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I am submitting herewith a dissertation written by Michael Thomas Carver entitled "Effects of Chlorobenzoate Counterions on the Structure and Properties of Hexadecyltrimethylammonium Surfactant Solutions." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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EFFECTS OF CHLOROBENZOATE COUNTERIONS ON THE STRUCTURE
AND PROPERTIES OF HEXADECYLTRIMETHYLAMMONIUM
SURFACTANT SOLUTIONS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
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Michael Thomas Carver

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To the memory of my grandfather,

H. S. Head

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ABSTRACT

Hexadecyltrimethylammonium surfactants with a number of mono- and dichlorobenzoate counterions were prepared by ion-exchange methods. Solutions of these surfactants were characterized by a number of techniques. Small-angle neutron scattering experiments were carried out to determine the size and shape of the micelles formed by several of the surfactants in water. Measurements of the electrical conductivity of the surfactant solutions were performed to determine their critical micelle concentrations and extents of counterion binding. Viscosity measurements, as a function of concentration, shear rate, and pH were made; proton and Carbon-13 nuclear magnetic resonance spectra of the solutions were recorded.

The results of these experiments indicate a strong dependency of the properties of the micellar solutions on the precise structure of the counterion of the surfactant. Solutions of a number of the surfactants exhibited strongly viscoelastic behavior; these solutions had low CMC values, high extents of counterion binding, and contained long cylindrical micelles. Solutions of the other surfactants exhibited normal viscometric behavior, contained approximately spherical micelles and had relatively low extents of counterion binding. Suggestions were advanced as to the cause of the observed counterion specificity.

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CHAPTER I

INTRODUCTION

A. General Remarks

The synonymous terms "surfactant" and "amphiphile" refer to substances whose molecules consist of two distinct parts--a hydrophobic tail, usually a straight or branched hydrocarbon chain, and a polar hydrophilic head, which may be either charged or uncharged. The significant property of these substances is their tendency to aggregate in solution--most importantly, in aqueous solution. In water, the hydrophobic tails of the surfactant molecules cluster together, creating a particle containing a hydrocarbon core, with polar groups at the surface serving to maintain solubility. The term "micelle" is generally applied to particles in solution consisting of aggregated amphiphilic molecules. Reverse micelles also exist; in these, the surfactant is dissolved in an organic solvent such as an aliphatic hydrocarbon, and the roles of the polar head group and the hydrocarbon tail are reversed. Surfactants, and the micelles they form, are often classified by their head groups as either ionic or nonionic. In this work, discussion will generally be limited to solutions of ionic surfactants in water.

Micelles in water may be small spheres, ellipsoids, or finite bilayer disks, depending upon factors such as concentration, added salt, and the structure of the surfactant molecules. The various

micelle structures are illustrated in Figure 1. A spherical ionic micelle may be described in terms of three geometric parameters.^{1,2} First, there is a characteristic optimum area per head group, which arises due to electrostatic repulsions between the head groups. Next, there is the micellar radius which cannot exceed a certain critical length, l_c , which is roughly equal to the length of the extended hydrocarbon chain. Finally, there is the volume per hydrocarbon chain in the core, v . Since a sphere has a fixed surface-to-volume ratio, there is, for any given l_c (and v) a maximum aggregation number N if the micelle is to be spherical. For a spherical micelle of mean aggregation number $\bar{N}$, the volume of the sphere is

$$\bar{N}v = (4/3)\pi l_c^3 . \quad (1)$$

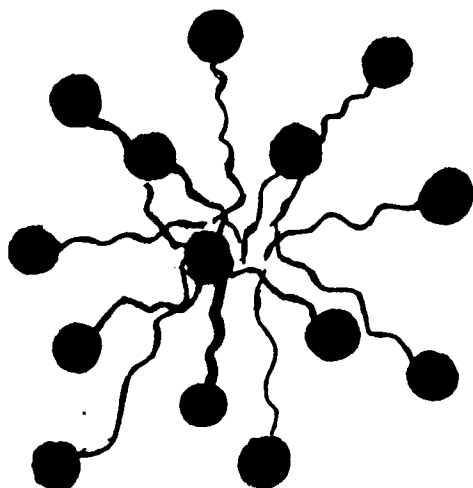
The surface area of the sphere is

$$\bar{N}a = 4\pi l_c^2 . \quad (2)$$

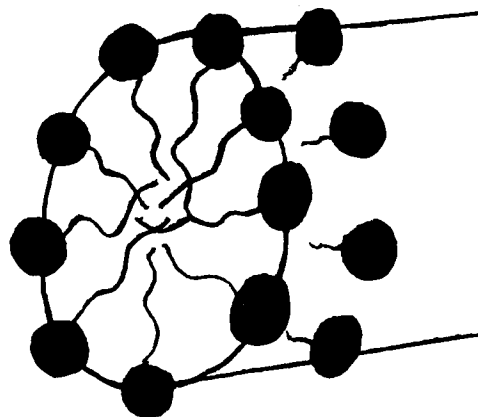
Dividing Equation 1 by Equation 2 yields the critical condition for spherical micelles,

$$v/(al_c) = 1/3 \quad (3)$$

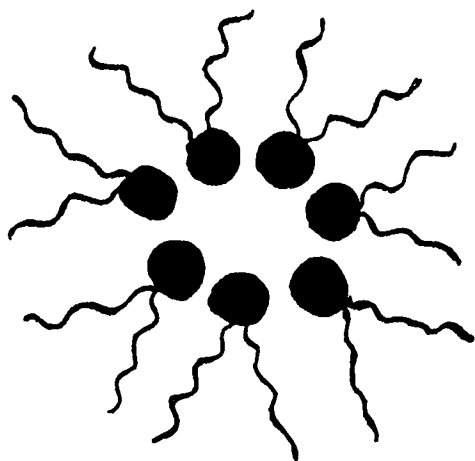
It is apparent from Equation 3 that once v/al_c becomes greater than one-third, spherical micelles will not be able to form.



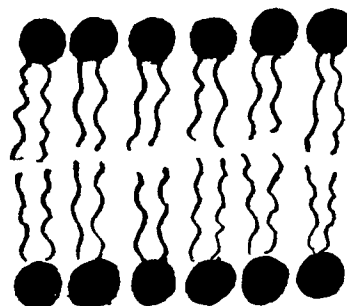
(a) Sphere



(b) Cylinder



(c) Inverse micelle



(d) Bilayer

Figure 1. Various micellar shapes.

In the case of cylindrical micelle of length, L , the volume and area equations are

$$\bar{N}_v = \pi l_c^2 L \quad (4)$$

and

$$\bar{N}_a = 2\pi l_c L \quad (5)$$

Thus, the critical condition for the formation of cylinders is

$$v/(al_c) = 1/2 \quad (6)$$

Similarly, it can be shown that for bilayers and reverse micelles the critical conditions are, respectively,

$$v/(al_c) = 1 \quad (7)$$

and

$$v/(al_c) > 1 \quad (8)$$

Hartley proposed that the microenvironment of an ionic micelle is composed of three distinct features,³ as shown in Figure 2. The core of the micelle is made up of the hydrophobic portions of the surfactant molecules. The radius of the core is approximately equal to the length of the extended hydrocarbon chain. Calorimetric,⁴ X-ray,⁵ and NMR^{6,7} measurements have confirmed that the hydrocarbon core is liquid in

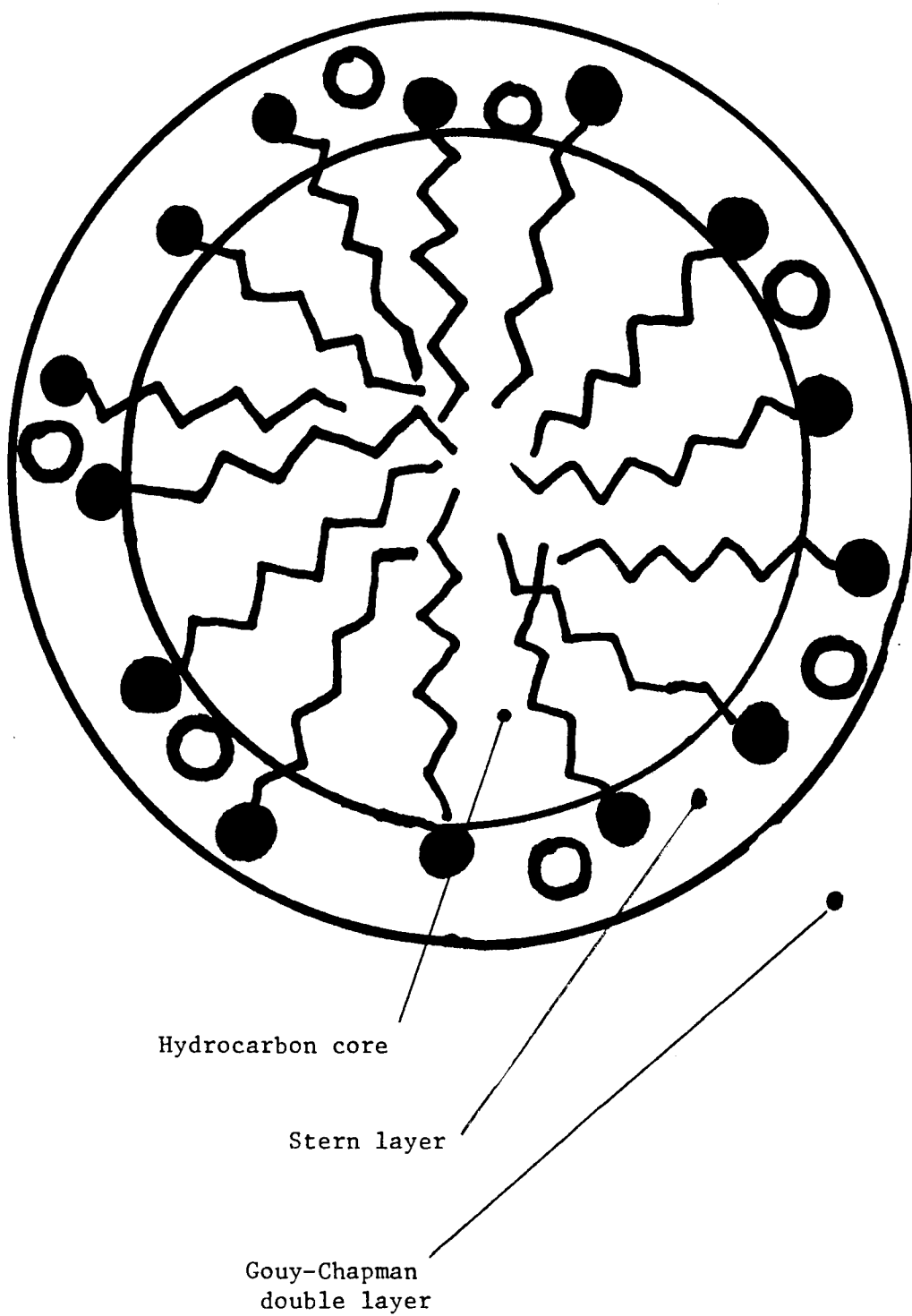


Figure 2. The Hartley model of the micelle.

nature. In addition a number of attempts to measure the effective viscosity or "microviscosity" of the core have been made,^{8,9,10} but conclusions drawn from these experiments vary widely.¹¹ At the surface of the micelle is the Stern layer, made up of the ionic head groups and some fraction of the counterions. Both the head groups and the bound counterions are assumed to be hydrated, with water penetrating among the polar groups.¹² The remainder of the counterions is contained in the Gouy-Chapman double layer, where they are dissociated from the micelle and are free to exchange with ions in the bulk aqueous phase.

The Hartley model suggests that the micellar core is dry, that is, free of water, and that the core is surrounded by a smooth, relatively thin layer of polar head groups and counterions. This view has been seriously questioned by a number of investigators. By constructing CPK models, Menger¹¹ deduced micellar structures having considerable water penetration and a much rougher micellar surface than that of the Hartley model. Fromherz¹³ rationalized structures of the micelles in terms of a surfactant-block model. Again this model predicts more wetting and surface roughness than the Hartley model. Much of this is explained by empty sites in the cubic structure due to head group repulsions. Dill and Flory^{14,15} discussed molecular organization of surfactants in terms of a statistical theory using a lattice model. The micelle is considered to contain a number of chains with $n + 1$ segments connected by n flexible bonds. The segments are assigned to locations on a three-dimensional curved lattice such that each lattice site accommodates one chain segment. This results in an ordered center

and a disordered surface of the micelle. This model also supports the postulate of some degree of water penetration into the micellar core.

Recently, Chen et al.¹⁷ stated that, based on NMR and small-angle neutron scattering data, "The evidence is unambiguous that the (micellar) cores are virtually devoid of internal water." The authors evaluated the various micellar models on the basis of their experimental results and discounted the notion of significant water penetration into the micellar core. In addition, their results indicate that the hydrocarbon chains in the micellar core are largely disordered.

Micelles first appear in surfactant solutions over a narrow range of concentration called the critical micelle concentration, CMC. Below this range, a number of physical properties such as conductance, surface tensions, and self-diffusion coefficients indicate that there is no appreciable aggregation of the surfactant. Above the CMC, these properties change in a way indicating that extensive association to large aggregates is commencing. Because of this relatively sharp change in physical properties over a small concentration range, a number of techniques can be employed to determine the CMC. The most popular of these include conductimetry, surface tension measurements, fluorescence, and solubilization of a compound having a low solubility in water. The value of the CMC, which falls within the transition zone, is assigned by empirical graphical techniques, and tends to be somewhat dependent upon the method chosen for its determination.¹⁸ An extensive tabulation of CMC values for a number of surfactants and experimental

techniques has been published by Mukerjee and Mysels.¹⁹ Some typical CMC values for a number of surfactants are given in Table I.

For single alkyl chain surfactants, the factor primarily determining the CMC is the length of the hydrocarbon chain. For many classes of surfactants, the expression

$$\log \text{CMC} = a - bn_c \quad (9)$$

gives the dependence of the CMC on the number of carbon atoms n_c in the alkyl chain.²⁰ The constant a is related to the head group identity and b depends upon the energy change involved in transferring a methylene group from water to the hydrocarbon environment. Chain branching and the introduction of double bonds in the chain have been observed to lead to an increased CMC in comparison with the corresponding n -alkyl compounds.²¹ For ionic surfactants, there are rather small differences between different head groups.²²

Counterions of ionic micelles can also affect the CMC. Mukerjee et al.²³ noted that the CMC of alkali dodecylsulfates increases slightly with decreasing counterion atomic number, while with tetraalkylammonium counterions, the CMC decreases with increasing ion size. For cationic micelles the counterion effects are more pronounced. For alkyltrimethylammonium salts, the CMC generally follows the sequence $\text{NO}_3^- < \text{Br}^- < \text{Cl}^-$.²⁴ Organic anions have in a number of cases been found to decrease the CMC markedly. For hexadecyltrimethylammonium salts, the CMC is lowered by a factor of 5-10 on substitution of salicylate or

TABLE I
CMC VALUES FOR VARIOUS SURFACTANTS AT 25°C

Amphiphile	CMC
Sucrose monostearate	1.1×10^{-5} M
Hexadecyltrimethylammonium bromide	9.2×10^{-4}
Sodium tetradecylsulfate	2.1×10^{-3}
Sodium dodecylsulfate	8.3×10^{-3}
Dodecylammonium chloride	1.5×10^{-2}
Dodecyltrimethylammonium bromide	1.6×10^{-2}
Dodecyltrimethylammonium chloride	2.0×10^{-2}
Potassium octanoate	3.9×10^{-1}

^aTaken from reference 19.

other substituted benzoates for bromide.²⁵ Low CMC values have also been found for tetradecylpyridinium salts with organic counterions.²⁶

For a given surfactant, the addition of salt may have the dual effect of decreasing the CMC and increasing the micellar size. The added salt reduces the micellar surface potential, and promotes micelle formation. The dependence of the CMC on electrolyte concentration may be expressed by the equation^{27,28}

$$\log \text{CMC} = -(m/n)\log(\text{CMC} + C_a) + \text{constant} \quad (10)$$

where m/n represents the fraction of counterions bound to the micelle and C_a equals the concentration of counterions contributed by added salt. At sufficiently high electrolyte or surfactant concentration, spherical micelles may change to rod-shaped micelles. The sphere-to-rod transition leads to a decreased area per head group and thus a higher surface potential. This potential is diminished by a higher degree of counterion binding for rodlike micelles than for spheres. In the absence of added salt, the sphere-to-rod transition occurs with increasing surfactant concentration due to two effects: (1) intermicellar interactions, which become important at higher surfactant concentrations, and (2) more efficient hydrocarbon chain packing, leading to a more favorable hydrophobic interaction term in the free energy of micellization.² In the case of added salt, the factor influencing the aggregation number is the closest approach of the counterions to

the site of charge of the head group. Upon the addition of small, hydrophobic counterions such as bromide ions at constant surfactant concentration, the sphere-to-rod transition may occur due to the presence of additional counterions, which screen the electrostatic head group repulsions and lower the surface potential of the micelles.^{29,30}

Numerous thermodynamic theories have been advanced to account for the self-assembly of surfactants in solution. The work of Tanford, with emphasis on the hydrophobic effect and the principle of opposing forces, has tended to dominate contemporary thinking.¹ Recently, some additions and amendments have been suggested by Israelachvili et al.²

According to Tanford, one may envision a thermodynamic equilibrium between the free monomers in solution and the associated monomers within a micelle. The free energy of an amphiphile in water may be expressed as

$$\mu_w = \mu_w^0 + RT \ln(X_w) \quad (11)$$

Where X_w is the mole fraction of monomeric solute in water and μ_w^0 is the standard chemical potential.

To relate thermodynamic parameters for micelle formation to experimental data, it is sometimes assumed that the micelle can be treated as a separate phase; thus,

$$\mu_{mic} = \mu_{mic}^0 + RT \ln(X_{mic}) \quad (12)$$

If micelles are considered a pure, separate phase, then $\ln(X_{\text{mic}})$ goes to zero and $\mu_{\text{mic}} = \mu_{\text{mic}}^{\circ}$. In this case, the Gibbs phase rule would apply, and micelles and free amphiphiles could be in equilibrium at a given temperature and pressure at only a single fixed value of X_w , which would effectively be a "solubility." Since at equilibrium $\mu_w = \mu_{\text{mic}}^{\circ}$,

$$\mu_{\text{mic}}^{\circ} - \mu_w^{\circ} = RT \ln(X_w) \quad . \quad (13)$$

This equation is, however, incorrect. Micelles do not exist as a separate phase but are in fact dispersed in solution. Tanford¹ points out that Equation 13 neglects the contribution to μ_{mic} that arises from the mixing of micelles with the solvent. The equation can be corrected by considering that all micelles, regardless of their size, are a single component of the solution. In that case, the contribution to the free energy per mole of micelles would be $RT \ln(\text{mole fraction of micelles})$. For micelles of average aggregation number $\bar{N}$,

$$\mu_{\text{mic}} = \mu_{\text{mic}}^{\circ} + (RT/\bar{N}) \ln(X_{\text{mic}}/\bar{N}) \quad , \quad (14)$$

and Equation 13 becomes

$$\mu_{\text{mic}} - \mu_w^{\circ} = RT \ln(X_w) - (RT/\bar{N}) \ln(X_{\text{mic}}/\bar{N}) \quad . \quad (15)$$

Because micelle formation is not equivalent to phase separation, a plot of total amphiphile concentration versus concentration of free

amphiphile in solution does not yield a single sharp break at the CMC. However, if $\bar{N}$ is reasonably large, X_w changes very slowly as X_{mic} increases, and the transition from the predominately unassociated amphiphile to micelles does in fact occur over a narrow range of concentration, approaching true phase separation in sharpness. Because X_w changes only slowly above the CMC, the approximation of $X_w \approx \text{CMC}$ can be made over a wide range of conditions. Equation 15 can then be written

$$\mu_{mic}^o - \mu_w^o = [(\bar{N}-1)/\bar{N}]RT\ln(\text{CMC}) + (RT/\bar{N})\ln(X_{mic}/\bar{N}) \quad (16)$$

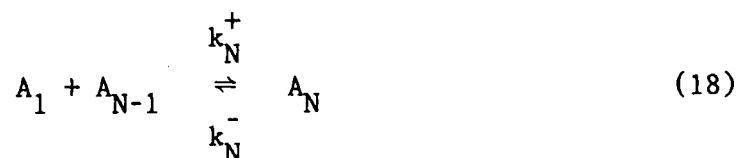
As $\bar{N}$ becomes large (>50), the last term in Equation 16 becomes negligible, and $(\bar{N} - 1)/\bar{N}$ approaches unity. For large micelles, then

$$\mu_{mic}^o - \mu_w^o = RT\ln(\text{CMC}) \quad (17)$$

which is the same as Equation 13. Thus it is seen that treating micelle formation as a true phase separation becomes a progressively better approximation as $\bar{N}$ increases.

A consequence of the liquid-like structure of the micelle is that the equilibrium with monomers in the solution is a highly dynamical one. The amphiphiles constantly protrude from and leave the micelle while monomers in the solution recombine with the micelle.^{31,32} A theoretical analysis of the kinetics of micelle formation was developed by Aniansson and co-workers^{31,33-36} and has been found consistent with a number of experimental results.^{31,37-40} The crucial assumption in the theoretical model is that the elementary kinetic process that

determines the dynamic behavior of the system is the equilibrium between a monomer and a micellar aggregate



where k_N^+ and k_N^- are the forward and reverse rate constants, respectively. A basic observation in the analysis is that micellization is a cooperative process. As a consequence, the distribution curve for aggregate sizes has a strong minimum for aggregation numbers lower than the optimal size.

When a micellar solution at equilibrium is subjected to a sudden stress, such as a sudden temperature change, a redistribution of micellar sizes occurs to accommodate the new conditions. When there is a strong minimum in the micelle size distribution, the redistribution of micelle sizes is a two-step process. In the first and faster step, relaxation occurs to a quasi-equilibrium state which is formed under the constraint that the total number of micelles remains constant. Thus the fast process involves reactions in Equation 18 for aggregates of sizes close to the maximum in the distribution. This process is characterized by an exponential relaxation with a time constant τ_1 equal to

$$\tau_1^{-1} = k^-/\sigma + ak^-/\bar{N} \quad (19)$$

Here k^- is the reverse rate constant for the micelle at the mean aggregation number $\bar{N}$ and σ is the standard deviation of the assumed Gaussian micelle size distribution. a is the relative amount of micellized monomer,

$$a = (A_{\text{tot}} - \bar{A}_1)/\bar{A}_1 \quad (20)$$

where $\bar{A}_1$ is the equilibrium concentration of A_1 . Experimentally the value of τ_1 depends strongly on both surfactant concentration and the length of the alkyl chain, but it is usually in the range $10^{-3} - 10^{-8}$ sec.

When the system has reached its quasi-equilibrium state, a slower process, involving relaxation to the true equilibrium state, becomes measurable. This process involves a change in the number of micelles. Aniansson and Wall showed that this process is also characterized by an exponential decay with a relaxation time τ_2 ,

$$\tau_2^{-1} = (N^2/\bar{A}_1)R^{-1}[1 + \sigma^2 a/\bar{N}]^{-1} \quad (21)$$

Here R is a "resistance" for aggregate flow through the region of intermediate aggregate sizes,

$$R = \sum_{N_1+1}^{N_2} (k_N^- \bar{A}_N) \quad (22)$$

where $\bar{A}_N$ is the mean concentration of aggregate A_N and N_1 and N_2 are aggregation numbers between monomer and the proper micelles. Typical values of τ_2 are in the range 10^{-7} - 1 sec.

For ionic micelles there is also rapid exchange of counterions between the micellar surface and the bulk solution. The exchange is very rapid, with rate constants on the order of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for the counterion association.¹⁸

B. Statement of the Problem

It is well known that the structure of both the hydrophobic and hydrophilic moieties of surfactant molecules has a large effect on the size and shape of the micellar aggregates formed by surfactants in aqueous solutions. For cationic micellar solutions where the amphiphilic moiety is an alkylpyridinium or an *n*-alkyltrimethylammonium ion, marked counterions specificity has been noted for the production of the sphere-to-cylinder transition, and for the onset of viscoelasticity and flow birefringence, where the counterion is a substituted aromatic counterion.

The purpose of this dissertation is to investigate the special interaction between quaternary ammonium cations and aromatic anions as it affects micellar structure and properties. Hexadecyltrimethylammonium surfactants with a series of mono- and dichlorobenzoate counterions have been studied to determine the relationship between the counterion structure and the properties of the aqueous solutions of the corresponding surfactant. These properties include the shape and size

of the micelles in solution, the extent of counterion binding to the micelles, and the viscosity and viscoelasticity of the solutions. In addition, a number of anionic surfactants with aromatic head groups and quaternary ammonium counterions were prepared, to determine whether solutions of these surfactants might have similar properties in aqueous solutions. These will be further discussed in Chapter V.

For this study, the hexadecyltrimethylammonium ion will be abbreviated, according to the commonly used convention, by CTA^+ (for cetyltrimethylammonium); thus hexadecyltrimethylammonium bromide is abbreviated as CTAB. The counterions used in this study, and their abbreviations (in parentheses) are as follows: 4-chlorobenzoate (4Cl^-); 2-chlorobenzoate (2Cl^-); 2,4-dichlorobenzoate ($2,4\text{Cl}^-$); 2,6-dichlorobenzoate ($2,6\text{Cl}^-$); 3,4-dichlorobenzoate ($3,4\text{Cl}^-$); 3,5-dichlorobenzoate ($3,5\text{Cl}^-$); salicylate (or 2-hydroxybenzoate) (Sal^-); 4-hydroxybenzoate (4OH^-); and 4-methoxybenzoate (4OMe^-). Hexadecyltrimethylammonium 2,4-dichlorobenzoate, then, is abbreviated by $\text{CTA}_{2,4\text{Cl}}$. The abbreviation CTAX will occasionally be used, where X refers to any or all counterions in general. Table II lists the structures, names, and abbreviations of the CTAX's in this study.

The choice of these counterions is not arbitrary. Gravsholt has reported that CTASal and $\text{CTA}_{4\text{Cl}}$ form viscoelastic solutions, while $\text{CTA}_{4\text{OH}}$ and $\text{CTA}_{2\text{Cl}}$ do not.²⁵ In addition, Bain and Hyde⁴¹ found that solutions of CTAB became viscoelastic when sodium 4-chlorobenzoate was added. It is reasonable, then, to further extend the chlorobenzoate series to a number of dichlorobenzoate counterions in order to further

TABLE II

CTAX'S USED IN THIS STUDY

Compound Name	Abbreviation	Structure
Hexadecyltrimethylammonium 2-hydroxybenzoate	CTASa1	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{OH}$
Hexadecyltrimethylammonium 4-hydroxybenzoate	CTA4OH	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{OH}$
Hexadecyltrimethylammonium 4-methoxybenzoate	CTA4OMe	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{OCH}_3$
Hexadecyltrimethylammonium 3,5-dichlorobenzoate	CTA3,5Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_2(\text{Cl})_2$
Hexadecyltrimethylammonium 2-chlorobenzoate	CTA2Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{Cl}$
Hexadecyltrimethylammonium 2,6-dichlorobenzoate	CTA2,6Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_2(\text{Cl})_2$
Hexadecyltrimethylammonium 2,4-dichlorobenzoate	CTA2,4Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_2(\text{Cl})_2$
Hexadecyltrimethylammonium 4-chlorobenzoate	CTA4Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{Cl}$
Hexadecyltrimethylammonium 3,4-dichlorobenzoate	CTA3,4Cl	$\text{N}^+(\text{CH}_3)_3 - \text{C}_{16}\text{H}_{33} - \text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_2(\text{Cl})_2$

elucidate the relationship between the number and position of the substituents on the ring, and the corresponding properties of the resulting surfactant solutions. In addition, the only viscoelastic surfactant systems which have been well characterized have employed the salicylate counterion.⁴²⁻⁴⁴ Characterization of the CTA-chlorobenzoate series in terms of the various properties mentioned above will shed further light on the phenomena of counterion specificity and the formation and growth of cylindrical micelles, and may provide valuable new insight into the elusive problem of discovering the source and mechanism of viscoelasticity in surfactant solutions.

The problem, then, may be discussed in three parts. First it must be determined whether viscoelastic effects similar to those seen in other systems can also be seen in these systems, and whether the results of viscosity measurements made on other surfactant systems are quantitatively similar to those from viscosity measurements of some of the CTA-chlorobenzoates. Second, the role of the counterion and the reason for the observed counterion specificity in these and other systems need to be explored. Finally, the issue of the size and shape of the micelles in both the viscoelastic solutions and in the nonviscoelastic solutions needs to be addressed, in order to give insight into the role of micellar geometry in determining the rheological properties of the solutions. Of course these three areas of interest cannot be wholly separated. The ability of a surfactant to form cylindrical micelles is largely dependent upon the nature of the counterion and its affinity for the micellar surface. In turn, the occurrence of viscoelasticity

in micellar solutions has almost always been linked to the presence of rod-shaped micelles. For the purpose of this work, however, each area will first be examined separately, then an overview of the entire work will be given.

Chapter II of this dissertation deals with the topic of rheology and includes a brief discussion of the theory of viscosity and viscoelasticity, a literature review of the recent work in the area of viscoelastic surfactant solutions, and the results of visual observations and viscometry measurements of some of the CTAX's prepared for this study. Chapter III involves the area of counterion binding and specificity and is limited to the case of cationic amphiphiles with aromatic counterions. A review of the recent literature is given and the results of conductivity and NMR measurements on the CTA-chlorobenzoates are presented. In addition, measurements to determine the effect of pH on the surfactant solutions are included in this chapter. The third topic to be discussed concerns the presence and growth of nonspherical aggregates in these solutions. To this end a number of small-angle neutron scattering (SANS) measurements were made on the CTA-chlorobenzoate solutions. These measurements provide information on micellar size and shape, aggregation number, and micellar charge. Because SANS is a relatively new and powerful technique for the study of micellar solutions, the theory and application of this technique are presented in some detail in Chapter IV. In Chapter V, a discussion of the results is presented, along with suggestions for further study.

CHAPTER II

VISCOSITY AND VISCOELASTICITY OF SURFACTANT SOLUTIONS

A. Definition of Viscosity and Viscoelasticity1. Newtonian and Non-Newtonian Viscosity

Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called "shear." Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading or mixing. Highly viscous fluids, therefore, require more force to move than less viscous materials.

Newton modeled viscosity by considering two parallel planes of fluid of equal area A separated by a distance dX and moving in the same direction at different velocities. The difference in these velocities is dV . Newton assumed that the force required to maintain this difference in speed was proportional to the velocity gradient, dV/dX ,

$$\frac{F}{A} = \eta \frac{dV}{dX} \quad (23)$$

where η is a constant for a given material and is called its viscosity. The velocity gradient is a measure of the speed at which the layers move with respect to each other. It describes the shearing the liquid experiences and is thus called the shear rate, S , and has units of

reciprocal seconds (sec^{-1}). The F/A term indicates the force per unit area required to produce the shearing action. It is referred to as shear stress σ , and is generally expressed in units of dynes per square centimeter (dynes/cm^2). Thus a material requiring a shear stress of one dyne per square centimeters to produce a shear rate of one reciprocal second has a viscosity of one poise, or 100 centipoise.

A Newtonian fluid is one for which the viscosity is independent of shear rate. For a Newtonian liquid, a doubling of the shear stress will cause a doubling of the shear rate. A non-Newtonian fluid, then, is broadly defined as one for which the relationship σ/S is not a constant. In other words, the viscosity of a non-Newtonian fluid will change when the shear rate is varied. The measured viscosity of such a fluid is called its "apparent viscosity" and is accurate for only one explicit set of experimental parameters.⁴⁵

Non-Newtonian liquids are classified as dilatant, pseudoplastic, thixotropic, or rheopectic liquids.⁴⁶ In dilatant liquids, the apparent viscosity, η_{app} , rises as the shear stress increases (shear-thickening), whereas for pseudoplastic liquids, it falls (shear-thinning). At very low shear rates these effects become very small and approach a limiting value. In both cases, a change in the shear stress brings about an almost instantaneous change in viscosity. In some liquids, however, a noticeable induction time is required; that is, the viscosity also depends on time. If, at a constant shear rate, the viscosity falls as the time increases, then the liquid is termed thixotropic. Liquids are termed rheopectic, on the other hand, when the

apparent viscosity increases with time. Both thixotropy and rheopexy may occur in combination with any of the previously discussed flow behaviors, or only at certain shear rates. In addition, the time element is extremely variable; under conditions of constant shear some fluids will reach their final viscosity value in a few seconds, while others may take up to several days.

2. Viscoelasticity

The classical theory of elasticity deals with mechanical properties of perfectly elastic solids, for which, in accordance with Hooke's law, stress is always directly proportional to strain but independent of the rate of strain. The theory of hydrodynamics deals with properties of perfectly viscous liquids, for which, in accordance with Newton's law, the stress is always directly proportional to the rate of strain but independent of the strain itself. These categories are idealizations, however; all real solids show deviations from Hooke's law under suitably chosen conditions, and any real liquid shows deviations from Newtonian flow if subjected to sufficiently precise measurements. One important type of deviation from these ideal behaviors is that in which the stress depends upon both the strain and the rate of strain together. Such time-dependent anomalies reflect a behavior which combines liquid-like and solid-like characteristics, and are therefore called viscoelastic.

In a viscoelastic body, the state of deformation at a given point is specified by a strain tensor which represents the relative changes

in dimensions and angles of a small cubical element at that position.⁴⁷ Similarly, the state of stress is specified by a stress tensor which represents the forces acting on different faces of the cubical element from different directions. If the strains are small, the components of the two tensors are related in a simple manner by certain moduli of elasticity which are properties of the material alone and not of the external geometry of the body. For viscoelastic materials, the moduli are time-dependent.

The most important type of deformation in studies of viscoelastic bodies is simple shear, which produces a change in the shape of the body but no change in its volume. In a simple shear experiment, the shear stress is $\sigma = f/A$ where f is a lateral force acting parallel to an area A . The shear modulus is $G = \sigma/\gamma$, where γ , the shear strain, is the tangent of the angle of deformation. An example of a simple shear experiment for a viscoelastic solution involves constant shear between coaxial cylinders, corresponding to a constant stress σ .

A second example of a simple shear experiment involves a sinusoidally oscillating shear between coaxial cylinders. If the stress is small, the strain will also alternate sinusoidally but will be out of phase with the stress. The stress can be decomposed vectorially into two components, one in phase with the strain and the other 90° out of phase; when these are divided by the strain the modulus is separated into an in-phase component, G' , and an out-of-phase component, G'' . G' is related to the energy cyclically stored and released in the periodic deformation and is called the storage modulus. G'' is associated with

the dissipation of energy as heat and is called the loss modulus. From these, a complex viscosity is calculated,

$$\eta^* = \sqrt{\frac{G'^2 + G''^2}{\omega}}, \quad (24)$$

where ω is the angular frequency of the oscillation.

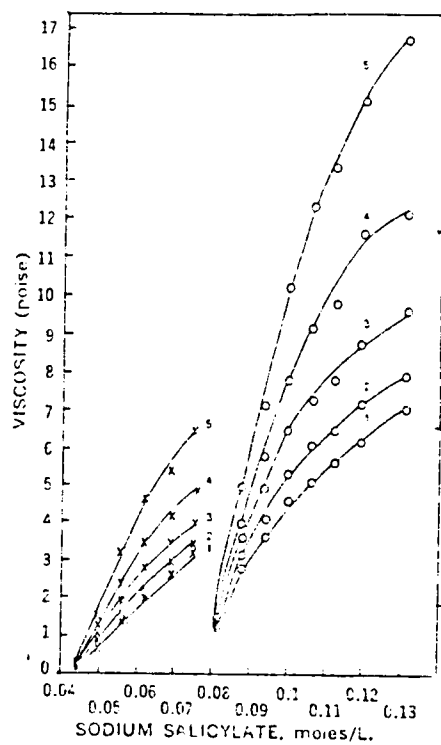
The occurrence of viscoelasticity in surfactant solutions is often detected by the "swirl test."²⁵ When surfactant solutions are swirled in a flask or beaker, air bubbles are trapped in the solution and travel in the direction of the flow. When the swirling, or shearing, is stopped, the bubbles generally continue in the direction of the shear until their forward motion is slowed to a stop by viscous forces in the solution. For solutions exhibiting elasticity, however, the trapped bubbles recoil when shearing is stopped, and depending upon surfactant concentration, temperature, and other factors, the bubbles may continue to travel in the reverse direction for times on the order of seconds before the motion ceases. Though simple, the test is a very sensitive indicator of viscoelasticity, even for dilute solutions with viscosities very nearly equal to that of the solvent.

B. Literature Review of Viscoelastic Surfactant Solutions

The occurrence of strongly viscoelastic behavior in dilute aqueous surfactant solutions is relatively rare. Gravsholt²⁵ lists a number of references to viscoelastic surfactant systems prior to 1976. The

majority of these share common elements. Most involve cationic surfactants, either alkyltrimethylammonium or alkylpyridinium, and, in all cases involving dilute surfactant systems, a third or fourth component is required to induce viscoelastic behavior. Larsen and co-workers⁴⁸ reported large increases in viscosity when certain organic solutes were added to solutions which were 0.1 M in CTAB and 0.1 M in NaBr. Solute which induced the increase in viscosity included naphthalene (0.001 m), benzene (0.025 M), 1-hexanol (0.029 M), and benzoic acid (0.025 M). In the absence of NaBr, however, none of these solutes alone caused an increase in the viscosity of the CTAB solution. Wan^{49,50} reported the effect of a number of aromatic acid solutes in the viscosity of dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide. She found viscosity increases for each surfactant solution in the presence of salicylic acid. The effect was even more pronounced for sodium salicylate than for salicylic acid. Other aromatic acids, including 3-hydroxy-, 4-hydroxy-, 2-chloro-, and 4-chlorobenzoic acid, displayed no tendency to cause an increase in viscosity for the surfactant solutions. For the surfactant-salicylic acid systems, peak viscosities were seen at 4 to 6% (w/v) surfactant and 1 to 2% (w/v) solute. These results are shown in Figure 3 which indicates that the solutions are shear-thinning, or pseudoplastic.

Though Wan found no viscosity increase for the chlorobenzoic acids, Bain and Hyde⁴¹ noted a strong viscoelastic effect for CTAB solutions to which sodium 4-chlorobenzoate was added. Light scattering and flow birefringence indicated that for a system of 2 moles Na₄Cl:



Key: X, 0.081 M CTAB; O, 0.162 M CTAB. Shear rates: 1, 234.6 sec.^{-1} ; 2, 195.9 sec.^{-1} ; 3, 155.1 sec.^{-1} ; 4, 117.35 sec.^{-1} , 5, 78.56 sec.^{-1} . From reference 49.

Figure 3. Effect of sodium salicylate on the viscosity of CTAB solutions at 25°C.

1 mole CTAB, the micelles of the solution are cylindrical. Also, as the concentration of the solutions was increased, interactions between the micelles became strong enough that a relaxation time for individual rods could no longer be seen; instead, only a relaxation time for the entire system could be observed. Tiddy and co-workers,⁵¹ in preparing a phase diagram for an octyltrimethylammonium bromide/sodium dodecylsulfate/H₂O system, discovered a viscoelastic region in the water-rich portion of the phase diagram. Rotational and oscillatory rheological measurements revealed that the non-Newtonian solutions were pseudoplastic. In addition, line broadening seen in proton NMR measurements indicated the possible presence of cylindrical micelles. Similar results were seen with a zwitterionic/anionic surfactant system, hexadecyldimethylammoniopropanesulfonate and sodium dodecylsulfate in water.⁵²

In the past decade, interest in viscoelastic surfactant solutions has centered primarily on binary systems containing only water and surfactant. The Gravsholt paper in 1976²⁵ introduced a number of hexadecyltrimethylammonium surfactants with aromatic counterions, including 2-hydroxy-, 3-hydroxy-, 4-hydroxy-, 2-chloro-, 3-chloro-, and 4-chlorobenzoate. Of these, the surfactants which formed viscoelastic solutions in water were CTASal, CTA3Cl, and CTA4Cl. It was noted that the effect is temperature dependent, with an increase in temperature causing an increase in the minimum surfactant concentration required for the onset of viscoelastic behavior. For CTASal at 25°C, viscoelasticity was first observed at a surfactant concentration of 0.19 mM; at

40°C, viscoelasticity was first observed at 0.26 mM. A number of rheological measurements on CTASal solutions have been carried out by Gravsholt.⁵³⁻⁵⁵ For dilute solutions (from 0.1 to 1.0 mM) at very low constant shear rates, Newtonian behavior was observed. That is, at sufficiently low concentration and shear rates, the shear stress remains constant over time. Figure 4 shows the behavior of a 0.0006 M CTASal solution as the shear rate was increased. At a given critical shear rate, an initial period of constant shear stress was followed by a marked rise in shear stress, until a second plateau was reached. As the concentration of the CTASal solutions was decreased, higher shear rates were required to induce the rheopectic behavior, which was seen for solutions with concentrations as low as 0.3 mM.

