain length), the size of the head group[67] and on the presence of added electrolyte[68] (it increases solubilization). Solubilization is important physiologically in explaining the action of bile salts on the transport of fats.[55]

Because of certain similarities to globular proteins, micellar systems have been used in the catalysis of a variety of organic reactions.[1,69] Although the rate enhancements produced by micellar catalysis do not approach those which enzymes are capable of producing, certain features of enzymatic catalysis are found. These include catalyst-substrate specificity, saturation of catalyst with substrate

and vice-versa, catalyst-substrate and catalyst-inhibitor complexes, and proximity effects.[69] In general, hydrophobic interactions and electrostatic effects (concentration in or exclusion from the micellar phase for a charged reactant) can be used to explain these phenomena. In particular, very high Ks for certain micelle-substrate complexes are found. Micellar systems can be used to carry out reactions which require a reasonable dielectric constant but whose reagents are not significantly soluble in water or other polar solvents.

CHAPTER II

PROPERTIES OF THE HEXADECYLTRIMETHYLAMMONIUM BROMIDE, SODIUM DODECYLSULFATE AND DODECYLTRIMETHYLAMMONIUM BROMIDE MICELLAR SYSTEMS

Because of the vast amount of data available in the literature on the properties of various surfactants, this chapter of the Introduction will be confined to the three ionic surfactants chiefly studied in this work: hexadecyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (NaLS) and dodecyltrimethylammonium bromide (DTAB).

A. Micellar Shape and Size: Counterion Binding and the Effects of Added Salts

1. Hexadecyltrimethylammonium Bromide

The size of the CTAB micelle has been determined by Ekwall[70] using light scattering; it contains 95 surfactant molecules per micelle immediately above the CMC at 25°. Keh[71] on the other hand quotes an aggregation number of 80; Hyde and Robb report 61[72] - 72.[73] When a salt such as potassium bromide is added to the system higher values are obtained: 174[74] in the presence of 0.013 M KBr, 207[75] with 0.0125 M KBr; at 30° 80[76] in the presence of 0.003 M KBr, and 270[76] - 288[77] in the presence of 0.025 M KBr. At higher salt concentrations rodlike micelles are observed; Granath[78] has used viscosity and sedimentation data to characterize these micelles, and Scheraga has used flow birefringence.[79] Debye and Anacker[80] report micellar molecular weights for CTAB in 0.178 M KBr and 0.233 M KBr at 30° which correspond to

aggregation numbers of 2200 and 5110 respectively. Some workers feel these values are anomalously high, however.[81] CTAB itself has a transition from spherical to rodlike micelles at a concentration of approximately 5% by weight.[19,82,83]

Light scattering gives molecular weights for the unhydrated micelles, from which the aggregation numbers above are then calculated. The effects of charge, particularly with regard to the refractive index increment, must be taken into account[84] since one is dealing with ionic surfactants. It is not clear in all cases whether the workers whose values are reported above have done this. Viscosity and sedimentation measurements on the other hand give data on the hydrated micelle; Ekwall claims that the CTAB micelle is very strongly hydrated, having about 70 water molecules associated with each surfactant molecule in the micelle. A monolayer of water of hydration corresponds to 10-12 water molecules per monomer; this value has been found for potassium laurate,[85] the sodium salt of sulfonated di(2-hexyl)succinate[86] and sodium dodecylsulfate.[87] Granath, working with CTAB in the presence of 0.2-0.4 M KBr, found the hydration to be 40 molecules of water per molecule of surfactant. These data suggest the hydration requirements of cationic and anionic micelles are quite different.[36] However, work with mixed cationic surfactants in carbon tetrachloride shows water binding of only 10-15 molecules per molecule of surfactant, as shown by IR.[88] CTAB was not included in this study, but DTAB was.

Even for CTAB at very low concentrations the micelles are probably not spherical. Tanford[21] has calculated the maximum aggregation

number consistent with a spherical micelle for various surfactant chain lengths. CTAB must have ellipsoidal micelles according to his calculations. The more methylene groups which are still exposed to bulk water at the surface of the micelles, the more pronounced the deviation from spherical will be. This fact, together with neglecting the electroviscous[81,89,90] effect on viscosity results for CTAB in the absence of salt, may contribute to Ekwall's high estimate of hydration for its micelles.

There is evidence that CTAB molecules form dimers below the critical micelle concentration. Bair and Kraus[91] found that a plot of equivalent conductivity versus $\sqrt{C}$ at concentrations below the CMC exhibited a slope greater than that predicted for a 1:1 electrolyte; Czerniawski[92] has computed a dimerization constant of 2,171 from conductivity measurements. Dimerization may partially account for the fact that the free energy of transfer per methylene group for CTAB methylene groups from water to the micelle is only -1.13 kT[45] instead of the theoretically possible -1.4 kT. Another important factor is of course the water present in the micelles.

At higher salt concentrations there is evidence that the sizes of the micelles present in CTAB solutions vary, i.e., that the system is polydisperse.[22,79] The variation may be as much as a factor of two[22] about the average micellar molecular weight, which is given by light scattering. Polydispersity is considered to be reasonable when one considers the formation and dissolution of micelles: binary collisions (micelle plus one molecule of surfactant) are much more likely than

multiple collisions.[23,93] At low salt concentrations, Attwood[74] and Birdi[94] find no evidence for polydispersity in the CTAB micellar system. Birdi finds that the aggregation number of CTAB micelles increases as the temperature decreases.

The CMC for CTAB has been determined by a variety of techniques;[92,95-99] many of the values fall closely around 0.0009 M at 25°. The technique used by Malik[100] is especially worthy of mention for the simplicity of data collection and presentation. He measures the bromide ion activity in solutions of varying CTAB concentrations using a mercury, mercurous bromide cell. The measured cell voltage is a measure of a_{Br^-}; a plot of a_{Br^-} versus -log C_{CTAB} shows a change in slope at log CMC. Using this technique, Malik obtains a value of 0.000912 M for the CMC at 30°. The addition of urea is found to increase the CMC of CTAB.[99]

As mentioned in Chapter I, an appreciable fraction of a surfactant's counterions will be bound to the micelles in solution. These bound counterions are considered to be part of the kinetic micelle, the micelle upon which hydrodynamic and electrokinetic measurements are made. For CTAB solutions at 75°, two different kinds of counterions have been observed, as indicated by two superimposed resonance lines in the NMR.[101] Presumably one line corresponds to bromide ion in the Stern layer, the other to bromide ion in the diffuse double layer. The fraction of free counterions, α, for CTAB micelles has been determined by light scattering as 0.116[102] and 0.0915,[74] the latter being in the presence of 0.013 M KBr. Values determined by

osmotic pressure measurements[23] and use of a bromide ion selective electrode[103] agree closely with 0.116. These values were all obtained at 30°; since counterion binding is exothermic, α should increase with increasing temperature.[104] Keh,[71] using potentiometric measurements, has found α to be 0.22; Hyde[105] and Mathews[106] report 0.20-0.25. Hartley[107] and coworkers, by interpreting conductivity measurements, found that α depends on the concentration of CTAB, being 0.26 at 0.02 M CTAB but 0.35 at 0.1 M CTAB. The reported values differ because the methods of measurement differ. Light scattering apparently takes into account a greater fraction of the counterions bound in the double layer than conductivity measurement for example. Mukerjee has commented on the differences in degrees of dissociation obtained.[48]

Values of α may be used to calculate the free energy of micellization for CTAB, using Phillips'[108] equation, Equation 8. The

$$\Delta G^{\circ}_{mic} = 2.3(2 - \alpha)kT \log CMC \qquad (8)$$

CMC is to be expressed in mole fraction units; using $\alpha = 0.11$, ΔG°_{mic} = -20.8 kT = -12.4 kcal/mole at 25°. For $\alpha = 0.25$, ΔG°_{mic} = -19.3 kT = -11.5 kcal/mole. Phillips' equation may be derived from Equation 3 (p 9) neglecting activity coefficients and [M], setting $[X^-]=[S^+]$ and $m/n = 1 - \alpha$. Czerniawski[92] has reported the enthalpy and entropy of micellization for CTAB over the temperature range 25-35°. The enthalpy of micellization is -3.77 kcal/mole; the entropy is -12.4 eu, a very surprising result since micellization is generally considered to be entropy-controlled.[1] The associated ΔG°_{mic} would be -0.70 kcal/mole.

Assuming the correct entropy value is +12.4 eu, ΔG°_{mic} is still only -7.47 kcal/mole. Phillips is using unit mole fraction as the standard state, but Czerniawski most probably is not.

Adding salts to micellar systems is known to decrease the CMC[1,39] and increase the aggregation number, as has been seen for CTAB; one might also expect some effect on α. Pearson[103] has assumed that α is independent of CTAB concentration, with good results, while Hartley, as mentioned earlier, found a concentration dependence. Cohen,[109] using light scattering, found α to increase with the addition of KBr to a CTAB solution.

The surface potential for the micelle (ψ_o) depends on the total concentration (C_i) of counterions present in the solution (in equivalents of effective ions per liter) and on the surface charge density of the micelle (σ) according to Equation 9. The electrical free energy

$$\psi_o = (kT/e)\ \{\ln\ (2000\ \sigma^2/DNkT) - \ln C_i\} \qquad (9)$$

of micellization depends on the fraction of counterions, m/n (see Chapter I) bound to the micelle:[2] $E_{el} = (m/n)e\ \psi_o$. The higher the concentration of added salt, the smaller E_{el} will be; this operates through ψ_o.[110] The above expression for ψ_o implies that a counterion's effect on ψ_o depends upon its charge only. This might imply that a counterion's effectiveness in decreasing a surfactant's CMC or increasing its aggregation number should depend on charge only also. That this is not generally the case can be seen by considering Cohen's[109] work on the CMC of CTAB in the presence of $NaClO_3$, $NaNO_3$, NaBr and NaSCN. Sodium chlorate

is the least effective in lowering the CMC per mole added; NaSCN is the most effective. For CTAB, one can also note a study on the effects of added quaternary alkylammonium bromides on its CMC at 30°.[111] Initial addition of salt produces a decrease in CMC, but this situation is reversed as additional salt is added. The observed behavior is attributed to the solvent-organizing properties of the higher quaternary alkylammonium bromides. In a well-organized solvent, the entropy of micellization decreases, and the CMC increases.

2. Lyotropic Series Effects

Specific effects of ions on the properties of surfactants are considered in this section, effects which do not depend upon differences in ionic charge. In order to more fully consider these effects, the so-called lyotropic or Hofmeister series of ions[50,51] will be briefly discussed before considering DTAB and NaLS. (It turns out that even ions of the same charge as the surfactant involved have a slight effect on the CMC.)[112,113]

The Hofmeister series was first constructed by observing the order of effectiveness of a series of anions or cations in denaturing euglobulins.[52] An effective ion is said to salt in the hydrophobic portion of the protein chains, decreasing the free energy of transfer for these portions from the hydrophobic environment of the native protein's interior to the bulk solvent, water. Typical lyotropic series are:

anions: $SO_4^{2-} < C_2H_3O_2^- < Cl^- < Br^- < NO_3^- < ClO_4^- < I^- < CNS^-$

cations: $(CH_3)_4N^+ < NH_4^+ < Rb^+, K^+, Na^+, Cs^+ < Li^+ < Mg^{2+} < Ca^{2+} < Ba^{2+}$

with the ions at the right being the most effective denaturants.

Lyotropic series are also observed for the solubility of nonelectrolytes in aqueous salt solutions.[44] The results can be expressed in terms of the Setchenow equation, Equation 10. S_o is the solubility of the nonelectrolyte in pure water; S is its solubility in a salt solution of

$$\log \gamma = \log(S_o/S) = K_s C_s \qquad (10)$$

molarity C_s. K_s is the salting-out coefficient for a given salt; it also depends on the nonelectrolyte. If K_s is positive, the nonelectrolyte is said to be salted out; it is less soluble in aqueous salt solution than in pure water. Salting-in is the opposite behavior. Virtually all salts tested salted out compounds such as benzene.[44]

According to Long and McDevit[44] the internal pressure concept, Equation 11, can be used to explain the relative magnitudes of the K_s

$$K_s = \bar{V}_i^{\,o}(V_s - \bar{V}_s^{\,o})/2.3\ \beta_o RT \qquad (11)$$

values, where $(V_s - \bar{V}_s^{\,o})/\beta_o$ is the internal pressure factor. The compressibility of the solvent is given by β_o, $\bar{V}_i^{\,o}$ is the partial molar volume of the nonelectrolyte solution at infinite dilution, V_s is the molar liquid volume of the pure salt and $\bar{V}_s^{\,o}$ is the partial molar volume of the salt in solution at infinite dilution.

For polar nonelectrolytes and for proteins, whose molecules contain polar and nonpolar regions, salting-in is observed. Any salt which is an effective denaturant for a protein will have a negative K_s for that protein. Studies by Schrier and Schrier[114] on simple amides indicated that an observed K_s could be divided into contributions from

the amide group and the nonpolar groups in the molecule; every salt of a given charge type salted the amide group in to the same extent, while a typical lyotropic series was observed for the salting-out constants for methylene and methyl groups. Jencks and Robinson,[115,116] using a tetrapeptide derivative, acetyltetraglycyl ethyl ester (ATGEE), came to a quite different conclusion. Their results suggest direct salt-amide dipole interactions, with the importance of these interactions forming a lyotropic series. Certain salts, especially those with large organic anions or cations, show curved lines when log γ for ATGEE is plotted against C_s. Jencks sees this as intervention of the following association (the ion I binds directly to an amide group):

$$\text{ATGEE} + \text{I} \rightleftarrows \text{ATGEE}\cdot\text{I};\ K = [\text{ATGEE}\cdot\text{I}]/[\text{ATGEE}][\text{I}] \qquad (12)$$

von Hippel and Schleich[50] have measured binding constants for a series of anions and cations with polyacrylamide; they observe lyotropic series. No such series are observed with materials lacking amide groups, such as polystyrene. Duynstee and Grunwald[117] have observed direct solute-salt interactions in the hydrolysis of methyl 1-naphthanoate. Moss[118] has observed a lyotropic series effect on the stereochemistry of the nitrous acid deamination reaction in micelles. Voet[119] has attempted to put lyotropic series on a quantitative basis, by assigning lyotropic numbers to the various cations and anions. Hydrolysis rates for an ester in the presence of a salt, as well as properties of the ions themselves, such as heat of hydration, are then linear functions of these lyotropic numbers.

For proteins, interactions of added cations or anions with the charged groups are not considered very important in determining the extent of denaturation, as the majority of these groups should be in contact with bulk solvent before and after denaturation. For micelles such interactions are important, however; lyotropic series effects on the micellar properties of NaLS and DTAB will be considered below. For simple tetraalkylammonium salts the association constant for ion pairs follows a lyotropic series, with ion pair formation being much more extensive for an iodide salt than for a chloride salt.[120-122] The specific adsorption of certain anions at the water-hydrocarbon interface occurs for monolayers of CTAB; the ionic potential and dipole moment in the double layer are influenced by the nature of the anion.[123] The effectiveness of a counterion in promoting association seems to be correlated with its hydrated radius.[124] The work of Cohen and Vassiliades,[109] considered earlier, and the work of Bungenberg de Jong[125,126] on coacervation of CTAB solutions containing various salts shows the operation of a lyotropic series. Anions such as NO_3^-, I^-, and SCN^- are most effective at producing coacervation.

3. Sodium Dodecylsulfate

Sodium dodecylsulfate micelles contain 40^{81}-$62^{76,93}$ monomers in the absence of added salt (the higher value is generally accepted); the aggregation numbers increase as sodium chloride is added, reaching 126^{29}-142^{93} in the presence of 0.50 M NaCl. Anacker[127] has a good compilation of aggregation numbers determined by several workers using a

a range of sodium chloride concentrations. The CMC is 0.0081 M,[4,29,53] with a second CMC at 0.065 M.[128] Viscometric studies indicate the presence of an electroviscous effect up to 0.12 M NaCl;[129] the hydration of micellar NaLS is considered by some workers to be 10-12 molecules of water per molecule of surfactant, as mentioned earlier. Mukerjee, using Kushner's viscosity data,[129] computes the hydration to be six moles water per mole of surfactant; he considers this value to be the same before and after micellization.[36] The micelles are thought to be spherical in the absence of salt; this is not supported by Tanford's[21] calculations, which predict a slightly ellipsoidal shape. Dimer formation at concentrations below the CMC occurs, as indicated by deviation of the conductance of very dilute solutions from Onsager's theory.[130]

Stigter and Mysels[13] first proposed the concept of the rough micellar surface, with one or two methylene groups from the monomers sticking up from the surface into the water solution. Mukerjee[48] calculates the portion of the micellar surface which consists of hydrocarbon groups to be approximately two-thirds of the total micellar surface area. Counterions bound in the Stern layer of the NaLS micelles are considered to be fully hydrated;[6] the water molecules in the hydration sheath rapidly exchange with bulk solvent molecules.[131]

The degree of dissociation α of the sodium ions, determined by several methods, ranges from 0.14[132] (pH 12.3) to 0.54,[39] with most of the values falling around 0.2-0.3.[13,29,37,130,133-137] The degree of dissociation increases slightly as sodium chloride is added to the system;[13,29] it also increases slightly as the concentration of NaLS

is increased,[130,135] or decreased, depending on the work under consideration.[37]

In the presence of cations other than sodium, α for the sodium ions increases, i.e., there is a competition for binding sites on the micelles. This effect has been studied for added magnesium ions[133] using a sodium ion sensitive glass electrode; when the molar concentration of magnesium sulfate reaches one-half the molar concentration of NaLS, α = 0.86. Since this technique gives α = 0.25 for NaLS only, the competition is quite striking. Venable[138] has investigated the effects of Mg^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} on NaLS micelles; they all give micelles of similar size and α (0.16). Urea also increases α for NaLS, presumably because it increases the dielectric constant of the solution.

Goddard[53] determined the effect of added salts containing various cations on the CMC of NaLS. Dye solubilization was used to determine the CMC in each case. Although the method is reputed to give anomalously low values, these workers obtained a CMC for NaLS only of 0.008 M, which agrees with the values obtained by other methods. The cationic order of effectiveness (anions have little[112] or no effect) in lowering the CMC forms a lyotropic series:

$$Li^+ < Na^+ < K^+ < Cs^+ < (CH_3)_4N^+I^- < C_4H_9N^+(CH_3)_3Br^- < PhN^+(CH_3)_3I^- .$$

Recall that tetra-n-butylammonium bromide has the opposite effect on CTAB: it increases the CMC.[111]

For the alkali metal cations, plots of log CMC versus the reciprocal of the cations' hydrated radii give reasonably straight lines, but plotting against the reciprocal of the distances of closest approach

of the cations (from the Debye-Hückel approach) gives an even better one. It is felt that the smaller the distance of closest approach the more effectively the micellar charges will be screened.

Mukerjee[48] has further amplified the importance of the size of the hydrated cation in a study on the MLS surfactants, where M is a variety of univalent cations. The CMC values, determined by conductivity, decrease in a manner consistent with the lyotropic series for alkali metal cations reported by Goddard for NaLS. The following order of effectiveness for decreasing the CMC for tetraalkylammonium ions was found: $(CH_3)_4N^+ < (C_2H_5)_4N^+ < (C_3H_7)_4N^+$. The degree of dissociation of the counterions, determined from the conductivity measurements, is lowest for the ions most effective at decreasing the CMC. The variation in α is much larger when light-scattering data are used. The closer the approach of an alkali metal cation to the charged head groups on the micellar surface, the lower the degree of dissociation is and the more compact the double layer surrounding the micelle will be. For the tetraalkylammonium ions on the other hand, the ion most effective at decreasing the CMC has the largest Stokes' Law hydrated radius. Mukerjee suggests that hydrophobic interactions of the ion's alkyl groups with the exposed hydrocarbon on the micellar surface are responsible for these ions' effectiveness. In light of results with CTAB, it would be interesting to examine the effects of large added concentrations of the tetraalkylammonium salts. Presumably, if the sites available for the interaction of cations with the NaLS micellar surface could be saturated, water structure effects on the CMC might show up. Interestingly, data

obtained for α for the tetramethyl- and tetraethylammonium surfactants by using a Corrin plot[39] indicate a larger α for the tetraethylammonium compound. Although Mukerjee reports some α values for the dodecylsulfate surfactants in the presence of added common ion salts, no large effects are seen.

Mukerjee calculated the free energy of micellization for the various surfactants investigated, using the mass-action approach. He finds that micelles form more easily as the size of the hydrated ion becomes smaller. Unfortunately, size data are not available for all the surfactants. Mysels and Princen[93] did find the micelles of the sodium, lithium and tetramethylammonium surfactants to be very close to the same size. Mukerjee's value for NaLS is ΔG°_{mic} = -14.5 kT = -8.6 kcal/mole, for α = 0.31. Phillips[108] obtained the value -15.9 kT using Equation 8 (p 22) and an α value of 0.15, obtained from light scattering. Obviously one needs to choose α values determined by a single experimental technique in order to reliably compare free energies of micellization calculated using them.

Mukerjee[3] has also used the Loeb, Overbeek and Wiersema method (Equation 4, p 10) for calculating the electrical free energy contribu- to micellization and hence to ΔG°_{mic}. The value, -13 kT, is different from the value calculated using the mass-action approach. Mukerjee thinks this is the result of neglecting the loss of translational entropy by the counterions upon micelle formation. Rehfeld[37] has investigated micelle formation for NaLS calorimetrically; he finds that for α = 0.29 (determined by electrophoresis), the enthalpy of micellization

(ΔH°_{mic}) at 25° is 0.52 ± 0.04 kcal/mole and the entropy of micellization (ΔS°_{mic}) is 18.3 ± 0.3 gibbs/mole, using a 1 M standard state. The ΔH°_{mic} value agrees well with the 0.6 kcal/mole obtained from the temperature dependence of the CMC for NaLS.[133] This corresponds to ΔG°_{mic} = -4.93 kcal/mole; this value differs from Mukerjee's because the latter's calculations are based on a standard state of mole fraction one.

Rehfeld has determined the enthalpy, entropy and free energy of binding of sodium ion to the dodecylsulfate anion: ΔH°_{p} = -1.09 ± 0.14 kcal/mole, ΔS°_{p} = 7.8 ± 0.5 gibbs/mole and ΔG°_{p} = -3.4 kcal/mole. For sodium sulfate, ΔS for the interaction is 1.3 gibbs/mole, and ΔH is -0.49 kcal/mole, from which Rehfeld concludes that the high affinity of NaLS micelles for sodium ions is primarily an entropy effect. He feels that the micelle interacts with the solvent over a very large volume, although he gives no values for hydration. In contrast to Stigter's view on full hydration in a micelle's Stern layer, Rehfeld feels the solvation in the immediate vicinity of the sulfate groups is reduced.

Jones and coworkers[139,140] have studied micellization of NaLS in the presence of sodium chloride and urea. They also present a good tabulation of ΔH°_{mic} values obtained by previous workers using calorimetry. The values range from -0.45 kcal/mole to 0.10 kcal/mole. Their own calorimetric value for ΔH°_{mic} at 25° is 0.087 kcal/mole, which does not agree with Rehfeld's work. The value of ΔH°_{mic} is very sensitive to the temperature, being -0.609 kcal/mole at 30°, according to Jones. The ΔH°_{mic} value is -0.153 kcal/mole in 0.023 M sodium chloride and

-1.443 kcal/mole in 3 M urea at 25°. For the urea case, ΔS°_{mic} decreases from 17.2 eu for NaLS in water to 10.9 eu in the urea solution. This is interpreted to occur because of urea's partial breakdown of the iceberg region around the hydrocarbon in water. Jones points out that α increases with temperature, indicating the removal of counterions from the micelle is endothermic. This is consistent with Rehfeld's data.

4. Dodecyltrimethylammonium Bromide

Dodecyltrimethylammonium bromide micelles contain roughly 40-60 monomers; the two best values come from light scattering data in which the micellar charge was taken into account, but they differ widely: 43[32] and 61[127] at 25°. Anacker[127] has compiled the values obtained by previous workers, none of whom considered charge effects. The micelles are not very strongly hydrated, according to Mukerjee's[36] calculations using the viscosity data of Kushner[81] on dodecyltrimethylammonium chloride (DTACl). The size of the DTAB micelle increases with the addition of various electrolytes; as in the case of NaLS, the increase is not particularly sharp. In the presence of 0.1 M sodium bromide, reported aggregation numbers range from 72[29] to 78.[32] At high concentrations of sodium bromide (2.0 M), there is evidence for a polydisperse micellar system.[127] DTACl micelles are considerably smaller, having 37 monomers per micelle in pure water and 62 in 0.1 M sodium chloride.[81,127] For DTAB the CMC is 0.0146 M;[2,32,104] DTACl has a CMC of 0.0185 M.[81] The CMC of DTAB is temperature-dependent, reaching a minimum at 25°, but the aggregation number decreases with increasing temperature in the range 15-55°.[32]

The degree of dissociation α of the bromide counterions is 0.15[127]-0.171[32] at 25° when determined by light scattering; use of membrane electrodes gives 0.24[103]-0.256.[104] An increase in temperature produces an increase in α, regardless of the method by which it is measured. Addition of sodium bromide, however, does not produce regular changes in α.[32] From the temperature dependence of α the enthalpy of desorption of bromide ions from the DTAB micellar surface has been calculated to be 2.0[104]-2.2[32] kcal/mole. For DTACl α is 0.24 at 25°, as calculated from the electrophoretic mobility of the micelles.[141]

Jones and coworkers[142] have measured the enthalpy of micellization for DTAB in pure water and in the presence of sodium bromide and urea. At 25° ΔH°_{mic} in water is -0.333 $\pm$ 0.022 kcal/mole; in 0.1 M sodium bromide it is -0.491 kcal/mole. Urea[140] further decreases ΔH°_{mic}, to -0.633 kcal/mole, but ΔS°_{mic} is less favorable, 10.6 eu compared to 13.3 eu in water. As for NaLS, this change in ΔS°_{mic} may be attributed to partial destruction of the iceberg regions formed about the surfactant hydrocarbon chains in water. Urea increases the CMC of DTAB, as would be expected;[143] the favorable decrease in ΔH°_{mic} is not sufficient to counteract the unfavorable decrease in ΔS°_{mic}. It is not certain whether urea increases or decreases α for the DTAB micelles. Jones has found both effects, having measured an α of 0.244 in the presence of 3 M urea on one occasion,[110] 0.277 on another.[140] Both of these values were obtained using membrane electrodes.

Jones[32] has attempted to calculate the electrostatic (F_{el}) and hydrophobic contributions (ΔG_{hc}) to the free energy of micellization

for DTAB, using the equation $RT \ln CMC = F_{el} - \Delta G_{hc}$. Emerson and Holtzer[29,144] have used the same treatment, but their method of calculating F_{el} has been very elegantly criticized by Mukerjee.[145] Jones used the method developed by Verwey, Overbeek and Stigter[146] for calculating F_{el}; the micellar surface potential and charge density, which are needed in the computations are obtained from the tables of Loeb, et al.[18] This method assumes the micelles are completely ionized.

The average value of ΔG_{hc} at 25° for DTAB is -6.34 ± 0.1 kcal/mole, much less than the -9.5 kcal/mole calculated by Emerson and Holtzer. Some of the methylene groups near the charged head groups are certainly exposed to the bulk solution; Jones' value is much less than that obtained from the solubilization of simple hydrocarbons in micellar systems.[147] The value of ΔG_{hc} is independent of the concentration of added sodium bromide. Jones attempted to break ΔH°_{mic} into an electrostatic and hydrocarbon contribution, but the numbers obtained were small and the attendant errors large.

Lyotropic effects on the dodecyltrimethylammonium micelle may be seen by considering the CMCs and aggregation numbers reported for DTAX, X being a variety of counterions. Anacker and Ghose[47] have determined the CMCs, aggregation numbers and degree of dissociation for DTAB in the presence of 0.5 m NaX by light scattering. Surfactant concentrations did not exceed 0.06 M; all calculations were done taking charge effects into account. Assuming that only X^- were bound to the micelle, or X^- and Br^- in proportion to their stoichiometric concentrations produced no differences in the calculated values of the aggregation

numbers. The effectiveness of the added anions in decreasing DTAB's CMC followed this order:

$$F^- < CHO_2^- < IO_3^- < Cl^- < BrO_3^- < Br^- < NO_3^- \quad .$$

This is a lyotropic series. Although the measurements were carried out at 31-32°, NaI and NaSCN caused the DTAB to precipitate. The anions' effectiveness in increasing the aggregation number was somewhat different:

$$IO_3^- < CHO_2^- < BrO_3^- < F^- < Cl^- < NO_3^- < Br^- < ClO_3^- < SCN^- \quad .$$

In the case of thiocyanate, the micelles were quite large: 8700 monomers per micelle. The decrease in degree of dissociation α showed the same order as the increase in the micellar aggregation number, although the effects were quite small. For 0.5m sodium bromide α was 0.17, which is the same α obtained for DTAB by light scattering in the absence of added salt. Muller has found that F^- and Br^- are equally bound to micelles of 12,12,12-trifluorododecyltrimethylammonium ions; he gets values for α of 0.50, using an NMR technique.[148]

For 0.5 m NaCl, NaBr and $NaNO_3$, Anacker's aggregation number results for DTAB agree quite closely with Holtzer's[29] for the surfactant DTAX in 0.5 m NaX, X = Cl^-, Br^-, NO_3^-. For X = Cl^-, Anacker obtains 62, Holtzer 68; for Br^- 84 versus 88; for NO_3^- 79 versus 86.

In view of the influence of the nature of the counterion on the free energy of micellization, as manifested through variations in the CMC and the degree of dissociation of the counterion, it would be very informative to have additional data on counterion interactions with micelles. These interactions could be studied by the use of ion-specific

electrodes to determine the nature of the counterion binding when more than one kind of anion or cation is present. Calorimetric techniques could also be profitably used to measure enthalpies of binding to the micelle surface for various counterions.

B. Solubilization

The general characteristics of solubilization by micelles have been presented in Chapter I. Accordingly, this section will, in large part, be restricted to solubilization studies carried out using CTAB. Where appropriate, conclusions from work with DTAB and NaLS will also be included.

The complete phase diagram for two ternary systems containing CTAB have been worked out, the CTAB-1-hexanol-water system[149] and the CTAB-hexanoic acid-water system.[150,151] Lawrence and Pearson[152] have looked at a four-component system, CTAB-cyclohexylammonium bromide-1-hexanol-water. Only one aspect of this work is really of interest with respect to dilute CTAB solutions containing small amounts of solubilizates, with which we will be mainly concerned. This aspect is the high viscosity observed in the L_1 solution phase (the water-rich phase) for CTAB-hexanoic acid-water.[151]

CTAB solubilizes a variety of organic solutes;[153-156] it has been used in commercial preparations[54,157] to keep normally insoluble materials in aqueous solutions. The sites for solubilization have been studied by a variety of spectroscopic techniques; the methods all involve measuring a parameter for the solubilizate which is sensitive

to solvent polarity and then comparing this parameter's value in a micellar solution with its value in water and other solvents. Dorrance and Hunter[98] have studied the monomer and excimer fluorescences of pyrene in DTAB and CTAB; the spectra obtained are identical to those obtained in hydrocarbon solvents, which indicates pyrene is solubilized in the micellar interiors. Pyrene mobility is considered to be quite low; DTAB appears to present a more rigid arrangement of hydrocarbon chains (over a period of time) than CTAB. Perylene is also solubilized in the interior of CTAB micelles, while anthracene is solubilized at the surface.[158] ESR measurements[9] using a nitroxide free radical containing a steroid ring system solubilized in 0.15 M CTAB give a spectrum which correlates with the radical's spectrum in hexadecane at -22° (hexadecane is solid at this temperature). This indicates a very rigid micellar interior for CTAB; the use of the same free radical with NaLS indicated a relatively fluid and more polar environment for solubilizates in its micelles. Calorimetric data[159] on the heat of solution of shorter chain alkyltrimethylammonium bromides (C_8-C_{10}) in CTAB micellar systems supports a liquid nature for the micellar interior. The enthalpy of transfer from water to the micelle is -0.1 kcal/mole of methylene groups. If the micellar interior were solid the enthalpy of transfer should be at least -1 kcal/mole, reflecting the heat of crystallization of a methylene group, according to Aveyard and Lawrence.[159]

Thakkar and Hall[66] have investigated the site of solubilization of testosterone by DTAB and CTAB by using the UV absorption of the steroid's carbonyl chromophore. The wavelength at which maximum

absorption (λ_{max}) occurs in the surfactant solutions is compared to the λ_{max} in solvents for which Kosower's Z values are known. Below the surfactants' CMC, Z is essentially that of pure water; above the CMC it drops to 85 at approximately five times the CMC and then remains constant as the surfactant concentration increases. This Z value corresponds to 90% methanol, indicating that testosterone's carbonyl group is in a very polar environment. Thakkar and Hall feel that testosterone is essentially solubilized at the micellar surface, because of results with potassium laurate. Potassium laurate is even better on a mole per mole basis than CTAB (and CTAB is better than DTAB) at solubilizing testosterone; Thakkar and Hall invoke hydrogen bonding between the C-17 hydroxyl group of testosterone and the carboxylate head groups of the potassium laurate.

Eriksson and Gillberg[56] have studied the solubilization of benzene, N,N-dimethylaniline, nitrobenzene, isopropylbenzene and cyclohexane in 0.1729 M CTAB solutions at 35° by NMR. The micelles involved in this study cannot be spherical.[14,20] Solubilization of the first three compounds significantly affects the chemical shift of the methylene group adjacent to nitrogen; these solubilizates are considered to be adsorbed at the micelle-water interface up to concentrations of 0.7-1.0 mole per mole of CTAB, at which point transition to solubilization in the hydrocarbon core occurs. This is supported by the differential UV spectroscopy work of Rehfeld.[160,161] Gordon and coworkers[162] have calculated a Z value for benzene in CTAB from Eriksson's data; in this case $Z = (\delta_{mic} - \delta_{H_2O})/(\delta_{hydrocarbon} - \delta_{H_2O})$,[163] where δ refers to

the chemical shift of benzene in the appropriate medium. They compute Z = 0.18, which indicates a very polar environment for benzene. With 0.4 M sodium decanoate, Z = 0.33; with 0.4 M sodium decanoate in 1 M sodium chloride, Z = 0.55, a very interesting salt effect. NMR studies on benzene in the presence of NaLS indicate a lifetime in the micelle of 10^{-4} sec or less for the solubilizate;[57] differential spectroscopic measurements[60] indicate that benzene on the average occupies the hydrocarbon core of the NaLS micelle. It is thought to be at varying distances from the hydrocarbon center, however.

For isopropylbenzene and cyclohexane, the preferred site of solubilization with CTAB is the micelle interior. Initially, however, some isopropylbenzene is solubilized by interfacial adsorption; Eriksson and Gillberg suggest that the benzene rings are oriented towards the water with the isopropyl groups in a more hydrocarbon-like environment. The solubilization by adsorption is thought to displace some of the water molecules present in the hydrocarbon core near the micellar surface. The nuclear quadrupole relaxation of ^{81}Br in CTAB solutions containing benzene, N,N-dimethylaniline and 1-hexanol indicate that these solubilizates displace bromide ions from the micelle surface.[83] Very high CTAB concentrations, around 12-20% by weight are required. Cyclohexane has no effect on the counterion binding.

Mankowich[164] has investigated dye solubilization and has calculated ΔH and ΔS for the process of adsorption onto a micellar surface. He finds that solubilization is not a true adsorption, since he calculates a positive entropy change.

The effect of solubilization on micellar size has been studied by light scattering and by conductivity. Götz and Heckmann[165] have observed the growth of rodlike CTAB micelles (0.4 M CTAB) upon addition of benzene or 1-heptanol. The micelle size is considered to increase because the solubilizate is located near the surfactant's head groups, spreading them apart and hence decreasing their repulsive electrostatic interactions. Hyde and Robb[72,73] have investigated the size of the CTAB micelle by light scattering in solutions containing simple hydrocarbons. The hydrocarbon concentrations used were all below saturation; micellar molecular weights were determined by simple Debye plots. Addition of solubilizates is known to affect α for CTAB in certain cases;[83,105,106,166] the counterion activity for NaLS is increased by the addition of alcohols,[167] according to conductivity measurements. Upon addition of n-octane, n-decane and cyclohexane the aggregation numbers of the CTAB micelles increase only slightly, with n-decane being the most effective on a molar basis. Initial solubilization of benzene causes a decrease in micellar size, from 72 monomers per micelle to 52 monomers per micelle when the benzene is present to the extent of 15 molecules per micelle. The size then increases with further addition of benzene. The concentration of benzene at the transition from decreasing to increasing micellar size does not correspond to the concentration at the transition from surface to interior solubilization. The same decrease in aggregation number is observed with the solubilizate 1-decanol, which should have its hydroxyl group located at the micellar surface.

Conductivity measurements have also provided useful data on solubilization sites in the CTAB micelle. Hyde and Lawrence[166] found that the equivalent conductivity of CTAB solutions increases with the addition of several polar solubilizates: phenyl ethyl alcohol, m-cresol, aniline, and various aliphatic alcohols. Nonpolar additives such as ethylbenzene produced a linear decrease in equivalent conductivity with increasing additive concentration. Hyde and Lawrence interpreted the increases in conductivity in terms of increased dissociation of counterions from the CTAB micelles; emf measurements using silver, silver bromide electrodes in the case of phenyl ethyl alcohol substantiated this claim. Increased counterion dissociation has been observed by NMR for 1-hexanol in CTAB[83]. Nonpolar additives were considered to cause an increase in micelle size, which would lead to decreased micellar mobility, and hence decreased conductivity.

Hyde and Stevenson[105] studied several nonpolar additives' effects on the conductivity of CTAB solutions; they found results identical to those for ethylbenzene in the case of n-hexane, n-octane, n-decane, cyclohexane, toluene, p-xylene and isopropylbenzene. They presented two interpretations of the conductivity decrease, one the size increase mentioned earlier and a second interpretation based on a decrease in α for the micelles. Tentative emf measurements indicated that a decrease in α did indeed occur for CTAB micelles containing solubilized hydrocarbons. Ward and Chitale[168] found that naphthalene, 2-naphthylamine and 2-naphthol all lower the equivalent conductivity of CTAB solutions, which is certainly not consistent with the other results discussed here.

Benzene solubilized in CTAB produces conductivity behavior intermediate between the two types discussed above.[105,166] Initial additions of benzene produce no change in equivalent conductivity, followed by a linear decrease at higher benzene concentrations (beyond a 1:1 molar ratio with surfactant). The plateau region appears only at CTAB concentrations of 0.02 M and above. Hyde and Stevenson[105] do not have an explanation for the behavior of CTAB solutions containing benzene. They do note that the plateau and decreasing conductivity regions correspond roughly, with respect to benzene concentration, to the two regions observed by Eriksson and Gillberg in their NMR studies. It should also be noted that similar behavior is observed with benzene in NaLS, although a true plateau region is not present. CTAB solutions containing benzene in a 1:1 molar ratio are viscoelastic.[166]

Two studies in which large viscosity increases were observed upon the solubilization of certain aromatic compounds in CTAB micelles should also be mentioned. Although this is not a quantitative technique for determining solubilization sites, it is generally accepted[1,165] that solubilizates which are located at or near the micellar surface are the most effective at decreasing micellar surface charge density and hence increasing micellar size. An increase in viscosity of a CTAB solution containing certain solubilizates then indicates a qualitative increase in micellar size.

Nash[169,170] observed large viscosity increases for CTAB in the presence of phenol and naphthols; Wan[171] found similar effects for salicylic acid (o-hydroxybenzoic acid). DTAB and the C_{14} homologue,

tetradecyltrimethylammonium bromide, also showed large viscosity increases in the presence of salicylic acid. Neither the m- nor p-isomers show these viscosity increases; benzoic acid, acetyl salicylic acid, nitro-, chloro- and aminobenzoic acids are also not effective. The solubility of salicylic acid in the surfactant solutions is independent of chain length, but the maximum viscosity increase is not. Because low pH was used, 1.6-2.2, the acids were unionized in all cases. Bungenberg de Jong and coworkers[172] have observed viscoelasticity with CTAB and sodium salicylate, but coacervation does not occur. They suggest the salicylate ions are adsorbed on the micellar surface at low concentration, with the aromatic ring penetrating into the micelle at higher salicylate concentrations.

For solubilizates possessing ionizable groups, pK may be affected by incorporation into CTAB micelles. Nash found a lowering of the observed pK_a for phenol and the naphthols in the presence of CTAB, using a titration technique.[169] Mukerjee,[12] on the other hand, found an increase in the observed pK_a (decrease in ionization) for the dyes bromophenol blue and bromocresol green. He feels that the actual pK_a at the surface of the micelle for these dyes is greater than in the bulk solution. This increase is ascribed to the difference in dielectric constants for the two environments. Bunton[55] has preliminary NMR evidence for the solubilization of phenol at the micellar surface, the benzene ring being between CTAB head groups.

Although some properties of CTAB micelles in the presence of some solubilizates have been studied, there is very little work on enthalpies

of solubilization[159] or on counterion binding in ternary systems containing CTAB. It is the purpose of this work to partially fill these gaps.

CHAPTER III

MICELLAR CATALYSIS

A. Background

Systematic investigation of catalysis by micelles of ionic and nonionic surfactants began in 1959, with the work of Duynstee and Grunwald on the alkaline fading of cationic triphenylmethane dyes.[173] Since that time many other studies have appeared[1] which provide insight into several important effects which operate in micellar catalysis, namely: (1) hydrophobic interactions, (2) electrostatic interactions, (3) proximity effects, (4) salt effects, (5) substrate saturation with surfactant and so forth.

An understanding of hydrophobic interactions important to micellar catalysis must include an explanation for a homologous series ' increasing catalytic effectiveness with increasing chain length, for the free energy and enthalpy changes involved in the transfer of a substrate from the aqueous to the micellar phase (and hence a knowledge of K, the distribution coefficient for the substrate, also called the substrate-micelle association constant) and for the dependence of micellar catalysis on micellar size. The location of the substrate in the micelle is also important. With regard to electrostatic interactions, one needs to consider the preferential accumulation of counterions at the micelle surface. One also needs to consider the stabilizing effect the micellar charge has on a transition state bearing the opposite

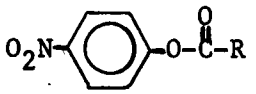
charge. Enthalpies and entropies of activation for the catalyzed and uncatalyzed reactions are relevant here. Salt effects on the reactions need to be examined not only in terms of changes in micelle structure and in surface charge density, but also in terms of competition for the binding sites on the micelles normally occupied by substrate molecules. Salt effects have been used to rationalize the observed rate versus surfactant concentration profiles for several reactions; this merits closer examination. In general, micellar catalysis does not alter the products formed in a reaction, but there are exceptions.[118,174-176]

It is generally assumed that reactions catalyzed by micelles take place in the Stern layer, because the two reagents necessary need to be in reasonable proximity to one another. This is particularly true for reactions involving a neutral substrate and a charged nucleophile. There is no evidence for the incorporation of charged nucleophiles or other small ions into the micelle interior. One would expect very high activity coefficients indeed for these species. Furthermore, there is NMR evidence that solubilizates such as benzene, N,N-dimethylaniline and nitrobenzene are adsorbed onto the surface of CTAB micelles.[56] Cordes[58] has found that orthoesters and acetals occupy water-rich sites in DTAB and NaLS micelles, sites where substrate-solvent hydrogen bonding can occur. The dielectric constant at the micellar surface, while less than that of bulk water, is nevertheless substantial. Mukerjee has found a value of 36 for micelles of an N-alkylpyridinium surfactant;[177] this is generally quoted for a variety of other micelles.

It is not the intention of this Chapter to review all the papers which have appeared on micelle-catalyzed reactions. It will concentrate instead on those reactions which have been studied using the cationic surfactant, CTAB and its homologues. For these surfactants certain characteristics which they all share when participating in catalysis will be emphasized, but the differences which are found will also be pointed out. This is particularly important when comparing one class of micelle-catalyzed reaction to another. To a lesser extent, the use of the anionic surfactant NaLS will also be considered.

B. Reactions Catalyzed by Hexadecyltrimethylammonium Bromide and Related Surfactants

Cordes and coworkers have investigated the alkaline hydrolysis of some p-nitrophenyl esters I in the presence of several cationic



I

Ia R = CH_3-
Ib R = C_5H_{11}-
Ic R = $C_{11}H_{23}$ -

surfactants,[178,179] $R'N^+Me_3X^-$ (R' = C_8H_{17}- to $C_{18}H_{35}$-). All reactions were carried out at 25°, in the presence of 0.01 M KCl and 0.01 M carbonate buffer, 50% base; the rate of reaction was determined by monitoring the appearance of the p-nitrophenolate ion spectrophotometrically. The substrate concentrations used were in the 10^{-5} M range, so that the hydrolysis could be considered as a pseudo first-order reaction. Since the CMC for these surfactants are quite low, only one molecule of substrate is considered to be solubilized per micelle. Rates for each

ester were obtained at several surfactant concentrations; for all the surfactants investigated, Ia(p 48) showed little rate enhancement in the presence of micelles. No catalysis for any of the substrates was observed below a surfactant's CMC. Catalytic effectiveness depends on both R and R', with the hydrolysis rate increasing for either an increase in R or R'. Rate maxima are observed as the concentration of surfactant is increased. With increasing chain length of the surfactant, the maxima occurred at lower and lower surfactant concentrations. This is a reflection of the decrease in CMC with increase in surfactant chain length. The lower the CMC, the larger the concentration of micelles at a given total surfactant concentration. The concentration at which the maxima occurred is also dependent on the substrate, decreasing for a given surfactant as one goes from Ib to Ic. Cordes concludes that the dependence of the rate on substrate is due to varying degrees of incorporation into the micellar phase. He used molecular sieve chromatography[65] to measure K for Ia and Ib in the presence of tetradecyltrimethylammonium chloride; K = 33 M^{-1} for Ia, but 16,000 M^{-1} for Ib. Cordes defines K using Equation 13. Other workers have used

$$K = [\text{ester}]_{mic}/[\text{ester}]_{bulk}\ (\text{C-CMC}) \qquad (13)$$

the concentration of micelles instead of surfactant;[55,180] this requires knowledge of the aggregation number of the surfactant under the experimental conditions used in the kinetic studies. When comparing K values from different sources this difference should be kept in mind. The large difference in K when going from Ia to Ib supports Cordes' explanation of the observed rate dependence on the substrate chain length. Hydrophobic

interactions are considered to be the reason for the variations in K. The value of ΔG for transfer of Ib (p 48) to the micellar phase is 3.7 kcal/mole more favorable than the transfer of Ia; if one considers this as due entirely to the four additional methylene groups in Ib, the ΔG_{CH_2} = -0.925 kcal/mole (free energy of transfer per methylene group). This corresponds to -1.56 kT per methylene group for the transfer; the accepted value for complete transfer of a methylene group from water to hydrocarbon solvents is about -1.4 kT[3,27,108] (not -1.4 kcal, as Cordes indicates). Thus some other factor must also be involved in explaining the size of the difference in the two Ks. One must invoke stabilization for the transition states produced from Ia and Ib in the hydrolysis, since the observed catalysis would not occur otherwise. The hydrolysis of Ic has been studied by other workers[181] in the ternary system CTAB-1-butanol-water, pH 11.5 (phosphate buffer). Here the maximum rate enhancement (1500) is much larger; catalysis occurs in the reversed micelles also.

For studies on the inhibitory effects of added salts, Cordes used Ib, 0.009 M tetradecyltrimethylammonium chloride and a 0.02 M triethylamine-ammonium chloride buffer. In addition, the solvent contained 3% acetonitrile by volume, which certainly must be solubilized to some extent by the micelles present, altering their properties. It is not clear whether any acetonitrile was present in the chain-length dependence work done with Ia-Ic and various surfactants. The chloride ion containing surfactant was used because bromide ion was found to be an effective inhibitor of the hydrolysis reaction. It is assumed only

the anions of the added salts are effective inhibitors; the order of effectiveness then follows the lyotropic series for anions.[50,51] For a sufficient concentration of bromide and nitrate ions the rate of hydrolysis actually drops below the rate in the absence of surfactant. The anions are much more effective inhibitors at low concentrations (say below 0.1 M) than they are at higher concentrations. The order of effectiveness is $F^- < SO_4^{2-} < Cl^- < Br^- < NO_3^-$.

Added anions may exert two effects on the hydrolysis in the micellar phase. Due to the positive charge of a CTAB micelle, one would expect hydroxide ion to be concentrated at the micellar surface. One would also expect the positive charge to electrostatically stabilize the negatively charged transition state for ester hydrolysis. The added anions may alter both of these phenomena. The anions may compete with hydroxide ions for binding sites within the Stern layer; they may reduce the surface charge density (and surface potential) of the micelle, thus reducing the electrostatic stabilization of the transition state. It should be emphasized that this stabilization must be fairly substantial in order for $\Delta G_m^{\ddagger}$ (reaction in the micellar phase) to be lower than $\Delta G_{bulk}^{\ddagger}$ (maximum rate enhancement for Ib, p 48 with CTAB is about five), because starting ester is stabilized considerably by incorporation into the micelles. Exclusion of the substrate from the micelles by added salt is not a factor, as K values measured in the presence of salts are substantially the same as in their absence. Further, exclusion of substrate from the micellar phase cannot explain the results obtained with added nitrate and bromide ions. Lapinte,[176] in a study of hydroxide ion

catalyzed elimination and substitution reactions for 1-bromo-2-phenylpropane in the presence of CTAB, has found the explanation of electrostatic stabilization as a major factor in micellar catalysis inadequate.

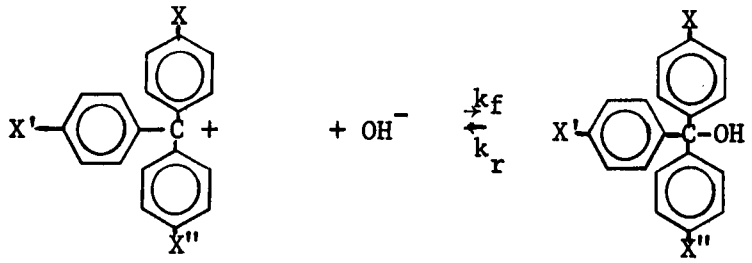
The order of inhibitory effectiveness for the anions is the same as their ability to decrease the CMCs and raise the aggregation numbers for cationic surfactants (i.e., the anions form a lyotropic series);[29,47,67] the fraction of bound counterions should increase in the same order.

The rate maxima with varying surfactant concentration observed with these ester hydrolyses can be explained by counterion inhibition, according to Cordes, since the counterion concentration increases as the surfactant concentration increases. If the total counterion concentration is maintained constant, while the surfactant concentration increases, no inhibition is observed.

Cordes[179] has also investigated the hydrolysis of Ia and Ib (p 48) in the presence of CTAB with leucine and morpholine. The reactions with leucine are accelerated (it bears a negative charge), while the reaction of Ib with morpholine is slightly inhibited by CTAB. The pK_a of the corresponding conjugate acids of leucine and morpholine are unaffected by the presence of surfactant. These results seem to point to the importance of proximity effects (getting the reagents together) even though some bimolecular reactions can occur when one reagent is incorporated into the micellar phase and the other excluded from it.[65] This is indicated for CTAB by a study of azo dye formation involving p-nitrobenzenediazonium ion and naphtholsulfonates.[182] The authors

assume the organic cation is not incorporated into the CTAB micelle. Letsinger[183] has also looked at proximity effects in the CTAB micelle, observing fluorescence quenching for certain aromatic groups in the presence of 4-methoxy-1-nitronaphthalene.

Another class of bimolecular reactions studied in the presence of CTAB is the alkaline fading of triphenylmethane dyes. The original work is that of Duynstee and Grunwald,[173] who used a series of dyes; the reaction has recently been reexamined by Cordes[184] for crystal violet with CTAB and its homologues. The fading reaction, Equation 14, involves conversion of a cation into an alcohol. One-hundredth molar



(14)

CTAB accelerates the rate of the fading reaction for crystal violet [X,X',X" = $-N(CH_3)_2$], malachite green [X = H, X', X" = $-N(CH_3)_2$], brilliant green [X = H, X',X" = $-N(C_2H_5)_2$] and rosaniline (X,X',X" = NH_2; 3-CH_3); the ratios of the pseudo first-order reaction rates with hydroxide ion in the presence of CTAB to the rates in water are 14.1 (pH 12), 8.6 (pH 10.2), 18.2 (pH 10.2), and 1.2 (pH 10.2) respectively.[173] Note particularly the wide variation in the ratios with small variations in substrate structure. In this connection only the values at a single pH should be directly compared; pH 10.2 was produced using a 0.05 M boric acid-sodium borate buffer, while pH 12 was produced using sodium hydroxide. The reaction of water with these dyes is inhibited by the presence

of CTAB micelles. The equilibrium between cation and alcohol is shifted to the right in the presence of CTAB, which is consistent with Hartley's rules[185] for micellar effects on the position of equilibria involving charged reactants and products: $+ \rightleftarrows 0$ will be shifted to the right. Duynstee and Grunwald found no effect of CTAB on the position of the visible absorption bands for the dyes studied. With NaLS in contrast there was a significant red shift. They still feel, however, that some sort of short-range interactions is operating, so that most of the dyes' molecules are associated with micelles in some way. Apparently electrostatic repulsion between the positively charged micellar surface and the dye's cationic form is overcome by hydrophobic interactions. This work was carried out using substrate concentrations of 10^{-5} M, ensuring enough micelles to obviate any saturation effects.

Cordes[184] concentrated on one dye, crystal violet, and studied the effects of surfactant concentration, chain length, and the addition of salts on the rate of the alkaline fading reaction. Alkyltrimethylammonium bromides, $RN^{+}Me_3X^{-}$ from R = $C_{10}H_{21}^{-}$ to $C_{18}H_{35}^{-}$, were used; the reactions were run at 30°, while Duynstee and Grunwald's work was carried out at 25°. For a given surfactant, the rate versus surfactant concentration plot reaches a maximum then decreases; the ratio k_m/k_o (rate in micellar phase divided by rate in bulk solvent) depends on the chain length of the surfactant. For CTAB, C_{max} (the concentration at which maximum rate enhancement occurs) is 0.008 M, and $k_m/k_o = 27.5$. As the chain length of the surfactant increases C_{max} is displaced to lower concentrations, the same behavior observed in ester hydrolysis. Cordes

finds, however, that even after corrections for decreasing CMC values are made, the equilibrium constant for adsorption of crystal violet onto the micelles increases rapidly with increasing chain length of the surfactant; he characterizes his results as the most striking example of chain length dependence yet observed. Even when complete association with the micelle occurs, the substrate reacts more rapidly in the presence of the more hydrophobic[184] (i.e., longer chain) surfactants; Cordes originally felt this was not associated with direct hydrophobic contributions to the activation energy, but rather to electrostatic or medium effects. The reason for his conclusion was that a plot of k_{max}, the maximum observed rate for the fading reaction, versus N, the number of carbon atoms in a surfactant monomer, begins to level off at N = 18, even though hydrophobic interactions (judged by rate versus concentration profiles) should still be increasing. Cordes[186] has recently revised his position on hydrophobic contributions to the activation energy, however, admitting that hydrophobic interactions may play a direct role in the catalysis.

The fading reaction is quite sensitive to added salts. At 0.01 M CTAB the series $F^- < Cl^- < Br^- < N_3^- < NO_3^-$ is observed for inhibitory effectiveness, the same series observed for ester hydrolyses. The same explanations for the series are used.

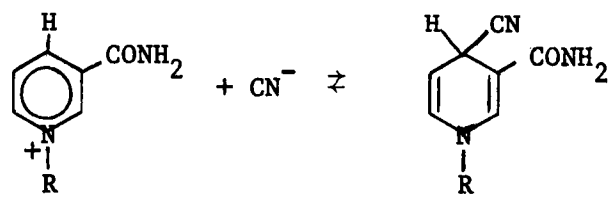
Bunton[187] and coworkers have looked at another triphenylmethane dye ($X,X',X'' = -OCH_3$) in the presence of CTAB; they found the same effects observed by Duynstee and Grunwald on the equilibrium between cation and alcohol. CTAB was found to have no effect on the rate of the reaction of

the cation with water, Equation 15. However, k_r is sharply decreased

$$R^+ + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ROH + H^+ \qquad (15)$$

in the presence of CTAB. Bunton interprets the absence of any cationic micellar effect on k_f to mean that R^+ is excluded from the micellar pseudophase. The CTAB concentrations used in these experiments were very low, generally 10^{-3} M or less. Because of the presence of added electrolytes, it is assumed that the concentrations are above the CMC for CTAB. Bunton also finds that CTAB has little effect on the reaction of the tri-p-anisyl carbonium ion with hydroxide or azide ions, but the maximum CTAB concentration used was 10^{-3} M. It is assumed that this work is not incompatible with that of Cordes and Duynstee and Grunwald. Bunton's surfactant concentrations were at a level which may have produced only a slight rate increase.

Cordes has investigated another system in which hydrophobic substrate-micelle interactions may contribute to the lowering of a reaction's activation energy: the addition of cyanide ion to N-substituted 3-carbamoylpyridinium ions,[188,189] Equation 16. CTAB and its



(16)

II

IIa R = C_8H_{17}- IIc R = $C_{12}H_{25}$- IIe R = $C_{16}H_{33}$-

IIb R = $C_{10}H_{21}$- IId R = $C_{14}H_{29}$- IIf R = $C_{18}H_{37}$-

homologues, $R'N^+Me_3Br^-$ ($R' = C_{10}H_{21}-$, $C_{12}H_{25}-$, $C_{14}H_{29}-$) were found to increase the rate of addition and the magnitude of the equilibrium constant K for the reaction. Appearance of the initial product (it undergoes slow rearrangement to adducts with the cyano group at the 2- or 6- position) was monitored spectrophotometrically; concentrations of substrate were around 10^{-4} M, and the pH of the solutions was approximately 10 to 11. A wide range of surfactant concentrations was used.

The catalytic effects observed are quite large. For IIe (p 57) and 0.02 M CTAB (C_{max}, approximately), k_m/k_o (ratio of second-order rate constants for the addition of cyanide) is 950; K_m/K_o, the ratio of the equilibrium constants in the micelles and bulk solution is 25,000. Plots of k_m versus surfactant concentration show the characteristic rate maxima seen with other bimolecular reactions. It is interesting to note that C_{max} for CTAB in this case is much higher than it was in the ester hydrolysis work. A simple explanation would be a difference in substrate-micelle association constant, so that complete incorporation in the case of II requires a higher concentration of CTAB than in the ester case.

Both the rate and equilibrium constant for the addition of cyanide increase for a given surfactant on going from IIa through IIe. The pyridinium ions as the bromide salts do show a slight shift of UV absorption maxima ($\simeq$ 271-272 nm) to higher wavelength in the presence of CTAB as the chain length of R increases (IIa to IIe). This suggests an increasingly polar environment for the pyridinium groups, which is to be expected, since the radius of the CTAB micelle is assumed fixed by the length of its extended hydrocarbon monomer chains.

The effect of surfactant concentrations up to 0.08 M was studied for the case of tetradecyltrimethylammonium bromide (C_{max} = 0.02 M) at 25°. Both k_m and K_m decrease with increasing surfactant concentration, but the effects are not nearly as large as in the case of ester hydrolysis. Studies of IIa-IIe (p 56) in the presence of 0.174 M CTAB show a chain length dependence for k_m and K_m (i.e. increasing hydrophobicity of the substrate), but the effect is not as marked as at the lower concentrations of CTAB. The CTAB micelles cannot be spherical at the higher concentration.[13,20,70]

Salt effects on the addition reaction are not nearly as marked as in the case of ester hydrolysis, and a different order of inhibitory effectiveness is found: $F^- < NO_3^- < Cl^- < Br^-$. Nitrate ion is out of place. The salt effects were studied using 0.02 M $C_{14}N^+Me_3Br^-$ with IIc at 30°. Concentrations of added salt went as high as 0.5 M; under these conditions spherical micelles are probably unlikely.

Cordes cites a number of possible contributing factors to the large rate enhancements in the presence of surfactants observed in the addition of cyanide ion to N-substituted 3-carbamoylpyridinium ions: (1) electrostatic destabilization of the ions (compared to the transition state for addition) by the positively charged micelle surface, (2) concentration of cyanide ion at the micelle surface by electrostatic attraction and (3) hydrophobic interactions between substrate and micelle (and transition state and micelle), contributing to a lower overall free energy change. He initially suggests that since the k_m and K_m depend on surfactant chain length for a given substrate, and electrostatic factors

are important, the effect may be explained by better organized micelle surfaces (higher surface charge density?). However, increasing substrate hydrophobicity is also important. This may be an orientation effect, with the pyridinium group being brought closer to the micelle surface (by increasing micelle-substrate hydrophobic interactions), where increased electrostatic destabilization can be felt. This argument seems a bit surprising, since one would expect the pyridinium group to be as close to the micellar surface as possible from dielectric constant considerations. In addition, the ring position to be attacked by cyanide ion must be accessible.

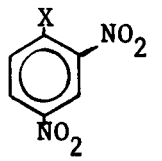
Substrate-micelle hydrophobic interactions were also observed by Gitler and Ochoa-Solano[190] in their work on p-nitrophenyl ester hydrolysis using mixed micelles of CTAB and N^{α}-myristoyl-L-histidine. Their interpretation of the lowering of the activation energy for the hydrolysis by these interactions is worth considering. They found that the logarithm of the second-order rate constant for the ester hydrolysis in the micellar phase increased linearly with the chain length of the ester (see Ia,b,c, p 48). The free energy change per methylene group necessary to account for the change in the rate constant was 0.442 kcal/mole, which is a reasonable value[191] for the transfer from water to the micellar interior. Note that no differences in orientation of the ester substrate were invoked to explain the chain length dependence.

Cordes concludes that the results he obtains at high surfactant concentrations are independent of micellar shape and size because no sharp transitions in dependence of k_m on surfactant concentration are

observed for tetradecyltrimethylammonium bromide over the concentration range studied. He makes no comment on the substrate chain length dependence for k_m and K_m obtained at two different concentrations of CTAB, noting only that k_m and K_m increase with increasing chain length at both concentrations. The magnitude of the variations is certainly much smaller at the higher CTAB concentration.

In contrast to the results observed with pyridinium ions and triphenylmethane dyes, reactions between a cation and anion are not always catalyzed by CTAB. Thus hydrolysis of some Schiff bases in the alkaline pH region is unaffected by CTAB.[192] In some cases, marked inhibition of the hydrolysis is observed (this is for the reaction of water with the protonated Schiff base).[193,194] At the alkaline pHs the rate-determining step in this reaction is found to be the attack of hydroxide ion on the protonated form of the Schiff base. However, the association constant for a protonated Schiff base with the CTAB micelle is less than for the neutral molecule; the protonated Schiff base has a significantly lower pK_a in the micellar phase than in water. Cordes[192] used fairly high concentrations of substrate in his Schiff base studies; he observed no saturation of the micelles with substrate, indicating that the association constants are true constants.

There are a number of other bimolecular reactions which are catalyzed by CTAB micelles which should be considered. Nucleophilic aromatic substitution reactions using III as substrate and both neutral



IIIa X = F
IIIb X = Cl

III

and anionic nucleophiles as the attacking species have been studied.[195-199] Bunton's publications dealing with III (p 60) will be considered together; a few cationic surfactants related to CTAB (modified head groups) will also be included.

This reaction shows the characteristic rate maxima when k_2, the observed second-order rate constant, is plotted against the concentration of surfactant used. For CTAB C_{max} is much higher for the reaction of IIIa or IIIb with hydroxide ion than the C_{max} values found for ester hydrolysis by Cordes. For IIIa, C_{max} = 0.02 M, and the rate enhancement is 60; for IIIb, C_{max} = 0.015 M, and the rate enhancement is 61.[199] The reactions are followed spectrophotometrically; hydroxide ion concentration is generally 0.01 M, with the substrate concentration in the 10^{-4} M range. Bunton finds the C_{max} values reasonable, commenting that one would expect a lower substrate-micelle association constant for the fluoro compound. He measured K for IIIb by solubility measurements, but IIIa is too reactive for this method to be applied: it undergoes hydrolysis slowly in the presence of CTAB even at low pH.[196] The reported K for IIIb is 4600;[195] since Bunton erroneously uses Anacker's value of n = 61 (for DTAB)[127] for CTAB,[70,105] K is actually 7125. In addition, one cannot directly compare a K quoted by Bunton with one quoted by Cordes (Equation 13, p 49), since Bunton uses the concentration of micelles, not the concentration of surfactant, in calculating K (Equation 17). When K is determined from kinetic data,

$$K = [\text{substrate}]_{mic}/[\text{substrate}]_{bulk}\ (C\text{-}CMC)/n \qquad (17)$$

n is the aggregation number of the micelles only when one assumes binding of one substrate molecule per micelle.[55] If more than one binding site per micelle is available, n is smaller than the aggregation number.

Fendler and Fendler[1] have pointed out that solubility measurements are inferior to gel filtration as a method for determining K. Solubility measurements rely on data for saturated solutions only; one must certainly worry about the difference in the activity coefficient of a substrate in the micellar phase under conditions of saturation versus more dilute conditions. For Schiff bases Cordes has observed a constant K in the presence of CTAB as the concentration of substrate increased, indicating no activity coefficient problem in at least one case.[192] There is also the problem of substrate-induced alterations of micellar properties: a decrease in CMC and an increase or decrease in the size of the micelles is probably to be expected.[2] Data should be obtained for a variety of substrate concentrations below saturation in order to obtain Ks which apply to kinetic conditions. The substrate-micelle association constant K may also be obtained from the variation of k_2 (the observed second-order rate constant) with surfactant concentration, according to an equation developed by Menger and Portnoy.[180] The term C_n represents micellar

$$\begin{array}{ccccc} C_n + S & \overset{K}{\rightleftharpoons} & C_nS & & \\ \downarrow k_2^{w} & & \downarrow k_2^{m} & & \\ P & & P & & \end{array} \qquad (18)$$

surfactant, S is free substrate and C_nS represents substrate incorporated into the micellar phase. The rate constants k_2^w and k_2^m are for the second-order reaction in water and the micelle respectively. The concentration of C_n is equal to (C-CMC)/n where C is the total concentration of surfactant. This treatment also involves the assumption that only one molecule of substrate will be associated with one micelle. This is a reasonable assumption for the systems studied by both Bunton and Cordes. Equation 19 describes this kinetic scheme.

$$1/(k_2^w-k_2) = 1/(k_2^w-k_2^m) + 1/(k_2^w-k_2^m)K[C_n] \quad (19)$$

Plots of $1/(k_2^w-k_2)$ versus $1/[C_n]$ can then be used to obtain both k_2^m and K. This equation is adequate only for cases where a plateau in the k_2 (observed second-order rate constant) versus surfactant concentration plot is observed, since rearranging it gives Equation 20.

$$k_2 = (k_2^w + k_2^m K[C_n])/(1 + K[C_n]) \quad (20)$$

In cases where a rate maximum is observed, e.g., IIIb (p 60) plus hydroxide ion, an additional term is added to the denominator, of the form $a[C_n]^2$. At C_{max}, k_2^w can be neglected; this enables a to be determined: $a = n^2/(C-CMC)^2$. Bunton finds the K obtained using this approach for IIIb to agree rather closely with that obtained with solubility measurements. K for IIIa could not be obtained by this method either.[196]

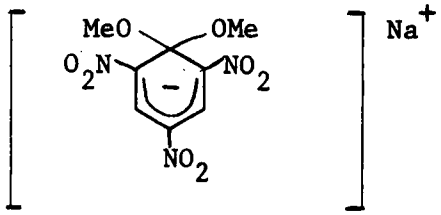
There is an unfortunate result of Bunton's K and C_{max} values for the reaction of IIIb with hydroxide ion in the presence of CTAB.

It is conventionally assumed that at C_{max} virtually all of the substrate is incorporated into the micellar phase. This is the case for the hydrolysis of p-nitrophenyl hexanoate, for example. However, for IIIb (p 60), $K = 7125 = [S]_{mic}/[S]_{bulk}[C_n]$; $[C_n] = 1.525 \times 10^{-4}$ M (CMC is chosen as 0.0005 M because under kinetic conditions considerable NaOH is present; n = 95).[70] Therefore $[S]_{mic}/[S]_{bulk} = 1.09$; the substrate is about equally distributed between the micelle and the bulk solvent. If one could assume that IIIa and IIIb are largely incorporated into the micellar phase at C_{max}, the difference between their binding constants and that of p-nitrophenyl hexanoate, for example, could be used to explain the variation in C_{max}.

Bunton has investigated the effect of surfactants related to CTAB on the reaction of IIIa and IIIb with hydroxide ion. One type contains an aromatic ring in place of one of the N-methyl groups:[198] $ArN^{+}RMe_2Br^{-}$ or $ArCH_2N^{+}RMe_2Br^{-}$ (R = $C_{16}H_{33}$-), while the second group are dicationic surfactants:[199] $RMe_2N^{+}(CH_2)_nN^{+}Me_2R2Br^{-}$ (R = $C_{16}H_{33}$-, n = 2,4,6). All of these materials have lower CMCs than CTAB. For the first group of surfactants Bunton finds increased substrate-micelle binding, but no difference in k_2^m when compared to CTAB. However, k_2 is higher at C_{max} for the aromatic head group surfactants, due to the increase in K. The observed rate constant k_2 is also significantly increased for the reaction in the presence of the dicationic detergents n = 4,6; the rate enhancements are two to three times what they were in the presence of CTAB. In both cases there is increased substrate-micelle interaction, presumably of the hydrophobic sort; C_{max} is therefore lowered (assume

this is the result of increased Ks) but the environment where the reaction takes place is little changed on going from one of these cationic detergents to another. It is perhaps appropriate to note that the rate-determining step in the reaction of IIIa and IIIb (p 60) with hydroxide ion is attack of the nucleophile, rather than decomposition of the intermediate. If decomposition were rate-determining, one might expect to see retardation of the reaction by CTAB.

Fendler and Fendler[200] have observed that CTAB stabilizes the related Meisenheimer complex IV against decomposition. The observed



IV

rate enhancement is exclusively an enthalpy effect in the case of IIIa: $\Delta H^{\ddagger}$ decreases from 16.0 kcal/mole in water to 13.2 kcal/mole in the micelle (at C_{max}); the entropy change is 1 eu, from -9 to -10. For IIIb in the other hand $\Delta H^{\ddagger}$ decreases from 21.3 to 16.5 kcal/mole, but $\Delta S^{\ddagger}$ changes from -5.2 eu to -14.3 eu, an unfavorable entropy change. This is surprising in light of the fact that the substrate should have lost most of its translational entropy upon incorporation into the micellar phase. In order to obtain activation parameters one must investigate a reaction at more than one temperature; in the case of micellar systems this certainly leads to changes in micellar structure.[32,33]

CTAB also catalyzes the reactions of IIIa and IIIb (p 60) with neutral nucleophiles such as aniline, glycine, glycylglycine and glycylglycylglycine,[197] although the rate enhancements observed are more modest: approximately 3 to 30. The last three nucleophiles bear a negative charge on their free hydroxyl groups, but the reacting amino groups are uncharged. In fact, this series was investigated in order to determine whether the carboxylate group could serve as a means of "concentrating" nucleophile at the CTAB micellar surface. The rate enhancements are about the same in the three cases and significantly larger (30 versus 8) than those observed with aniline. Reactions with IIIb and these nucleophiles were carried out at 85° in order to get conveniently measurable rate constants; temperature effects on the micelles may be a problem.

The observed second-order rate constant k_2 decreases as the concentration of glycine, glycylglycine or glycylglycylglycine is increased; Bunton observed the same phenomenon with hydroxide ion. He interprets this effect as an increase in aggregation number of the micelles, hence leaving fewer micelles available for catalysis.

Bunton has used CTACl as a catalyst for the reactions of IIIa and IIIb with aniline and hydroxide ion; CTACl is more effective in both cases. However, the difference in effectiveness is much less in the case of aniline, indicating that a counterion inhibition mechanism is in operation. Bunton feels that a CTACl solution has more micelles at a given concentration than CTAB; he expects this to contribute to the rate difference also. It must be mentioned, however, that CTACl has

a higher CMC than CTAB, which would predict the opposite result. Aggregation numbers do not support Bunton's contention either.[71]

Cordes would explain the difference between CTAB and CTACl as lying in the difference of their counterions' affinity for the micelle surface; he feels counterions compete with hydroxide ion for binding sites. Bunton interprets inhibition by electrolytes as competition only when additional electrolyte, over and above what is present by virtue of partially dissociated counterions from the micelles, is added. Thus observed rate maxima for IIIa and IIIb (p 60) with hydroxide ions, for example, are due to the hydroxide ions being bound by micelles not containing a substrate molecule. In other words, as the surfactant concentration continues to increase above C_{max}, micelles containing no substrate compete for hydroxide ions with micelles containing substrates. Berezin[201,202] has also proposed that rate retardations at high surfactant concentrations are a consequence of decreased substrate concentration (the micelles now occupy a larger portion of the solution volume). The weakness in this argument is its inability to explain the difference between CTACl and CTAB mentioned above. For the acid-catalyzed hydrolysis of p-nitrobenzaldehyde diethyl acetal in the presence of NaLS, Bunton[203] has computed the true second-order rate constants in the micellar phase, taking into account the actual concentrations of hydrogen ions bound to the micelles. When this is done, there is no decrease in rate constant as the concentration of NaLS increases.

Bunton observes the typical lyotropic series in his electrolyte inhibition work; he finds the reactions of IIIa and IIIb with neutral

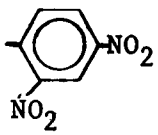
nucleophiles are much less sensitive to salt effects than the reaction with hydroxide ions. He has used several salts containing bulky organic anions of low charge density; these are more effective at inhibition than ordinary salts containing simple anions. Only small concentrations of the low charge density salts are needed for a significant rate decrease, and the magnitude of the decrease is larger for the salts containing organic anions. For IIIa (p 60) in 0.01 M NaOH, 0.025 M CTAB[196] the order of inhibitory effectiveness is as follows: $F^- < Cl^- < CH_3SO_3^- \approx SO_4^{2-} < Br^- < NO_3^- < C_5H_5CO_2^- \approx \underline{o}\text{-}C_6H_4(CO_2)_2^{2-} < \underline{p}\text{-}C_7H_7SO_3^- < C_{10}H_7SO_3^-$.

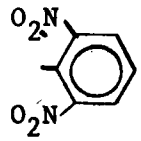
A few examples of modest catalysis of nucleophilic aliphatic substitution by CTAB or its homologues have also been observed. The second order rate constant for the reaction of n-pentyl bromide with thiosulfate ion in 25:75 w/w ethanol-water shows the characteristic rate maximum when plotted against CTAB concentration; $k_{obs}/k_{H_2O} = 9.5$.[195] The reaction of thiosulfate with sodium bromoacetate is even less sensitive to catalysis; CTAB is more effective than DTAB, indicating a dependence on the surfactant's hydrocarbon chain length.[204] When k_2, the observed second-order rate constant, is plotted against CTAB concentration for this reaction, one finds that the rate maximum has not yet been reached. Finally, Winters and Grunwald[205] have found that the reaction of cyanide ion with methyl bromide is accelerated by 0.302 M DTAB at 20°. The substrate-micelle association constant is 3.1 M^{-1} (Cordes' convention), and the second-order rate constant for reaction in the micellar phase decreases with increasing cyanide concentration. Obviously k_{obs}/k_{H_2O} then also decreases with increasing cyanide concentration.

In the case of neutral substrates, it is fairly well established that added electrolytes do not exclude the substrate from incorporation into the micelles. However, in studies of the spontaneous hydrolysis of aryl phosphate monoester dianions V[206] competitive inhibition was

$ArOPO_3^{2-}$

V

Va Ar = 

Vb Ar = 

found, with the anions (presumably) of added salts preventing incorporation of substrate into the micelle. The kinetic data could be described using Equation 21. It is assumed that incorporation of one molecule of inhibitor into the micelle is sufficient to prevent incorporation of substrate. This is a weak assumption, particularly for a simple anion such as chloride ion. Equation 22 relates k_{obs}, the first-order rate constant for hydrolysis of V by water at pH 9 (CTAB does not catalyze the reaction with hydroxide ions), to the remainder of the rate and equilibrium constants. The rate constants for the reaction in the micellar phase,

$$\begin{array}{ccccc} S + C_n & \underset{}{\overset{K}{\rightleftharpoons}} & C_nS & \xrightarrow{k^m} & P \\ \downarrow k^w & & I\downarrow\uparrow K_I & & \\ P & & C_nI & & \end{array} \qquad (21)$$

$$(k^m-k^w)/(k_{obs}-k^w) = 1 + n/K(C-CMC) + K_I[C_I]n/K(C-CMC) \qquad (22)$$

k^m, can be determined by the Menger and Portnoy treatment described earlier. The concentration of added inhibiting salt is $[C_I]$; a plot of $(k^m-k^w)/(k_{obs}-k^w)$ versus $[C_I]$ enables K_I to be determined. These plots are in general linear, with an intercept of unity, since $n/K(C-CMC)$ is a constant and small compared to one when working at a

single surfactant concentration. Bunton obtains K_I for the hydrolysis of Va and Vb (p 69) in the presence of 0.003 M CTAB at pH 9, 25° ranging from four for NaCl to 2800 for sodium tosylate.

