Surface and Micellar Phenomena in Some Quaternary Ammonium-Bromides.

Gary K. Brashier
Louisiana State University and Agricultural & Mechanical College

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BRASHIER, Gary K., 1937–
SURFACE AND MICELLAR PHENOMENA IN SOME QUATERNARY AMMONIUM BROMIDES.

Louisiana State University, Ph.D., 1964
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan
SURFACE AND MICELLAR PHENOMENA IN SOME QUATERNARY AMMONIUM BROMIDES

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

Gary K. Brashier
B.S., Northeast Louisiana State College, 1960
August, 1964
ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. R. V. Nauman, his major professor, for his guidance throughout the course of this study.

Recognition is made of the helpful suggestions and discussions from Raymond L. Venable, Joseph W. Goerner, and Frank E. Collins, Jr.

Financial assistance from the Texas Eastman Company and the Celanese Corporation of America is gratefully acknowledged.

The author also wishes to express his appreciation to his wife, Pat, for her patience and untiring efforts which made this work possible.
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<td>TTMAB</td>
<td>Tetradecyltrimethylammonium bromide</td>
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<td>TTEAB</td>
<td>Tetradecyltriethylammonium bromide</td>
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<tr>
<td>TTPAB</td>
<td>Tetradecyltripropylammonium bromide</td>
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<tr>
<td>TTBAB</td>
<td>Tetradecyltributylammonium bromide</td>
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<tr>
<td>HTMAB</td>
<td>Hexadecyltrimethylammonium bromide</td>
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<tr>
<td>HTBAB</td>
<td>Hexadecyltributylammonium bromide</td>
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The surface properties and micellar phenomena associated with detergent solutions were investigated for two series of quaternary ammonium bromides. The long paraffin chain was either tetradecyl or hexadecyl and the three short alkyl chains were varied from methyl to ethyl, propyl, and butyl. Surface tension experiments, light scattering experiments, and solubilization experiments were conducted on these compounds in water and in sodium bromide solutions.

The surface tension-logarithm of concentration curves were used to evaluate the critical micelle concentration (c.m.c.) for each compound and the area occupied by each surface active molecule in the air-solution interface. A linear dependence of c.m.c. on the total number of carbon atoms in the short alkyl chains was found for both the tetradecyl and hexadecyl series. The area per molecule calculations showed a linear dependence on the square of the number of carbon atoms in each short alkyl chain which indicates a constant effectiveness of additional methylene groups within each series. The well-known log-log relationship between the c.m.c. and the added salt concentration was
verified using tetradecyltriethylammonium bromide and hexadecyltriethylammonium bromide. The maximum lowering of surface tension and the monomer head size of all compounds were found to decrease with increasing added salt concentration. This effect was discussed in terms of the Debye-Hückel theory.

Light scattering measurements on all compounds in water gave a decreasing micellar molecular weight as the monomer head size increased. The micellar molecular weights were then calculated from surface tension data with the aid of two similar models. Agreement between measured and calculated micellar molecular weights was better when the micelle was assumed to be spherical with a radius equal to the length of the long chain minus the linear extension determined by the number of carbon atoms in each short alkyl chain. Indications were found that there exists an optimum salt concentration above which micelles do not grow. In all systems a lower micellar molecular weight was found in water than in added salt solutions. Lower micellar molecular weights were found for the hexadecyl series of compounds than for the tetradecyl series for a given head size when the solvent was water. However, in extraneous electrolyte solutions, the reverse was true.
Benzene was chosen as the solubilizate for the solubilization experiments. Detergent solubilizing power was discussed in terms of the number of benzene molecules solubilized per detergent monomer in micellar form. The size of the hydrophilic head of the monomer did not change the solubilizing power within each series when the solvent was water. This effect coupled with the decreasing micellar molecular weight as the head size was increased suggested that the void space within the interior of the micelle is a factor to be considered in evaluating solubilizing power. Simple calculations based on the model described above showed that this void space per detergent monomer increased with increasing head size.

The efficiency of solubilization was found to increase with an increase in added salt concentration. For a given salt concentration and a given head size the hexadecyl compounds were found to solubilize more benzene than the tetradecyl compounds.

Hexadecyltrimethylammonium bromide gave an anomalously low c.m.c. as measured by the surface tension experiments and its solubilization curve in 0.0500 M sodium bromide solutions showed a decreasing efficiency for solubilizing benzene at higher detergent concentrations. These results led to the
conclusion that this detergent may form microcrystals before it forms true micelles.

The solubility of benzene in detergent solutions below the c.m.c. was measured as $2.38 \pm 0.04 \times 10^{-2}$ moles/liter.

Experiments using tetra-n-butylammonium bromide showed that the size of the added cation has no effect upon detergent behavior.
CHAPTER I

INTRODUCTION AND SURVEY OF THE LITERATURE

The physical and chemical phenomena which are exhibited by a solution of a surface active agent in some suitable solvent have comprised a field of extensive scientific research for the past thirty years. Surface active agents have found applications in diverse areas of industry and technology and an almost formidable volume of literature has accompanied this growth. While many of the principles involved are now understood, many remain a matter of conjecture.

The characteristic features of surface active agents are (1) their relatively small maximum concentration of monomeric species; (2) their ability to lower surface and interfacial tension in the region where only monomers exist; (3) their reversible aggregation of monomers to form micelles at a certain concentration, generally called the critical micelle concentration; and (4) their ability to solubilize water-insoluble materials by the action of the micelles.
It will be the purpose of this literature survey to outline the progress in these areas. Special emphasis will be placed on the forces responsible for micellization, surface phenomena, the structure of micelles, and solubilization.

Detergents, one group of surface active agents, are generally classified according to the electrical nature of the aggregating species as non-ionic, anionic, and cationic. The last of these will be of primary interest here. Work reported on the other two types will be included when necessary for comparison and when applicable to cationic systems.

A. Micellization

When any of a number of properties of a given detergent is investigated as a function of its concentration, a pronounced change occurs at a particular concentration, the critical micelle concentration (c.m.c.). At concentrations lower than the c.m.c. monomeric cationic detergent molecules are believed to be completely dissociated into


ions and remain in solution as positively charged paraffin chain ions and negatively charged gegenions. Some investigators interpret enhanced electrical conductivity in this region as evidence for a small degree of aggregation of the cations to dimers, trimers and perhaps other small aggregates. There is general agreement that at the c.m.c. a greater aggregation begins and thermodynamically stable micelles are formed. However the mechanism of their formation and their size and shape have been in question for quite some time.

At this point a qualitative picture of the forces responsible for micellization would be helpful. In this discussion the solvent will be assumed to be water unless otherwise stated. The effect of added electrolyte will be discussed at the end of this section.

The paraffin chain cation is made up of a long hydrocarbon chain to which is attached a polar, ionic group

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which will be referred to as the "head" of the ion. This arrangement leads to the participation of several kinds of forces in micelle formation.\textsuperscript{6,7}

As the paraffin chains come together the water-hydrocarbon surface is diminished. Energy is liberated due to both the attraction of the chains for each other and the large cohesive forces between water molecules which tend to expel from the water all species that have energetically disruptive influences. These forces are the short-range van der Waals forces. Since each paraffin chain carries along a polar end group, any aggregation process brings these similarly charged groups into closer proximity. This results in Coulombic repulsion and the expenditure of energy.

Ooshika\textsuperscript{8} points out that the hydrophilic nature of the head groups produces a surface interaction between the aggregating species and the water. This leads to a surface energy which must be considered in the counterplay of forces.

Reich\textsuperscript{9} shows that since aggregation reduces the

\begin{itemize}
\item \textsuperscript{6}P. Debye, \textit{J. Phys. and Coll. Chem.}, LIII (1949), 1.
\item \textsuperscript{7}H. V. Tartar, \textit{J. Phys. Chem.}, LIX (1955), 1195.
\item \textsuperscript{8}Y. Ooshika, \textit{J. Coll. Sci.}, IX (1954), 254.
\item \textsuperscript{9}I. Reich, \textit{J. Phys. Chem.}, LX (1956), 257.
\end{itemize}
number of independent particles in solution, a decrease in total entropy will occur and the entropy effects must be included in any theoretical treatment of micellar stability. The same author noted that the adhesion energy per ion gained by coalescence of hydrocarbon chains increases as the micelle grows.

When equilibrium between all these forces is reached with an attendant decrease in free energy of the whole system, the micelle can be considered as a thermodynamically stable species. The theories advanced by these investigators attempt to explain not only why micelles form but also why they do not grow to infinite size.

The critical micelle concentration is the narrow concentration range over which monomers reversibly aggregate. Its value depends on a number of factors. Several investigators\(^{10-13}\) have found empirically that the logarithm of the c.m.c. is a linear function of the number of carbon atoms, m,

\[^{10}\text{Debye, loc. cit.}\]
\[^{11}\text{H. B. Klevens, J. Am. Oil Chemists Soc., XXX (1953), 74.}\]
\[^{12}\text{A. B. Scott and H. V. Tartar, J. Am. Chem. Soc., LXVI (1943), 292.}\]
\[^{13}\text{M. L. Corrin and W. D. Harkins, ibid., LXIX (1947), 683.}\]
in the paraffin chain, that is

\[ \log \text{c.m.c.} = A - Bm \quad (1) \]

in which \( A \) and \( B \) are constants for a particular homologous series at a given temperature. From theoretical principles Hobbs\textsuperscript{14} derived the equation

\[ \log \text{c.m.c.} = -0.5 \log (\text{c.m.c.} + C_a) - 0.435M + 2.45 \quad (2) \]

in which \( C_a \) is the concentration of added electrolyte in solution and \( m \), as before, is the number of carbon atoms in the paraffin chain. The coefficient of \( \log (\text{c.m.c.} + C_a) \) is shown to be related to the average charge contributed by each molecule to the micelle. The last two terms are described in terms of the charge density on the surface of the micelle, the number of moles of water per liter, and the van der Waals interactions due to the presence of hydrocarbon chains. For a given value of \( m \), Equation (2) can be written

\[ \log \text{c.m.c.} = A - B \log (\text{c.m.c.} + C_a). \quad (3) \]

If no added salt is present, Equation (2) reduces to the form of Equation (1).

Small differences in the c.m.c. of cationic detergents having the same length hydrocarbon chain result from the variations in the number of charges on and the nature of the gegenion, the number of ionic groups on each chain, and the structural differences of isomeric molecules. Shinoda\textsuperscript{15} reviews these factors in some detail.

Klevens\textsuperscript{16} and Ralston\textsuperscript{17} report that the values of the c.m.c. are not changed appreciably by substitution near the hydrophilic head. This conclusion is based on results from experiments in which the amine hydrogens of alkylammonium halides were replaced by one, two, or three groups, some of which were as large as the hydroxyethyl group. This conclusion was not confirmed by Venable\textsuperscript{18} who noted that as the three alkyl groups around the head of quaternary detergents were changed from methyl to propyl the c.m.c. decreased. Results will be presented in a later section to show that the head size does affect the c.m.c. and that the c.m.c. is

\textsuperscript{15}Shinoda, op. cit., pp. 42-79.

\textsuperscript{16}Klevens, loc. cit.

\textsuperscript{17}A. W. Ralston, \textit{et al.}, J. Am. Chem. Soc., LXIX (1947), 2095.

\textsuperscript{18}R. L. Venable, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1963, p. 58.
a definite function of the number of carbon atoms in the
three short alkyl chains.

Quantitative descriptions of micellization from a
theoretical point of view have followed two basic approaches,
the mass law approach and the pseudophase equilibrium ap-
proach. The mass law approach considers micelles to be the
equilibrium product of the reaction of single molecules to
form large clusters of monomers. There is the usual equi-
librium constant associated with the reaction. The process
may be formulated by an equation of the following type for
cationic surfactants:

\[ m \, B^+ + n \, A^- = A_n B_m^+ (m-n) \] (4)

in which \( B^+ \) represents the paraffin chain cation, the aggreg-
gating species, \( A^- \) is the gegenion, and \( A_n B_m^+ (m-n) \) is the
micelle. Since \( m \) is greater than \( n \), the micelle carries a
formal positive charge, a fact which is verified by many
experiments. The equilibrium constant \( K \) is then given in
terms of the activities of the various species by

\[ K = \frac{(a_{B^+})^m (a_{A^-})^n}{(a_{A_n B_m})} . \] (5)
This is the approach used by Bury and his associates\textsuperscript{19} to explain the abrupt transitions in colloidal properties at the c.m.c. Reich\textsuperscript{20} and Vold\textsuperscript{21} explain the stability of micelles and a possible spread in molecular weights by this treatment.

