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STUDIES OF MICELLAR SOLUTIONS OF CATIONIC DOUBLE-TAILED SURFACTANTS AND INVESTIGATIONS OF BICONTINUOUS MICROEMULSIONS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Joi Louise Phelps

August 1986

DEDICATION

This work is dedicated to my family, John, Pam, Neal and René, whose unconditional love, encouragement, and support have brought me this far.

ACKNOWLEDGMENTS

The author wishes to express her sincere gratitude and appreciation to Dr. Linda J. Magid for her patience and advice during the course of this work.

Appreciation is also extended to The University of Tennessee, Knoxville, for a teaching assistantship.

Finally, thanks to all the people in the chemistry department who kept this ordeal humorous.

ABSTRACT

The micellar properties of three double-tailed cationic surfactants were studied. All three surfactants were found to be insoluble in water. Two of the compounds, diesters, were soluble in n-hexane and isooctane; however, the reverse micelles formed in these solutions did not solubilize a measurable amount of water. The third compound, a diamide, was insoluble in n-hexane and isooctane. Small-angle neutron scattering was used to determine the size and shape of the reverse micelles formed in isooctane by the diesters. The aggregates were found to be approximately spherical with radii of 12-13 Å.

Phase studies were carried out on the mixed surfactant system involving SDS and AOT. In a molar ratio of 25% SDS and75% AOT a one phase microemulsion region was determined for the system using n-octane and water. Conductivity measurements indicated that the system was water-continuous.

Attempts to use gelatinization to determine the microstructure of DDAB/n-octane/water microemulsions are also reported. These systems are believed to undergo a phase transition from water-continuous to water-discontinuous as the water content increases. The gelatinization technique was not successful due to the inability of the system to incorporate the gelatin.

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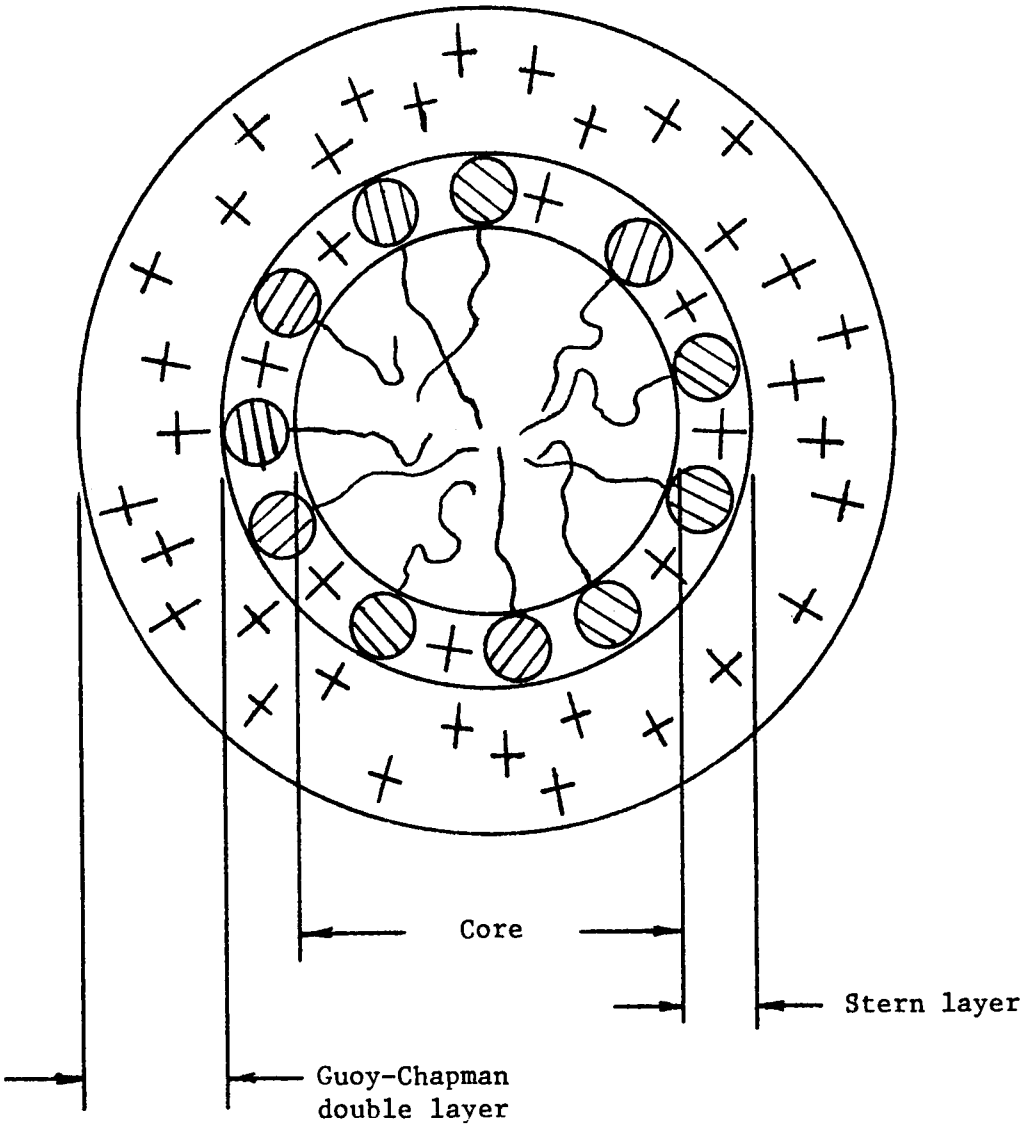
CHAPTER I

INTRODUCTION

Surfactants belong to the class of compounds known as amphiphiles.[1-4] An amphiphile is any molecule which contains a hydrophobic part and a hydrophilic part. The word surfactant is a contraction of the phrase surface active agent. This refers to the tendency of these molecules to concentrate themselves at interfaces (air/water, oil/water, etc.). Surfactant molecules contain a nonpolar or hydrophobic tail and a polar or hydrophilic head group. The head group can be: (1) cationic (e.g., ammonium); (2) anionic (e.g., sulfate); (3) zwitterionic; (4) nonionic (e.g., polyethylene oxide). The hydrocarbon tail may be of varying length and structure. The molecule may also contain more than one hydrocarbon tail. In solution, the opposing solvation properties of the polar heads and nonpolar tails become the driving forces for the association of the molecules into organized assemblies. The exact nature of the aggregate formed depends on the surfactant and the solvating medium.

Many surfactants aggregate into small spherical micelles in water at very low concentrations. The driving force for the formation of these spherical micelles is the decrease in surface area of the hydrocarbon tail in contact with the solvent. The formation of amphiphilic aggregates can be seen as a compromise between the tendency of the alkyl chains to avoid contact with water and the strong affinity of the polar groups for water. An ionic micelle is depicted in Figure 1.[5] The



Shaded circles: surfactant head groups.
Crosses: counterions.
Zigzag lines: surfactant hydrocarbon tails.

Figure 1. Schematic representation of a typical ionic micelle.

hydrophobic tails are buried in the core, the hydrophilic heads are located in the Stern layer with some bound counterions. The Guoy-Chapman double layer contains the remaining associated counterions. Approximately 60-70% of the counterions are associated with the micelle. Many surfactants also associate into aggregates in nonpolar or hydrocarbon solvents.[6-8] The aggregates formed in these systems are called reverse or inverted micelles. In general, single-tailed surfactants form normal micelles and double-tailed surfactants form reverse micelles. In the case of inverted micelles, the polar portion of the molecule resides in the aggregates' cores while the hydrocarbon tails form the outer shell.

There is no appreciable aggregation of the surfactant in aqueous solutions at low concentrations. Properties such as self-diffusion coefficients, activities, turbidity, conductance, surface tension and NMR spectral features undergo an abrupt change as the concentration of the surfactant is increased.[1] Figure 2 shows a typical graph obtained from conductivity data. The concentration at which there is a sharp break in the conductance, known as the critical micelle concentration (CMC), indicates the onset of extensive association into large aggregates.

To better understand the existence of CMC's it is necessary to review the theories for self-assembly of surfactants in solutions.[1,7] The CMC has the most clear-cut interpretation within the (pseudo) phase separation model of micelle formation. Although the micelles and the surrounding solution form a single phase, the amphiphile association shows a cooperativity that makes an analogy with phase transition useful. Within this model, the CMC is the concentration at which the system

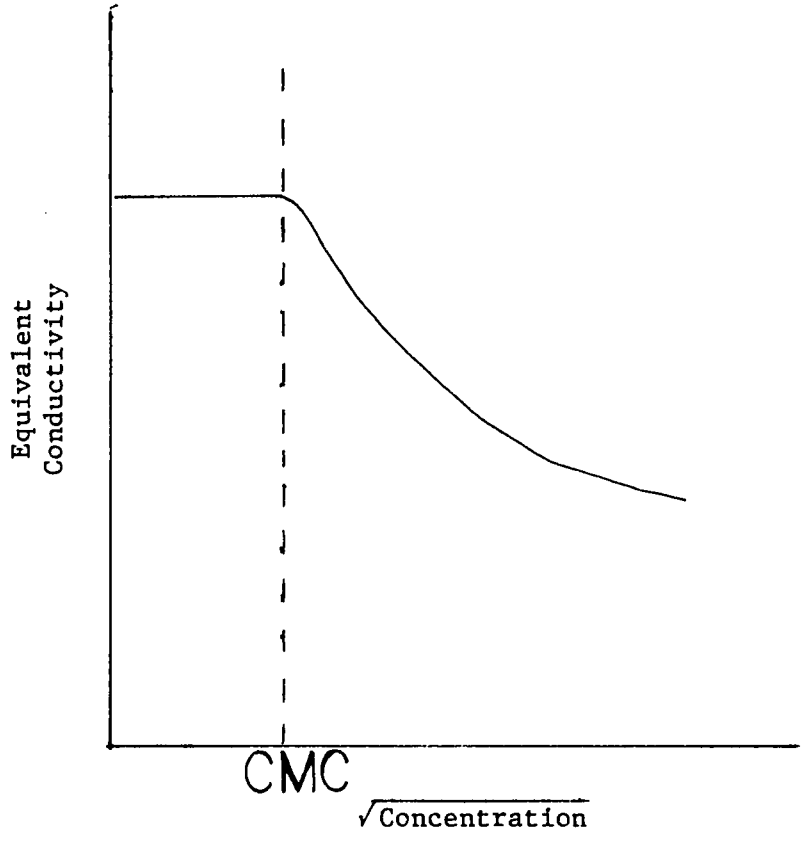


Figure 2. Equivalent conductivity vs. $\sqrt{\text{concentration}}$ for a typical aqueous surfactant solution.

enters a two phase region; the two pseudophases formed are the aqueous system and the micelles.

Another model for surfactant association is based on the mass action law. In this model it is assumed that a single micellar species, of aggregation number $\bar{n}$, is in equilibrium with the monomers:

$$nS_1 \rightleftharpoons S_n \tag{1a}$$

$$K = [S_n]/[S_1]^n \tag{1b}$$

In reality several aggregation numbers of the micelles occur, but from the simple equilibrium in (1a) one can conclude that the larger the value of $\underline{n}$, the more cooperative is the association and the more one approaches phase separation behavior. The CMC here would be the point of formation of aggregates with size S_n.

An alternative to these two models is the multiple self-association model, which assumes that micelles are formed through a stepwise aggregation process. This model can be formulated as a number of equilibria between aggregates of increasing size.

$$S_1 \overset{K_1}{\rightleftharpoons} S_2 \overset{K_2}{\rightleftharpoons} S_3 \overset{K_3}{\rightleftharpoons} \cdots \overset{K_{n-1}}{\rightleftharpoons} S_n \quad ; \tag{2a}$$

The equilibrium constants are given by

$$K_i = [S_{i+1}]/[S_i][S_1] \quad ; \tag{2b}$$

and all the equilibrium constants are related by

$$K = \prod_{i=2}^{n} K_i \quad . \tag{2c}$$

According to this model aggregation should continue indefinitely, with the micelles becoming larger and larger. A modification must be made to account for the possibility of a range of K_n dependence on n. In this model it is more difficult to define a CMC, since there is no distinct onset of extensive aggregation into large aggregates. Most surfactants which form reverse micelles do not have well-defined CMC's, so reverse micellar systems have best been described using the multiple self-association model of aggregate formation.[9] As mentioned above this model (and type of aggregation) does not allow for a CMC value to be obtained directly.

One of the most striking effects encountered in surfactant solutions is their ability to solubilize normally insoluble or only slightly soluble compounds. Water-insoluble compounds are solubilized when surfactant is added. In apolar solvents, the reverse micelles are able to solubilize water. The extent of solubilization depends on the solubilizate and the surfactant. Solubilizing ability usually increases with increasing hydrocarbon chain length in the surfactant. If a normal micelle solubilizes a large amount of hydrocarbon (oil) it becomes an oil-in-water microemulsion. On the other hand, when a reverse micelle solubilizes a large amount of water it becomes a water-in-oil microemulsion. The distinction between a micelle and a microemulsion

is operational and the size of the aggregate is most often used to differentiate the two structures. Microemulsions have been defined as collodial dispersions with particle radii in the range of 50-200 Å.[10]

The solvophobic interactions described above actually lead to a myriad of organized assemblies. Recently, Ninham and co-workers[8,11,12] have defined a surfactant packing parameter, $v/\underline{a}l_c$; v is the volume of the surfactant's hydrocarbon chain, $\underline{a}$ is the head group area in the planar bilayer, which is determined by a balance of opposing forces, chiefly a minimization of hydrocarbon-water contact vs. head group repulsions and l_c is an optimal length close to that of the fully extended chain. Figure 3 shows the aggregates expected for various parameter values in binary and ternary systems. We see an evolution of structures from those having positive curvature (normal spherical or cylindrical micelles and oil-in-water microemulsions) to those with zero net interfacial curvature (lamellar liquid crystals or bicontinuous microemulsions) and finally evolving to structures possessing negative curvature (reverse micelles and water-in-oil microemulsions). Negative and positive curvature are operational definitions based on the relationship of the head group to the water phase. Normal structures are defined as having positive curvature and reverse structures are defined as having negative curvature. The $v/\underline{a}l_c$ values come from simple geometric considerations: the use of surface-to-volume relationships for the various aggregate shapes. Consider a normal spherical micelle containing n surfactant monomers and having a hydrocarbon core volume (in the

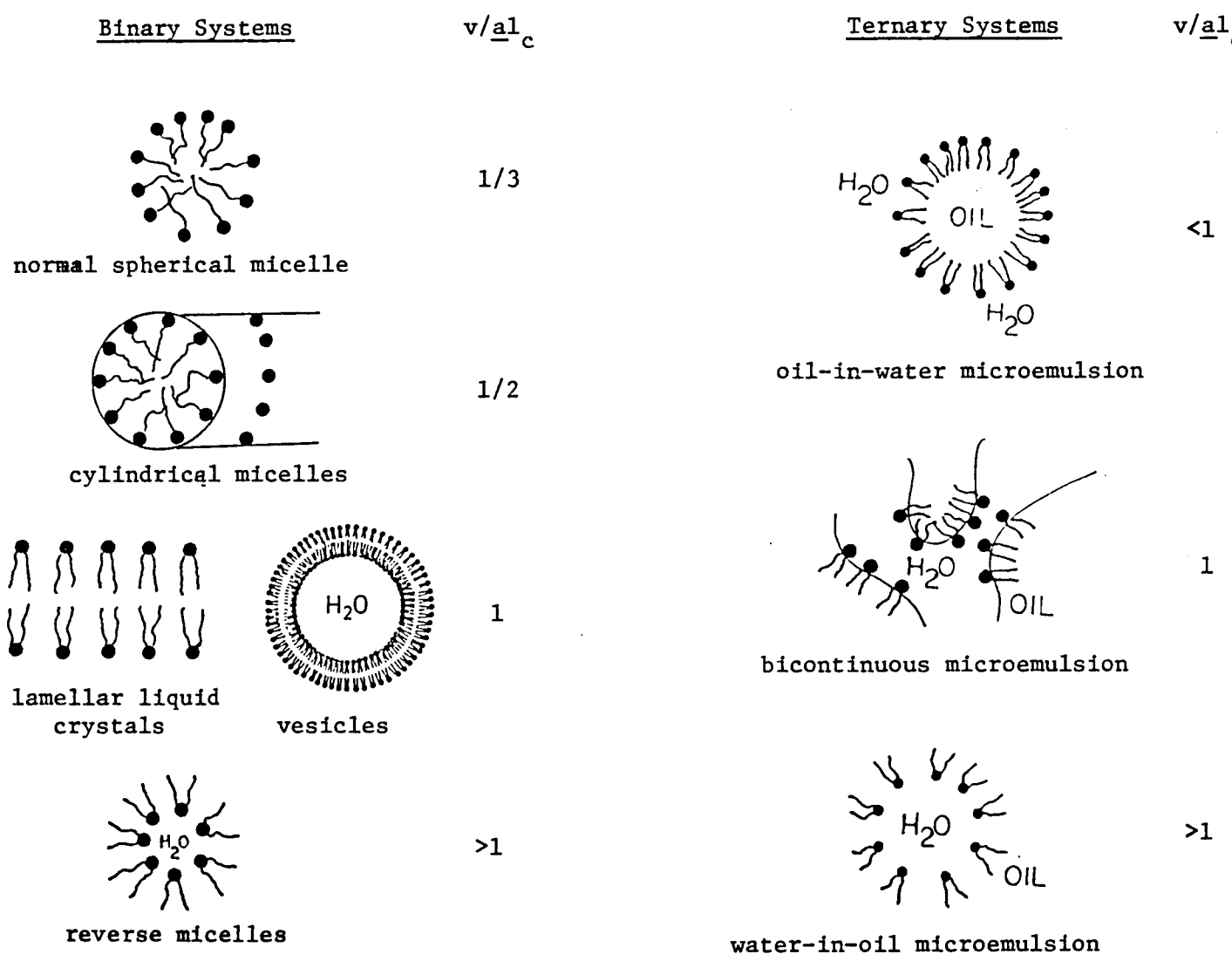
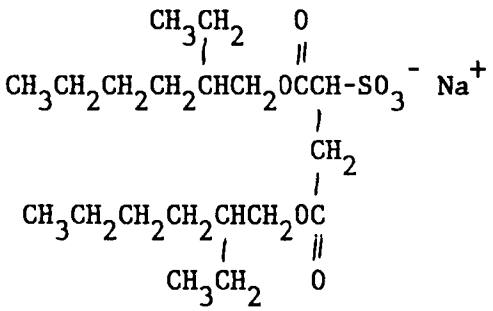


Figure 3. Schematic of aggregate structures with packing parameter values.

absence of oil) of $nv = (4/3)\pi l^3$ and a core surface of $na = 4\pi l^2$. Rearrangement gives $v/(4/3)\pi l^3 = a/4\pi l^2$, which rearranges to $v/\underline{a}l_c = 1/3$. This treatment ignores curvature corrections: that is, the recognition of the fact that head group repulsion is different at curved than at planar interfaces. Also, intermicellar interactions affect the structural changes observed.

