To the Graduate Council:

I am submitting herewith a thesis written by H. Lynn Button Tepley entitled "An Investigation of the Binding of Organic Salts and Solutes to Ionic Micelles." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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AN INVESTIGATION OF THE BINDING OF ORGANIC SALTS AND SOLUTES TO IONIC MICELLES

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Degree

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H. Lynn Button Tepley

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ABSTRACT

The complete thermodynamic characterization of the binding of sodium p-toluenesulfonate, sodium p-toluate, sodium benzenesulfonate, and disodium phenyl phosphate to hexadecyltrimethylammonium bromide micelles (0.01 M) was done using the equilibrium constants determined by Sepulveda and calorimetric measurements of the heats of transfer from water to the micelles. The small enthalpies, similar free energies, and large positive entropies obtained indicate that the binding is entropy-controlled. The transfers also exhibit typical enthalpy-entropy compensation (slope of 312°K). Although qualitatively similar, the thermodynamic results obtained for phenyl phosphate differ somewhat from those of the other salts. No explanation is proposed for this observation. In the case of sodium p-toluenesulfonate, the heats of transfer from water to the micelles were found to be dependent on soap concentration.

Counterion binding to hexadecyltrimethylammonium bromide micelles (0.01 M) was measured in the presence of increasing concentrations of the four salts. The plot of each set of data was a straight line having a break at a certain concentration ratio of soap to salt. The break point

differed with each salt but occurred in the approximate vicinity of the n_s predicted by Sepulveda.

Viscosity measurements showed that large increases in micelle size occur in the solutions containing sodium p-toluenesulfonate and sodium p-toluate at these same soap to salt ratios, while none occurs in the solutions containing sodium benzenesulfonate and disodium phenyl phosphate. This difference is attributed to a different mode of binding beginning to occur in these solutions at salt concentrations above that associated with the break point. The p-methyl groups are thought to be responsible for the observed changes in micelle size in the systems containing sodium p-toluenesulfonate and sodium p-toluate.

Finally, the heat of transfer of some organic solutes to sodium dodecyl sulfate micelles (0.04 M) is reported. There is no discernible relationship between solute structure and heat of transfer. The only generality which may be made is that the heats of transfer of these organic solutes to sodium dodecyl sulfate micelles is less favorable than that to hexadecyltrimethylammonium bromide micelles.

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LIST OF SYMBOLS

a_f	Unbound solute molecule
a_b	Bound solute molecule
$(CTA)_s$	Unoccupied micellar site
C_{a_f}	Concentration of free solute
C_{a_b}	Concentration of bound solute
$C_{(CTA)_s}$	Number of unoccupied micellar sites
L	Langmuir parameter
K_L	Equilibrium constant for Langmuir adsorption
K_p	Equilibrium constant based on partitioning of solute
ΔG_{trans}	Free energy of transfer
ΔH_{trans}	Enthalpy of transfer
ΔS_{trans}	Entropy of transfer
C_at	Total concentration of solute
C_{CTAB}	Total concentration of CTAB
CTAB	Hexadecyltrimethylammonium bromide
NaLS	Sodium dodecyl sulfate
f	Fraction of bound counterions
n_s	Sepulveda's number of CTAB molecules at a binding site
k	Boltzmann constant
n	Number of CTAB molecules in a system

T	Temperature in Kelvin degrees
F_{el}	Change in electrical free energy for a single molecule undergoing association with the micelle
f_z	Activity coefficient of solution component z
K_s	Equilibrium constant derived by Sepulveda
A	Absorbance
E_{a_f}	Absorptivity of free solute
E_{a_b}	Absorptivity of bound solute
X_{mic}	Solute in the micellar phase
X_{aq}	Solute in the aqueous phase
$[Z]$	Concentration of quantity Z
S^+	Surfactant molecule without counterion
X^-	Counterion
M	Micelle
m	Total number of counterions
K_m	Equilibrium constant for micelle formation
n_L	Langmuir parameter
ΔG_{mic}	Free energy of micellization
R	Gas constant
TOS	Sodium p-toluenesulfonate
TOL	Sodium p-toluate
BS	Sodium benzenesulfonate
PP	Disodium phenyl phosphate
η_{KE}	Viscosity

ρ	Solution density
E	Potential of solution
E_a	Standard potential of the solution
F	Faraday
a_{Br^-}	Activity of bromide ions
n_e	Electrons transferred per molecule

CHAPTER I

INTRODUCTION

A. General Properties of Micelles

Micelles, aggregates of surfactant molecules, have properties similar to those of certain biological systems, i.e., lipid-protein interfaces and enzymes, and have been of interest as models for these systems for many years. Surfactant molecules are amphipathic: they have a hydrophobic part (consisting of a long hydrocarbon chain, usually unbranched, unsubstituted, and saturated) attached to a hydrophilic polar head group. The nature of the head group distinguishes the three major surfactant classifications: (1) cationic, having a positively charged head group such as the trimethylammonium ion; (2) anionic, having a negatively charged head group like sulfate or carboxylate; and (3) non-ionic in which the head group contains a polar uncharged group such as an ether oxygen. This work will consider only ionic surfactants. Strictly speaking, a soap is a molecule having a carboxylate head group while a surfactant is one having some other type of head group. In this work, however, the two terms will be used interchangeably.

In very dilute solutions soap molecules exist primarily as monomers, dissociated from their counterions. At a certain concentration (depending upon the surfactant) known as the critical micelle concentration (CMC), large numbers of these molecules aggregate into micelles. Each micelle contains approximately 20 to 100 monomers; however, no system contains micelles of exactly the same size, i.e., they are polydisperse.[1,2] Also, at the CMC only about 2 percent of the surfactant is in micelles; the rest is monomeric or in some other premicellar form.[3] As micelles form, some of the free counterions reassociate with the head groups producing a decrease in the micellar surface charge density and enabling the head groups to be closer together. CMC values range from about 10^{-4} to 10^{-2} M for ionic surfactants depending upon the soap.[4] Since a number of physical and chemical properties of the solution change at the CMC, this point may be observed through a variety of techniques, including surface tension, viscosity, conductivity, and solubilization.[5,6] The measurement of these parameters over a range of soap concentrations gives two lines whose intersection is the CMC.

Micelles are usually spherical at a concentration slightly above the CMC and become more ellipsoidal or rod-shaped at higher concentrations. However, this is not always the case. Even in very dilute solutions, some micelles are

rod-shaped.[7] The ends of rod-shaped micelles, known as Debye micelles,[6] are thought to be hemispherical. Tanford[8] has ascribed this difference in shape between spherical and rod-shaped micelles to the length of the hydrocarbon chain and the number of surfactant molecules per micelle. Since even small chains cannot be radially arranged in a spherical micelle, larger chains, having more volume, may necessitate less surface area per head group and thus a more ellipsoidal shape. That the micellar core has a constant density throughout[6] would support this theory.

Micelles have three main regions[9,10] as shown in Figure 1: the internal hydrocarbon core formed by the association of the hydrocarbon chains; the Stern layer, surrounding the core and including the hydrated head groups, their associated hydrated counterions,[10] and solvent; and the outer Guoy-Chapman layer consisting of solvent and free counterions. The hydrocarbon core is thought to be liquid in nature,[6,11-14] to have a constant density, and to contain some water.[15] Substances which are insoluble or slightly soluble in water are often soluble in the micelle interior. The Stern layer is about as thick as the radius of the hydrated head groups. It has a dielectric constant lower than that of the bulk solution[16] possibly due to the fact that parts of the hydrocarbon core protrude into it,[17] as well as due to dielectric saturation effects resulting from

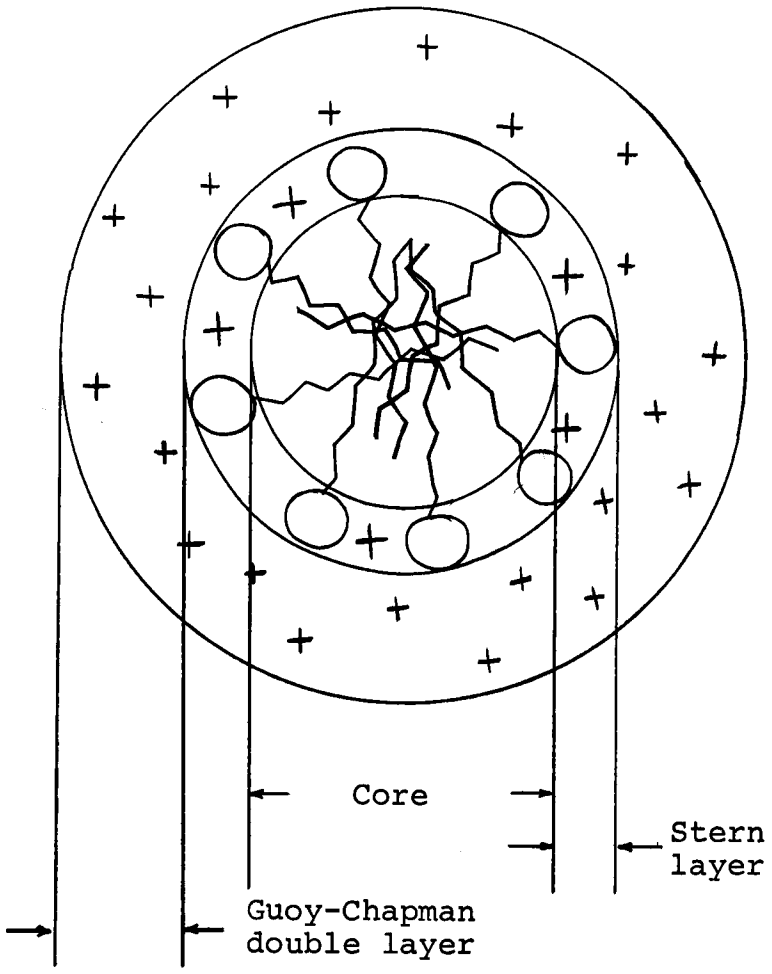


Figure 1. Two-dimensional schematic representation of a typical ionic micelle.

A cross represents a counterion; small circles are the polar head groups; and jagged lines are the alkyl chains.

the high charge density.[18] This has been substantiated by studies on electrophoretic mobilities, micellar surface area per head group,[19] and free energy of transfer for methylene groups from water to micelles.[20-22] The Guoy-Chapman layer contains the dissociated counterions and may be quite thick depending on the electrical properties of the micellar surface.

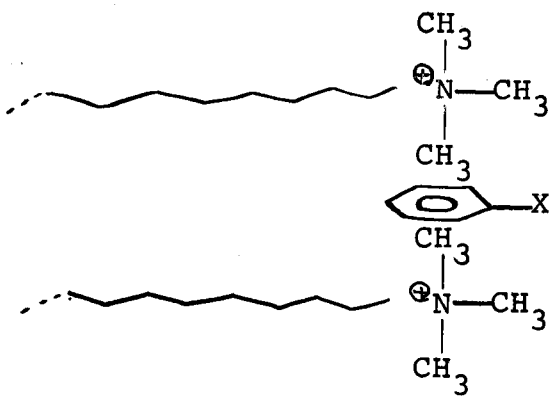
The driving force for micellization is the hydrophobic interaction of the hydrocarbon chains, as long as it is stronger than the Coulombic repulsion between the head groups.[23] An increase in the chain length increases hydrophobic interactions and lowers the CMC[6] as long as repulsion factors are constant. Micelles are not fixed structures but are dynamic in nature. Their formation and dissociation is very fast, having a rate constant of 10^5-10^6 sec^{-1} for the dissociation of one monomer from the micelle, as measured by temperature-jump,[24] EPR,[25] and NMR.[26] The energetics of micellization have been thoroughly discussed by Magid.[27]

B. Factors Affecting Micellar Solutions

Micellar properties are a function of many factors including the nature of the head group, the length of the hydrocarbon chain (usually C_8 to C_{18}), solvent, temperature, and added solutes. As the head group and its counterions vary, so do the electrical properties of the system,

resulting in alterations of the CMC, micelle size and shape, solubilization, and other properties. Similarly, variations in surfactant chain length also affect these parameters. Temperature affects the CMC such that for a range of temperatures the CMC usually is at a minimum at 25°. Such a minimum indicates that micelles are most stable at 25°C. Temperature also affects micellar size which decreases as the temperature increases.[28]

Organic and inorganic additives greatly alter the properties of micellar solutions, depending upon the nature of the solute. At sufficiently high concentrations of electrolyte, micelles often become more rod-shaped owing to the inclusion of more monomers per micelle. This is possible since added counterions decrease the surface potential and thus allow more head groups to become incorporated. This, in turn, decreases the area per head group. Similar changes in the CMC, solubilization, and other properties occur. Organic solutes affect the solution as well, but the mechanism is uncertain. It has been postulated that certain organic solutes are solubilized in the micellar core; some are oriented radially; while others, especially aromatic solutes, are sorbed in the Stern layer as illustrated below:



The solvent has a primary effect on the micellar system and determines the relative orientation of the head groups and alkyl chains. Water solutions produce micelles as have been described thus far and are the concern of this study. Organic solvents often produce reversed micelles in which the polar groups make up the core. A more thorough discussion of the changes on micelles, produced by changes in the micellar environment, will be presented later.

C. Enthalpy-Entropy Compensation

In a number of systems similar to micellar systems, the free energy change of a process changes monotonically over a range of systems while the enthalpy and entropy undergo large swings. A plot of enthalpy versus entropy yields a straight line with slope ranging from about 285° to 320°K, called the compensation temperature. This phenomenon, known as enthalpy-entropy compensation, explains that the driving force of an unfavorable process (in terms of enthalpy) is a

favorable change in entropy, and vice versa. Thus, if a solute becomes more ordered in the final medium, giving a negative or unfavorable ΔS, the enthalpy change is relatively favorable. Likewise, a favorable entropy change compensates for an unfavorable enthalpy. This compensation is thought to be a function of changes in water structure and their effects on the studied properties.[29] It has been observed in various processes involving small solutes, including the solvation of ions and organic solutes, hydrolysis, oxidation-reduction, and the ionization of weak electrolytes, especially when the bulk solution contains proteins or other large molecules whose properties may be controlled to a large extent by water structure. In this regard, binding of solutes to micelles may be affected by changes in water structure since the head groups and counterions are hydrated and the bulk solution is primarily water. If so, binding should show compensation behavior. An excellent review of this problem is available.[29]

D. Purpose

Although the interaction between micelles and solutes has been well researched, very little is known about the nature or the interaction of the forces involved. It has been established that simple anions or cations interact with the oppositely charged head groups while remaining in a

predominantly aqueous environment. However, with organic solutes, especially aromatic compounds and their salts, the mechanism is less clear. From many experimental results, it appears that nonpolar compounds are solubilized in the micellar core. Compounds having some polar component as well as a hydrocarbon chain are thought to orient themselves radially, i.e., the polar component lies in or near the Stern layer and the chain is projected into the core. Aromatic molecules and other small polar solutes are thought to sorb to the micelle near the surface. There has been much experimental evidence for these theories but why and how solutes bind where they appear to bind is less understood.