Shinoda\textsuperscript{22} and Corrin and Harkins\textsuperscript{23} point out the shortcomings of this approach when concentrations are substituted for activities in Equation (5).

The second approach is to consider the micelles as forming a pseudophase much like a liquid hydrocarbon phase. The problem is attacked by applying the thermodynamics of phase equilibria. This theory is particularly attractive in dealing with solubilization phenomena. Water-insoluble substances are known to be made more soluble by the addition of micelle forming agents to the solution.

Tartar\textsuperscript{24} suggests that the micelle has a liquid

\textsuperscript{19} C. R. J. Bury and J. Grindley, \textit{J. Chem. Soc.}, CXXXI (1929), 679; CXXXII (1930), 2263.

\textsuperscript{20} I. Reich, \textit{J. Phys. Chem.}, LX (1956), 257.


\textsuperscript{22} Shinoda, \textit{Colloidal Surfactants}, pp. 25-30.


hydrocarbon interior of practically unordered arrangement and a density comparable to that of the corresponding liquid hydrocarbon of like chain length. The interior is surrounded by a surface of hydrophilic head groups in contact with the solvent. This model is supported by Sasaki,\textsuperscript{25} Stainsby and Alexander,\textsuperscript{26} Matijevic and Pethica,\textsuperscript{27} and Hartley.\textsuperscript{28}

Aranow\textsuperscript{29} develops a statistical mechanical treatment which reveals the relationships between these two approaches and discusses some of the uncertainties underlying the interpretation of micelle behavior. Other statistical mechanical treatments will be mentioned in the survey of the light scattering literature.

Concerning existing knowledge of the geometry of micelles in 1955, McBain and Hutchinson say, "At the present time we really do not know the actual size and shape of micelles in solution. No single experimental technique so far developed can provide unequivocal evidence on either of

\begin{itemize}
  \item R. H. Aranow, \textit{J. Phys. Chem.}, LXVII (1963), 556.
\end{itemize}
these factors, and the results of different experimental
techniques often yield conflicting evidence, and from others
widely differing conclusions may be drawn."\textsuperscript{30} This statement
is still true nearly ten years later.

The various models for micelle structure all have two
things in common. The hydrophilic head groups are on the
surface of the micelle at the micelle-water interface, while
the hydrocarbon chains are associated in the interior in
some fashion. In 1938 Hartley\textsuperscript{31} proposed a spherical micelle
with a radius approximately the length of the hydrocarbon
chain. He suggested that further addition of surfactant
after a certain micelle size had been attained only increased
the number of such micelles. This model has been supported
in later years by the light scattering data of Tartar,\textsuperscript{32} the
conductivity and diffusion measurements of Vetter,\textsuperscript{33} the

\begin{itemize}
\item \textsuperscript{30}M. E. L. Mc Bain and E. Hutchinson, \textit{Solubilization
and Related Phenomena} (New York: Academic Press, Inc.,
\item \textsuperscript{31}Hartley, \textit{loc. cit.}
\item \textsuperscript{32}H. V. Tartar, \textit{J. Coll. Sci.}, XIV (1959), 115; \textit{J.
Phys. Chem.}, LIX (1955), 1195.
\item \textsuperscript{33}R. J. Vetter, \textit{J. Phys. and Coll. Chem.}, LI (1947),
262.
\end{itemize}
collection of evidence cited by Philippoff,34 and by Nash.35

In 1950 McBain36 presented evidence for a lamellar micelle in solutions above the c.m.c. A lamellar micelle is analogous to a peanut butter sandwich with the hydrocarbon tails representing an overly generous amount of peanut butter and the ionic heads forming the bread. Philippoff37 and Harkins38 explained results of X-ray experiments by this model. Later Harkins39 proposed a cylindrical shape to agree with further X-ray data. This structure is analogous to a bundle of wheat the length of which is twice that of the hydrocarbon tails.

A sausage shaped micelle was suggested by the light scattering experiments of Debye and Anacker40 and the

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birefringence studies of Backus and Scheraga.\textsuperscript{41} Other models which have been advanced are the plate-like micelle by Hoeve and Benson\textsuperscript{42} and the ellipsoid of revolution by Müller.\textsuperscript{43}

Disagreement also exists over the presence or absence of micelles below the c.m.c. A wide variety of experiments\textsuperscript{44-47} seem to indicate a large number of smaller micelles in this region. However most investigators, principle among whom is Tartar,\textsuperscript{48} believe that no such aggregates exist.

To this writer the most logical description of the

\begin{itemize}
\item \textsuperscript{41} J. K. Backus and H. A. Scheraga, \textit{J. Coll. Sci.}, VI (1951), 508.
\item \textsuperscript{42} C. A. J. Hoeve and G. C. Benson, \textit{J. Phys. Chem.}, LXI (1957), 1149.
\item \textsuperscript{43} F. H. Müller, \textit{Koll. Zeit.}, CVIII (1944), 66.
\item \textsuperscript{44} J. W. McBain, \textit{Colloid Science} (Boston: H. C. Heath and Co., 1950), p. 256.
\item \textsuperscript{45} C. W. Hoerr and A. W. Ralston, \textit{J. Am. Chem. Soc.}, LXV (1943), 976.
\item \textsuperscript{46} E. D. Goddard, \textit{et al.}, \textit{J. Phys. Chem.}, LXI (1957), 593.
\item \textsuperscript{47} E. F. Williams, \textit{et al.}, \textit{J. Coll. Sci.}, XII (1957), 452.
\end{itemize}
physical state of micelles is that given by Schick\textsuperscript{49} and similarly by Corkill and Herrmann.\textsuperscript{50} These investigators suggest that when the detergent concentration exceeds the c.m.c., the micelles formed initially are spherical. Somewhere below the maximum turbidity a gradual elongation sets in accompanied by an increasing alignment of elongated micelles. Orientation increases with surfactant concentration until a well-ordered phase appears. These ideas are strengthened by experiments on the effect of added electrolyte on micellar geometry. These experiments will be discussed shortly. Recently Reiss-Husson and Luzzati\textsuperscript{51} studied a number of anionic and cationic detergents using X-rays and reported exactly this same phenomenon for sodium lauryl sulfate, five sodium saturated soaps, and cetyltrimethylammonium bromide. These authors report, however, that cetyltrimethylammonium chloride remains spherical throughout the concentration range, from about a 5 per cent solution until


\textsuperscript{50} J. M. Corkill and K. W. Herrmann, \textit{J. Phys. Chem.}, LXVII (1963), 934.

\textsuperscript{51} Fr. Reiss-Husson and V. Luzzati, Centre de Recherches, sur les Macromolecules, Strasbourg, France, quoted from \textit{Abstracts of Papers}, 147th Meeting, American Chemical Society, Philadelphia, 1964, No. 19, p. 10 H.
a separate phase appeared. To this writer's knowledge, this is the first report where a change in gegenions changes the shape of the micelle.

The preceding discussion has been concerned primarily with solutions of detergents in pure water. Much work on solutions of detergents in water containing various concentrations of extraneous electrolytes has been reported, however. The change in the properties of detergent solutions due to added salt will be discussed briefly here and in more detail in the following sections.

The effect of added salt is intimately related to the charge effects displayed by ionic detergents. In 1913 McBain\textsuperscript{52} suggested correctly that soaps in aqueous solution form electrically charged aggregates. Since micellization depends upon the counterbalancing of forces among electrically charged species, it is reasonable to expect that a change in the ionic atmosphere in solution will affect this aggregation process.

Tartar's\textsuperscript{53} qualitative description of such a change would be helpful at this point. In dilute solution the detergent is completely ionized. To minimize the energy


associated with the water-hydrocarbon interface, the paraffin chains curl up. According to the Debye-Hückel theory each ion is surrounded by an ionic atmosphere of equal and opposite charge. The thickness of the ionic atmosphere depends upon the concentration and charges of the various ions in solution. It decreases with increasing concentration of and increasing charge on the ions. The distance over which a charged paraffin chain ion can "see" another of its kind is proportional to the thickness of the ionic atmosphere. The addition of extraneous electrolyte with a common gegenion decreases this thickness and with enough added salt, it is reduced to the point where paraffin chains can approach closely enough to coalesce into larger aggregates. This results in a reduction of the water-hydrocarbon surface and consequently lowers the energy of the system due to the van der Waals cohesive forces between water molecules. Corrin and Harkins\textsuperscript{54} present a similar explanation in terms of ionic strength.

Such a picture is used to justify the validity of Equation (3) and the repeated reports of decrease in c.m.c. with increase in added salt. Data will be presented later.

to show that this same discussion is adequate to explain the
effects of added salt on the c.m.c.'s that were obtained in
this work.

Controversy exists however about the effect of added
salts on micelle size and shape. Among those who believe
that added salt increases the micellar molecular weight are
Debye,\textsuperscript{55} Anacker,\textsuperscript{56} and Hobbs.\textsuperscript{57} On the other hand Kushner
and Hubbard\textsuperscript{58} find that there exists a maximum salt concen-
tration above which the micelle does not appear to grow.
More will be said about this paper later where similar evi-
dence will be presented by this writer.

Philippoff\textsuperscript{59} cites much evidence concerning the effect
of added electrolyte on micelle geometry. He concludes that
for shorter chain detergents in water throughout the entire
concentration range, for longer chain detergents in water at

\begin{itemize}
\item \textsuperscript{55}P. Debye, \textit{J. Phys. and Coll. Chem.}, LIII (1949),
1; LV (1951), 644.
\item \textsuperscript{56}E. W. Anacker, \textit{J. Coll. Sci.}, VIII (1953), 402;
\item \textsuperscript{57}M. E. Hobbs, \textit{J. Phys. and Coll. Chem.}, LX (1951),
675.
\item \textsuperscript{58}L. M. Kushner and W. D. Hubbard, \textit{J. Coll. Sci.}, X
(1955), 428.
\item \textsuperscript{59}W. Philippoff, \textit{Dis. Far. Soc.}, No. 11 (1951), p. 96.
\end{itemize}
lower concentrations, and for both of these in moderate content of added salt the detergent micelles are essentially spherical. He further concludes that for the longer chain compounds in water and high detergent concentration and in all systems with high added salt content, the spherical shape gives way to some other structure.

B. **Surface Tension**

The dependence of surface tension on surfactant concentration has been used as a method to detect the c.m.c.\(^6\) Surface tension decreases rapidly until the c.m.c. is reached and stays approximately constant at higher concentrations. The accuracy of this method to locate the c.m.c. compared with other techniques such as conductivity, refractive index, and partial molal volume is discussed by Shinoda\(^6\) and found to be better for a wider range of c.m.c. values.

\(^{60}\) R. L. Venable, Ph.D. Dissertation, pp. 57-63.


\(^{65}\) Shinoda, *Colloidal Surfactants*, p. 11.
General and quite detailed treatments of surface thermodynamics can be found by Gibbs, Guggenheim, and Moillet, Collie, and Black.

A plot of surface tension versus log concentration of detergent is frequently used to arrive at the area each molecule occupies at the air-solution interface. This calculation makes use of the well-known Gibbs adsorption equation given by

$$\Gamma = - \frac{1}{2.303 RT} \cdot \frac{d \gamma}{d \log C}$$  \hspace{1cm} (6)

in which \(\Gamma\) is the number of moles of solute in a volume having unit area in the interface in excess of the number of moles of solute in a volume of the bulk solution which contains an equal quantity of solvent, \(\gamma\) is the surface tension, and \(C\) is the detergent concentration. The assumptions necessarily imposed to arrive at this form of the equation and the limitations of this treatment are given by Venable. The


reciprocal of $\Gamma$ then represents the effective area of the surface occupied by each molecule. When the solvent is a solution of high added salt content, the area calculated by this method must be multiplied by the factor 2.

It has long been convenient to think of ionic surfactants as having their polar heads oriented at the air-solution interface and their hydrocarbon tails directed into the air. If this picture is correct, one should be able to measure changes in effective head sizes by this method. Data will be given later to show that this is indeed the case.