Similar measurements on more concentrated solutions (3.0 and 5.0 mM) of CTASal revealed considerably more complex behavior.⁵⁵ Gravsholt reports that for the 3.0 mM CTASal solution, the solutions are pseudoplastic at low shear rates ($0.01-0.06 \text{ sec}^{-1}$) and pseudoplastic and thixotropic at intermediate shear rates ($0.21-2.48 \text{ sec}^{-1}$). At high shear rates ($3.37-4.59 \text{ sec}^{-1}$), the solutions are first thixotropic, then rheopectic. Gravsholt could give no explanation for the behavior of the CTASal solutions at high concentrations. However, Gravsholt et al.⁴² proposed that, for the dilute solutions at the critical shear rate, a shear-induced structure consisting of a periodic network of rod-shaped micelles may be formed. This network would be responsible for the abrupt rise in viscosity at the critical shear rate and the observed viscoelastic properties of these solutions.

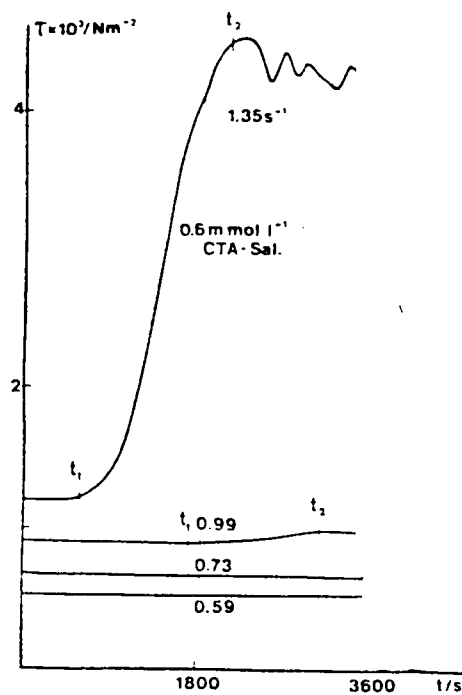


Figure 4. Shear stress (τ) versus time (t) and shear rate for a 0.6 mM CTASal solution at 25°C. From reference 54.

The presence of nonspherical aggregates in CTASal solutions with concentrations greater than 0.2 mM was confirmed by Johansson et al.,⁵⁶ using linear dichroism. Above a certain threshold shear gradient, an LD signal was observed, indicating the presence of nonspherical aggregates which could be aligned upon flow. For concentrations below that at which viscoelasticity could be observed, no LD signal was seen. Likewise, as the temperature of the solution was raised, a decrease and eventual disappearance of the LD signal was noted.

Hoffmann and co-workers^{43,44,57} made similar measurements on dilute solutions of cetylpyridinium salicylate. For a 0.9 mM solution of the surfactant, Newtonian behavior was observed at a shear rate of 0.1 sec^{-1} . At intermediate shear rates, rheopectic behavior similar to that seen by Gravsholt was observed. At still higher shear rates, as shown in Figure 5, the viscosity of the solution rose to a maximum value, η_{max} , then underwent a thixotropic decrease in viscosity, until a plateau was reached, at which a constant viscosity, η_{∞} , was maintained. Hoffmann explains this phenomenon by postulating the formation of a supermolecular structure during flow. The state of this structure is evidently complex. It is continuously broken by the shearing forces but is also reforming all the time. When the shearing is stopped, the shear-induced structure decays with very long time constants which are on the order of a few hundred seconds.

The rheopectic behavior of the cetylpyridinium salicylate solutions could be measured at detergent concentrations of up to 7.7 mM. Above this concentration, the viscous resistance increases rapidly and

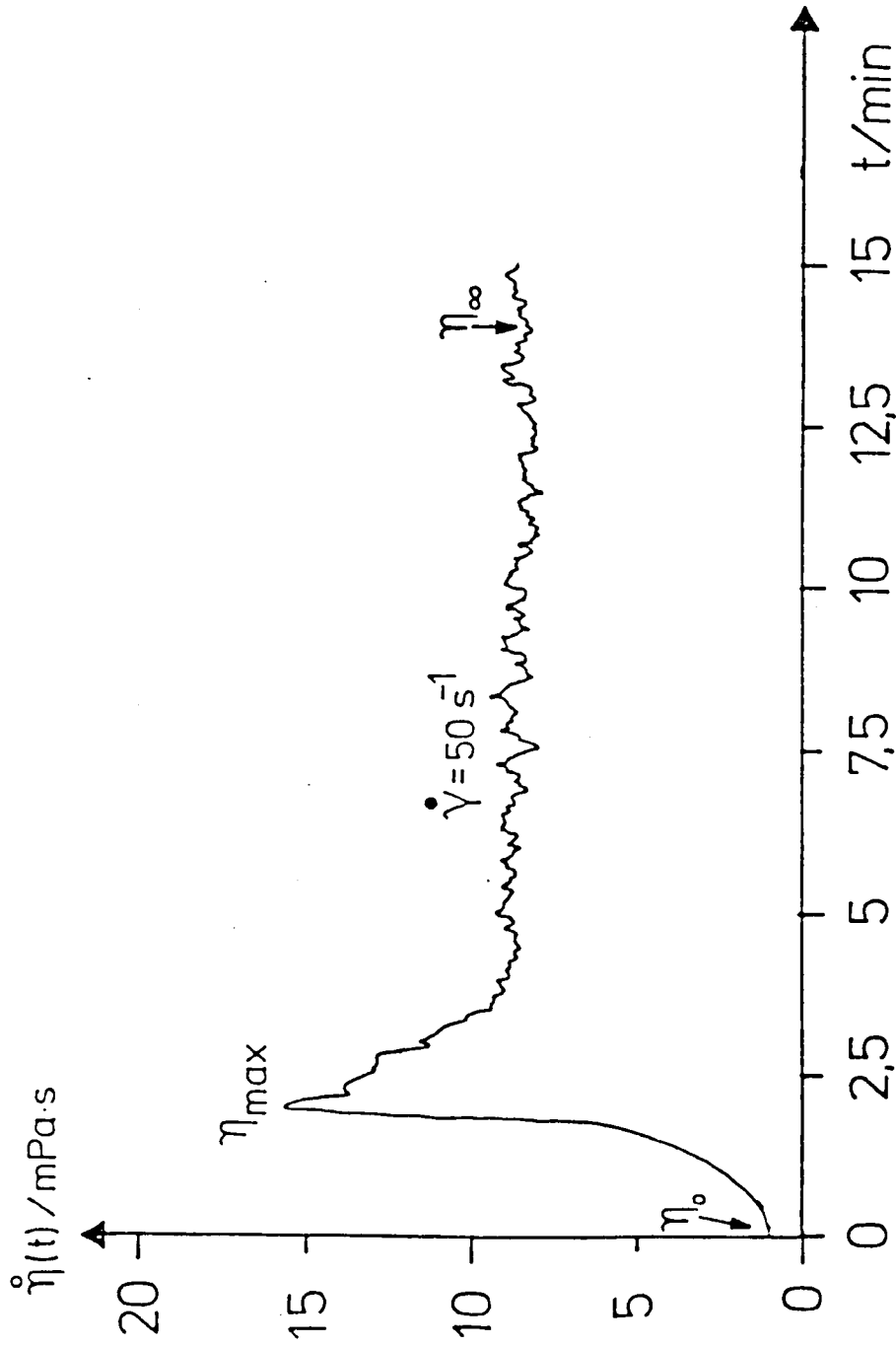


Figure 5. Dependence of the transient viscosity on time of shearing. Solution: 0.9 mM cetylpyridinium salicylate; $\dot{\gamma}$ = shear rate. From reference 57.

the solutions show a thixotropic behavior. Previous studies had shown that 7.7 mM was the concentration at which the rodlike micelles start to overlap. It was postulated that, at this concentration, a network is formed in the unsheared solution, giving rise to the rheological properties seen for the solutions above 7.7 mM. To support this observation, a number of experiments were made employing oscillating, sinusoidal deformations.⁴⁴ Unlike measurements at constant shear, these dynamic measurements shear the solutions through very small angles at a low angular frequency. The solutions, therefore, experience extremely small shear stresses. Figure 6 shows the results of these measurements on a number of alkyltrimethylammonium salicylates. For each, a sharp increase of the viscous resistance was noted at a well-defined characteristic concentration, c^* . Solutions below c^* were not elastic in the unperturbed state. However, for alkyltrimethylammonium salicylates with C_{14} or C_{16} alkyl chains, elasticity could be induced by shearing the solutions at concentrations below c^* .

C. Visual Observation and Rheological Measurements on CTAX Surfactant Solutions

This section includes the results of two studies. First visual observation of the CTAX surfactant solutions prepared for this study were made to determine which of the surfactants exhibited viscoelastic properties in solution. Second, measurements of viscosity were made for CTASal; CTA2,4Cl; and CTA3,4Cl. The purpose of these measurements was to compare the dependence of their apparent viscosities on changes

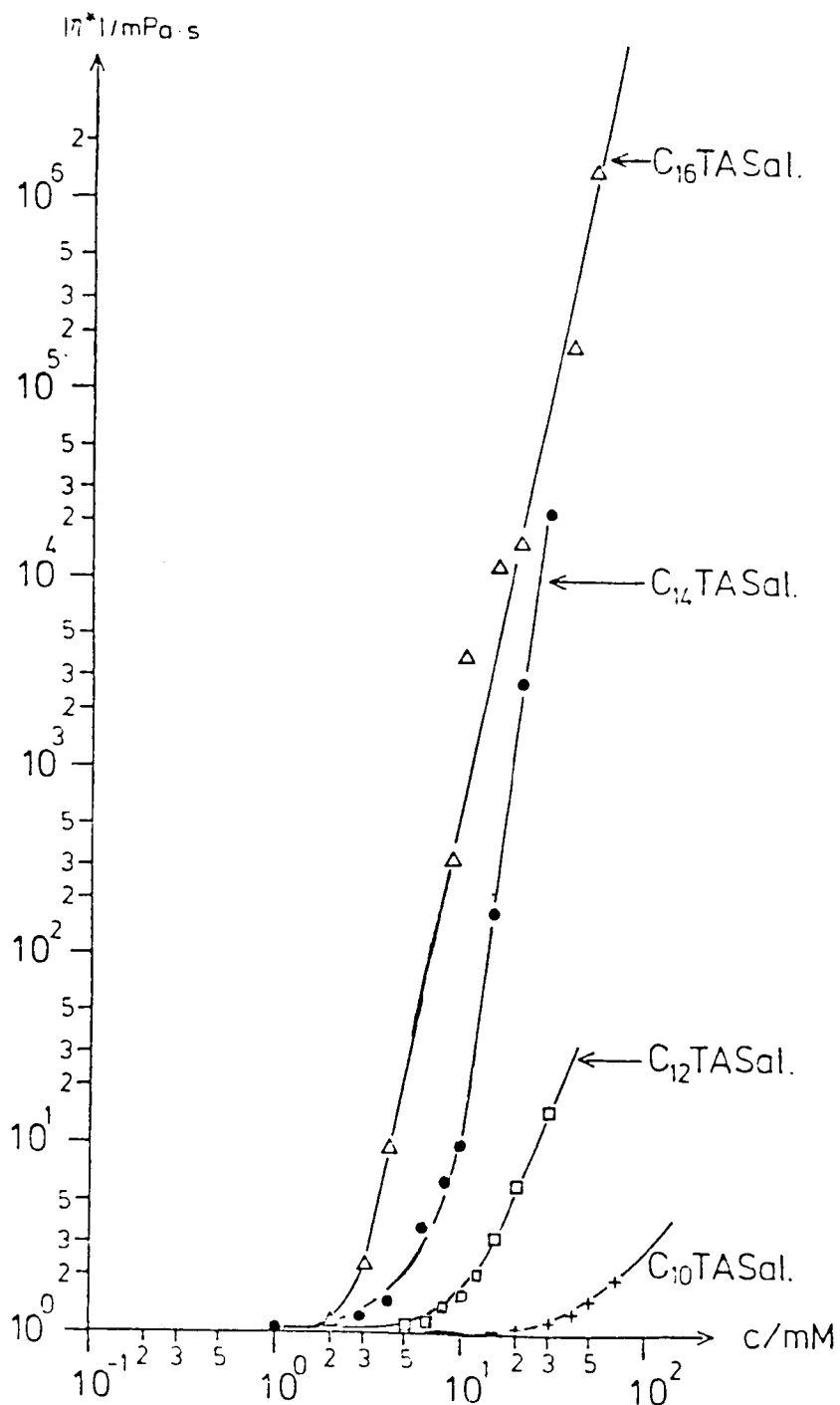


Figure 6. The magnitude of the complex viscosity as a function of the detergent concentration for different alkyltrimethylammonium salicylates. From reference 44.

in shear rate and concentration, and to determine whether the rheological behavior of these compounds is similar to that seen by Gravsholt and Hoffmann for alkyltrimethylammonium and alkylpyridinium salicylates.

1. Visual Observation of Solutions of CTAX Surfactants

In order to classify micellar solutions as viscoelastic or non-viscoelastic, dilute solutions of each of the cationic surfactants prepared for this study were subjected to the swirl test. At a concentration of 0.5 mM, CTASal; CTA4Cl; CTA2,4Cl; CTA3,4Cl; and CTA3,5Cl displayed viscoelastic behavior. Above this concentration, solution of these five surfactants remained viscoelastic and, at sufficiently high concentrations, they formed nonflowing gels. The gel point was different for each of the surfactants--being highest, for example, for the CTA2,4Cl--but precise determinations of the gel point concentrations were not attempted. However, solutions CTA3,4Cl; CTA4Cl; and CTA3,5Cl did not flow at concentrations above 30 mM, while solutions of CTA2,4Cl, though extremely viscous, were not completely gelled at this concentration. From these visual observations, these solutions can be ranked according to the apparent strength of their viscoelastic behavior. This order, from strongest to weakest, appears to be CTA3,4Cl; CTA3,5Cl > CTASal; CTA4Cl > CTA2,4Cl.

On the other hand, viscoelasticity was not observed for solutions of CTA2Cl; CTA2,6Cl; CTA4OH; and CTA4OMe, even at concentrations as high as 0.2 M. However, solutions of CTA2Cl and CTA2,6Cl became

noticeably more viscous at concentrations above about 0.15 M. The most concentrated solution prepared was a 0.2 M solution of CTA2C1. The solution was very viscous, but did not exhibit the "recoil" seen in solutions classified as viscoelastic.

2. Viscosity Measurements on Solutions of CTAX Surfactants

Rotational viscometry measurements were made on solutions of CTASal; CTA2,4C1; and CTA3,4C1. The measurements were consistently made at 25°C and 30 minutes after shear was begun, at each shear rate. All samples appeared to have reached their final viscosity values by this time. These measurements allow a comparison to be made between CTA3,4C1 solutions, which were strongly viscoelastic even at low concentrations, and CTA2,4C1 solutions, which required higher surfactant concentrations to achieve similar properties. In addition, measurement of CTASal solutions allowed quantitative comparisons of the effectiveness of each of the counterions in inducing viscosity in these solutions.

The data from viscometry measurements at constant shear are given in Tables III-V. Figure 7 shows the results from these measurements on CTASal solutions at three concentrations and four different shear rates. At a concentration of 0.5 mM, the apparent viscosities of the solution at all the shear rates employed are only slightly higher than the viscosity of water. At 1.0 mM, there is a large increase in the viscosities of the solution at all shear rates. At 5.0 mM, the viscosities are still higher, but the rate of increase in apparent viscosity

TABLE III
ROTARY VISCOMETRY OF CTASa1

Shear Rate	Shear Stress	Apparent Viscometry
0.0005 M		
73.42 sec ⁻¹	1.188 dynes/cm ²	1.404 cP
36.71	0.6600	1.971
14.68	0.2779	2.060
7.34	0.1121	2.211
3.67	0.1121	3.072
1.83	0.1042	5.648
0.001 M		
36.71	5.523	16.50
14.68	2.786	20.61
7.34	1.563	22.64
3.67	1.000	27.64
1.83	5.836	31.64
0.005 M		
14.78	3.091	22.87
7.34	1.799	26.04
3.67	1.084	29.94
1.83	.861	46.69

TABLE IV

ROTARY VISCOMETRY OF CTA2,4C1

Shear Rate	Shear Stress	Apparent Viscosity
0.0003 M		
73.42 sec ⁻¹	1.334 dynes/cm ²	1.577 cP
36.71	0.3432	1.025
14.68	0.1112	0.824
7.34	0.0694	1.006
3.67	0.0694	1.919
1.83	0.0556	3.013
0.0006 M		
73.42	1.626	1.922
36.71	0.9378	2.800
14.68	0.1806	1.339
7.34	0.1042	1.509
3.67	0.1112	3.071
1.83	0.1389	7.522
0.001 M		
73.42	2.433	2.924
36.71	1.181	3.526
14.68	0.1389	1.030
7.34	0.1250	1.811
3.67	0.1667	4.607
1.83	0.1667	9.038
0.003 M		
14.68	0.7642	5.664
7.34	0.2570	3.721
3.67	0.1389	3.839
1.83	0.1112	6.025
0.006 M		
14.68	4.404	32.64
7.34	2.154	31.19
3.67	0.1042	2.879
1.83	0.1112	6.025
0.01 M		
14.68	4.717	34.96
7.34	2.563	37.12
3.67	1.188	32.82
1.83	0.1181	6.402

TABLE V
ROTARY VISCOMETRY OF CTA3,4C1

Shear Rate	Shear Stress	Apparent Viscosity
0.0003 M		
73.42 sec^{-1}	4.634 dynes/cm^2	5.5478 cP
36.71	2.418	7.218
14.68	1.612	11.94
7.34	0.8684	12.58
3.67	0.6461	17.85
1.83	0.5210	28.24
0.0006 M		
36.71	5.662	16.90
14.68	2.529	18.74
7.34	1.501	21.73
3.67	0.9031	24.95
1.83	0.5766	31.26
0.004 M		
14.68	5.182	38.41
7.34	2.306	33.40
3.67	1.112	30.71
1.83	0.7642	41.76
0.008 M		
14.68	5.377	39.85
7.34	2.320	33.60
3.67	1.570	43.38
1.83	1.139	61.76
0.01 M		
14.68	5.419	40.16
7.34	2.730	39.54
3.67	1.841	50.86
1.83	1.257	68.16

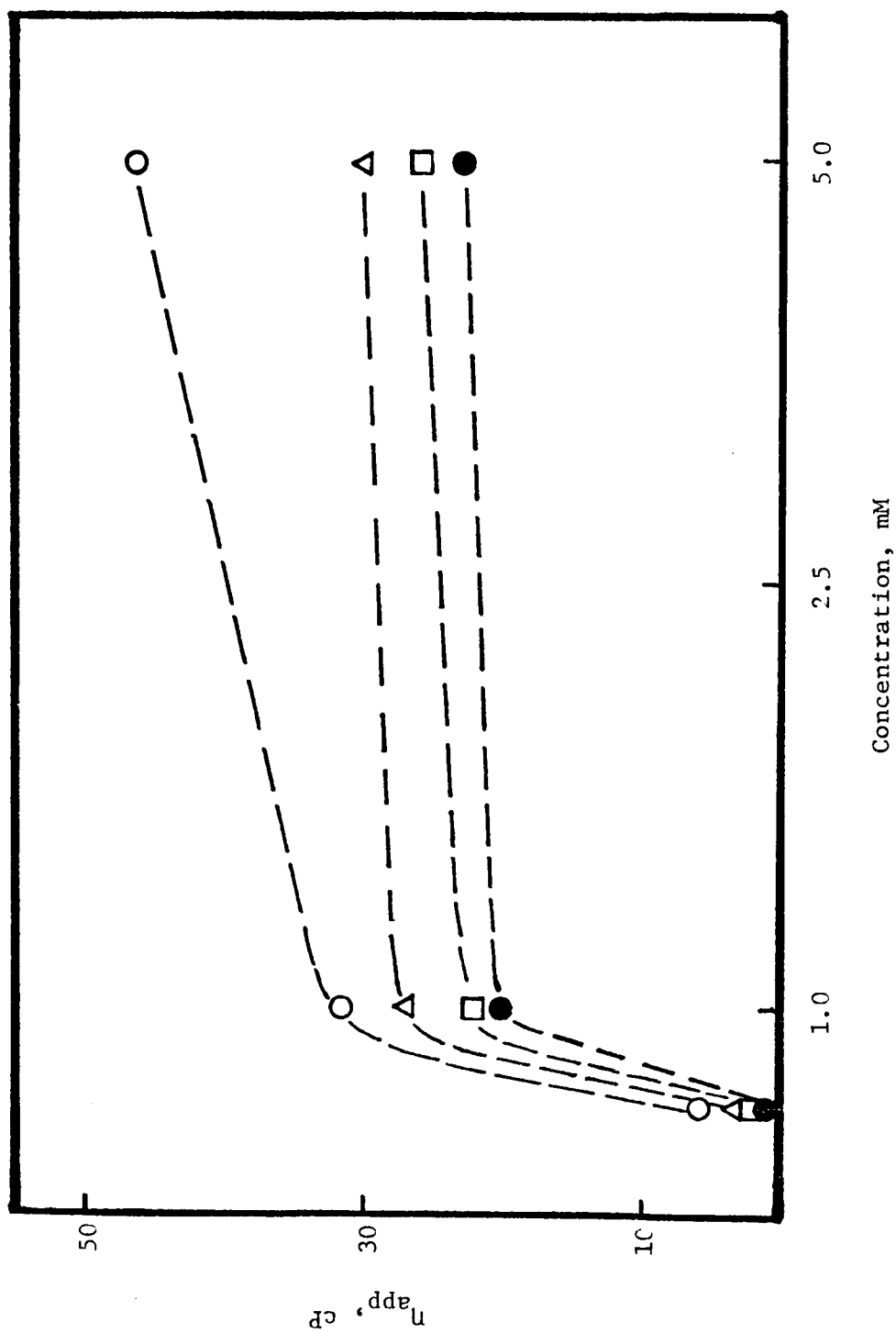


Figure 7. Rotational viscometry measurements of CTASal solutions. Shear rates: 0, 14.63 sec^{-1} ; Δ , 7.34 sec^{-1} ; $\square$, 3.67 sec^{-1} ; and $\bullet$, 1.83 sec^{-1} .

with increasing concentration is much lower in the range from 1.0 mM to 5.0 mM than in the range from 0.5 mM to 1.0 mM. The solutions exhibit pseudoplastic behavior at all three concentrations.

Figure 8 demonstrates the more complex behavior of CTA2,4Cl solutions. (The curves are meant to single out the points of a particular shear rate, not to imply that the precise functional dependence of the apparent viscosity on the solution concentration is known. Gaps in the curves indicate that no measurements were made in this region and a high degree of uncertainty exists as to the precise shape of the curve at this point.) At concentrations below 3.0 mM, a change in the behavior of the solution is seen at the two higher shear rates. At this concentration, the viscosities corresponding to shear rates of 14.63 sec^{-1} and 7.34 sec^{-1} have increased noticeably. At 6.0 mM the apparent viscosity at these two shear rates is quite large. For shear rates of 3.67 sec^{-1} and 1.83 sec^{-1} , however, there is essentially no increase in viscosity up to 6.0 mM. As the solution concentration is increased from 6.0 mM to 10 mM a large increase in viscosity is now seen for the 3.67 sec^{-1} shear rate. However, even at a shear rate 1.83 sec^{-1} of no similar large increase in apparent viscosity can be seen.

These results appear to be similar to those reported by Gravsholt. For dilute solutions, there is a minimum shear rate for each solution concentration at which rheopectic behavior can be seen. In other words, for any given surfactant concentration (below the critical concentration for rod overlap, c^*), a certain minimum shear rate is required to induce the proposed supermolecular network structure in the

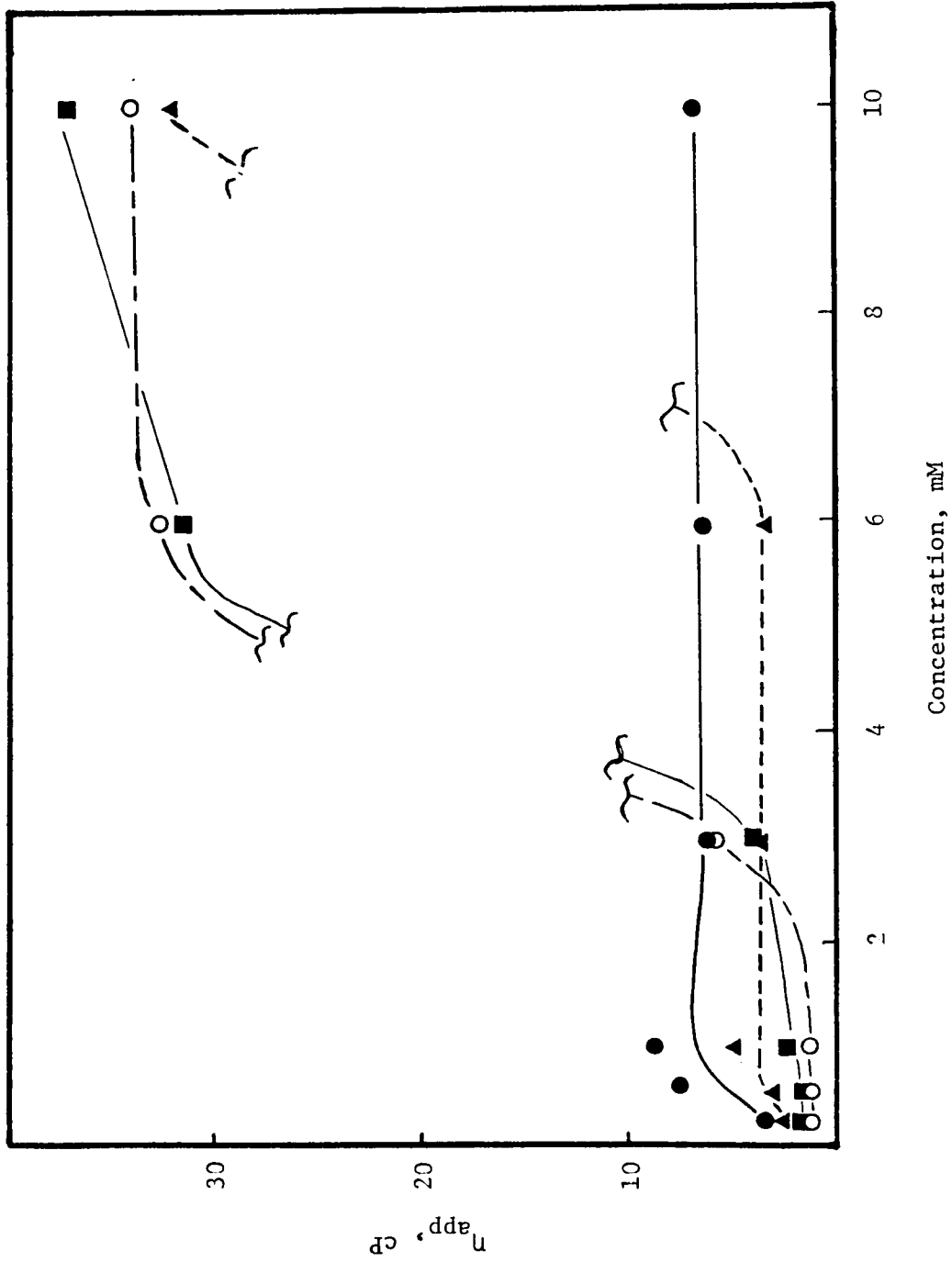


Figure 8. Rotational viscometry measurements of CTA2,4Cl-f solutions. Shear rates: 0, 14.63 sec⁻¹; ■, 7.34 sec⁻¹; ▲, 3.67 sec⁻¹; ●, 1.83 sec⁻¹.

solution. For CTA2,4Cl at a concentration of 6.0 mM, shear rates of 14.63 and 4.34 sec^{-1} are apparently sufficient to induce this structure, which causes an increase in apparent viscosity of about 25 cP at this concentration. At the same concentration, shear rates of 3.67 and 1.83 sec^{-1} are apparently not sufficient to cause the shear-induced structure to be formed. In contrast, rheopectic behavior has been observed for a 0.6 mM solution of CTASal at a shear of 1.35 sec^{-1} .

Results of viscosity measurements of CTA3,4Cl solutions are shown in Figure 9. In this case, the apparent viscosities are already quite high at 0.3 mM. (In capillary viscometry measurements, discussed below, a 0.3 mM solution of CTA3,4Cl had a much lower viscosity, 1.41 cP.) At the higher shear rates the apparent viscosities have reached (evidently) plateau values at a concentration of about 4.0 mM, while at the lower shear rates the viscosity is continuing to increase at concentrations as high as 10 mM.

A comparison of the shear stresses at a shear rate of 14.63 sec^{-1} for CTASal; CTA2,4Cl; and CTA3,4Cl is shown in Figure 10. The shear stresses of CTASal and CTA3,4Cl become quite high at concentrations of 1.0 mM or less, while for CTA2,4Cl solutions, higher concentrations are required before a large increase in shear stress is seen. Interestingly, however, when the plateau shear stress value for CTA2,4Cl is reached, it is higher than the apparent plateau value for CTASal and similar to that of CTA3,4Cl.

Capillary viscometry measurements were made on a series of CTA3,4Cl solutions at concentrations varying from 0.13 mM to 4.0 mM. A

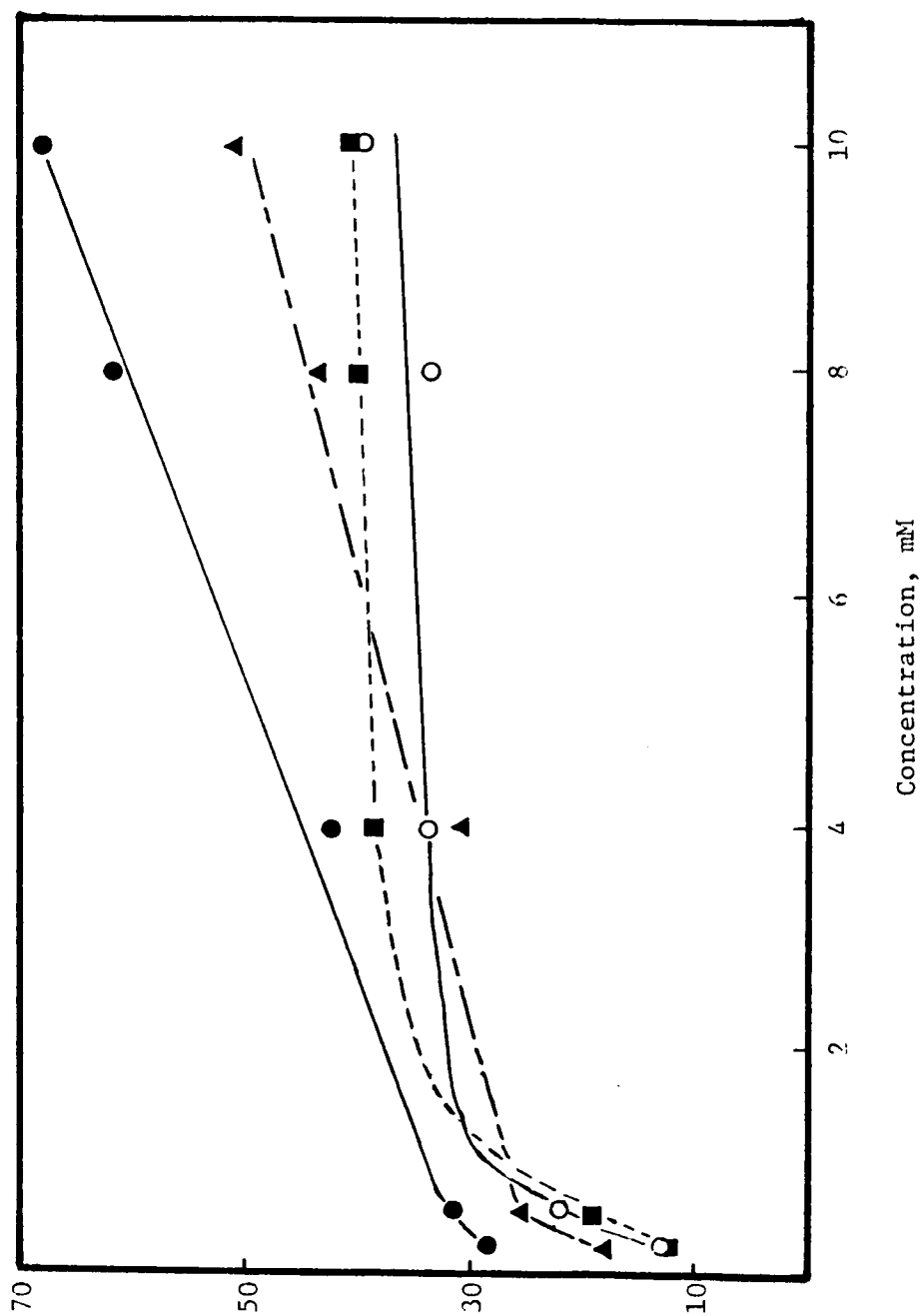


Figure 9. Rotational viscometry measurements of CTA3,4Cl1 solutions. Shear rates: $\blacksquare$, 14.63 sec^{-1} ; $\bullet$, 7.34 sec^{-1} ; $\blacktriangle$, 3.67 sec^{-1} ; $\circ$, 1.83 sec^{-1} .

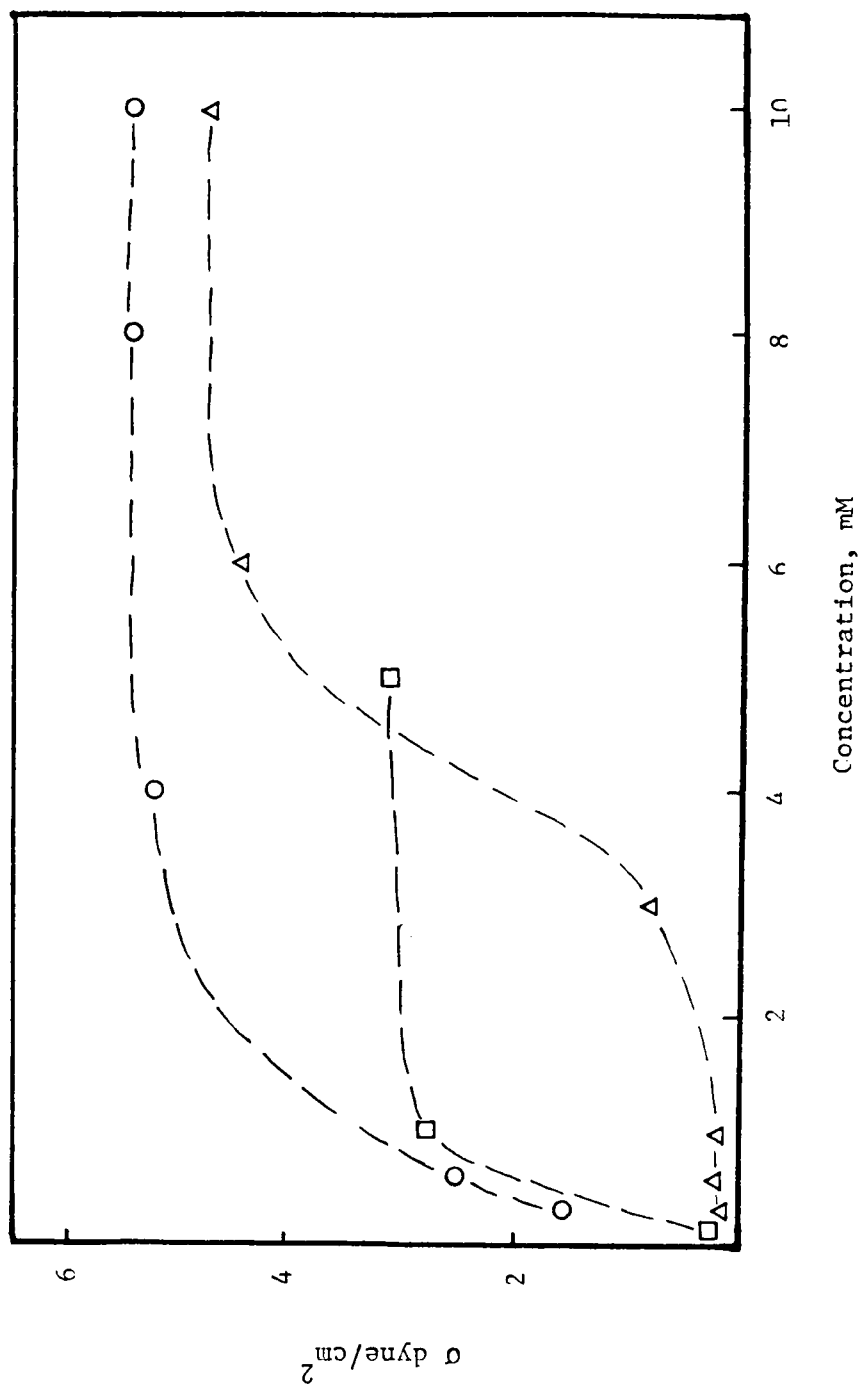


Figure 10. Shear stress versus concentration for CTASal, CTA2,4Cl and CTA3,4Cl at a shear rate of 14.63 sec^{-1} . $\square$, CTASal; Δ , CTA2,4Cl; $\circ$, CTA3,4Cl.

plot of the viscosity of these solutions versus concentration is shown in Figure 11. The results reveal a critical concentration for the CTA3,4Cl solutions at a concentration of about 3.0 mM. It must be pointed out that a value for c^* obtained by capillary viscometry measurements cannot be compared directly to values obtained by measurements of complex viscosity. However, the shear stress imparted to the solution by the capillary is sufficiently small that rheopectic behavior is not induced at concentrations below the observed critical concentration. As has been shown, solutions of CTA3,4Cl at very small concentrations are quite viscous (≈ 30 cP) under constant shear conditions. Below the observed critical concentration, then, the CTA3,4Cl solutions are essentially Newtonian in behavior under the conditions of the capillary experiment. Above the observed critical concentration, the viscosities of the solutions rise very rapidly. Due to the non-Newtonian behavior of the solutions above c^* , a considerable amount of error is introduced in viscometry measurements with the capillary viscometer at higher concentrations, as shown in Table VI. (The error associated with the absolute viscosity values in Table VI is the sample standard deviation of five viscosity measurements at each concentration.) Nevertheless, it is obvious that the rapid rise in viscosity at this point is real, and that c^* corresponds to a major change in the structure of the solution.