A great deal of the present work is centered around the surfactant Aerosol OT (AOT, sodium bis(2-ethylhexyl)sulfosuccinate), 1; a double-tailed anionic surfactant.[13-18] AOT has a low solubility in water, tending to form liquid crystals at low amphiphile concentrations.



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This surfactant is very soluble in hydrocarbons and will solubilize large amounts of water in its inverted micelles. The phase behavior and aggregate characteristics of AOT have been studied extensively. Figure 4 is a ternary phase diagram of AOT/n-decanol/water. The micellar solubility limit is reached at 1.35% AOT in the absence on n-decanol, therefore the L_1 (normal micelle) region is small. AOT dissolves in the nominally water-free organic solvent and solubilizes considerable amounts of water giving an extensive L_2 (reverse micellar)

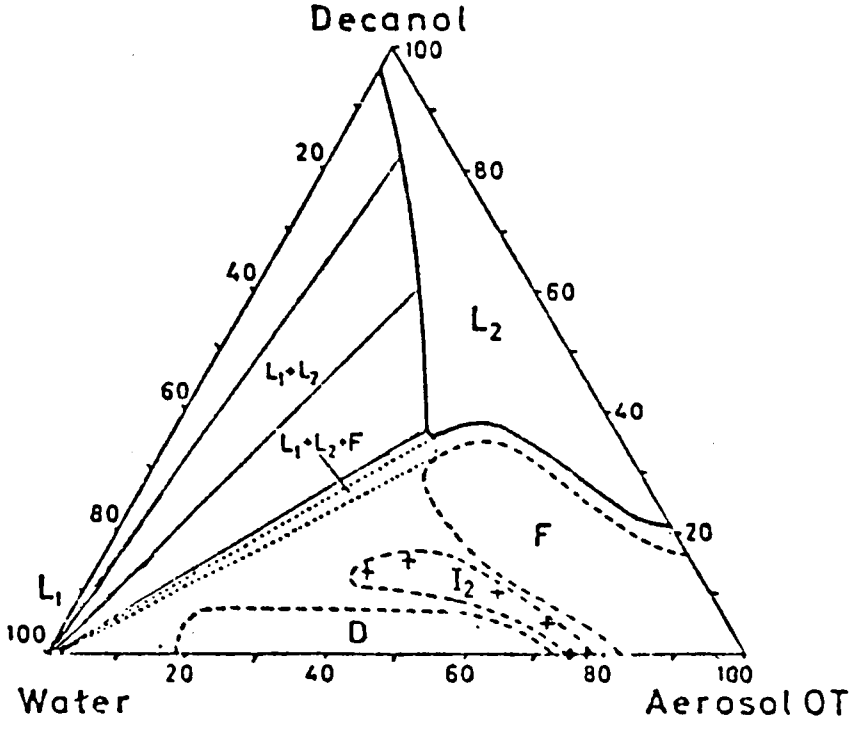


Figure 4. AOT/n-decanol/water ternary phase diagram.

region. The regions marked F, I_2, and D represent liquid-crystalline mesophases. AOT requires approximately 4 moles of water per mole of monomer for hydration of the sulfonate head group.[19] Solutions of AOT in nonpolar solvents are able to solubilize water beyond the requirement for hydration of the head group, therefore forming water-in-oil microemulsions. AOT is unusual because these microemulsion systems form without the use of cosurfactant. A cosurfactant[8] is an amphiphilic molecule (frequently a medium chain length alcohol). It is desirable for structural studies whenever possible, to work with systems not containing cosurfactant, because the cosurfactant partitions among the continuous phase, the surfactant monolayer and the water pool. If the hydrocarbon chain of the alcohol is sufficiently long it may function as the oil, thus confusing observations concerning oil specificity. We will be concerned with certain aspects of AOT's ability to form reverse micelles and microemulsions.

Despite the research of the last 20 years concerning nonpolar surfactant solutions, there is still a great deal of controversy concerning the necessity of water for stabilization of the aggregate.[20] AOT is one of the few surfactants for which CMC values for nonpolar solutions can be measured. It has been determined that the CMC value is dependent on the amount of water present, increasing exponentially as the water content decreases. Even under the most particular conditions minute amounts of water will be present in an organic system. Around the CMC (10^{-4} - 10^{-5} M) there is a 1:1 surfactant to water ratio. It has been suggested that aggregation occurs through hydration

interactions followed by hydrogen bond formation. Some water would therefore be necessary to support growth of the reverse micelles. Actually, in surfactant/hydrocarbon systems we are looking at a ternary system around the CMC, where water and surfactant are present in equal amounts. If this is the case then the "CMC" would lose its significance with respect to a binary surfactant/solvent property since it is changing with water content.

Surfactants are used extensively in many applications because of their solubilizing and wetting properties. They are used in pharmaceutical work as drug delivery systems. Micelles are used to mimic cell membranes and to carry out in vitro studies in membrane research. Surfactants are used as emulsifying agents in paint, toothpaste, lubricants, and in the soaps and detergents used by people every day. Furthermore, functionalized surfactants have been used for catalysis in organic reactions. Because of their overwhelming importance in science and technology, micelles and microemulsions are the topics of extensive research. There is still a great deal to learn about these unique and versatile systems. The research presented in this thesis deals with three different, but related subjects. Chapter II will report on the solubility in water, n-hexane, and isooctane of three cationic surfactants, which are similar in structure to AOT. Also in Chapter II, we will discuss the ability of the reverse micelles formed by these surfactants to solubilize water and present results of small-angle neutron scattering (SANS) experiments which were carried out on the

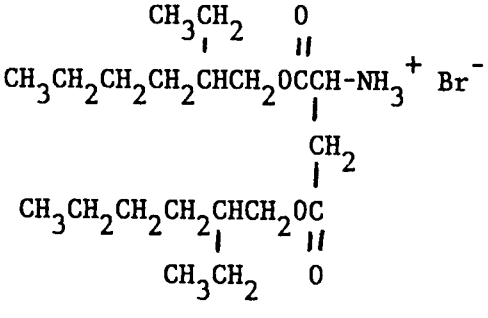
hydrocarbon solutions. Chapter III presents the results of an investigation of a pseudoternary microemulsion system involving AOT and the surfactant sodium dodecylsulfate (SDS); also in Chapter III the use of gelatin to detect water continuous phases in microemulsion systems will be discussed.

CHAPTER II

REVERSE MICELLES FORMED BY DOUBLE-TAILED CATIONIC SURFACTANTS

A. Introduction

The series of surfactants in this research are cationic analogues of sodium dialkylsulfosuccinates. The micellar properties of these surfactants had not been studied previously. Reasoning by analogy to the behavior of AOT discussed in Chapter I, it was thought that these surfactants would be excellent candidates for the efficient solubilization of polar and nonpolar substances. The three surfactants, 2-4, shown here were synthesized.



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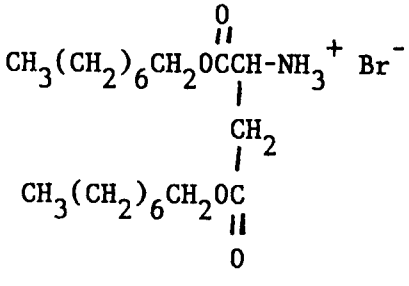

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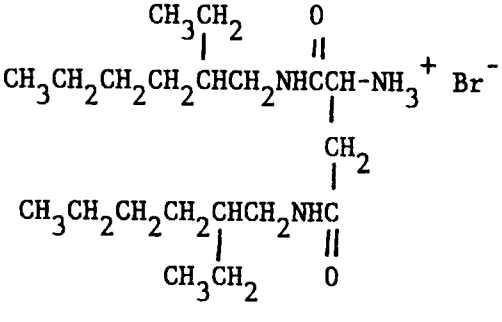

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Compound 2 (BC8ASP) is the cationic analogue of AOT and compound 3 (NC8ASP) is a straight chain compound analogous to 2. Compound 4 (BC8AMD) differs in that it is a diamide rather than a diester. The expected advantage of the diamide compound was that it would not hydrolyze as readily as the diester compounds.[21] In this chapter the solubility of compounds 2-4, in water and hydrocarbon, and their ability to solubilize water in hydrocarbon solvents will be discussed. Small-angle neutron scattering data will be presented from which the size and approximate shape of the reverse micelles formed by BC8ASP and NC8ASP can be deduced.

B. Solubility and Solubilization of Cationic Surfactants

The three cationic surfactants, 2-4, were not soluble in water. The lowest concentration attempted for the three surfactants was 0.03 M; none of the compounds were soluble at this concentration. The two diesters formed turbid suspensions in water and hydrolyzed within 30 minutes. The hydrolysis was easily detected by the strong odor of the free alcohol, either 2-ethyl-1-hexanol or 1-octanol. The diamide could not even be dispersed in water: it appeared to swell into a thick viscous clump of gel-like solid. The above were the results at room temperature; warming to 45°C only served to facilitate the hydrolysis of the diesters and no apparent effect on the water solubility of the diamide was observed. The aqueous dispersions of the surfactants were also sonicated in an attempt to solubilize the compounds. The sonication was unsuccessful. In n-hexane and 2,2,4-trimethylpentane

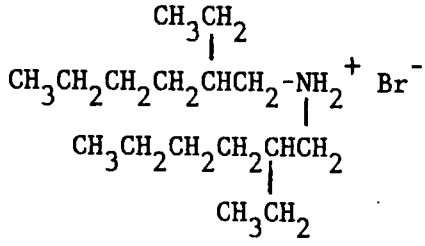
(isooctane) the two diesters showed increased solubility, but the diamide remained insoluble and no further work was performed. BC8ASP was readily soluble in isooctane and n-hexane forming solutions at concentrations up to 0.4 M (this was the highest concentration attempted). The straight chain analogue however was not as soluble: in the same solvents only 0.1 M solutions could be obtained.

The amount of water solubilized by a reverse micellar solution can be expressed using the parameter w_0, which is the molar ratio of water to surfactant. When enough water to obtain a w_0 of two was added to the hydrocarbon solutions above, they became cloudy. This indicated that all of the water was not taken up. Therefore, the reverse micelles formed by NC8ASP and BC8ASP were not able to solubilize appreciable amounts of water.

Since the surfactants were not soluble in water, no CMC values were determined. As mentioned earlier, the exact point at which aggregation begins in nonpolar media is not easily measurable. Therefore, we did not attempt to determine CMC values for the n-hexane and the isooctane solutions of the surfactants.

The most obvious question concerning the results described above is why does an ammonium head group cause such a dramatic change in water-solubilizing ability when compared to AOT? This is easily understood by considering that the hydration number for a sulfonate ion is higher than that of an ammonium ion. Also, the hydration number for a sodium ion is higher than that of a bromide ion. These two factors would lead to the anionic head group having a higher affinity for water. Therefore,

the AOT reverse micelles would be able to solubilize more water than the cationic surfactants. Furthermore, Kon-no and Kitahara[22] carried out experiments comparing the ability of cationic and anionic surfactants to solubilize water. Their work comparing AOT and di-2-ethylhexylammonium bromide, 5, is of particular interest. Compound 5 is similar to BC8ASP.



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Kon-no and Kitahara found the anionic surfactant (AOT) had a much higher affinity for water than the cationic surfactant, 5. Our results are in agreement with this observation.

The second question to ask is, why were NC8ASP and BC8AMD less soluble in hydrocarbon than BC8ASP? First, consider the fact that BC8ASP formed a poor crystal, resembling AOT. That is, the BC8ASP appeared to have a liquid-crystalline structure. NC8ASP formed a white powder and BC8AMD formed a very hard solid which, when dried, resembled glass. The more crystalline the materials were, the less soluble they were in hydrocarbons. This has been noted by others. We can also discuss the effects of hydrocarbon tail structure on solubility. AOT has been shown to be more soluble in hydrocarbon solvents than the straight chain analogue, sodium bis(n-octyl)sulfosuccinate.[23] This is in agreement with the observations made for the cationic surfactants. Furthermore, BC8AMP

probably had extensive intermolecular hydrogen bonding due the hydrogen attached to the nitrogen. It seems then that the slight changes in molecular structure are responsible for the difference in solubility properties between the three compounds.

It appeared that the cationic surfactants, despite the similarity of their structure to AOT, did not have the attraction between the head groups to be extensively soluble in polar or nonpolar solvents. Furthermore, the cationic head groups hindered the solubilization of water by inverted micelles. The effect of the cationic head group was dominant here, with the tail structure playing only a minor role in the solubility and solubilization ability of the cationic surfactants.

C. Static Small-Angle Neutron Scattering

Static small-angle neutron scattering (SANS) was used to study the structure of the reverse micelles formed by BC8ASP and NC8ASP. The structure of AOT had been studied extensively.[13,15,24-26] We made measurements for AOT in deuterated isooctane for comparison. Deuterated solvent was used in order to visualize the particles in solution. This was possible because hydrogen and deuterium have different scattering properties. The scattering from hydrogen is largely incoherent. The coherent scattering lengths (b_{coh}) for hydrogen and deuterium are -0.374 and +0.667 x 10^{-12} cm, respectively. The scattering amplitude for particles in solution depends on the contrast $(1/V_{part})(\Sigma b_{part})-(1/V_{solv})(\Sigma b_{solv})$, where V_{part} and V_{solv} are the molar volumes of the particle and the solvent and Σb_{part} and Σb_{solv} are the sums of the

coherent scattering lengths for all the atoms in the particle and the solvent. Therefore the deuterated isooctane will contrast with the protiated particles making the particles visible.[27]

Recently, Chen and co-workers[24] carried out an extensive SANS study on AOT reverse micelles in n-decane. Their study gave a detailed picture of the reverse micelles formed by AOT in n-decane including size, shape, aggregation number, and internal structure. Figure 5 illustrates the structure of the AOT reverse micelle as described by Chen and co-workers. The micelle was approximately spherical in shape with an aggregation number of 22 ±2 monomers per micelle. Each monomer was determined experimentally to have a solvent-excluded volume of 612 Å. The micellar core consisted of a monolayer of polar heads close packed on the faces of an icosahedron, enclosing a region of bound water having a radius of about 4.4 Å. The micelle was coated by an 8 Å layer of surfactant tails. The AOT used by Chen and co-workers was determined to contain residual water, 0.7 moles per mole AOT.