For some time reports of surface tension measurements from different laboratories were quite discordant. Some surface tension-concentration curves showed minima in the neighborhood of the c.m.c. accompanied by surface aging prior to the c.m.c. Others reported neither of these phenomena throughout the entire region. Shedlovsky\(^{73}\) and Haydon


and Phillips\textsuperscript{74} attribute both effects to impurities, either in the detergent or in the water. McBain and Hutchinson\textsuperscript{75} explain the minima in terms of progressive solubilization of the impurities by micelles after the c.m.c. is exceeded.

C. \textit{Light Scattering}

The theory of light scattering has its origin in the last half of the nineteenth century before the advent of quantum mechanics. Maxwell's electromagnetic theory of light permitted the linking together of electric and optical phenomena. If an electromagnetic wave passes over a small elastically bound charged particle, the particle will be set into motion by the electric field. When the frequency of the wave is equal to the natural frequency of vibration of the particle absorption occurs. If the wave is of a different frequency from that of the particle, the latter undergoes forced vibration at primarily the same frequency of the wave. The wave emitted at exactly the same frequency as the incident one is known as scattered radiation.


The first quantitative study of the scattering of light by small particles was made by Rayleigh\footnote{Lord Rayleigh, \textit{Phil. Mag.}, XLI (1871), 447; XII (1881), 81.} in 1871 and applied to the molecules in a gas in 1881. He was thus able to explain such phenomena as the color of the sky and polarization of scattered light.

For the next several decades investigators in this field were concerned with highly theoretical and mathematical formulation of complex phenomena rather than physical insight into simple systems. Debye was the last of the classical masters of this era which had begun with Rayleigh. A detailed review of this period is given by Oster.\footnote{G. Oster, \textit{Chem. Reviews}, XLIII (1948), 319.}

Unlike the scattering by gaseous systems treated by Rayleigh,\footnote{Lord Rayleigh, \textit{loc. cit.}} a detergent solute in water can be considered as a system that contains non-independent particles. One cannot merely sum over the scattered intensity from all particles to get the total intensity of scattered light. Destructive interference occurs and the amount of scattered light decreases. Although the phase relationships between the scattered wavelets from the various parts of a condensed
system can be theoretically deduced, the mathematical difficulties are sufficient to encourage one to look for other solutions to the problem.

Scattering has been treated by the theory of spontaneous fluctuations in density and composition. Debye's classic papers\(^7^9\) and the review by Oster\(^8^0\) should be consulted for the details of this theory. Only those ideas and equations pertinent to the work done by the present writer will be discussed.

If the scattering particles are small compared with the wavelength of the light impinging upon them and if they are isotropic, only the intensity of the scattered light will be significant. The decrease in intensity of the incident light by scattering is often expressed by an integrated form of Lambert's law:

\[ I = I_0 e^{-\tau x} \]

where \(I_0\) is the initial intensity of the incident beam, \(I\) is its intensity after it has traveled a distance \(x\) in the medium, and \(\tau\) is the turbidity of the sample, an extinction coefficient which is related to the number and size of the


\(^{8^0}\)Oster, *loc. cit.*
scattering species.

For light scattered at $90^\circ$ with respect to the incident beam, Debye$^{81}$ derived the following expression for non-interacting particles:

$$\tau = \frac{32\pi^3 \mu_o^2 (\mu - \mu_o)^2}{3 \lambda^4 n}$$

(7)

where $\mu_o$ and $\mu$ are the indices of refraction of the pure solvent and the solution, respectively, $\lambda$ is the wavelength of the incident light, and $n$ represents the number of scattering particles per cubic centimeter of solution.

Expressing $n$ in terms of its molecular weight $M$, its concentration $C$ in units of grams per cubic centimeter, and Avogadro's number $N$, such that $n = \frac{NC}{M}$, then Equation (7) becomes

$$\tau = \frac{32\pi^3 \mu_o^2 (\mu - \mu_o)^2}{3 \lambda^4} \cdot \frac{M}{NC}.$$

This equation is usually written in the form

$$\tau = HMC$$

(8)

with $H$, called the refraction constant, defined by

$^{81}$Debye, loc. cit.
These equations were derived on the assumption that the scattering particle does not interact with the solvent; this is an assumption of solution ideality.

Deviations from ideality can be incorporated into this expression by starting with the equation due to Smoluchowski and Einstein:

\[ H = \frac{32\pi^3 \mu_0^2}{3N\lambda^4} \left( \frac{\mu - \mu_0}{C} \right)^2 \] (9)

\[ \tau = \frac{32\pi^3 \mu_0^2}{3N\lambda^4} \cdot \frac{C}{C} \left( \frac{d\mu}{dc} \right)^2 \cdot \frac{\frac{\partial}{\partial c} \left( \frac{P}{RT} \right)_T}{(P/RT)_T} \] (10)

The change in refractive index of the solution with the change in concentration is now expressed in differential form and a concentration gradient of osmotic pressure \( P \) appears. In many cases \( \frac{d\mu}{dc} \) can be replaced by \( \frac{\mu - \mu_0}{C} \) as before. Making this approximation and substituting Equation (9) gives

\[ \frac{H_c}{\tau} = \frac{\partial}{\partial c} \left( \frac{P}{RT} \right)T \] (11)

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For the ideal case van't Hoff's law is written

\[ P = \frac{C}{M} \text{RT} \]

and so Equation (11) reduces to Equation (8). However, even in dilute solutions of large molecules, deviation from ideality of osmotic pressure is known to be significant. An expression often used to account for small deviations is

\[ \frac{P}{RT} = \frac{C}{M} + BC^2. \]

Substitution into Equation (11) gives

\[ \frac{HC}{\tau} = \frac{1}{M} + 2BC \quad (12) \]

which is a better equation for the study of scattering of light by detergent solutions. The constant B is a measure of non-ideality due to the interactions between solute and solvent.

The value of H is determined from refractive index measurement and \( \tau \) is measured for a range of concentrations. Then a plot of \( \frac{HC}{\tau} \) versus C is extrapolated to infinite dilution and the reciprocal of the intercept is the molecular weight of the scattering species. A large slope B of such a plot indicates good dissolution properties of the solvent.

However, in detergent solutions this procedure must be modified to account for the absence of large scattering species (micelles) below the c.m.c. This is done by
subtracting $\tau_0$, the turbidity at the c.m.c., and $C_0$, the concentration of monomers at the c.m.c. Then a plot of $\frac{H(C-C_0)}{(T-T_0)}$ against $C-C_0$ will reflect the properties of the micelles only. The micellar molecular weight obtained by this method is a weight average one. 84

Opinions differ on whether the slopes of the conventional light scattering plots are influenced by a dispersion of molecular weights. 85,86 Detergent solutions are generally regarded as being practically monodispersed. Recent work by Anacker 87 indicates however that hexadecyltrimethylammonium bromide in high added salt solutions forms polydispersed micelles. Sasaki 88 concludes from his spectral studies with dyes that increasing the surfactant concentration increases the number of detergent molecules per micelle and not the number of micelles. He further concludes that the systems are virtually monodispersed.

Other points of controversy are the magnitude of the charge carried by the micelles, particularly in added salt solutions, and the effect of charge on micelle size and growth. The above treatment applies strictly only to uncharged particles. Many authors, including Anacker, apply it in this form to colloidal electrolytes.

Hutchinson and Shinoda believe that if sufficient extraneous salt is added to the solution, the charge on the micelle is neutralized. Others cite evidence that micelles remain charged in salt solutions.

Attempts to derive theoretical relationships to account for the fact that colloidal electrolytes are indeed electrolytes have been made by Prins and Hermans, Doscher and

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From these papers come equations for calculating the magnitude of the effective charge on the micelle and for correcting the molecular weight obtained by the treatment given above. These equations will be given and discussed later.

Another complication arises over the lack of justification for the assumption that dilute solutions of colloidal electrolytes are ideal. Vrij and Overbeek develop equations which do not assume ideality but, as Venable points out, their theory is difficult to test experimentally. Stigter discusses the relationships from the various treatments of light scattering from multicomponent systems.

In this discussion of charge effects no details have been included because the required space would be prohibitive, little would be gained in so doing, and this writer is

\[95^{95} L. H. Princen and K. J. Mysels, J. Coll. Sci., XII (1957), 594.\]
\[96^{96} D. Stigter, J. Phys. Chem., LXIV (1960), 842.\]
\[98^{98} R. L. Venable, Ph.D. Dissertation, p. 17.\]
much less capable of presenting the various cases than are the authors of the papers cited. The reader is referred to the original papers for specific points of interest.

D. **Solubilization**

Many substances which are normally relatively insoluble in a given solvent are much more soluble in a dilute solution of colloidal material. This process is called solubilization. The otherwise insoluble material is generally considered to be incorporated within or upon the colloidal particles. This property of detergent solutions is found to increase rapidly with detergent concentration above the c.m.c. Below the c.m.c. the solubility of the foreign material is essentially the same as it is in pure solvent. This behavior indicates the presence of micelles in solutions, concentrations of which exceed the c.m.c. and is often used to get an approximate value of the c.m.c.

McBain and Hutchinson,100 Klevens,101 and Harris102

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give excellent reviews of the investigations in this area. The different kinds of solubilization are categorized by Harkins\textsuperscript{103} as (1) solubility of non-polar solutes such as hydrocarbons in the non-polar interior of the micelle; (2) solubility of polar-non-polar molecules such as long chain alcohols in a position similar to that occupied by the detergent molecules in the micelle; and (3) adsorption at the surface of the micelle. The first of these is supported by X-ray data which indicates a thickening in the aggregate dimensions. The second type requires that the molecules of the material solubilized, the solubilize, locate themselves between the detergent molecules. The third type is exhibited by some dyes.

The turbidimetric data of Stearns\textsuperscript{104} on anionic detergents and normal hydrocarbon solubilizes in water indicates that solubilization increases rapidly with paraffin chain length. He also found that the rate of increase of solubilization with detergent concentration increases with concentration. On this latter point Venable\textsuperscript{105} found a


\textsuperscript{104} R. S. Stearns, \textit{et al.}, \textit{J. Chem. Phys.}, XV (1947), 497.

\textsuperscript{105} Venable, Ph.D. Dissertation, pp. 94-97.
similar phenomenon for cationic detergents in water.

Detergent micelles have been described previously as having a liquid-like hydrocarbon interior. Hartly specifically states that "the part of it (the micelle) which is responsible for the solvent action (solubilization) is not diluted by the water in the sense of being intimately dispersed as separate ions,"\textsuperscript{106} and cites other works to confirm this conclusion. However, Sasaki\textsuperscript{107} finds from dye adsorption studies on all three classes of detergents that micelles contain some water, at least up to concentrations of surfactant as large as 10 per cent.

The size of the charged head group was indicated by Drott\textsuperscript{108} to be a factor in solubilization. Venable\textsuperscript{109} studied the various properties of tetradecylpyridinium bromide (TPB) and TTPAB in water and in 0.050 M sodium bromide solution. In both solvents the head size calculations gave a much smaller value for TPB as expected. In water both detergents had comparable molecular weights but TTPAB

\textsuperscript{108}E. Drott, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1959, p. 111.
\textsuperscript{109}Venable, Ph.D. Dissertation, p. 112.
solubilized fewer benzene molecules per micelle than did TPB. He suggested that this could possibly be caused by the propyl side chains bending down into the interior of the micelle, thereby reducing the void space which is presumably capable of receiving benzene molecules. In 0.050 M sodium bromide solution the molecular weights were quite different, so he chose as the criterion for solubilizing power the ratio of benzene molecules solubilized to detergent monomers in the micelle. On this basis TTPAB was found to be a more efficient solubilizer. This discussion will be continued in Chapter III where solubilization results obtained by this writer will be presented.

One's inability to determine micelle size leads to complications in comparing solubilizing power of different detergents and of the same detergent in different added salt concentrations. Using the criterion of ratio of moles of solubilize to moles of micellar molecules, the solubilizing power generally increases with added salt concentration. This point will also be discussed in Chapter III where evidence for its validity will be presented.

Harkins\textsuperscript{111} ascribed the increased solubilizing power of potassium laurate in added salts to the depression of the c.m.c. and the consequent formation of more micelles of the type which were present before the salt was added. However, he admits that at higher detergent concentrations, solubilization is too great to be accounted for in this way. He also notes that the molar volume of the solubilizate is inversely proportional to the amount solubilized.