In the past few years, increasing interest has developed in this problem. Since micelles have been found to produce rate enhancements for certain chemical reactions,[27,30] a knowledge of the nature of the interaction between micelles and the substances undergoing reaction would enable chemists to better control and enhance this catalytic phenomenon. Similarly, micelles have been used as models for certain biological systems such as lipid-protein interfaces. Since micelles are affected by solutes, as are membranes, but are structurally simpler and more easily manipulated, a study of the interactions between solutes and the micelles and of the effects of solutes on micelles should provide insight into those properties of membranes.

Thus, in an effort to extend the characterization of those interactions and the forces involved, studies on counterion binding to hexadecyltrimethylammonium bromide (CTAB) in the presence of aromatic salts as well as changes in viscosity and heats of transfer have been employed. Such a study should produce a more complete picture of the factors involved in binding as well as the effects on the micelles produced by binding.

Also, the heat of transfer of certain organic solutes from water to sodium dodecyl sulfate (NaLS) micelles has been studied and a comparison drawn between these results and those for CTAB. Differences in the interactions between the two types of micelle systems should result and aid in differentiating which effects are due to surface interactions and which are due to the micellar environment as a whole.

CHAPTER II

PROPERTIES OF HEXADECYLTRIMETHYLAMMONIUM BROMIDE AND SODIUM DODECYL SULFATE

There is a large volume of information on surfactants of all types. Since this study is concerned with only one cationic surfactant, hexadecyltrimethylammonium bromide, and one anionic surfactant, sodium dodecyl sulfate, the following discussion will be limited to these.

A. Hexadecyltrimethylammonium Bromide

Hexadecyltrimethylammonium bromide (CTAB) has a CMC of approximately 0.0009 M at 25°, determined by several techniques.[31-36] Two CMCs have been observed in the presence of 0.1 M NaBr and 0.025 M benzoic acid: 7.95×10^{-5} M from surface tension and 1.57×10^{-3} M using viscometry.[27] Several workers have estimated the aggregation number: Ekwall[37] found 95 monomers per micelle using light scattering: Keh[38] found 80; and Hyde and Robb report 61[39]-72.[40] Bair and Kraus[41] have shown that below the CMC, dimers may form. They plotted equivalent conductivity versus $\sqrt{c}$ below the CMC and found a slope different from that expected for a simple 1:1 electrolyte. Tanford[8] determined the maximum number of monomers in a spherical micelle and since the

aggregation number of CTAB exceeds this, CTAB micelles are probably ellipsoidal even at low concentrations and undergo a transition to rod-shaped micelles at a concentration of about 5 percent by weight.[23,42,43] The fraction of counter-ions bound to the micelle depends on concentration of the surfactant, temperature, additives, and method of determination. The following values have been obtained: 0.884 at 30° using light scattering,[44] osmotic pressure,[1] and a bromide-ion electrode;[45] 0.78[38] and 0.75-0.80[46,47] at 25° from potentiometry; and with conductivity, 0.74 at 0.02 M CTAB and 0.65 at 0.1 M CTAB.[48] Variations may be attributed to the different methods used.

The head groups on the micellar surface are heavily hydrated, according to Ekwall,[37] having approximately 70 water molecules per group, measured by viscometry and sedimentation. In the presence of 0.2-0.4 M KBr, the micelles had 40 molecules of water per head group.[49]

With added inorganic salts, the CMC decreases in most cases and the aggregation number increases.[50] For example, with KBr the following aggregation numbers were found: 174[51] with 0.013 M KBr and 207[52] with 0.0125 M KBr at 25°; and 80[53] in 0.003 M KBr and 270[53]-288[54] with 0.025 M KBr at 30°. Salts also alter the micellar shape, producing rod-like micelles at high concentrations.[49,55] This would be expected since an increase in the anion

concentration of the bulk solution increases counterion binding, produces a lower surface potential and consequently allows more head groups to become incorporated into the Stern layer. Likewise, an increase in aggregation number usually produces a shape change.

NaBr produces an increase in viscosity[27] indicative of an increase in micelle size. Magid[27] found that other salts produced similar changes according to the lyotropic series. In the presence of 0.1 M NaBr, 0.1 M CTAB solutions also increase in viscosity with certain added organics including benzoic acid, 1-hexanol, and benzene.[27] Certain organic salts such as sodium p-toluenesulfonate and sodium p-toluate produce large increases in viscosity with subsequent decreases, while others do not.[56,57] It has been postulated[56] that those which do produce an increase in viscosity do so because they are sorbed in the Stern layer and decrease the distance between the head groups. Some organic solutes similarly increase viscosity while others do not. It is thought that those which do, are surface solubilized, and those which produce no change are solubilized in the micellar core or not at all. Strictly speaking, solubilization refers to the transfer of a solute in its pure state to the micellar phase while binding of the solute to the micelle means transfer of the solute from the aqueous phase to the micellar phase.[58]

Counterion binding is affected by solutes as well. Competition for binding to the micelle between added salt anions and those initially bound has been studied extensively, and displacement of bromide by other anions follows the lyotropic series.[27] In CTAB solutions containing NaBr, a small change in counterion binding with added organic solutes was observed in one study[27] while no change was observed in another.[47] Bunton[59] found that 75 percent of added sodium p-toluenesulfonate, a large organic anion, binds to the micelles (0.003 M CTAB) and interacts with the head groups.[60] He has observed this from NMR data.[57,60]

The heat of transfer of inorganic anions to CTAB micelles also follows the lyotropic series such that the anions which are least hydrated have the ability to approach the head groups more closely and show the most favorable binding.[27] Organic compounds produce changes in heats of binding which do not correspond to the viscosity changes. The ΔH_{trans} of NaBr from water to 0.1 M CTAB decreases slightly in the presence of benzoic acid or carbon tetrachloride, while the viscosity increases significantly.[27] In general, organic solutes are proposed to be initially surface solubilized and undergo a transfer to the micelle interior at higher solute concentrations. Aromatic compounds are thought to interact with the head group as has been illustrated. This postulate has been strengthened by

spectral studies.[61] Sepulveda[61] further proposed that the binding of organic anions to CTAB is via sorption in the Stern layer with a certain number of CTAB head groups associated with each anion. This number, n_s, varies with the anion.

When n-hexane is transferred from water to micelles, a large positive entropy change results which may be due to the loss of water of hydration accompanying the normal transfer of methylene groups from water to a hydrocarbon environment.[27] In a comparison of the heats of transfer of a number of organic compounds to CTAB micelles and to organic solvents, Magid[27] suggested that phenol and p-nitrophenol undergo surface solubilization to CTAB micelles since their heats of solution in CTAB are similar to those in methanol, which would have a dielectric constant similar to that of the CTAB surface.

B. Sodium Dodecyl Sulfate

The CMC of sodium dodecyl sulfate (NaLS) is 8.2×10^{-3} M[5] as determined by surface tension. There are approximately 40[62] to 62[53,63] monomers per micelle increasing to between 126[64] to 142[63] in the presence of 0.50 M NaCl. Tanford's[8] calculations indicate that slightly above the CMC the micelles are slightly ellipsoidal. They become rod-like at concentrations above 25 percent surfactant by weight.

Courchene[65] estimated that the head groups are hydrated with 10-12 water molecules per anion, but Mukerjee found only six molecules per group, being the same before and after micellization.[66] The fraction of bound counterions has been determined by various techniques. The values average 0.7-0.8[17,64,67-73] but vary widely from 0.46[50] to 0.86[74]. The fraction of bound counterions also varies with concentration and added solutes. The counterions in the Stern layer are completely hydrated[9] and the water molecules undergo rapid exchange with those in the solvent. The micellar surface is rough since approximately two thirds of it consists of the hydrocarbon portions of the molecules in contact with water.

In the presence of different cations, there is competition for binding between those of the original solution and those which have been added. A lyotropic series is followed by the heats of transfer of cations from water to the micelles. The ions which are least solvated, and thus have the possibility of closest approach to the head groups, give the most favorable heats of binding.[27]

The viscosity of 0.1 M NaLS solutions containing 0.025 M 1-hexanol and KBr did not change.[27] Similarly, no change resulted in 0.1 M to 0.3 M NaLS solutions containing NaBr and organic solutes.

Counterion binding studies indicate that organics like benzene are solubilized in the micellar core[75] while incorporation of 1-hexanol causes a release in counterions indicating it to be radially arranged.[76]

A more thorough discussion of the properties of NaLS, especially those concerning the thermodynamics of micellization in the presence of added solutes, may be found in Magid.[27]

CHAPTER III

EXPERIMENTAL SECTION

A. Basic Equipment

The melting points of organic compounds were measured on a Thomas Hoover Capillar Melting Point Apparatus (6406-H) equipped with a 6407-A Periscopic Thermometer Reader. The apparatus was calibrated prior to each determination. Distilled water for the experiments was provided by a Kontes WS-2 continuous water still. Weighings were done on a Mettler H20T analytical balance having an accuracy of ± 0.01 mg.

A constant temperature bath maintained at 24.95 ± 0.06°C was used for viscometry and counterion binding studies. The temperature was measured with a Beckmann thermometer, calibrated against a platinum resistance thermometer. The platinum thermometer was calibrated at the freezing and boiling points of water.

All glassware was washed with soap, rinsed repeatedly with tap water, rinsed with deionized distilled water and dried in an oven. No organic solvents were employed.

Diluted solutions were prepared by pipetting stock solution into a volumetric flask and then filling to the mark.

B. Statistical Methods

When a number of physical determinations of an experimental quantity was made, certain values were neglected based on the 95 percent confidence level criterion.[77] Standard deviations were computed using Equation 1.

$$\sigma = \sqrt{\sum_{i=1}^{n} (X_i - M)^2/(N-1)} \quad . \tag{1}$$

When calculations involving two or more numbers and their associated standard deviations were done, the standard deviation of the result (σ_p) was calculated according to the method found in Daniels.[78] Equations 2, 3, and 4 were used to calculate the associated standard deviations for the operations of addition (subtraction), multiplication, and division, respectively.

$$\sigma_p = \pm \sqrt{a^2 + b^2} \tag{2}$$

$$\sigma_p = \pm \sqrt{(Ab)^2 + (Ba)^2} \tag{3}$$

$$\sigma_p = \pm 1/A \sqrt{b^2 + B^2a^2/A^2} \tag{4}$$

Capital letters stand for numbers while small letters represent their associated standard deviations. In Equation 4, A represents the divisor.

C. Calorimetry

The calorimetric measurements were made in a system which has been previously described.[79,80] A typical run consisted of filling each of the twin calorimeters with 200.0 ml of the solvent using a volumetric pipet, inserting the flasks into metal cans, and, in turn, inserting the cans into large polyethylene Dewar flasks filled with ice water. In this way the temperature inside the calorimeters could be controlled well over long periods of time (several hours) and variations in room temperature. In this study all measurements were made at 25 ± 1°C. The stirred solutions were allowed to equilibrate for 30 minutes after the initial temperature adjustment to 25° and between runs for 15 minutes.

Solid injections were made with airtight 3 cc syringes with the tips cut off and fitted with teflon plugs. The samples were weighed into the syringes approximately one hour before use. Liquid samples were delivered from a 500 µl Hamilton syringe with a Chaney adaptor and teflon needle on a Luer tip. The syringes were calibrated using brass stops by weighing several injections of absolute ethanol into a stoppered Erlenmeyer flask.

The NaLS solutions were prepared immediately before use. CTAB solutions were often prepared as much as an hour

earlier to allow complete solution without excessive heating. Warming the solutions to about 26° was necessary to speed this process.

Experimental heats were measured from deflections on a strip chart recorder which was calibrated prior to each injection. During a calibration, a heating curve was run by introducing a known amount of heat in calories from an electrical heater. The calculations were made according to Equation 5 in which I is the current through the heater, Q_e is the heat introduced into the system from the heater in calories, c is the calorimeter constant, and t is the time of heating in seconds. (C is simply the heater resistance divided by the conversion factor 4.184 joules per calorie.)

$$Q_e = I^2 \, t \, c \, . \tag{5}$$

Dividing Q_e by Δ^C, the deflection of the strip chart recorder in millimeters, gives the calories per millimeter of pen deflection for a run. The enthalpy of solution was then determined according to Equation 6 in which Δ^R is the pen deflection of a run in millimeters, MW is the molecular weight of the solute, and mg is the weight of the sample in milligrams. The calculation of ΔH_s using the above units

$$\Delta H_s = Q_e/\Delta^C \cdot \Delta^R \cdot MW/mg \tag{6}$$

gives the enthalpy change in kcals per mole.

D. Determination of Critical Micelle Concentrations from Surface Tension Measurements

The purity of NaLS samples was determined by measuring the CMC of each batch from the surface tension of solutions of different concentrations. A number of concentrations above and below the CMC were used and the CMC determined from the intersection of the two lines obtained. The measurements were made on a Du Noüy tensiometer equipped with a platinum-iridium ring which was rinsed in distilled water and blotted dry between runs. It was handled with forceps at all times. At least three determinations were made on each solution and the average used. All solutions were at the same temperature, approximately 23°, and prepared immediately before use.