We did not do the sort of work which allows this much detail. However, we will use the work done by Chen and co-workers to support our results and to compare data for AOT in isooctane with data for the cationic surfactants in isooctane. Furthermore, several aspects of our data analysis are justified by the results from the AOT/n-decane system. It should be pointed out that the AOT used in our SANS measurements was purified by high pressure liquid chromatography and contained only 0.3 moles of residual water per mole of AOT.[28] The aspartates were believed to be virtually water free, based on the results of elemental analysis.

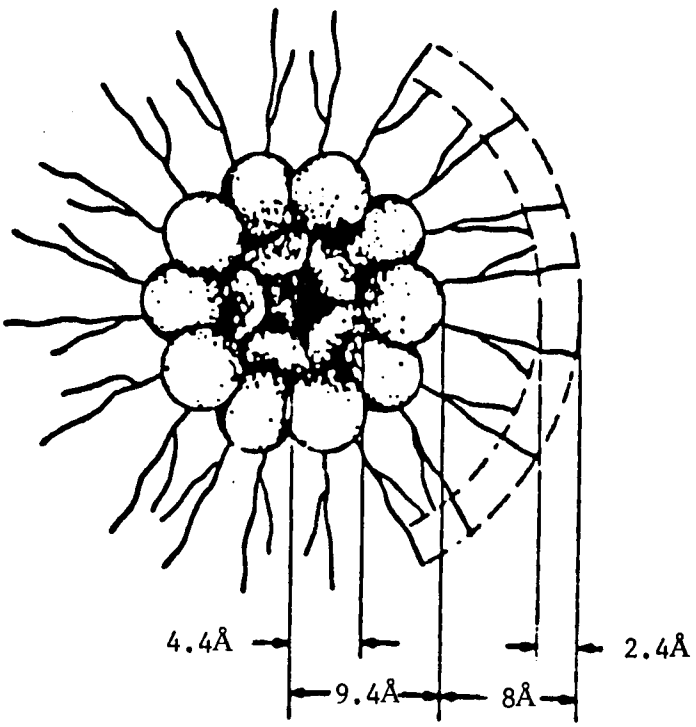


Figure 5. AOT reverse micelle.

The scattering curves were fit, using as the micellar model, interacting monodisperse, homogenous spheres. The scattering intensity as a function the scattering wavevector is given by

$$I(Q) = (\text{conc-cmc}) \cdot AGG \cdot \{(\Sigma b_{mon}) - \rho_{solv} V_{mon}\}^2 \cdot S(Q) \cdot [F(Q)]^2 + B \quad (3)$$

where Q is related to the scattering angle θ, as $Q = 4\pi/\lambda \sin\theta/2$ and AGG is the aggregation number, Σb_{mon} denotes the sum of the scattering lengths for the monomer, ρ_{solv} is the mean scattering length density of the solvent, V_{mon} is the volume of the visible part of the monomer, and B is the residual incoherent scattering. F(Q) is the particle form factor and is given by

$$F(Q) = 3.0[\sin QR - QR \cdot \cos QR]/(QR)^3 \quad (4)$$

where R is the radius of the particle. S(Q) is the structure factor, which measures the interparticle interaction. Since there was no interaction peak at intermediate Q we assumed there were no interparticle interactions in our initial fitting. This would mean setting S(Q) = 1. This, however, gave poor fits. We then tried using a hard-spere interaction ($S_{HS}(Q)$) model, which also gave poor fits. We therefore refit the data using equation 5

$$S(Q) = \frac{I_{0,crit}}{1 + Q^2\xi^2} + S_{HS}(Q) \quad (5)$$

where ξ is a correlation length (a sort of range parameter for our purposes) and $S_{HS}(Q)$ denotes the hard sphere contribution to S(Q). This is a well-established procedure in treating scattering from micellar and microemulsion systems. The first term in equation 5 is formally equivalent to an attractive Yukawa tail potential.[29-32] Figures 6-9 present intensity vs. Q plots for each of the solutions measured.

Table I gives the fitting parameters, which were determined from nonlinear least squares fitting of the data. A is proportional to the number particle density (N_p) and the contrast factor ($(\rho_{part}-\rho_{solv})^2$). B is the residual incoherent scattering used in equation 3. R is the radius of the particles. ξ is the correlation length used in equation 5 and $I_{0,crit}$ is critical intensity at zero scattering angle. Plots of the fitted data are shown in Figures 10-15.

The results of the fits were tested for consistency by comparing the aggregation number ($\bar{n}_1$) obtained from I(0) with $\bar{n}_2$ obtained from the finite Q data (i.e., from the value of R). The value for $\bar{n}_1$ was calculated using I(0) by the following equations

$$I(0) = (\text{conc-cmc}) \cdot AGG \cdot \{(\Sigma b_{mon}) - \rho_{solv} V_{mon}\}^2 \qquad (6)$$

where

$$I(0) = A \cdot V_{part}^2 \quad . \qquad (7)$$

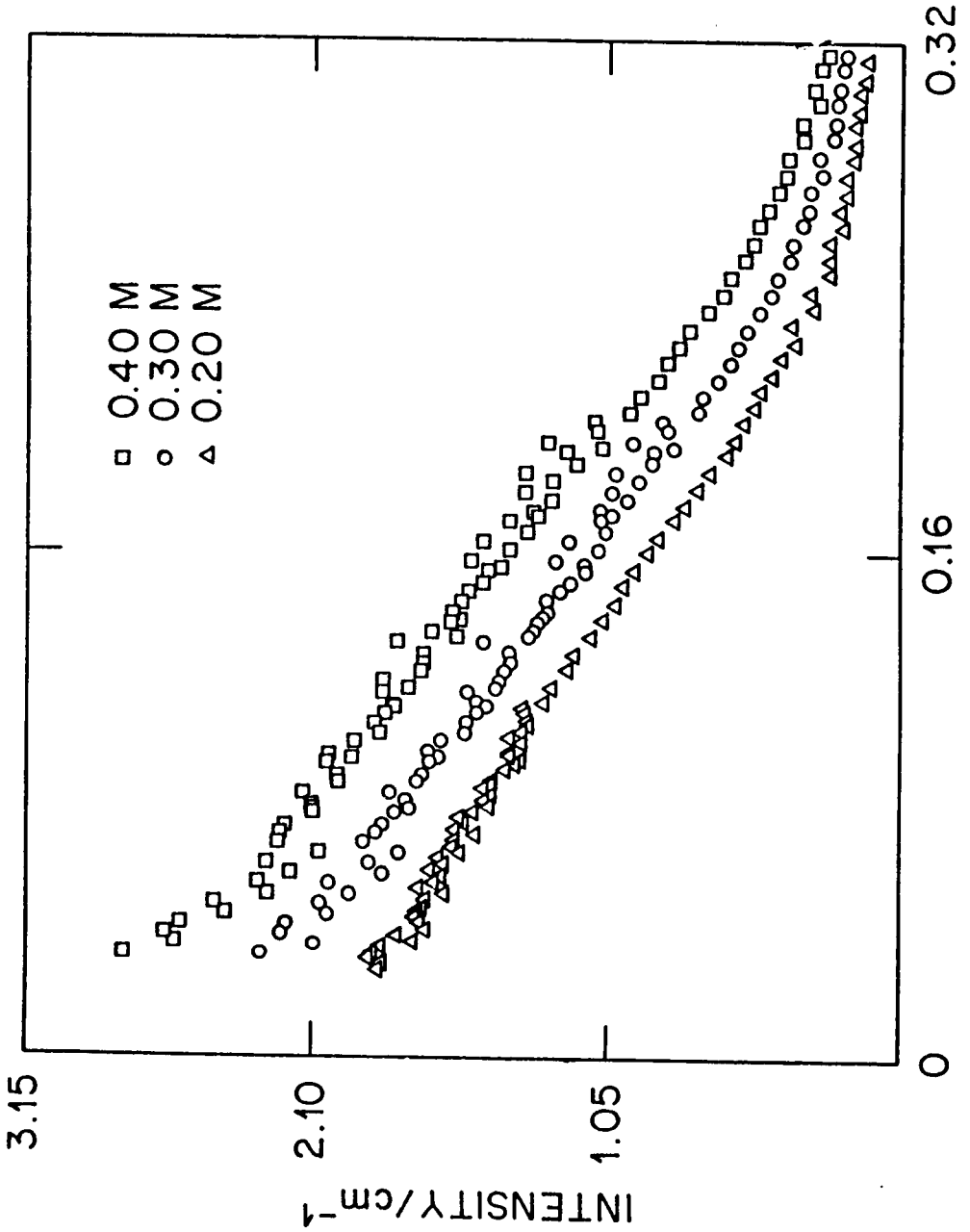


Figure 6. Intensity vs. Q plot for 0.4 M, 0.3 M, and 0.2 M BC8ASP.

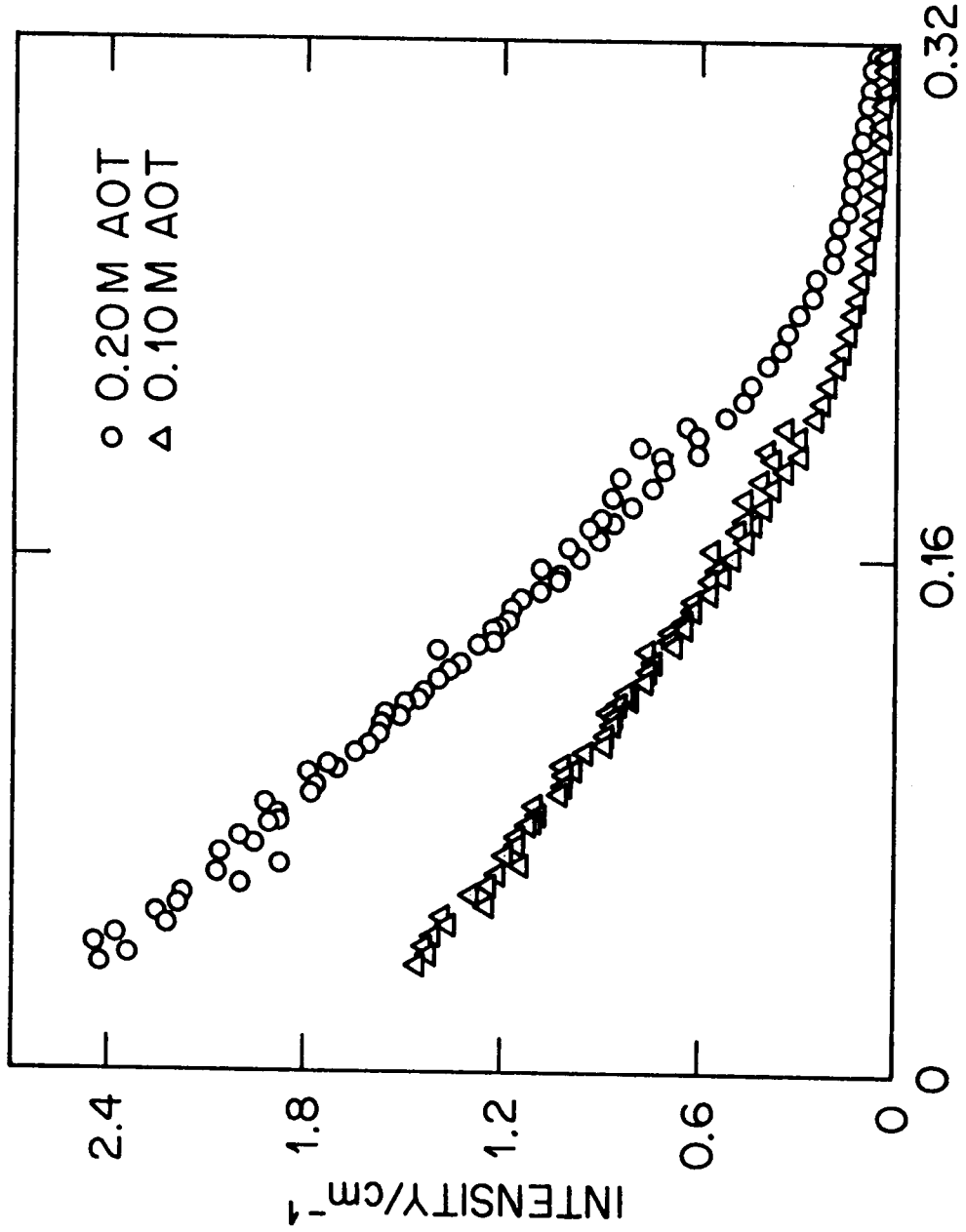


Figure 7. Intensity vs. Q plot for 0.2 M and 0.1 M AOT.

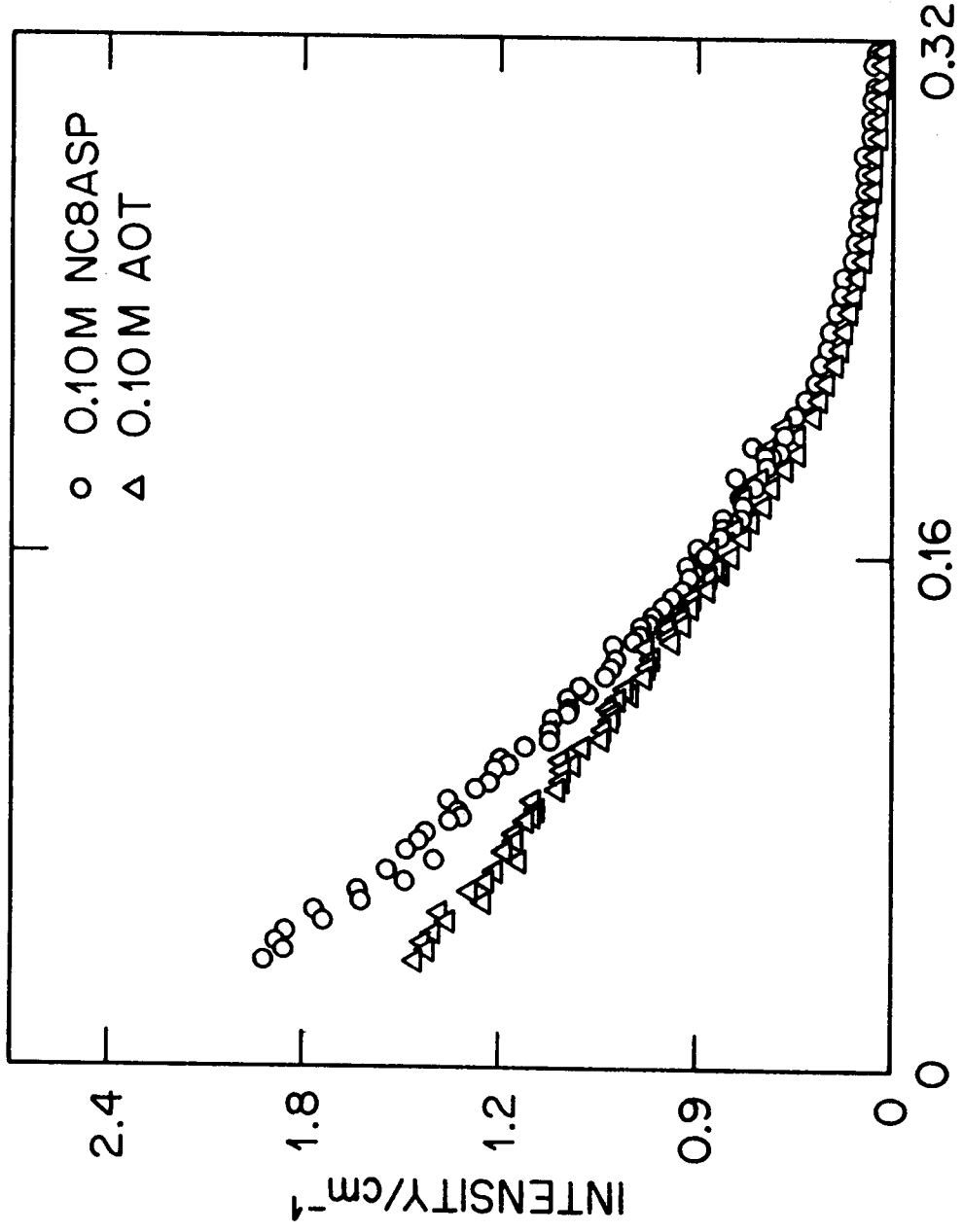


Figure 8. Intensity vs. Q plot for 0.1 M NC8ASP and 0.1 M AOT.