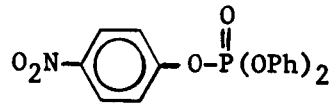
A rate plateau in the plot of k_{obs} versus CTAB concentration comes at 0.004 M CTAB. A maximum is apparently not observed because the mechanism is thought to involve Equation 23 as the rate-determining step. The maximum rate enhancement is about 25-fold and decreases with

$$ArOPO_3^{2-} \rightarrow ArO^- + PO_3^- \qquad (23)$$

increasing substrate concentration;[198] catalysis arises wholly as a result of a lowering of the enthalpy of activation for the reaction when carried out in the micellar phase. The substrate-micelle association constants (K) for Va and Vb are 1.1×10^5 M^{-1} and 3.9×10^4 M^{-1} respectively; these were calculated using kinetic data. Corrected to aggregation number 95 for CTAB they are 1.7×10^5 M^{-1} and 6.1×10^4 M^{-1}. At 0.004 M CTAB Va is 85% incorporated into the micellar phase. The fact that Bunton gets Ks indicating significantly less than 100% incorporation of substrate into the micelles may say something about the precision of the kinetic method for determining Ks.

Bunton has investigated a number of other phosphate ester hydrolyses[198,199,207-211] and reactions of these esters with other nucleophiles in the presence of CTAB and surfactants related to it (the related surfactants have already been mentioned in connection with nucleophilic aromatic substitution). Only a few features of this work will be considered here.

In general, the modified surfactants are found to be more effective catalysts than CTAB, both for the hydrolysis of Va and Vb (p 69) and for the reaction of fluoride or hydroxide ions with VI.[198,199]



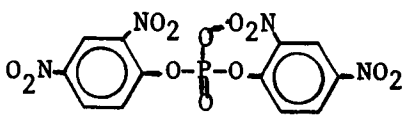
VI

The origin of this effect is increased substrate-micelle binding. The activation parameters for the reaction of VI with both fluoride and hydroxide ions indicate that the observed rate enhancement is due totally to the more favorable $\Delta S^{\ddagger}$ observed in the micellar phase (about -10 eu versus -23 eu in the bulk phase). $\Delta H_m^{\ddagger}$ is actually higher than $\Delta H_o^{\ddagger}$. Exactly the same entropy effect is observed with NaLS, which inhibits the reaction of fluoride and hydroxide ions with VI. Here $\Delta H_m^{\ddagger}$ is much larger than $\Delta H_o^{\ddagger}$ for the reaction. A chain length effect is also observed, because DTAB is not nearly as effective as a catalyst as CTAB is.[210] This indicates substrate-micelle hydrophobic interactions are important.

Bunton observes salt effects on these reactions analogous to those mentioned for the hydrolysis of Va and Vb (p 69). In the case of fluoride and hydroxide ions reacting with VI, $PhOPO_3^{2-}$ and $\underline{p}\text{-}\underline{t}BuC_6H_4OPO_3^{2-}$ are also very effective inhibitors.[208] Bunton mentions the importance of hydrophobic interactions in this connection. In his studies on the reaction of VI with hydroxide ions Bunton calculated ψ, the surface potential of the CTAB micelle, by assuming an hydroxide ion distribution of the form $C_{OH^-}^{\ m} = C_{OH^-}^{\ bulk}\, e^{-z\varepsilon\psi/kT}$, where ε is the

electronic charge. From this equation, $\psi = 2.3\ kT/\varepsilon\ [\log(k_\psi' - k_1) - \log k_2 - pH + 14]$, where k_ψ' ($k_\psi' = k_1' + k_2' C_{OH^-}$), k_1 and k_2 are rate constants for the following reactions: (1) spontaneous hydrolysis of VI (p 71), k_1, no detergent, k_1' in the presence of CTAB and (2) attack on VI by hydroxide ion, k_2, no detergent, k_2', in the presence of CTAB. He obtains $\psi = 107$ mV, which is in excellent agreement with the value 103 mV for the zeta potential for CTAB calculated by applying Booth's equation to electrophoretic mobility measurements.[212] However, Bunton compares it to values of the Guoy-Chapman potential and zeta potential for NaLS, which does not seem appropriate. Bunton uses the ratio of k_2'/k_2 for attack of hydroxide ions on VI as equivalent to the enhancement of the nucleophilicity of hydroxide ion in the presence of CTAB. This simple approach ignores the specific stabilizing effects of the micelle on the transition state for the reaction.

Hydrolysis of VII in the presence of CTAB and CTACl has been investigated[209] at high concentrations of these surfactants. One is considering the spontaneous hydrolysis reactions given by Equations 24(a) and 24(b). Plots of k_1 and k_2 versus surfactant concentration



VII

$$\text{(a)}\ (ArO)_2PO_2^- \xrightarrow[k_1]{H_2O} ArO^- + ArOPO_3^{2-} \qquad (24)$$

$$\text{(b)}\ ArOPO_3^{2-} \xrightarrow{k_2} ArO^- + H_2PO_4^- \ (H_2O + PO_3^-)$$

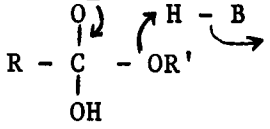
both exhibit plateaux. At high NaOH concentration, say 0.01 M, attack on VII (p 72) by hydroxide ions is observed. At pH 9, the use of CTAB up to 0.4 M has no effect on the hydrolysis rates: in fact, k_2 is increased by about 20% at about 0.1 M CTAB, and the plot of k_2 versus CTAB concentration again levels off. This is near, although slightly lower than the concentration at which the CTAB micelle changes from spherical to rodlike.[20] CTACl gives the same results as CTAB, which contrasts with their differing catalytic abilities in the nucleophilic aromatic substitution reactions discussed earlier. Salt effects on the hydrolysis are much larger in the case of attack by hydroxide ions, which occurs at high pH; they follow the lyotropic series pattern in both cases. However, their presence, even for the hydrolysis with water, must imply some sort of change in the micelles, for example a reduction of surface charge density. This makes the CTAB-CTACl results surprising. Bunton concludes that bromide ion does not have a significant kinetic effect on this reaction. This reinforces his belief that rate maxima observed in reactions where an anionic nucleophile is the attacking species come from inhibition of the nucleophile, i.e., it is bound to micelles not containing a molecule of substrate and hence inactivated. This is in contrast to Cordes' emphasis on competition for binding sites. Bunton further concludes that micellar size and shape effects are not kinetically significant, at least for this reaction.

In the ester hydrolyses considered thus far, the alcohol released upon hydrolysis is a substituted phenol. This offers distinct advantages in terms of ease in doing kinetics, obtaining rate constants

of convenient magnitude, and in using low concentrations of substrate. However, it is fortuitous for another reason: alkaline hydrolysis of simple alkyl esters, at least simple carboxylic acid esters, is not catalyzed by CTAB. Even in cases where benzene rings or a significant number of methylene groups are present in the substrate, rate enhancements have not been observed. For carboxylic acid esters possessing good leaving groups (pK_a of R'OH is low) the rate-determining step in a B_2 hydrolysis is attack of hydroxide ion on the carbonyl carbon of the ester, Equation 25. It is unlikely that B_1 hydrolysis is involved

$$R - \overset{O}{\overset{\|}{C}} - OR' + OH^- \xrightarrow{\text{slow}} R - \overset{O^-}{\underset{OH}{C}} - OR' \rightarrow R - \overset{O}{\overset{\|}{C}} - OH + {}^-OR' \qquad (25)$$

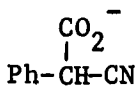
with any of the carboxylic acid esters considered to date. For simple alkyl esters however, slow assisted removal of OR' is possible,[213] as in VIII. In the micellar phase, less water would be available to serve as



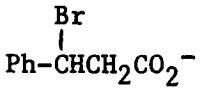
VIII

a proton source. However, significant inhibition is not observed, except in cases where one would predict the ester group is buried in the micelle core, e.g., Riegelman's work[214] on the alkaline hydrolysis of ethyl p-aminobenzoate (benzocaine). Furthermore, at least for long chain alcohols interaction with micelles is quite favorable,[159] which should enhance the rate of the reaction to the extent the transition state of the rate-determining step resembles the products (unfortunately, this is likely to be small).

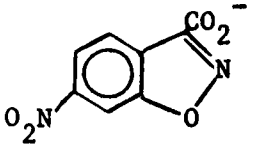
Bunton has examined micellar effects on another type of reaction, decarboxylation. The substrates (IX,[215] X,[215], XI[216-218]) studied are particularly interesting because positive salt effects occur for the micelle-catalyzed decarboxylations, rather than rate retardations by a lyotropic series of inhibitors. For IX and XI decarboxylation is much



IX

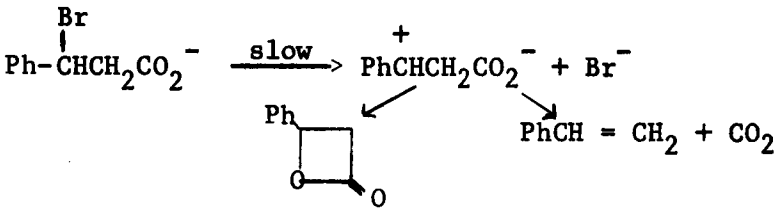


X



XI

faster in dipolar aprotic solvents than it is in water. This is thought to reflect differing solvation requirements for the initial and transition states. For X, the rate determining step, Equation 26, is loss of bromide ion, which is then followed by rapid decarboxylation or lactone formation. The product distribution is the same in the presence of



(26)

micelles as in their absence. Furthermore, the decomposition of X is farily insensitive to the nature of the solvent. Decarboxylations for all three substrates were followed spectrophotometrically; for IX and XI a plot of k_{obs} versus CTAB concentration shows a plateau.

The rate of decarboxylation for IX at pH 8 is enhanced 660-fold by CTAB at 25°, 360-fold at 33.2°. Activation parameters for the reaction in the presence of 0.15 M CTAB (note the very high surfactant

concentration) indicate that a favorable change in the enthalpy of activation is responsible: $\Delta H_m^{\ddagger}$ = 20 kcal/mole, $\Delta S_m^{\ddagger}$ = -8.5 eu. In the absence of CTAB the parameters are $\Delta H_o^{\ddagger}$ = 31.5 kcal/mole, $\Delta S_o^{\ddagger}$ = 21 eu. Bunton does not comment on the very large difference in entropies of activation, although it is unprecedented in view of other reactions studied. The rate enhancement is considered to reflect the greater stabilizing effect of CTAB micelles on the transition state for the decarboxylation compared to the starting material; CTAB is known to be very effective at interacting with low charge density anions, as indicated previously in the discussion of numerous salt effect studies. The transition state for decarboxylation of IX (p 75) will have negative charge spread over several atoms.

The course of IX's decarboxylation was followed spectrophotometrically at 235 nm; due to a low extinction coefficient, the substrate concentration used was in the 10^{-3} M range, which precluded doing an analysis of the kinetics in order to obtain K. The assumption of one molecule of substrate per micelle does not hold over the range of CTAB concentrations studied. In addition the salt effects of added benzoate and tosylate ions could not be studied, since these anions absorb at 235 nm. Of the salts which were studied (all at 0.15 M CTAB, 33.2°), all were found to modestly (less than a factor of two) increase the rate of decarboxylation: Na_2SO_4, NaCl, KCl, KH_2PO_4, and K_2HPO_4. Bunton interprets this as the result of a reduction of surface charge density for the micelles, which stabilizes the transition state more than the starting material, as well as

destabilization of the starting material by anion-anion repulsions experienced by the carboxylate group in the Stern layer. It is felt that Bunton has the Guoy-Chapman double layer and the Stern layer mixed up in this case:

> "On the other hand, this negative charge becomes delocalized into the carbanionlike transition state where it will be closer to the quaternary ammonium groups of the surfactant and therefore relatively unaffected by the anions in the Stern layer."[215]

The head groups are part of the Stern layer. Considering Bunton's choice of salts, it is felt that the reduction in surface charge density will be minimal, except perhaps for sulfate. Lapinte[176] disagrees with Bunton's interpretation of micellar stabilization of delocalized charge. He predicts that an S_N2 reaction will be catalyzed more effectively than an E2 reaction by CTAB because the transition state of the former reaction has charge spread over fewer atoms. Experimentally, however, he observes the opposite result.

The decarboxylation of X (p 75) is inhibited by CTAB; a plot of k_{obs} versus CTAB concentration levels off with increasing CTAB, indicating that its decarboxylation is slower in the micellar phase than in bulk solution. This is to be expected, since the rate-determining step for decarboxylation has considerable zwitterionic character. The addition of salts decreases the magnitude of the inhibition, with sodium tosylate being by far the most effective. Bunton interprets these results in terms of exclusion of substrate by salt from the micellar phase; why this should be important for X but not for IX (p 75) is unclear. Reduction of the micellar surface charge density might be expected to

improve the situation with respect to the zwitterionic transition state.

Decarboxylation of XI (p 75) is the most interesting in light of the salt effects observed. CTAB produces a 100-fold rate enhancement at 25°; the characteristic plateau is obtained. Changes in pH, buffer and substrate concentration (only to 1.5×10^{-4} M) have little effect, provided the pH is high enough to ensure the substrate being present in the ionized form only. The reaction was monitored spectrophotometrically at 410 nm; this enabled the use of a large number of salts.[217] At 0.02 M CTAB, using 0.002 M NH_3 buffer (pH 9) a number of salts were found to increase k_{obs} at all salt concentrations studied (0.0 to 0.8 M). Their order of effectiveness was CNS^- < pivalate < no salt < OH^- < acetate ≃ F^- < Cl^- < Br^- < SO_4^{2-}, which is a lyotropic series, except for the position of sulfate and possibly CNS^-.[218] The rate effects were again modest; the nature of the cation had no effect. Bunton feels the salt effects operate through increases in micellar size, which force the surfactant head groups closer together, resulting in stronger binding with molecules of XI. For another group of salts, those containing hydrophobic anions, the rate of decarboxylation was increased until a certain salt concentration, characteristic of the anion, was reached. Above these concentrations rather strong inhibition was observed. The following order of effectiveness was found: benzoate < $PhOPO_3^{2-}$ ≃ β-naphthalenesulfonate < tosylate. The C_{NaOTs} at which the maximum rate occurs is about 0.05 M; for 0.015 M CTAB addition of sodium tosylate causes increases in viscosity which reach a maximum at 0.03 M

NaOTs. Bunton believes the viscosity effects indicate a sphere to rod transition for the micelles, followed by tosylate binding converting the cationic micelles to anionic and once again spherical micelles. Transport experiments[55,218] support the formation of anionic micelles at high tosylate concentrations. NMR measurements show that the benzene ring interacts strongly with the N-methyl groups in the CTAB micelle. Other salts do not show these strong interactions.

Bunton interprets the salt effects[55,218] in terms of relative stabilization of the transition state for XI (p 75)(compared to the ground state) by the anions present at the micellar surface. At high tosylate concentrations anionic micelles are present; this prevents incorporation of XI into the micelles. Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decrease for this decarboxylation upon incorporation of the substrate into the CTAB micelles.[218] The value of $\Delta H_o^{\ddagger}$ is 29.4 kcal/mole; $\Delta H_m^{\ddagger}$ is 21.3 kcal/mole. Bunton believes that the decrease in free energy of the transition state upon incorporation into the micelles is greater than the decrease in free energy for the starting material upon incorporation. Since this difference is partially due to electrostatic interactions, $\Delta H^{\ddagger}$ changes. The value of $\Delta S_o^{\ddagger}$ is 15 eu; $\Delta S_m^{\ddagger}$ is -2.7 eu. Bunton feels that as negative charge is delocalized in the transition state for decarboxylation there are increased interactions between the charged head groups and the substrate. This leads to loss of freedom and the decrease in $\Delta S^{\ddagger}$.

C. Reactions Catalyzed by Sodium Dodecylsulfate

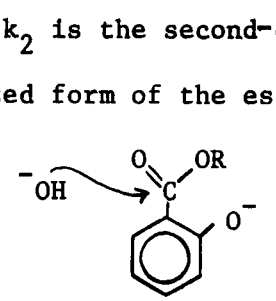
Thus far all discussion of catalysis by micelles of NaLS, the anionic surfactant commonly used for micellar catalysis studies, has been omitted. In general, the reactions catalyzed by NaLS are of a charge type opposite to those catalyzed by CTAB; the reactions will involve protonic attack and/or transition states bearing a positive charge. NaLS frequently inhibits reactions which are catalyzed by CTAB and vice-versa. Hydrophobic interactions between micelle and substrate are important; catalysis is sensitive to the nature of the cation of an added salt. The inhibitory effectiveness of salts frequently follows the lyotropic series for cations. Hydrophobic interactions between the cation and micelle can also be important, as indicated by the increasing inhibitory effectiveness of tetraalkylammonium salts as the length of the alkyl groups is increased. Cordes' work on the hydrolysis of orthoesters by NaLS and its homologues illustrates these considerations.[179,219,220]

D. Salicylate Ester Hydrolysis

In view of the strong and specific interactions observed for CTAB with salicylic acid (see Chapter II, Section B), it was felt that hydrolysis of salicylate esters in the presence of CTAB micelles might result in significant rate enhancements. Studies on the hydrolysis of acetyl salicylic acid,[221] acetyl salicylate[222] and phenyl salicylate[223] in water in the presence of CTAB and related surfactants showed no catalytic effects. Likewise alkaline hydrolysis of diethyl phthalate and

ethyl and propyl benzoate showed no acceleration in the presence of tetradecyltrimethylammonium bromide (TTMAB).[224] However, no data on micellar catalysis of alkaline hydrolysis of aliphatic salicylate esters has been obtained; it was expected that the favorable micelle-salicylic acid interactions might give a different result for these esters. In addition, the chain length of the ester's alcohol portion might have a considerable effect. To this end, the alkaline hydrolysis of methyl and hexyl salicylate was to be investigated in the presence of CTAB.

Several studies on the alkaline hydrolysis of salicylate esters have appeared; the dependence of the rate on the pH of the hydrolysis medium is especially noteworthy. Tommila[225] has investigated the hydrolysis of methyl, ethyl and isopropyl salicylates at high hydroxide ion concentrations (up to 1.6 M in the presence of 0.4 M ester); he finds the observed rate constant to have the form $k_1 = k_1' + k_2[OH^-]$, where k_2 is the second-order rate constant for attack of OH^- on the ionized form of the ester, XII, and k_1' is the



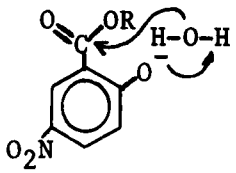
XII

first order rate constant for some unspecified hydrolysis process. For the m- and p-hydroxy esters, k_2 is much larger, so that only hydroxide ion attack on ionized ester is important.

Bender has investigated the hydrolysis of p-nitrophenyl salicylates over the entire pH range,[226] and he has studied the

alkaline hydrolysis of methyl salicylate.[227] As mentioned previously, for a good leaving group such as p-nitrophenoxide ion, the rate-determining step in the hydrolysis is clearly formation of the tetrahedral intermediates. For poor leaving groups, on the other hand, decomposition of the tetrahedral intermediate to give acid plus alcohol may be rate-determining. The rate of decomposition should at least be equal to the rate of formation. In the hydrolysis of p-nitrophenyl 5-nitrosalicylate two pH-independent regions are observed; only the one in the alkaline region is of importance to this work. For methyl salicylate there is no region where the rate is completely independent of pH, only an inflection point. See Figure 3 for the pH-rate profiles.

For the p-nitrophenyl ester Bender has good evidence that the mechanism in the pH-independent region involves intramolecular general base catalysis, XIII. He finds that when the hydroxyl group is replaced



XIII

by a methoxy group or a hydrogen, the hydrolysis in this pH region is only 1/1000th and 1/200th as fast, respectively (calculated assuming hydroxide ion attack on the unionized ester). For the ethyl ester, on the other hand, the large effect of the o-hydroxyl group is not seen; Bender has no explanation for this. Furthermore, use of sulfite ion, azide ion and imidazole as nucleophiles gives $k_{salicylate}/k_{benzoate}$ ratios close to one; if no general base catalysis is occurring these

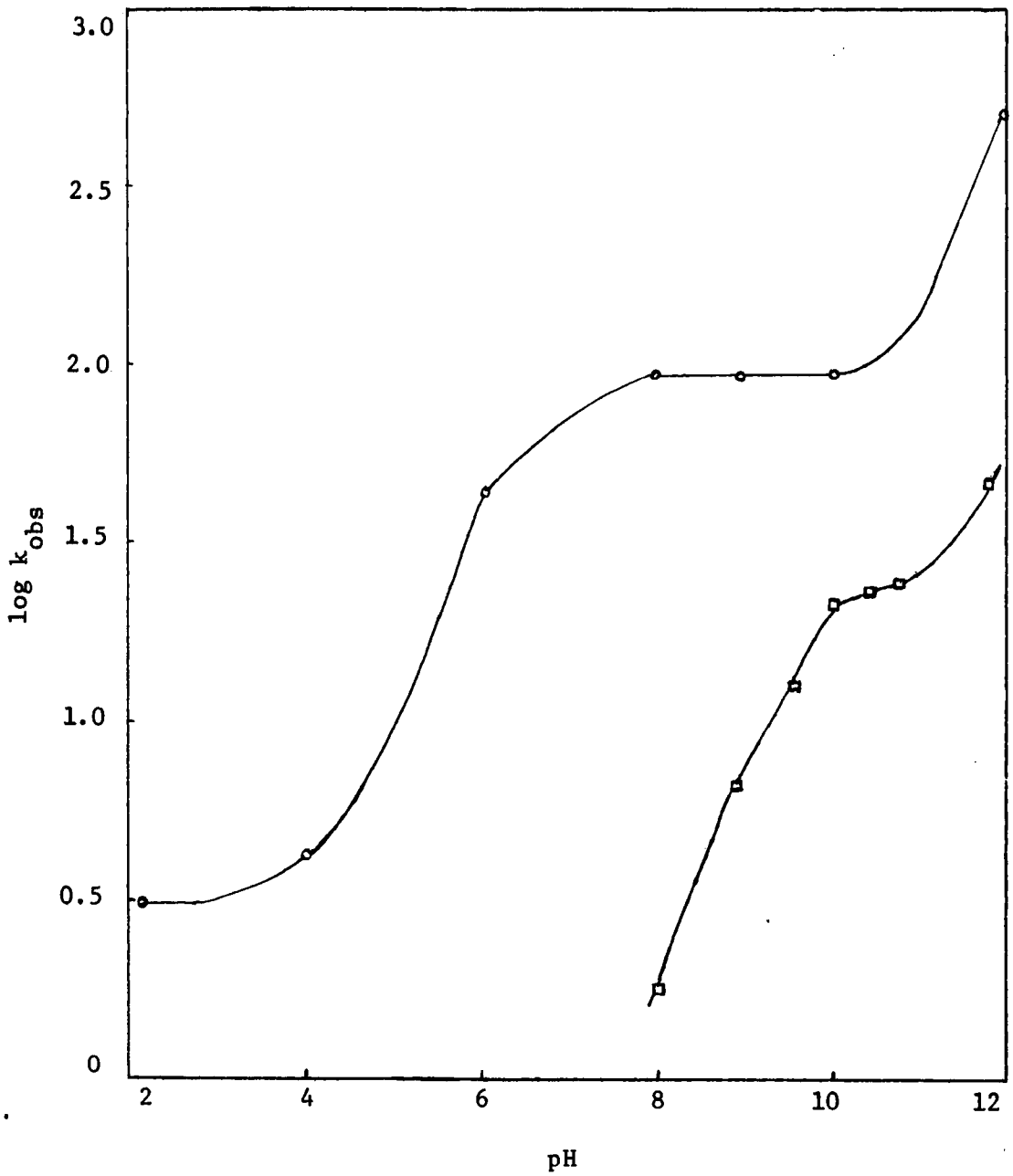


Figure 3. pH-rate profiles for the hydrolysis of p-nitrophenyl salicylate and methyl salicylate.

Circles: log k_{obs} + 6 for p-nitrophenyl 5-nitrosalicylate in 34.4% dioxane-water at 25°, squares: methyl salicylate in 1.15% acetonitrile-water at 60°.

ratios should be large: the o-hydroxyl group should exert its special effect, whatever it is, in all cases. Bender makes no suggestions as to the mechanism of hydrolysis in the case of methyl salicylate, but it can be reasonably supposed that both intramolecular general base catalysis and attack by hydroxide ion are occurring. This is compatible with Tommila's results. It is important to have a working picture of the mechanism, particularly in the region pH 9-12, where the studies on micellar catalysis of this reaction will be carried out.

The difference in pH-rate profiles for p-nitrophenyl 5-nitrosalicylate and methyl salicylate can be rationalized using the differences in their pK_as and the difference in rate-determining step. For the good leaving group in the plateau region above the pK_a, one has the following scheme (presumably 27 and 28 occur simultaneously):

$$\underset{(E)}{\text{ester}} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \underset{(T)}{\text{tetrahedral intermediate}} \xrightarrow{k_3} \underset{(P)}{\text{acid + alcohol (product)}} \qquad (27)$$

$$\underset{(E)}{\text{ester}} \underset{k_{-2}}{\overset{k_2[OH^-]}{\rightleftharpoons}} \underset{(T)}{\text{tetrahedral intermediate}} \xrightarrow{k_4} \underset{(P)}{\text{acid + alcohol (product)}} . \qquad (28)$$

Applying the steady-state assumption:

$$\frac{dP}{dt} = k_3[T] \quad \frac{dT}{dt} = k_1'[E] - k_{-1}'[T] - k_3[T] = 0; \quad [T] = \frac{k_1'[E]}{k_{-1}' + k_3}$$

$$\frac{dP}{dt} = \frac{k_3 k_1'[E]}{k_{-1}' + k_3} \quad \text{and } k_3 \gg k_{-1}'$$

$$\therefore \quad \frac{dP}{dT} = k_1'[E] \qquad (29)$$

$$\frac{dP}{dt} = k_4[T] \quad \frac{dT}{dt} = k_2[OH^-][E] - k_{-2}[T] - k_4[T] = 0; \quad [T] = \frac{k_2[OH^-][E]}{k_{-2} + k_4}$$

$$\frac{dP}{dt} = \frac{k_4 k_2[OH^-][E]}{k_{-2} + k_4} \quad \text{and } k_4 >> k_{-2}$$

$$\therefore \frac{dP}{dt} = k_2[OH^-][E] \quad . \tag{30}$$

Above the pK_a, E will be mostly in the ionized form; the overall observed first-order rate constant will be $k_1 = k_1' + k_2[OH^-]$. If the relative magnitudes of k_1' and k_2 are such that an hydroxide ion concentration greater than ca. 10^{-4} M is needed in order for the second term to make a significant contribution to k_1, then the plateau observed for p-nitrophenyl 5-nitrosalicylate is explained. For a poor leaving group on the other hand, the simplifying assumption about k_3 and k_4 cannot be made. (In addition, there will be protonation prior to decomposition of the tetrahedral intermediate.) However, the observed first-order rate constant will still be of the form $k_{obs} = k_5 + k_6[OH^-]$ where $k_5 = k_3k_1'/(k_{-1}' + k_3)$ and $k_6 = k_4k_2/(k_{-2} + k_4)$. For methyl salicylate the pK_a is 9.22[227] -10.2;[225] the $k_6[OH^-]$ term will be much larger than $k_2[OH^-]$ is at the pK_a of p-nitrophenyl 5-nitrosalicylate, provided that k_2 and k_6 are of comparable magnitude. To be of comparable magnitude, $k_4/(k_{-2} + k_4)$ should be approximately equal to one; this is reasonable.[202] The greater importance of the term containing $[OH^-]$ in k_{obs} for methyl salicylate is reflected in the presence of only an inflection point in its log k_{obs} versus pH plot.

In conclusion, one is dealing with both the reaction of water with ionized ester (intramolecular general base catalysis) and the reaction of hydroxide ion with ester, ionized or unionized. The higher the pH, the more important the latter reaction is.

CHAPTER IV

PROPERTIES OF CATIONIC MICELLES IN THE PRESENCE OF SODIUM BROMIDE

A. Hexadecyltrimethylammonium Bromide Micelle Sizes

Our early work in this area used viscosity measurements to get a rough indication of CTAB micelle sizes in the presence of sodium bromide. The impetus for this work was provided by Mr. Victor Payton, of these laboratories, who observed a large viscosity increase when benzene was added to 0.1 M CTAB in 0.1 M NaBr. It was of interest to determine the concentrations of various salts and organic solutes required for the production of solutions of high viscosity. In this Chapter the effect of NaBr only on the structure of the CTAB micelles will be emphasized. The effect of organic solutes and of salts other than NaBr will be dealt with in Chapters V and VI. A variety of techniques can be used to determine the size and shape of macromolecules and other colloidal particles. While not the most reliable technique, viscosity measurements can be made rapidly and cheaply. Also, since micellar size changes were first observed in these laboratories as viscosity changes, further exploration of this phenomenon was desirable.

Table I shows the changes in viscosity which occur when NaBr is added to a 0.1 M CTAB solution. The observed increases in viscosity are quite large. Solutions containing 0.15 M NaBr and up are non-Newtonian, that is the viscosity is some function of the rate of shear at which it is measured (in a Newtonian system the viscosity is

TABLE I

VISCOSITY OF 0.1 M CTAB SOLUTIONS AS A FUNCTION OF SODIUM BROMIDE CONCENTRATION AT 25°

[NaBr], M	η_{KE} (cP)	η_{rel} (to no salt)
--	1.234 ± 0.037	--
0.0010	1.184 ± 0.004	0.960 ± 0.029
0.0100	1.102 ± 0.003	0.893 ± 0.027
0.0500	1.520 ± 0.020	1.232 ± 0.044
0,0750	2.078 ± 0.047	1.684 ± 0.063
0.1000	4.422 ± 0.026	3.583 ± 0.110
0.1500	17.40 ± 0.28, 19[a]	14.10 ± 0.48, 15
0.2000	73[a]	59
0.5000	637[a]	516
1.0032	919[a]	745

[a]Shear rate is 25.3 sec^{-1}; data obtained using the Haake Rotovisco. All other points were obtained using capillary viscometers.

independent of the rate of shear). Appendix I, Table XLV gives apparent viscosities at several rates of shear for these non-Newtonian solutions. Table II shows the effect of adding NaBr to solutions containing 0.1 M CTAB and 0.025 M benzoic acid. Note that the presence of benzoic acid greatly enhances the effectiveness of NaBr in increasing the viscosity of this system.

A better indication of the micelle sizes in these systems could be obtained using constant concentrations of NaBr but varying the concentration of CTAB so that the intrinsic viscosities could be determined. The intrinsic viscosity $[\eta]$ for solutions containing macromolecules or colloidal particles is defined according to Equation 31,[228] where η

$$[\eta] = \lim_{C \to 0}(\eta - \eta_{solvent})/\eta_{solvent}C \qquad (31)$$

is the viscosity of a solution containing concentration C of the solute being studied. The viscosity of the solvent is $\eta_{solvent}$. In studying micellar solutions one uses a solution at the CMC as the solvent and C_m as the concentration of surfactant in micellar form ($C_m = C - CMC$). The expression for $[\eta]$ thus becomes Equation 32, where $\eta_{sp} = (\eta - \eta_{CMC})/\eta_{CMC}$

$$[\eta] = \lim_{C_m \to 0}(\eta - \eta_{CMC})/\eta_{CMC}C_m \text{ or } [\eta] = \lim_{C_m \to 0} \eta_{sp}/C_m \qquad (32)$$

or $\eta/\eta_{CMC} - 1$ or $\eta_{relm} - 1$. The resulting intrinsic viscosity is a measure of the shape and size of the micelles (or other particles) in solution. Equations which may be used to determine the particles' shape in solution have been tabulated.[228] Some estimate of the amount of water of hydration associated with each particle is required. Common shapes include spheres, prolate ellipsoids and rods; the tabulated equations

TABLE II

VISCOSITY OF 0.1 M CTAB-0.0250 M BENZOIC ACID SOLUTIONS AS A FUNCTION OF SODIUM BROMIDE CONCENTRATION AT 25°

[NaBr], M	η_{KE} (cP)
0.0049	1.263 ± 0.018
0.0104	1.718 ± 0.118
0.0450	110[a]
0.0511	98.35 ± 0.76
0.1000	460[a]
0.2027	924[a]

[a]Shear rate is 25.3 sec^{-1}; data obtained using the Haake Rotovisco. All other points were obtained using capillary viscometers.

enable calculation of axial ratios (p) for the particles. In the case of micelles aggregation numbers (sizes) are then obtained by assuming that the micelles' short axis is equal to the length of an extended surfactant molecule. The partial specific volume ($\bar{V}_{sp}$) for the micelles is also needed. This is determined by the variation of the specific volume (reciprocal of the density) of the micellar solution with concentration of the surfactant.

All of the systems listed in Table III have been investigated previously with KBr as the added electrolyte by at least one of the following methods: light scattering,[78,80] sedimentation,[78] diffusion[78] or viscosity.[70,78] It was of interest to compare results obtained solely by viscosity with the results obtained by other methods. In addition, it was desirable to extend the intrinsic viscosity work to CTAB-NaBr solutions containing organic solutes, an area where few micellar size data are available. It was therefore important to compare some of our experimental results with previously published results, as a check on technique.

The data in Table III were all obtained using capillary viscometers, even though some of the solutions are certainly non-Newtonian. Because of the short flow times of the viscometers used, it was difficult to work at concentrations close to the CMCs of these systems. Large deviations from a straight line or a higher-degree polynomial were observed in the η_{sp}/C_m versus C_m plots at low concentrations. See Appendix II, Tables XLVI, XLVII, XLVIII and XLIX and Figures 12, 13, 14, 15 and 16 for the raw data. Because the CMC was so low when high concentrations of NaBr were present, $\eta_{solvent}$ was used for η_{CMC}; a CMC of 10^{-5} M was

TABLE III

INTRINSIC VISCOSITIES [η] AND AXIAL RATIOS (p) FOR CTAB IN THE PRESENCE OF SODIUM BROMIDE AND POTASSIUM BROMIDE AT 30°

[NaBr], M	[η], ml/g[b]	p[g] prolate ellipsoids	p[g] rods	[η], ml/g[h]	p[g] prolate ellipsoids	p[g] rods	p (light scattering)[i] prolate ellipsoids	p (light scattering)[i] rods	KBr [η], ml/g	KBr p
--[a]	--	--	--	11.8 ± 0.2[f]	1.25	--	--	--	11.3[j]	1.0[j]
0.1000[a]	9.11 ± 1.5,[c] 9.25 ± 1.5[c,d]	7.5	10.	--	--	--	15	10.	--	--
0.1780	15.8 ± 0.4[c]	11.0	13.5	21.7 ± 0.5[c]	13.9	16.8	29.9	19.9	--	--
0.2000	11.3 ± 0.2[e]	8.8	10.7	26.8 ± 0.5[e]	16.0	19.3	33.6	22.4	20[k]	12.7[k]
0.2330	28.9 ± 2.8[f]	16.8	20.1	36.3 ± 3.2[b]	19.4	23.3	38.9	25.9	--	--
0.3000	40.7 ± 3.9[f]	20.8	25.0	54.4 ± 1.9[f]	25.0	30.0	48.6	32.4	45[k]	24.4[k]
0.4000	106.7 ± 4.0[c]	37.2	45.0	160.5 ± 6.0[c]	47.3	57.1	60.9	40.6	60[k]	23.1[k]

[a] Run at 25°.

[b] Calculated from relative viscosities computed using the viscosity of the appropriate NaBr solution (0.1780-0.4000 M NaBr only).

[c] Raw data fit to a fourth order polynomial, Appendix II, Table XLIX.

TABLE III (Continued)

[d]First value CMC = 7.95×10^{-5} M, second value CMC = 1.78×10^{-5} M.

[e]Raw data fit to a third order polynomial, Appendix II, Table XLIX.

[f]Determined by linear least squares analysis, Appendix II, Table XLIX.

[g]For prolate ellipsoids and rods respectively, "C. Sadron, Progr. in Biophysics, 3, 237 (1950).

[h]Relative viscosities computed using the viscosity of water (0.1780-0.400 M NaBr only).

[i]Calculated from micelle sizes obtained by light scattering, assuming prolate ellipsoids and rods respectively.

[j]P. Ekwall, L. Mandell and P. Solyom, J. Colloid Interface Sci., 35, 519 (1971).

[k]K. Granath, Acta. Chem. Scand., 7, 297 (1953).

used throughout the work at NaBr concentrations of 0.178 M and above. This introduces negligible error into the results. A plot of η_{rel} versus C for CTAB solutions gives a straight line, indicating no particle-particle interactions are occurring. However, interactions do occur in the CTAB-0.1 M NaBr solutions, indicating[229] that the CTAB concentration is really higher than it should be for intrinsic viscosity determinations. See Appendix II, Figures 17 and 18.

For CTAB without added salt Ekwall[70] has proposed that the micelles are very strongly hydrated. Assuming spherical micelles, the intrinsic viscosity may be expressed by Equation 33, where $\Lambda(p)$, a tabu-

$$[\eta] = (\bar{V}_{sp} + w/\rho)\Lambda(p) \qquad (33)$$

lated function of the suspended particles' axial ratio,[228] equals 2.5 and p is one. This results in w = 3.53 g/g of CTAB, where w is the associated water of hydration for the particles. On a molar basis, this is 71 moles of water per mole of CTAB. Ekwall supports his contention of strong hydration by using Eiler's relation for the voluminosity (V_o) of a suspended particle: the ratio between its hydrodynamically effective volume and its dry volume (i.e. $\bar{V}_{sp}$ for the micelles, obtained from density measurements). The viscosity data presented here also give a high voluminosity of CTAB without added salt: 4.16 ± 0.22 (4.1 ± 0.1, Ekwall[70]), i.e., CTAB seems to have strongly hydrated micelles. See Appendix II, Table L. Ekwall used Vand's equation[230] (Equation 34) for suspensions of spherical particles, where $A_3 = \Lambda(p)\bar{\nu}/2.303$, $\bar{\nu}$ is

$$\log \eta_{rel} = A_3C/(1 - Q'C) \qquad (34)$$

the hydrodynamic molar volume of the solute and η_{rel} is η_{relm} when micellar solutions are being investigated. Both methods indicate the hydrated micelle occupies about four times the volume of the unhydrated micelle.

It is important to point out that there will certainly be an electroviscous effect (E) operating in this system. Electroviscous effect is the term[5,90,231,232] used to describe the electrostatic contribution made by charged colloidal particles to the viscosity of a solution. The contribution is proportional to the square of the electrokinetic potential of the particles. The thicker the particles' double layers (the lower the ionic strength of the medium) the more pronounced the effect is. It is estimated that this effect for CTAB at 25° without added salt would reduce the intrinsic viscosity by a factor of 2.37. See Appendix II for the calculation of E. Therefore $[\eta]$ = 11.8 ml/g should be divided by E^5 prior to applying the equation which determines hydration. Doing this gives 4.98 ml/g = $(\bar{V}_{sp} + w/\rho)\Lambda(p)$. Furthermore, the CTAB micelle is probably slightly ellipsoidal,[21] with $\Lambda(p) = 2.55$. With $\bar{V}_{sp}$ = 0.980 ml/g,[70] and correcting for the electroviscous effect, the hydration of the CTAB micelle is then 0.97 g/g CTAB (twenty moles of water per mole of surfactant). This is much closer to hydration values reported for other surfactants[85,86,87] and seems much more reasonable than the value of 3.53 g/g CTAB reported by Ekwall. The value derived here is lower than Granath's hydration value of 2 g/g CTAB, obtained by ultrafiltration.[78] This may be the result of the use of different hydrodynamic methods involving different hydrodynamic entities. It is not surprising that Ekwall computes the same hydration values by three different methods, since all three methods use raw viscosity data. Each

experimental point should also be corrected for the electroviscous effect before computing the voluminosity.

Table III (p 92) also lists the axial ratios for CTAB micelles computed by Granath[78] using diffusion measurements and assuming the micelles are prolate ellipsoids. These computed axial ratios are not consistent with her reported intrinsic viscosity numbers. Granath also calculated the micellar molecular weights for the hydrated and unhydrated CTAB micelles at 30° in the presence of 0.2 M, 0.3 M and 0.4 M KBr from sedimentation and diffusion measurements. The weights for the unhydrated micelles were used along with Debye's[80] values for CTAB micelles in 0.178 M and 0.233 M KBr (determined by light scattering) to prepare a plot of the dependence of micelle size on salt concentration. Potassium bromide and sodium bromide should have similar effects on micellar size. A second-order polynomial from a nonlinear least squares fit of a plot of micellar size (literature values) versus log [salt] was used to obtain micelle sizes to be used in calculating axial ratios. These sizes, as aggregation numbers, are presented in Appendix II, Table LII.

From the aggregation numbers of CTAB micelles at various salt concentrations (determined from the second-order polynomial), axial ratios were computed. To do this, the volume per micelle was first computed for each aggregation number; these volumes were then used in computation of the micellar dimensions (see Appendix II, Table LIII). The axial ratios obtained using both a prolate ellipsoid model (minor half axis 24 Å, the length of an extended CTAB chain) and a rod model (radius 24 Å) for the CTAB micelles appear under the heading p (light scattering) in Table III.

Simha's equations as presented by Sadron[228] were used in calculation of axial ratios from our viscosity data; they should strictly be applied only to data obtained at low shear rates. Although capillary viscometers do not fulfill this requirement, the calculations of p were carried out in order to be able to do qualitative comparisons of micellar sizes in the presence of varying NaBr concentrations. The equations are also good only for large axial ratios (despite contrary statements by Sadron[228]); this is probably why our experimental axial ratios are smaller in the case of the prolate ellipsoid model than in the rod model case. The equation for $\Lambda(p)$ for prolate ellipsoids presented by Sadron is slightly in error; the correct equation (presented by Eirich[229]) is used.

The axial ratios corresponding to the intrinsic viscosity measurements in Table III (p 92) were computed neglecting hydration. Corrections for hydration would make the observed axial ratios even lower. For simplicity, $\bar{V}_{sp}$ was set equal to 1 ml/g in all cases. No correction for the electroviscous effect should be necessary at high salt concentrations. See Appendix II for the p calculations (Table LIV) and the actual partial specific volumes of CTAB in the various NaBr solutions (Tables LV and LVI). Comparison of the axial ratios obtained from intrinsic viscosity measurements and those computed from literature data on micelle size [p (light scattering)] shows reasonable agreement only for the rod model. The agreement is best for p (rod) values obtained from intrinsic viscosity values based on extrapolation of $(\eta/\eta_{H_2O} - 1)/C_m$, i.e. η_{sp}/C_m, to C_m equals zero. That is, η_{CMC} was approximated by the viscosity of water at 30°. The other set of

intrinsic viscosity values (column 2, Table III, p 92) was obtained using η_{CMC} equals $\eta_{x\ M\ NaBr}$. It is not surprising that the intrinsic viscosities and hence axial ratios obtained using different η_{CMC}s should be so different. At low concentrations of CTAB the experimentally observed η will be very close to η_{CMC}; a small error in η can produce a large error in η_{sp}/C_m. Mukerjee[36] has pointed out that the numerical values of intrinsic viscosities are very sensitive to the value of η_{CMC} also. Because the $[\eta]$ values have not been extrapolated to zero shear rate they are probably smaller than they should be. For non-Newtonian systems the viscosity decreases as the shear rate increases.

In drawing conclusions about the effect of added NaBr on CTAB micelle sizes (as expressed through p) it is probably safe to compare only $[\eta]$s determined using the same η_{CMC}, i.e. down a column in Table III. With regard to our p values obtained by intrinsic viscosity measurements being lower than those obtained from light scattering, Kushner[81] has observed the same sort of situation. For the surfactant dodecylamine hydrochloride he found that light scattering consistently gives larger micelle sizes than intrinsic viscosity measurements. For our purposes qualitative information is sufficient. Since the ability of increasing concentrations of NaBr to increase micelle sizes does show up nicely, all the values of $[\eta]$ being low is not serious. It should be pointed out that the intrinsic viscosities listed in Table III refer to micelles of average size in each case. Mukerjee[22] has determined that a range of micelle sizes exists for CTAB at high salt concentrations; this size distribution can be as large as a factor of two about the average micellar molecular weight.

An attempt was made to apply Vand's treatment, Equation 34 (p 94), to CTAB in the presence of 0.1 M, 0.178 M and 0.3 M NaBr. The values of A_3 obtained were 15.6, 26.6 and 43.9 ml/g respectively. These correspond to intrinsic viscosities of 35.9, 61.3 and 101 ml/g, assuming no hydration (see Appendix II, Table LVII). Since Vand's equation was derived for spherical particles and is good only up to relative viscosities five to ten times that of water,[233] the lack of agreement with the experimental results is not surprising.

The intrinsic viscosity results obtained in this work, while certainly not in quantitative agreement with other data on micellar size (e.g., data obtained by sedimentation, diffusion and light scattering) are useful in drawing qualitative conclusions about the effect of NaBr on the sizes of CTAB micelles. Clearly the micelles are not spherical (indicated by axial ratios greater than one), with the possible exception of the CTAB micelles in the absence of NaBr. The more NaBr is added to a CTAB solution, the larger the micelles become; this is indicated by the observed increases in $[\eta]$. In the case of CTAB micelles in aqueous solutions there is an electroviscous effect on the intrinsic viscosity; an attempt was made to estimate its magnitude. No great significance should be attached to the actual numerical value of the effect, but the fact that it does exist cannot be overemphasized. Neglecting it has previously[70] led to unreasonably high values for the hydration of CTAB micelles.

B. Temperature Dependence of the Interaction of Sodium Bromide with Hexadecyltrimethylammonium Bromide

Table IV contains data on the enthalpies of solution of sodium bromide in 0.1 M CTAB solutions containing 0.05 M and 0.1 M sodium bromide. It is not fully understood why the significant temperature dependence of $\Delta H_{s,NaBr}$ is found in the latter system. Micellar size is known to decrease with increasing temperature for ionic surfactants,[32] but enthalpies of micellization are ordinarily quite small, so that formation of additional micelles should not make a significant contribution to the observed heats. Some structural change in the micelles which is temperature-dependent may be responsible.

One can associate large heat capacities in aqueous solutions with a highly structured medium. A structure-making process in aqueous solution is associated with a loss of entropy occasioned by formation of clusters of water molecules about the added solutes. Our data suggest that the medium containing 0.1 M NaBr is more highly structured than the medium containing 0.05 M NaBr. Increased structure may be due to the formation of large rodlike micelles which induces an ordering effect, since the rods will tend toward a parallel orientation in solution. However, it is not possible to explain the inflection point between 38° and 42° on this basis. There is evidence which suggests that water structure decreases in the region from roughly 30° to 40°. The evidence includes a shallow minimum in the heat capacity of water at 35°,[234] inflection points in the intensity of an intermolecular IR absorption band for H_2O[235] and D_2O[236] in the region 30° to 40°, and maxima in ΔH and

TABLE IV

TEMPERATURE DEPENDENCE OF THE ENTHALPY OF SOLUTION FOR ADDITION OF SODIUM BROMIDE TO 0.1 M CTAB SOLUTIONS

Surfactant	T, °C	$\Delta H_{s,NaBr}$ kcal/mole
0.1 M CTAB	25 ± 1	-1.43 ± 0.12[a]
0.1 M CTAB-0.05 M NaBr	28.0 ± 0.2	-0.942 ± 0.025[a]
0.1 M CTAB-0.05 M NaBr	33.75 ± 0.25	-0.892 ± 0.069
0.1 M CTAB-0.05 M NaBr	37.65 ± 0.25	-0.895 ± 0.066
0.1 M CTAB-0.05 M NaBr	42.2 ± 0.2	-0.969 ± 0.107
0.1 M CTAB-0.1 M NaBr	28.25 ± 0.25	-0.281 ± 0.088
0.1 M CTAB-0.1 M NaBr	33.4 ± 0.1	-0.548 ± 0.062[a]
0.1 M CTAB-0.1 M NaBr	37.7 ± 0.03	-1.10 ± 0.01[a]
0.1 M CTAB-0.1 M NaBr	42.45 ± 0.15	-0.755 ± 0.033

[a]Concentration dependent. Extrapolated to infinite dilution by least squares analysis, see Appendix III, Tables LVIII and LIX.

ΔS at 34° for hydrocarbon-water interface formation.[237] The change in direction of $\Delta H_{s,NaBr}$ in the 0.1 M CTAB-0.1 M NaBr system between 38° and 42° may be a manifestation of this decrease (or "melting") of water structure. If this is true, water structure effects are more important in 0.1 M CTAB-0.1 M NaBr than in 0.1 M CTAB-0.05 M NaBr.

C. Bromide Ion Binding to Micelles of Decyltrimethylammonium Bromide, Dodecyltrimethylammonium Bromide and Hexadecyltrimethylammonium Bromide

Our earliest studies of bromide ion binding to the micelles of these surfactants were initiated to investigate whether the cationic head groups could be titrated with bromide ion. This was an attempt to investigate micelle structure in a manner analogous to protein titrations. Equation 35, adapted from the potentiometric behavior of poly-

$$\log(\alpha/1 - \alpha) - pBr = pBr_{int} - 0.868wn\alpha \qquad (35)$$

electrolytes containing basic groups,[238] was to be used to describe the results and determine the surface potential of the micelles involved. This requires values for the degree of dissociation (α) and the aggregation number (n) of the micelles. The surface potential of micelles containing dimethyldodecylamine oxide monomers[239] has actually been worked out in this fashion. In this case the titration behavior of the micelles was described by Equation 36, where ψ_o is the surface potential of the

$$pH + \log(\alpha/1 - \alpha) = pK_{int} - (0.434/kT)e\psi_o\alpha \qquad (36)$$

micelles. The effect of NaBr on α for the C_{10}, C_{12} and C_{16} trimethylammonium bromide micelles was also of interest because of Cordes',[178]

explanation of bromide ion inhibition of certain micellar catalyses with these surfactants. He explains inhibition of ester hydrolysis by NaBr in the presence of C_{10}-C_{18} trimethylammonium bromide micelles by invoking increased bromide ion binding to the micelles with increased NaBr concentration. It will become clear later that the observed dependence of α on NaBr concentration for $C_{10}NMe_3Br$, DTAB and CTAB is not of a form suitable for use in Equation 35 (p 102). While our work was in progress, Jones and Piercy[32] reported that α for DTAB was not dependent in any regular way on the concentration of added NaBr.

Table V presents the results for α at the CMC for the C_{10}, C_{12} and C_{16} trimethylammonium bromide surfactants. Pearson[103] has looked at these surfactants in the absence of added salt at 30°; he obtains α of 0.27, 0.24 and 0.12 respectively. Because CTAB has such a low CMC, it was not investigated in the presence of added salts.

The raw experimental data (a_{Br^-} at several concentrations of surfactant, above and below the CMC) were treated in two different ways to obtain α values. The first is due to Botré;[135] it requires independent knowledge of the CMC for the system under consideration. The necessary CMCs may be obtained by surface tension measurements or, in cases where the CMC is fairly high, from plots of log a_{Br^-} versus log total surfactant concentration.[103] The raw data were converted into experimental activity coefficients (γ_{expt}) by dividing a_{Br^-} by total surfactant concentration (C). Plots of γ_{expt} versus 1/C for concentrations above the CMC gave straight lines (Equation 37). The slopes (S) and

$$\gamma_{expt} = \alpha\gamma_s + \gamma_s CMC(1 - \alpha)(1/C) \qquad (37)$$

intercepts (I) of these straight lines could be used to determine αs,

TABLE V

INFLUENCE OF SODIUM BROMIDE ON COUNTERION BINDING FOR n-ALKYLTRIMETHYLAMMONIUM BROMIDE SURFACTANTS AT THE CRITICAL MICELLE CONCENTRATIONS AT 25°

[NaBr], M	CMC, M	γ_s	α
$C_{10}NMe_3Br$	0.0626 ± 0.0067[a]	0.736 ± 0.082[d]	0.240 ± 0.028[d]
	0.0626 ± 0.0067[a]	0.732 ± 0.078	0.248 ± 0.028
	0.059[b]	0.763 ± 0.028	0.238 ± 0.026
	0.050 ± 0.004[c]	0.869 ± 0.073	0.209 ± 0.019
0.0400	0.0510 ± 0.0081[a]	0.757 ± 0.070[d]	0.241 ± 0.023[d]
	0.0510 ± 0.0081[a]	0.756 ± 0.070	0.243 ± 0.023
	0.042[b]	0.818 ± 0.006	0.224 ± 0.019
	0.0385 ± 0.0015[c]	0.847 ± 0.018	0.217 ± 0.007
0.1000	0.0403 ± 0.0062[a]	0.743 ± 0.034[d]	0.227 ± 0.012[d]
	0.0403 ± 0.0062[a]	0.748 ± 0.034	0.234 ± 0.014
	0.030 ± 0.003[c]	0.794 ± 0.019	0.221 ± 0.010
$C_{12}NMe_3Br$(DTAB)	0.0139 ± 0.0006[a]	0.891 ± 0.040[d]	0.223 ± 0.012[d]
	0.0139 ± 0.0006[a]	0.896 ± 0.041	0.222 ± 0.010
	0.0145[b]	0.865 ± 0.002	0.230
	0.0105 ± 0.0015[c]	1.118 ± 0.163	0.178 ± 0.026
0.0300	0.00676 ± 0.00096[a]	0.867 ± 0.023[d]	0.266 ± 0.008[d]
	0.00676 ± 0.00096[a]	0.863 ± 0.024	0.279 ± 0.014
	0.0064 ± 0.0006[c]	0.868 ± 0.015	0.278 ± 0.015
0.1000	0.00440 ± 0.00035[c]	0.793 ± 0.020[d]	0.258 ± 0.087[d]
	0.00440 ± 0.00035[c]	0.791 ± 0.003	0.274 ± 0.012

TABLE V (Continued)

[NaBr], M	CMC, M	γ_s	α
$C_{16}NMe_3Br$(CTAB)	0.000910 ± 0.000011[a]	0.891 ± 0.011[d]	0.222 ± 0.005[d]
	0.000910 ± 0.000011[a]	0.896 ± 0.013	0.209 ± 0.003
	0.000789 ± 0.000003	0.921 ± 0.004[d]	0.215 ± 0.002[d]
	0.000789 ± 0.000003[a]	0.956 ± 0.130	0.203 ± 0.019
	0.00080 ± 0.00005[b,c]	0.996 ± 0.121	0.188 ± 0.023

[a]Determined from a plot of a_{Br^-} versus total surfactant concentration.

[b]Determined from a plot of log a_{Br^-} (millivolts) versus log total surfactant concentration.

[c]Determined by surface tension.

[d]Determined from a plot of a_{Br^-} versus total surfactant concentration; all others in γ_s and α columns determined from γ_{expt} versus (total surfactant concentration)$^{-1}$, where γ_{expt} is equal to a_{Br^-} divided by (total surfactant concentration).

using Equation 38. The intercept gives the product of α and γ_s, where

$$\alpha = CMC/(S/I + CMC) \qquad (38)$$

γ_s is the activity coefficient of the bromide ions at the CMC. For cases where NaBr was present, the slope of the γ_{expt} versus 1/C line is $\gamma_s CMC(1 - \alpha) + (x\ M\ NaBr)(\gamma_s)$. Assuming γ_s is a constant, which amounts to assuming a pseudophase model for micellization, the intercept of the line may be used in the form $\gamma_s = I/\alpha$ and substituted into the expression for the slope, from which α may be obtained.

The second method for calculating α and γ_s is due to Tokiwa and Moriyama,[240] who demonstrated that a plot of a_{Br^-} versus total surfactant concentration above the CMC has the slope $\alpha\gamma_s$. This again assumes that γ_s is a constant. The a_{Br^-} versus C plot including concentrations below the CMC can be used and the CMC located by the intersection of the two straight lines. From the activity at the CMC γ_s may be calculated; α is then obtained from the slope for the plot above the CMC. When added NaBr is present, the a_{Br^-} at the CMC is γ_s(CMC + added NaBr); it is assumed that the slope of the a_{Br^-} versus C line above the CMC is not affected by the presence of added salt. Note that the determination of γ_s by the Tokiwa method does not include the possibility of pre-CMC dimerization. The raw data, as straight lines determined by least squares analysis, as well as representative plots illustrating the two methods may be found in Appendix IV, Tables LXI and LXII and Figures 19, 20 and 21.

The results for counterion binding for the C_{10}, C_{12} and C_{16} trimethylammonium bromides at 25° without any added NaBr agree roughly with Pearson's results at 30°. With the exception of CTAB our α values

are slightly lower than his; this agrees with the dissociation of counterions from the micellar surface being endothermic. This work's value for CTAB does not agree with Pearson's value of 0.12 at all.[103] Two runs were made for this surfactant; the first run is represented in Table V by CMCs 9.1×10^{-4} M and 8.0×10^{-4} M, the second by 7.89×10^{-4} M. How long the CTAB solutions are allowed to stand prior to readings being taken can have a significant effect on the values of α obtained (they increase with time); fresh solutions were used in both cases (three to four hours old). The effect of solution age can be illustrated by a_{Br^-} values obtained for solutions over 24 hours old versus a_{Br^-} values obtained for fresh solutions: for 0.005 M CTAB, 0.00208 M versus 0.00157 M, for 0.002 M CTAB, 0.00118 M versus 0.00097 M and for 0.0015 M CTAB, 0.0010 M versus 0.000865 M.

The value taken for the CMC of a surfactant has an effect on the values of α and γ_s, so that only values obtained using a single experimental method for CMC determination should be compared. Doing this, one sees that α decreases slightly as the number of carbons in the long alkyl chain of the surfactant increases, but the effect is not nearly so large as that reported by Pearson. Pearson attributes the decrease in α to a closer packing of the ionic head groups in the micelles as the chain length of the surfactant increases. This results in an increase in the surface charge density of the micelles, which gives rise to a smaller α. An alternative explanation is possible. The free energy of micellization can be regarded as having three principal contributions: (1) hydrophobic interactions, especially between hydrocarbon chains, (2) Coulombic repulsion between the head groups

and (3) counterion association. Hydrophobic interactions favor closer packing of the surfactant chains (decrease in ΔG), but Coulombic repulsion opposes closer packing. Increased counterion binding decreases ΔG. If the hydrophobic term is large it is possible to have a more compact micelle without any contribution due to increased counterion binding. Pearson seems to conclude that an increase in the compactness of a micelle must result in an increase in counterion binding.

For the C_{10} and C_{12} surfactants the effect of added NaBr on α at the CMC is small or nonexistent, within experimental error, and there is no regular increase or decrease in α as NaBr is added. As mentioned earlier, the low CMC of CTAB precluded using the Botré or Tokiwa treatments in the presence of added NaBr. However, by using single concentrations of CTAB above the CMC and varying the concentration of added NaBr the desired effect of NaBr on α could be observed. The same technique was also used for the C_{10} and C_{12} surfactants. These data are presented in Tables VI, VII and VIII. The fraction of dissociated counterions, α, due to the micelle is equal to the free Br^- concentration due to the micelle divided by the concentration of surfactant in micellar form. The data were originally collected to use with the titration equation, Equation 35 (p 102), for polyelectrolytes, but the dependence of α on NaBr concentration is not of the proper form for use in the Equation for any of the surfactants. As the concentration of NaBr increases, micelle sizes will increase and closer packing of the head groups might be expected. This does not necessarily require increased counterion binding, as was discussed earlier.

Before the α values in Tables VI, VII and VIII could be calculated,

TABLE VI

COUNTERION BINDING FOR 0.2 M DECYLTRIMETHYLAMMONIUM BROMIDE IN THE PRESENCE OF SODIUM BROMIDE

[NaBr, M]	$[C_{10}NMe_3Br]$, M[a]	Free $[Br^-]$, M[b]	α	$[C_{10}NMe_3Br]$, M[c]	Free $[Br^-]$, M[b]	α	a_{Br^-}, M[d]	Free $[Br^-]$, M[e]	α	γ[f]	Free $[Br^-]$, M[g]	α
0.2000	0.1764	0.0504	0.29	0.1690	0.0430	0.25	0.1975	0.0340	0.20	0.720	0.0510	0.29
0.1000	0.1694	0.0460	0.27	0.1596	0.0366	0.23	0.1375	0.0442	0.28	0.800	0.0409	0.24
0.0750	0.1664	0.0454	0.27	0.1560	0.0350	0.22	0.1160	0.0367	0.24	0.820	0.0330	0.20
0.0500	0.1627	0.0457	0.28	0.1520	0.0350	0.23	0.1025	0.0396	0.26	0.837	0.0355	0.22
0.0200	0.1563	0.0388	0.25	0.1440	0.0265	0.18	0.0815	0.0330	0.23	0.860	0.0318	0.20
0.0100	0.1537	0.0391	0.25	0.1410	0.0264	0.19	0.0768	0.0341	0.24	0.865	0.0320	0.21

[a]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension used in the calculations.

[b]Due to micelles only; standard activity coefficients were used.

[c]Concentration of surfactant in micellar form; CMC values from Corrin plots of Br^- specific electrode results.

[d]Total observed activity from all sources of Br^-.

TABLE VI (Continued)

[e]Due to micelles only; calculated using $\gamma_s = 0.745$ and CMC values from Br^- specific electrode results.

[f]From observed dependence of γ_s on salt concentration when Br^- specific electrode results were used with surface tension CMCs. See Appendix IV, Figure 24.

[g]Usual corrections applied.

TABLE VII

COUNTERION BINDING FOR 0.075 M DTAB IN THE PRESENCE OF SODIUM BROMIDE

[NaBr], M	[DTAB], M[a]	Unstirred Free $[Br^-]$, M[b]	α	Stirred Free $[Br^-]$, M[b]	α	a_{Br^-}, M[c]	γ[d]	Unstirred Free $[Br^-]$, M[e]	α	Stirred Free $[Br^-]$, M[e]	α
0.1000	0.0709	0.0040	0.056	0.021	0.30	0.0845	0.795	0.0022	0.031	0.0185	0.26
0.0800	0.0705	0.0050	0.071	0.023	0.33	0.0725	0.812	0.0048	0.067	0.0187	0.27
0.0480	0.0696	0.0106	0.15	0.0201	0.29	0.0540	0.847	0.0103	0.15	0.0190	0.27
0.0200	0.0688	0.0140	0.20	0.020	0.29	0.0350	0.875	0.0128	0.19	0.0185	0.27
0.0100	0.0665	0.0160	0.24	0.0183	0.28	0.0290	0.885	0.0142	0.21	0.0174	0.26
0.0048	0.0655	0.0162	0.25	0.0187	0.29	0.0255	0.890	0.0144	0.22	0.0173	0.27
0.0020	0.0648	0.0150	0.23	0.0203	0.31	0.0235	0.892	0.0141	0.22	0.0173	0.27

[a]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension data.

[b]Due to micelles only; standard activity coefficients were used.

[c]Total observed activity from all sources of Br^-.

TABLE VII (Continued)

[d]From the observed dependence of γ_s on salt concentration when Br^- specific electrode results were used with appropriate CMCs. See Appendix IV, Figure 25.

[e]Usual corrections applied.

TABLE VIII

COUNTERION BINDING FOR CTAB IN THE PRESENCE OF SODIUM BROMIDE

[NaBr], M	0.005 M CTAB [CTAB], M[a]	Free [Br^-], M[b]	α	0.01 M CTAB [CTAB], M[a]	Free [Br^-], M[b]	α	0.1 M CTAB[c] [NaBr], M	α
0.0480	0.00497	0.0038	0.76	0.0100	0.0053	0.53	0.1000	0.19
0.0200	0.00493	0.0029	0.59	0.00993	0.0049	0.49	0.0800	0.14
0.0100	0.00488	0.0028	0.57	0.00989	0.0037	0.37	0.0480	0.20
0.0050	0.00481	0.0016	0.33	0.00981	0.0028	0.28	0.0200	0.22
0.0020	0.00465	0.0020	0.43	0.00965	0.0025	0.26	0.0100	0.23
0.0010	0.00450	0.0016	0.36	0.00950	0.0024	0.25	0.0080	0.23
							0.0048	0.23

[a]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension data.

[b]Due to micelles only; standard activity coefficients were used.

[c]No CMC corrections necessary; free [Br^-] corrected for added NaBr prior to calculation of α.

the concentration of surfactant and the amount of free bromide ion present in each solution had to be corrected for the amount of surfactant present as monomers, i.e., for the CMC. The dependence of the CMC on the concentration of NaBr was determined by using Corrin plots,[39] Equation 5 (p 12). The concentration of surfactant in micellar form is then total surfactant concentration minus the CMC. For each surfactant the Corrin plots were constructed by determining the CMCs at four different concentrations of added NaBr by surface tension measurements, and the best straight line was obtained by least squares analysis. See Appendix IV, Table LXIII and Figures 22 and 23 for these data. For decyltrimethylammonium bromide, which has the highest CMC of the surfactants studied, a Corrin plot was also constructed using CMC values obtained using the bromide ion specific electrode. This method generally gives higher values for the CMCs than surface tension does.

There are three sources of free bromide ion in surfactant solutions to which NaBr has been added. They are (1) Br^- due to the surfactant monomers of concentration equal to the CMC, (2) the Br^- from NaBr and (3) the Br^- present due to the dissociation of the micellar counterions. The concentration of added NaBr and the CMC are subtracted from the experimentally observed concentration of Br^- in each case in order to give the Br^- concentration due to source (3) only.

A number of different approaches were tried for converting the observed a_{Br^-} for each sample into a Br^- concentration. It was deemed important to determine whether the choice of activity coefficients would have a significant effect on the calculated values of α. In Table VI the first and second set of α values correspond to Br^- concentrations

obtained using standard activity coefficients for NaBr.[241] The third set of α values were computed assuming a constant γ_s (γ for Br^- at the CMC) of 0.745, the average of three γ_ss reported for decyltrimethylammonium bromide in Table V (p 104). These γ_ss were computed using CMCs from a_{Br^-} versus concentration plots for the surfactant. It is amazing that γ_s was found to be independent of NaBr concentration in this particular instance. The fourth set of α values were determined with γ_s values computed in Table V for decyltrimethylammonium bromide's surface tension CMCs. These γ_s values give a straight line when plotted against (added salt + CMC); the plot appears in Appendix IV, Figure 24. To get γ_s at the appropriate NaBr concentrations interpolation was used.

The resultant α values for decyltrimethylammonium bromide do not show a strong dependence on added NaBr concentration. Values computed using standard activity coefficients and using the nonconstant γ_s values from Table V show a slight increase in α with increasing concentration of NaBr. Use of a constant activity coefficient produced no trend at all.

It is felt that the α values obtained for DTAB (Table VII, p 111) in the presence of 0.08 M and 0.10 M NaBr are in error. These low values were obtained only in unstirred solutions. Such low values have never been reported for DTAB, even in light scattering experiments (Anacker and Ghose[47] report α equal to 0.17 for DTAB in 0.5 m NaBr). The concentration of DTAB in the micellar form was determined using surface tension CMCs only. The CMCs obtained from the bromide ion specific electrode gave a nonlinear Corrin plot. Again, one sees that the choice of γ makes very little difference in α. The effect of stirring on

counterion binding in surfactant solutions will be considered again later.

It is apparent that the choice of activity coefficients is not the determining factor in the values of α which will be obtained. This is useful when one works with a surfactant such as CTAB having a CMC (in the presence of NaBr) too low to determine activity coefficients by the Botré or Tokiwa methods. It is assumed this result can be extrapolated to work with CTAB.

For CTAB three different concentrations of surfactant were investigated; standard activity coefficients were used throughout. At the lowest concentrations of CTAB α increases with increasing NaBr concentration; these are in the concentration range commonly used to investigate micellar catalysis. Only for 0.1 M CTAB does any trend toward decreased dissociation (increased counterion binding) appear (Table VIII, p 113); the effect of stirring on counterion binding in this system is discussed later. Cohen[109] has also observed an increase in α for CTAB as bromide ion is added. He looked at the micellar charge of CTAB (concentration unspecified) as a function of added KBr concentration at 30° using light scattering; he found the charge to increase with increasing KBr concentration. A leveling off was observed (α equals 0.16) at 0.09 M KBr.

The results of the α determinations for $C_{10}NMe_3Br$, DTAB and CTAB do not support Cordes',[178] contention of increased Br^- binding to micelles of these surfactants when NaBr is added. Thus some other explanation for the inhibitory effect of NaBr on cationic micelle-catalyzed reactions

having charged transition states needs to be found. One possible suggestion would be micellar size effects.

The dependence of α on CTAB concentration in salt-free solutions is presented in Table IX; a slight increase in α is observed with increasing CTAB concentration. These data were obtained from the experimental points used for CTAB (CMC, 7.89×10^{-4} M) in Table V (p 104). Cordes has argued that the dependence of rates of ester hydrolyses on the concentration of CTAB and homologous cationic surfactants is due to a decreasing α with increasing surfactant concentration (the same explanation used for the effect of added NaBr). The data in this work do not support this contention. It is felt that the decrease in rates observed as the concentration of surfactant increases is due to a decrease in concentration of the reacting species in the micellar phase. Bunton[203] and Berezin[202] have commented on this phenomenon; data will be presented later for hydroxide ion as a reacting species which also supports this contention.

CTACl shows increasing αs with increasing concentration of added NaCl; this result is still observed at 0.1 M CTACl (see Table X). It is recognized that α values greater than one are not possible. There were some difficulties with the chloride ion specific electrode used in these measurements (Nernst factor -48 mV); these may have contributed to the erroneous result. The data were included to show the influence of added salt on α for this surfactant. It is felt that the qualitative trend in the α values is correct; it is interesting to note that the increase in α with increasing NaCl concentration persists to a higher

TABLE IX

COUNTERION BINDING FOR CTAB ONLY

[CTAB], M[a]	Free [Br^-], M[b]	α
0.1000	0.0215	0.22
0.0092	0.00191	0.21
0.00421	0.000831	0.20
0.00321	0.000631	0.20
0.00121	0.000211	0.17
0.00091	0.000164	0.18
0.00071	0.000107	0.15
0.00041	0.000036	0.09

[a]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension data.

[b]Due to micelles only.

TABLE X

COUNTERION BINDING FOR CTACl IN THE PRESENCE OF SODIUM CHLORIDE

0.01 M CTACl				0.1 M CTACl[c]		
[NaCl], M	[CTACl], M[a]	Free [Cl^-], M[b]	α	[NaCl], M	Free [Cl^-], M	α
0.0480	0.0100	0.0137	1.37	0.2000	0.105	1.05
0.0200	0.0099	0.0060	0.60	0.1000	0.060	0.60
0.0100	0.00988	0.0044	0.45	0.0480	0.0465	0.47
0.0048	0.00981	0.0034	0.35	0.0200	0.0345	0.35
0.0020	0.00965	0.0029	0.30	0.0100	0.026	0.26
0.0010	0.0095	0.0028	0.30	0.0048	0.026	0.26

[a]Concentration of surfactant in micellar form; CMC values from CTAB's Corrin plots of surface tension data were used.

[b]Due to micelles only; standard activity coefficients were used.

[c]No CMC corrections necessary; free [Cl^-] corrected for added NaCl prior to calculation of α.

concentration of CTACl than was the case with CTAB in NaBr solutions.

The counterion binding data discussed above were obtained in unstirred solutions unless specifically noted otherwise in Chapter VIII. Table XI presents some data obtained for 0.075 M DTAB and 0.1 M CTAB to specifically illustrate the effects of magnetic stirring in these systems. Stirring increases α in both cases; the effect on CTAB appears at lower concentrations of added salt than the effect on DTAB. It may be that bromide ions are literally sheared off the micellar surfaces by the stirring. For DTAB an attempt to look at the effects of stirring on some solutions containing up to 0.3 M NaBr was made. A paddle stirrer with a variable speed motor was used; no reproducibility in α values could be achieved.

In protein chemistry several examples of denaturation by mechanical treatment are known.[242] Stirring could certainly be considered an example of such mechanical treatment. It is possible that the stirring effects on α for micelles may be the same general sort of phenomenon. Stirring may result in a breakdown of large micelles and/or an increase in CMC. Both factors would increase α.

TABLE XI

THE EFFECTS OF STIRRING ON COUNTERION BINDING TO MICELLES

0.075 M DTAB						0.1 M CTAB[c]				
		Unstirred		Stirred			Unstirred		Stirred	
[NaBr], M	[DTAB], M[a]	Free [Br^-], M[b]	α	Free [Br^-], M[b]	α	[NaBr], M	Free [Br^-], M	α[d]	Free [Br^-], M	α
0.1000	0.0710	0.020	0.28	0.029	0.41	0.1000	0.019	0.19	0.032	0.32
0.0400	0.0692	0.0192	0.28	0.0177	0.26	0.0800	0.014	0.14	0.027	0.27
0.0200	0.0678	0.019	0.28	0.018	0.27	0.0480	0.020	0.20	0.024	0.24
--	0.0640	0.018	0.28	0.0177	0.28	--	0.022	0.22	0.022	0.22

[a]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension data.

[b]Due to micelles only; standard activity coefficients were used.

[c]No CMC corrections necessary; free [Br^-] corrected for added NaBr prior to calculation of α.

[d]From Tables VIII (p 113) and IX (p 118).

CHAPTER V

LYOTROPIC SERIES EFFECTS IN MICELLAR SYSTEMS

A. Background

As discussed in Chapter II, different anions influence the CMCs, aggregation numbers and degree of counterion binding for cationic surfactants in accordance with the anion's position in a lyotropic series. The same is true of the effect of cations on anionic surfactants. In certain cases ions of the same charge as the surfactants also affect these properties.[112,113] These lyotropic series effects have been looked at by viscometry (aggregation number), counterion binding measurements (degree of counterion binding) and calorimetry (thermodynamics of counterion binding) in the course of this work. Most of the work was done with CTAB; for DTAB and the anionic surfactant NaLS only calorimetric investigations were carried out. Much more information on lyotropic series effects for DTAB and NaLS than for CTAB is available in the literature.

B. Viscosity and NMR Results

The viscosity results for CTAB will be considered first. Although none of the data are reported as intrinsic viscosities, one may still draw at least qualitative conclusions about micelle size from data taken at a single surfactant concentration. For example, in the raw data for the intrinsic viscosities of CTAB-NaBr solutions (see Appendix II,

Table XLVIII) the viscosities of 0.1 M CTAB-x M NaBr solutions increase with increasing x. Realizing the limitations of these qualitative conclusions, an increase in viscosity with an increase in salt concentration at constant surfactant concentration will be regarded as evidence for an increase in micelle size. Note that the electroviscous effect would act in the opposite direction in the absence of other effects, with an increase in salt concentration decreasing the viscosity.

Table XII compares the viscosities of 0.1 M CTAB solutions containing NaBr and $NaNO_3$ respectively; added NO_3^- appears to be more effective at increasing the micellar size than added Br^- on a mole for mole basis. Table XIII presents data on the effectiveness of several other salts at increasing the viscosity of 0.1 M CTAB solutions. The observed order for 0.1 M salts is F^- < NaBr < HBr < NO_3^- < ClO_3^-; the effects of sodium iodide and sodium perchlorate could not be investigated because they cause CTAB to precipitate from solution, even when working at low concentrations of CTAB.

The proton is not generally included in lyotropic series for cations. The viscosity difference between 0.1 M CTAB-0.1 M NaBr and 0.1 M CTAB-0.1 M HBr may indicate the existence of a cationic lyotropic series for CTAB. The proton is classified as a structure maker in water, while Na^+ is a structure breaker.[51] The 0.1 M CTAB-0.1 M $KClO_3$ system exhibits a form of hysteresis when run in the Haake Rotovisco. The viscometer is commonly operated in the low shear rate to high shear rate direction; for some of our systems following this by a return to low shear rate gives differing apparent viscosities for the same shear rate (Appendix I, Table XLV).

TABLE XII

COMPARISON OF SODIUM BROMIDE AND SODIUM NITRATE: VISCOSITY OF 0.1 M CTAB SOLUTIONS

[NaBr], M	η_{KE}, cP	[$NaNO_3$], M	η_{KE}, cP
0.0100	1.102 ± 0.003	0.0100	1.092 ± 0.002
		0.0250	1.051 ± 0.001
0.0500	1.520 ± 0.020	0.0500	1.849 ± 0.003
0.0750	2.078 ± 0.047	0.0750	5.804 ± 0.068

TABLE XIII

VISCOSITY OF 0.1 M CTAB AND 0.1 M CTACl SOLUTIONS IN THE PRESENCE OF ADDED SALTS

0.1 M CTAB				0.1 M CTACl		
Salt	[Salt], M	η_{KE}, cP	η_{rel} (to no salt)[d]	Salt	[Salt], M	η_{KE}, cP
NaBr	0.4999	600 ± 20[a,b]	486 ± 16	NaBr	0.5001	232 ± 15[a,b]
NaF	0.1025	1.050 ± 0.001	0.851 ± 0.025	NaBr	0.3996	250[a]
NaBr	0.09997	4.697 ± 0.079	3.806 ± 0.130	NaCl	0.5014	1.177 ± 0.002
HBr	0.10	15.14 ± 0.14	12.27 ± 0.38			
$NaNO_3$	0.1003	22.58 ± 0.38	18.30 ± 0.63			
$KClO_3$	0.0992	355,394[a,c]	288,319			

[a]Shear rate is 25.3 sec^{-1}; data obtained using the Haake Rotovisco.

[b]These values are independent of the time elapsed between preparation of the solutions and measurements of the viscosities; the average value is reported.

[c]Second value is for Rotovisco run from high shear rate to low shear rate.

[d]η_{KE} for CTAB, no salt is 1.234 ± 0.037 cP.

