1966

Aggregation and Solubilization Properties of Decyl, Dodecyl and Tetradecyl Quaternary Ammonium Salts.

Joseph William Goerner
Louisiana State University and Agricultural & Mechanical College

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QUATERNARY AMMONIUM SALTS

A Dissertation

Submitted to the Graduate Faculty of the 
Louisiana State University and 
Agricultural and Mechanical College 
in partial fulfillment of the 
requirements for the degree of 
Doctor of Philosophy 
in 
The Department of Chemistry

by
Joseph William Goerner
B.A., Rice University, 1957
August, 1966
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<td>DTMAB</td>
<td>Decyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>DTEAB</td>
<td>Decyltriethylammonium Bromide</td>
</tr>
<tr>
<td>DTPAB</td>
<td>Decyltripropylammonium Bromide</td>
</tr>
<tr>
<td>DTBAB</td>
<td>Decyltributylammonium Bromide</td>
</tr>
<tr>
<td>DDTMAB</td>
<td>Dodecyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>DDTEAB</td>
<td>Dodecyltriethylammonium Bromide</td>
</tr>
<tr>
<td>DDTPAB</td>
<td>Dodecyltripropylammonium Bromide</td>
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<tr>
<td>TTMAB</td>
<td>Tetradecyltrimethylammonium Bromide</td>
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<td>TTPAB</td>
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<td>TTMAC</td>
<td>Tetradecyltrimethylammonium Chloride</td>
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The aggregation and solubilization characteristics of a series of quaternary ammonium salts were studied in the hope of determining more factors which would help devise a model for explaining the properties of colloidal electrolyte aggregates. Both the length of the hydrophobic tail and the size of the hydrophilic head were varied in the investigation. Solubilization, surface tension and spectral studies were performed.

The critical micelle concentration (cmc) was determined for some decyl, dodecyl and tetradecylammonium bromides in pure water by means of surface tension measurements. The cmc was determined for the same substances in the presence of benzene by means of a spectrophotometric technique.

Head size parameters were calculated from the surface tension data. The linear relationship between the head size parameter and square of the number of carbon atoms in the short alkyl side chain was verified. A linear relationship between the ln cmc determined in the presence of benzene and chain length of hydrophobic tail was reconfirmed.

Spectra of benzene in a variety of solvents,
including numerous detergent solutions, were determined. By subtracting the spectrum due to the benzene in the aqueous phase, the spectrum of the micellar benzene was obtained. It was concluded from the character of the spectra that the benzene was located in the organic interior of the micelle.

The following model was proposed to explain the results of this work and previous work in this laboratory. The aggregate is spherically shaped and has a liquid organic core that is surrounded by an organic-water interface. The water penetrates into the micelle and surrounds the first five to six methylene groups in the hydrophobic tail. This penetration reduces the effective solubilizing volume of the aggregate.

Miscellaneous studies were done on the partitioning of quaternary salts between water and benzene and on the analysis of detergent-benzene solution by means of a radioisotope technique.
CHAPTER I

INTRODUCTION AND SURVEY OF THE LITERATURE

Colloidal electrolytes exhibit peculiar properties in both the bulk of the solution and the surface phase. All these substances have approximately the same molecular design, a large lyophobic part on one end and a lyophilic part on the other end. In this discussion, the only solvent to be discussed will be water, therefore the more specific terms hydrophobic and hydrophilic will be used.

These substances form large thermodynamically stable aggregates called micelles which form over a narrow concentration range known as the critical micelle concentration (cmc) and they exist at concentrations higher than the cmc. They are also adsorbed in the liquid-air interface with a reduction of the surface tension. Above the cmc, these substances solubilize water insoluble
The factors that control the cmc, aggregate size, and solubilizing power are not well determined and evaluated. Many kinds of experiments, and theoretical investigations have been conducted and many models have been suggested in attempts to better understand this aggregation process. The gross structure of the aggregate consists of a protective hydrophilic surface layer around a hydrophobic core. Further discussion of the size and shape and their relation to the length of the hydrophobic tail and size of the hydrophilic head follows; first, however, a short discussion on water structure seems to be in order.

A. Water Structure and Solubility of Organic Molecules

At one time it was thought that water did little more than act as a high dielectric medium that reduced the forces between ionic groups in solution. Even after the structural characteristics of water were well known, many investigators still considered water to have a secondary effect on aggregation processes. Today, however the effects of water structure are being introduced into the explanation of most aqueous thermodynamic, kinetic, mechanistic and structural phenomena.
Water's unusual properties maximum density at $4^\circ\text{C}$, high boiling point, volume change at fusion have been the focal point of theoretical works over the last half century. The first structural model was that of long hydrogen bonded polymers.$^1$ Later, Bernal and Fowler$^2$ postulated the broken down ice structure which assumes that most of the hydrogen bonding in the solid phase remains in the liquid state. Adaptations of this model have been presented by numerous investigators in attempts to explain the properties of water.

One of the more recent approaches by Nemethy and Scheraga$^3$ uses a model similar to one proposed by Frank and Wen.$^4,5$ Water is pictured as being composed of an equilibrium distribution of short lived clusters, which are highly hydrogen bonded, and monomer molecules that

$^1$For a review of earlier theories, see for example, H. M. Chadwell, Chem. Revs., IV (1927), 375.


have a high coordination number. These clusters have half lives of the order of $10^{-10}$ second.

Dissolution of substances in water and the mechanism by which water structure aids the solubility of paraffin hydrocarbons are the real interests. A solute particle can either be dissolved interstitially or fit into the water structure. Frank and Evans\(^6\) proposed that organic material was located in the holes in the ice-like structure, and in fact, proposed that the presence of the organic molecules facilitated the formation of an ice structure around the molecule. This structuring of the water in the presence of the organic molecule is called the "iceberg effect." This region of water around the organic molecule has a low enthalpy and a low entropy.

Nemethy and Scheraga\(^7\) proposed a similar explanation. The energy levels of the completely hydrogen bonded water molecules are lowered by the presence of the hydrocarbon. All the other species of water have higher energy, therefore, the ice-like sheath is stabilized in the presence of the hydrocarbon.

---


The ionic and organic portions of the detergent molecules will be considered to interact with the water as two separate particles. The water surrounding the ionic head is considered to be similar to that around any singly charged cation. The water around the organic portion is assumed to have the iceberg structure. If the organic portions are removed from the water and are placed together and if the ionic groups form a protective surface layer, the entropy of the water should increase and the enthalpy should increase; thus the dissolution is an entropically driven reaction.