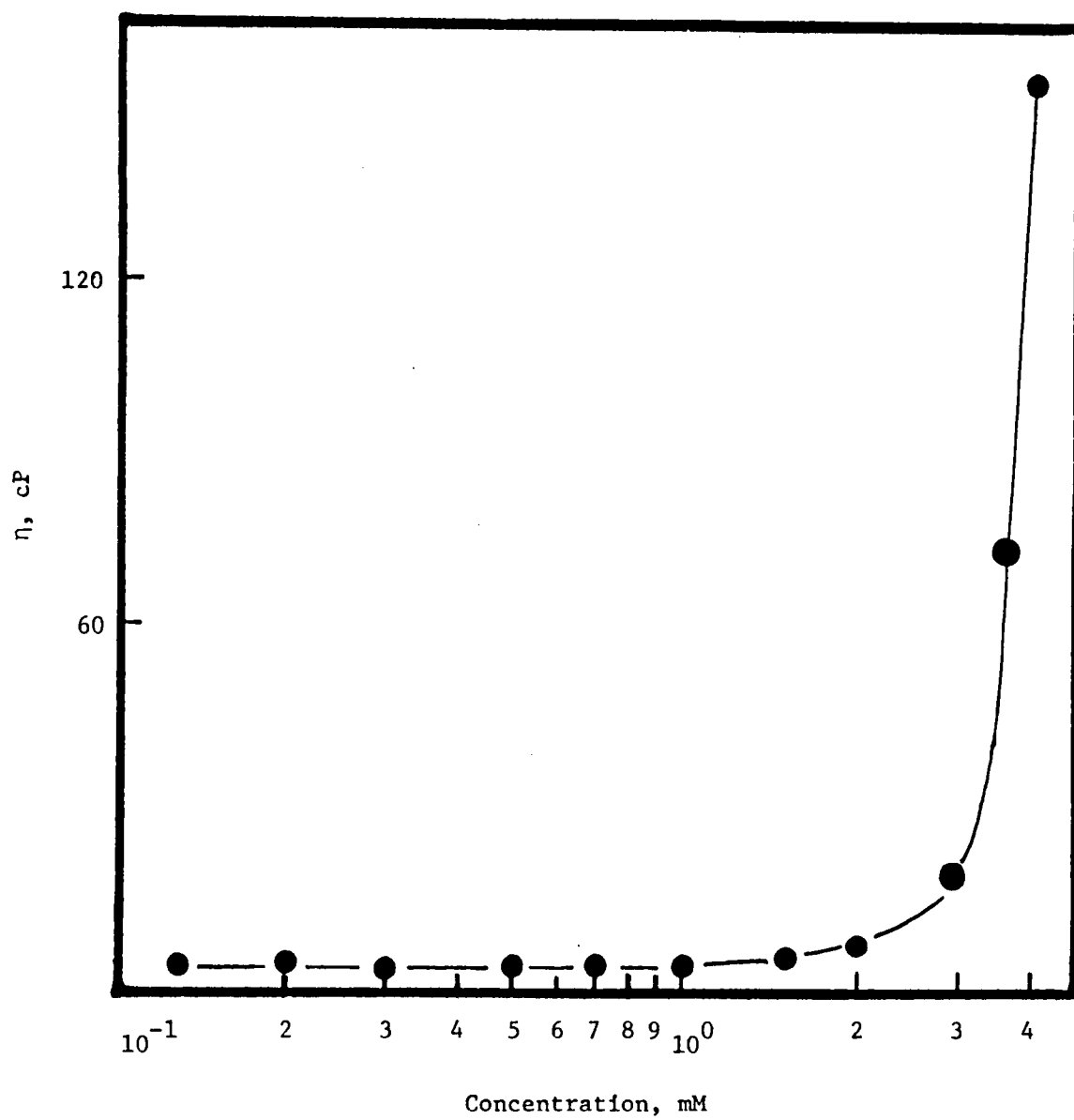


Figure 11. Capillary viscometry of CTA3,4Cl.

TABLE VI
CAPILLARY VISCOMETRY OF CTA3,4Cl

Concentration	Viscosity
4.00 mM	155.6 ± 66.47 cP
3.50	75.09 ± 18.72
3.00	18.71 ± 3.95
2.00	7.520 ± 0.268
1.50	4.530 ± 0.240
1.00	2.752 ± 0.234
0.70	2.346 ± 0.2160
0.50	1.888 ± 0.0510
0.30	1.360 ± 0.017
0.20	1.390 ± 0.046
0.13	0.964 ± 0.0046

CHAPTER III

COUNTERION EFFECTS IN CTAB MICELLAR SOLUTIONS

A. Aromatic Counterions in Cationic Surfactant Solutions

The special affinity between quaternary ammonium cations and aromatic moieties, especially aromatic anions, has been noted by a number of authors.^{41,49,50,58-61} Larsen and Magid⁵⁹ measured the heats of transfer of a number of organic and inorganic salts from water to the surface of CTAB micelles. They noted a marked affinity of tosylate ions for CTAB micelles; furthermore, counterion binding measurements revealed that the tosylate anion completely displaced Br^- from the surface of the micelles. By comparison, acetate and citrate anions demonstrated a weaker affinity for the micellar surface than did Br^- . Bunton^{47a} noted that among solutes added to CTAB, aromatic acids shifted the proton NMR absorbances of the N-methyl and N-methylene groups further upfield than aliphatic acids, and aromatic acid salts shifted the absorbances further upfield than aromatic acids did. The larger upfield shift induced by aromatic compounds is due to the anisotropy of the aromatic ring. The chemical shift changes become pronounced upon ionization because repulsive electrostatic forces are replaced by attractive forces, decreasing the average distance between the aromatic molecule and the CTA^+ head groups. The ring current effect has quite precise geometrical requirements and only those surfactant protons situated in the field of the ring are substantially shifted, thus only

N-methyl and N-methylene protons are affected. In measurements of positive surface potentials for a cationic surfactant monolayer, Goddard⁵⁸ found little or no evidence of strong interaction for aliphatic acid salts with docosyltrimethylammonium bromide (docosyl = $n - C_{20}H_{41}-$) head groups, whereas aromatic carboxylates and sulfonates interacted very strongly with the surfactant.

Among the effects of increased interactions between cationic amphiphilic moieties and their counterions are a decrease in CMC values, a greater tendency to form cylindrical micelles than for surfactants with more weakly interacting counterions and, occasionally, the appearance of strongly viscoelastic properties. Even among aromatic counterions, these effects can be quite specific, depending strongly upon the structure of the counterion. For example Gravsholt²⁵ determined CMC values by conductimetry for a number of aromatic CTAX's. In every case the CMC was lower than that of CTAB; but for CTA4OH and CTA2Cl, the CMC was about half that of CTAB, while for CTASal and CTA4Cl the CMC values were much lower. In addition, the latter surfactant solutions were strongly viscoelastic, whereas the former solutions exhibited normal viscosity behavior. Underwood and Anacker⁶² noted similar behavior in CMC determinations of decyltrimethylammonium surfactants with a series of twenty different aromatic counterions. Again, in every case, the CMC value was lower for the aromatic CTAX than for CTAB. Among the benzoate counterions, the variation of the CMC values was dependent upon the hydrophobicity of the counterion, with the lower CMC values corresponding to the more hydrophobic

counterions. Goddard also noted specificity among aromatic counterions toward interactions with quaternary ammonium head groups in surface monolayers.⁵⁸ He noted stronger interaction for aromatic sulfonates than for aromatic carboxylates and stronger interaction for 4-chlorobenzoate than for 2-chlorobenzoate. He also found stronger interaction for 4-hydroxybenzoate than for 2-hydroxybenzoate, a result that conflicted with Gravsholt's findings. Underwood and Anacker⁶³ pointed out that it might not always be possible to predict results for experiments on micelles from studies of other types of organized assemblies. Their light scattering experiments confirmed Gravsholt's observation of a stronger interaction of salicylate with the micellar surface than for 4-hydroxybenzoate. Their studies suggest that decyltrimethylammonium salicylate forms cylindrical micelles, whereas decyltrimethylammonium 4-hydroxybenzoate does not. Similar results had already been observed for other amphiphilic cations.^{42,64} Ulmius and co-workers⁴² showed by means of linear dichroism and nuclear magnetic resonance that CTASal forms long rod-like micelles at surfactant concentrations as low as 1.0 mM, while CTA4OH does not, even at ten times the CTASal concentration. Small-angle neutron scattering measurements performed by Hoffmann and co-workers indicate that cetylpyridinium salicylate also forms cylindrical micelles at concentrations as low as 3.0 mM.⁶⁴ Bain and Hyde⁴¹ demonstrated through flow birefringence and light scattering measurements that solutions of CTAB form rod-like micelles upon the addition of sodium 4-chlorobenzoate.

Attempts have been made to explain, in terms of counterion structure, the specificity of the micellar head group region toward various counterions. Ulmius et al.⁴² speculated that the salicylate anion is somewhat amphiphilic itself, and can be oriented at the micellar surface such that the hydroxyl and carboxylate groups are exposed to the aqueous environment at the micelle surface, while the remainder of the anion, the hydrophobic portion, can position itself somewhat below the surface, in a more favorable environment. On the other hand, no such favorable orientation can be envisioned for the 4-hydroxybenzoate counterion, since solubilization of the aromatic ring in the hydrophobic portion of a micelle forces the hydroxyl group into an unfavorable apolar environment. Johnson and Olofsson⁶⁵ determined the difference between the apparent molar heat capacities of CTASal and NaSal and between CTA4OH and Na4OH. In the absence of specific counterion interactions in the micellar solutions, the two differences should have nearly the same value. However, the difference is significantly lower for the salicylate anion than for the 4-hydroxybenzoate anion. The authors interpreted this to mean that the salicylate anion penetrates into the head group region with an accompanying loss of hydration, while the more hydrated 4-hydroxybenzoate anion remains outside the palisade layer. Underwood and Anacker⁶³ reach essentially the same conclusion and point out that the model is only valid if the Stern layer is thin, with an abrupt transition from the hydrocarbon core to the Stern region. If, as in Menger's model,¹⁰ a small hydrophobic core is "surrounded by a much larger region composed of hydrocarbon, water,

head groups, and counterions," then it is difficult to see why one hydroxybenzoate interacts more favorably with the Stern region than any other.

B. Conductimetric Measurements of CTAX Surfactant Solutions

Conductimetry is a commonly applied technique for the determination of CMC values.¹⁹ The utility of this method for solutions of ionic surfactants arises from a change in the concentration dependence of the specific conductivity of the solution, L , with increasing surfactant concentration. At concentrations below the CMC, the unaggregated surfactant molecules are dissociated into individual ions, while at concentrations above the CMC, a majority of the counterions are bound to the micelles. When a plot of specific conductivity versus concentration is made, two straight lines of differing slopes are obtained. The point of intersection of the two lines, determined graphically or analytically by a linear least squares fit of the data points of each slope, is taken to be the CMC. In addition, the ratio of the slopes above and below the CMC is considered a good approximation of the degree of counterion binding.

In some cases, more than one break in the L vs. concentration curve has been noted. Hoffmann et al. performed conductivity measurements on hexadecylpyridinium salicylate⁴³ and tetradecylpyridinium heptanesulfonate.⁶⁷ In both cases, two breaks in the conductivity curves were noted. According to Hoffmann, the surfactants form

spherical micelles at the first break, or CMC_I , then undergo a shape transition from spherical micelles to cylindrical micelles at the CMC_{II} . Magid et al.⁶⁶ reported two "operational" CMC's for both sodium bis(n-hexyl)sulfosuccinate and sodium bis(n-octyl)sulfosuccinate. In both cases, the breaks at lower concentration corresponded to the value of the CMC found by an EMF method. The second break points were attributed to a continuous decrease in degree of counterion dissociation, rather than a transition in shape.

In this work, conductivity measurements have been carried out on seven surfactants: CTASal; CTA2Cl; CTA4Cl; CTA2,4Cl; CTA2,6Cl; CTA3,4Cl; and CTA3,5Cl. Plots of specific conductivity versus concentration are shown in Figures 12-18. Table VII tabulates values for the CMC_I and CMC_{II} as well as α_L , the degree of counterion dissociation derived from slope ratios of the specific conductivity plots. $\alpha_{L,I}$ is the ratio of slopes II and I, and $\alpha_{L,II}$ is the ratio of slopes III and I. Two breaks in the conductivity plots were seen in the cases of CTASal; CTA4Cl; and CTA2,4Cl. Previously, Gravsholt²⁵ reported CMC values from conductimetry measurements of CTASal (0.152 mM), CTA2Cl (0.496), and CTA4Cl (0.163 mM); however, she reported that only one break was seen in all her conductivity plots, including CTASal and CTA4Cl. Since repeated measurements by this author of these surfactants consistently gave two breaks in their conductivity curves, it is difficult to explain the failure of Gravsholt to note a second break. Other than CMC values, she presented no other data or plots in her paper.

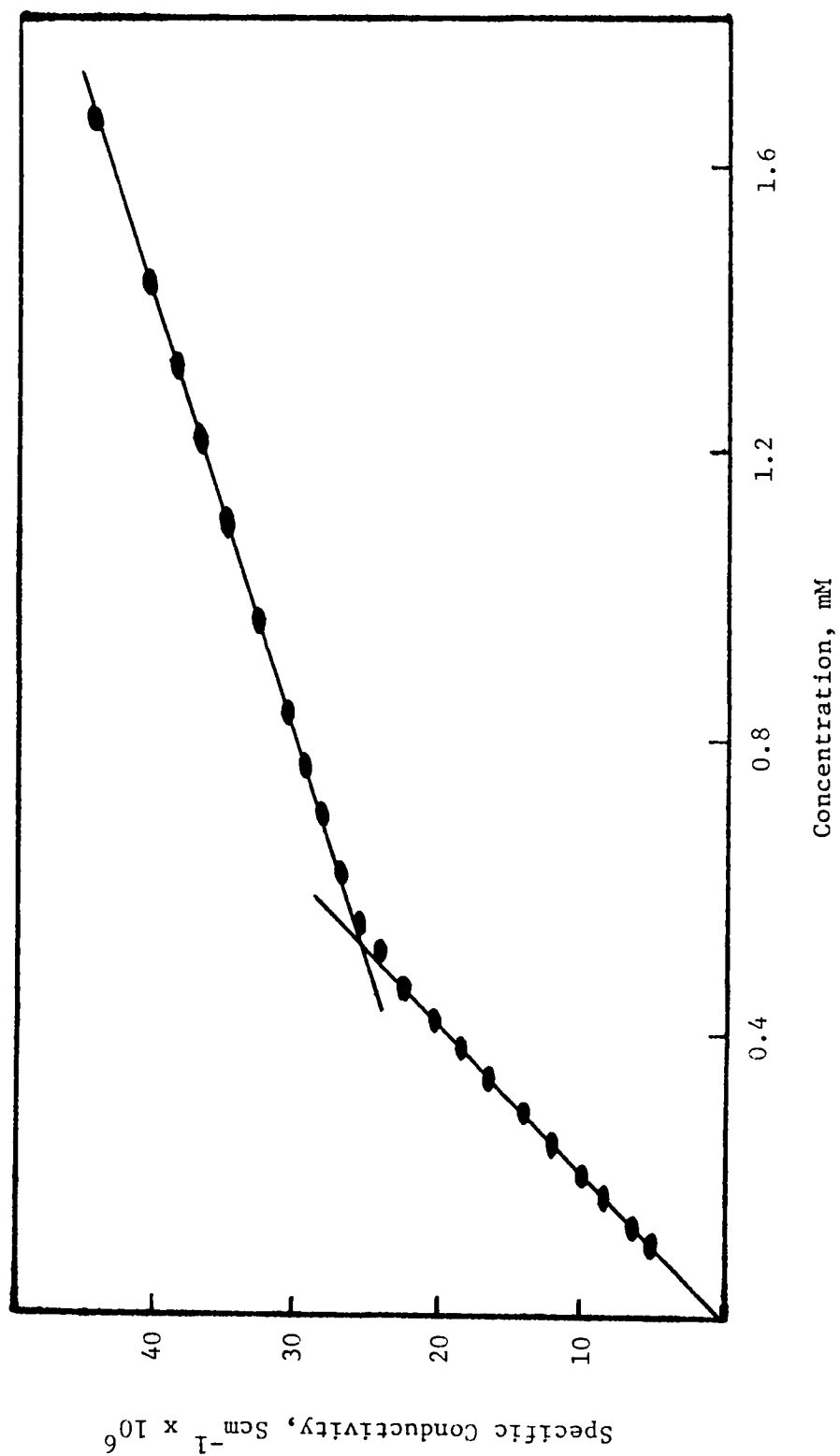


Figure 12. Specific conductivity of CTA2Cl.

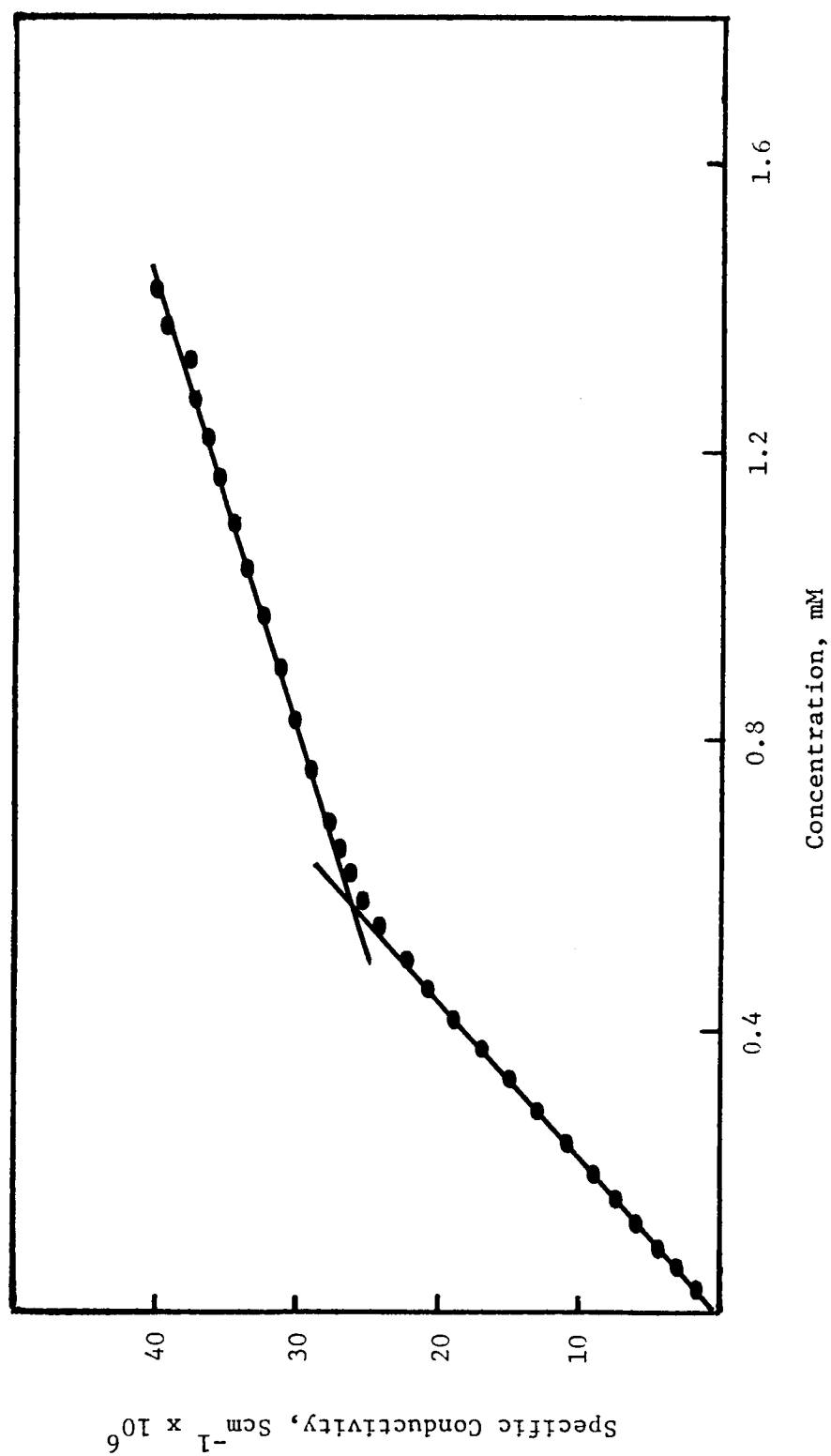


Figure 13. Specific conductivity of CTA2,6Cl.

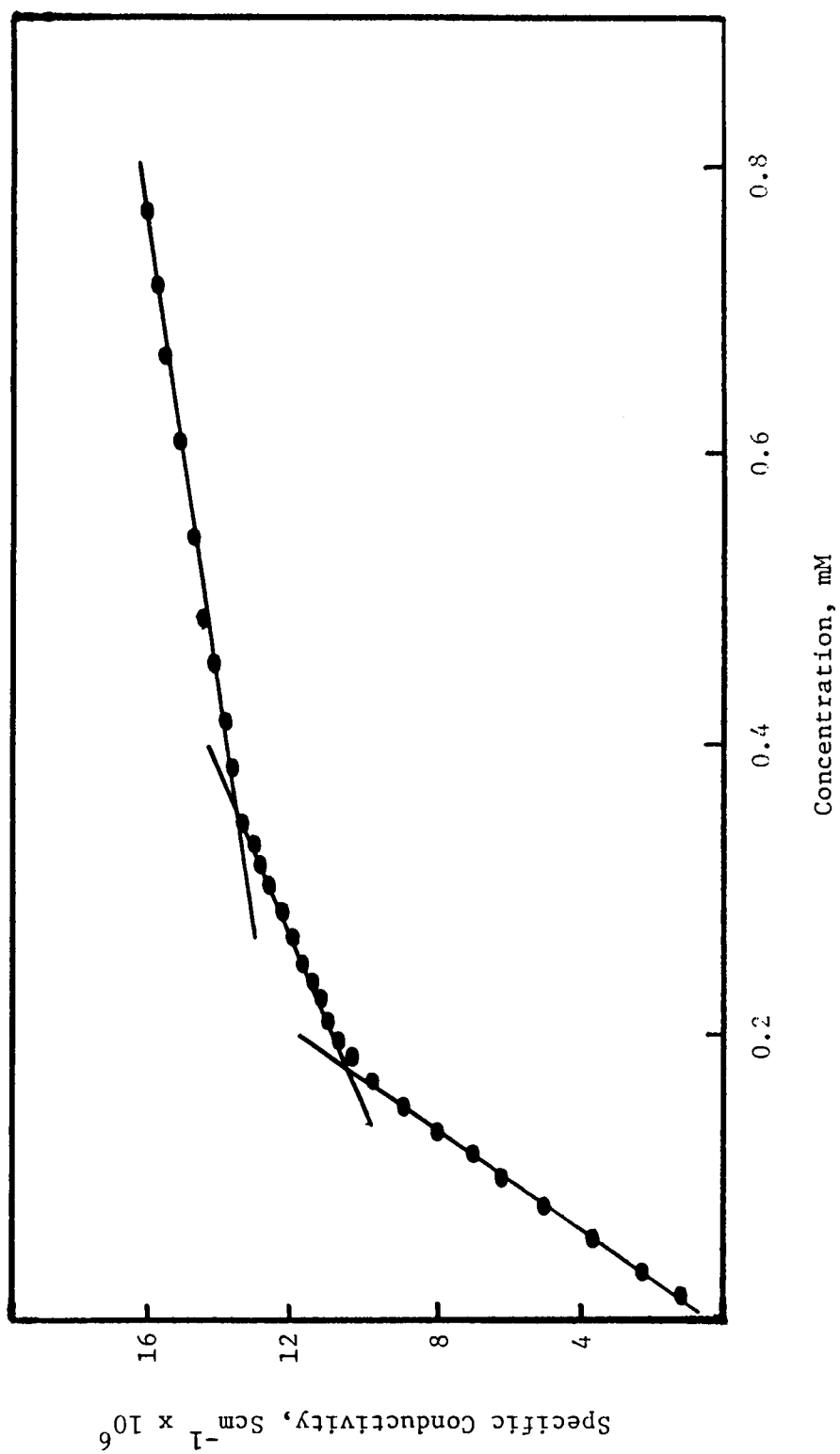


Figure 14. Specific conductivity of CTA2,4Cl.

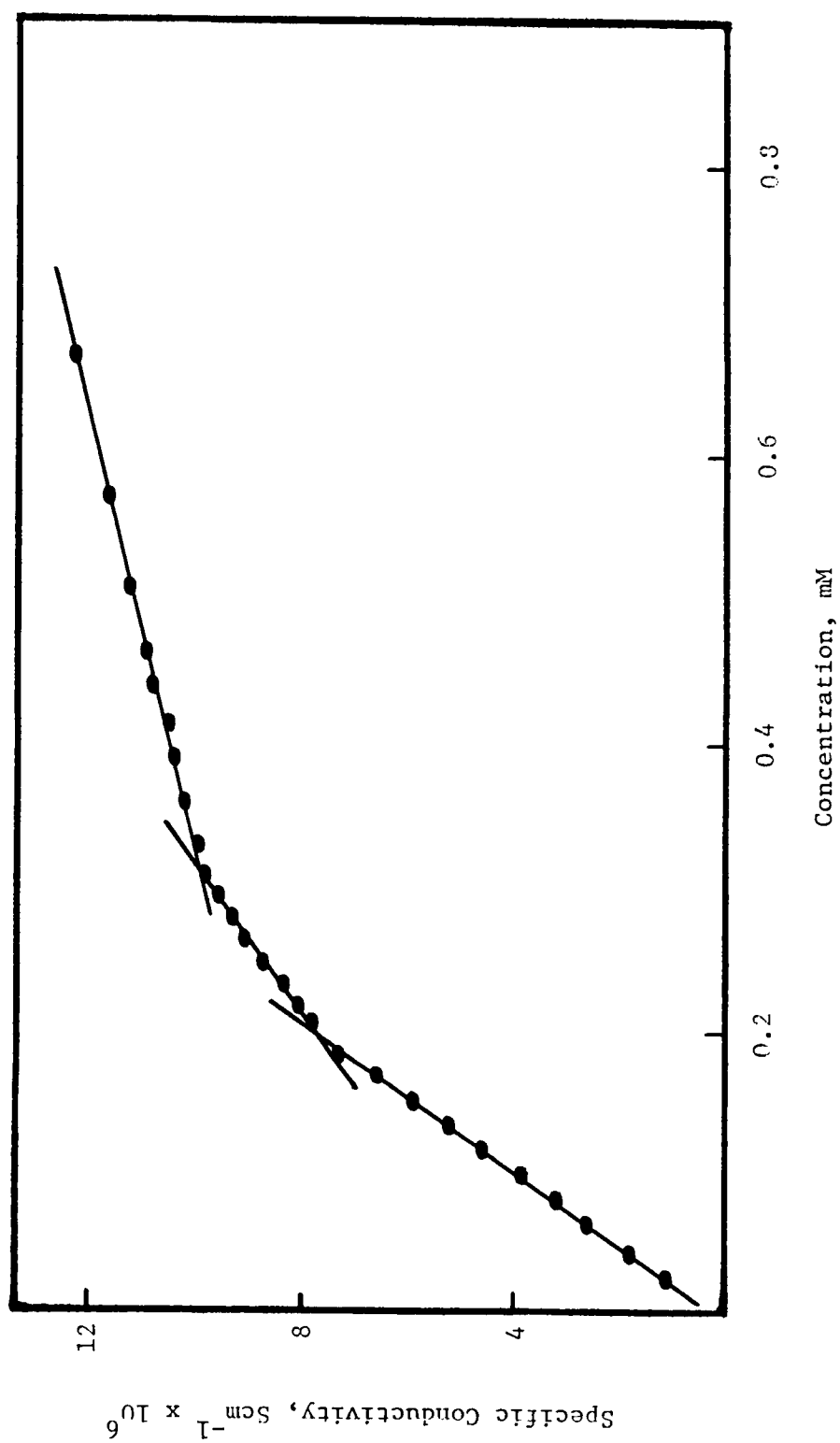


Figure 15. Specific conductivity of CTA4Cl.

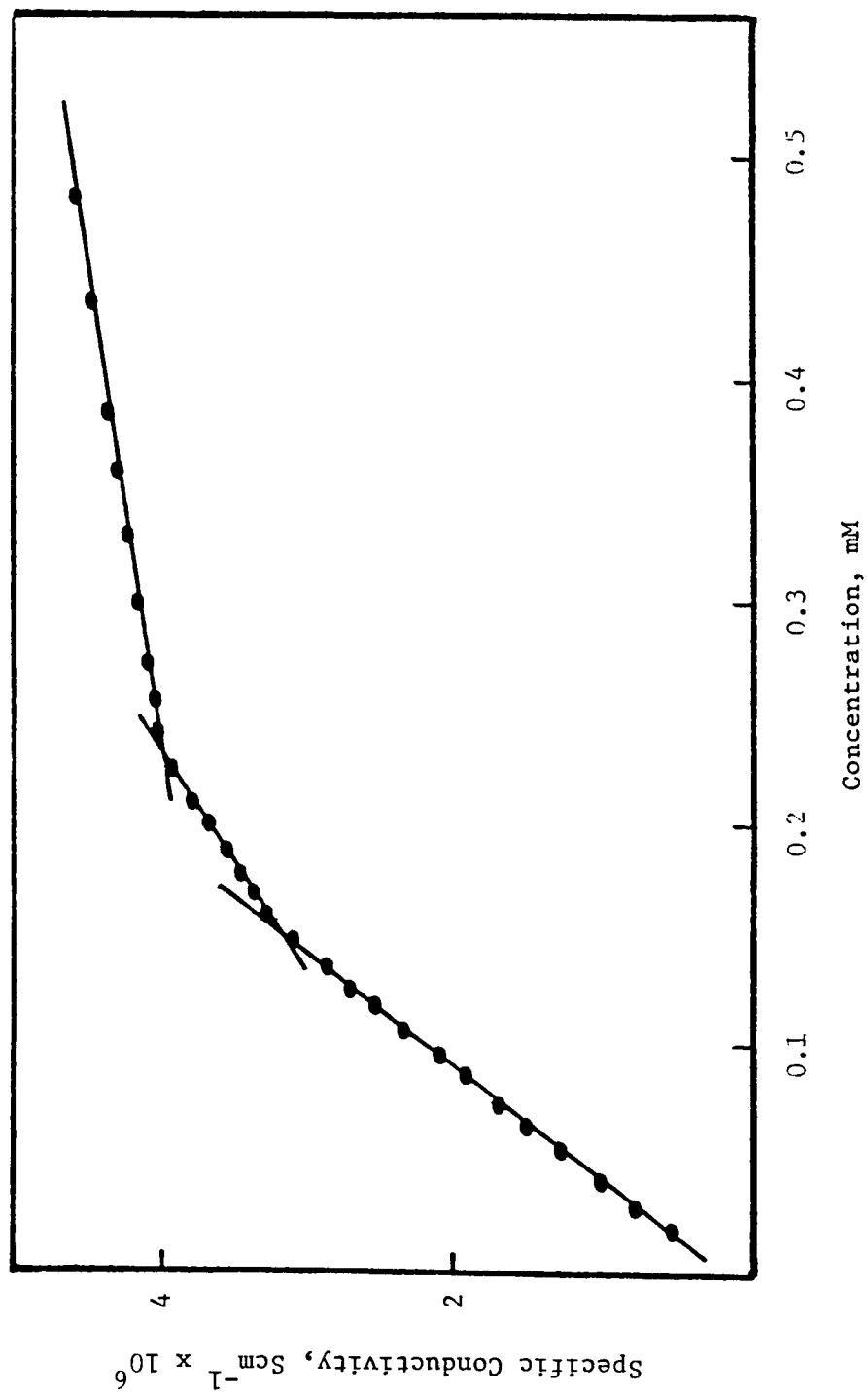


Figure 16. Specific conductivity of CTASal.

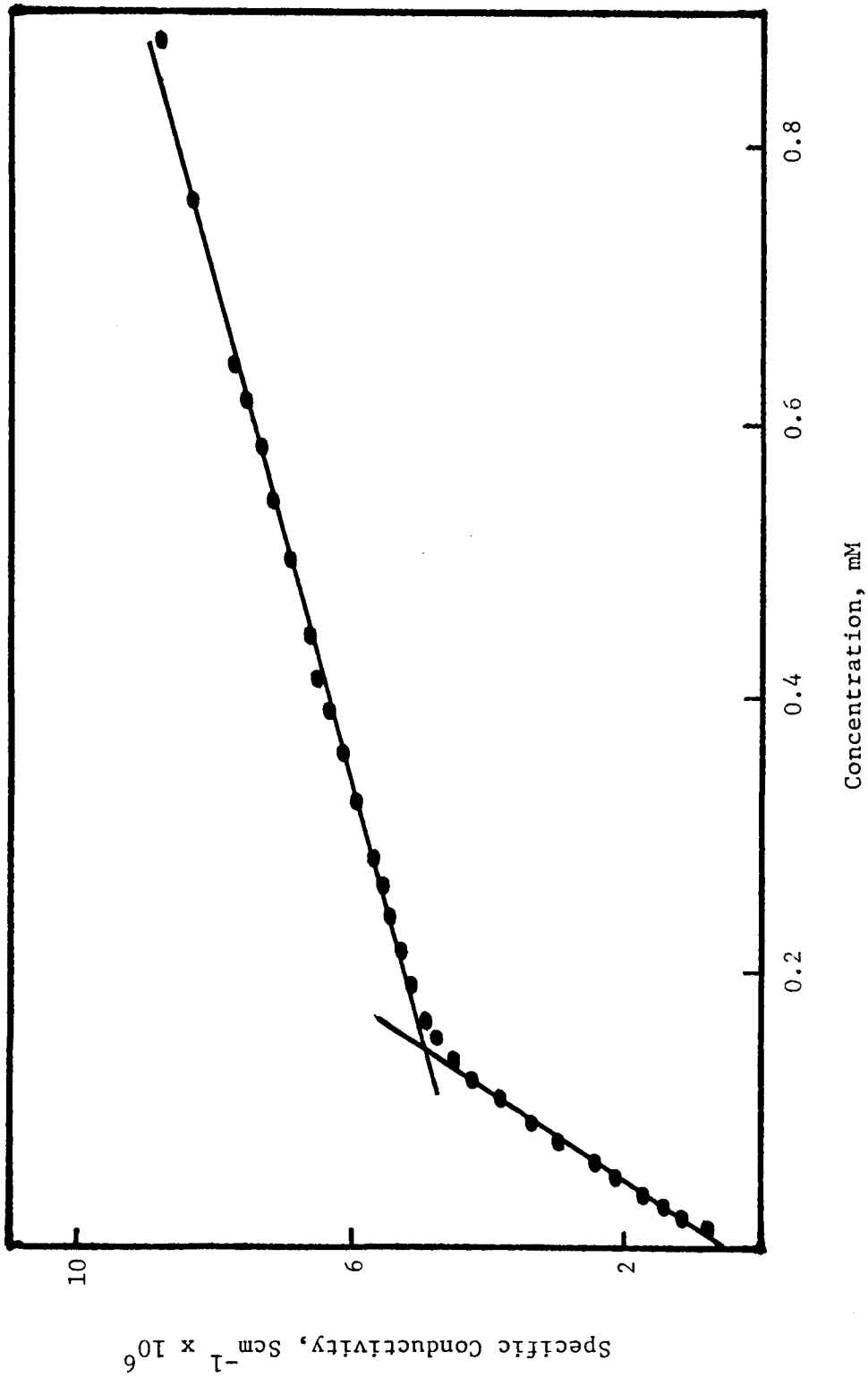


Figure 17. Specific conductivity of CTA3,4Cl.

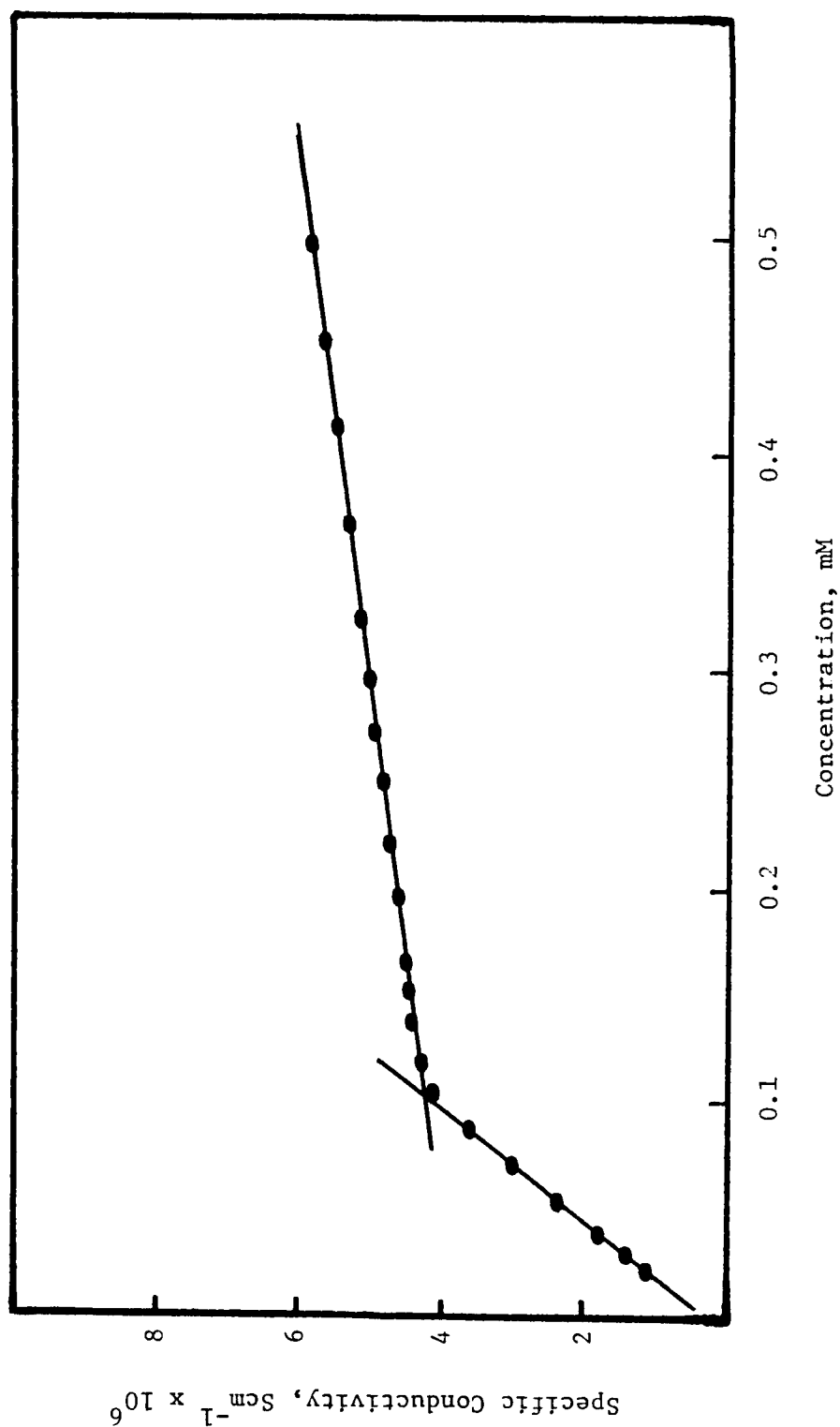


Figure 18. Specific conductivity of CTA3,5Cl.

TABLE VII

CMC'S AND COUNTERION DISSOCIATIONS OF CTAX'S

Compound	CMC _I	CMC _{II}	$\alpha_{L,I}$	$\alpha_{L,II}$
CTA2C1	0.502 mM	--	0.32	--
CTA2,6C1	0.562	--	0.36	--
CTA2,4C1	0.162	0.365 mM	0.32	0.10
CTA4C1	0.196	0.312	0.43	0.18
CTASa1	0.154	0.236	0.22	0.12
CTA3,4C1	0.134	--	0.15	--
CTA3,5C1	0.104	--	0.10	--

Certain trends may be seen in the data of Table VII. CTA2C1 and CTA2,6C1 have similar CMC and α values, and have only one break in their conductivity plots. Both surfactants have counterions with chlorine atoms in the ortho position only. CTA3,4C1 and CTA3,5C1, whose counterions have their chlorine atoms in meta and para positions, also have only one break in their conductivity curves. In this case, however, the CMC values are considerably lower than for CTA2C1 and CTA2,6C1, and the degree of counterion dissociation is much less.

For CTA4C1 and CTA2,4C1, which undergo a second transition after micellization, the $\alpha_{L,I}$ values correspond closely to the $\alpha_{L,I}$ values of CTA2C1 and CTA2,6C1, while the $\alpha_{L,II}$ values of CTA4C1 and CTA2,4C1 closely match those of CTA3,4C1 and CTA3,5C1. These results indicate that CTA4C1 and CTA2,4C1 undergo a transition to form aggregates with a degree of counterion dissociation similar to the aggregates of CTA3,4C1 and CTA3,5C1. Aggregates with similar properties have been shown to form cylindrical micelles.⁶³ Table VIII lists CMC and α values determined by Underwood and Anacker for solutions of decyltrimethylammonium surfactants with substituted benzoate counterions. The CMC's are higher, as expected for solutions of the shorter-chained surfactant, but the same trend is seen as for the CTAX's. The degree of counterion dissociation values were determined from light scattering measurements experiments and are remarkably similar to those for the CTAX's in Table VII.

Values of α may also be obtained from the conductivity data by using Evans's equation:²¹

TABLE VIII

CMC'S AND COUNTERION DISSOCIATIONS OF
DECYLTRIMETHYLAMMONIUM SURFACTANTS

Counterion	CMC	α
Benzoate	5.3 mM	0.21
Salicylate	1.9	0.08
<u>p</u> -hydroxybenzoate	15.0	0.25
<u>o</u> -hydroxybenzoate	3.8	0.34
<u>m</u> -chlorobenzoate	1.0	0.10
<u>p</u> -chlorobenzoate	0.63	0.14

$$(1000)S_2 = \frac{(\bar{N} - m)^2}{\bar{N}^{4/3}} (1000S_1 - \Lambda_X^-) + \frac{\bar{N} - m}{\bar{N}} \Lambda_X^- \quad (25)$$

where S_1 and S_2 are the slopes below and above the CMC, respectively, Λ_X^- is the equivalent conductivity of the counterion at 25°C, $\bar{N}$ is the average micellar aggregation number, and m is the average number of bound counterions. Hence, in Evans's terminology, $\alpha = (\bar{N} - m)/\bar{N}$ and Equation 25 can be rewritten

$$(1000)S_2 = \bar{N}^{2/3} (1000S_1 - \Lambda_X^-) \alpha^2 + \Lambda_X^- \alpha \quad (26)$$

Values of Λ_X^- for the 2-chlorobenzoate anion and the 2,6-chlorobenzoate anion were taken from the literature,^{68,69} and values for the mean aggregation numbers near the CMC for CTA2Cl and CTA2,6Cl were taken from small-angle neutron scattering experiments (see Chapter IV, section E.2). Table IX lists the mean aggregations numbers, the equivalent conductances for the counterions, and the degree of counterion dissociation calculated from Equation 26 for CTA2Cl and CTA2,6Cl.

