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Solubilization and Related Phenomena in Quaternary Ammonium Halides.

Raymond Leslie Venable
Louisiana State University and Agricultural & Mechanical College

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in

The Department of Chemistry

by

Raymond Leslie Venable
B.S., Southern State College, 1955
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LIST OF ABBREVIATIONS

LPB  Laurylpyridinium Bromide
TPB  Tetradecylpyridinium Bromide
TTMAB  Tetradecyltrimethylammonium Bromide
TTPAB  Tetradecyltripropylammonium Bromide
HTPAB  Hexadecyltripropylammonium Bromide
The factors which control the amount of an organic substance that can be solubilized by a detergent have never been established. The primary aim of this work was to determine some of these factors.

Micellar molecular weights were determined for three quaternary salts each having one fourteen-carbon chain and for one salt with a twelve-carbon chain. The idea was to determine if the void space inside the micelle was a factor in controlling the amount of benzene solubilized.

Critical micelle concentrations were determined from surface tension measurements and from turbidity measurements and found to be $1.18 \times 10^{-3}$ g/ml for tetradecyltrimethylammonium bromide, $0.92 \times 10^{-3}$ g/ml for tetradecylpyridinium bromide, $0.86 \times 10^{-3}$ g/ml for tetradecyltripropylammonium bromide, and $4.00 \times 10^{-3}$ g/ml for laurylpyridinium bromide.

In 0.05 N sodium bromide the critical concentrations are $1.40 \times 10^{-4}$ g/ml, $0.86 \times 10^{-4}$ g/ml, $1.16 \times 10^{-4}$ g/ml, and $1.10 \times 10^{-3}$ g/ml respectively.

Micellar molecular weights were determined by light scattering. In water these were found to be 27,200 for
tetradecyltrimethylammonium bromide, 26,000 for tetradecylpyridinium bromide, 25,000 for tetradecyltripropylammonium bromide, and 17,700 for laurylpyridinium bromide. In 0.05 N sodium bromide the micellar molecular weights were found to be 50,400; 97,600; 40,700; and 20,800 respectively.

In water the number of benzene molecules solubilized per micelle increased with increase in detergent concentration. This led to the tentative conclusion that one of the factors affecting solubilization is the concentration of ionic species and that micelles can be considered as a microphase and solubilization an extraction process.

Fewer benzene molecules were solubilized per micelle for tetradecyltripropylammonium bromide than for tetradecylpyridinium bromide or for tetradecyltrimethylammonium bromide. This indicated that possibly the presence of propyl groups around the nitrogen atom decreases the void space inside the tetradecyltripropylammonium bromide micelle relative to the void space in the micelles of the other two detergents with less bulky head groups. At a given concentration surface tension was found to decrease drastically with time for tetradecyltripropylammonium bromide even though the detergent was pure. This led to the conclusion that the area occupied by each molecule of this detergent in the air-water interface
decreased until an equilibrium value was reached which was much lower than the initial area of 90 square angstroms per molecule. This lends support to the above conclusion.

The area occupied per molecule in the air-water interface was found to be 61 square angstroms for tetradecyltrimethylammonium bromide, 59 units for tetradecylpyridinium bromide and for laurylpyridinium bromide. Very slow changes of surface tension with time were observed with these latter compounds and indications were found that this was due to trace impurities.

The number of benzene molecules solubilized per micelle in 0.05 N sodium bromide was found to be independent of detergent concentration and equal to 661 for tetradecyltrimethylammonium bromide, 1246 for tetradecylpyridinium bromide, and 634 for tetradecyltripropylammonium bromide. Although there are fewer benzene molecules per micelle for the latter compound the micelle is much smaller. The ratio of benzene molecules to detergent monomers per micelle is 6.53 for the tripropyl salt, 4.54 for the pyridinium salt, and 4.41 for the trimethyl salt, indicating that in the presence of a high concentration of extraneous electrolyte the tripropyl salt is a more efficient solubilizing agent. This may also indicate
that the micelle of the tripropyl salt can swell to a greater
degree than can the micelles of the other two salts.

Indications also were found that trace impurities were
responsible for the emulsion formation encountered in the
solubilization determinations.
CHAPTER I

INTRODUCTION AND REVIEW OF THE LITERATURE

When organic molecules containing polar or ionic groups are placed in aqueous media there is a force of attraction between the polar or ionic portion of the organic molecule and the water molecules. This attractive force tends to render the solubility of the organic molecule in water greater than that of a pure hydrocarbon of similar molecular weight.

It is often stated that hydrocarbon molecules are repelled by water molecules. Strictly speaking this is incorrect. There will actually be an attractive force between the water molecules and the hydrocarbon portions of organic molecules. This force is of the same order of magnitude as the force of attraction between hydrocarbons. However, water molecules are known to exhibit large cohesive forces toward each other. The presence of a hydrocarbon group tends to disrupt these cohesive forces. As a result of the greater attraction of water molecules for water molecules, hydrocarbon portions of organic molecules tend to be expelled from aqueous
phases. This tendency for hydrocarbons to be expelled is the force that causes the solubility of a given series of compounds to decrease with increasing hydrocarbon chain length.

This counterplay of forces causes many organic molecules to concentrate in interfacial regions. In such instances the polar or ionic group will be oriented toward the aqueous or polar phase and the hydrocarbon group will normally be oriented toward the less polar phase. Substances which behave in this fashion are termed surface active and play a very important role in many technical processes.

Equilibrium between the forces attracting the polar or ionic groups and the cohesive forces between water molecules can be achieved in many instances by the formation of aggregates of the organic molecules. Such aggregates are termed micelles. Again the polar or ionic groups will be oriented toward the water molecules while the hydrocarbon groups will be oriented toward each other in what is sometimes considered a microphase. This will be discussed more fully later.

These aggregates usually form when the concentration exceeds a particular value called the critical micelle concentration (cmc). Strictly speaking this is a concentration range but it is generally a very narrow range. The value of the cmc for a given type of detergent will depend largely on
the length of the hydrocarbon chain.

For cationic detergents the cmc has also been found to depend on the nature of the gegenion. For instance the cmc for laurylpyridinium chloride has been found\(^1\) to be 0.02 moles per liter while the cmc of laurylpyridinium bromide is reported in the present work to be 0.012 moles per liter and laurylpyridinium iodide has a cmc of 0.005 moles per liter.\(^2\) These values are all for aqueous solution with no added electrolyte.

Data will be presented later to show that the critical concentration of cationic detergents also depends on the size of the charged head group.

For aqueous solutions of these materials plots of turbidity, surface tension, osmotic pressure, and several other physical properties measured as functions of detergent concentration show rather distinct changes of slope at the cmc. These changes of slope are part of the evidence that suggests aggregation. The abruptness of these changes of slope indicates that this aggregation takes place over a rather narrow concentration range. The term critical micelle concentration

\[^{1}\text{A. P. Brady and H. Huff, J. Phys. Chem., LXII (1958), 644.}\]

\[^{2}\text{H. V. Tartar, J. Colloid Sci., XIV (1959), 115.}\]
consequently is not rigorous and refers to a concentration range that depends slightly upon the method of detection.

The discussion which follows will deal with some of the various types of measurements which yield useful information about detergent solutions.

A. Surface Thermodynamics

Throughout this work the term surface tension will be used to refer to vapor-liquid or gas-liquid interfaces. The expression interfacial tension will be reserved for interfaces between condensed phases.

Moilliet, Collie, and Black\textsuperscript{3} give an excellent review of the thermodynamics of surfaces and the reader is referred to this work for details and for the completely general treatment. This work will follow the convention of Guggenheim\textsuperscript{4} as do Moilliet, Collie, and Black.\textsuperscript{5} It is believed that this treatment gives a clearer physical picture than any other treatment.


\textsuperscript{4} E. A. Guggenheim, \textit{Trans. Faraday Soc.}, XXXVI (1940), 397.

\textsuperscript{5} Moilliet, Collie, and Black, \textit{op. cit.}, p. 70.
In the discussion below the following assumptions are explicit.

1. Temperature and pressure are held constant.

2. The interface in question is an air-liquid interface.

3. The components of the air are considered to be "inert components" in Guggenheim's original treatment and do not enter into the calculations.

4. The interface has a finite thickness and all transition from the properties of the bulk phases to the properties of the physical interface occur within this "interfacial phase."

5. No limitation is placed on the location of the boundary between the bulk liquid phase and the interfacial phase except the one given in 4.

6. In the equations below $\sum_i$ represents the number of moles of solute species $i$ per unit interfacial area in excess of the number of moles of $i$ contained in a volume of bulk solution containing an equal quantity of solvent.

Under the special conditions given above, Guggenheim's treatment reduces to essentially that of Gibbs.\(^7\) The

---

\(^6\)Guggenheim, *loc. cit.*

equation given below relating changes in surface tension to changes in concentration (really changes in activity) is therefore universally called the Gibbs adsorption equation or just the Gibbs equation.

This equation can be expressed in the following form

\[ d\gamma = - \sum_i \gamma_i d\mu_i \]  \hspace{1cm} (1)

The differential of the chemical potential can be related to the activity by

\[ d\mu_i = RTd\ln a_i \]  \hspace{1cm} (2)

In this equation \( R \) is the gas constant in ergs per degree per mole, \( T \) is the absolute temperature, and \( a_i \) is the activity of the \( i \)th component. When equation (2) is substituted into equation (1) and natural logarithms converted to common logarithms, the following result is obtained:

\[ d\gamma = - 2.303 RT \sum_i \gamma_i d\log a_i \]  \hspace{1cm} (3)

As a first approximation concentrations can be substituted for activities. For a two component system the subscripts and summation sign can be dropped. Thus equation (3) becomes

\[ d\gamma = - 2.303 RT \gamma d\log C \]  \hspace{1cm} (4)

where \( C \) is in moles per liter. This can be solved for \( \gamma \) as to
\[ \gamma = - \frac{1}{2.303RT} \frac{d\gamma}{d\log C} \] (5)

A plot of surface tension versus the logarithm of the concentration (in moles per liter) usually gives two straight line segments intersecting at the cmc. From the slope of the line at concentrations lower than the critical concentration it is possible to obtain an approximate value for the excess concentration of surfactant molecules in the surface. This would be an exact determination if activities were used in the place of concentrations.

The reciprocal of the surface excess concentration should give a fair approximation of the area occupied by each molecule. Since the size of the charged head group should determine the area occupied by a molecule, one really ought to be able to measure the effective sizes of charged head groups by this method.

The reciprocal of the surface excess concentration really gives one a measure of the area per excess molecule. However, if the substance under investigation is very surface active, the surface excess concentration will be so near the total surface concentration as to be practically indistinguishable.
Since the development of radioactive tracers, it has become possible to measure surface concentrations directly. With this technique Dixon et al.\textsuperscript{8} report that surface concentrations continue to rise after the critical micelle concentration is reached. They find values of surface concentrations which correspond to the formation of several monolayers in systems where the surface excess concentrations calculated from the Gibbs equation correspond to single monolayer formation. According to these writers this casts doubts on the validity of the Gibbs equation. In the opinion of the present writer there is nothing in these results which contradicts results based on the Gibbs equation. This equation was developed for very thin layers and cannot be expected to predict multilayer adsorption.

On the other hand Roe and Brass\textsuperscript{9} report surface concentrations obtained by radiotracer techniques which are in agreement with the results calculated from the Gibbs equation. At the present time it is not possible to decide which results are the most reliable.


For a solute which is preferentially adsorbed in the interface, equations 1-3 require that the surface tension decrease as the activity of the solute increases. Conversely, for a solute which is negatively adsorbed, these equations require that the surface tension increase as the activity of the solute increases.

Experimentally the surface tension is found to decrease quite rapidly with increase in detergent concentration until the cmc is reached. After the cmc is reached the surface tension decreases very slowly, if at all, with increasing detergent concentration. This is good evidence that aggregation takes place and that the monomer concentration is approximately constant at concentrations higher than the cmc.