B. Micellization

Micellization results from the counterbalancing of two or more forces. The first simple explanation was given by Debye.\(^8,9\) He suggested that the two opposing forces were the van der Waals attractive force of the hydrocarbon tails and the coulombic repulsive force of the ionic heads. An expression for the free energy of the micelle was derived and then minimized to obtain the most stable aggregate. The final expression contained

\(^8\)P. Debye, \emph{J. Phys. Chem.}, \textbf{LI\textsc{II}}, (1949), 1.
\(^9\)P. Debye, \emph{Ann. N. Y. Acad. Sci.}, \textbf{LI} (1949), 575.
parameters that could be evaluated with the use of experimental results. These calculated parameters were consistant with results from other experiments; thus, Debye's model gained considerable support.

Ooshika,¹⁰ Hobbs,¹¹ and Shinoda¹² modified this technique by adding surface effects and the entropy contribution which Debye had neglected.

Reich¹³ pointed out that there was a fundamental error in Debye's work because Debye had minimized the free energy of the micelle instead of that of the solution. Also, Reich extended the theory to include non-ionic detergents and postulated that the surface of the micelle must be covered with the polar heads of the surfactant molecules. This conclusion agrees nicely with a model used by Tartar¹⁴ to predict the molecular weights of detergents. This model and modifications of it have been

used by previous investigators\textsuperscript{15,16} in this laboratory.

Benson and Hoeve\textsuperscript{17} presented the first statistical mechanical approach in which they used the McMillan-Mayer theory of solutions. In this particular technique, the solvent is considered to be similar to the vacuum in imperfect gas calculation.

Using Hill's theory of physical clusters, Aranow\textsuperscript{18} developed a more general theoretical treatment of micelle statistics. This more general theory provides a common foundation for the previous approaches and reveals the relationship between them. His approach summarizes the nature of the approximations that are normally used, and the appropriate interaction terms necessary for improving the existing theories are displayed.

Recently, Poland and Scheraga\textsuperscript{19,20} have published

\textsuperscript{15}R. L. Venable, Ph. D. Dissertation, Louisiana State University, Baton Rouge, 1963.

\textsuperscript{16}G. K. Brashier, Ph. D. Dissertation, Louisiana State University, Baton Rouge, 1964.


\textsuperscript{18}R. H. Aranow, J. Phys. Chem., LXVII (1963), 556.

\textsuperscript{19}D. C. Poland and H. A. Scheraga, J. Phys. Chem., LXIX (1965), 2431.

two papers about the statistical nature of both non-ionic and ionic detergents. Their work is by far the most readable statistical approach for the person who is not adept in statistical mechanics. In their works, they also used cluster theory and considered the solvent to be a continuous dielectric medium. They divided the partition function for the aggregate into four parts which are the external (translational and rotational), the solvent (hydrophobic bonding), the internal (mobility of hydrophobic tails in aggregate) and the electrostatic portion. They explained the effect of each part of the total partition function. In conclusion, they postulated that the change in the hydration sphere for the polar part of the micelle should be included in the treatment.

C. Shape

Spheres,21,22,23 lamellae,24,25,26,27 and

26J. Stauff, Kolloid-Z LXXXIX (1939), 224, XCVI (1942),
244.
platelets\textsuperscript{28} and rods\textsuperscript{29} have been postulated to be possible shapes for the micelles in order to explain the results of a manifold of experiments such as x-ray diffraction, light scattering, diffusion, electrophoretic mobility, and flow birefringence.

There is still disagreement about the shape of micelles. The majority of investigators today would not argue against the use of spherical micelles as a model for the aggregates in dilute solutions, however, most would agree that larger nonspherical micelles form in the more concentrated solutions.

D. Critical Micelle Concentration

The micellar shape, stability and size have been considered; next, the equilibrium between those aggregates and the monomer in solution will be discussed. The abrupt formation of aggregates can be explained by either the mass action law\textsuperscript{30,31} or a pseudophase separation.\textsuperscript{32}

\textsuperscript{28}G. A. Hoeve and G. C. Benson, \textit{loc. cit.}
\textsuperscript{32}E. Hutchinson, \textit{et. al.}, \textit{Z physik Chem. (Frankfurt)}, \textbf{V} (1955), 344.
The abrupt changes in properties such as surface tension, equivalent conductance and solubilization of organics are all reminiscent of those in phase separations. A transition of this character can also be explained by the application of the mass action law to the equilibrium between the single species and the micelles as long as the aggregates have large aggregation numbers. Both models have been used to explain experimental data, but the controversy remains.

There is also disagreement concerning the existence of aggregates below the cmc. In this laboratory, no evidence that supports the existence of such aggregates has been found. It has been assumed that no micellization occurs until the cmc is reached.

Numerous factors control the cmc. By far the most extensively studied factor is the effect that the length of the hydrophobic tail has on the cmc. It has been found both experimentally and theoretically that the logarithm of the cmc is proportional to the negative of the number of methylene groups in the hydrophobic

\[33^3\]

J. W. McBain, loc. cit.

\[34^3\]

\[35^3\]
chain. Results obtained in this laboratory by Brashier and Venable reconfirm the following equation.

$$\log \text{cmc} = A - Bm$$

in which

$m$ is the number of carbon atoms in the hydrophobic chain and $A$ and $B$ are constants that are discussed below.

The constant $B$ is directly proportional to the change in free energy of transferring a methylene group from water to the hydrocarbon core. In Scheraga's terminology, $B$ is proportional to the free energy of formation of the hydrophobic bond. The constant $A$ depends upon the nature of the hydrophilic of the head. Another empirical relationship of the same form between the log cmc and the total length of the detergent molecule was presented by Klevens.\textsuperscript{36}

Brashier also found an empirical relationship similar to the one above, but the log cmc was related to the total number of methylene groups in the hydrophilic head when the tail length was constant.

Studies of the effects on the cmc due to structural characteristics of the detergent molecule have been

\textsuperscript{36}H. B. Klevens, \textit{J. Am. Oil Chemists' Soc.}, XXX (1953), 76.
conducted. The cmc increases as the number of polar
groups is increased.\textsuperscript{37} The cmc increases as the ionic
head is moved from the terminal position toward the
middle of the hydrophobic chain.\textsuperscript{38} Brashier and Venable
found that the cmc decreased as the head size was
increased.

The cmc is also affected by both organic and
ionic additions. The cmc decreases with addition of
salt.\textsuperscript{39,40} As the result of experiments, the following
empirical relationship has been found.

\[ \ln \text{cmc} = K_g \ln C_i + \text{const.} \]

in which $K_g$ is an experimental constant and $C_i$ is the
concentration of the gegenions. A similar equation was
derived by Hobbs.\textsuperscript{41}

It has also been found that the cmc decreases

\textsuperscript{39}M. L. Corrin and W. D. Harkins, J. Am. Chem.
\textsuperscript{40}E. Hutchinson and L. Winslow, Z physik Chem.
(Frankfurt), II(1957), 165.
\textsuperscript{41}Hobbs, loc. cit.
in the presence of long chain alcohols, paraffin hydrocarbons and aromatic hydrocarbons. Similar relationships between the logarithm of cmc and the total number of carbons in the hydrophobic chain have been presented.