Plots of surface tension (γ) versus surfactant concentration gave two interesting lines, and the CMC was the point of intersection. The same result was obtained by plotting the direct readings from the tensiometer versus surfactant concentration. To convert the tensiometer readings to surface tension in dynes per centimeter, the dynes per scale division was determined by loading the ring with weighed pieces of wire and measuring the amount of force necessary to just lift the weight. The force per scale reading was then calculated by dividing the weight by the

scale reading and multiplying by 981 (the appropriate proportionality constant).

E. Viscometry

The viscosity of the soap solutions was measured using Ostwald Capillary Viscometers which had been rinsed several times with distilled water and dried in an oven. To each viscometer was added 5.5 ml of the solution to be run, and the solutions were allowed to equilibrate in a constant temperature bath for at least 30 minutes. In measuring flow times, the solution was drawn up into the bulb of the viscometer using a rubber squeeze bulb, attached to a piece of Tygon tubing into which a small wad of cotton had been inserted. Flow times were obtained using a Haydon electronic stop clock and recorded to the nearest tenth of a second. At least five determinations were made on each solution and the average calculated.

Equation 7, which takes kinetic energy into account, was used to calculate the viscosities (η_{KE}). A and B are constants, ρ is the solution density, and t is the flow time in seconds.

$$\eta_{KE} = A\rho t - B\rho/T \ . \qquad (7)$$

A and B were determined by measuring the flow times and densities of carbon tetrachloride, distilled water, benzene,

and methanol and using their viscosities at 25° obtained from the Handbook of Chemistry.[81] The constants for each viscometer were calculated from the resulting four simultaneous equations. A was the same in all cases while B varied. Only the standard deviation in the flow time was used in the final calculations since those associated with A and B were relatively insignificant. Densities were determined using a 25 ml jacketed pycnometer after equilibration of the solution for 30 minutes in the constant temperature bath.

F. Counterion Binding Studies

Counterion binding to CTAB micelles was measured with the Orion Model 701 digital pH/mV meter, the Orion Model 94-35 bromide-ion electrode, and the Orion Model 90-02 double junction reference electrode. The reference electrode has two chambers. The inner chamber was filled with solution 90-00-02 and the outer chamber was filled with solution 90-00-03, 10% KNO_3. These solutions were changed weekly.

Theoretically, the measured potential of a solution containing Br^- using an electrode sensitive to Br^- can be calculated from Equation 8 in which Ea depends on the reference electrode and filling solution employed.

$$E = Ea + 2.3\ RT/n_eF\ (\log a_{Br^-}) \ . \qquad (8)$$

Experimentally, a series of NaBr solutions was prepared, and their potentials were measured and plotted versus log a_{Br^-} of the surfactant solution. The a_{Br^-} of the standard solutions was obtained from Latimer.[82] At 25° the slope of the calibration plot should be -59.16 mv; it was actually -57 mv. The effect of liquid junction potentials is expected to be very small and was neglected.

Bound bromide was calculated by subtracting the measured free bromide from the original soap concentration. The concentration of nonmicellar molecules was neglected.

The soap and salt solutions were prepared, poured into 50 ml beakers, and placed in a constant temperature bath at 25° for at least 30 minutes before measuring the potential. A calibration plot of standards was prepared before each set of soap solutions was run, and the potential of a standard solution was measured directly before each soap solution measurement. When the electrodes were moved from one solution to the next, they were rinsed several times with deionized distilled water and blotted. It took up to ten minutes to obtain a constant millivolt reading since a slight initial drift often occurred.

G. Preparation and Purification of Surfactants

1. Hexadecyltrimethylammonium Bromide (CTAB)

The surfactant CTAB (City Chemical Corporation) was recrystallized twice from carbon tetrachloride and dried in

vacuo at 55°. The resulting crystals were fine white needles. This method was chosen since it gives no minimum in the surface tension plot as did other methods.[27] Titration of the surfactant with $AgNO_3$ yielded a molecular weight of 364.7 ± 1.3 (true molecular weight 364.5).

2. Sodium Dodecylsulfate (NaLS)

The surfactant NaLS was prepared by the method of Kurz.[83] Using a 1000 ml three-necked flask fitted with a dropping funnel, condenser and drying tube containing 4Å molecular sieves, chlorosulfonic acid (Eastman--0.28 moles) was added slowly with stirring to 90 ml of anhydrous diethyl ether (Fisher) maintained at 0° with an ice bath. 1-Dodecanol (0.225 moles--Eastman, showed only one peak in gas chromatograph) was added to 160 ml ether, and this solution was added (dropping funnel) to the acid-ether solution held at 0° over a period of 45 minutes. This mixture was stirred at room temperature for one hour, poured over ice, neutralized with 5 N NaOH, extracted with 1-butanol, and dried over sodium sulfate. The crude surfactant was collected by evaporating the 1-butanol and recrystallized in 1-butanol. During collection of the final product, repeated washings of the crystals with ether was done to remove any unreacted 1-dodecanol. This method provided 49.1 grams (75.7 percent) of surfactant with a CMC of 7.2×10^{-3} M, measured by surface tension (lit.[5] 8.2×10^{-3} M).

H. Organic Compounds Used in Calorimetry

The organic solutes used without purification are listed in Table I. Those which were purified and the methods of purification are as follows:

1. p-Aminobenzoic Acid

p-Aminobenzoic acid (Matheson, Coleman, Bell) was recrystallized twice from 95 ~~percent~~ ethanol and dried *in vacuo* at 55° overnight, m.p. 186.5-187.0° (lit.[84] 187-188°).

2. Benzamide

Benzamide (Matheson, Coleman, Bell) was recrystallized twice from acetone-water and dried *in vacuo* at 55°, m.p. 125.5-127.0° (lit.[85] 130°).

3. o-Chlorobenzoic Acid

o-Chlorobenzoic acid (Eastman) was recrystallized from carbon tetrachloride-acetone and dried *in vacuo* at 55°, m.p. 139.3-139.8° (lit.[86] 140.2°).

I. Salts Used in Calorimetry, Viscometry, and Counterion Binding Studies

The organic salts used in this study were purified as is discussed below. NMR and infrared data indicated only one compound to be present in the purified materials.

TABLE I

ORGANIC COMPOUNDS USED IN CALORIMETRIC STUDIES

Compound	Source and Grade	Melting Point, °C
Benzoic acid	Fisher Scientific, Certified A. C. S.	122.0-122.5 (lit.[b] 122.4)
2-Butanone	Mallinckrodt, Analyzed Reagent	--
Catechol	Matheson, Coleman, Bell	103.2-103.5 (lit.[b] 105)
Chlorobenzene	Matheson, Coleman, Bell	--
p-Chlorobenzoic acid	Eastman	240-241 (lit.[b] 240)
Chloroform	Baker Analyzed	--
Cytosine	Aldrich, Chromatographically pure	--
1-Hexanol[a]	Eastman	--
Hydroquinone	Baker Chemicals	171.5-172.0 (lit.[b] 172.3)
p-Hydroxybenzoic acid	Matheson	213.5-214.3 (lit.[b] 214.5-215.5)
Methyl butyrate	Eastman	--
Methyl salicylate	Fisher Scientific U. S. P.	--
Methylene chloride	Baker, Analyzed	--
Nitrobenzene	Fisher Scientific Certified A. C. S.	--
p-Nitrobenzoic acid	Eastman	238.0-239.0 (lit.[b] 240)

TABLE I (Continued)

Compound	Source and Grade	Melting Point, °C
p-Nitrophenol	Matheson, Coleman, Bell	112.5-113.5 (lit.[b] 113-114)
Uracil	Aldrich, Chromatographically pure	--

[a]Major component 75 percent by gas chromatography.

[b]"Handbook of Chemistry," 10th ed., N. A. Lange, Ed., McGraw Hill, New York, N. Y., 1967.

1. Phenyl Disodium Phosphate

Phenyl disodium phosphate (Fisher A. C. S. Reagent) was stored in a cold room and used without purification.

2. Sodium Benzenesulfonate

Sodium benzenesulfonate (Eimer and Amend) was recrystallized twice from absolute ethanol, dried overnight at 120° and stored over Drierite.

3. Sodium Bromide

Sodium bromide (Mallinckrodt, Analytical Reagent), used in the standardizations for counterion binding studies, was dried to constant weight and stored over Drierite.

4. Sodium p-Toluate

Sodium p-toluate was prepared from p-toluic acid by neutralization with NaOH. The crude toluate was collected by evaporating the water and was recrystallized from ethanol-water. The final product was dried in an oven (120°) for 24 hours and stored over Drierite.

5. Sodium p-Toluenesulfonate

Sodium p-toluenesulfonate (Eastman) was dried to constant weight and stored over Drierite until used.

CHAPTER IV

RESULTS AND DISCUSSION

Even though a vast amount of experimental data has been gathered concerning the interactions of organic compounds and salts with CTAB micelles, the nature of these interactions and the forces involved is still uncertain. In a recent article[61] Sepulveda derived an equation for the equilibrium constant (K_s) for binding of some aromatic salts to CTAB micelles based on UV absorbance measurements. He determined K_s for each of four anions: sodium p-toluenesulfonate (TOS), sodium p-toluate (TOL), sodium benzenesulfonate (BS), and disodium phenyl phosphate (PP). Since the complete thermodynamics of binding to CTAB for this group of compounds would aid in the characterization of these interactions, this study was undertaken combining Sepulveda's K_s values with calorimetric measurements of ΔH_{trans} from water to CTAB.

In determining K_s, Sepulveda employed the mass-action model for micelle systems. There are, in fact, at least three thermodynamic models for micelles:[27] (1) the pseudo-phase model, in which the CMC represents a saturation point (for monomers in the solution) at which micelles form and become a separate phase; (2) the mass-action model, based

on multiple equilibria between micelles, monomers, and counterions, which takes into account physical parameters such as aggregation number and counterion binding; and (3) a modification of the mass-action model which includes the calculation of the electrical free energy of the micelles.

For micelles having large aggregation numbers, the pseudophase model may be used.[6] This model assumes that the micelles are a completely separate phase in the overall system and thus a partitioning of added solute between the two phases occurs. The free energy of micellization (ΔG_{mic}) is calculated by RT ln(CMC) where the CMC is expressed in mole fractions units.[3] In this treatment the loss of entropy experienced by the monomers is accounted for but similar effects on the counterions are ignored.[58,87] The change in free energy on binding (ΔG_{trans}) of the solute to the micelle is calculated from the partition coefficient (K_p):

$$K_p = [X_{mic}]/[X_{aq}] \quad . \qquad (9)$$

$[X_{mic}]$ is the concentration of the solute in the micellar phase and $[X_{aq}]$ is the concentration of solute in the aqueous phase. Thus, ΔG_{trans} is $-RT \ln(K_p)$. Some writers[3] oppose this model because it predicts that changes occurring at the CMC will be very sharp, it gives different results for the chain length dependence of the free energy of micellization for ionic and nonionic surfactants, and it predicts

enthalpies of micellization which are contrary to experimental results. There are those, however, who defend it.[28,64]

The mass-action model is represented by Equation 10 in which S^+ is a surfactant monomer, X^- is a counterion, M is the micelle containing n monomers and m counterions and thus having a net charge of n-m. Activity coefficients of

$$nS^+ + mX^- \rightleftharpoons M^{(n-m)+}; \quad K_M = \frac{f_M[M]}{f_{S^+}{}^n[S^+]^n \, f_{X^-}{}^m[X^-]^m} \tag{10}$$

the various components are designated by f with the corresponding subscript. The expanded form of the equation for ΔG_{mic} is given in Equation 11, but it is usually written

$$\Delta G_{mic} = (-kT/n)(\ln f_M + \ln[M] - n \ln f_{S^+} - n \ln[S^+] - m \ln f_{X^-} - m \ln[X^-]) \tag{11}$$

as follows:

$$\Delta G_{mic}/kT = (-\ln f_M)/n - (\ln[M])/n + \ln f_{S^+} + \ln[S^+] + (m \ln f_{X^-})/n + (m \ln[X^-])/n . \tag{12}$$

Since the CMCs are small, f may often be neglected. $[S^+]$ is the concentration of unassociated surfactant (CMC), [M] is often taken as 2 percent of the surfactant at the CMC, and

m/n denotes the fraction of bound counterions and may be experimentally determined.

A modification of the mass-action model takes the electrical free energy of the micelles into account.[3] In this model, X^- and f_{X^-} are replaced in Equation 12 by F_{el}/kT as shown in Equation 13. nF_{el} represents the changes in electrical free energy during micelle formation.

$$\Delta G_{mic}/kT = -(\ln f_M)/n - (\ln[M])/n + \ln f_{S^+} + \ln[S^+] - F_{el}/kT \qquad (13)$$

Both the mass-action model and modified mass-action model have been used by Mukerjee[3] with NaLS. They give different results. Mukerjee favors the former since it gives a value closest to that experimentally observed. The latter may ignore the loss of entropy of the counterions which is taken into account by $\ln[X^-]$ in the mass-action model.

An alternative and more flexible treatment of binding to micelles uses the Langmuir adsorption equation which also takes the effects of counterion binding and aggregation number into account. The Langmuir parameters for a certain system, K_L and n_L, are calculated as in Equation 14 and ΔG_{trans} for this type of system is $-RT \ln(K_L)$.

$$K_L = \{[X_{mic}]/(1 + K_L[X_{aq}])\}/([X_{aq}]n_L) \; . \qquad (14)$$

Therefore, Sepulveda's K_s, derived from a model based on binding sites similar to the Langmuir model, will give an accurate thermodynamic characterization of the system at the concentrations used in his experiments. His initial equilibrium expression (Equation 15) describes the association of a free anion with an unoccupied micellar site, $(CTA)_s$, to give a bound anion (a_b).

$$a_f + (CTA)_s \rightleftharpoons a_b \tag{15}$$

The equilibrium constant (K_s) is

$$K_s = C_{a_b}/C_{a_f} C_{(CTA)_s} \tag{16}$$

in which the concentrations of a_f, a_b, and $(CTA)_s$ are, respectively, C_{a_f}, C_{a_b}, and $C_{(CTA)_s}$. The total concentration of CTAB (neglecting the small amount of unassociated monomers) is C_{CTAB} (Equation 17).

$$C_{CTAB} = n_s(C_{(CTA)_s} + C_{a_b}) \tag{17}$$

In this equation Sepulveda assumes that at each site there are n_s molecules of CTAB and thus the number of CTAB molecules at a site (n_s) times the total number of sites should equal the total CTAB concentration. From UV absorbance measurements he derived an expression for the fraction of solute (f) bound to the micelle (Equation 18) in which $C_a{}^t$

is the total concentration of anions ($C_{a_b} + C_{a_f}$), A is the total absorbance, and E_{a_b} and E_{a_f} are the absorptivities of the bound and free anions, respectively:

$$f = (A - C_a^t E_{a_f})/\{C_a^t (E_{a_b} - E_{a_f})\} . \qquad (18)$$

Combining Equations 16, 17, and 18, he obtained an equilibrium expression (K_s) based not on a simple partitioning of the solute between two phases but on a dynamic equilibrium involving micelles, bound anions, and free anions:

$$K_s = n_s f/(1 - f)(C_{CTAB} - n_s f C_a^t) . \qquad (19)$$

Rearranging, he obtained the following form of the equation which gives K_s and n_s when experimental data are plotted:

$$C_a^t(1 - f) = -1/K_s + (C_{CTAB}/n_s)\{(1 - f)/f\} . \qquad (20)$$

Thus, the K_s obtained is one describing not a simple partitioning of the solute between two phases but the multiple equilibria between the anions and micelles, and the ΔG_{trans} calculated from it defines the same process. Therefore, in this study the thermodynamic parameters reported will be for this model.