Several authors\textsuperscript{10,11,12} have reported that the curve of surface tension versus detergent concentration reaches a minimum at or near the cmc and then rises again before it flattens out. There is nothing in the Gibbs equation that can account for this. Naturally this caused a great deal of


speculation, and many attempts were made to explain the phenomenon. None of the explanations that were proposed could be reconciled with all the facts.

Miles and Shedlovsky\textsuperscript{13} reported that no minimum occurred if the detergents were extremely pure. Other authors\textsuperscript{14,15,16} have verified these results. Since in most if not all cases where a minimum occurred a surface active impurity was probably present, the most likely explanation seems to be that this surface active impurity contributes to the lowering of the surface tension at concentrations lower than the cmc. After the cmc is reached the impurity is progressively solubilized by the micelles of the detergent so the surface tension rises to approximately the value it would have if no such impurity were present.

The same authors who found minima in surface tension versus concentration curves also found that, at concentrations lower than the cmc, the surface tension changed slowly

\textsuperscript{13}G. D. Miles and L. Shedlovsky, \textit{J. Phys. Chem.}, XLVIII (1944), 57.

\textsuperscript{14}A. P. Brady, \textit{J. Phys. Chem.}, LIII (1949), 56.


with time, sometimes for a period of several weeks. However, Shedlovsky and coworkers\textsuperscript{17} have found that, for carefully purified detergents, no change occurs in the surface tension after about thirty minutes. No satisfactory explanation has been offered for this effect.

B. Light Scattering

When an atom, molecule, or other particle is exposed to light, its electrons are set into periodic oscillations at the frequency of the incident light if the incident light does not have a frequency near an adsorption band for the particle. Any oscillating charge must emit light of the same frequency as the oscillations. As a result particles will emit light of the same wavelength as that of the impinging light. This radiative process is referred to as light scattering. Some light will be radiated at a different frequency due to the Raman effect, but this is such a small fraction that it can be ignored in the present discussion.

The scattering of light by particles was first discussed by Rayleigh.\textsuperscript{18} His treatment was primarily for the scattering of light by gaseous particles. Debye\textsuperscript{19} showed

\textsuperscript{17}L. Shedlovsky, J. Ross, and C. W. Jakob, J. Colloid Sci., IV (1949), 25.

\textsuperscript{18}Lord Rayleigh, Phil. Mag., XII (1881), 81.

\textsuperscript{19}P. Debye, J. Applied Phys., XV (1944), 338.
that light scattering could be used to investigate particles in solution. The general theory of light scattering is treated in a second paper by Debye\textsuperscript{20} and is reviewed by Oster.\textsuperscript{21} A detailed mathematical review has been given by Aguirre.\textsuperscript{22} The application of light scattering to detergent solutions has been reviewed by the present writer in a previous work.\textsuperscript{23} A brief summary of the general ideas will be presented here.

The angular distribution, the intensity, and the polarization of the scattered light can be used to gain information about the sizes, shapes, and interactions of particles in solution. The angular distribution and the polarization of the scattered light give useful information only if the particles have one dimension equal to \(1/20\)th to \(1/10\)th the wavelength of the incident light or are non-isotropic.

Since detergent micelles are generally small and are isotropic and practically monodisperse, the only experimental quantity of any interest in this work will be the intensity of

\textsuperscript{22}F. Aguirre, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1962, p. 106.
\textsuperscript{23}R. L. Venable, M. S. Thesis, Louisiana State University, Baton Rouge, 1958, p. 10.
the light scattered at 90° with respect to the incident beam.

An equation of the same form as Lambert's law can be written for the reduction in intensity due to scattering.

This equation can be written as

\[
\frac{dI}{dx} = - \tau I
\]

or in integrated form

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

where \(I\) is the intensity of the incident beam at the point \(x\), \(I_0\) is the intensity of the incident beam and \(x\) is the distance the beam has traveled in the medium. The quantity \(\tau\) is an extinction coefficient for scattering and depends on the number and size of the scattering particles.

Debye\(^24\) showed that for 90° scattering this extinction coefficient can be expressed in the following way:

\[
\tau = \frac{32\pi^3}{3} \frac{u_o^2(u-u_o)^2}{\lambda^4} \frac{1}{n}
\]

In this equation \(u\) and \(u_o\) are the refractive indexes of the solution and of the pure solvent respectively; \(\lambda\) is the wavelength of the incident light in vacuo; and \(n\) is the number of scattered particles.

scattering particles per cubic centimeter. The quantity $\frac{1}{n}$ can be replaced by $\frac{M}{NC}$ where $M$ is the molecular weight of the scattering species, $N$ is Avogadro's number, and $C$ is the concentration of scattering material in grams per cubic centimeter.

After making this substitution for $n$, equation (7) becomes

$$\tau = HMC $$  \hspace{1cm} (8)$$

where

$$H = \frac{32\pi^3}{3} \frac{u_o^2}{N\lambda^4} \left( \frac{u-u_o}{C} \right)^2 $$  \hspace{1cm} (9)$$

The quantity $H$ is evaluated from the experimental measurement of the difference in refractive index between solvent and solution. Equation (8) is for small non-interacting particles. For non-ideal solutions a better equation is

$$\frac{HC}{\tau} = \frac{1}{M} + 2BC $$  \hspace{1cm} (10)$$

The constant $B$ is a measure of the interactions between particles and is dependent on the solvent used.

These equations are applicable to solute species which do not undergo a change of size with change in concentration. The fact that the turbidity of aqueous solutions of detergents rises extremely slowly with concentration in very dilute solutions and then increases rather sharply over a narrow
concentration range is further evidence that aggregation takes place. However, it is necessary to modify equation (10) to take this into account. The concentration of the scattering species of interest is really \( C - C_0 \) where \( C_0 \) is the critical micelle concentration. The turbidity due to the micelles would likewise be \( T - T_0 \) where \( T_0 \) is the turbidity at the cmc. Generally the turbidity due to the solvent is subtracted from the total turbidity \( T \) and from \( T_0 \). The reciprocal of the intercept of a plot of \( \frac{H(C-C_0)}{T-T_0} \) versus \( C - C_0 \) gives the value of the weight average molecular weight of the scattering species. From the slope of this plot some information can be gained about the interactions of the scattering particles with the solvent and indirectly some information about interactions between particles.

It is generally conceded that detergent micelles possess a residual charge in aqueous solution to which no extraneous electrolyte has been added. However, some authors such as Hutchinson\(^{26,27}\) believe that the micellar charge is completely neutralized in the presence of sufficient quantities of added


\(^{26}\)E. Hutchinson, \textit{J. Colloid Sci.}, IX (1954), 191.

electrolyte. However, the electrophoresis measurements of Stigter and Mysels$^{28}$ indicate that some micelles are charged even in salt solutions.

The above light scattering equations were developed by means of the fluctuation theory of light scattering and are applicable to uncharged particles or micelles. The fluctuation treatment was extended to charged micelles by Prins and Hermans$^{29}$ and less elegantly by Mysels$^{30}$ and by Princen and Mysels.$^{31}$ These writers assume that a micelle has an effective charge which is much less than the number of charged monomers making up the micelle. They further assume ideal behavior of the solutions. The results of these treatments are summarized very well by Anacker.$^{32}$ It is felt that nothing would be gained by reproducing the details of these treatments here. By using these treatments it is possible to obtain an approximate value for the number of effective charges on the micelle. Also the micellar molecular weights obtained


are 10-20 per cent higher than those obtained by using the modified form of equation (10).

Vrij and Overbeek\textsuperscript{33} criticize the above treatments because of the assumption that the solutions are ideal. These workers develop light scattering equations for charged particles which avoid this assumption. However, their treatment requires that the refractive index increment \( \frac{\Delta n}{c} \) of equation (9) be measured at constant chemical potential instead of at constant salt concentration which is the normal procedure in the presence of added electrolyte. The refractive index increment can be measured at constant chemical potential in a straightforward fashion for polymeric materials by use of a Donnan membrane. Experimentally this would be much more difficult for an association colloid because of passage of the monomer through the membrane.

The theoretical treatment of Vrij and Overbeek\textsuperscript{34} will have to be adapted before it can be used for work with association colloids. It will not be possible to compare their treatment with that of Prins and Hermans\textsuperscript{35} until this adaptation has been made.


\textsuperscript{34}\textit{Ibid.}

\textsuperscript{35}Prins and Hermans, \textit{loc. cit.}
C. Conductivity

When the equivalent conductance is plotted as a function of the square root of the detergent concentration, a decrease in slope is usually observed at the cmc. This is the result of a decrease in the number of charges capable of carrying current. Because of a reduction in the frictional resistance to motion, a charged particle bound into a micelle should be a more effective current carrier than an unbound particle with the same charge. The reduction in equivalent conductance at the critical concentration is attributed to ion pair formation between the ions forming the micelle and the gegenions. This would reduce the effectiveness of the micelle as a charge carrier.

However, McDowell and Kraus\textsuperscript{36} report cases where the equivalent conductance shows a sharp rise at the cmc. These authors were working with a series of octadecyltri-n-alkylammonium bromates. The short n-alkyl chain was varied from methyl to n-amyl. An increase in equivalent conductance was observed for octadecyltripropylammonium bromide and the rise in equivalent conductance was more pronounced with the longer alkyl chains. They attribute the rise in equivalent conductance

\textsuperscript{36}M. J. McDowell and C. A. Kraus, \textit{J. Am. Chem. Soc.}, LXXIII (1951), 2173.
to the fact that the large bulk of the alkyl groups around the quaternary nitrogen prevents ion pair formation between the ions of the micelle and the gegenions. The aggregated charges are a more effective current carrier than the individual charges would be.

The size of the gegenion can also affect the equivalent conductance at the cmc. Kraus and coworkers\textsuperscript{37,38} have found that octadecylpyridinium chloride does not exhibit this sharp increase in equivalent conductance but octadecylpyridinium iodate does show this sharp increase. This increase in equivalent conductance is also attributed to the formation of a highly charged aggregate.

An alternate way of plotting conductivity data is to plot the specific conductivity versus the concentration. Such a plot will usually give just a decrease in slope at the cmc. A plot of this type usually gives two straight line segments which intersect at the cmc. The cmc determined by this method will usually differ slightly from the value determined from equivalent conductance plots.


Both Kraus\textsuperscript{39} and Mysels\textsuperscript{40} interpret the slope of the equivalent conductance versus the square root of the concentration plots for certain compounds as indicative of the formation of dimers or in some cases trimers below the critical concentration. At the very low concentrations under discussion these uni-univalent detergents should give limiting equivalent conductances as predicted by the Onsager theory for ordinary 1-1 electrolytes. Both groups report compounds with limiting equivalent conductances corresponding to 2-1 or 3-1 electrolytes.

McDowell and Kraus\textsuperscript{39} report no evidence for dimerization of quaternary ammonium salts where the long alkyl chain contained fewer than sixteen carbon atoms. However, Mukerjee and Mysels\textsuperscript{41} report dimerization of sodium dodecyl sulfate. Mukerjee\textsuperscript{42} attempts to explain deviations in osmotic coefficients and solubilities of many detergents as well as the deviations in conductivity on the basis of dimerization. This latter author considers dimerization rather commonplace. Much of the data cited by Mukerjee is admitted to be inaccurate and

\textsuperscript{39}M. J. McDowell and C. A. Kraus, \textit{loc. cit.}
\textsuperscript{41}\textit{Ibid.}
this clouds any interpretation he may make based on these data.