E. Surface Tension

The surface free energy or surface tension of water is one of the physical properties that is most affected by the addition of detergents to water. These substances are strongly adsorbed in the air-liquid interface or organic-aqueous interface. In this discussion, only the air(inert gas)-liquid interface will be considered. All the following statements could also be applied with few changes to organic-aqueous interfaces.

The "surface phase" will be considered to be a separate phase in equilibrium with the bulk phase. The detergent molecules in solution are distributed between these two phases. Since the molecular surface energy can be reduced by the expulsion of the hydrophobic tail into the gas phase, the concentration of the detergent


molecules in the surface phase is much greater than that in the bulk.

Thermodynamic expressions that relate surface tension and bulk activities can be derived. Comprehensive discussions of surface thermodynamics are given by Guggenheim\(^{44}\) and Adams.\(^{45}\) For more specific discussions of the adsorption of detergents in interfaces, the reader is referred to books by J. L. Moillet,\(^{46}\) et. al., and L. I. Osipow.\(^{47}\)

The following differential equation has been derived by Gibbs with the aid of thermodynamic principles

\[
\frac{d\gamma}{d\ln a_2} = -2RT \Gamma_2
\]

in which

\(\gamma\) = surface tension

\(a_2\) = activity of detergent in bulk phase

\(\Gamma_2\) = surface excess of detergent molecule


The above equation is applicable to ionic detergent solutions that contain no extraneous salt. The surface excess possibly needs explanation. $\Gamma_i$ is the excess number of moles of component $i$ in a portion of the liquid containing unit area of surface compared to a portion in the bulk which contains exactly the same number of molecules of solvent. In other words, the surface excess of the solvent equals zero. The reciprocal of the surface excess is interpreted to be a size parameter.

Due to the rapid change in surface tension with change in detergent concentration below the cmc and the slight or insignificant change above the cmc, surface tension measurements have been extensively used to determine the cmc. If the surface tension of the solution is plotted versus the logarithm of concentration (an approximation of activity) of the detergent, a head size parameter can also be obtained along with the cmc. The reciprocal of $\Gamma_2$ is interpreted to be a measure of the head size.

There are numerous methods for determining the surface tension - Wilhelmy plate, drop weight, ring, static drop, oscillating jet, capillary rise and maximum bubble pressure. In this laboratory, the ring method has been used. All pertinent information concerning this technique will be covered in the experimental
F. Solubilization

Solubilization is the process by which insoluble material is brought into solution by the action of a surfactant. This is not to be confused with increased solubility of insoluble materials by gross changes in the solvent media. The solubility of the insoluble materials is not greatly changed until the detergent concentration exceeds the cmc. The solubilize is supposedly incorporated in the micelle.

During the last fifty years numerous studies have been conducted on a variety of detergents and solubilizates. Both the nature of the detergent and that of the solubilize have been studied in order to determine their effects on the solubilization process. Excellent reviews covering all this work have been given by McBain and Hutchinson,48 Klevens49 and Harris.50

In this discussion, the term solubilizing power

---


will be used. Solubilizing power is defined as the ratio of the number of moles of solubilizate in the micelle to the number of moles of detergent in micellar form.

It has been postulated that the solubilizate can be located in the interior of the micelle, inside but near the hydrophilic heads, and also in the aqueous-micellar interface. Nonpolar organic molecules are sometimes located in the interior of the micelle; x-ray studies demonstrate the expansion of the micelles that occurs when solubilization takes place in concentrated solutions. Absorption spectra can be interpreted to support an interior location of nonpolar solubilizates.

The solubilizing power increases as the hydrophobic chain length increases. The amount of solubilized material depends also on the molecular character of the solubilizate. The size, polarizability


\[5_3^3\] Venable, loc. cit.

\[5_4^4\] Brashier, loc. cit.


\[5_6^6\] Ibid.
and polar character\textsuperscript{57} of the solubilizate influence
the amount that is incorporated in the micellar phase. The type of hydrophilic head and gegenion also influence
the solubilizing power.

Brashier\textsuperscript{58} and Venable\textsuperscript{59} showed that the solu-
bilizing power of a series of quaternary ammonium bromides
that has the same chain length but different head sizes
was constant. These results indicate that the solu-
bilizing power does not depend on the head size of the
hydrophilic head.

The solubilizing power increases greatly as the
extraneous salt concentration is increased. This is one
of the most difficult observations to explain.

Numerous models have been postulated in attempts
to correlate the large amount of experimental data on
solubilization. These shapes correspond to the ones
mentioned previously. Most of the published material
has been based on x-ray diffraction data\textsuperscript{60} which indicates
the micelle swells as nonpolar organic material is solu-
bilized. Other data for polar organics can be interpreted

\textsuperscript{57}J. W. McBain, \textit{Frontiers in Chemistry}, (Vol. 8,

\textsuperscript{58}Venable, \textit{loc. cit.}

\textsuperscript{59}Brashier, \textit{loc. cit.}

\textsuperscript{60}Harkins, Mattoon and Corrin, \textit{loc. cit.}
in a manner that suggests an opening of the micelle around the head and indicates that the materials are solubilized between the detergent molecules near the surface of the micelle.

G. Position of the Solubilizate in the Micelle

In the previous section on solubilization it was stated that nonpolar organic molecules were located in the interior of the micelle, that polar materials are located near the polar heads and that large dye molecules are adsorbed at the micellar-aqueous interface. Since the absorption spectrum of substances depends upon the solvent medium in which the absorbing particle is located, the environment of the solubilized molecules can be determined; therefore, the location in the micelle should become apparent.

Thorough characterization of the interactions between the absorbing particle and the medium has been presented by Bayliss and McRae. These interactions,

\[\text{Ibid.}\]
\[\text{N. S. Bayliss and L. Hulme, Aust. J. of Chem., VI (1953), 257.}\]
\[\text{E. S. McRae, J. Phy. Chem., LXI (1957), 562-572.}\]
which cause shifts in the spectrum, can be related to the index of refraction, the dipole-moment and the absorption spectrum of the solvent system. A general rule applicable to the system that was studied is that \( \pi \rightarrow \pi^* \) benzoid transitions are shifted more to the red in polar solvents than in nonpolar solvents. This rule is followed as long as the solvent system has an amorphous liquid structure. Since water has a highly crystalline structure, especially around organic molecules, it is not surprising to find that the rule is not applicable.

Spectral studies have been done on a few systems in an effort to ascertain their position in the micelle. Ethylbenzene\(^{64}\) was the only small organic molecule used as a solubilizate in such studies. The observed shifts suggested that it was positioned in the interior. The naphthalene spectrum indicated that naphthalene is located between the heads and is positioned so that the long axis runs approximately parallel to the surface and the short axis is perpendicular to the surface.