The surfactant CTACl, despite differing from CTAB only in the nature of its counterions, shows very different viscosity behavior from CTAB. High concentrations of NaCl have no viscosity increasing effects for CTACl (Table XIII); this is in agreement with small angle X-ray scattering data for CTACl in the absence of salt, which indicates spherical micelles are present from 5 to 38% concentration of CTACl by weight.[20] High concentrations of added NaBr do cause viscosity increases for CTACl. The resulting high viscosity, at least for 0.5 M NaBr, is time-independent (data collected over two weeks), indicating that slow exchange (on this time scale) of bound Br^- ions for bound Cl^- ions is not occurring. That the viscosity of 0.1 M CTACl-0.5 M NaBr is so much smaller than the viscosity of 0.1 M CTAB-0.5 M NaBr is an example of a lyotropic series.

The system 0.1 M CTACl-0.1 M NaBr contains 0.0535 M free Br^- shortly after being made; it contains 0.0575 M free Br^- a week later. The corresponding values for 0.1 M CTAB-0.1 M NaCl are 0.0415 M and 0.0452 M free Br^-. The upward drift in free Br^- concentration seems to be a consequence of the age of the solutions. These data will be discussed more fully in a later section. These counterion binding results, since they were determined in systems containing equal total concentrations of Cl^- and Br^-, suggest that the micelles in each system do not freely exchange their tightly bound counterions with ions from bulk solvent. This conjecture requires one assume that some surfactant molecules are always present as tight ion-pairs, since micelle formation

and breakdown is known to be rapid. An explanation based on slow exchange rates for the micelles or the ion-pairs is formally possible, but completely at odds with independent data on the rates of such exchanges. It seems quite possible that there is some other, experimentally related, explanation which has to date escaped us. Patterson,[158] using the fluorescence lifetime of anthracene as a probe, has found that Cl^- ions are poorly bound to CTAB micelles, but Br^- ions bind fairly well to CTACl micelles.

Tables XIV, XV and XVI present viscosity results obtained for CTAB and CTACl in the presence of salts as well as certain organic solutes. Urea is known to increase the CMC for CTAB,[99] an effect which operates through a lowered entropy of micellization. The viscosity data indicate it also decreases the size of the micelles. The viscosity of a 0.1 M CTAB-0.1 M urea solution is much less than the viscosity of a 0.1 M CTAB-0.1 M NaBr solution. Note also that the viscosity of 0.1 M CTAB decreases as the concentration of urea present in the solution increases. Where necessary, the appropriate 0.1 M CTAB-x M NaBr viscosity was obtained from a graph of the viscosity dependence of 0.1 M CTAB on NaBr concentration. See Appendix V, Figure 26, for the graph.

As Table XV indicates, 0.1 M CTACl solutions containing either 0.1 M NaCl or 0.1 M NaBr have low viscosities in the presence of benzene, benzoic acid and 1-hexanol. This implies the presence of small, spherical micelles, which may arise because the solutes are solubilized in the CTACl micellar interior. This is not a very realistic assumption

TABLE XIV

EFFECT OF UREA ON VISCOSITY OF 0.1 M CTAB SOLUTIONS

[Urea], M	[Additive], M	η_{KE}, cP	η_{rel} (to 0.1 M CTAB, x M NaBr[a])
0.0335	--	3.591 ± 0.019	2.87 ± 0.015[b]
0.1008	--	1.245 ± 0.053	0.329 ± 0.020[c]
0.1008	0.0115 M benzene	1.218 ± 0.008	0.323 ± 0.016[c]

[a] x equals [urea], M.

[b] The appropriate sodium bromide viscosity was interpolated from the dependence of η for 0.1 M CTAB on [NaBr]. See Table I (p 88) and Appendix V, Figure 26.

[c] Appropriate sodium bromide viscosity from Table I.

TABLE XV

EFFECTS OF ADDITIVES ON 0.1 M CTACl SOLUTIONS CONTAINING 0.1 M SODIUM CHLORIDE OR 0.1 M SODIUM BROMIDE

Additive	NaBr [Additive], M	NaBr η_{KE}, cP	NaBr η_{rel} (to no additive)	NaCl [Additive], M	NaCl η_{KE}, cP	NaCl η_{rel} (to no additive)
--	--	1.137 ± 0.015	--	--	1.152 ± 0.004	--
Benzene	0.0250	1.281 ± 0.009	1.127 ± 0.017	0.0245	1.157 ± 0.002	1.004 ± 0.004
Benzoic acid	0.0248	2.243 ± 0.052	1.973 ± 0.053	0.0249	1.193 ± 0.051	1.036 ± 0.044
1-Hexanol	0.0275	1.891 ± 0.008	1.663 ± 0.022	0.0267	1.157 ± 0.013	1.004 ± 0.018

TABLE XVI

VISCOSITIES OF 0.1 M CTAB SOLUTIONS CONTAINING VARIOUS SALTS AND ADDITIVES

Additive	[Additive], M	Salt	[Salt], M	η_{KE}, cP	η_{rel} (to no additive)[d]
Benzene	0.0249	NaF	0.1025	1.056 ± 0.003	1.006 ± 0.003
	0.0253	NaBr	0.0999	310[a]	82
	0.0254	HBr	0.10	490[a]	32.4
	0.0241	$NaNO_3$	0.1003	426,403[a,b]	18.9,17.8
	0.0242	$KClO_3$	0.0992	553,553[a,b,c]	≃ 1.6
Benzoic acid	0.0251	NaF	0.1025	1.672 ± 0.008	1.592 ± 0.008
	0.0250	NaBr	0.1000	460[a]	102
	0.0251	HBr	0.10	624[a]	41.2
	0.0249	$NaNO_3$	0.1003	474[a]	21.0
	0.0250	$KClO_3$	0.0992	861[a]	≃ 2.4
1-Hexanol	0.0246	NaF	0.1025	1.088 ± 0.002	1.036 ± 0.002
	0.0290	NaBr	0.0999	583[a]	154
	0.0289	HBr	0.10	695[a]	45.9
	0.0192	$NaNO_3$	0.1003	482,442[a,b]	21.3,19.5
	0.0259	$KClO_3$	0.0992	774[a]	≃ 2.2

TABLE XVI (Continued)

[a]Shear rate is 25.3 sec^{-1}; data obtained using the Haake Rotovisco.

[b]Second value is for Rotovisco run from high shear rate to low rate shear rate.

[c]Other shear rates give unequal values for these two numbers.

[d]See Table XIII (p 125) for the 0.1 M CTAB, 0.1 M NaX viscosities, except for NaBr (benzene and 1-hexanol), where $\eta_{0.1\ M\ NaBr}$ = 3.787 cP was used (these data are for unrecrystallized soap) and for NaBr, benzoic acid where η = 4.494 cP was used (recrystallized soap).

for 1-hexanol with its polar hydroxyl group, and it is not realistic at all for benzoic acid, which should be appreciably ionized in solution. For the latter two solubilizates, positions close to the micellar surface (at least the polar groups being in contact with water) are much more likely; for CTAB this kind of solubilization is considered[165] to lead to decreased surfactant head group repulsions and hence the growth of large micelles. Table XVI indicates that increases in micelle size do indeed occur for 0.1 M CTAB-0.1 M NaBr solutions containing benzene, benzoic acid and 1-hexanol, in direct contrast to the same solutes in CTACl solutions. This worker has no reasonable explanation for the large difference in viscosity behavior observed when the counterion for CTA^+ ions is changed from Cl^- to Br^-. It was, to say the least, unexpected. It may be connected with the ability of the counterion to effectively interact with the solutes. Further experimental exploration of this phenomenon is needed.

The 0.1 M CTACl-0.1 M NaBr-0.025 M benzene system also exhibits NMR behavior strikingly different from the corresponding 0.1 M CTAB system. Preliminary results show very significant broadening of the N-methyl and methylene protons for the CTAB system in the presence of benzene. The methylene region is beginning to split into two regions of unequal area. Because the benzene protons' resonance is not broadened relative to its line width in 0.1 M CTAB without salt (not a viscous system), the effect on the CTAB proton resonances mentioned is due to more than viscosity broadening. Bunton[55,218] sees the same behavior with sodium tosylate in CTAB solutions: the CTAB resonances are

broadened but the resonances due to tosylate ion are not. He proposes that tosylate ions lie between adjacent surfactant chains, with the sulfonate group in contact with solvent. He describes the electron-rich aromatic ring of tosylate ion as "solvating" the hydrophobic N-methyl groups of the surfactant.

In 0.1 M CTACl-0.1 M NaBr-0.025 M benzene no broadening of the CTACl resonances occurs. The methylene region (includes all methylene groups except the one α to nitrogen) shows three peaks where the CTAB system shows only one. The NMR spectra are shown in Appendix V, Figures 27, 28, 29 and 30.

The resonances in the spectra were assigned using the NMR data of Eriksson and Gillberg[56] for 0.1729 M CTAB in the presence of benzene at 35°. These workers observed relative line widths up to 50 for equimolar quantities of benzene and CTAB. Compounds solubilized in the CTAB micelle interior do not give line broadening of the CTAB resonances. See Appendix V, Table LXIV for the chemical shift assignments. Eriksson and Gillberg report all chemical shifts in cycles per second relative to the proton resonance of water as internal standard. The external standard is chloroform (7.27 δ or 436.2 cps at 60 Mc). From the relative chemical shifts and the value for chloroform, the values in ppm (δ) for each CTA^+ proton resonance and for benzene could then be assigned. The position of the benzene resonance does not change appreciably on the addition of NaBr in either the CTAB or CTACl case.

The salts which form a lyotropic series in their effects on the viscosity of 0.1 M CTAB solutions were looked at again by viscometry

with benzene, benzoic acid and 1-hexanol present. The lyotropic series has now changed in one respect: HBr is now more effective than $NaNO_3$ in causing viscosity increases. It is not known why this reversal in order occurs when solubilizates are present. The form of hysteresis commented on earlier is also seen for some systems in Table XVI (p 130). The $KClO_3$-benzene system shows it at rates of shear other than 25.3 sec^{-1} (see Appendix I, Table XLV).

C. Calorimetric Investigations

An investigation of lyotropic effects on the thermodynamics of counterion binding to micelles was carried out for CTAB, DTAB and NaLS. The results, expressed as enthalpies of transfer for the salts involved from water to aqueous solutions of the surfactants, are collected in Tables XVII and XVIII. In order to make quantitative comparisons of the enthalpies of binding of the various ions used, it would be necessary to correct the observed enthalpies of transfer for the fraction of counterions which are actually bound to the micelles. All of the data collected represent competition between two different counterions, rather than binding of a counterion in solutions of micelles containing only that counterion. Data of the latter type could be obtained by dilution experiments on surfactant solutions, according to Rehfeld.[37] This would require preparation of a surfactant corresponding to each counterion. Rehfeld's method also assumes that α changes as the concentration of surfactant changes, which is not always the case.

Note that only ions having charges opposite to the surfactant

TABLE XVII

ENTHALPIES OF TRANSFER FOR SALTS FROM WATER TO 0.1 M CTAB SOLUTION AT (25 ± 1)°

Salts	$\Delta H_{s,0.1\ M\ CTAB}$, kcal/mole	$\Delta H_{s,\ H_2O}$, kcal/mole[b]	ΔH_{trans}, kcal/mole
$Na_3C_6H_5O_7 \cdot 2H_2O$	5.02 ± 0.47	1.97 ± 0.32[c]	3.05 ± 0.57
Na_2CO_3	-2.07 ± 0.11[a]	-4.541 ± 0.090[d]	2.47 ± 0.14
Na_2SO_4	1.49 ± 0.12	-0.560 ± 0.010[e]	2.05 ± 0.12
$NaC_2H_3O_2$	-3.09 ± 0.18	-4.140 ± 0.050	1.05 ± 0.19
NaF	1.10 ± 0.04[a]	0.218 ± 0.010	0.88 ± 0.04
NaOH	-9.84 ± 0.02	-10.637 ± 0.010	0.80 ± 0.02
$NaHCO_2$	0.878 ± 0.059	0.203 ± 0.024[c]	0.68 ± 0.06
NaCl	1.32 ± 0.02	0.928 ± 0.005	0.39 ± 0.02
$NaNO_3$	3.93 ± 0.20	4.900 ± 0.050	-0.97 ± 0.20
NaBr	-1.43 ± 0.12	-0.144 ± 0.015	-1.29 ± 0.12
$NaSO_3C_7H_7$	-0.965 ± 0.045	0.535 ± 0.099[a,c,f]	-1.50 ± 0.11
KBr	4.08 ± 0.27	4.750 ± 0.020	-0.67 ± 0.27
LiBr	-12.38 ± 0.14[a]	-11.670 ± 0.050	-0.71 ± 0.15
$(CH_3)_4NBr$	4.80 ± 0.18	5.800 ± 0.100	-1.00 ± 0.20
NH_4Br	2.41 ± 0.06[a]	4.010 ± 0.100	-1.60 ± 0.12
$MgBr_2$	-39.63 ± 1.77	-37.69 ± 0.77[c]	-1.94 ± 1.93
$CaBr_2$	-25.90 ± 0.96	-23.34 ± 0.69[c]	-2.56 ± 1.03

[a]Extrapolated to infinite dilution using linear least squares analysis, see Appendix III, Tables LVIII and LIX.

TABLE XVII (Continued)

[b]V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards 2.

[c]This work.

[d]Linear least squares analysis (ΔH versus $\sqrt{I}$) on the data of J. P. Rupert, H. P. Hopkins and C. A. Wulff, J. Phys. Chem., 69, 3059 (1965).

[e]K. S. Pitzer and L. V. Coulter, J. Amer. Chem. Soc., 60, 1310 (1938).

[f]ΔH versus C_{salt}, not $\sqrt{C_{salt}}$, gives a straight line.

TABLE XVIII

ENTHALPIES OF TRANSFER FOR SALTS FROM WATER TO DTAB AND NaLS SOLUTIONS AT (25 ± 1)°

0.075 M DTAB			0.04 M NaLS		
Salts	ΔH_s, 0.075 M DTAB kcal/mole	ΔH_{trans}, kcal/mole[b]	Salts	ΔH_s, 0.04 M NaLS, kcal/mole	ΔH_{trans}, kcal/mole[b]
Na_2CO_3	-0.830 ± 0.147	3.71 ± 0.17	$NaSO_3C_7H_7$	0.682 ± 0.175	0.15 ± 0.20
Na_2SO_4	0.996 ± 0.117	1.56 ± 0.12	$NaC_2H_3O_2$	-4.33 ± 0.07[a]	-0.19 ± 0.08
$NaC_2H_3O_2$	-3.20 ± 0.07	0.94 ± 0.09	$NaNO_3$	4.36 ± 0.16[a]	-0.54 ± 0.17
$NaHCO_2$	0.617 ± 0.170	0.41 ± 0.17	Na_2SO_4	-1.70 ± 0.08[a]	-1.14 ± 0.08
$NaNO_3$	4.44 ± 0.09	-0.46 ± 0.10			
NaBr	-0.955 ± 0.082[a]	-0.81 ± 0.08			
$NaSO_3C_7H_7$	-0.517 ± 0.294	-1.05 ± 0.31			
LiBr	-11.62 ± 0.19	≃ 0	LiBr	-11.07 ± 0.16	0.60 ± 0.17
NH_4Br	3.61 ± 0.13	-0.40 ± 0.17	NaBr	-0.333 ± 0.077	-0.19 ± 0.08
KBr	4.20 ± 0.10	-0.55 ± 0.10	NH_4Br	3.65 ± 0.15	-0.36 ± 0.18
$(CH_3)_4NBr$	5.01 ± 0.22	-0.79 ± 0.25	KBr	3.94 ± 0.22[c]	-0.81 ± 0.22
$CaBr_2$	-24.17 ± 0.28	-0.83 ± 0.74	$(CH_3)_4NBr$	3.40 ± 0.15[a]	-1.40 ± 0.18
$MgBr_2$	-38.58 ± 0.27	-0.89 ± 0.82	$CaBr_2$	-24.90[d]	-1.56

TABLE XVIII (Continued)

[a]Extrapolated to infinite dilution using linear least squares analysis. See Appendix III, Tables LVIII and LIX.

[b]See Table XVII (p 135) for $\Delta H_{s,H_2O}$.

[c]Precipitation of surfactant occurred at $\leq$ 0.0175 M KBr (fourth injection)

[d]Based on one injection. Addition of further $CaBr_2$ caused precipitation of surfactant.

head groups can be bound. It has been possible to determine the fraction of added counterions bound only for NO_3^- and OH^- added to CTAB. These results will be considered in Section D. The necessary ion-specific electrodes to do the remaining ions were not available. The enthalpies of transfer should also be corrected for the amount of bromide or sodium ions, depending on the surfactant being used, which dissociate as a result of the added counterions binding to the micelles' surfaces. The dissociation of bromide ions from DTAB micelles[32,104] and sodium ions from NaLS micelles[37] is an endothermic process.

Finally, since added salts are known to lower the CMCs of surfactants, a correction for additional surfactant undergoing micellization should be considered. The small ΔH_{mic} observed for NaLS and DTAB makes this last correction unnecessary. For CTAB, Czerniawski[92] reports ΔH_{mic} equal to -3.77 kcal/mole, but because of CTAB's low CMC very little additional surfactant will be micellized during the course of salt addition. Estimates on enthalpies for structural changes in the micelles have not been made with any reliability.

Lacking the necessary data on fraction of counterions bound for all the salts investigated, the salts studied have been arranged in lyotropic series based on their observed enthalpies of transfer. For each surfactant the effects of cations and anions were studied. One ion is more effective than another (and hence is placed higher in the lyotropic series) if the ΔH_{trans} for the more effective ion is the more negative of the two. Note that when cations were studied the anion of the added salts was kept constant; the reverse was true for studying the anions.

For CTAB the observed lyotropic series on the basis of the ΔH_{trans} in Table XVII is citrate < CO_3^{2-} < SO_4^{2-} < $C_2H_3O_2^-$ < F^- < OH^- < HCO_2^- < Cl^- < NO_3^- < Br^- < $SO_3C_7H_7^-$. This series closely parallels the one given for protein denaturation in Chapter II. Being able to observe such a lyotropic series for observed ΔH_{trans} (no corrections applied) is indeed gratifying. The series seems to reflect the ability of these anions to bind to the CTAB head groups on the micellar surface. The closer the approach of the ion, the more favorable ΔH_{trans} will be. Hydrophobic interactions may also be important in certain cases, e.g., tosylate ion. Indeed a plot of ΔH_{trans} versus Stokes' Law hydrated radii[124] (omitting OH^- because of its high equivalent conductivity) for the anions studied gives a reasonable straight line: see Figure 4. Only tosylate ion is a significant distance off the line. The Stokes' Law hydrated radius for the benzoate ion was used to approximate the tosylate ion's radius.[124] The contention concerning close approach of the counterions will be supported later by our work on competitive counterion binding.

The position of citrate and tosylate obtained agrees with Jenck's and Robinson's[115,116] work with the tetrapeptide acetyltetraglycyl ethyl ester (ATGEE). Nitrate ion is observed to be less effective than Br^-; this same result was obtained by Cohen[109] in a study on the effectiveness of NO_3^- and Br^- in lowering the CMC of CTAB. Wan[112] found an order of effectiveness in lowering the CMC of tetradecyltrimethylammonium bromide different from ours for CTAB: SO_4^{2-} < Cl^- < citrate < Br^-. The qualitative observation that sodium citrate will produce systems

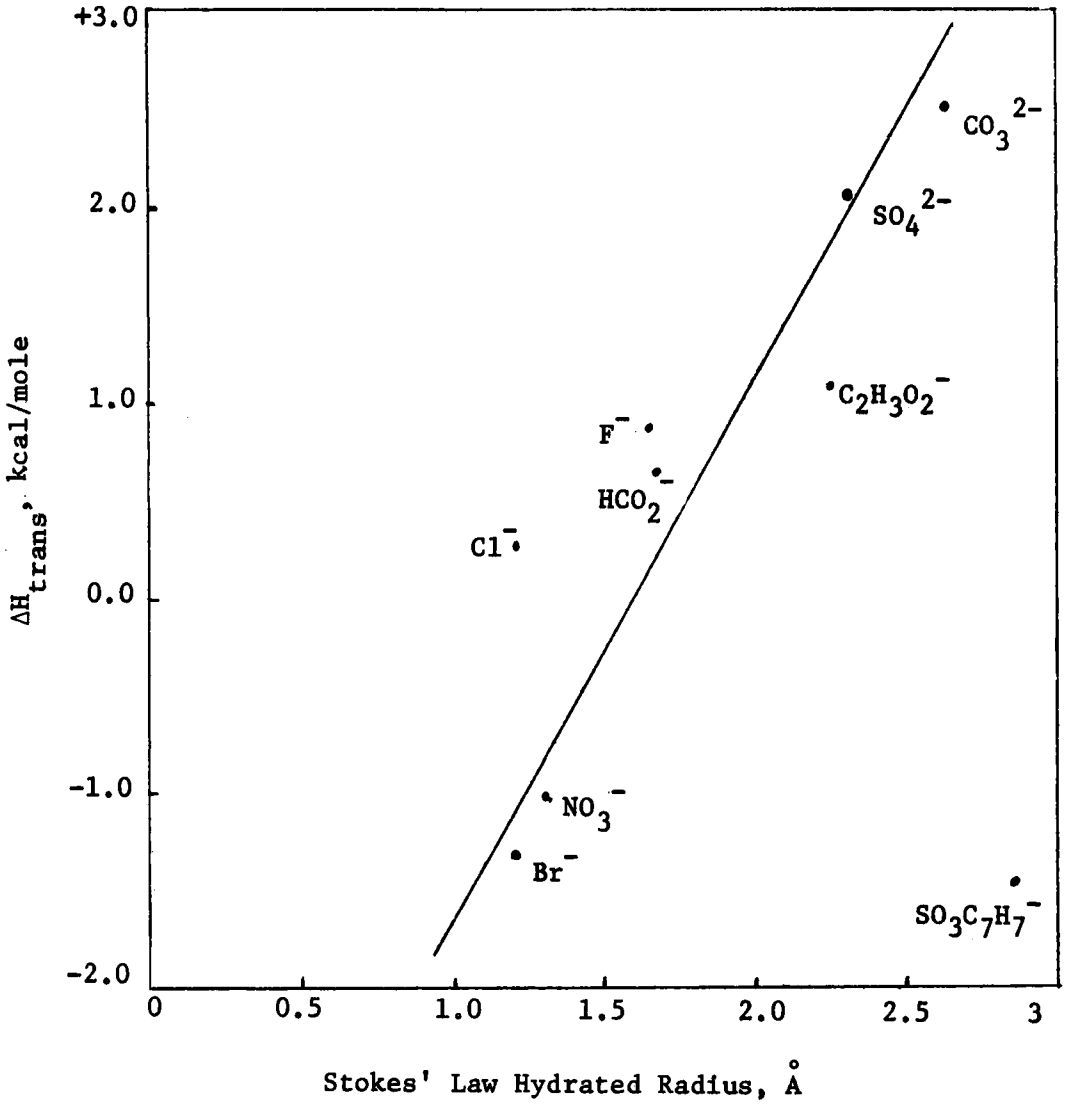


Figure 4. ΔH_{trans} (to 0.1 M CTAB) for NaX versus the Stokes' law hydrated radii for the anions.

of high viscosity when added to CTAB in large amounts has been made in these laboratories. Citrate ion thus has different positions in a lyotropic series, depending on whether viscosity results or binding results are considered. This is probably not the result of our inability to correct for the fraction of citrate ions actually bound to the CTAB micelles. The anions which are poorly solvated are the ones which show the best binding, indicating a dependence on distance of closest approach to the cationic head groups. This suggests that competition between two different counterions for micellar binding sites is largely electrostatic in nature.

The lyotropic series observed for cations with CTAB is $K^+ < Li^+ < (CH_3)_4N^+ < Na^+ < NH_4^+ < Mg^{2+} < Ca^{2+}$. The tetramethylammonium and ammonium ions are out of place compared to the series commonly observed for proteins (see Chapter II). Wan[112] has found that $K^+ < NH_4^+ < Na^+$ in effectiveness of lowering the CMC of tetradecyltrimethylammonium bromide. Since the cations are not bound to the CTAB micellar surface [with the possible exception of $(CH_3)_4N^+$, where hydrophobic interactions may play a role] the observed order must be rationalized in terms of indirect effects. A good candidate for these indirect effects is the influence of the cations studied on the structure of water. The cations include structure makers: Mg^{2+}, Ca^{2+} and $(CH_3)_4N^+$ and structure breakers: Li^+, Na^+ and K^+.[51] These ions are classified on the basis of their effect on the near IR of HOD; other techniques give slightly different results. Tetramethylammonium bromide is known to decrease the CMC of CTAB at concentrations up to 0.09 M; thereafter it increases the

CMC.[111] This is explained on the basis of micellization being more difficult in a well-organized solvent (operates through a decrease in ΔS_{mic}). Malik takes the opposite view: a well-ordered solvent promotes micellization.[113] He finds that the CMC of cetylpyridinium bromide is lowered the most by Li^+, followed by Na^+, then K^+. The order of the cations in their ability to increase water structure is $K^+ < Na^+ < Li^+ < (CH_3)_4N^+ < Ca^{2+} < Mg^{2+}$. Ammonium ion has not been looked at by many techniques; it comes between K^+ and Mg^{2+} on the basis of measurement of the activity of water in salt solutions.[51]

The observed order of ΔH_{trans} for cations in this work agrees roughly with the water structure ordering properties of the ions, with only Na^+ and perhaps NH_4^+ significantly out of line. What is ΔH_{trans} measuring? If the CTAB micelles are strongly hydrated, ΔH_{trans} may represent enthalpy effects resulting from structural changes in this water of hydration (increase or decrease in hydrogen-bonded structure for example). If this is true, it is hard to imagine why the ΔH_{trans} are the most favorable for the structure-making ions. For structure-making ions $\Delta H_{s,H_2O}$ is favorable (but $\Delta S_{s,H_2O}$ is unfavorable) while $\Delta H_{s,0.1\ M\ CTAB}$ would not be expected to be particularly favorable. In the latter case the ion is entering a medium which is already fairly highly structured, due to the presence of the micelles. The quantity ΔH_{trans} may also be measuring structural changes in the micelles. The possibility that it represents ΔH_{mic} for additional surfactant going into micelles as a result of the CMC decreasing can probably be ruled out. Unfortunately, ΔH_{mic} values for CTAB in the presence of each of

the salts are not available. Because of CTAB's low CMC, however, this last possibility is considered much less probable than the others.

It should be noted that anions also affect water structure, with the ability to increase it following the order ClO_4^- < I^- < Br^- < NO_3^- < Cl^- < $C_2H_3O_2^-$ < F^- < OH^-.[51] This is the reverse of the observed lyotropic series for ΔH_{trans} for the anions with CTAB, indicating that water structure is not playing a primary role in this case.

The results in Table XVIII (p 137) for DTAB and NaLS were run at surfactant concentrations of five times the CMC in both cases, in an attempt to utilize solutions containing about the same number of micelles. Since DTAB and NaLS also both have 12 carbon atoms in their long alkyl chains, it was felt that the comparison might reveal a significant difference in behavior toward added salts for cationic and anionic surfactants, if any such difference existed. The magnitudes of the ΔH_{trans} are very similar in the two cases.

For DTAB the anionic series is CO_3^{2-} < SO_4^{2-} < $C_2H_3O_2^-$ < HCO_2^- < NO_3^- < Br^- < $SO_3C_7H_7^-$, the same order which was found for these anions with CTAB. Since 0.075 M DTAB has only 65% as many micelles as 0.1 M CTAB (assuming similar aggregation numbers) one might expect the ΔH_{trans} value for an anion in DTAB to be 65% of what it is in CTAB (this of course also assumes that the enthalpy of binding for the anions is independent of surfactant chain length). With the exception of Na_2CO_3, the ΔH_{trans} for DTAB are 47 to 89% of the corresponding ΔH_{trans} values for CTAB. This seems to indicate that the binding characteristics of the two micellar surfaces are not radically different.

The ΔH_{trans} values for the anions studied with DTAB roughly follow their order of effectiveness in decreasing the CMC and α and in increasing the aggregation numbers of DTAB.[47] In particular, NO_3^- was found to be more effective than Br^- in decreasing the CMC, but less effective in increasing the aggregation number.[47] Holtzer[29] disagrees with Anacker[47] on the effect of anions on α for DTAB. Holtzer finds, using light scattering (also the technique used by Anacker), that α increases as the counterion changes from Cl^- to Br^- to NO_3^-. The degree of dissociation for DTAB in the presence of any of the salts studied by calorimetry, with the exception of NaBr, has not been studied. A plot of ΔH_{trans} for the anions versus their Stokes' Law hydrated radii[124] again gives a reasonable straight line (see Figure 5), with carbonate and tosylate ions deviating markedly. The carbonate data for DTAB has a very unusual concentration dependence (Figure 6); a second method of extrapolation (see Appendix III, Table LVIII) puts the carbonate point much closer to the straight line (marked by x in Figure 5).

The observed cationic series for DTAB is $Li^+ < NH_4^+ < K^+ < (CH_3)_4N^+ < Na^+ < Ca^{2+} \simeq Mg^{2+}$. For the last two ions the standard deviation of ΔH_{trans} is very bad. Lithium ion and potassium ion have changed places, compared to the results with CTAB, and NH_4^+ is also out of place. Lithium ion is a structure maker and should be located with Ca^{2+} and Mg^{2+} if the effect being seen has to do with water structure. Since different methods[51] of detecting the effects of ions on water structure give different orders for structure makers and breakers, too much significance should not be attached to the order obtained in

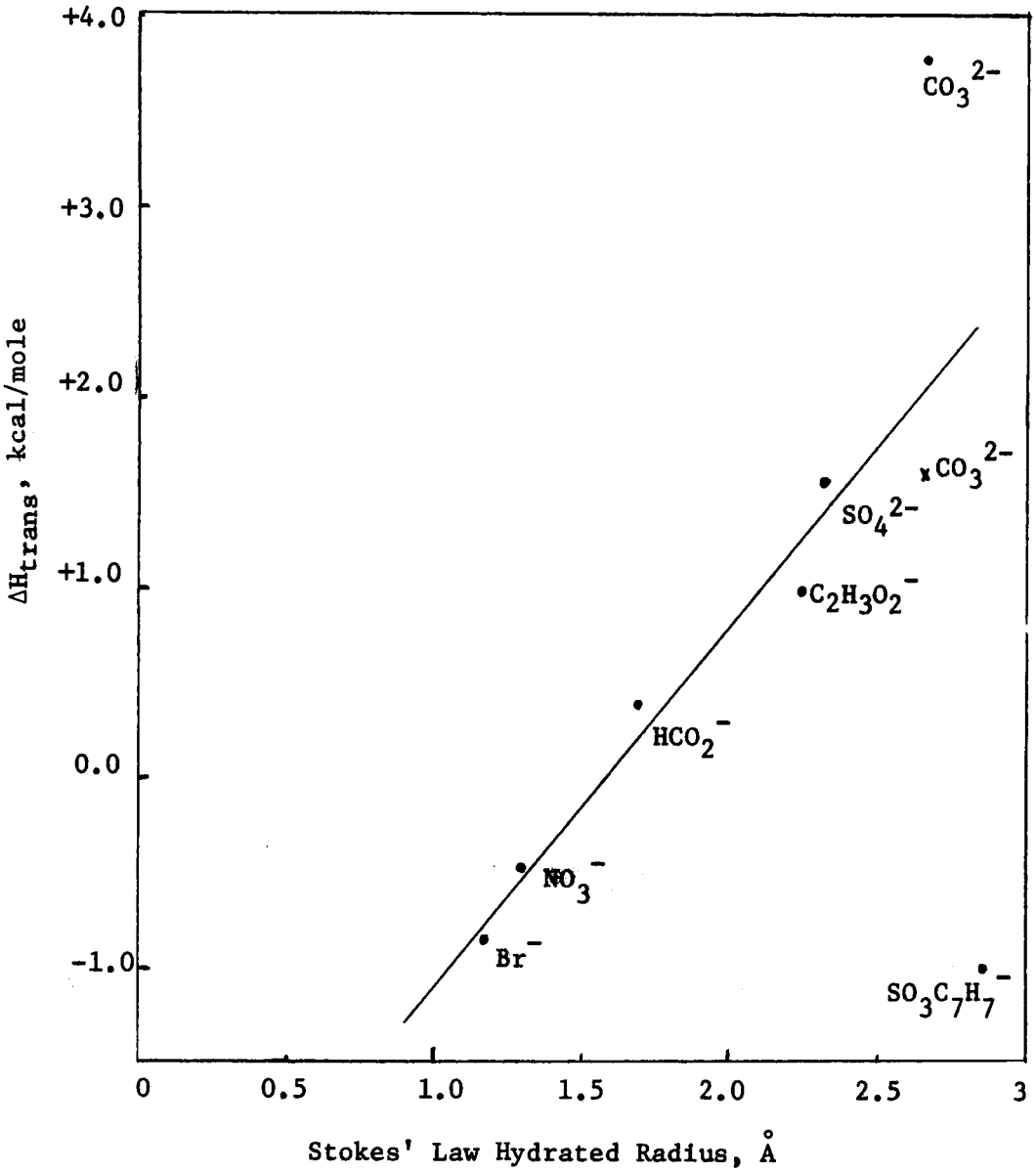


Figure 5. ΔH_{trans} (to 0.075 M DTAB) for NaX versus the Stokes' law hydrated radii for the anions.

X: ΔH_{trans} for CO_3^{2-} determined by extrapolation of ΔH_s, 0.075 M DTAB values at high CO_3^{2-} concentrations.

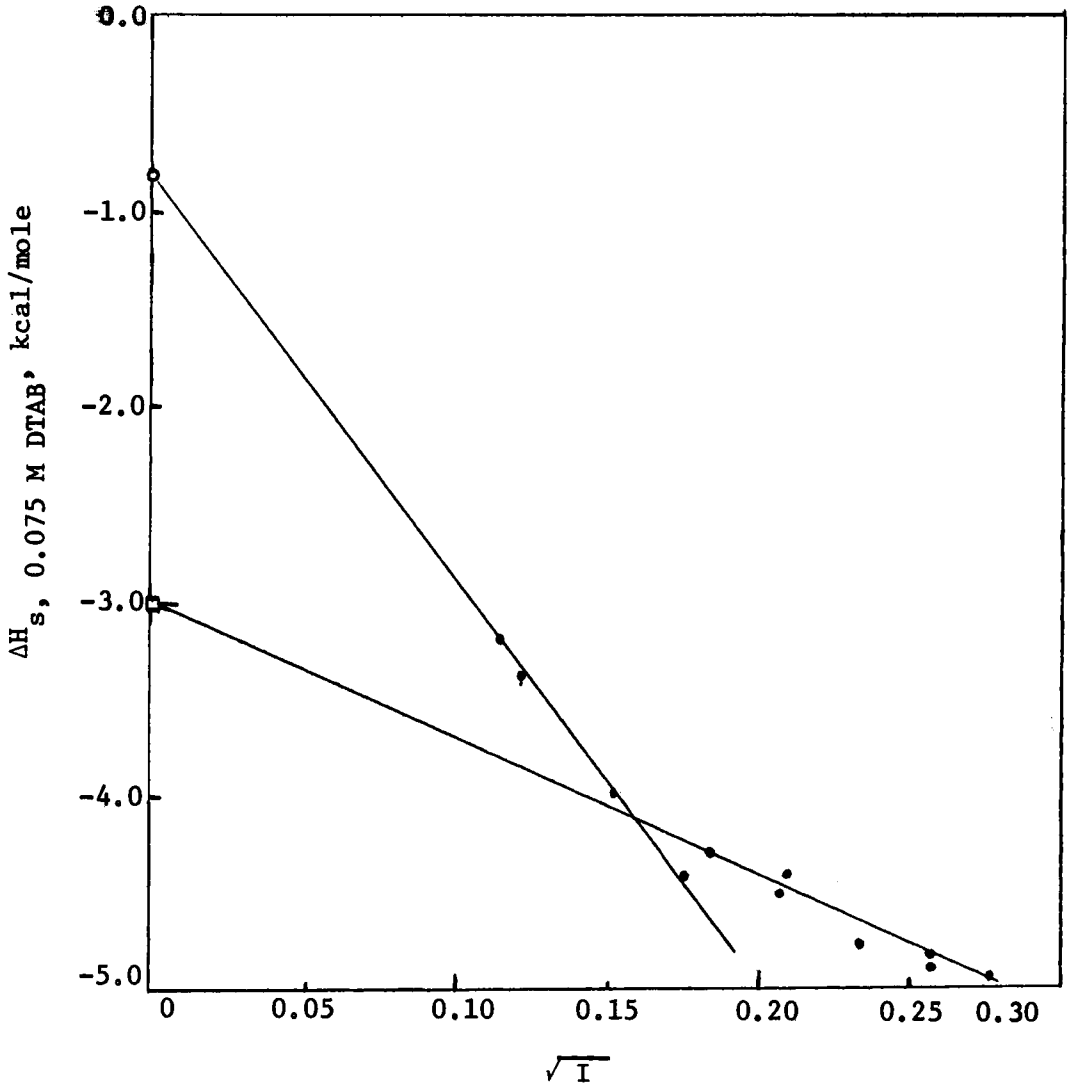


Figure 6. $\Delta H_{s,\ 0.075\ M\ DTAB}$ versus the square root of the ionic strength for Na_2CO_3.

Open circle: $\Delta H_{s,0.075\ M\ DTAB} = -0.830 \pm 0.147$ kcal/mole, square: $\Delta H_{s,0.075\ M\ DTAB} = -2.97$ kcal/mole.

a particular case. It is disturbing, however, that DTAB and CTAB show different series of ΔH_{trans} for the cations.

The results with NaLS definitely show a lyotropic series for the cations. The observed ΔH_{trans} for the anions studied may correlate with the effect of these anions on the structure of water if one assumes that tosylate ion will behave the way perchlorate ion does (i.e., as a structure breaker): $SO_3C_7H_7^- < C_2H_3O_2^- < NO_3^- < SO_4^{2-}$. This assumption about tosylate ion's behavior may be invalid because of water structure induced by tosylate's aromatic ring.

The cationic results for NaLS give $Li^+ < Na^+ < NH_4^+ < K^+ < (CH_3)_4N^+ < Ca^{2+}$. The reported ΔH_{trans} for Ca^{2+} is based on a single injection in the calorimeter, since addition of $CaBr_2$ causes NaLS to precipitate. The same problem, to a lesser extent, was observed with KBr. The order observed for ΔH_{trans} agrees with the effectiveness of these cations in lowering the CMC[48,112] of NaLS and in decreasing α for it.[48,53] It is assumed that ΔH_{trans} is measuring the binding of some fraction of the added cations to the NaLS micellar surface. Satake[133] has observed that large amounts of the Na^+ bound to NaLS can be displaced by addition of Mg^{2+}. Unfortunately, he did not look at what fraction of the Mg^{2+} added was bound to the micelles. Goddard[53] found that the decrease in CMC with the addition of various ions correlates very well with the distance of closest approach of the ions to the charged surfactant heads. The closer the approach, the more the surface potential of the micelles and the free energy of micellization decreased. It is felt that the ΔH_{trans} values give the correct order

for the actual enthalpies of binding of the cations to the NaLS micellar surface. The ions which can approach the head groups most closely, such as K^+, give the most favorable ΔH_{trans}. In support of this, the ΔH_{trans} for the alkali-metal cations versus their Stokes' Law hydrated radii[48,124] have been plotted; the result is a straight line (Figure 7). The value for NH_4^+ is not on the line. It is interesting to note that Cordes[219] found the same order of effectiveness in inhibition by these cations of the hydrolysis of methyl orthobenzoate in the presence of NaLS: $Li^+ < Na^+ < NH_4^+ < K^+$.

For a surfactant already in the presence of high concentrations of an added salt, one might be able to obtain enthalpies of binding for a second salt added in small quantities, without having to take large structural changes or significant additional micellization into account. Table XIX presents the experimental results of adding NaBr to 0.1 M DTAB in the presence of 0.5 M NaCl, NaF and $NaBrO_3$. Anacker and Ghose[47] have found these three systems to have micelles of very similar size, using light-scattering techniques. The ΔH_{trans} for NaBr is the most exothermic in the NaF case, followed by $NaBrO_3$ and NaCl. This corresponds to the lyotropic series $F^- < BrO_3^- < Cl^-$. Assuming that at least some F^- is bound to the DTAB micelles, the ΔH_{trans} indicate it is most easily displaced by Br^-. The difference in ΔH_{trans} for displacement of F^- and BrO_3^- is surprising since their Stokes' Law hydrated radii are the same, which should indicate they are bound equally well. It is of course plausible that their ΔGs for binding are the same but their entropies and enthalpies of binding are not.

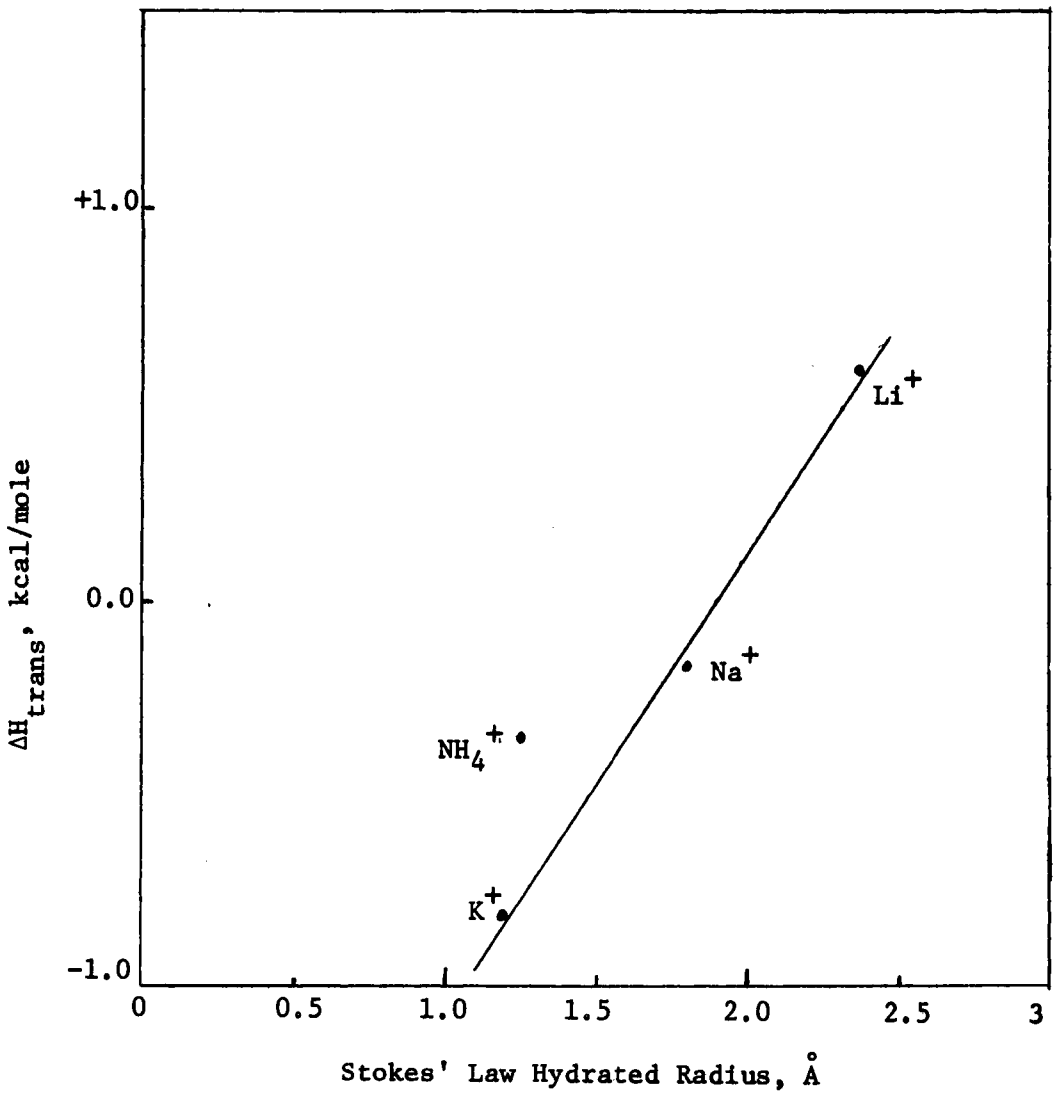


Figure 7. ΔH_{trans} (to 0.04 M NaLS) for salts of alkali metals versus the Stokes' law hydrated radii for the cations.

TABLE XIX

ENTHALPIES OF TRANSFER FOR SALTS FROM WATER TO VARIOUS SURFACTANT SOLUTIONS AT (25 ± 1)°

Surfactant	Salt	Injected Salt	ΔH_s, kcal/mole	$\Delta H_{s,H_2O}$, kcal/mole	ΔH_{trans}, kcal/mole
0.1 M DTAB	0.5 M NaCl	NaBr	-0.620 ± 0.056	-0.152 ± 0.036[d]	-0.47 ± 0.07
	0.5 M NaF	NaBr	-1.04 ± 0.07	-0.147 ± 0.020[d]	-0.89 ± 0.07
	0.5 M $NaBrO_3$	NaBr	-0.808 ± 0.066	-0.144 ± 0.015[e]	-0.66 ± 0.07
0.0015 M HACl	--	$NaSO_3C_7H_7$	-0.460 ± 0.516[a]	0.535 ± 0.099[a,f]	-1.00 ± 0.69[g]
	--	NaCl	-2.99 ± 0.47[b]	0.928 ± 0.005[e]	-3.91 ± 0.47[g]
	--	NaCl	0.417 ± 0.077[c]	0.928 ± 0.005[e]	-0.51 ± 0.08[g]

[a]Extrapolated to infinite dilution using linear least squares analysis. See Appendix III, Tables LVIII and LIX.

[b]Linear least squares analysis for ΔH versus $\sqrt{C_{NaCl}}$, where C_{NaCl} equals one-half the concentration of a given injection plus the concentration of NaCl already present prior to the injection.

[c]Data at high concentrations of NaCl. See Figure 8 (p 154) for complete graph of concentration dependence.

[d]In the presence of 0.5 M NaCl and 0.5 M NaF respectively.

TABLE XIX (Continued)

[e]V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards 2.

[f]This work.

[g]At 36.5° because of surfactant solubility problems.

Lyotropic series effects are also observed for the addition of salts to 0.0015 M hexadecylammonium chloride (HACl), CMC equal to 0.0011 M.[4] The ΔH_{trans} for added NaCl at low concentrations is -3.91 kcal/mole; it is -0.51 kcal/mole at higher concentrations of added NaCl. The unusual form of the concentration dependence (Figure 8) may be due to large structural changes in the micelles, specifically to a change in micelle size. Addition of sodium tosylate also gives an exothermic ΔH_{trans}; when compared to -0.51 kcal/mole for NaCl this fits in with lyotropic series effects which were observed with CTAB and DTAB.

The enthalpy of micellization of CTAB in 0.1 M CTAB in the presence and absence of sodium tosylate was studied; the results are presented in Table XX. The enthalpy of micellization in taken as the difference of the enthalpy of solution of CTAB in water below the CMC and in the appropriate 0.1 M CTAB solution. In the latter case, all the added CTAB is assumed to form micelles, since the existing solution will already contain monomers equal to the CMC. The $\Delta H_{s,H_2O}$ was obtained by a single injection technique, changing the calorimeter water for each new addition of CTAB. The reproducibility of the values was not good (see Appendix V, Table LXV). No correction is made for pre-CMC dimerization. In the presence of $SO_3C_7H_7^-$ ΔH_{mic} is more favorable than in its absence. These values lend further support to our neglecting enthalpies of micellization in considering our ΔH_{trans} numbers for the addition of salts to 0.1 M CTAB. Our ΔH_{mic} does not agree very well with that reported by Czerniawski[92] (-3.7 kcal/mole), which was undoubtedly obtained by the temperature dependence of the CMC, since

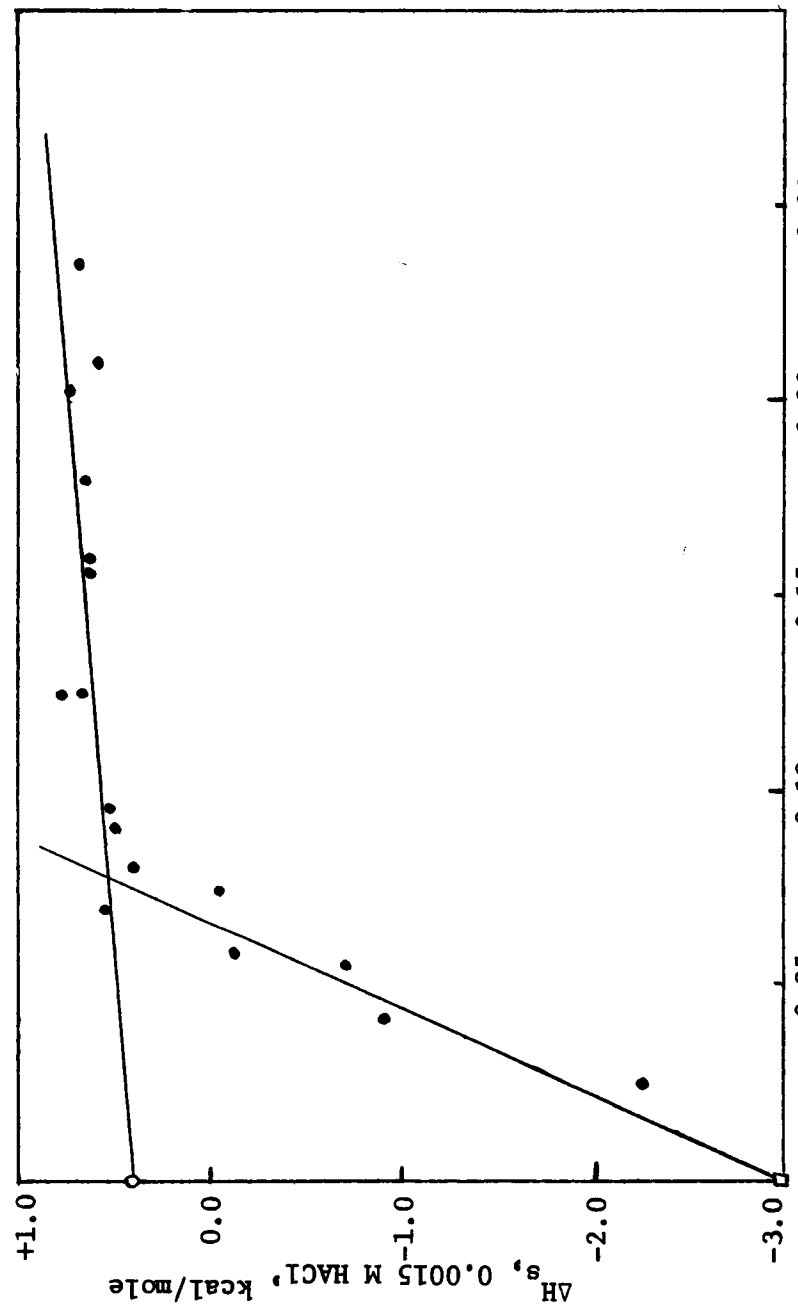


Figure 8. ΔH_s, 0.0015 M HACl versus the square root of concentration for NaCl.

Open circle: ΔH_s, 0.015 M HACl = -2.99 $\pm$ 0.47 kcal/mole, square: ΔH_s, 0.015 M HACl = 0.417 $\pm$ 0.077 kcal/mole.

TABLE XX

THERMODYNAMICS OF MICELLIZATION FOR CTAB IN 0.1 M CTAB SOLUTION AT (25 ± 1)°

Solvent	ΔH_s, kcal/mole	ΔH_{mic}, kcal/mole	α	ΔG_{mic}, kcal/mole[b]	ΔS_{mic}, eu
H_2O	15.67 ± 0.44[a]				
0.1 M CTAB	13.91 ± 0.61	-1.76 ± 0.75	0.22	-10.2	28
0.1 M CTAB, 0.01 M $NaSO_3C_7H_7$	12.70 ± 0.73	-2.97 ± 0.85	0.20	-11.3	28

[a] Obtained using a single injection technique. See Appendix V, Table LXV.

[b] $\Delta G_{mic} = 2.3\ RT\{\log[S^+] + (1-\alpha)\ \log[X^-]\}$, where $[S^+]$ = CMC and $[X^-]$ represents total free counterion. Both quantities are expressed in mole fraction units. For 0.1 M CTAB $[X^-] = 3.96 \times 10^{-4}$ mole fraction units (0.022 M); for 0.1 M CTAB, 0.01 M $NaSO_3C_7H_7$ $[X^-] = 5.40 \times 10^{-4}$ mole fraction units (0.03 M).

it is reported for 25° to 35°. To obtain information on ΔG_{mic} it would be necessary to know the CMC of CTAB in the presence of 0.01 M $NaSO_3C_7H_7$; this has not been determined. For 0.1 M CTAB, α is 0.22; for 0.1 M CTAB-0.01 M $NaSO_3C_7H_7$ the lowest possible α is 0.20 (assuming 100% of the tosylate ion added is bound to the micelles, see p 161). Using Equation 3 (p 9) (ignoring activity coefficients and [M]), and the CMC for 0.1 M CTAB-0.01 M NaBr (1.15×10^{-4} M, mole fraction 2.08×10^{-6}) to approximate the CMC for 0.1 M CTAB-0.01 M $NaSO_3C_7H_7$, the ΔG_{mic} listed in Table XX were calculated. The CMC for CTAB only used was 8.0×10^{-4} M, mole fraction 1.44×10^{-5}. The ΔS_{mic} for the two systems is the same, probably indicating no significant water-structure effects on micellization exerted by the tosylate ion.

D. Counterion Binding in Hexadecyltrimethylammonium Bromide Solutions Containing Two Counterions

To reinforce the belief that the anions of salts added to cationic surfactant solutions are bound to the micelles in these solutions and to obtain true enthalpies of transfer for some of the anions studied with CTAB, the degree of counterion binding was determined for a few salts other than NaBr. The anions which could be studied were limited by ion-specific electrodes available in these laboratories and to a lesser exent by the interferences from certain ions to which the ion-specific electrodes are subject.

The competition between NO_3^- and Br^- for binding to CTAB micelles was examined at two concentrations of CTAB. See Table XXI for the

TABLE XXI

COMPETITIVE COUNTERION BINDING FOR CTAB:
BROMIDE IONS VERSUS NITRATE IONS

Surfactant	$[NaNO_3]$, M	[CTAB], M[b]	Bound $[Br^-]$, M[c]	%	Bound $[Br^-]$, M[d]	%	Bound $[NO_3^-]$, M[c]	%	Bound $[NO_3^-]$, M[d]	%	$1-\alpha^{c,e}$	$1-\alpha^{d,e}$
0.01 M CTAB	0.04001	0.00996	0.0023	23	0.0018	18	0.0080	20	0.0070	18	1.03	0.89
	0.02001	0.00993	0.0028	28	0.0024	24	0.0055	28	0.0058	29	0.84	0.83
	0.01000	0.00988	0.0038	38	0.0035	35	0.0046	46	0.0043	43	0.85	0.79
	0.00480	0.00980	0.0050	50	0.00495	50	0.0027	56	0.0027	56	0.79	0.78
	0.00201	0.00965	0.00605	61	0.0061	61	0.0014	72	0.0014	70	0.78	0.78
	0.0010	0.00950	0.0066	66	0.0066	66	0.00078	78	0.00077	77	0.77	0.78
0.1 M CTAB[a]	0.03148		0.0575	58	0.0568	57	0.0237	75	0.0228	70	0.81	0.81
	0.02000		0.0625	63	0.0626	63	0.0162	81	0.0157	79	0.79	0.78
	0.01000		0.0665	67	0.0670	67	0.0088	88	0.0088	88	0.75	0.76
	0.00480		0.0720	72	0.0720	72	0.0046	96	0.0045	94	0.77	0.77
	--		0.0780	78								

TABLE XXI (Continued)

[a]No CMC corrections needed.

[b]Concentration of surfactant in micellar form; CMC values from Corrin plots of surface tension data for added NaBr were used.

[c]Standard activity coefficients were used. See Appendix V, Table LXVI.

[d]Estimated activity coefficients were used. See Appendix V, Table LXVII.

[e]Includes both kinds of ions; $1-\alpha$ = (bound $[NO_3^-]$ + bound $[Br^-]$)/[CTAB].

results and Appendix V, Tables LXVI and LXVII for the calculations. It was found that part of the added NO_3^- is bound, and this is accompanied by displacement of some Br^-. For both 0.01 M and 0.1 M CTAB the fraction of NO_3^- bound is higher at low total concentrations of NO_3^-. At both concentrations of CTAB the amount of bound Br^- steadily decreases as NO_3^- is added. As noted earlier, an ion high in a lyotropic series is expected to be more effectively bound than an ion lower in the series. For 0.01 M CTAB α does get smaller as the concentration of NO_3^- increases; at the higher concentrations of added $NaNO_3$, NO_3^- ions are the bulk of the ions bound to the micellar surface. This is not the behavior which was found when Br^- was added to 0.01 M CTAB. There α increased with increasing concentration of added salt; see Table VIII (p113). Thus α decreases upon addition of nitrate ions and increases upon addition of bromide ions. For 0.1 M CTAB α remains virtually constant as the concentration of NO_3^- is increased. The results with 0.01 M CTAB and to a lesser extent with 0.1 M CTAB support Cordes'[178] contention that anions such as NO_3^- act in micellar inhibition of certain reactions by decreasing micellar charge density. The values of α when NO_3^- is present are smaller than when NaBr is the only salt present (see Table VIII).

Competition between OH^- and Br^- for binding sites on the CTAB micelles was also investigated: see Table XXII and Appendix V, Tables LXVIII and LXIX. Bunton[203] unsuccessfully tried this same sort of experiment for CTAB. Hydroxide ion, although quite low on the lyotropic series, is effectively bound to CTAB micelles. For 0.005 M CTAB α is

TABLE XXII

COMPETITIVE COUNTERION BINDING FOR CTAB: BROMIDE IONS VERSUS HYDROXIDE IONS

0.005 M CTAB									0.1 M CTAB[f]									
[NaBr], M	[CTAB], M[a]	Free [Br^-], M[b]	1-α	Free [Br^-], M[c]	1-α	Bound [OH^-], M[c]	%[d]	$1-\alpha^e$	[NaOH], M	Bound [Br^-], M[g]	%	Bound [Br^-], M[h]	%	Bound [OH^-], M[g]	%	Bound [OH^-], M[h]	%	$1-\alpha^{g,i}$	$1-\alpha^{h,i}$
--	0.00420	0.00088	0.79	0.00104	0.75	0.000073	39	0.78	0.05652	0.0660	66	0.0653	65	0.0310	55	0.0290	51	0.97	0.94
0.00250	0.00470	0.00110	0.77	0.00140	0.70	0.000020	15	0.71	0.04037	0.0720	72	0.0714	71	0.0131	32	0.0116	29	0.85	0.88
0.00500	0.00480	0.00156	0.68	0.00216	0.55	0.000052	39	0.56	0.03028	0.0740	74	0.0736	74	0.0103	34	0.0095	31	0.84	0.85
									0.02019	0.0715	72	0.0718	72	0.0172	85	0.0165	82	0.89	0.83
									0.01009	0.0750	75	0.0758	76	0.00998	100	0.0090	90	0.85	0.83

[a] CTAB in micellar form; CMC values from Corrin plots of surface tension data were used([NaOH] is neglected).

[b] Due to micelles only; no NaOH present.

[c] In the presence of approximately 10^{-4} M NaOH; standards contained NaOH.

[d] Calculated using the NaOH solution's pH in the absence of CTAB.

[e] Includes both OH^- and Br^-.

[f] No CMC corrections necessary.

[g] Standard activity coefficients were used. See Appendix V, Table LXVIII.

[h] Estimated activity coefficients were used. See Appendix V, Table LXIX.

[i] Includes both kinds of ions; 1-α = (bound [OH^-] + bound [Br^-])/[CTAB].

increased only slightly when OH^- is added; some of the Br^- bound to the micelles is displaced. For 0.1 M CTAB a decrease in α with an increase in NaOH concentration is seen. The difference between competition with NO_3^- and with OH^- seems to be the amount of Br^- they are able to displace from the micelle surfaces. Hydroxide ion is much less effective than NO_3^- at displacing Br^- ions from CTAB micelles. This probably indicates that OH^- is less firmly bound to the micelle surfaces than NO_3^-, which can get closer to the surfactant head groups.

Table XXIII presents the effect of tosylate ion on Br^- bound to the CTAB micelles in 0.1 M CTAB. The calculations appear in Appendix V, Table LXX. Lack of a tosylate ion specific electrode prohibits complete characterization of this system. Tosylate ion behaves like NO_3^- in that it is very effective at freeing Br^- from the CTAB micellar surfaces. It is so effective that the smallest possible α (including both ions) for the micelles in these systems is 0.20, assuming 100% of the added tosylate ion is bound. This value was arrived at by adding the bound Br^- and the total added $SO_3C_7H_7^-$ for each solution reported on in Table XXIII and then dividing the sum in each case by 0.1 M, the concentration of CTAB. For 0.1 M CTAB-0.012 M $NaSO_3C_7H_7$ this gives 1 - α equal to 0.80, the largest 1 - α value obtained. Hence an α of 0.20 is the smallest possible degree of dissociation. Bunton,[206] using kinetic data and treating tosylate ion as an inhibitor, found that about 75% of the tosylate present was bound (this was for 0.003 M CTAB). Because of tosylate ion's interaction with the surfactant heads[55] it should be very effective at reducing the micellar charge

TABLE XXIII

COMPETITIVE COUNTERION BINDING FOR CTAB: BROMIDE IONS IN THE PRESENCE OF SODIUM TOSYLATE

	0.1 M CTAB					
$[NaSO_3C_7H_7]$, M	Bound $[Br^-]$, M[a]	1-α	Δ bound $[Br^-]$, M[b]	$[NaSO_3C_7H_7]$, M	[CTAB], M[c]	Free $[Br^-]$, M
--	0.0785	0.78	--	0.0125	0.00618	0.00619
0.0020	0.0770	0.77	-0.0015	0.0200	0.00620	0.00624
0.0040	0.0757	0.76	-0.0028			
0.0052	0.0750	0.75	-0.0035			
0.0080	0.0720	0.72	-0.0065			
0.0100	0.0702	0.70	-0.0083			
0.0120	0.0680	0.68	-0.0105			

[a]Estimated activity coefficients were used. See Appendix V, Table LXX.

[b]Computed by subtracting bound $[Br^-]$ in the absence of $NaSO_3C_7H_7$ from the values in column two.

[c]These solutions are very viscous; CTAB in micellar form, CMC values from Corrin plots of surface tension data for added NaBr were used.

density: it spreads the charged head groups apart. This is a mechanism not available to simple ions such as NO_3^- or OH^-. When the molar ratio of tosylate to CTAB is greater than one, very viscous solutions are observed; the micelles actually bear a negative charge.[55,218] It is found that under these conditions there is almost no Br^- bound to the CTAB micelles.

Because Br^- interferes with the chloride ion specific electrode, a complete study of Cl^- and Br^- competition could not be made. Table XXIV presents some of the very early counterion binding work; it is felt that the αs obtained, especially at low CTAB concentrations, are too high. Concentrating on the data for 0.005 M and 0.01 M CTAB (entries three and five respectively) one sees that Cl^- does indeed displace Br^- from the CTAB micellar surfaces. It is not nearly as good at it as NO_3^- or $SO_3C_7H_7^-$ however; Patterson[158] also has observed that Cl^- is not very effective in its interactions with CTAB. Chloride ion is about as effective as OH^-, when one considers the amount of Br^- displaced divided by the total amount of an added anion which could potentially bind to the micelles.

The use of both CTAB and CTACl solutions with the bromide ion specific electrode was investigated, hoping that the amount of Cl^- bound to the CTAB micelles could be determined. However, as Table XXV shows, two systems identical in the number and kinds of ions they contain do not give equal amounts of free Br^-. Perhaps there are some ions in each case which are not freely exchanged; this was discussed earlier in connection with the viscosity results. Undoubtedly a more reasonable

TABLE XXIV

COMPETITIVE COUNTERION BINDING FOR CTAB: BROMIDE IONS IN THE PRESENCE OF 0.02 M SODIUM CHLORIDE[a]

[CTAB], M[b]	Free [Br^-], M	α	α^c
0.000956	0.000892	0.93	
0.00351	0.00268	0.76	
0.00501	0.00368	0.73	0.59
0.00599	0.00433	0.72	
0.00988	0.00603	0.61	0.49

[a]This concentration of NaCl does not interfere with the operation of the bromide ion specific electrodes; the standards contained 0.02 M NaCl.

[b]CTAB in micellar form; CMC $\simeq 6.8 \times 10^{-5}$ M (from Corrin plot of surface tension data for added NaBr).

[c]Values from Table VIII (p 113) for CTAB in the presence of 0.02 M NaBr.

TABLE XXV

COMPETITIVE COUNTERION BINDING FOR HEXADECYLTRIMETHYLAMMONIUM ION: BROMIDE IONS VERSUS CHLORIDE IONS[a]

Time elapsed	0.1 M CTAB, 0.1 M NaCl Free [Br^-], M	0.1 M CTACl, 0.1 M NaBr Free [Br^-], M
0 Days	0.0415	0.0535
6 Days	0.0452	0.0575

[a]These data were obtained with the bromide ion specific electrode.

explanation is some change (decomposition) of the solutions with time. The solutions were stored in stoppered volumetric flasks, so that evaporation was not a factor.

The effectiveness of the ions studied at displacing Br^- from the CTAB micellar surfaces follows a lyotropic series: $Cl^- \simeq OH^- < NO_3^- < SO_3C_7H_7^-$. Whether α values for CTAB micelles in the presence of two counterions depend on the counterions' position in the lyotropic series is less clear. Addition of OH^- to 0.1 M CTAB and of NO_3^- to 0.01 M CTAB decreases α, but addition of NO_3^- to 0.1 M CTAB results in α values independent of the NO_3^- concentration.

The observed fraction of counterions bound for NO_3^- and OH^- was used to compute true enthalpies of transfer for these ions from water to 0.1 M CTAB solutions. The calorimetric results were corrected for the enthalpy of displacement of Br^- using a value of 2 kcal/mole. This was the value determined for DTAB.[32,104] For tosylate ion Bunton's[206] estimate of 75% of the added tosylate being bound to the micelles was used. Table XXVI presents the results of these calculations; the details may be found in Appendix V, Tables LXXI and LXXII. Note that an expression for K, the distribution coefficient for the ions between the bulk and the micellar phases, of the form $[X^-]_{mic}/[X^-]_{bulk}$ was used. Activity coefficient effects are neglected; since the concentration of X^- in the micellar phase will be quite high, this introduces an error into the calculations of the free energy of binding.[64] The entropies of transfer are quite intriguing; they may be related to the position of the ions in the lyotropic series. Rehfeld[37] observes a positive entropy

TABLE XXVI

THERMODYNAMICS OF BINDING TO THE CTAB MICELLES[a]

Ion	ΔH, kcal/mole	ΔG, kcal/mole	ΔS, eu
NO_3^-	-3.14	-2.52	-2.1
OH^-[b]	0.76	-2.08	9.5
OH^-[b]	1.97	-1.51	12
$SO_3C_7H_7^-$	-4.57	-2.60	-6.6
Na^+ to NaLS[c]	-1.09	-3.4	7.8

[a]See Appendix V, Tables LXXI and LXXII for the calculations.

[b]OH^- results are for 55% and 32% respectively of total [OH^-] being bound to the micelles.

[c]Data for binding of Na^+ to NaLS micelles, D. J. Eatough and S. J. Rehfeld, Thermochimica Acta, 2, 443 (1971).

of transfer for Na^+ ions binding to NaLS micelles. Although it is frequently considered that there is no loss in solvation when a counterion binds to a micelle,[6,36] loss of solvation might be a possible explanation for the observed entropies. This predicts OH^-, a very well-solvated ion, would have a positive entropy of binding; this is observed. Nitrate ion and tosylate ion, although poorly solvated in aqueous solution and not expected to show an increase in solvation upon binding, may be very tightly bound to the CTAB micellar surfaces. This is reflected in their ΔS_{trans} values. All of the ions will of course lose translational entropy upon binding. It must also be pointed out that the ΔGs do not necessarily refer to the same standard state, because the added ions in each case may be binding to micelles containing different amounts of bromide ion already on the micellar surface.

In an effort to gain further insight into the binding of OH^-, NO_3^- and $SO_3C_7H_7^-$ to the CTAB micelles, an attempt has been made to calculate the surface potentials "seen" by these ions (and Br^- in their presence) in the bound state. The more closely they are bound to the head groups, the larger the surface potential they should see. The surface potential of a charged particle is the potential difference between the interior of the bulk solvent in which the particle is immersed and some charged surface associated with the particle. For micelles, the surface may include the charged head groups only or it may include the bound counterions and associated water of hydration (i.e., it may be the boundary of the Stern layer). The Boltzmann's Law distribution of counterions,[243] Equation 39, was used to compute the surface

potentials; this distribution holds for all surface potentials.[243]

$$[X^-]_{mic}/[X^-]_{bulk} = e^{-ze\psi/kT} = e^{+e\psi/kT} \qquad (39)$$

The concentration of X^- in the micellar phase, $[X^-]_{mic}$, was computed using the concentration (in moles/liter of the entire solution) of X^- found to be bound to the micelles divided by the volume fraction of the solution (ϕ) occupied by the micelles. The use of the volume fraction attempts to take into account the finite thickness of the micelles' Stern layers. Actually, the surface area for a CTAB micelle is less than a factor of ten smaller than its volume, and relative, not absolute, comparisons are the goal of these calculations. For $[X^-]_{bulk}$ the uncorrected values for the concentration of free X^- as determined by the ion-specific electrodes were used. When only one kind of counterion is present in solution, the calculations are straightforward: all ions are included in either $[X^-]_{mic}$ or $[X^-]_{bulk}$.[244] When two or more counterions are present they have been considered separately and a surface potential (ψ) has been calculated for each kind of ion in solution. This does not correspond to thermodynamic reality, in that the micelles would be expected to have only one associated surface potential in a given solution. However, if the effectiveness of an ion in the lyotropic series has to do with how close it can get to the surfactant head groups, one might expect the ψs seen by different ions to be different. Other workers[202,208] have used this kind of separate consideration of the ions present. An effective ion is said to cause a decrease in the observed ψ for the micelle (this might show up in the magnitude of the electrokinetic potential at the boundary of the

Stern layer). However, the ion itself, through the expression given above, will experience a high surface potential if it is close to the head groups on the micelle surface, a lower one if it is loosely bound (farther out in the Stern layer, farther away from the head groups).

The results of the surface potential calculations using the counterion binding data presented earlier are given in Table XXVII. Appendix V, Tables LXXIII, LXXIV, LXXV and LXXVI contains the complete calculations. The first data were included to indicate that the surface potential depends inversely on the ionic strength of a solution. The results using CTACl and CTAB may be compared directly (because all counterions were included in computing ψ) to get an idea of how closely the two kinds of ions approach the hexadecyltrimethylammonium head groups. Clearly, the bromide ion is located closer to the head groups than the chloride ion, at least at the higher concentrations of added electrolyte.

The data on the binding of NO_3^- and OH^- to the CTAB micelles and of Br^- to the micelles in the presence of $SO_3C_7H_7^-$ should be used only to establish relative positions in the Stern layer for the particular system under consideration. The NO_3^- data should not be compared with the OH^- data, for example. With these limitations in mind, it can be seen that NO_3^- and Br^- "see" similar surface potentials for 0.01 M CTAB, while NO_3^- sees consistently higher potentials than Br^- in the presence of 0.1 M CTAB. Hydroxide ion also sees lower surface potentials than bromide ion at some concentrations of added hydroxide ion. It is felt that the latter two ψs (at NaOH concentrations of 0.02 M and 0.01 M) are probably in error; the corresponding binding data are

TABLE XXVII

LYOTROPIC EFFECTS IN CTAB SOLUTIONS AS MEASURED BY SURFACE POTENTIALS "SEEN" BY VARIOUS COUNTERIONS[a]

[CTAB], M	ψ, mV	0.1 M CTACl [NaCl], M	ψ, mV	0.1 M CTAB [NaBr], M	ψ, mV	Surfactant	[$NaNO_3$], M	$\psi(NO_3^-)$, mV	$\psi(Br^-)$, mV	[NaOH], M	$\psi(OH^-)$, mV	$\psi(Br^-)$, mV	[$NaSO_3C_7H_7$], M	$\psi(Br^-)$, mV
0.1000	118	0.010	107	0.010	107	0.01 M CTAB	0.04001	105	106					
0.0100	172	0.020	93	0.020	101	0.01 M CTAB	0.02001	121	115					
0.0050	185	0.048	74	0.048	89	0.01 M CTAB	0.01000	137	129					
0.0040	189	0.100	53	0.100	75	0.01 M CTAP	0.00480	151	144					
0.0020	199					0.01 M CTAB	0.00201	167	157					
0.0017	200					0.01 M CTAB	0.00100	176	163					
0.0015	202					0.1 M CTAB	0.03148	110	92	0.05652	90	102	0.0120	104
0.0012	206					0.1 M CTAB	0.02000	118	98	0.04037	66	109	0.0100	107
						0.1 M CTAB	0.01000	136	103	0.03028	68	112	0.0080	109
						0.1 M CTAB	0.00480	156	109	0.02019	130	109	0.0052	113
										0.01009	201	113	0.0040	114
													0.0020	116

[a]See Appendix V, Tables LXXIII, LXXIV, LXXV and LXXVI for the calculation of the surface potentials.

therefore probably also in error. It seems that the values for OH^-, if the assumptions of the limited validity of these surface potentials are correct, should be appreciably smaller than those for Br^-. This is true only at two concentrations of added NaOH, 0.04 M and 0.03 M. To the extent to which comparison from one system to another can be made, it is seen that addition of nitrate ion (0.01 M) is more effective than either 0.01 M tosylate ion or 0.01 M hydroxide ion at excluding Br^- (as measured by its surface potential) from close binding to the CTAB head groups in 0.1 M CTAB.

Bunton[208] has computed ψ to be 107 mV for the OH^- ion in 0.003 M CTAB-0.015 M borate buffer; he compares this value to the Guoy-Chapman potential (151 mV) and electrokinetic potential (81 mV) for CTAB. Unfortunately, he uses the wrong values for these potentials. At the CMC for CTAB the electrokinetic potential (ζ) is 103 mV;[212] using $\zeta = 0.55\psi_{GC}$, the Guoy-Chapman potential is 187 mV. As the concentration of CTAB and added electrolyte increases these potentials will both decrease. The values obtained in our work for ψ for OH^- are probably just within the value of the electrokinetic potential, indicating fairly loose binding for OH^-.

It is felt that the work discussed in this Chapter has established the usefulness of calorimetric investigation and the use of ion-specific electrodes for characterizing surfactant systems containing more than one species of counterion. Certainly the large differences in properties observed when the counterion for CTAB is changed to Cl^- (giving CTACl) are remarkable. Finding cationic lyotropic series operating

for CTAB and DTAB was unexpected. Addition of counterions such as NO_3^-, OH^- and $SO_3C_7H_7^-$ were found to either decrease or not affect α for the CTAB micelles. A decrease in α with these additions has been widely invoked by those who study micellar catalysis.

CHAPTER VI

PROPERTIES OF MICELLES IN THE PRESENCE OF ORGANIC SOLUTES

A. Background

The effect of various organic solutes on micelle size and counterion binding for CTAB and to a lesser extent NaLS are of considerable interest for a variety of reasons. Some reports about solutes either increasing or decreasing the extent of counterion binding have appeared.[83,105,106,166] This kind of data could explain the results of micellar catalyses where electrostatic stabilization by a micellar surface of a transition state for the reaction has been invoked. Data on the thermodynamics of solute binding to CTAB micelles were also thought to be of potential value in explaining some aspects of micellar catalysis. In particular, some information about the position of solubilizates within the micelles might be obtained from these binding data. Strictly speaking, binding of an organic solute to a micelle means transfer from the bulk solution to the micellar phase, while solubilization refers to transfer of the solute from its pure state to the micellar phase.[64]

B. Viscosity Results

Our early work on the interaction of organic solutes with micelles was directed toward effects on micellar size. Table XXVIII presents the results of a viscosity study using 0.10 M to 0.30 M NaLS with 0.1 M NaBr and a variety of organic solutes. None of these solutes produces a significant viscosity increase over the value for the solution without

TABLE XXVIII

EFFECTS OF ORGANIC SOLUTES ON THE VISCOSITY OF NaLS SOLUTIONS CONTAINING 0.1 M SODIUM BROMIDE AT 25°

[NaLS], M	Organic solute	[Solute], M	η_{KE}, cP	η_{rel} (to no solute)
0.1000	--	--	1.000 ± 0.005	--
	Benzene	0.0261	0.998 ± 0.017	0.998 ± 0.018
	Benzene	0.0339	1.045 ± 0.003	1.045 ± 0.006
	Benzene	0.0800	1.044 ± 0.002	1.044 ± 0.006
	Benzene	0.1540	1.036 ± 0.006	1.036 ± 0.008
	Benzoic acid	0.0220	1.014 ± 0.001	1.014 ± 0.005
	1-Hexanol	0.0242	1.021 ± 0.002	1.021 ± 0.006
0.2000	--	--	1.135 ± 0.004	--
	Benzene	0.0294	1.139 ± 0.019	1.004 ± 0.017
	1-Hexanol	0.0285	1.194 ± 0.039	1.052 ± 0.034
0.3000	--	--	1.305 ± 0.023	--
	Benzoic acid	0.0240	1.435 ± 0.017	1.100 ± 0.023

organic solutes; such an increase would indicate a change in micellar size. These viscosities are not a strong function of the cation of the added electrolyte. Thus 0.1 M NaLS-0.025 M 1-hexanol with KBr up to the concentration at which NaLS starts to precipitate (0.02 M KBr), is not a viscous system. This is a qualitative observation.