D. Partial Molal Volumes

Very careful and accurate measurements of the densities of detergent solutions reveal a decrease in the slope of the plot of density versus surfactant concentration at the cmc. This means that the partial molal volumes of the surfactants are greater in the micellar form than in the monomeric form. Hamann\textsuperscript{43} reports that the change in partial molal volume may be as much as 11 cc per mole in agreement with the results of Kushner \textit{et al.}\textsuperscript{44} who report a change in partial molal volume of 10 cc per mole.

Goddard, Hoeve, and Benson\textsuperscript{45} suggest that this increase in volume might arise from the release of water molecules held in an ice-like structure around the hydrocarbon chains. On the other hand, Hamann\textsuperscript{43} suggests that the volume change occurs as a result of the release of water of hydration around the ionic portions of the monomers when aggregation takes place.


E. Solubilization

Relatively dilute solutions of detergents can often dissolve relatively large quantities of a great many materials which are quite insoluble in the pure solvent. In this discussion emphasis will be on aqueous solutions, but detergents are being used in nonaqueous media in a variety of applications.

The type of dissolution process referred to above is normally called solubilization. When a material has been solubilized, the system is thermodynamically stable and is reproducible. This is contrasted with emulsion formation which results in an unscable or metastable state. Solubilization is also to be contrasted with rendering a material soluble in "aqueous" media by the addition of large quantities of a substance which is a solvent for the material in question and which is also miscible with water.

The literature on solubilization up to about 1950 is ably reviewed by Klevens.\(^{46}\) McBain and Hutchinson\(^{47}\) also review the literature in this field as does Harris.\(^{48}\) The reader is referred to these reviews for the details of the


work done in this area.

It has generally been found that the solubility of materials such as benzene or cyclohexane in a detergent solution is not appreciably greater than the solubility of these materials in water unless the detergent concentration exceeds the critical concentration. The solubility of hydrocarbons such as the ones mentioned increases markedly with increase in detergent concentration after the cmc has been exceeded. This sharp increase in the solubility of such materials has sometimes been used to get an approximate value of the cmc.

The mechanism of solubilization is not completely understood. It is highly probable that the mechanism of solubilization depends on the nature of the solubilizate and it may depend on the structure and nature of the solubilizer.

Riegelman et al.\(^49\) present spectroscopic information which in their opinion indicates that ethylbenzene is incorporated into the hydrocarbon interior of the micelle while naphthalene is incorporated in what is called the palisade layer just below the charged heads. Aromatic compounds with such substituents as nitro groups are reported to be located right at the surface of the micelle and exposed to the aqueous medium. Certain large and highly polar organic dye molecules

are reported adsorbed on the surface of the micelle.

Their interpretation is based on the changes in fine structure and shifts of adsorption peaks with changes in the polarity of the medium. In the words of the authors "the conclusions drawn in this paper are by no means final, nor entirely unambiguous."

Ward and Chitale\textsuperscript{50} interpret their viscosity and conductivity data as indicating that naphthalene is incorporated in the interior of the micelle. These latter workers find that the solubility of naphthalene in aqueous solutions of hexadecyltrimethylammonium bromide can be correlated with the solubility of naphthalene in hydrocarbon solutions.

Drott\textsuperscript{51} found indications that the solubility of organic solubilizates depends on the size of the charged head group or ultimately on the volume available within the micelle for receiving foreign material.

All workers seem to be in agreement on certain general rules about the solubility of various classes of hydrocarbons in a given detergent at a particular concentration.


\textsuperscript{51}E. Drott, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1959, p. 111.
1. For a given homologous series the solubility decreases with increasing chain length.

2. Benzene is more soluble than cyclohexane.

3. Cyclic compounds are more soluble than their straight chain homologues.

4. Compounds with multiple bonds are more soluble than saturated compounds of equal chain length.

5. Branched chain compounds are as soluble as their straight chain isomers.

6. Polycyclics are less soluble than straight chain compounds with an equal number of carbon atoms.

Harris\textsuperscript{52} makes the comment that solubilization does not seem to play a very important role in the industrial applications of detergents.

F. Theory of Micelle Structure

In the foregoing discussion reference was made to incorporation into the hydrocarbon interior of the micelle, solubilization in the palisade layer or in the charged head area, and to adsorption on the surface of the micelle. No such discussion could be complete without some consideration of the structure and shape of detergent micelles. It is generally accepted that, for ionic detergents, the polar

\textsuperscript{52}J. C. Harris, \textit{loc. cit.}
groups are oriented toward the water molecules and the hydrocar­
bon portions away from the water or towards each other.

Hartley⁵³ proposes a spherical model for the micelle in which the hydrocarbon chains are directed toward the center and the charged heads form the surface of this sphere. The radius of this spherical micelle is approximately twice the length of the hydrocarbon chain. This is the model that is championed by Tartar.⁵⁴

McBain⁵⁵ proposed a small spherical micelle of the Hartley type for dilute solutions but contended for a lamellar micelle in concentrated solutions. This micelle was described as being analogous to two brushes placed together bristles to bristles. The bristles represent hydrocarbon chains and the backs of the brushes represent the hydrated ionic layer.

On the basis of some early X-ray studies Harkins et al.⁵⁶ proposed a model for the micelle which consisted of these double layers. Later Harkins and coworkers⁵⁷ after

further X-ray measurements proposed a cylindrical model which is somewhat different from the spherical model already discussed. This model can sometimes be thought of as a "bundle of wheat." The cylinder is approximately twice the length of the hydrocarbon chain.

It should be pointed out that, to get X-ray diffraction patterns, it is necessary to use very concentrated solutions on the order of 15-30 per cent detergent. On the other hand light scattering measurements are usually done at concentrations not exceeding five per cent.

Phillipoff\(^{58}\) surveys all X-ray data which existed at the time along with other types of data. He concludes that the X-ray diffraction patterns are consistent with some sort of small micelle such as the spherical or cylindrical models. No data available at that time indicated a transition from one of these small micelles to any of the larger lamellar ones.

Various theories have been proposed to explain why micelles form and why they do not grow to infinite size or show a dispersion of sizes. One of the first such theories is due to Debye.\(^{59}\) He proposed that the driving force in micelle formation is the decrease in the hydrocarbon-water


interfacial area and the resulting lowering of the free energy. This is offset by coulombic repulsion between the charged heads. A fundamental thermodynamic error was made in the development of this theory; Debye minimized the free energy of the micelle instead of the free energy of the whole system.

Reich\textsuperscript{60} points out two other errors in Debye's theory. These are neglect of entropy effects and the assumption that each hydrocarbon chain added to the micelle contributes a constant amount of energy. A rather involved theory is developed which takes into account these factors as well as the effect of the area of the polar head groups. The word polar is used here instead of ionic since Reich developed his theory for nonionic detergents. The reader is referred to the original literature for the details of these theories.

\textsuperscript{60}I. Reich, \textit{J. Phys. Chem.}, LX (1956), 257.
CHAPTER II

MATERIALS AND EXPERIMENTAL METHODS

A. Preparation of Detergents

The detergents used in this work were all prepared by the same general method. The long-chain alkyl bromides were refluxed with 30-40 per cent excesses of the appropriate amines. In most cases methanol was used as the solvent but in some cases ethanol was used. After refluxing, the solvent was evaporated and ether added. Usually this was sufficient to precipitate the quaternary salt, but in some cases it was necessary to chill the mixture before precipitation would take place.

The detergents were further purified by repeated recrystallizations. These precipitations were accomplished by dissolving the detergents in the minimal amount of methanol and adding ether as described above. This was repeated until reproducible light scattering curves could be obtained after further recrystallizations.

Attempts were made to prepare tetradecylquinolinium bromide by the method described above using methanol as the
solvent. After the mixture of tetradecyl bromide, quinoline, and methanol had been refluxed for several hours a pink color developed which darkened on standing. At first this was thought to be formation of a charge transfer complex. However, essentially the same results were obtained using tetradecyl chloride. The absorption spectra for both of the colored reaction mixtures were very similar. If formation of charge transfer complexes were involved, the absorption peaks for the tetradecyl chloride mixture should have been in the UV.

In addition to the pink color mentioned previously, a green fluorescence was observed in the methanol solutions of the tetradecyl bromide-quinoline reaction mixture. The absorption spectra in the visible region showed the general characteristics of organic dyes. The colored products have never been identified, but it is believed that a side reaction involving the methanol was responsible for the color formation and fluorescence. No such phenomena was observed if the reaction was carried out in benzene.

Extremely low yields were obtained in these attempts. As a result efforts to prepare tetradecylquinolinium bromide were abandoned.

B. Surface Tension Measurements

All surface tension measurements were made by measuring
the maximum pull on a ring. This method was perfected by Harkins and Jordan.\textsuperscript{1} The relationship between surface tension and experimentally measurable quantities is

$$\gamma = \frac{Mg}{2\pi R} \cdot F$$  \hspace{1cm} (11)

where $\gamma$ is the surface tension in dynes per centimeter, $M$ is the mass required to pull the ring from the surface, $g$ is the acceleration due to gravity, $R$ is the radius of the ring, and $F$ is a factor which accounts for the shape of the surface of the liquid pulled up by the ring. The factor $F$ is a dimensionless ratio of $R/r$ where $r$ is the radius of the wire of which the ring is made.

If surface tensions are to be obtained from equation (11), the quantities $R$ and $r$ will have to be known very accurately in addition to $M$. Harkins and Jordan\textsuperscript{2} give tables of values of the factor $F$ for various values of the ratio $R/r$.

In the present work an alternative procedure has been used. The surface tension of water has been determined by many different workers using a variety of methods at many temperatures. If one uses a particular ring on a particular balance at a given temperature, one can use the relationship

\textsuperscript{1}W. D. Harkins and H. F. Jordan, \textit{J. Am. Chem. Soc.}, LII (1930), 1751.

\textsuperscript{2}Ibid.
\[ \gamma = kw. \] In this equation \( \gamma \) is the known surface tension of water and \( w \) is the weight required to pull the ring free. Since \( \gamma \) is known and \( w \) can be measured, one can easily evaluate the proportionality constant \( k \). Then the surface tensions of detergent solutions can be measured relative to the surface tension of pure water. Since the primary use of surface tension data is the determination of critical micelle concentrations, this method is certainly adequate for this purpose.

To measure the pull on the ring a chainomatic balance manufactured for the purpose by Christian Becker, Inc., was used. The balance was equipped with a platform which could be raised and lowered as needed. The sample container was designed so that it could be thermostated by pumping a thermostated fluid through it.

Triply distilled water which had been distilled once from potassium permanganate solution was used in the preparation of all solutions. The water which was pumped around the sample container was maintained at 30.0° ± 0.01°C. All glassware was cleaned with chromic acid before use. Water was pumped around the sample container for several hours before a series of measurements was begun and all solutions were stored in the water bath for a similar period.

The method follows: The ring was immersed in the solution by raising the platform on which the sample container
rested. The platform was lowered slightly until the ring began to rise above the liquid level. The beam arrest was lowered partially and weights added until the needle was returned approximately to zero. Then the beam arrest was lowered all the way and the platform lowered as weights were added with the chain. The maximum pull was obtained when the ring pulled free of the surface.

The gear mechanism which raises and lowers the sample platform did not operate as smoothly as it should. As a result the pointer tended to swing unduly wildly. It was found that, if the platform was lowered while the needle was swinging from the left back toward zero, this swinging could be greatly reduced and most of the time eliminated completely.

Probably a better method for measuring surface tensions is the Wilhelmy plate method as modified by Padday.3,4 This method does not involve breaking the surface as does the ring method used here. However, a suitable apparatus for the modified Wilhelmy plate method was not available.

C. Turbidity Measurements

The light scattering photometer used for these measurements was designed by Brice et al.\(^5\) and manufactured by the Phoenix Precision Instrument Company of Philadelphia, Pennsylvania.

This instrument uses an AH-3 mercury arc as a light source. A Sorenson Model 250 electronic voltage regulator was used to maintain a constant voltage for both the lamp and the photomultiplier power supply. The photomultiplier tube was a 1P21 mounted on a rotating arm so that it could be rotated about the scattering cell from 0 to 135° in either direction.