Figures 19-24 are plots of the equivalent conductivity Λ , in $\text{Scm}^2\text{mol}^{-1}$, versus the square root of the surfactant concentration. The upper portions of the curves give an indication of the tendency of the ions to associate in solutions of surfactant monomers below the CMC. Where the CMC is sufficiently high, there is a general tendency for the upper curve to be relatively flat at concentrations between $0.01 \text{ M}^{1/2}$ and $0.02 \text{ M}^{1/2}$, as for CTA2Cl; CTA2,6Cl; and CTA4Cl. At lower

TABLE IX

COUNTERION DISSOCIATIONS FROM EQUIVALENT CONDUCTIVITIES

Compound	$\bar{N}$	Λ_X^-	α
CTA2Cl	84.3	29.6	0.53
CTA2,6Cl	91.0	28.2	0.56

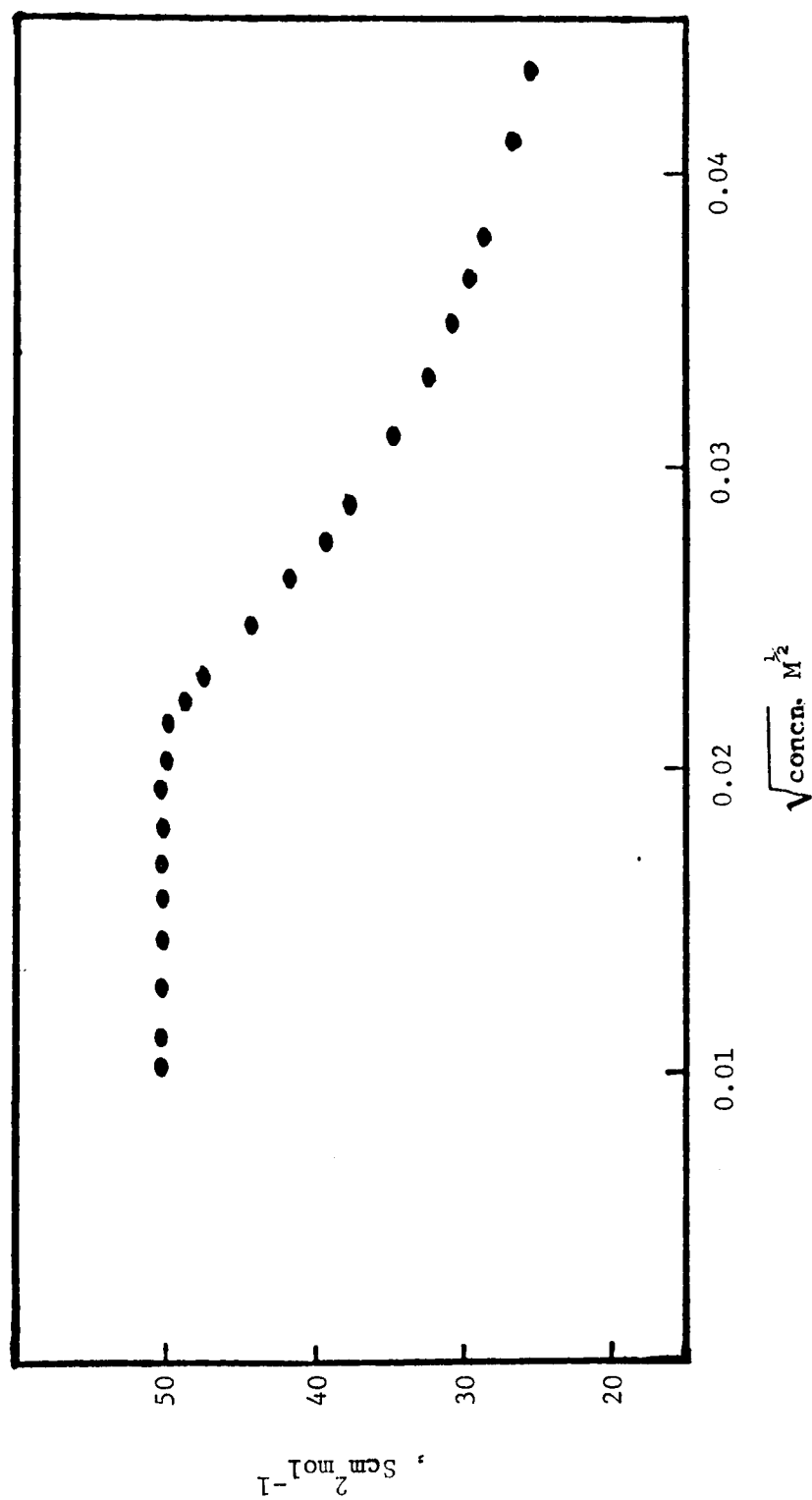


Figure 19. Equivalent conductivity of CTA2Cl.

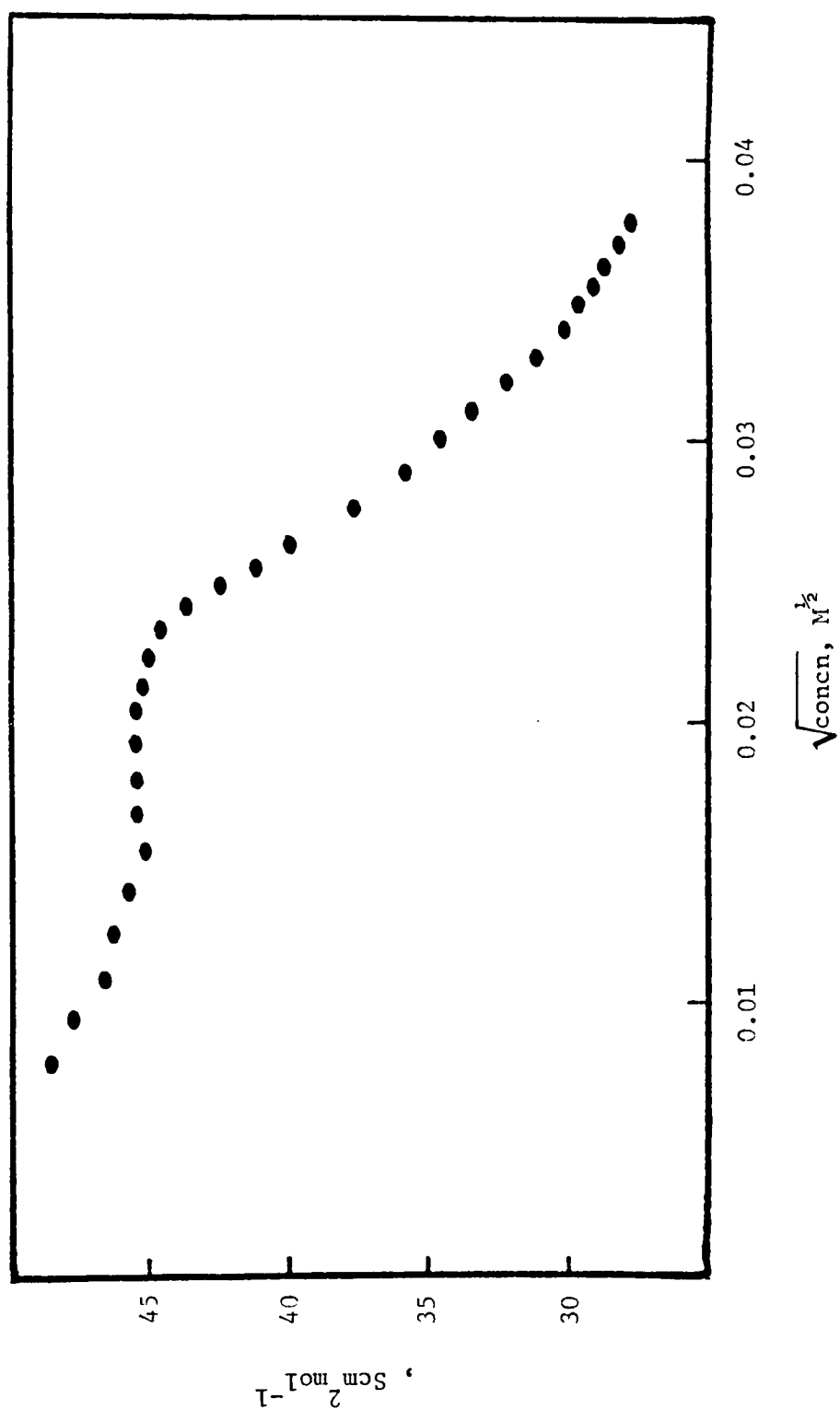


Figure 20. Equivalent conductivity of CTA2,6Cl.

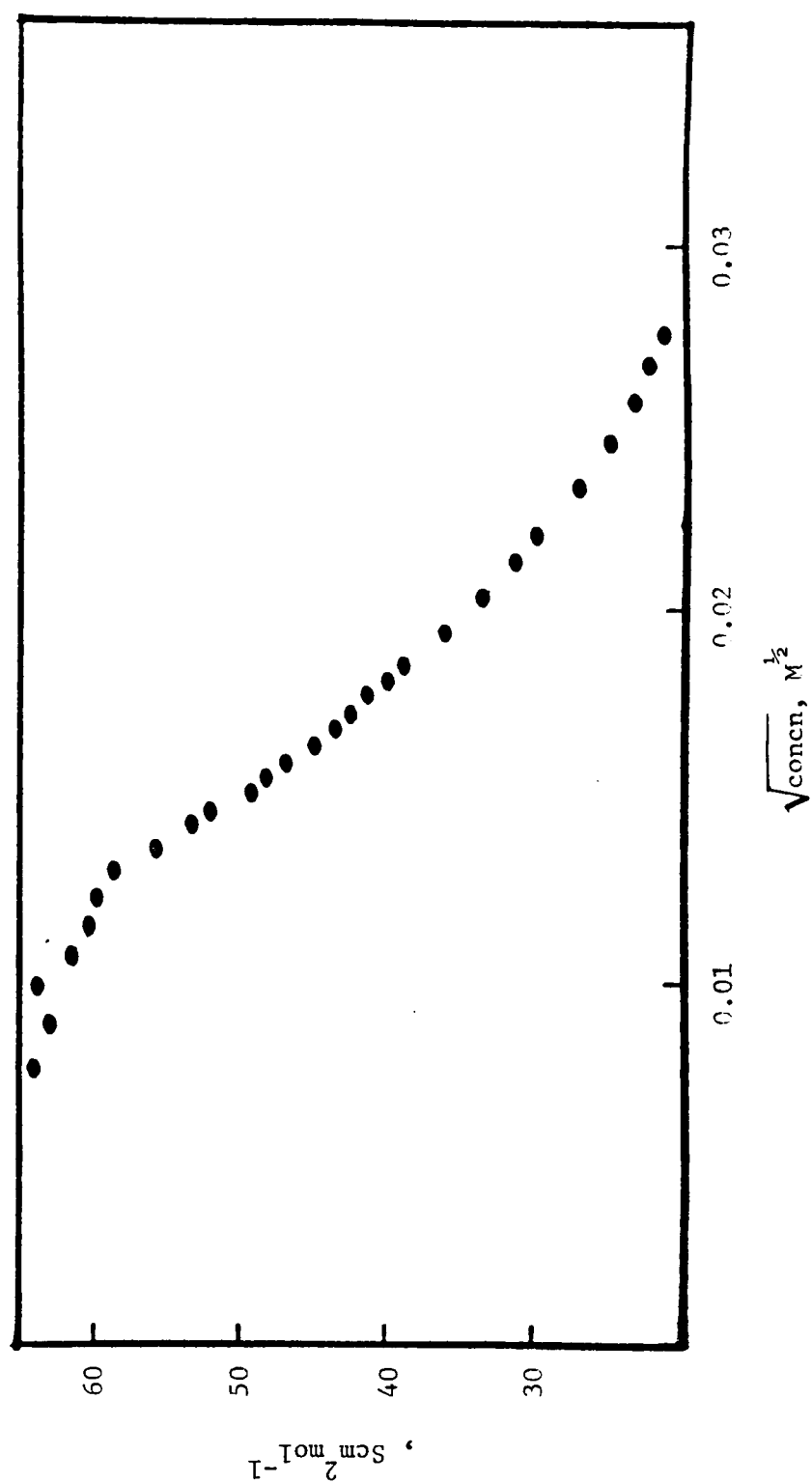


Figure 21. Equivalent conductivity of CTA2,4Cl.

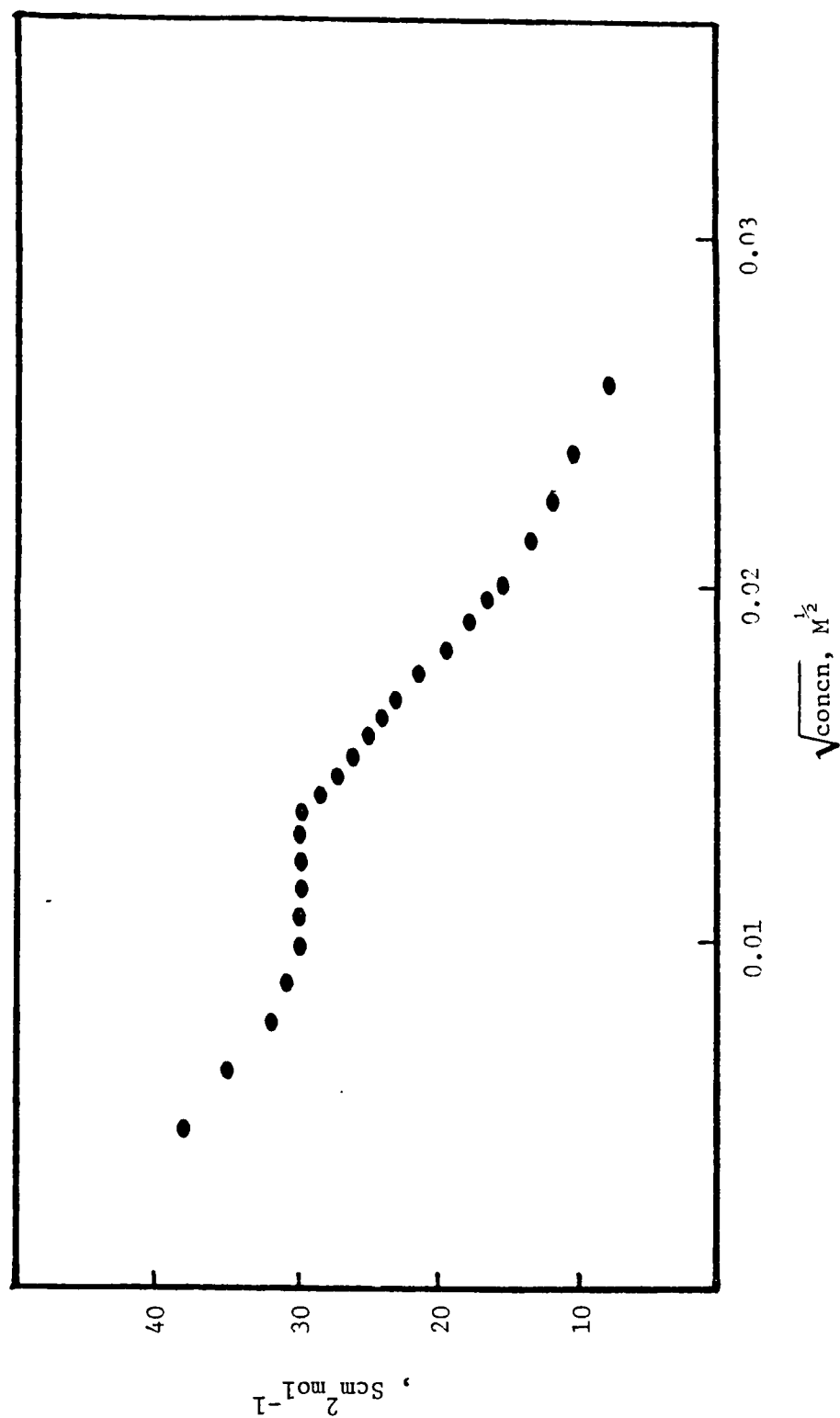


Figure 22. Equivalent conductivity of CTA4Cl.

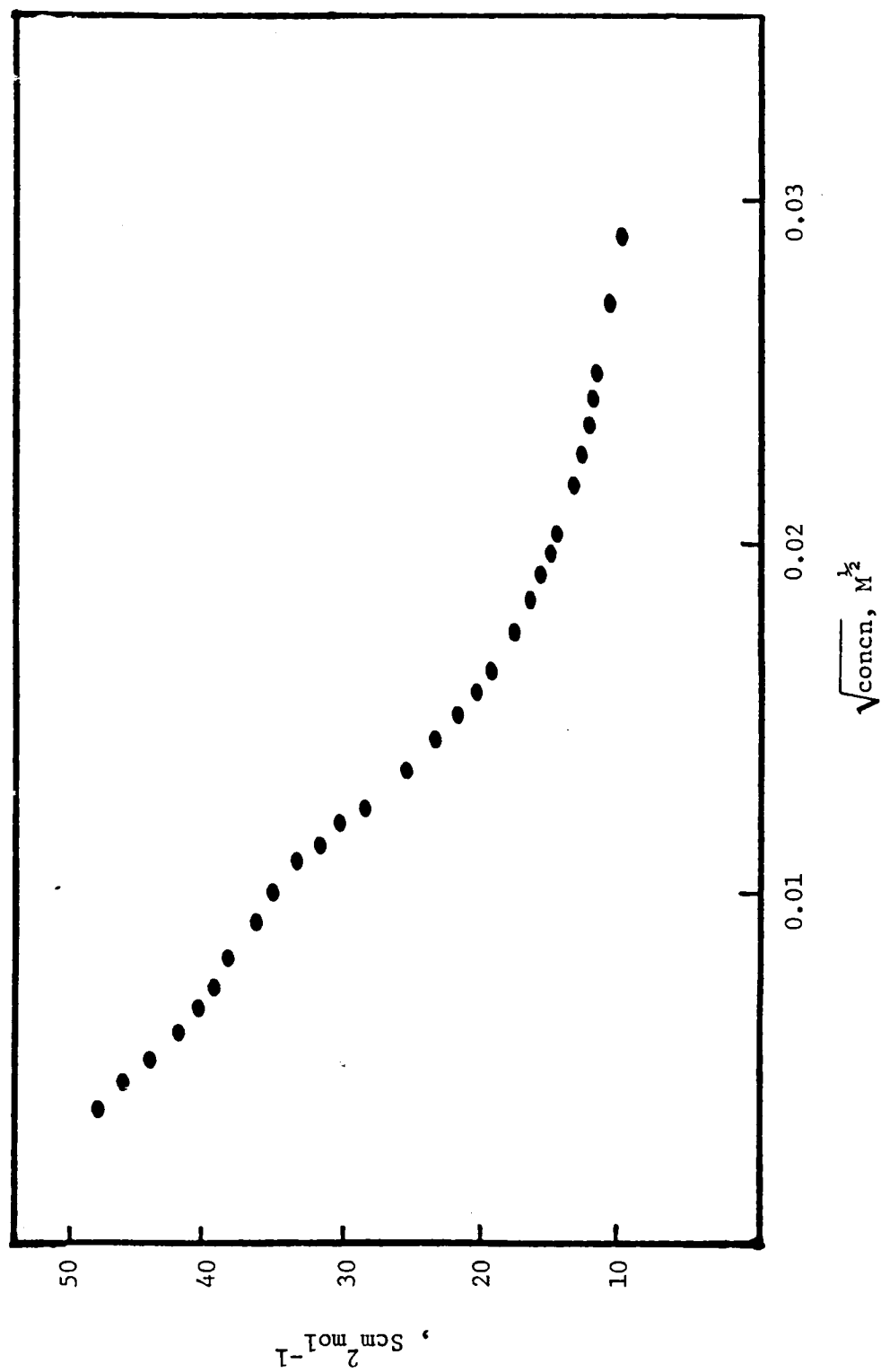


Figure 23. Equivalent conductivity of CTACl.

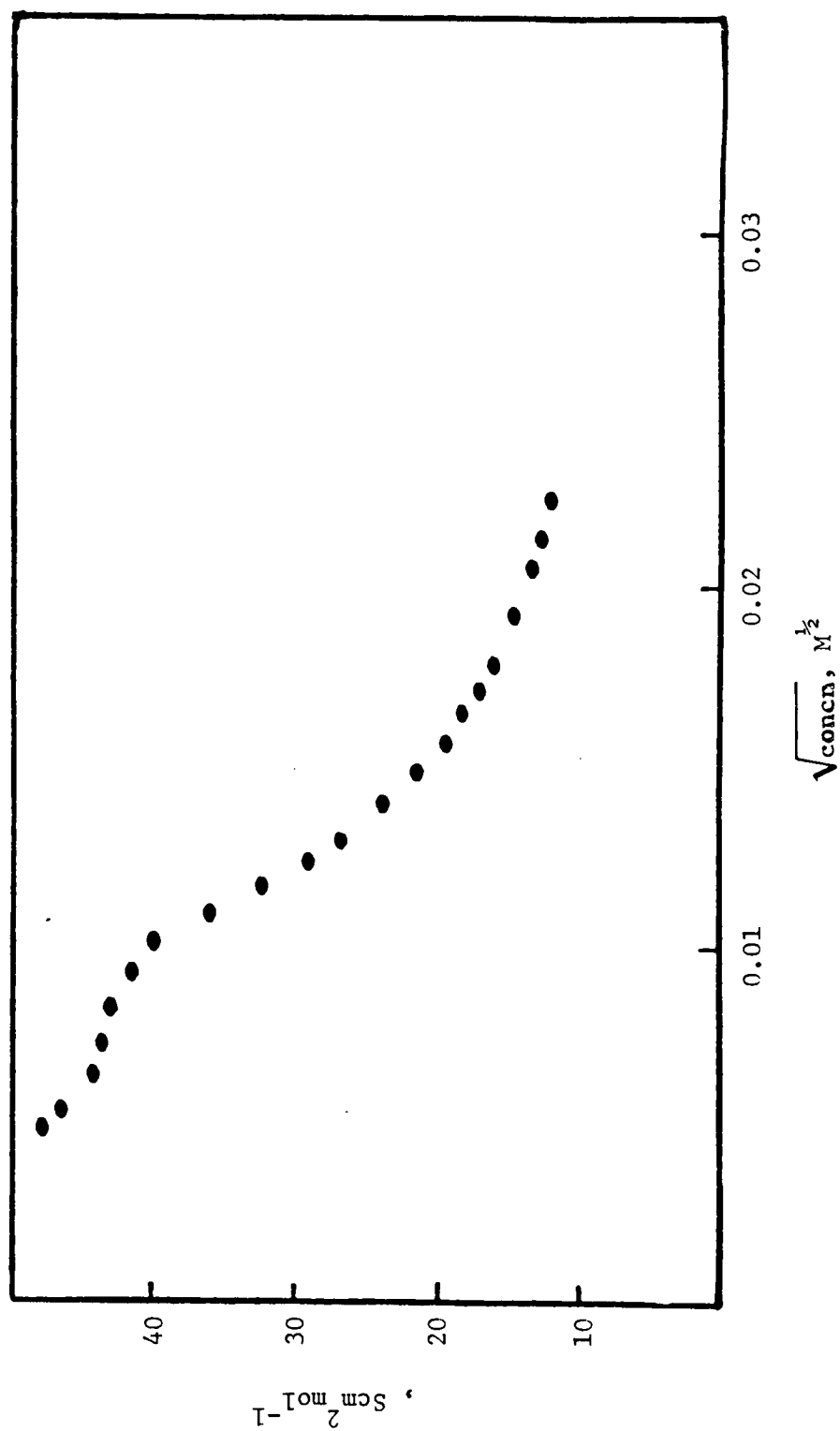


Figure 24. Equivalent conductivity of CTA3,5Cl.

concentrations, below about $0.01 \text{ M}^{1/2}$, there is an upturn in the curve for all the surfactant solutions. This is similar to the behavior seen in solutions of weak electrolytes such as aqueous acetic acid. At high concentrations the equivalent conductivity curve for aqueous acetic acid is relatively flat, but at lower concentrations the plot curves upward, indicating that the acetic acid is becoming increasingly dissociated into ions. Solutions of strong 1:1 electrolytes, on the other hand, yield equivalent conductivity slopes which are flat or gently curving over all concentrations. The curves for the CTAX's indicate that these surfactants have a tendency to associate, either as ion pairs, or as premicellar aggregates at concentrations above $0.01 \text{ M}^{1/2}$ and below the CMC. Below $0.01 \text{ M}^{1/2}$, the surfactant monomers are becoming increasingly dissociated with decreasing concentration.

Finally, Figure 25 shows the specific conductivity data for CTA2Cl at high concentrations. The deviation from linearity of the points above 15 mM may be due to a gradual shape change as the spherical micelles become ellipsoidal in shape. More evidence for a shape transition at these concentrations is seen for CTA2Cl and CTA2,6Cl from small-angle neutron scattering measurements and will be discussed in Chapter IV.

C. Nuclear Magnetic Resonance of Aqueous CTAX Surfactant Solutions

Proton nuclear magnetic resonance spectra of aqueous micellar solutions of CTAB have been made by Ulmuis and Wennerstrom.⁷⁰ At 28°C,

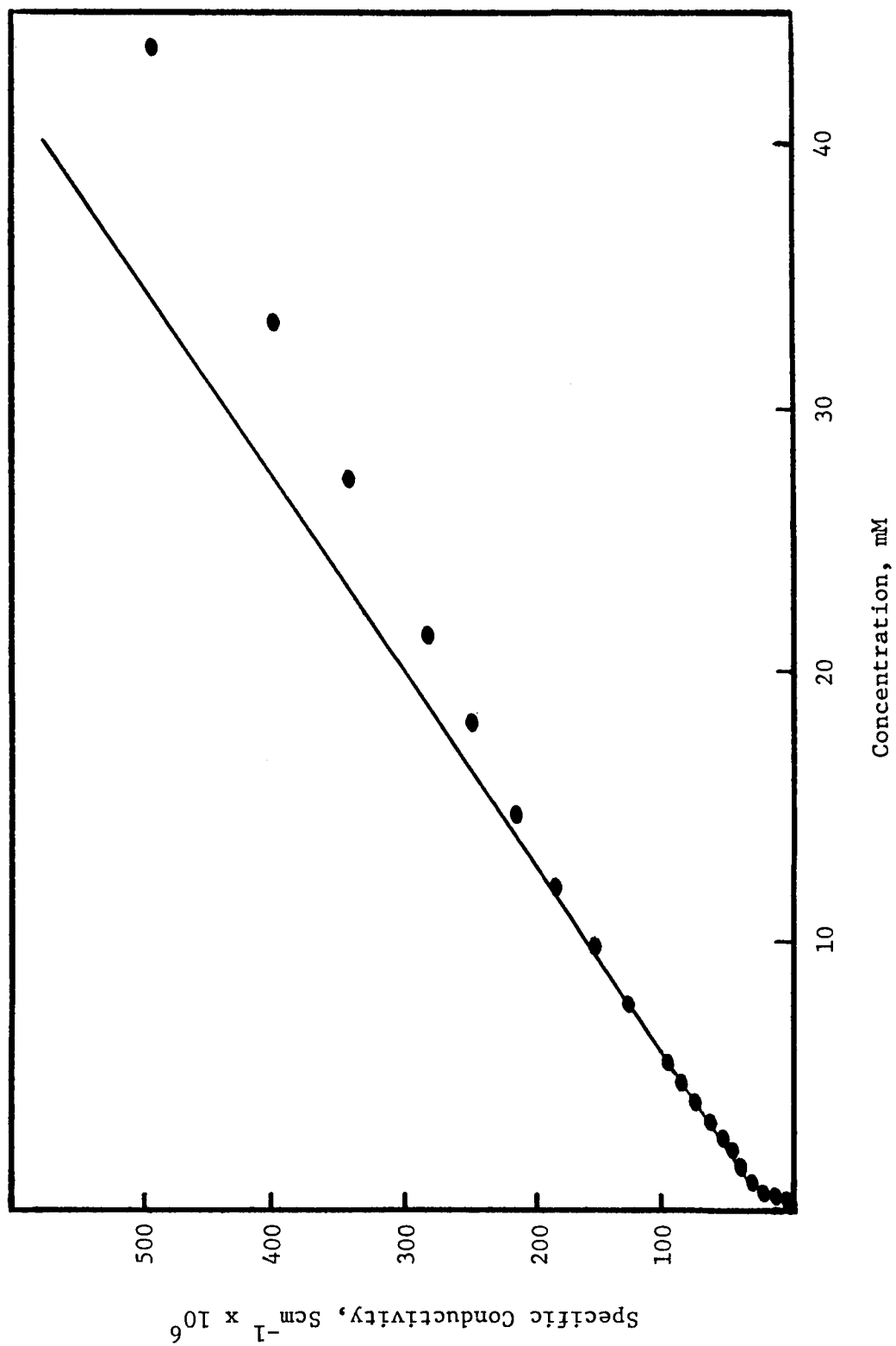


Figure 25. Specific conductivity of CTA2Cl at high concentrations.

solutions from 1.0 mM to approximately 0.27 M contain small spherical micelles. Above 0.27 M, the micelles begin to grow and become rod-shaped. In the lower concentration range, the proton spectra show typical high-resolution features with Lorentzian band shapes. The spectra of the rod-shaped micelles have broadened resonance peaks, with the peaks becoming broader as the CTAB concentration increases. Ulmius et al.,⁴² made proton NMR spectra of aqueous solutions of CTASal and CTA4OH, both at concentrations of 12 mM. For the CTA4OH solution, the spectrum is similar to that of CTAB at low concentrations, with well-defined resonance peaks. The peaks of the CTASal spectrum, on the other hand, are broadened and most of the detail is lost. The authors claim that the peak broadening and loss of detail is due to the presence of large rod-shaped aggregates. Bunton and Minch⁶¹ noted that the N-methyl and N-methylene protons of CTAB head groups are shifted up-field when aliphatic or aromatic carboxylate ions are added. The shift of the methyl groups was about 0.1 ppm for aliphatic ions and about 0.4 ppm for aromatic ions.

In this work, proton NMR measurements were primarily made to determine whether differences in the positioning of the counterions near the surfactant head groups could be detected. Johnson and Olofsson⁶⁵ have predicted that the counterions lie either outside the head group region (in the case of CTA4OH) or between the head groups (in the case of CTASal). If this is true, the N-methylene group should experience different environments and be shifted to different extents, depending upon the counterion orientation. In addition, the NMR

measurements will give some evidence as to the shape of the micelle as shown by Ulmius and Wennerstrom⁷⁰ and Bunton and Minch.⁶¹

In the CTA-chlorobenzoate surfactants of this study, the surfactants which do not form viscoelastic solutions, CTA2C1 and CTA2,6C1, show the same type of high resolution features in their spectra as in the spectrum of CTA4OH obtained by Ulmius et al.⁴² On the other hand, the spectra of CTA4C1; CTA2,4C1; CTA3,4C1; and CTA3,5C1 have broad featureless peaks, similar to that of CTASal or CTAB at concentrations above 0.27 M. Figure 26 is a proton spectrum of a 0.01 M CTAB solution. Figures 27-32 are spectra of the CTA-chlorobenzoates. In addition, the chemical shifts of some the proton resonances of these surfactants are listed in Table X. As can be seen from the table, the N-methyl protons are shifted upfield by about 0.1 ppm for all the surfactants with aromatic counterions. The N-methylene signal can be seen in the spectra of CTA2C1 and CTA2,6C1 only; however, for these the upfield shift is about 0.25 ppm. There appears to be no difference in the N-methyl shifts between the surfactants that form viscoelastic solutions and those that do not. Unfortunately, it was not possible to distinguish the N-methylene peak in the spectra of those surfactants that form viscoelastic solutions.

Carbon-13 NMR spectra were obtained for 0.15 m CTAB; CTA2C1; and CTA2,6C1. For the surfactants which form viscoelastic surfactant solutions, obtaining Carbon-13 NMR spectra proved to be very difficult. Solutions of these surfactants had to be either very dilute, in which case the signal-to-noise ratio was very low, or very viscous, in which

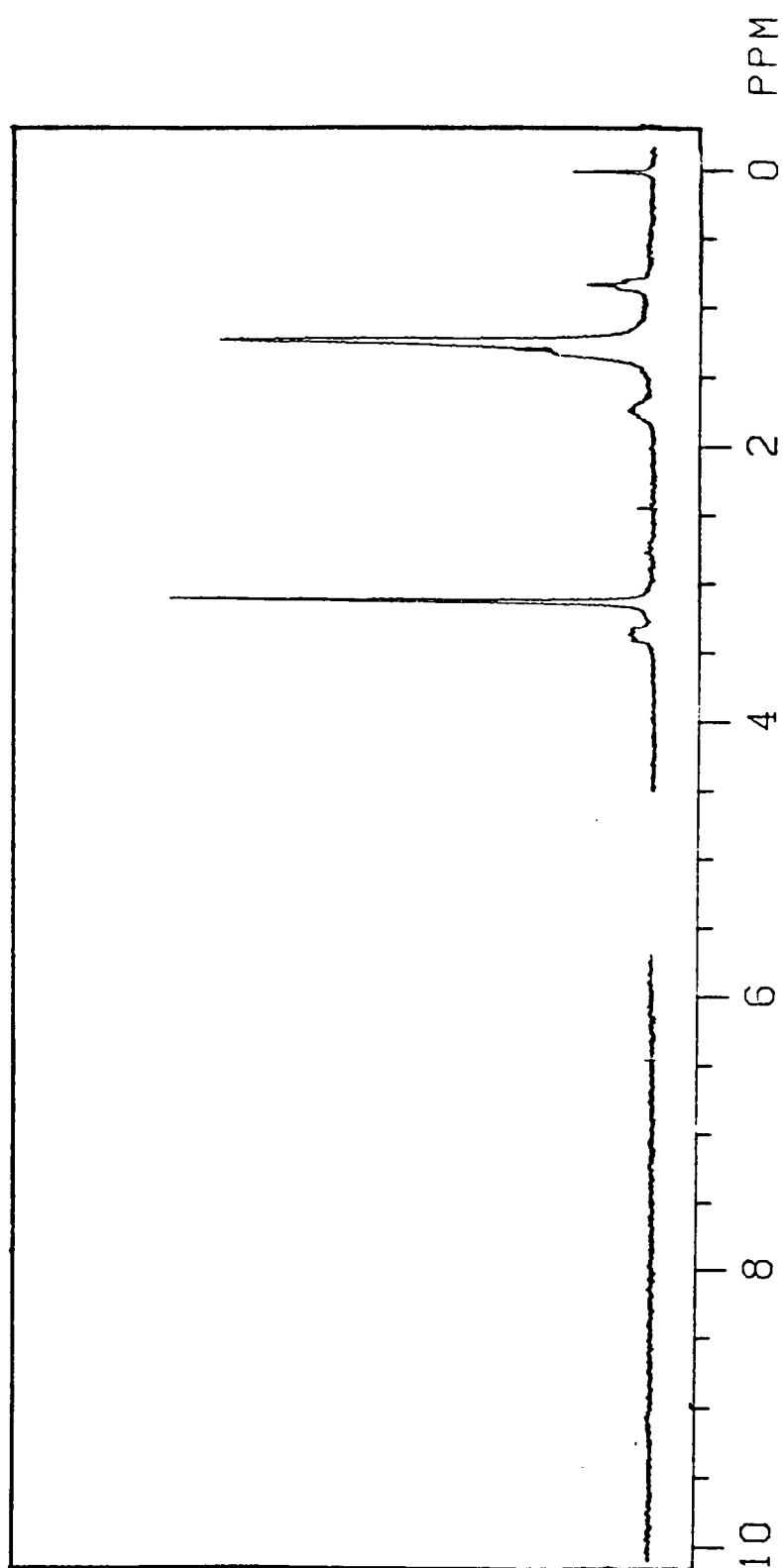


Figure 26. Proton NMR spectrum of CTAB.

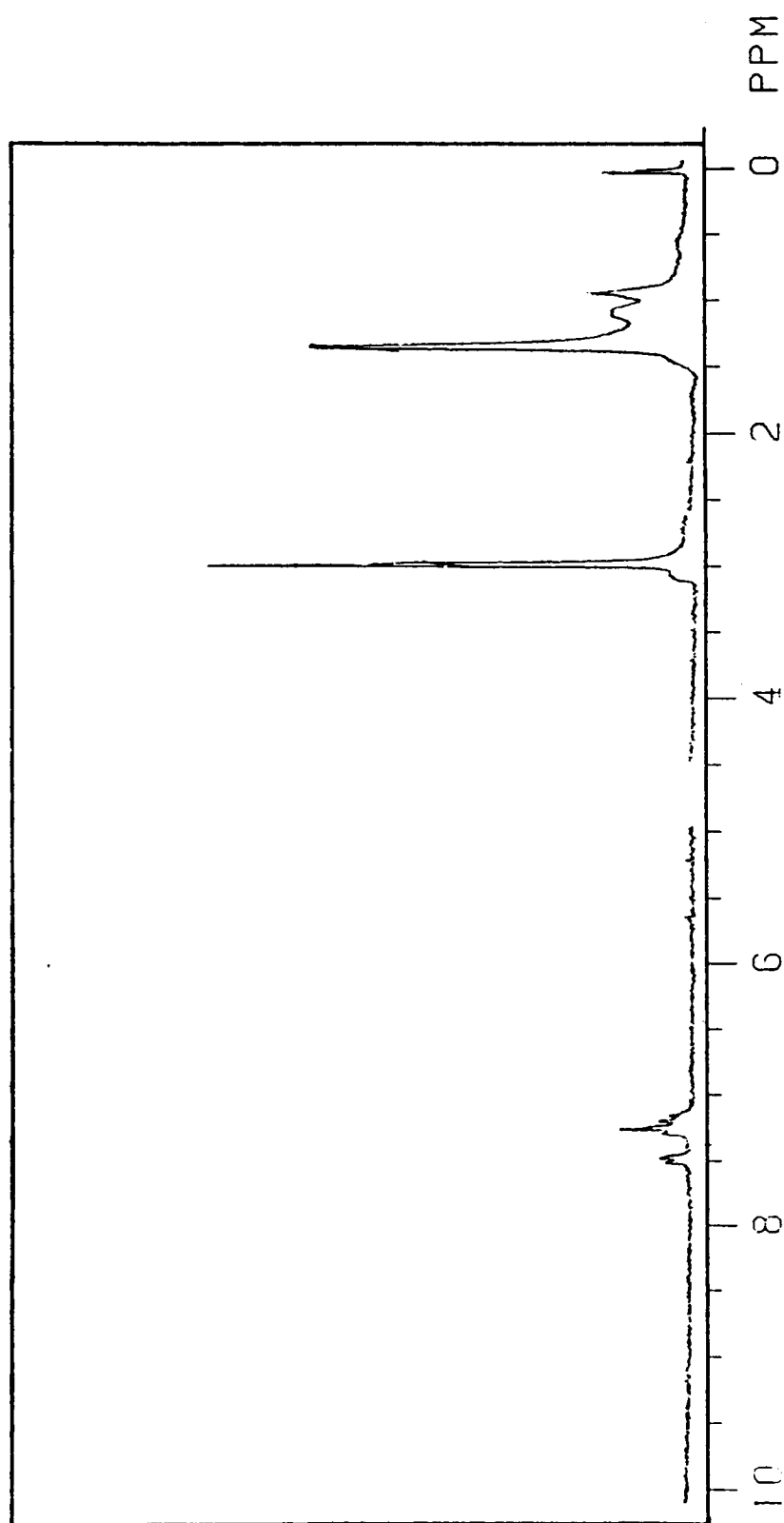


Figure 27. Proton NMR spectrum of CTA2Cl.