For CTAB, on the other hand, the solutes studied fall fairly cleanly into two classes: those which cause little or no viscosity increase and those which cause significant viscosity increases. The results appear in Table XXIX. Members of the latter class of solutes include benzene, naphthalene, benzoic acid, 1-hexanol, carbon tetrachloride, chloroform and methylene chloride.

The compounds which produce little viscosity change when added to 0.1 M CTAB-0.1 M NaBr may either be solubilized in the micellar interior or not solubilized at all. The compounds which produce viscosity increases include some, such as benzene, which are known to be solubilized at or near the CTAB micellar surface[56] (see the NMR data discussed in Chapter V, Section B). Presumably this mode of solubilization would increase the distance between the charged surfactant head groups, decreasing their electrostatic repulsion and allowing micellar size to increase. This <u>should</u> perhaps also result in decreased counterion binding.[83] Mathews[106] has looked at the effect of carbon tetrachloride and 1-hexanol on counterion binding for 0.1 M CTAB-0.1 M NaBr; he finds that the addition of organic solutes does not alter the counterion binding. Lindblom[83] has explained this as the result of competition between increased counterion binding caused by a sphere to rod transition for

TABLE XXIX

EFFECTS OF ORGANIC SOLUTES ON THE VISCOSITY OF 0.1 M CTAB SOLUTIONS CONTAINING 0.1 M SODIUM BROMIDE AT 25°

Organic solute	[Solute], M	η_{rel} (to no solute)[e]
n-Hexane	0.00805	1.152 ± 0.011
Ethanol	0.01033	0.979 ± 0.007
Sucrose	0.00889	0.981 ± 0.003
Ethyl acetate	0.00724	1.003 ± 0.004
Acetic acid	0.01345	0.942 ± 0.013
d,ℓ-Alanine	0.01028	0.990 ± 0.019
ℓ-(-)-Tyrosine	0.00204[a]	0.914 ± 0.013
Naphthalene	<0.00995[a]	1.791 ± 0.045
Benzene	0.0097[b]	4.006 ± 0.66, 7.4[f]
	0.01107	3.430 ± 0.216
	0.01107[c]	9.789 ± 0.044
	0.0253[b]	82[f]
Benzoic acid	0.00872	8.550 ± 0.094
	0.0250[b]	102[f]
1-Hexanol	0.00881[d]	3.942 ± 0.166
	0.0290[b]	154[f]
Carbon tetrachloride	0.0184[b]	71.8[f]
Chloroform	0.0158[b]	36.8[f]
Methylene chloride	0.0318[b]	26[f]

TABLE XXIX (Continued)

[a]Not very soluble.

[b]These systems are non-Newtonian.

[c]After warming the solution to 62° and allowing it to cool.

[d]This system is Newtonian.

[e]Some of the early work used unrecrystallized CTAB. η_{rel} is independent of the method of purification, as was verified using different samples of CTAB for the same additive.

[f]Shear rate is 25.3 sec^{-1}; data were obtained using the Haake Rotovisco. $\eta_{no\ solute}$ = 3.787 cP, except for benzoic acid, where $\eta_{no\ solute}$ = 4.494 cP and the chlorinated hydrocarbons, where $\eta_{no\ solute}$ = 4.290 cP.

the micelles (the area per head group decreases from 76 $Å^2$ to 51 $Å^2$ in the case of CTAB micelles having 95 monomers, see Appendix VI, Table LXXVII) and decreased counterion binding caused by 1-hexanol's mode of solubilization.

Naphthalene, although not very soluble, clearly falls into the second class of solutes. This is interesting in light of fluorescence data which indicates that pyrene, an even larger aromatic hydrocarbon, is solubilized in the interior of CTAB micelles.[98] The chlorine-substituted methanes produce an interesting series of relative viscosities: the more chlorines which are present, the higher the viscosity. This may be the result of London dispersion interactions between the N-methyl groups of the CTAB head groups and the chlorine atoms of the solutes.

NaLS is known to form rod-shaped micelles, but only at concentrations above 25% of surfactant by weight. It is also thought to solubilize benzene in its hydrocarbon interior,[60] but the position of 1-hexanol in the NaLS micelle is almost certainly radial orientation, with the hydroxyl group situated at the micellar surface. This is supported by counterion release from NaLS micelles containing 1-hexanol.[152] Because of this, it is surprising that no evidence of micellar size increase is detected. Although NaLS has a higher CMC than CTAB, the difference in the number of micelles present in 0.1 M solutions of the two surfactants is probably not sufficient to account for the low viscosities observed with NaLS. If large micelles were present in the NaLS systems, the viscosities obtained would reflect this.

The intrinsic viscosities were determined for CTAB solutions

containing a few solutes from the two classes of solutes which could be differentiated using the viscosity results in Table XXIX (p 177). These systems are presented in Table XXX; the raw data appear in Appendix VI, Tables LXXVIII and LXXIX. Chronologically the first system which was examined was CTAB in the presence of 0.1 M NaBr and 0.025 M benzoic acid. This system has two CMCs, the first at 7.95×10^{-5} M, determined by surface tension, the second at 1.57×10^{-3} M, determined from the intersection of the two polynomials (see Appendix VI, Table LXXX and Figure 31) which describe the intrinsic viscosity data. This system is characterized by very high intrinsic viscosities; they correspond to axial ratios of 65 and 146 in the two regions. Next CTAB with 0.02 M NaBr and 0.025 M benzoic acid was investigated; an η_{sp}/C_m versus C_m plot resulted which was unlike any which had previously been observed. The data for this system are presented in graphical form in Appendix VI, Figure 32. Because structural changes in the micelles might be occurring as the molar ratio of benzoic acid to CTAB changed in this system, it was decided to do the remaining intrinsic viscosity work using a constant molar ratio of organic solute to CTAB: 0.25. The resulting intrinsic viscosities can be used to divide the solutes into two classes, just as the results in Table XXIX could be used. The hydrocarbons n-hexane and n-octane give intrinsic viscosities which are lower than the intrinsic viscosity, 9.11 ml/g, for CTAB in 0.1 M NaBr. The micelles in these systems are nearly spherical; their aggregation numbers are probably lower than the aggregation numbers for CTAB micelles in 0.1 M NaBr. In the absence of NaBr n-octane increases the aggregation number of CTAB micelles (as observed by light scattering).[72,73]

TABLE XXX

I NTRINSIC VISCOSITIES OF CTAB SOLUTIONS CONTAINING SODIUM BROMIDE AND VARIOUS ORGANIC SOLUTES

[NaBr], M	Organic solute[a]	[η], ml/g	p[f]
0.1000	n-Hexane	3.11 ± 1.05[b]	≈2
0.1000	n-Octane	3.90 ± 0.19[b]	≈3
0.0200	Benzoic acid	4.45 ± 0.20[c]	3.6
0.1000	Benzoic acid	13.3 ± 0.5[d]	9.9
	1-Hexanol	16.7 ± 0.5[d]	11.6
	0.025 M benozic acid	199,828[e]	65,146

[a]The organic solute is maintained at 25% of [CTAB] throughout the experiments, except where indicated.

[b]Determined by linear least squares analysis, Appendix VI, Table LXXIX.

[c]Raw data fit to a third order polynomial, Appendix VI, Table LXXIX.

[d]Raw data fit to a fourth order polynomial, Appendix VI, Table LXXIX.

[e]This system exhibits a second CMC at 1.57×10^{-3} M; the raw data fit two third order polynomials which intersect at the second CMC. See Appendix VI, Table LXXX.

[f]Calculated assuming prolate ellipsoids, with the exception of 0.1 M NaBr, 0.025 M benzoic acid, where the rod model was used. See Appendix VI, Table LXXXI.

Benzoic acid and 1-hexanol probably both increase the aggregation number of the CTAB micelles over its value in CTAB-0.1 M NaBr. 1-Hexanol is more effective in this regard than benzoic acid. The difference in behavior of the two kinds of solubilizates almost certainly reflects their different solubilization sites in the CTAB micelles. The actual values of p reported for these systems should be considered in a qualitative sense only, because the equations for $\Lambda(p)$ hold only for $p >> 1$.[229]

C. Effect of Organic Solutes on Counterion Binding

Release of a micelle's counterions, as mentioned earlier, is one way in which solubilization at the micellar surface can be detected. Lindblom[83] has shown that the counterion binding of CTAB micelles containing 1-hexanol depends on their size. In order to completely characterize such a system a range of CTAB concentrations would have to be investigated. However, work done at a single concentration may also be useful; an example is counterion binding measurements taken in "kinetic" systems. By this is meant studying the effects on counterion binding of reactants and products for a reaction which is catalyzed by the CTAB micelles. If the reactant and/or product cause an increase in α, and a high degree of dissociation for the micelles is important to the micellar catalysis, useful insight into the course of the reaction has been gained.

Appendix VII, Tables LXXXII, LXXXIII and LXXXIV contain the effects of methyl salicylate and salicylic acid on α for CTAB micelles. Catalysis by CTAB of alkaline hydrolysis of methyl salicylate has been

investigated; the results are presented in Chapter VII. The α values for CTAB in the presence of the carbonate buffer used are also included in Appendix VII, Table LXXXII. Although the α values seem much too high, their relative values have significance. This comparison shows that salicylic acid probably displaces a small amount of bromide ion from CTAB micelles in 0.001 M to 0.01 M solutions of CTAB; methyl salicylate is less effective. In any event the effects are certainly not large.

Counterion binding to very large CTAB micelles has also been investigated, using 0.1 M CTAB-0.1 M NaBr in the presence of benzene and benzoic acid. Table XXXI presents these results. It should be noted that some displacement of bound bromide ions by the solutes used was observed, since α is 0.19 for 0.1 M CTAB-0.1 M NaBr. Values of α of 0.41 and 0.43 for benzene and benzoic acid respectively were observed at 25°; these solute concentrations are higher than those used by Mathews,[106] who observed no solute effect on α for the 0.1 M CTAB-0.1 M NaBr system. An increase in α is also seen with an increase in temperature, which is consistent with the enthalpy of bromide ion binding being exothermic. The most interesting aspect of the results presented in Table XXXI is the observed dependence of the counterion binding on the rate at which the solutions are stirred. A small paddle stirrer with a variable speed motor was used. Stirring consistently increases α, except for the benzoic acid system at 39.2°. In some cases after stirring was stopped α continued to increase or decrease, then "changed" direction, approaching what it was prior to stirring. In other cases

TABLE XXXI

EFFECT OF STIRRING ON CTAB COUNTERION BINDING: 0.1 M CTAB-0.1 M NaBr-0.070 M BENZENE AND 0.1 M CTAB-0.1 M NaBr-0.0540 M BENZOIC ACID

T, °C	Rate of Stirring, rpm	α before Stirring	α after Stirring	Nature of decay[b]
	Benzene:[a]			
25	No solute	0.19		
25	500	0.43	0.55	Simple decay back to 0.43
25	700	0.41	0.53	Simple decay back to 0.41
25	900	0.45	0.52	Simple decay back to 0.45
40	500	0.85	1.03	Decay back to 1.0, then reversed to 1.12
40	700	>1.0		
	Benzoic acid:[a]			
25	400	0.43	0.45	Simple decay back to 0.43
25	500	0.42	0.44	Simple decay back to 0.38
25	500	0.38	0.42	Fluctuation, then simple decay
25	700	0.38	0.42	No decay
25	700	0.38	0.42	Very little decay
39.2	400	0.56	0.61	No decay
39.2	500	0.52	0.47	Simple decay past 0.52
39.2	500	0.74	0.70	Simple decay back to 0.90
39.2	700	0.65	0.55	Simple decay back to 0.62 then reverses to 0.52

TABLE XXXI (Continued)

T, °C	Rate of Stirring, rpm	α before Stirring	α after Stirring	Nature of decay[b]
39.2	700	0.62	0.63	α increases to 0.82, then simple decay back to 0.74

[a]NaBr standards for preparing calibration plot were used at the listed temperatures.

[b]See Appendix VII, Figures 33, 34, and 35 for plots of the decay. For benzoic acid only the first run at each stirring rate is plotted.

α may ultimately end up smaller or larger than it was before stirring was begun. This behavior is described as decay behavior in Table XXXI; the complete time dependence for each system appears in Appendix VII, Figures 33, 34 and 35. The experimental readings in millivolts versus seconds elapsed after stirring was stopped have been plotted; the larger the millivolt reading (in a negative sense) the more free bromide ion is present in the solutions. After taking readings at 25° for the solution containing benzene, a new solution was prepared for the readings at 40°, because benzene is quite volatile.

The increase in α for both benzene and benzoic acid seems to indicate that stirring either causes some of the bound bromide ions to be sheared off the micellar surfaces or causes a decrease in micelle size. Certainly the micelles present in these systems are quite large and are interacting with one another during the stirring. As considered in Chapter IV, Section C, stirring can affect α even in systems which are not very viscous, such as 0.1 M CTAB-0.1 M NaBr. The slow decay behavior for α which is seen in the systems presented in Table XXXI contradicts the widely held belief that processes such as micelle formation and solute binding are very rapid. The decay behavior of the bromide ion binding may either reflect slow binding of counterions to the micellar surfaces or the reformation of large micelles from small micelles produced by the stirring (this is the sort of shear denaturation discussed in Chapter IV, Section C, which may also be reflected in an increase in CMC). There is evidence for the formation of large CTAB micelles being a slow process.[169,170] Lindblom[83] has indicated that large CTAB micelles show lower α values than small CTAB micelles.

D. Calorimetric Investigations

In studies of micellar catalysis the distribution coefficient K for the starting material (between micellar and bulk phases) is frequently determined by using gel filtration chromatography.[65] The concern is to establish that a significant fraction of the material undergoing reaction is actually solubilized by the micelles at the surfactant concentrations where significant rate enhancements are observed. However, little attention has been directed toward complete thermodynamic characterization of the binding of organic solutes to the micelles. When such characterization is attempted, it is common to obtain enthalpies of binding by determining K for a system at several temperatures. However, this introduces the possibility of temperature-induced size changes in the micelles being studied. No studies are available for CTAB.

Binding of solutes to micelles may be of two types,[64] one following a distribution law, $K = [\text{solute}]_{mic}/[\text{solute}]_{bulk}$ and the other being of the Langmuir type, Equation 40, where K_L and n are Langmuir parameters

$$[\text{solute}]_{mic} = K_L[\text{solute}]_{bulk}n/(1 + K_L[\text{solute}]_{bulk}) \qquad (40)$$

for the system under investigation. The former type of binding has been assumed for the solutes in this work for which attempts to calculate $\Delta G_{binding}$ are made.

The enthalpies of binding to CTAB micelles for a wide range of organic solutes have been investigated calorimetrically. The concentration of CTAB used was 0.1 M CTAB; because of this high concentration, application of the results to systems used in micellar catalysis may

be inappropriate. One-tenth molar CTAB was chosen because considerable data (using other experimental techniques) had been previously collected at this concentration. It is also a convenient concentration because amounts of solutes sufficient to get experimentally detectable heat evolution or absorption due to binding may be used. This would not be possible using very low concentrations of CTAB.

The ΔH_{trans} values reported here are uncorrected for the fraction of solute which actually binds to the micelles, but for materials of low water solubility the fraction can be expected to be close to one. The effects of two organic solutes, benzoic acid and carbon tetrachloride, on ΔH_{trans} for NaBr in 0.1 M CTAB were also briefly investigated. The results are presented in Table XXXII; both solutes decrease ΔH_{trans} from its value in 0.1 M CTAB alone. This phenomenon has little to do with decreased counterion binding per se.[106] It may reflect a change in the nature of the binding sites available to Br^- on the CTAB micelles: the distance of closest approach for Br^- and the charged head groups may be increased.

Table XXXIII includes several solutes which had been investigated by viscometry previously. It is interesting to note that the observed ΔH_{trans} from water to 0.1 M CTAB do not correlate with a solute's ability to induce micellar growth (as measured by viscometry) in 0.1 M CTAB-0.1 M NaBr. The calorimetric investigation was not carried out using added NaBr precisely because of these large viscosity changes. It was impossible experimentally to maintain an adequate baseline (due to heat of stirring effects) when solute injections caused a large change in viscosity.

TABLE XXXII

ENTHALPY OF SOLUTION OF SODIUM BROMIDE IN 0.1 M CTAB SOLUTIONS CONTAINING ORGANIC SOLUTES AT (25 ± 1)°

Organic Solute	ΔH_s, 0.1 M CTAB', kcal/mole	ΔH_{trans}, kcal/mole[a]
--	-1.43 ± 0.12	-1.29 ± 0.12
0.010 M benzoic acid	-1.32 ± 0.07	-1.18 ± 0.07
0.010 M carbon tetrachloride	-1.11 ± 0.16	-0.97 ± 0.16

[a] $\Delta H_{s,H_2O}$ for NaBr is -0.144 ± 0.015 kcal/mole. See Table XVII (p 135).

TABLE XXXIII

ENTHALPIES OF SOLUTION OF MISCELLANEOUS ORGANIC SOLUTES IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°

Solute	ΔH_s, 0.1 M CTAB, kcal/mole	ΔH_s, H_2O, kcal/mole	ΔH_{trans}, kcal/mole
n-Hexane	0.858 ± 0.511[a]	0.112 ± 0.029[c]	0.75 ± 0.51
Cyclohexane	0.604 ± 0.307[a]	0.062 ± 0.020[c]	0.54 ± 0.31
1-Hexanol	-0.714 ± 0.047	-1.11 ± 0.08[d]	0.40 ± 0.09
Carbon tetrachloride	0.048 ± 0.045	-1.022 ± 0.407[e]	1.07 ± 0.41
Chloroform	-1.38 ± 0.17	-0.167 ± 0.068	-1.21 ± 0.19
Methylene chloride	-0.171 ± 0.085	-0.349 ± 0.100	0.18 ± 0.13
Bromoform	-2.32 ± 0.19	-0.177 ± 0.055[b]	-2.14 ± 0.20
Uracil	6.39 ± 0.11[b]	6.40 ± 0.20[b]	-0.01 ± 0.23
Cytosine	5.15 ± 0.17	5.15 ± 0.06	0.00 ± 0.18

[a]Average of five and four runs respectively, two for each compound at very high stirring rates in the calorimeter, in order to attain solution.

[b]Extrapolated to infinite dilution by linear least squares analysis. See Appendix III, Tables LVIII and LIX.

[c]F. Frank, Nature, 224, 1293 (1969).

[d]R. Aveyard and A. S. C. Lawrence, Trans. Faraday Soc., 60, 2265 (1964).

[e]Computed by least squares analysis of the temperature dependence of solubility. See Appendix III, Table LX.

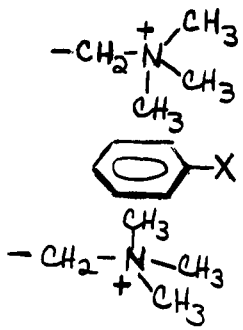
Assuming that ΔG_{trans} for n-hexane from water to the CTAB micelle interior is -1.4 kT (-839 kcal/mole) per methylene group,[45] n-hexane has a large positive ΔS_{trans} (19 eu). This is to be expected because of the break-up of the iceberg regions which form around hydrocarbon chains in aqueous solution.

The results for carbon tetrachloride, chloroform and methylene chloride were expected to parallel the results obtained in the viscosity studies, Table XXIX (p 177), with carbon tetrachloride having the most exothermic ΔH_{trans}. Presumably the ΔG_{trans} values do parallel the viscosity results. The order of the ΔH_{trans} obtained for these solutes may reflect differences in their water solubility. Since methylene chloride is more soluble than the other solutes in water, a smaller fraction of methylene chloride would be expected to be bound to the CTAB micelles. There may also be significant desolvation of the micellar surface caused by binding of these solutes.[56] The desolvation, as well as the solute's effect on counterion binding, would contribute to the observed ΔH_{trans} values. Bromoform has a very favorable ΔH_{trans}; comparing it with chloroform indicates the importance of London dispersion interactions, bromine being more polarizable than chlorine.

The effects of a number of functional groups on solute binding were studied using C_4 and C_5 compounds. Originally C_6 compounds were tried, but their low solubility in water precluded easy determination of their $\Delta H_{s,H_2O}$ values. Because of hydrogen bonding possibilities and/or electrostatic stabilization the functional groups studied were expected to be located at or near the CTAB micellar surface. The

hydrocarbon chain would then be oriented radially between surfactant chains. No strong dependence of ΔH_{trans} on the nature of the functional groups present was found, as the data in Table XXXIV show.

Aromatic solutes are known to interact strongly with CTAB micelles; surface solubilization occurs first, followed by transition to interior solubilization at high concentrations of added solute.[56] For the solutes which were studied by calorimetry the molar ratio of solute to CTAB was considerably less than one, so that surface solubilization was expected to be operative. Attempts were made to get enthalpies of binding for biphenyl, naphthalene, phenanthrene and anthracene, but these aromatic hydrocarbons were not sufficiently soluble in 0.1 M CTAB for this purpose. All of the solutes in Table XXXV showed favorable enthalpies of binding. It is felt that in all cases the aromatic rings are interacting with the N-methyl groups of the surfactant molecules and the positively charged nitrogen:



If X can be a negatively charged group, the interaction should be especially favorable. In this connection, Nash[169] has observed a shift in pK_a toward increased dissociation for phenol in the presence of CTAB; Bruice[245] however did not observe this shift. One might also expect

TABLE XXXIV

ENTHALPIES OF SOLUTION OF ORGANIC SOLUTES CONTAINING REPRESENTATIVE FUNCTIONAL GROUPS IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°

Solute	ΔH_s, 0.1 M CTAB, kcal/mole	ΔH_s, H_2O, kcal/mole	ΔH_{trans}, kcal/mole
Butyric acid	-0.384 ± 0.048	-0.391 ± 0.036[b]	0.01 ± 0.06
Valeric acid	-0.391 ± 0.100	-0.089 ± 0.019[c]	-0.30 ± 0.10
Methyl butyrate	-1.29 ± 0.12	-1.85 ± 0.13	0.56 ± 0.17
Butyramide	2.17 ± 0.22	1.94 ± 0.27	0.23 ± 0.34
Valeramide	2.62 ± 0.11	2.23 ± 0.14	0.39 ± 0.18
Butyraldehyde	-3.09 ± 0.25	-3.98 ± 0.17	0.89 ± 0.30
2-Butanone	-2.63 ± 0.10[a]	-2.71 ± 0.03[a]	0.08 ± 0.10
Butyronitrile	-0.509 ± 0.017	-0.754 ± 0.055	0.25 ± 0.06
n-Butylamine	-5.31 ± 0.25	-5.576 ± 0.002[c]	0.26 ± 0.25

[a]Extrapolated to infinite dilution by linear least squares analysis. See Appendix III, Tables LVIII and LIX.

[b]J. Konicek and I. Wadso, Acta. Chem. Scand., 25, 1541 (1971) report -0.350 ± 0.001 kcal/mole.

[c]Same work cited in footnote b above.

TABLE XXXV

ENTHALPIES OF SOLUTION OF AROMATIC ORGANIC SOLUTES IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°

Solute	ΔH_s, 0.1 M CTAB, kcal/mole	ΔH_s, H_2O, kcal/mole	ΔH_{trans}, kcal/mole
Methyl salicylate	0.107 ± 0.046	0.489 ± 0.629	-0.38 ± 0.63
Nitrobenzene	0.155 ± 0.081	1.050[a]	-0.90 ± 0.08
Chlorobenzene	-0.792 ± 0.050	-0.053[a]	-0.74 ± 0.05
Aniline	-1.40 ± 0.08	0.275[a]	-1.68 ± 0.08
Benzaldehyde	-0.124 ± 0.062	1.47 ± 0.14	-1.59 ± 0.15
Benzamide	3.73 ± 0.12	4.60 ± 0.39	-0.87 ± 0.40
2-Naphthol	-1.45 ± 0.31	1.970[a]	-3.42 ± 0.31

[a]A. Katayama, T. Takagishi, K. Konishi and N. Kuroki, Kolloid Z.-Z. Polym., 210, 126 (1966), measured at 25.8°.

such a shift in dissociation constant for substituted phenols and benzoic acids.

Table XXXVI presents observed ΔH_{trans} (binding) for several benzoic acids. These compounds were studied because of Wan's[171] report that only salicylic acid (of those presented in Table XXXVI) produces significant viscosity effects when added to CTAB (no salt present). The enthalpies of binding which were observed do not reflect this selectivity. It had been hoped that the increase in micellar size observed when salicylic acid is added to CTAB, because it does indicate strong binding for this solute, would result in a large exothermic ΔH_{trans}. All of the acids studied do show favorable ΔH_{trans}.

Wan[171] has determined the solubilities of these substituted benzoic acids in CTAB solutions of varying concentration; applying Equation 41[65] to her data one can determine the distribution coefficient K for each substituted benzoic acid. The quantity C_m refers to the

$$y = y_s + y_s(K - 1)\bar{\nu}C_m \qquad (41)$$

concentration of surfactant in micellar form; $\bar{\nu}$ is the partial specific volume of surfactant in solution. When C_m is expressed in grams of micellized surfactant per milliliter of solution and $\bar{\nu}$ is expressed in milliliters/gram $\bar{\nu}C_m = \phi$, which is the volume fraction of solution occupied by the micelles. The concentration of solute in bulk solution is y_s, and the total concentration of solute is y. Use of Equation 41 is made necessary by the way in which Wan's solubility data are presented: as plots of solute concentration (w/v) versus CTAB concentration (w/v). This work assumes that K is of the form $[solute]_{mic}/[solute]_{bulk}$, but

TABLE XXXVI

ENTHALPIES OF SOLUTION OF BENZOIC ACIDS IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°

Solute	ΔH_s, 0.1 M CTAB, kcal/mole	ΔH_s, H_2O, kcal/mole	ΔH_{trans}, kcal/mole
Benzoic acid	2.30 ± 0.20	6.92 ± 0.04[a]	-4.62 ± 0.21
Benzoic acid	2.30 ± 0.20	6.577 ± 0.412[c]	-4.28 ± 0.46
o-Nitrobenzoic acid	3.34 ± 0.51	5.06 ± 0.60	-1.72 ± 0.79
o-Chlorobenzoic acid	4.69 ± 0.20[a]	6.44[d]	-1.75 ± 0.20
o-Aminobenzoic acid	2.44 ± 0.26	6.39 ± 0.61	-3.95 ± 0.66
p-Aminobenzoic acid	4.40 ± 0.16	5.58 ± 0.70	-1.18 ± 0.72
o-Hydroxybenzoic acid (salicylic acid)	2.42 ± 0.11[a,b]	7.74 ± 0.20[a,e]	-5.32 ± 0.24
p-Hydroxybenzoic acid	1.70 ± 0.22	6.83 ± 0.12	-5.13 ± 0.25

[a]Extrapolated to infinite dilution by linear least squares analysis. See Appendix III, Tables LVIII and LIX.

[b]Average of two runs.

[c]Computed by least squares analysis of the temperature dependence of solubility. See Appendix III, Table LX.

[d]International Critical Tables, 5, 148 (1929).

[e]Temperature dependence of the solubility gives slightly different results. See Appendix III, Table LX. Reference d gives 6.38 kcal/mole.

it is impossible to verify this using only solubility data in saturated systems.[64] The K which is chosen should always include the true concentration of solute in the micellar phase. Neither the expression for K chosen by Cordes[178] nor the expression chosen by Bunton[195] fulfills this requirement. Activity coefficients have been assumed to be unity in both the bulk solvent and micellar phases.

The Ks determined from Wan's data appear in Table XXXVII; the calculations appear in Appendix VII, Table LXXXV. Salicylic acid has the highest partition coefficient of the acids studied, but the quantitative differences are not large. Note that Wan's work was done at pH 2. From these Ks the free energies of binding were calculated (Appendix VII, Table LXXXVI); the observed enthalpies were corrected for the fraction of material actually transferred to the micelles. The calorimetric data were not corrected for any possible increase in ionization which might accompany the transfer. The enthalpies of ionization for these acids range from -3 to +1 kcal/mole;[246,247] except for benzoic acid (0.0) they should be taken into account. The case of o-nitrobenzoic acid illustrates the maximum magnitude for this heat of ionization effect. The pK_a for o-nitrobenzoic acid in water is 2.16;[248] addition of 0.004 mole of acid (typical amount used in calorimetry) to 200 ml water would result in 31% ionization for the acid. If 0.1 M CTAB shifts the pK_a one unit, to 1.16, addition of 0.004 mole of acid to 200 ml 0.1 M CTAB would result in 80% ionization for the acid. The observed heat for 0.002 mole of acid ionizing would be - 3 kcal/mole[246] x 0.002 mole or 6 cal. The observed heat of transfer

TABLE XXXVII

THERMODYNAMICS OF BINDING FOR BENZOIC ACIDS TO THE MICELLES IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°[a]

Solute	True ΔH_{trans}, kcal/mole	K	ΔG, kcal/mole	ΔS, eu
o-Nitrobenzoic acid	-2.29	79	-2.58	0.97
o-Chlorobenzoic acid	-2.22	100	-2.72	1.7
o-Aminobenzoic acid	-5.09	91	-2.66	-8.1
p-Aminobenzoic acid	-1.78	52	-2.33	1.8
o-Hydroxybenzoic acid	-6.19	163	-3.01	-11
p-Hydroxybenzoic acid	-9.25	33	-2.06	-24

[a]See Appendix VII, Tables LXXXV and LXXXVI for the calculations.

for 0.004 mole of o-nitrobenzoic acid from 200 ml water to 200 ml 0.1 M CTAB would be ΔH_{trans} x 0.004 mole transferred, or 7 cal. The effect of the pK_a shift is overestimated in this case because only the acid actually bound to the micelles would be expected to have its degree of ionization affected. In addition, o-nitrobenzoic acid has the lowest pK_a of any acid studied. Attempts were made to measure pK_as for the benzoic acids in 0.1 M CTAB, with no success.

o-Aminobenzoic acid, salicylic acid and p-hydroxybenzoic acid have negative entropies of transfer, suggesting a rigid orientation upon binding. None of these compounds would be expected to experience increased solvation when bound to the micellar surface, so the negative ΔS_{trans} cannot arise from a tie-up of solvent molecules. Loss of translational entropy and the entropy change arising from some loss of water of hydration should act in opposing directions for all solutes upon transfer of the solutes to the micellar phase.

The enthalpies of binding for a series of phenols have also been looked at; these results are presented in Table XXXVIII. As in the case of the benzoic acids, these compounds show strong interactions with the CTAB micelles. The true ΔH_{trans} may be very large indeed, since phenols do have an appreciable solubility in water. In 1% CTAB solution 65% of the phenol added is associated with the micelles.[249] Bunton[55] has found that phenols and phenoxide ions affect the rate of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion, Compound XI (p 75), in the presence of CTAB. Phenoxide ions increase the rate of decarboxylation. Considering the calorimetric and counterion binding

TABLE XXXVIII

ENTHALPIES OF SOLUTION OF PHENOLS IN 0.1 M CTAB SOLUTIONS AT (25 ± 1)°

Solute	ΔH_s, 0.1 M CTAB, kcal/mole	ΔH_s, H_2O, kcal/mole	ΔH_{trans}, kcal/mole
Phenol	0.961 ± 0.022[a]	2.97 ± 0.09[c]	-3.93 ± 0.09
Catechol	-1.25 ± 0.27	4.05 ± 0.19	-5.30 ± 0.33
Hydroquinone	1.52 ± 0.05	4.97 ± 0.10	-3.45 ± 0.11
o-Chlorophenol	-6.07 ± 0.29	0.132 ± 0.075	-6.20 ± 0.29
p-Chlorophenol	-1.92 ± 0.09[b]	4.04 ± 0.08	-5.96 ± 0.12
o-Nitrophenol	1.94 ± 0.33	4.49 ± 0.22[d]	-2.55 ± 0.39
p-Nitrophenol	-0.867 ± 0.089[a]	5.16 ± 0.27[e]	-6.03 ± 0.29

[a]Extrapolated to infinite dilution by least squares analysis. See Appendix III, Tables LVIII and LIX.

[b]Based on only four injections, due to a sharp viscosity increase.

[c]L. P. Fernandez and L. G. Hepler, J. Amer. Chem. Soc., 81, 1783 (1959) report 3.10 kcal/mole.

[d]Computed by least squares analysis of the temperature dependence of solubility. See Appendix III, Table LX.

[e]Reference c reports 5.40 kcal/mole.

results with added electrolytes and CTAB and the data on interactions of organic solutes with CTAB, it is clear that effects of additives on micelle structure have been greatly underestimated in explaining micellar catalysis results.

For phenol and catechol, which exhibit concentration-dependent ΔH_s in 0.1 M CTAB, attempts were made to get distribution coefficients from the concentration dependence. This unsuccessful work appears in Appendix VIII. Using Good and Milloy's results[249] for ΔG for phenol in 1% CTAB and our ΔH_{trans} for phenol to various CTAB solutions (see Appendix VIII, Section F and Table LXXXVIII) a true ΔH_{trans} of -2.65 kcal/mole and ΔS_{trans} of 1.1 eu were computed for phenol going from water to 1% CTAB (0.0274 M) solution. The interpolated value for the observed ΔH_{trans} of phenol going from water to 1% CTAB solution was -1.72 kcal/mole, using our data (Appendix VIII, Figure 36). The distribution coefficient K for this system was computed using the expression $[phenol]_{mic}/[phenol]_{bulk}$.[64] Most of the phenols are sufficiently weak acids so that a change in ionization upon transfer to the CTAB micelles would not materially affect the calorimetric results. p-Nitrophenol is the only possible exception to this; its enthalpy of ionization is significant.[250]

Many micellar catalysis investigations employ p-nitrophenyl esters because their hydrolysis is very convenient to follow spectrophotometrically. It is intriguing to consider the possibility that the p-nitrophenoxide ion released in these hydrolyses has an effect on micellar structure and hence on the rate[55] of the reaction being studied. The

concentration of the starting esters is probably too small for this to be a factor,[178] but in many cases it appears that a range of substrate concentrations was not investigated. Hydrolysis of p-nitrophenyl laurate in the presence of CTAB and 1-butanol shows a larger maximum rate enhancement than in the presence of CTAB only.[181]

Although it is considered very likely that both the phenols and benzoic acids studied are solubilized at the micellar surface, this assumption was briefly looked at by calorimetric means. The results are presented in Table XXXIX. The dielectric constant of micellar surfaces is commonly quoted as 36;[12] Thakkar and Hall[66] found the environment of testosterone solubilized by CTAB corresponds to 90% methanol. Table XXXIX lists the enthalpies of solution which were determined for several aromatic solutes in n-hexane and carbon tetrachloride (dielectric constant 2.2 at 20°,[251] but a highly polarizing solvent leading to significant London dispersion interactions between solvent and solute). If a solute were solubilized in the CTAB micelles' interior one might expect the enthalpies of solution in 0.1 M CTAB and in n-hexane or carbon tetrachloride to be at least qualitatively similar. The same statement holds for a solute solubilized close to the micellar surface, but still not in contact with a great deal of water. The values of ΔH_s for phenol and p-nitrophenol in methanol are in closest agreement with observed enthalpies of solution for these compounds in 0.1 M CTAB. It is felt this supports surface solubilization for these compounds. The position of ultraviolet absorption maxima for phenol and catechol in the presence of CTAB also supports solubilization in a region of

TABLE XXXIX

ORGANIC SOLVENTS AS MODELS FOR THE MICELLAR PHASE:
ENTHALPIES OF SOLUTION OF SELECTED ORGANIC
SOLUTES IN ORGANIC SOLVENTS
AT (25 ± 1)°

Solute	ΔH_s, MeOH, kcal/mole [a]	ΔH_s, n-hexane kcal/mole	ΔH_s, 0.1 M CTAB, kcal/mole [d]	Solute	ΔH_s, CCl_4, kcal/mole	ΔH_s, 0.1 M CTAB, kcal/mole [d]
Phenol	0.88	7.65 ± 0.15 [b]	-0.961 ± 0.022	p-Chlorophenol	6.40 ± 0.20	-1.92 ± 0.09
Catechol		8.48 [c]	-1.25 ± 0.27	Catechol	9.06 ± 0.05	-1.25 ± 0.27
p-Nitrophenol	1.83	2.03 [c]	-0.867 ± 0.089	p-Nitrophenol	3.71 ± 1.35	-0.867 ± 0.089
Nitrobenzene		2.77 ± 0.17	0.155 ± 0.081	o-Nitrophenol	5.52 ± 0.29	1.94 ± 0.33
Chlorobenzene		0.667 ± 0.041	-0.792 ± 0.050	2-Naphthol	7.90 ± 0.13	-1.45 ± 0.31
Benzoic acid		4.55 ± 0.11 [b]	2.30 ± 0.20			

[a] G. H. Parsons, C. H. Rochester and C. E. C. Wood, J. Chem. Soc. (B), 533 (1971).

[b] Extrapolated to infinite dilution by least squares analysis. See Appendix III, Tablex LVIII and LIX.

[c] Values from one injection since these compounds showed low solubility in n-hexane.

[d] See Tables XXXV (p 194), XXXVI (p 196), and XXXVIII (p 200).

intermediate dielectric constant (between hydrocarbon and water). See Appendix VIII, Table LXXXVII for these data. Némethy and Ray[252] reached the same conclusions about phenol solubilized by nonionic surfactants. More benzoic acids and phenols were not investigated in the nonpolar solvents because of solubility problems.

CHAPTER VII

HEXADECYLTRIMETHYLAMMONIUM BROMIDE AS A CATALYST FOR THE ALKALINE HYDROLYSIS OF ALKYL SALICYLATES

The hydrolysis of methyl and hexyl salicylate has been investigated at three pHs, using CTAB concentrations in the range 0.001 M to 0.01 M. Attempts to use calcium hydroxide (pH 12) gave very poor experimental results. A phosphate buffer system (pH 11.2) was also tried, but $FePO_4$ is not a very soluble compound, and the analytical technique for following the hydrolysis involved the reaction of ferric ion with salicylic acid.[253] Because of the similarities of the ultraviolet spectra[254] for the acid and esters, this chelation reaction had to be employed. Chapter VIII, Section G, gives details on experimental procedure and on adherence to Beer's Law for the systems studied.

In order to obtain the pseudo first-order rate constants for the hydrolyses log $(A_\infty - A_t)$ was plotted versus time elapsed in minutes for each kinetic run. Representative raw data and least squares analyses for all kinetic runs appear in Appendix IX, Tables LXXXIX and XC. In general, the kinetic data are of poor quality. Methyl salicylate, Table XL, gave much poorer results than hexyl salicylate, Table XLI. This is probably due almost completely to the dependence on pH of the observed absorbance of the complex formed between ferric ion and salicylic acid. The rate constants for hydrolysis of hexyl salicylate in the absence of CTAB could not be obtained, due to the ester's extreme

TABLE XL

HYDROLYSIS OF METHYL SALICYLATE AT 25°[a]

[CTAB], M	pH	$k \times 10^5$, sec^{-1}	$t_{1/2} \times 10^{-4}$, sec
--	9.2[b]	1.59 ± 0.02	4.36 ± 0.06
--	9.2[b]	1.69 ± 0.03	4.10 ± 0.08
0.00497	9.2[b]	1.12 ± 0.05	6.17 ± 0.30
0.00500	9.2[b]	0.605 ± 0.036	11.5 ± 0.70
0.0505	9.2[b]	0.281 ± 0.009	54.1 ± 3.8
--	10.0[c]	1.95 ± 0.09	3.56 ± 0.16
--	10.0[c]	3.24 ± 0.09	2.14 ± 0.06
--	10.0[c]	1.88 ± 0.09	3.69 ± 0.17
--	10.0[c]	3.66 ± 0.15	1.89 ± 0.08
0.00500	10.0[c]	1.67 ± 0.05	4.14 ± 0.13
0.00500	10.0[c]	2.60 ± 0.34	2.67 ± 0.35
--	10.25[d]	1.69 ± 0.09	4.11 ± 0.22
--	10.25[d]	5.49 ± 0.08	1.26 ± 0.02
--	10.25[d]	4.94 ± 0.48	1.41 ± 0.14
0.00501	10.25[d]	2.16 ± 0.09	3.22 ± 0.14
0.00497	10.25[d]	2.20 ± 0.12	3.16 ± 0.18
0.00501	10.25[d]	2.40 ± 0.05	2.89 ± 0.06

[a] All solutions contain 0.02 M NaCl.

[b] 0.02 M borax buffer.

[c] 0.02 M carbonate buffer, 50% base.

[d] 0.03 M carbonate buffer, 75% base.

TABLE XLI

HYDROLYSIS OF HEXYL SALICYLATE AT 25°[a]

[CTAB], M	pH	k x 10^6, sec^{-1}	$t_{1/2}$ x 10^{-5}, sec
0.00503	9.2[b]	1.32 ± 0.05	5.24 ± 0.18
0.00111	10.0[c]	1.43 ± 0.06	4.86 ± 0.22
0.00348	10.0[c]	2.06 ± 0.06	3.36 ± 0.09
0.00454	10.0[c]	2.21 ± 0.04	3.13 ± 0.05
0.00500	10.0[c]	1.92 ± 0.04	3.62 ± 0.07
0.00551	10.0[c]	2.37 ± 0.02	2.93 ± 0.02
0.00654	10.0[c]	1.88 ± 0.08	3.70 ± 0.17
0.01000	10.0[c]	1.87 ± 0.07	3.71 ± 0.13
0.00501	10.25[d]	2.26 ± 0.06	3.07 ± 0.08

[a]All solutions contain 0.02 M NaCl.

[b]0.02 M borax buffer.

[c]0.02 M carbonate buffer, 50% base.

[d]0.03 M carbonate buffer, 75% base.

insolubility in water. This undoubtedly indicates a large distribution coefficient for hexyl salicylate, with the micellar phase being greatly favored.

Methyl salicylate may not be appreciably associated with the CTAB micelles in 0.005 M CTAB, because the ester concentrations which were used (10^{-3} M) do not exceed the ester's solubility in water. The ester concentration does not affect the observed rate constants in any regular fashion when CTAB is present, indicating that structural effects such as those mentioned in Chapter VI, Section D are not operating or are not detectable. The methyl salicylate concentration used is quite high when compared with the CTAB concentration; this is also a consequence of our analytical technique. Use of these high ester concentrations violates the desirable situation of having only one molecule of substrate per micelle.[1] However, the results with hexyl salicylate, where the CTAB concentration increases and the ester concentration does not, indicate no substantial effects on the hydrolysis rates at a high ester to CTAB molar ratio.

CTAB slightly retards the rate of methyl salicylate hydrolysis; this effect was observed at all pHs studied. This is consistent with the results of other workers on alkaline hydrolysis of simple aliphatic esters.[222-224] In the presence of 0.05 M CTAB (borax buffer) the rate of hydrolysis is further decreased compared to its value at low CTAB concentrations. This result has been frequently observed by other workers.[1] Hydrolysis of hexyl salicylate is not affected by changes in CTAB concentration, as the results at pH 10 show. The difference

in chain length of the alcohol portions of the ester seems to have no influence on the effect of CTAB on their hydrolyses. One would have expected hydrophobic interactions of the substrate methylene groups with surfactant molecules to be important. This mode of solubilization should still leave the aromatic ring at the micellar surface, "sandwiched" between surfactant head groups; the ester group and hydroxyl group should still be accessible to bulk solvent.

Figure 9 shows the observed rate constants for methyl salicylate hydrolysis with and without CTAB and for hexyl salicylate with CTAB plotted versus the hydroxide ion concentrations used. Except for methyl salicylate in the presence of CTAB, the data follow the equation $k_{obs} = k_1 + k_2[OH^-]$. For methyl salicylate in water k_2 equal to 0.22 M^{-1} sec^{-1} (lit[225] 0.51 M^{-1} sec^{-1}) was obtained; for hexyl salicylate in 0.005 M CTAB, k_2 was 0.058 M^{-1} sec^{-1}. It is felt that the non-linear k versus $[OH^-]$ plot for methyl salicylate with CTAB reflects the pK_a of the ester's hydroxyl group; apparently a region of pH corresponding to the inflection point observed by Bender[227] in the log k_{obs} versus pH plot for methyl salicylate in water has been investigated. In Bender's study the relatively flat portion of the rate profile stretched from pH 10 to pH 11.5. In this work a leveling off at approximately pH 10 is seen also. CTAB may or may not be affecting the pK_a of the ester's hydroxyl group. However, because the plot for methyl salicylate without CTAB is a straight line, a shift in pK_a caused by CTAB is a likely proposal. It is likely that no plateau is observed in the hexyl salicylate case because the pK_a of this ester's hydroxyl

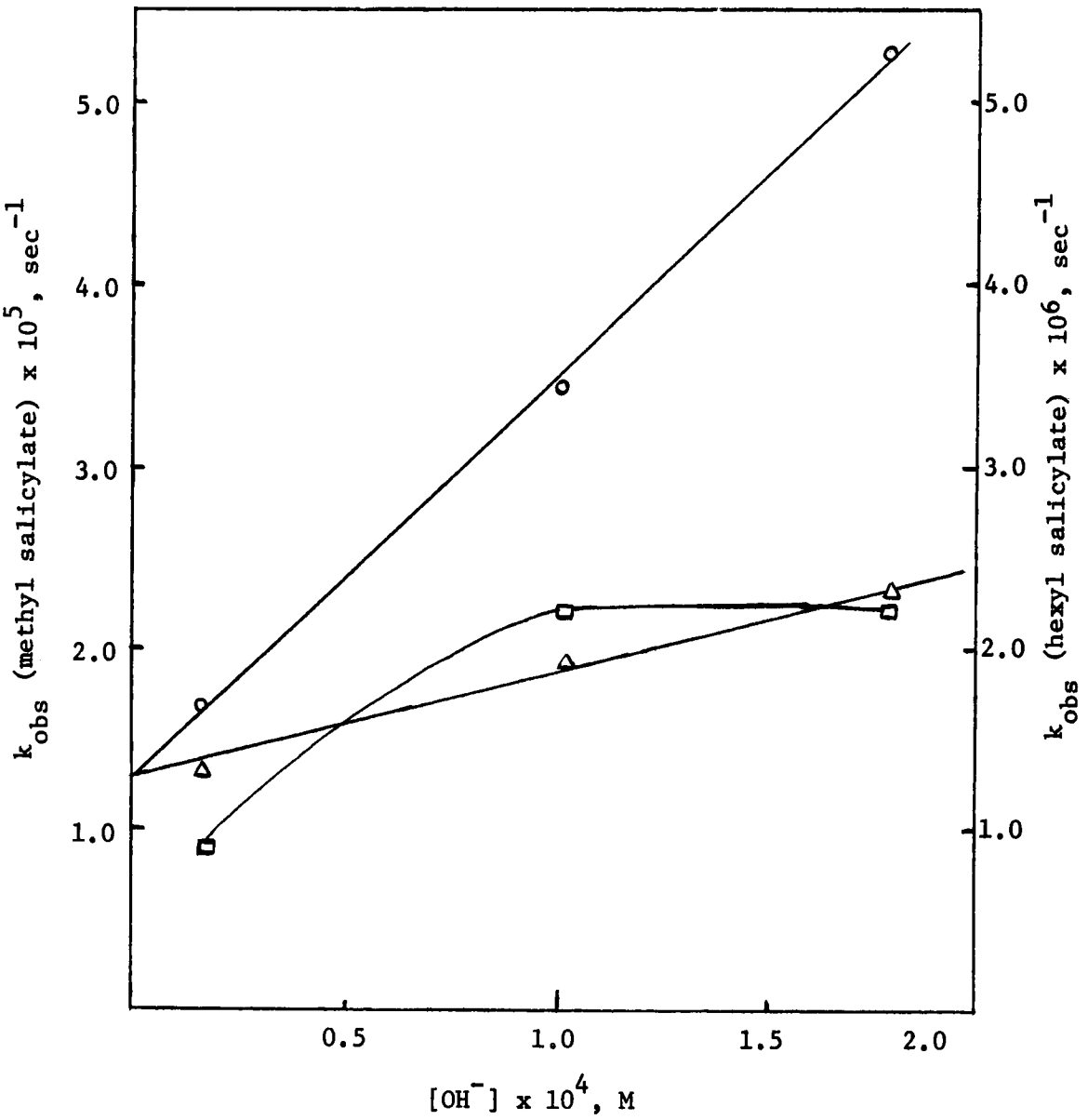


Figure 9. Hydrolysis of methyl and hexyl salicylate in the presence of CTAB.

Circles: methyl salicylate in water, squares: methyl salicylate in 0.005 M CTAB, triangles: hexyl salicylate in 0.005 M CTAB.

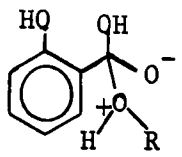
group is significantly higher than that of methyl salicylate. Tommila[225] reports a pK_a of 10.2 for methyl salicylate and 10.5 for ethyl salicylate; one might expect the trend to continue as the chain length of the alcohol involved in the ester increases.

One might propose that initial release of salicylic acid by hydrolysis in the presence of CTAB acts to inhibit further hydrolysis by strong binding to the micellar surface, decreasing its surface potential. Use of the distribution coefficient calculated for salicylic acid using Wan's data, Table XXXVII (p 198), shows that most of the salicylic acid released when the concentration of CTAB is 0.005 M will go into bulk solvent, however. Neither the esters nor salicylic acid displace significant amounts of Br^- from the CTAB micellar surfaces (see Appendix VII, Tables LXXXIII and LXXXIV).

In order to explain the absence of significant rate enhancement in the hydrolysis of methyl and hexyl salicylate in the presence of CTAB, one needs to consider certain characteristics of the CTAB micellar surfaces. It has been seen that hydroxide ion is significantly bound to the surface; it is known that the dielectric constant at the surface is appreciably lower[12,66] than it is in bulk solution and hence water molecules may be somewhat more scarce than they are in bulk solution. The high concentration of OH^- at the micellar surface means that the concentration of protons will be low. Table XXIV (p 164) indicates that 0.005 M CTAB in the presence of approximately 10^{-4} M NaOH has 7.3×10^{-5} M OH^- bound to the micelles; this corresponds to an actual concentration of OH^- in the micellar phase of at least 0.04 M. The surface concentration

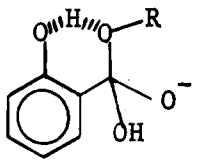
is probably even higher. Without making any assumptions about the ion-product constant for water at the micellar surface one can see that the proton concentration will be quite low.

In hydrolysis of an alkyl salicylate the rate-determining step is loss of alcohol from the tetrahedral intermediate, Structure XIV.[213]



XIV

Note that the alcohol's oxygen in the ester needs to be protonated prior to loss of the alcohol. In hydrolysis of p-nitrophenyl esters the rate-determining step is formation of the tetrahedral intermediate; the p-nitrophenol is lost as the anion, because of its low pK_a. The rate of formation of the tetrahedral intermediate should be enhanced for both kinds of esters when their hydrolysis occurs at a positively charged micelle surface. For the simple alkyl esters this is of no consequence, since decomposition of the tetrahedral intermediate is rate-determining. The necessary protonation of the alcohol oxygen may actually be difficult, given the low concentration of protons available. One could invoke proton transfer from the ester's hydroxyl group, which would have a six-centered transition state, Structure XV, but this should only be possible at pHs below the pK_a of the ester when bound to the micellar surface. The suggested proton transfer would probably be slow, since protonated ethers are much stronger acids than phenols. Because of this the lowest possible energy of activation for proton transfer is



XV

the difference in free energy of the phenol and the protonated ether. The major difference in behavior for hydrolysis of the two kinds of esters in the presence of surfactants certainly is the rate-determining step.

When the study of salicylate ester hydrolysis was begun it was felt that the interactions of salicylic acid with CTAB would produce significant rate enhancements, to the extent those interactions were felt in the transition state of the rate-determining step of the hydrolysis. Clearly this interaction is not felt to any significant extent. It was also felt that solubilization of a substrate by micelles would of itself predict inhibition rather than rate enhancements for any reaction susceptible to micellar catalysis, by virtue of a decrease in free energy for the substrate. The substrate binding after all decreases the substrate's free energy, relative to the situation in bulk solution. Apparently the micelles will have much the same stabilizing effect on transition states as on the ground states. On top of this effect will be electrostatic and proximity effects, where appropriate. This affords a reasonable explanation for catalysis of p-nitrophenyl ester hydrolyses as well as several other systems. There are of course systems[184] where

hydrophobic bonding effects between substrate and micelles appear to directly influence the magnitude of the rate enhancements observed. In these cases differences in stabilization for ground state and transition state as a result of solubilization could be invoked. These sorts of effects on transition states cannot be measured by calorimetry.

In conclusion, the inhibition of methyl salicylate hydrolysis caused by 0.05 M CTAB will be briefly discussed. One view of this kind of effect deals with counterion inhibition,[178] another with concentrations of the reactants.[201,202] The concentration of hydroxide ion may be lower on the CTAB micelles in 0.05 M CTAB compared to 0.005 M CTAB (say 0.0049 M versus 0.04 M), and there should be at least one molecule of ester per micelle. Data for the kinetic system, presented in Appendix VII, Table LXXXII, show the decrease in OH^- concentration in the micellar phase with increasing CTAB concentration very nicely. Unfortunately, these measurements could not be obtained in the presence of buffer solutions. For NaLS, however, Bunton[203] finds that buffer effects are not a large factor in altering hydrogen ion concentration at the NaLS micellar surface. Since the overall reaction follows the rate law $k_{obs} = k_1 + k_2[OH^-]$, this decrease in OH^- concentration causes a decrease in the observed rate of reaction. This of course assumes that methyl salicylate is appreciably bound to the micelles. It is not clear why hexyl salicylate does not show a similar dependence on the concentration of CTAB. Perhaps a sufficient range of CTAB concentrations was not studied.

Bunton[203] has treated reactions catalyzed by hydrogen ions in

the presence of NaLS in the same way: he has computed the concentration of bound hydrogen ions in the micellar pseudophase. He uses these concentrations to compute second-order rate constants for reaction of substrate plus hydrogen ion in the micelles. When this is done over a range of NaLS concentrations, what appears as inhibition with increased surfactant concentration for k_{obs} disappears and a true plateau region is observed. It is felt that Cordes' thoughts on counterion inhibition with increasing surfactant concentration have been laid to rest. The important effects in micellar catalysis are proximity of reactants, dielectric constant, micellar charge density and micellar structural effects. With respect to this last variable, workers who obtain activation parameters for reactions catalyzed by micelles are erroneously disregarding the effects of temperature on micelle size and degree of counterion binding.

CHAPTER VIII

EXPERIMENTAL SECTION

A. Basic Equipment

A Kontes WS-2 continuous water still was used to provide water for the experiments. Weighings were done using a Mettler H20T analytical balance having an accuracy of $\pm$ 0.01 mg. When a series of solutions were needed containing one solute in varying concentrations, but other solutes at a constant concentration, serial dilutions were made using volumetric pipettes and a stock solvent containing the solutes to be held at constant concentration. Solutes having low water solubility and/or high vapor pressures were handled by individual weighings.

The constant temperature baths used for viscometry, counterion binding studies and micellar catalysis were maintained at $24.95 \pm 0.06)^{\circ}$, except where noted otherwise in the Results and Discussion Chapters. The temperature was recorded using a Beckmann thermometer calibrated against a platinum resistance thermometer which had in turn been calibrated using the freezing and boiling points of water. At 30° and 40° temperature control was certainly somewhat poorer. For work using the Haake Rotovisco a Neslabs Instruments, Inc. circulating constant temperature bath was used.

For pH readings either a Sargent Model LS pH meter, a Beckman Expandomatic pH meter or an Orion Model 701 pH/mV meter was used. Sargent S-30072-15 combination electrodes were employed in the pH

measurements. For the counterion binding studies only the Orion meter was used.

Beakers, flasks and pipettes used in experiments involving surfactants were not cleaned with organic solvents unless absolutely necessary. In general distilled water was used, followed by oven drying.

B. Statistical Methods

When a number of determinations of an experimental quantity was made values were neglected using the 95% confidence level criterion.[255] Standard deviations were computed using Equation 42. When

$$\sigma = \sqrt{\sum_{i=1}^{N} (X_i - M)^2 / N-1} \qquad (42)$$

mathematical operations involving two or more numbers, each with an associated standard deviation, were carried out the standard deviation (σ_p) associated with the result of the mathematical operation was calculated using the equations found in Daniels, et al.[256] Equations 43, 44, and 45 were used for the operations of addition (subtraction), multiplication and division respectively. Capital letters represent the numbers and the corresponding small letters represent their associated standard deviations. In Division A represents the divisor.

$$\sigma_p = \pm \sqrt{a^2 + b^2} \qquad (43)$$

$$\sigma_p = \pm \sqrt{(Ab)^2 + (Ba)^2} \qquad (44)$$

$$\sigma_p = \pm \quad (1/A) \sqrt{b^2 + B^2a^2/A^2} \qquad (45)$$

C. Viscometry

1. Ostwald Capillary Viscometers

The viscometers used were cleaned by soaking in warm cleaning solution ($K_2Cr_2O_7$ in conc. H_2SO_4) for at least two hours, followed by copious rinsing with distilled water and oven drying. The viscometers were charged with 5.5 ml of the liquid whose viscosity was to be determined and placed in a constant temperature bath 30 minutes prior to the time at which readings were taken. The liquid was drawn into the upper bulb of the viscometer by means of a rubber squeeze bulb and a piece of tygon tubing containing a wad of cotton. Flow times for the liquid were obtained using either a Heuer stopwatch or a Lab-chron (Lab-Line Instruments, Inc.) electric timer. Times were reported to the nearest one-tenth of a second. A minimum of five determinations were made for each liquid. The viscosity (η) of each liquid was calculated using Equation 46.[257] This equation takes kinetic energy corrections into account. The flow time (t) was an average of the five determinations and the density (ρ) of the liquid was obtained using a 10 ml or 25 ml jacketed pycnometer thermostated in the constant temperature bath. The values of A and B, the viscometer constants, were

$$\eta_{KE} = A\rho t - B\rho/t \qquad (46)$$

determined by measuring the flow times for water, carbon tetrachloride, benzene and methanol in the viscometers. The viscosities of these liquids, in centipoise (cP), were obtained from the Handbook of Chemistry and Physics.[258] Where necessary, interpolation with respect to temperature

was performed on the tabulated viscosities. Using the flow times and viscosities for these liquids, four simultaneous equations (unknowns A and B) could be set up and solved for each viscometer. For the viscometers used, the flow time for water ranged from 80 to 109 sec. In computing standard deviations for η only the standard deviation of the time was used. Standard deviations for A and B were much less significant. For η values below 1 cP only three figures are significant, because these values correspond to flow times of less than 100 sec.

Particularly for CTAB, a range of viscosities was observed for different batches of soap. For this reason several η_{KE} values for the 0.1 M CTAB-0.1 M NaBr system have been used. Unrecrystallized CTAB had a viscosity of 3.787 cP under these conditions; for the recrystallized CTAB values from 4.290 cP to 4.697 cP were observed. Where η_{rel} (to no solute) values were reported for 0.1 M CTAB-0.1 M NaBr-solute systems care was taken to use the appropriate value of η_{KE} for 0.1 M CTAB - 0.1 M NaBr.

2. Determination of Intrinsic Viscosities

In determining intrinsic viscosities by extrapolating plots of η_{sp}/C_m versus C_m to zero concentration (Equation 32, p 89) for CTAB in various concentrations of NaBr, there were generally a few experimental points which were located above or below the best curve. Those points showing a serious positive deviation from the curve determined by the remaining points were neglected on the basis that there was an error in η_{CMC}.[36] Those points showing serious negative deviations

were also neglected; this has been done by other workers[259] in determining the intrinsic viscosity of potassium myristate. See Appendix II, Figures 15 and 16, for examples of both kinds of deviation.

3. Haake Rotovisco

The Rotovisco was equipped with the SVI series cup and bob, thermostated to 25° using the circulating constant temperature bath. The cup was charged using a pipet with the liquid whose viscosity was to be determined; any trapped air bubbles were allowed to escape before placing the cup into the Rotovisco. After allowing 30 minutes for the Rotovisco to warm up and the liquid in the cup to come to constant temperature, viscosity measurements were begun. The Rotovisco was operated in the direction of increasing rate of shear (and hence decreasing gear position number). The shearing stress, as a scale reading S, was recorded at each gear position using a strip chart recorder. The Rotovisco was allowed to run for a few minutes at each position.

The apparent viscosity at each rate of shear was calculated using Equation 47, where U is the number of the gear position, S is the scale reading (0 to 100) and K is the instrument constant. Some

$$\eta_{apparent}(\text{poise}) = U \times S \times K \qquad (47)$$

of the viscosity data were obtained by using a ruler to measure S from the recorder paper, because the number of significant figures attainable could thereby be increased. This is the origin of the varying number

of significant figures for the viscosities reported in Appendix I, Table XLV.

The instrument constant K is equal to A/B where A and B are two additional instrument constants; A = 11.52584 dynes/cm^2 and B = 455.6293 sec^{-1} for the SVI cup and bob used under the conditions of this work. The constants A and B may be used to calculate the shearing stress and rate of shear respectively for each apparent viscosity determined. The shearing stress is equal to A x S and the rate of shear is equal to B/U. Data for the solutions examined by rotational viscometry appear in Appendix I, Table XLV. Plots of shearing stress versus rate of shear (Appendix I, Figures 10 and 11) for some of these solutions indicate that they are pseudoplastic.[260]

From the constants A and B K may be calculated to be 0.02530. The value of K was also determined experimentally, however, using a Newtonian oil with η = 209 poise at 25°. This determination required that the torsion spring used to detect viscous drag on the rotor be made less sensitive by a factor of ten (A = 115.2584 dynes/cm^2). The value of K so determined was 0.2572, corresponding to K = 0.02572 for A = 11.52584 dynes/cm^2. This was good agreement with the value 0.02530. It should be pointed out that using a Newtonian instrument constant to calculate apparent viscosities for non-Newtonian systems is not strictly correct. However, this work was aimed at determining relative viscosity differences for different systems, rather than their absolute viscosities.

D. Determination of Critical Micelle Concentrations Using Surface Tension

Surface tension measurements on surfactant solutions were carried out using a Du Nuoy tensiometer equipped with a platinum-iridium ring. The ring was cleaned briefly with cleaning solution, then washed copiously with distilled water. The ring was handled at all times with forceps. Four or five determinations were made on each solution (contained in a small crystallizing dish) according to the procedure of Daniels, et al.[261] Special efforts were made to keep the bar from which the ring was suspended horizontal with respect to the desk top. After each determination the ring was rinsed with distilled water and blotted dry using filter paper.

Good temperature control was not possible; measurements were made at ambient temperature, but each solution (in a volumetric flask) was brought to 25° in the constant temperature bath first. The surfactant solutions used which had concentrations near the CMC were made ca. 30 minutes before readings were taken so that the characteristic dip in the surface tension (γ) versus log (surfactant concentration) plot could be avoided.

In order to determine the CMC of a surfactant plots of γ versus log C (surfactant concentration) were used: two lines or curves were obtained in each case, having the CMC as their point of intersection. Plots of the scale reading, directly from the tensiometer, versus log C gave the same result. Representative plots appear in Appendix X, Figures 37, 38 and 39. In order to obtain γ from the scale readings the

dynes per scale division had to be determined. To do this the ring was loaded with weighed pieces of wire and the amount of force necessary to just lift the horizontal bar from its support was measured. The dynes per scale division were then calculated by dividing the weight of the wire pieces by the observed scale reading and multiplying by 981 (the applicable proportionality constant).

1. Use of Surface Tension Critical Micelle Concentrations in Intrinsic Viscosity Calculations

For each system whose intrinsic viscosity was investigated it was necessary to know the CMC in order that η_{CMC} could be determined. For the CTAB-0.1 M NaBr system there are two good candidates for the CMC; these are indicated in Appendix X, Figure 37. For the CTAB-x M NaBr systems a constant CMC of 10^{-5} M was used; actual values from the Corrin plot for CTAB at 25° are: 0.178 M NaBr, CMC = 1.3×10^{-5} M and 0.400 M NaBr, CMC = 7.2×10^{-6} M (see Appendix IV, Figure 23).

E. Counterion Binding Studies

The reference electrode used (except for pH measurements) was the Orion Model 90-02 double junction reference electrode. The inner chamber was filled with solution 90-00-02 and the outer chamber was filled with solution 90-00-03, 10% KNO_3, except for measurements of NO_3^- and Br^- competition, where 10% KCl was used. These filling solutions were changed every one to two weeks. The effect of liquid-junction potentials was neglected. The specific-ion electrodes used were the Orion Model 94-35 bromide-ion electrode, the Orion Model 94-17

chloride-ion electrode and the Orion Model 92-07 nitrate-ion electrode. The latter electrode is of the liquid membrane type. All emf measurements were recorded using the Orion Model 701 pH/mV meter, except for studies reported in Appendix VII, Tables LXXXII, LXXXIII and LXXXIV, and in Tables XXII (p 160) (0.005 M CTAB only) and XXIV (p 164). For these studies a Keithley microvolt null detector was used.

The measured potential of a solution containing X^- using an electrode sensitive to X^- is given by Equation 48. The term E_a is due to the choice of reference electrode and internal filling solutions for that reference electrode.

$$E = E_a + 2.3RT/nF \ (\log a_{X^-}) \qquad (48)$$

In practice a series of standard solutions containing varying concentrations of the salt NaX were prepared. Their potentials were measured and plotted against log a_{X^-} in the surfactant sample solutions. The a_{X^-} for the standards were obtained using activity coefficients (γ) for NaX from Latimer.[241] Where interpolation was necessary (because γ for a particular concentration was not given in Latimer) a plot of γ versus concentration was constructed and used. For NaOH the activity coefficients for NaCl were used; they are quite similar at concentrations of the two salts where comparisons can be made. The slope of the resulting straight line should be -59.16 mV at 25°. In practice slopes slightly less than this (ca. -58 mV) were observed. Least squares analysis was not applied to the calibration plots because of their good quality. See Appendix X, Figure 40 for a calibration plot.

It was assumed in these experiments that ions bound to the micelles present in surfactant solutions do not contribute to a_{X^-} for that solution. For the studies appearing in Appendix VII, Tables LXXXII, LXXXIII and LXXIV and in Table XXIV (p 164) plots of emf versus log C_{X^-} were used for the standards, because they contained all other salts present in the sample solutions.

Both samples and standards were allowed to come to constant temperature by placing them in a constant temperature bath 30 minutes prior to taking readings. A series of standards or samples were always read starting with the least concentrated solution and proceeding to the most concentrated one. Because the millivolt readings do drift slowly toward a constant value with time, a waiting period of up to ten minutes was sometimes necessary before a reliable reading could be obtained. When transferring the electrodes from one solution to another they were either rinsed with distilled water and blotted with a tissue or simply blotted.

Readings on sample solutions were frequently taken interspersed with readings on standard solutions, because of the problem of electrode drift with time. Appendix X, Figure 41 illustrates the technique which was then used to get the value of a_{X^-} for each sample solution: millivolt readings for standards read directly before and after each sample were used in the calibration lines.

The problem of the reproducibility of the measured potential for a particular solution was most important for the studies of α for alkyltrimethylammonium bromide surfactants in the presence of salts. For

most of the NaBr standard solutions used in these studies two or more readings, taken within one to two hours of each other, are available. For a few of the experimental runs these readings for each standard have been averaged; Appendix X, Table XCI reports the average millivolt readings and associated maximum deviations for a series of NaBr standard solutions used in the study of free Br^- in 0.1 M CTAB containing added NaBr. In this study the total range of millivolt readings for the samples was -94.0 mV to -125.7 mV.

In the determination of $a_{NO_3^-}$ in CTAB solutions containing $NaNO_3$ the maximum deviation for repeated readings for $NaNO_3$ was $\pm$ 0.5 mV. The worst reproducibility was observed in the study of 0.2 M $C_{10}NMe_3Br$ in the presence of NaBr. Deviations of up to $\pm$ 1.6 mV from the average values were observed for the millivolt readings of the standards. In this study the millivolt readings of the samples ranged from -101.9 mV to -126.8 mV. Furthermore, when an entire series of measurements were repeated, the observed a_{X^-} for the samples were in good agreement ($\pm$ 10%) for the two runs. This was done in the study of α and γ_s for CTAB, for example (Table V, p 104).

For the work on OH^- binding in 0.1 M CTAB solutions pH readings were obtained for a series of NaOH solutions and plotted against log a_{OH^-}. The resulting straight line should have a slope close to one; Appendix X, Figure 42 shows that this was the case. Values of a_{OH^-} for the samples were then obtained from this straight line by interpolation. For the OH^- binding data in Table XXII (p 160) for 0.005 M CTAB a different procedure was followed. The pH of a solution with and

without CTAB was determined and the resulting difference in OH^- concentration used as the amount of OH^- bound to the micelles.

In the use of the nitrate ion specific electrode corrections to the observed $a_{NO_3^-}$ for samples containing Br^- had to be made because Br^- interferes with the nitrate ion specific electrode according to Equation 49.[262] These corrections were necessary for 0.01 M and 0.1 M

$$E_{obs} = E_a - 2.3RT/F \ (\log[a_{NO_3^-} + 0.13a_{Br^-}]) \qquad (49)$$

CTAB solutions studied in the presence of $NaNO_3$. The necessary a_{Br^-} for each sample was obtained using the bromide ion specific electrode, which is not susceptible to interference by nitrate ion. A calibration plot of E_{obs} versus log $a_{NO_3^-}$ (standards) was used to get the quantity $[a_{NO_3^-} + 0.13a_{Br^-}]$ for each sample. The observed a_{Br^-} for the sample was then multiplied by 0.13 and subtracted from $[a_{NO_3^-} + 0.13a_{Br^-}]$ to give the actual $a_{NO_3^-}$ for each sample.

Stirring can have some effect on values of α obtained for the micelles in surfactant solutions. Readings were taken in the following systems while they were being stirred magnetically: (1) 0.2 M $C_{10}NMe_3Br$ (Table VI, p 109) and (2) some of the competitive counterion binding for 0.1 M and 0.01 M CTAB (NO_3^- versus Br^-, Table XXI, p. 157). Stirring effects (Table XI, p 121) cannot account for all of the Br^- displaced by NO_3^- or OH^- ions, however. No estimate of the fractions of Br^- which might be displaced by stirring in the competition experiments was made.

In order to convert a_{X^-} for samples into C_{X^-}, plots of a_{X^-} versus C_{X^-} constructed from data in Latimer[241] were used. The errors encountered

in carrying out this sort of interpolation should be within the reproducibility of a millivolt reading for a given sample. For binding studies in two-counterion systems a_{X^-} for each counterion was first converted into C_{X^-} without taking the other counterion's presence into account. The resulting C_{X^-} (one for each ion in each sample) were then added together and a γ for each ion determined. These γ values took into account both kinds of ions; they were used to convert the a_{X^-} for each ion into a final C_{X^-} for each ion. In the case of 0.1 M CTAB containing $NaSO_3C_7H_7$ and NaBr it was assumed that 25% of the total added tosylate ion was free in solution.

F. Calorimetric Procedure

The construction and operating principles of the calorimeter used have been described.[263,264] In a typical run twin calorimeters were each filled with 200 ml of solvent, delivered by volumetric pipet. When the solvent was a 0.04 M solution of NaLS the solution was prepared just prior to placing it in the calorimeter. Solutions of CTAB frequently had to be warmed to 26° in order to get all of the CTAB into solution, then cooled below 25° prior to introduction into the calorimeter. For temperatures around 25° no temperature control was usually necessary: $(25 \pm 1)°$ could easily be achieved by holding the ambient temperature at 22°. For solutes having highly exothermic ΔH_s values, the calorimeter was inserted into a metal can, and the can was placed in a polyethylene Dewar containing water at 10°. For operating temperatures significantly above 25° the polyethylene Dewar was filled with water 15° above the desired operating temperature.

After the solvents were allowed to equilibrate, with stirring, for about 15 minutes, the solute injection procedure was begun. Solid samples were injected by means of a 3 cc plastic Jelco syringe with the tip cut off and replaced by a silicone rubber septum. After weighing each sample into a syringe the syringes were stored in a desiccator containing either Drierite or P_2O_5. Hygroscopic solutes were handled in a Dry Box or glove bag, except for actual weighing of the filled syringes. Liquid samples were injected into the calorimeter using a 500 µl Hamilton syringe with a Chaney adaptor and a Teflon needle on a Luer tip. The injections were calibrated by using machined brass stops; the volume of each injection was determined by weighing repeated injections of absolute ethanol into a stoppered Erlenmeyer flask.

The heat evolved or absorbed during operation of the calorimeter was recorded using a strip chart recorder. Before each injection of a solid sample a heating curve was run for the purpose of calibration; before and after each three injections of a liquid sample two heating curves were run. The calibrated injections of liquid samples were preceded by a small injection designed to remove any solute contaminated by solvent from the Teflon needle of the syringe. An electrical heater was used to introduce a measured amount of heat (in calories) according to Equation 50, where I is the current through the heater resistance R, and t is the time of heating in seconds. Dividing Q_e by Δ^c, the

$$Q_e = I^2Rt/4.184 \qquad (50)$$

length of the heating curve in millimeters, gives the calories per unit

pen deflection. The enthalpy of solution for a solute was calculated using Equation 51, where Δ^R is the length of the pen deflection, in millimeters, upon sample injection, MW is the molecular weight of the

$$\Delta H_s \text{ (kcal/mole)} = (Q_e/\Delta^c)\Delta^R MW/mg \qquad (51)$$

solute and mg is the weight of the injected sample in milligrams. For liquid samples the weight is obtained by multiplying the density of the sample by the volume of the injection.

In some cases ΔH_s was dependent on the concentration of the solutes; the raw data and the necessary extrapolations to infinite dilution appear in Appendix III, Tables LVIII and LIX. Six determinations of ΔH_s were made for each solute whenever possible. For some solutes whose ΔH_s were determined in surfactant solutions fewer than six injections were made because the solute caused precipitation of the surfactant.

G. Salicylate Ester Hydrolysis

The increase in salicylic acid concentration during the hydrolysis reactions was followed by allowing the salicylic acid to react with $FeCl_3$ in acidic solution.[253] The absorbance of the resulting complex in acidic solution was monitored at 532 nm, its experimentally determined λ_{max} (A at 520 nm up to 545 nm was examined) using a Beckman DU spectrophotometer. The blank used contained $FeCl_3$ in acidic solution.

The absorbance of the complex was found to obey Beer's Law in the presence of borax buffer, NaCl and CTAB: see Appendix X, Figure 43 for the plots of A versus salicylic acid concentration. The presence of

CTAB in the blank was not necessary. The presence of CTAB did alter the extinction coefficient of the complex: $\varepsilon_{\text{no CTAB}} = 1611$, but $\varepsilon_{0.005\ \text{M CTAB}} = 1473$. Methyl salicylate also gave rise to a very weak absorbance: $\varepsilon = 95$ (see Appendix X, Figure 43). The absorbance of the ester presented no problem however, as the analysis in Equation 52 shows (the path length of the cells used was 1 cm). The concentrations c_1 and c_2 are for acid and ester respectively; ε_1 and ε_2 are their respective extinction coefficients. The total concentration of acid and ester is $c_{\text{total}} = c_1 + c_2$.

$$\begin{aligned} A_{\text{total}} &= \varepsilon_1 c_1 + \varepsilon_2 c_2 \\ &= \varepsilon_1 c_1 + \varepsilon_2 (c_{\text{total}} - c_1) \\ &= c_1(\varepsilon_1 - \varepsilon_2) + \varepsilon_2 c_{\text{total}} \end{aligned} \tag{52}$$

Two-hundredths molar borax buffer was prepared using $Na_2B_4O_7 \cdot 10H_2O$ (Merck Reagent); 0.02 M carbonate buffer (pH 10) was prepared using equimolar amounts of Na_2CO_3 (Baker reagent) and $NaHCO_3$ (Baker reagent). Carbonate buffer, 0.03 M and 75% base, contained 0.0225 M Na_2CO_3 and 0.0075 M $NaHCO_3$. All solutions used in the kinetic studies contained 0.02 M NaCl, oven-dried. The water for the buffer solutions was boiled prior to use.

For each run the ester and CTAB, if used, was weighed into a 100 ml volumetric flask, which was filled to volume using a stock solution containing buffer and NaCl. After vigorous mixing, the flask was placed in the constant temperature bath. Five milliliter aliquots were withdrawn periodically; the pH of each was recorded. It was found

that the pH remained constant over the entire course of the reaction. Each aliquot was treated with 0.5 ml of 1% w/v $FeCl_3 \cdot 6H_2O$ (Fisher Scientific, Certified A.C.S.) made up in 0.1 N HCl, delivered from a burette. The aliquot was then titrated with 1 N HCl to a final pH of 3.1 to 3.4 and diluted to volume in a 10 ml volumetric flask. The absorbance of the aliquot was then measured as described previously. The A_∞ values were determined after ten half-lives, and they are the average of at least two determinations. Some difficulty in obtaining consistent color development (formation of the complex) was encountered. This is thought to be due to the sensitivity of the salicylic acid-ferric ion reaction to the pH of the solution.