The output current of the photomultiplier tube was registered on a galvanometer. The sensitivity of the galvanometer and the photomultiplier tube could be varied as needed.

The instrument was equipped with four neutral filters to reduce the intensity of the incident beam as needed. The 436 mu line of mercury as isolated by a Corning glass filter was used throughout this work.

The instrument is supplied with three types of cells. Small square cells which can be used only for ninety degree scattering are available. Much larger semioctagonal cells are

available which permit measurement of the intensities of the light scattered at 45° and 135° with respect to the incident beam as well as the 90° scattering. The cell used throughout this work was a cylindrical cell with flat faces for the entrance and exit of the incident light. Other cells are available from the manufacturer.

The instrument was aligned so that the light beam passed down the center of the collimating assembly and illuminated the slits uniformly. This alignment also gave a maximum in intensity at zero degrees on the rotating disc carrying the photomultiplier tube. While it may seem obvious that this should be the case, these conditions have not always been fulfilled in past work with this instrument.

After the light source was properly aligned the cylindrical cell was aligned on its base so that the incident light was approximately perpendicular to the flat entrance and exit faces. This alignment of cell and light source also gave a symmetrical scattering pattern when triply distilled carbon tetrachloride was used.

To calibrate this instrument a solution of Cornell polystyrene was used. A solution of this material containing 0.5g of polystyrene per 100 ml of solution with triply distilled toluene as the solvent was used. Such a solution has come to be an internationally accepted standard of turbidity
and it is considered to have a turbidity due to the Styron (polystyrene) of $3.49 \times 10^{-3}$ cm$^{-1}$ at 26°C for light of 436 m$m$.

The following procedure was used in calibrating the instrument. Triply distilled toluene was placed in the cell and the ratio $I_{90}/I_0$ was determined. $I_{90}$ is the intensity of the light scattered at 90° with respect to the incident beam and $I_0$ is the intensity of the incident beam. The toluene was replaced by the Styron solution and the ratio $I_{90}/I_0$ for the solution was determined. The difference in these two ratios is called X and is proportional to a turbidity of $3.49 \times 10^{-3}$ cm$^{-1}$. To find the turbidity of an unknown solution it is necessary to measure $I_{90}/I_0$ for the solution and use the following relationship:

$$
\tau = \frac{Y}{X} (3.49 \times 10^{-3}) \quad (12)
$$

where $Y$ represents the ratio of $I_{90}/I_0$ for the solution of unknown turbidity. This calibration should be performed periodically and must be done every time a change is made in the optical alignment of the instrument.

In light scattering work it is very desirable to have dust free solutions. For measurements of the intensity of light scattered at various angles this condition is almost a necessity unless the particles under investigation are much
larger than the dust particles. However, it is well known that dust particles have a much smaller effect on the intensity of the light scattered at $90^\circ$ than on the intensity scattered at smaller angles. Many workers go to extremes to obtain dust free water. Prins\textsuperscript{6} tried repeated distillations in a closed system but found this unsatisfactory for his purposes. He, along with many others, uses the criterion that a satisfactory solvent must have a dissymmetry ratio of unity or essentially unity. Normally the dissymmetry ratio is understood to mean the ratio of intensities at two angles symmetric about $90^\circ$, usually $45^\circ$ and $135^\circ$. This same author found ultracentrifugation satisfactory but quite time consuming. Repeated filtration through membrane filters of the polypore or millipore types gives fair results. Some workers use repeated filtration through ultrafine fritted glass filters.

All of the above methods are no doubt superior to the methods used in this present work. However, the proof of the method lies in the results obtained by the method. Water which had been distilled once from alkaline potassium permanganate followed by a second distillation without permanganate

\textsuperscript{6}W. Prins, Ph.D. Dissertation, University of Leiden, 1956, p. 66.
gave as good results as the more elaborate methods. This statement is based on the fact that the micellar molecular weights obtained in this laboratory agree very well with the values obtained by workers using the more elaborate techniques.

Detergent solutions were filtered once through ultra-fine sintered glass filters. Single filtrations gave just as reproducible results as repeated filtrations. The solutions were filtered into carefully cleaned glassware and used immediately.

Actual turbidity measurements were made in the following way. A carefully measured volume of solvent was placed in the cell. The turbidity of the solvent was determined and then carefully measured volumes of a concentrated detergent solution were added. The resulting solution was stirred with a carefully cleaned polyethylene stirring rod. The turbidity was measured after each such addition.

There is a greater chance for the introduction of lint and dust using this procedure than would be involved in filtering individual solutions directly into the cell. However, as will be discussed later, the addition of lint and dust can be accounted for and when this is done the two methods give the same results.
Anacker\(^7\) has found that detergents are adsorbed onto glass frits. This is not a surprising result, and the concentration changes caused by the adsorption can be taken into account in either of the following ways. First the amount of detergent adsorbed is small so that filtration of concentrated solutions results in small relative changes in concentration, and these small changes can be ignored. Secondly the actual concentration of the detergent in the filtered solution can be determined by measuring the refractive index difference between the solvent and the solution. These measurements will be described in detail in the following pages. This refractive index increment is proportional to concentration and if the proportionality constant is known the concentration can be calculated.

**D. Refractive Index Measurements**

In order to evaluate the constant \(H\), known as the refraction constant, in the equations relating turbidity to molecular weight, accurate measurement of the refractive index difference, \(\Delta n\), between solvent and solution is necessary. For this purpose a differential refractometer designed by

Brice and Speiser⁸ and manufactured by the Phoenix Precision Instrument Company was used.

The refractive index differences between solvent and aqueous solutions of potassium chloride are known very accurately at a wavelength of 436 μm. This is the wavelength used throughout this work. Solutions of potassium chloride were therefore used to calibrate the instrument.

In making such refraction measurements a sample of pure detergent was carefully weighed and diluted to a known volume at the temperature at which measurements were to be made. Samples of this stock solution were then carefully diluted to give solutions covering the desired concentration range. A plot of refractive index increment, \( \Delta n \), versus concentration gives a straight line with slope \( \Delta n/C \). Such graphs also provide the means of determining the concentrations of a detergent in solutions of unknown concentration.

E. Solubilization Measurements

For a number of reasons benzene was chosen as the material to be solubilized. First of all, both Drott⁹ and


⁹E. Drott, Ph.D. Dissertation, Louisiana State University, 1959, p. 93.
Sardisco\textsuperscript{10} have studied the solubility of benzene in solutions of various detergents. It was hoped to compare our data with theirs and further generalize the conclusions. Also it is relatively easy to analyze quantitatively for benzene by use of the ultraviolet absorption spectra. A third and really less important reason is that benzene is relatively soluble even in distilled water so that random errors of observation were much smaller than the changes in solubility observed.

For these studies detergent solutions were sealed in glass ampoules with quantities of benzene which were in excess of the amount which could be solubilized. The sealed ampoules were shaken for 48 hours on a wrist action shaker. After this the samples were placed in a water bath at 30.0 ± 0.01°C and kept there until any emulsions formed during shaking were broken. Usually the samples remained in the water bath for a week or more. According to Klevens\textsuperscript{11} solubility equilibrium is usually reached within 48 hours when benzene is the solubilizate. Thus the above waiting period should be sufficient.

Because of the rapid loss of benzene from the detergent solutions upon exposure to air, it was necessary to

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

transfer the solution saturated with benzene directly from the ampoule to the container of cyclohexane which was to be used in extracting the benzene from the aqueous detergent solution. In all cases approximately one ml of detergent solution was extracted, and the exact amount was determined by weighing. After extraction the absorbency of the cyclohexane layer was measured on a Beckman D U spectrophotometer at 255 mu. This is the wavelength at which the maximum absorbance of benzene is observed. The amount of benzene present in the cyclohexane was determined from a previously prepared curve of absorbancy versus concentration of benzene.
A. Instrumentation

When making turbidity measurements one really needs to measure the intensity of the light scattered at 90° and the intensity of the incident light or something proportional to these quantities. What one actually measures is a quantity proportional to the total amount of light striking the phototube. This will be proportional to the intensity if the light source is a point source. In the particular case of light scattering it will be proportional to intensity to a good approximation if the volume of scattering solution viewed by the photomultiplier tube is constant.

The volume of solution viewed by the photomultiplier tube will be constant for solutions of a given refractive index. However, when solutions having greatly different refractive indexes are used the volume of solution viewed by the photomultiplier tube will not be the same for all solutions. This is important in the present case because the instrument was calibrated with a solution of polystyrene in
toluene while experimental measurements were made with aque­
ous solutions.

A second factor which will affect the apparent inten­
sity of the light scattered at 90° is that the amount of light
reaching the phototube from a given volume element of constant
size will vary when the refractive index of the scattering
solution is changed appreciably. Changes of the refractive
index of the scattering solution due to changes in solute con­
centration will not usually be of sufficient magnitude to
cause the effects mentioned here.

The significance of these effects can perhaps be
grasped more clearly by reference to Figure 1. Figure 1a
shows how the effect of change in volume will be compensated
for, while Figure 1b shows the effect of refractive index on
the amount of light reaching the phototube from a given volume
element.

The regular scattering volume in Figure 1a is that
volume defined by the width w and height h of the incident
light beam and the width l₁ of the first slit in the photo­
multiplier collimating assembly. Other definitions could
possibly have been used but this one will be shown to be com­
pletely satisfactory for present purposes.

The volume designated by the crosshatched areas in
Figure 1a will be referred to as the excess volume.
Fig. 1a Effect of the Refractive Index of the Solution on the Volume of Solution Viewed by the Photomultiplier Tube

1b Effect of the Refractive Index of the Solution on the Amount of Light Reaching the Phototube from a given Volume Element
Scattering centers located in this excess volume will be only half as effective on the average as scattering centers located in the regular scattering volume. The effectiveness of scattering centers decreases linearly with their distance from the regular scattering volume so that scattering centers located near the regular volume are almost as effective as centers located in the regular volume while centers near the outer edge of the excess volume do not have much effect on the amount of light reaching the phototube. As a result it will only be necessary to consider half of the volume indicated by the crosshatched areas. This then will be referred to as the excess volume. In speaking of these variations in volume, etc., reference has always been made to the intensity of the scattered light and never to variation in the apparent intensity of the incident beam. This is because no such variation in the intensity of the incident beam will be caused by these factors.

It will be necessary to calculate an intensity correction factor for both toluene and aqueous solutions for both of the above effects. The volume correction factor will have the following general form \( F_V = \frac{V}{V + V_{ex}} \) where \( V \) represents the regular scattering volume and \( V_{ex} \) represents the excess volume as defined above. \( V \) can be replaced by \( \frac{l_1wh}{dwh} \) and \( V_{ex} \) by \( \frac{l_1wh}{dwh} \). The correction then becomes \( F_V = \frac{l_1wh}{l_1wh + dwh} \).
The quantity \( \frac{l_1}{l_1 + d} \). The quantity \( l_1 \) is easily measured so that the only real problem is the evaluation of the quantity \( d \). This can be done using Snell's law and ordinary trigometric relations among the measurable slit widths and other distances on the instrument. The principles are the same for all shapes of cells supplied with the instrument.

It would seem that there should be a similar correction for a possible change in the height of the volume element viewed by the photomultiplier. However, when this correction was calculated it was found that instrument geometry is such that this correction was negligible.