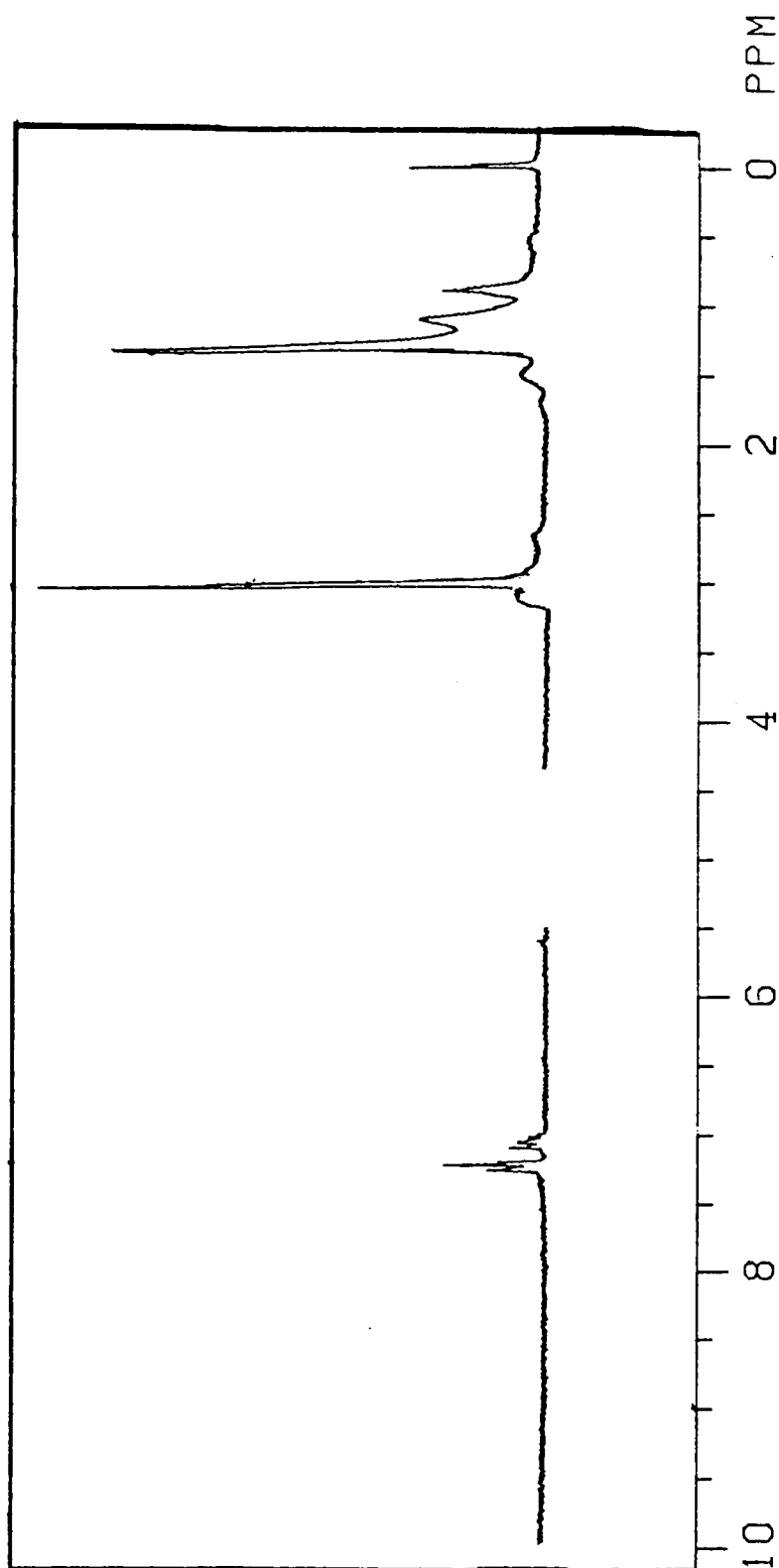


Figure 28. Proton NMR spectrum of CTA2,6Cl.

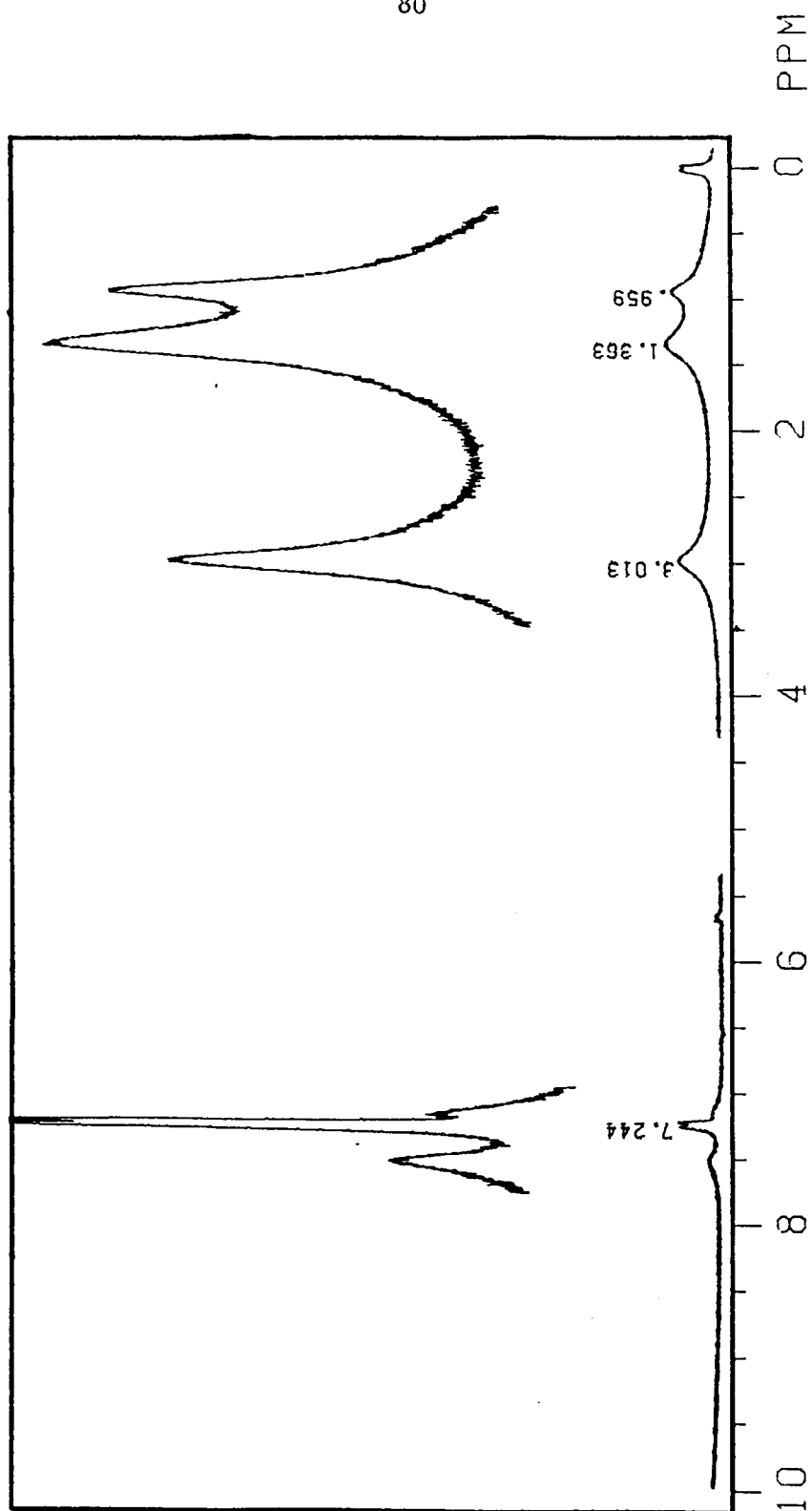


Figure 29. Proton NMR spectrum of CTA2,4Cl.

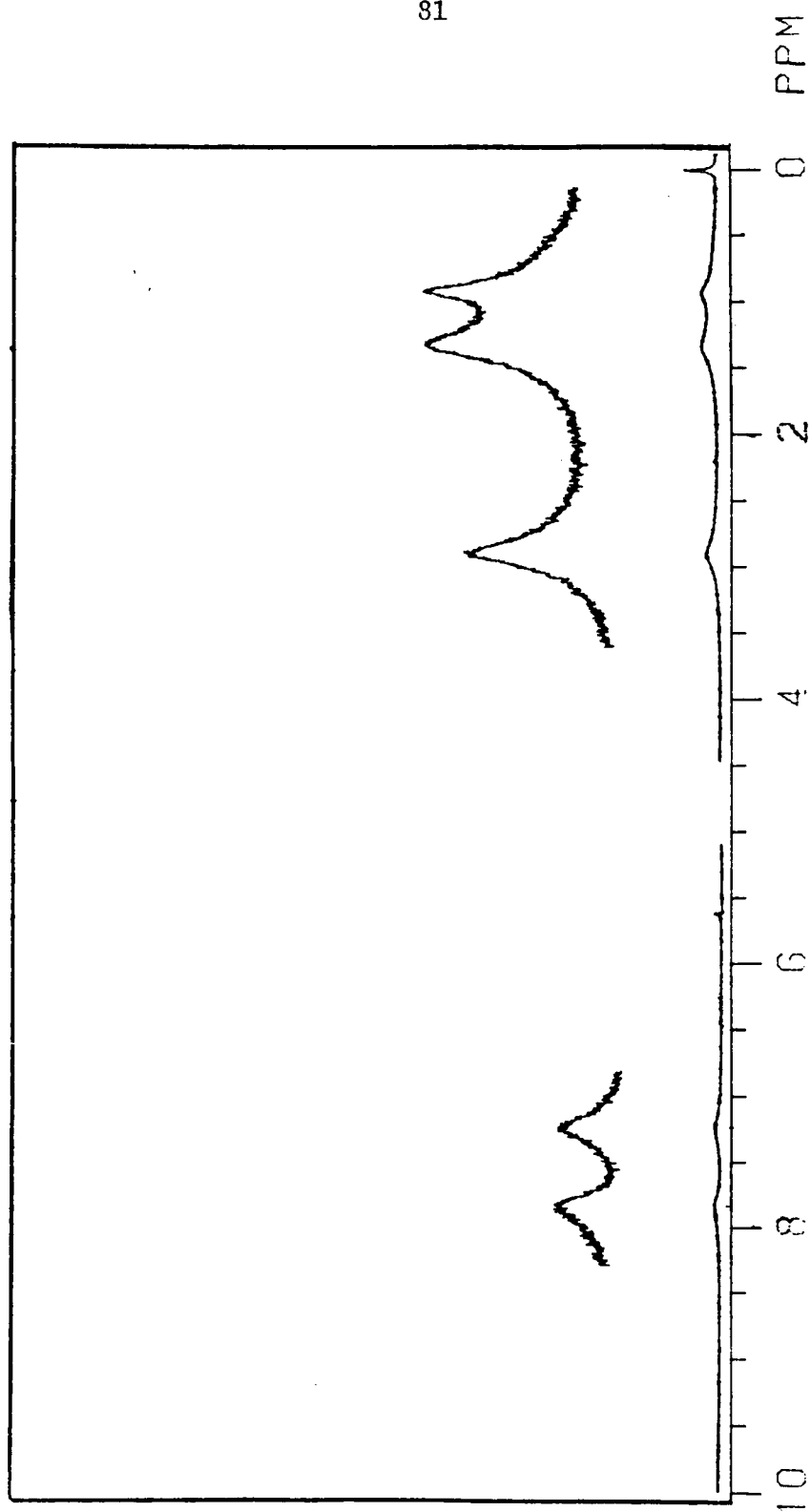


Figure 30. Proton NMR spectrum of CTA4Cl.

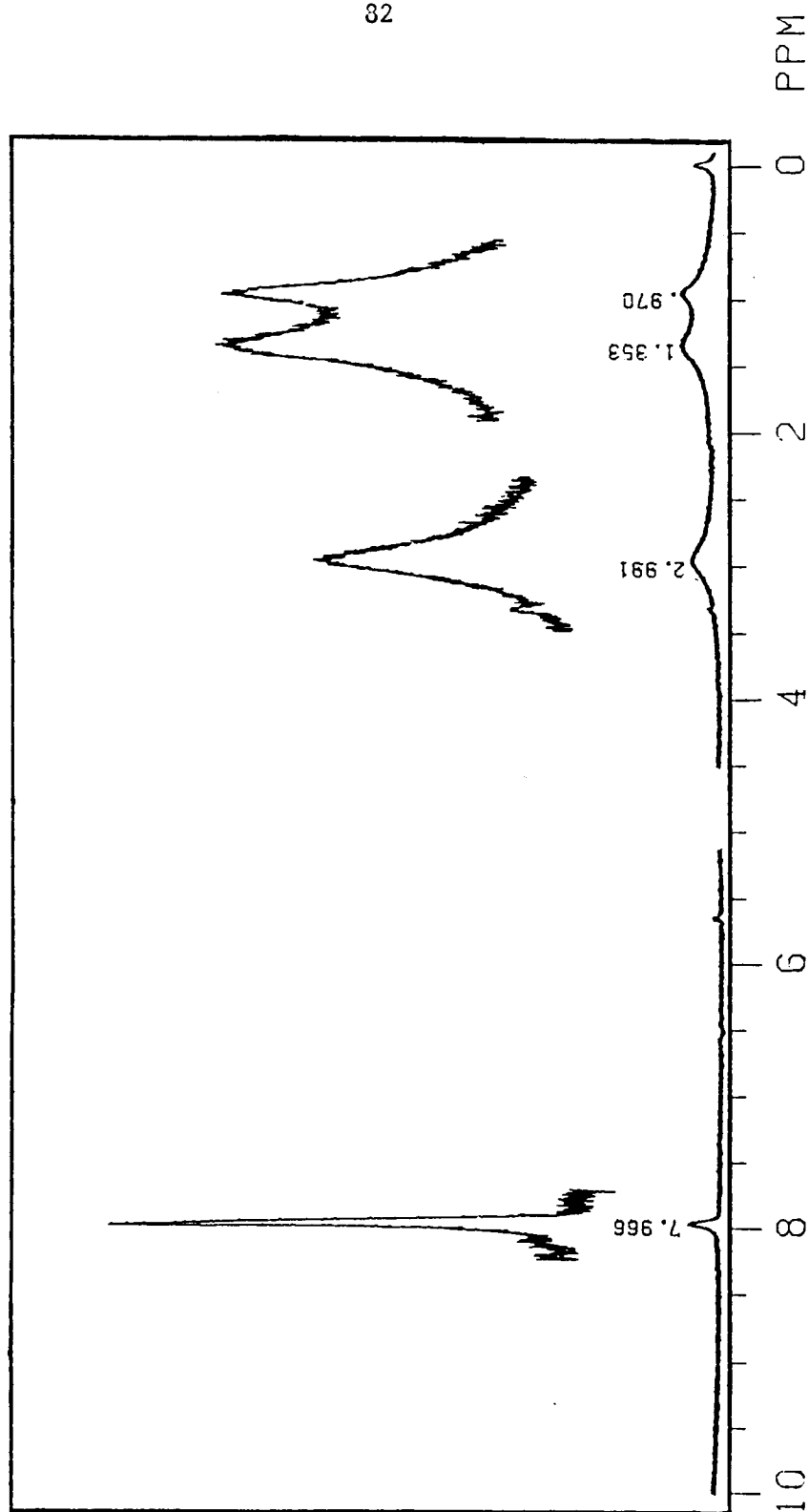


Figure 31. Proton NMR spectrum of CTA3,4Cl.

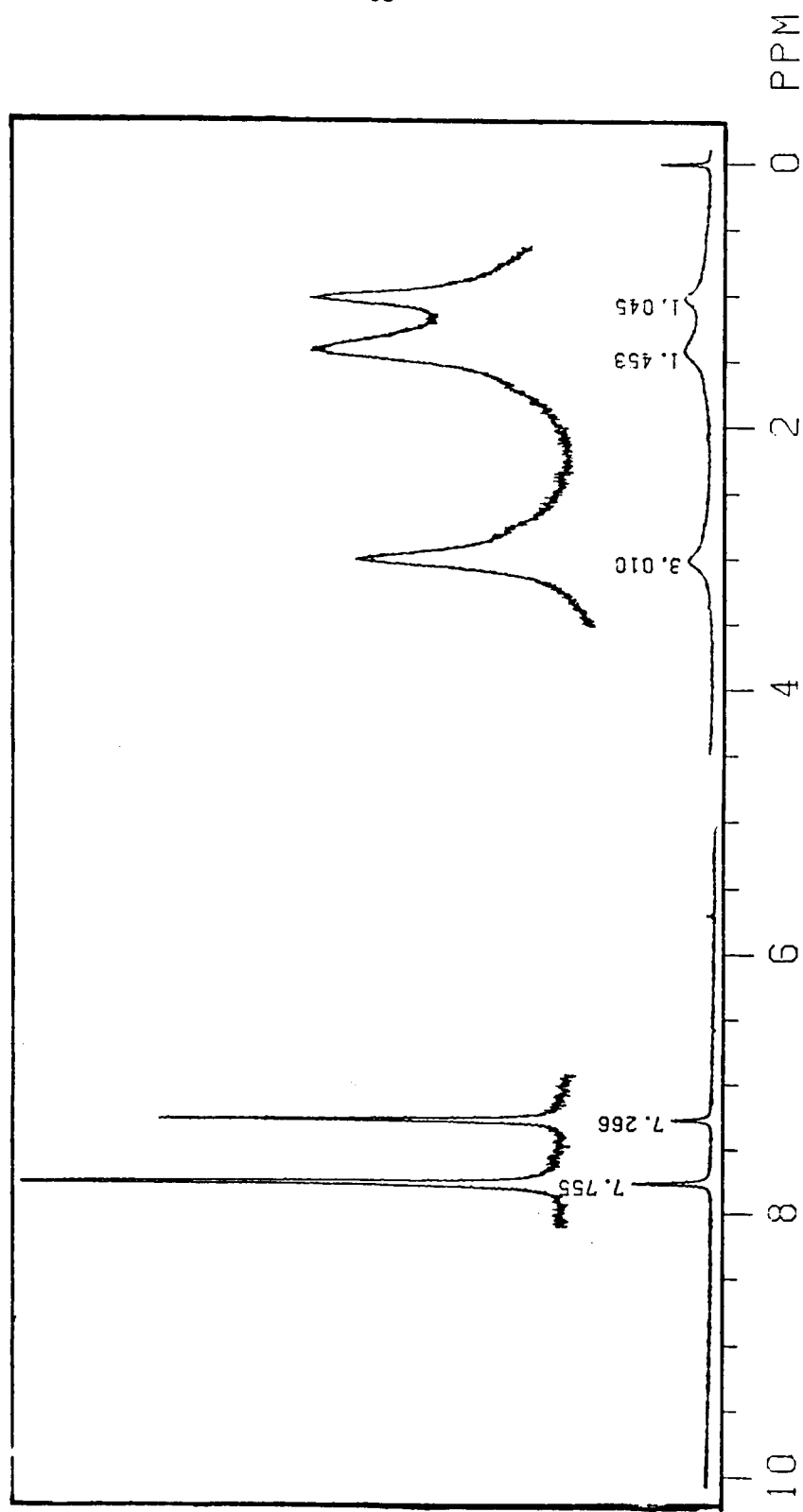
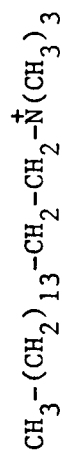


Figure 32. Proton NMR spectrum of CTACl.

TABLE X

PROTON NMR SHIFTS^a OF THE CTAX'S

a b c e d

	CTAB	CTA2C1	CTA26C1	CTA4C1	CTA24C1	CTA34C1	CTA3,5C1
a	0.839	0.956	0.897	0.944	0.959	0.970	1.045
b	1.236	1.345	1.301	1.361	1.363	1.353	1.453
c	1.700	-- ^b	1.490	-- ^b	-- ^b	-- ^b	-- ^b
d	3.106	2.984	3.018	2.917	3.010	2.991	3.010
e	3.350	3.100	3.120	-- ^b	-- ^b	-- ^b	-- ^b

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^aThe chemical shifts are measured on the δ scale.^bThese peaks could not be seen.

case the peaks were broadened into the baseline. Nevertheless, it was possible to collect some data from spectra of CTA3,4Cl and CTA3,5Cl. These data, and those from the spectra of CTAB, CTA2Cl and CTA2,6Cl are listed in Table XI. Again a small shift can be seen for the N-methyl groups associated with aromatic counterions, but there is no obvious difference between the surfactants that do and those that do not form viscoelastic solutions. Once again, no peaks can be seen for the N-methylene group in the spectra of the viscoelastic solutions.

D. pH Effects on CTAX Surfactant Solutions

Experiments were performed to determine the effect of changes in pH on the viscosity and viscoelasticity of some of the surfactant solutions. In particular, it has been seen by other authors^{49,61,71} that some neutral aromatic solutes, including aromatic acids, cause an increase in the viscosity of CTAB solutions. The present measurements were made to determine what effects ionization or neutralization of the counterions might have on the viscosity of the solutions and what the mechanism of these effects might be. Visual observation was used to evaluate the changes in viscoelasticity and viscosity in a number of CTAX solutions or solutions of CTAB plus either 2-chlorobenzoic acid or 4-chlorobenzoic acid. In addition, capillary viscometry was used to detect the relative changes in viscosity.

A solution of 0.05 M CTAB adjusted to a pH of 3.0 with concentrated hydrochloric acid demonstrated no visible change in viscosity over that of the CTAB solution at a pH of 7.0. To four 10 mL aliquots of

TABLE XI
CARBON-13 NMR SHIFTS^a OF THE CTAX'S
 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}\overset{+}{\text{N}}(\text{CH}_3)_3$
a b f e d c h g

	CTAB ^b	CTAB	CTA2C1	CTA2,6C1	CTA3,4C1	CTA3,5C1
a	14.0	14.1	14.4	14.1	14.0	14.1
b	22.7	22.9	23.0	23.0	23.0	22.9
c	23.3	-- ^c	-- ^c	-- ^c	-- ^c	-- ^c
d	26.4	26.4	26.2	26.2	-- ^c	-- ^c
e	29.8	30.5	30.4	30.4	30.4	30.3
f	32.0	32.3	32.3	32.3	--	32.4
g	53.5	53.3	52.9	52.9	52.8	52.8
h	66.9	66.5	66.2	66.3	-- ^c	-- ^c

^aChemical shifts are measured on the δ scale.

^bCTAB chemical shifts from literature.

^cThese peaks could not be seen.

the 0.05 M CTAB solution, sufficient solute amounts were added to give: (1) 0.025 M 2-chlorobenzoic acid; (2) 0.05 M 2-chlorobenzoic acid; (3) 0.025 M 4-chlorobenzoic acid; and (4) 0.05 m 4-chlorobenzoic acid. 2-Chlorobenzoic acid is completely soluble at both concentrations chosen (samples 1 and 2); however, the samples containing 4-chlorobenzoic acid are saturated at an acid concentration below that of sample 3. Even when sample 3 was diluted to twice its original volume, it still contained excess acid. In addition, no change in viscosity, relative to the original CTAB solution, was apparent in samples 3 or 4 either before or after the dilution. These observations agree with those of Wan,⁴⁹ who reported very low solubility for 4-chlorobenzoic acid in CTAB solutions and also detected no visible increase in the viscosity of the CTAB solution upon addition of the acid.

Samples 1 and 2, containing 2-chlorobenzoic acid, on the other hand, exhibit a dramatic increase in viscosity over the CTAB-only solution. When the pH of samples 1, 2, and 3 was reduced to 2.0 by the addition of concentrated HCl, the samples containing 2-chlorobenzoic acid appeared still more viscous, while the sample containing 4-chlorobenzoic acid showed no change.

A 0.04 M solution of CTA2Cl was titrated with successive additions of 6 N HCl, and visual observations of the change in viscosity were made. Table XII describes these observations. It is apparent that for CTA2Cl, addition of hydrochloric acid to the solution causes an increase in viscosity. This observation is verified by capillary viscometry. Table XIII lists viscosity values for a 0.04 M CTA2Cl

TABLE XII

VISUAL OBSERVATION OF pH EFFECTS ON CTA2C1 SOLUTIONS^a

pH	Observation
1.73	No visible increase in viscosity ^b
1.39	No visible increase in viscosity
1.22	No visible increase in viscosity
1.05	Increase in viscosity first seen
0.93	Increasing viscosity
0.86	Very viscous solution

^aSolution concentration is 0.04 M.^bRelative to same concentration solution at pH = 7.0.

TABLE XIII

VISCOMETRIC EFFECTS OF pH ON CTA2C1 SOLUTIONS^a

pH	Viscosity
6.58	0.992 cP
4.00	1.02
2.56	0.994
2.08	1.08
1.91	1.09
1.75	1.32
1.39	3.24

^aSolution concentration is 0.04 M.

solution titrated with 6 N HCl. The viscosity of the solution is relatively constant as the pH is lowered, until a pH of about 1.75 is reached. At this point, the viscosity increases rapidly as the pH decreases. Figure 33 is a plot of the data in Table XIII. It is possible that the increase in viscosity in this case is due merely to the increase in electrolyte in the solution rather than being a result of the decrease in pH. As a test of this hypothesis, sufficient NaCl to make a solution of CTA2Cl (0.04 M) which was 0.1 M in NaCl was prepared. This is approximately the same number of moles of added electrolyte as for the pH = 1.39 solution, where HCl is the added electrolyte. However, the measured viscosity of the solution with added NaCl was essentially the same as for the pure CTA2Cl solution in the absence of added electrolyte, 0.998 cP and 0.992 cP, respectively. The measured viscosity of the pH = 1.39 CTA2Cl solution is 3.24 cP, indicating that the effect of HCl on the viscosity of the CTA2Cl solution is not simply an added electrolyte effect. These results also negate the possibility that the viscous behavior of the CTA2Cl solution is the result of some unique property of the chloride anion.

In contrast to the behavior of the CTA2Cl solution, a 0.001 M solution of CTA3,4Cl is viscoelastic in the absence of added acid. In this case, addition of concentrated HCl causes a rapid loss of viscosity and the solution becomes cloudy, indicating precipitation of at least one of the components. Apparently it is the relatively easily protonated 3,4-dichlorobenzoate anion (see pKa values for the various CTAX's in Table XIV) which precipitates as 3,4-dichlorobenzoic acid,

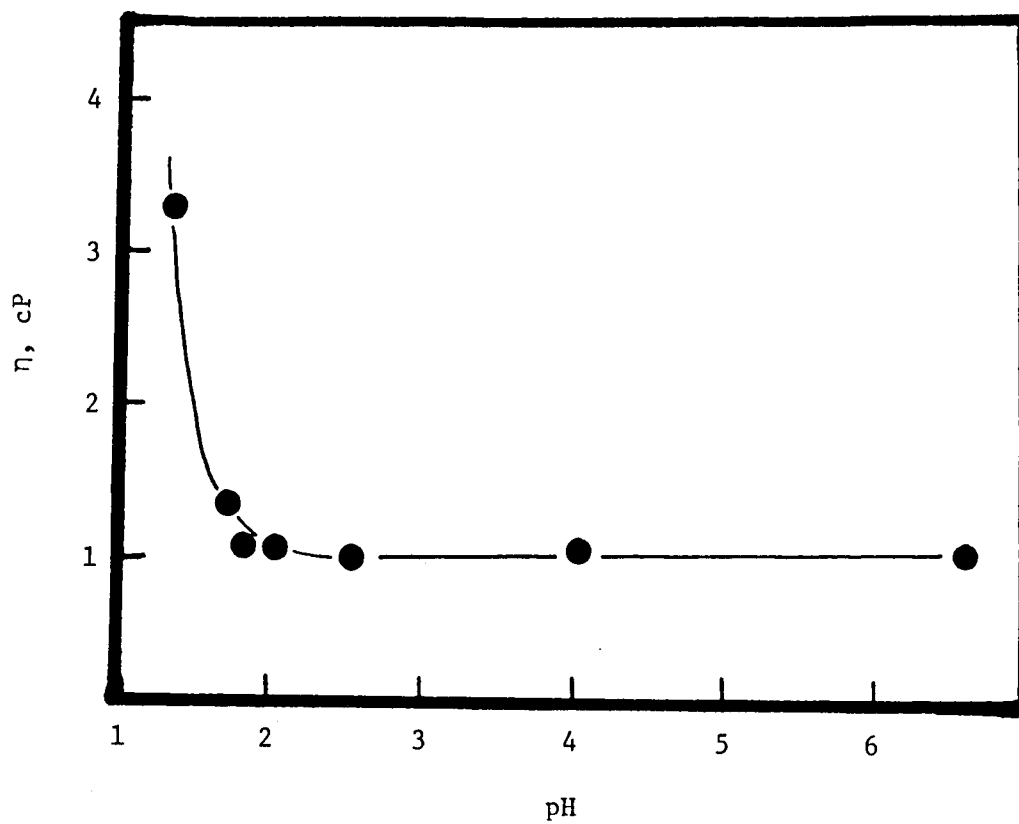


Figure 33. Effect of pH on viscosity of a 0.04 M CTA2Cl solution.

TABLE XIV

pKa VALUES OF CHLOROBENZOIC ACIDS

Acid	pKa
2-chlorobenzoic acid	2.45
4-chlorobenzoic acid	3.98
2,6-dichlorobenzoic acid	2.45
3,4-dichlorobenzoic acid	3.67
3,5-dichlorobenzoic acid	3.45

since it is unlikely that the CTA^+ cation would precipitate in the presence of the Cl^- anion. The result of a decrease in pH may be seen in Table XV.

The addition of NaOH to a solution of 0.001 M $\text{CTA}_{3,4}\text{Cl}$ also results in a reduction of viscosity. In this case, however, no precipitation occurs when small amounts of NaOH are added. Interestingly, despite the fact that the solution viscosity is reduced to that of pure water, some viscoelastic recoil can still be seen when these solutions are swirled. Since the 3,4-dichlorobenzoate counterion is essentially completely ionized at a pH of 6.65 (99.9% ionized), it seems unlikely that the change in pH is the cause of the decrease in viscosity. A comparison of the effect of NaCl versus that of NaOH on the viscosity of a solution of $\text{CTA}_{3,4}\text{Cl}$ was made. As shown in Table XVI, the effects of the two additives are of about the same magnitude. Thus it appears that the reduction in viscosity is a result of an electrolyte effect, rather than an increase in the pH.

TABLE XV
pH EFFECTS ON CTA3,4Cl SOLUTIONS^a

pH	Additive	Viscosity
2.25	HCl ^b	0.929, cP
2.40	HCl	1.436
2.57	HCl	1.502
6.65	--	2.370
11.30	NaOH ^c	1.470
11.65	NaOH	1.070
11.85	NaOH	0.975
12.55	NaOH	0.949
12.76	NaOH	0.948
12.85	NaOH	0.948

^aThe CTA3,4Cl solution was 0.001 M.

^bFrom a 6N solution of HCl.

^cFrom a 4N solution of NaOH.

TABLE XVI
SALT EFFECT ON CTA3,4Cl SOLUTIONS^a

Additive	Viscosity
--	3.335, cP
NaCl; 0.04 M	2.214
NaCl; 0.08	2.063
NaCl; 0.12	1.912
NaOH; 0.03 M	1.896
NaOH; 0.08	1.814
NaOH; 0.12	1.769

^aCTA3,4Cl concentration is 0.0015 M.

CHAPTER IV

SIZE AND SHAPE OF MICELLES OF CATIONIC
SURFACTANTS WITH AROMATIC COUNTERIONSA. Literature Review of Solutions of Rodlike Micelles

A number of workers have advanced theories concerning the size and shape of micelles in solution, based on thermodynamic and geometric considerations. Tartar,⁷² and more recently, Tanford^{1,73} have examined the way amphiphilic ions can pack into prolate and oblate spheroids once they can no longer pack into spheres. The shorter ellipsoid semi-axis is set equal to l_c (see Chapter I, page 2) and the longer axis is determined by applying the criterion that the total hydrocarbon core volume of the micelle, V , and the total surface area of the micelle, A , must satisfy $V/v = A/a_o = N$, where v is the volume of an individual chain in the core, a_o is the optimum area per head group, and N is the aggregation number of the structure. Both oblate and prolate spheroids were found to satisfy this criterion. Israelachvili et al.² challenged these findings, pointing out that packing should be favorable over all parts of an aggregate and not only on the average. Their analysis suggested that micelles form "ellipses of revolution," particles which do not have the sharp edges and ends of oblate and prolate ellipsoids. With increasing concentration, these particles eventually become cylindrical micelles with globular ends. This leads to a very polydisperse system whose mean aggregation number increases rapidly with amphiphile

concentration. In addition, $\bar{N}$ is predicted to increase rapidly with amphiphile concentration; $\bar{N}$ is also predicted to increase rapidly with increasing amounts of added salts and with increasing hydrocarbon chain length.

Quasielastic light scattering measurements on sodium dodecylsulfate solutions with high NaCl concentrations were performed by Benedek and co-workers.⁷⁴⁻⁷⁷ Their evidence confirmed the existence of long prolate ellipsoids and rods in the solutions. The dependence of the sphere-to-rod transition on the surfactant concentration, the concentration of added NaCl, and on temperature were measured. The results also indicated that there was a considerable degree of polydispersity in these systems. Based on their experimental observation that the micelles have the shape of a prolate spherocylinder, they developed a thermodynamic theory of micelle formation and growth,⁷⁶ which allowed them to reproduce their experimental results ($\bar{N}$ and micellar dimensions) over the range of temperature, salt concentration and surfactant concentration studied.

Porte and Appell⁷⁸⁻⁸² have investigated rod-shaped cetylpyridinium micelles, primarily with bromide as the counterion. For cetylpyridinium bromide (CPBr) solutions in the presence of high NaBr concentrations, they noted evidence for flexible, rather than rigid, rods, when the rod length exceeded a certain value, l_p , the persistence length of the rod.^{78,79} They also found that while large cylindrical micelles were formed in CPBr + NaBr solutions, the micelles in solutions of CPCl + NaCl stayed small and nearly spherical even at very

high salt concentrations.⁷⁸ Fluoride ion was found to be unable to induce micellar growth, while NO_3^- and ClO_3^- were more efficient than Br^- at inducing large rod-like micelles to form.⁸⁰ The authors demonstrated that these results could be predicted within the framework of a multiple equilibrium description of micellar elongation, incorporating a counterion binding approximation which includes the nature of the electrical and chemical interactions between the micelles and the various counterions.⁸¹ The general predictions of the theory stated that the mean aggregation number of the surfactant is proportional to the square root of the detergent concentration, and the width of the micellar size distribution increases dramatically with increasing mean aggregation numbers. In addition, the theory accounted for the strong influence of the added salt concentration on the mean aggregation number. This theory depends upon screening of the intermicellar interactions by the high concentrations of added salt present in the solutions, and it was experimentally verified for surfactant concentrations from 1.5×10^{-3} M up to 2.0×10^{-2} M. Porte et al.⁸² have offered a theoretical analysis of the sphere-to-cylinder transition in solutions of increasing surfactant concentrations, in the absence of added salts. In this case, the electrostatic repulsions between neighboring, similarly charged micelles are not screened, as they are in the case of high concentrations of added salts. This model suggests that the appearance of a second critical micelle concentration, rather than a smooth monotonic elongation with increasing surfactant concentration can be explained in a manner similar to the abrupt appearance of the

first CMC. Just as premicellar aggregates with aggregation numbers less than that of the smallest stable micelles, N_0 , are energetically unfavorable, the existence of the second CMC is related to the fact that elongated micelles with moderate aggregation numbers greater than N_0 but less than some N'_0 (where N'_0 is the minimum aggregation number for a stable elongated micelle), are likewise energetically disfavored. As the concentration of the surfactant is increased above the first CMC, the micelles remain small until increasing premicellar interactions reach a point that an energy barrier is overcome, and the second CMC is reached.

Ikeda and co-workers have published a number of studies on aqueous dodecyldimethylammonium chloride (DDAC) and bromide (DDAB) solutions at high NaCl and NaBr concentrations.⁸³⁻⁸⁶ According to their interpretation of the results of these experiments, the rodlike micelles of DDAB are fairly monodisperse. Ikeda⁸⁷ developed a theory of the salt- or temperature-induced sphere-to-rod transition and the reversible linear aggregation of surfactant into rodlike micelles on the basis of a simple treatment of the law of mass action in terms of statistical thermodynamics. He considers the theories developed by Benedek et al.⁷⁶ and Porte and Appell⁸¹ inadequate, because they fail to include the reversibility of the association of monomers into the aggregates. He presented experimental verification of his theory; however, Ikeda's interpretation of his light scattering results have been questioned by Porte and co-workers.^{78,82}

The appearance of viscoelastic properties in surfactant solutions has generally been linked to the presence of rod-shaped micelles. Cylindrical micelles have been detected in solutions of CTASal by NMR,⁴² viscometry,⁵³ and linear dichroism⁵⁶; in solutions of CTAB plus sodium 4-chlorobenzoate by flow birefringence⁴¹; and in cetylpyridinium salicylate (CPS) solutions by light scattering,⁴³ small-angle neutron scattering,^{64,88} and electric birefringence.⁴³ The latter solutions have been investigated primarily by Hoffmann and co-workers,⁴³ who have reported that the rodlike micelles of CPS are relatively monodisperse, according to their electric birefringence measurements. SANS^{64,88} measurements indicate that intermicellar interactions in these solutions are strong, and that the micelles (which are assumed to be rigid rods) grow with increasing surfactant concentrations until their lengths are approximately equal to the average distance between the centers of mass of the nearest-neighbor micelles. At this overlap point Hoffmann believes that the micelle lengths stop growing and seem to even contract somewhat in response to increased intermicellar interactions. In order to explain the elasticity of the solutions, a three-dimensional dynamic network formed by the rods as soon as the point of overlap is reached was proposed.

B. The Theory of Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) was the method chosen to determine micellar sizes for the CTA-chlorobenzoates in this study. A number of reviews dealing with the theoretical aspects of SANS⁸⁹⁻⁹⁵ as

well as small-angle x-ray scattering^{96,97} have been published. These and other reviews^{98,99} also detail techniques and applications for polymeric, biological, and micellar systems. The following sections of this dissertation briefly reviews the basic theory of SANS and its advantages over small-angle light scattering and small-angle x-ray scattering as a means of studying micellar size and shape.

1. The Basis of SANS Theory

The basic theory has been described previously.^{89,92-97} An incident neutron wave is represented by

$$\psi_i = \exp(i\vec{k}_i \cdot \vec{r}) \quad , \quad (27)$$

with $\vec{k}_i$ being the incident wave vector, having a magnitude of $2\pi/\lambda$. Thermal neutrons incident on a sample of N nuclei may interact in one of two ways--they may be absorbed or scattered. While the absorption cross section, i.e., the number of neutron capture events per second, is high for a few nuclei such as cadmium and the lanthanides, it is small for many nuclei, including those most commonly encountered in organic compounds.

For the case of scattering, the scattered wave is expressed by

$$\psi_f = \left(\frac{b}{r}\right) \exp(i\vec{k}_f \cdot \vec{r}) \quad , \quad (28)$$

where $\vec{k}_f$ is the scattered wave vector and b is the scattering length for the nucleus. Figure 34 represents scattering from a particle. The incident beam $\vec{k}_i$ strikes the particle at point 0 resulting in a

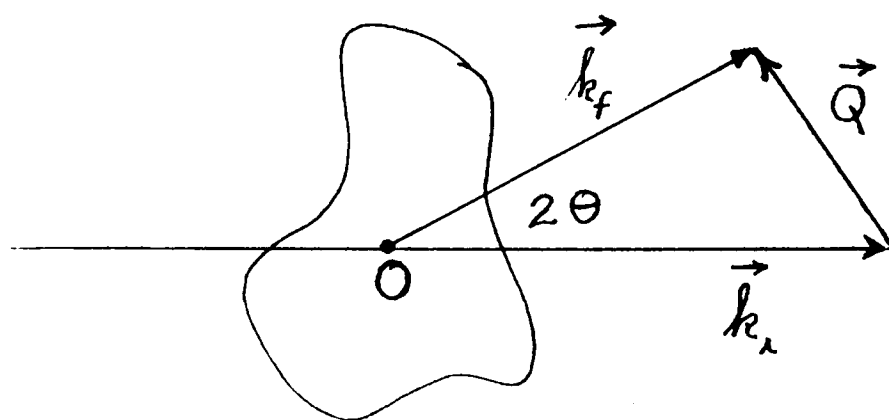


Figure 34. Scattering from a particle.

scattered wave at some angle θ . The momentum transferred in the scattering event is

$$\vec{Q} = \vec{k}_i - \vec{k}_f . \quad (29)$$

The magnitude of Q is

$$|\vec{Q}| = Q = (4\pi/\lambda)\sin\frac{\theta}{2} . \quad (30)$$

The scattered waves interfere; interferences associated with the incoherent part of the cross section are averaged and give rise to an isotropic scattering, which generates a background contribution. The superposition of the coherent scattered waves (coherence means the amplitudes are added) is a function of atomic distribution in the sample and hence contains some information about intraparticle structure and interparticle correlations. For coherent scattering, a nucleus's scattering cross sections is given by

$$\sigma_{\text{coh}} = 4\pi b_{\text{coh}}^2 \quad (31)$$

where b_{coh} is the characteristic coherent scattering length of that nucleus.