The other parameter obtained from this plot (n_s) is supposedly the number of CTAB molecules associated with each anion at a binding site. According to this definition, at

at a certain concentration of CTAB, the number of micelles, and thus the number of sites, should be fixed and added anion should sorb to these sites until a saturation point is reached. After this point additional salt should not be sorbed but should instead be dissolved in the bulk solution or become solubilized in the micellar core. If this were indeed occurring, counterion binding to the micelles should reflect such a change. Bound counterions are freed when salts, which sorb to the micelle, are added. If further additions of salt cannot be sorbed and must become dispersed in some other way, this change should be observed. Therefore, we have studied the change in counterion binding which occurs in these solutions over a range of concentrations around n_s. The changes observed in both counterion binding and viscosity indicate that what occurs in these systems is more complicated than the simple saturation of micellar sites.

We have also undertaken the complete thermodynamic characterization of this system using K_s, based on the multiple-equilibria model, and calorimetric measurements of ΔH_{trans}. This study will be discussed first.

A. Thermodynamics of Transfer for Aromatic Anions from Water to Hexadecyltrimethylammonium Bromide Micelles

The heats of transfer from water to 0.01 M CTAB were measured calorimetrically at 25°C for four salts: sodium

p-toluenesulfonate (TOS), sodium p-toluate (TOL), sodium benzenesulfonate (BS), and disodium phenyl phosphate (PP). This CTAB concentration was used since Sepulveda's study[61] showed that this was the minimum concentration at which a maximum amount of the added salt should interact with the micelles. Also, calculations of the percent bound bromide at the salt and soap concentrations employed in this study showed that greater than 99.9 percent of the salt is bound.

The enthalpies, free energies (calculated from Sepulveda's K_s), and the entropies of transfer from water to the micelle are given in Tables II and III. The equilibrium constants and therefore the calculated free energies (which are large and negative) indicate that the anions have a high affinity for the micelles. The corresponding enthalpies are small and show no discernible pattern. The striking part of these data is the large positive entropy which accompanies all transfers and provides the driving force for the transfer. Thus, the transfer of these salts from water to CTAB micelles (at 0.01 M CTAB) is entropy-controlled.

What is the source of the entropy control? If the solute interacts with or sorbs in the Stern layer of the micelle and displaces some of the water of hydration around the head groups, the liberation of the hydrating water should provide a favorable ΔS of transfer. At the same time any solvent structuring due to the anion itself would also be

TABLE II

ΔH_{trans} FOR BINDING OF ORGANIC ANIONS TO 0.01 M CTAB AT 25°C

Salt	$\Delta H_{s(CTAB)}$ kcal/mole	$\Delta H_{s(H_2O)}$[a] kcal/mole	ΔH_{trans} kcal/mole
PP	-0.550 ± 0.131	-3.82 ± 0.21	3.27 ± 0.25
TOL	-1.64 ± 0.14	-1.17 ± 0.11	-0.47 ± 0.18
BS	0.445 ± 0.173	1.70 ± 0.18	-1.25 ± 0.25
TOS	1.17 ± 0.23	2.54 ± 0.60	-1.37 ± 0.64

[a]Obtained from Magid, Reference 27.

TABLE III

THERMODYNAMIC PARAMETERS FOR BINDING OF AROMATIC ANIONS TO 0.01 M CTAB AT 25°C

Salt	ΔH_{trans} kcal/mole	ΔG_{trans}[a] kcal/mole	ΔS_{trans} eu
PP	3.27	-5.61	29.8
TOL	-0.47	-5.92	18.3
BS	-1.25	-5.80	15.3
TOS	-1.37	-5.92	15.3

[a]Calculated from equilibrium constants derived by Sepulveda, Reference 61.

diminished. (On the basis of one diffusion study,[88] it has been argued that BS is a structure breaker rather than a structure maker. The method is untested and this conclusion is regarded as somewhat questionable in the absence of supporting data.) If the solute solubilizes in the core, rather than in the Stern layer, only the former change may occur; i.e., the solute loses its effect on the bulk solution but the head groups remain hydrated. Finally any changes produced by added salt on the system as a whole will have a large effect on any measured parameters. (Large salt concentrations have been shown to produce marked changes in micelle systems.[27]) We will assume, however, that at the salt concentrations employed ($\leq 10^{-3}$ M) there is little, if any, effect on the bulk solution produced by the added salt. We can assume this because the salt concentrations are very small and calculations indicate that essentially all of the salt is bound to the micelle. Therefore, the salts should produce no change in the bulk solution which would disturb the micellar systems as a whole, and any observed changes should occur as a result of the binding of the salts to the micelles.

Since it is known that most aromatic compounds bind in the Stern layer, the above description of entropy control (in which sorption of the solute causes a certain amount of dehydration of the head groups as well as the solute) would

appear to be reasonable. Exactly how these anions are oriented in the Stern layer is of considerable interest. It is known that at a concentration of 0.01 M, CTAB micelles are slightly ellipsoidal,[8] have approximately 75 percent of their counterions bound,[38,46-48] and are the main form of CTAB in the solution.[61] When TOS is added to the system, it almost quantitatively interacts with the micelles, as observed by Sepulveda[61] and calculated in this study. Most experimental work[59-61] indicates that TOS is sorbed in some fashion to the Stern layer such that the sulfonate anion is oriented toward the outer surface of the micelle and the p-methyl substituent is aimed toward the core. The exact mode of orientation which has been proposed[61] for TOS (but which may be used for all of these salts) is that the anionic portion of the salt is located between the cationic head groups, and the ring and connected p-methyl group are submersed in the hydrocarbon core. This postulate is based on the UV absorbances of the aromatic anions in solutions of varying dielectric constant.[61] When TOS (and other aromatic anions) interact with CTAB micelles, their absorbances are similar to those in a solvent of very low dielectric constant. The Stern layer is thought to have a dielectric constant of around 36[16] and since the absorbances indicate the rings to be in a medium of much lower dielectric constant, they are probably in the core.

The results of this thermodynamic study are consistent with this model. Strong entropy control of the binding process comes from a decrease in the solvent structure around the head groups and solute, when the solute is sorbed. In addition, systems in which water structuring is thought to be a major factor, exhibit enthalpy-entropy compensation.[29] When the data in Table III (page 39) were plotted as ΔH_{trans} versus ΔS_{trans}, a typical straight line with a slope of 312°K was observed, as shown in Figure 2. (A similar plot, having a slope of 285°K, was obtained in a study of the binding of certain organic solutes to 0.1 M CTAB micelles.[89]) If plots of this type do indicate water structure effects, then the binding of the aromatic anions to CTAB micelles is largely controlled by solvent structuring.

The only other observation which may be made concerning the thermodynamics of these systems is that phenyl phosphate is quite different from the other three anions. Its heat of transfer is positive and its entropy of transfer is almost twice that of any of the other salts. Also, even though the K_s for binding of PP to the micelles is quite large, it is the smallest of the series. A study of the competition between these salts for binding on the micelle should show that the other salts displace PP. Something to this effect has been observed in catalysis studies,[59] where it was shown that certain aromatic sulfonates and carboxylates suppress

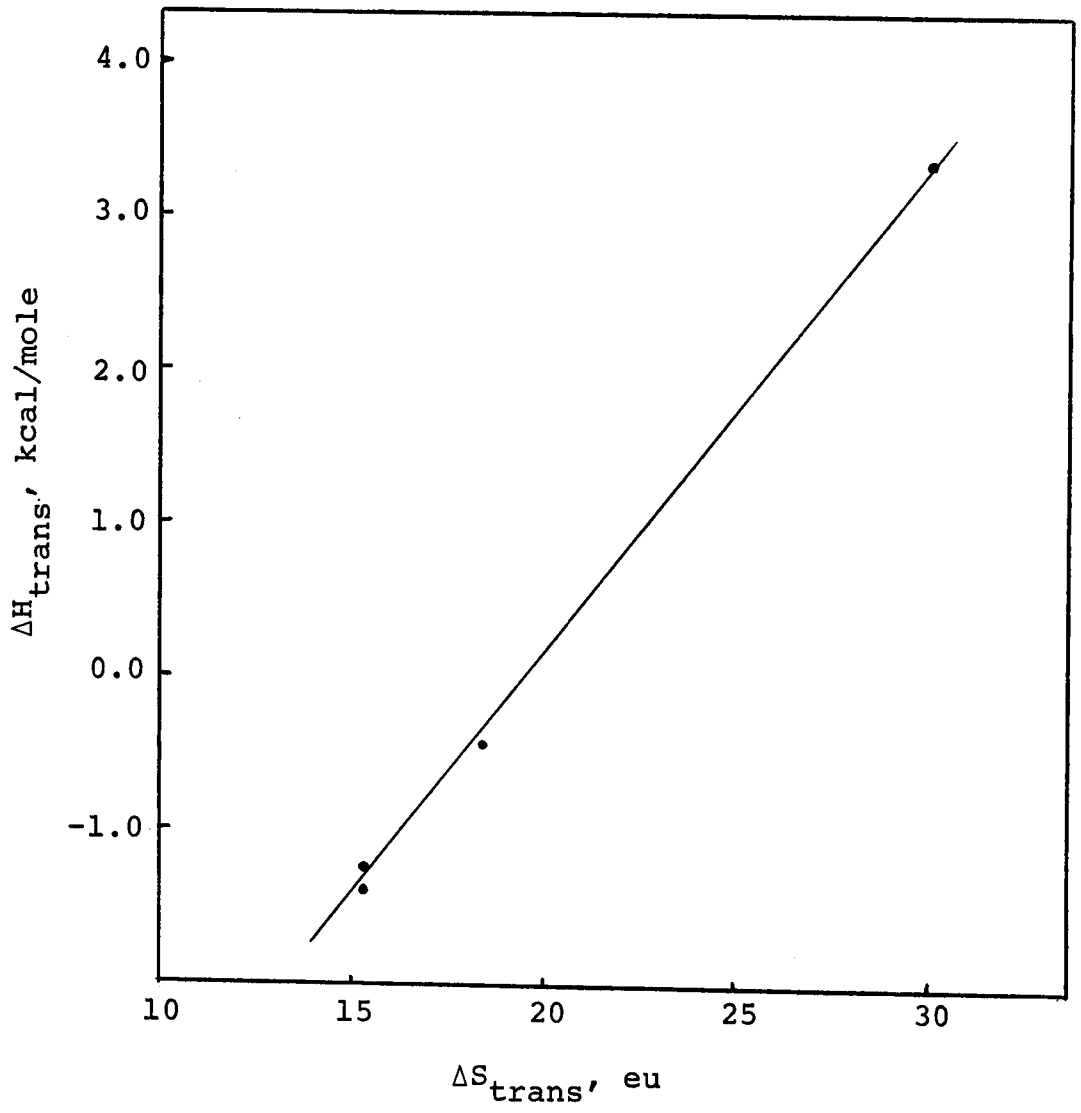


Figure 2. ΔH_{trans} versus ΔS_{trans} of organic anions from water to 0.01 M CTAB at 25°C.

the hydrolysis of some aryl phosphates. What the difference between phenyl phosphate and the other anions is which causes PP to be catalytically and thermodynamically distinct is unknown.

Finally, it was found that the heat of transfer of TOS to CTAB micelles is dependent on surfactant concentration. The data are listed in Table IV and plotted in Figure 3. A concentration of approximately 0.001 M TOS was used for each determination. Why there is an apparent minimum at about 0.06 M CTAB is unknown. Since the heat of solution of TOS in water is positive (2.54 kcal/mole), this minimum must represent the most favorable binding in terms of enthalpy. The curve might represent the effect of structural changes in CTAB micelles in the presence of 0.001 M TOS from spherical to rod-shaped with increasing concentrations. It would be interesting to see if the other salts in this series have similar dependences.

B. Counterion Binding and Viscosity Studies on Hexadecyltrimethylammonium Bromide Solutions Containing Aromatic Anions

Sepulveda[61] proposed that every micelle is composed of a certain number of sites at which n_s molecules of CTAB associate with each sorbed anion. He observed that n_s varies with the anion added. If indeed what Sepulveda was observing

TABLE IV

CONCENTRATION DEPENDENCE OF ΔH_{trans} FOR 0.001 M TOS IN CTAB

[CTAB], M	$-\Delta H_{s(CTAB)}$ kcal/mole	ΔH_{trans}[a] kcal/mole
0.100	0.564 ± 0.232	-1.98 ± 0.64
0.060	0.316 ± 0.380	-2.22 ± 0.71
0.030	0.654 ± 0.133	-1.89 ± 0.61
0.010	1.17 ± 0.23	-1.37 ± 0.63

[a] $\Delta H_{s(H_2O)}$ = 2.54 ± 0.60 kcal/mole.