A detailed examination of equation (12) of the preceding section will show that it contains a ratio of the intensity of the light scattered from an aqueous solution to the intensity of the light scattered from a solution of polystyrene in toluene. The ratio also contains quantities proportional to the intensity of the respective incident beams but this does not affect the present argument. Since the quantity \( F_v \) described above is a correction to the scattered intensity, the modified form of equation (12) will contain the ratio \( F_v(w)/F_v(t) \) where \( F_v(w) \) is the correction factor for aqueous solutions and \( F_v(t) \) the factor for toluene solutions. If this latter ratio is called \( C_v \) equation (12) will
now read

$$\tau = C_V (Y/X) \times 3.49 \times 10^{-3}. \quad (13)$$

The quantity $C_V$ has been calculated to be 0.92 for the cylindrical cell available with the instrument for the solvent pair toluene and water. Therefore equation (13) becomes simply

$$\tau = (Y/X) \times 3.21 \times 10^{-3}. \quad (14)$$

Because of refraction effects only that light scattered through the angle $\theta_1$ of Figure 1b will reach the phototube whereas if no refraction occurred all light scattered through the angle $\theta_2$ would reach the phototube. The angle $\theta_2$ is fixed by the slit widths $l_1$ and $l_2$ and the distances $r_1$, $r_2$, and $r_3$ where $r_1$, $r_2$, and $r_3$ are the distances shown in Figure 1a, while $\theta_1$ depends on the refractive index of the scattering medium. The correction to be applied is of the form $F_n = \theta_1/\theta_2$ for a cylindrical cell. For a rectangular cell $F_n = (\theta_1/\theta_2)^2$ since there is a correction in both the horizontal and the vertical direction.

Carr and Zimm$^1$ and also Brice, Halwer and Speiser$^2$

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show the angles $\theta_1$ and $\theta_2$ are related to instrument parameters in the following way

$$F_n = n \left[ 1 - \frac{b}{r} \frac{(n-1)}{n} \right]$$  \hspace{1cm} (15)

where again this is for the cylindrical cell and the correction must be squared for a square cell. In this equation $n$ is the refractive index of the scattering solution, $b$ is the distance from the center of the scattering volume to the edge of the cell (equal the $r_1$ of Figure 1a) and $r$ is the distance from the center of the scattering volume to the photomultiplier tube.

As was the case with the excess volume correction factors, equation (12) will contain the ratio $F_n(w)/F_n(t)$ where as before $F_n(w)$ is the correction to the apparent intensity for aqueous solutions and $F_n(t)$ is for toluene solutions. If this ratio is designated as $C_n$, equation (12) becomes

$$\tau = C_n \left( \frac{Y}{X} \right) 3.21 \times 10^{-3}.$$  \hspace{1cm} (16)

The factor $C_n$ has been calculated to be 0.91 for the cylindrical cell for the particular pair of solvents used. Therefore equation (12) becomes in its final form

$$\tau = \left( \frac{Y}{X} \right) 2.92 \times 10^{-3}.$$  \hspace{1cm} (17)

This is the form of the equation which has been used throughout
this work. The effect these corrections have on the molecular weight obtained will be discussed later.

Mention has been made of the fact that this particular light scattering photometer is equipped with four neutral filters for reducing the intensity of the incident beam. It is necessary that the transmittances of these neutral filters be known very accurately. In the past there has been much discussion\(^3\),\(^4\),\(^5\) concerning the correct value to use for the transmittances of these filters.

The instruction manual supplied with the instrument gives the values listed in Table I under "Manual Values." When attempts were made to verify these transmittance values, using the light scattering photometer, rather wide discrepancies were found. The values obtained with the light scattering photometer are recorded in Table I under "Instrument Values."

These "Instrument Values" were obtained in the following way. The photomultiplier tube was set at zero degrees

\(^3\)R. L. Venable, M.S. Thesis, Louisiana State University, Baton Rouge, 1958, pp. 36-40.

\(^4\)F. Aguirre, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1962, pp. 50-54.

\(^5\)E. Drott, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1959, pp. 41-47.
<table>
<thead>
<tr>
<th>Filter Number</th>
<th>Manual Value</th>
<th>Instrument Value</th>
<th>Cary Value</th>
<th>Ninety Degree Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.450</td>
<td>0.419</td>
<td>0.453</td>
<td>0.455</td>
</tr>
<tr>
<td>2</td>
<td>0.194</td>
<td>0.202</td>
<td>0.195</td>
<td>0.198</td>
</tr>
<tr>
<td>3</td>
<td>0.121</td>
<td>0.129</td>
<td>0.125</td>
<td>0.125</td>
</tr>
<tr>
<td>4</td>
<td>0.0525</td>
<td>0.0598</td>
<td>0.0547</td>
<td>0.0569</td>
</tr>
</tbody>
</table>
with respect to the incident beam or, in other words, directly in the light path. The photomultiplier and galvanometer sensitivity knobs were set in such positions that the galvanometer gave approximately full scale deflection with no neutral filters in the light path. This deflection was carefully determined. Then filter 1 was inserted into the light path and the galvanometer deflection again determined. The ratio of this latter deflection to the deflection without the filter is termed the transmittance of filter 1.

To determine the transmittance of filter 2, filter 1 was inserted in the light path and the sensitivity knobs set so that the galvanometer again gave approximately full scale deflection. The deflection with filter 1 in the light path was carefully measured and filter 1 was removed and filter 2 inserted into the light path. The calculation of the transmittance of filter 2 can probably be made clearer by the use of an example. Suppose that the galvanometer deflection with filter 1 in the light path was 98.0 units and that the transmittance of filter 1 is 0.450 (the manual value). This means that, if the galvanometer had a sufficiently large scale, and if filter 1 had not been in the light path, the galvanometer would have read 217.8 units. If the galvanometer deflection with filter 2 alone in the light path was 43.3 units, the transmittance of filter 2 is 43.3/217.8 or 0.199.
To determine the transmittance of filter 3 by this method the sensitivity knobs were set such that the galvanometer gave approximately full scale deflection with filter 2 in the light path. The calculations illustrated above are repeated except that this galvanometer reading is now divided by the transmittance of filter 2 to get the "real" galvanometer deflection. This process is repeated using the transmittance of filter 3 obtained in this way to determine the transmittance of filter 4. One can easily see that any errors made in determining the transmittance of filter 1 are compounded greatly using this procedure.

This does not remove the dilemma of the discrepancies between the "Manual Values" and the "Instrument Values." In an effort to remedy this difficulty the light source from the light scattering photometer was placed behind the Cary Model 14 Spectrophotometer so that the very fine optical system of this instrument could be used to determine the transmittances of these filters.

The filters in their usual mountings were taped in position in the optical path of the Cary and the percent transmission measured as a function of wavelength from 4300 to 4400 Angstroms. The wavelength of the incident light was simply that of the light scattering photometer lamp transmitted by the blue (436 mu) filter. The values of the filter
transmittances were found by calculating the ratio of the heights of the peaks with and without the neutral filter in the light path. The values so obtained are recorded under "Cary Values" in Table I. It is obvious that these values agree much better with the "Manual Values" than do the "Instrument Values."

The filter transmittances determined using the Cary are considered to be just as accurate and perhaps more accurate than the values listed in the manual. However, this still does not resolve the difficulty of which values to use in calculations because the possibility exists that the "Instrument Values" contain some factor from the detector system of the light scattering photometer which affects all measurements made with this instrument. Happily this difficulty has been resolved.

The light scattering photometer was calibrated and used in such a way that in the measurement of the apparent intensity of the incident beam, all four neutral filters were always used. Therefore the transmittance of this filter combination canceled out of equation (17). The only time that the exact value of the filter transmittance was needed was when the apparent intensity of the light scattered at ninety degrees with respect to the incident beam was calculated. As a result it was decided to determine the filter
transmittances with the photomultiplier tube in this position. The measurements and calculations were performed in the manner used previously to calculate the "Instrument Values" except that it was necessary to have some fairly turbid solution in the light path. The values obtained in this fashion are listed in Table I under "Ninety Degree Values." These values are averages obtained using three different cells with a different solution in each cell. These values and the values obtained from the Cary are in much better agreement than the values listed under "Instrument Values."

The agreement between the "Ninety Degree Values" and the "Cary Values" is good enough to convince the writer that the photomultiplier and galvanometer of the light scattering photometer give essentially linear response as indeed they must if measurements made on this instrument are to have any meaning.

Mention has been made of the fact that errors in determining the transmittance of each filter are compounded in the determination of the transmittances of subsequent filters using the light scattering photometer. In determining the "Ninety Degree Value" this was minimized as much as possible in the following way. The "Ninety Degree Value" for filter 1 is 0.455 as compared to 0.453 from the Cary. The "Cary Value" is considered to be the correct value since the
Cary spectrophotometer is a much better instrument than the light scattering photometer for this purpose. Therefore the value 0.453 was used in the calculation of the transmittance of filter 2 in the way shown by the numerical example above. While this may not be the ideal way to handle this situation, the writer feels that it is the best way suggested to date.

The finding that the "Ninety Degree Values" agree very nicely with the "Cary Values" and fairly well with the "Manual Values" is in direct contradiction to the findings of Drott who found that "Ninety Degree Values" differed from the "Manual Values" even more than the transmittances which he determined and which correspond to the results designated here as "Instrument Values." The instrument was found to be in very poor alignment at the beginning of this work with the light source shifted far to one side with respect to the collimating tubes. This poor alignment is believed to be the cause for his finding inconsistent "Ninety Degree Values."

B. Surface Tension

Surface tension measurements were made primarily for the purpose of determining the critical micelle concentrations. The data obtained were also used to calculate an approximate

\[ \text{Cary spectrophotometer is a much better instrument than the light scattering photometer for this purpose. Therefore the value 0.453 was used in the calculation of the transmittance of filter 2 in the way shown by the numerical example above. While this may not be the ideal way to handle this situation, the writer feels that it is the best way suggested to date.} \]

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B. Surface Tension

Surface tension measurements were made primarily for the purpose of determining the critical micelle concentrations. The data obtained were also used to calculate an approximate

\[ \text{Drott, op. cit., p. 7.} \]
value for the area occupied by each molecule in the interface after a monolayer was formed. These measurements were made in water and 0.05 N sodium bromide. The results are summarized in Table II.

Plots of surface tension versus the logarithm of surfactant concentration in moles/liter are shown in Figures 2-6 which are referenced in Table II, where the results are summarized. No measurements were made on HTPAB in 0.05 N sodium bromide solution because quaternary salts of this chain length are salted out of solution at this concentration of added electrolyte. The critical concentrations determined from these data are in excellent agreement with the values found by light scattering.

Mention has been made of the fact that in aqueous solutions of surface active molecules the surface tension often changes slowly with time. Changes of 0.5 dynes/cm or more over a period of thirty minutes were observed in most cases in the present work. In all cases the data presented in Figures 2-5 are for the initial points, which were determined by the procedure described in the previous chapter. However, there are some indications that even these small changes of surface tension with time are caused by the presence of traces of impurities. Surface tension measurements on all compounds were made on samples having the
TABLE II

SUMMARY OF THE RESULTS OF SURFACE TENSION MEASUREMENTS ON THE VARIOUS DETERGENTS USED IN THIS STUDY

<table>
<thead>
<tr>
<th>Compound</th>
<th>CMC in g/ml</th>
<th>Area/Molecule in sq. A</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. In water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPB</td>
<td>$3.97 \times 10^{-3}$</td>
<td>58.9</td>
<td>2</td>
</tr>
<tr>
<td>TPB</td>
<td>$0.915 \times 10^{-3}$</td>
<td>59.5</td>
<td>3</td>
</tr>
<tr>
<td>TTMAB</td>
<td>$1.18 \times 10^{-3}$</td>
<td>6.12</td>
<td>4</td>
</tr>
<tr>
<td>TTPAB</td>
<td>$0.86 \times 10^{-3}$</td>
<td>88.6</td>
<td>5</td>
</tr>
<tr>
<td>HTPAB</td>
<td>$2.58 \times 10^{-4}$</td>
<td>91.0</td>
<td>6</td>
</tr>
<tr>
<td><strong>B. In 0.05 N Sodium Bromide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPB</td>
<td>$1.20 \times 10^{-3}$</td>
<td>48.3</td>
<td>2</td>
</tr>
<tr>
<td>TPB</td>
<td>$0.86 \times 10^{-4}$</td>
<td>47.5</td>
<td>3</td>
</tr>
<tr>
<td>TTMAB</td>
<td>$1.43 \times 10^{-4}$</td>
<td>38.6</td>
<td>4</td>
</tr>
<tr>
<td>TTPAB</td>
<td>$1.16 \times 10^{-4}$</td>
<td>64.4</td>
<td>5</td>
</tr>
</tbody>
</table>
Fig. 2. Surface Tension vs. Logarithm of the Concentration for LPB
Fig. 3. Surface Tension vs. Logarithm of the Concentration for TPB
Fig. 4. Surface Tension vs. Logarithm of the Concentration for TTMAB
Fig. 5. Surface Tension vs. Logarithm of the Concentration for TTPAB
Fig. 6. Surface Tension vs. Logarithm of the Concentration for HTPAB
composition indicated in Table III. Changes of surface tension with time in aqueous and salt solutions were observed in every instance. After further purification, measurements were made on LPB in water and TPB in 0.05 N potassium bromide solution. In both of these latter cases the surface tension at each concentration was found to be constant for periods of at least ten minutes. The surface tension values found here agree well with the initial values found in those cases where changes with time occurred. This is by no means conclusive evidence that the small changes of surface tension with time were caused by impurities in every case but it does indicate that this is a good possibility.