CHAPTER II

MATERIALS AND EXPERIMENTAL METHODS

A. Preparation and Purification of Materials

All the quaternary salts were prepared by a method similar to that described by Tartar and Scott. The alkyl halides (Eastman) were analyzed with a gas chromatograph and found to be pure. The trialkylamines were vacuum distilled in order to obtain pure material.

When the materials were mixed, a thirty-three percent excess of amine was used in either ethyl or methyl alcohol as solvent. The mixtures were refluxed three days to a week. The alcohol was then removed by distillation and ether was added to the mixture. In some cases a white precipitate formed and in others a viscous oil separated.

\footnote{A. B. Scott and H. V. Tartar, \textit{J. Am. Chem. Soc.}, \textbf{LXV} (1943), 692.}
The purification of the trimethyl and triethyl salts consisted of repeated recrystallizations from alcohol by the addition of ether in a manner similar to that used previously in this laboratory. This technique, however, was not at all satisfactory for the tripropyl and tributyl salts.

Many solvent systems and extraction techniques were used to purify the compounds. Recrystallizations were done from room temperature to Dry-Ice acetone bath temperatures. The work at low temperatures was done in a dry box and all the work on the tripropyl and tributyl salts was also performed in a controlled atmosphere. The solvent systems used were methyl, ethyl and isopropyl alcohol, alcohol-ether, dioxane, ethyl acetate, alcohol-hexane and chloroform-ether. After filtration, the materials were dried at 80°C under high vacuum.

The materials were also dissolved in water and extracted with cyclohexane. The mixture was separated and the water was evaporated under vacuum in a rotary drier. A cationic exchange column in the hydrogen form was used to purify the material; however, once the quaternary salt was absorbed on a site, it could not be removed by eluting with 0.5 N HBr.

Some materials that were finally used gave a
slight minimum in their surface tension curves; thus slight impurities were indicated. This would affect the surface area and cmc values, but the impurities should have little effect on the solubilization work.

The benzene and bromobenzene used for all the solubilization work were reagent grade materials. All the solvents used in the spectral studies were classified as spectrograde. The water was triply distilled.

B. Surface Tension Measurements

The surface tension measurements were made with a ring type tensiometer that has a Christian Becker chainomatic balance for determining the weight necessary to detach the ring from the surface of the solution. This weight was related to the surface tension by the following equation

\[ \sqrt{\frac{Mg}{4R}} \cdot F \]

in which \( \sqrt{\cdot} \) is surface tension in dynes per centimeter;


R is the mean radius of the ring; M is the maximum weight of the liquid; F is a correction factor for correcting for the shape of the liquid held up by the ring and g is the acceleration due to gravity.

The maximum force downward on the ring is equal to the weight added to the beam; therefore, the surface tension is directly proportional to the weight added.

There are some other very small corrections that are suggested by Harkins and Jordan[4], however, they are not necessary in this case. The same ring is used for all measurements; consequently, the following simple expression

\[ \sqrt{V} = kM \]

can be used to determine the surface tension. The value of k is obtained by standardizing with the triply distilled water surface tension of which is known accurately. The solution was placed in a glass water bath through which 30°C water was pumped. Twenty milliliters of triply distilled water was placed in the bath and allowed to come to equilibrium. Then measured amounts of detergent solution were added to the solution. The solution was stirred by a motor driven paddle wheel. The solution was

[4] Ibid.
raised to wet the ring and then lowered. At this point, weight was added to the opposite side of the beam to keep it horizontal. The solution was lowered and weight was added simultaneously until the ring was detached. Great care was taken to eliminate both the vertical and the horizontal motion of the ring.

The value of individual points varied slightly with time and also slight minima were obtained for some of the detergents. Both of these variations are usually the result of small impurities.

C. Absorbancy Measurements

The following experimental procedure was used both for determination of the cmc in the presence of solubilized material and in the determination of the solubilizing power of the detergents. The detergent stock solutions were prepared by weighing the detergents on a Mettler balance and dissolving them in a volumetric flask. The other solutions were prepared by placing aliquots of the standard solution in a volumetric flask and diluting to the mark.

Ten to fifteen milliliters of the detergent solutions were placed in ampules to which approximately 0.2 ml. of benzene was added. The ampules were sealed
and then were shaken periodically by hand.

Previously the solutions had been shaken with a wrist action shaker; however, in many cases quite stable suspensions formed and would not break for weeks or more. To prevent these emulsions from forming, the samples were shaken until a fine dispersion of benzene appeared in the mixture, then they were placed in a rack to separate; in this manner no long lived emulsions formed. The solubilization result for tetradecyltrimethylammonium bromide checked closely with that obtained by the procedure that involved more rigorous shaking; thus attainment of equilibration was assumed.

The ampules were changed slightly to facilitate removal of the solution with less disturbance. Previously the bottom exit tube was pulled down to an outer diameter of approximately 2 mm. and the top tube was 7-8 mm. tubing. When the upper tube was broken, frequently the sudden jolt disturbed the benzene layer on the top and caused a small dispersion of droplets to be mixed in solution. This made it impossible to use the sample until the droplets rose to the top of the solution. For this work both the top and bottom were pulled down to a smaller diameter of 1 mm. These fragile extensions could be broken quite easily without disturbing the solution.
After three or more days of periodic shaking, the solutions were transferred directly to absorbancy cells. By breaking the top tube of the ampule and then breaking the bottom tube, the solution could be drained directly into the cell with no loss of benzene. The absorbance of these samples was recorded with the Cary 15 spectrophotometer. In order to cancel the absorbance of the benzene that was dissolved in the aqueous phase, a water reference saturated with benzene was used. The benzene spectrum from 2650 Å to 2300 Å was recorded in order that the spectral shifts, the absorbancy and the general character of the spectra could be observed. These results will be discussed separately under different headings. In this section only the experimental technique will be covered.

First and foremost it had to be determined whether the saturated benzene solution does or does not subtract out the effect of the aqueous benzene in the surfactant solution. In the concentrated detergent solutions the concentration of the micellar benzene is much greater than that of the aqueous benzene so small errors in subtraction are not noticeable; however, in the more dilute solutions the complete subtraction is quite important since the aqueous benzene concentration is
approximately that of the micellar benzene. For many of the detergents one or more benzene detergent solutions were run at concentrations below the cmc. A straight base line was obtained, and thus equal benzene concentration in both cells was indicated. In addition, when detergent solutions barely more concentrated than the cmc were analyzed, the wave length of the peak of maximum absorption was approximately 2547 Å, which is approximately that of benzene in hydrocarbon, and the peak to valley ratio was approximately equal to that for all the higher concentrations. Both these results indicate that there was complete subtraction of the aqueous benzene from the solution containing benzene in the micelle and in the aqueous media. More discussion concerning the fixed absorption maximum and the peak to valley ratio will follow.