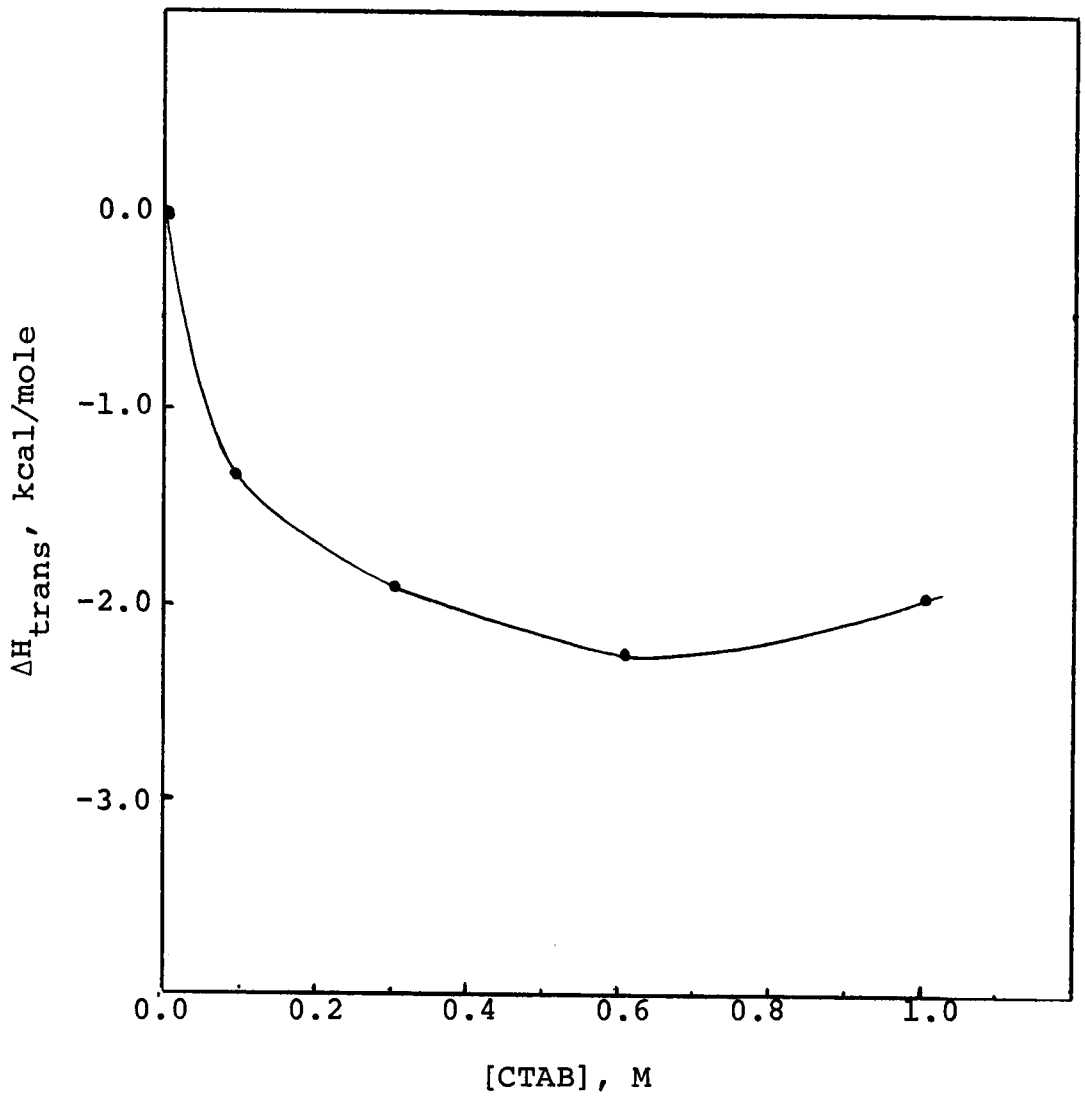


Figure 3. Concentration dependence of ΔH_{trans} for 0.001 M TOS to CTAB solutions.

at n_s was a saturation of sites on the micelle, it seemed probable that this could also be observed in the counterion binding. Thus the percentage of counterions bound to the micelle at a concentration of 0.01 M CTAB was determined over a range of concentrations of Sepulveda's salts. As was mentioned in the previous section, this CTAB concentration was used since at that concentration the maximum amount of added anion (approximately 100 percent) is associated with the micelle, according to Sepulveda's absorbance studies[61] and calculations of percent bound anion.

The percentage of counterions bound to the micelles of 0.01 M CTAB with increasing concentrations of the four anions was determined. The results (see Appendix Tables VIII, IX, X, and XI) were plotted as shown in Figures 4, 5, 6, and 7. In all solutions there was a decrease in bound bromide with added salt; however, in each case a break point in the plot was observed. The concentration of the salt required to produce such a break was different in each case, and calculation of the ratios of soap concentration to salt concentration producing each break point gave the following numbers: TOS, 1.8; TOL, 2.0; PP, 3.0; and BS, 2.3. These are strikingly close to the n_s values determined by Sepulveda: TOS, 1.3; TOL, 1.3; PP, 2.0; and BS, 2.5. It would therefore appear that the change in these systems, observed in the counterion binding, is related to the parameter measured by Sepulveda.

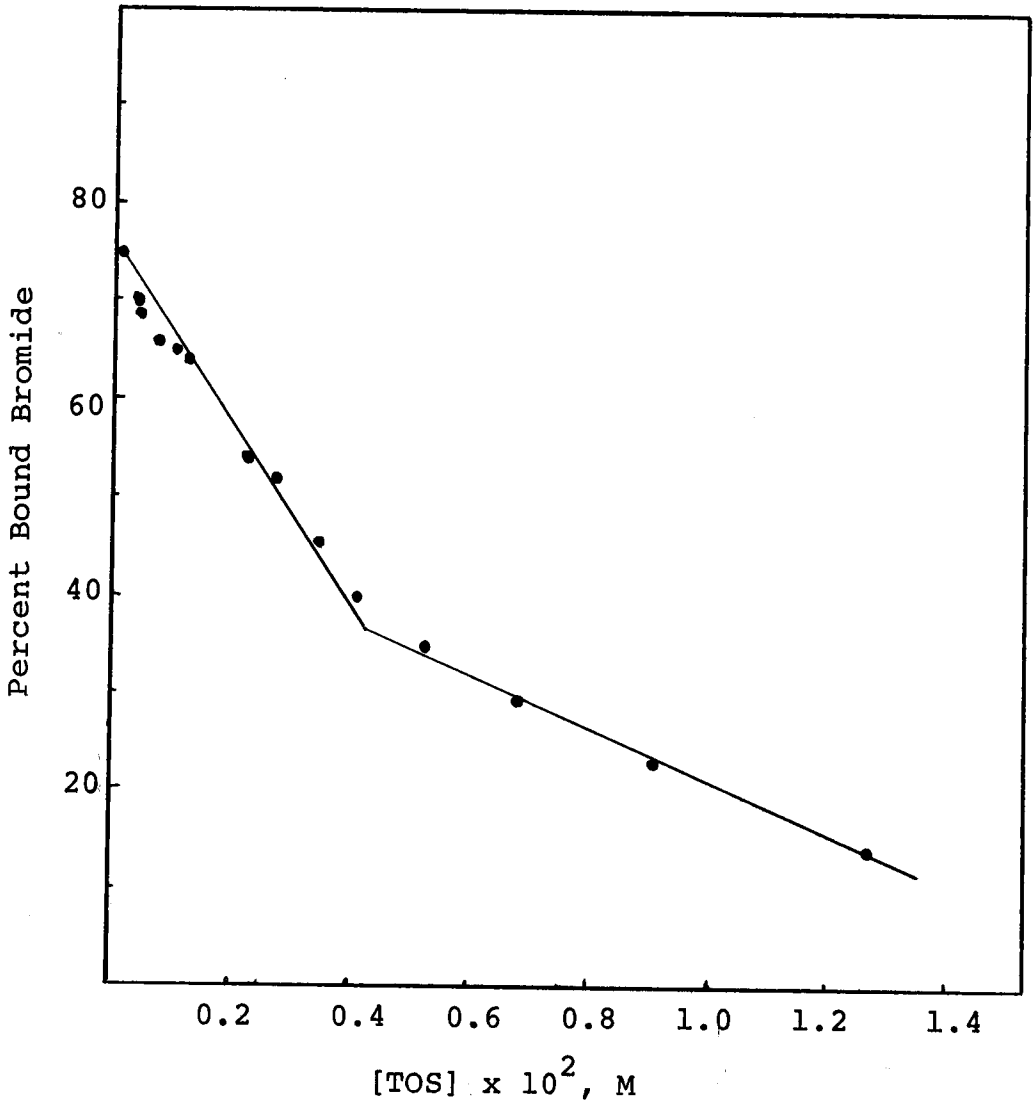


Figure 4. Dependence of bromide binding to 0.01 M CTAB micelles on TOS concentration.

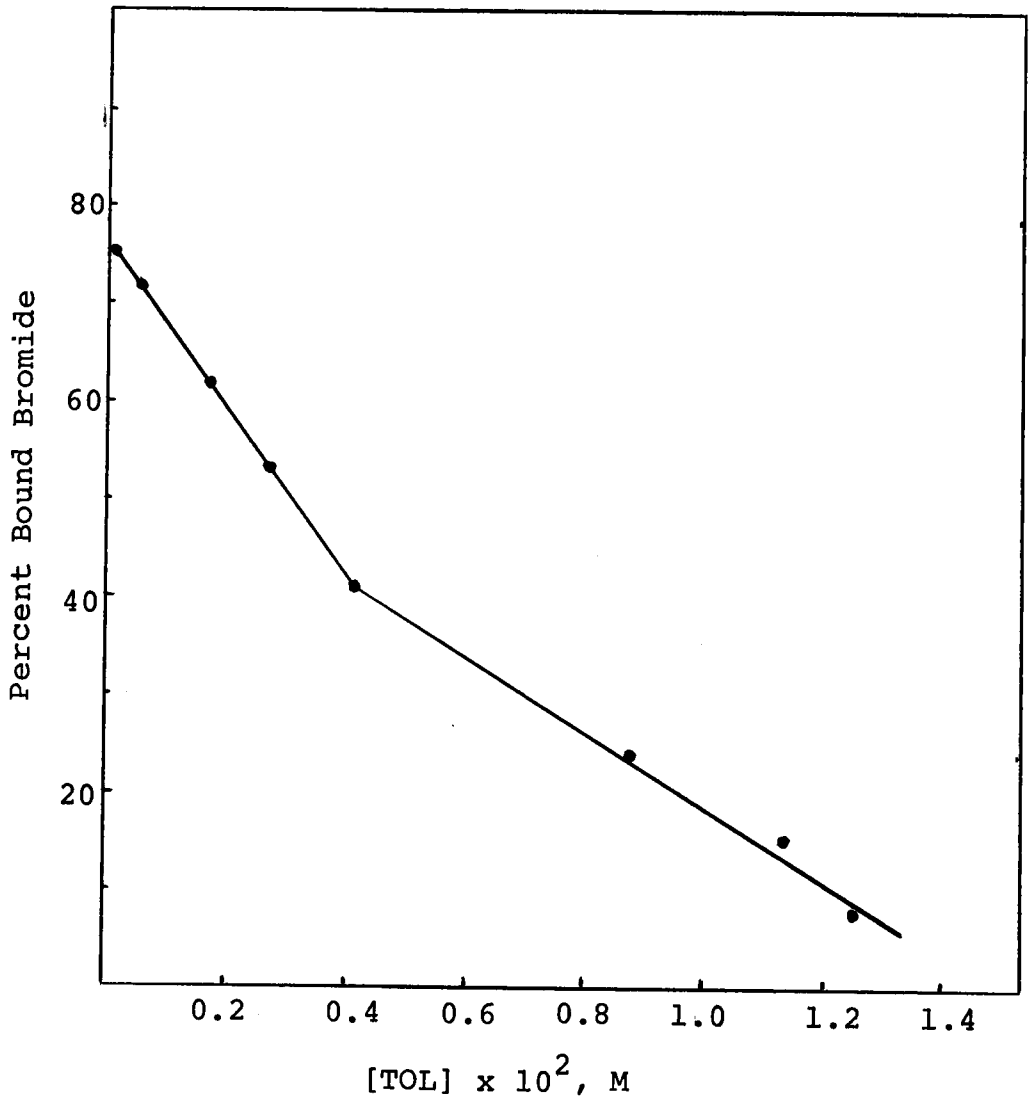


Figure 5. Dependence of bromide binding to 0.01 M CTAB micelles on TOL concentration.