Least squares analysis of a plot of log $(A_\infty - A_t)$ versus time (minutes) for each kinetic run was carried out; the results appear in Appendix IX, Table XC. To convert the slope of each line into a pseudo first-order rate constant (k) in $(\text{seconds})^{-1}$ the slope was multiplied by 2.303 and divided by 60 (the number of seconds per minute). The half life $(t_{1/2})$ corresponding to each k was determined by Equation 53.

$$t_{1/2} = 0.693/k \tag{53}$$

H. Preparation and Purification of Surfactants

Melting points are not generally a reliable test of surfactant purity. Determination of the CMC is the most widely used criterion for purity;[4] molecular weight determinations are also suitable. Titration of a known weight of surfactant with a standardized $AgNO_3$ solution

was used in this work for molecular weight determinations. The bromide ion specific electrode was used to follow the course of the titration. The emf reading at x ml of added $AgNO_3$ was recorded; the equivalence point was found in the conventional manner. A representative titration curve is presented in Appendix X, Figure 44. The $AgNO_3$ used was standardized against NaBr which had been dried to constant weight.

1. Decyltrimethylammonium Bromide ($C_{10}NMe_3Br$)

Decyltrimethylammonium bromide (Eastman) was used as received. CMC values were 5.0×10^{-2} M (surface tension) and 6.26×10^{-2} M by bromide ion specific electrode (a_{Br} - versus C). Literature values cluster around 6.4×10^{-2} M.[4]

2. Dodecyltrimethylammonium Bromide (DTAB)

The surfactant DTAB was prepared from 1-bromododecane (Matheson, Coleman, Bell 97%) and trimethylamine (Eastman, 25% aqueous solution) by the method of Scott and Tartar.[265] Dry trimethylamine was obtained by distillation from the 25% aqueous solution. The vapors were allowed to pass through a CaO plug and then condensed in a receiver cooled with Dry Ice-acetone. The trimethylamine could then be introduced, by warming the receiver, into a 1000 ml three-necked round-bottom flask fitted with a drying tube, Dry Ice-acetone condenser and addition funnel and containing 300 ml absolute ethanol. The amount of trimethylamine introduced (0.643 mole) was determined by weighing the reaction flask before and after addition. The 1-bromododecane (0.470 mole) was added dropwise in 45 minutes, with the reaction mixture held at 0°.

The reaction mixture was then allowed to warm to room temperature and stirred for five hours.

After the excess trimethylamine and ethanol had been removed by evaporation, the resulting DTAB was recrystallized from acetone-ethanol mixtures. Nice white flakes were obtained; these were dried in vacuo for 24 hours at 60°. Yield 59.5 g, 41%; m.p. 245°. Titration with $AgNO_3$ gave a molecular weight of 311 (actual 308.3). Other syntheses gave M.W. 307. The CMC was 1.05×10^{-2} M by surface tension and 1.45×10^{-2} M by bromide ion specific electrode (log a_{Br} - versus log C). Literature values cluster around 1.45×10^{-2} M.[4]

3. Hexadecylammonium Chloride (HACl)

The surfactant HACl was prepared by Mrs. Lynn Tepley.

4. Hexadecyltrimethylammonium Chloride (CTACl)

The surfactant CTACl (City Chemical Corp., Practical, 50% aqueous solution) was used as recieved. Titration using $AgNO_3$ and the chloride ion specific electrode gave an actual value of 50.09% by weight for the solution.

5. Hexadecyltrimethylammonium Bromide (CTAB)

The surfactant CTAB (City Chemical Corp.) was slurried with CCl_4, filtered by suction filtration and the filtrate was warmed to produce a clear solution. CTAB crystallized from this solution as fine white needles; it was dried in vacuo for at least 24 hours at 60°.

The CTAB used had CMCs ranging from 6×10^{-4} M to 8×10^{-4} M by surface tension; 8×10^{-4} M has been observed by other workers.[4]

Titration of the CTAB having a CMC of 8×10^{-4} M using $AgNO_3$ gave a molecular weight of 363 (actual 364.5). This batch of surfactant had a CMC value of 9.1×10^{-4} M using the bromide ion specific electrode (a_{Br^-} versus C).

The use of other recrystallization techniques gave less satisfactory results. Recrystallization from 2-butanone gave a marked dip in the γ (surface tension) versus log C plot at concentrations near the CMC. Addition of 2% hexadecanol (2% of CTAB on a concentration basis) gave the same behavior. See Appendix X, Figures 45 and 46 for the plots.

6. Sodium Dodecylsulfate (NaLS)

The NaLS (City Chemical Corp.) for the viscosity studies was used as received; its CMC was 2.5×10^{-3} M. Attempts to raise the CMC value by recrystallization from isopropyl alcohol were unsuccessful. Repeated extraction with diethyl ether to remove the possible contaminant 1-dodecanol was also unsuccessful,[266] as was lengthy drying *in vacuo*.

For use in calorimetric experiments NaLS was prepared from 1-dodecanol (Eastman, Technical) and chlorosulfonic acid (Eastman, Practical) according to the method of Kurz[267] and Dreger, *et al.*[268] The 1-dodecanol was purified by distillation at reduced pressure through a Nestor-Faust spinning-band column. The center cut showed only one peak by GC analysis.

The chlorosulfonic acid (0.280 mole) was added dropwise to 90 ml of anhydrous diethyl ether held at 0° in a 1000 ml three-necked

round-bottom flask equipped with reflux condenser, addition funnel and drying tube filled with 4 Å molecular sieves. The 1-dodecanol (0.225 mole) in 160 ml diethyl ether was added dropwise over a period of 30 minutes. After stirring an additional hour the reaction mixture was poured over crushed ice and neutralized using 5 N NaOH (the reaction mixture was cooled in an ice bath during this operation). The NaLS was extracted into 1-butanol; the extract was dried over Na_2SO_4. After drying, the extract was filtered, evaporated to dryness and the resulting white solid recrystallized from 1-butanol. During collection of the crystals copious washing with diethyl ether was performed to remove any unreacted 1-dodecanol. Drying in vacuo at 55° for 24 hours gave 25.2 g of NaLS, 39% yield.

This material had a CMC of 6.7×10^{-3} M as measured by surface tension (literature value 8.2×10^{-3} M[4]). When the CMC was determined using NaLS solutions which were 72 hours old a dip in the γ versus log C plot occurred near the CMC. This is thought to be due to 1-dodecanol produced by hydrolysis of NaLS.[266]

I. Compounds Used in Viscosity Studies

The compounds listed in Table XLII were used without purification in the viscosity studies. In addition, NaF, $NaNO_3$, $KClO_3$ (Baker and Adamson), NaCl and NaBr were used without drying in the viscosity studies.

J. Salts Used in Calorimetric and Counterion Binding Studies

The salts listed in Table XLIII were used in calorimetric and counterion binding studies after drying to constant weight where necessary.

TABLE XLII

SOME OF THE COMPOUNDS USED FOR VISCOSITY STUDIES

Compound	Source and Grade
Acetic acid, glacial	Baker and Adamson, Reagent
d,l-Alanine	Eastman
Ethyl acetate	Mallinckrodt, Analytical Reagent
Hydrogen bromide, 47% solution	Fisher Scientific, Certified
Naphthalene	J. T. Baker, Analyzed Reagent
n-Octane	Aldrich, puriss.
Sucrose	Mallinckrodt, Analytical Reagent
Tyrosine	Eastman
Urea	J. T. Baker, CP

TABLE XLIII

SALTS USED IN CALORIMETRIC AND COUNTERION-BINDING STUDIES

Salt	Source and Grade
NH_4Br[a]	J. T. Baker, Reagent
$CaBr_2$[b]	Matheson, Coleman, Bell, N.F.
LiBr[b]	Research Organic/Inorganic Chemicals Corp., 99.7%
$MgBr_2$[c]	Research Organic/Inorganic Chemicals Corp.
KBr[a]	J. T. Baker, Reagent
$NaC_2H_3O_2$[a]	Baker and Adamson, Reagent
$NaBrO_3$	--
NaBr[a]	J. T. Baker, Reagent
Na_2CO_3[a]	J. T. Baker, Analyzed Reagent
NaCl[d]	Mallinckrodt, Analytical Reagent
$Na_3C_6H_5O_7 \cdot 2H_2O$	Fisher Scientific, Certified
NaF[a]	J. T. Baker, Analyzed Reagent
$NaHCO_2$[a]	Merck, Reagent
NaOH[c]	Fisher Scientific, electrolytic pellets
$NaNO_3$[a]	J. T. Baker, Reagent
Na_2SO_4[a]	Baker and Adamson, anhydrous powder
$NaSO_3C_7H_7$[a]	Matheson, Coleman, Bell, Technical
$(CH_3)_4NBr$[a]	Matheson, Coleman, Bell, 99%

[a]Dried to constant weight *in vacuo* at 55°.

[b]Dried to constant weight *in vacuo* at 100°.

[c]From a freshly opened bottle.

[d]Dried at 100° for 22 hours.

All salts were stored in desiccators containing Drierite or P_2O_5 until use. Sodium hydroxide, lithium bromide, magnesium bromide and calcium bromide were handled in a Dry Box when syringes were filled with them for use in calorimetry.

K. Organic Compounds Used in Calorimetric, Counterion Binding and Micellar Catalysis Studies

All organic liquids were dried over 4 Å molecular sieves prior to use. Purity for these liquids was checked by gas chromatography using a Varian Aerograph Model 1444 gas chromatograph equipped with a flame ionization detector and a column packed with 5% SE-30 on Chromosorb W (60/80 mesh) acid-treated and DMCS (dimethylchlorosilane) treated. In some cases NMR spectra using a Varian A-60 spectrometer were obtained. For solids melting points were taken on a "Mel-Temp" apparatus; they are uncorrected. Table XLIV lists compounds which were used without purification. Unless otherwise stated, only one compound could be detected by GC or NMR. In addition, phenol and p-chlorophenol (Eastman) were dried to constant weight over P_2O_5 and used without further purification.

The following compounds required purification. All organic liquids were dried over 4 Å molecular sieves; all solids were stored in desiccators over either Drierite or P_2O_5.

1. p-Aminobenzoic Acid

p-Aminobenzoic acid (Matheson, Coleman, Bell) was recrystallized

TABLE XLIV

ORGANIC COMPOUNDS USED IN CALORIMETRIC AND MICELLAR CATALYSIS STUDIES

Compound	Source and Grade	Melting Point, °C
o-Aminobenzoic acid	Matheson, Coleman, Bell	145-146 (lit.[c] 145)
Benzoic acid	Fisher Scientific, Certified A.C.S.	122.4[d]
2-Butanone	Mallinckrodt, Analytical Reagent	--
n-Butylamine	Eastman	--
Butyronitrile[a]	Matheson, Coleman, Bell	--
Catechol	Matheson, Coleman, Bell	103.5-104.5 (lit.[d] 105)
Chlorobenzene	Matheson, Coleman, Bell	--
Cyclohexane	Mallinckrodt, Analytical Reagent	--
Cytosine	Aldrich, chromatographically pure	--
Hexane	Phillips Petroleum	--
1-Hexanol[b]	Eastman	--
o-Hydroxybenzoic acid	Eastman	157.5-159.5 (lit.[d] 159)
p-Hydroxybenzoic acid	Eastman	213.5-215 (lit.[d] 214.5-215.5)
Methyl butyrate	Eastman	--
Methyl salicylate	Fisher Scientific, U.S.P.	--
Nitrobenzene	Fisher Scientific, Certified	--

TABLE XLIV (Continued)

Compound	Source and Grade	Melting Point, °C
o-Nitrobenzoic acid	Eastman	145.5-146.5 (lit.[d] 147-148)
o-Nitrophenol	Matheson, Coleman, Bell	44.0-46.0 (lit.[d] 45.3-45.7)
p-Nitrophenol	Mallinckrodt	112.0-113.5 (lit.[c] 113-114)
Uracil	Aldrich, chromatographically pure	

[a]Six percent impurities present by gas chromatography.

[b]Major isomer 73% by gas chromatography.

[c]D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966.

[d]"Handbook of Chemistry and Physics," 50th ed., R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1969-1970, C-75-C-542.

from 95% ethanol. After drying *in vacuo* at 55° the melting point was 186.0-187.5° (lit.[269] 187-188°).

2. Aniline

Aniline (Fisher Scientific, Certified A.C.S.) was distilled through a short Vigreaux column at reduced pressure, b.p. 103°/25 mm (lit.[270] 68.3°/10 mm, 184°/760 mm). Gas chromatography showed only one peak.

3. Benzaldehyde

Benzaldehyde (Matheson, Coleman, Bell) was distilled through a short Vigreaux column at reduced pressure, b.p. 92.5-93.5°/17 mm (lit.[270] 62°/10 mm, 178°/760 mm). Following distillation, a very small amount of hydroquinone was added to suppress oxidation. Gas chromatography just prior to calorimetry showed only a trace of benzoic acid.

4. Benzamide

Benzamide (Matheson, Coleman, Bell) was recrystallized from acetone-water and dried *in vacuo* at 55°, m.p. 125.0-126.5° (bottle: 125-126°).

5. Bromoform, $CHBr_3$

Bromoform (J. T. Baker, Purified) was distilled through a short Vigreaux column at reduced pressure, b.p. 82.5-84.5°/56 mm (lit.[270] 46°/15 mm, 149°/760 mm). Following distillation, a very small amount of absolute ethanol was added as a stabilizer. Gas chromatography showed only one peak.

6. Butyraldehyde

Butyraldehyde (Eastman) was distilled through a short Vigreaux column. Its NMR spectrum was satisfactory.

7. Butyramide

Butyramide (Eastman) was recrystallized from methanol-benzene-pentane, m.p. 113-115° (lit.[270] 114.8°). There was no smell of butyric acid after recrystallization.

8. Butyric Acid

Butyric acid was distilled through a long metal-packed column; the second cut was used in calorimetry. Gas chromatography showed only one peak.

9. Carbon Tetrachloride

Carbon tetrachloride (Fisher Scientific, Certified A.C.S.) was obtained from Mr. Paul Bouis. n_D^{20} 1.4600 (lit.[271] 1.46005).

10. o-Chlorobenzoic Acid

o-Chlorobenzoic acid (Matheson, Coleman, Bell) was recrystallized from carbon tetrachloride-acetone, m.p. 139.0-139.5° (lit.[269] 139-140°).

11. Chloroform

Chloroform (Fisher Scientific, Certified A.C.S.) was used without purification. n_D^{20} 1.4461 (lit.[272] 1.44593).

12. o-Chlorophenol

o-Chlorophenol was distilled through a short Vigreaux column at

reduced pressure, b.p. 86-88°/25 mm (lit.[270] 56.4°/10 mm, 175°/760 mm). Gas chromatography showed only one peak.

13. n-Hexane

n-Hexane (Chemical Samples, 95%) to be used as a calorimetry solvent was washed with small portions of conc. H_2SO_4 until the wash remained colorless. It was then washed with water, followed by 10% Na_2CO_3 and more water. It was dried over $CaCl_2$ and distilled through a Vigreaux column. The distillate was stored over $CaCl_2$.

14. n-Hexyl Salicylate

n-Hexyl salicylate was prepared according to the method of Gel'shtein and Krivosheeva.[273] Salicylic acid (0.492 mole) and 1-hexanol (0.801 mole) were heated to reflux with a catalytic amount of p-toluenesulfonic acid and p-toluenesulfonyl chloride in a 300 ml single-necked round-bottom flask equipped with reflux condenser. After refluxing for seven hours the reaction mixture was cooled and 200 ml 10% Na_2CO_3 added. The organic layer was separated and the aqueous layer extracted with small portions of diethyl ether. The combined organic material was dried over $MgSO_4$. Distillation at reduced pressure through a glass helices packed column removed most of the unreacted 1-hexanol. Two cuts were then collected by distillation through a short Vigreaux column, b.p. 90-93°/0.05 mm, 9% yield. Gas chromatography showed both cuts to contain about 88% ester.

15. Hydroquinone

Hydroquinone (J. T. Baker, Purified) was recrystallized from acetone and dried *in vacuo*, m.p. 171.5-173.5° (lit.[270] 173-174°).

16. Methylene Chloride

Methylene chloride (Fisher Scientific, Certified) was used without purification. n_D^{20} 1.4242 (lit.[269] 1.42456).

17. 2-Naphthol

2-Naphthol (Fisher Scientific, Certified) was recrystallized twice from carbon tetrachloride-acetone and dried *in vacuo* at 50°, m.p. 120.5-121.5° (bottle: 122.0°).

18. Valeric Acid

Valeric acid (Eastman) was distilled through a long metal-packed column. Gas chromatography showed only one peak.

19. Valeramide

Valeramide (Eastman) was recrystallized once from ethanol-acetone and once from acetone-pentane. It was then sublimed twice, m.p. 100.5-102.0° (bottle: 105°).

LIST OF REFERENCES

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1. J. H. Fendler and E. Fendler, Adv. Phys. Org. Chem., 8, 271 (1970).

2. K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, Chapter 1.

3. P. Mukerjee, Advan. Colloid Interface Sci., 1, 241 (1967).

4. P. Mukerjee and K. J. Mysels, "Critical Micelle Concentrations of Aqueous Surfactant Systems," NSRDS-NBS 36, U. S. Government Printing Office, Washington, D. C., 1971.

5. D. Stigter, J. Colloid Interface Sci., 23, 379 (1967).

6. D. Stigter, J. Phys. Chem., 68, 3603 (1964).

7. O. H. Griffith and A. S. Waggoner, Accounts Chem. Res., 2, 17 (1969).

8. J. Oakes, J. Chem. Soc., Faraday Trans. 2, 1464 (1972).

9. M. J. Povich, J. A. Mann and A. Kawamoto, J. Colloid Interface Sci., 41, 145 (1972).

10. J. Clifford and B. A. Pethica, Trans. Faraday Soc., 60, 1483 (1964).

11. J. Clifford, ibid., 61, 1276 (1965).

12. P. Mukerjee and K. Banerjee, J. Phys. Chem., 68, 3567 (1964).

13. D. Stigter and K. J. Mysels, ibid., 59, 45 (1955).

14. H. V. Tartar, ibid., 59, 1195 (1955).

15. D. Stigter and J. Th. G. Overbeek, Proc. 2nd Intern. Congr. Surf. Act., 1, 311 (1957).

16. K. Shinoda, Bull. Chem. Soc. Jap., 26, 101 (1953).

17. M. E. Hobbs, J. Phys. Chem., 55, 675 (1951).

18. A. L. Loeb, J. Th. G. Overbeek and P. H. Wiersema, "The Electrical Double Layer around a Spherical Colloid Particle," the M. I. T. Press, Cambridge, Mass., 1961.

19. P. Debye, J. Phys. and Colloid Chem., 53, 1 (1949).

20. F. Reiss-Husson and V. Luzatti, J. Phys. Chem., 68, 3504 (1964).

21. C. Tanford, ibid., 76, 3020 (1972).

22. P. Mukerjee, ibid., 76, 565 (1972).

23. M. J. Vold, J. Colloid Sci., 5, 506 (1950).

24. N. Muller, J. Phys. Chem., 76, 3017 (1972).

25. K. K. Fox, Trans. Faraday Soc., 67, 2802 (1971).

26. J. Lang, J. J. Auborn and E. M. Eyring, J. Colloid Interface Sci., 42, 484 (1972).

27. N. Muller in "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York - London, 1973.

28. J. E. Gordon, J. Phys. Chem., 74, 3823 (1970).

29. M. F. Emerson and A. Holtzer, ibid., 71, 1898 (1967).

30. K. Shinoda and E. Hutchinson, ibid., 66, 577 (1962).

31. C. Tanford, J. Mol. Biol., 67, 59 (1972).

32. M. N. Jones and J. Piercy, J. Chem. Soc., Faraday Trans. 1, 1839 (1972).

33. K. Kuriyama, Kolloid-Z. Z. Polym., 180, 55 (1962).

34. M. F. Emerson and A. Holtzer, J. Phys. Chem., 71, 3320 (1967).

35. D. C. Poland and H. A. Scheraga, J. Colloid Sci., 27, 273 (1966).

36. P. Mukerjee, ibid., 19, 722 (1964).

37. D. J. Eatough and S. J. Rehfeld, Thermochimica Acta., 2, 443 (1971).

38. E. W. Anacker and R. D. Geer, J. Colloid Interface Sci., 35, 441 (1971).

39. M. L. Corrin, J. Colloid Sci., 3, 333 (1948).

40. D. Stigter, Recl. Trav. Chim. Pays-Bas, 73, 593 (1954).

41. P. Mukerjee, J. Phys. Chem., 66, 1733 (1962).

42. N. Pilpel, J. Colloid Sci., 9, 285 (1954).

43. P. Mukerjee, J. Phys. Chem., 69, 4038 (1965).

44. F. A. Long and W. F. McDevit, Chem. Rev., 51, 119 (1952).

45. I. J. Lin and P. Somasundran, J. Colloid Interface Sci., 37, 731 (1971).

46. D. C. Robins and I. L. Thomas, ibid., 26, 422 (1968).

47. E. W. Anacker and H. M. Ghose, J. Phys. Chem., 67, 1713 (1963).

48. P. Mukerjee, K. J. Mysels and P. Kapauan, ibid., 71, 4166 (1967).

49. G. Hartley, J. Chem. Soc., 1968 (1938).

50. P. H. von Hippel and T. Schleich, Accounts Chem. Res., 2, 257 (1969).

51. P. H. von Hippel and T. Schleich in "Biological Macromolecules," Vol. 3, S. Timasheff and G. Fasman, Eds., Marcel Dekker, New York, N. Y., 1969.

52. F. Hofmeister, Arch. Exptl. Pathol. Pharmakol., 24, 247 (1888).

53. E. D. Goddard, O. Harva and T. G. Jones, Trans. Faraday Soc., 49, 980 (1953).

54. M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, New York, N. Y., 1955.

55. C. A. Bunton in "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York - London, 1973.

56. J. C. Eriksson and G. Gillberg, Acta. Chem. Scand., 20, 2019 (1966).

57. T. Nakagawa and K. Tori, Kolloid-Z. Z. Polym., 194, 143 (1964).

58. P. A. Arrington, A. Clouse, D. Doddrell, R. B. Dunlap and E. H. Cordes, J. Phys. Chem., 74, 665 (1970).

59. S. Riegelman, N. A. Allawala, M. K. Hrenoff and L. A. Strait, J. Colloid Sci., 13, 208 (1958).

60. S. J. Rehfeld, J. Phys. Chem., 74, 117 (1970).

61. S. J. Rehfeld, J. Amer. Chem. Soc., 95, 4489 (1973).

62. M. Donbrow and C. T. Rhodes, J. Chem. Soc., 6166 (1964).

63. M. Donbrow, P. Molyneux and C. T. Rhodes, J. Chem. Soc. A, 561 (1967).

64. P. Molyneux and C. T. Rhodes, Kolloid-Z. Z. Polym., 250, 886 (1972).

65. D. G. Herries, W. Bishop and F. M. Richards, J. Phys. Chem., 68, 1842 (1964).

66. A. L. Thakkar and N. A. Hall, J. Pharm. Sci., 57, 1394 (1968).

67. R. L. Venable and R. V. Nauman, J. Phys. Chem., 68, 3498 (1964).

68. H. B. Klevens, J. Amer. Chem. Soc., 72, 3780 (1950).

69. E. H. Cordes and R. B. Dunlap, Accounts Chem. Res., 2, 329 (1969).

70. P. Ekwall, L. Mandell and P. Solyom, J. Colloid Interface Sci., 35, 519 (1971).

71. E. Keh, C. Gavach and J. Gustalla, C. R. Acad. Sci., Ser. C., 263, 1488 (1966).

72. A. J. Hyde and D. J. M. Robb, J. Phys. Chem., 67, 2093 (1963).

73. A. J. Hyde and D. J. M. Robb, Int. Congr., 4th (1964) Chem. Phys. Appl. Surface Active Subst., Proc., 2, 743 (1967).

74. K. J. Mysels, J. Colloid Sci., 10, 507 (1955).

75. H. J. L. Trap and J. J. Hermans, Proc. Koninkl. Ned. Akad. Wetenschap, 58B, 97 (1955).

76. H. V. Tartar, J. Colloid Sci., 14, 115 (1959).

77. D. Attwood, P. H. Elworthy and S. B. Kayne, J. Phys. Chem., 74, 3529 (1970).

78. K. Granath, Acta. Chem. Scand., 7, 297 (1953).

79. H. A. Scheraga and J. K. Backus, J. Amer. Chem. Soc., 73, 5108 (1951).

80. P. Debye and E. W. Anacker, J. Phys. and Colloid Chem., 55, 644 (1951).

81. L. Kushner, W. Hubbard and R. Parker, J. Res. Nat. Bur. Stand., 59, 113 (1957).

82. K. G. Götz and K. Heckmann, J. Colloid Sci., 13, 266 (1958).

83. G. Lindblom, B. Lindman and L. Mandell, J. Colloid Interface Sci., 42, 400 (1973).

84. K. J. Mysels, J. Phys. Chem., 58, 303 (1954).

85. J. W. McBain, Y. Kawakami and H. P. Lucas, J. Amer. Chem. Soc., 55, 2762 (1933).

86. R. J. Vetter, J. Phys. and Colloid Chem., 51, 262 (1947).

87. W. L. Courchene, J. Phys. Chem., 68, 1870 (1964).

88. O. F. Bezrukov and A. N. Potanin, Dokl. Akad. Nauk SSSR, 192, 353 (1970).

89. D. Stigter, J. Phys. Chem., 70, 1323 (1966).

90. F. Booth, Proc. Roy. Soc., Ser. A, 203, 533 (1950).

91. E. J. Bair and C. A. Kraus, J. Amer. Chem. Soc., 73, 1129 (1951).

92. M. Czerniawski, Rocz. Chem., 40, 1935 (1966).

93. K. J. Mysels and L. H. Princen, J. Phys. Chem., 63, 1696 (1959).

94. K. S. Birdi, Kolloid-Z. Z. Polym., 250, 731 (1972).

95. N. H. Choulis, Can. J. Pharm. Sci., 5, 24 (1970).

96. G. A. Davis, J. Amer. Chem. Soc., 94, 5089 (1972).

97. D. G. Duff and C. H. Giles, J. Colloid Interface Sci., 41, 407 (1972).

98. R. C. Dorrance and T. F. Hunter, J. Chem. Soc., Faraday Trans. 1, 1312 (1972).

99. W. U. Malik and S. P. Verma, Kolloid-Z. Z. Polym., 233, 985 (1969).

100. W. U. Malik and A. K. Jain, J. Electroanal. Chem., 16, 442 (1968).

101. J. C. Erikkson, A. Johansson and L. Anderson, Acta. Chem. Scand., 20, 230 (1966).

102. M. Czerniawski, Rocz. Chem., 41, 119 (1967).

103. J. T. Pearson and K. J. Humphreys, J. Pharm. Pharmacol., 22, Suppl. 126S (1970).

104. T. Ingram and M. N. Jones, Trans. Faraday Soc., 65, 297 (1969).

105. A. J. Hyde and D. M. Stevenson, Kolloid-Z. Z. Polym., 232, 797 (1969).

106. W. K. Mathews, J. W. Larsen and M. J. Pikal, Tetrahedron Lett., 513 (1972).

107. G. S. Hartley, B. Collie and C. S. Samis, Trans Faraday Soc., 32, 795 (1936).

108. J. N. Phillips, ibid., 51, 561 (1955).

109. I. Cohen and T. Vassiliades, J. Phys. Chem., 65, 1774, 1781 (1961).

110. J. Piercy, M. N. Jones and G. Ibbotson, J. Colloid Interface Sci., 37, 165 (1971).

111. J. Steigman, I. Cohen and F. Spingola, J. Colloid Sci., 20, 732 (1965).

112. L. S. C. Wan and P. K. C. Poon, J. Pharm. Sci., 58, 1562 (1969).

113. W. U. Malik and A. K. Jain, J. Indian Chem. Soc., 46, 631 (1969).

114. E. E. Schrier and E. B. Schrier, J. Phys. Chem., 71; 1851 (1967).

115. D. R. Robinson and W. P. Jencks, J. Amer. Chem. Soc., 87, 2470 (1965).

116. P. K. Nandi and D. R. Robinson, ibid., 94, 1299, 1308 (1972).

117. E. F. J. Duynstee and E. Grunwald, Tetrahedron, 22, 2401 (1965).

118. R. A. Moss and C. J. Talkowski, J. Amer. Chem. Soc., 94, 4767 (1972).

119. A. Voet, Chem. Rev., 20, 169 (1937).

120. S. Lindenbaum and G. E. Boyd, J. Phys. Chem., 68, 911 (1964).

121. I. Paligoric and I. J. Gal, J. Chem. Soc., Faraday Trans. 1, 1093 (1972).

122. M. Azzarri and C. A. Kraus, Proc. Natl. Acad. Sci., U. S., 42, 590 (1956).

123. S. Minc and Z. Koczorowski, Rocz. Chem., 39, 469 (1965).

124. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London, 1968, pp. 124-126 and App. 6.1, 6.2.

125. H. G. Bungenberg de Jong and A. Recourt, Proc. Koninkl. Ned. Akad. Wetenschap, 56B, 303 (1953).

126. H. G. Bungenberg de Jong and W. W. H. Weijzen, ibid., 57B, 192 (1954).

127. E. W. Anacker, R. M. Rush and J. S. Johnson, J. Phys. Chem., 68, 81 (1964).

128. M. Miura and M. Kodama, Bull. Chem. Soc. Jap., 45, 428 (1972).

129. L. M. Kushner, B. C. Duncan and J. I. Hoffman, J. Res. Nat. Bur. Stand., 49, 85 (1952).

130. K. J. Mysels and C. I. Dulin, J. Colloid Sci., 10, 461 (1955).

131. I. D. Robb, J. Colloid Interface Sci., 37, 521 (1971).

132. M. E. Feinstein and H. L Rosano, ibid., 24, 73 (1967).

133. I. Satake, T. Tahara and R. Matuura, Bull. Chem. Soc. Jap., 42, 319 (1969).

134. L. Shedlovsky, C. W. Jakob and M. B. Epstein, J. Phys. Chem., 67, 2075 (1963).

135. C. Botré, V. L. Crescenzi and A. Mele, ibid., 63, 650 (1959).

136. J. N. Phillips and K. J. Mysels, ibid., 59, 325 (1955).

137. K. Shirahama, Kolloid-Z. Z. Polym., 250, 620 (1972).

138. M. U. Oko and R. L. Venable, J. Colloid Interface Sci., 35, 53 (1971).

139. G. Pilcher, M. N. Jones, L. Espada and H. A. Skinner, J. Chem. Thermodyn., 1, 381 (1969).

140. M. N. Jones, G. Pilcher and L. Espada, ibid., 2, 333 (1970).

141. H. W. Hoyer and A. Marmo, J. Phys. Chem., 65, 1807 (1961).

142. L. Espada, M. N. Jones and G. Pilcher, J. Chem. Thermodyn., 2, 1 (1970).

143. W. Bruning and A. Holtzer, J. Amer. Chem. Soc., 83, 4865 (1961).

144. M. F. Emerson and A. Holtzer, ibid., 69, 3718 (1965).

145. P. Mukerjee, ibid., 73, 2054 (1969).

146. J. Th. G. Overbeek and D. Stigter, Recl. Trav. Chim. Pays-Bas, 75, 1263 (1956).

147. A. Wishnia, J. Phys. Chem., 67, 2079 (1963).

148. N. Muller, J. H. Pellerin and W. W. Chen, ibid., 76, 3012 (1972).

149. P. Ekwall, L. Mandell and K. Fontell, J. Colloid Interface Sci., 29, 639 (1969).

150. A. S. C. Lawrence, B. Boffey, A. Bingham and K. Talbot, Chem. Phys. Appl. Surface Active Subst., Proc. Int. Congr., 4th 2, 673 (1964).

151. B. J. Boffey, R. Collison and A. S. C. Lawrence, Trans. Faraday Soc., 55, 654 (1959).

152. A. S. C. Lawrence and J. T. Pearson, Chem. Phys. Appl. Surface Active Subst., Proc. Int. Congr., 4th 2, 709 (1964).

153. C. T. Iacobelli, Ric. Sci., 39, 252 (1969).

154. P. Massini and G. Voorn, Biochim. Biophys. Acta, 153, 589 (1968).

155. D. Guerritore, L. Bellelli and M. L. Bonacci, Giorn. Biochim., 13, 231 (1964).

156. G. Amici and D. Franzini, Sett. med., 47, 48 (1959).

157. Neth. Appl. 6,610,468, Chem. Abstr., 68, 81413r (1968).

158. L. K. Patterson and E. Vieil, J. Phys. Chem., 77, 1191 (1973).

159. R. Aveyard and A. S. C. Lawrence, Trans. Faraday Soc., 60, 2265 (1964).

160. S. J. Rehfeld, J. Phys. Chem., 75, 3905 (1971).

161. J. H. Fendler and L. K. Patterson, ibid., 75, 3907 (1971).

162. J. E. Gordon, J. C. Robertson and R. L. Thomas, ibid., 74, 957 (1970).

163. N. Muller and R. H. Birkhahn, ibid., 71, 957 (1967).

164. A. M. Mankowich, J. Am. Oil Chemists Soc., 42, 185 (1965).

165. K. G. Götz and K. Heckmann, Z. Phys. Chem. (Frankfurt am Main), 20, 42 (1959).

166. A. J. Hyde and A. S. C. Lawrence, Vortraege Originalfassung Intern. Kongr. Grenzflaechenaktive Stoffe, 3, Cologne, Ger., 1, 21 (1960).

167. A. S. C. Lawrence and J. T. Pearson, Trans. Faraday Soc., 63, 495 (1967).

168. A. F. H. Ward and A. G. Chitale, Proc. Intern. Congr. Surface Act., 2nd, London, 1, 319 (1957).

169. T. Nash, J. Appl. Chem., 6, 539 (1956).

170. T. Nash, J. Colloid Sci., 14, 59 (1959).

171. L. S. C. Wan, J. Pharm. Sci., 55, 1395 (1966).

172. H. G. Bungenberg de Jong, H. J. van den Berg and W. W. H. Weijzen, Proc. Koninkl. Ned. Akad. Wetenschap, 58B, 135, 147 (1955).

173. E. F. J. Duynstee and E. Grunwald, J. Amer. Chem. Soc., 81, 4540, 4542 (1959).

174. R. A. Moss and D. W. Reger, ibid., 91, 7539 (1969).

175. R. A. Moss and C. J. Talkowski, Tetrahedron Lett., 703 (1971).

176. C. Lapinte and P. Viout, ibid., 1113 (1973).

177. P. Mukerjee and A. Ray, J. Phys. Chem., 70, 2144 (1966).

178. L. R. Romsted and E. H. Cordes, J. Amer. Chem. Soc., 90, 4404 (1968).

179. M. T. A. Behme, J. G. Fullington, R. Noel and E. H. Cordes, ibid., 87, 266 (1965).

180. F. M. Menger and C. E. Portnoy, ibid, 89, 4698 (1967).

181. S. Friberg, L. Rydhag and G. Lindblom, J. Phys. Chem., 77, 1280 (1973).

182. M. Poindexter and B. McKay, J. Org. Chem., 37, 1674 (1972).

183. R. R. Hautala and R. L. Letsinger, ibid., 36, 3762 (1971).

184. J. Albrizzio, J. Archila, T. Rodulfo and E. H. Cordes, ibid., 37, 871 (1972).

185. G. S. Hartley, Trans. Faraday Soc., 30, 444 (1934).

186. J. Baumrucker, M. Calzadilla and E. H. Cordes, in "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York - London, 1973.

187. C. A. Bunton and S. K. Huang, J. Org. Chem., 37, 1790 (1972).

188. J. Baumrucker, M. Calzadilla, M. Centeno, G. Lehrmann, P. Lindquist, D. Dunham, M. Price, B. Sears and E. H. Cordes, J. Phys. Chem., 74, 1152 (1970).

189. J. Baumrucker, M. Calzadilla, M. Centeno, G. Lehrmann, M. Urdaneta, P. Lindquist, D. Dunham, M. Price, B. Sears and E. H. Cordes, J. Amer. Chem. Soc., 94, 8164 (1972).

190. C. Gitler and A. Ochoa-Solano, ibid., 90, 5004 (1968).

191. G. Némethy and H. A. Scheraga, J. Phys. Chem., 66, 1773 (1962).

192. M. T. A. Behme and E. H. Cordes, J. Amer. Chem. Soc., 87, 260 (1965).

193. K. G. van Senden and C. Koningsberger, Tetrahedron Lett., 7 (1960).

194. K. G. van Senden and C. Koningsberger, Tetrahedron, 22, 1301 (1966).

195. C. A. Bunton and L. Robinson, J. Amer. Chem. Soc., 90, 5972 (1968).

196. C. A. Bunton and L. Robinson, J. Org. Chem., 34, 780 (1969).

197. C. A. Bunton and L. Robinson, J. Amer. Chem. Soc., 92, 356 (1970).

198. C. A. Bunton, L. Robinson and L. Sepulveda, J. Org. Chem., 35, 108 (1970).

199. C. A. Bunton, L. Robinson, J. Schaak and M. F. Stam, ibid., 36, 2346 (1971).

200. J. H. Fendler, E. J. Fendler and M. V. Merritt, ibid., 36, 2172 (1971).

201. A. K. Yatsimirski, K. Martinek and I. V. Berezin, Tetrahedron, 27, 2855 (1971).

202. K. Martinek, A. K. Yatsimirski, A. P. Osipov and I. V. Berezin, ibid., 29, 963 (1973).

203. C. A. Bunton and B. Wolfe, J. Amer. Chem. Soc, 95, 3742 (1973).

204. F. Sebba and J. H. Wigill, J. Colloid Interface Sci., 21, 116 (1965).

205. L. J. Winters and E. Grunwald, J. Amer. Chem. Soc., 87, 4608 (1965).

206. C. A. Bunton, E. J. Fendler, L. Sepulveda and K.-U. Yang, ibid., 90, 5512 (1968).

207. C. A. Bunton and L. Robinson, J. Org. Chem., 34, 773 (1969).

208. C. A. Bunton, L. Robinson and L. Sepulveda, J. Amer. Chem. Soc., 91, 4813 (1969).

209. G. J. Buist, C. A. Bunton, L. Robinson, L. Sepulveda and M. Stam, ibid., 92, 4072 (1970).

210. C. A. Bunton, L. Robinson and M. Stam, ibid., 92, 7393 (1970).

211. C. A. Bunton and L. G. Ionescu, ibid., 95, 2912 (1973).

212. M. Czerniawski, Rocz. Chem., 41, 817 (1967).

213. S. L. Johnson, Adv. Phys. Org. Chem., 5, 237 (1967).

214. S. Riegelman, J. Am. Pharm. Assoc., Sci. Ed., 49, 339 (1960).

215. C. A. Bunton, A. Kamego and M. J. Minch, J. Org. Chem., 37, 1388 (1972).

216. C. A. Bunton and M. J. Minch, Tetrahedron Lett., 3881 (1970).

217. C. A. Bunton, M. Minch and L. Sepulveda, J. Phys. Chem., 75, 2707 (1971).

218. C. A. Bunton, M. J. Minch, J. Hidalgo and L Sepulveda, J. Amer. Chem. Soc., 95, 3262 (1973).

219. R. B. Dunlap and E. H. Cordes, ibid., 90, 4395 (1968).

220. R. B. Dunlap and E. H. Cordes, J. Phys. Chem., 73, 361 (1969).

221. N. Nakajima, Yakugakio Zasshi, 81, 1684 (1961).

222. H. Nogami and S. Awazu, Chem. Pharm. Bull. (Tokyo), 10, 1158 (1962).

223. E. Ullmann, K. Thomas and R. Rombach, Arch. Pharm. (Weinheim), 301, 363 (1968).

224. A. G. Mitchell, J. Pharm. Pharmacol., 14, 172 (1962).

225. L. Pekkarinen and E. Tommila, Acta. Chem. Scand., 13, 1019 (1959).

226. M. L. Bender, F. J. Kézdy and B. Zerner, J. Amer. Chem. Soc., 85, 3017 (1963).

227. F. L. Killian and M. L. Bender, Tetrahedron Lett., 1255 (1969).

228. C. Sadron, Progr. in Biophysics, 3, 237 (1950).

229. H. L. Frisch and R. Simha in "Rheology: Theory and Applications," Vol. I, F. R. Eirich, Ed., Academic Press, Inc., New York, N. Y., 1956.

230. V. Vand, J. Phys. Chem., 52, 279 (1948).

231. R. A. Parker and S. P. Wasik, ibid., 62, 967 (1958).

232. B. E. Conway and A. Dobry-Duclaux in "Rheology: Theory and Applications," Vol. III, F. R. Eirich, Ed., Academic Press, Inc., New York, N. Y., 1960;

233. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London, 1968, p 305.

234. D. C. Ginnings and G. T. Furukawa, J. Amer. Chem. Soc., 75, 522 (1953).

235. G. Salama and D. A. Goring, J. Phys. Chem., 70, 3838 (1966).

236. R. Oder and D. A. I. Goring, Can. J. Chem., 48, 3790 (1970).

237. F. Franks and D. J. G. Ives, J. Chem. Soc., 741 (1960).

238. C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 549-554.

239. F. Tokiwa and K. Ohki, J. Phys. Chem., 70, 3437 (1966).

240. F. Tokiwa and N. Moriyama, J. Colloid Interface Sci., 30, 338 (1969).

241. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952.

242. M. Joly, "A Physico-Chemical Approach to the Denaturation of Proteins," Academic Press, London, 1965, p 13.

243. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London, 1968, pp 74-79.

244. F. Oosawa, "Polyelectrolytes," Marcel Dekker, Inc., New York, N. Y., 1971, pp 13-17.

245. T. C. Bruice, J. Katzhendler and L. R. Fedor, J. Amer. Chem. Soc., 90, 1333 (1968).

246. L. P. Hammett, J. Chem. Phys., 4, 613 (1936).

247. J. Hermans, Jr., S. J. Leach and H. A. Scheraga, J. Amer. Chem. Soc., 85, 1390 (1963).

248. "Handbook of Chemistry and Physics," 50th ed., R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1969-1970, D-118.

249. W. Good and M. H. Milloy, Chem. and Ind., 872 (1956).

250. L. P. Fernandez and L. G. Hepler, J. Amer. Chem. Soc., 81, 1783 (1959).

251. Reference 248, E-62.

252. G. Némethy and A. Ray, J. Phys. Chem., 77, 64 (1973).

253. J. D. DeMarco and A. D. Marcus, J. Pharm. Sci., 51, 1010 (1962).

254. L. Lang, "Absorption Spectra in the Ultraviolet and Visible Region," Academic Press, Inc., New York, N. Y.

255. J. D. Hinchen, "Practical Statistics for Chemical Research," Methuen and Co., Ltd., London, 1969, pp 25-27.

256. F. Daniels, J. H. Mathews, J. W. Williams, P. Bender and R. A. Albetty, "Experimental Physical Chemistry," McGraw Hill, New York, N. Y., 1956, pp. 324-328.

257. Reference 256, pp 379-382.

258. "Handbook of Chemistry and Physics," 38th ed., C. D. Hodgman, Ed., The Chemical Rubber Co., Cleveland Ohio, 1956-1957, pp 2031-2037.

259. K. Granath, Acta. Chem. Scand., 4, 103 (1950).

260. J. R. Van Wazer, J. W. Lyons, K. Y. Kim and R. E. Colwell, "Viscosity and Flow Measurement," Interscience Publishers, New York, N. Y., 1963, pp 12-22.

261. Reference 256, pp 55-56.

262. "Instruction Manual, Nitrate Ion Electrode," Orion Research Inc., Cambridge, Mass., 1971.

263. A. V. Metzner, M. S. Thesis, The Unversity of Tennessee, Knoxville, Tennessee, 1971.

264. D. B. Glass, M. S. Thesis, The University of Tennessee, Knoxville, Tennessee, 1971.

265. A. B. Scott and H. V. Tartar, J. Amer. Chem. Soc., 65, 692 (1943).

266. S. P. Harrold, J. Colloid Sci., 15, 280 (1960).

267. J. L. Kurz, J. Phys. Chem., 66, 2239 (1962).

268. E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky and J. Ross, Ind. Eng. Chem., 36, 610 (1944).

269. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966.

270. Reference 248, C-75-C-542.

271. I. H. Heilbron, "Dictionary of Organic Compounds," Oxford University Press: New York, N. Y., 1953; 1965.

272. "Physical Properties of Chemical Compounds," R. R. Dreisbach, Ed., Advances in Chemistry Series, Number 22, American Chemical Society, Washington, D. C., 1959.

273. R. M. Gel'shtein and N. F. Krivosheeva, Metody Polucheniza Khim. Reaktivov i Preparatov, 13, 5 (1965); Chem. Abstr., 65, 5395b (1966).

274. T. F. Bolles and R. S. Drago, J. Amer. Chem. Soc., 87, 5015 (1965).

APPENDIXES

APPENDIX I

SYSTEMS HAVING NON-NEWTONIAN VISCOSITIES

TABLE XLV

COMPLETE VISCOSITY DATA FOR SYSTEMS SHOWING NON-NEWTONIAN BEHAVIOR

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
0.1 M CTAB-0.15 M NaBr	2.81	11	31
	5.63	4.4	25
	8.44	2.2	19
	16.9	0.51	8.6
	25.3	0.19	4.8
	50.6	0.12	6.1
	75.9	0.11	8.3
	152	0.14	21
	228	0.14	32
	455	0.084	38
0.1 M CTAB-0.20 M NaBr	2.81	6.5	18
	5.63	4.4	25
	8.44	3.9	33
	16.9	1.4	24
	25.3	0.73	18
	50.6	0.51	26
	75.9	0.50	38
	152	0.44	67
	228	0.37	84
	455	0.27	120
0.1 M CTAB-0.50 M NaBr	2.81	52.0	146
	5.63	23.6	133
	8.44	17.9	151
	16.9	9.62	163
	25.3	6.37	161
	50.6	3.33	168
	75.9	2.27	172
	152	1.18	179
	228	0.821	187
	455	0.408	186
0.1 M CTAB-1.0032 M NaBr	2.81	70.0	197
	5.63	38.7	218
	8.44	25.8	218
	16.9	13.3	225
	25.3	9.19	233
	50.6	5.03	255

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	75.9	3.76	285
	152	1.77	269
	228	1.33	303
	455[b]	--	--
0.1 M CTAB-0.025 M Benzoic acid-0.045 M NaBr	2.81	8.7	24
	5.63	5.3	30.
	8.44	3.5	30.
	16.9	1.8	30.
	25.3	1.1	28
	50.6	0.83	42
	75.9	0.68	52
	152	0.53	81
	228	0.45	100
	455	0.289	131
0.1 M CTAB-0.025 M Benzoic acid-0.10 M NaBr	2.81	37	100
	5.63	22.3	126
	8.44	14	120
	16.9	7.1	120
	25.3	4.6	120
	50.6	2.4	120
	75.9	1.62	123
	152	0.875	133
	228	0.599	137
	455	0.27	123
0.1 M CTAB-0.025 M Benzoic acid-0.2027 M NaBr	2.81	76.1	214
	5.63	39.1	220
	8.44	26.0	219
	16.9	13.3	225
	25.3	9.24	234
	50.6	4.91	248
	75.9	3.50	266
	152	2.01	306
	228[b]	--	--
	455[b]	--	--
0.1 M CTAB-0.4999 M NaBr - one of the time-dependent studies	2.81	37.	100
	5.63	24.1	136
	8.44	16.8	142
	16.9	8.83	149
	25.3	6.03	153
	50.6	3.11	157

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	75.9	2.15	163
	152	1.13	172
	228	0.794	181
	455	0.403	183
0.1 M CTAB-0.0992 M $KClO_3$[a]	2.81	11	31
	5.63	7.82	44.0
	8.44	6.40	54.0
	16.9	4.62	78.1
	25.3	3.55	89.8
	50.6	2.05	104
	75.9	1.32	100.
	152	0.842	128
	228	0.684	156
	455	0.342	156
	228	0.614	140.
	152	0.895	136
	75.9	1.66	126
	50.6	2.41	122
	25.3	3.95	100.
	16.9	5.33	90.1
	8.44	8.29	70.0
	5.63	11.0	61.9
	2.81	17.1	48.1
0.1 M CTACl-0.5001 M NaBr- one of the time-dependent studies	2.81	11	31
	5.63	6.6	37
	8.44	4.4	37
	16.9	2.7	46
	25.3	2.2	56
	50.6	1.9	96
	75.9	1.82	138
	152	1.34	204
	228	1.04	237
	455	0.616	280
0.1 M CTACl-0.3996 M NaBr	2.81	10.	28
	5.63	8.3	47
	8.44	4.7	40.
	16.9	2.8	47
	25.3	2.5	63
	50.6	2.0	100
	75.9	1.77	134

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	152	1.32	201
	228	1.06	242
	455	0.627	285
0.1 M CTAB-0.0253 M Benzene-0.0999 M NaBr	2.81	7.9	22
	5.63	6.5	37
	8.44	5.3	45
	16.9	3.9	66
	25.3	3.1	78
	50.6	2.0	100
	75.9	1.5	110
	152	0.858	130
	228	0.636	145
	455	0.356	162
0.1 M CTAB-0.0254 M Benzene-0.10 M HBr	2.81	23.5	66.0
	5.63	14.9	83.9
	8.44	11.1	93.7
	16.9	6.87	116
	25.3	4.90	124
	50.6	2.53	128
	75.9	1.74	132
	152	0.895	136
	228	0.614	140.
	455	0.329	150.
0.1 M CTAB-0.0241 M Benzene-0.1003 M $NaNO_3$[a]	2.81	31.3	88.0
	5.63	14.6	82.2
	8.44	11.6	97.9
	16.9	6.28	106
	25.3	4.26	108
	50.6	2.17	110.
	75.9	1.47	112
	152	0.790	120.
	228	0.553	126
	455	0.298	136
	228	0.570	130.
	152	0.803	122
	75.9	1.47	112
	50.6	2.17	110.
	25.3	4.03	102
	16.9	5.80	98.0
	8.44	10.2	86.1

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	5.63	13.5	76.0
	2.81	22.0	61.8
0.1 M CTAB-0.0242 M Benzene-0.0992 M $KClO_3$[a]	2.81	46.2	130.
	5.63	24.9	140.
	8.44	16.8	142
	16.9	8.17	138
	25.3	5.53	140.
	50.6	2.76	140.
	75.9	1.84	140.
	152	0.961	146
	228	0.667	152
	455	0.338	154
	228	0.693	158
	152	1.03	157
	75.9	1.95	148
	50.6	2.80	142
	25.3	5.53	140.
	16.9	8.76	148
	8.44	18.0	152
	5.63	26.6	150.
	2.81	44.1	124
0.1 M CTAB-0.0251 M Benzoic acid-0.10 M HBr	2.81	65.4	184
	5.63	29.5	166
	8.44	19.0	160.
	16.9	9.47	160.
	25.3	6.24	158
	50.6	3.16	160.
	75.9	2.16	164
	152	1.09	166
	228	0.798	182
	455	0.478	217
0.1 M CTAB-0.0249 M Benzoic acid-0.1003 M $NaNO_3$	2.81	54.7	154
	5.63	24.9	140.
	8.44	15.2	128
	16.9	7.22	122
	25.3	4.74	120.
	50.6	2.45	124
	75.9	1.66	126

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	152	0.829	126
	228	0.667	152
	455	0.439	200.
0.1 M CTAB-0.0250 M Benzoic acid-0.0992 M $KClO_3$	2.81	65.4	184
	5.63	34.1	192
	8.44	24.2	204
	16.9	12.7	215
	25.3	8.61	218
	50.6	4.46	226
	75.9	3.00	228
	152	1.75	266
	228	1.35	308
	455	0.921	419
0.1 M CTAB-0.0290 M 1-Hexanol-0.0999 M NaBr	2.81	28	79
	5.63	20.	110
	8.44	15.3	129
	16.9	8.76	148
	25.3	5.83	147
	50.6	2.93	148
	75.9	1.98	150.
	152	1.04	158
	228	0.708	161
	455	0.351	160.
0.1 M CTAB-0.0289 M 1-Hexanol-0.10 M HBr	2.81	47.6	134
	5.63	29.8	168
	8.44	19.4	164
	16.9	10.1	171
	25.3	6.95	176
	50.6	3.63	184
	75.9	2.50	190.
	152	1.28	195
	228	0.904	206
	455	0.509	232
0.1 M CTAB-0.0192 M 1-Hexanol-0.1003 M $NaNO_3$[a]	2.81	24.9	70.0
	5.63	16.0	90.1
	8.44	11.1	93.7
	16.9	6.75	114
	25.3	4.82	122
	50.6	2.61	132

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	75.9	1.76	134
	152	0.921	140.
	228	0.640	146
	455	0.338	154
	228	0.693	158
	152	0.855	130.
	75.9	1.63	124
	50.6	2.37	120.
	25.3	4.42	112
	16.9	6.28	106
	8.44	9.95	84.0
	5.63	12.4	69.8
	2.81	14.9	41.8
0.1 M CTAB-0.0259 M 1-Hexanol-0.0992 M $KClO_3$	2.81	46.9	132
	5.63	30.6	172
	8.44	21.1	178
	16.9	11.4	193
	25.3	7.74	196
	50.6	4.07	206
	75.9	2.79	212
	152	1.45	220.
	228	1.08	246
	455	0.671	305
0.1 M CTAB-0.0097 M Benzene-0.1 M NaBr	2.81	2.6	7.3
	5.63	1.5	8.4
	8.44	1.5	13
	16.9	0.58	9.8
	25.3	0.29	7.3
	50.6	0.19	9.6
	75.9	0.080	6.1
	152	0.13	20.
	228	0.14	32
	455	0.089	40.
0.1 M CTAB-0.0184 M CCl_4-0.1 M NaBr	2.81	22.0	61.8
	5.63	12.1	68.1
	8.44	8.05	67.9
	16.9	4.26	72.0
	25.3	3.08	77.9
	50.6	1.97	99.7
	75.9	1.40	106

TABLE XLV (Continued)

System	Rate of shear, sec^{-1}	$\eta_{apparent}$, poise	Shearing stress, $dynes/cm^2$
	152	0.882	134
	228	0.685	150.
	455	0.347	158
0.1 M CTAB-0.0158 M $CHCl_3$-0.1 M NaBr	2.81	11	31
	5.63	6.0	34
	8.44	4.0	34
	16.9	1.9	32
	25.3	1.58	40.0
	50.6	1.15	58.2
	75.9	0.947	71.9
	152	0.618	93.9
	228	0.482	110.
	455	0.303	138
0.1 M CTAB-0.0318 M CH_2Cl_2-0.1 M NaBr	2.81	14.9	41.9
	5.63	6.0	34
	8.44	3.6	30.
	16.9	1.3	22
	25.3	1.1	28
	50.6	0.59	30.
	75.9	0.47	36
	152	0.368	56
	228	0.307	70.0
	455	0.228	104

[a]Rotovisco was run from low rates of shear to high rates of shear and back down again; a form of hysteresis in the $\eta_{apparent}$ values was observed.

[b]Readings too eratic to obtain an $\eta_{apparent}$ value.

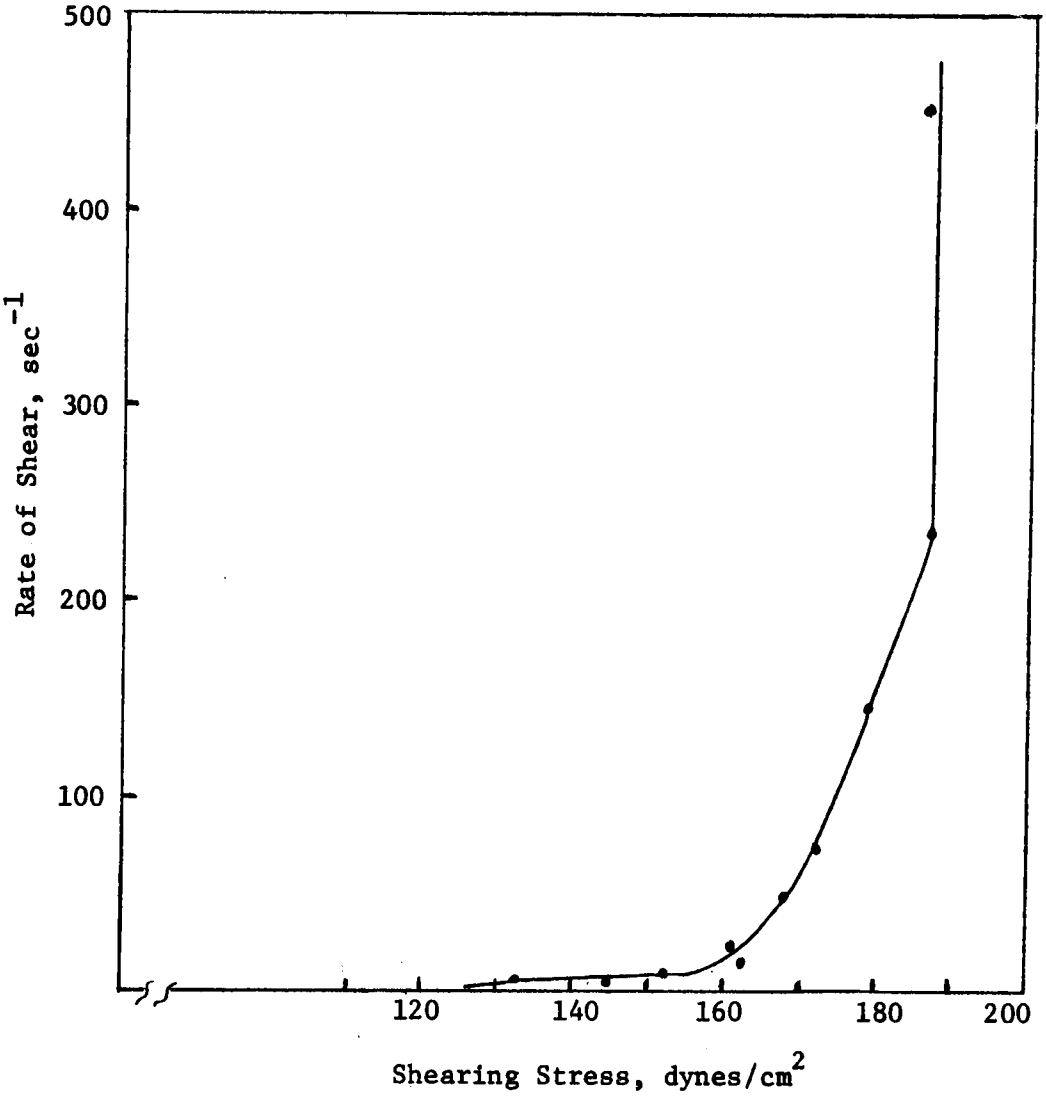


Figure 10. Flow curve for 0.1 M CTAB-0.5 M NaBr.

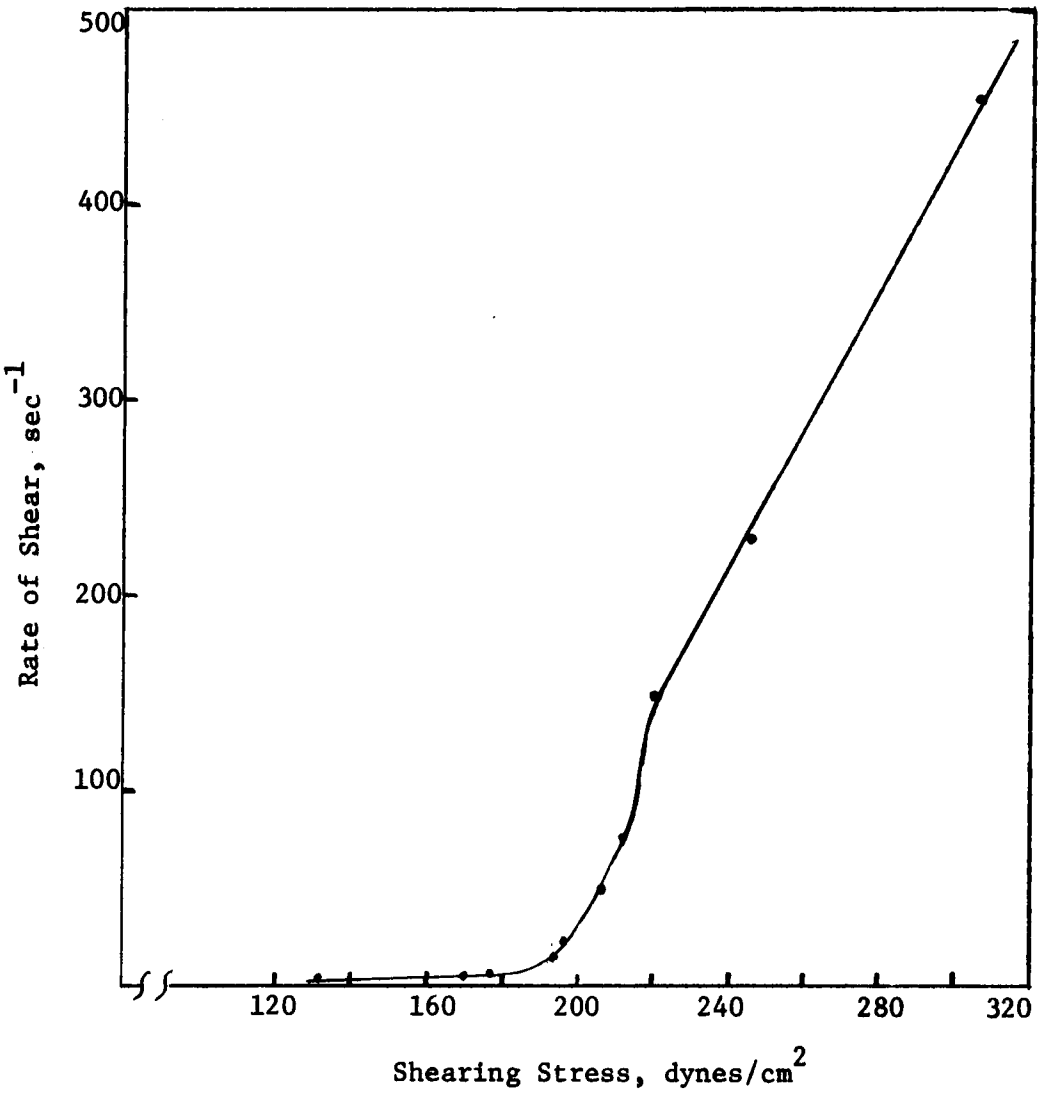


Figure 11. Flow curve for 0.1 M CTAB-0.0259 M 1-hexanol-0.0992 M $KClO_3$.

APPENDIX II

VISCOSITY DATA FOR HEXADECYLTRIMETHYLAMMONIUM BROMIDE-SODIUM BROMIDE SOLUTIONS

TABLE XLVI

VISCOSITY DATA FOR CTAB IN AQUEOUS SOLUTION AT 25°[a,b]

C_m, moles/ℓ[c]	η_{relm}[d]	η_{sp}[e]	η_{sp}/C_m, ℓ/mole
0.0994	1.381	0.381	3.83
0.05366	1.202	0.202	3.77
0.02653	1.109	0.109	4.12
0.01026	1.044	0.044	4.32
0.007542	1.0318	0.0318	4.21
(0.005425)	(1.015)	(0.015)	(3.3)
0.002116	1.0092	0.0092	4.35

[a] Linear least squares analysis gives $[\eta] = 4.29 \pm 0.08$ ℓ/mole or 11.8 ± 0.2 ml/g.

[b] Neglected points are in parentheses.

[c] C_m = C-CMC; CMC = 5.97×10^{-4} M by surface tension measurements.

[d] $\eta_{relm} = \eta_{exptl}/\eta_{CMC}$; $\eta_{CMC} = 0.891$ cP.

[e] $\eta_{sp} = \eta_{relm} - 1$.

TABLE XLVII

VISCOSITY DATA FOR CTAB IN
0.1 M NaBr AT 25°[a,b]

$C_m \times 10^2$, g/ml[c]	η_{rel}	η_{sp}	η_{sp}/C_m, ml/g[c]	$C_m \times 10^2$, g/ml[d]	η_{sp}/C_m, ml/g[d]
6.519	40.21	39.21	601.5	6.517	601.6
5.835	22.56	21.56	369.5	5.833	369.6
5.104	13.92	12.92	253.1	5.102	253.2
4.374	8.332	7.332	167.6	4.372	167.7
3.644	5.186	4.186	114.9	3.642	114.9
3.259	4.143	3.143	96.4	3.257	96.5
2.625	2.703	1.703	64.9	2.623	64.9
2.189	2.147	1.147	52.4	2.186	52.4
1.629	1.606	0.606	37.2	1.627	37.25
1.095	1.268	0.268	24.5	1.093	24.53
0.7293	1.127	0.127	17.4	0.7271	17.47
0.4067	1.044	0.044	10.8	0.4045	10.88
0.3251	1.026	0.026	8.0	0.3229	8.05
0.2438	1.019	0.019	7.8	0.2416	7.86
0.1089	1.004	0.004	3.67	0.1067	3.75
(0.07234)	(1.012)	(0.012)	(16.6)	(0.07012)	(17.1)
(0.06047)	(1.023)	(0.023)	(38.0)	(0.05822)	(39.5)
(0.02992)	(1.004)	(0.004)	(13.4)	(0.02770)	(14.4)
(0.02380)	(1.009)	(0.009)	(37.8)	(0.02158)	(41.7)
(0.01563)	(1.003)	(0.003)	(19.2)	(0.01341)	(22.4)

TABLE XLVII (Continued)

$C_m \times 10^2$ g/ml[c]	η_{relm}	η_{sp}	η_{sp}/C_m, ml/g[c]	$C_m \times 10^2$, g/ml[d]	η_{sp}/C_m, ml/g[d]
(0.01155)	(1.003)	(0.003)	(26.0)	(0.00933)	(32.2)
(0.00665)	(1.008)	(0.008)	(120.2)	(0.00440)	(182)
(0.00261)	(1.007)	(0.007)	(268.3)	(0.00361)	(1940)

[a]Nonlinear least squares analysis (fourth order polynomial) gives $[\eta] = 9.11 \pm 1.5$ ml/g for CMC = 2.897×10^{-5} g/ml or 9.25 ± 1.5 ml/g, for CMC = 6.487×10^{-6} g/ml.

[b]Neglected points are in parentheses.

[c]CMC = 6.487×10^{-6} g/ml; $\eta_{CMC} = 0.894$ cP.

[d]CMC = 2.897×10^{-5} g/ml; $\eta_{CMC} = 0.891$ cP.

TABLE XLVIII

VISCOSITY DATA FOR CTAB IN x M NaBr AT 30°[a,b]

$C_m \times 10^2$, g/ml	$\eta_{rel}{}^h$	$\eta_{sp}{}^h$	η_{sp}/C_m, ml/g[h]	$\eta_{rel}{}^i$	$\eta_{sp}{}^i$	η_{sp}/C_m, ml/g[i]
x=0.1780 M NaBr[c]						
3.644	17.04	16.04	440.1	17.28	16.28	446.7
2.915	8.369	7.369	252.8	8.489	7.489	256.9
2.369	5.245	4.245	179.2	5.320	4.320	182.4
1.822	3.345	2.345	128.7	3.393	2.393	131.3
1.458	2.403	1.403	96.26	2.438	1.438	98.7
0.7285	1.390	0.390	53.53	1.410	0.410	56.3
0.3641	1.114	0.114	31.31	1.130	0.130	35.7
0.2915	1.079	0.079	27.27	1.095	0.095	32.6
0.1819	(1.035)	(0.035)	(19.08)	1.0496	0.0496	27.3
0.1456	(1.022)	(0.022)	(15.11)	1.037	0.037	25.2
0.07253	(1.003)	(0.003)	(4.25)	1.017	0.017	24.1
0.03608	(0.998)	(-0.002)	(-6.62)	(1.012)	(0.012)	(33.2)
0.02882	(0.994)	(-0.006)	(-20.12)	(1.0085)	(0.0085)	(29.5)
x=0.2000 M NaBr[d]						
1.822	4.279	3.279	179.9	4.325	3.325	182.5
0.9108	1.810	0.810	88.9	1.830	0.830	91.1
0.3641	1.165	0.165	45.2	1.177	0.177	48.6
0.2730	1.103	0.103	37.9	1.115	0.115	42.1
0.1819	1.053	0.053	29.2	1.064	0.064	35.4
0.09075	(1.018)	(0.018)	(20.3)	1.029	0.029	32.3
0.07253	(1.011)	(0.011)	(15.3)	1.022	0.022	30.3
0.03609	(1.0022)	(0.0022)	(6.1)	(1.013)	(0.013)	(36.0)
0.02697	(1.000)	(0)	(0)	(1.011)	(0.011)	(39.8)
x=0.2330 M NaBr[e]						
1.821	(6.234)	(5.234)	(287.4)	(6.339)	(5.339)	(293.2)
0.9104	2.181	1.181	129.7	2.218	1.218	133.8
0.3639	1.248	0.248	68.1	1.269	0.269	73.6
0.2729	1.170	0.170	62.3	1.189	0.189	69.6
0.1818	1.079	0.079	43.4	1.097	0.097	53.5
0.09071	1.035	0.035	38.7	(1.053)	(0.053)	(58.0)
0.03607	1.0098	0.0098	27.3	(1.027)	(0.027)	(74.6)
0.02696	1.011	0.011	40.4	(1.028)	(0.028)	(103.7)

TABLE XLVIII (Continued)

$C_m \times 10^2$, g/ml	$\eta_{relm}{}^h$	$\eta_{sp}{}^h$	η_{sp}/C_m, ml/g^h	$\eta_{relm}{}^i$	$\eta_{sp}{}^i$	η_{sp}/C_m, ml/g^i
x=0.3000 M NaBr[f]						
0.9074	2.776	1.776	195.7	2.831	1.831	201.8
0.5462	1.787	0.787	144.1	1.822	0.822	150.5
0.3642	1.390	0.390	107.1	1.417	0.417	114.5
0.2729	1.248	0.248	90.9	1.273	0.273	100.
0.1819	1.128	0.128	70.4	1.151	0.151	82.9
0.1272	1.074	0.074	58.6	1.096	0.096	75.3
0.09077	(1.039)	(0.039)	(42.7)	1.059	0.059	65.4
0.03609	(1.0050)	(0.0050)	(13.9)	(1.025)	(0.025)	(69.2)
0.02697	(1.0042)	(0.0042)	(15.4)	(1.024)	(0.024)	(89.4)
x=0.4000 M NaBr[g]						
0.9110	5.140	4.140	454.4	5.343	4.343	476.7
0.5465	2.415	1.415	258.9	2.510	1.510	276.3
0.3642	1.743	0.743	204.0	1.812	0.812	222.9
0.2730	1.438	0.438	160.4	1.495	0.495	181.3
0.1819	1.247	0.247	135.8	1.296	0.296	162.7
0.1272	(1.114)	(0.114)	(89.6)	1.158	0.158	124.2
0.09077	1.087	0.087	95.4	1.129	0.129	142.1
0.03609	1.038	0.038	105	(1.079)	(0.079)	(218)
0.02698	(1.017)	(0.017)	(62.6)	(1.057)	(0.057)	(212)

[a] A CMC of 10^{-5} M (3.644×10^{-6} g/ml) was used throughout.

[b] Neglected values are in parentheses.

[c] $\eta_{CMC} = \eta_{0.1780\ M\ NaBr} = 0.8122$ cP and $\eta_{CMC} = \eta_{H_2O}$, respectively.

[d] $\eta_{CMC} = \eta_{0.2000\ M\ NaBr} = 0.8093$ cP and $\eta_{CMC} = \eta_{H_2O}$, respectively.

[e] $\eta_{CMC} = \eta_{0.2330\ M\ NaBr} = 0.8142$ cP and $\eta_{CMC} = \eta_{H_2O}$, respectively.

[f] $\eta_{CMC} = \eta_{0.3000\ M\ NaBr} = 0.8166$ cP and $\eta_{CMC} = \eta_{H_2O}$, respctively.

[g] $\eta_{CMC} = \eta_{0.4000\ M\ NaBr} = 0.8323$ cP and $\eta_{CMC} = \eta_{H_2O}$, respectively.

[h] Computed using $\eta_{CMC} = \eta_{x\ M\ NaBr}$.

[i] Computed using $\eta_{CMC} = \eta_{H_2O}$.

TABLE XLIX

POLYNOMIAL COEFFICIENTS ($\eta_{sp}/C_m = AC_m^4 + BC_m^3 + CC_m^2 + DC_m + [\eta]$) DESCRIBING THE RAW VISCOSITY DATA FOR CTAB IN THE PRESENCE OF SODIUM BROMIDE

[NaBr], M	[η], ml/g[a]	A[a,d]	B[a,d]	C[a,d]	D[a,d]
--	11.8 ± 0.2	--	--	--	-5.783 ± 1.613
0.1000	9.11 ± 1.5[b]	9.902×10^7	-8.491×10^6	2.913×10^5	-11.31
0.1000	9.25 ± 1.5[c]	9.994×10^7	-8.618×10^6	2.931×10^5	-12.13
0.1780	15.8 ± 0.4	3.943×10^8	-1.763×10^7	3.400×10^5	3200
0.1780	21.7 ± 0.5	4.037×10^8	-1.828×10^7	386.56	26.31
0.2000	11.3 ± 0.2	--	1.625×10^7	-3.610×10^5	10496
0.2000	26.8 ± 0.5	--	-4.399×10^6	2.826×10^5	4860
0.2330	28.9 ± 2.8	--	--	--	11.02 ± 0.72
0.2330	36.3 ± 3.2	--	--	--	10.72 ± 0.62
0.3000	40.7 ± 3.9	--	--	--	17.61 ± 0.81
0.3000	54.4 ± 1.9	--	--	--	16.57 ± 0.42

TABLE XLIX (Continued)

[NaBr], M	[η], ml/g[a,d]	A[a,d]	B[a,d]	C[a,d]	D[a,d]
0.4000	106.7 ± 4.0	3.015×10^{11}	-5.167×10^{9}	2.897×10^{7}	-25650
0.4000	160.5 ± 6.0	3.914×10^{11}	-6.895×10^{9}	4.004×10^{7}	-57600

[a]The values which appear first for each [NaBr] are for $\eta_{CMC} = \eta_{NaBr}$ unless otherwise noted; the second values are for $\eta_{CMC} = \eta_{H_2O}$ unless otherwise noted.

[b]$C_{MC} = 7.95 \times 10^{-5}$ M.

[c]$C_{MC} = 1.78 \times 10^{-5}$ M.

[d]True standard deviations are reported only in the cases where A=B=C=0. All others obtained by inspection of experimental η_{sp}/C_m values and the corresponding η_{sp}/C_m values computed by the nonlinear least squares program. The polynomials were selected on the basis of the smallest sum of the deviations squared for all coefficients.

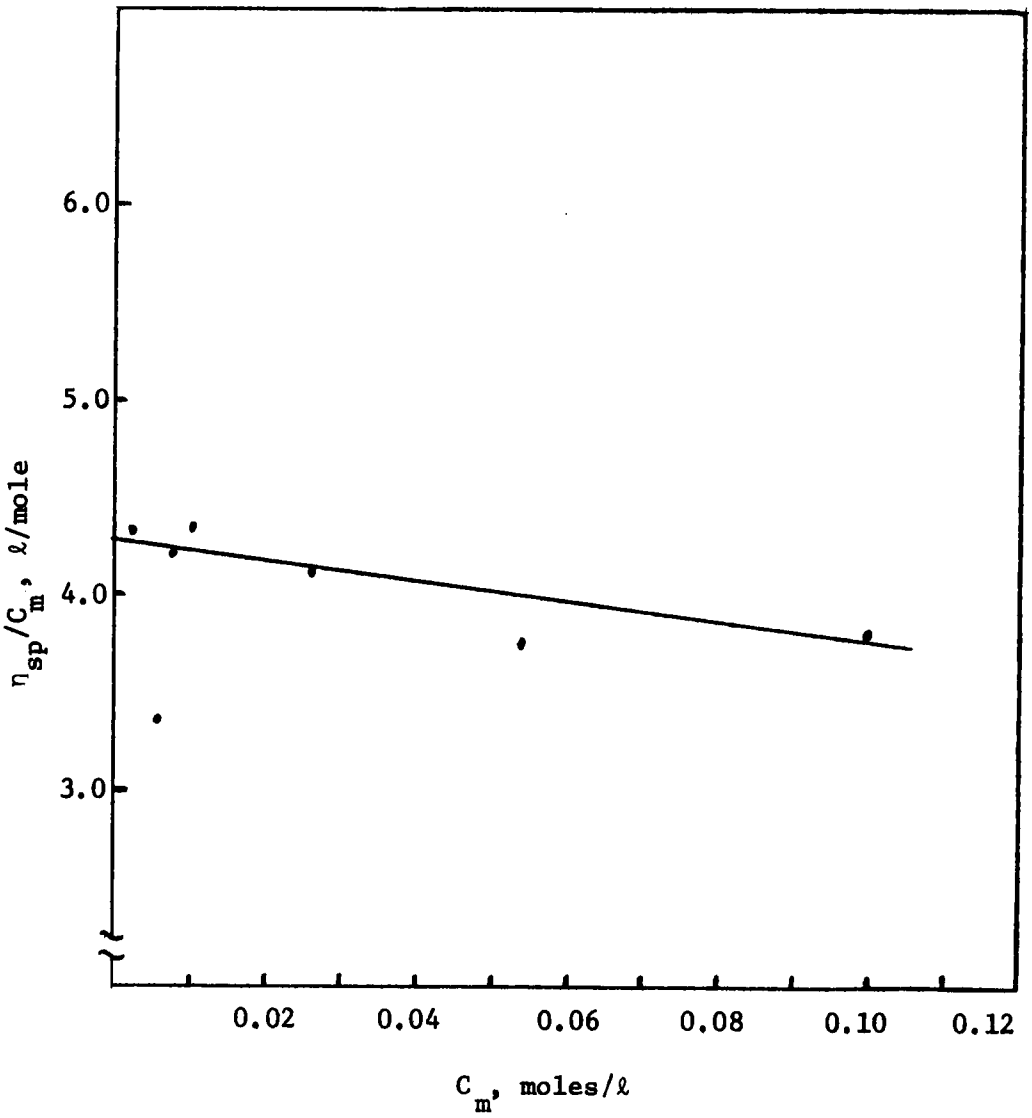


Figure 12. Plot of η_{sp}/C_m versus C_m for CTAB in H_2O at 25°.