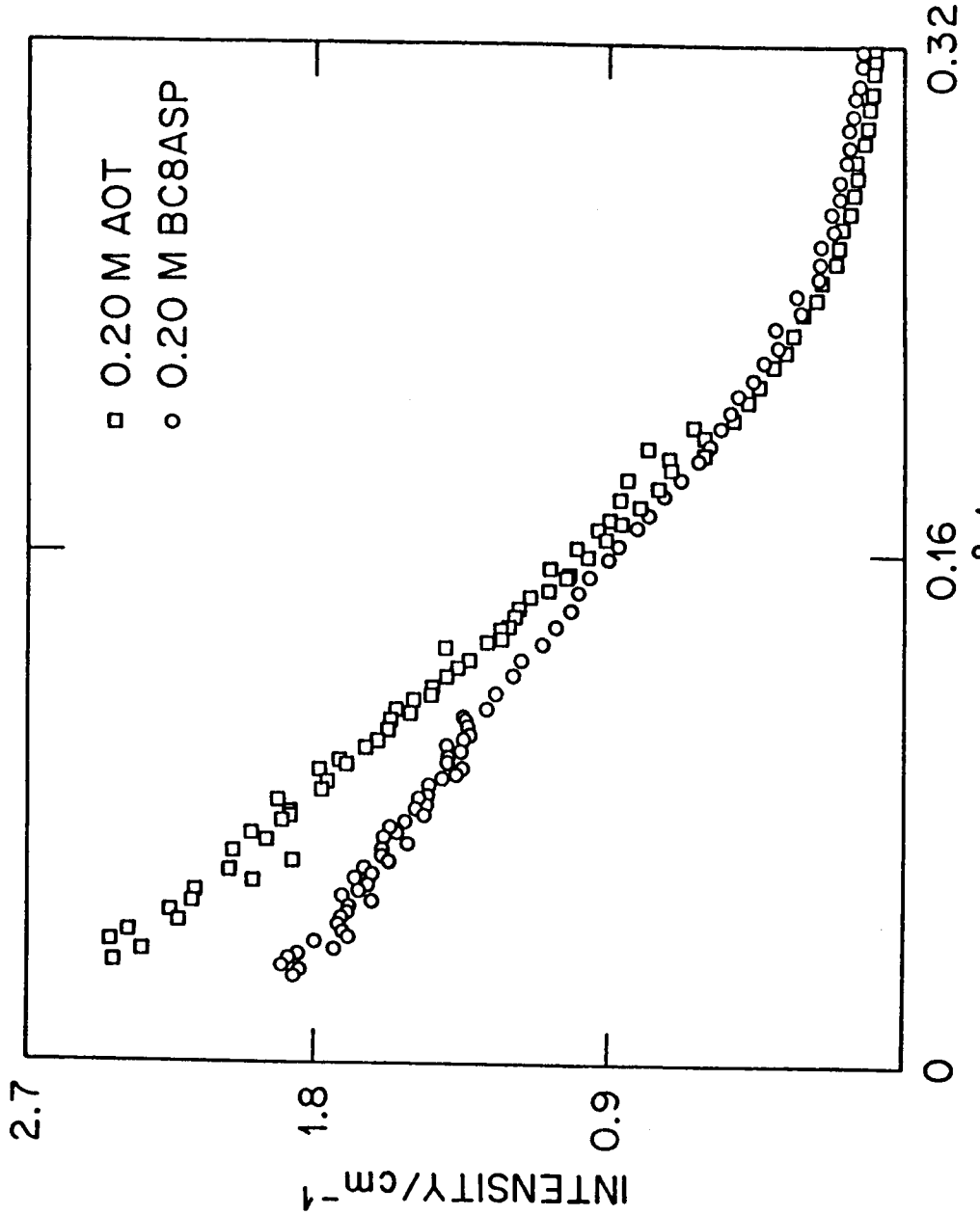


Figure 9. Intensity vs. Q plot for 0.2 M BC8ASP and 0.2 M AOT.

TABLE I

VALUES OBTAINED FOR FITTING PARAMETERS FROM NONLINEAR LEAST SQUARES FITS OF SANS DATA

Sample	$A(x10^{-8})$	B	R	ξ	$I_{0,crit}$	CHI
0.1 M AOT	1.016 ± 0.126	0.0344 ± 0.0117	13.56 ± 0.59	9.45 ± 5.5	0.619 ± 0.311	2.04
0.2 M AOT	2.008 ± 0.449	0.072 ± 0.031	13.16 ± 0.79	7.28 ± 5.2	0.784 ± 0.520	2.53
0.1 M NC8ASP	1.057 ± 0.149	0.063 ± 0.015	13.31 ± 0.71	10.1 ± 3.4	1.22 ± 0.53	2.12
0.2 M BC8ASP	2.080 ± 0.340	0.093 ± 0.016	12.38 ± 0.27	5.0 ± 1.4	0.784 set	2.13
0.3 M BC8ASP	3.021 ± 0.844	0.158 ± 0.046	11.93 ± 0.47	5.5 ± 1.5	0.949 set	2.34
0.4 M BC8ASP	3.632 ± 1.822	0.249 ± 0.125	12.18 ± 1.45	5.03 ± 5.23	0.831 ± 0.729	3.00

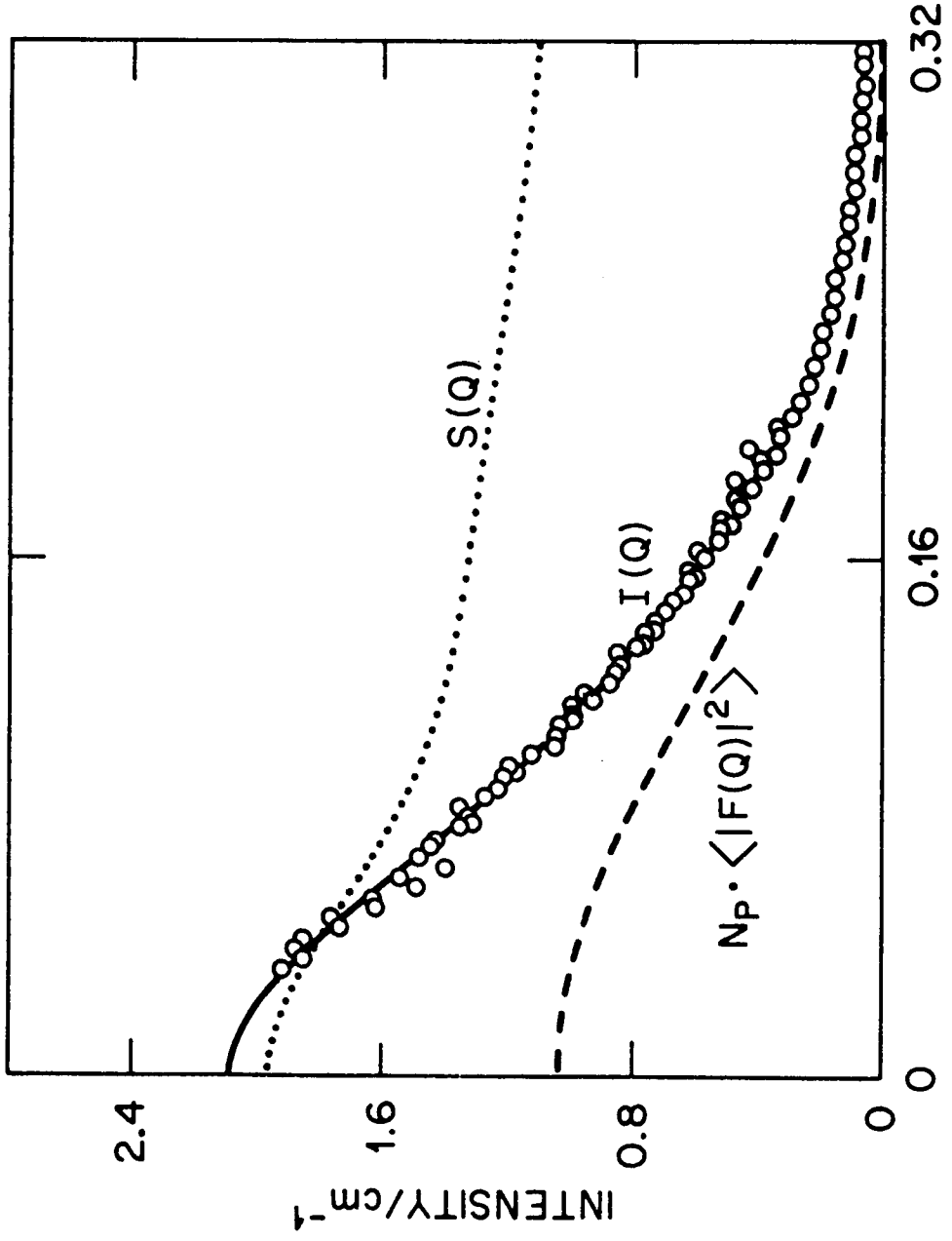


Figure 10. Fit of scattered intensities for 0.1 M NC8ASP.

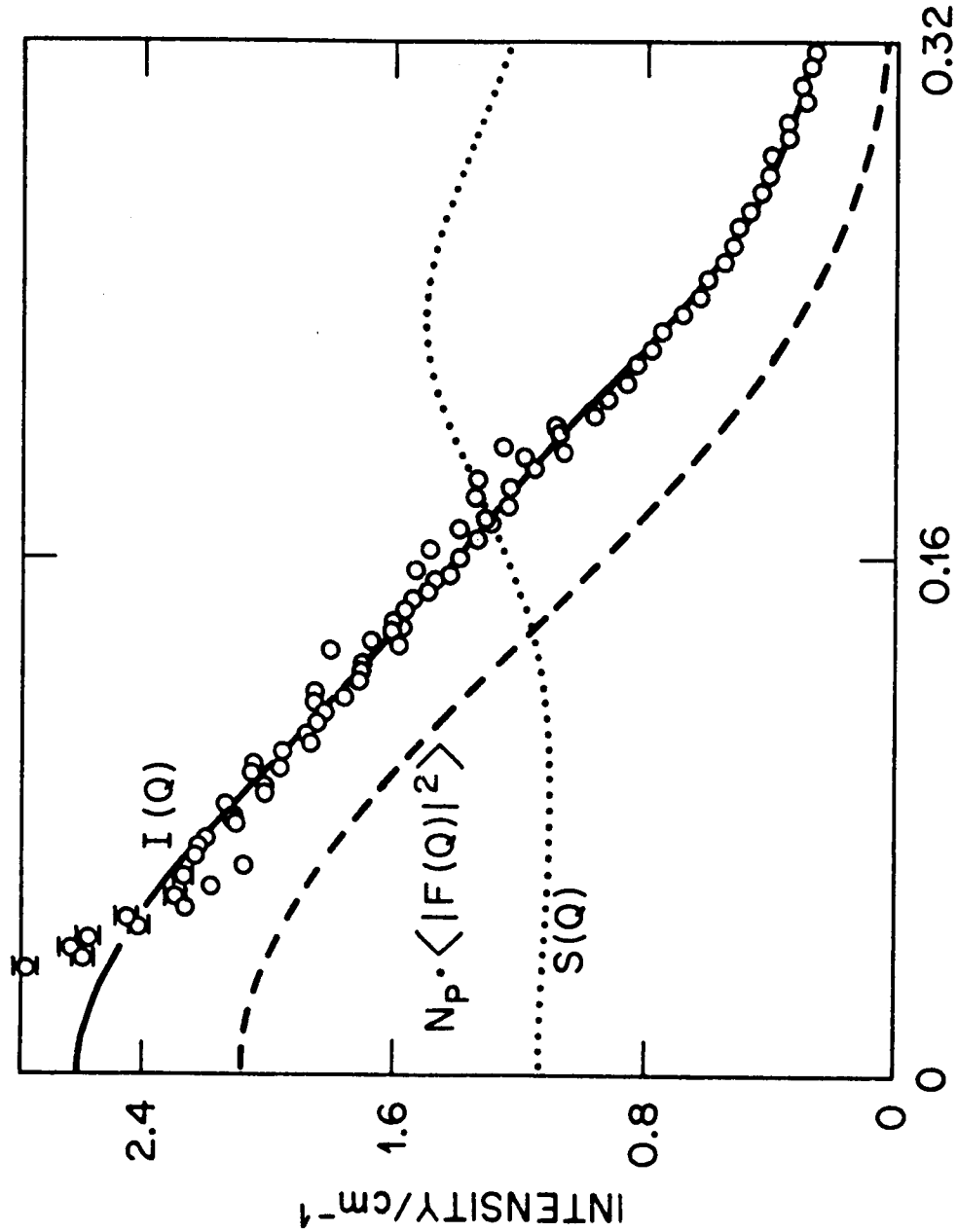


Figure 11. Fit of scattered intensities for 0.4 M BC8ASP.

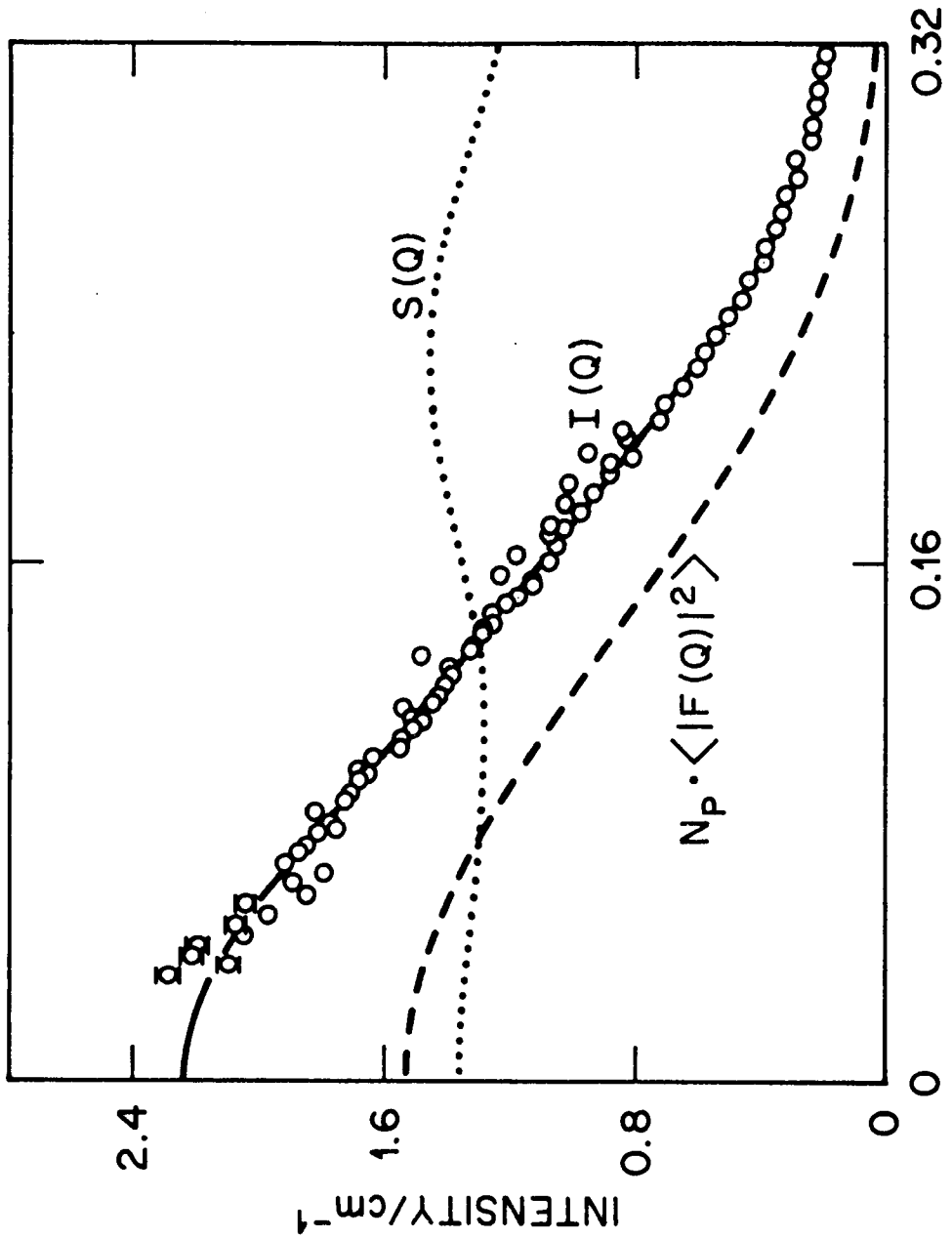


Figure 12. Fit of scattered intensities for 0.3 M BC8ASP.