If an absorption spectrum is a combination of two superimposed spectra, one can record either of the spectra independently by using a reference solution containing the other absorbing substance at the proper concentration. If the absorption peaks of the two substances are located at different wave lengths, the differential spectrum will be noticeably different from the parent. The absorption spectrum of the benzene in water is shifted with respect to that in the micelle
so that the peaks of aqueous benzene correspond to the valleys of the micellar benzene. One can tell by inspection if complete subtraction has occurred because the wave length of the maximum will be shifted as the ratio of the two absorbing species is changed. One can also check complete subtraction by calculating the peak to valley ratio for the spectrum and this should be a constant for a particular detergent for all concentrations.

In this work far u. v. Sargent cells were used. The path lengths varied from 0.1 mm. to 5 mm. The slit width was 0.01 mm. The gain was set at 2. Base lines were obtained for all cells and the appropriate corrections were applied. In no case were the corrections greater than 0.004 absorbancy units.

The above procedure was used for the solutions that contained either the benzene or the bromobenzene. The bromobenzene presented one difficulty because it is more dense than water and therefore the excess bromobenzene settled to the bottom of the ampule. The first portion of these samples was discarded because the excess bromobenzene drained out first; then the upper water layer was introduced into the cell and the spectrum was determined.
D. Critical Micelle Concentration with Solubilizate Present

In the previous section, the general experimental handling of the detergent-benzene solutions was discussed. In this section only the procedure for determining the cmc from the absorbancy data will be covered.

The absorbancy of the micellar benzene at a particular wave length is plotted against the detergent concentration. The intersection of the curve drawn through these points with the abscissa will be the cmc because benzene has no absorption at this wave length when no micelles are present.

E. Solubilization

In order to determine the amount of micellar benzene in the detergent-benzene solutions, the well known Beer-Lambert law was used.

\[ A = \varepsilon cl \]

- \( A \) = absorbancy
- \( \varepsilon \) = extinction coefficient
- \( c \) = concentration in moles/liter
- \( l \) = path length in cm

The extinction coefficients for the benzene in the micelles were not available. They were obtained by
determining the amount of solubilized benzene in the solution by another technique, measuring the absorbancy of the solution and back calculating the extinction coefficients with the Beer-Lambert Law.

The extraction method used by Venable and Brashier was the alternate technique utilized to determine the benzene concentration. One to three milliliters of benzene-detergent solution was added to known volumes of cyclohexane. These mixtures were then shaken for 4 to 6 hours. The absorbancy of the cyclohexane layer was determined by means of a Cary 15 spectrophotometer. The amount of benzene was determined from calibration curves that had been obtained. The absorbancy of the same benzene-detergent solutions which were analyzed by the extraction technique was determined. The extinction coefficients of the micellar-benzene were then calculated with the Beer-Lambert Law.
A. Surface Tension

The surface tension data are plotted in the manner discussed previously, i.e., the surface tension versus the logarithm of the concentration. Some of the curves show small minima at the cmc which indicate small amounts of impurities. Figure 1 shows curves for decyltrimethyl, triethyl, tripropyl and tributyl ammonium bromides. The surface areas and the cmc's obtained from these plots are given in Table I.

The cmc of the DTPAB appears to be in error since it falls below that of DTBAB. The hump in the DTPAB curve indicates some irregularity in the data; however, the head size parameter for DTPAB fits nicely with the values obtained for the other three decyl salts.
Surface Tension vs. Logarithm of the Concentration for Decyl Series

Figure 1: Surface Tension vs. Logarithm of the Concentration for Decyl Series
### TABLE I

**SUMMARY OF RESULTS FROM SURFACE TENSION MEASUREMENTS ON DECYL AND DODECYL SALTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>cmc in moles/liter $\times 10^2$</th>
<th>Area/Molecule in sq. Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTMAB</td>
<td>5.0</td>
<td>64</td>
</tr>
<tr>
<td>DTEAB</td>
<td>2.0</td>
<td>89</td>
</tr>
<tr>
<td>DTPAB</td>
<td>1.0</td>
<td>107</td>
</tr>
<tr>
<td>DTAB</td>
<td>1.8</td>
<td>143</td>
</tr>
<tr>
<td>DDTAB</td>
<td>1.3</td>
<td>60</td>
</tr>
<tr>
<td>DDAB</td>
<td>0.37</td>
<td>63</td>
</tr>
</tbody>
</table>
The surface areas are consistent with the values obtained by Brashier and Venable. The decyltrimethyl cmc is 2% lower than the literature values.

Figure 2 gives dodecyltrimethyl and triethyl ammonium bromide plots. The size parameters and cmc's are also tabulated in Table I.

All the data points were time dependent. This dependence has been pointed out before by Venable and numerous other investigators. The values obtained for the first readings after 3-5 minutes of equilibration were used to plot the curves, since the surfactants should have diffused from the bulk in this time. The change in the surface tension was attributed to the slower diffusion of the impurities to the surface.

Figure 3 illustrates the linear relationship between the surface area and the square of the number of methylene groups for the decyl salts. This was first observed by Brashier.¹

B. Absorbancy Results

The general character of the results will be discussed in this section. The cmc's with solubilizate

¹Brashier, loc. cit.
Figure 2 Surface Tension vs. Logarithm of the Concentration for Dodecyl Series
Figure 3  Area per Molecule vs. the Square of the Number of Carbon Atoms per Side Chain for the Decyl Salts
and the solubilizing powers of the detergents will be covered in the following section.

Table II shows the wavelength of the absorption peak of benzene for eight detergent solutions at three different concentrations. The particular concentrations are not given in the table. For each one of the detergents the first value in the table is for a solution just above the cmc and the other two are those for more concentrated solutions. The wavelength in water is also included to illustrate the shifts in the benzene spectra.

Table III includes the peak to valley ratio for benzene in six detergents, for benzene in water and for benzene-detergent solutions that were compared with a pure water reference. The table gives ratios at different detergent concentrations with the dilute solutions appearing on the left and the more concentrated ones on the right. Again the concentrations are not given because the only real interest was to determine if the values were constant over concentrations ranging from those near the cmc to those of concentrated solutions.