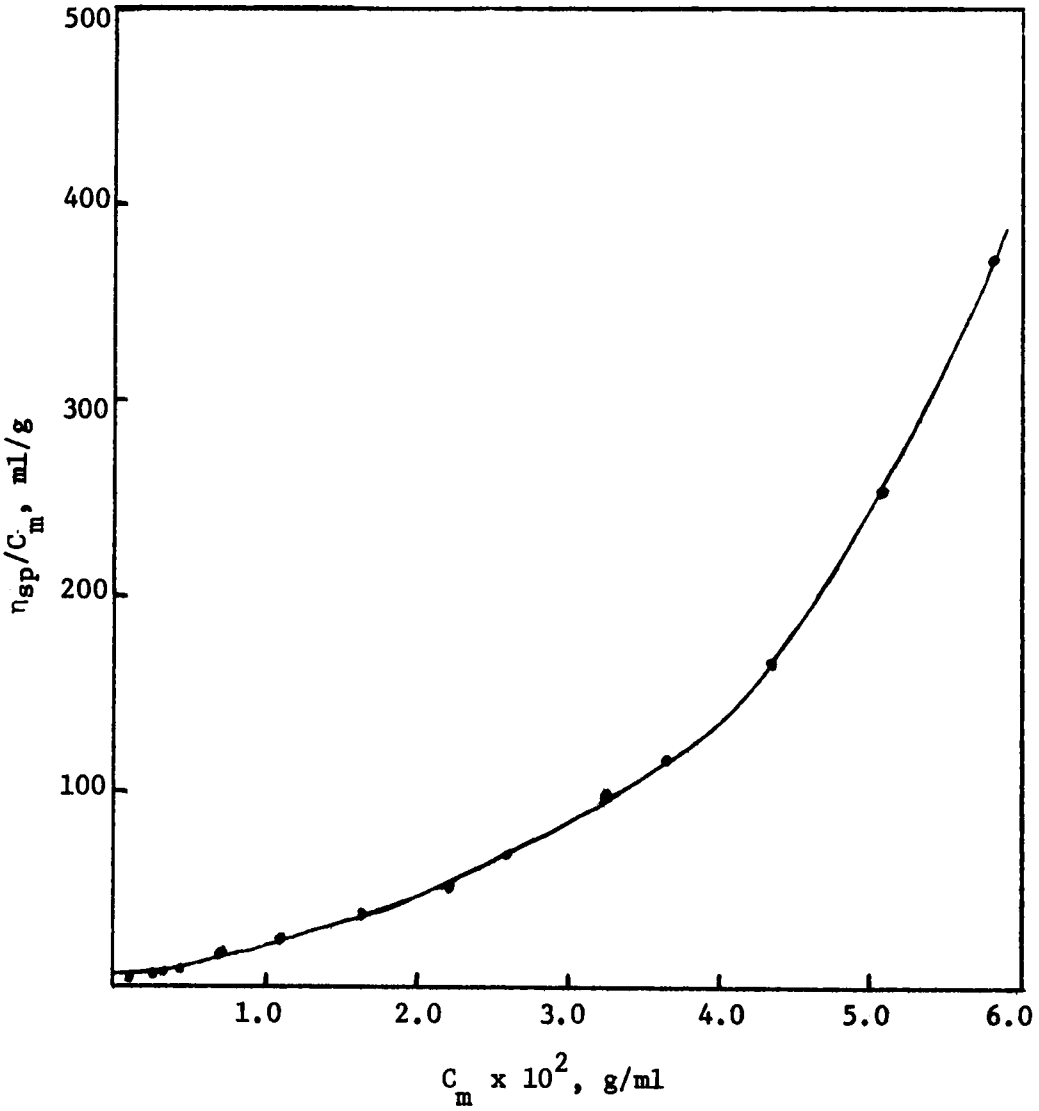


Figure 13. Plot of η_{sp}/C_m versus C_m for CTAB (high concentration) in 0.1 M NaBr at 25°.

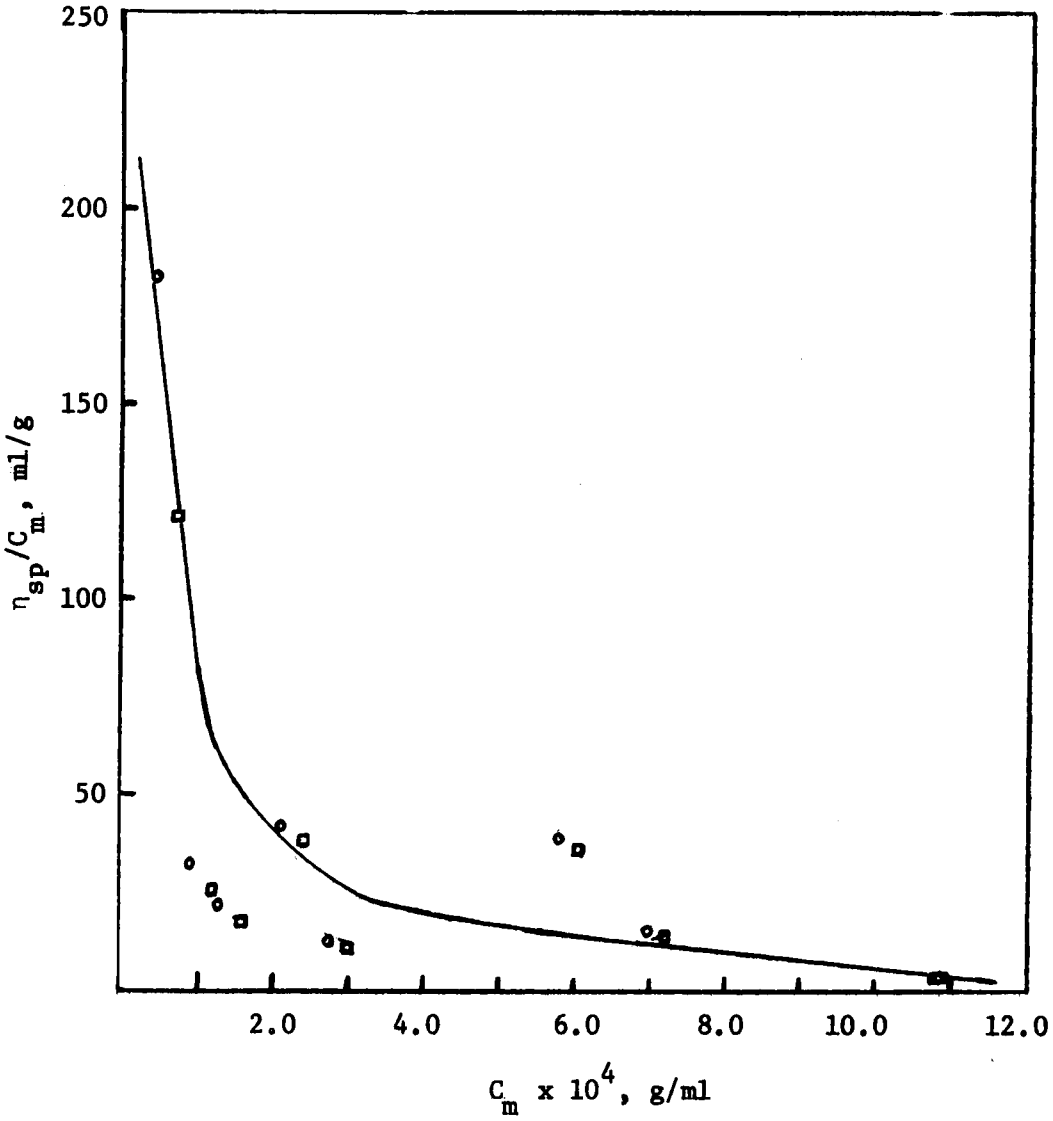


Figure 14. Plot of η_{sp}/C_m versus C_m for CTAB (low concentration) in 0.1 M NaBr at 25°.

Circles: CMC = 2.897×10^{-5} g/ml, squares: CMC = 6.487×10^{-6} g/ml.

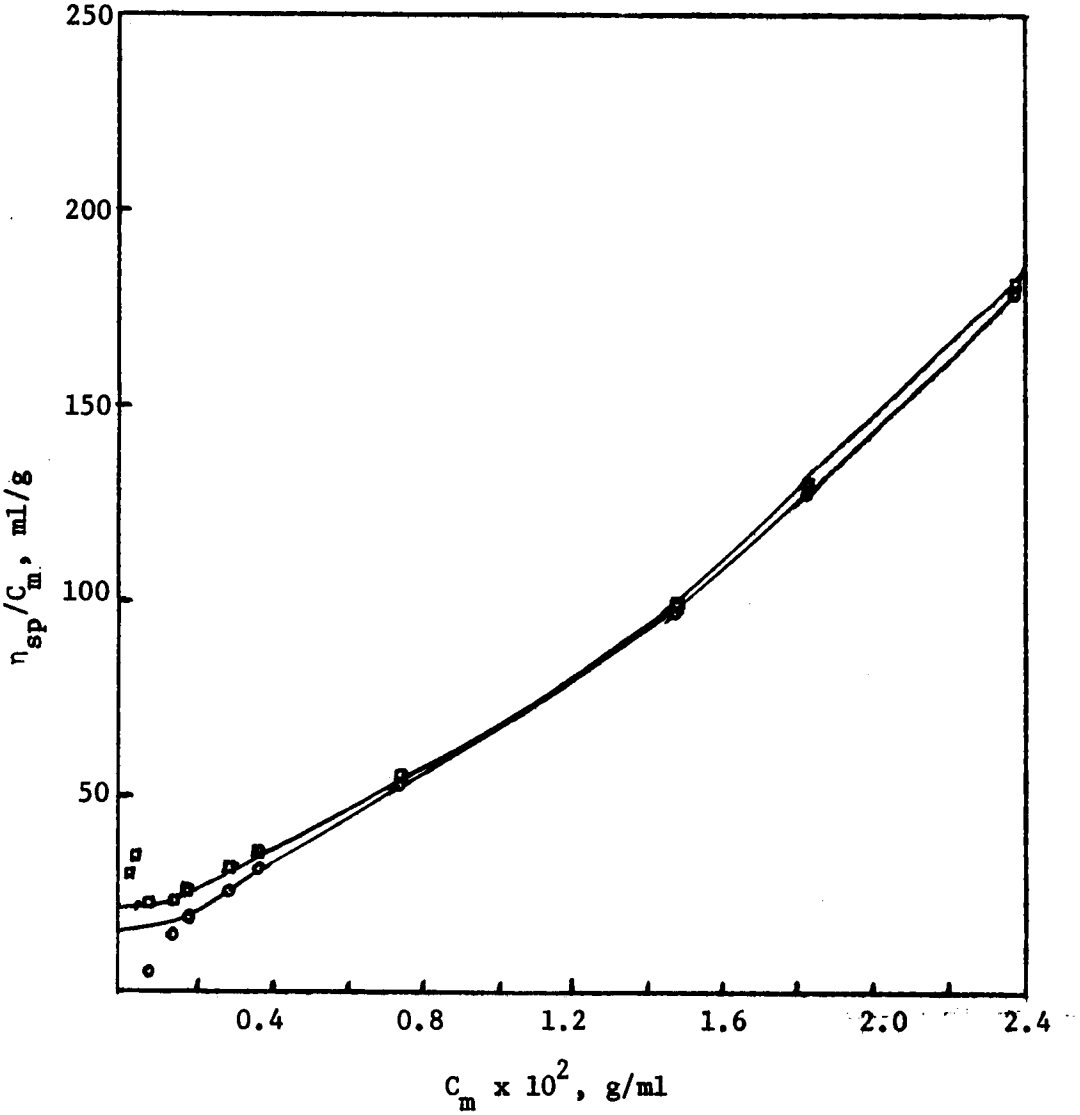


Figure 15. Plot of η_{sp}/C_m versus C_m for CTAB in 0.178 M NaBr at 30°.

Circles: $\eta_{CMC} = \eta_{0.178\ M\ NaBr}$, squares: $\eta_{CMC} = \eta_{H_2O}$.

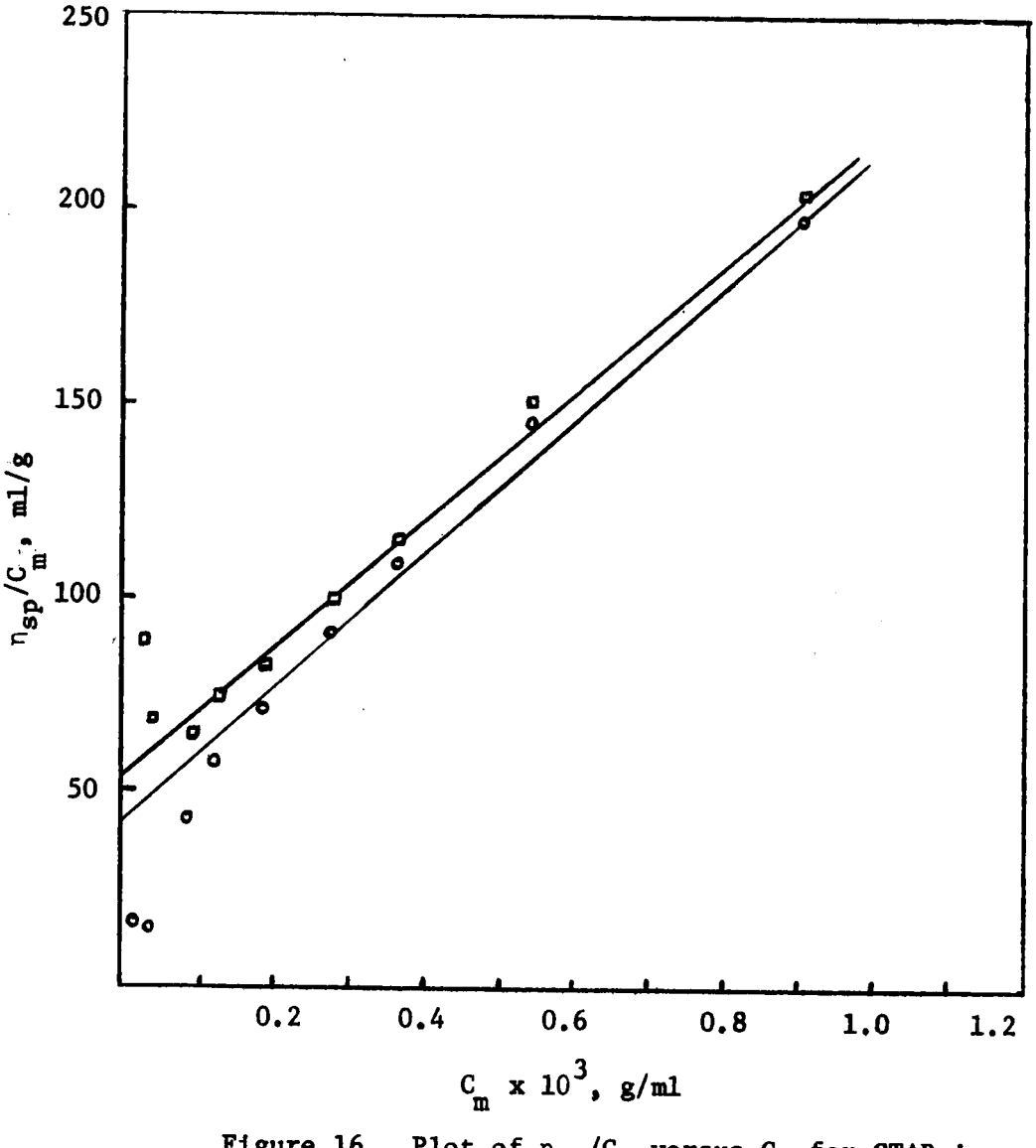


Figure 16. Plot of η_{sp}/C_m versus C_m for CTAB in 0.3 M NaBr at 30°.

Circles: $\eta_{CMC} = \eta_{0.3\ M\ NaBr}$, squares: $\eta_{CMC} = \eta_{H_2O}$.

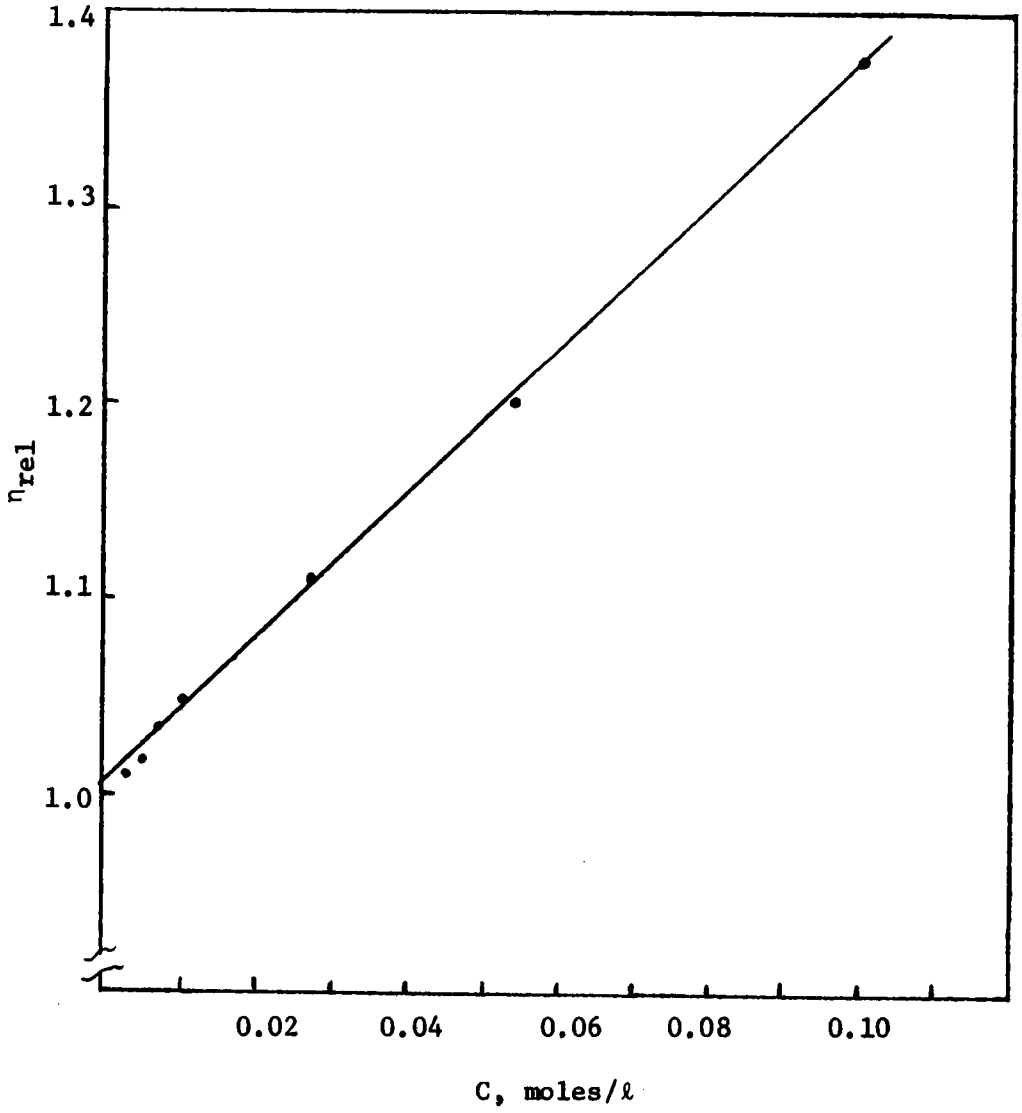


Figure 17. Plot of η_{rel} versus C for CTAB in H_2O at 25°.

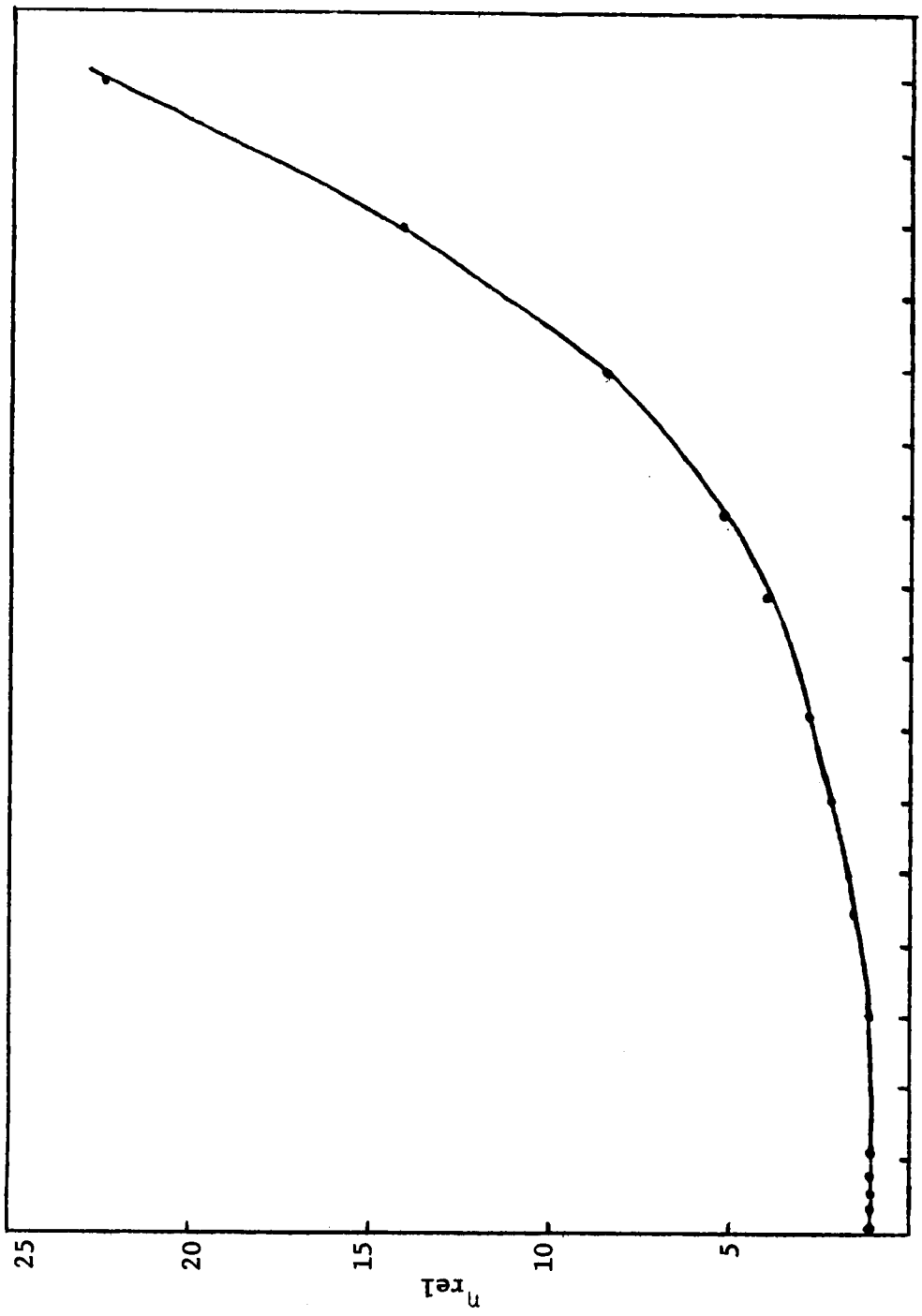


Figure 18. Plot of η_{rel} versus C for CTAB in 0.1 M NaBr at 25°.

TABLE L

CALCULATED VOLUMINOSITY (V_o) DATA FOR THE CTAB MICELLES IN THE ABSENCE OF ADDED ELECTROLYTE[a]

[CTAB], g/ℓ	η_{rel}	ϕ[b]	A x 10^3[c]	B[d]	V_o[e,f]
36.44	1.381	0.03655	3.345	0.1290	(0.299)
19.77	1.202	0.01983	0.856	0.06039	4.96
9.886	1.109	0.009916	0.197	0.02776	4.06
3.955	1.044	0.003967	0.298	0.01039	4.36
2.966	1.0318	0.002975	0.0165	0.007694	4.32
1.977	1.0155	0.001983	0.00723	0.005040	3.46
0.9886	1.0092	0.0009916	0.00180	0.002298	3.90

[a] $(1.82\ \phi^2\ \eta_{rel} - 0.01\ \phi^2)\ V_o^2 - (2.7\ \phi\ \eta_{rel} - 0.2\phi)V_o + \eta_{rel} - 1 = 0$; this comes from rearranging the expression $\eta_{rel} = (1 - 0.1\ V_o\ \phi)^2 / (1 - 1.35\ V_o\ \phi)^2$, see P. Ekwall, L. Mandell and P. Solyom, J. Colloid. Interface Sci., 35, 519 (1971).

[b] Volume fraction occupied by CTAB in solution. $\phi = \{[CTAB](g/\ell) \times \bar{V}_{sp}\}/1000$. $\bar{V}_{sp} = 1.003$ ml/g for CTAB.

[c] $A = 1.82\ \phi^2\ \eta_{rel} - 0.01\ \phi^2$.

[d] $B = 2.7\ \phi\ \eta_{rel} - 0.2\ \phi$.

[e] Solved for by using the quadratic formula on the equation $AV_o^2 - BV_o + \eta_{rel} - 1 = 0$; only the solution $[B - \sqrt{B^2 - 4A(\eta_{rel} - 1)}]/2A$ is reasonable.

[f] The average value of V_o is 4.18 ± 0.50, neglecting the value in parentheses, 4.16 ± 0.22, neglecting V_o 4.96, 3.46 also.

Estimation of the Electroviscous Effect for Hexadecyltrimethylammonium Bromide Micelles in Aqueous Solution

The electroviscous effect (E) for a suspension of colloidal particles is given by Equation 54,[5,90] where $q^* = \varepsilon kT \sum_{i=1}^{s} n_i z_i^2 w_i^{-1} / \eta_o e^2 \sum_{i=1}^{s} n_i z_i^2$, e is the electronic charge, ζ is the electrokinetic potential of the particles, κ is the reciprocal of the Debye length, a is the radius of the particles and Z is a tabulated function[90] of κa.

$$E = 1 + q^* (e\zeta/kT)^2 Z(\kappa a)(1 + \kappa a)^2 \qquad (54)$$

The symbols ε and η_o represent the dielectric constant of the medium and the viscosity of the medium respectively. The absolute mobility of ion i is represented by w_i; n_i and z_i represent the number of ions of kind i and the charge on ion i respectively.

Table LI gives a list of the quantities needed to calculate E for CTAB at its CMC. The value of κ was computed using Equation 55;[243] the

$$\kappa^2 = (4\pi e^2 \sum_{i=1}^{s} n_i z_i^2)/\varepsilon kT \qquad (55)$$

concentration of micelles present at the CMC was neglected, as its inclusion gave rise to an unrealistic value for E when calculations were completed. The limiting equivalent conductivity ($\lambda°$) for Br^- in CTAB solutions at 35° is 95 cm^2 ohm^{-1} $equiv^{-1}$.[107] The value for Br^- in aqueous solutions at 35° is 94 cm^2 ohm^{-1} $equiv^{-1}$.[124] It was therefore considered satisfactory to use 78.14 cm^2 ohm^{-1} $equiv^{-1}$ (the value for

TABLE LI

QUANTITIES NEEDED FOR THE ESTIMATION OF THE ELECTROVISCOUS EFFECT FOR CTAB

Quantity	Numerical value
κ	9.30×10^{5} cm^{-1}
κa[a]	2.23×10^{-1}
$Z(\kappa a)(1 + \kappa a)^{2}$[b]	1.16×10^{-2}
ζ[c]	1.036×10^{2} mV
$(e\zeta/kT)^{2}$[d]	1.607×10^{1}
$\epsilon kT/e^{2}$ [e]	1.40×10^{7} cm^{-1}
η_o[f]	8.94×10^{-3} poise
$\lambda°(CTA^{+})$[g]	2.082×10^{1} cm^{2} ohm^{-1} equiv^{-1}
$w_i(CTA^{+})$[h]	1.347×10^{8} cm sec^{-1} dynes^{-1}
$\lambda°(Br^{-})$[i]	7.814×10^{1} cm^{2} ohm^{-1} equiv^{-1}
$w_i(Br^{-})$[h]	5.072×10^{8} cm sec^{-1} dynes^{-1}
CMC	8.0×10^{-4} moles ℓ^{-1}.

[a] For the CTAB micelles a is 2.4×10^{-7} cm.

[b] From graph of this quantity versus κa in F. Booth, Proc. Roy. Soc., Ser. A, 203, 533 (1950).

[c] M. Czerniawski, Rocz. Chem., 41, 817 (1967).

[d] The value of kT/ϵ at 25° is 25.69 mV.

[e] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London, 1968, App. 7.1.

TABLE LI (Continued)

[f]The viscosity of the solution at the CMC may be approximated by the viscosity of water.

[g]E. J. Bair and C. A. Kraus, J. Amer. Chem. Soc., 73, 1129 (1951).

[h]$w_i = 6.469 \times 10^6 \lambda^\circ$, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London, 1968, p 43

[i]value in G. S. Hartley, B. Collie and C. S. Samis, Trans. Faraday Soc., 32, 795 (1936), extrapolated to 25°.

Br^- in aqueous solutions at 25°)[124] to approximate $\lambda°(Br^-)$ in CTAB solutions at 25°.

In calculating q* the concentration of micelles at the CMC was again neglected, as was pre-CMC dimerization. Thus a solution of CTAB at the CMC was considered to contain 8×10^{-4} M each of Br^- and CTA^+ ions. The resulting value of q* was 7.37, and the value of E is then 2.37 using Equation 54.

TABLE LII

CALCULATION OF CTAB MICELLE SIZES AT 30°
FROM LITERATURE DATA

[NaBr], M	n(lit)[a]	n(calc)[d]	MMW x 10^{-6} g/mole[e]
0.100	--	1430	0.521
0.178	2200[b]	2862	1.043
0.200	3380[c]	3221	1.174
0.233	5110[b]	3727	1.358
0.300	3470[c]	4651	1.695
0.400	6130[c]	5835	2.126

[a]Aggregation number of the micelles.

[b]P. Debye and E. W. Anacker, J. Phys. and Colloid Chem., 55, 644 (1951).

[c]K. Granath, Acta. Chem. Scand., 7, 297 (1953).

[d]n(lit) and log [NaBr] were fit to the following polynomial: $n = 10{,}543 + 13.625 \log [NaBr] + 4507 (\log [NaBr])^2$.

[e]Micellar molecular weight (n_{calc} x 364.45 g/mole).

TABLE LIII

CALCULATION OF AXIAL RATIOS (p) FOR CTAB MICELLES AT 30° FROM LITERATURE DATA

[NaBr], M	MMW x 10^{19}, g/micelle	Prolate ellipsoids[a] a, Å	p[b]	Rods[c] h, Å	p[d]
0.100	8.66	359	15.0	478	10.0
0.178	17.32	718	29.9	957	19.9
0.200	19.49	808	33.6	1077	22.4
0.233	22.54	934	38.9	1246	25.9
0.300	28.14	1166	48.6	1555	32.4
0.400	35.30	1463	60.9	1951	40.6

[a]For a prolate ellipsoid, $V = 4/3\ \pi\ ab^2$; b = 24 Å for CTAB and a is the major axis of the ellipsoid. V is computed from MMW using $\bar{V}_{sp}$ = 1 ml/g and the conversion factor 1 ml = 10^{24} Å^3.

[b]p = a/b for a prolate ellipsoid; b = 24 Å.

[c]For a rod, $V = \pi r^2 h$; r = 24 Å for CTAB. V is computed from MMW using $\bar{V}_{sp}$ = 1 ml/g and the conversion factor 1 ml = 10^{24} Å^3.

[d]p = h/2r for a rod; r = 24 Å.

TABLE LIV

CALCULATION OF AXIAL RATIOS (p) FROM INTRINSIC VISCOSITY DATA, ASSUMING UNHYDRATED MICELLES ($\bar{V}_{sp}$ = 1 ml/g)[a]

[NaBr], M	[η], ml/g[b]	Prolate ellipsoids p	Prolate ellipsoids Λ(p)[c]	1.5 [η][d]	Rods p	Rods Λ(p)[e]	[η], ml/g[g]	Prolate ellipsoids p	Prolate ellipsoids Λ(p)[c]	1.5[η][d]	Rods p	Rods Λ(p)[e]
0.1000	9.11	(7.5)	9.13	13.66	10.	13.6[f]	--	--	--	--	--	--
0.1780	15.8	(11.0)	15.8	23.7	14.5	26.2	21.7	14.5	23.09	32.55	17	33.29
					(13.5)	23.65		13.5	20.72		(16.8)	32.7
								(13.9)	21.67			
0.2000	11.3	8.5	10.7	16.95	11.5	18.86	26.8	15.5	25.59	40.2	(19.3)	40.44
		(8.8)	11.24		(10.7)	17.08		(16.0)	26.57			
0.2330	28.9	16	26.57	43.35	19.5	41.09	36.3	19.2	35.79	54.45	22.5	51.42
		17	29.5		20.5	44.49		(19.4)	36.38		(23.3)	54.35
		(16.8)	28.99		(20.1)	43.07						
0.3000	40.7	21	41.31	61.05	26	64.78	54.4	24.5	53.05	81.6	(30)	81.72
		20.9	40.99		(25)	60.82		(25)	54.8			
		(20.8)	40.68									

TABLE LIV (Continued)

[NaBr], M	[η], ml/g[b]	Prolate ellipsoids p	Prolate ellipsoids Λ(p)[c]	1.5 [η][d]	Rods p	Rods Λ(p)[e]	[η], ml/g[g]	Prolate ellipsoids p	Prolate ellipsoids Λ(p)[c]	1.5 [η][d]	Rods p	Rods Λ(p)[e]
0.4000	106.7	37	105.4	160.5	(45)	160.4	160.5	48	164	240.75		239.8
		37.4	107.3					47.6	162.0		(57.1)	240.7
		(37.2)	106.4					(47.3)	160.3			

[a]Values of p were estimated and Λ(p) then calculated using equations from C. Sadron, Progr. in Biophysics, 3, 237 (1950); values circled appear in Table III (p 92). For ellipsoids $[\eta] = \Lambda(p)\bar{V}_{sp}$, for rods $[\eta] = 2/3\ \Lambda(p)\bar{V}_{sp}$.

[b]For $\eta_{CMC} = \eta_{xM\ NaBr}$, 0.178-0.400 M NaBr.

[c]$\Lambda(p) = p^2/15\ [1/(\ln 2p-1.5)] + p^2/5\ [1/(\ln 2p-0.5)] + 0.933$.

[d]For rods $[\eta] = 2/3\ \Lambda(p)\ \bar{V}_{sp}$; $\bar{V}_{sp} = 1$ ml/g for our purposes.

[e]$\Lambda(p) = p^2/15\ [1/\ln 2p-1.8)] + p^2/5\ [1/(\ln 2p-0.8)] + 0.933$.

[f]From tabulated values in C. Sadron, Progr. in Biophysics, 3, 237 (1950).

[g]For $\eta_{CMC} = \eta_{H_2O}$, 0.178-0.400 M NaBr.

TABLE LV

RAW DATA FOR THE DETERMINATION OF THE PARTIAL SPECIFIC VOLUME OF CTAB IN x M NaBr SOLUTIONS

[CTAB], g/100 ml	Density (ρ) g/ml	V_{sp} (1/ρ) ml/g	Weight % of CTAB
x = 0.1000 M NaBr[a]			
6.51965	1.00588	0.994154	6.4815
5.83557	1.00554	0.994491	5.803
5.10449	1.00541	0.994619	5.077
4.37449	1.00539	0.994639	4.351
3.64486	1.00519	0.994837	3.626
3.25982	1.00527	0.994758	3.2427
2.62586	1.00514	0.994886	2.612
2.18925	1.00502	0.995005	2.178
1.62989	1.00476	0.995263	1.6222
1.09554	1.00491	0.995114	1.0902
0.72999	1.00475	0.995272	0.7265
0.40746	1.00474	0.995282	0.4055
0.32582	1.00475	0.995272	0.3243
0.24448	1.00478	0.995243	0.2433
0.10955	1.00477	0.995253	0.1090
x = 0.1780 M NaBr			
3.6442	1.00997	0.9901	3.608
2.9154	1.00995	0.9901	2.887
2.3686	1.00996	0.9901	2.345
1.8219	1.00981	0.9903	1.804
1.4575	1.00968	0.9904	1.443
0.72853	1.00998	0.9901	0.7213
0.36408	1.00975	0.9903	0.3606
0.29151	1.00975	0.9903	0.2887
0.18186	1.00984	0.99025	0.1801
0.14559	1.00989	0.9902	0.1442
0.07253	1.00960	0.9905	0.07184
0.03608	1.00977	0.9903	0.03573
0.02882	1.00966	0.9904	0.02854
x = 0.2000 M NaBr			
1.8224	1.01166	0.9885	1.801
0.91116	1.01169	0.9884	0.9006
0.36449	1.01142	0.9887	0.3604

TABLE LV (continued)

[CTAB], g/100 ml	Density (ρ) g/ml	V_{sp} (1/ρ) ml/g	Weight % of CTAB
0.27335	1.01147	0.9887	0.2702
0.18224	1.01146	0.9887	0.1802
0.091116	1.01147	0.9887	0.0901
0.072897	1.01133	0.9888	0.0721
0.036449	1.01134	0.9888	0.0360
0.027335	1.01133	0.9888	0.0270
x = 0.2330 M NaBr			
1.8215	1.01417	0.9860	1.796
0.91076	1.01403	0.9862	0.8982
0.3643	1.01421	0.9860	0.3592
0.27323	1.01401	0.9862	0.2694
0.18215	1.01393	0.9863	0.1796
0.09107	1.01399	0.9862	0.08981
0.03643	1.01402	0.9862	0.03593
0.027323	1.01391	0.9863	0.02695
x = 0.3000 M NaBr			
0.91102	1.01929	0.9811	0.8938
0.5466	1.01917	0.9812	0.5363
0.36452	1.01926	0.9811	0.3576
0.27331	1.01915	0.9812	0.2682
0.18226	1.01919	0.9812	0.1788
0.12758	1.01916	0.9812	0.1252
0.091131	1.01928	0.9811	0.08941
0.036452	1.01891	0.9814	0.03578
0.027331	1.01925	0.9811	0.02681
x = 0.4000 M NaBr			
0.91134	1.02638	0.9743	0.8879
0.54682	1.02704	0.9737	0.5324
0.36452	1.02695	0.9741	0.3549
0.2734	1.02661	0.9741	0.2663
0.18227	1.02671	0.9740	0.1775
0.12758	1.02685	0.9739	0.1242
0.09113	1.02671	0.9740	0.08876
0.03645	1.02668	0.9740	0.03550
0.02734	1.02689	0.9738	0.02662

[a]Data determined at 25°, all other data at 30°.

TABLE LVI

PARTIAL SPECIFIC VOLUME OF CTAB IN NaBr SOLUTIONS

[NaBr], M	m[a]	b[a]	$\bar{V}_{sp}$, ml/g[b]
0.1000	-0.00016 ± 0.00001	0.99534 ± 0.00003	0.979
0.1780	-0.0001 ± 0.00003	0.99033 ± 0.00004	0.980
0.2000	-0.0002 ± 0.00005	0.98876 ± 0.00004	0.969
0.2330	-0.0001 ± 0.00006	0.98623 ± 0.00004	0.976
0.3000	--	--	0.981[c]
0.4000	0.0003 ± 0.00021	0.97391 ± 0.00004	1.004

[a] V_{sp} = m(weight percent of CTAB) + b (see Table LV, p 297 for raw data). m and b were determined by least squares analysis.

[b] Value of V_{sp} at weight percent of CTAB equal to 100.

[c] For 0.3000 M NaBr, V_{sp} was constant.

TABLE LVII

DETERMINATION OF A_3 (EQUATION 34, P 94) FOR CTAB IN NaBr SOLUTIONS

[NaBr], M	[CTAB], M	Log $\eta_{rel m}$ [d]	(Log $\eta_{rel m}$)/C ℓ/ mole	A_3 ℓ/mole	[η], ml/gg
0.1000[a]	0.17889	1.604	8.97	5.68 ± 0.10[e]	35.9
	0.16012	1.353	8.45		
	0.14006	1.144	8.16		
	0.12003	0.9207	7.67		
	0.10001	0.7148	7.14		
	0.08944	0.6172	6.90		
0.1780[b]	0.10000	1.238	12.3	9.7[f]	61.3
	0.08000	0.9290	11.6		
	0.06500	0.7259	11.2		
	0.05000	0.5302	10.6		
0.3000[c]	0.024997	0.4434	17.7	16[f]	101
	0.014998	0.2521	16.8		

[a] $\eta_{rel m}$ from Table XLVII (p 275).

[b] $\eta_{rel m}$ from Table XLVIII (p 277), Column 5.

[c] $\eta_{rel m}$ from Table XLVIII, Column 2.

[d] Only those data points lying on a straight line are included; A_3 is the intercept for (log $\eta_{rel m}$)/C versus C.

[e] Determined by linear least squares analysis; slope of line = 2.075 ± 0.093; A_3 is the intercept.

TABLE LVII (Continued)

[f]Determined graphically.

[g]Since $A_3 = \Lambda(p)\ \bar{V}_{sp}/2.303$, $\Lambda(p)$ may be calculated and hence $[\eta]:[\eta] = \Lambda(p)\ V_{sp}$ (assume $\bar{V}_{sp} \simeq 1$ ml/g). To convert A_3 from ℓ/mole into ml/g multiply by (1000 ml/ℓ /364.45 g/mole).

APPENDIX III

CONCENTRATION-DEPENDENT ENTHALPIES OF SOLUTION

TABLE LVIII

ENTHALPIES OF SOLUTION

Solute and Solvent	[Solute],[f,g] M	$\Delta H_{s,\ solute}$,[g] kcal/mole
NaBr in 0.1 M CTAB	0.003741	-1.363
	0.005490	-1.383
	0.008977	-1.086
	0.01036	-1.047
	0.01440	-0.871
	0.01708	-0.982
	0.02038	-0.747
	(0.02086)	(-1.803)
	(0.02418)	(-1.706)
	0.02513	-0.683
	(0.02828)	(-3.169)
	0.02912	-0.595
	0.03333	-0.825
	0.03399	-0.538
	(0.03813)	(-1.812)
	0.03918	-0.588
	0.04237	-0.753
	0.04337	-0.596
	0.04717	-0.884
	0.05210	-0.623
	0.05990	-0.798
NaBr in 0.1 M CTAB-0.05 M NaBr at (28.0 ± 0.2)°	(0.005659)	(-0.425)
	0.008970	-0.684
	0.01400	-0.611
	0.01843	-0.582
	0.02203	-0.526
	0.02644	-0.499
NaBr in 0.1 M CTAB-0.1 M NaBr at (33.4 ± 0.1)°	0.005163	-0.469
	0.009677	-0.547
	0.01428	-0.526
	0.01865	-0.473
	0.02283	-0.465
	0.02772	-0.456
NaBr in 0.1 M CTAB-0.1 M NaBr at (37.7 ± 0.3)°	0.004648	-0.824
	0.009192	-0.717
	0.01380	-0.624

TABLE LVIII (Continued)

Solute and Solvent	[Solute],[f,g] M	$\Delta H_{s,\ solute}$, kcal/mole[g]
	0.01877	-0.553
	(0.02319)	(-0.639)
	(0.02811)	(-0.586)
Na_2CO_3 in 0.1 M CTAB	0.004114	-3.234
	0.009207	-3.632
	0.01301	-4.061
	0.01806	-4.454
	0.02294	-4.653
	0.02516	-4.848
Na_2CO_3 in H_2O[a]	0.01451	5.039
	0.01595	5.121
	0.01662	5.152
	0.01754	5.184
	0.01848	5.274
	0.02017	5.369
	0.02234	5.356
	0.02552	5.448
NaF in 0.1 M CTAB	(0.008345)	(0.748)
	0.01586	0.784
	0.02633	0.724
	0.03442	0.658
	0.04275	0.609
	0.05096	0.540
$NaSO_3C_7H_7$ in H_2O[b]	0.002811	0.729
	0.005087	0.759
	0.006991	0.699
	0.009474	0.852
	0.01228	0.940
	0.01438	1.220
LiBr in 0.1 M CTAB	0.004165	-11.75
	0.008007	-11.72
	0.01170	-11.50
	0.01522	-11.29
	0.02194	-11.09
	(0.03073)	(-11.49)

TABLE LVIII (Continued)

Solute and Solvent	[Solute], M [f,g]	$\Delta H_{s,\ solute}$, kcal/mole
NH_4Br in 0.1 M CTAB	0.003911	2.810
	0.008125	2.947
	0.01462	3.201
	0.02080	3.340
	0.02565	3.482
	0.03010	3.452
Na_2CO_3 in 0.075 M DTAB [c]	0.004492	-3.166
	0.004943	-3.378
	0.008057	-4.013
	0.01019	-4.421
	0.01127	-4.279
	0.01403	-4.575
	0.01501	-4.411
	0.01832	-4.783
	0.02206	-4.920
	0.02214	-4.847
	0.02532	-4.957
	(0.02730)	(-4.583)
NaBr in 0.075 M DTAB	0.003471	-0.709
	0.006645	-0.744
	0.01138	-0.549
	0.01837	-0.497
	0.02216	-0.488
	0.02576	-0.343
$NaC_2H_3O_2$ in 0.04 M NaLS	0.005216	-4.151
	0.01149	-4.140
	0.01796	-4.098
	0.02302	-4.088
	0.03003	-3.990
	0.03581	-3.913
$NaNO_3$ in 0.04 M NaLS	0.007134	4.395
	0.01345	4.563
	0.01728	4.589
	0.02171	4.654
	0.02632	4.482
	0.03273	4.575

TABLE LVIII (Continued)

Solute and Solvent	[Solute], M [f,g]	$\Delta H_{s,\ solute}$, kcal/mole
Na_2SO_4 in 0.04 M NaLS	0.002497	-1.207
	0.004634	-1.172
	0.008219	-0.950
	0.01117	-0.864
	0.01543	-0.655
	0.01934	-0.467
$(CH_3)_4NBr$ in 0.04 M NaLS	0.002215	3.965
	0.005382	4.370
	0.008439	4.408
	0.01096	4.800
	0.01464	4.981
	0.01716	4.936
$NaSO_3C_7H_7$ in 0.0015 M HACl[d]	0.000684	-0.481
	0.002118	0.925
	0.003856	1.248
	0.005947	0.955
	0.008261	1.275
	0.009936	1.317
NaCl in 0.0015 MHACl [d] (low concentration)	0.000576	-2.261
	0.001765	-0.916
	0.002984	-0.701
	0.003344	-0.0822
	0.005010	0.564
	0.00598	-0.0498
	0.00672	0.399
NaCl in 0.0015 M HACl[d] (high concentration)	0.005010	0.564
	0.00672	0.399
	0.00863	0.459
	0.009138	0.508
	0.01528	0.599
	0.01564	0.788
	0.02326	0.653
	0.02426	0.645
	0.03150	0.631
	0.04002	0.729
	0.04433	0.621
	0.05275	0.687

TABLE LVIII (Continued)

Solute and Solvent	[Solute],[f,g] M	$\Delta H_{s,\ solute}$, kcal/mole
Bromoform in H_2O	0.002416	-0.147
	0.005311	-0.061
	0.008270	-0.045
Uracil in 0.1 M CTAB	0.004106	6.139
	0.007769	6.024
	0.01024	5.686
	0.01333	5.682
	0.01738	5.553
	0.02105	5.115
Uracil in H_2O [e]	0.003006	6.413
	0.006439	5.751
	0.01015	5.355
	0.01358	5.546
	0.01641	5.206
	0.02037	4.907
2-Butanone in 0.1 M CTAB	0.002350	-2.611
	0.005167	-2.358
	0.008045	-2.396
	0.01040	-2.504
	0.01321	-2.238
	0.01609	-2.133
2-Butanone in H_2O	0.00235	-2.722
	0.00517	-2.659
	0.00804	-2.632
	0.01040	-2.681
	0.01321	-2.660
	0.01609	-2.604
Benzoic acid in H_2O	0.001887	(5.458)
	0.005868	5.568
	0.007617	5.195
	0.009769	4.705
	0.01112	4.370
	0.01264	(4.692)

TABLE LVIII (Continued)

Solute and Solvent	[Solute],[f,g] M	$\Delta H_{s,\ solute}$, kcal/mole
o-Chlorobenzoic acid in 0.1 M CTAB	0.000846	4.546
	0.001478	3.829
	0.001711	3.910
	0.002419	3.500
	0.003193	3.233
	0.003220	2.993
	0.003964	3.289
	(0.004475)	(4.106)
	0.004615	2.506
	(0.006617)	(2.738)
	(0.01019)	(2.538)
Salcylic acid in 0.1 M CTAB, run 1	0.002802	1.856
	0.005919	1.924
	0.009551	1.551
	0.01302	1.152
	0.01671	1.001
	0.02045	0.523
Salicylic acid in 0.1 M CTAB, run 2	(0.002048)	(1.814)
	0.003745	1.934
	0.005653	1.813
	0.007434	1.489
	0.009685	1.072
	0.01133	0.831
Salicylic acid in H_2O	0.002583	7.004
	0.004530	6.098
	0.006320	5.805
	0.009460	4.705
Phenol in 0.1 M CTAB	0.002523	-0.905
	0.006537	-0.769
	0.01134	-0.649
	0.01420	-0.521
	0.01855	-0.427
	0.02163	-0.374
p-Nitrophenol in 0.1 M CTAB	0.003061	-0.690
	0.004904	-0.386
	0.007466	-0.370
	0.01062	-0.198

TABLE LVIII (Continued)

Solute and Solvent	[Solute], M [f,g]	$\Delta H_{s,\ solute}$, kcal/mole
	0.01230	+0.069
	0.01472	0.241
Phenol in n-hexane	0.004089	7.409
	0.009279	7.162
	0.01175	7.127
	0.01518	7.000
	0.01790	6.509
	0.02136	6.619
Benzoic acid in n-hexane	0.002580	4.530
	0.004116	4.139
	0.006717	4.228
	0.008824	4.054
	0.01057	3.989
	0.01225	3.876
Phenol in 0.01 M CTAB	0.003931	1.944
	0.009121	2.029
	0.01339	2.143
	0.01982	2.304
	0.02527	2.432
	0.02999	2.478
Catechol in 0.01 M CTAB	(0.001361)	(5.073)
	0.002622	1.731
	0.004177	2.254
	0.005394	2.147
	0.006760	2.363
	0.008190	2.458
Phenol in 0.05 M CTAB	0.005810	0.520
	0.01144	0.798
	0.01621	1.125
	0.01901	0.985
	0.02249	1.126
	0.02771	1.093

[a]Data from J. P. Rupert, H. P. Hopkins and C. A. Wulff, J. Phys. Chem., 69, 3059 (1965); solute column reports $\sqrt{I}$.

TABLE LVIII (Continued)

[b] ΔH_s is plotted versus [solute].

[c] Recorded line in Table XVIII (p 135) uses only the first four points; points 3-11 give $\Delta H = -2.97 \pm 0.19$ kcal/mole.

[d] C_{NaX} is one-half the concentration of a given injection plus the concentration of NaX already present prior to injection.

[e] ΔH_s is plotted versus $\sqrt{\text{solute}}$.

[f] Data for inorganic solutes plotted against $\sqrt{C}$ or $\sqrt{I}$ except where noted; data for organic solutes plotted against C([solute]), except where noted.

[g] neglected points are in parentheses.

TABLE LIX

ENTHALPIES OF SOLUTION FOR SOLUTES AT INFINITE DILUTION[a]

Solute and Solvent	m[b]	ΔH_s, solute, kcal/mole[b]
NaBr in 0.1 M CTAB	3.649 ± 0.729	-1.429 ± 0.123
NaBr in 0.1 M CTAB-0.05 M NaBr at (28.0 ± 0.2)°	2.744 ± 0.190	-0.942 ± 0.025
NaBr in 0.1 M CTAB-0.1 M NaBr at (33.4 ± 0.1)°	0.472 ± 0.485	-0.548 ± 0.062
NaBr in 0.1 M CTAB-0.1 M NaBr at (37.7 ± 0.3)°	3.976 ± 0.081	-1.095 ± 0.009
Na_2CO_3 in 0.1 M CTAB	-100.1 ± 4.9	-2.071 ± 0.106
Na_2CO_3 in H_2O	37.17 ± 4.69	4.541 ± 0.090
NaF in 0.1 M CTAB	-2.426 ± 0.198	1.103 ± 0.037
$NaSO_3C_7H_7$ in H_2O	38.96 ± 10.60[c]	0.535 ± 0.100[c]
LiBr in 0.1 M CTAB	8.553 ± 1.309	-12.38 ± 0.14
NH_4Br in 0.1 M CTAB	6.381 ± 0.487	2.406 ± 0.064
Na_2CO_3 in 0.075 M DTAB	-20.55 ± 1.02	-0.830 ± 0.147
NaBr in 0.075 M DTAB	3.482 ± 0.678	-0.955 ± 0.082
$NaC_2H_3O_2$ in 0.04 M NaLS	1.949 ± 0.458	-4.332 ± 0.066
$NaNO_3$ in 0.04 M NaLS	1.375 ± 1.133	4.355 ± 0.159
Na_2SO_4 in 0.04 M NaLS	4.844 ± 0.458	-1.695 ± 0.080
$(CH_3)_4NBr$ in 0.04 M NaLS	12.38 ± 1.54	3.403 ± 0.152
$NaSO_3C_7H_7$ in 0.0015 M HACl	19.88 ± 7.19	-0.460 ± 0.516
NaCl in 0.0015 M HACl (low concentrations)	43.62 ± 7.68	-2.986 ± 0.472

TABLE LIX (Continued)

Solute and Solvent	m^b	ΔH_s, solute, kcal/mole[b]
NaCl in 0.0015 M HACl (high concentration	1.330 ± 0.510	0.417 ± 0.077
Bromoform in H_2O	17.38 ± 7.01	-0.177 ± 0.041
Uracil in 0.1 M CTAB	-55.90 ± 8.12	6.388 ± 0.110
Uracil in H_2O	-74.89 ± 15.33[d]	6.403 ± 0.200[d]
2-Butanone in 0.1 M CTAB	28.06 ± 9.67	-2.632 ± 0.100
2-Butanone in H_2O	5.784 ± 2.735	-2.713 ± 0.028
Benzoic acid in H_2O	-227.7 ± 4.6	6.916 ± 0.041
o-Chlorobenzoic acid in 0.1 M CTAB	-451.9 ± 67.8	4.687 ± 0.199
Salicylic acid in 0.1 M CTAB, run 1	-79.62 ± 9.16	2.243 ± 0.118
Salicylic acid in 0.1 M CTAB, run 2	-153.8 ± 12.7	2.592 ± 0.102
Salicylic acid in H_2O	-321.2 ± 32.1	7.742 ± 0.201
Phenol in 0.1 M CTAB	28.35 ± 1.56	-0.961 ± 0.022
p-Nitrophenol in 0.1 M CTAB	72.90 ± 9.12	-0.867 ± 0.089
Phenol in n-hexane	-51.55 ± 10.04	7.654 ± 0.145
Benzoic acid in n-hexane	-54.50 ± 13.59	4.545 ± 0.112
Phenol in 0.01 M CTAB	21.86 ± 1.13	1.852 ± 0.022
Catechol in 0.01 M CTAB	115.7 ± 34.2	1.563 ± 0.197
Phenol in 0.05 M CTAB	26.48 ± 7.91	0.488 ± 0.147

TABLE LIX (Continued)

[a]The ΔH_s values are actually good only to three significant figures, except for values >10 kcal/mole. This table includes an extra significant figure (in some cases) from the computer printout of linear least squares analysis.

[b]ΔH_s (conc) = m (conc) + ΔH_s (infinite dilution). The intercepts are presented in Column 3. The expression (conc) may take a variety of forms: for inorganic solutes it is $\sqrt{C}$ or $\sqrt{I}$ unless otherwise noted, for organic solutes it is C unless otherwise noted (C = [solute], M and I = ionic strength).

[c]ΔH_s was plotted against C.

[d]ΔH_s was plotted against $\sqrt{C}$.

TABLE LX

TEMPERATURE DEPENDENCE OF SOLUBILITY IN WATER FOR ORGANIC SOLUTES[a]

Solute	T, °C	Concentration	m^b	b^b	ΔH_s, H_2O, kcal/mole[c]
Carbon tetrachloride	0	0.00631 M	223.7 ± 89.0	-3.045 ± 0.308	-1.022 ± 0.407
	10	0.00540 M			
	15	0.00501 M			
	20	0.00520 M			
	25	0.00501 M			
	30	0.00527 M			
Benzoic acid	0	0.170 g/100 g H_2O	-1437.3 ± 90.0	5.391 ± 0.295	6.577 ± 0.412
	10	0.210 g/100 g H_2O			
	20	0.290 g/100 g H_2O			
	25	0.345 g/100 g H_2O			
	30	0.410 g/100 g H_2O			
	40	0.555 g/100 g H_2O			
	50	0.775 g/100 g H_2O			
	60	1.155 g/100 g H_2O			
	80	2.715 g/100 g H_2O			
o-Hydroxybenzoic acid	0	0.8 g/ℓ	-1671.6 ± 58.6	6.964 ± 0.190	7.649 ± 0.268
	10	1.2 g/ℓ			
	20	1.8 g/ℓ			
	25	2.2 g/ℓ			
	30	2.7 g/ℓ			
	40	3.7 g/ℓ			
	50	5.4 g/ℓ			

TABLE LX (Continued)

Solute	T, °C	Concentration	m^b	b^b	ΔH_s, H_2O kcal/mole[c]
	60	8.2 g/ℓ			
	70	13.2 g/ℓ			
	80	20.5 g/ℓ			
o-Hydroxybenzoic acid	0	1.24 g/1000 g H_2O	-1494.6 ± 57.6	5.444 ± 0.087	6.839 ± 0.263
	5	1.29 g/1000 g H_2O			
	10	1.35 g/1000 g H_2O			
	15	1.84 g/1000 g H_2O			
	20	2 g/1000 g H_2O			
	25	2.48 g/1000 g H_2O			
	30	2.98 g/1000 g H_2O			
	35	3.51 g/1000 g H_2O			
	40	4.16 g/1000 g H_2O			
	45	4.89 g/1000 g H_2O			
	50	6.38 g/1000 g H_2O			
	55	7.44 g/1000 g H_2O			
	60	9 g/1000 g H_2O			
	65	10.94 g/1000 g H_2O			
	70	13.70 g/1000 g H_2O			
	75	17.55 g/1000 g H_2O			
o-Nitrophenol	50	0.388g/1000 g H_2O	-982.0 ± 47.8	3.621 ± 0.140	4.494 ± 0.219
	60	0.463g/1000 g H_2O			
	70	0.560g/1000 g H_2O			
	80	0.685g/1000 g H_2O			
	90	0.856g/1000 g H_2O			

TABLE LX (Continued)

[a]A. Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand Co., New York, N.Y., 2nd ed., 1919, 3rd, 1940.

[b]Log sol = m[1/T(°K)] + b.

[c]$\Delta H_{s,\ H_2O} = -2.303\ R\ m$.

APPENDIX IV

COUNTERION BINDING IN SURFACTANT-SALT SOLUTIONS

TABLE LXI

COUNTERION BINDING DATA FOR n-ALKYLTRIMETHYLAMMONIUM BROMIDES IN THE FORM OF STRAIGHT LINES: BOTRÉ METHOD

Surfactant	[NaBr], M	m[a]	b[a]	Experimental points	Number Neglected
$C_{10}NMe_3Br$	--	0.0344 ± 0.0008	0.1816 ± 0.0071	4	0
	0.0400	0.0594 ± 0.0005	0.1836 ± 0.0048	4	1
	0.1000	0.0979 ± 0.0005	0.1753 ± 0.0070	4	0
DTAB	--	0.0096 ± 0.00001	0.1990 ± 0.0004	4	0
	0.0300	0.0301 ± 0.0001	0.2413 ± 0.0095	5	0
	0.1000	0.0816 ± 0.00009	0.2168 ± 0.0092	6	0
CTAB	--	0.000645 ± 0.000001[b]	0.1872 ± 0.0004[b]	4	1
	--	0.000602 ± 0.000037[c]	0.1941 ± 0.019[c]	8	1

[a] Slope and intercept respectively for equation of the form $\gamma_{exptl} = m(1/C_{surfactant}) + b$. $\gamma_{exptl} = a_{Br^-}/C_{surfactant}$ for each experimental point.

[b] For CMCs except 7.89×10^{-4} M.

[c] For CMC = 7.89×10^{-4} M.

TABLE LXII

COUNTERION BINDING DATA FOR n-ALKYLTRIMETHYLAMMONIUM BROMIDES IN THE FORM OF STRAIGHT LINES: TOKIWA AND MORIYAMA METHOD

Surfactant	[NaBr], M	Below the CMC		Experimental points	Number neglected	Above the CMC		Experimental points	Number neglected
		m[a]	b[a]			m[a]	b[a]		
$C_{10}NMe_3Br$	—	0.7170 ± 0.0167	0.00115 ± 0.0046	4	0	0.1768 ± 0.0061	0.03499 ± 0.0084	4	0
	0.0400	0.6739 ± 0.0074	0.03452 ± 0.00008	4	0	0.1823 ± 0.0028	0.05958 ± 0.00038	4	1
	0.1000	0.6372 ± 0.0669	0.07961 ± 0.00077	4	0	0.1685 ± 0.0050	0.09851 ± 0.00061	4	0
DTAB	—	0.8824 ± 0.0059	0.00011 ± 0.00004	4	0	0.1985 ± 0.00055	0.00964 ± 0.00004	4	0
	0.0300	0.8769 ± 0.0799	0.02593 ± 0.00024	3	0	0.2309 ± 0.0040	0.03030 ± 0.00017	5	0
	0.1000	6.66	0.075	2	0	0.2029 ± 0.0047	0.08206 ± 0.00018	6	0
CTAB	—	0.8939[b] ± 0.0076	-2.7793×10^{-6}[b] ± 2.0982×10^{-6}	4	0	0.1876[b] ± 0.0004	0.00064[b] ± 0.00000	4	1
	—	0.9152[c] ± 0.0028	4.290×10^{-6} ± 7.74×10^{-7}	4	0	0.1979[c] ± 0.0009	0.00057[c] ± 0.00000	8	1

[a] Slope and intercept respectively for equation of the form $a_{Br^-} = mC_{surfactant} + b$.

[b] For CMC s except 7.89×10^{-4} M.

[c] For CMC = 7.89×10^{-4} M.

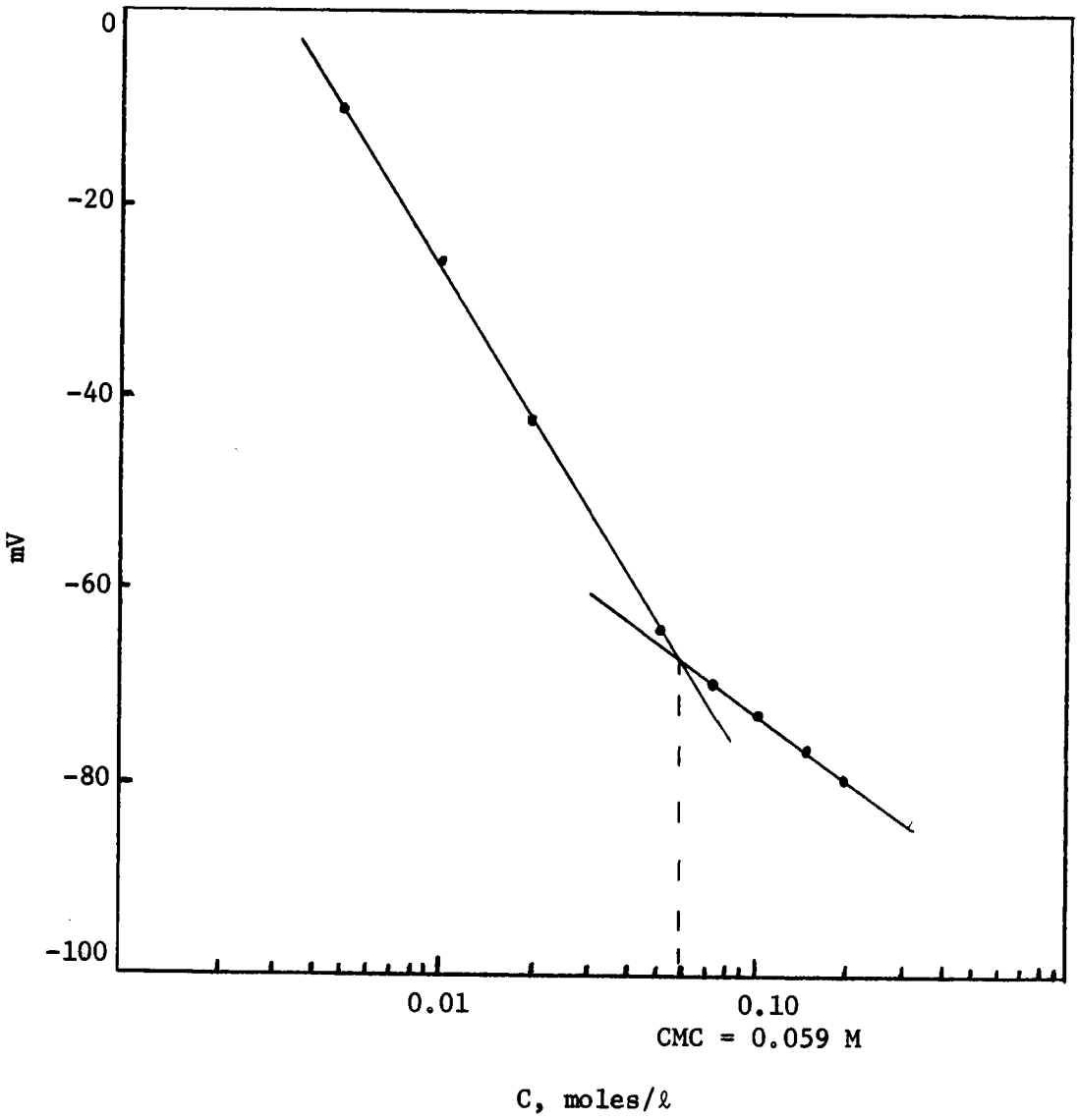


Figure 19. Plot of log a_{Br^-} (in millivolts) versus log C for $C_{10}NMe_3Br$ in H_2O at 25°.

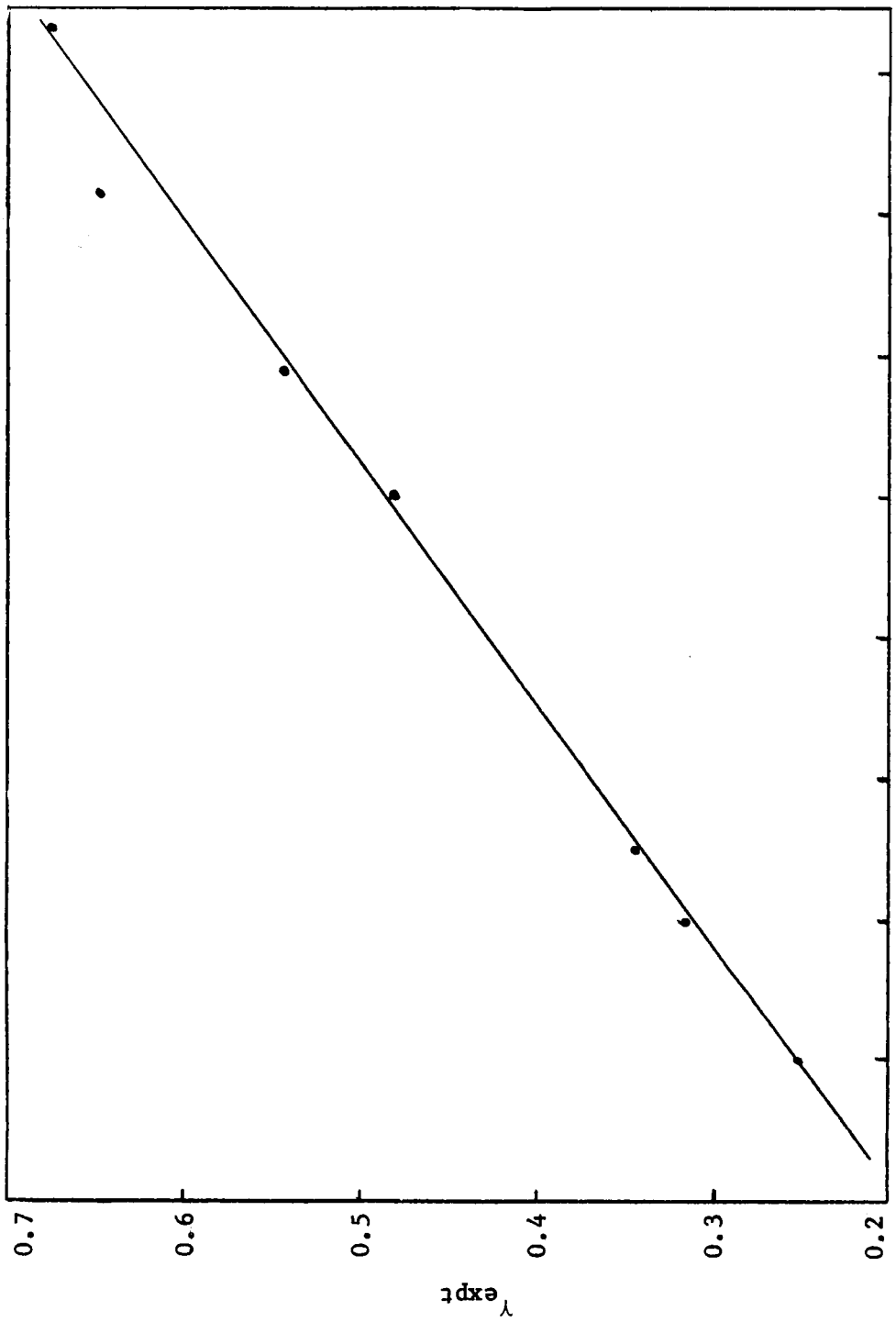


Figure 20. Plot of γ_{expt} versus 1/C for CTAB in H_2O at 25°.

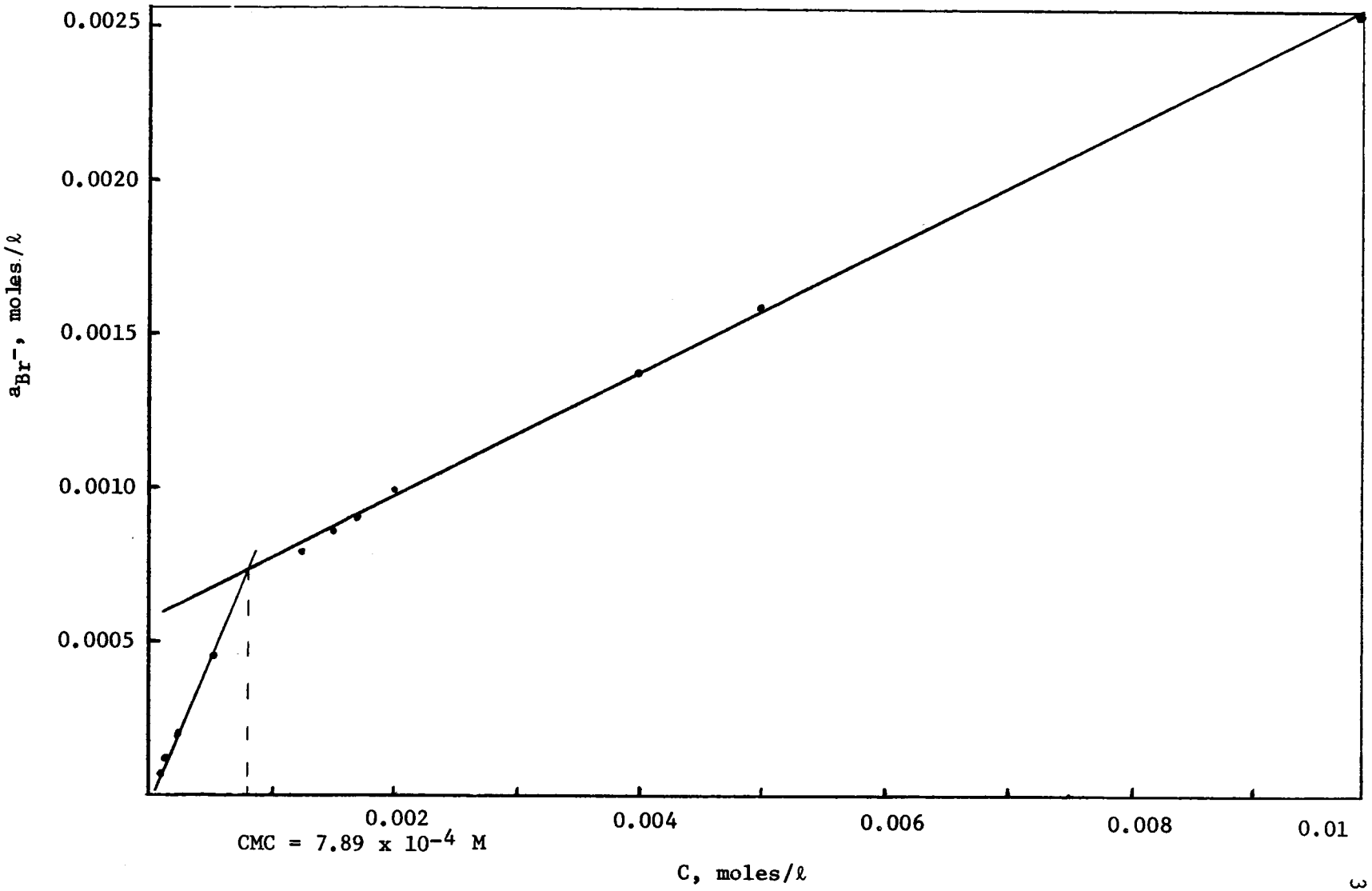


Figure 21. Plot of a_{Br^-} versus concentration for CTAB in H_2O at 25°.

TABLE LXIII

CORRIN PLOTS FOR n-ALKYLTRIMETHYLAMMONIUM BROMIDES IN THE PRESENCE OF SODIUM BROMIDE

Surfactant	[NaBr], M	CMC, M[a]	m[c]	b[c]
$C_{10}NMe_3Br$	--	0.050 ± 0.004	-0.488 ± 0.026	-1.9459 ± 0.0269
	0.0400	0.0385 ± 0.0015		
	0.1000	0.030 ± 0.003		
	0.2000	0.024 ± 0.002		
DTAB	--	0.0105 ± 0.0015	-0.420 ± 0.025	-2.7987 ± 0.0338
	0.0300	0.0064 ± 0.0006		
	0.1000	0.0044 ± 0.0003		
	0.3000	0.0025 ± 0.0002		
CTAB	--	0.00080 ± 0.00005	-0.765 ± 0.038	-5.4606 ± 0.0768
	0.0100	0.000115 ± 0.00001		
	0.0500	0.000040 ± 0.000006		
	0.1000	0.0000178[b]		

[a]All determined by surface tension measurements at approximately 25°.

[b]From early work done in connection with intrinsic viscosity studies.

[c]Determined by linear least squares analysis of the data in the following form: log CMC = m log (CMC + C_a) + b, where C_a = [NaBr].