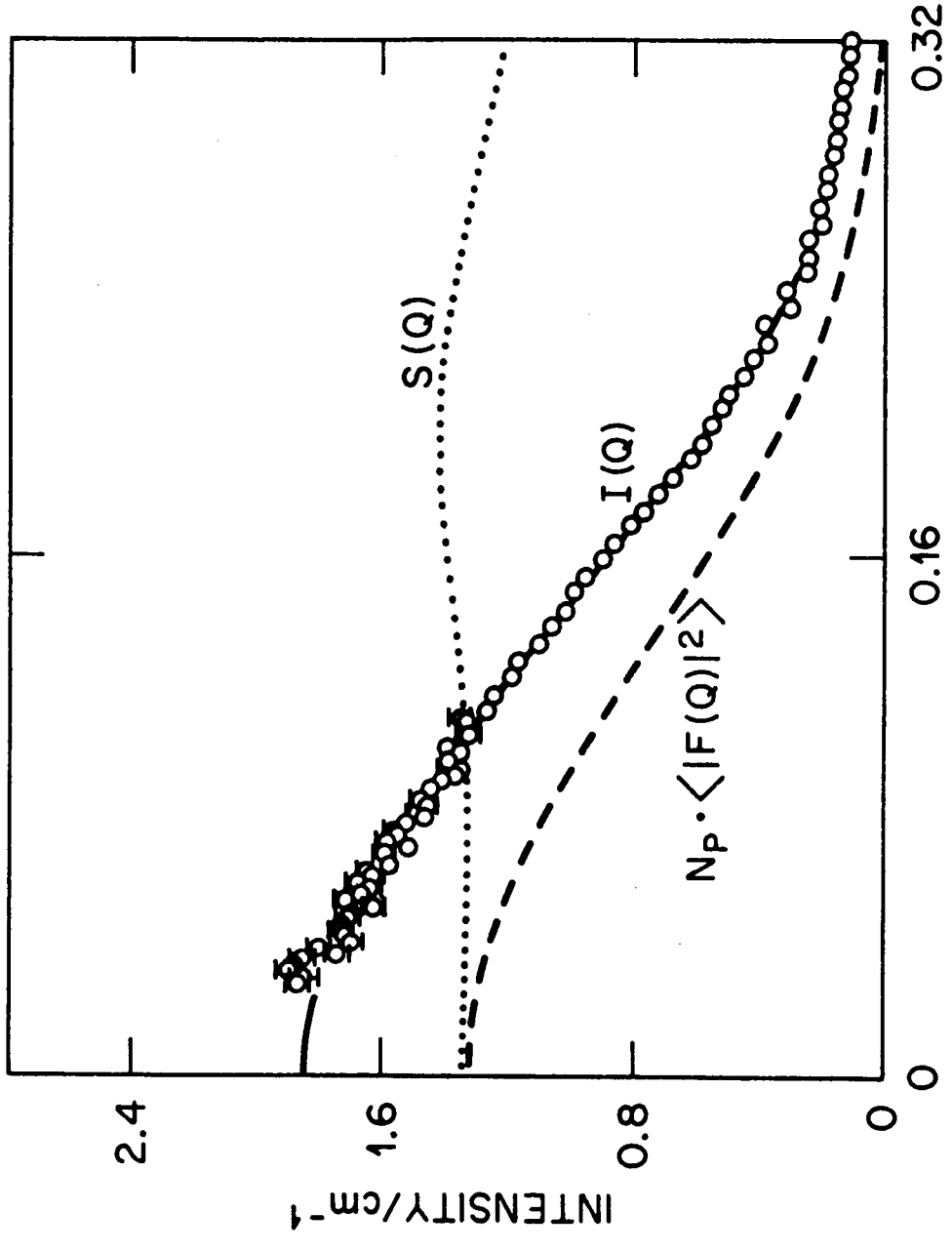


Figure 13. Fit of scattered intensities for 0.2 M BC8ASP.

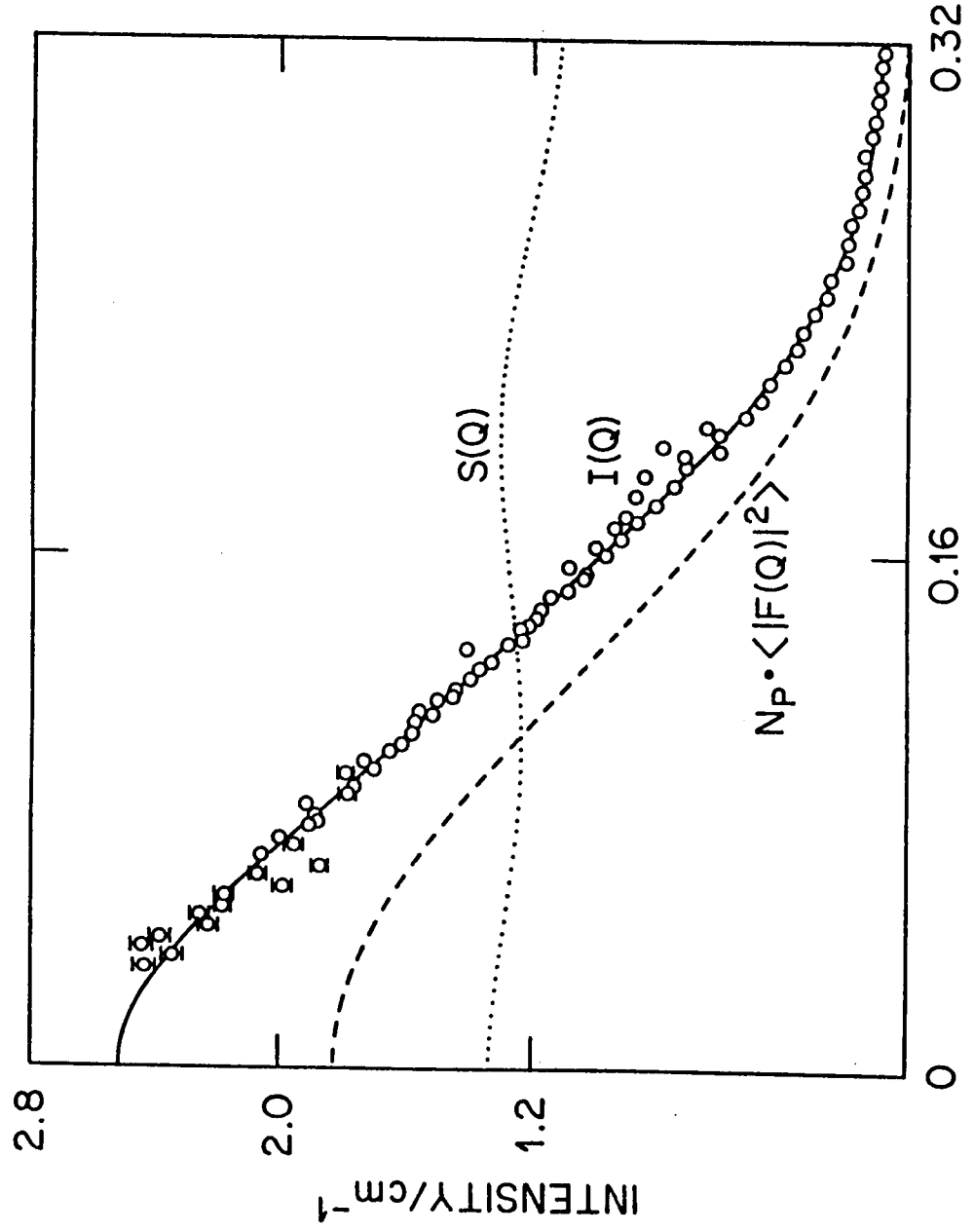


Figure 14. Fit of scattered intensities for 0.2 M AOT.

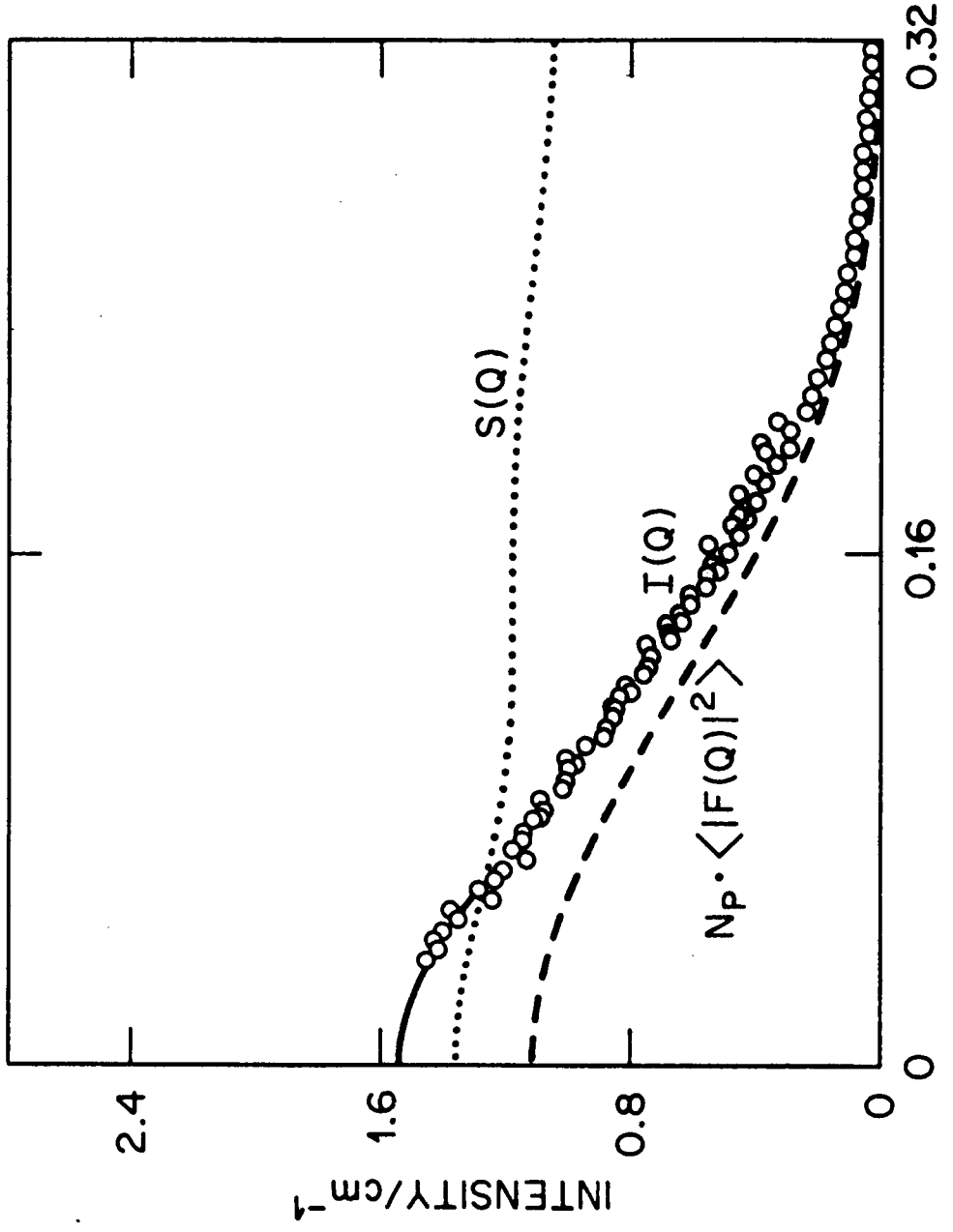


Figure 15. Fit of scattered intensities for 0.1 M AOT.

A was obtained from the fit as parameter 1. $V_{part} = (4/3)\pi R^3$. Dividing V_{part} by V_{mon} gave the value of $\bar{n}_2$. The values used for V_{mon} and the scattering lengths (Σb_{mon}) for each of the surfactants are given in Table II. These values were obtained using standard scattering lengths and volumes for each of the atoms in the surfactants.[33,34] Chen and co-workers[24] established that n-decane penetrates AOT reverse micelles very effectively to a "depth" of 2.4 Å, so that the radius visible to SANS measurement (i.e., the solvent excluded particle) should be a few Å less than the extended length of the tails for the three surfactants studied. However, in the AOT/n-decane study it was pointed out that the interpenetration distance may be limited by the branching of the tail groups. If this is the case then more penetration by the solvent would be expected for NC8ASP. This would lead to a smaller volume per monomer, which would increase the aggregation number slightly. However, this would not effect the agreement between $\bar{n}_1$ and $\bar{n}_2$.

Table III gives the values for $\bar{n}_1$ and $\bar{n}_2$. The agreement between the two $\bar{n}$ values were excellent for the AOT and the NC8ASP solutions. However, the results were not as good for the BC8ASP. Several reasons for the discrepancy were considered. Since the only difference between BC8ASP and AOT was the head group, we investigated the sensitivity of the agreement between $\bar{n}_1$ and $\bar{n}_2$ to the volume of the head group. Two possible variations were considered. The calculations were first carried out assuming that each head group had one molecule of bound water. This would increase the volume of the monomer. Although no water was added to the solution there was the possibility of a small amount of

TABLE II

SCATTERING LENGTHS AND VOLUMES PER MONOMER

	AOT	NC8ASP	BC8ASP
Σb, cm	5.249×10^{-12}	3.353×10^{-12}	3.353×10^{-12}
V_{mon}, $\AA^3$	561.3	498.3	540.5

TABLE III

AGGREGATION NUMBERS FOR REVERSE MICELLES FORMED BY CATIONIC SURFACTANTS

Sample	$\bar{n}_1$	$\bar{n}_2$	$Q_{maximum}$
0.1 M AOT	20.1 ± 3.27	18.6 ± 1.40	0.331
0.2 M AOT	16.6 ± 4.44	17.0 ± 1.76	0.331
0.1 M NC8ASP	21.6 ± 4.15	19.8 ± 1.83	0.331
0.2 M BC8ASP	11.5 ± 1.96	14.7 ± 0.297	0.283
0.3 M BC8ASP	8.9 ± 2.63	13.2 ± 0.520	0.331
0.4 BC8ASP	9.1 ± 5.27	14.0 ± 1.66	0.331

$\bar{n}_1$ is from I(0).

$\bar{n}_2$ is from R at finite Q.

water being bound to the head group as in the case of AOT described earlier. The second possibility was hydrogen bonding existing between the head group hydrogens and the carbonyl oxygens. This would make the effective area of the head group larger, but the net effect would be to decrease the volume of the monomer.[34] Calculations using either variation did not succeed in improving the agreement between the two n values.

The most obvious observation in looking at the values for n and R was that the micelles were very small. In comparison with AOT the radii of the micelles formed by the aspartates were reasonable. In the AOT samples as the concentration was increased, the radii decreased slightly. Referring to Table III it can be seen that n also decreased when the AOT concentration was increased. Therefore, the micelles in the 0.2 M sample were smaller than those in the 0.1 M sample. The decrease in $\bar{n}$ with increasing surfactant concentration is counterintuitive. We currently have no explanation for it. The 0.1 M sample of NC8ASP formed aggregates which were larger in size than those of the 0.1 M AOT solution. Figure 8, p. 25, gives the intensity vs. Q plots for these two solutions, and the curve for NC8ASP was just slightly below the AOT curve. This could be understood by looking at the respective aggregation numbers for AOT and NC8ASP. NC8ASP had an $\bar{n}$ value which was slightly larger than that of AOT. This was due to the straight chain vs. the branched chain tail of the two surfactants. The straight chains packed better,[23] therefore more monomers could aggregate. The data for BC8ASP showed similar size variations with increasing surfactant

concentration. The 0.2 M solution had the largest aggregates and the largest $\bar{n}$ of the three solutions measured. The 0.3 M solution showed a slight decrease in size and $\bar{n}$, but the 0.4 M solution showed an increase in size and $\bar{n}$. However, the particles in the 0.4 M solution were still smaller than those of the 0.2 M solution. If we compared the 0.2 M samples of AOT and BC8ASP we found that AOT had the larger $\bar{n}$ and the larger radii. This point was illustrated by Figure 9, p. 26, which gave the intensity vs. Q plot for the two solutions. In the study[22] mentioned earlier, comparing anionic surfactants (i.e., AOT) and cationic surfactants (i.e., di-2-ethylhexylammonium bromide) having the same tail structure, it was shown that $\bar{n}$ was greater for anionic surfactants. The results obtained in this work were in agreement with this observation, since AOT reverse micelles had $\bar{n}$ values almost 1.5 times those of BC8ASP. The $\bar{n}$ values obtained for AOT reverse micelles were smaller than that reported by Chen and co-workers, but we used a different solvent, which may account for the difference.

In conclusion, it has been shown using SANS that the cationic surfactants, BC8ASP and NC8ASP formed small spherical reverse micelles in isooctane. The radii for the reverse micelles formed in isooctane were in the range of 12-13 Å. Furthermore, it seemed correct to assume that the cores of the inverted micelles formed by BC8ASP and NC8ASP were relatively free of water. The aggregation numbers found for NC8ASP were higher than those for the branched chain surfactant. Finally, the cationic analogue of AOT, BC8ASP, formed smaller aggregates than AOT in isooctane.