Several anionic detergents and dye systems were studied by Mankowich.\textsuperscript{112} No correlation was found between the polarity of the solubilizate and the slope of the log solubilization-log concentration plot or between polarity and the magnitude of solubilization.

\textsuperscript{111} W. D. Harkins, et al., \textit{J. Chem. Phys.}, XV (1947), 496.

CHAPTER II

MATERIALS AND METHODS

A. Synthesis of Detergents

All the quaternary ammonium bromide detergents were prepared by a method similar to that of Scott and Tartar.¹

The long chain alkyl bromide was mixed with a 35-40 per cent excess of the appropriate trialkylamine and this solution was added to a particular volume of reaction solvent, either methanol or ethanol. The resulting solution was heated under total reflux from seven hours to three days. After the reaction mixture cooled, most of the alcohol and excess amine were boiled off, in some cases, under reduced pressure. Ether was added to precipitate the detergent crystals.

Purification was effected by repeated recrystallization from alcohol by adding ether, by Soxhlet extraction using ether for as long as twenty hours, or by a combination

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of the two methods. The ether was then filtered from the crystals. The last traces of ether were removed from the crystals by heating under vacuum at approximately 35°C for twenty-four hours.

If precipitation was allowed to occur very slowly by gradual chilling, the crystals were larger and more easily filtered. This technique enhances purification and so reduces the number of recrystallizations necessary. Soxhlet extraction has the advantages of being less time consuming, and less detergent is lost.

When ethanol was substituted for methanol as the reaction solvent, the reflux temperature was increased sufficiently to enhance the detergent yield greatly, in some cases by as much as 100 per cent.

The starting materials were reagent grade products of either Eastman Organic Chemicals or Matheson, Coleman, and Bell. In those cases in which the gas chromatogram of the alkyl bromide showed more than one large peak, the compound was purified by vacuum distillation.

The primary criterion for purity of the detergents was the absence of a minimum in the surface tension-concentration curve. The ultimate criterion was to obtain a reproducible turbidity-concentration curve containing no peaks nor change
in shape prior to the c.m.c. before and after a given re-
crystallization.

B. **Surface Tension Experiments**

All surface tension measurements were made by the ring
method. A chainomatic balance made by Christian Becker, Inc.
was used to measure the weight necessary to lift a platinum
ring from the solution-air interface. This weight is line-
early related to the surface tension of the liquid by the
theory developed by Harkins, Young, and Cheng\(^2\) and refined
by Harkins and Jordan.\(^3\) This theory furnishes the equation

\[
\gamma = \frac{f}{2\pi R} \cdot F = \frac{Mg}{4\pi R} \cdot F
\]

(13)
in which \(\gamma\) is the surface tension in dynes per centimeter;
\(f\), the maximum force exerted on the ring; \(R\), the mean radius
of the ring; \(M\), the maximum weight of liquid raised above
the free surface of the liquid; \(F\), a correction factor to
account for the shape of the liquid held up by the ring and
the ring dimensions; and \(g\), the acceleration due to gravity.

LXIV (1926), 33.

\(^3\) W. D. Harkins and H. F. Jordon, *J. Am. Chem. Soc.*,
LII (1930), 1751.
The maximum force exerted on the ring can be shown to be the maximum weight of the liquid held up by the ring multiplied by \( g/2 \). A measure of this downward force will be the equivalent upward force exerted by the weights added to the beam. Therefore the surface tension and weight added are directly proportional.

This relationship was used in calculating the surface tension of all solutions. By using the same ring throughout this work, all factors except \( M \) could be held constant. Equation (13) may be written

\[
\gamma = k M \tag{14}
\]

where \( k = gF/4\pi R \). Since all solutions were aqueous and the surface tension of water is known accurately, Equation (14) was employed to calculate the surface tension of detergent solutions relative to that of water.

The correct technique in using the ring method is described by Harkins and Jordon.\(^4\) However, the cell platform of the balance available could not be raised and lowered smoothly. Consequently the ring underwent horizontal and vertical oscillations. Since the beam release mechanism

\(^4\)Ibid.
could be operated with no noticeable oscillation of the ring, the following technique was used.

The sample cell and platinum ring were cleaned in chromic acid solution, rinsed copiously with triply distilled water and dried. The cell was thermostated by pumping water from a constant temperature bath at 30.0 ± 0.1°C around it for approximately one hour prior to an experiment. Twenty-five ml. of distilled water were pipetted into the cell and allowed to equilibrate for thirty minutes or until a constant measurement was obtained.

Increments of a stock solution of detergent were added and each new solution stirred vigorously by means of a motor driven paddlewheel mounted above the instrument. The cell was then raised so that the solution surface just contacted the ring. The solution and ring were allowed to equilibrate for 10-15 minutes. Weights were added to the beam and the beam arrest mechanism carefully released. Additional weight was slowly added by the chain until the ring pulled free of the solution.

This method gives values of the weight added which are slightly high. However this only causes the proportionality constant in Equation (14) to be lowered. Neither the break in the surface tension-log concentration curve which gives
the c.m.c. nor the slope of the curve from which is calculated the area per detergent molecule in the surface is changed. The technique used here gave values of $1.20 \times 10^{-3}$ gm/cc and 56 $\text{Å}^2$ for the c.m.c. and area per molecule, respectively for TTMAB in water. The same experiment by Venable\textsuperscript{5} using the conventional operating technique gave the values of $1.18 \times 10^{-3}$ gm/cc and 61 $\text{Å}^2$ for the same quantities. The two sets of results are consistent within the limits of experimental error.

C. Light Scattering Experiments

Turbidity measurements were made on an Aminco absolute light-scattering photometer. This instrument uses a mercury vapor lamp as a source of the incident beam. It is equipped with several filters to permit operation at various wavelengths. The 4360 Å line was used throughout this work.

The light beam from the lamp passes through a collimating assembly comprised of an aperture stop, a field stop, an achromatic lens, and an incident baffle. The receiver assembly containing a 1P21 photomultiplier tube is mounted on an arm which can be rotated 135° in either direction about the incident beam.

\textsuperscript{5}R. L. Venable, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1963, p. 58.
A cell holder is located between the collimating and receiver assemblies and houses the cell containing the solution. The cell can be positioned so that its flat faces are perpendicular to the incident and exit beams. A single 125 ml. capacity semi-octagonal cell was used in all measurements.

A part of the light leaving the solution is intercepted by the photomultiplier tube and converted into a current signal which is fed into a photomultiplier microphotometer. Here it is sent through one of seven resistors connected to the microphotometer control. The corresponding voltage drop which is proportional to intensity is read from the per cent transmission scale on the face of the microphotometer. All measurements were made at maximum sensitivity.

The light scattering photometer was calibrated periodically with a solution of 0.5 gm of Cornell polystyrene diluted to 100 ml with triply distilled toluene. The turbidity of the polystyrene in such a solution has been determined by many investigators and found to be $3.49 \times 10^{-3}$ cm$^{-1}$. Turbidity is proportional to $I_{90}/I_0$, the ratio of intensities measured at 90° and 0° with respect to the incident beam, that is
\[ \tau = C \frac{I_{90}}{I_0} \]

in which \( C \) depends only upon the instrument, its optical alignment and geometry, and the cell used. By measuring \( \frac{I_{90}}{I_0} \) and knowing \( \tau \) for the polystyrene, \( C \) can be evaluated. Then by measuring \( \frac{I_{90}}{I_0} \) for a detergent solution, its turbidity can be calculated from Equation (15). The corrections which have to be applied when the instrument is calibrated with a solution of refractive index different from that of the solution the turbidity of which is to be determined will be discussed in detail in the next chapter.

Between periodic calibrations a more frequent and much easier check of the instrument was accomplished with the aid of an opal glass diffuser manufactured by the Phoenix Precision Instrument Company. Ratios of \( \frac{I_{90}}{I_0} \) and \( \frac{I_{135}}{I_{45}} \) were determined immediately after a calibration to get accurate values which could be checked prior to a light scattering experiment. If these ratios change, recalculation is necessary.

The water used throughout the course of this work was triply distilled. One of the distillations was made on a basic permanganate solution. The turbidity of the water was repeatedly checked and found to be \( 0.80 \pm 0.04 \text{ cm}^{-1} \). This
value is higher than that reported by Phillips and Mysels\textsuperscript{6} who used more elaborate purification techniques. Venable\textsuperscript{7} who used water from the same container that the present writer used found that this higher turbidity did not influence his results.

The specific conductivity of the water used here was measured by Yarborough\textsuperscript{8} and found to be $1.22 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Haydon and Phillips\textsuperscript{9} investigated the effect of impure water on surface tension. Their water from a Manesty still with a specific conductivity of $4.0 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ was passed twice through a column of Biodeminrolit which reduced the value to $0.9 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Further purification by distillation in pyrex and condensation in silica gave the water a specific conductivity of $0.55 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. They found that the water from the last two treatments gave identical surface tension-concentration curves. From a comparison of


\textsuperscript{7}R. L. Venable, Ph.D. Dissertation, pp. 37-38.

\textsuperscript{8}K. Yarborough, Department of Chemistry, Louisiana State University, Baton Rouge.

these conductivities it seems likely that the water used here was sufficiently pure for use in surface tension, light scattering and solubilization work.

All glassware was scrupulously cleaned in a hot chromic acid bath, rinsed copiously with triply distilled water, and dried. All stock solutions were filtered through ultrafine fritted glass filters to remove dust and large foreign particles. Fritted filters are known to adsorb detergents from solution. Consequently the true concentration of stock solutions was determined by use of a differential refractometer described below.

The actual turbidity measurements on detergent solutions were made by the following procedure. Fifty ml. of filtered solvent was pipetted into the large semioctagonal cell and $I_{90}$ and $I_0$ measured. Subsequent aliquots of a detergent solution contained in a burette fitted with a Teflon stopcock were run into the cell, stirred vigorously with a glass rod, and the measurements repeated. It was found that the addition and stirring technique did not introduce sufficient dust to affect the measurements. Several runs were made in which the detergent was omitted from the system. No measurable increase in turbidity was found.
D. Differential Refractometer Measurements

The need for a differential refractometer was twofold in this work. The refraction constant $H$, defined by Equation (9) contains the quantity $\frac{\mu - \mu_0}{C}$, the change in index of refraction with detergent concentration. This factor must be evaluated for each detergent in order to calculate micellar molecular weights from light scattering data. Also this instrument provides a convenient method of determining accurate concentrations of filtered stock solution.

The refractometer used for these purposes was a Brice-Phoenix visual laboratory-type, model BP-1000-V made by the Phoenix Precision Instrument Company, Inc. Description of this instrument can be found in the manual supplied by the manufacturer.

Calibration was accomplished with a series of aqueous potassium chloride solutions for which the difference in refractive index between the potassium chloride solutions and water is known. A plot of refractive index difference against concentration for each detergent was made and $\frac{\mu - \mu_0}{C}$ calculated. These same plots were used to determine detergent concentration of filtered stock solutions by measuring the refractive index difference and reading concentration from the graph.
Although this difference in refractive index should be independent of the solvent, the importance of this quantity warranted a comparison of the results for a given detergent in water and 0.0500 M sodium bromide solution. The two results were identical as predicted. While light scattering measurements were made in solutions as high as 0.0500 M in added salt, H was evaluated only once for each detergent.

E. Solubilization Experiments

The only solubilizate used in this work was spectroscopic grade benzene. This was due primarily to two reasons. Other workers in this laboratory\textsuperscript{10,11,12} have studied similar systems using benzene. A comparison of their results with those obtained here seemed desirable. In addition benzene in aqueous solutions can be easily determined by spectrophotometric methods.

An excess of benzene was added to a series of solutions of varying detergent concentration contained in glass

\textsuperscript{10}J. Sardisco, M.S. Thesis, Louisiana State University, Baton Rouge, 1958, p. 44.

\textsuperscript{11}E. Drott, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1959, p. 93.

ampules. The ampules were sealed and shaken on a wrist action shaker for forty-eight hours. They were then transferred to a water bath maintained at $30.0 \pm 0.1^\circ C$ and allowed to equilibrate for one week or until the emulsions broke, whichever was longer. Klevens$^{13}$ reports that equilibrium in such systems is attained within forty-eight hours.