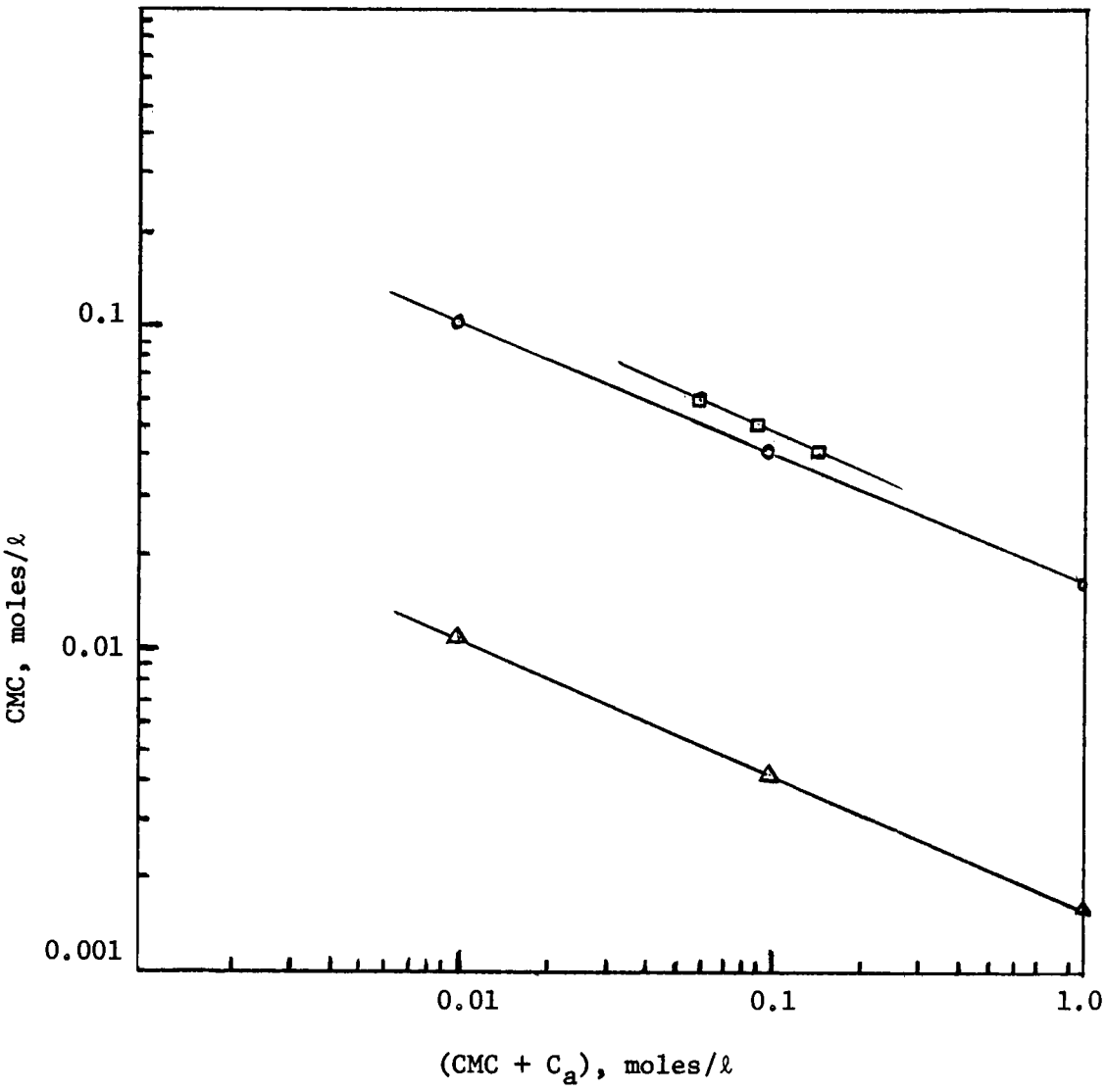


Figure 22. Corrin plots for $C_{10}NMe_3Br$ and DTAB.

Circles: CMCs of $C_{10}NMe_3Br$ determined by surface tension, squares: CMCs of $C_{10}NMe_3Br$ determined by ion-specific electrode, triangles: CMCs of DTAB determined by surface tension.

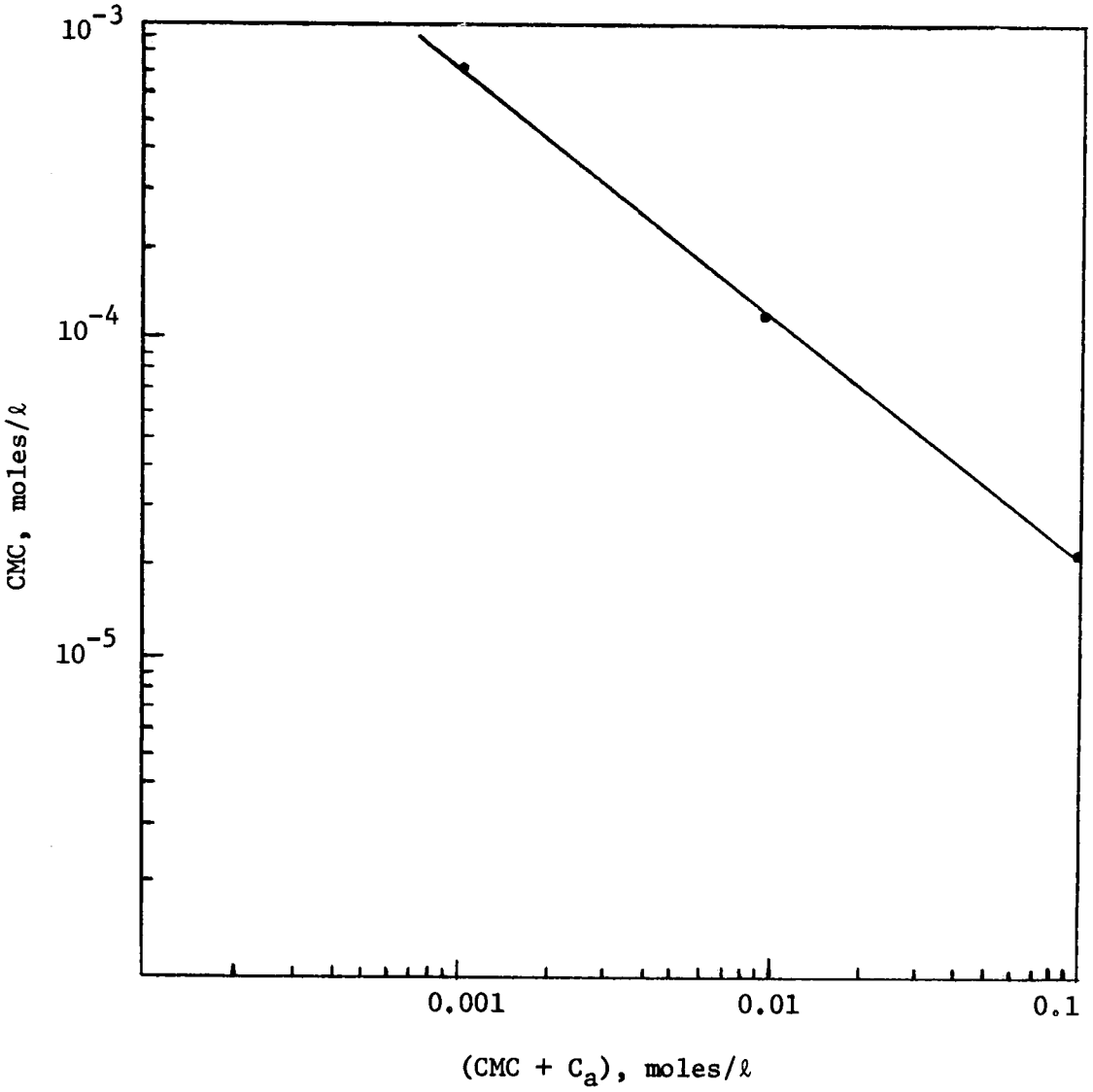


Figure 23. Corrin plot for CTAB.

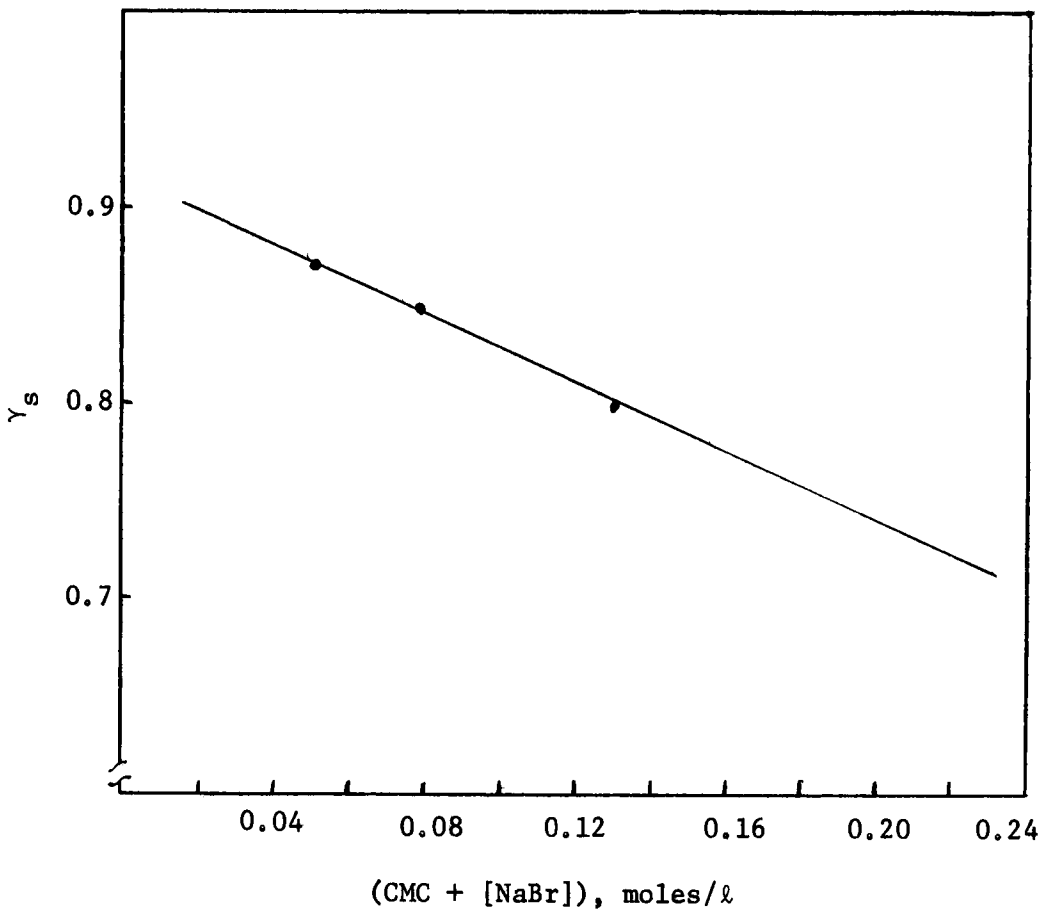


Figure 24. Plot of γ_s versus CMC + [NaBr] for $C_{10}NMe_3Br$.

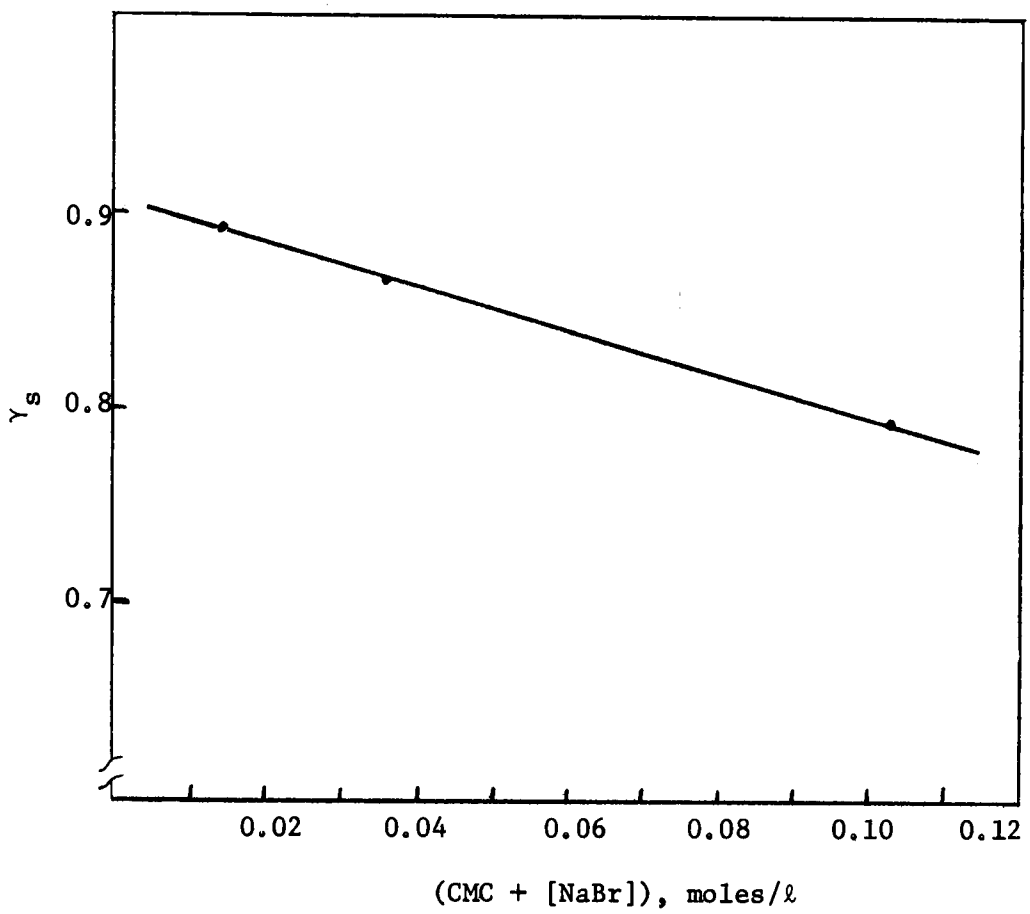


Figure 25. Plot of γ_s versus CMC + [NaBr] for DTAB.

APPENDIX V

NMR DATA AND COMPETITIVE COUNTERION BINDING CALCULATIONS

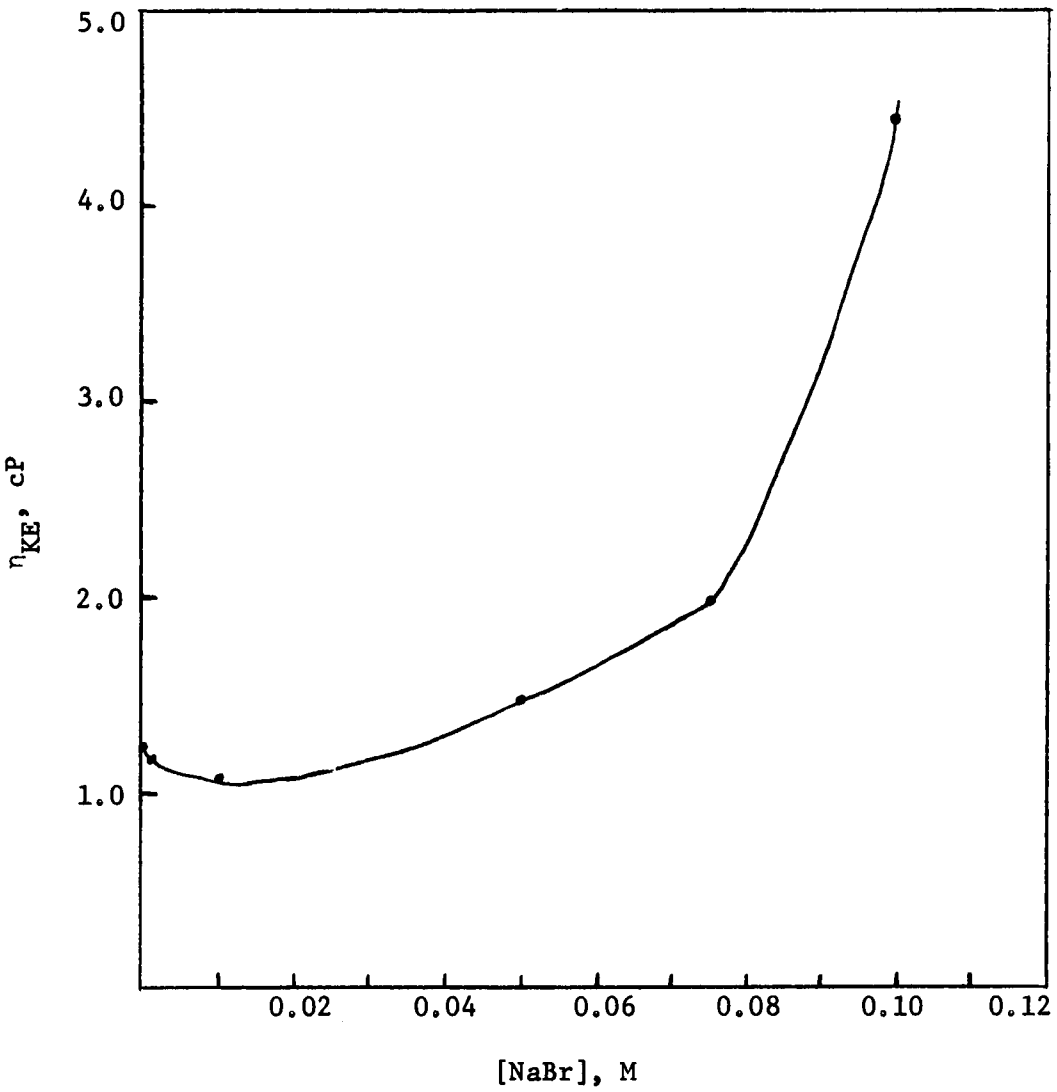


Figure 26. Dependence of η_{KE} for 0.1 M CTAB on the NaBr concentration.

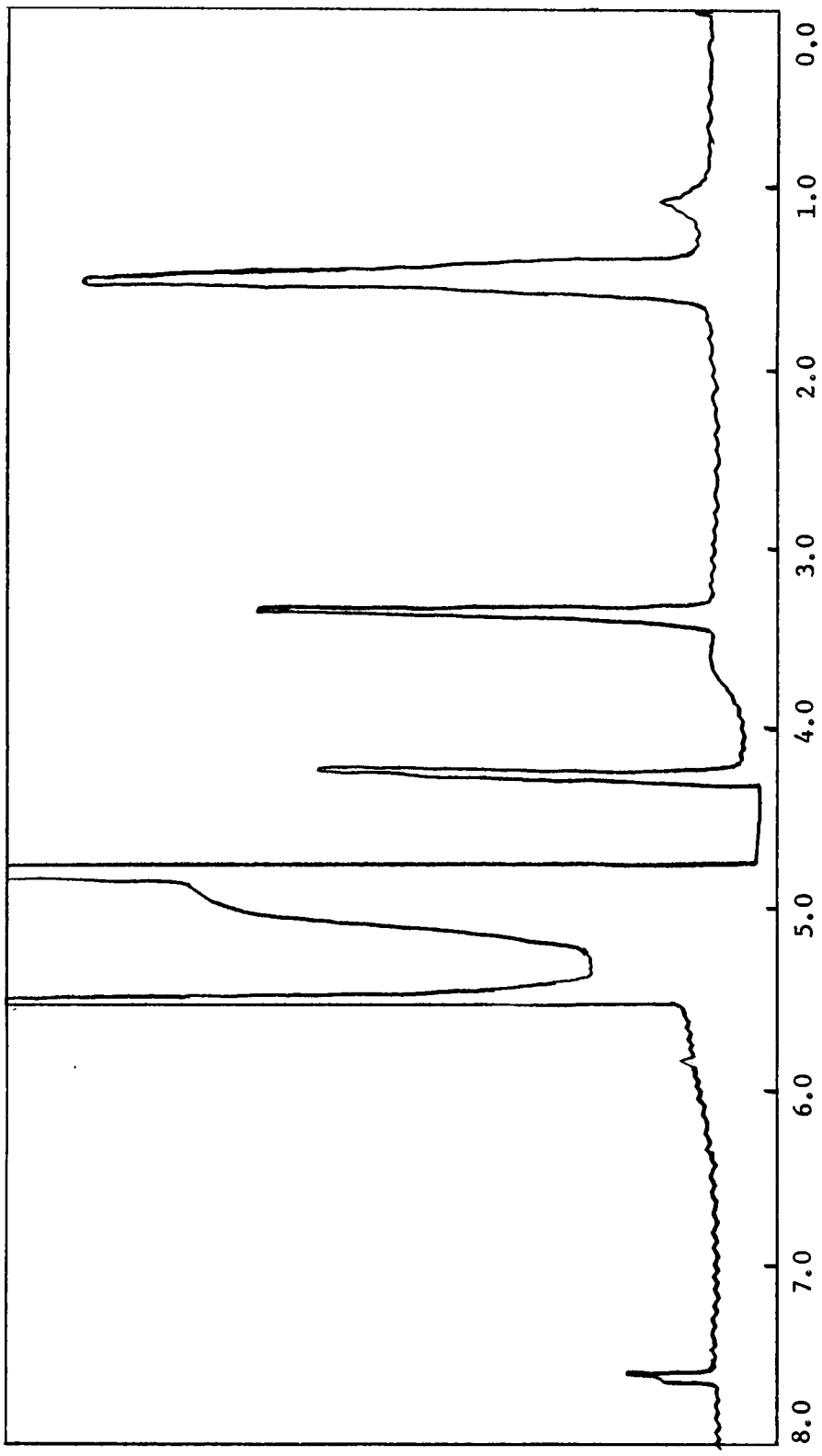


Figure 27. NMR spectrum of 0.1 M CTAB-0.025 M benzene.

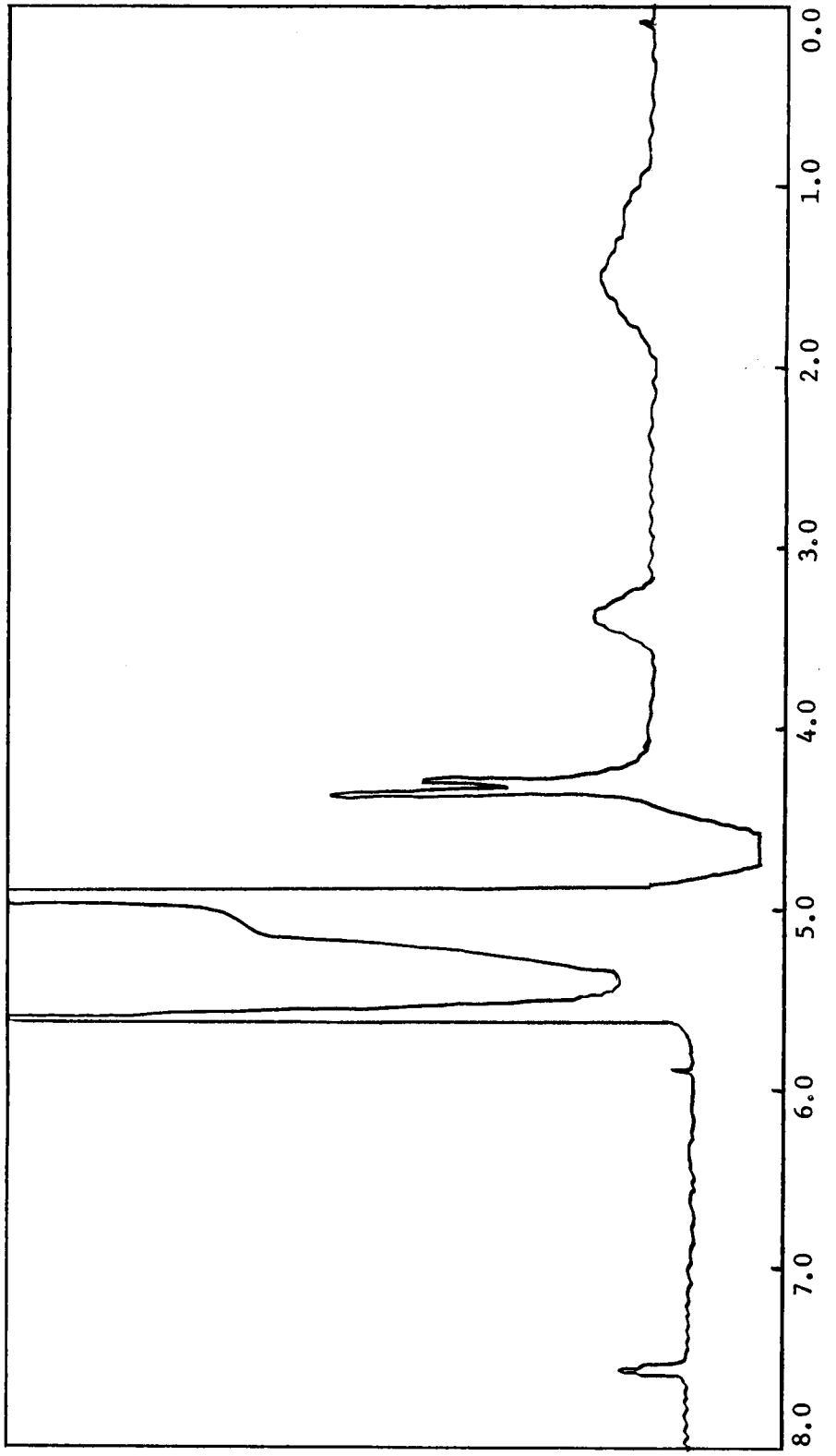


Figure 28. NMR spectrum of 0.1 M CTAB-0.025 M benzene-0.1 M NaBr.

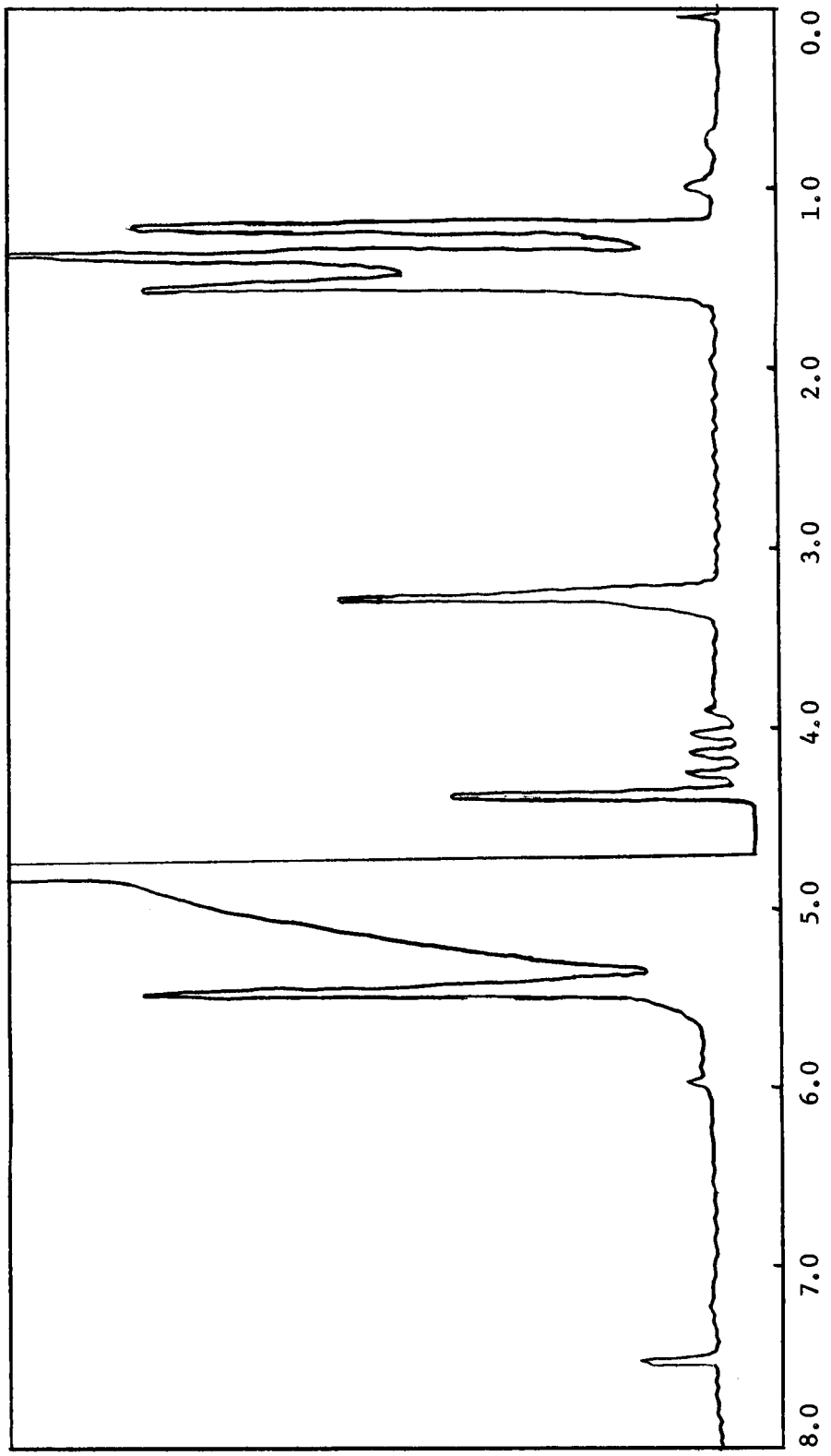


Figure 29. NMR spectrum of 0.1 M CTACl-0.025 M benzene.

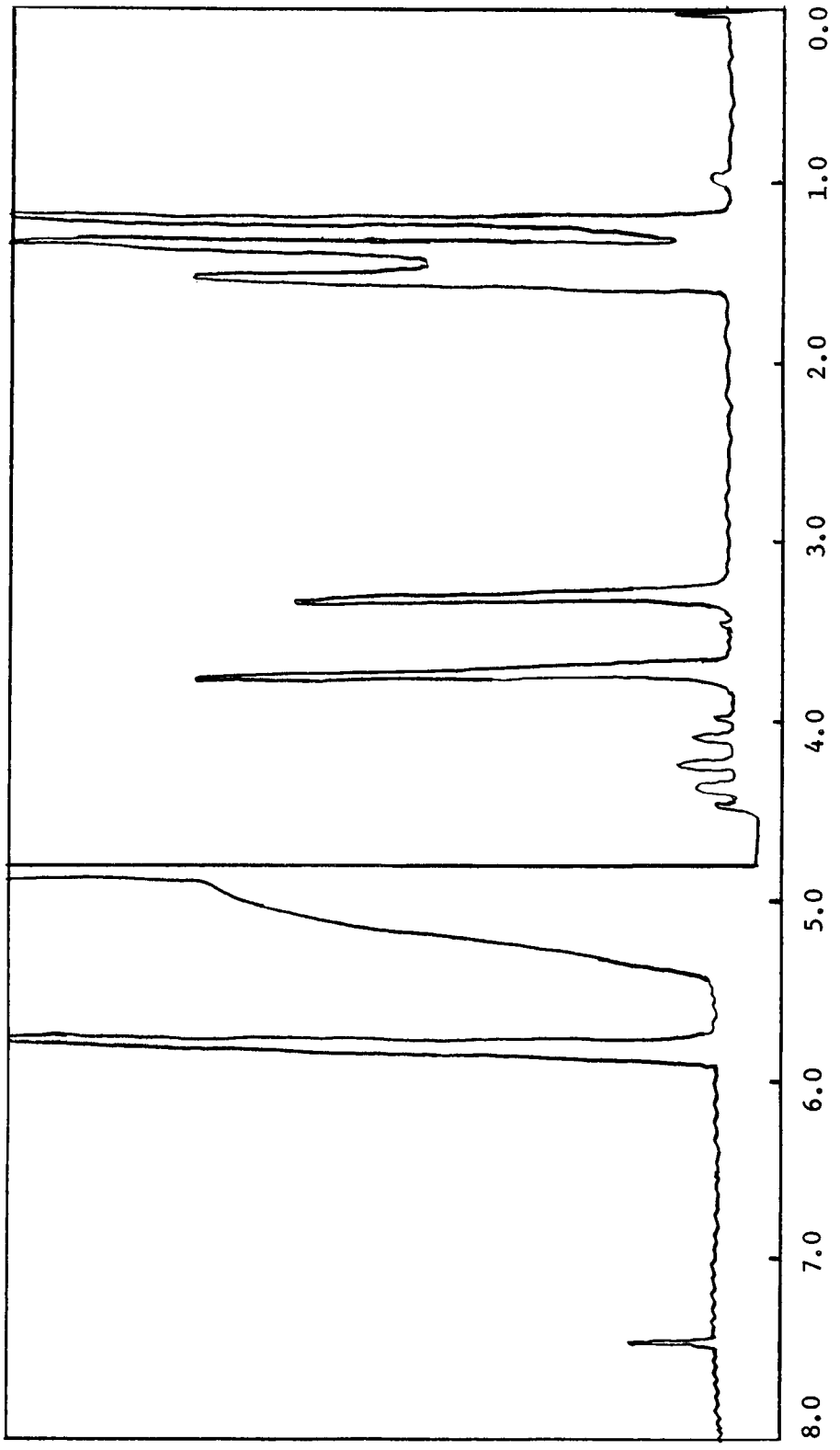


Figure 30. NMR spectrum of 0.1 M CTACl-0.025 M benzene-0.1 M NaBr.

TABLE LXIV

NMR CHEMICAL SHIFT ASSIGNMENTS FOR SPECTRA OF CTAB AND CTACl SOLUTIONS CONTAINING SODIUM BROMIDE AND BENZENE

Solution	Protons[c]	$\lvert\nu_p-\nu_{H_2O}\rvert$, cps[a,d]	ν_p[d,e]	δ, ppm[d,f]	$\lvert\nu_p-\nu_{H_2O}\rvert$, cps[a,g]	ν_p[e,g]	δ, ppm[f] (No NaBr)	δ, ppm (0.1 M NaBr)
0.17 M CTAB[a]	N-methyl	89	192.4	3.21	91	190.4	3.17[g]	
	Terminal methyl	228	53.4	0.89	228	53.4	0.89[g]	
	Methylenes	202	79.4	1.32	203.5	77.9	1.30[g]	
	α-Methylene	74.5	206.9	3.49	91	190.4	3.17[g]	
	Benzene	--	--	--	160.5	441.9	7.37[g]	
0.1 M CTAB[b]	N-methyl						3.30[h]	3.25[h]
	Terminal methyl						0.98[h]	0.98[h]
	Methylenes						1.42[h]	1.30[h]
	α-Methylene						3.55[h]	3.7[h]
	Benzene						7.52[h]	7.48[h]
0.1 M CTACl[b]	N-methyl						3.21[h]	3.25[h]
	Terminal methyl						0.95[h]	0.92[h]
	Methylenes						1.38,1.27, 1.17[h]	1.36,1.29, 1.17[h]
	α-Methylene						4.1(t)[h]	4.12(m)[h]
	Benzene						7.48[h]	7.48[h]

TABLE LXIV (Continued)

[a] J. C. Eriksson and G. Gillberg, Acta Chem. Scand., 20, 2019 (1966) at 35°.

[b] Solutions contain 0.025 M benzene.

[c] A CTA^+ ion has the following formula: $\underset{a}{CH_3}\underset{b}{(CH_2)_{14}}\underset{c}{CH_2}\overset{+}{\underset{d}{N}}(CH_3)_3$; d are the N-methyl protons, a the terminal methyl protons, b the methylene protons and c the α-methylene protons.

[d] No benzene present.

[e] since $|\nu_{H_2O}-\nu_{CHCl_3}| = 158.8$ cps (Erikkson and Gillberg) and $\nu_{CHCl_3} = 436.2$ cps ($CHCl_3$ as external standard in Eriksson's and Gillberg's work), $\nu_{H_2O} = 281.4$ cps. $\nu_p = 281.4 - |\nu_p-\nu_{H_2O}|$, for all proton resonances except benzene, where $\nu_p^2 = 281.4 + |\nu_p-\nu_{H_2O}|$.

[f] $\delta,\text{ppm} = \nu_p/60$.

[g] Molar ratio benzene/CTAB is 0.25.

[h] Relative to TMS as internal standard. TMS was used sparingly as it tends to extract benzene out of the aqueous solutions.

TABLE LXV

ENTHALPY OF SOLUTION OF CTAB IN H_2O USING A SINGLE INJECTION TECHNIQUE[a,b]

CTAB, mg/200 ml H_2O	$\Delta H_{s,\ H_2O}$ kcal/mole[c]
46.05	16.26
41.01	16.09
52.48	(12.29)
49.73	15.45
55.03	15.45
43.75	16.20
45.29	15.25
38.13	(17.89)
38.08	15.54
43.56	15.15

[a]Fresh water placed in the calorimeter prior to each injection.

[b]Neglected points are in parentheses.

[c]Average $\Delta H_{s,H_2O}$ = 15.67 kcal/mole.

TABLE LXVI

CALCULATION OF NITRATE AND BROMIDE IONS BOUND TO CTAB MICELLES, USING STANDARD ACTIVITY COEFFICIENTS

$[NaNO_3]$, M	[CTAB], M[a]	a_{Br^-}, M[b]	$a_{NO_3^-}$ M[b]	Free $[Br^-]$, M[c]	Free $[NO_3^-]$, M[c]	Bound $[Br^-]$, M[d]	%[e]	Bound $[NO_3^-]$, M[f]	%[e]
0.04001	0.00996	0.0070	0.0276	0.00768	0.0320	0.00232	23	0.0080	20
0.02001	0.00993	0.0066	0.0124	0.0072	0.0145	0.0028	28	0.0055	28
0.01000	0.00988	0.0057	0.00511	0.0062	0.00542	0.0038	38	0.00458	46
0.00480	0.00980	0.00468	0.00194	0.0050	0.0021	0.0050	50	0.0027	56
0.00201	0.00965	0.00365	0.000565	0.00395	0.000575	0.00605	61	0.00143	72
0.00100	0.00950	0.0032	0.000221	0.00342	0.000224	0.00658	66	0.00078	78
0.03148	0.1000	0.0365	0.0072	0.0425	0.0078	0.0575	58	0.0237	75
0.02000	0.1000	0.0320	0.0036	0.0375	0.0038	0.0625	63	0.0162	81
0.01000	0.1000	0.0285	0.0010	0.0335	0.00125	0.0665	67	0.0088	88
0.00480	0.1000	0.0245	0.00025	0.0280	0.00026	0.0720	72	0.0046	96

[a]Concentration in micellized form.

TABLE LXVI (Continued)

[b]Experimentally observed; $a_{NO_3^-}$ corrected for electrode interference by Br^-.

[c]Calculated from a_{Br^-} and $a_{NO_3^-}$ respectively, using activity coefficients found in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N.Y., 1952.

[d]Bound $[Br^-]$ = total [CTAB]-free $[Br^-]$.

[e]Percent of an ion bound = (bound [ion]/total [ion]) x 100%.

[f]Bound $[NO_3^-]$ = total $[NO_3^-]$-free $[NO_3^-]$.

TABLE LXVII

CALCULATION OF NITRATE AND BROMIDE IONS BOUND TO CTAB MICELLES, USING ESTIMATED ACTIVITY COEFFICIENTS

[CTAB], M	[$NaNO_3$] M	Total [salt], M[a]	a_{Br^-}, M[b]	γ_{Br^-}[c]	Free [Br^-], M	$a_{NO_3^-}$, M[b]	$\gamma_{NO_3^-}$[c]	Free [NO_3^-], M	Bound [Br^-], M[d]	%[e]	Bound [NO_3^-] M[f]	%[e]
0.01	0.04001	0.040	0.0070	0.857	0.00817	0.0276	0.837	0.033	0.00183	18	0.0070	18
	0.02001	0.0217	0.0066	0.868	0.0076	0.0124	0.873	0.0142	0.0024	24	0.0058	29
	0.01000	0.0116	0.0057	0.883	0.00646	0.00511	0.897	0.0057	0.00354	35	0.0043	43
	0.00480	0.0071	0.00468	0.926	0.00505	0.00194	0.916	0.00212	0.00495	50	0.0027	56
	0.00201	0.00453	0.00365	0.938	0.00389	0.000565	0.933	0.000606	0.00611	61	0.00139	70
	0.00100	0.00364	0.0032	0.943	0.00339	0.000221	0.940	0.000235	0.00661	66	0.00077	77
0.1	0.03148	0.0050	0.0365	0.844	0.0432	0.0072	0.823	0.0087	0.0568	57	0.0228	70
	0.02000	0.0413	0.0320	0.856	0.0374	0.0036	0.835	0.0043	0.0626	63	0.0157	79
	0.01000	0.0347	0.0285	0.864	0.0330	0.0010	0.846	0.0012	0.0670	67	0.0088	88
	0.00480	0.0283	0.0245	0.873	0.0280	0.00025	0.859	0.00029	0.0720	72	0.0045	94

[a]Total free Br^- and NO_3^-, computed by adding Columns 5 and 6 in Table LXVI (p 337).

[b]Experimentally observed; $a_{NO_3^-}$ corrected for electrode interference by Br^-.

TABLE LXVII (Continued)

[c]From activity coefficients listed in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N.Y., 1952, for NaBr and $NaNO_3$, using $[salt]_{total}$, M as the concentration at which γ is desired.

[d]Bound $[Br^-]$ = total [CTAB]-free $[Br^-]$.

[e]Percent of an ion bound = (bound [ion]/total [ion]) x 100%.

[f]Bound $[NO_3^-]$ = total $[NO_3^-]$-free $[NO_3^-]$.

TABLE LXVIII

CALCULATION OF HYDROXIDE AND BROMIDE IONS BOUND TO CTAB MICELLES, USING STANDARD ACTIVITY COEFFICIENTS

[CTAB], M[a]	[NaBr], M	[NaOH], M	pH[b]	a_{OH^-}[c]	Free $[OH^-]$, M	Bound $[OH^-]$, M	χ[g]	a_{Br^-}, M[c]	Free $[Br^-]$, M (No OH^-)	Bound $[Br^-]$, M (OH^- present)	χ[j]
--	--	0.000187	10.270	--	0.000187	--	--	--	--	--	--
0.00420	--	0.000187	10.057	--	0.000114	0.000073[e]	39	--	0.00088[h]	0.00104[h]	--
--	0.0025	0.000132	10.120	--	0.000132	--	--	--	--	--	--
0.00470	0.0025	0.000132	10.050	--	0.000112	0.000020[e]	15	--	0.00110[h]	0.0014[h]	--
--	0.0050	0.000132	10.120	--	0.000132	--	--	--	--	--	--
0.00480	0.0050	0.000132	9.905	--	0.000080	0.000052[e]	39	--	0.00156[h]	0.00216[h]	--
0.1000	--	0.05652	--	0.0222	0.0255[d]	0.0310[f]	55	0.0290	--	0.034[d]	0.066[i]	66
	--	0.04037	--	0.0235	0.0272[d]	0.0131[f]	32	0.0240	--	0.028[d]	0.0720[i]	72
	--	0.03028	--	0.0172	0.020[d]	0.0103[f]	34	0.0225	--	0.026[d]	0.07[illegible][i]	74
	--	0.02019	--	0.00310	0.0032[d]	0.0172[f]	85	0.0245	--	0.0285[d]	0.0715[i]	72
	--	0.01009	--	0.00098	0.0011[d]	0.00998[f]	100	0.0212	--	0.0245[d]	0.0750[i]	75

[a]CTAB in micellized form.

[b]Determined using a Beckman expandomatic pH meter at 23° (ambient temperature).

TABLE LXVIII (Continued)

[c] Experimentally observed from millivolt versus log $[X^-]$ calibration plot.

[d] Calculated from a_{Br^-} and a_{OH^-} respectively, using activity coefficients from W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, INc., New York, N.Y., 1952. For OH^- activity coefficients for NaCl were used; where comparison is possible the two sets of coefficients are very similar.

[e] Bound $[OH^-]$ = $[OH^-]_{no\ CTAB}$ - free $[OH^-]$.

[f] Bound $[OH^-]$ = total $[OH^-]$ - free $[OH^-]$.

[g] Percent of OH^- bound = (bound $[OH^-]/[OH^-]_{no\ CTAB}$) x 100%.

[h] The calibration plots for the bromide ion specific electrodes were of the form millivolts versus log $[Br^-]$, so that concentrations could be read directly from the plots; for samples containing OH^- the standards also contained OH^-.

[i] Bound $[Br^-]$ = 0.1 M-free $[Br^-]$.

[j] Percent of Br^- bound = (bound $[Br^-]/0.1$ M) x 100%.

TABLE LXIX

CALCULATION OF HYDROXIDE AND BROMIDE IONS BOUND TO CTAB MICELLES IN 0.1 M CTAB USING ESTIMATED ACTIVITY COEFFICIENTS

[NaOH], M	Total [Salt], M[a]	a_{Br^-}, M[b]	γ_{Br^-}[c]	Free $[Br^-]$, M	a_{OH^-}, M[b]	γ_{OH^-}[c]	Free $[OH^-]$, M	Bound $[Br^-]$, M[d]	%[e]	Bound $[OH^-]$, M[f]	%[e]
0.05652	0.0595	0.0290	0.836	0.0347	0.0222	0.809	0.0275	0.0653	65	0.0290	51
0.04037	0.0552	0.0240	0.840	0.0286	0.0235	0.815	0.0288	0.0714	71	0.0116	29
0.03028	0.0460	0.0225	0.850	0.0264	0.0172	0.829	0.0208	0.0736	74	0.0095	31
0.02019	0.0317	0.0245	0.868	0.0282	0.00310	0.852	0.00364	0.0718	72	0.0165	82
0.01009	0.0256	0.0212	0.877	0.0242	0.00098	0.865	0.00113	0.0758	76	0.0090	90

[a] Total free Br^- and OH^-, computed by adding the values for free Br^- and OH^- presented in Table LXVIII (p 341).

[b] Experimentally observed.

[c] From activity coefficients listed in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N.Y., 1952, for NaBr and NaCl (used for NaOH), using total [salt], M as the concentration at which γ is desired.

[d] Bound $[Br^-]$ = 0.1 M-free $[Br^-]$.

[e] Percent of an ion bound = (bound [ion]/total [ion]) x 100%.

[f] bound $[OH^-]$ = total $[OH^-]$ - free $[OH^-]$.

TABLE LXX

CALCULATION OF BROMIDE IONS BOUND TO CTAB MICELLES IN THE PRESENCE OF TOSYLATE IONS, USING ESTIMATED ACTIVITY COEFFICIENTS

[CTAB], M	$[NaSO_3C_7H_7]$, M	a_{Br^-}, M[a]	Free $[Br^-]$, M[b]	Total [Salt], M[c]	γ_{Br^-}[d]	New free $[Br^-]$, M	Bound $[Br^-]$, M[e]
0.1 M	--	0.0184	0.0215	--	--	--	--
	0.0020	0.0198	0.0230	0.0235	0.868	0.0230	0.0770
	0.0040	0.0210	0.0242	0.0252	0.865	0.0243	0.0757
	0.0052	0.0216	0.0250	0.0263	0.867	0.0250	0.0750
	0.0080	0.0240	0.0280	0.0300	0.860	0.0280	0.0720
	0.0100	0.0256	0.0295	0.0320	0.859	0.0298	0.0702
	0.0120	0.0265	0.0320	0.0350	0.857	0.0320	0.0680
0.00625 M	0.0125	0.0056	0.00619				
	0.0200	0.0057	0.00624				

[a]Experimentally observed.

[b]Calculated from a_{Br^-} using activity coefficients found in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N.Y. 1952.

[c]Total free Br^- (Column 4) and $SO_3C_7H_7^-$ in solution; 25% of added $SO_3C_7H_7^-$ is considered to be free.

TABLE LXX (Continued)

[d]From activity coefficients listed in W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, N.Y., 1952, for NaBr; total [salt], M gives the concentration at which γ_{Br^-} is desired.

[e]Bound $[Br^-]$ = 0.1 M - new free $[Br^-]$, M.

TABLE LXXI

CALCULATION OF THE ENTHALPIES OF BINDING OF VARIOUS IONS TO CTAB MICELLES IN 0.1 M CTAB SOLUTIONS

Quantity	Numerical Value for $NaNO_3$	Numerical Value for NaOH	Numerical Value for $NaSO_3C_7H_7$
[NaX] under calorimetric conditions	0.03148 M	0.05652 M	0.0120 M
ΔH_s, 0.1 M CTAB, kcal/mole, for NaX	3.93 ± 0.20	-9.84 ± 0.02	-0.965 ± 0.045
Moles of NaX added under calorimetric conditions[a]	0.00631	0.0113	0.0024
Observed heat, in cal, for solution of NaX in 200 ml of 0.1 M CTAB[b]	24.8	-111.1	-2.32
Moles of X^-[c] bound in 200 ml of 0.1 M CTAB	0.00442	0.0062 (55%) 0.0036 (32%)	0.0018
$\Delta H_{s,H_2O}$, kcal/mole, for NaX	4.900 ± 0.050	-10.637 ± 0.010	0.535 ± 0.099
Observed heat, in cal, for solution of NaX in H_2O[d]	30.9	-120.2	1.71
Moles of Br^- displaced in 200 ml of 0.1 M CTAB solution[e]	0.0039	0.0022 (55% OH^- bound) 0.0010 (32% OH^- bound)	0.0021
Estimated heat, in cal, of displacement[f]	7.8	4.4 (55%) 2.0 (32%)	4.2
Calculated heat, in cal, of binding of X^- to the micelles in 200 ml of 0.1 M CTAB solution[g]	-13.9	4.7 (55%) 7.1 (32%)	-8.2
ΔH of binding, kcal/mole, for NaX[h]	-3.14	0.76 (55%) 1.97 (32%)	-4.57

TABLE LXXI (Continued)

[a][NaX], M x 0.2, since the calorimeter operates with 200 ml of solution. In all cases the value of [NaX] corresponds to a concentration at which counterion binding studies have been carried out.

[b]ΔH_s, 0.1 M CTAB for NaX x moles of NaX added.

[c]Determined by multiplying percentage of counterions bound (as determined by binding studies) by moles of NaX bound under calorimetric conditions. Percentages are NO_3^-: 43%, OH^-: 55% and 32% and $SO_3C_7H_7^-$ 75%. The tosylate value comes from C. A. Bunton, E. J. Fendler, L. Sepulveda and K.-U. Yang; J. Amer. Chem. Soc., 90, 5512 (1968).

[d]$\Delta H_{s,H_2O}$ for NaX x moles of NaX added.

[e]Determined from counterion binding data: for NO_3^-, 0.077 M-0.0575 M are displaced, for OH^- 0.0077 M-0.066 M and 0.077 M-0.072 M respectively; for $SO_3C_7H_7^-$ 0.0785 M-0.0680 M. Each of these numbers was then multiplied by 0.2.

[f]Calculated using $\Delta H_{displacement}$ = 2 kcal/mole, T. Ingram and M. N. Jones, Trans. Faraday Soc., 65, 297 (1969).

[g]Heat of solution of NaX in H_2O + heat of displacement of Br^- + heat of binding of X^- = observed heat for solution of NaX in 0.1 M CTAB.

[h](Calculated heat of binding for X^-/1000)/moles of X^- bound.

TABLE LXXII

FREE ENERGIES AND ENTROPIES OF BINDING OF VARIOUS IONS TO CTAB MICELLES IN 0.1 M CTAB SOLUTIONS

Ion	Bound [ion], M	Free [ion], M	$[Ion]_{mic}$, M[b]	K[c]	ΔG, kcal/mole[d]	ΔH, kcal/mole	ΔS, eu
NO_3^-	0.0228	0.00868	0.626	72.1	-2.52	-3.14	-2.1
OH^-	0.0310 (55%)[a]	0.025[a]	0.854	33.6	-2.08	0.76	9.5
	0.0181 (32%)[a]	0.0384[a]	0.497	12.9	-1.51	1.97	12
$SO_3C_7H_7^-$	0.009	0.003	0.247	82.3	-2.60	-4.57	-6.6

[a] For total $[OH^-]$ = 0.0565 M.

[b] $[Ion]_{mic}$, M = bound [ion], M/volume fraction of CTAB micelles in 0.1 M CTAB; the volume fraction = 0.0364.

[c] $K = [ion]_{mic}$/free [ion].

[d] $\Delta G = -RT\ln K$.

TABLE LXXIII

CALCULATION OF SURFACE POTENTIALS FOR BROMIDE AND CHLORIDE IONS BOUND TO CTAB AND CTACl MICELLES

[CTAB], M[a]	$\phi \times 10^2$[b]	Bound $[Br^-]$, M	$[Br^-]_{mic}$, Mc	Free $[Br^-]$, Md	K[e]	$\psi(Br^-)$, mV[f]	Surfactant	[NaX], Mg	Bound $[X^-]$, Mg	$[X^-]_{mic}$, Mc,g,h	Free $[X^-]$, Md,g	K[e]	$\psi(X^-)$, mV[f,g]
0.1000	3.645	0.0785	2.15	0.0215	100	118	0.1 M CTACl	0.010	0.0740	2.31	0.0360	64.2	107
0.0092	0.3353	0.00731	2.18	0.00269	810	172	0.1 M CTAB	0.010	0.0770	2.11	0.0330	64.1	107
0.0042	0.1534	0.00338	2.20	0.00162	1360	185	0.1 M CTACl	0.020	0.0655	2.05	0.0545	37.6	93
0.0032	0.1170	0.00258	2.21	0.00142	1553	189	0.1 M CTAB	0.020	0.0780	2.14	0.042	51.0	101
0.0012	0.0441	0.00101	2.29	0.00099	2313	199	0.1 M CTACl	0.048	0.0535	1.67	0.0945	17.8	74
0.0009	0.0352	0.000756	2.28	0.000944	2415	200	0.1 M CTAB	0.048	0.0800	2.20	0.0680	32.4	89
0.0007	0.0259	0.000603	2.33	0.000897	2597	202	0.1 M CTACl	0.100	0.0400	1.25	0.160	7.82	53
0.0004	0.0149	0.000374	2.50	0.000826	3030	206	0.1 M CTAB	0.100	0.0810	2.22	0.119	18.7	75

[a]Corrected for CMC: CMC = 0.0008 M, as determined by surface tension.

[b]Fraction of the solution's volume occupied by the micelles; assuming $\bar{V}_{sp}$ = 1 ml/g, ϕ = ([CTAB], M x 364.45 g/mole x $\bar{V}_{sp}$)/ 1000.

[c]$[X^-]_{mic}$ = bound $[X^-]/\phi$.

[d]Includes added NaX and ions contributed by surfactant monomers.

[e]K = $[X^-]_{mic}$/free $[X^-]$.

[f]$K = e^{+\varepsilon\psi/kT}$; 2.303 log K = + $\varepsilon\psi/kT$ or ψ = (+ kT 2.303/ε) log K. For ψ in mV, kT/ε = 25.69 at 25°.

[g]X^- is Cl^- for CTACl, Br^- for CTAB.

[h]ϕ is 0.0320 for 0.1 M CTACl, 0.0364 for 0.1 M CTAB.

TABLE LXXIV

CALCULATION OF SURFACE POTENTIALS FOR NITRATE AND BROMIDE IONS BOUND TO CTAB MICELLES

$[NaNO_3]$, M	[CTAB], M[a]	$\phi \times 10^2$[b]	Bound $[NO_3^-]$, M	$[NO_3^-]_{mic}$, M[c]	Free $[NO_3^-]$, M	K[d]	$\psi(NO_3^-)$, mV[e]	Bound $[Br^-]$, M	$[Br^-]_{mic}$, M[c]	Free $[Br^-]$, M	K[d]	$\psi(Br^-)$, mV[e]
0.04001	0.00996	0.3630	0.0070	1.93	0.033	58.5	105	0.00183	0.504	0.00817	61.7	106
0.02001	0.00993	0.3619	0.0058	1.60	0.0142	113	121	0.0024	0.663	0.0076	87.2	115
0.01000	0.00988	0.3601	0.0043	1.19	0.0057	209	137	0.00354	0.983	0.00646	152	129
0.00480	0.00980	0.3572	0.0027	0.756	0.00212	357	151	0.00495	1.39	0.00505	275	144
0.00201	0.00965	0.3517	0.00139	0.395	0.000606	652	167	0.00611	1.74	0.00389	447	157
0.00100	0.00950	0.3462	0.00077	0.222	0.000235	945	176	0.00661	1.91	0.00339	563	163
0.03148	0.1000	3.64	0.0228	0.626	0.0087	72.0	110	0.0568	1.56	0.0432	36.1	92
0.02000	0.1000	3.64	0.0157	0.431	0.0043	100	118	0.0626	1.72	0.0374	46.0	98
0.01000	0.1000	3.64	0.0088	0.242	0.0012	202	136	0.0670	1.84	0.0330	55.8	103
0.00480	0.1000	3.64	0.0045	0.124	0.00029	428	156	0.0720	1.98	0.0280	70.7	109

[a] Concentration of CTAB in micellar form; CMC values from Corrin plots of surface tension data, assuming $NaNO_3$ affects the CMC in the same manner NaBr does.

[b] ϕ = ([CTAB], M x 364.45 g/mole x $\bar{V}_{sp}$)/1000, assuming $\bar{V}_{sp} \cong 1$ ml/g.

[c] $[X^-]_{mic}$ = bound $[X^-]/\phi$.

[d] $K = [X^-]_{mic}/\text{free } [X^-]$.

[e] $K = e^{+\epsilon\psi/kT}$; for ψ in mV, $kT/\epsilon = 25.69$ at 25°.

TABLE LXXV

CALCULATION OF SURFACE POTENTIALS FOR HYDROXIDE AND BROMIDE IONS BOUND TO CTAB MICELLES IN 0.1 M CTAB

[NaOH], M	Bound $[OH^-]$, M	$[OH^-]_{mic}$, M[a]	Free $[OH^-]$, M	K[b]	$\psi(OH^-)$, mV[c]	Bound $[Br^-]$, M	$[Br^-]_{mic}$, M[a]	Free $[Br^-]$, M	K[b]	$\psi(Br^-)$, mV[c]
0.05652	0.0310	0.851	0.0255	33.4	90	0.0660	1.81	0.0340	53.3	102
0.04037	0.0131	0.359	0.0273	13.2	66	0.0720	1.98	0.0280	70.6	109
0.03028	0.0103	0.283	0.0200	14.2	68	0.0740	2.03	0.0260	78.1	112
0.02019	0.0172	0.472	0.0030	157	130	0.0715	1.96	0.0285	68.8	109
0.01009	0.00998	0.274	0.00011	2490	201	0.0750	2.06	0.0250	82.3	113

[a] $[X^-]_{mic}$ = bound $[X^-]/\phi$. ϕ = 0.0364 for 0.1 M CTAB, with no corrections for the CMC necessary.

[b] $K = [X^-]_{mic}/\text{free } [X^-]$.

[c] $K = e^{+\varepsilon\psi/kT}$; for ψ in millivolts, $kT/\varepsilon = 25.69$ at 25°.

TABLE LXXVI

CALCULATION OF SURFACE POTENTIALS FOR BROMIDE IONS BOUND TO CTAB MICELLES (0.1 M CTAB) IN THE PRESENCE OF TOSYLATE IONS

$[NaSO_3C_7H_7]$, M	Bound $[Br^-]$, M	$[Br^-]_{mic}$, M[a]	Free $[Br^-]$, M	K[b]	$\psi(Br^-)$, mV[c]
0.0120	0.0680	1.87	0.032	58.3	104
0.0100	0.0702	1.93	0.0298	64.6	107
0.0080	0.0720	1.98	0.0280	70.6	109
0.0052	0.0750	2.06	0.0250	82.3	113
0.0040	0.0757	2.08	0.0243	85.5	114
0.0020	0.0770	2.11	0.0230	91.9	116

[a] $[Br^-]_{mic}$ = bound $[Br^-]/\phi$; ϕ = 0.0364 for 0.1 M CTAB, with no corrections for the CMC necessary.

[b] $K = [Br^-]_{mic}/\text{free } [Br^-]$.

[c] $K = e^{+\varepsilon\psi/kT}$; for ψ in millivolts, kT/ε = 25.69 at 25°.

APPENDIX VI

VISCOSITY DATA FOR HEXADECYLTRIMETHYLAMMONIUM BROMIDE-SOLUTE-SODIUM BROMIDE SOLUTIONS

TABLE LXXVII

CALCULATED AREA PER HEAD GROUP FOR SPHERICAL AND ROD-SHAPED CTAB MICELLES[a]

Shape	Volume[c]	h[d]	Surface area[e]	Area per head group[f]
Sphere[b]	5.8×10^4 Å^3	--	7250 Å^2	76.4 Å
Rod[b]	5.8×10^4 Å^3	32. Å	4830 Å^2	51 Å

[a]Containing 95 monomers.

[b]r = 24 Å.

[c]Computed from $4/3\ \pi r^3$; used for both the sphere and the rod.

[d]For the rod $V = \pi r^2 h$.

[e]Surface of sphere is $4\pi r^2$, surface of rod is $2\pi rh$.

[f](Surface area)/95 monomers.

TABLE LXXVIII

VISCOSITY DATA FOR CTAB IN SOLUTIONS CONTAINING 0.1 M NaBr AND VARIOUS ORGANIC SOLUTES[a,b]

Solute	C_m (CTAB) x 10^2, g/ml	η_{rel}	η_{sp}	η_{sp}/C_m, ml/g
n-hexane[c]	3.643	(4.954)	(3.954)	(108.3)
	2.732	1.602	0.602	22.0
	1.821	1.257	0.257	14.1
	0.9829	(1.223)[i]	(0.223)	(22.7)
	0.8182	1.066	0.066	8.1
	0.6542	(1.096)[i]	(0.096)	(14.7)
	0.3626	1.023	0.023	6.3
	0.2714	(1.008)[i]	(0.008)	(2.9)
n-Octane[d]	3.643	1.147	0.147	4.03
	2.732	1.105	0.105	3.84
	1.821	1.075	0.075	4.1
	1.456	1.052	0.052	3.6
	0.8183	1.035	0.035	4.2
	0.5449	1.024	0.024	4.4
	0.3627	1.014	0.014	3.8
	0.2715	1.0096	0.0096	3.5
Benzoic acid;[e] 0.02 M NaBr not 0.1 M NaBr	3.643	4.165	3.165	86.9
	2.768	2.062	1.062	38.4
	1.821	1.237	0.237	13.0
	1.383	1.105	0.105	7.6
	1.091	1.058	0.058	5.3
	0.8182	1.039	0.039	4.8
	0.7271	1.030	0.030	4.2
	0.5521	1.027	0.027	4.8
	0.3625	1.015	0.015	4.2
	0.2768	(1.019)	(0.019)	(6.7)
	0.1802	(1.013)	(0.013)	(7.1)
Benzoic acid[f]	0.9104	6.411	5.411	594.3
	0.7280	3.410	2.410	331.0
	0.4053	1.510	0.510	126
	0.2722	1.181	0.181	66.6
	0.2020	1.086	0.086	43
	0.1123	1.022	0.022	19.5
	0.07156	1.009	0.009	13
	0.03928	(1.056)	(0.056)	(144)
	0.02597	1.030	(0.030)	(116)

TABLE LXXVIII (Continued)

Solute	C_m (CTAB) x 10^2, g/ml	η_{relm}	η_{sp}	η_{sp}/C_m, ml/g
1-Hexanol[g]	0.9094	2.938	1.938	213.1
	0.5450	1.510	0.510	93.6
	0.3627	1.190	0.190	52.3
	0.2716	1.093	0.093	34.3
	0.1805	1.045	0.045	25.2
	0.1441	1.021	0.021	14.3
	0.08940	(1.003)	(0.003)	(3.1)
	0.07118	(1.0017)	(0.0017)	(2.4)
	0.03473	1.0052	0.0052	14.9
0.025 M Benzoic acid[h]	0.7282	(214.3)	(213.3)	(29,407)
	0.4035	19.46	18.46	4575
	0.3616	13.47	12.47	3449
	0.3221	10.38	9.38	2912
	0.1793	3.785	2.785	1553
	0.1067	2.127	1.127	1057
	0.06991	1.635	0.635	907.9
	0.05808	1.406	0.406	870.9
	0.05196	1.310	0.310	597
	0.04284	1.185	0.185	432
	0.03355	1.087	0.087	259.6
	0.02961	1.065	0.065	218.7
	0.02463	1.049	0.049	198
	0.01894	1.038	0.038	198.1
	0.01533	1.029	0.029	187.3
	0.01174	(1.014)	(0.014)	(118)
	0.00803	(1.031)	(0.031)	(389)
	0.00438	(1.022)	(0.022)	(512)

[a]Points neglected are in parentheses.

[b]All CMCs were determined by surface tension measurements.

[c]η_{CMC} = 0.898 cP; CMC = 5.31 x 10^{-5} M.

[d]η_{CMC} = 0.888 cP; CMC = 5.01 x 10^{-5} M.

[e]η_{CMC} = 0.885 cP; CMC = 5.62 x 10^{-5} M.

[f] η_{CMC} = 0.891 cP; CMC = 3.80×10^{-5} M.

[g] η_{CMC} = 0.890 cP; CMC = 4.07×10^{-5} M.

[h] η_{CMC} = 0.896 cP; CMC = 7.95×10^{-5} M.

[i] Neglected because n-hexane present had evaporated.

TABLE LXXIX

POLYNOMIAL COEFFICIENTS ($\eta_{sp}/C_m = A\,C_m^4 + BC_m^3 + CC_m^2 + DC_m + [\eta]$)

DESCRIBING THE RAW VISCOSITY DATA FOR CTAB IN THE PRESENCE OF ORGANIC SOLUTES AND 0.1 M NaBr

Solute	[η], ml/g[a]	A[a]	B[a]	C[a]	D[a]
n-Hexane	3.11 ± 1.05	--	--	--	663 ± 62
n-Octane	3.90 ± 0.19	--	--	--	2.091 ± 10.191
Benzoic acid, 0.02 M NaBr	4.45 ± 0.20	--	1.993×10^6	-9.888×10^3	-23
Benzoic acid	13.3 ± 0.5	2.083×10^{11}	-3.053×10^9	1.920×10^7	-1.338×10^4
1-Hexanol	16.7 ± 0.5	5.181×10^{10}	-1.014×10^9	8.266×10^6	-9.072×10^3
0.025 M Benzoic acid	199	--	5.708×10^{12}	-1.382×10^9	1.050×10^4
	828[b]		1.005×10^{11}	-4.150×10^8	1.078×10^6

[a]True standard deviations are reported only in the cases where A=B=C=0. All others were obtained by inspection of experimental η_{sp}/C_m values and the corresponding η_{sp}/C_m values computed by the nonlinear least squares program. The polynomials were selected on the basis of the smallest sum of the deviations squared for all coefficients.

[b]Value of η_{sp}/C_m, ml/g for the concentration where the two polynomials intersect; second polynomial includes concentrations of 5.808×10^{-4} g/ml and above, while the first polynomial includes concentrations of 5.808×10^{-4} g/ml and lower concentration.

TABLE LXXX

DETERMINATION OF THE SECOND CMC FOR THE CTAB-0.1 M NaBr-0.025 M BENZOIC ACID SYSTEM

Trial value for second CMC, g/ml	Calculated value of F(c) (=0 at CMC)[b]
5.8×10^{-4}	23.5
5.7×10^{-4}	-10.3
5.73×10^{-4}[a]	- 0.5

[a]Value used in Table XXX (p 181).

[b]F(c) is obtained by setting the two polynomials for the system (presented in Table LXXVIII, p 355) equal and then rearranging to give $5.607 \times 10^{12}\ c^3 - 9.67 \times 10^8\ c^2 - 1.063 \times 10^6\ c - 128.6 = F(c)$. At the point where the two polynomials intersect, F(c) = 0.

TABLE LXXXI

CALCULATION OF AXIAL RATIOS (p) FOR CTAB MICELLES IN THE PRESENCE OF ORGANIC SOLUTES AND 0.1 M NaBr ($\bar{V}_{sp}$ = 1 ml/g)[a]

Solute	[η], ml/g	Prolate ellipsoids p	Prolate ellipsoids Λ(p)[c]	1.5 [η], ml/g[d]	Rods p	Rods Λ(p)[e]
n-Hexane	3.12 ± 1.05	2[b]	2.91[b]			
n-Octane	3.88 ± 0.17	3[b]	3.68[b]			
Benzoic acid, 0.02 M NaBr	4.45 ± 0.20	3.8	4.64			
		(3.6)	4.51			
Benzoic acid	13.3 ± 0.5	9.8	13.03	19.95	12	20.01
		(9.9)	13.22			
1-Hexanol	16.7 ± 0.5	11.5	16.36	25.05	15	27.59
		(11.6)	16.56		(14)	24.93
0.025 M Benzoic acid	199			298.5	64.5	296.5
					(65)	300.5
	828			1242	150	1302
					147	1256
					(146)	1242

[a] Values of p were estimated and Λ(p) then calculated using equations from C. Sadron, Progr. in Biophysics, 3, 237 (1950); values circled appear in Table XXX (p 181). For ellipsoids [η] = $\Lambda(p)\bar{V}_{sp}$; for rods [η] = 2/3 $\Lambda(p)\bar{V}_{sp}$.

[b] From tabulated values in C. Sadron, Progr. in Biophysics, 3, 237 (1950).

[c] $\Lambda(p) = p^2/15\ [1/(\ln 2p-1.5)] + p^2/5\ [1/(\ln 2p-0.5)] + 0.933.$

[d] For rods [η] = 2/3 $\Lambda(p)\bar{V}_{sp}$.

[e] $\Lambda(p) = p^2/15\ [1/(\ln 2p-1.8)] + p^2/5\ [1/(\ln 2p-0.8)] + 0.933.$

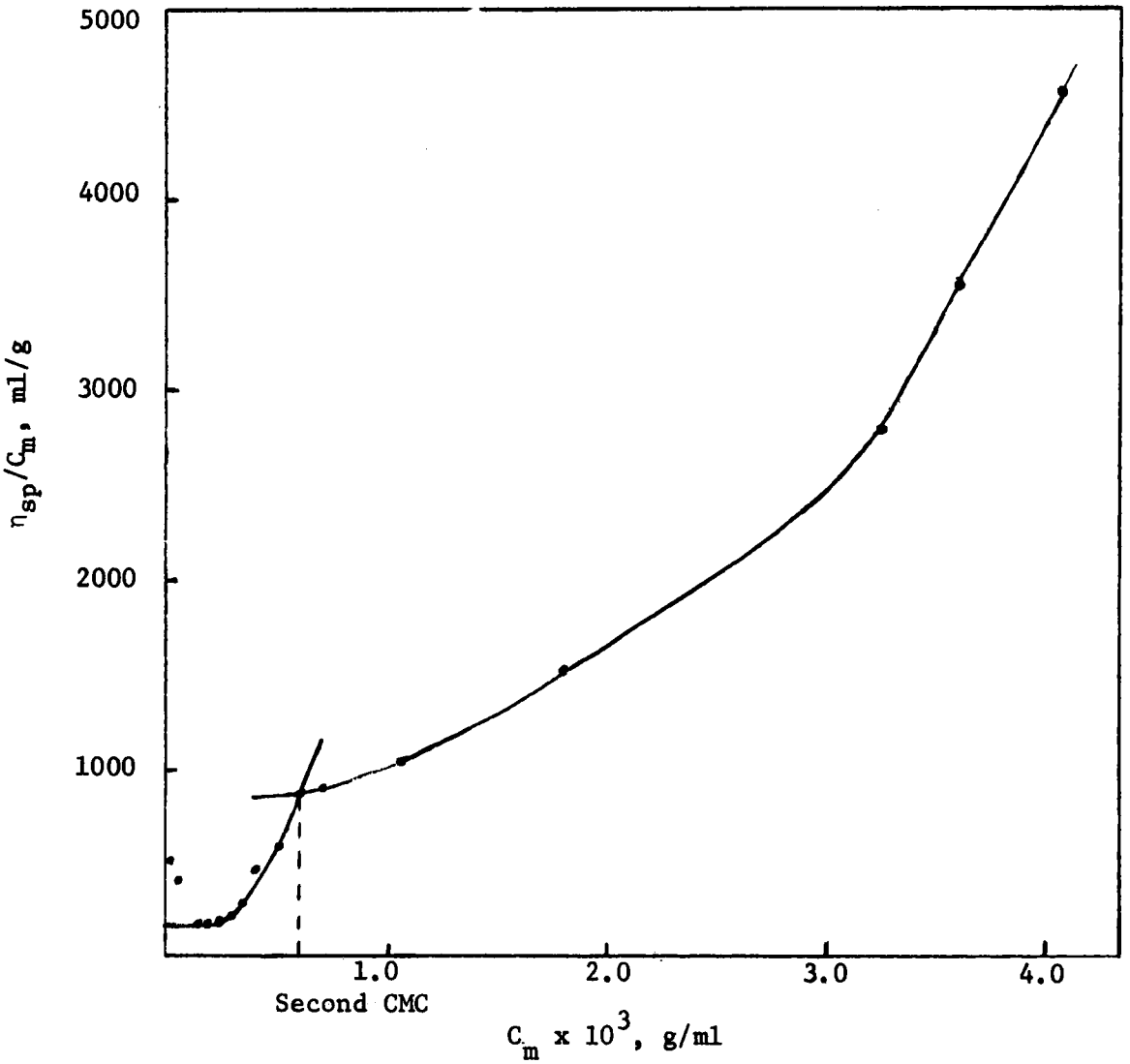


Figure 31. Plot of η_{sp}/C_m versus C_m for CTAB in 0.025 M benzoic acid and 0.1 M NaBr at 25°.

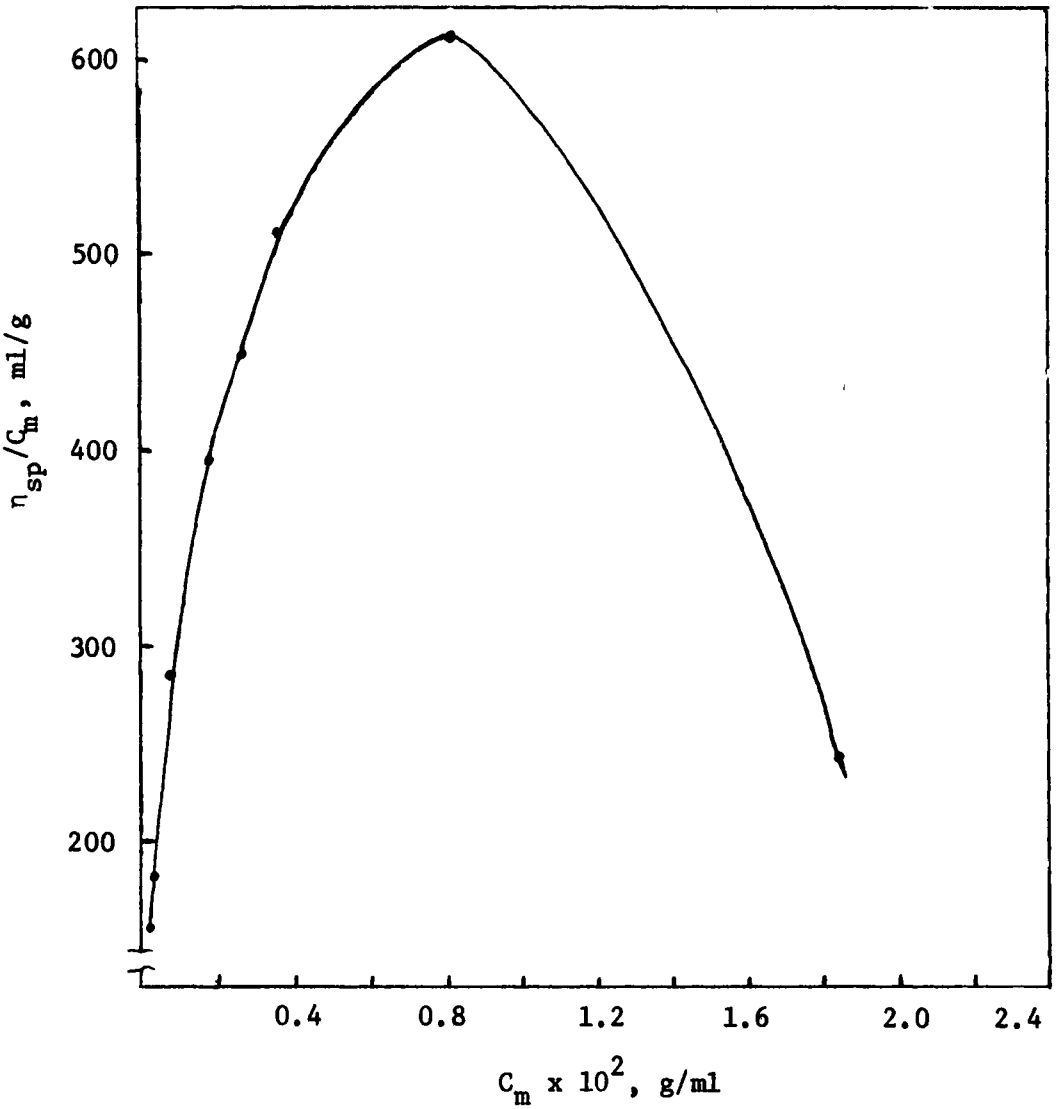


Figure 32. Plot of η_{sp}/C_m versus C_m for CTAB in 0.025 M benzoic acid and 0.02 M NaBr at 25°.

APPENDIX VII

COUNTERION BINDING EFFECTS AND TRUE ENTHALPIES OF SOLUTION FOR BENZOIC ACIDS IN HEXADECYLTRIMETHYLAMMONIUM BROMIDE SOLUTIONS

TABLE LXXXII

COMPETITIVE COUNTERION BINDING FOR CTAB IN VARIOUS BASIC SOLUTIONS

$[CTAB] \times 10^4$, M[a]	$\phi \times 10^4$[b]	pH[c]	Bound $[OH^-] \times 10^6$, M	%	$1-\alpha$[d]	$[OH^-]_{mic}$, Me[e]	$[CTAB] \times 10^4$, M	Free $[Br^-] \times 10^4$, M[h]	α	α, No OH^-[i]
—	--	9.638	--	--	--	--	9.56[f]	9.52	0.996	0.93
9.70	3.535	9.555	7.5	17	0.00773	0.0212	9.84[g]	8.1	0.82	--
31.0	11.30	9.528	9.7	22	0.00312	0.00858	34.9[g]	29.2	0.84	--
48.2	17.57	9.474	13.6	31	0.00282	0.00774	35.1[f]	27.8	0.79	0.76
72.1	26.28	9.392	18.8	43	0.00261	0.00715	49.7[g]	41.2	0.83	--
99.2	36.15	9.188	28.0	64	0.00282	0.00774	50.1[f]	38.8	0.79	0.73
							59.0[f]	44.8	0.75	--
							64.9[g]	51.2	0.79	0.72
							98.8[f]	62.8	0.64	0.61

[a]Concentration of surfactant in micellized form in the presence of 0.02 M NaCl and 4.35×10^{-5} M NaOH; CMC values from Corrin plots of surface tension data for CTAB.