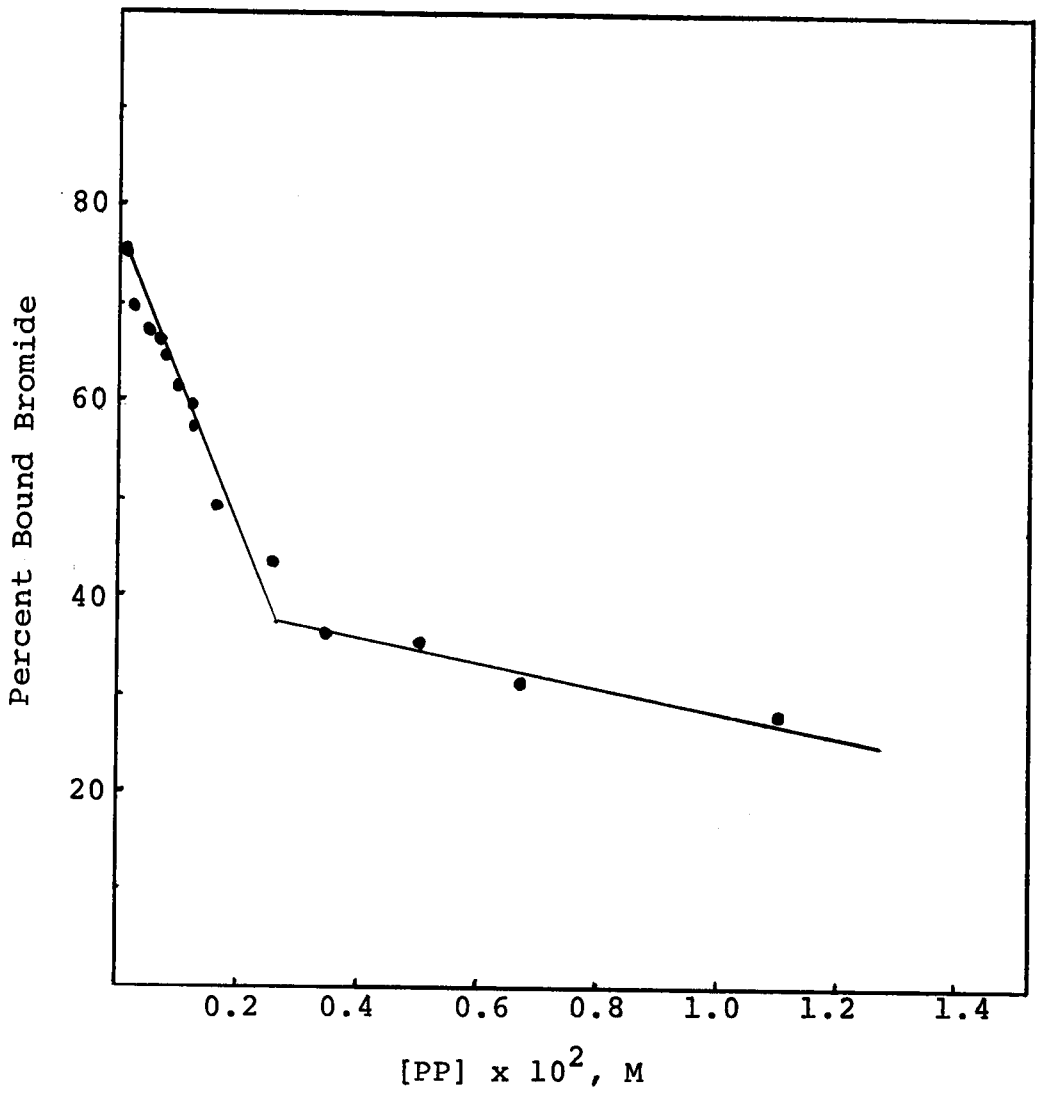


Figure 6. Dependence of bromide binding to 0.01 M CTAB micelles on PP concentration.

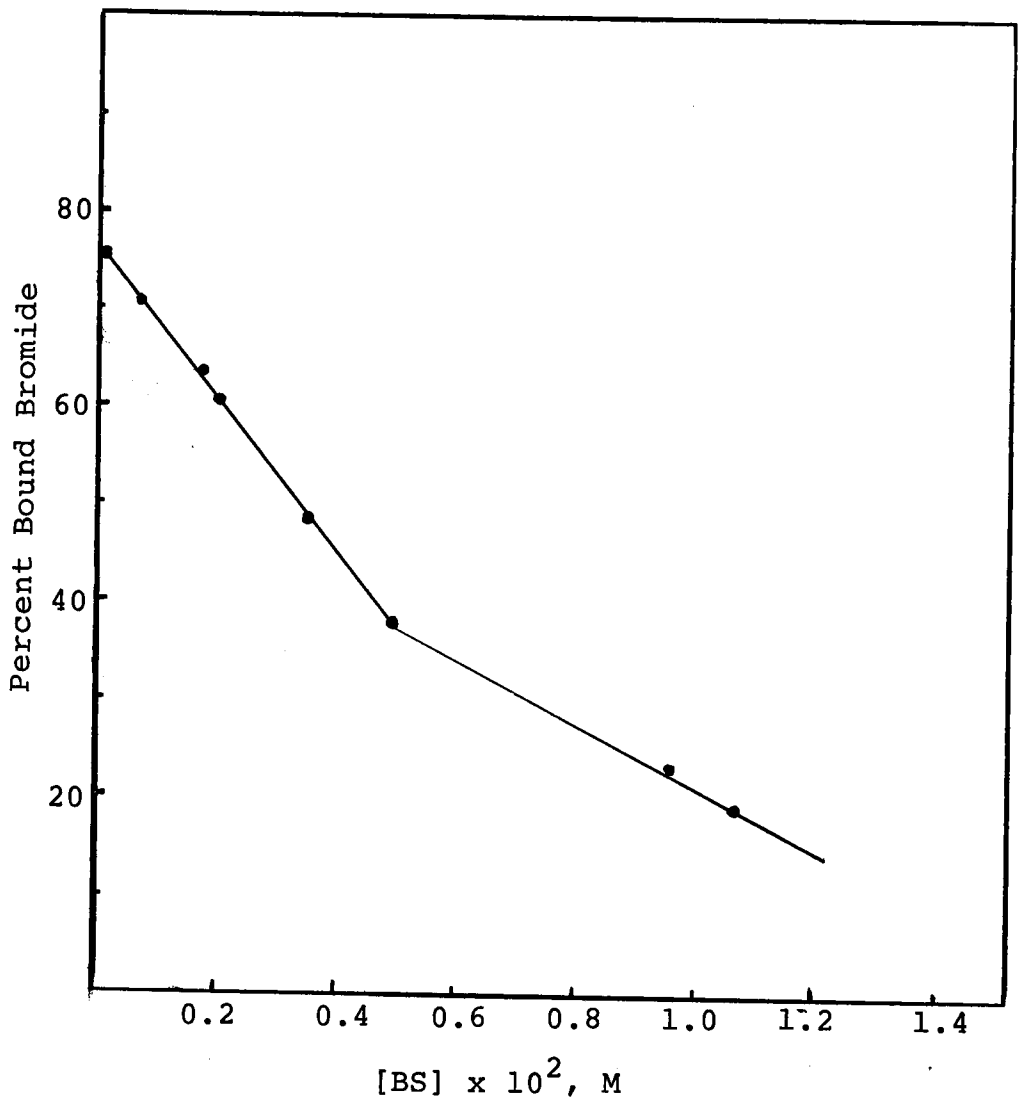


Figure 7. Dependence of bromide binding of 0.01 M CTAB micelles on BS concentration.

Changes in counterion binding may be observed in conjunction with a number of changes in the micellar environment including changes in micellar size and shape,[45] decreases in surface potential,[27] solubilization,[27,43,46,47,90] and binding of substances to the micellar surface.[27] Any type of surface sorption of the anions is expected to decrease bound bromide. A change in the type of sorption, ease of sorption, or micellar size might produce a break in the plot. However, if there are a certain number of sites, each containing n_s CTAB molecules, then at a salt concentration large enough to saturate these sites, the counterion binding to the micelle should reach a minimum. No such minimum is observed. Also, Bunton has shown that CTAB micelles undergo a large increase in size at high concentrations of certain anions followed by a decrease with additional salt.[56,57] He also found that at high TOS concentrations, the micelles have a negative charge.[57,60] Neither of these facts would support the existence of a saturation point. Thus the break point in counterion binding in the system, if not a saturation point, must reflect a change in either mode of binding or micellar size. To check this hypothesis a further study was made.

During the counterion binding measurements, it was observed that changes in viscosity occurred in solutions containing TOS and TOL while none appeared to occur with BS

and PP. To quantitatively measure these changes and thus any changes in micellar size and shape, the viscosities of solutions having the same CTAB to salt concentration ratios, as were studied with counterion binding, were measured. The results (Table XI, Appendix), illustrated in Figures 8, 9, 10, and 11, show large increases in viscosity occurring in solutions containing TOS and TOL at a concentration ratio of CTAB to salt of n_s (TOS: 1.5, TOL: 1.3) with no corresponding change with BS or PP.

Thus there is a major difference between the binding of TOS and TOL to CTAB micelles and that of BS and PP. The binding in all four systems yields basically similar thermodynamic properties, counterion binding tendencies, equilibrium constants, and UV absorbances, but the changes in viscosity between the two pairs of anions are vastly different. The viscosity increases in TOS and TOL solutions, indicative of increases in micellar size or elongation, have been attributed to their p-methyl groups.[61] What effect these substituents have and how they alter the micelle in such a way to produce such drastic changes is not known; however, the size change may be due to micellar elongation. This explanation would account for the large initial decrease in bound bromide, i.e., the displacement of bound bromide by the salt is favorable and results in micellar stabilization and decreased repulsions between the head groups. As the

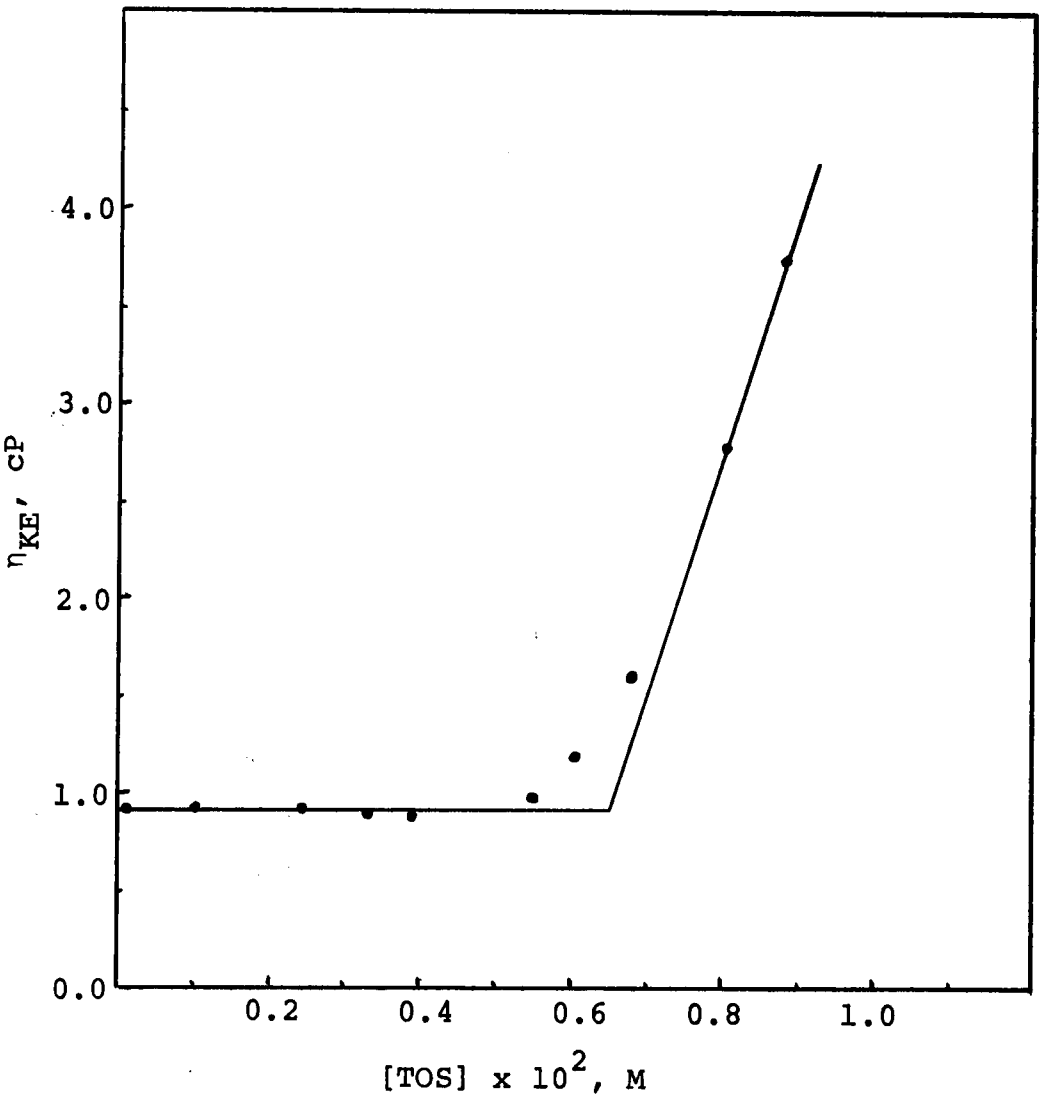


Figure 8. Dependence of viscosity of 0.01 M CTAB solutions on TOS concentration at 25°C.

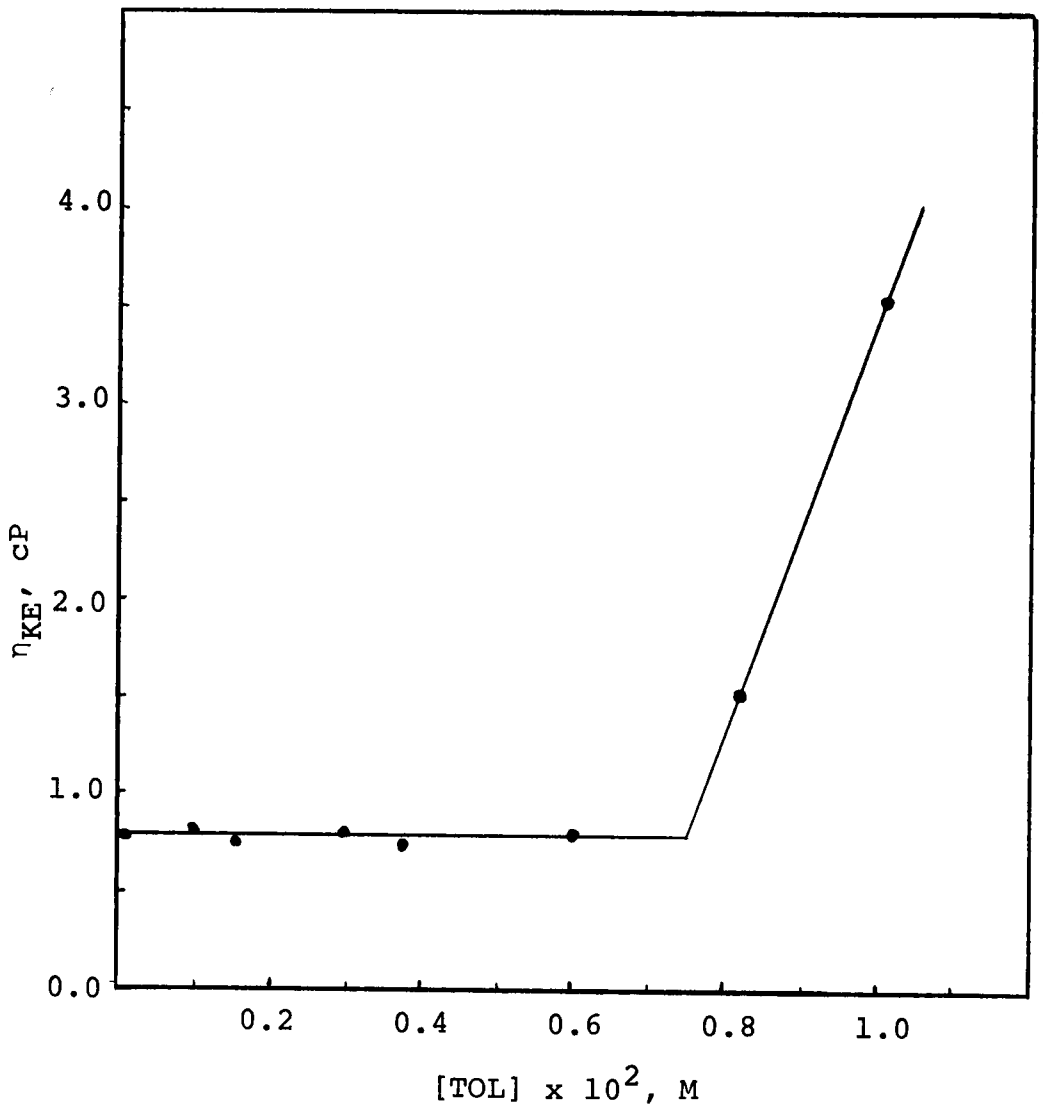


Figure 9. Dependence of viscosity of 0.01 M CTAB solutions on TOL concentration at 25°C.