The tips of each ampule were then snapped off and approximately one ml. of the detergent solution was run into a weighed amount of reagent grade cyclohexane contained in a volumetric flask. The flask was reweighed to determine the amount of the aqueous phase. A single extraction was carried out by placing the flask on a wrist action shaker for six to eight hours.

The cyclohexane layer was subsequently analyzed by means of a Beckman DU Spectrophotometer to determine the amount of benzene in the cyclohexane. Absorbance was measured at the 255 m\(\mu\) absorption band of benzene. From a calibration curve of absorbance versus known concentration of benzene, the amount of benzene in the cyclohexane phase was determined. Subsequently the amount of benzene solubilized by the detergent solution was calculated.

Quite stable emulsions were formed by the TTBAB-H$_2$O

and HTBAB-H₂O systems, the former required nineteen days to break and the latter was abandoned after three months.
A. Surface Tension

A graph of surface tension of detergent solutions versus the logarithm of detergent concentration shows two intersecting straight lines. The point of intersection is assumed to be the c.m.c. and the slope of the line at concentrations below the c.m.c. is used to calculate a parameter known as the effective area per molecule in the interface.

The c.m.c.'s and the effective areas obtained from measurements on solutions of members of the tetradecyl and hexadecyl series are given in Tables I and II, respectively. The figures referred to in these tables show the linear dependence of surface tension on the log concentration for the systems studied. All concentrations are in gram per ml. TTBAB was suspected of containing impurities; a minimum occurred in the surface tension-log concentration curve and aging effects were observed when the surface tension of solutions below the c.m.c. was measured. The impurities could not be removed by the methods discussed in Chapter II.


<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>c.m.c. in gm/ml x 10^4</th>
<th>c.m.c. in moles/liter x 10^4</th>
<th>Area molecule in A^2</th>
<th>( \gamma^* ) in dyne/cm at c.m.c.</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTMAB</td>
<td>0</td>
<td>12.0</td>
<td>35.7</td>
<td>56</td>
<td>40.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>(1.43)</td>
<td>(4.25)</td>
<td>(39)</td>
<td>(37)</td>
<td></td>
</tr>
<tr>
<td>TTEAB</td>
<td>0</td>
<td>10.6</td>
<td>28.0</td>
<td>67</td>
<td>42.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>4.0</td>
<td>10.6</td>
<td>61</td>
<td>41.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>2.5</td>
<td>6.6</td>
<td>64</td>
<td>40.6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>1.6</td>
<td>4.2</td>
<td>55</td>
<td>40.4</td>
<td>2</td>
</tr>
<tr>
<td>TTPAB</td>
<td>0</td>
<td>9.1</td>
<td>21.6</td>
<td>83</td>
<td>42.7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>(1.2)</td>
<td>(2.85)</td>
<td>(64)</td>
<td>(39)</td>
<td></td>
</tr>
<tr>
<td>TTBAB</td>
<td>0</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>


1Values given in parentheses were determined by R. L. Venable, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1963, p. 58, and are listed here for comparison.
TABLE II
RESULTS OF SURFACE TENSION MEASUREMENTS ON THE HEXADECYL SERIES OF DETERGENTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>c.m.c. in gms/ml x 10^4</th>
<th>c.m.c. in moles/liter x 10^4</th>
<th>Area/molecule in A^2</th>
<th>γ in dyne/cm at c.m.c.</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTMAB</td>
<td>0</td>
<td>1.80</td>
<td>4.94</td>
<td>57</td>
<td>39.4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>0.20</td>
<td>0.55</td>
<td>--</td>
<td>35.0</td>
<td>-</td>
</tr>
<tr>
<td>HTEAB</td>
<td>0</td>
<td>3.02</td>
<td>7.4</td>
<td>77</td>
<td>43.8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>0.41</td>
<td>1.0</td>
<td>65</td>
<td>41.1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>0.23</td>
<td>0.57</td>
<td>73</td>
<td>40.3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>0.20</td>
<td>0.49</td>
<td>62</td>
<td>39.7</td>
<td>4</td>
</tr>
<tr>
<td>HTPAB</td>
<td>0</td>
<td>2.49</td>
<td>5.56</td>
<td>92</td>
<td>43.4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>0.10</td>
<td>0.22</td>
<td>66</td>
<td>38.6</td>
<td>5</td>
</tr>
<tr>
<td>HTBAB</td>
<td>0</td>
<td>1.53</td>
<td>3.12</td>
<td>132</td>
<td>41.7</td>
<td>6</td>
</tr>
</tbody>
</table>
FIGURE 1. Surface Tension versus Log C for the Tetradecyl Series in H₂O
FIGURE 2. Surface Tension versus Log C for TTEAB in NaBr Salt Solutions
FIGURE 3. Surface Tension versus Log C for HTMAB and HTEAB in H₂O
FIGURE 4. Surface Tension versus Log C for HTEAB in NaBr Salt Solutions
FIGURE 5. Surface Tension versus Log C for HTPAB in H₂O and NaBr Salt Solutions
FIGURE 6. Surface Tension versus Log C for HTBAB in H₂O
Consequently this compound is omitted from the discussions concerning surface tension.

Equation (1) given in the first chapter indicates a linear relationship between log c.m.c. and the number of carbon atoms in the long paraffin chain. Using the values of c.m.c. listed in Tables I and II a similar linear relationship is suggested when the total number of carbons in the three short alkyl chains is plotted versus the logarithm of the critical micelle concentration in pure water; see Figure 7. Concentrations are in moles per liter. The apparent discrepancy for HTMAB may be found in the nature of this detergent. Hill and Hunter\(^2\) found the maximum lowering of surface tension for this detergent to occur at \(1.5 \times 10^{-4}\) gm/cc which is not too different from the value of \(1.80 \times 10^{-4}\) gm/cc given above. Debye and Anacker\(^3\) noted that this compound precipitated from aqueous solutions around 30\(^\circ\)C. It may be that this break in the surface tension curve is not a true c.m.c., but the point at which some sort of microcrystals form.


FIGURE 7. Total Number of Carbon Atoms in Side Chains versus Log c.m.c.
Different linear relationships for the tetradeyl and hexadecyl series suggest that the length of the long chain affects both the slope and the intercept of such plots. Although Shinoda\(^4\) discusses the theoretical basis for Equation (1), no explanation for the similar phenomena described here will be attempted.

The area occupied by a detergent molecule in the interface can be determined from the surface tension data. As the nature of the three alkyl groups at the head of the monomer was changed from methyl to ethyl, propyl and butyl, a corresponding increase in this head size parameter occurred. The results from the fifth columns of Tables I and II are presented in Figure 8. The ordinate of each point is the square of the number of carbon atoms in each short alkyl chain. If one visualizes a monomer head in the interface to be contained within a circle whose radius is proportional to the length of the short alkyl chain, the area of this circle will be proportional to the square of the length of the alkyl chain. This length will, in turn, be proportional to the number of carbon atoms in each chain, N. Although this is a very elementary picture, Figure 8 verifies the prediction

FIGURE 8. Area per Molecule versus the Square of the Number of Carbon Atoms per Side Chain
that the area per molecule calculated from surface tension data increases linearly with $N^2$. The same type behavior is exhibited by both the tetradecyl and hexadecyl series.

Equation (3) in Chapter I, which is derived from theoretical principles, predicts a linear dependence of log c.m.c. on log (c.m.c. + $C_a$), where $C_a$ is the concentration of added electrolyte. All concentrations must be expressed in moles per liter. In the quantity (c.m.c. + $C_a$), which is the total concentration of unassociated electrolyte, the concentration of unaggregated colloid is represented by the first term. If the micelle carries a residual charge, the aggregation number will be larger than the number of bound gegenions. This leaves an excess of gegenions of the same nature as that of the added salt. This contribution is not accounted for but is negligibly small.

Figure 9 is a plot of log c.m.c. versus log (c.m.c. + $C_a$) for TTEAB and HTEAB in various solutions of NaBr, the results for which are taken from Tables I and II. The form of Equation (3) is seen to be verified.

The applicability of the Gibbs adsorption relation, Equation (6), when applied to solutions containing added salts is questionable. This is due primarily to the fact that this form of the equation was derived on the assumption
FIGURE 9. Log c.m.c. versus Log (c.m.c. + C_a) for TTEAB and HTEAB
that concentrations could be substituted for activities. Dilute solutions of detergents in the presence of added salts are less ideal than if the solvent is pure water and consequently the assumption is less valid.

However, it is evident from Tables I and II that this head size parameter decreases with increasing added salt concentration for all detergents. It is possible that this effect has its explanation in the Debye-Hückel theory. In the interionic theory of strong electrolytes, increasing the electrolyte concentration is known to exhibit a shielding effect which reduces the electrical Coulombic repulsion between ions. On this premise Debye\(^5\) explained the decrease in c.m.c. with added electrolyte in terms of a reduction in electrical work done against the Coulombic forces. In other words, micellization can occur at a lower surfactant concentration than if the salt were absent.

It seems probable that a similar argument could account for the increasing number of detergent molecules in the interface. A larger number of molecules at the surface would reduce the effective area each head could occupy there. No quantitative expression for this phenomenon will be given here.

The last point of interest in this series of experiments concerns the maximum lowering of the surface tension by each detergent-solvent system. These values are shown in the sixth columns of Tables I and II, labeled "γ in dyne/cm at c.m.c." Only one regular trend was observed, that of a small but significant decrease with increase in added salt in all cases. This effect parallels the decrease in area per molecule as the added salt concentration increases. The argument given above for the increase in number of surface active species at the interface due to the shielding effect of added electrolyte is supported by this trend. A higher concentration of detergent monomers at the interface would both reduce the effective area each head could occupy there as well as increase the maximum lowering of the surface tension for a particular concentration of detergent.

B. Light Scattering

When turbidity measurements are made on a solution having a refractive index which is different from that of the solution used to calibrate the light scattering instrument, several corrections must be applied to the data in order to get accurate molecular weights. In this work calibration was effected by means of solutions of polystyrene in toluene while measurements were made on detergents
dissolved in water. The necessary corrections are given by Edsall\textsuperscript{6} and by Carr and Zimm.\textsuperscript{7} Only those which apply here will be discussed.

A refractive index correction is necessary because refraction occurring at the cell faces changes with the index of fraction of the solution. Consequently the spreading of the light rays leaving the cell will not be the same from toluene solutions and water solutions. The quantity $C_n$ by which the $\frac{I_{90}}{I_0}$ measurements in water must be multiplied is

\begin{equation}
C_n = \left[ \frac{n_1 \left[ 1 - \frac{r'}{R} \left( \frac{n_1-1}{n_1} \right) \right]^2}{n_2 \left[ 1 - \frac{r'}{R} \left( \frac{n_2-1}{n_2} \right) \right]} \right].
\end{equation}

In this equation the subscripts 1 and 2 refer to water and toluene, respectively. The $n$'s represent the corresponding indices of refraction of the two solvents, $r'$ is the distance from the center of the cell to its outer edge, and $R$ is the distance from the center of the cell to the photomultiplier aperture. This equation is applicable in this form to a square cell.


A volume correction factor must be applied to the measurements to account for the variation in the total volume of liquid which the photomultiplier tube "sees" as the refractive index of the solution in the cell changes. This correction $C_v$ has the form

$$C_v = \frac{1 - \frac{r'(a+L)}{(R-r')}}{1 - \frac{r'(a+L)}{(R-r')}} \cdot \frac{2 \left[ n_1 L + r'(a+L) \right]/(R-r')}{2 \left[ n_2 L + r'(a+L) \right]/(R-r')}.$$  \hspace{1cm} (17)

In this equation $a$ and $L$ are the widths of the receiver stops on the entrance and exit sides of the cell, respectively, while the other quantities are defined above. The numerical values of the constants are:

- $n_1 = 1.340 \, (\lambda = 436 \, \text{m\AA}, \, T = 25^\circ \text{C})$
- $n_2 = 1.515 \, (\lambda = 436 \, \text{m\AA}, \, T = 25^\circ \text{C})$
- $r' = 2.21 \, \text{cm}$
- $R = 7.366 \, \text{cm}$
- $A = L = 0.4039 \, \text{cm}$
- $C_n = 0.844$
- $C_v = 0.984$
In Chapter II, the following equation for the turbidity \( \tau \), in terms of the ratio of measured intensities, \( \frac{I_90}{I_0} \), for detergent solutions was given:

\[
\tau = C \frac{I_90}{I_0} . \quad (18)
\]

C is the calibration constant determined by measuring \( \frac{I_90}{I_0} \) for a particular polystyrene solution the turbidity of which is \( 3.49 \times 10^{-3} \) cm\(^{-1} \). Since the value of C often changes from one calibration to the next, the working equation which is derived below will contain this quantity as a parameter that must be evaluated periodically.