Table XVII is a compilation of the relevant values for several isotopes. It reveals a number of important points. The neutron scattering lengths may be negative or positive, but all are of about the same order of magnitude, 10^{-12} cm. Thus, unlike the case of x-ray scattering, where the contribution of an atom to the scattering

TABLE XVII

SCATTERING LENGTHS AND INCOHERENT AND ABSORPTION
CROSS SECTIONS OF SOME ISOTOPES AND ELEMENTS^a

Element or Isotope	Scattering Length (b_{coh})	Incoherent Cross Section (σ_{inc})	Absorption Cross Section (σ_{abs})
^1H	$-0.3740 \times 10^{-12} \text{ cm}$	79.7 barn	0.33 barn
$^2\text{H} = \text{D}$	0.6674×10^{-12}	2.0	0.00046
B	$(0.535 + 0.21i) \times 10^{-12}$	0.7	755.
C	0.665×10^{-12}	<0.018	0.0033
N	0.936×10^{-12}	0.46	1.88
O	0.5803×10^{-12}	<0.015	<0.0002
Cl	0.958×10^{-12}	5.9	33.6
Br	0.677×10^{-12}	<0.5	6.7
Cd	$(0.37 + 0.16i) \times 10^{-12}$	--	2450.

^aValues taken from Kostorz.⁸⁹

intensity increases with increasing atomic number, the contribution of H is about the same as those of C, N, and O. Furthermore, there is a relatively large difference between hydrogen and deuterium scattering lengths. For hydrogen, the length is negative, which indicates a phase shift of 180° between waves scattered by hydrogen and those scattered by deuterium. Finally, the incoherent scattering length of hydrogen is exceptionally high, much higher than its coherent scattering length.

The difference in the coherent scattering of hydrogen and deuterium is significant, since the substitution of a hydrogen atom in a molecule for a deuterium atom effects a large change in the coherent scattering of the molecule. This power to generate high contrast in a sample (e.g., by deuterating only the solvent, or only the solute in a solution) by simple H/D substitution provides a minimum perturbation to the system and allows much shorter data gathering times than with x-ray scattering (in systems where only light atoms are present).

Another advantage of the SANS technique is the relative ease with which the scattered intensities can be put on an absolute scale. There are relatively simple procedures to calibrate neutron detector efficiencies and to normalize the data to absolute terms. Due to the short wavelength of thermal neutrons, the scattered intensities at small angles is not contaminated by sample container imperfections or by dust particles in the solutions, both of which are difficult problems to handle in small-angle light scattering. Furthermore, most samples of interest are sufficiently transparent to thermal neutrons when contained in a 1 mm (or up to several millimeters) quartz cell. One

usually adjusts the transmission to higher than 80% by varying the cell thickness; under such conditions, multiple scattering is negligible.

2. The Coherent Cross Section

The partial coherent cross section with respect to the solid angle Ω is defined by

$$\frac{d\sigma}{d\Omega} = \langle \sum_{i,j} b_i b_j \exp[i\vec{Q} \cdot (\vec{r}_i - \vec{r}_j)] \rangle . \quad (32)$$

Equation 32 is a sum of amplitude-weighted phase shifts over all the atoms in the sample. As shown in Figure 35, $\vec{r}_i$ and $\vec{r}_j$ are atomic positions relative to an arbitrary origin in the sample, and the sum is extended over all pairs of atoms with coherent scattering lengths $b_{i,j}$ and position defined by $\vec{r}_{i,j}$.

Equation 32 may be expressed as

$$\frac{d\sigma}{d\Omega} = \langle \sum_{p,q} \sum_{i(p)}^{n_p} \sum_{j(q)}^{n_q} b_i b_j \exp(i\vec{Q} \cdot \vec{r}_{i,j}) \rangle , \quad (33)$$

which is a means of writing all atomic positions in a given micelle relative to its geometric center. Here $\vec{r}_{i,j}$ is the relative separation of two atoms. Atoms i and j may be within the same particle or in two different particles, e.g., p and q . Then $\vec{r}_{i,j}$ may be expressed as

$$\vec{r}_{i(q),j(p)} = \vec{R}_p - \vec{R}_q + \vec{r}_{j(p)} - \vec{r}_{i(q)} , \quad (34)$$

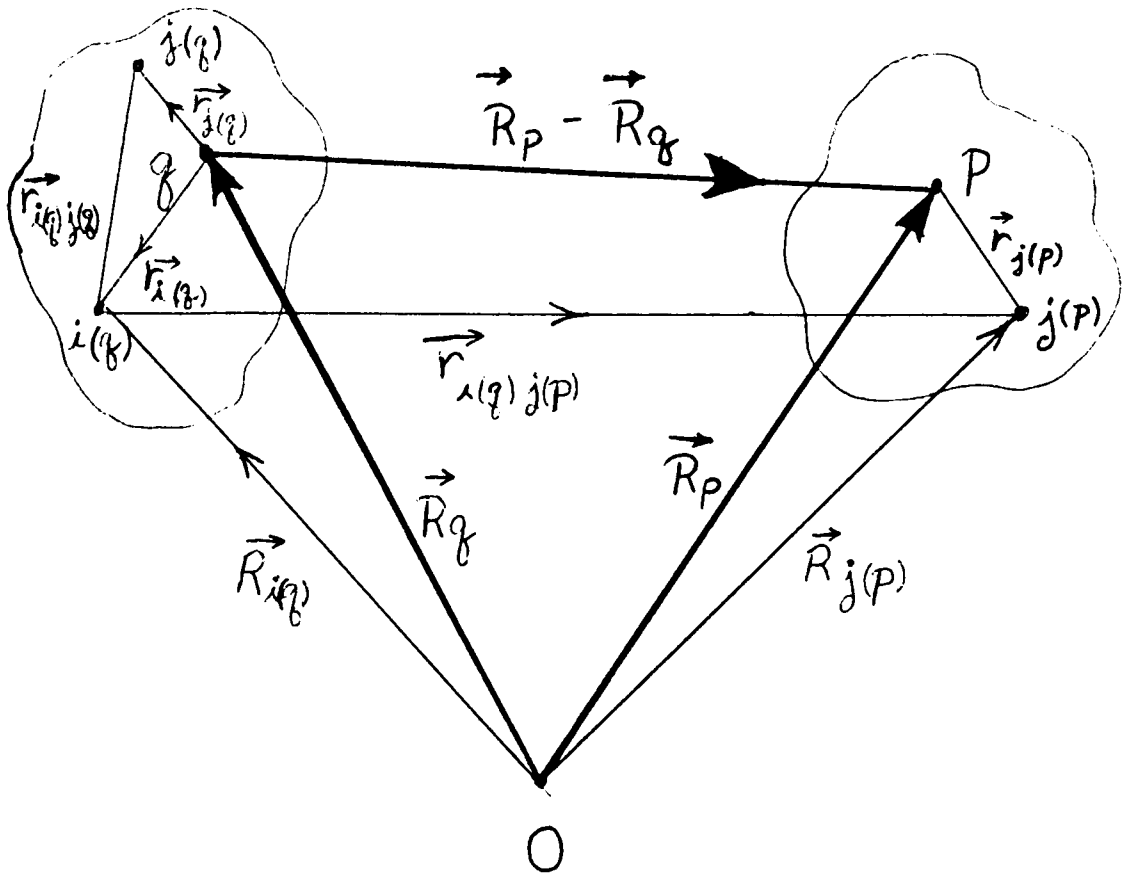


Figure 35. Scattering interaction between two particles.

where p and q refer in general to different micelles separated by a center-to-center distance $\vec{R}_p - \vec{R}_q$. Equation 33 can then be separated into intraparticle and interparticle terms:

$$\begin{aligned} \frac{d\sigma}{d\Omega} = & \left\langle \sum_{i(p)}^{n_p} \sum_{j(p)}^{n_p} b_i b_j \exp[i\vec{Q} \cdot (\vec{r}_j - \vec{r}_i)] \right\rangle \\ & + \left\langle \sum_{p \neq q=1}^N \exp[i\vec{Q} \cdot (\vec{R}_p - \vec{R}_q)] \right. \\ & \cdot \left. \sum_{i(p)}^{n_p} \sum_{j(q)}^{n_q} b_i b_j \exp[i\vec{Q} \cdot (\vec{r}_j - \vec{r}_i)] \right\rangle . \end{aligned} \quad (35)$$

The interparticle term in Equation 35 is the number of micelles N_m , times the square of the single particle form factor, defined as:

$$F(Q) = \sum_{j(q)} b_j \exp(i\vec{Q} \cdot \vec{r}_j) , \quad (36)$$

where the sum is over all atoms in the micelle and the distances are relative to the micelle's center. For particles in solution, it is the difference $\rho_p(r) - \rho_{\text{solv}}$ which is of interest; here $\rho_p(r)$ is the scattering length density of the solvent. In terms of ρ , Equation 36 can be rewritten

$$F_p(Q) = \int [\rho_p(r) - \rho_{\text{solv}}] \exp[i\vec{Q} \cdot \vec{r}] d^3r , \quad (37)$$

where the integral is over the volume of the particle only.

The first term of Equation 35, page 106, is calculable for any micelle geometry; the second term, however, cannot be evaluated exactly for any type of interparticle interaction. Nevertheless, the sum of the second term may be averaged separately if one assumes that there is little correlation between the size and orientation of the particle and the interparticle distance. For charged particles interacting through a screened Coulombic repulsive potential, this decoupling approximation works well, since contact among the neighboring particles is unlikely. Equation 35 then becomes

$$\begin{aligned} \frac{d\sigma}{d\Omega} = N_m < |F(Q)|^2 > + < \sum_{p \neq q} \exp[i\vec{Q} \cdot (\vec{R}_p - \vec{R}_q)] > \\ \cdot < \sum_{i(p)}^{n_p} \sum_{j(q)}^{n_q} b_i b_j \exp[i\vec{Q} \cdot (\vec{r}_j - \vec{r}_i)] > . \end{aligned} \quad (38)$$

The term involving different micelles $p \neq q$ is

$$N_m [S(Q) - 1] < \sum_{j(q)} b_j \exp(i\vec{Q} \cdot \vec{r}) >^2 ,$$

where the structure factor, $S(Q)$, averaged over all orientations and positions is defined as

$$S(Q) = 1 + N_m^{-1} < \sum_{p \neq q} \exp[i\vec{Q} \cdot (\vec{R}_p - \vec{R}_q)] > . \quad (39)$$

In the absence of particle-particle interactions, e.g., at very low particle concentrations, the averaged term equals zero and $S(Q)$ is equal to one.

Provided that $\vec{r}_{i(p)}$ and $\vec{r}_{j(q)}$ are statistically independent, Equation 38 becomes

$$\frac{d\sigma}{d\Omega} = N_m \langle |F(Q)|^2 \rangle + N_m [S(Q) - 1] \langle \sum_{j(q)} b_j \exp(i\vec{Q} \cdot \vec{r}_j) \rangle^2 \quad (40a)$$

$$= N_m \langle |F(Q)|^2 \rangle + N_m [S(Q) - 1] \cdot |\langle F(Q) \rangle|^2 \quad (40b)$$

$$= N_m [\langle |F(Q)|^2 \rangle - |\langle F(Q) \rangle|^2] + N_m \cdot S(Q) \cdot |\langle F(Q) \rangle|^2 \quad (40c)$$

The quantity $F(Q)$ is the Fourier transform of the radial average distribution of distances $p(r)$ within one particle; $S(Q)$ is the Fourier transform of the radial distribution function $g(r)$ for the centers of mass of the particles.

3. Form Factors

For a solution of monodisperse spheres where $\langle |F(Q)|^2 \rangle = |\langle F(Q) \rangle|^2$,

$$\frac{d\sigma}{d\Omega} = I(Q) = N_p \cdot S(Q) \cdot P(Q) \quad , \quad (41)$$

where N_p is the number particle density, and $P(Q)$ is equivalent to $\langle |F(Q)|^2 \rangle$ and is called the "form factor" (sometimes $F(Q)$ itself is also called the form factor). The function $P(Q)$ contains information about the shape of the scattering particle, and its mathematical form depends upon that shape.

For homogeneous spheres of radius R :

$$F_p(Q) = \Delta\rho \int_0^R \frac{\sin \theta r}{Qr} 4\pi r \, dr \quad (42a)$$

$$= \Delta\rho \cdot \frac{4}{3}\pi R^3 \cdot \phi(QR) \quad (42b)$$

where

$$\phi(QR) = 3 \left[\frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right] \quad (43)$$

and $\Delta\rho$ is $\bar{\rho} - \rho_{\text{solv}}$, where $\bar{\rho}$ is the mean scattering density of the solvent-excluded particle.

In the case of spherical particles with scattering length density inhomogeneities, a centrosymmetric distribution of scattering length density may be modeled by a set of N concentric shells:

$$F_p(Q) = (\rho_1 - \rho_2)V_1\phi(QR_1) + (\rho_2 - \rho_3)V_2\phi(QR) \dots \\ (\rho_N - \rho_{\text{solv}})V_N\phi(QR_N) \quad (44)$$

For the cases of monodisperse ellipsoids or cylinders, or polydisperse spheres, the inequality $\langle |F(Q)|^2 \rangle \neq |\langle F(Q) \rangle|^2$ holds; for a polydisperse sample, one must average over the particle size distribution.¹⁰⁰⁻¹⁰³

Scattering from a collection of monodisperse ellipsoids is often difficult to distinguish from an equivalent collection of polydisperse spheres because for each orientation of an ellipsoid relative to Q , the form factor is identical to that of a sphere with an equivalent radius, which varies with orientation.

The orientational averages are computed according to

$$\langle |F(Q)|^2 \rangle = \int_0^1 |F(Q, a, ECC, t, \mu)|^2 d\mu \quad (45)$$

$$|\langle F(Q) \rangle|^2 = \left| \int_0^1 F(Q), a, ECC, t, \mu) d\mu \right|^2 \quad (46)$$

The function F is given by

$$F(Q, a, ECC, a', ECC', t, \mu) = V_c(\rho_1 - \rho_2)\phi(u') + V_T(\rho_2 - \rho_{solv})\phi(u) \quad (47)$$

where the ellipsoids' core (of volume V_c) has axes of a' , a' , and $ECC \cdot a'$ (semiminor for prolate, semimajor for oblate). The thickness of the shell region is given by t ; ECC is the eccentricity (axial ratio) of the ellipsoid. The quantity $u(a, ECC)$ is $Q[(ECC \cdot a \cdot \mu)^2 + a^2(1 - \mu^2)]^{\frac{1}{2}}$.

For monodisperse rigid cylinders of homogeneous scattering length density, one may write

$$\begin{aligned} \langle |F(Q)|^2 \rangle &= \Delta \rho^2 V_p^2 \\ &\cdot \int_0^{2\pi} \left[\frac{\sin(QH \cos \beta)}{QH \cos \beta} \cdot 3\phi(QR \sin \beta) \right] \sin \beta d\beta \quad (48) \end{aligned}$$

with H equal to the half-length of the cylinder.

4. The Structure Factor

For solutions of ionic micelles in the absence of added salt, intermicellar Coulombic interactions are already appreciable at the CMC. These particle-particle interactions produce correlations between the centers of different particles; $S(Q)$, the interparticle structure factor, is sensitive to these correlations. Discussion of the analysis of $S(Q)$ must be restricted from the outset to spherical particles,

which may be mono- or polydisperse. In these cases, theories have been developed for the analysis of interparticle interactions based on a number of approximations, which turn out to be very accurate in practice. However, interacting particles with a moderate or high degree of asphericity--including disks and rods--cannot be treated quantitatively at present, using liquid state theories.

For a solution of macroions, the weakly attractive van der Waals part of the true colloidal potential will have little effect because the repulsive screened Coulombic potential is generally larger than thermal energies at small interparticle separations, and the attractive forces rarely come into play. For spherical macroions of diameter σ , the repulsive Coulombic potential, $U(r)$, due to the interaction of their electric double layers, has the Yukawa form,

$$U(r) = \pi \epsilon_0 \epsilon \sigma \psi_s^2 \exp[-\kappa \sigma(x-1)] x^{-1}, \quad x > 1, \quad (49)$$

where ψ_s is the surface electrostatic potential, and κ is the Debye-Huckel inverse screening length, determined by the ionic strength of the solution, ϵ_0 is the permittivity of free space, ϵ is the dielectric constant of the solvent medium and $x = r/\sigma$, where r is the separation between two particles. At low κ , the electrostatic repulsion is long ranged, while at higher ionic strength, the repulsive energy term decays more rapidly. For micellar solutions, $U(r)$ is dependent upon the micellar charge.

Hayter and Penfold¹⁰⁴ have solved Equation 49 in the Mean Spherical Approximation¹⁰⁶ to obtain closed analytical forms for $S(Q)$. At low volume fractions, a rescaled version of the MSA must be used.¹⁰⁵

Klein et al.¹⁰⁷ have recently published an attempt to derive the static structure factor for a solution of charged rods. In this case, the equations are far more complicated than for spherical particles and the analysis is only valid for weakly coupled systems at low concentrations, where the center-to-center distances between the particles are greater than the length of the individual rods. An additional problem for the determination of the structure factor for elongated micelles has been pointed out by Porte and Appell.^{79,81} In light scattering investigations, they noted that systems of cylindrical micelles may be very polydisperse, considerably complicating the analysis of $S(Q)$.

C. Literature Review of Applications of SANS to Micellar Systems

Before the development of a means to calculate the structure factor directly, other workers had used extrapolation of $I(Q)$ to zero concentration (where $S(Q) = 1$) or the addition of salts to the solutions to eliminate correlation effects. Hayter and Penfold¹¹⁰ pointed out that for the case of micelles, extrapolation to zero concentration becomes intractable, since the micellar phase disappears below the CMC, whereas, at the CMC, the concentration is still significantly high for there to be significant intermicellar interactions. Also, micelle size and shape generally depend on concentration and ionic strength; thus, addition of salt is not a suitable procedure for overcoming the problem. Bendedouche et al.¹¹¹ have pointed out one alternative to the analytical solution of Hayter and Penfold. By combining the techniques of light scattering and small-angle neutron scattering, one can

indirectly derive $S(Q)$ by obtaining the value of $P(Q) \cdot S(Q)$ at very small values of Q using light scattering, then obtaining the value of $P(Q)$ at high values of Q (where $S(Q)$ is identical to one) using SANS.

A number of ionic micellar systems have been evaluated by SANS. Magid and co-workers^{66,112} have investigated solutions of double-tailed anionic surfactants: sodium dialkylsulfosuccinates and branched chain *p*-alkylbenzenesulfonates. In the former case, where the alkyl group is either *n*-hexyl or *n*-octyl, a concentration dependence of micellar aggregation number was observed, but contrary to predictions that might be made based on Israelachvili's packing constraint theory,² no sphere-to-disk shape transition was observed. The authors concluded also that the micellar interiors were quite disordered and the micellar surface was quite rough. For the branched alkylbenzenesulfonates, sodium *p*-(1-pentylheptyl)benzenesulfonate and sodium *p*-(1-heptylnonyl)benzenesulfonate were conclusively shown to form small micelles of 13.7 Å - 16.6 Å and 17 Å radii, respectively, despite earlier evidence to the contrary for the latter surfactant.¹¹³ Triolo et al.¹¹⁴ reported SANS results from sodium *p*-(1-pentylheptyl)benzenesulfonate in D₂O-H₂O solutions of 57% to 100% (volume percent) D₂O. By varying the constant between the micelle and the solvent in this way, they obtained good fits by taking into account hard-sphere and electrostatic repulsions with the MSA, and they concluded that the micelles of this study have rough surfaces and cores containing only half of each chain, thus differing substantially from the two-shell Hartley model of micelle structure.

Hayter and Zemb¹¹⁵ investigated micellar solutions of sodium octanoate by SANS for solutions from 0.6 M to 1.2 M in surfactant concentration. Finding that a roughened, two-shell model provided a satisfactory description of the micelle geometry, they were able to verify the model by using it to successfully predict the results of isotopic substitution experiments. Hayter and Zemb¹¹⁶ also found that for sodium dodecylsulfonate, the micellar surface is rough and grows rougher with increasing concentration. For dodecyltrimethylammonium bromide and chloride, on the other hand, they found smooth micelles with no tendency to grow with increasing concentration. The authors suggested that this might indicate an optimal packing geometry for this combination of chain length and head group, since the hexadecyltrimethylammonium chloride micelles again show a tendency to grow with increased concentration.

Chevalier and co-workers¹¹⁷ used SANS measurements to analyze several important features of the interfacial and structural characteristics of micelles in an aqueous solution of sodium octylphosphate. By varying the pH of the solutions, the structural charge of the head group could be altered from 0.8 to 2 without altering the surfactant molecule. The SANS technique allowed quantification of changes in aggregation number, micelle shape, and area per head group as a function of the charge of the head group.

Chen et al.¹¹⁸ chose to study aqueous solutions of lithium dodecylsulfate, LDS, because micelles from this surfactants have been shown to be nearly monodisperse at moderate concentrations.

Information regarding size, shape, aggregation number, and polydispersity of the micelles, as well as the water content of the inner hydrocarbon core was extracted. The authors concluded, from internal contrast experiments, that the spatial distribution of end groups of the dodecyl chains was essentially Gaussian, and that the core has a degree of order between that for a completely disordered liquid state and a fully ordered all-trans radial configuration. In subsequent work with LDS micelles, Chen et al.^{119,120} evaluated the structure factor for the system and extended the interpretation of the analysis of $S(Q)$ to solutions of sufficiently high salt content that the potential between particles has become essentially attractive. The authors found that they were able to fit their data satisfactorily with the Hayter-Penfold $S(Q)$ even for solutions of high ionic strength. They offered a partial explanation for these results¹¹⁹ and later extended the theory to include the effect of an attractive potential on the interparticle structure of ionic micellar solutions at very high salt concentrations.¹²¹

Of particular interest to the present work is the SANS measurements on rodlike micelles of cetylpyridinium salicylate performed by Hoffmann and co-workers.^{64,88} Based on measurements made over a range of concentrations, they concluded that the micelles were rigid rods which grow with increasing surfactant concentration until the rod lengths are equal to the average center-to-center distance between micelles. At this point the micelles no longer grow and may even contract somewhat. The analysis and results of Hoffmann's work are described in the following sections.

D. Protocol for Data Analysis in This Work

Figure 36 shows a typical experimental intensity curve which has been corrected point by point for solvent and background scattering (see Chapter VI, section A.6.b.). The major features of interest are, at low values of Q , the intensity maximum $Q_{I_{\max}}$, also called the interaction peak, and, at high Q values beyond the interaction peak, the tail of the curve. Because of the reciprocal relationship between the magnitude of the scattering vector Q and the distance, r , from the center of the scattering particle ($Q = 2\pi/r$), the curve at low Q yields information about intermicellar interactions at distances generally greater than the radius of the particle ($QR < 2\pi$, where R is the micellar size). Thus it is at these low Q values that the structure factor, $S(Q)$, has its greatest effect; the Q dependence of the maximum in the $S(Q)$ curve reflects the center-to-center distance between nearest neighbor particles. This in turn results in the interaction peak in the $I(Q)$ curve, whose form is dominated by the Q dependence of $S(Q)$ at low Q values. At higher Q values (smaller values of r) the structure factor approaches a constant value of one. In this high Q range, the intensity curve of the solution is simply proportional to the form factor, $P(Q)$. Thus information about the size and shape of the micelles, contained in the $P(Q)$ function, can be obtained from this portion of the curve.

The goal of small-angle neutron scattering experiments on micellar solutions is to gather information regarding micellar size, shape, mass, scattering density distribution and interparticle interactions

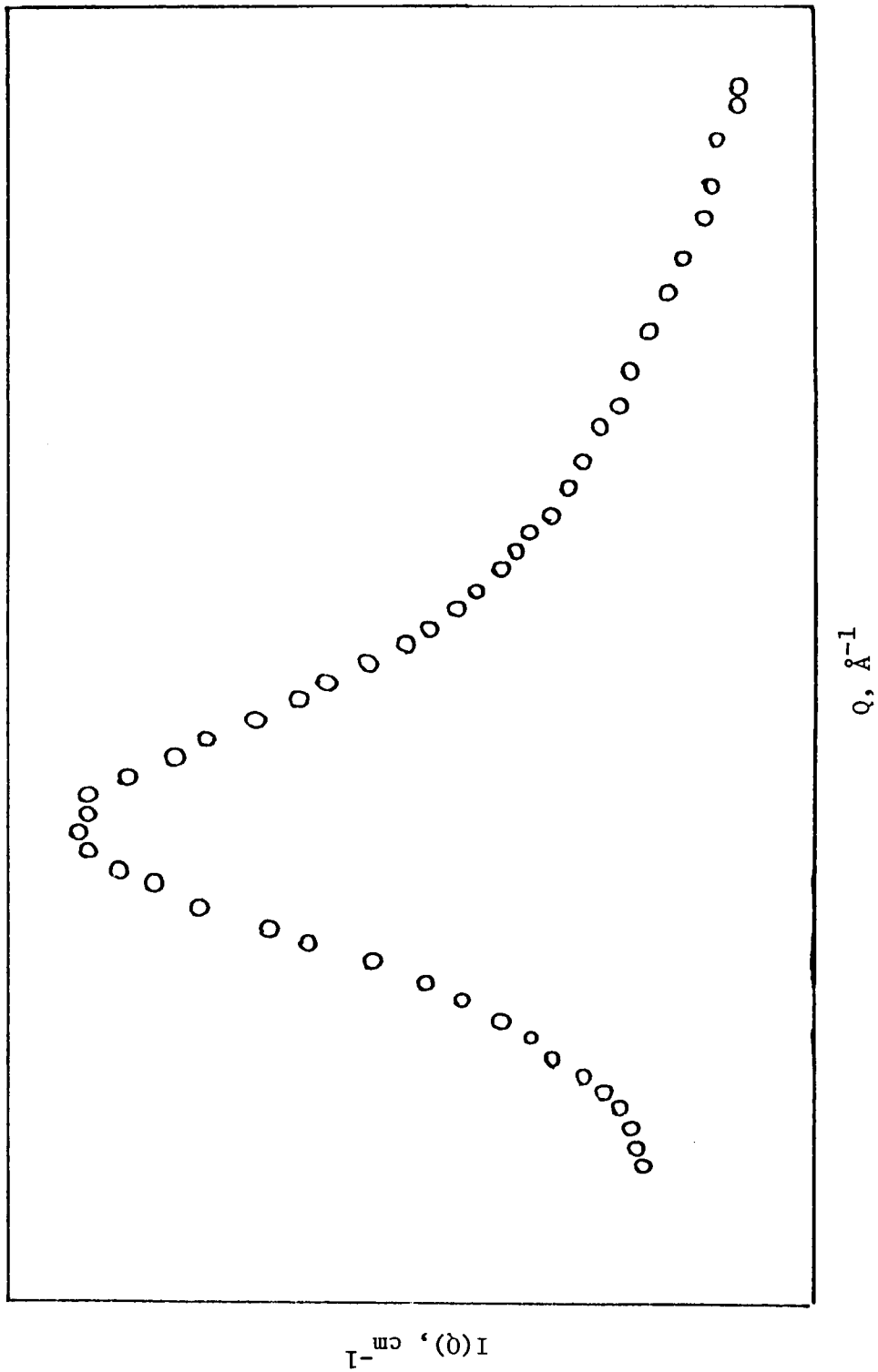


Figure 36. Experimentally obtained scattered intensity data.

from $P(Q)$ and $S(Q)$. Each of these functions contains information about the micelles and the micellar solutions. To exploit this store of information, one has to find a model particle (sphere, cylinder, etc.) which is "equivalent in scattering" with the particle in solution; in other words, a solution of the model particles should have a scattering curve which agrees within experimental error with the experimental curve. A complete solution to the problem of finding a model equivalent in scattering means selecting the proper forms for the structure and form factors, and frequently requires several cycles of approximation.

For the present analysis, all three models (spheres, ellipsoids, and cylinders) discussed in Section B.2 of this chapter were used. The surfactants and models employed for this study are summarized in Table XVIII. CTA2,6Cl and CTA2Cl were fit to the spherical core-plus-shell model of Figure 37. This model is characterized by a dry core of radius R_1 , and a hydrated outer shell consisting of the head groups, the bound counterions, a fraction of each of the C_{16} hydrocarbon chains, and the water of hydration. R_1 has a maximum value of l_c , the length of the extended hydrocarbon chain⁷³:

$$l_c = (2.765 + 1.265 n_c) \text{ \AA} \quad (50)$$

where n_c is the number of methylene groups in the hydrocarbon chain. For a $n\text{-}C_{16}$ chain, $n_c = 15$ and $l_c = 21.7 \text{ \AA}$. However, Hayter and Penfold¹²² have pointed out that even when $R_1 = l_c$, not all of each hydrocarbon chain is in the dry core; rather, some portion of the

TABLE XVIII
MODELS USED FOR SANS ANALYSIS

Sphere Model	Ellipsoid Model	Rigid Rod Model
CTA2C1	CTA2C1	CTA3,4C1
CTA2,6C1	CTA2,6C1	CTA4C1
	CTA4C1	
	CTA3,4C1	

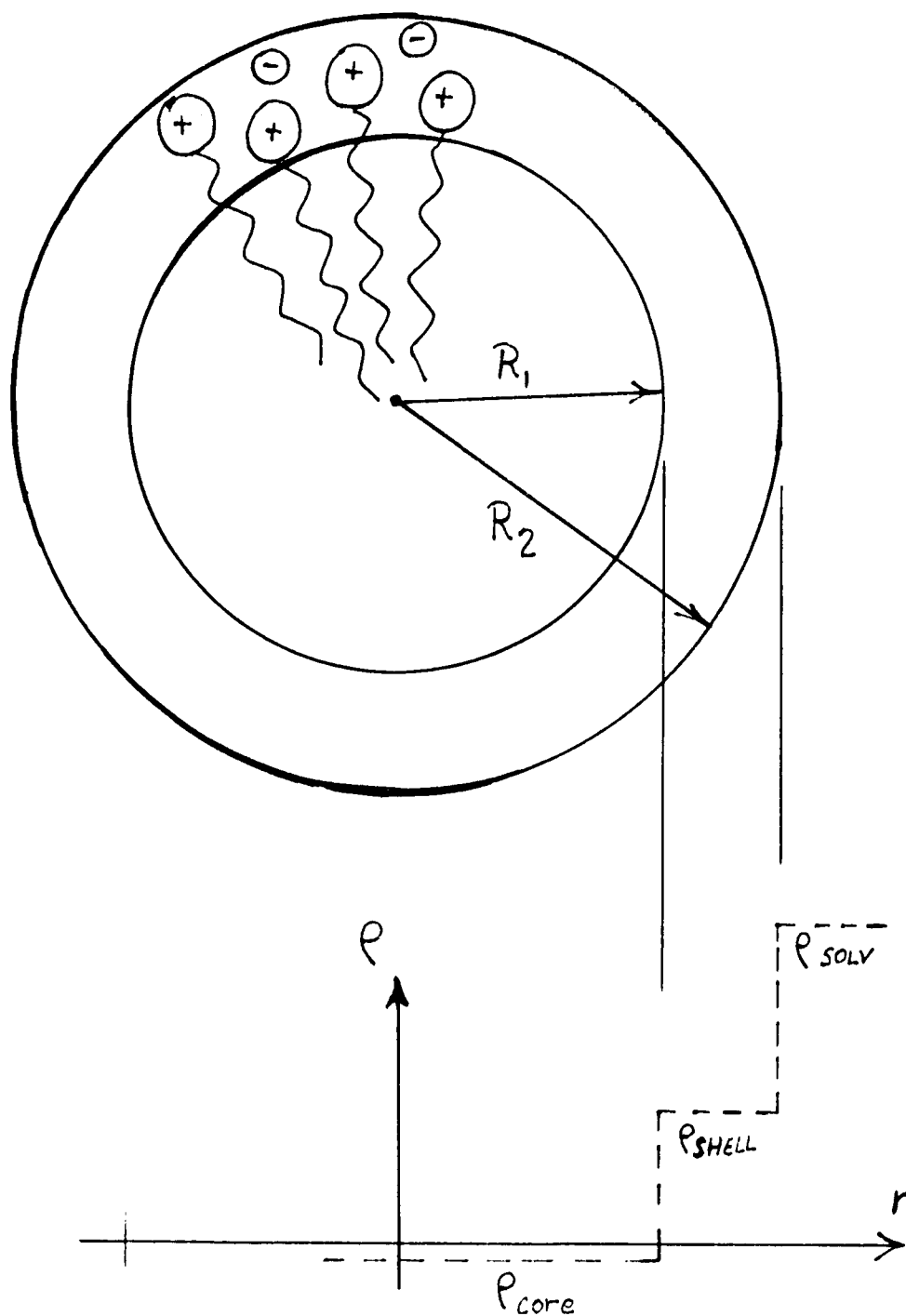


Figure 37. Core-plus-shell spherical model. ρ is the scattering length density; R_1 is the radius of the hydrocarbon core; and R_2 is the radius of the entire micelle.

chains are in the hydrated Stein layer. For the analysis, the volume of the CTA^+ ion was assumed to be $560 \text{ \AA}^3$; the volume of the 2Cl^- anion was $177 \text{ \AA}^3$; and the volume of the $2,6\text{Cl}^-$ anion was $200.7 \text{ \AA}^3$. The volumes were calculated from the group volumes listed by Immirzi and Perini.¹²³ For both surfactants, the hydration number for the head groups was set at 1.5 water molecules and at four water molecules for the associated counterions.

The parameters obtained in the computation of this model include R_1 , R_2 , the aggregation number N , the charge on the micelle ZED , and the number of methylene groups per monomer in the dry portion of the hydrocarbon core. In addition, the statistical parameter CHI , a weighted nonlinear least squares fit of the computed model to the experimental data, is given. In the analysis, R_1 was fixed at the value of l_c , $21.7 \text{ \AA}$, and the aggregation number and micellar charge were allowed to vary. The scattering length density of the dry core is simply equivalent to the scattering length density of the hydrocarbon chains in the core; for the shell, the scattering length density is calculated from the water, head groups, and counterions bound to this layer. The extent of counterion binding is $1 - ZED/N$.

The form factor for the core-plus-shell model is given in Equation 44, page 109. Figure 38 shows a typical fit for $\text{CTA}2\text{Cl}$ at a concentration of 0.02 M . The solid line is the calculated $I(Q)$ for the core-plus-shell model with R_1 equal to the extended hydrocarbon chain length. While $P(Q)$ alone cannot account for the shape of the entire curve, it is nearly identical to $I(Q)$ at Q values greater than Q_{Imax} .

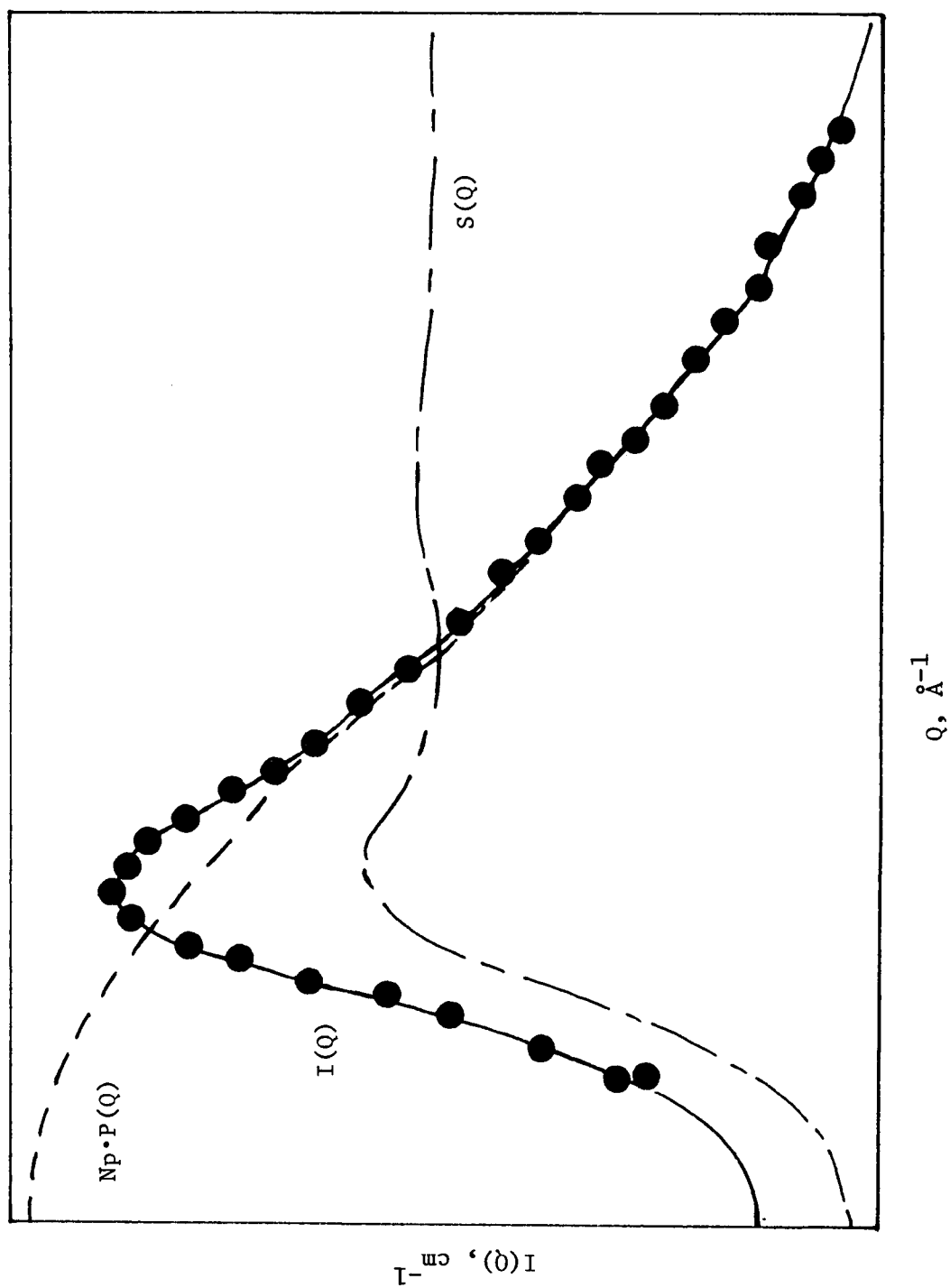


Figure 38. Fit of experimental data to a sphere model.

In order to fit the entire curve, however, it is necessary to calculate $S(Q)$ using Hayter and Penfold's analytical solution, as discussed in Section B.4 of this chapter. The parameters of interest here are the diameter, σ , of the micelles, modeled as charged hard spheres; and the ionic strength, X , of the solution, given by

$$X = \text{CMC} + \frac{1}{2}\alpha(C - \text{CMC}) \quad (51)$$

where α is the degree of counterion dissociation and C is the total surfactant concentration. As long as the micelles are roughly spherical in shape, σ can simply be approximated by $2 \times R_2$.

The scattering curves of four surfactants--CTA2Cl; CTA2,6Cl; CTA4Cl; and CTA3,4Cl--were fit to a core-plus-shell ellipsoid model, pictured in Figure 39. Again a number of parameters may be varied, including the eccentricity ECC , the aggregation number, the micellar charge and a , the semiminor axis of the prolate ellipsoid. It must be pointed out that, in cases of large eccentricity the Haytor-Penfold model for the structure factor is at best a poor approximation of the function.^{95,107} In addition systems containing large prolate or cylindrical micelles have been shown in general to be polydisperse,^{75,79,81} further complicating the computation of $S(Q)$.