If there is any general validity to the suggestion in the previous paragraph, surface tension measurements on TTPAB in water certainly provide an interesting exception. Figure 7 shows how surface tension changed with time at three concentrations below the cmc. These are by far the most drastic changes of surface tension with time that were observed in this work. The possibility that traces of impurities were responsible for these changes cannot be overlooked but it is felt that this is a very unlikely cause. One possible explanation for these effects lies in the relatively long and "floppy" propyl chains. It is suggested that because of this the charged head group can be compressed or in other words,
<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Composition</th>
<th>Observed Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPB</td>
<td>62.18% carbon 9.21% hydrogen 4.27% nitrogen 24.34% bromine</td>
<td>62.02% carbon 9.33% hydrogen 4.12% nitrogen</td>
</tr>
<tr>
<td>TPB</td>
<td>64.03% carbon 9.62% hydrogen 3.93% nitrogen 22.42% bromine</td>
<td>63.89% carbon 9.96% hydrogen 3.91% nitrogen</td>
</tr>
<tr>
<td>TTMAB</td>
<td>60.69% carbon 11.39% hydrogen 4.16% nitrogen 23.76% bromine</td>
<td>61.04% carbon 11.04% hydrogen 4.07% nitrogen</td>
</tr>
<tr>
<td>TTPAB</td>
<td>65.68% carbon 11.98% hydrogen 3.33% nitrogen 19.00% bromine</td>
<td>65.62% carbon 12.02% hydrogen 3.46% nitrogen</td>
</tr>
</tbody>
</table>

*These analyses were performed by Galbraith Laboratories Inc. of Nashville, Tennessee.
Fig. 7. Change of Surface Tension with Time for TTPAB at Concentrations Below the CMC
that during the time when the surface tension is changing so drastically, the propyl chains are coiling back toward the central nitrogen atom. This would result in or be caused by additional surface active molecules appearing in the interface. One would expect there to be an energy barrier to such a compression and this could possibly lead to the observed time effects. The writer knows of no experiment which could be used to clarify the situation.

The two humps presented on curve III of Figure 7 were caused by swirling the surface tension cell. The first hump results from a gentle swirling and the second hump from a vigorous swirling of the cell. It will be observed that these swirlings took place after the surface tension had reached a minimum and was going back up slowly. It is proposed that the vigorous swirling effectively created a new surface. The surface tension did not go as high upon swirling as it had originally been and neither did it drop as low afterwards as it did the first time. As a matter of fact the low reached after each swirling is approximately that which would be obtained by extrapolation of the curve obtained before the solution was stirred. No explanation is offered for this effect.

Figure 3 shows a curve for surface tension vs. the logarithm of the concentration for TPB in 0.05 N potassium
bromide. The critical concentration in potassium bromide solution apparently is $1.05 \times 10^{-4}$ g/ml while in sodium bromide solution it is $0.86 \times 10^{-4}$ g/ml. These measurements were occasioned by the fact that Trapp and Hermans report the cmc for TPB in 0.05 N potassium bromide to be $5.34 \times 10^{-4}$ g/ml. It was thought that possibly the difference in results might be due to the difference in the salts added. As shown above, however, the difference in the effects of the two salts is not nearly that great. This latter conclusion is in qualitative agreement with the finding that in general the added ion having the same charge as the aggregating species has no effect on the critical concentration. Most workers have not used as high salt concentrations as have been used here and the possibility exists that such an effect may be real at these high salt concentrations. Further work will be necessary before this can be definitely established.

The summary in Table II shows that the value calculated for the area occupied by each molecule in the interface is very nearly the same for the trimethyl salt and the two pyridinium salts in water. This is consistent with qualitative observations on Stuart-Brieglieb molecular models for these

---

two head groups. Likewise there is good agreement concerning this parameter for the two tripropyl salts. There is a rather large difference between the trimethyl salt and the two pyridinium salts in 0.05 N sodium bromide solution although there is good agreement between the two pyridinium salts. The area per molecule calculations in salt solution are probably less reliable than in aqueous solution because the substitution of concentrations for activities in the Gibbs equation is no doubt a much poorer approximation in the presence of a high concentration of added electrolyte.

If one assumes that the area occupied by each charged group in the surface of a micelle occupies the same area that the group occupies in the air-water interface, one can predict micellar molecular weights based on a particular model. Most of the data currently available for micelle formation is compatible with a spherical model for the micelle. This model has a radius equal to the length of the long hydrocarbon chain of the monomer. Tartar\(^8\) states that the linear extension of a methylene group is 1.27 A while that of a methyl group is 2.00 A. Using these figures one finds that the linear extension of a twelve carbon chain is 16 A while that of a fourteen carbon chain is 18.5 A and that of a sixteen

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\(^8\)H. V. Tartar, *J. Colloid Sci.*, XIV (1959), 115.
carbon chain is 21 A.

The predicted micellar molecular weights were calculated in the following way. The surface area of a sphere having a radius equal to the chain length under consideration was divided by the area occupied by the charged head of each monomer. This gave the predicted number of monomers in the micelle which when multiplied by the monomer molecular weight gave the micellar molecular weight.

Table IV shows the predicted micellar molecular weights. A spherical model with the indicated radii was assumed. These predicted molecular weights are compared with the weights determined by light scattering. No predictions are made for micellar molecular weights in sodium bromide solution. One reason for this is a lack of confidence in the area per molecule calculations and the other is the lack of a suitable model.

The predicted and observed micellar molecular weights are in very close agreement for the two pyridinium salts. The predicted values are considerably lower than the observed values for TTMAB and TTPAB which causes one to suspect that the close agreement for the pyridinium salts is fortuitous. No light scattering measurements were made on HTPAB because it has generally not been possible to get reproducible turbidity measurements for hexadecyl salts in the absence of
### TABLE IV

**COMPARISON OF PREDICTED AND OBSERVED MICELLAR MOLECULAR WEIGHTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Predicted MMW</th>
<th>Observed MMW</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPB</td>
<td>17,900</td>
<td>17,700</td>
</tr>
<tr>
<td>TPB</td>
<td>25,900</td>
<td>26,000</td>
</tr>
<tr>
<td>TTMAB</td>
<td>23,700</td>
<td>27,200</td>
</tr>
<tr>
<td>TTPAB</td>
<td>20,100</td>
<td>25,600</td>
</tr>
<tr>
<td>HTPAB</td>
<td>24,800</td>
<td></td>
</tr>
</tbody>
</table>
extraneous electrolyte. From the amount the observed micellar molecular weights are above the predicted values, it is estimated that the micellar molecular weight for HTPAB is probably approximately 30,000. This is in agreement with the findings of Tartar who reports micellar molecular weights of 29,000 for hexadecyltrimethylammonium bromide (HTMAB) and 33,500 for hexadecylpyridinium bromide (HPB). These later measurements were made in 0.003 N potassium bromide solution. This salt concentration is reported to be the most dilute salt solution which is a satisfactory solvent for stable micelle formation.

One possible explanation for the differences in the predicted and observed micellar molecular weights is that the micelles are not really completely spherical as assumed in the model. There is an uncertainty in the values for the area occupied by each charged head group because of the assumptions made in calculating this parameter. In addition the assumption was made that the charged head group occupied the same area in the air-water interface and in the surface of the micelle. This latter assumption is certainly not necessarily valid and the differences in the predicted and observed micellar molecular weights could be caused by the charged head groups occupying smaller areas in the surface

\[9\text{Ibid.}\]
of the micelle than they occupy in the air-water interface.

The conclusion is that prediction of micellar molecular weights by the method described above is not entirely satisfactory. However, this method can be used to obtain a rough approximation of the micellar molecular weight if no light scattering data are available as in those situations where turbidity measurements are not possible.

C. Light Scattering

In order to calculate micellar molecular weights from turbidity measurements it is necessary to evaluate the refraction constant $H$ defined by equation (9). The only experimental quantity involved is the refractive index increment $(u-u_0)/C$ or $dn/dc$ since $u_0$ is fixed for a given solvent. The results of differential refractive index measurements are given in Table V. No results are presented for HTPAB because no turbidity measurements were made on this compound.

The results of turbidity measurements are summarized in Table VI. The various symbols used in this table will be defined in the following discussion where data are presented.

Turbidity data for LPB in aqueous solution and in 0.05 N sodium bromide solution are presented in Figure 8. Figure 9 shows the plots of $H(C-C_0)/(\tau-\tau_0)$ vs. $(C-C_0)$. When such a plot is extrapolated to $(C-C_0)$ equal to zero,
TABLE V
REFRACTIVE INDEX INCREMENTS AND
REFRACTION CONSTANTS

<table>
<thead>
<tr>
<th>Compound</th>
<th>dn/dc</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPB</td>
<td>0.174</td>
<td>8.27 x 10^{-6}</td>
</tr>
<tr>
<td>TPB</td>
<td>0.175</td>
<td>8.36 x 10^{-6}</td>
</tr>
<tr>
<td>TTMAB</td>
<td>0.154</td>
<td>6.47 x 10^{-6}</td>
</tr>
<tr>
<td>TTPAB</td>
<td>0.1595</td>
<td>6.945 x 10^{-6}</td>
</tr>
</tbody>
</table>
### TABLE VI

**SUMMARY OF THE RESULTS OF TURBIDITY MEASUREMENTS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>1/A</th>
<th>B</th>
<th>P</th>
<th>m</th>
<th>mM</th>
<th>cmc in g/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. In Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPB</td>
<td>14,900</td>
<td>1.156x10^-2</td>
<td>9</td>
<td>54</td>
<td>17,700</td>
<td>4.0x10^-3</td>
</tr>
<tr>
<td>TPB</td>
<td>22,300</td>
<td>3.69x10^-2</td>
<td>10</td>
<td>73</td>
<td>26,000</td>
<td>0.92x10^-3</td>
</tr>
<tr>
<td>TTMAB</td>
<td>23,300</td>
<td>3.03x10^-2</td>
<td>12</td>
<td>84</td>
<td>27,200</td>
<td>1.18x10^-3</td>
</tr>
<tr>
<td>TTPAB</td>
<td>22,700</td>
<td>1.79x10^-2</td>
<td>7</td>
<td>61</td>
<td>25,600</td>
<td>0.86x10^-3</td>
</tr>
<tr>
<td>TPB*</td>
<td>26,300*</td>
<td>2.84x10^-2*</td>
<td>11*</td>
<td>83*</td>
<td>29,500*</td>
<td>0.92x10^-3*</td>
</tr>
<tr>
<td><strong>B. In 0.05 N Sodium Bromide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPB</td>
<td>20,800</td>
<td>0</td>
<td>0</td>
<td>63.4</td>
<td>20,800</td>
<td>1.10x10^-3</td>
</tr>
<tr>
<td>TPB</td>
<td>90,400</td>
<td>8.25x10^-3</td>
<td>85</td>
<td>274</td>
<td>97,600</td>
<td>0.86x10^-4</td>
</tr>
<tr>
<td>TTMAB</td>
<td>49,700</td>
<td>1.25x10^-3</td>
<td>6</td>
<td>150</td>
<td>50,400</td>
<td>1.40x10^-4</td>
</tr>
<tr>
<td>TTPAB</td>
<td>39,200</td>
<td>1.87x10^-3</td>
<td>.3</td>
<td>97</td>
<td>40,700</td>
<td>1.16x10^-4</td>
</tr>
</tbody>
</table>