Insertion of the fraction and volume correction factors into Equation (18) gives

\[
\tau = C_n \ C_v \frac{I_90}{I_0} C . \quad (19)
\]

After substitution of 0.844 and 0.984 for \( C_n \) and \( C_v \), respectively, the working equation becomes

\[
\tau = (0.844)(0.984) \frac{I_90}{I_0} C
\]

or

\[
\tau = (0.841) \frac{I_90}{I_0} C . \quad (20)
\]
The turbidities of all detergent solutions were calculated from measured quantities by the use of this equation.

The refraction constant H defined by Equation (9) contains only one experimental quantity, \( \frac{\mu - \mu_0}{C} \), the change in index of refraction with concentration called the refractive index increment. The values of \( \frac{\mu - \mu_0}{C} \) and H for all the detergents studied are listed in Table III. Also shown is the change in refractive index with concentration for NaBr, a quantity needed in calculating the charge on the micelle. The procedure will be explained later.

Results of the light scattering measurements on the tetradecyl and hexadecyl series of detergents are summarized in Table IV and Table V, respectively. The quantity \( \frac{1}{A} \) is the reciprocal of the intercept of a plot of \( H(C-C_0)/(\tau-\tau_0) \) against \( (C-C_0) \). Its value represents an apparent micellar molecular weight. B is the initial slope of such a plot. P is the charge per micelle and m is the number of monomers per micelle; both of these quantities are calculated from equations discussed below. The corrected micellar molecular weight is then nM, where M is the monomer molecular weight. The c.m.c. values listed are those determined by the breaks in the turbidity-concentration curves.

The \( H(C-C_0)/(\tau-\tau_0) \) versus \( (C-C_0) \) plots for the various
### TABLE III

**REFRACTIVE INDEX INCREMENTS AND REFRACTION CONSTANTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\frac{\mu - \mu_0}{C}$</th>
<th>$H \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTMAB</td>
<td>(0.154)</td>
<td>(6.47)</td>
</tr>
<tr>
<td>TTEAB</td>
<td>0.155</td>
<td>6.57</td>
</tr>
<tr>
<td>TTPAB</td>
<td>0.160</td>
<td>6.95</td>
</tr>
<tr>
<td>TTBAB*</td>
<td>0.157</td>
<td>6.73</td>
</tr>
<tr>
<td>HTMAB</td>
<td>0.153</td>
<td>6.39</td>
</tr>
<tr>
<td>HTEAB</td>
<td>0.156</td>
<td>6.61</td>
</tr>
<tr>
<td>HTPAB</td>
<td>0.164</td>
<td>7.34</td>
</tr>
<tr>
<td>HTBAB</td>
<td>0.162</td>
<td>7.16</td>
</tr>
<tr>
<td>NaBr</td>
<td>$1.48 \times 10^{-2}$</td>
<td>----</td>
</tr>
</tbody>
</table>

*TTBAB contained some impurities which makes these values less reliable.

---

*Values in parentheses were determined by R. L. Venable, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1963, p. 74.*
## TABLE IV

RESULTS OF LIGHT SCATTERING MEASUREMENTS ON THE TETRADECYL SERIES OF DETERGENTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>$\frac{1}{A}$ x $10^3$</th>
<th>$B$ x $10^3$</th>
<th>$P_m$</th>
<th>$\frac{P}{m}$</th>
<th>$mM_1$ in gms/cc x $10^4$</th>
<th>C.M.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTMAB</td>
<td>0</td>
<td>(23,300)</td>
<td>(30.3)</td>
<td>(12)</td>
<td>(84)</td>
<td>(0.14)</td>
<td>(27,200)</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>(49,700)</td>
<td>(1.25)</td>
<td>(6)</td>
<td>(150)</td>
<td>(0.04)</td>
<td>(50,400)</td>
</tr>
<tr>
<td>TTEAB</td>
<td>0</td>
<td>15,200</td>
<td>16.4</td>
<td>5</td>
<td>45</td>
<td>0.12</td>
<td>17,100</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>20,700</td>
<td>25.1</td>
<td>10</td>
<td>63</td>
<td>0.16</td>
<td>23,700</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>31,300</td>
<td>5.0</td>
<td>12</td>
<td>81</td>
<td>0.14</td>
<td>30,000</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>26,500</td>
<td>2.2</td>
<td>10</td>
<td>73</td>
<td>0.13</td>
<td>27,500</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>27,600</td>
<td>1.2</td>
<td>10</td>
<td>76</td>
<td>0.13</td>
<td>28,700</td>
</tr>
<tr>
<td>TTPAB</td>
<td>0</td>
<td>8,000</td>
<td>29.7</td>
<td>3</td>
<td>22</td>
<td>0.15</td>
<td>9,300</td>
</tr>
<tr>
<td></td>
<td>(22,700)</td>
<td>(17.9)</td>
<td>(7)</td>
<td>(61)</td>
<td>(0.12)</td>
<td>(25,600)</td>
<td>(8.6)</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>(39,200)</td>
<td>(1.87)</td>
<td>(18)</td>
<td>(97)</td>
<td>(0.19)</td>
<td>(40,700)</td>
</tr>
<tr>
<td>TTBAB*</td>
<td>0</td>
<td>3-5,000</td>
<td>0</td>
<td>0</td>
<td>6-11</td>
<td>0</td>
<td>3-5,000</td>
</tr>
</tbody>
</table>

*These values for TTBAB are based on a single experiment.

---

9Ibid., p. 75.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>$\frac{1}{A}$ x 10^3</th>
<th>B x 10^3</th>
<th>P</th>
<th>M</th>
<th>$\frac{P}{m}$</th>
<th>mM$_1$</th>
<th>c.m.c. in gms/cc x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTEAB</td>
<td>0</td>
<td>12,600</td>
<td>18</td>
<td>2.4</td>
<td>33</td>
<td>0.071</td>
<td>13,500</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>17,100</td>
<td>26</td>
<td>5.2</td>
<td>45</td>
<td>0.12</td>
<td>18,200</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>43,900</td>
<td>9.5</td>
<td>23</td>
<td>114</td>
<td>0.20</td>
<td>46,400</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>44,900</td>
<td>4.1</td>
<td>22</td>
<td>137</td>
<td>0.16</td>
<td>55,700</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>41,500</td>
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<td>0</td>
<td>103</td>
<td>0</td>
<td>41,500</td>
<td>0.30</td>
</tr>
<tr>
<td>HTPAB</td>
<td>0</td>
<td>7,000</td>
<td>137</td>
<td>3.4</td>
<td>19</td>
<td>0.18</td>
<td>4,500</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>32,300</td>
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<td>0</td>
<td>72</td>
<td>0</td>
<td>32,300</td>
<td>0.70</td>
</tr>
</tbody>
</table>
systems are shown in Figures 10-14. These graphs were constructed from selected turbidity-concentration data points which were also used to plot turbidity-concentration curves similar to those in Figure 15. These graphs will be referred to as necessary throughout the remainder of this discussion.

All values listed in Tables IV and V are averages of two or more determinations. For the molecular weight values, the reproducibility was within 5 per cent except for the TTEAB-0.0130 M NaBr and HTEAB-0.0500 M NaBr systems, in which cases it was 8 per cent and 10 per cent, respectively. Phillips and Mysels\(^\text{10}\) studied the effects of various errors in the different steps of light scattering experiments. They estimate the absolute accuracy of the micellar molecular weight determination as \(\pm 10\) per cent. Tartar\(^\text{11}\) agrees and notes that the same errors can cause different results to vary by as much as \(\pm 10\) per cent.

In Table IV the numbers in parentheses for TTMAB and TTPAB were obtained by Venable\(^\text{12}\). His surface tension


\(^{12}\)Venable, Ph.D. Dissertation, p. 75.
FIGURE 10. $\frac{H(C-C_0)}{(\tau-\tau_0)}$ versus $(C-C_0)$ for TTEAB and TTPAB in H₂O
FIGURE 11. $H(C-C_0)/(\tau-\tau_0)$ versus $(C-C_0)$ for TTEAB in NaBr Salt Solutions
FIGURE 12. $\frac{H(C-C_0)}{(\tau - \tau_0)}$ versus $(C-C_0)$ for HTEAB in H$_2$O
FIGURE 13. $H(C-C_0)/(\tau-\tau_0)$ versus $(C-C_0)$ for HTEAB in NaBr Salt Solutions
FIGURE 14. $H(C-C_0)/(\tau-\tau_0)$ versus $(C-C_0)$ for HTPAB in H$_2$O and NaBr Salt Solutions
FIGURE 15. \((\tau - \tau_0)\) versus \((C - C_0)\) for TTEAB in NaBr Salt Solutions
measurements on TTPAB\textsuperscript{13} showed a decrease with time for all concentrations prior to the c.m.c. Although he offers an alternative explanation for this time dependence of surface tension, he does not preclude the possibility of impurities in the detergent. His light scattering results\textsuperscript{14} on the same compound were reproducible and did not indicate impurities.

This writer found no such changes in surface tension with time. These results were obtained from material made in a new preparation of TTPAB and, as shown in Table IV, a much smaller micellar molecular weight was obtained. Therefore it is likely that the difference between the two sets of values may be due only to impurities. The smaller value will be taken as the correct one.

A similar discussion concerning TTBAB in this writer's work must be included. The surface tension measurements for this compound showed aging effects at concentrations lower than the c.m.c. and the surface tension-concentration curve showed a minimum. The light scattering results given in Table IV for TTBAB are based on a single run and should be regarded as dubious at this time.

\textsuperscript{13}\textit{Ibid.}, p. 64. \textsuperscript{14}\textit{Ibid.}, pp. 83, 85.
Light scattering work was not done on HTMAB for two reasons. In water this detergent behaves peculiarly as noted previously in the discussion of the surface tension results. Added salt solutions of this detergent have been studied extensively.

Debye\textsuperscript{15} found that in 0.0130 M KBr HTMAB gave a micellar molecular weight of 61,700. The light scattering data of Trap and Hermans\textsuperscript{16} gave values of 75,600 and 98,400 for the micellar molecular weight of this detergent in 0.0125 M KBr and 0.0250 M KBr, respectively. (See also references 17–19).

No light scattering results are listed in Table V for HTBAB. Solubilization work on this compound was abandoned after emulsions with benzene did not break over a period of three months. Since there was no basis for correlating light scattering and solubilization data, only preliminary


turbidity measurements were made. A single experiment indicated very small aggregates comparable to those of TTBAB.

It is possible to obtain with the aid of surface tension data an approximate micellar molecular weight with which to compare those from turbidity measurements. If the area occupied by each monomer head at the air-water interface is assumed to be the same as that on the surface of the micelle, and if the micelle is spherical with a radius equal to the length of the long hydrocarbon chain, the number of monomers per micelle can be determined. The linear extensions of tetradecyl and hexadecyl chains can be taken as 18.5 Å and 21 Å, respectively. Division of the surface areas of each sphere by the area each molecule occupies there gives the number of monomers per micelle which, when multiplied by the monomer molecular weight, gives the micellar molecular weight.