Finally solutions of CTA3,4Cl and CTA4Cl were fit to a rigid cylinder model shown in Figure 40. Because of the intractability of the calculation of $S(Q)$ for solutions of long cylindrical micelles, the fits were made by employing a method suggested by Hoffman et al.⁸⁸ in which only the high- Q portion of the curve, beyond the interaction

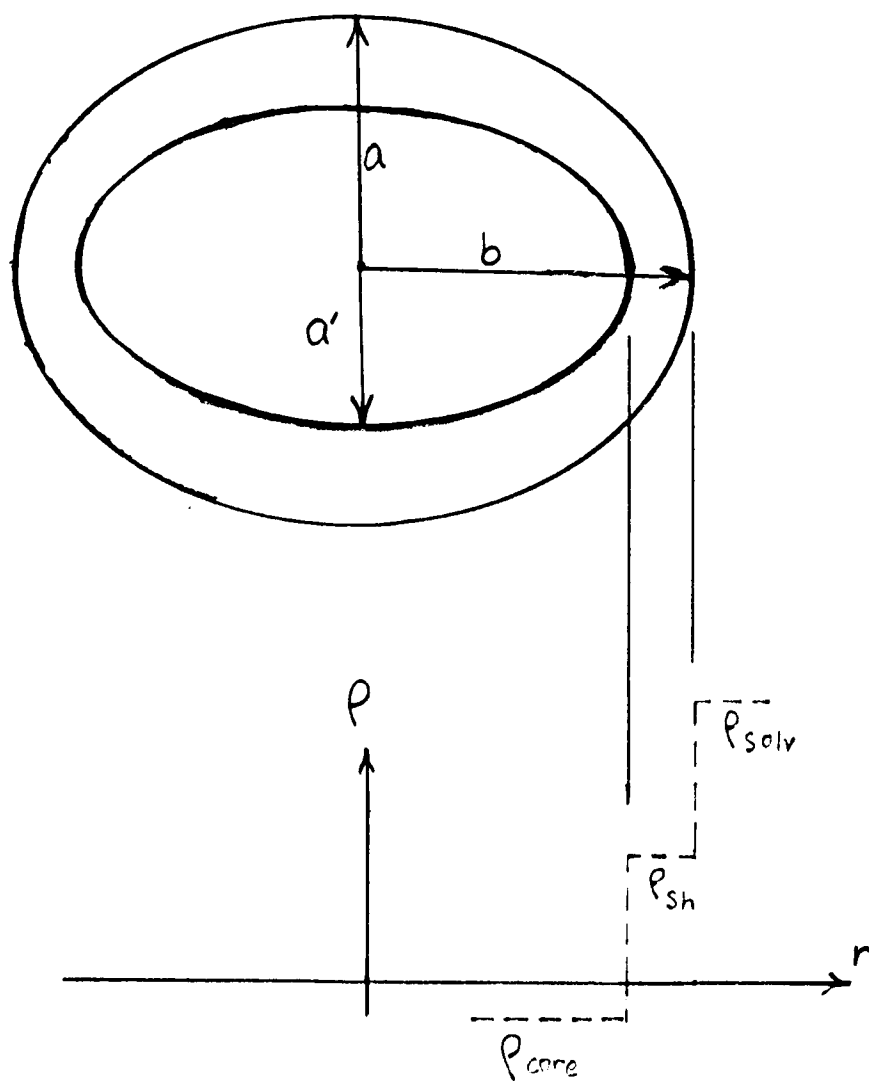


Figure 39. Core-plus-shell ellipsoidal model. a is the semiminor axis of the entire particle; a' is the semiminor axis of the hydrocarbon core; and b , the semimajor axis of the particle, is $2 \cdot a \cdot \text{ECC}$.

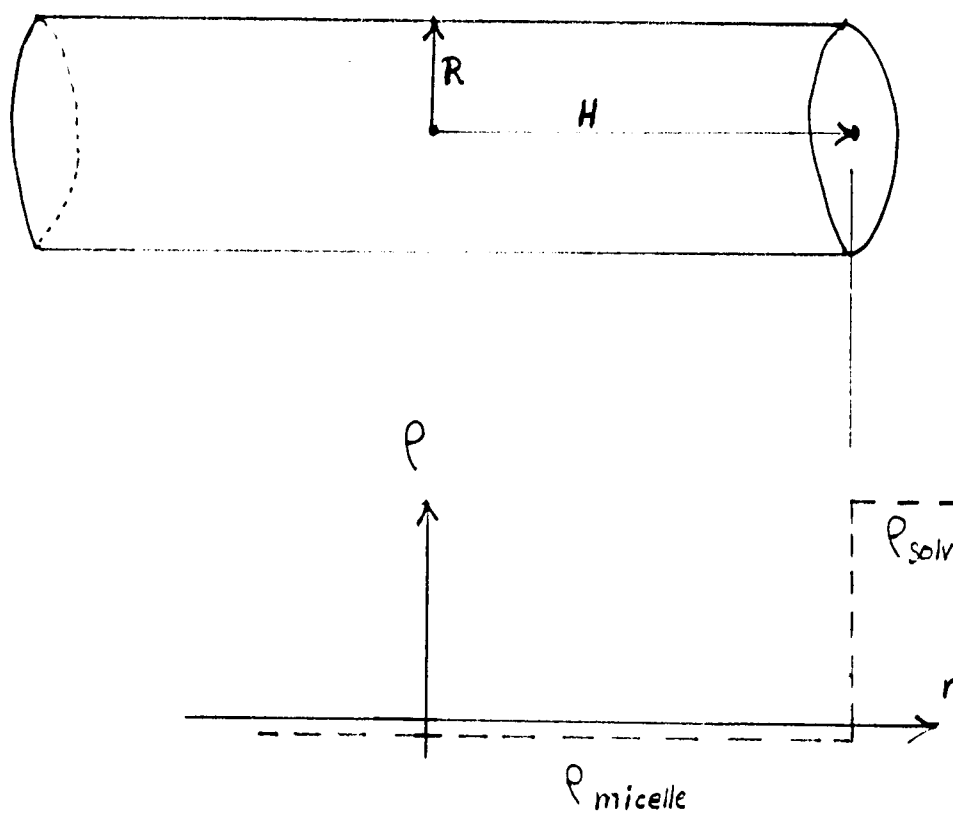


Figure 40. Cylinder model. H is the half-length of the particle and R is the radius of the particle.

peak, was fit. For this portion of the curve, $S(Q)$ approaches a value of one and the intensity function is given by

$$I(Q) = N_p \cdot \langle |F(Q)|^2 \rangle + B \quad (52)$$

where $\langle |F(Q)|^2 \rangle$ is given by Equation 48, page 110, and B is the background correction (see Chapter VI, Section A.6.b). In practice, it was necessary to obtain the values of the half-length of the cylinder from $I(0)$, where the integral in the form factor is a constant, since the H values were too large to be obtained reliably from the fittable Q range. Among the parameters which could be varied were the cylinder radius R , the half length H , the number particle density N_p , and the volume of the particle V_p . The micelles were treated as dry homogeneous cylinders, assuming no water penetration into the micelle. This was necessary because it is not possible to separate the scattering from the core and the shell for very asymmetrical, randomly oriented particles.

E. Results of SANS Measurements

1. CAT4C1 and CTA3,4C1

SANS measurements of solutions of CTA3,4C1 and CTA4C1 were made on solutions having concentrations ranging from 0.007 M to 0.05 M. Some of the experimentally obtained $I(Q)$ curves for the CTA4C1 solutions are shown in Figure 41. Similar curves were obtained for solutions of CTA3,4C1. As the concentrations of the solutions increases, an interaction peak begins to appear, with the value of $Q_{I_{max}}$ shifting to

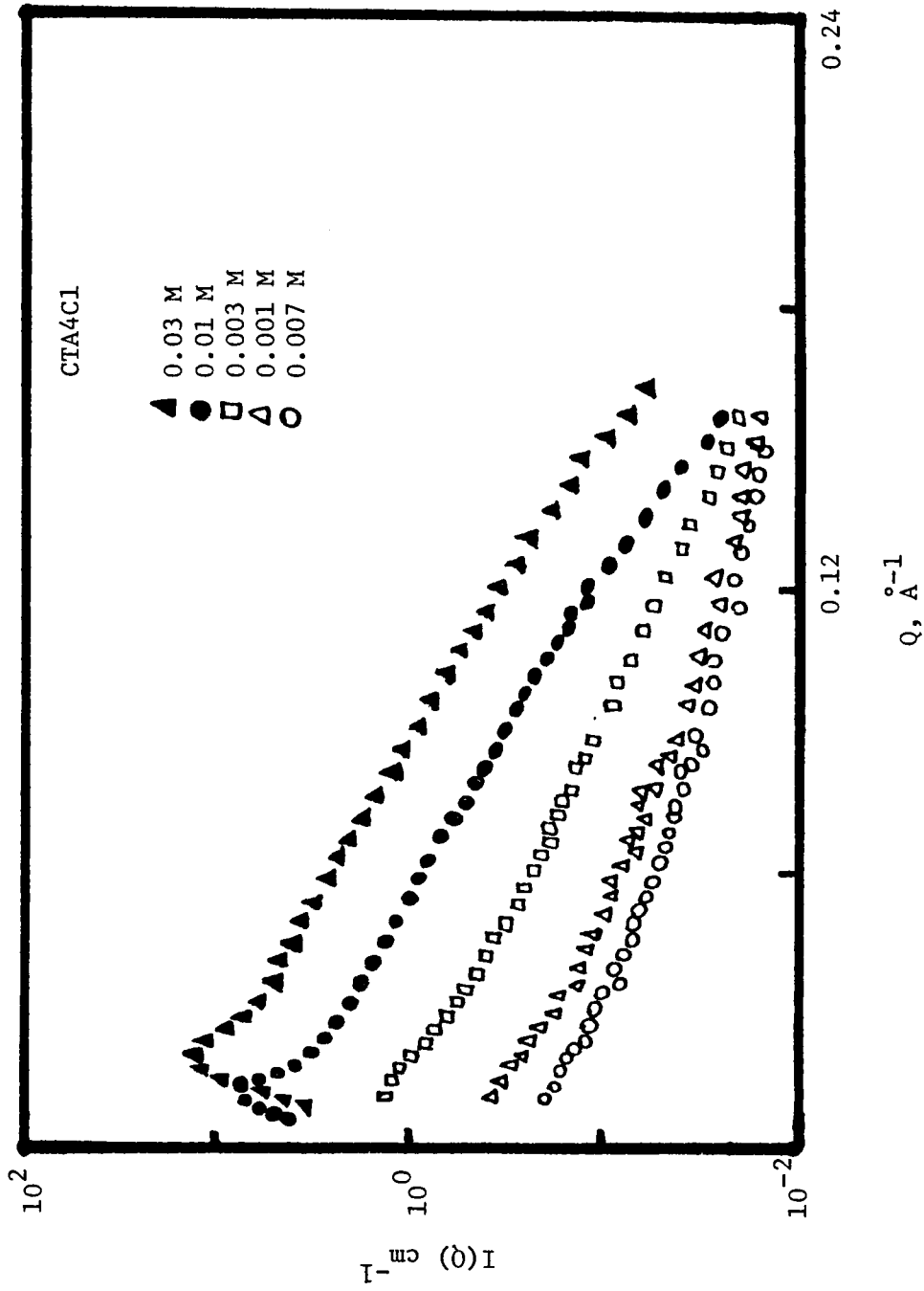


Figure 41. SANS data for a number of CTA4Cl solutions.

higher Q values as the concentration increases. For the solutions of lower concentration, the interaction peaks are shifted to values of Q too low to be observed at the sample-to-detector distances used in this experiment (1.4 m to 12 m). In order to observe the interaction peaks for the less concentrated samples, it would be necessary to perform experiments at even larger sample-to-detector distances. The shift of the interaction peak to higher Q values with increasing concentration indicates that the center-to-center distance between nearest neighbor micelles is decreasing. This distance can be approximated from Q_{Imax} according to

$$r_{\text{Imax}} = \frac{2\pi}{Q_{\text{Imax}}} \quad (53)$$

In turn, it is possible to obtain the average aggregation number of the micelles from r_{Imax} and the surfactant concentration:

$$\bar{N} = N_A r_{\text{Imax}}^3 (C - \text{CMC}) \quad (54)$$

where N_A is Avogadro's number. The values of $\bar{N}$ are not exact because Equation 53 is only an approximation. Table XIX presents the results of calculations of r_{Imax} and $\bar{N}$ for the CTA4Cl and CTA3,4Cl solutions with distinguishable interaction peaks. The values of $\bar{N}$ are clearly much too high for the micelles to be of spherical shape. If the micelles are assumed to be rigid cylinders, the lengths of the micelles can be calculated from the total volume of the micelles and the radius of the cylinder by the equation

TABLE XIX
 $Q_{I\max}$ VALUES, AGGREGATION NUMBERS AND LENGTHS FOR CTA4C1 AND CTA3,4C1

Solution	$Q_{I\max}$	r	$\bar{N}$	L
CTA4C1, 0.01 M	$0.011 \text{ \AA}^{-1}$	$571 \text{ \AA}$	1121	$336 \text{ \AA}$
CTA4C1 0.03	0.019	331	655	196
CTA4C1 0.05	0.023	273	612	183
CTA3,4C1 0.007	0.009	698	1433	429
CTA3,4C1 0.02	0.014	449	1090	326
CTA3,4C1 0.05	0.24	262	541	162

$$L = \frac{\bar{N}V_{\text{mon}}}{\pi R^2} \quad (55)$$

where V_{mon} is the volume of a single CTA⁺ monomer ($560 \text{ \AA}^3$) and R is taken as $24.4 \text{ \AA}$. Table XIX also includes the L values for the CTA4Cl and CTA3,4Cl micelles calculated by Equation 55.

Hoffmann et al.⁸⁸ have pointed out that Q_{Imax} is affected not only by the maximum in the $S(Q)$ function, Q_{Smax} , but also, to a lesser, but noticeable, extent, by the $P(Q)$. They warn that for strong interactions, wrong conclusions could be drawn by using Q_{Imax} rather than Q_{Smax} for the calculation of $\bar{N}$ and L . The results of Hoffmann's analysis for cetylpyridinium salicylate solutions are shown in Table XX. A comparison of the r_{Imax} values and the r_{Smax} values of his data indicates that the value of Q_{Smax} is a factor of about 1.13 times larger than Q_{Imax} . This correction was made for the data in Table XIX and the results are shown in Table XXI.

A final value which can be obtained from Q_{Imax} (or Q_{Smax}) is the number particle density, N_p , from the relation

$$N_p = \frac{[C - \text{CMC}]N_A}{N} = \frac{1}{r^3} \quad (56)$$

Clearly, this relationship indicates that the number of micelles is increasing with increasing concentration. At the same time, it is apparent from Tables XIX and XXI that the aggregation numbers and lengths of the micelles are decreasing with increasing concentration.

TABLE XX
CETYLPIRIDINIUM SALICYLATE $Q_{I\max}$ AND $Q_{S\max}$ VALUES^a

Conc	$Q_{I\max}$	$\bar{N}_{I\max}$	$L_{I\max}$	$Q_{S\max}$	$\bar{N}_{S\max}$	$L_{S\max}$
0.010 M	$0.0110 \text{ }^{\circ}\text{A}^{-1}$	1115	$623 \text{ }^{\circ}\text{A}$	--	--	--
0.020	0.0151	857	479	$0.0185 \text{ }^{\circ}\text{A}^{-1}$	759	$426 \text{ }^{\circ}\text{A}$
0.040	0.0197	776	429	0.0220	561	312
0.080	0.0284	517	290	0.0321	362	205
0.160	0.039	400	230	0.0449	264	152

^aValues from reference 88.

TABLE XXI
 Q_{Smax} VALUES, AGGREGATION NUMBERS, AND LENGTHS FOR CTA4Cl AND CTA3,4Cl

Solution	Q_{Smax} $^{\circ} \text{Å}^{-1}$	r $^{\circ} \text{Å}$	$\bar{N}$	L $^{\circ}$
CTA4Cl, 0.01 M	0.0124	506	780	233
CTA4Cl, 0.03	0.0215	292	450	134
CTA4Cl, 0.05	0.0261	241	421	107
CTA3,4Cl 0.007	0.0102	616	985	295
CTA3,4Cl 0.02	0.0158	398	759	227
CTA3,4Cl 0.05	0.0271	232	376	113

An alternative to this picture is that, rather than rigid rods, the micelles are growing, flexible cylinders of some persistence length, l_p ; if so, the decrease in r with increasing concentration may be due to the growing number of segments of length, l_p , rather than a growing number of micelles of decreasing length. In this case, as the micelles draw near to and surpass c^* , r^3 corresponds not to the volume per micelle but only to the volume of a portion of the micelle. No calculation of micelle size can be made from $Q_{I\max}$ alone in this situation.

Tables XXII and XXIII show the results of fitting the $I(Q)$ data from solutions of CTA4Cl and CTA3,4Cl to a rigid rod model similar to the one used by Hoffmann on the CPS system. These fits were made by setting R equal to $24.4 \text{ \AA}$ and allowing the half-length, H of the cylinder to vary. Clearly, the values of L from the model fits are quite different from those calculated from $Q_{I\max}$ or $Q_{S\max}$. In fact, while the trend in the latter cases was toward smaller rod lengths and aggregation numbers with increasing concentration, no such trend can be discerned from the values of the model fitting. If anything, the trend appears to be toward larger micelles with increasing concentration. If this is truly the case, then the CTA3,4Cl and the CTA4Cl solutions behave differently from the CPS solutions of Hoffmann. As his results, given in Table XXIV, indicate, he found that the micelle lengths of CPS first increase, then decrease with increasing surfactant concentration. According to Hoffmann, the point at which the rod lengths pass over their maximum corresponds to the point at which the rod lengths are equal to the center-to-center distance between the micelles, c^* . For

TABLE XXII

RIGID ROD FITS OF CTA4C1 WITH R CONSTANT

Concentration	R	L	CHI
0.0007	24.4 $\overset{\circ}{\text{\AA}}$	150 $\overset{\circ}{\text{\AA}}$	1.13
0.001	24.4	392	1.28
0.003	24.4	396	2.20
0.010	24.4	616	2.90
0.030	24.4	566	5.89
0.050	24.4	1394	6.58

TABLE XXIII

RIGID ROD FITS OF CTA3,4C1 WITH R CONSTANT

Concentration	R	L	CHI
0.0007	24.4 $\overset{\circ}{\text{\AA}}$	582 $\overset{\circ}{\text{\AA}}$	1.07
0.001	24.4	400	1.35
0.003	24.4	504	2.09
0.007	24.4	606	3.96
0.020	24.4	336	4.39
0.050	24.4	942	13.8

TABLE XXIV

CETYLPIRIDINIUM SALICYLATE RIGID ROD FITS^a

Concentration	R	L
0.003 M	21.37 $\overset{\circ}{\text{\AA}}$	320 $\overset{\circ}{\text{\AA}}$
0.005	21.31	526
0.020	21.5	557
0.040	21.6	550
0.080	21.4	395
0.160	21.2	300

^aValues taken from References 64 and 88.

the CTAX's it becomes increasingly difficult to accurately fit the experimental curves to the rigid rod model as the solution concentration increases, as is reflected in the growing CHI values.

When the experimental data for CTA4C1 and CTA3,4C1 are fit by varying both R and H, the R values show some scatter but average about 24.6 Å for CTA3,4C1 and 23.2 Å for CTA4C1. These results are shown in Tables XXV and XXVI. Here again, no definite trends can be detected for the rod lengths, except to indicate that the micelles are indeed much too large to be spherical in shape.

Some of the experimental data from CTA3,4C1 and CTA4C1 were also fit to a model for prolate ellipsoids. While this model is generally used for ellipsoids of low eccentricity and includes the computation of a structure factor $S(Q)$, which should not work well for highly elongated micelles, the fits in the present case are astonishingly good, as shown in Figure 42 for 0.01 M CTA4C1. The results of the analysis along with CHI for each fit, are shown in Table XXVII. For CTA4C1 solutions, the aggregation numbers obtained from the ellipsoid fits are quite similar to those obtained from $Q_{I_{max}}$, and the values for the length of the major axis of the ellipsoids, $2 \cdot a \cdot ECC$, though larger than those calculated from $Q_{I_{max}}$, do decrease with increasing concentration. In addition, values for the semiminor axis, a , average 24.6 Å, about the same as the value obtained from the rigid rod fits. ZED, the micellar charge obtained from the ellipsoid fits, is probably too low ($\alpha = 2$ to 4%) for these solutions, but only by a few percent.

TABLE XXV

RIGID ROD FITS OF CTA4C1 WITH R VARYING

Concentration	R	L
0.0007 M	20.0 $\text{\AA}$	197 $\text{\AA}$
0.001	22.5	410
0.003	22.8	1102
0.010	24.4	544
0.030	23.6	636
0.050	25.7	544

TABLE XXVI

RIGID ROD FITS OF CTA3,4C1 WITH R VARYING

Concentration	R	L
0.0007 M	25.2 $\text{\AA}$	780 $\text{\AA}$
0.001	23.8	704
0.003	24.3	590
0.007	26.1	340
0.020	23.9	658
0.050	24.5	438

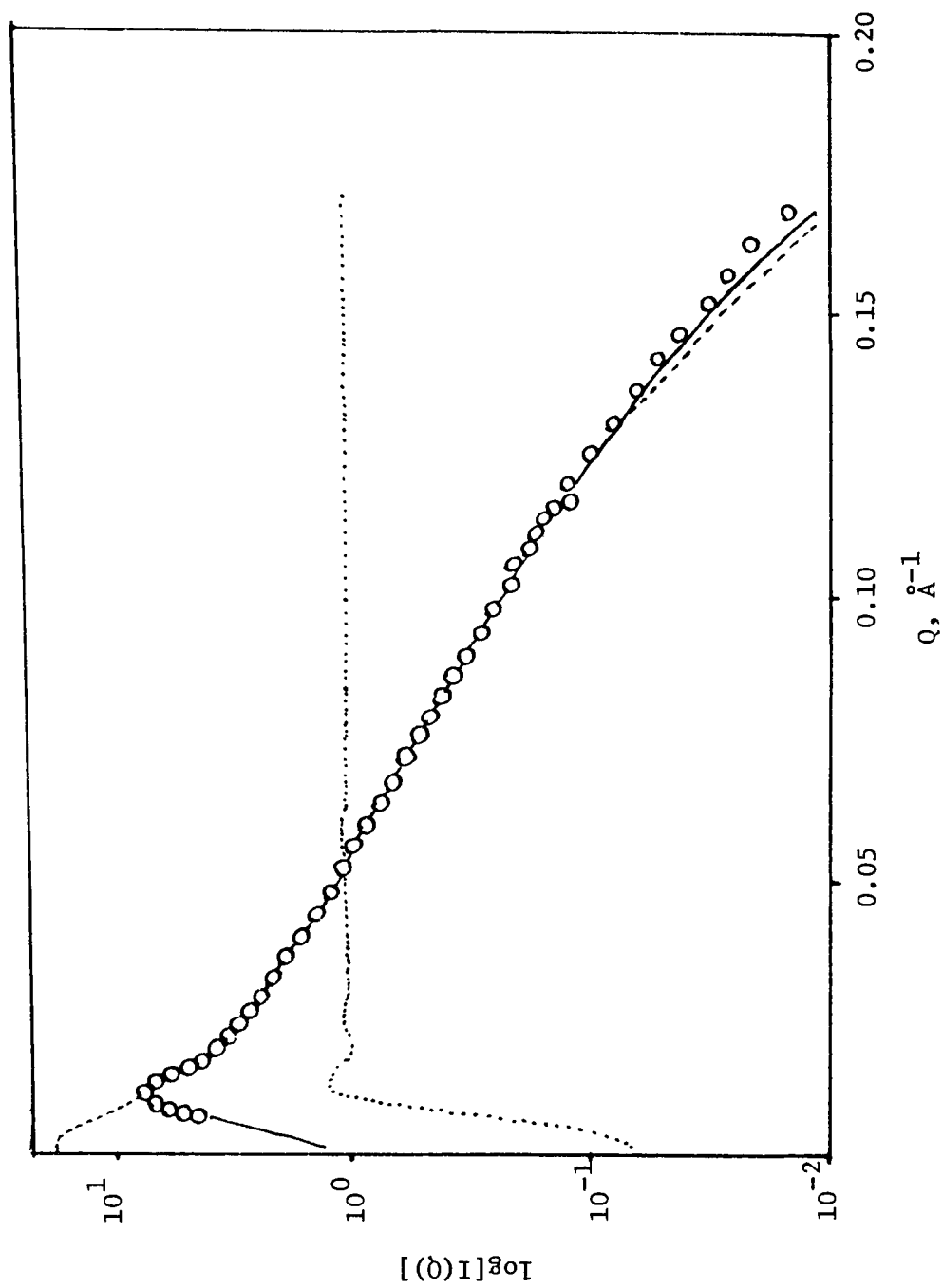


Figure 42. Ellipsoid fit of 0.01 M CTA4Cl.

TABLE XXVII

ELLIPSOID FITS OF CTA4C1 AND CTA3,4C1

Concentration	AGG	ZED	a	2aECC	CHI
0.04 M CTA34C1	617	23	25.7 Å	408 Å	10.38
0.01 M CTA4C1	1473	43	24.45	1052	2.38
0.03 M CTA4C1	888	37	24.37	635	4.27
0.05 M CTA4C1	665	23	25.00	226	5.78

It is difficult to explain the failure of the rigid rod model to fit successfully the experimental data. One possible source of difficulty may lie in the question of the polydispersity of these systems. Hoffmann et al. have found evidence that the CPS system is essentially monodisperse,⁴³ but other authors have found similar cylindrical cationic micellar systems to possess a high degree of polydispersity, and the same cannot be ruled out for the CTAX systems. Nevertheless, the rigid rod model used for these fits do not account for polydispersity, which, as pointed out in Section B.3 of this chapter, requires special methods of computation. Another problem is that, especially for the higher concentrations, a great deal of the intensity curve must be truncated to eliminate the effect of the structure factor before the fit is performed. Finally, there is the possibility that the micelles are not rigid rods at all, but are instead flexible cylinders which continue to grow above c^* .

2. CTA2C1 and CTA2,6C1

Results of the fits of CTA2C1 and CTA2,6C1 solutions indicate that these surfactants do, indeed, form spherical micelles at concentrations up to 0.06 M. The results of fitting the data from solutions of CTA2C1 and CTA2,6C1 to a spherical core-plus-shell model are presented in Table XXVIII. These figures are the results of setting R_1 equal to the extended hydrocarbon chain length, as calculated by Equation 50, page 118.

The results indicate that the aggregation numbers remain relatively constant over an intermediate range of concentration, then begin to

TABLE XXVIII
 SPHERE FITS FOR CTA2C1 AND CTA2,6C1

Concn	R_1	R_2	AGG	ZED	ALF	CHI
CTA2C1						
0.020 M	21.7 $\overset{\circ}{\text{\AA}}$	28.9 $\overset{\circ}{\text{\AA}}$	122	16	12.1	1.69
0.035	21.7	29.2	126	17.4	11.6	1.40
0.050	21.7	29.4	128	17.3	10.5	1.47
0.070	21.7	30.1	137	20	10.5	3.46
0.100	21.7	35.5	221	17	5.7	2.50
CTA2,6C1						
0.007 M	19.8 $\overset{\circ}{\text{\AA}}$	23.9 $\overset{\circ}{\text{\AA}}$	74	23	15.0	1.19
0.010	21.7	26.8	96	17	15.0	0.99
0.020	21.7	27.6	104	17	13.9	1.17
0.035	21.7	27.5	103	15	13.7	1.33
0.058	21.7	27.6	105	16	13.9	1.70
0.090	21.7	30.5	141	23	10.1	1.78

increase around 0.06 M. Above this concentration, a marked increase is seen in the aggregation numbers and R_2 values of the micelles, indicating that growth is occurring. When the 0.10 M CTA2Cl solution was fit to the spherical model, the result was a shell thickness of 13.8 Å and an ALF of only 5.7, indicating that more than half of the methylene groups are wet. This is clearly an unfavorable situation and it is unlikely that these micelles are actually spherical at this concentration. CTAB micelles have been demonstrated to form cylindrical micelles at concentrations of 0.27 M. The less hydrophilic counterions of CTA2Cl and CTA2,6Cl might be expected to condense to the micellar surface at lower concentrations than the Br^- ion, thus the sphere-to-cylinder (or prolate ellipsoid) transition would occur at a somewhat lower concentration than for CTAB. Conductivity measurements of CTA2Cl at high concentrations (Chapter III, Figure 26, page 77) reveal a gradual deviation from the straight line (of specific conductivity vs. concentration) formed by the data at small concentrations above the CMC. The conductivity data indicate that, unlike the sudden sphere-to-rod transition of CTA4Cl, the change to elongated micelles is relatively gradual for CTA2Cl. This also appears to be the case from the SANS results, particularly the aggregation numbers and the R_2 values.

Solutions at still higher CTA2Cl and CTA2,6Cl concentrations were analyzed by SANS and fit to ellipsoid models. These results, given in Table XXIX, indicate that the micelles are ellipsoidal in shape with eccentricities between 3.5 and 6 for solutions of concentrations from 0.167 M to 0.302 M. The micelles apparently pass through a maximum in

TABLE XXIX

ELLIPSOID FITS OF CTA2C1 AND CTA2,6C1

Concn	AGG	ZED	a	a'	ECC	2aECC	r	CHI
CTA2C1								
0.167 M	290	22.2	22.24 Å	17.88 Å	5.55	246 Å	132 Å	2.97
0.234	236	28.9	22.69	18.34	4.17	189	112	7.47
CTA2,6C1								
0.201	208	3.85	22.56 Å	18.09 Å	3.85	174 Å	114	5.30
0.302	197	3.49	22.83	18.35	3.49	159	96.7	7.19

size and then decrease in size somewhat. This may be the result of increasing electrostatic repulsion between the growing micelles as the concentration increases. The lengths of these micelles, $2 \cdot a \cdot \text{ECC}$, are considerably smaller than those obtained from fits of CTA3,4C1 and CTA4C1 solutions; however the number particle densities for the CTA2C1 and CTA2,6C1 solutions are much higher than for the larger micelles. The r values, obtained from Q_{Imax} and included in Table XXIX, indicate that these systems may be near or above the overlap concentration.

Again it should be mentioned that the ellipsoid model employed in this study includes the $S(Q)$ function and assumes monodispersity. The $S(Q)$ approximation of Hayter and Penfold gives good results at modest eccentricities; nevertheless, the values of ECC found in the ellipsoid fits of CTA2C1 and CTA2,6C1 are probably near the frontier of this range. It is also likely that the solutions at higher concentrations are somewhat polydisperse, affecting both the $P(Q)$ and the $S(Q)$ to a small extent.

CHAPTER V

DISCUSSION AND CONCLUSIONS

A. Discussion of the Results

The results of the foregoing experiments clearly indicate that there is a marked specificity of micellar solution properties toward various mono- and dichlorobenzoate counterions. Solution viscosity and viscoelasticity, extent of counterion binding, CMC values, NMR line broadening, response to changes in pH, and micellar size and shape have all been demonstrated to depend upon the precise molecular structure of the counterion. The deciding structural characteristic is the position of the chlorine atom or atoms on the aromatic ring of the counterion. Counterions with chlorine atoms only in the ortho positions induce the formation of "normal" micelles, approximately spherical in shape and remaining relatively small over a wide range of surfactant concentration. Surfactants with these counterions have relatively low extents of counterion binding and exhibit normal rheological properties; that is, they exhibit no signs of viscoelasticity and have viscosities similar to that of CTAB solutions of the same concentration. (However, they do exhibit an increase in viscosity at sufficiently low values of pH). In addition, ^1H NMR spectra of D_2O solutions of these surfactants resemble the spectra of aqueous solutions of CTAB at similar concentrations. The peaks of these spectra are narrow, indicative of the presence of spherical micelles.

In contrast, counterions having chlorine atoms in the meta and para positions induce, at sufficiently high surfactant concentrations, large cylindrical micelles that grow with increasing surfactant concentration, at least to the point at which the rod lengths are equal to the average center-to-center distance of neighboring micelles. Conductivity measurements reveal that counterion binding for these cylindrical micelles is quite high (ca. 90%). Solutions of these surfactants also have unusually high viscosity and remarkable viscoelastic properties. Their ^1H NMR spectra have very broad, featureless peaks, and there appears to be no pH effect for these solutions. One counterion, the 2,4-dichlorobenzoate anion includes both an ortho and a para chlorine on the aromatic ring of the counterion. Predictably, the properties of CTA2,4Cl fall between those of the two preceding extremes. The solutions of CTA2,4Cl first form spherical micelles, then undergo a transformation to form cylindrical micelles at higher concentrations. Also, solutions of CTA2,4Cl are visibly less viscoelastic than solutions of CTA3,4Cl or CTA4Cl at the same concentration, over a large range of concentration, and higher concentrations and shear rates are required for the apparent viscosity of CTA2,4Cl solutions to obtain a value similar to that of CTA3,4Cl solutions at lower concentrations.

Finally, these structural effects are additive. When the 2-chlorobenzoate counterion is replaced by the 2,6-dichlorobenzoate counterion, the resulting micelles are smaller and show less tendency to grow at high surfactant concentrations. On the other hand, CTA4Cl, though ultimately forming strongly viscoelastic solutions and large

cylindrical micelles, first forms spherical micelle and undergoes a sphere-to-rod transition, while solutions of CTA3,4Cl and CTA3,5Cl form cylindrical micelles from the onset of micellization, and at concentrations below that at which CTA4Cl forms cylindrical micelles.

It has been suggested that the counterion specificity of CTA⁺ micelles toward the hydroxybenzoate counterions may be due to the position of the counterion relative to the micellar surface.⁴² The surface of alkyltrimethylammonium micelles is smooth, with little water penetration beyond the Stern region of the micelle. The 2-hydroxybenzoate counterion can itself be considered amphiphilic, with a hydrophilic portion, the polar functional groups, and a hydrophobic portion, the aromatic ring. Thus for CTASal micelles, the counterion is pictured as occupying a position between the head groups in the Stern layer, with its aromatic ring protruding through the Stern region, into the hydrocarbon core. In contrast, the 4-hydroxybenzoate counterion does not possess a structure that allows it such a favorable interaction with the micellar surface. It thus must sit at the outer surface of the micelle, where it is less effective at screening the repulsions between the charged head groups. Indications from calorimetric studies⁶⁵ that the 4-hydroxybenzoate anion remains hydrated at the micellar surface while the 2-hydroxybenzoate anion sheds its waters of hydration at the micellar surface help explain why the 4-hydroxybenzoate anion is less strongly bound (has a lower extent of counterion binding) than the salicylate anion.

For the chlorobenzoates, the situation is less easily explained. Here the positions of the substituents and their roles are reversed. The 2-hydroxybenzoate counterion induces viscoelasticity; the 2-chlorobenzoate counterion does not. The 4-chlorobenzoate counterion induces the formation of large micelles; the 4-hydroxybenzoate counterion does not. When the chlorobenzoate counterions have chlorine atoms only in the meta or para positions, however, the position of the counterions is probably similar to that of the salicylate counterion. The chlorine atom substituents, being hydrophobic, are able to penetrate into the hydrocarbon core of the micelle, while the carboxyl group remains at the micelle-water interface. The penetration into the hydrocarbon core probably extends even further than for the salicylate counterion.

It is not clear why the 2-chlorobenzoate anion, which is structurally similar to the salicylate anion, would not be able to orient itself in a similar position. The chlorine substituent is somewhat larger than the hydroxy group, but simple steric problems can almost certainly be ruled out, since the head groups are free to move. In addition to the head groups and counterions in the Stern region, there is also a certain amount of highly structured water. Underwood and Anacker⁶³ pointed out that the hydroxyl group of the salicylate anion can form hydrogen bonds with the water in the Stern layer while the chlorine substituent of 2-chlorobenzoate cannot. They suggested that the hydrogen bonding is sufficiently important to be the deciding force in anchoring the salicylate anion to the Stern region. Another explanation is that one of the resonance structures which can be drawn for

the 2-chlorobenzoate anion places a positive charge on the chlorine atom. This resonance contribution may be enhanced by the close proximity of the negatively charged carboxyl group. It may be that this slightly positive chlorine substituent is unable to remain near the positively charged head groups and is thus unable to position itself in an orientation similar to that taken by the salicylate anion. Though a similar resonance contributor exists for the para-chlorobenzoate anion, the chlorine atom is too far removed from the negatively charged carboxyl group and this resonance contributor would not be particularly enhanced.

In addition to having higher counterion binding, which leads rod-shaped micelles, the meta and para chlorobenzoate solutions are also viscoelastic. Viscoelasticity is not simply the result of the presence of large micelles. Porte and Appell and co-workers,⁷⁸⁻⁸² and Benedek and co-workers⁷⁴⁻⁷⁷ have studied numerous surfactant solutions which contain rodlike micelles, but none of these are viscoelastic. Hoffmann found that solutions of cetylpyridinium heptanesulfonate were not viscoelastic, despite evidence from SANS and conductivity measurements that these solutions contain large cylindrical micelles.¹²⁴ On the other hand, results from measurements of viscometry and conductivity clearly indicate that rods must be present in order for large increases in viscosity to occur. This is best seen for solutions of CTA2,4Cl. A comparison of the conductivity versus concentration curve (Figure 14, page 57) and the viscosity versus concentration curve (Figure 8, page 42) shows that for the two highest shear rates, the viscosity is

low in the region below the CMC_I , increases slightly in region where small spherical micelles are normally formed, then undergoes a large increase just above the CMC_{II} . Apparently the higher shear rates can induce a temporary network of the CTA₂,4Cl rodlike micelles even below c^* .

It is clear, then, that the occurrence of viscoelasticity is dependent upon both the presence of rod-like micelles and the identity of the counterion. The nature of the contacts between the cylindrical micelles of viscoelastic solutions is not fully understood, but the contacts appear to be sensitive to the counterion structure. The surface of a CTA-chlorobenzoate micelle consists of relatively hydrophobic trimethylammonium head groups and is about 90% charge-neutralized by the bound counterions, which are themselves relatively hydrophobic. Thus, despite long-range repulsions between micelles, local contacts between overlapping rods may be attractive. However, more study must be undertaken to explain the counterion specificity for intermicellar contacts.

The pH measurements were made primarily to determine the role of ionization of the counterions. Several neutral aromatic solutes induce increases in viscosity (but not viscoelasticity) in CTAB solutions. CTA₂Cl solutions at moderate (1-10 mM) concentrations are not exceptionally viscous, but at pH values less than 2, they become increasingly viscous with decreasing pH. This is probably due to the presence of neutral 2-chlorobenzoic acid which can penetrate the outer shell of the micelle and position itself at least partially in the hydrocarbon

region. This is in agreement with the results found by Bunton and Minch,⁴⁷ who reported that neutral arenesulfonic acid molecules are buried more deeply in the micelle, on average, than are arenesulfonate anions, because hydration is less important with the acid. For CTA3,4Cl solutions, the counterions are already in position between the head groups and penetrating into the hydrocarbon region; protonation of these counterions only results in the precipitation of very insoluble 3,4-dichlorobenzoic acid. As the 3,4-dichlorobenzoate counterions are replaced by Cl^- counterions from the added HCl, the viscosity of the solution is rapidly lost.

A clear picture of the growth or shrinkage of the micelles at concentrations above c^* was not obtained in this work. The trend, noted by Hoffmann,⁸⁸ of micelle lengths that grow to a maximum at c^* , then decrease in size with increasing concentration was not observed. The micelles of the CTA3,4Cl and CTA4Cl solutions were obviously quite large above and below the overlap concentration, but, especially above c^* , no single trend could be established. An alternative explanation to the trend observed by Hoffmann may be found in recent work by Candau and co-workers.^{125,126} They propose that semidilute CTAB solutions containing 0.1 M or 0.25 M KBr have highly flexible micelles which behave in a fashion analogous to overlapping polymer coils. The micelles continue to grow with increasing surfactant concentration above c^* ; however, the scattered intensities no longer depend upon the size of individual rods, but upon the correlation length (or mesh size) of the network. As the micelle size increases (above c^*) the

correlation length decreases, and hence the results noted by Hoffmann. It should be pointed out, however, that Hoffmann's cetylpyridinium salicylate solutions contain no added electrolyte, and he found no evidence for flexible micelles in these systems. In the present work, flexible CTA-chlorobenzoate micelles would help to explain the increasingly poor fit, with increasing concentration, of the SANS data to the rigid rod model.

B. Other Surfactants Involving Interactions Between Aromatic and Ammonium Ions

One logical extension of this work was to seek other examples of surfactant-water systems which display viscoelasticity. In particular, it was of interest to find an anionic amphiphilic moiety which, with the proper cationic counterion, would be able to form viscoelastic solutions. A number of surfactants with benzoate or salicylate head groups and ammonium counterions were prepared, to determine whether such an arrangement might have interesting rheological properties in solution. The compounds are shown in Table XXX.