CHAPTER III

MICROEMULSIONS

A. Introduction

Mixtures of oil and water are practically immiscible. However they can be stabilized by the addition of surfactants, which concentrate at the oil-water interface and thereby drastically decrease the interfacial tension.[35] In most cases this decrease in interfacial tension stops at some point. The reason is that beyond a certain concentration the added surfactant does not go to the interface but prefers to stay in one of the bulk phases in the form of micelles. At low concentrations of oil (or water) this occurs in the form of swollen micelles or microemulsions. The system behaves like a transparent fluid of low viscosity, which is a favorable feature for most applications.

There are three types of microemulsions. An oil-in-water (o/w) microemulsion is water continuous and oil discontinuous. Alternatively, a water-in-oil (w/o) microemulsion is oil discontinuous and water discontinuous. In a bicontinuous microemulsion both the water and the oil phases are continuous. In chapter I we discussed the concept of packing parameters[8,11,12] which describe structures which form in surfactant systems in terms of curvature. It is possible to use the packing rules for $v/\underline{a}l_c$ to explain factors which allow the interface to curve to give stable microemulsions.[36]

Curvature can be induced by the oil[37] used in the microemulsion system. For this factor to be important the length of the surfactant

tail must exceed that of the oil. This allows for solubilization of the oil in the hydrocarbon tails which swells the surfactant layer and effectively increases v. This makes the effective surfactant parameter $(v_{eff}/\underline{a}l_c) >> 1$. The oil then induces the formation of reverse structures, i.e., negative curvature. Mixtures of surfactants, with opposite $v/\underline{a}l_c$ values can be used to achieve a desired value by adjusting the mole fractions of the surfactants in the mixture. Single-tailed surfactants typically form normal micelles, i.e., $v/\underline{a}l_c < 1/3$, while double-tailed surfactants have a larger hydrocarbon tail volume and form reverse structures, i.e., $v/\underline{a}l_c > 1$. For a surfactant mixture containing a single- and a double-tailed surfactant the value of the packing parameter (P_{mixt}) can be determined by the following equation:

$$P_{mixt} = X_1 P_1 + X_2 P_2 \qquad (8)$$

where X_1 and X_2 are the mole fractions of the single- and the double-tailed surfactant respectively and P_1 and P_2 are packing parameters for the pure components. By adjusting the mole fractions it is possible to change the microstructure of the system. Cosurfactants have been widely used with single-tailed surfactants to form o/w microemulsions. Alcohols of medium chain length are typical candidates. Alcohols have little effect on the head group area: the cosurfactant simply acts to swell the effective chain volume sufficiently to allow substantial oil uptake. Cosurfactants allow for considerable flexibility in inducing changes in structure, but it is difficult to perform structural studies

on these systems due to the complications involved when using cosurfactant. Finally, salt may be added to the system. Salt reduces the electrostatic repulsions of the head groups, and therefore effectively decreases the head group area. This increases the $v/\underline{a}l_c$ value.

Manipulation of four and (with salt) five component systems poses formidable experimental and theoretical difficulties. Theory predicts, however that it should be possible to obtain three component (oil/water/surfactant) microemulsion systems by simply using a surfactant having $v_{eff}/\underline{a}l_c = 1$. This would specify the use of a surfactant which is sparingly soluble in water and in oil. The tails should be fluid at room temperature to allow oil uptake, and the chains should be long enough to solubilize large amounts of short chain alkanes.

Finally, even if all the above requirements are met, a microemulsion will not form unless the flexibility of the interfacial boundary is sufficient to allow curvature. When the system forms some sort of macrocrystal the interface is rigid. It is relatively simple to control the spontaneous curvature using steric effects and solvent qualities. It is much more difficult to control interfacial flexibility.

Until recently AOT was the only surfactant known to form microemulsions[18,38] in three component systems. As mentioned in chapter I, AOT is capable of solubilizing large quantities of water in its reverse micelles, which eventually swell to sizes operationally defined as microemulsions. Recently, Evans and Ninham[36,37,39-41] have reported that the cationic surfactant didodecyldimethylammonium bromide (DDAB), 6, forms three component microemulsions. DDAB satisfies the theoretical

$$(C_{12}H_{29})_2\text{-}\overset{+}{N}\ Br^-$$
$$|$$
$$(CH_3)_2$$

<u>6</u>

requirement for forming microemulsions by having a $v/\underline{a}l_c = 0.82$ ($\underline{a}$ is determined by x-ray diffraction). Furthermore, DDAB is sparingly soluble in both water and oil. The DDAB/oil/water microemulsions exhibit properties which are very different from those exhibited by other microemulsion systems. A typical phase diagram is shown in Figure 16. In the one phase region the microemulsions are conducting at low water content, but along the dotted line there is a percolation type transition to a nonconducting state with increasing water content. A percolative transition[42,43] has been characterized as a steep increase over five orders of magnitude in electrical conductance for a microemulsion system as water is added. When a system undergoes a transition of this type something has happened to the structure, making the water in the system connect. The DDAB system shows the opposite behavior in that the percolative transition is from conducting to nonconducting with increased water content. Parallel behavior is exhibited by the viscosity. At very high water content the one phase system becomes a rigid gel instead of more fluid as would be expected. Three component systems containing DDAB, water, and oils ranging from <u>n</u>-hexane to <u>n</u>-tetradecane have been studied. The length of the alkane chain of the oil has a large effect on these systems, as would be expected from the discussion above concerning curvature. Conductance studies and NMR

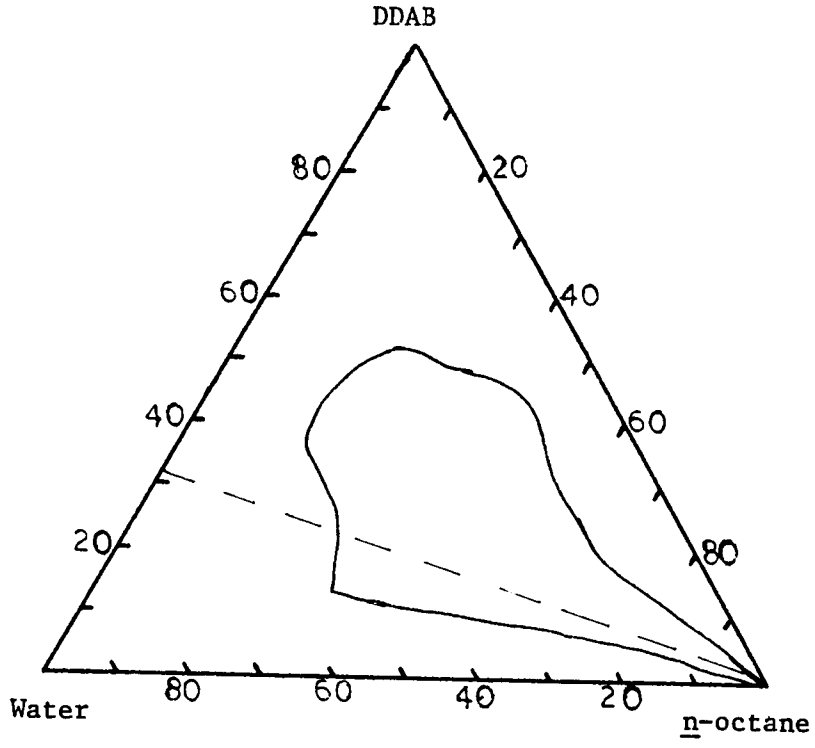


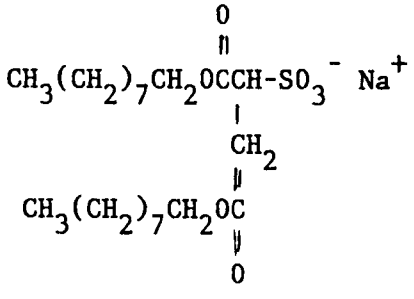
Figure 16. DDAB/n-octane/water ternary phase diagram.

self diffusion measurements have been used to determine the structure of the DDAB microemulsions. At low water content a bicontinuous phase is formed. As water is added the conduits disconnect and form w/o spheres. The abrupt conducting/nonconducting transition which is observed signals the change in structure.

This unique system prompted two separate projects. First, we were interested in finding another surfactant which would form microemulsions in a three component system and perhaps exhibit properties similar to the DDAB system. Secondly, the research group of Professor Luisi[44] at Eidgenossische Technische Hochschule Zurich has been using gelation to indicate the presence of a water-continuous phase in AOT systems. We hoped this technique could be used to detect the structure transition from bicontinuous to water discontinuous.

B. Mixed Surfactant Microemulsions

DDAB is insoluble in water as well as nonpolar solvents, and as a result the oil-water interfacial area can be set by the amount of surfactant. The surfactant sodium bis(n-nonyl)sulfosuccinate, 7,



7

has solubility properties similar to DDAB. It is virtually insoluble in both polar and nonpolar media. This surfactant therefore appeared to be a good candidate for producing three component microemulsions. However, all attempts to create such systems failed. In an attempt to create a surfactant system mimicing the hydrophilic-lipophilic properties of DDAB we began mixing surfactants with opposing solubility properties. AOT is extremely soluble in oil, but only 1.35% soluble in water.[13,14] We therefore attempted to form microemulsions using varying mole ratios of AOT to compound 7. The mole ratios tried are summarized in Table IV. None of the mixed surfactant systems yielded a one phase system with water and n-hexane. Since mixing compound 7 with a hydrophobic surfactant did not produce a microemulsion, we went to the other extreme and used an extremely hydrophilic surfactant, i.e., sodium dodecylsulfate (SDS), 8. SDS is opposite in solubility properties from AOT in that is is

$$CH_3(CH_2)_{11}OSO_3^- \ Na^+$$

8

soluble in water and insoluble in hydrocarbon. We tried a 50:50 mole ratio of the two surfactants in a system with water and n-hexane with no success.

Since the attempts to form a microemulsion using compound 7 failed, we decided to try combining the AOT and SDS. We hoped that this combination of an extremely lipophilic surfactant, AOT, and an extremely hydrophilic surfactant, SDS, might be successful in producing a microemulsion system. The best results were obtained using a 25:75 mole

TABLE IV

SUMMARY OF MOLE RATIOS USED IN ATTEMPTING TO FORM AOT/SODIUM BIS(n-NONYL)SULFOSUCCINATE MICROEMULSIONS

Sodium Bis(n-nonyl)sulfosuccinate	AOT
80	20
50	50
65	35
75	25

ratio of SDS:AOT, with n-octane as the oil. Initially, several mixtures of SDS/AOT/n-octane/water were prepared in ampules. The points are shown in the phase diagram, Figure 17. The observations for each ampule are summarized in Table V. These ampules were observed at room temperature for several months and at 45°C for one week. There were no changes in the systems over time; at the elevated temperature the systems became more fluid but never underwent any phase changes. By observing the compositions indicated we were able to narrow down a possible one phase region in the oil corner of the phase diagram. This one phase region was further defined by titration of surfactant and octane suspensions with water to clarity. Figure 18 shows the one phase region. It has an extremely irregular shape, which may be attributed to experimental uncertainty. Determining the exact location of the phase boundaries was difficult for two reasons. First as the solutions were titrated with water some surfactant would precipitate out of solution. Rapid stirring would resolubilize the solid. The second problem arose as one moved towards the water corner of the phase diagram through the one phase region: the solution became very viscous and eventually became a rigid gel. This difficulty along with the constant precipitation described above made it extremely difficult to delineate the phase boundaries.

Beyond the line AB in Figure 18, the system is one phase at first. As water is added the system becomes increasingly viscous as the second boundary, line CD, is reached. Inside the one phase region the system is a clear, apparently stable, microemulsion. The conductivities were determined for the points marked with an x in Figure 18. The results of the conductance measurements are given in Table VI. The system was

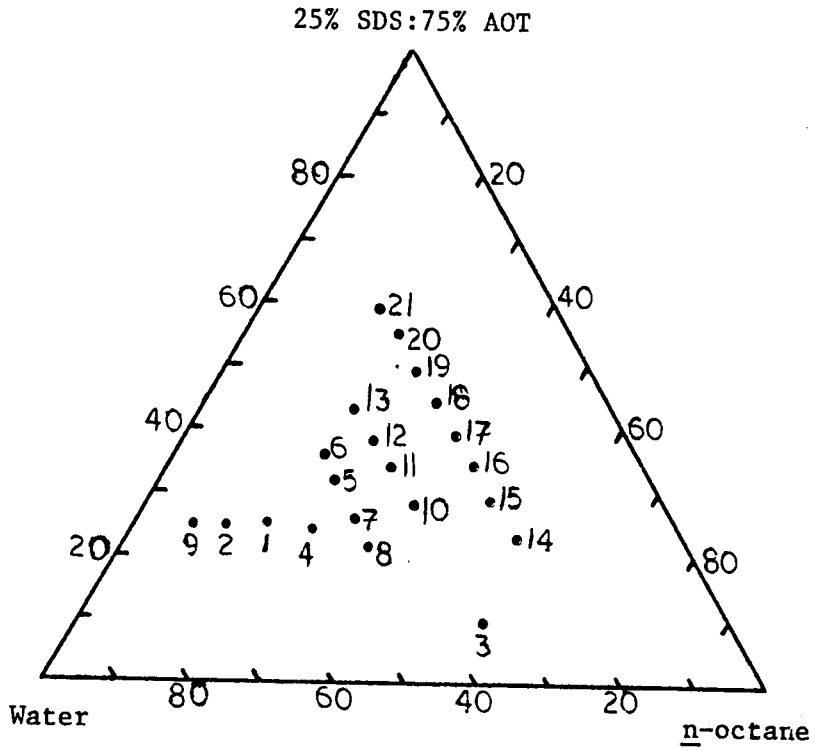


Figure 17. SDS/AOT/n-octane/water ternary phase diagram showing the specific mixtures prepared.

TABLE V

DESCRIPTIONS OF SPECIFIC MIXTURES OF SDS/AOT/WATER/n-OCTANE SHOWN IN FIGURE 17

Ampule Number	Description
1	two phase liquid with clumps of gel
2	milky liquid
3	white solid gel
4	solid gel cloudy/clear
5	clear gel
6	clear gel
7	gel and liquid
8	opaque gel
9	milky liquid
10	viscous liquid, solid surfactant
11	one phase viscous liquid
12	one phase slightly thick liquid
13	one phase almost gel liquid
14	one phase liquid
15	one phase liquid, thicker
16	one phase liquid, thicker
17	one phase gel
18	slightly cloudy gel
19	two phase gel
20	two phase gel
21	two phase gel

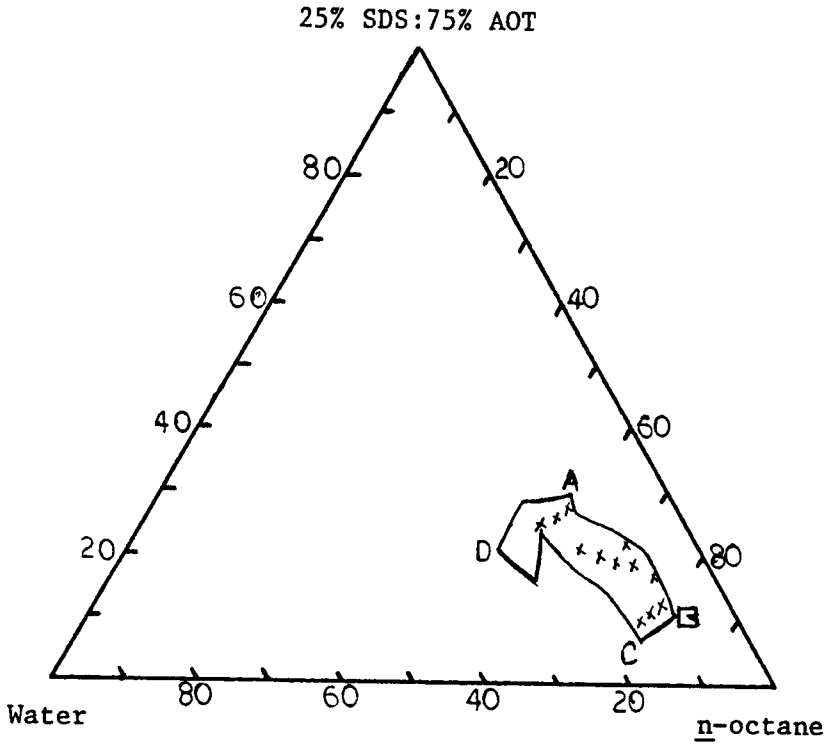


Figure 18. SDS/AOT/n-octane/water ternary phase diagram showing the one phase region.