The micellar molecular weights calculated by this method are shown in Table VI in the column labeled "Calculated MMW I." The measured values are listed for comparison. The column labeled "Calculated MMW II" will be discussed at the end of this section. It is evident that these calculated values are quite approximate. The degree of approximation is

---

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>Measured MMW*</th>
<th>Calculated MMW (I)</th>
<th>Calculated MMW (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTEAB</td>
<td>0</td>
<td>17,000</td>
<td>24,000</td>
<td>18,200</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>30,000</td>
<td>27,000</td>
<td>19,900</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>27,500</td>
<td>25,000</td>
<td>19,000</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>28,700</td>
<td>30,000</td>
<td>22,100</td>
</tr>
<tr>
<td>TTPAB</td>
<td>0</td>
<td>9,300</td>
<td>22,000</td>
<td>13,800</td>
</tr>
<tr>
<td>HTEAB</td>
<td>0</td>
<td>13,500</td>
<td>29,000</td>
<td>23,000</td>
</tr>
<tr>
<td></td>
<td>0.0130</td>
<td>46,400</td>
<td>35,000</td>
<td>27,000</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>55,700</td>
<td>31,000</td>
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<td>0.0500</td>
<td>41,500</td>
<td>36,000</td>
<td>28,300</td>
</tr>
<tr>
<td>HTPAB</td>
<td>0</td>
<td>8,500</td>
<td>27,000</td>
<td>18,400</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>32,300</td>
<td>37,000</td>
<td></td>
</tr>
</tbody>
</table>

*MMW refers to micellar molecular weight.
governed not only by the explicit assumptions given above for this calculation but also by the assumptions made in the application of the Gibbs adsorption equation to these systems. Agreement is poorest for the tripropyl detergents in water.

Princen and Mysels\(^{21}\) develop equations for calculating the unneutralized charge \(P\) on the micelle and the corrected micellar molecular weight in terms of this charge in both the absence and presence of extraneous electrolyte. In the absence of added salt, \(P\) can be determined from

\[
P = \frac{B M_1 n_1 + (2Bn_1)^{1/2}}{A (1 - \frac{AM_1}{2})}
\]  

(21)

In the presence of added salt Equation (21) becomes

\[
P = \frac{B M_1 (n_1 + fn_3) + [2B(n_1 + n_3)]^{1/2}}{A (1 - \frac{AM_1 E}{2})}
\]  

(22)

The number of monomers per micelle \(m\) in the absence of added salt is given by

\[
m = \frac{1}{2} \left( P + \frac{1}{AM_1} \right) + \frac{1}{2} \left[ \left( P + \frac{1}{AM_1} \right)^2 - (P^2 + P) \right]^{1/2}
\]  

(23)

and in the presence of added salt by

\[ m = \frac{1}{2} \left( PE + \frac{1}{AM_1} \right) + \frac{1}{2} \left[ (PE + \frac{1}{AM_1})^2 - (p^2 + p) E^2 \right]^{\frac{1}{2}} . \]  

Equations (21) through (24) the various quantities are:

- \( P \) = charge per micelle,
- \( B \) = the initial slope of the \( \frac{H(C-C_0)}{(\tau-\tau_0)} \) vs. \( (C-C_0) \) plot,
- \( M_1 \) = monomer molecular weight,
- \( n_1 \) = c.m.c. in moles/liter,
- \( A \) = the intercept of the \( \frac{H(C-C_0)}{(\tau-\tau_0)} \) vs. \( (C-C_0) \) plot,
- \( n_3 \) = concentration of added salt in moles/liter,
- \( f \) = the ratio of molar refractive index increments of the added salt to that of the detergent,

and \( E = \frac{n_1 + fn_3}{n_1 + n_3} \).

Comparisons between the various light scattering results shown in Tables IV and V and Figures 10-15 provide some interesting cases for discussion.

Figures 11 and 13 show the \( \frac{H(C-C_0)}{(\tau-\tau_0)} \) versus \( (C-C_0) \) plots for TTEAB and HTEAB in various added salt solutions, respectively. In both cases the three systems of highest added salt concentration show approximately the same intercept or micellar molecular weight. This agrees with the results on sodium lauryl sulfate given by Kushner and
Hubbard. They believe that there exists an optimum concentration of added salt above which the micelle does not grow.

All the light scattering results can be compared in terms of the slope $B$, the charge per micelle $P$, and the concentration of added salt. Princen and Mysels develop an equation which relates these variables:

$$B = \frac{P^2 d_3 + Pd_3 - P}{2n_3 M_1^2 d_3^2}$$ (25)

In this equation $n_3$ is the concentration of added salt, $M_1$ is the micellar molecular weight, and $d_3$ is given by:

$$d_3 = 1 - f\xi + f^2 \frac{\xi^2}{4} + f^2 \frac{\xi}{4m}$$

where $\xi$ is the charge per micelle divided by the aggregation number and $f$ is the ratio of molar refractive index increment of the added salt to that of the detergent.

From Equation (25) it is obvious that as $P \rightarrow 0$, $B \rightarrow 0$, but also $B$ approaches zero at a constant $P$ as the

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23 Princen and Mysels, loc. cit.
added salt concentration increases. Consequently a negligible slope in high added salt concentration does not necessarily mean that $P = 0$.

In all systems studied here $B$ decreases with increase in added salt (see Tables IV and V). For TTEAB in the various added salt solutions $P$ remains essentially constant and therefore the decrease in slope can be explained by Equation (25). However, for HTEAB over the same added salt range, $P$ increases initially and then goes to zero at 0.0500 M NaBr. While the slope decreases in this system with increase of added salt, the nonconstant charge also affects $B$.

The magnitudes of the charge per micelle in many cases is quite high. Chandler and McBain say, "No evidence has been uncovered to indicate that micelles of unusually high effective valence exist. The strong tendency toward aggregation of ions of one sign to form micelles of high net charge is automatically held in check by electrostatic forces which attract and fix gegenions. As a result, the effective net charge on micelles is of the same order as that of ordinary ions."\textsuperscript{24} In this writer's opinion it should be the

values of $\frac{P}{m}$, the charge per monomer in the micelle, and not $P$ which should be small. This is the case for all systems studied; $\frac{P}{m}$ is 0.20 or less. This agrees well with the values for similar compounds that are listed by Shinoda.  

Comparisons of the micellar molecular weight of a given detergent in water with those in added salt solutions in Tables IV and V consistently show a smaller value in water. This behavior is discussed in Chapter I and it is generally agreed by the investigators in this field that such should be the case.

However, it is also generally agreed that the longer is the paraffin chain, the higher is the micellar molecular weight. In this investigation when the solvent was water, TTEAB and TTPAB were found to have higher micellar molecular weights than HTEAB and HTPAB, respectively. In the three highest concentrations of added salt for TTEAB and HTEAB, the trend was reversed; HTEAB gave higher values than TTEAB.

It can also be seen that for either the tetradecyl or hexadecyl compounds that, as the head size of the monomer increased, the micellar molecular weight decreased. In water the micellar molecular weight for TTEAB was 17,100; for

---

TTPAB it was 9,300; and for TTBAB it was approximately 4,000. Similarly HTEAB in water gave a value of 13,500 compared to 8,500 for HTPAB in water. This same phenomena was observed by Venable on TTMAB and TTPAB in both water and 0.0500 M NaBr. This is not what was anticipated and it is difficult to offer a logical explanation.

The increase in monomer head size for a series of detergents with a given long chain not only shields the repulsive interactions between charged heads in the micelle but also increases the monomer molecular weight. These factors tend to increase the micellar molecular weight if the volume of the hydrocarbon interior of the micelle remains constant. On the other hand the greater bulkiness of the larger head groups decreases the number of such heads which can occupy the surface of a given sphere. This would tend to decrease the micellar molecular weight. This presupposes that the micelles are spherical with a constant radius equal in length to the linear extension of the long paraffin chain. If these assumptions are valid, it would appear that the latter effect is predominant. This argument finds some support in the micellar molecular weight values calculated

26 Venable, Ph.D. Dissertation, p. 75.
by Method I and shown in Table VI. As the area per monomer head increases (see Tables I and II) the calculated micellar molecular weight decreases to some extent. However the effect is too small to account for the larger differences between the measured micellar molecular weights and those calculated by Method I.

This discrepancy leads one to consider a slightly different model for predicting micellar molecular weights from surface tension data. If the monomer heads in the micelle surface are considered to be spherical rather than planar, then the effective long chain length will be shortened by the number of carbons in each short alkyl chain. For example, the radius of TTPAB micelles should be taken as the extension afforded by eleven carbon atoms rather than fourteen because three of them will contribute to the spherical head in the same manner as the propyl side chains.

This model gives values which are listed in Table VI under the column labeled "Calculated MMW II." It is evident that Method II gives much better approximations of the micellar molecular weights for detergents in water than does Method I. However, the reverse is true in added salt solution. Since the area per molecule calculations are less reliable in extraneous electrolyte, this writer feels that in
added salt solutions the fair agreement between the micellar molecular weights calculated by Method I and those measured by light scattering is fortuitous and that the second model is better. This point will be discussed in the following section.

C. Solubilization

The criterion of solubilizing power which will be used here is the ratio of the number of benzene molecules solubilized to the number of detergent molecules in micellar form. It is expressed as $\frac{S-S_0}{C-C_0}$, in which $S$ is the total number of benzene molecules found at a given detergent concentration $C$ and $S_0$ is the solubility of benzene at $C_0$ (the c.m.c.). The quantity $S-S_0$ then represents the amount of benzene which is made soluble by the presence of micelles. Likewise $C-C_0$ represents the amount of detergent in micellar form if one assumes that $C_0$ remains constant with increasing benzene and detergent concentrations.

The merits of using this ratio as a measure of solubilizing power as well as those of other criteria are discussed in some detail by McBain and Hutchinson.27

One criterion of solubilizing power which is sometimes used in the number of molecules of solubilize per micelle. This has been used to compare different detergents which have the same micellar molecular weights. Using benzene as an example, it is obvious that if \( \frac{S-S_0}{C-C_0} \) in units of molecules of benzene per molecule of detergent monomer in micellar form is multiplied by the aggregation number in units of molecules of detergent per micelle, the result is the number of molecules of benzene per micelle. Therefore a comparison of solubilizing power for different detergents of the same aggregation number (and micellar molecular weight) in terms of the number of molecules of solubilize per micelle is merely a special case of the criterion of \( \frac{S-S_0}{C-C_0} \). Any change in solubilizing power which is reflected in the former will also be reflected in a comparison of \( \frac{S-S_0}{C-C_0} \) values. Only this latter criterion will be used in this discussion. It should be kept in mind that it would be nonsensical to compare solubilizing power in terms of the amount of solubilize per micelle for detergents of different micellar molecular weights.

In the figures and tables in this section the values used for \( C_0 \) were those found by surface tension measurements. The value of \( S_0 \) was determined experimentally and was slightly
different in different systems. When S was plotted against C (see for example Figure 21), the curve was flat below \( C_0 \). This constant value of S at low concentrations is \( S_0 \).

The average of all \( S_0 \) values was found to be \( 2.38 \pm 0.04 \times 10^{-2} \) moles of benzene per liter of solution. The literature\(^{28}\) value for the solubility of benzene in water is \( 0.177 \pm 0.002 \text{ gm/100 ml} \) or \( 2.26 \times 10^{-2} \) moles/liter. Venable\(^{29}\) says that the increase in this value due to the presence of detergent monomers can be taken as \( 0.09 \times 10^{-2} \) moles/liter. This would mean that \( S_0 \) should be around \( 2.35 \times 10^{-2} \) moles/liter, a figure which agrees with the values found in this work.

Figures 16 and 17 show the experimental curves of \( S-S_0 \) plotted against \( C-C_0 \) for the tetradecyl and hexadecyl series of detergents, respectively, in water. The values of these two quantities taken at particular intervals together with their ratio are shown in Table VII. These and following figures which show solubilization results were constructed from selected but representative data points.


\(^{29}\) Venable, Ph.D. Dissertation, p. 93.
FIGURE 16. \((S-S_0)\) versus \((C-C_0)\) for the Tetradecyl Series of Detergents in \(H_2O\)
FIGURE 17. \((S-S_0)\) versus \((C-C_0)\) for the Hexadecyl Series of Detergents in \(H_2O\)
# TABLE VII

SOLUBILIZATION RESULTS FOR THE TETRADECYL AND HEXADECYL DETERGENTS IN WATER

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C - C_0$ x 10^3</th>
<th>$S - S_0$ x 10^2</th>
<th>$S - S_0$ x $C - C_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTMAB, TTEAB,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and TTPAB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.15</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.27</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>3.42</td>
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<td></td>
</tr>
<tr>
<td>20</td>
<td>4.55</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>HTMAB, HTEAB,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and HTPAB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>2.65</td>
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<td>4</td>
<td>1.06</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>1.59</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.12</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>
It is obvious that for a given chain length, the monomer head size makes no difference. However, the longer paraffin chain detergents are seen to be more efficient solubilizers. It is interesting to note that, while the micellar molecular weight decreases as the head size increases for a given chain length (see Tables IV and V), \( \frac{S-S_0}{C-C_0} \) remains approximately constant within each series.