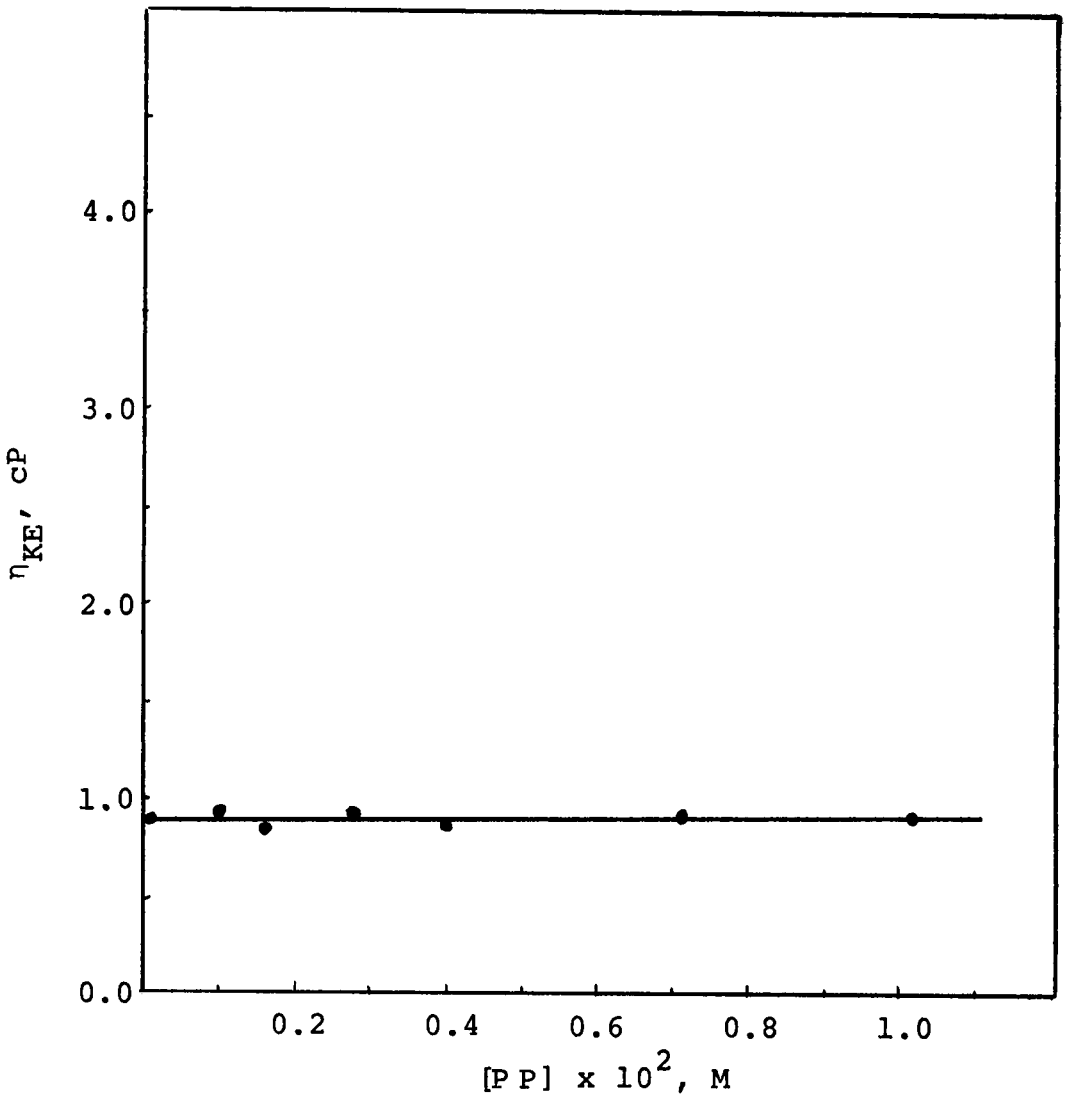


Figure 10. Dependence of viscosity of 0.01 M CTAB solutions on PP concentration at 25°C.

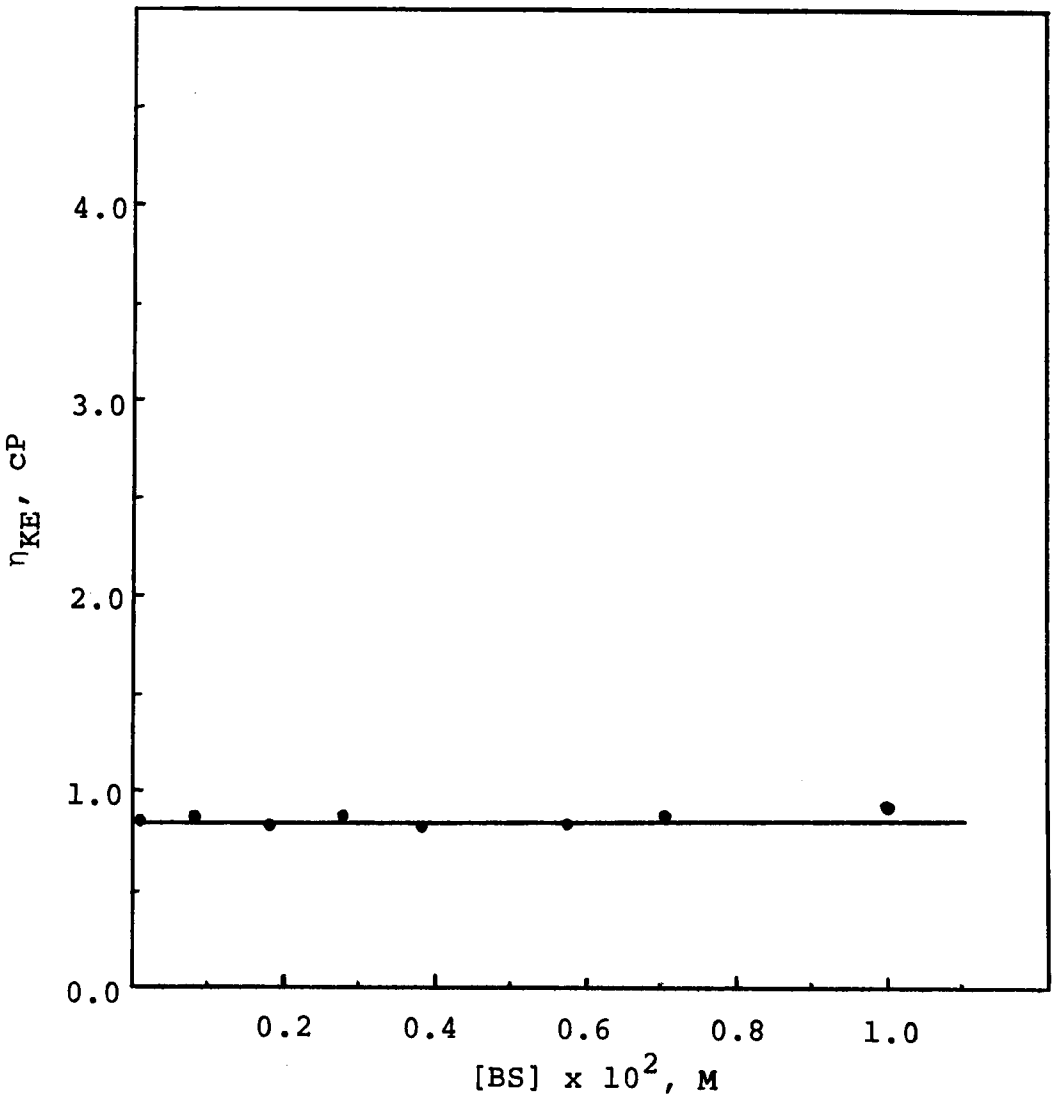


Figure 11. Dependence of viscosity of 0.01 M CTAB solutions on BS concentration at 25°C.

salt concentration is increased, a point is reached at which maximum stabilization of the micelles, due to incorporation of the salt, has been achieved and further incorporation initiates a change in size and shape.

What happens with BS and PP is less certain. A similar change in counterion binding occurs but there is no corresponding change in size or shape. It would appear that in these systems, some other mode of orientation of the anions in the micelle exists after the break point.

If it is true, that the p-methyl group on TOS and TOL causes the micelle to change shape and size, one might expect an even more pronounced viscosity change in systems in which the salt has a p-isopropyl or p-t-butyl substituent. Such a study would prove interesting.

C. Calorimetry of Binding of Organic Compounds to Sodium Dodecyl Sulfate

Many studies of the interaction between organics and CTAB have been done, however, very little is known about the thermodynamic transfer of organics from water to NaLS. Since CTAB and NaLS have similar carbon chains and differ mainly in their head groups, a comparison of the transfer of organic molecules to each might provide an insight into which interactions are controlled by the nature of the head group and which are associated with the alkyl chain. (The

comparison of the results in 0.1 M CTAB and 0.04 M NaLS should be reasonable since at that concentration each has approximately the same aggregation number and micelle shape.[8,37-40,53,63] Using a larger concentration of NaLS might complicate the system since NaLS has a second CMC at about 0.065 M.[91]) Magid[27] studied the heats of transfer to CTAB for a number of organics. The ΔH_{trans} for many of the same compounds to NaLS were measured in this study and are reported.

There is a major problem associated with measurements of this type: i.e., we assume that all of the added solute in some way associates itself with the micelle. The assumption that the heats measured are those of a 100 percent transfer of the solute from the bulk solution to the micelle may not be valid. It is important to know what portion of the added solute associates with the micelle and how much remains in the bulk solution. If essentially all of the solute is found in the micelle, the ΔH_{trans} will be the single difference between the heats of solution in the micellar solution and in the water. However, if significant amounts of solute are present in the aqueous part of the micellar solution, the measured ΔH's must be recalculated to take this difference into account. Unfortunately, in most cases this information is not available. The problems involved with measuring this partitioning are substantial. In fact,

to this writer's knowledge the relative solubilities of the compounds studied in NaLS at 0.04 M are unknown. However, the solubilities of the compounds studied in water are generally quite low and therefore most should undergo association with the micelles. Also, in most cases, the observed heats were not concentration dependent suggesting that the solutes were associated with the micelles. We shall assume then that the added solute is completely associated with the micelle recognizing that further data in these systems may vitiate this assumption. Based on current knowledge, it seems reasonable.

The results are shown in Table V. As a whole, the heats are small and show no logical relationship to the compounds and their structures. In Table VI the heats of transfer of the aromatic solutes to CTAB and to NaLS are compared. These data are plotted in Figure 12. Since the aromatic ring is thought to play an important role in the binding, this comparison should be of importance. The only generality which may be drawn, however, is that the heats of transfer of the aromatic compounds to CTAB are more negative (except for o-chlorobenzoic acid) than to NaLS. Thus the interaction of the cationic head groups with these solutes must be more favorable than the corresponding sulfate-aromatic solute interaction. In fact, it has been shown that a favorable interaction between tetrasubstituted

TABLE V

ΔH_{trans} FOR ORGANIC SOLUTES FROM WATER TO 0.04 M NaLS MICELLES

Solute	$\Delta H_{s(NaLS)}$ kcal/mole	$\Delta H_{s(H_2O)}$ [b] kcal/mole	ΔH_{trans} kcal/mole
Chlorobenzene	0.278 ± 0.076[a]	-0.053	0.328
o-Nitrobenzoic acid	5.36 ± 0.66	5.06 ± 0.60	0.30 ± 0.89
Nitrobenzene	1.32 ± 0.10[a]	1.050	0.27
Methyl salicylate	0.667 ± 0.066	0.489 ± 0.629	0.178 ± 0.153
Uracil	6.55 ± 0.21[a]	6.40 ± 0.20	0.15 ± 0.29
Methylene chloride	-0.243 ± 0.015	-0.349 ± 0.100	0.106 ± 0.100
2-Butanone	-2.61 ± 0.04	-2.71 ± 0.03	0.10 ± 0.05
Methyl butyrate	-1.82 ± 0.04	-1.85 ± 0.13	0.03 ± 0.14
Benzamide	4.59 ± 0.14	4.60 ± 0.39	-0.01 ± 0.41
1-Hexanol	-1.21 ± 0.05	-1.11 ± 0.08	-0.10 ± 0.09
Cytosine	4.87 ± 0.16	5.15 ± 0.06	-0.28 ± 0.17
Hydroquinone	4.60 ± 0.23	4.97 ± 0.10	-0.37 ± 0.25
Chloroform	-0.683 ± 0.018	-0.167 ± 0.068	-0.516 ± 0.070
p-Nitrophenol	4.47 ± 0.23	5.16 ± 0.27	-0.69 ± 0.35
p-Aminobenzoic acid	4.80 ± 0.26	5.58 ± 0.70	-0.78 ± 0.75
o-Nitrophenol	3.65 ± 0.20	4.49 ± 0.22	-0.84 ± 0.30
Catechol	0.41 ± 0.06	2.23 ± 0.19	-1.82 ± 0.20
p-Hydroxy-benzoic acid	4.98 ± 0.21	6.83 ± 0.12	-1.85 ± 0.24
o-Chlorobenzoic acid	4.30 ± 0.26	6.44	-2.14
Benzoic acid	4.39 ± 0.15	6.92 ± 0.04	-2.53 ± 0.16
o-Hydroxy-benzoic acid	4.41 ± 0.46	7.70 ± 0.20	-3.29 ± 0.50

[a] Linear least squares analysis. See Appendix, Table XIII.