TABLE VI

SPECIFIC CONDUCTIVITY DATA FOR SDS/AOT/WATER/n-OCTANE MICROEMULSIONS

Solution Number	wt% Oil	wt% Water	wt% Surfactant	Specific Conductivity $\Omega^{-1}cm^{-1}$ (x 10^{-4})
1	74	13	13	2.85
2	62	20	18	2.81
3	64	17	19	1.27
4	63	19	18	2.51
5	62	20	18	3.18
6	61	21	18	3.50
7	59	23	17	0.174 (two phase)
8	79	11	10	1.29
9	78	12	10	1.94
10	77	13	10	0.224 (two phase)
11	58	20	22	1.35
12	53	27	20	8.93
13	56	23	21	2.88

found to be conducting throughout the one phase region. As water was added there was a slight drop in conductance but, nothing like the percolative effect seen in the DDAB system. Recall that in percolation a change in conductance of several orders of magnitude is generally observed.[43] When the system went into two phases, there was a dramatic drop in conductance. This is to be expected since the surfactant is coming out of solution and is no longer stabilizing the water conduits.

Several potential microemulsion systems have been presented. In all our attempts we were trying to produce a system with a surfactant that had the curvature requirements from the packing parameter. The sodium bis(n-nonyl)sulfosuccinate was chosen because of its solubility properties. However, this surfactant was not able to form a microemulsion in n-hexane. The solvent met the specifications in that it was a shorter alkane chain than the nine carbon tail of the surfactant. Therefore, the solvent should have been taken up by the hydrocarbon tails. The sulfosuccinate is an anionic surfactant while DDAB is a cationic surfactant. The difference in headgroups would cause the greatest difference in the hydrophile-lipophile balance. The sulfonate head group is more hydrophilic[22] than the ammonium head group which would affect the way in which the surfactant would partition itself along the water-oil interface. In order for a microemulsion to form the surfactant must saturate the oil-water interface and not prefer to partition itself into one of the bulk phases. The sulfosuccinate apparently was not as efficient at meeting this requirement as DDAB.

When we mixed surfactants we were trying to pull from opposite ends of the packing parameter spectrum to find an intermediate value. AOT would be expected to have a $v/\underline{a}l_c > 1$. Hence, if the problem with 7 (p. 44) was that it had a $v/\underline{a}l_c < 1$ then it should be possible to vary the mole fractions and obtain a value of approximately 1. This would meet the theoretical requirements for a bicontinuous system. When this system did not work, our mixture was changed to SDS and compound 7 (p. 44). The SDS would have a $v/\underline{a}l_c = 1/3$. Hence, if 7 was opposite having a $v/\underline{a}l_c > 1$, we should have been able to adjust the mole fractions and obtain the bicontinuous system. Both mixed surfactant systems failed. This was probably due to lack of flexibility of the interfacial boundary, which prevented the surfactant layer from curving. Instead we had macrocrystals which would not melt, resulting in thick geled systems. Finally, the AOT/SDS mixture produced a microemulsion with n-octane and water. It was interesting to note that the mole fractions used, 0.75 AOT and 0.25 SDS, give a packing parameter value of 0.83 assuming values of 1 and 1/3 for AOT and SDS respectively. This is very close to the value reported for DDAB by Evans and Ninham. The AOT/SDS/n-octane/water system was one phase at high oil content. We therefore expected to have an oil continuous system with inverted micelles by analogy to an AOT system. This would have been a non-conducting system. The fact that the system was conducting was surprising. The SDS must be having some effect on the hydrophile-lipophile balance relative to pure AOT. There are several possible explanations, the system could be bicontinuous or if there are in fact reverse

structures containing the water they must be involved in "sticky" collisions. A "sticky" collision would entail two particles colliding, becoming one particle, and then splitting into two particles again. When the particles combine they are able to exchange contents of their water pools. Furthermore, we may not be observing a percolative transition due to extremely viscous systems which were produced as the water content increased.

In conclusion we have found that mixing 25% SDS and 75% AOT produces one phase systems with water and n-octane. The exact structure of the system was not known. However, conductance measurements indicated that the system had connected water paths. The exact structure could be determined using SANS.

C. Gelatinization of Water-Continuous Phases

In Switzerland the research group of Professor Luisi[44] has reported the use of gelatin to indicate the presence of a water-continuous phase. Their work has been concerned with systems containing AOT/isooctane/water. AOT forms w/o aggregates at room temperature. However, when these systems are heated to between 45 and 60°C phase separation occurs producing a water-continuous phase. If gelatin in water is present as the water phase when phase separation occurs, it is possible to produce a rigid gel by rapidly mixing the two phases while cooling the system in ice. Figure 19 shows the region of water content where a 0.140 M solution of AOT in isooctane will gel by this process. This is the region where heating gives the phase separation to the water continuous phase.

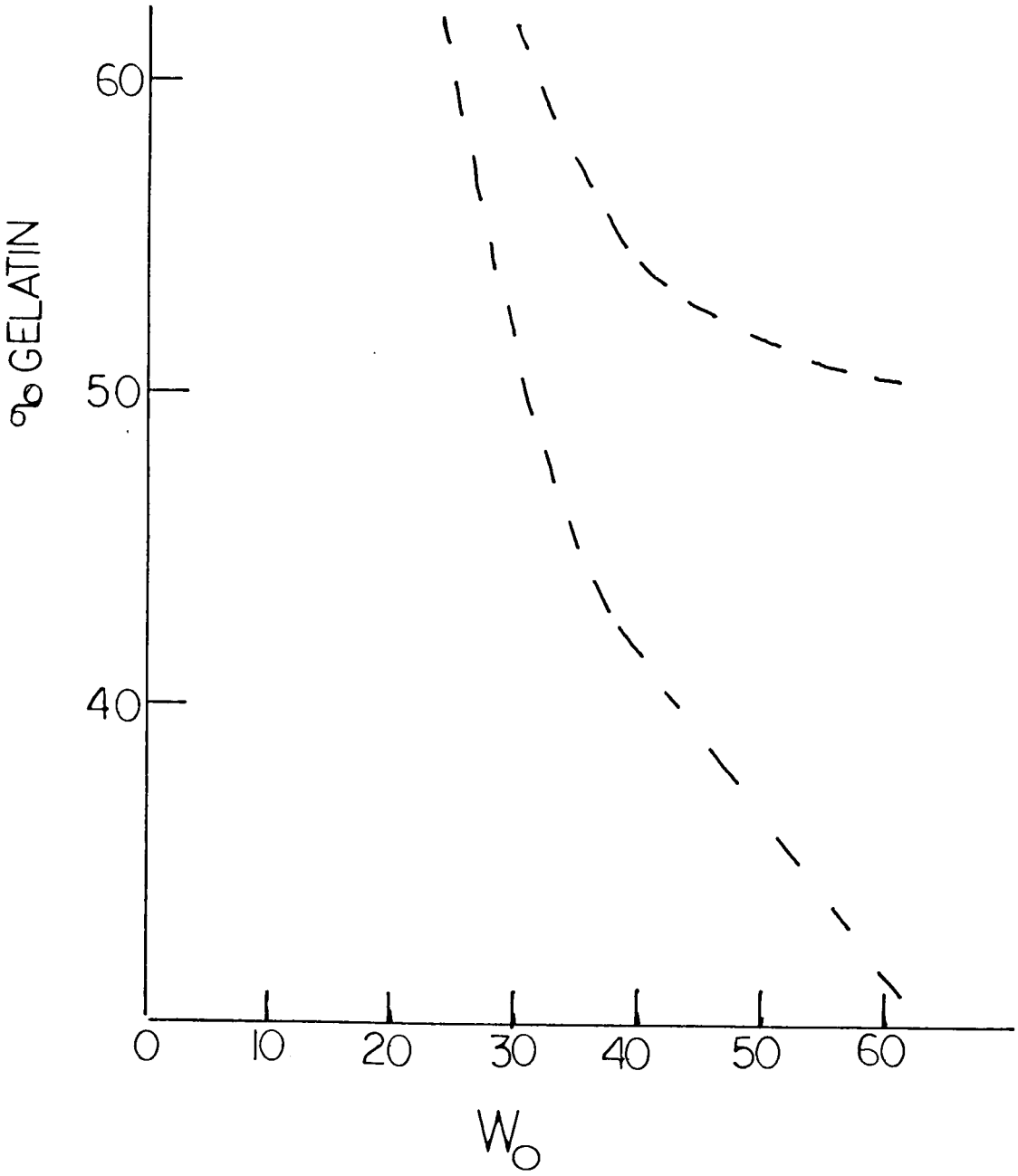


Figure 19. Phase diagram for gelatinization of 0.140 M AOT/isooctane/water. (% gelatin is the percent gelatin present in the water phase and W_o is the molar ratio of surfactant to water.)

The basis for this work is as follows: if the water is connected and it has gelatin dissolved in it then it should be possible to gel the system through the interconnecting water pathways. This approach works very nicely with AOT. We hoped that we could distinguish the two types of microstructure present in the DDAB microemulsion system using this technique. The conducting region is bicontinuous and should therefore form a gel. The nonconducting region is made up of water in oil spheres and should not form a gel.

There are two techniques for gelatinization of the AOT system. If there is 35-40% gelatin present in the water, then the water and gelatin are slurried before addition of the AOT/isooctane solution. If there is greater than 40% gelatin present in the water, then the gelatin is added to the AOT/water/isooctane system all at once. Figure 17 (p. 47) is the phase diagram for the DDAB microemulsion system with n-octane as the oil. All the points marked were tested for gelation. Both of the above techniques were used for 35%, 25%, 15%, 10%, 5%, and 1% gelatin in water. None of the attempts to gelatinize the DDAB system were successful. Once the gelatin was introduced the system could not be made one phase.

These results did not mean that the premise of being able to gel water-continuous phases was wrong. The results do however point out that the DDAB microemulsions are very sensitive to added substances. Apparently the system requires an exact interaction between the three components; the forth component, gelatin, disturbs this. DDAB is very insoluble in oil while AOT is soluble in oil up to extremely high

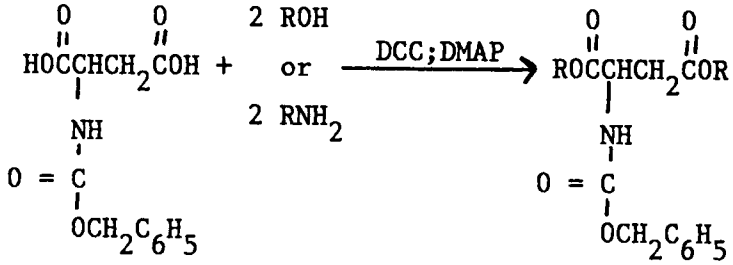
concentrations. Neither surfactant is particularly soluble in water. The AOT systems which form gels, have a lower surfactant-to-oil ratio and higher water to surfactant ratio than the DDAB system. In preparing the DDAB systems it was observed that the one phase solution was formed slowly. They took anywhere from 30 minutes to an hour to clear. Addition of water precipitated surfactant which took an equivalent amount of time to redissolve in the solution. Therefore for two reasons, (1) insolubility of the DDAB in oil and water and (2) sensitivity of the interfacial balance, introduction of gelatin preturbed the system and could not be used for detection of water-continuous phases.

CHAPTER IV

METHODS AND MATERIALS

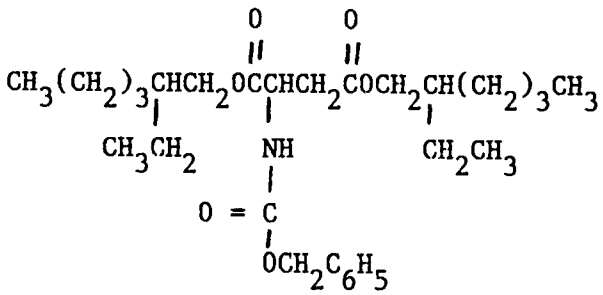
A. Synthesis and Characterization of Cationic Surfactants

1. The dicyclohexylcarbodiimide coupling reaction[45]



The experimental conditions used for the esterification of N-carbobenzoxy-L-aspartic acid with either 2-ethyl-1-hexanol or 1-octanol were the same. A 500 mL flask was charged with 200 mL of methylene chloride, 0.10 mole of 1,3 dicyclohexylcarbodiimide (DCC), 0.04 mole of N-carbobenzoxy-L-aspartic acid, and 0.004 mole of 4-dimethylamino-pyridine (DMAP). To this solution was added 0.06 mole of alcohol (dissolved in 50 mL of methylene chloride) through an addition funnel over a period of 20 minutes at which time the addition funnel was replaced with a stopper. The reaction was stirred with a magnetic stirring bar under a nitrogen atmosphere for twelve hours. During this time the by-product of the coupling reaction, dicylohexylurea, precipitated. The reaction mixture was filtered to remove the precipitate. The filtrate was washed consecutively with 100 mL water, twice with 100 mL 5% acetic acid, and 100 mL saturated sodium chloride. The washed solution was then dried over anhydrous magnesium sulfate for several hours, after

which time the solution was filtered and the solvent removed. This process afforded a yellowish to brown oil which was placed on a silica gel column and eluted with 5% acetone in hexanes. The silica gel column was prepared using 30 g of 200 mesh silica gel per gram of compound and was packed using hexanes. The first 250 mL fraction was always discarded. The pure aspartates were isolated from the next 400 mL fraction; after that a mixture of compounds came off the column with were not further characterized. This process produced the pure protected aspartates, 9, and 10, shown below in approximately 50% overall yield.



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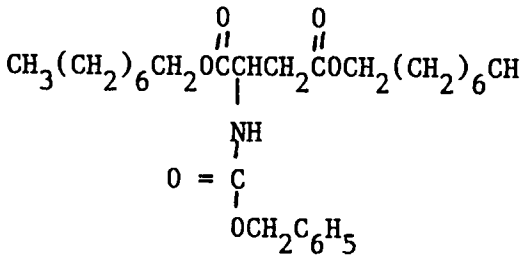
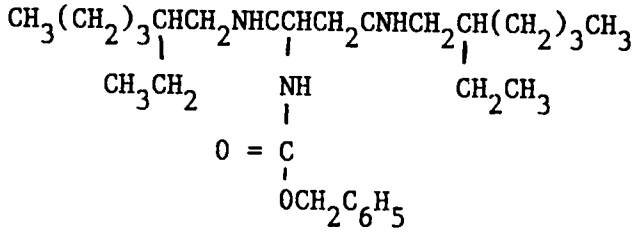


10

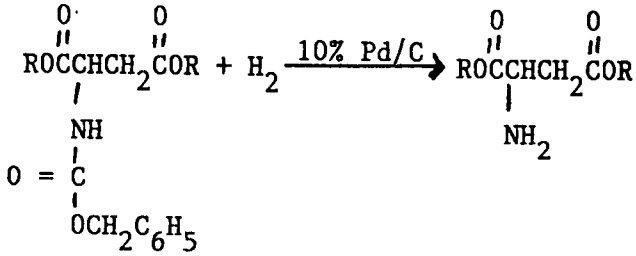
Synthesis of the diamide[46] was carried out similarly. A 500 mL flask was charged with 200 mL methylene chloride, 0.04 mole

N-carbobenzoxy-L-aspartic acid, 0.080 mole of 2-ethyl-1-hexylamine, 0.004 mole DMAP. This solution was cooled to 0°C, at which time 0.08 mole DCC was added. The mixture was stirred with a magnetic stirrer for 30 minutes at 0°C. After this time the reaction mixture was allowed to warm up to room temperature and left to stir for 18 hours. Again, the dicyclohexylurea precipitate formed and was removed by filtration. Removal of the solvent yielded a white solid which was purified by multiple recrystallizations from ethyl acetate. The pure protected diamide, 11, shown below was finally isolated with an overall yield of 30-40%.



11

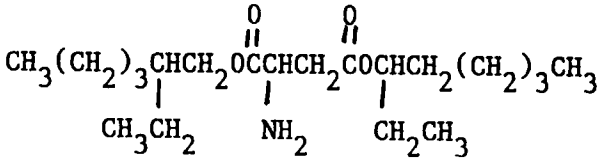
2. Removal of the carbobenzoxy protecting group[47]



(10)

Approximately 0.007 mole of protected compound was dissolved in 70 mL of t-butyl alcohol, and one gram of the catalyst (10% Pd on carbon) was suspended in the solution. The reaction vessel was then placed on a hydrogenator and charged to 30 psi. The reaction vessel was shaken

for 24 hours then filtered to remove the catalyst. Removal of the solvent yielded a clear viscous oil which was placed on a vacuum line to insure removal of all solvent. No further purification was needed and the protected compounds, 12-14, shown below were obtained in at least 90% yield.