Compounds I-IV have n -C₁₂ hydrocarbon tails and *p*-aminobenzoate or *p*-aminosalicylate head groups connected by an amide linkage. The salicylate head group was chosen to simulate the interaction present between the salicylate counterion and the ammonium head group in CTASal. Following the analogy the benzoate head group was not expected to form viscoelastic solutions. Two different ammonium counterions were employed: a tetramethylammonium cation and a cyclohexylammonium

TABLE XXX
OTHER SURFACTANTS PREPARED IN THIS STUDY

Number	Structure
I.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{N}(\text{CH}_3)_4$
II.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{N}(\text{CH}_3)_4$
III.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{NH}_3-\text{C}_6\text{H}_{11}$
IV.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{NH}_3-\text{C}_6\text{H}_{11}$
V.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{N}(\text{C}_2\text{H}_5)_4$
VI.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{N}(\text{C}_2\text{H}_5)_4$
VII.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{NH}_3-\text{C}_6\text{H}_{11}$
VIII.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{NH}_3-\text{C}_6\text{H}_{11}$
IX.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad +\text{NH}_3-\text{C}_6\text{H}_{11}$
X.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \quad (\text{CH}_3)_3\text{N}^+\text{C}_6\text{H}_{13}$

cation. The latter is less hydrophilic and might be expected to exhibit a greater preference for the micellar surface. However, none of the compounds, I-IV, were at all soluble in water. Therefore surfactants with shorter hydrocarbon chains were prepared, since amphiphilic ions generally become more hydrophilic as the size of the hydrocarbon chain is reduced. Compounds VI-VIII represent this change. In addition, a new counterion, the tetraethylammonium cation, was employed, along with the cyclohexylammonium cation. Of the latter four surfactants, only compound VIII, with the combination of a salicylate head group and a cyclohexylammonium counterion, was at all soluble. The highest measured solubility for this compound was 0.1183 molal at 45°C. All the other surfactants, I-VII, were insoluble at concentrations as low as 0.005 molal at 45°C. Solutions of compound VIII were not viscoelastic at either 45°C or 25°C.

The dissolution of a solid in a solvent generally requires that sufficient solvent-solute interaction forces exist to disrupt the crystalline lattice of the solid. Generally, the more efficiently the solid can pack in crystalline form, the greater the forces required to dissolve the solid. The extensive conjugation of the amphiphilic anion in compounds I-VIII causes a relatively large portion of the ion to be planar. This fact, and the fact that each ion has a single, linear hydrocarbon tail, might well lead to very efficient packing of these anions. In an attempt to reduce the efficiency of the packing of the ions, a short side chain was added to the amphiphile in compound VIII, near the head group. However, this change in structure actually led to

reduction in solubility; compound IX was entirely insoluble. Finally, the amphiphilic ion in compound IX was paired with another counterion, the hexyltrimethylammonium cation. This counterion might be expected to situate itself at the micellar surface with its short hydrocarbon chain penetrating into the micelle, thus "anchoring" the counterion in place. This compound, a viscous oil, also proved to be insoluble. Undoubtedly, the structure of the amphiphilic anion has an effect on the solubility of these compounds, but similar surfactant with sodium counterions have been shown to be soluble in water.¹²⁷ Thus the counterion also plays a role in the problem.

Possible improvements in the amphiphilic ion would include replacing the amide linkage with a direct graft of the hydrocarbon chain to the phenyl ring of the head group. This would increase the flexibility of the molecule and should improve its solubility. In addition, the hexyltrimethylammonium cation and other quaternary ammonium counterions should be tried with other, more soluble amphiphilic anions.

Besides the anionic surfactants, one other cationic surfactant, N-decyl-N,N-dimethyl-N-hexadecylammonium 3,5-dichlorobenzoate was prepared, but it, too, has extremely low solubility in water. Nevertheless, it would be of interest to expand this examination to other branched or double-tailed surfactants, in combination with salicylate or chlorobenzoate counterions.

C. Summary

The present research into the effect of the chlorobenzoate counterion structure on the properties of hexadecyltrimethylammonium surfactant solutions has revealed the following points.

1. There are major differences in the properties of the CTA-chlorobenzoate surfactant solutions, depending upon the structure of the counterion. Among the properties significantly affected by the identity of the counterion are the CMC, the extent of counterion binding, viscosity and viscoelasticity, and micellar size and shape.
2. In general, it is the position of the chlorine atom or atoms on the benzene ring which determines what properties the surfactant solution will possess. Counterions with chlorine atom only in the ortho position do not induce micellar growth or viscoelasticity, while counterions with chlorine atoms in the meta or para positions only do induce micellar growth and viscoelasticity in the surfactant solutions. Counterions with chlorine atoms in both the ortho and para positions have the former properties at low concentrations, and the latter properties at high concentrations.
3. For the solutions displaying significant viscoelasticity, their rheological properties are quite similar to those of CTASal, and have even higher shear stresses at a given shear rate. There is a critical concentration c^* at which the viscosity of the unsheared solutions increases sharply.

Tables XXXI and XXXII show the concentration and shear dependence for inducing apparent network structures in CTA2,4Cl and CTA3,4Cl solutions, respectively. A description of the unsheared solutions, as determined from conductivity measurements, is given for each concentration. No viscosity measurements were made for either solution in the concentration region below the CMC. For CTA2,4Cl, no structure was induced at any shear rate in the region of concentration where spherical micelles were present. At slightly higher concentrations, the network structure is induced at high shear rates, but absent at low shear rates. As the concentration is increased further, lower shear rates are able to induce the network structure. Even at 10 mM, however, a shear rate of 1.83 sec^{-1} was not sufficient to induce a network structure in CTA2,4Cl solutions. In contrast, for CTA3,4Cl solutions, a network structure can be induced at all shear rates and concentrations used in this study. Evidence that this structure is shear-induced and not present in unsheared solutions at low concentrations is given in the results of capillary viscometry, shown in Table VI, page 48. Here, under conditions of very low shear, no network structure is induced until c^* is reached.

4. For the solutions displaying significant viscoelasticity, a very high extent of counterion binding (ca. 90%) and long rod-shaped micelles were found. In some cases a sphere-to-rod

TABLE XXXI

CONCENTRATION AND SHEAR DEPENDENCE FOR INDUCED NETWORK STRUCTURES
IN CTA2,4Cl SOLUTIONS

Concentration	Results of Conductimetry	Structure at Various Shear Rates			
		14.68 sec ⁻¹	7.34 sec ⁻¹	3.67 sec ⁻¹	1.83 sec ⁻¹
0.1 mM	monomers	-	-	-	-
0.3	sphere region	no structure	no structure	no structure	no structure
6.0	cylinder region	induced structure	induced structure	no structure	no structure
10.0	cylinder region	induced structure	induced structure	induced structure	no structure

TABLE XXXII

CONCENTRATION AND SHEAR DEPENDENCE FOR INDUCED NETWORK STRUCTURES
IN CTA3,4C1 SOLUTIONS

Concentration	Results of Conductimetry	Structure at Various Shear Rates			
		14.68 sec ⁻¹	7.34 sec ⁻¹	3.67 sec ⁻¹	1.83 sec ⁻¹
0.1 mM	monomer region	-	-	-	-
0.3	cylinder region	induced structure	induced structure	induced structure	induced structure
6.0	cylinder region	structure ^(a)	structure	structure	structure
10.0	cylinder region	structure	structure	structure	structure

transition was observed; in other cases the surfactants appeared to form cylindrical micelles from the outset of micellization.

In addition, a number of questions have been raised. Answers to questions about the extent of flexibility and growth of the micellar rods above c^* ; the nature of the intermicellar contacts and the micellar surface characteristics that give rise to viscoelasticity; and the molecular origin of the growth-promoting abilities of the chlorobenzoates and certain other counterions, would add valuable knowledge to the information already obtained by this work. The following section describes a number of techniques which could be employed for further work in this area.

D. Suggestions for Further Work

This section describes a number of experiments which would give further insight into the remaining questions about counterion selectivity, the mechanism of viscoelasticity, and the growth of the cylindrical micelles.

1. Time-Dependent Rheological Measurements

In addition to the viscometric measurements of this work, time-dependent, oscillating-shear rheological measurements for the viscoelastic CTA-chlorobenzoate solutions would yield values of η^* , G' and G'' , and τ , the structural relaxation time. A plot of the complex viscosity versus log concentration should yield the critical concentration, c^* . τ is of interest also, since Hoffmann has suggested that it

is changes in τ which give rise to the remarkable changes in viscosity caused by changes in the head group, counterion, or chain length of the hydrocarbon tail.¹²⁷

2. UV Linear Dichroism

UV linear dichroism has proven useful for determining the orientation of aromatic solutes at the micelle-solvent interface of flow-oriented cylindrical micelles.⁵⁶ Similar measurements could be made to determine whether the counterions of these micelles are positioned parallel or perpendicular to the direction of flow. If present theories of the positioning of the counterions between the head groups (for the rod formers) are correct, one would expect the counterions to be perpendicular to the direction of flow, since the rods should be aligned parallel to the flow.

3. Surface Force Measurements

The results of the present work indicated that there are significant counterion effects on intermicellar interactions. An apparatus commonly called "the box"¹²⁹ can be used to measure the forces (down to a few Angstroms) between opposing planar surfaces onto which cationic surfactants have been adsorbed. Incubation of well-separated mica surfaces in aqueous cationic surfactants at concentrations well below the CMC causes adsorption of a surfactant monolayer; near or above the CMC, a second monolayer adsorbs, giving a bilayer, so that each surface is charged and hydrophilic. It has been shown¹³⁰ that when acetate is the counterion, the bilayers are completely ionized and the bilayer

forces are purely repulsive, while with bromide as the counterion, the bilayer is about 90% charge-neutralized and the bilayer interaction energy shows an attractive minimum due to van der Waals forces. For the chlorobenzoates, the absorption of the counterions should also be quite high. The relative counterion specificity could be determined from the dependence of the depth and position of the van der Waals minimum on the counterion structure.

4. Light Scattering Experiments

Essentially all of the light scattering measurements performed to date on solutions containing rodlike micelles have involved ionic strengths high enough to screen the Coulombic repulsions between the micelles. In most of these cases, very large, flexible, and polydisperse micelles were found. However, in both the present work and the work of Hoffmann, the SANS data for the case of strongly repulsive solutions (containing no added salt) were well fit assuming a monodisperse micelle population. Dynamic and static light scattering could be employed to determine the dependence of polydispersity, as well as rod length and flexibility on supporting electrolyte concentration and on surfactant concentration. A suitable electrolyte for this purpose is NaCl since it screens repulsions between micelles but does not induce micellar growth. With the CTA-chlorobenzoates it is possible to screen the electrostatic repulsions and yet keep the total ionic strength of the solution low enough so that the rods should still be quite stiff. This screening has the effect of reducing $S(Q)$ to 1; then Equation 52 (page 126) can be employed. At even lower ionic strength

(where repulsions are becoming significant) the formalism for $S(Q)$ proposed by Klein¹⁰⁷ could be included. Appropriate relations to account for polydispersity¹⁰¹⁻¹⁰³ and micelle flexibility⁸⁸ should also be applied, as necessary.

5. Microscopy

Very recently Y. Talmon has succeeded in obtaining electron micrographs of micelles in vitrified ice.¹³¹ This cryomicroscopy removes the possibility of observing artifacts generated in conventional electron microscopy and appears to be a promising method of observing the structure of micellar aggregates. A few preliminary measurements have already been made on CTA-chlorobenzoates by Talmon. For 0.01 M CTA3,5Cl one can clearly see very long threadlike structures, while for 0.01 M CTA2,6Cl, only small "specks," which could be approximately spherical micelles, could be seen. Clearly, further work in this area should be pursued.

CHAPTER VI

EXPERIMENTAL SECTION

A. Instrumental Methods1. Conductimetry

Conductivity measurements were performed with a Wayne-Kerr Automatic Precision Bridge, model number B904. The measurements were made at a frequency of 1 kHz in the resistance mode. The accuracy of the instrument at 1 kHz is $\pm 0.05\% \pm 5 \text{ m}\Omega$ for a resistance range of 0 to 10 M Ω . After a warm up period of approximately one hour, the instrument was trimmed to remove residual lead impedances in the circuit. Resistance values, R, were read directly from the digital display after connecting leads from the bridge to the cell containing the sample. The sample solutions were contained in a 500 mL Kraus-Erlyenmayer conductivity cell. The cell constant, as determined by Kim Daus of these laboratories, was 0.5814 cm^{-1} . The cell was placed in a thermostatted oil bath and measurements were made at $25.00 \pm 0.01^\circ\text{C}$.

Solutions for conductivity measurements were prepared with water obtained by passing distilled water through a Millipore Mille-Q reagent Water Filtration System. Water thus obtained had a specific conductivity of $(9.1 \text{ to } 12.0) \times 10^{-7} \text{ S cm}^{-1}$ at 25°C . Sample concentrations were varied by adding small aliquots of concentrated surfactant solutions to a dilute solution in the cell to incrementally increase the solution concentration. Measurements were made about one minute after

each addition. Specific conductivity values were calculated using the equation

$$L = k \left(\frac{1}{R_{\text{Sam}}} - \frac{1}{R_{\text{H}_2\text{O}}} \right) \quad (57)$$

where k is the cell constant, and $1/R_{\text{Sam}}$ and $1/R_{\text{H}_2\text{O}}$ are the reciprocal resistances for the sample and the water, respectively. Equivalent conductivity values were calculated using the equation

$$\Lambda = L/C \quad (58)$$

where C is the sample concentration. The results of the conductivity measurements are presented in Chapter III.

2. Capillary Viscometry

Cannon-Fenske type viscometers were prepared for viscometry measurements by cleaning in a chromic acid solution followed by extensive rinsing with distilled water and oven drying. Between samples, the viscometers were cleaned with distilled water or methanol followed by distilled water, then oven dried. The viscometers were calibrated with water or glycerol/water mixtures in a thermostatted water bath at $25.00 \pm 0.1^\circ\text{C}$. The viscometer constants were determined by dividing the literature value of viscosity for the water or glycerol/water mixtures by the average time in seconds of the determination.

The viscometer was charged with 10.0 mL of the sample 10 minutes prior to taking readings. Flow time for the liquid were obtained with

a Heuer stopwatch. Times were reported to the nearest one-tenth of a second. A minimum of three measurements was made for each sample. The viscosity of the solution was calculated by multiplying the average flow time for the sample by the viscometer calibration constant.

3. Rotary Viscometry

The Brookfield model LV rotary viscometer was equipped with a UL cup and spindle adapter, thermostatted to $25 \pm 0.01^\circ\text{C}$ in a circulating constant temperature bath. The cup was charged with 18 mL samples of the liquid whose viscosity was to be determined; trapped air bubbles were removed by tilting the apparatus slightly and tapping it lightly. Measurements were made in the direction of increasing rate of shear. At each shear rate, a scale reading (0 to 100) was recorded. The shear stress σ and the apparent viscosity η_{app} may be calculated from Equations 59 and 60, respectively.

$$\sigma = \frac{M(673.7 \text{ dyne}\cdot\text{cm})}{2\pi R_b^2 \cdot L} \quad (59)$$

$$\eta_{\text{app}} = \sigma/S \quad (60)$$

Here M is the dial reading, R_b the radius of the spindle, and L the effective length of the spindle. Data and plots of shear rates, shearing stresses, and apparent viscosities of the samples measured appear in Chapter II.

The viscometer was calibrated at each shear rate position with glycerol/water mixtures of known viscosity. The procedure for calibration was that suggested in the Brookfield publication "More Solutions to Sticky Problems"⁴⁵; the booklet also provided values for the constants R_b , L , and S .

4. Nuclear Magnetic Resonance

NMR spectra were obtained on a Nicolet NT 200 system consisting of an Oxford magnet (field strength 4.7 T), a NIC 293C programmable pulser, a NIC 1180E data processor, and a Control Data Corporation cartridge disk drive.

Typical parameters for a proton spectrum were: sweep frequency = 200.068 MHz, sweep width = ± 1100 Hz, pulse length = 7.5 μ sec, delay time = 2.5 sec, and number of acquisitions = 256. Five millimeter sample tubes were employed. Samples were prepared with Aldrich Gold Label deuterium oxide and 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt was used as a reference. Samples were locked on D_2O .

Typical ^{13}C spectra were obtained at 50.3108 MHz with a sweep width of ∓ 6024 Hz. Broad band proton decoupling was used in the BILEV experiment. The pulse and first and second delays were 6.5 μ sec, 100 μ sec, and 1.0 sec, respectively. For nonviscous solutions a 5 mm probe was used and the number of acquisitions were typically under 1000. For viscous solutions 12 mm sample tubes were used and the number of acquisitions was 40,000 to 70,000. For ^{13}C spectra, methanol was used as an external reference and samples were locked on D_2O .

5. pH Measurements

Measurements were made on an Orion 701 digital pH meter with a Fisher polymer-body combination pH electrode.

6. Small-Angle Neutron Scattering

SANS measurements on aqueous solutions of CTA2C1, CAT4C1, CTA2,4C1, CAT2,6C1, CTA3,4C1, and CTA3,5C1 were made at the National Center for Small-Angle Scattering Research. Measurements were made on the instrument at the High Flux Isotope Reactor, which is described in Chapter IV.

The samples were contained in quartz spectrophotometric cells of 2 mm pathlength. Scattering from samples and from the D₂O (Norell) solvent was corrected for detector sensitivity, empty cell scattering, background scattering, calculated incoherent scattering and sample transmission. Solvent intensity was subtracted from that of the sample at each position. These differences were converted to radial average intensities versus Q, and absolute cross sections $d\sigma/d\Omega$ (or $I(Q)$) in cm^{-1} were computed from calibrations based on scattering from standard samples. Equations and procedures for data correction and calculation are described in detail in Chapter IV. The corrected data were then fit to the models for monodisperse spheres, ellipsoids, and cylinders which are also described in Chapter IV.

a. The Instrument. The 30 meter SANS apparatus at the National Center for Small-Angle Scattering Research (NCSASR), Oak Ridge National

Laboratory is depicted in Figure 43. The neutron source is located at the High Flux Isotope Reactor (HFIR) core, from which a thermal neutron beam emerges. The beam passes through a beryllium filter followed by a set of graphite monochromator crystals which select a wavelength $\lambda = 4.75\text{\AA}$ with a spread of $\Delta\lambda/\lambda = 6\%$.

The nuclear reactor provides a neutron beam with a large cross-sectional area, thus specimens of large cross sections can be used to increase the scattered intensity. The incident beam flux is continuously monitored by a low efficiency neutron proportional counter before entering a double slit evacuated flight path of 7.6 m. The entrance slit S_1 has a circular diameter ranging from 0.5 cm to 3.5 cm. The flight path has three removable beam guides; the beam passes through a second slit (the sample slit) before impinging upon the sample. The diameter of the sample slit, S_2 , may be varied from 0.4 cm to 2.0 cm. Solutions are typically studied in cylindrical or rectangular spectrophotometric cells having path lengths of 1 mm to 5 mm. The cells are generally constructed from quartz; the extremely high absorption cross section of boron precludes the use of borosilicate glass. The cells are mounted on a motor-driven slide (with six sample positions) which can be lowered into a removable thermostated well inserted through the top part of the permanent sample chamber. The two-slit geometry defines a spot of the transmitted beam at the center of the detector which is covered by a cadmium beam stop (4 or 8 centimeters in diameter). Neutrons which are scattered at an angle θ are detected by the area detector elements situated on a ring at a distance d from the

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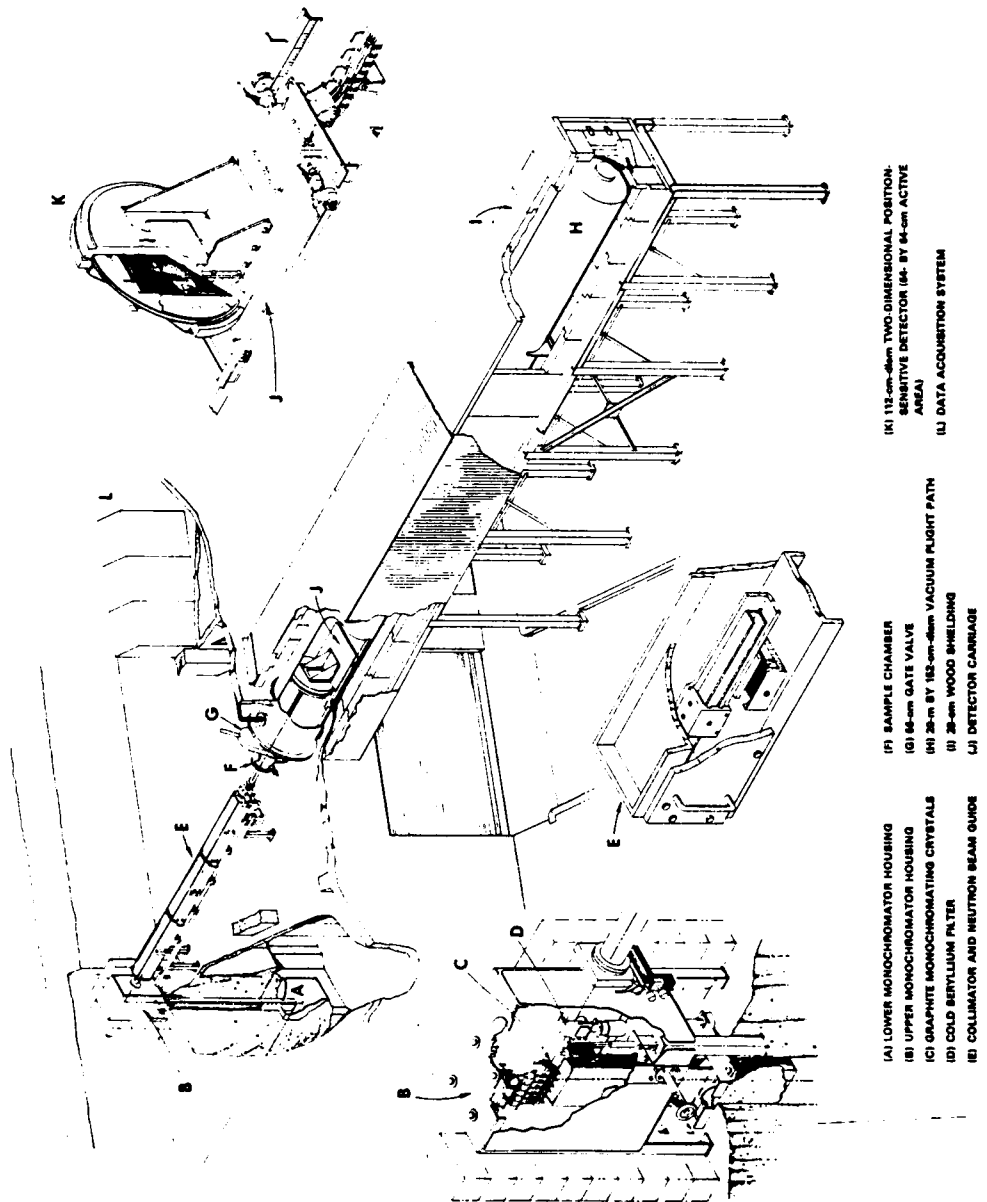


Figure 43. Schematic drawing of the 30 m SANS facility at NCSASR.

center of this detector, as shown in Figure 44. The multidetector consists of 4096 detector elements covering an area of $64 \times 64 \text{ cm}^2$. The sample-to-detector distance L_2 can be varied from 1.4 m to 19 m; at large L_2 , Q is approximated by

$$Q = \frac{2\pi}{\lambda} \tan\theta = \frac{2\pi}{\lambda} \cdot \frac{d}{L_2}$$

so that the total accessible range of NCSASR's 30 m spectrometer is $0.002 \text{ \AA}^{-1}$ to $0.6 \text{ \AA}^{-1}$. Figure 45 shows a representation of a typical intensity map (contour plot) for a micellar solution and the one-dimensional radial average of the contour plot, which is the conventional scattering curve, $I(Q)$ vs. Q , generally presented in the literature.

The choice of scattering geometry is predicated on two factors. At constant S_2 , the flux at the sample is proportional to the area S_1 . However, a large S_1 can only be used in combination with a small L_2 because of the finite size of the beam stop. Also, the Q -resolution, $\Delta Q/Q$, has to be kept at a reasonably small value. This means that Q should be kept relatively large. The net result is that it is always preferable to work at the largest possible Q consistent with the size of the particle, namely $0.5 < QR < 5.0$, where R is the particle size. In this way, L_2 can be kept at the minimum and S_1 at the maximum value.

A computer is interfaced with the instrument for machine control and data acquisition and handling. Data recorded in the memory can be processed by a variety of online programs developed by staff members of

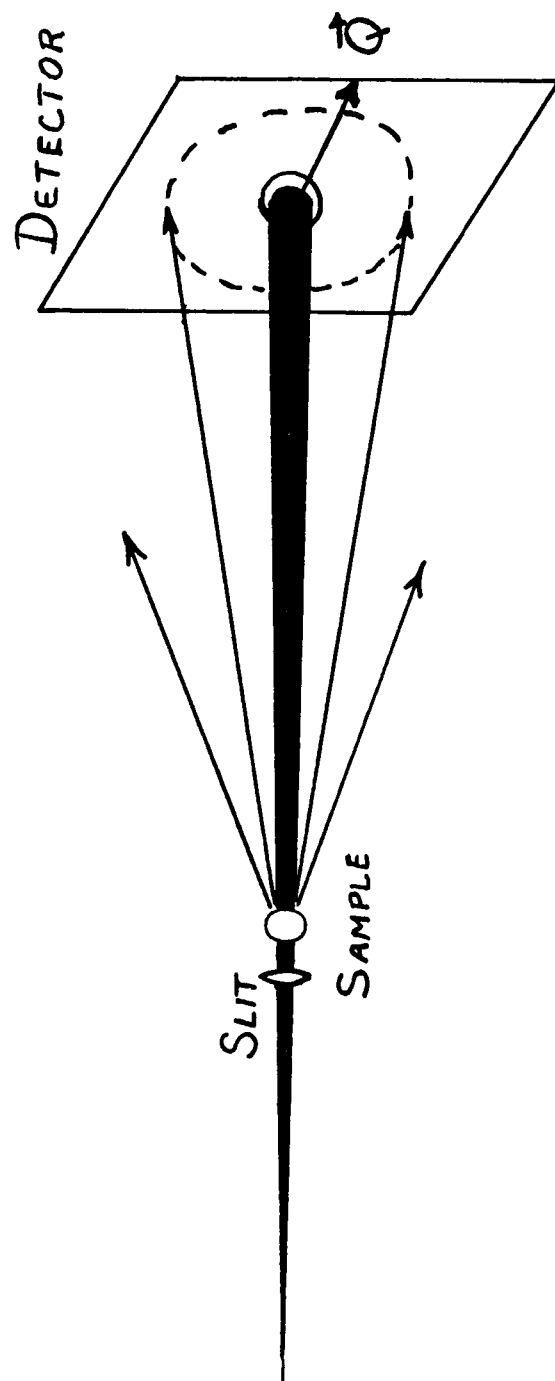
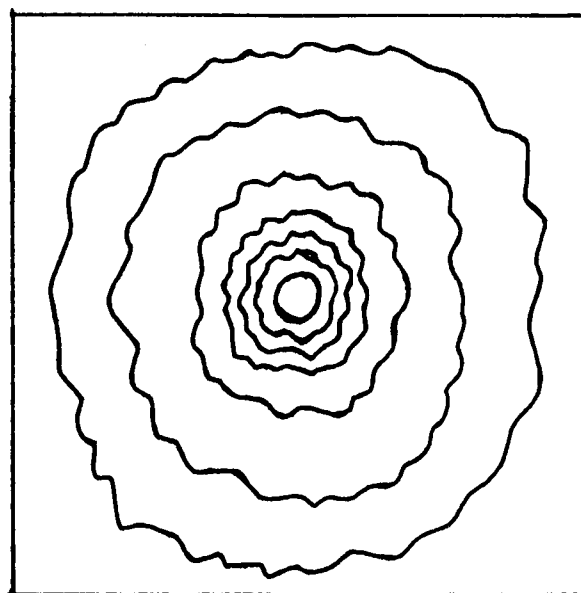


Figure 44. Representation of scattering from a sample.



a

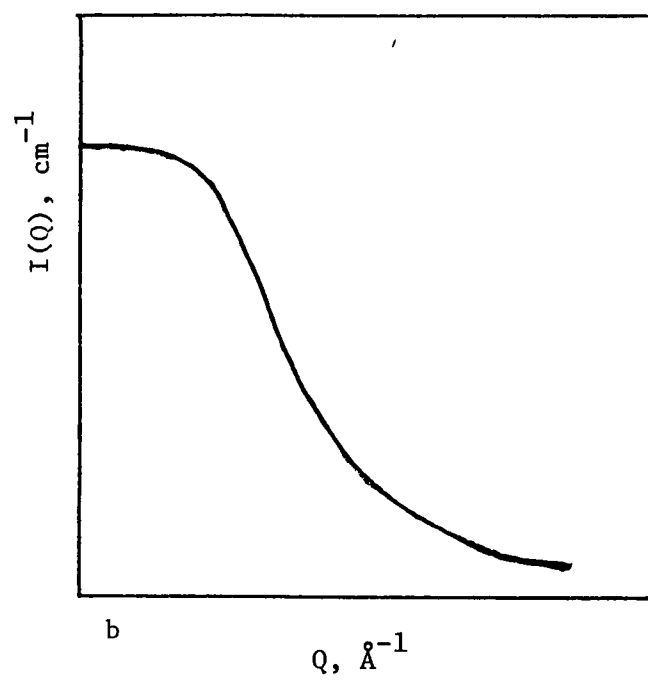


Figure 45. Contour map (a) and radial intensity plot (b).

NCSASR. Among these are routines for background and detector sensitivity corrections, various averaging schemes for circular or one-dimensional averages, and plotting routines.

b. Treatment of data. The total scattered intensity for a sample contains contributions not only from the solute, but also from the solvent, the empty cell, and the background. The scattering due to each of these is measured and computer programs are used to correct the raw data for background and empty beam scattering,

$$I_{\text{corr}} = (I_{\text{tot}} - I_b) - T_s/T_e(I_e - I_b) \quad , \quad (61)$$

where I_{tot} = total scattered intensity

I_b = intensity due to background

I_e = intensity due empty cell

T_s = sample transmission coefficient

T_e = empty cell transmission coefficient.

I_{corr} is computed for each detector element by Equation 61. Programs are also available to subtract the calculated incoherent scattering level for the solution and the solvent's contribution to the coherent scattered intensity.

Corrections must also be made for the sensitivity of the detector elements. Ideally each element should respond identically to the same number of scattered neutrons; however, this is not the case in reality. The sensitivity of the detector is usually determined by using a strong

isotropic scatterer; in general, H_2O is used. The incoherent scattering of H_2O is relatively strong and has negligible angular dependence. The counting probability of an element is then defined as the number of neutrons recorded in that detector element, divided by the average number of neutrons recorded per unit element.

The corrected scattered intensity may be reduced to an absolute scale by using a standard scatterer to calibrate the detector. This provides the neutron calibration constant K_N . The intensity $I(Q)$ in absolute units is then given by

$$I(Q) = \frac{I_{\text{corr}}(Q)}{t \cdot T_s} \cdot \frac{L_2^2}{K_N A} \quad (62)$$

with t equal to the sample's thickness, L_2 the sample-to-detector distance, and A equal to the area of the sample slit, S_2 . At small L_2 (< 7 meters) the standard scatterer generally used was H_2O . For longer distances, the absolute calibration was performed with the scattering from a single crystal of aluminum in which voids had been produced by irradiation.

In summary, then, the following corrections are generally made:

1. Calibration of the detector elements for sensitivity,
2. Correction of the scattered intensity for background and empty cell scattering, and for the incoherent scattering of the solvent.

3. Subtraction of the corrected solvent scattering from the corrected scattering of the sample, and
4. Calibration of the data to an absolute scale by Equation 62.

B. Materials and Syntheses

1. Synthesis of Cationic Surfactants

a. Ion exchange method. The following surfactants were prepared by an ion exchange method: CTASal, CTA2Cl, CTA4Cl, CTA2,4Cl, CTA2,6Cl, CTA3,4Cl, CTA3,5Cl and CTA4OMe. Dowex anion exchange resin in the OH⁻ form was packed on a column holding approximately 150 cm³ of resin. Ten grams of CTAB dissolved in water were poured onto the column. The column was then washed with about four liters of water. The CTAOH solution was collected, and the H₂O was removed on a rotary evaporator. Ethanol was added to the solution during evaporation to prevent excessive foaming. The CTAOH residue was a hygroscopic gel which could not be crystallized. In order to determine the amount of CTAOH collected, the CTAOH was dissolved in H₂O and an aliquot was titrated with a standard solution. When the moles of CTAOH were determined, an equivalent number of moles of 3,4-dichlorobenzoic acid (or other chloro- or hydroxybenzoic acids) was added to the solution to form CTA3,4Cl in H₂O. The solution was evaporated to dryness, recrystallized twice from acetonitrile, then dried and weighed. Elemental analysis for CTA3,4Cl by this method gave 66.05% C and 10.22% H. (Theoretical, 65.79% C and 9.56% H.)

b. Synthesis employing silver salts. As an alternative to the previous synthesis, a method employed by Underwood and Anacker was used to synthesize the 4-methoxy- and all of the chlorobenzoate surfactants. This second method required less time and resulted in cleaner, more crystalline compounds.

An example of the method is as follows. Sodium 3,4-dichlorobenzoate was prepared by titrating 4.20 g of recrystallized 3,4-dichlorobenzoic acid with 3 N NaOH. The aqueous salt solution was then treated with an excess of silver nitrate (dissolved in a small amount of water) to precipitate silver 3,4-dichlorobenzoate. The silver salt was washed with water and dried. Three grams of CTAB dissolved in 50 mL of methanol were stirred with the silver 3,4-dichlorobenzoate for three hours. The silver salts were removed by filtration and the methanol solution was stirred over charcoal overnight. The solution was then evaporated to dryness. The solid CTA_{3,4}Cl was recrystallized from acetonitrile, vacuum dried, and stored in a desiccator. Table XXXIII shows the results of elemental analysis of surfactants prepared by this procedure.

2. Other Syntheses

In addition to the CTAX's, a number of other compounds were prepared. These compounds and their structures are shown in Table XXXIV.

Compounds I, II, VII, VIII, and XIV (see Table XXXIV) were prepared by a procedure described by Pelizzetti et al.¹²⁷ For example, Compound II was prepared by dropping tetradecanoyl chloride into a

TABLE XXXIII
ELEMENTAL ANALYSES OF THE CTAX'S

Compound		Theoretical	Found
CTA2C1	%C	70.96	70.45
	%H	10.54	10.75
CTA4C1	%C	70.96	69.44
	%H	10.54	10.72
CTA2,6C1	%C	65.79	65.72
	%H	9.56	9.61
CTA2,4C1	%C	65.79	65.70
	%H	9.56	9.59
CTA3,4C1	%C	65.79	66.02
	%H	9.56	9.82
CTA3,5C1	%C	65.79	64.47
	%H	9.56	9.78

TABLE XXXIV
ANIONIC SURFACTANTS AND THEIR PRECURSORS

Number	Structure
I.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$
II.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$
III.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+(\text{CH}_3)_3$
IV.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+(\text{CH}_3)_3$
V.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+\text{H}_3-\text{C}_6\text{H}_{11}$
VI.	$\text{CH}_3-(\text{CH}_2)_{11}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+\text{H}_3-\text{C}_6\text{H}_{11}$
VII.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$
VIII.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$
IX.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+(\text{C}_2\text{H}_5)_3$
X.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+(\text{C}_2\text{H}_5)_3$
XI.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+\text{H}_3-\text{C}_6\text{H}_{11}$
XII.	$\text{CH}_3-(\text{CH}_2)_8-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+\text{H}_3-\text{C}_6\text{H}_{11}$
XIII.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$
XIV.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{OH})-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$
XV.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+\text{H}_3-\text{C}_6\text{H}_{11}$
XVI.	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}(\text{C}_2\text{H}_5)-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- \text{N}^+(\text{CH}_3)_3(\text{C}_6\text{H}_{13})$

pyridine solution of 4-amino-2-hydroxybenzoic acid (equimolar amounts) under stirring at room temperature. The reaction mixture was kept overnight, poured into distilled water and slightly acidified with acetic acid. The precipitate was slurried in water in the presence of a little amount of acetic acid, collected and recrystallized twice from ethanol.

Compounds V, VI, XI, XII, and XV were prepared by addition of cyclohexylamine to a methanol solution containing an equimolar amount of the corresponding acid (Compounds I, II, VII, VIII, and XIV). The solutions were warmed to 40°C overnight, then the solvent was removed and the precipitate recrystallized twice from acetonitrile.

Compounds III, IV, IX, and X were prepared by addition of equimolar amounts of either tetramethylammonium hydroxide or tetraethylammonium hydroxide to methanol solutions of the proper acids (Compounds I, II, VII, and VIII). The solutions were stirred several hours at room temperature. The solvent was removed and Compounds II, IV, and IX were recrystallized twice from acetonitrile. Compound X was a viscous oil which did not crystallize even after several days.

Compound XVI was prepared by the following procedure. Hexyltrimethylammonium bromide was converted to hexyltrimethylammonium hydroxide by passage over Dowex-1 ion exchange resin in the OH^- form. The eluted solution was evaporated and the residue was freeze-dried overnight. The solid hexyltrimethylammonium hydroxide was then added to an equimolar amount of Compound XIV in a methanol solution. The

solution was stirred overnight. The solvent was removed, leaving a viscous oil which could not be crystallized.

Compound XIII was prepared by dropping 2-ethyldecanoic acid into a small excess of thionyl chloride. The mixture was heated at reflux for several hours. The excess thionyl chloride was removed by distillation at 760 Torr and 75°C. The residual material was distilled at 3.5 Torr over a boiling range of 77-80°C.

3. Materials

a. Hexadecyltrimethylammonium bromide (CTAB). CTAB from Sigma was recrystallized from an 80/20 (volume %) acetone-methanol mixture. The CMC for CTAB was determined by surface tension measurements at 25°C. A value of 9.6×10^{-4} M was found, compared to a literature value of 9.2×10^{-4} M. The molecular weight of CTAB was determined by titration with AgNO_3 ; the value found was 361.9 g/mol compared to a theoretical value of 364.5 g/mol.

b. Dowex-1 resin. Ion exchange resin was purchased from Sigma in the chloride form. It was treated with 12 N HCl, 6 N HCl, H_2O , 3 N NaOH, H_2O , methanol and then H_2O again. The methanol wash was to remove the amines generated when the resin was converted to the hydroxide form. The presence of the amines was detected by their characteristic odor.

c. Chlorobenzoic acids. The following acids were obtained from Aldrich and recrystallized twice from acetonitrile before use:

2-chlorobenzoic acid

4-chlorobenzoic acid

2,4-dichlorobenzoic acid

2,6-dichlorobenzoic acid

3,4-dichlorobenzoic acid

3,5-dichlorobenzoic acid.

d. Salicylic acid. Salicylic acid was obtained from Aldrich and recrystallized twice from acetonitrile before use.

e. 4-Methoxybenzoic acid. This acid was obtained from Sigma and recrystallized twice from acetonitrile.

f. Myristoyl chloride. Myristoyl chloride was used as purchased from Aldrich.

g. Decanoyl chloride. Decanoyl chloride was used as purchased from Aldrich.

h. 4-Aminosalicylic acid. 4-Aminosalicylic acid was obtained from Aldrich and recrystallized from acetonitrile.

i. 4-Aminobenzoic acid. 4-Aminobenzoic acid was Fisher certified grade. The acid was recrystallized from acetone.

j. 2-Ethyldecanoic acid. 2-Ethyldecanoic acid was used as purchased from Wiley Organics.

k. Thionyl chloride. Reagent grade thionyl chloride from Fisher was distilled twice before use.

l. Hexyltrimethylammonium bromide. Hexyltrimethylammonium bromide was prepared by C. A. Martin in these laboratories, and used without further purification.

- m. Tetramethylammonium hydroxide. Tetramethylammonium hydroxide was obtained from Aldrich as a solution of 20 wt.% in methanol.
- n. Tetraethylammonium hydroxide. Tetraethylammonium hydroxide was obtained from Eastman Kodak as a solution of 25 wt.% in methanol.
- o. Silver nitrate. Silver nitrate from Fisher was A.C.S. reagent grade.
- p. Cyclohexylamine. Aldrich Gold Label cyclohexylamine was used as purchased.
- q. 3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt (DSS). Aldrich Gold Label DSS was used as an NMR standard.
- r. Glycerine. Fisher certified A.C.S. grade glycerine was used without further purification.
- s. Acetonitrile. Fisher certified A.C.S. grade acetonitrile was used as purchased.
- t. Acetone. Reagent grade acetone from Baker was used as purchased.
- u. Methanol. Certified A.C.S. grade methanol from Fisher was used as purchased.
- v. Ethanol. Ethanol was used as purchased from AAPER Alcohol and Chemical Company.
- w. Deuterium oxide. D_2O from either Aldrich or Norell was 99+% isotopically pure.
- x. Water. H_2O was distilled or passed through a Millipore filtration system.

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