Considering the constant value for the wavelength of the micellar benzene absorption peak and the approximately constant peak to valley ratio, one can assume that there was complete subtraction of the aqueous benzene
<table>
<thead>
<tr>
<th>Detergent Benzene Solubilized in</th>
<th>Approximate Detergent Concentrations</th>
<th>Wavelength of Maximum Absorption Peak in Angstroms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Just above the cmc</td>
<td>Intermediate times cmc</td>
</tr>
<tr>
<td>DTMAB</td>
<td>2547</td>
<td>2547</td>
</tr>
<tr>
<td>DTEAB</td>
<td>2547</td>
<td>2548</td>
</tr>
<tr>
<td>DDTMAB</td>
<td>2547</td>
<td>2547</td>
</tr>
<tr>
<td>DDTEAB</td>
<td>2547</td>
<td>2548</td>
</tr>
<tr>
<td>DDTPAB</td>
<td>2547</td>
<td>2547</td>
</tr>
<tr>
<td>TTMAB</td>
<td>2546</td>
<td>2548</td>
</tr>
<tr>
<td>TTEAB</td>
<td>2547</td>
<td>2547</td>
</tr>
<tr>
<td>TTPAB</td>
<td>2548</td>
<td>2547</td>
</tr>
<tr>
<td>H₂O</td>
<td>2535</td>
<td></td>
</tr>
<tr>
<td>Detergent Benzene Solubilized in</td>
<td>Peak to Valley Ratio</td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Approximate Detergent Concentrations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Just above the cmc</td>
<td>Intermediate</td>
</tr>
<tr>
<td>DTMAB</td>
<td>3.09</td>
<td>3.16</td>
</tr>
<tr>
<td>DDTEAB</td>
<td>3.80</td>
<td>3.24</td>
</tr>
<tr>
<td>DDTMAB</td>
<td>3.00</td>
<td>2.94</td>
</tr>
<tr>
<td>TTMAB</td>
<td>3.05</td>
<td>3.21</td>
</tr>
<tr>
<td>TTPAB</td>
<td>3.06</td>
<td>3.00</td>
</tr>
<tr>
<td>TTPAB (salt)</td>
<td>3.19</td>
<td>3.26</td>
</tr>
</tbody>
</table>
absorption. The solubility of the benzene in the non-micellar aqueous phases that are equilibrated with all the various micellar phases of all the detergent concentration that were studied remains constant within the ± 2% the precision of the method.

C. Critical Micelle Concentration in Presence of Benzene

The absorbance of the micellar benzene was plotted versus detergent concentration for the various quaternary ammonium salts. The intersection of these curves with the abscissa gives the cmc of the detergent saturated with benzene. Figure 4 shows the absorbancy results obtained from detergent solutions with and without added salt. Figure 5 shows the absorbancy results from the dodecyl detergents in pure water and Figure 6 shows them from salt solutions. Figure 7 shows the results from the tetradecyl detergent solutions.

An empirical relationship similar to the one relating logarithm cmc to the hydrophobic chain length is obtained for the decyl, dodecyl and tetradecyl trimethyl salts in the presence of benzene and is shown in Figure 8. Also, if the log cmc's of decyl and dodecyl triethyl are plotted, a straight line parallel to those of the trimethyl results.

Table IV contains the cmc's for the detergent-
TABLE IV

CRITICAL MICELLE CONCENTRATIONS
IN THE PRESENCE OF BENZENE FOR DECYL-,
DODECYL- AND TETRADECYLMAMMONIUM SALTS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>cmc in water</th>
<th>cmc in 0.05 N NaBr Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTMAB</td>
<td>4.5</td>
<td>3.0</td>
</tr>
<tr>
<td>DTEAB</td>
<td>3.7</td>
<td>2.7</td>
</tr>
<tr>
<td>DDTMA</td>
<td>1.0</td>
<td>0.35</td>
</tr>
<tr>
<td>DDTEAB</td>
<td>0.92</td>
<td>0.30</td>
</tr>
<tr>
<td>DDTPAB</td>
<td>0.64</td>
<td>0.26</td>
</tr>
<tr>
<td>TMMAB</td>
<td>0.27</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1 | Absorbancy of Micellar Benzene vs. Concentration of Detergent for Decyl Series
Figure 5. Absorbancy of Micellar Benzene vs.
Concentration of Detergent for Dodecyl Series

Concentration of Detergent in moles per liter x $10^2$
Figure 6 Absorbancy of Micellar Benzene vs. Concentration of Detergent for Dodecyl Series

Concentration of Detergent in moles per liter x 10^2
Figure 7  Absorbancy of Micellar Benzene vs. Concentration of Detergent for Tetradecyl Series
Logarithm of the cmc

Figure 8 Log cmc in the presence of Benzene vs. the Number of Carbon Atoms in the Hydrophobic Tail
benzene aggregates. The cmc's in the presence of benzene are lower than those obtained from solutions of the pure detergents in the case of the trimethyl series; however, the reverse is true for the triethyls. No suitable explanation for this reversal has been found. One would expect the cmc to be reduced in the presence of solubilizate due to the decrease in free energy of the detergent when it mixes with the benzene in the micellar phase.

D. Solubilization Results

Figure 9 shows the experimental curves for the solubilization of benzene by decyl detergent solutions with and without added salt. The solubilizing power for the decyltrimethylammonium bromide and decyltriethylammonium bromide in pure water are approximately the same. The solubilizing powers of all the detergents that were studied are presented in Table V. The usual increases in the solubilizing power in the presence of 0.05 N NaBr were observed. The increase for the DTEAB is however, smaller than that expected.

Figure 10 shows the experimental curves for the solubilizing power of the dodecyl detergents in pure water. The solubilizing powers for dodecyltrimethylammonium bromide, dodecyltriethylammonium bromide and dodecyltripropylammonium bromide are approximately the
### TABLE V

SOLUBILIZATION RESULTS FOR DECYL, DODECYL AND TETRADECYL DETERGENTS IN WATER AND 0.05 N NaBr SOLUTIONS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water</th>
<th>0.05 N NaBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTMAB</td>
<td>0.96</td>
<td>1.44</td>
</tr>
<tr>
<td>DTEAB</td>
<td>0.90</td>
<td>1.06</td>
</tr>
<tr>
<td>DDTMAB</td>
<td>1.75</td>
<td>2.90</td>
</tr>
<tr>
<td>DDTETAB</td>
<td>1.55</td>
<td>1.76</td>
</tr>
<tr>
<td>DDTPAB</td>
<td>1.88</td>
<td>4.40</td>
</tr>
<tr>
<td>TTMB</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>TTMAC</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>TTPAB</td>
<td></td>
<td>6.60</td>
</tr>
</tbody>
</table>
Figure 9. Micellar Benzene vs. Micellar Detergent for Decyl Series in Water and in 0.05 N NaBr
Figure 10 Micellar Benzene vs. Micellar Detergent for Dodecyl Series in Water
same. The constant values of the solubilizing power for the decyl and dodecyl detergent agrees with the results of Brashier on the tetradecyl and hexadecyl detergents.

Figure 11 shows the experimental curves for the solubilization of benzene by dodecyl detergents in salt solutions. The solubilizing power for the DDTMAB and DDTPAB showed the usual large increases over those obtained from pure aqueous solutions; however, the DDTEAB results appeared to be low. This small increase of solubilizing power for the triethyl detergents was similar to the result obtained from the decyl detergent.