[b]Volume fraction of the solution occupied by micelles.

[c]Measured at 23°.

[c]For OH^- only.

[e]$[OH^-]_{mic}$ = (bound $[OH^-]$)/ϕ.

[f]Concentration of surfactant in micellized form in the presence of 0.02 M NaCl and 6.31×10^{-5} M NaOH.

[g]Concentration of surfactant in micellized form in the presence of 0.02 M carbonate buffer and 0.02 M NaCl; CMC values from Corrin plots of surface tension data for CTAB, using an ionic strength of 0.06 for these solutions.

[h]Due to the micelles only.

[i]From Table XXIV (p 164).

TABLE LXXXIII

EFFECT OF 0.001 M SALICYLIC ACID ON CTAB COUNTERION BINDING[a]

[CTAB] x 10^4, M[b]	No acid: Free [Br^-] x 10^4, M[c]	No acid: α	With acid-run 1: Free [Br^-] x 10^4 M[c]	With acid-run 1: α	With acid-run 2: Free [Br^-] x 10^4, M[c]	With acid-run 2: α	Average α
9.71	9.9	1.02	9.9	1.02	11.0	1.13	1.08 ± 0.06
29.7	26.2	0.88	28.1	0.945	28.8	0.959	0.95 ± 0.01
49.8	41.9	0.84	43.7	0.878	44.0	0.878	0.878
59.8	48.9	0.82	50.1	0.838	51.5	0.857	0.85 ± 0.01
100.	73.2	0.73	73.7	0.737	73.0	0.730	0.734 ± 0.004

[a]All solutions contain 0.02 M carbonate buffer and 0.02 M NaCl.

[b]Concentration of surfactant in micellized form; CMC values from Corrin plots of surface tension data for CTAB, using an ionic strength of 0.06 for these solutions.

[c]Due to the micelles only.

TABLE LXXXIV

EFFECT OF 0.001 M METHYL SALICYLATE ON CTAB COUNTERION BINDING[a]

[CTAB] x 10^4, M[b]	Run 1 Free $[Br^-]$ x 10^4, M[c]	Run 1 α	Run 2 Free $[Br^-]$ x 10^4, M[c]	Run 2 α	Average α
9.72	9.3	0.957	9.9	1.02	0.99 ± 0.03
29.8	26.7	0.897	27.3	0.917	0.91 ± 0.01
49.8	43.4	0.871	42.7	0.857	0.86 ± 0.01
59.8	48.2	0.806	50.2	0.839	0.82 ± 0.02
99.9	76.9	0.770	75.2	0.753	0.76 ± 0.01

[a]All solutions contain 0.02 M carbonate buffer and 0.02 M NaCl.

[b]Concentration of surfactant in micellized form; CMC values from Corrin plots of surface tension data for CTAB, using an ionic strength of 0.06 for these solutions.

[c]Due to the micelles only.

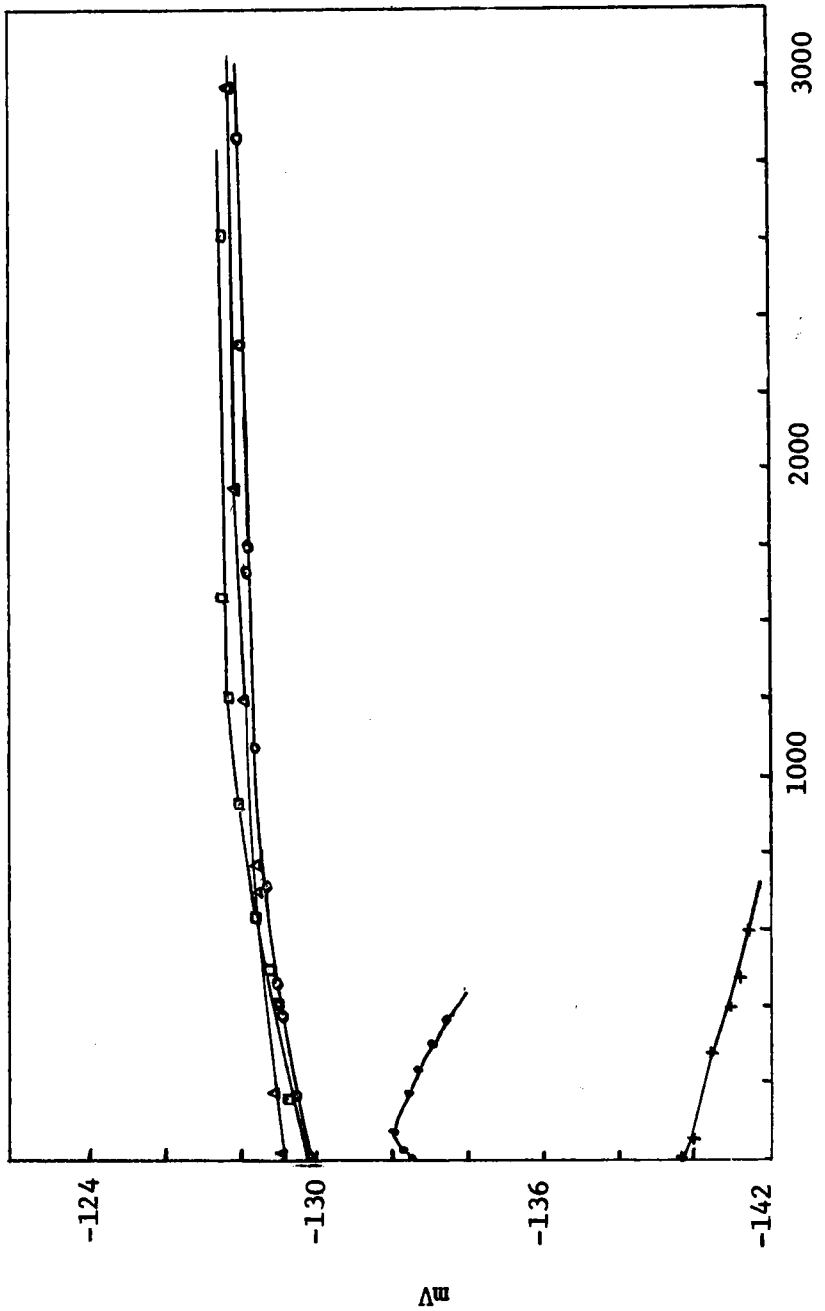


Figure 33. Dependence of free bromide ion concentration (expressed in millivolt readings) for 0.1 M CTAB-0.1 M NaBr-0.070 M benzene on time elapsed after stirring was stopped.

Open circles: 25°, stirring rate 500 rpm, squares: 25°, stirring rate 700 rpm, triangles: 25°, stirring rate 900 rpm, closed circles: 40°, stirring rate 500 rpm, crosses: 40°, stirring rate 700 rpm.

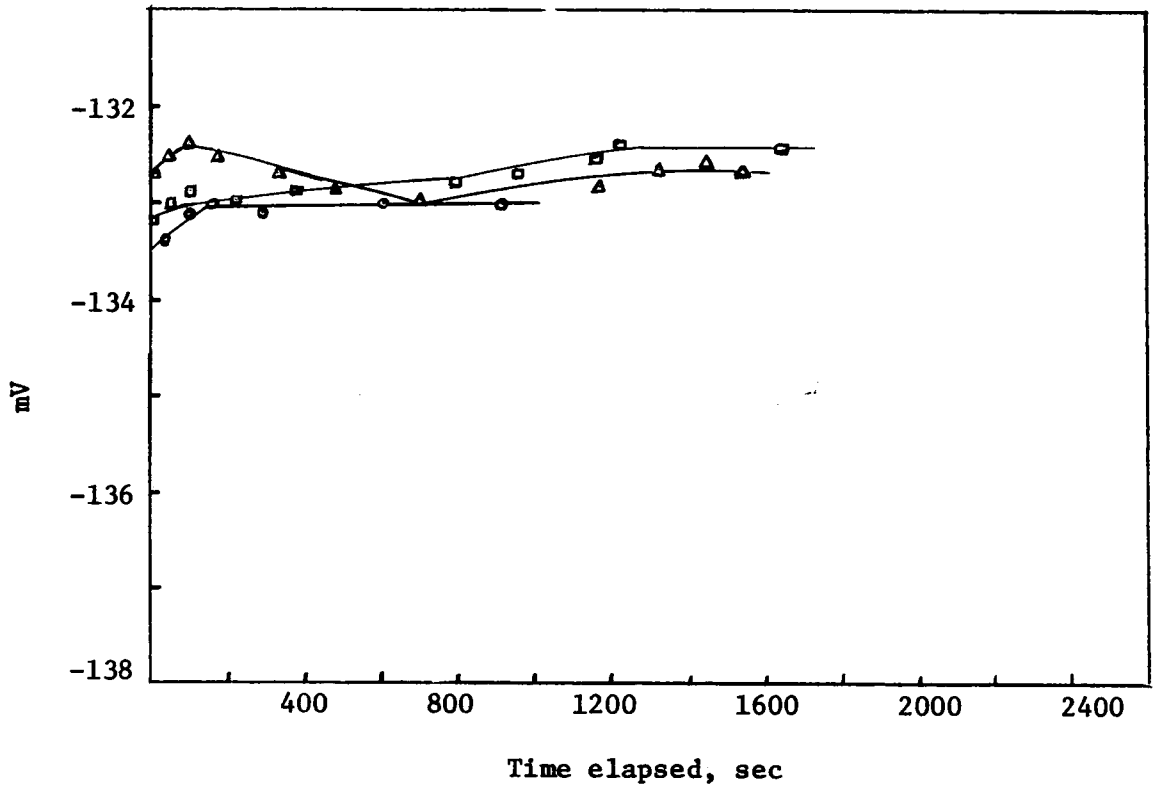


Figure 34. Dependence of free bromide ion concentration (expressed in millivolt readings) for 0.1 M CTAB-0.1 M NaBr-0.054 M benzoic acid at 25° on time elapsed after stirring was stopped.

Circles: stirring rate 400 rpm, squares: stirring rate 500 rpm, triangles: stirring rate 700 rpm.

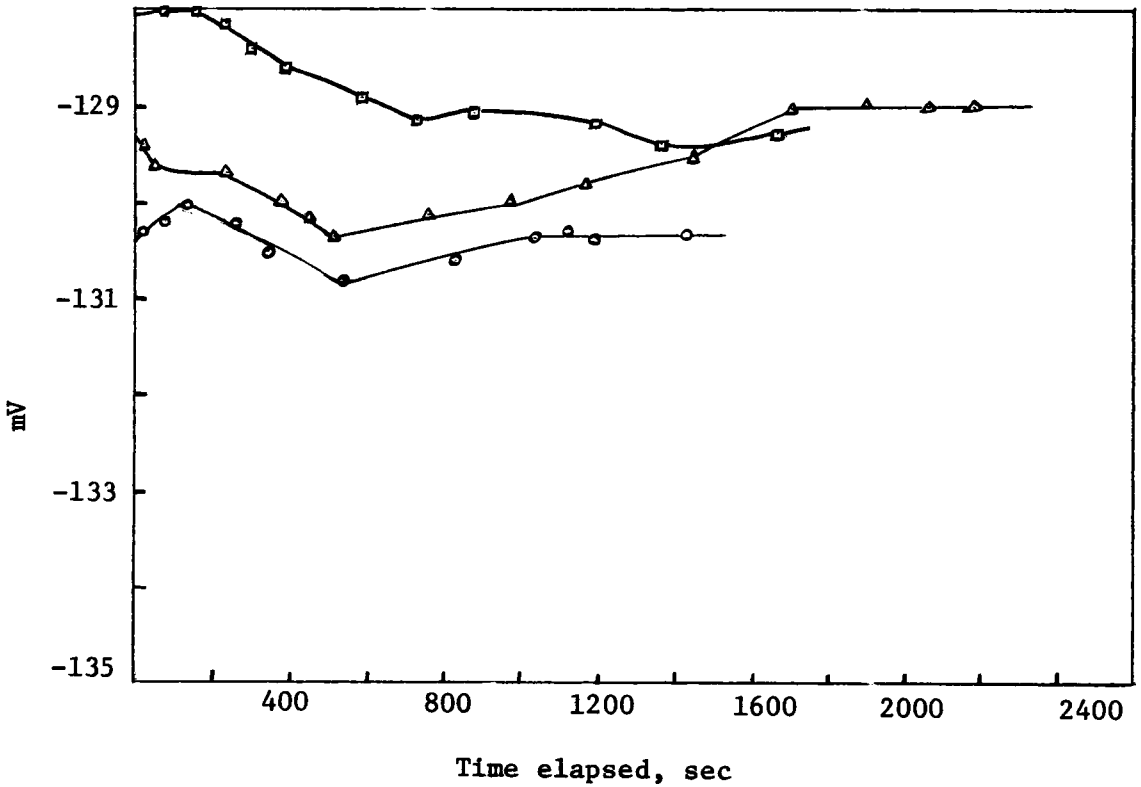


Figure 35. Dependence of free bromide ion concentration (expressed in millivolt readings) for 0.1 M CTAB-0.1 M NaBr-0.054 M benzoic acid at 39.2° on time elapsed after stirring was stopped.

Circles: stirring rate 400 rpm; squares: stirring rate 500 rpm, triangles: stirring rate 700 rpm.

TABLE LXXXV

DISTRIBUTION COEFFICIENTS FOR SUBSTITUTED BENZOIC ACIDS IN THE PRESENCE OF CTAB[a]

Solute	[Solute] at 5% w/v CTAB	y_s[b]	$y_s(K-1)\bar{\nu}$[c]	K[d]
o-Nitrobenzoic acid	3.1 g/100 ml	0.63 g/100 ml	0.494	79
o-Chlorobenzoic acid	1.97 g/100 ml	0.33 g/100 ml	0.328	100
o-Aminobenzoic acid	1.88 g/100 ml	0.41 g/100 ml	0.367	91
p-Aminobenzoic acid	1.22 g/100 ml	0.36 g/100 ml	0.184	52
o-Hydroxybenzoic acid	2.0 g/100 ml	0.22 g/100 ml	0.356	163
p-Hydroxybenzoic acid	1.6 g/100 ml	0.61 g/100 ml	0.198	33

[a]Data for the calculations from L. S. C. Wan, J. Pharm. Sci., 55, 1395 (1966).

[b]Saturation concentration of solute in water, extrapolated from plots of [solute] versus [CTAB] contained in reference cited in footnote a.

[c]([Solute] at 5% w/v CTAB)-y_s = $y_s(K-1)\bar{\nu}C_m$ where C_m is the concentration of CTAB in micellar form; $\bar{\nu}$ is the partial specific volume ($\simeq$ 1 ml/g). The equation is due to D. B. Herries, W. Bishop and F. M. Richards, J. Phys. Chem., 68, 1842 (1964).

[d]K is of the form $[\text{solute}]_{mic}/[\text{solute}]_{bulk}$; K = (moles of solute in micellar phase/moles of solute in bulk phase) x $(1-\phi)/\phi$, where ϕ is the volume fraction occupied by the micelles in solution.

TABLE LXXXVI

CORRECTED ENTHALPIES OF TRANSFER FOR SUBSTITUTED BENZOIC ACIDS IN THE PRESENCE OF CTAB

Solute	ΔH_{trans}, kcal/mole	K[a]	n_m/n_{bulk}[b]	% of Solute transferred[c]	True ΔH_{trans}, kcal/mole[d]
o-Nitrobenzoic acid	-1.72	79	2.98	75.3	-2.29
o-Chlorobenzoic acid	-1.75	100	3.77	79	-2.22
o-Aminobenzoic acid	-3.95	91	3.43	77.5	-5.09
p-Aminobenzoic acid	-1.18	52	1.96	66.5	-1.78
o-Hydroxybenzoic acid	-5.32	163	6.15	86	-6.19
p-Hydroxybenzoic acid	-5.13	33	1.24	55.5	-9.25

[a] $K = (n_m/n_{bulk}) \times (1-\phi)/\phi$, where n_m and n_{bulk} are the number of moles of solute in the micellar and bulk phases respectively; ϕ is the volume fraction occupied by the micelles in solution.

[b] $\phi = 0.0364$ at 0.1 M CTAB; $(1-\phi)/\phi = 26.5$ and $K/26.5 = n_m/n_{bulk}$.

[c] Percent transferred $= \dfrac{n_m}{n_m + n_{bulk}} \times 100\%$.

[d] ΔH_{trans} = (percent transferred/100) x ΔH_{true}.

APPENDIX VIII

ATTEMPTS TO CALCULATE DISTRIBUTION COEFFICIENTS FOR SOLUTES BETWEEN MICELLAR AND BULK PHASES USING CALORIMETRIC AND SPECTROSCOPIC DATA

A. The Bolles-Drago Approach

Bolles and Drago[274] found that both the equilibrium constant (K) and enthalpy of formation (ΔH°) for an adduct (C) could be determined calorimetrically. To do this, Equation 56 was derived, and reasonable values of ΔH° were chosen. This generated a family of straight lines of the form 1/K versus ΔH°; the point at which the lines intersected gave the true K and ΔH° for adduct formation. The following experimental quantities were used in Equation 56: (1) V, the volume of solution in milliliters, (2) $\Delta H'$, the measured heat of formation for an unknown amount of complex and (3) the initial concentrations A_o and B_o.

$$A + B \rightleftharpoons C \qquad K = [C]/[A][B]$$

$$C = (1000\Delta H'/V)/\Delta H^\circ$$

$$K = (1000\Delta H'/V\Delta H^\circ)/(A_o - 1000\Delta H'/V\Delta H^\circ)(B_o - 1000\Delta H'/V\Delta H^\circ)$$

$$K^{-1} = 1000\Delta H'/V\Delta H^\circ + A_oB_oV\Delta H^\circ/1000\Delta H' - (A_o + B_o) \qquad (56)$$

For studies of the equilibrium constant and true enthalpy of transfer from bulk to micellar phase for a solute, Equation 57 was derived. The quantity Q_{obst} (observed heat of transfer for an unknown amount of solute) corresponds to the Bolles-Drago $\Delta H'$. The quantity ΔH_{mt} is the true enthalpy of transfer for the solute in kcal/mole. The equilibrium

constant K is given by the expression $K = [\text{solute}]_{mic}/[\text{solute}]_{aq}$ or $[Y]/[X]$. It also equals $(n_m/n_{aq})(1 - \phi)/\phi$, where n_m is the number of moles of solute associated with the micelles, n_{aq} is the number of moles of solute in the bulk phase and ϕ is the volume fraction of the solution occupied by the micelles. Total added solute is n_{tot} $(n_m + n_{aq})$. The expression $(n_{tot} - 1000\ Q_{obst}/200\Delta H_{mt})$ is n_{aq}. Unfortunately, Equation 57

$$[Y] = 1000\ Q_{obst}/200\Delta H_{mt}$$

$$K = [Y]/[X]$$

$$K = (1000\ Q_{obst}/200\Delta H_{mt}\phi)/[n_{tot} - (1000\ Q_{obst}/200\Delta H_{mt})]/1 - \phi$$

$$= (1 - \phi)(5\ Q_{obst}/\Delta H_{mt}\phi)/(n_{tot} - 5\ Q_{obst}/\Delta H_{mt})$$

$$= 26.5\ (5\ Q_{obst}/\Delta H_{mt})/(n_{tot} - 5\ Q_{obst}/\Delta H_{mt}), \text{ since } \phi = 0.0364 \text{ for 0.1 M CTAB}$$

$$K^{-1} = (\Delta H_{mt}/26.5 \times 5\ Q_{obst})(n_{tot} - 5\ Q_{obst}/\Delta H_{mt})$$

$$= \Delta H_{mt} n_{tot}/(26.5 \times 5\ Q_{obst}) - 1/26.5 \qquad (57)$$

gives a family of straight lines (depending on what ΔH_{mt} is) which intersect only at -1/26.5, not a very realistic value for K^{-1}. The failure of this approach may be due to the form of our equilibrium constant being different from the equilibrium constant for adduct formation used by Bolles and Drago.[274]

B. Determination of Distribution Coefficients Using an Equation for a Solute's Observed Enthalpy of Solution in One-tenth Molar Hexadecyltrimethylammonium Bromide

For solutes whose enthalpies of solution are concentration

dependent, Q_{obs} will vary. Since Q_{obs} may be expressed in the form of Equation 58, a series of simultaneous equations containing two unknowns, ΔH_m and K are obtained. ΔH_m is the true enthalpy of solution for the solute in the micellar phase. Using Equation 58 for each of six Q_{obs}

$$Q_{obs} = \Delta H_{H_2O} n_{aq} + \Delta H_m n_m$$

$$K = (n_m/n_{aq})(1 - \phi)/\phi$$

$$= (n_m/n_{aq}) \times 26.5 \qquad \text{in 0.1 M CTAB}$$

$$K' = K/26.5 = n_m/n_{aq} = (n_{tot} - n_{aq})/n_{aq}$$

$$n_{aq}K' = n_{tot} - n_{aq};\ n_{aq} = n_{tot}/(1 + K')$$

$$n_m = K'n_{tot}/(1 + K')$$

$$Q_{obs} = \Delta H_{H_2O} n_{tot}/(1 + K') + \Delta H_m K' n_{tot}/(1 + K') \qquad (58)$$

obtained from calorimetric runs for phenol and o-chlorobenzoic acid in 0.1 M CTAB gave K' values of minus one, not a realistic number. Equation 57 was rearranged to give a left-hand side of the form $Q_{obs}(1 + K')$ prior to using it in calculations.

C. Ultraviolet Spectroscopy as a Tool for Determining Solute Distribution Coefficients

It was hoped that 0.1 M CTAB would alter the UV absorption bands of the solutes phenol and catechol sufficiently (compared to their spectra in water) so that the relative amount of these materials in the micellar and bulk phases could be determined. Table LXXXVII shows that a small

TABLE LXXXVII

THE EFFECT OF CTAB ON THE ULTRAVIOLET ABSORPTION SPECTRA OF PHENOL AND CATECHOL

Solute	[Solute] x 10^4, M	λ_{max}, nm	H_2O A	H_2O ε	0.1 M CTAB A	0.1 M CTAB ε
Phenol	2.789	269	1.043	1496		
	3.485	269	0.525	1506		
	6.971	269	0.416	1492		
	1.946	273			0.300	1541
	3.243	273			0.525	1619
	3.892	273			0.635	1632
	6.486	273			1.072	1653
Catechol[a]	4.505	275.5	1.021	2266		
	5.632	275	1.270	2255		
	1.123	278.5			0.275	2449
	2.246	278.7			0.560	2493
	2.808	279.0			0.720	2564
	4.212	278.7			1.105	2623
	5.616	279.3			1.426	2539

[a]"Sadtler Standard Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1969, reports λ_{max} = 277.5 nm and ε = 2673 in methanol.

shift in λ_{max} for both catechol and phenol was observed when the solvent was changed from water to 0.1 M CTAB, but no new peaks appeared.

An attempt was made to use the variation in extinction coefficients (ε) observed as the concentrations of phenol and catechol increased. The treatment developed parallels the procedure discussed in Section B. The expressions derived for n_m and n_{aq} in Section B are used in deriving Equation 59. V is the volume of the solution and $[n_{tot}]$ is the total concentration of solute in moles/liter. The path length of the cells used was 1 cm. By using Equation 59 for each concentration of solute a

$$A_{tot} = n_{tot}\varepsilon_{obs}/V = n_{aq}\varepsilon_{H_2O}/V + n_m\varepsilon_{mic}/V$$

$$A_{tot} = n_{tot}\varepsilon_{H_2O}/(1 + K')V + K'n_{tot}\varepsilon_{mic}/(1 + K')V$$

$$A_{tot} = [n_{tot}]\varepsilon_{obs} = [n_{tot}]\varepsilon_{H_2O}/(1 + K') + K'[n_{tot}]\varepsilon_{mic}/(1 + K') \quad (59)$$

series of simultaneous equations may be set up, each containing two unknowns, ε_{mic} (the extinction coefficient of solute in the micellar phase) and K'. Unfortunately, Equation 59 is again of the form where K' = -1 is the only possible solution with respect to that unknown.

D. Determination of Distribution Coefficients Using Enthalpies of Solution Obtained at Varying Concentrations of Hexadecyltrimethylammonium Bromide

Table LXXXVIII lists the ΔH_s values and ΔH_{trans} values for phenol and catechol at three different concentrations of CTAB. Figure 36 indicates that the values of ΔH_{trans} for phenol and catechol

TABLE LXXXVIII

ENTHALPIES OF SOLUTION OF PHENOL AND CATECHOL IN CTAB

[CTAB], M	Phenol		Catechol	
	ΔH_s, kcal/mole	ΔH_{trans}, kcal/mole[b]	ΔH_s, kcal/mole	ΔH_{trans}, kcal/mole[c]
0.100	-0.961 ± 0.022[a]	-3.93 ± 0.09	-1.25 ± 0.27	-5.30 ± 0.34
0.050	0.488 ± 0.147[a]	-2.48 ± 0.17	0.477 ± 0.222	-3.57 ± 0.29
0.010	1.85 ± 0.02[a]	-1.12 ± 0.09	1.56 ± 0.20[a]	-2.49 ± 0.28

[a]Extrapolated to infinite dilution by linear least-squares analysis. See Appendix III, Tables LVIII (p 303) and LIX (p 311).

[b]$\Delta H_{s,H_2O} = 2.97 \pm 0.09$ kcal/mole.

[c]$\Delta H_{s,H_2O} = 4.05 \pm 0.19$ kcal/mole.

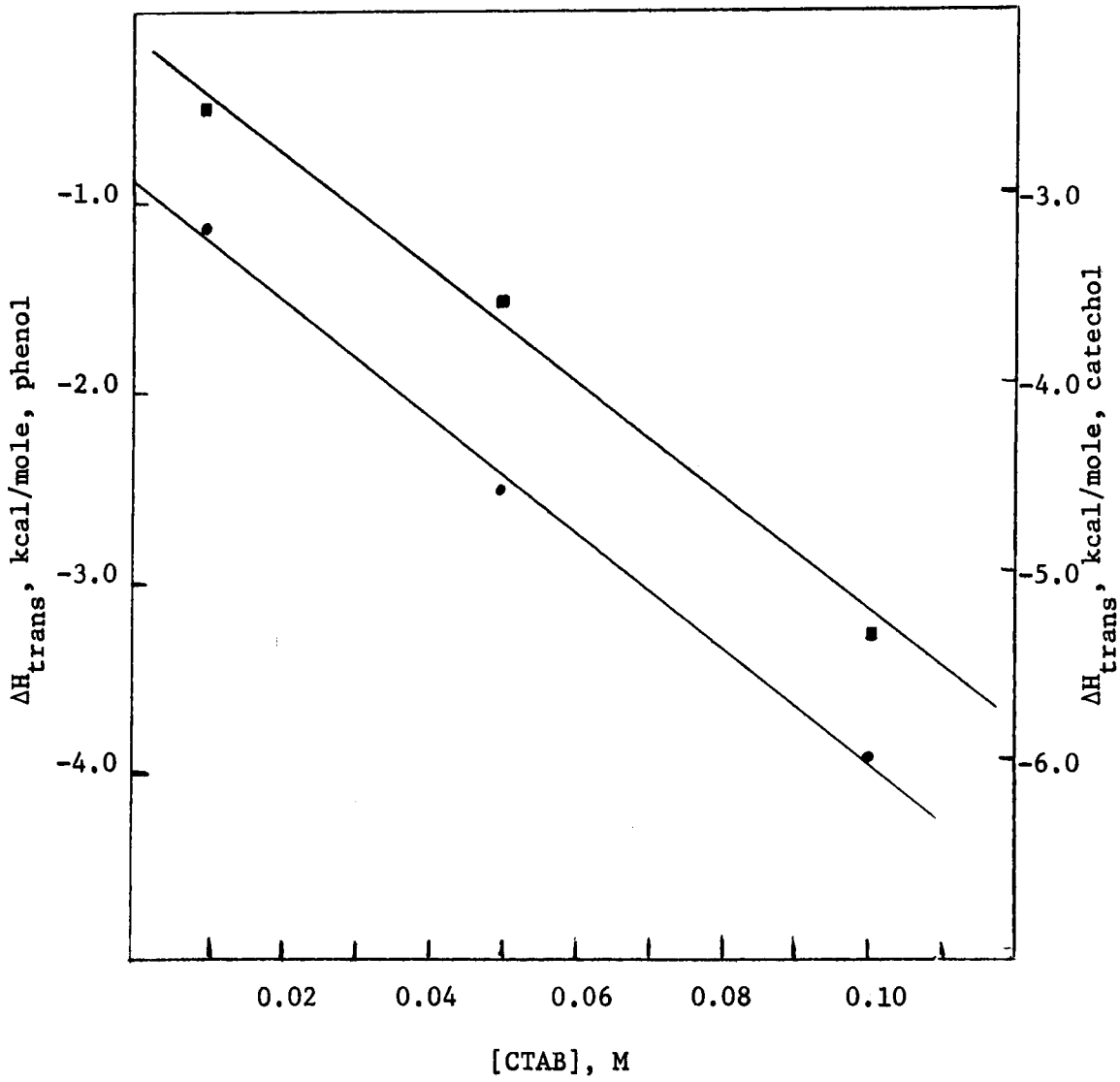


Figure 36. Dependence of ΔH_{trans} (water to CTAB) for phenol and catechol on CTAB concentration.

Circles: phenol, squares: catechol.

are linearly dependent on the concentrations of CTAB at which they were measured. Attempts were made to solve for $K = (n_m/n_{aq})(1-\phi)/\phi$ using simultaneous equations gotten from Equation 60. The expression $n_{tot}\Delta H_{s,CTAB}$ is the same as the Q_{obs} used in the derivation of Equation 58. The value of the quantity $(1-\phi)/\phi$ depends on the concentration of CTAB being used: 26.5 (0.1 M CTAB), 53.94 (0.05 M CTAB) and

$$n_{tot}\Delta H_{s,CTAB} = \Delta H_{H_2O} n_{aq} + \Delta H_m n_m \; ; \quad n_m = n_{tot} - n_{aq}$$

$$K = (n_{tot} - n_{aq})/n_{aq} \times (1-\phi)/\phi$$

$$n_{aq} = [(1-\phi)/\phi]n_{tot}/[K + (1-\phi)/\phi]$$

$$n_m = n_{tot} - [(1-\phi)/\phi]n_{tot}/[K + (1-\phi)/\phi]$$

$$= Kn_{tot}/[K + (1-\phi)/\phi]$$

$$\Delta H_{s,CTAB} = \Delta H_{H_2O} n_{aq}/n_{tot} + \Delta H_m n_m/n_{tot}$$

$$= \Delta H_{H_2O}[(1-\phi/\phi]/[K + (1-\phi/\phi] + \Delta H_m K/[K + (1-\phi)/\phi] \qquad (60)$$

273.7 (0.01 M CTAB). For each concentration of CTAB ϕ was computed using Equation 61, where $\bar{V}_{sp} = 1$ ml/g.

$$\phi = ([CTAB], M \times 364.45 \text{ g/mole} \times \bar{V}_{sp})/1000 \qquad (61)$$

It was hoped that the K obtained from Equation 60 (three equations per solute, one for each CTAB concentration) using the $\Delta H_{s,CTAB}$ values for phenol and catechol in Table LXXXVIII would be a constant. This was not the case; depending on which two equations were used a different K was obtained. For example, for phenol let Equation 60a denote the one obtained from data at 0.1 M CTAB, Equation 60b from data at 0.05 M CTAB and Equation 60c from data at 0.01 M CTAB. When Equations 60a and 60b were used to solve for K, K = 20.4; when Equations 60b and

60c were used, K = 127 and when Equations 60a and 60c were used, K = 72. The same result was obtained for catechol. Apparently K in the expression $K = (n_m/n_{aq})(1-\phi)/\phi$ is not a true equilibrium constant for micellar systems.

E. Summary of Distribution Coefficient Work

Attempts to calculate distribution coefficients for solutes between micellar and bulk phases were completely unsuccessful when data using only one concentration of CTAB were employed. Use of calorimetric data for phenol and catechol taken at three different CTAB concentrations met with more success. However, it was found that the behavior of these solutes as the concentration was varied could not be described by the use of a single K.

F. The True Enthalpy of Transfer of Phenol from Water to 0.0274 M Hexadecyltrimethylammonium Bromide

Good and Milloy[249] report an observed ΔG_{trans} for phenol from water to 0.0274 M CTAB of -0.360 kcal/mole; this corresponds to K = 1.84 where K is defined as n_m/n_{aq}. The phenol present in 0.0274 M CTAB is therefore divided into 65% associated with the micellar phase, 35% with the bulk, aqueous phase. The distribution coefficient $K = (n_m/n_{aq})(1-\phi)/\phi$ is then 182, since $\phi = 0.01$ for 0.0274 M CTAB. The true $\Delta G_{trans} = -RT\ln 182 = -3.07$ kcal/mole.

From Figure 36 the observed ΔH_{trans} for phenol is 0.0274 M CTAB is estimated to be -1.72 kcal/mole; correcting this to a true ΔH_{trans} requires dividing by 0.65, since only 65% of the phenol is actually

transferred to the micellar phase. The value of the true ΔH_{trans} is then -2.65 kcal/mole and ΔS_{trans} = 1.1 eu.

APPENDIX IX

MICELLAR CATALYSIS DATA

TABLE LXXXIX

REPRESENTATIVE RAW DATA FOR THE HYDROLYSIS OF METHYL AND HEXYL SALICYLATES AT 25°[a]

[Ester], M	[CTAB], M	t, min	$A_\infty - A_t$
Methyl salicylate			
0.002024[b]	--	20	1.522
		56	1.467
		85	1.381
		147	1.306
		255	1.181
		376	1.053
		1404	0.403
		1527	0.349
		1787	0.247
		2043	0.202
		2852	0.108
		3070	0.082
		∞	A=1.532
0.001033[c]	0.00500	100	0.708
		322	0.600
		382	0.594
		1111	0.264
		(1237)	(0.127)
		1343	0.217
		1491	0.182
		∞	A=0.772
0.000987[d]	0.00501	72	0.731
		162	0.721
		269	0.567
		343	0.535
		396	0.439
		1434	0.104
		1525	0.099
		1680	0.074
		∞	A=0.789
Hexyl salicylate			
0.001003[b]	0.00503	1191	0.756
		2625	0.687
		5505	0.538

TABLE LXXXIX (Continued)

[Ester], M	[CTAB], M	t, min	$A_\infty - A_t$
		8575	0.413
		10101	0.365
		11665	0.320
		14163	0.265
		15984	0.204
		19117	0.183
		21634	0.161
		∞	A=0.783
0.000991[c]	0.00454	1157	0.648
		1532	0.621
		4256	0.428
		7573	0.270
		9885	0.194
		12665	0.147
		15617	0.094
		(17656)	(0.063)
		∞	A=0.738
0.001070[d]	0.00501	1197	0.705
		2631	0.599
		5509	0.414
		8579	0.271
		10108	0.215
		11669	0.194
		14168	0.122
		15988	0.094
		∞	A=0.844

[a]Points neglected in the least squares analysis (to obtain rate constants) are in parentheses.

[b]0.02 M borax buffer.

[c]0.02 M carbonate buffer, 50% base.

[d]0.03 M carbonate buffer, 75% base.

TABLE XC

LINEAR LEAST SQUARES ANALYSIS OF KINETIC DATA FOR HYDROLYSIS OF METHYL AND HEXYL SALICYLATES AT 25°[a]

[Ester], M	[CTAB], M	$m' \times 10^4$[a]	b[a]
Methyl salicylate			
0.002024[b]	--	- 4.140 ± 0.057	0.1777 ± 0.0089
0.001154[b]	--	- 4.407 ± 0.081	-0.0409 ± 0.0092
0.002168[b]	0.00497	- 2.929 ± 0.141	0.1794 ± 0.0212
0.001178[b]	0.00500	- 1.577 ± 0.094	0.0162 ± 0.0110
0.001644[b]	0.0505	- 0.3337 ± 0.0232	0.0640 ± 0.0386
0.001113[c]	--	- 5.077 ± 0.222	0.0435 ± 0.0204
0.001035[c]	--	- 8.429 ± 0.230	-0.1879 ± 0.0230
0.001082[c]	--	- 4.891 ± 0.223	-0.0996 ± 0.0161
0.001423[c]	--	- 9.545 ± 0.393	0.0253 ± 0.0130
0.001033[c]	0.00500	- 4.358 ± 0.134	-0.0850 ± 0.0129
0.001218[c]	0.00500	- 6.769 ± 0.878	0.0228 ± 0.0201
0.001268[d]	--	- 4.390 ± 0.234	0.0854 ± 0.0195
0.001362[d]	--	-14.31 ± 0.204	0.0131 ± 0.0080
0.001044[d]	--	-12.86 ± 1.26	-0.0787 ± 0.0309
0.000945[d]	0.00501	- 5.615 ± 0.241	-0.1783 ± 0.0235
0.001374[d]	0.00497	- 5.719 ± 0.317	0.0502 ± 0.0211
0.000987[d]	0.00501	- 6.242 ± 0.138	-0.0751 ± 0.0134
Hexyl salicylate			
0.001003[b]	0.00503	-0.3448 ± 0.0119	-0.0857 ± 0.0152
0.000949[c]	0.00111	-0.3721 ± 0.0167	-0.0158 ± 0.0148
0.001134[c]	0.00348	-0.5372 ± 0.0147	-0.00065 ± 0.0132
0.000991[c]	0.00454	-0.5767 ± 0.0099	-0.1237 ± 0.0090
0.001090[c]	0.00500	-0.4993 ± 0.0096	0.0164 ± 0.0067
0.000996[c]	0.00551	-0.6165 ± 0.0047	-0.1144 ± 0.0049
0.001050[c]	0.00654	-0.4884 ± 0.0220	-0.1038 ± 0.0238

TABLE XC (Continued)

[Ester], M	[CTAB], M	$m \times 10^4$[a]	b[a]
0.000963[c]	0.01000	-0.4871 ± 0.0170	-0.1300 ± 0.0195
0.001070[d]	0.00501	-0.5889 ± 0.0148	-0.0664 ± 0.0148

[a] $\text{Log}(A_\infty - A_t) = mt + b$.

[b] 0.02 M borax buffer.

[c] 0.02 M carbonate buffer, 50% base.

[d] 0.03 M carbonate buffer, 75% base.

APPENDIX X

REPRESENTATIVE EXPERIMENTAL DATA

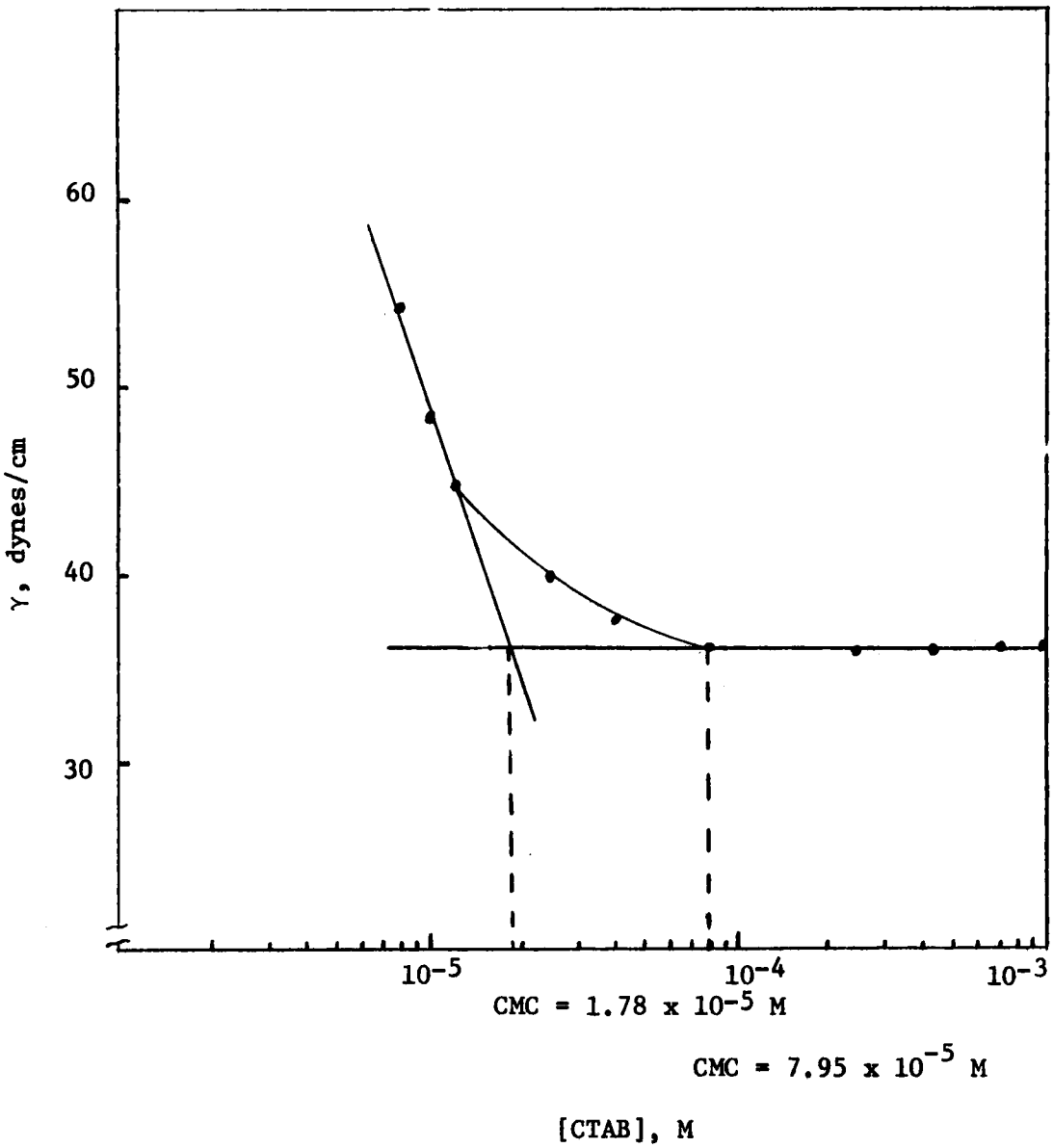


Figure 37. Surface tension of CTAB in 0.1 M NaBr.

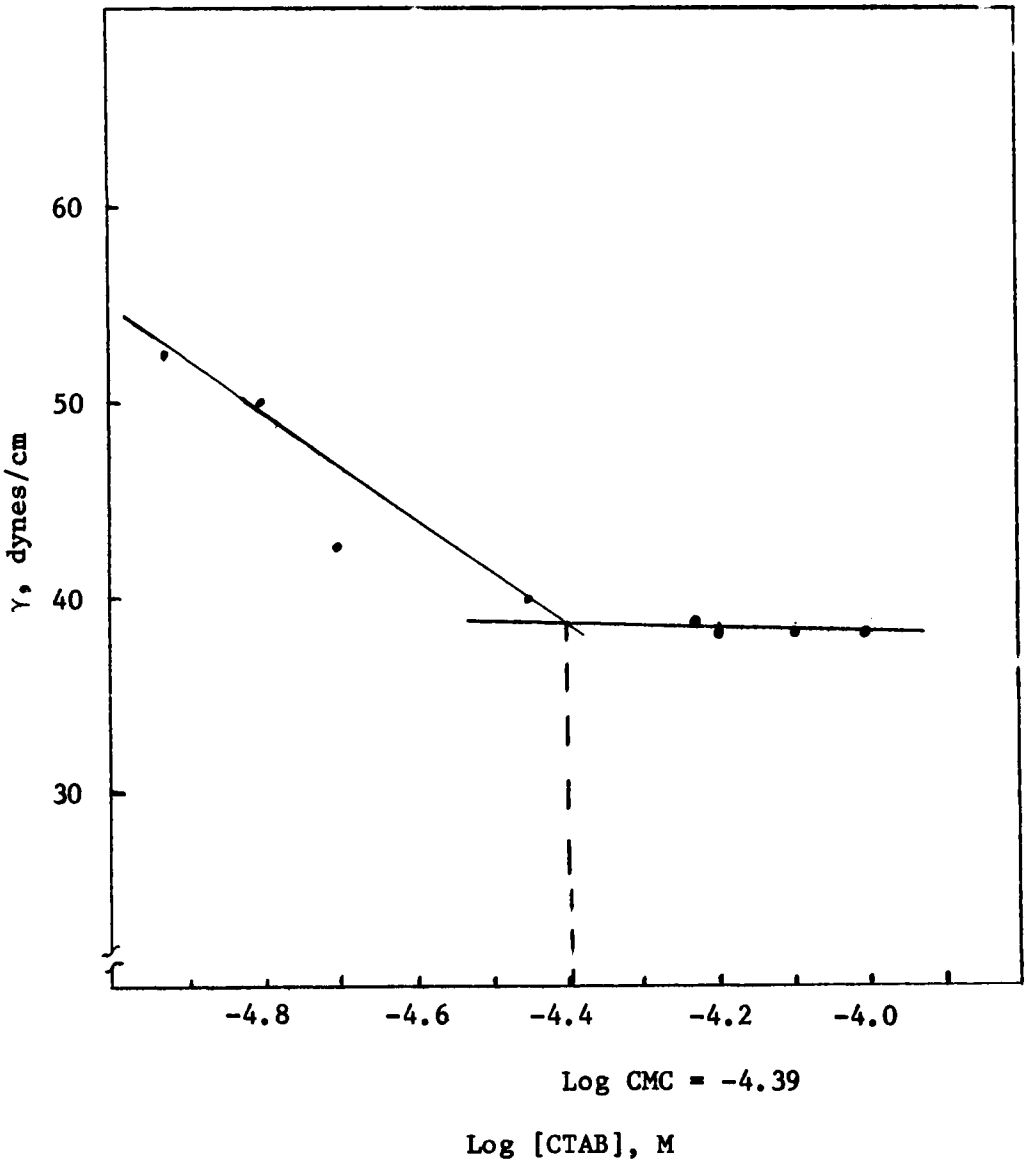


Figure 38. Surface tension of CTAB-1-hexanol (4:1 ratio) in 0.1 M NaBr.

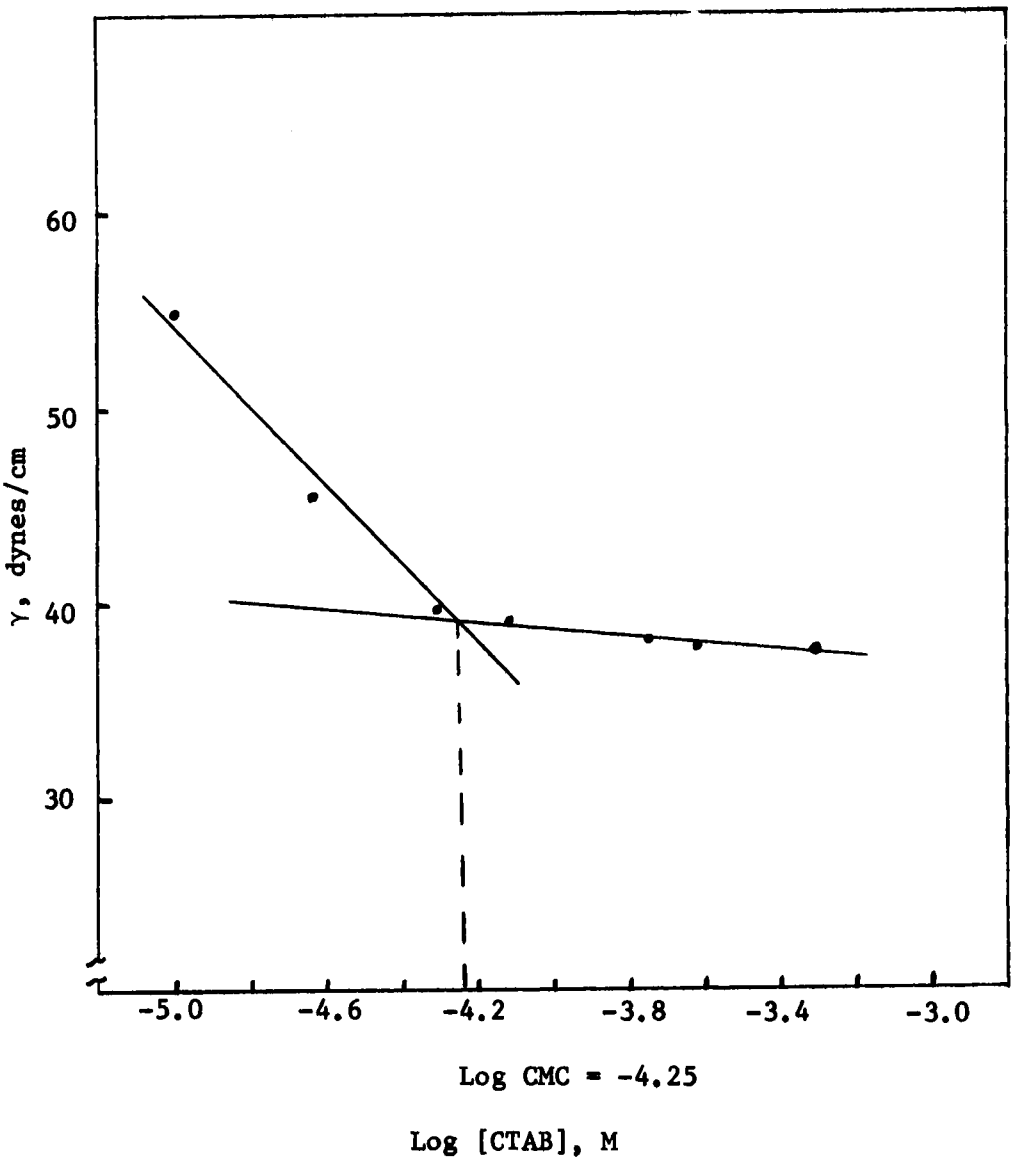


Figure 39. Surface tension of CTAB-benzoic acid (4:1 ratio) in 0.02 M NaBr.

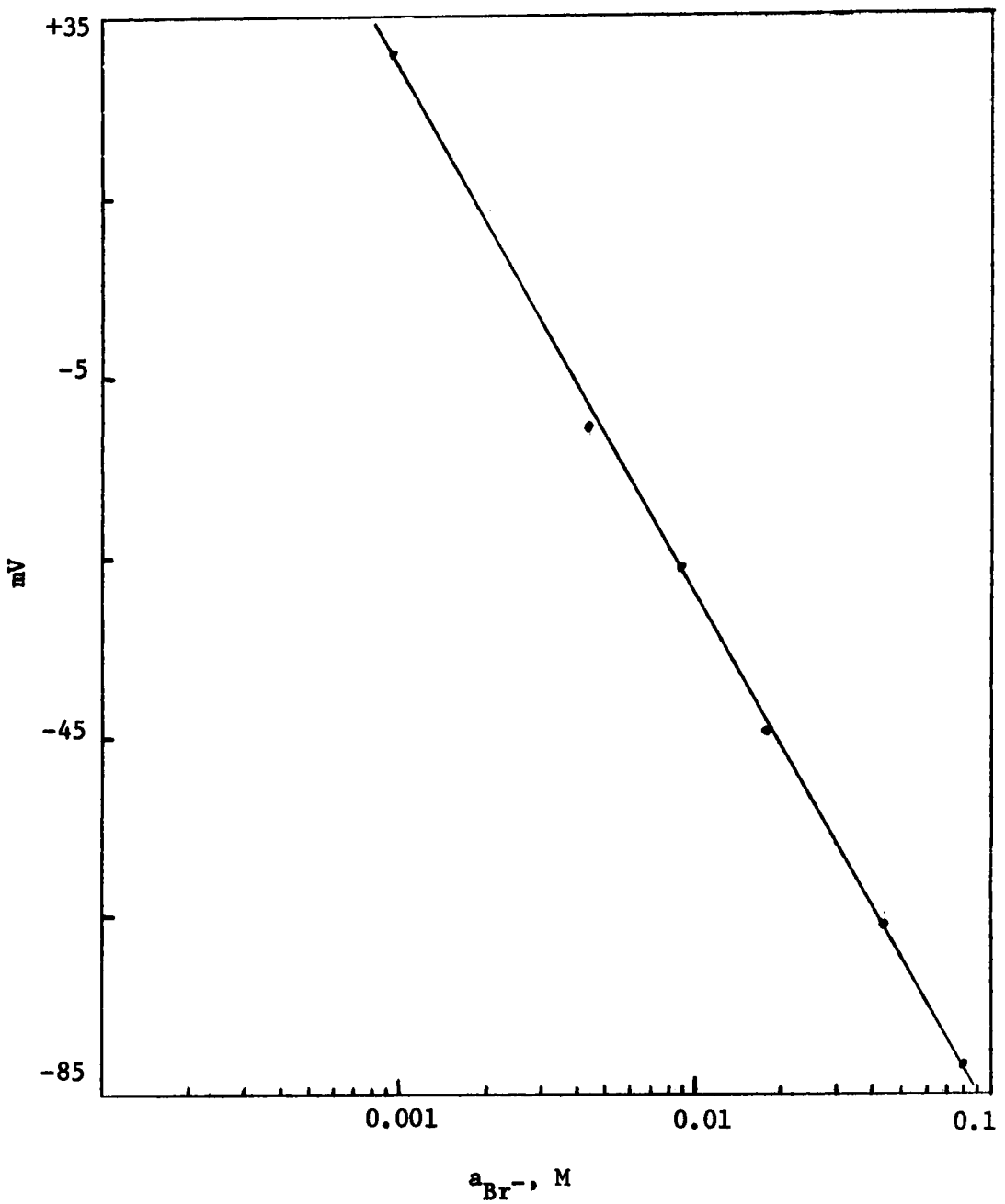


Figure 40. Plot of millivolts versus a_{Br^-} for NaBr standards used with the bromide ion specific electrode.

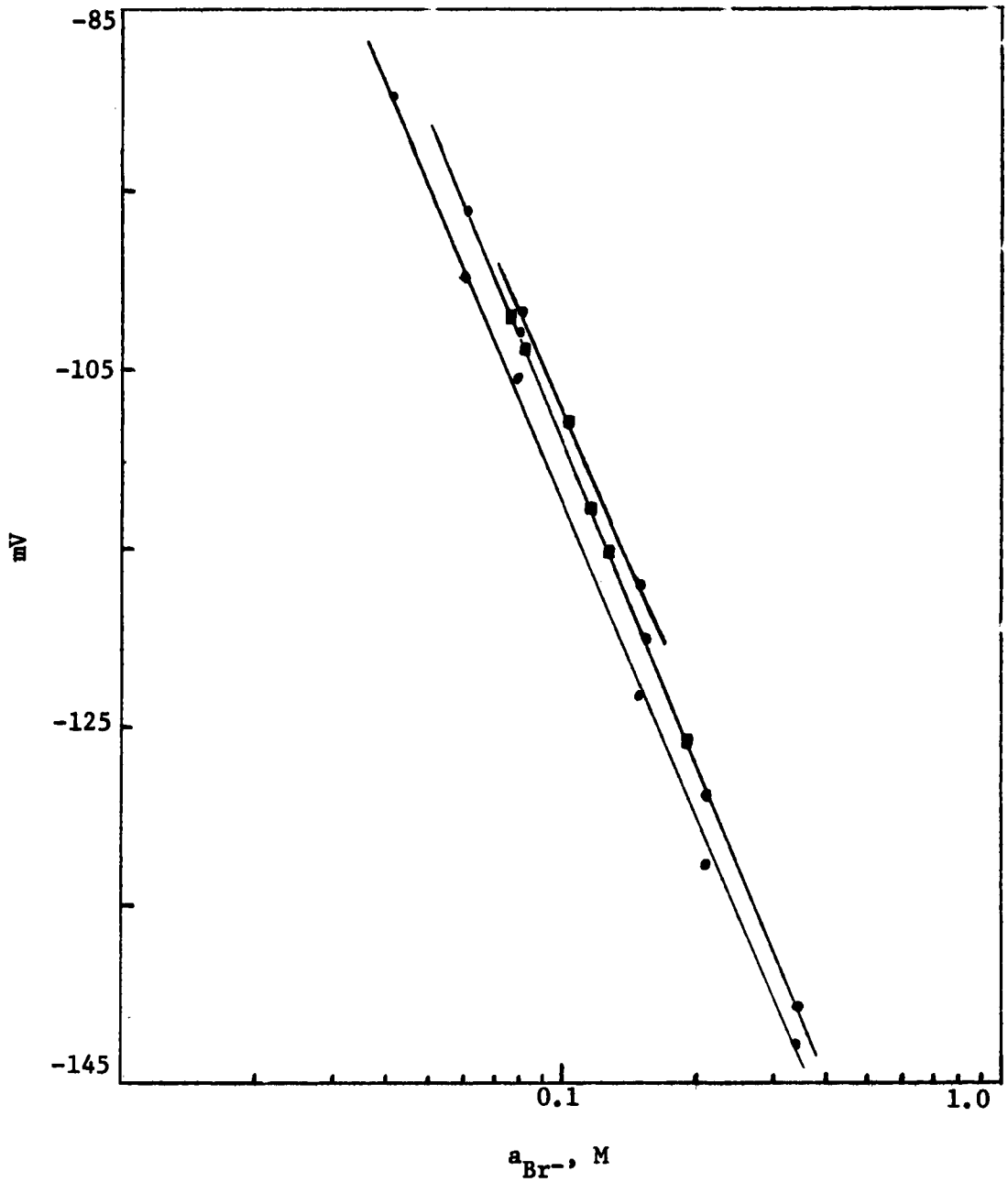


Figure 41. Use of NaBr calibration plots to determine a_{Br^-} in decyltrimethylammonium bromide solutions.

Circles: NaBr standard solutions, squares: decyltrimethylammonium bromide solutions.

TABLE XCI

AVERAGE MILLIVOLT READINGS AND MAXIMUM DEVIATIONS FOR A SERIES OF SODIUM BROMIDE SOLUTIONS USING THE BROMIDE ION SPECIFIC ELECTRODE

[NaBr], M	Reading, mV[a]
0.010	- 72.6 ± 0.5
0.020	- 87.4 ± 0.4
0.050	-107.3 ± 0.3
0.100	-122.3 ± 0.1
0.200	-136.9
0.500	-156.5 ± 0.1

[a]Average of two readings.

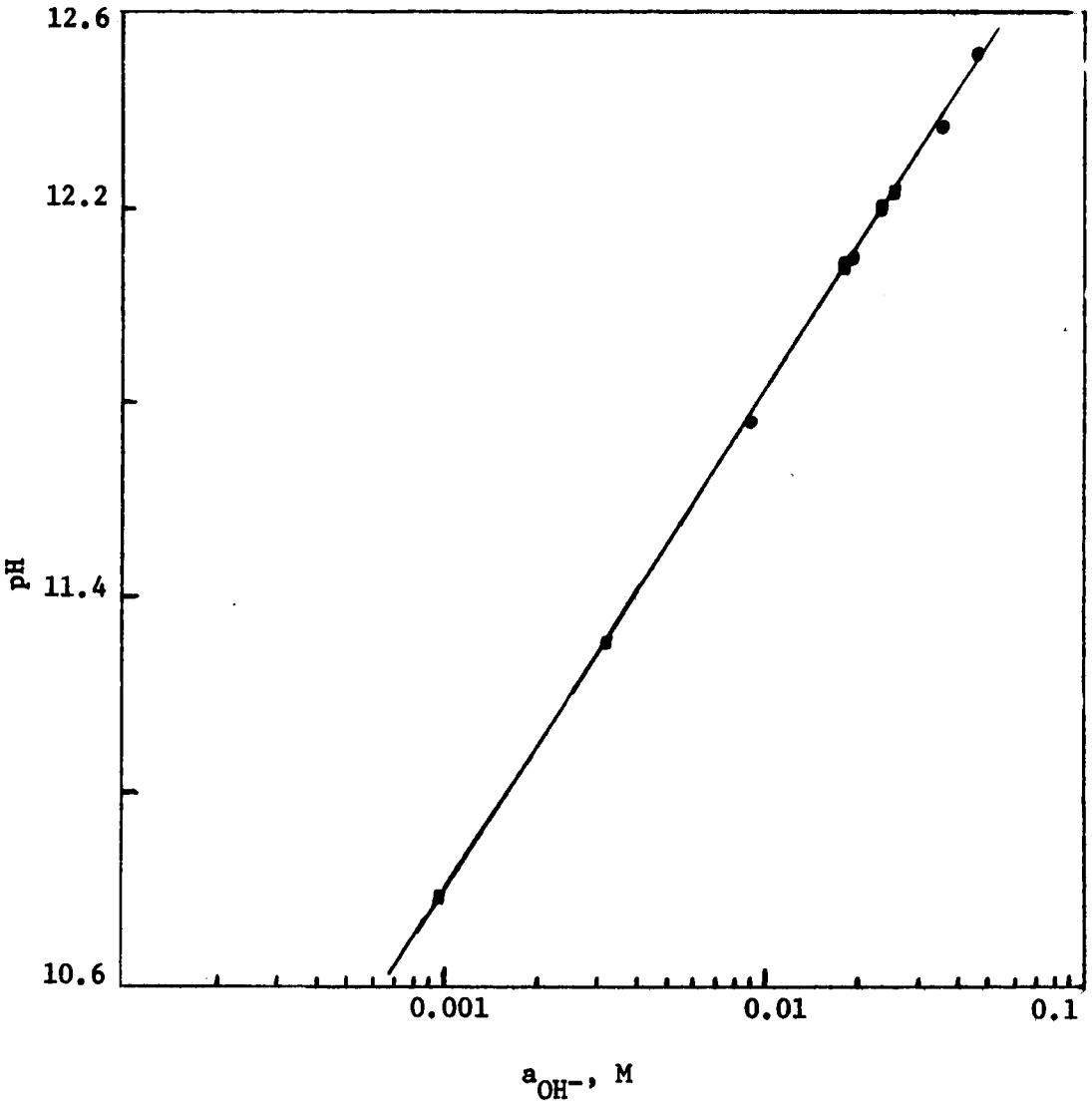


Figure 42. Plot of pH versus a_{OH^-} for NaOH standards and CTAB solutions containing NaOH.

Circles: NaOH standard solutions, squares: CTAB solutions.

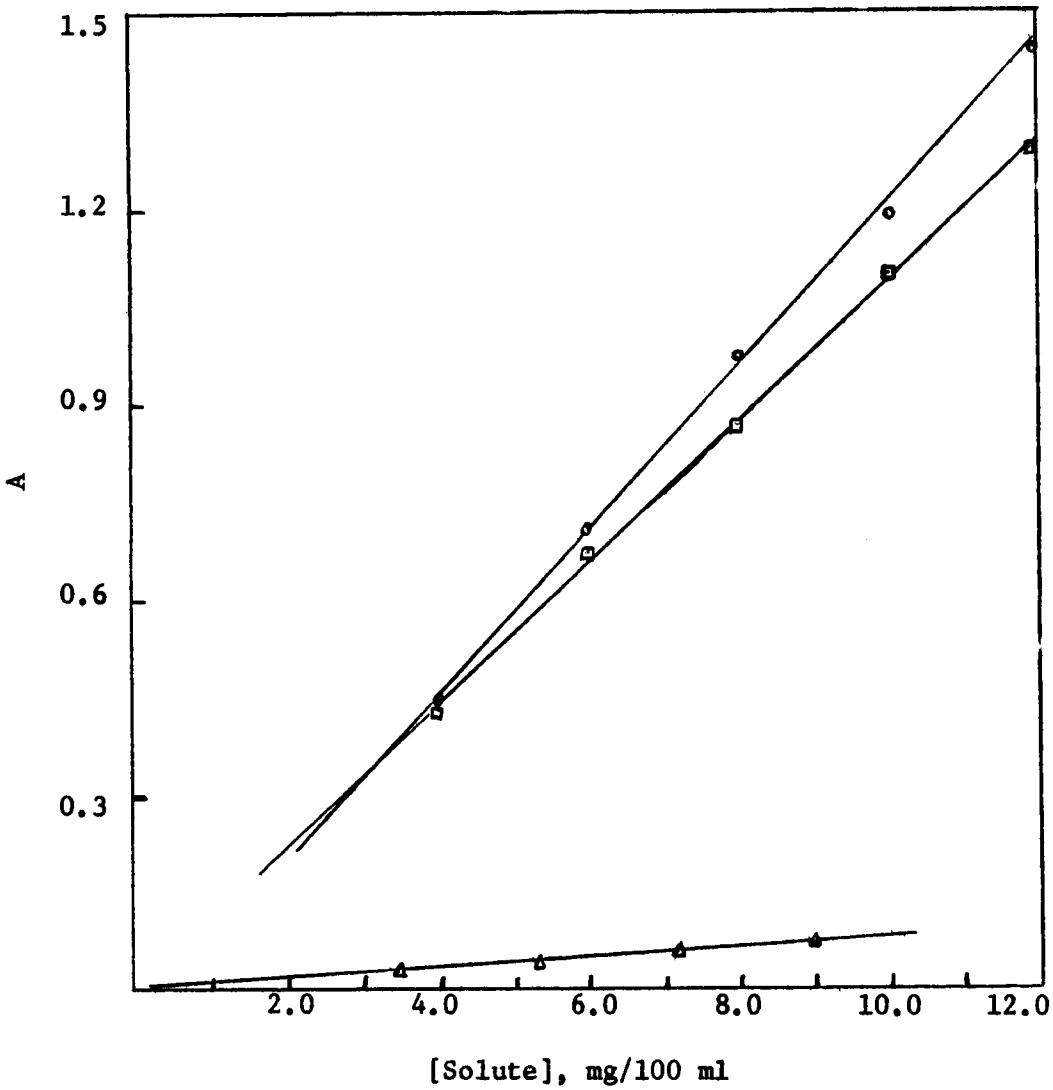


Figure 43. Adherence to Beer's law for the complex of $FeCl_3$ with salicylic acid and methyl salicylate.

Circles: salicylic acid in H_2O, squares: salicylic acid in 0.005 M CTAB, triangles: methyl salicylate in H_2O.

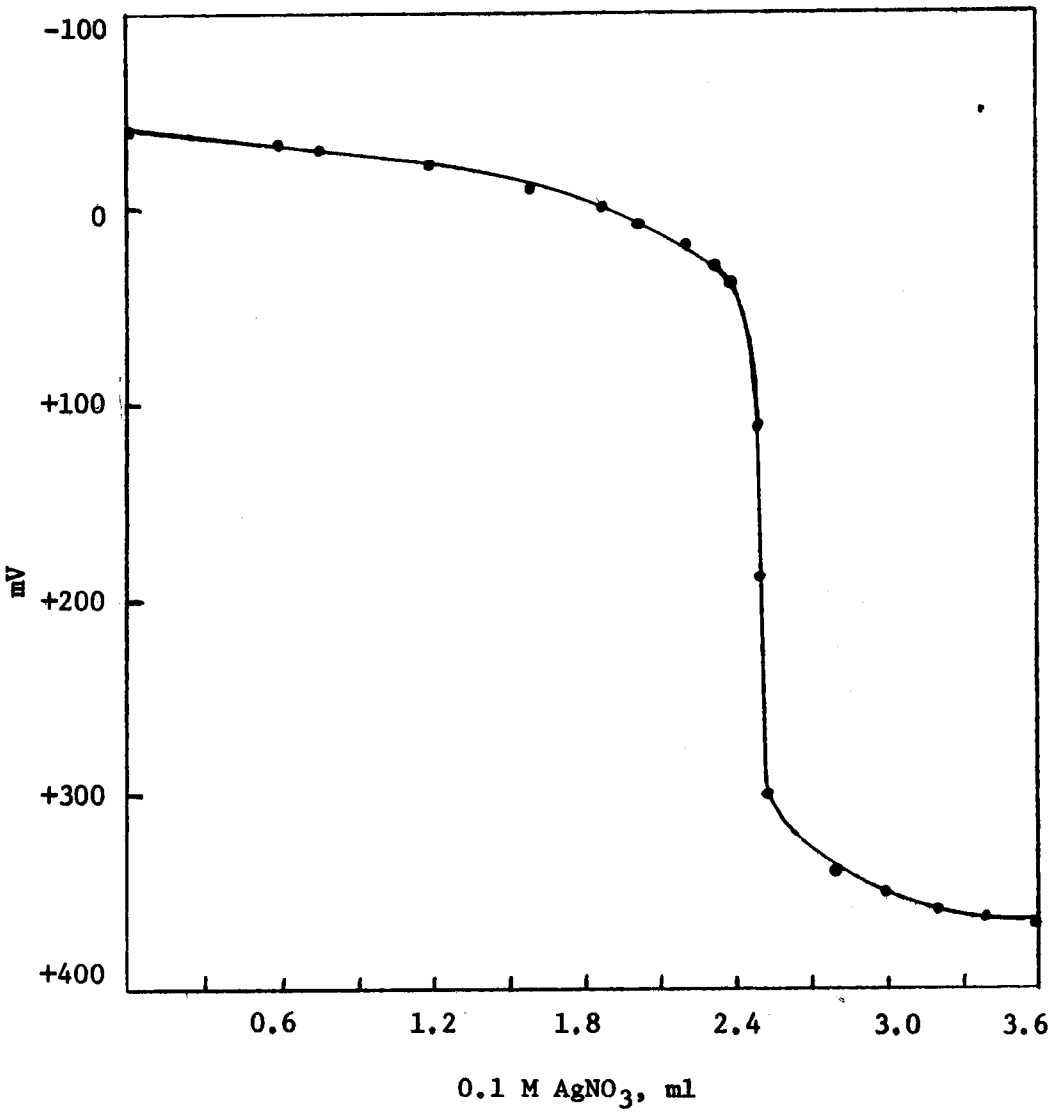


Figure 44. Titration of CTAB (2.5×10^{-4} mole) with 0.1 M $AgNO_3$.

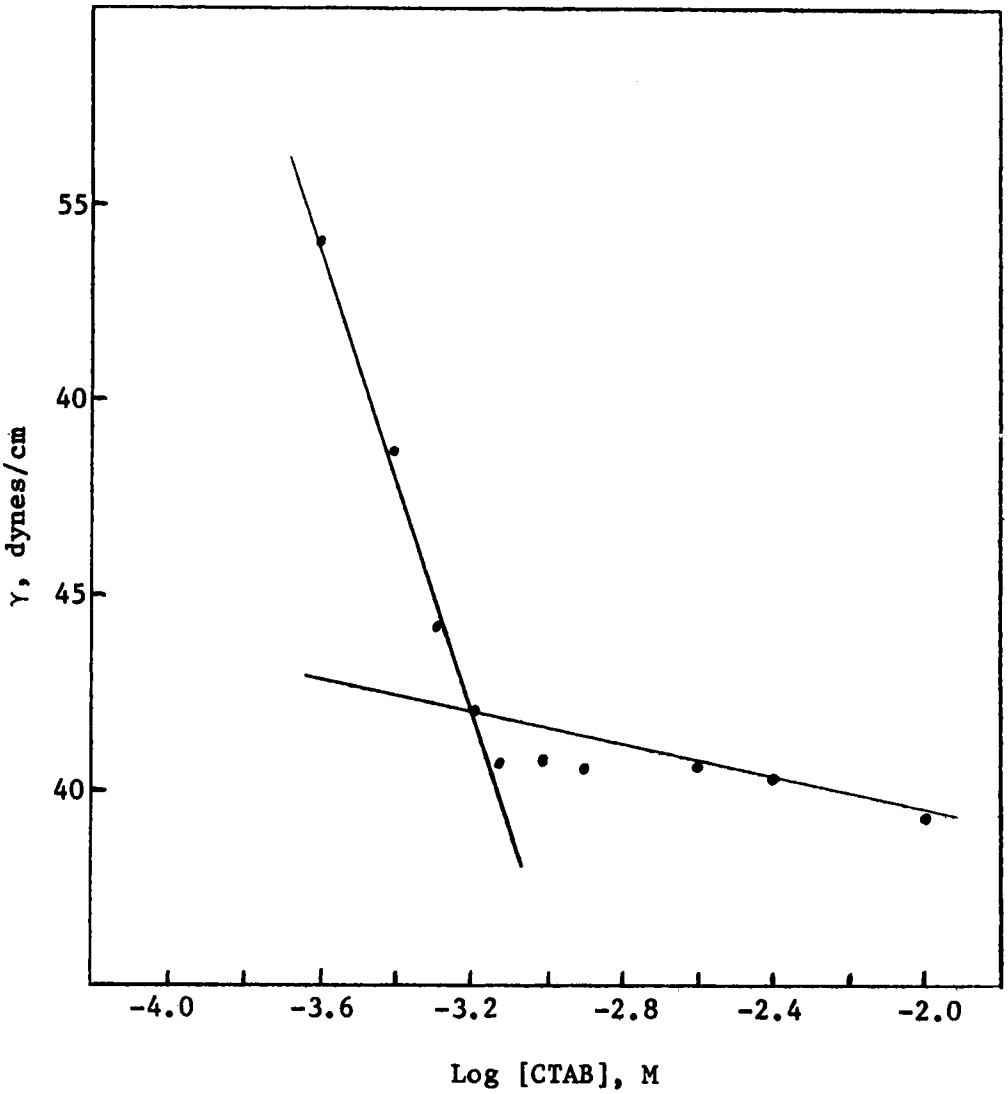


Figure 45. Surface tension of CTAB recrystallized from 2-butanone.

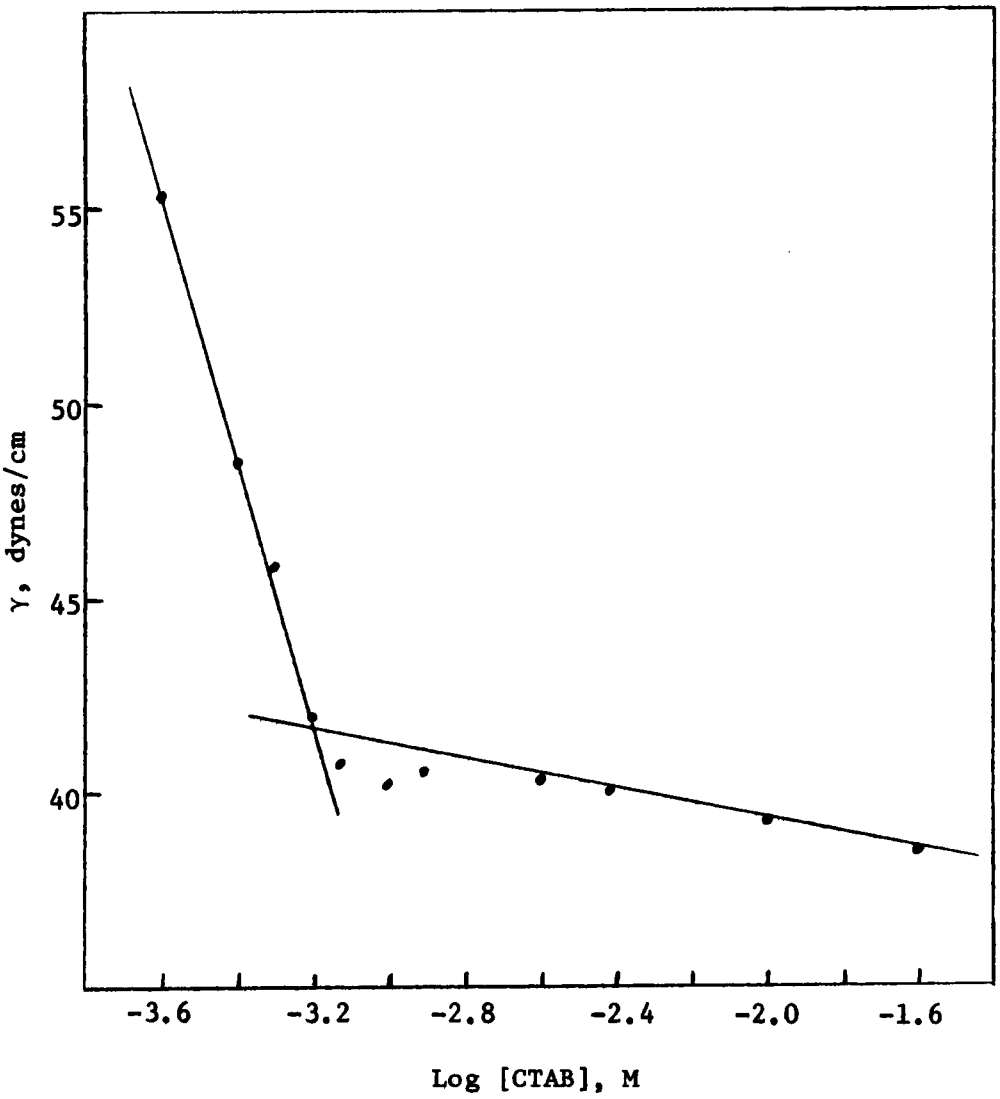


Figure 46. Surface tension of CTAB containing 2% hexadecanol.

VITA

Linda Jenny Magid was born on December 13, 1946 in Omaha, Nebraska. She attended public schools in Omaha and graduated from Benson High School, as class valedictorian, in June, 1965. Also in 1965 she was chosen as one of forty Outstanding Young Scientists by Westinghouse Corporation.

The author attended Rice University in Houston, Texas, receiving the B. A. summa cum laude in chemistry in May, 1969. While at Rice she was active in student government and was chosen one of fifteen Outstanding Seniors in 1969. She was chosen a Woodrow Wilson Fellow. At Rice she also met her husband Ron, whom she married in May, 1969.

The author spent one year in graduate school at Rice, then followed her husband to the University of Tennessee in 1970. She was a National Science Foundation Graduate Fellow from September 1969 through August 1972. From September 1972 to August 1973 she held a graduate teaching assistantship at the University of Tennessee.