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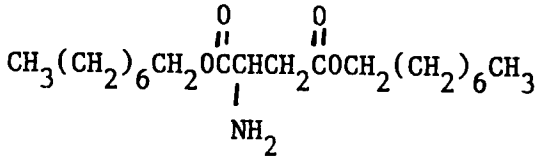

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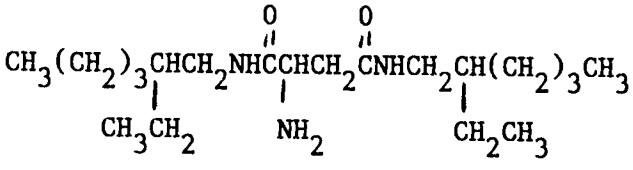
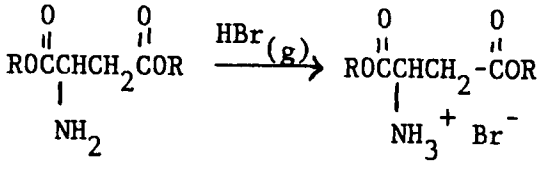


14

3. Formation of the hydrobromides



(11)

The hydrobromides of the deprotected compounds 12-14 were made by dissolving 2-3 grams of the compound in 15 mL of isooctane. HBr gas was

then bubbled into the solution. As the HBr was added the solutions were stirred with a magnetic stirring bar. The reactions were followed using thin layer chromatography (TLC). The diesters and the diamide were developed in 10% and 20% acetone in hexanes respectively. As the reactions proceeded samples from the reaction mixture showed the spot for the starting material fading after 30 minutes and a new spot appearing at the origin, which was indicative of the hydrobromide. For the two aspartates the solvent was removed to yield an orange oil which was placed on the vacuum line to insure removal of all the unreacted HBr. The oil was then dissolved in methanol and stirred with a magnetic stir bar for several hours with decolorizing carbon. After removal of the methanol a clear viscous oil was obtained which was then placed on a freeze dryer for 24 hours. This yielded compounds 2 and 3. Compound 3 was further purified by recrystallization from isooctane. When the solution containing the deprotected diamide was treated with HBr the product precipitated out of solution. Therefore, compound 4 was isolated directly by decanting the solvent and placing the precipitate on a vacuum line. This yielded a hard crystalline solid which was intractable.

4. Thin layer chromatography and characterization

All of the reactions described above were followed by thin layer chromatography. The diester compounds were developed in 10% acetone in hexanes and visualized with iodine. The diamide compounds were developed in 20% acetone in hexanes and visualized using 10% phosphomolybic acid in ethanol. The compounds were further characterized by proton

Nuclear Magnetic Resonance (NMR) spectroscopy and elemental analysis. These results along with R_f values are given in Table VII. All the NMR spectra were obtained using a Varian T60-A spectrometer. The compounds were run in $CDCl_3$ solutions with 1% tetramethylsilane (TMS) added. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

B. Purification of AOT

Aerosol OT was purified by the following method, which is an abbreviated form of the procedure followed by C. A. Martin.[15]

The AOT was dissolved in a minimum amount of anhydrous methanol and suction filtered through a 0.80 micron polycarbonate filter (Nucleopore) to remove any salts. The filtrate was stirred with decolorizing carbon for 12 hours and then filtered. After removal of the solvent the recovered AOT was dried in vacuo for 24 hours at 75°C.

C. Purification of DDAB

DDAB was purified by the following procedure, which was obtained from reference 39.

The DDAB was dissolved in anhydrous methanol and stirred for 12 hours with decolorizing carbon. The solution was filtered and the solvent removed. The recovered DDAB was recrystallized from ethyl acetate as a white powder which was dried for 24 hours in vacuo at 50°C.

TABLE VII

NMR DATA AND ELEMENTAL ANALYSES FOR ALL COMPOUNDS SYNTHESIZED

Compound	R_f	Elemental Analysis	calc.	expt.	^{1}H NMR ($CDCl_3$)
9	0.69	%C %H	68.45 9.16	68.53 9.21	δ 0.90 (12H,d), 1.4 (18H,s), 3.0 (2H,d), 4.1 (4H,t) 4.6 (1H,m), 5.2 (2H,s), 5.9 (1H,d), 7.4 (5H,s)
10	0.53	----------			δ 0.90 (12H,d), 1.4 (18H,s), 2.0 (2H,d), 2.8 (2H,m), 4.1 (4H,t), 4.5 (1H,m)
11	--	%C %H	54.84 9.13	54.70 9.23	δ 0.90 (12H,d), 1.4 (18H,s), 3.35 (2H,m), 4.1 (4H,t), 4.6 (1H,m), 8.5 (3H,br.s)
12	0.65	%C %H	68.45 9.16	68.29 9.11	δ 0.90 (6H,d), 1.4 (24H,s), 2.9 (2H,m), 4.1 (4H,t) 4.6 (1H,m), 5.2 (2H,s), 5.9 (1H,d), 7.4 (5H,s)
13	0.51	----------			δ 0.90 (6H,d), 1.4 (24H,s), 2.1 (2H,br.s) 2.8 (2H,m) 2.8 (2H,m), 4.2 (5Hbr.m)
14	--	%C %H	54.84 9.13	54.94 9.24	δ 0.90 (6H,d), 1.4 (24H,s), 3.4 (2H,br.s), 4.3 (4H,m), 4.8 (1H,br.s), 8.3 (3H,br.s)
2	0.43	%C %H	68.90 9.63	68.77 9.61	δ 0.90 (12H,d), 1.4 (18H,s), 2.6 (2H, m), 3.2 (4H,br.t), 4.5 (1H,br.m), 5.1 (2H,s), 6.6 (3H,br.m), 7.3 (5H,s)
3	0.34	----------			δ 0.90 (12H,d), 1.4 (18H,s), 2.2 (2H,s), 2.8 (2H,m), 3.3 (4H,br.m), 3.9 (1H,br.m), 7.0 (1H,br.s), 7.8 (1H,br.s)
4	--	%C %H	55.10 9.60	52.38 9.31	----------

Note: s = singlet; d = doublet; t = triplet; m = multiplet; br. = broad.

D. Conductivity

The conductimetric apparatus consisted of a Wayne-Kerr Automatic Precision Bridge model B904 and a 500 mL Kraus-Erlenmeyer cell. The cell constant was determined to be 0.5418 cm^{-1}. [48] The accuracy of the bridge at 1kHz was ±0.05% ±0.5 m for a resistance range of 0Ω to 10 MΩ. After a warm up time 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 the leads from the bridge to the cell containing the sample.

All of the conductivity measurements were made at 25.0°C ± 0.1°C. Prior to each measurement the cell containing the solutions was placed in a constant temperature oil bath and allowed to equilibrate for 20 minutes.

Solutions for conductivity measurements were prepared with water obtained by passing distilled water through a Millipore Milli-Q Reagent Water Filtration System. This water had a specific conductivity of 1.72 x 10^{-6} $cm^{-1}\Omega^{-1}$ at 25°C. All the hydrocarbons used to prepare the sample solutions were Aldrich spectroscopic grade. Specific conductivity values were calculated using: specific conductivity = 0.5814 cm / R - conductivity of water.

E. SDS/AOT/n-Octane/Water

Mixtures of SDS:AOT were prepared with a molar ratio of 25% SDS to 75% AOT. For each solution the SDS and AOT were weighed out separately.

The AOT was then dissolved in the n-octane and this solution was transferred to an ampule with contained the SDS. The water was added and the ampule was sealed. Use of sealed ampules permitted the samples to be studied at elevated temperatures.

When the general area of the one phase region had been determined by the above procedure the studies were carried out titrimetrically. This entailed titrating a mixture of SDS/AOT/n-octane with water. The mixture was stirred with a magentic stirring bar during the titration. By noting the point at which the solution became clear and the point at which it became turbid it was possible to determine the one phase region for the four component system.

F. Gelatinization of Water-Continuous Phases

The gelatinization of hydrocarbon solutions of AOT at relatively high water contents had been demonstrated by Luisi and co-workers.[42] Their experiments were reproduced using AOT purified as described above and two different experimental techniques which were demonstrated to us by G. Zampieri, a co-worker of Professor Luisi.[49]

The purified AOT was dissolved in isooctane as a 0.280 M solution. The experiments were carried out on a 5 mL scale. The amount of water was determined by the desired w_0. The percentage gelatin was based on the grams of gelatin per total grams of gelatin and water. For example, a typical experiment would call for 5 mL of 0.140 M AOT in isooctane, 38% gelatin at a w_0 of 55. This would require 2.5 mL of the 0.280 M AOT solution, which would be diluted to 0.140 M with isooctane. The w_0

would require 0.495 grams of water, therefore 0.303 grams of gelatin would be needed since (0.303/0.303 + 0.495) x 100 = 38%.

The two procedures for gelatinization of the AOT solutions are outlined below.

Procedure I for 35-40% gelatin

1. slurry the gelatin and the water
2. add 2.5 mL of 0.280 M AOT in isooctane
3. heat the mixture to 45-60°C in a water bath with stirring
4. add 2.5 mL of isooctane (diluting the solution to 0.140 M AOT) and continue heating and stirring until phase separation begins
5. cool in ice for 30 seconds
6. shake vigorously until gelatinization begins

Procedure II for greater than 40% gelatin

1. mix 2.5 mL of 0.280 M AOT in isooctane with the water and heat to 45-60°C in a water bath with stirring
2. add the gelatin
3. add 2.5 mL of isooctane (diluting the solution to 0.140 M AOT) and continue heating and stirring until phase separation begins
4. cool in ice
5. shake vigorously until gelatinization begins

The DDAB systems were treated in the manner described above using n-octane as the solvent. The only other variation was that the amounts of surfactant, hydrocarbon, and water were based on the weight percents as taken from the phase diagram.

G. Static Small-Angle Neutron Scattering

Figure 20 depicts the 30 m spectrometer at the National Center for Small-Angle Scattering Research (NCSASR) of the Oak Ridge National Laboratory (ORNL). The spectrometer design and operation have been described in several recent reviews.[27,50,51]

The scattered neutron intensity, I, was detected for many scattering angles, Q, at once by a helium-filled Kopp-Borokowski two-dimensional multidetector having an active area of 64 x 64 cm (thus 4096 detector elements).

SANS measurements were carried out on AOT, BC8ASP, and NC8ASP in fully deuterated isooctane at the concentrations shown in Table III (p. 35). The measurements were made with a neutron wavelength of 4.75 Å at three different sample-to-detector distances (SDD); 1.4 m, 2.4 m, and 12 m. The sample cells were quartz cells from NSG precision cells, Inc. and had a path length of 2 mm. Sample cells were mounted on a motor-driven slide which was lowered into the thermostated sample chamber. All measurements were made at 25.0 ± 0.1°C.

The raw scattering data were manipulated using programs developed by NCSASR's staff. First the data were corrected for background (I_b, determined with the beam blocked by a sheet of cadmium) and empty cell (I_e) scattering.

$$I_{s,corr} = (I_{s,total} - I_b) - (T_s/T_e)(I_e - I_b) \qquad (12)$$

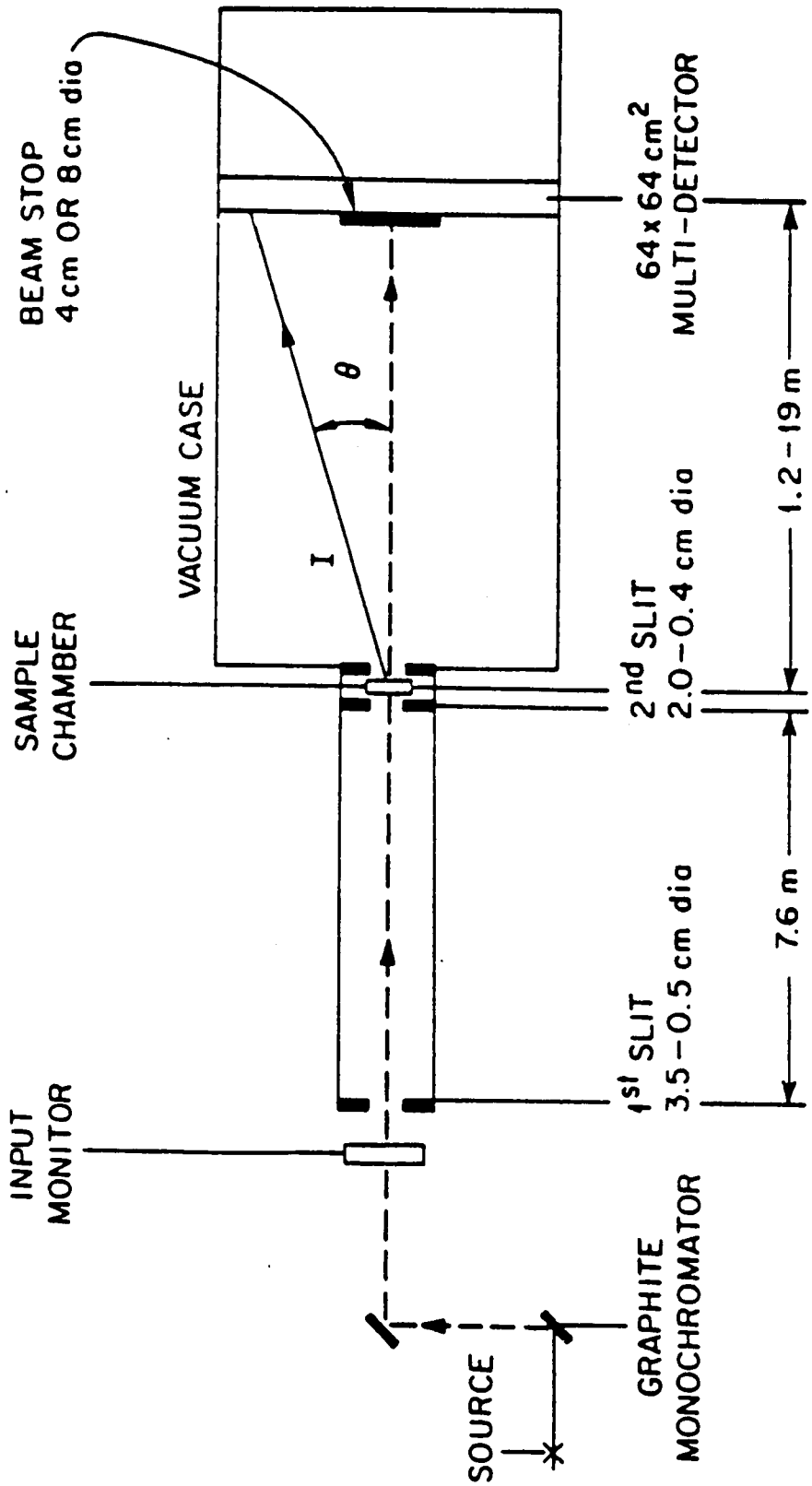


Figure 20. Schematic layout of 30-meter SANS instrument.

Here T_s and T_e are neutron transmission coefficients for the sample and the empty cell respectively; $I_{s,corr}$ was computed for each detector element using equation 11.

Since, the samples were in solution, an evaluation of the scattering intensity due to the solvent (I_{solv}) was also necessary. The raw data for measurements made on the pure sample were corrected as above. The sample solutions were then corrected for solvent contributions.

Each corrected array was then radially averaged to give values of the absolute scattering intensity vs. Q. Scattering was put on an absolute scale using water (at 1.4 m and 2.4 m) or Al-4 (at 12 m) for standard scattering.

H. Materials

Aerosol OT (AOT or sodium bis(2-ethylhexyl) sulfosuccinate) was purchased from Fluka, purification is described.

N-Carbobenzoxy-L-Aspartic Acid was purchased from Aldrich Chemical Company.

1,3 Dicyclohexylcarbodiimide, 99% (DCC) was purchased from Aldrich Chemical Company.

Didodecyldimethylammonium Bromide (DDAB) was purchased from Eastman Kodak, purification is described.

4-Dimethylaminopyridine, 99% (DMAP) was purchased from Aldrich Chemical Company and recyrystallized once from hexanes.

2-ethyl-1-hexylamine was purchased from Fluka.

Gelatine, granulated USP 250 Bloom was purchased from Fluka.

Methylene Chloride was purchased from Fisher Scientific Company.

1-Octanol was purchased from Fisher Scientific Company.

n-Octane, 99% was purchased from Aldrich.

10% Palladium on activated carbon was purchased from Aldrich.

Sodium dodecylsulfate, specially pure, (SDS) was purchased from BDH Biochemicals, LTD.

2,2,4-trimethylpentane, 98% mol d, was purchased from Cambridge Isotopes Laboratories.

2,2,4-trimethylpentane, spectrometric grade, was purchased from Fisher Scientific Company.

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