Figure 12 shows the experimental curves for the solubilization of benzene by the tetradecyl detergents that were studied. The solubilizing power for tetradecyltrimethylammonium bromide agreed with the value obtained by Brashier. The solubilizing power of tetradecyltrimethylammonium chloride was much lower than that expected; the only difference between these two detergents is the gegenion. Further studies on the effect of gegenion on the solubilizing power were initiated in this laboratory by John Brown and are being continued at Denison University. The solubilizing power of tetradecyltripropylammonium bromide in 0.05 N NaBr showed the expected increase.

The extinction coefficients for benzene in five
Figure 11  Micellar Benzene vs. Micellar Detergent for Dodecyl Series in 0.05 N NaBr.
Figure 12 Micellar Benzene vs. Micellar Detergent for Tetradecyl Series in Water and in 0.05 N NaBr
different detergents were determined and are given in Table VI. The average value for the different detergents was 188 liter/mole cm.

E. Spectral Shifts Results

The absorption spectra of benzene were determined in the cases of solutions in water, nonane cyclohexane, methyl alcohol, chloroform and the detergent-water mixtures. These spectra are presented on Figure 13. All the above spectra were obtained with solvent references except in the case of the benzene-water-detergent systems. As stated before, the reference solution in those cases was water saturated with benzene. Only one detergent system at one concentration is represented in the Figure 13. All the primary maxima for all the detergent systems, however, fell within 1 Å of 2547 Å. In all cases only the peak of maximum benzene absorption will be considered.

The wavelength for the maximum absorption peak of benzene is 2535 Å in water, 2546 Å in nonane and cyclohexane, 2547 Å in the micelle and 2552 Å in chloroform. The positions certainly indicated that the benzene molecule is located in the organic core of the micelle.

Bromobenzene spectra in water and in micelles are shown in Figure 14. Nothing new is learned because the shifts in the spectra are similar to those of benzene.
<table>
<thead>
<tr>
<th>Salt</th>
<th>Extinction Coefficient in liter per cm-moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTMAB</td>
<td>191</td>
</tr>
<tr>
<td>DTEAB</td>
<td>188</td>
</tr>
<tr>
<td>DDTMAB</td>
<td>190</td>
</tr>
<tr>
<td>DDTEAB</td>
<td>186</td>
</tr>
<tr>
<td>TTMAB</td>
<td>188</td>
</tr>
</tbody>
</table>
Figure 13 Benzene Spectra in Various Solvents
Figure 14. Bromobenzene Spectra in Detergent and in Water
It was hoped that the dipolar nature of the absorbing particle would cause the shifts to be much larger.

F. Distribution of Detergents between Benzene and Aqueous Solutions

The solubilization results obtained by Brashier for tetradecyltributylammonium bromide in pure water and hexadecyltripropylammonium bromide in 0.05 N NaBr were quite unusual. In both cases it was found that no benzene was solubilized; however, both these compounds had properties (surface activity, cmc's and large molecular weights) similar to those of the other detergents with smaller head sizes.

The solubilization experiments were all performed in a similar fashion which has been described previously. In all cases a small excess of benzene is added to the detergent solutions. It has always been considered that the chemical potential of the benzene in the pure benzene phase has remained constant and that the detergent was insoluble in the benzene. If, however, in the case of the detergents with the more organic character, their solubility in the benzene was enhanced, the above anomaly could be explained.

The following information given in Table VII substantiates this belief, and it also validates all the
<table>
<thead>
<tr>
<th>Hydrophobic Chain</th>
<th>Hydrophilic Head</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trimethyl</td>
<td>Triethyl</td>
<td>Tripropyl</td>
<td>Tributyl</td>
</tr>
<tr>
<td>Decyl</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyl</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>0</td>
<td>0</td>
<td>$10^{-1}$</td>
<td>15</td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>0</td>
<td></td>
<td>$10^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>
other solubilization work done in this laboratory.

The trimethyl and triethyl detergents were completely insoluble in benzene, and the tripropyl detergents were just barely partitioned between the two phases. The tributyl detergent, however, was quite soluble in the benzene, thus the chemical potential of the benzene was reduced. The partitioning was not determined in the presence of salt so hexadecyltripropylammonium bromide might also be more soluble in the benzene in the presence of extraneous salt.
CHAPTER IV

SUMMARY AND CONCLUSIONS

Two series of quaternary salts were prepared in order to study the aggregation and solubilization properties as both the hydrophobic tail and the hydrophilic head sizes were changed. Difficulties in purification of these substances made it necessary to use slightly impure compounds. The cmc's obtained by the analysis of surface tension data were all low and the head size parameters appeared a little large in comparison with previous values obtained in this laboratory. The linear relationship between the head size parameter and the square of the number of carbon atoms in the short alkyl chains was reconfirmed.

A new spectrophotometric technique for determining the micellar benzene was devised. This technique made it possible to obtain the cmc for the detergents in the
presence of benzene. With this information, the solubilizing power could be calculated for the different detergent solutions.

The absorption spectrum of benzene was obtained in organic solvents and in the micelle. The shifts of the absorption peaks indicated that the benzene was in the organic interior.

The following model is proposed to explain the data of the author and previous workers in this laboratory, Venable and Brashier. It has the same gross structural arrangement as that described previously. The hydrophilic part is the surface layer of the aggregate and the hydrophobic portion is divided between the surface layer and the liquid organic core. This aggregate is pictured as having a large amount of water around the ionic group and this water extends down into the micelle so that the first five to six methylene groups are ineffective as solubilizing groups in the liquid core.

Now this model must be tested to see if it can explain the data and if it is consistent with modern views. The depth of penetration might seem too deep because if this penetration exists, one would not expect detergent molecules of chain length six to five to condense in large aggregates. This is exactly the case.
Micellization usually occurs in substances when the hydrophobic chain contains more than five to six carbon atoms. For substances with shorter chains dimerization and trimerization and finally phase separation occur, but the large stable micelles do not form.

W.L. Courcheene, Proctor and Gamble, presented data at a seminar at Louisiana State University in 1962 that went even farther than this. He stated that the water penetrated to within the last four carbon atoms in the hydrophobic chain. He later presented diffusion, sedimentation and viscosity data that confirmed the existence of a large amount of water in the micelle.

In the introduction the different mechanical and statistical mechanical descriptions of these aggregates were given. It was shown then that the stability of the micelle can be explained by the counterbalancing of the repulsive electrostatic forces and the hydrophobic bonding forces. In the most recent attempt by Scheraga, the entire hydrophobic phase was not included in the bonding in the center of the micelle. Instead, he introduced a parameter to include some of the hydrophobic tail in the surface. One can see that this has exactly the same effect as introducing water around the first six methylene groups of the monomer in the aggregate.
This exclusion of a certain constant number of methylene groups from the organic core for a detergent molecule does not invalidate the previous empirical relationship

\[
\log \text{cmc} = A - Bm.
\]

For the decyl, dodecyl, tetradecyl and hexadecyl quaternary ammonium bromides, the solubilization power was seen to increase with increased chain length. This effect was expected and has been observed in other detergent series. It should be remembered that the chemical potential of the benzene in the micelle is controlled by the pure benzene in equilibrium with the solution; therefore, the activity of the benzene in the micellar phase is constant.