This result leads one to speculate about the void space in the micelle interior and how it changes with change in micellar geometry. Obviously the anchorage of the aggregating monomer head on the micelle surface prevents the interior of the micelle from being exactly analogous to a liquid hydrocarbon of similar density. The problem however is how to evaluate this void space.

The model chosen for the micelle was that one described in the preceding section during the discussion of Method II for calculating micellar molecular weights. The micelle is considered to be spherical with each of its component monomers having an effective chain length determined by the number of carbon atoms in the long chain minus the number of carbon atoms in each short alkyl group. The area per head group calculated from surface tension data was taken as the equitorial place through the spherical head on
the micellar surface. Two such heads were drawn to scale along with the paraffin chains the widths of which were taken as the linear extension of the methylene group, 1.27 Å. The paraffin chains were allowed to touch at their terminal groups. The area between these two "aggregated" monomers was calculated and this area raised to the power of 3/2 to get an approximate void space per monomer.

These crude calculations showed that as the head size increases the void space actually increases. This calculation suggests that the void space available for accepting solubilizate may indeed be a factor in determining the solubilizing power of micelles. Therefore, within a series of detergents of a given long chain of varying effectiveness, a constant $\frac{S-S_0}{C-C_0}$ may be controlled in part by the void space in the micelle.

Figures 18 and 19 show $S-S_0$ plotted against $C-C_0$ for TTEAB and HTEAB, respectively, with the added salt concentration varied from zero to 0.0500 M NaBr. Since all curves are straight lines, the value of $\frac{S-S_0}{C-C_0}$ will be constant at any point along a particular curve. These ratios are listed in Table VIII. It can be seen that the addition of extraneous electrolyte greatly enhances solubilization for both detergents. A comparison of the two compounds in the same added
FIGURE 18. \((S-S_0)\) versus \((C-C_0)\) for TTEAB in \(H_2O\) and NaBr Salt Solutions
FIGURE 19. \((S-S_0)\) versus \((C-C_0)\) for HTEAB in \(H_2O\) and NaBr Salt Solutions
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent in moles/liter of NaBr</th>
<th>$\frac{S-S_0}{C-C_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTEAB</td>
<td>0</td>
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</tr>
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<td>0.0130</td>
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</tr>
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<td>0.0250</td>
<td>2.83</td>
</tr>
<tr>
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<td>3.37</td>
</tr>
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<td>2.75</td>
</tr>
<tr>
<td></td>
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<td>4.29</td>
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</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>5.28</td>
</tr>
</tbody>
</table>
salt concentration shows that in each case the detergent with the longer chain is a more efficient solubilizer of benzene.

Some unexplainable anomalies were found in these experiments. The first of these is shown in Figure 20 for HTMAB. In 0.0500 M NaBr the curve exhibits a decreasing slope which means that \( \frac{S-S_o}{C-C_o} \) decreases with increasing concentration. Mention has already been made of the peculiarities of this detergent. Debye and Anacker\(^{30}\) noted that below 30°C this detergent precipitates. It was suggested earlier that its abnormally low c.m.c. value in water may be due to the formation of microcrystals and not to true micelles. However, the solubilization curve in water does not exhibit any unusual behavior. No explanation can be given for this result.

Figure 21 shows the solubilization curves for HTPAB in water and 0.0500 M NaBr and TTBAB in water. Whereas light scattering experiments give micellar molecular weights of 32,200 for HTPAB in 0.0500 M NaBr and approximately 4,000 for TTBAB in water, respectively, the solubilization results seem to indicate that no micelles are formed, or if they are

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FIGURE 20. \((S-S_0)\) versus \((C-C_0)\) for HTMAB in \(H_2O\) and 0.0500 M NaBr.
FIGURE 21. Benzene Solubilized versus Concentration for HTPAB and TTBAB in H₂O and HTPAB in 0.0500 M NaBr
formed for some reason do not solubilize benzene. These results cannot be rationalized.

D. Miscellaneous

It was thought that the effect of very large ions of the same sign as the aggregating species might change the properties of micelles drastically by interposing themselves into the micellar surface. Consequently tetra-n-butylammonium bromide was chosen as an added salt in order to compare its effects with those of NaBr.

A surface tension experiment for HTEAB was run in 0.0500 M solutions of tetra-n-burylammonium bromide and sodium bromide. Figure 22 shows the results. The weight added to the beam of the surface tension balance is directly proportional to the surface tension (see Equation (14)), and this quantity is plotted against detergent concentration. It is clear that the difference in the c.m.c. values, denoted by the breaks in the curves, is quite small. The fact that tetra-n-butylammonium bromide produces lower surface tension values than NaBr over the entire detergent concentration range can be understood by referring to Figure 23. Here it is seen that tetra-n-butylammonium bromide itself is surface active although formation of micelles is not indicated. The presence of NaBr is known to increase the surface tension of
FIGURE 22. Weight Added versus Concentration of HTEAB in 0.0500 M Solutions of NaBr and (n-Bu)$_4$NBr
FIGURE 23. Surface Activity of (n-Bu)$_4$ N Br in H$_2$O
water by only about 0.7 dyne/cm if the NaBr concentration is as large as 0.50 M.\textsuperscript{31}

A comparison of the solubilizing power of TTEAB in the presence of these same two added salts is shown in Figure 24. The much larger size of the tetra-n-butylammonium ion is seen to be of no consequence in solubilization. No light scattering experiments were done with this compound.

FIGURE 24. Benzene Solubilized versus Concentration of TTEAB in 0.0500 M Solutions of NaBr and (n-Bu)_4 N Br .
CHAPTER IV

SUMMARY AND CONCLUSIONS

Two series of quaternary ammonium bromides, one with the tetradecyl long chain and one with the hexadecyl long chain, were synthesized. The three alkyl groups at the hydrophilic head were increased by CH₂ increments from methyl through butyl in each series.

Surface tension-logarithm of concentration curves were obtained for all the detergents in water and various extraneous electrolyte concentrations. From each plot the critical micelle concentration and the area per molecule at the air-solution interface were determined.

A linear dependence of c.m.c. on the total number of carbon atoms in the head groups was found for both series of detergents in water. The slopes and intercepts of these plots were found to be dependent upon the length of the long paraffin chain. While a similar relationship has been proposed empirically and derived theoretically in the literature for the dependence of c.m.c. on the number of carbon atoms in the long chain, to the author's knowledge this is the.
first time such a relationship has been proposed for the head group carbons. In fact, it openly contradicts the opinions of some investigators. Both effects can be related to the decrease in the hydrocarbon-water interface and the cohesive forces between water molecules.

The area per monomer head calculations showed a linear dependence on the square of the number of carbon atoms in each short alkyl chain. This indicates that the effectiveness of additional methylene groups is constant from the methyl through the butyl side chains.

The surface tension results on TTEAB and HTEAB in various added salt solutions verified the well-known linear log-log relationship between the c.m.c. and concentration of added salt.

The maximum lowering of surface tension by all detergent solutions was greater in added salt solutions than in water. The monomer head size was smaller in added salt solutions than in water. Both of these effects can be explained by the increasing number of surface active ions at the interface in salt solutions. This increase can be explained by the shielding of Coulombic repulsion between surface active ions at the interface which is afforded by the addition of extraneous electrolyte to the detergent.
systems. This is essentially an adaptation of the Debye-Hückel theory. The same principles are involved when one rationalizes the decrease in c.m.c. with increasing added salt concentration.

Results of the light scattering experiments are presented in Tables IV and V. In all systems a lower micellar molecular weight was obtained in water than in added salt solution. It is generally agreed by the investigators in this area that such should be the case.

The data for TTEAB and HTEAB in added salt solution indicated that there exists an optimum added salt concentration above which micelles of these detergents do not grow. This observation supports the conclusions of some reports in the literature while it contradicts those from still other laboratories. The conflicting theories are discussed in the first chapter.

The micellar molecular weights of TTEAB and TTPAB were found to be higher than those of HTEAB and HTPAB, respectively, in water. Normally, however, the longer chain detergent exhibits the larger micellar molecular weight. At higher concentrations of added salt normal behavior was observed.

In both the tetradecyl and hexadecyl series in water,
a decrease in micellar molecular weight occurred upon increasing the monomer head size. The opposite effect was anticipated. These results suggested that the increasing bulkiness of the head groups led to smaller aggregation numbers. The micellar molecular weights calculated from a spherical model of radius equal to the length of the long hydrocarbon chain and surface area determined by the area per monomer head calculations supported this suggestion but could not account for the larger differences in measured molecular weights for different detergents.

A different model was chosen and found to be in better agreement. If the monomer heads on the surface of the micelle are considered as small spheres, the long paraffin chain will have an effective length determined by the number of carbon atoms in the long chain minus the number of carbon atoms in the short alkyl groups. This would effectively decrease the radius of the micellar sphere as the monomer head size increased. This model gave much better results when the solvent was water. In added salt solutions the first model gave better agreement between calculated and observed micellar molecular weight but the head size parameters are thought to be less valid in these systems.

Solubilization results were discussed in terms of the
number of benzene molecules solubilized per detergent molecule in micellar form, \( \frac{S-S_0}{C-C_0} \).

In water and for a given long chain length, increasing the size of the hydrophilic head did not change the solubilizing power of the detergent. This effect was correlated with the decreasing micellar molecular weight accompanied by increasing the monomer head size in terms of the void space calculated from the second model described above. For a given long paraffin chain, its effective length can be considered to decrease as the monomer head size increases. Simple calculations showed that the void space per monomer in the micelle increased as the head size increased. This led to the conclusion that the space available for receiving solubilized material is a factor in evaluating the efficiency of detergents.

For the TTEAB and HTEAB detergents solubilizing power increased with increasing added salt concentration. At any particular added salt concentration, HTEAB was found to be the more efficient solubilizer. Both of these observations are in accord with current theories relating detergent action to the effect of extraneous electrolyte.

The solubilization results of HTMAB and HTPAB in 0.0500 M NaBr and TTBAB in water were anomalous and no conclusions
were reached concerning these systems.

The solubility of benzene in all detergent solutions below the c.m.c. was measured and found to be $2.38 \pm 0.04 \times 10^{-2}$ moles/liter which is in agreement with the literature.

The break in the surface tension-log concentration curve for HTMAB and the decreasing slope of the solubilization curve at higher concentrations of this detergent in 0.0500 M NaBr led to the suggestion that this compound forms microcrystals before it forms true micelles. The literature references cited earlier also discuss the anomalous behavior of this detergent.

Experiments using tetra-n-butylammonium bromide as an added salt showed that this compound behaved very much like NaBr. The size of the extraneous cation was found to have no apparent effect upon surface and micellar phenomena.

The purpose of many of the experiments performed throughout this study was to determine the effect of the monomer head size upon various micellar phenomena. The head size was varied by increasing the number of carbon atoms in the short alkyl chains attached to the quaternary nitrogen. All three short chains were increased simultaneously. It would be interesting to repeat these experiments on series of these compounds in which one chain was
increased at a time. This was not done here primarily because of the difficulties involved in getting pure starting materials and in synthesizing these detergents. Also it has long been desirous to determine molecular weights in the presence of solubilizate but the analytical techniques are not available at this time for these experiments.
SELECTED BIBLIOGRAPHY


VITA

Gary K. Brashier was born on October 6, 1937 at Marion, Louisiana. His elementary and high school education was acquired at Marion High School from which he was graduated in May, 1956, as valedictorian. He was chosen as the recipient of the American Legion Award and the Danforth Leadership Award from his graduating class.

He entered Northeast Louisiana State College in Monroe, Louisiana, in September, 1956. In August, 1960, he was awarded, with honors, the degree of Bachelor of Science in Chemistry.

In September, 1960, he entered the Graduate School of Louisiana State University. On March 28, 1962, he married Mary Patricia King of Mangham, Louisiana. He became a member of Phi Lambda Upsilon, national honorary fraternity for chemists and chemical engineers in May, 1962. A daughter, Pamela Sheryl, was born on December 30, 1962. He is now a candidate for the degree of Doctor of Philosophy.
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Date of Examination: July 22, 1964