[b] From Magid dissertation, Reference 27.

TABLE VI

COMPARISON OF ΔH_{trans} OF AROMATIC SOLUTES TO NaLS AND CTAB MICELLES

Solute	ΔH_{trans} (NaLS) kcal/mole	ΔH_{trans} (CTAB)[a] kcal/mole
Nitrobenzene	0.49	-0.90 ± 0.08
o-Nitrobenzoic acid	0.30 ± 0.89	-1.72 ± 0.79
Chlorobenzene	0.32	-0.74 ± 0.05
Methyl salicylate	0.178 ± 0.633	-0.38 ± 0.63
Benzamide	-0.01 ± 0.41	-0.87 ± 0.40
Hydroquinone	-0.37 ± 0.25	-3.45 ± 0.11
p-Nitrophenol	-0.69 ± 0.35	-6.03 ± 0.29
p-Aminobenzoic acid	-0.78 ± 0.75	-1.18 ± 0.72
o-Nitrophenol	-0.84 ± 0.30	-2.55 ± 0.39
Catechol	-1.82 ± 0.20	-5.30 ± 0.33
p-Hydroxybenzoic acid	-1.85 ± 0.24	-5.13 ± 0.25
o-Chlorobenzoic acid	-2.14	-1.72 ± 0.79
Benzoic acid	-2.53 ± 0.16	-4.62 ± 0.21
o-Hydroxybenzoic acid	-3.29 ± 0.50	-5.32 ± 0.24

[a]From Magid dissertation, Reference 27.

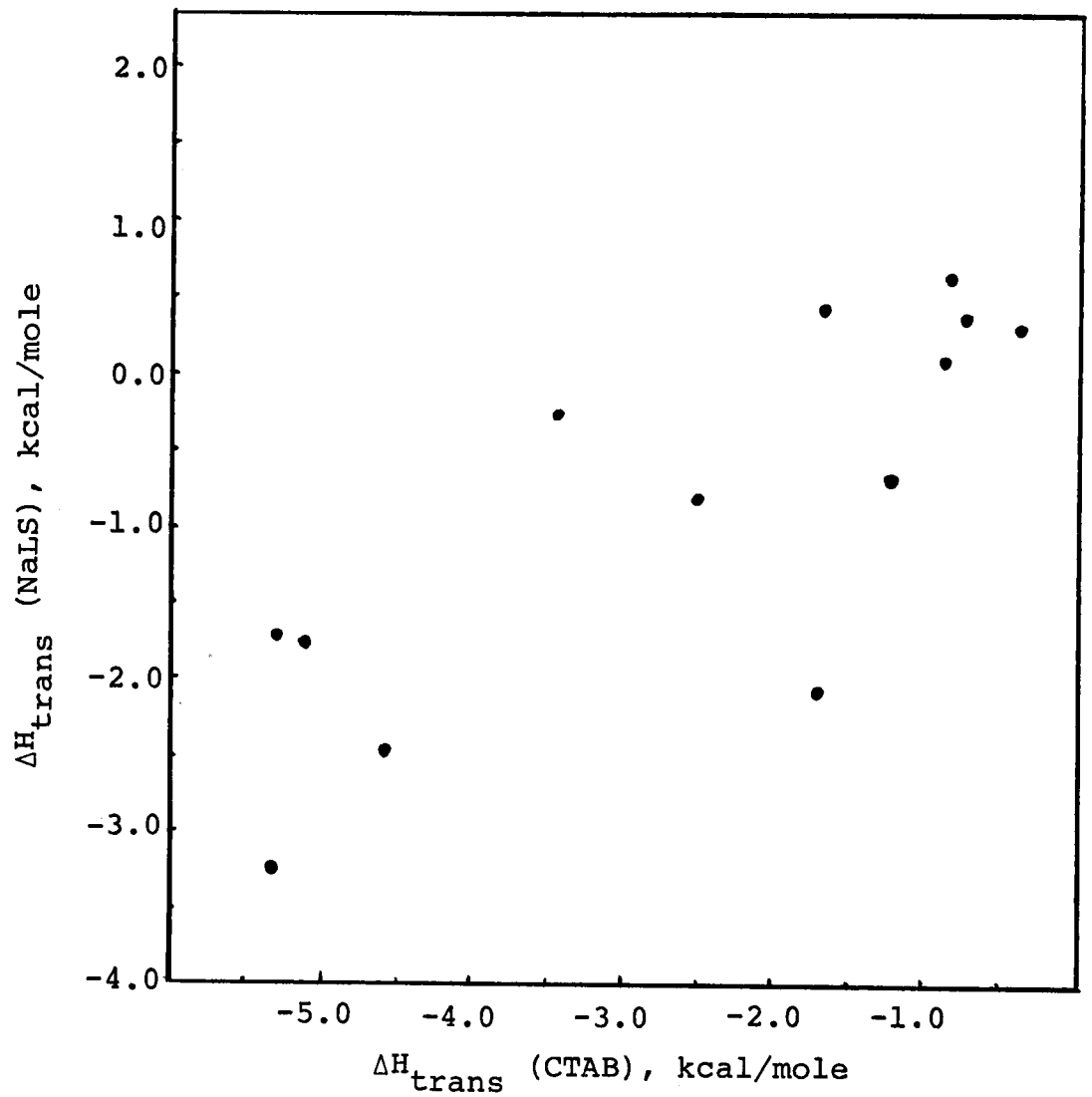


Figure 12. Comparison of ΔH_{trans} of organic solutes from water to NaLS and CTAB.

ammonium groups and aromatics does exist.[92] Whether such an interaction between sulfate and aromatics exists is not known to this writer's knowledge.

In Table VII the heats of solution in NaLS and CTAB of a few of these compounds are compared with those in solvents of differing dielectric constant and other properties. Again, there is no consistent similarity. However, several of the solutes have a heat of solution in NaLS which is quite close to that in n-hexane. These, chlorobenzene and benzoic acid, may be undergoing solubilization in the micellar core.

D. Conclusions

In this study, it has been shown that binding of aromatic anions to CTAB is entropy-controlled and exhibits typical enthalpy-entropy compensation behavior, indicative of a control on the binding produced by changes in water structure. It was observed that phenyl phosphate differs in some way from the other salts, and this difference makes it less readily sorbed in the Stern layer and yet makes its entropy of binding to the micelles almost twice as large as that of the other salts. No conclusions on this point could be drawn.

The decrease in counterion binding and the break points which occur indicate that some change in the system occurs when a certain concentration ratio of CTAB to salt is

TABLE VII

COMPARISON OF ΔH_s OF SOME AROMATIC SOLUTES IN NaLS, CTAB AND TWO SOLVENTS

Solute	ΔH_s, kcal/mole			
	NaLS (0.04 M)	n-Hexane[a]	Water[a]	CTAB[a] (0.1 M)
Catechol	2.23	8.48	4.05	-1.25
p-Nitrophenol	4.47	2.03	5.16	-0.87
Nitrobenzene	1.32	2.77	0.28	0.16
Chlorobenzene	0.278	0.67	-0.05	-0.79
Benzoic acid	4.39	4.55	6.92	2.30
o-Nitrophenol	3.65	-	4.49	1.94

[a]From Magid dissertation, Reference 27.

reached. This may be due to either a change in micellar size and shape or a change in solute orientation within the micelle depending on the salt. The observed increases in viscosity in TOS and TOL solutions reveal that, at least in these systems, the micelles are undergoing a change in size or shape. This change may be due to the p-methyl group on these compounds which produces a different orientation of the solute in the micelle in these systems (after the break point concentration ratio) compared with that of BS and PP.

The results of the transfers of organics to NaLS are inconclusive. The fact that the heats of transfer of the aromatic compounds to CTAB are more favorable than those to NaLS could be accounted for by the more favorable interaction of the N-methyl groups with the aromatic ring. An interesting extension of these results and those concerned with aromatic anion binding to CTAB would be the study of cationic aromatics binding to NaLS. Finally, from a comparison of the heats of transfer to NaLS and those to other solvents, it appears that certain aromatics (benzoic acid and chlorobenzene) may be solubilized in the micellar core in NaLS rather than sorbed.

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APPENDIX

TABLE VIII

COUNTERION BINDING TO 0.01 M CTAB MICELLES IN THE PRESENCE OF BS AT 25°C

[BS] x 10^2, M	[Free Br^-], M	[Bound Br^-], M	Percent Bound Br^-
1.07	0.0081	0.0019	19
0.962	0.0077	0.0023	23
0.489	0.0062	0.0038	38
0.363	0.0052	0.0048	48
0.187	0.0040	0.0060	60
0.167	0.0037	0.0063	63
0.0698	0.0030	0.0070	70
0.00	0.0025	0.0075	75

TABLE IX

COUNTERION BINDING TO 0.01 M CTAB MICELLES IN THE PRESENCE OF TOL AT 25°C

[TOL] x 10^2, M	[Free Br^-], M	[Bound Br^-], M	Percent Bound Br^-
1.24	0.0092	0.0008	8
1.13	0.0085	0.0015	15
0.870	0.0076	0.0024	24
0.417	0.0059	0.0041	41
0.264	0.0047	0.0053	53
0.176	0.0038	0.0062	62
0.0518	0.0028	0.0072	72
0.00	0.0025	0.0075	75

TABLE X

COUNTERION BINDING TO 0.01 M CTAB MICELLES IN THE PRESENCE OF PP AT 25°C

[PP] x 10^2, M	[Free Br^-], M	[Bound Br^-], M	Percent Bound Br^-
2.00	0.0076	0.0024	24
1.11	0.0072	0.0028	28
0.670	0.0069	0.0031	31
0.500	0.0065	0.0035	35
0.385	0.0064	0.0036	36
0.298	0.0057	0.0043	43
0.200	0.0051	0.0049	49
0.131	0.0043	0.0057	57
0.125	0.0041	0.0059	59
0.098	0.0039	0.0061	61
0.080	0.0036	0.0064	64
0.065	0.0034	0.0066	66
0.057	0.0033	0.0067	67
0.023	0.0031	0.0069	69
0.000	0.0025	0.0075	75

TABLE XI

COUNTERION BINDING TO 0.01 M CTAB MICELLES IN THE PRESENCE OF TOS AT 25°C

[TOS] x 10^2, M	[Free Br^-], M	[Bound Br^-], M	Percent Bound Br^-
1.26	0.0086	0.0014	14
0.905	0.0077	0.0023	23
0.666	0.0071	0.0029	29
0.519	0.0065	0.0035	35
0.407	0.0060	0.0040	40
0.339	0.0054	0.0046	46
0.274	0.0048	0.0052	52
0.217	0.0046	0.0054	54
0.120	0.0036	0.0064	64
0.105	0.0035	0.0065	65
0.0656	0.0034	0.0066	66
0.0360	0.0031	0.0069	69
0.0250	0.0030	0.0070	70
0.000	0.0025	0.0075	75

TABLE XII

VISCOSITY OF 0.01 M CTAB SOLUTIONS
CONTAINING ORGANIC SALTS

Solute	[Solute], M	η_{KE}, cP
TOS	0.00	0.881
	0.00114	0.898
	0.00235	0.924
	0.00324	0.895
	0.00391	0.896
	0.00546	1.04
	0.00605	1.22
	0.00663	1.54
	0.00783	2.72
	0.00825	3.73
TOL	0.00	0.881
	0.00111	0.927
	0.00168	0.910
	0.00296	0.931
	0.00379	0.893
	0.00608	0.906
	0.00814	1.64
	0.00985	3.47
BS	0.00	0.881
	0.00100	0.925
	0.00196	0.898
	0.00305	0.920
	0.00412	0.893
	0.00589	0.885
	0.00723	0.905
	0.00996	0.972
PP	0.00	0.881
	0.00126	0.913
	0.00185	0.887
	0.00301	0.916
	0.00426	0.888
	0.00721	0.893
	0.01173	0.904

TABLE XIII

DEPENDENCE OF $\Delta H_{s\,(NaLS)}$ FOR SOME ORGANIC SOLUTES ON CONCENTRATION

Solute	Grams Added	$\Delta H_{s\,(NaLS)}$ kcal/mole
Chlorobenzene	0.057	0.222
	0.171	0.167
	0.285	0.120
	0.399	(-0.138)
	0.513	-0.0463
Nitrobenzene	0.063	1.36
	0.189	1.07
	0.315	1.00
	0.441	0.835
	0.567	0.906
Uracil	0.04250	6.60
	0.08747	5.89
	0.13144	5.61
	0.17691	5.73
	0.21269	5.47
	0.25779	5.27

VITA

Helen Lynn Button Tepley was born on January 15, 1950, to Mr. and Mrs. Paul S. Button in Jackson, Tennessee. In 1951 they moved to Chattanooga, Tennessee, where she was raised and attended Hamilton County Schools. In June, 1968, she graduated from Central High School as class Torchbearer and Valedictorian.

The author attended the University of Tennessee, Knoxville and graduated magna cum laude with a B.S. in Chemistry in June, 1972. While at UT she was a Neyland Scholar, Rhenium Scholar, and a member of Kappa Alpha Theta Fraternity, Mortar Board, Phi Beta Kappa, Phi Kappa Phi, Sigma Xi, and the American Chemical Society. During her last three years, she worked as a Resident Assistant and Assistant Head Resident in the UT Residence Hall System. Prior to her freshman year she met Steve Tepley whom she married in June, 1972.

The author took her graduate studies in chemistry at UTK from September, 1972, to December, 1974, and held a teaching assistantship throughout that time. In January, 1975, she enters the UT Medical School in Memphis.