If the micelles are spherical in shape with a uniform surface layer, it appears that the organic core of substances differing only in chain length should have similar properties. The difference in solubilizing power will just depend, therefore, on the difference in the total number of methylene groups in the organic core. The ratio of the micellar benzene to the methylene groups in the core was calculated for the above series. It was found that the minimum average deviation for this ratio in the series occurred when six or seven carbon atoms were substracted
from the hydrophobic chain.

Above it was stated that the interiors of these micelles were similar to the solubilized material, a conclusion which appears to be verified by the constancy of wavelength of the absorption maxima and the constant value for the extinction coefficient. These constant values can not be attributed to the presence of small pure benzene droplets in the interior of the micelle because the same maximum was obtained for a dilute benzene solution in which there was only one benzene molecule per micelle.

The solubilization work in this laboratory has shown that the solubilizing power of a particular chain length does not appear to depend upon the head size. This is consistent with the results predicted by the model because the steric importance of the bulky head will be diminished by the additional water and six carbon atoms attaching the head to the organic core.

The solubilizing power increases greatly as the salt concentration is raised. This again is an obviously complex process. A few changes in the solution should be considered. (a) The internal pressure increases. (b) Hydrophobic bonding increases. (c) The double layer or charge distribution around the aggregate
collapses. (d) The activity of the water decreases. All these effects should cause the water to leave the interior of the micelle; therefore, the number of methylene groups in the liquid core is increased and more material can be solubilized. If enough of the water were removed and the effective charge on the monomers were reduced, the head size might play an important part in determining the solubilizing power. This was found to be the case for the TTEAB. For the dodecyls, however, there was a decrease in solubilizing power from the methyl to ethyl and then a sizable increase for the propyl. The same decrease was found for the decyl methyl to ethyl. If the solubilization changes going from ethyl to propyl and methyl to propyl are considered, the trends predicted by the model are correct. This, however, is not the case in going from methyl to ethyl. At this time, more solubilization results in the presence of salt are needed.

The information that is really needed is the micellar weights for the mixed aggregates. Some work has been done on this subject in the laboratory by Earl Pye.
APPENDIX

A. Ag-Ag Halide Electrode

Light scattering studies of detergent solutions in the presence of extraneous salt have been conducted in this laboratory to determine the molecular weight of the micelles. Numerous investigators have presented expressions with which the molecular weights of these micelles are calculated. A recent paper by Overbeek and Vrij¹ pointed out that one should obtain the differential refractive index for solutions at Donnan equilibrium rather than for solutions at equal salt concentration.

Differential refractometer measurements were attempted under these equilibrium conditions. The

solution containing the detergent and salt was placed in a vessel which was in contact with a solution containing only salt. These solutions were separated by an inert visking membrane. The salt solution concentration could be varied. The change in emf between the two Ag-AgBr electrodes inserted in the solutions was measured by means of a potentiometer. The results that were obtained were not satisfactory and this project was abandoned.

The electrodes were particularly satisfying; consequently, a short description of the technique used to prepare the electrodes follows.

B. Preparation of Electrodes

This information is included to assist persons who require mechanically and electrically stable Ag-Ag halide electrodes that have very small asymmetric potentials. This technique is not that of the author but results from the combined efforts of many experimenters and experiments at Shell Development Company, Houston.

One should use soft glass because it has the same thermal expansion coefficient as that of platinum and therefore no mechanical strain will be introduced as the temperature is varied. Platinum wire is sealed in a
glass tube and the wire is wrapped around the end of the glass tube two or three times. The electrode is placed in an annealing oven. The temperature is adjusted so that the glass will flow around the wire and give the electrode mechanical stability.

The end of the electrode is then covered with pure Ag$_2$O and is placed in a furnace at 400°C. The Ag$_2$O will decompose leaving a silver matrix in intimate contact with the platinum wire. Next, the electrode is anodized in a 0.05 N NaBr solution with a low current density of 4-6 milliamperes per square centimeter.

The electrodes should then be aged in a dilute halide solution and then rinsed and stored in distilled water. These electrodes will have an asymmetry potential of the order of 0.01 - 0.02 mv. They will have rapid equilibration times if the Ag$_2$O layer was not too thick. They will be quite stable mechanically.

C. Radioisotopic Studies

In this laboratory, solubilization limits have been measured by extracting the solubilizes with cyclohexane and determining the amount of material by u. v. absorption, by observing with the differential refractometer the abrupt change in the index of refraction
that results from adding increments of solubilizate and by direct determination of the u. v. absorption of the aqueous detergent. The two u. v. absorption techniques are obviously limited to those compounds that absorb in a convenient region. The refractive index technique is reasonably accurate and does not have the previous limitation, but it is tedious. Each determination requires six or more measurements in order to identify the solubilization limit.

In order to study paraffin hydrocarbons the index of refraction technique or some other procedure would have to be used. It was decided to investigate the possibility of using radioisotopes.

It was found that this technique would be quite satisfactory for these problems. The usual liquid scintillators were used, PPO and POPOP. The solution was composed of 158 ml. xylene, 71 ml. ethyl alcohol, 1.11 grams PPO and 11 mg. POPOP.

Two tenths of a milliliter of aqueous solution can be dissolved in 15 milliliters of this mixture without phase separation. This was the size sample used in the liquid scintillator. This small aqueous sample presented the problem that a very low radioactivity existed in the cases of the dilute solutions. For the
dilute solutions, however, more aqueous solution could be added and the solubilized material could be extracted into the xylene alcohol phase. The small amount of aqueous phase would not affect the geometry of the emitting solution.

Aqueous solutions of tagged benzoic acid were prepared and the above technique was used. The counts were recorded and the technique proved to be quite satisfactory for our purposes.

Since in the author's studies, reported herein, benzene was used exclusively, it was not necessary to use the radiotracer technique.
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VITA

Joseph W. Goerner was born on August 18, 1934 in Fort Worth, Texas. He received his primary and secondary education in several schools from Texas to New York. Graduating from Lamar High School, Houston, he entered Rice University and received his B. A. in Chemistry in 1957.

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EXAMINATION AND THESIS REPORT

Candidate: Joseph William Goerner

Major Field: Chemistry

Title of Thesis: Aggregation and Solubilization Properties of Decyl, Dodecyl, and Tetradecyl Quaternary Ammonium Salts.

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination: July 15, 1966