*These results on TPB ignore the volume and refraction corrections.*
Fig. 8. Turbidity vs. Concentration for LPB in Water and in 0.05 N Sodium Bromide
Fig. 9. $H(C-C_0)/(\tau-\tau_0)$ vs. $(C-C_0)$ for LPB in Water and in 0.05 N Sodium Bromide.
the intercept is called \( A \) and the initial slope of the line is \( B \). The reciprocal of the intercept, \( 1/A \), gives the micellar molecular weight as determined by the straightforward application of the modified form of equation (10). Application of the Princen-Mysels\textsuperscript{10} treatment allows one to estimate the number of unneutralized charges \( P \) on each micelle. In addition the treatment gives a corrected micellar molecular weight, \( mM_1 \), where \( m \) is the number of monomers in the micelle and \( M_1 \) is the monomer molecular weight.

In the absence of extraneous electrolyte the relationship between \( P \) and experimental quantities is

\[
P = \frac{BM_1n_1 + \sqrt{2Bn_1}}{A(1 - AM_1/2)}
\]  

(18)

in which the only undefined quantity is \( n_1 \), which is the critical concentration expressed in moles/ml. This quantity can be obtained from the critical concentrations given in Table VI simply by dividing by the monomer molecular weight. The quantity \( m \) is calculated from the expression

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

(19)

These equations take a more complicated form when

\textsuperscript{10}L. H. Princen and K. J. Mysels, \textit{J. Colloid Sci.}, XII (1957), 594.
extraneous electrolyte is present. In this case

\[
P = \frac{BM_1(n_1 + fn_3) + \sqrt{2B(n_1 + n_3)}}{A(1 - AM_1E/2)}
\]  

(20)

where \(n_3\) is the concentration of added electrolyte in moles/ml and \(f\) is the ratio of the molar refractive index increment of the added salt to that of the detergent. The only other new quantity encountered here is \(E\) which equals \((n_1+fn_3)/(n_1+n_3)\). The expression for \(m\) is

\[
m = \frac{1}{2}(PE + 1/AM_1) + \frac{1}{2} \sqrt{(PE + 1/AM_1)^2 - (P^2 + P)E^2}
\]  

(21)

From these equations it can easily be seen that when \(B\) is zero, \(P\) is also zero. It is also obvious that when \(P\) is zero, \(m\) is equal to \(1/AM_1\) and \(mM_1\) equals \(1/A\) and the micellar molecular weight obtained is simply that which is obtained from the modified form of equation (10).

The results of turbidity measurements for TPB and TTMAB in water are presented in Figure 10. The quantities \(A\) and \(B\) were determined for these compounds from the curves of Figure 11.

Turbidity data for TPB were obtained in two ways. The data represented by the squares of Figure 10 were obtained from measurements on individually prepared and filtered solutions. The data represented by the triangles were obtained
Fig. 10. Turbidity vs. Concentration for TPB and TTMAB in Water
Fig. 11. $\frac{H(C-C_0)}{(\tau-\tau_0)}$ vs. $(C-C_0)$ for TPB and TTMAB in Water
by starting with solvent in the light scattering cell and adding increments of a concentrated stock solution with stirring after each addition. As mentioned in the previous chapter there is greater chance for the addition of dust by this latter technique. This addition of dust and lint was accounted for as follows. Blank curves were run by placing solvent in the cell and adding more solvent and stirring just as was done in regular turbidity measurements. The turbidity was observed to increase slightly with each addition and the increase was independent of the volume of solvent added and depended only on the number of additions that had been made. To get the data represented by the triangles in Figure 10, the original data were corrected by subtracting from each turbidity measurement the amount of the turbidity increase incurred by the number of additions used to get the particular data point. Data obtained by the two methods agree very well and therefore this latter method is felt to be a valid experimental technique.

Turbidity data for TTPAB in aqueous solution are presented in Figure 12 while Figure 13 shows the plot of $H(C-C_0)/(\tau-\tau_0)$ vs. $(C-C_0)$ for this compound. Plots of turbidity vs. concentration for TPB, TTMAB, and TTPAB in 0.05 N sodium bromide are given in Figure 14 and the $H(C-C_0)/(\tau-\tau_0)$ plots appear in Figure 15.
Fig. 12. Turbidity vs. Concentration for TTPAB in Water
Fig. 13. $H(C-C_0)/(T-T_0)$ vs. $(C-C_0)$ for TTPAB in Water
Fig. 14. Turbidity vs. Concentration for TPB, TTMAB, and TTPAB in 0.05 N Sodium Bromide
Fig. 15. \[ \frac{H(C-C_0)}{(\tau-\tau_0)} \] vs. \( (C-C_0) \) for TPB, TTMAB, and TTPAB in 0.05 N Sodium Bromide
The number of charges calculated for each micelle in aqueous solution is approximately 10 units and is considered to be the same for all compounds within the probable limits of error of the calculations. The micellar molecular weight and charge per micelle for TPB in 0.05 N sodium bromide solution are far out of line with respect to the results on the other compounds. An unneutralized charge of 85 units in such a concentrated salt solution seems preposterous. Such a result casts doubt on either the validity of the treatment or of the experimental results. These results were obtained by exactly the same technique used for the other compounds. A charge of zero units per micelle for LPB is completely reasonable. The calculation of charge per micelle in 0.05 N sodium bromide solution seems to the writer to be dubious in most cases because the slope of the $H(C-C_0)/(T-T_0)$ vs. $(C-C_0)$ plot is so extremely low that relative errors in determining $B$ are rather large. It seems unreasonable that the charge per micelle could be larger in 0.05 N sodium bromide than in the absence of added electrolyte yet this is what appears to be the case for both TPB and TTPAB although the micellar molecular weight for TTPAB is completely reasonable.

When blank turbidity measurements were made to determine the effect of additions and stirrings on sodium bromide solution, it was found that the turbidity did not increase at
all. Therefore turbidity results in 0.05 N sodium bromide did not need to be corrected for additions and stirrings.

It is of interest to see the effect that the combined volume and refraction corrections had on the micellar molecular weights obtained. The data on TPB in aqueous solution have been used to illustrate this effect. Figure 16 gives turbidity data that is uncorrected for volume and refraction effects and Figure 17 shows the $\frac{H(C-C_0)}{(\tau-\tau_0)}$ vs. $(C-C_0)$ plot for these data. As shown in Table VI the micellar molecular weight obtained when the corrections are ignored is 29,500 compared to 26,000 when the corrections are used. The micellar molecular weight is 13.4 per cent larger when the corrections are ignored than when the corrections are used. This shows very definitely that the corrections cannot be ignored if reliable molecular weights are to be obtained when the instrument is calibrated as this one was using Styron in toluene.

D. Solubilization

One of the reasons for doing solubilization measurements is that Drott$^{11}$ found indications that the amount of material solubilized depended on the size of the charged head

$^{11}$E. Drott, Ph.D. Dissertation, Louisiana State University, Baton Rouge, 1959, p. 111.
Fig. 16. Turbidity vs. Concentration for TPB in Water Omitting Volume and Refraction Correction Factors
Fig. 17. $H(C-C_0)/(\tau-\tau_0)$ vs. $(C-C_0)$ for TPB in Water Omitting Volume and Refraction Correction Factors
group. The size of the charged head group should control, at a given chain length, the volume capable of receiving added materials.

Mention was made in the previous chapter of the necessity of running the sample to be extracted directly from the ampoule to the container of cyclohexane. The data presented in Figure 18 show very clearly why this was necessary. The data for curve I were obtained by means of the direct sampling technique. After this sample was taken the remaining detergent solution was run out into a beaker. Then a one milliliter pipette was used to take a sample for extraction. The data obtained in this fashion are shown by curve II. Clearly a serious loss of benzene occurred during the short period of time required to allow the solution to run into the beaker and then get the sample with the pipette.

Solubilization is a micellar phenomenon and therefore it is necessary to determine the amount of material soluble when no micelles are present and subtract this from the total solubility to get the amount solubilized by the micelles. To this end the solubility of benzene in water was determined and found to be $0.179 \pm 0.002$ g/100 ml or $2.29 \times 10^{-2}$ moles/liter. This compares very well with the literature\textsuperscript{12} value

Fig. 18. Solubility Data for TTMAB in Water Showing Effects of Exposure to Air
of $0.177 \pm 0.002 \text{ g/100 ml}$. A spectrophotometric technique similar to the one used in the present work was used to obtain the latter result. There is one important difference. In the present work the benzene was extracted into such a volume of cyclohexane that reasonable absorbance values were obtained on the spectrophotometer. Arnold et al.\textsuperscript{13} diluted the saturated solution directly with water. In view of this difference in method the writer feels that the agreement between the two results is truly excellent.

The solubility of benzene in 0.05 N sodium bromide was found to be $0.173 \pm 0.002 \text{ g/100 ml}$ or $2.22 \times 10^{-2}$ moles/liter. Naturally one would subtract these solubilities from the total amount of benzene present in solution to get the amount of benzene brought into solution by the detergent. There is one complicating factor. The solubility of benzene in solutions of detergents at concentrations lower than the critical concentration is slightly greater than the solubility in the pure solvents where for our purposes 0.05 N sodium bromide can be classed as a pure solvent. A survey of all available data indicates that the solubility of benzene in a detergent solution at the critical concentration is $0.09 \times 10^{-2}$ moles/liter higher than the solubility in the pure

\textsuperscript{13}\textit{Ibid.}
solvent and this quantity is called \( S_0 \) in the following dis-
cussion while \( S \) refers to the total amount of benzene rendered
soluble by the detergent at any given detergent concentration.
In other words \( S \) is the total solubility of benzene minus the
solubility of benzene in the pure solvent. Therefore \( (S-S_0) \)
represents the amount of benzene solubilized by the detergent
micelles.

In Figure 19 plots of \( (S-S_0) \) vs. \( (C-C_0) \) are presented
for TPB, TTMAB, and TTPAB in water with all concentrations
expressed in moles/liter. These results are summarized in
Table VII. In addition Table VII gives the results of calcu-
lations of the number of benzene molecules per micelle at
several concentrations. Inherent in these calculations are
two assumptions: (1) the number of detergent monomers per
micelle remains constant and (2) the critical micelle concen-
tration (cmc) is not affected by the presence of the benzene.
This latter assumption is probably not valid but no data are
available which can be used to determine the magnitude of any
change of cmc which may occur upon addition of benzene to the
system.

The slopes of the curves of Figure 19 increase with
increasing detergent concentration which indicates that the
relative molar amounts of benzene solubilized increases as
the detergent concentration increases. This corresponds to
Fig. 19. \((S-S_0)\) vs. \((C-C_0)\) for TPB, TTMAB, and TTPAB in Water
<table>
<thead>
<tr>
<th></th>
<th>(C-C₀) in moles/liter x 10²</th>
<th>(S-S₀) in moles/liter x 10²</th>
<th>Moles of micelles per liter x 10⁴</th>
<th>Benzene molecules per micelle</th>
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<td></td>
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</tr>
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saying that the number of benzene molecules per micelle increases as the detergent concentration increases if the assumptions stated in the previous paragraph are valid. However, the validity of these assumptions is open to question. Possible explanations for the increase in the slopes are considered below.

It is generally considered that the distribution of micellar molecular weights in a detergent solution is rather narrow or that all micelles of a given detergent have about the same size. However, if the addition of benzene to the system caused an increase in micellar molecular weight by causing an increase in the number of monomers per micelle, this could possibly cause the observed increase in the relative molar amount of benzene solubilized. Such an increase in micelle size could occur at the expense of the monomers present in equilibrium with the micelles and thereby result in a decrease in the concentration of unassociated monomers. This would correspond to a constantly changing critical concentration. Also the increased solubilization could possibly be caused by micelles becoming larger in size and fewer in number without affecting the concentration of monomers. Data will be presented later which the writer believes discredits the idea that a change in the distribution of micelle sizes affects the relative molar solubilization of benzene.
Therefore the assumption that the number of monomers per micelle remains constant is used in the remainder of this work.

Another possible explanation for the increase in the relative molar amount of benzene solubilized at higher detergent concentrations is partly of thermodynamic origin. As the number of micelles per unit volume increases the micelles approach each other more closely and interact with each other more strongly because of the unneutralized charges on the micelles. The writer suggests that possibly this increasing interaction results in a lowering of the chemical potential of the benzene in the micelle relative to that of the benzene in the aqueous surroundings thus favoring addition of more benzene to the micelle. Perhaps a more realistic suggestion is that the increase in the concentration of charged micelles as a result of increasing the detergent concentration has the same effect as addition of an ordinary salt would have. That is, the increase in the concentration of micelles tends to progressively salt the benzene out of solution just as the addition of sodium bromide does. However, as previously mentioned, a micelle can be considered as sort of a microphase and the solubilization phenomenon can be considered as an extraction process. A well known technique for increasing the efficiency of the extraction of an organic
solute from water to an organic solvent is the addition of salt to the aqueous phase to salt out the organic solute. Therefore this increase in the amount of benzene solubilized per micelle can be interpreted as supporting the view that a micelle is a microphase. It is of interest to observe that the \((S-S_0)\) vs. \((C-C_0)\) curve is approximately linear at low concentrations in all cases. The increase in slope begins to occur at a \((C-C_0)\) value of approximately \(1 \times 10^{-2}\) moles/liter. This is the concentration range in which the turbidity versus concentration curves become approximately linear because of interactions between micelles.

The micellar molecular weights of TPB and TTPAB are the same within the limits of experimental error and yet it is obvious that there are more benzene molecules solubilized per TPB micelle than there are per TTPAB micelle. The opposite result had been expected. The only alternative one has in such cases is to give a plausible explanation of why the expected results were not observed. In the introductory paragraphs mention was made of the fact that hydrocarbon chains tend to be expelled from an aqueous phase. Therefore the propyl chains of TTPAB could be expected to be oriented as shown schematically below.
This is an exaggerated sketch, but the point at hand is that the propyl groups should tend to bend down toward the hydro­
carbon-like interior of the micelle. This could actually reduce the expected void space inside the micelle, compared with the void space inside a TTMAB or TPB micelle instead of increasing it as expected.

The explanation given above is in conflict with the area per molecule calculations from surface tension measure­
ments which show that the TTPAB molecule occupies a much larger area than TPB or TTMAB molecules. However, as stated in that section, these calculations were based on initial surface tension measurements. The drastic changes of surface tension with time were considered to be possibly due to the kinetics of this squeezing together of the tripropyl head­
groups. Probably if the area per molecule calculations had been based on the minima in the surface tension curves, as shown in Figure 7, much lower values of area per molecule would have resulted. However, the time and effort involved in getting sufficient data points for these latter calcula­
tions would be almost prohibitive. The higher value of ben­
zene molecules per micelle for TTMAB is not surprising in view of the higher micellar molecular weight.

As previously stated the number of benzene molecules solubilized per micelle increases with increase in detergent
concentration. Over the concentration range from \((C-C_0)\) equal 0.50 moles/liter to \((C-C_0)\) equal to 3.00 moles/liter the number of benzene molecules solubilized per micelle increased by approximately 20 molecules per micelle for TPB and for TTMAB but by approximately 30 molecules per micelle for TTPAB. Thus it is obvious that the number of benzene molecules per micelle is increasing more rapidly with increase in concentration for TTPAB than for the other two. However, if one looks at the moles of micelles per liter, one finds that the micellar concentration at a given molar concentration of detergent is also higher for TTPAB. In other words the number of micelles per unit volume is higher for TTPAB. If one accepts the previous interpretation that increasing the number of micelles per unit volume has the same effect as increasing the salt concentration, one would expect the number of benzene molecules solubilized per micelle to increase more rapidly with increase in total detergent concentration for TTPAB than for the other two because the effective salt concentration is slightly higher at any given molar concentration of detergent.

The plots of \((C-C_0)\) vs. \((S-S_0)\) for TPB, TTMAB, and TTPAB in 0.05 N sodium bromide appear in Figure 20. It will be observed that these plots give straight lines. This means that the number of benzene molecules solubilized per
Fig. 20. $(S-S_0)$ vs. $(C-C_0)$ for TTPAB, TPB, and TTMAB in 0.05 N Sodium Bromide
micelle is the same for all detergent concentrations. For TPB there are 1246 benzene molecules per micelle while for TTMAB there are 661 and for TTPAB there are 634. If an effective increase in salt concentration due to an increase in the number of micelles per unit volume was responsible for the nonlinearity of the solubilization curves in water, then the linearity of the curves in 0.05 N sodium bromide indicates that the effective increase in salt concentration due to the increase in the concentration of micelles is negligible.

Since there are rather large differences in the micellar molecular weights obtained in salt solution, it is necessary to use some criterion other than benzene molecules per micelle in order to compare the effectiveness of the various compounds as solubilizers. Possibly the simplest criterion is the ratio of benzene molecules per micelle to detergent monomers per micelle. For TPB this ratio is 4.54 while for TTMAB the ratio is 4.41 and the ratio is 6.53 for TTPAB. The same idea could be shown by comparing ratios of micellar molecular weights. To the writer this indicates that in this case there is an increase in solubilizing power with increase in charged head size. It could also indicate that the TTPAB micelle can swell to a greater extent than can the micelles of the other two compounds.

The ratios of benzene molecules per micelle to monomers
per micelle are very close for TPB and TTMAB. In fact there is only a three per cent difference. Since the limit of experimental error in molecular weight determinations is five per cent, these ratios are the same within the limits of experimental error. This also means that the solubilization curves for TPB and TTMAB shown in Figure 19, although drawn separately, are really the same within the limits of experimental error. All curves in this figure were obtained by fitting a least squares line to the data points. The writer interprets this to mean that formation of large micelles from smaller ones would not affect the amount of benzene solubilized and therefore could not explain the curvature of the solubilization curves in water. Obviously the evidence presented here is not conclusive since it effectively involves an extrapolation from results obtained in 0.05 N sodium bromide to results obtained in water with no results from solutions of intermediate salt concentrations.

Solubilization data for LPB in water and 0.05 N sodium bromide are presented in Figure 21 and the results are summarized in Table VIII. Because of the differences in chain length these data do not contribute anything to the discussion of the effect of charged head size on solubilization and so no discussion of these results is given. The measurements were made as part of an abandoned study of the effect
Fig. 21. \((S-S_0)\) vs. \((C-C_0)\) for LPB in Water and in 0.05 N Sodium Bromide
### TABLE VIII

SUMMARY OF SOLUBILIZATION RESULTS FOR LPB IN WATER AND IN 0.05 N SODIUM BROMIDE

<table>
<thead>
<tr>
<th>(C - C₀) in moles/liter x 10²</th>
<th>(S - S₀) in moles/liter x 10²</th>
<th>Moles of micelles per liter x 10⁴</th>
<th>Benzene molecules per micelle</th>
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of chain length on solubilizing power. The results are presented here so that they will be available to other workers.

When aqueous solutions of LPB, TPB, and TTMAB were shaken with excess quantities of benzene, emulsions were formed. Subsequent light scattering measurements showed that these detergents were not completely pure when the solubilization measurements were made. This naturally cast doubts on the validity of the solubilization measurements. Therefore further solubilization measurements were made on a sample of TPB which had been purified sufficiently to give reproducible turbidity measurements. The results obtained with this purified sample reproduced the previous results. This leads the writer to conclude that traces of impurities do not affect the results of solubilization measurements. Another interesting feature of this last set of measurements on TPB is that no emulsions formed during the shaking operation. The TTPAB used in all solubilization measurements was pure enough to give reproducible turbidity measurements and no emulsions formed in this case. If this is not indicative that the formation of emulsions was due to the traces of impurities, it is certainly suggestive of that.
CHAPTER IV

SUMMARY AND CONCLUSIONS

A factor was determined to correct the intensity of scattered light for the difference in the volume of solution viewed by the phototube when solutions of greatly differing refractive index are compared. A similar correction was calculated to correct for the variation with refractive index of the amount of light reaching the phototube from a given volume element. The magnitude of the effect of these corrections on the molecular weight obtained was determined for one case, and the conclusion was reached that these corrections cannot be ignored if the instrument is calibrated with a toluene solution and experimental measurements are made in aqueous solution.

The transmittances of the four neutral filters of the B. S. Light Scattering Photometer were very carefully determined using the Cary Model 14 Recording Spectrophotometer. Values obtained with the Light Scattering Photometer were shown to be in good agreement with the values obtained from the Cary if the former were determined with the photomultiplier tube set at ninety degrees with respect to the incident
beam and the instrument properly aligned.

Critical micelle concentrations were determined for all detergents in water and for all except HTPAB in 0.05 N sodium bromide using surface tension measurements. In addition the area occupied by each molecule in the air-water interface was estimated using the Gibbs Adsorption Equation. These results are summarized in Table II and will not be repeated here. The area occupied by each molecule in the air-water interface was found to be approximately 60 square angstroms for LPB, TPB, and TTMAB molecules. Qualitative observations on Stuart-Brieglieb models indicate that these head groups have very nearly the same area. An area per molecule of approximately 90 square angstroms was found for both TTPAB and HTPAB using the initial surface tension points obtained at each detergent concentration.

Drastic changes of surface tension with time at constant concentration were observed in solutions of TTPAB at concentrations below the critical concentration even though the detergent was pure. This was interpreted to mean that additional molecules of TTPAB were entering the surface thereby increasing the surface excess concentration and decreasing the area occupied by each molecule in the air-water interface.

Slow changes of surface tension with time were observed with most of the detergents. However, a series of measurements
with very pure LPB and TPB indicates that these slow changes were due to trace impurities since no such changes were observed in these latter cases.

Micellar molecular weights were predicted for the detergents using a spherical model for the micelle and the areas per molecule from surface tension measurements. Very good agreement was found between the predicted and observed values of micellar molecular weights for LPB and TPB. The predicted micellar molecular weights were considerably lower than the observed ones for TTPAB and TTMAB. Since the prediction for TTPAB was based on the area per molecule determined from the initial surface tension points, it was postulated that perhaps better agreement between prediction and observation might have been obtained if the area per molecule had been calculated from the points represented by the minima in the surface tension vs. time curves for TTPAB. The difference between the predicted and observed micellar molecular weights for TTMAB can be explained in two ways, a departure of the micelle from a perfect sphere or bad data. Although every precaution was taken to prevent the latter, those familiar with light scattering techniques will recognize that this possibility cannot be overlooked. Certainly the first suggestion is highly possible.

Micellar molecular weights have been determined in
water and in 0.05 N sodium bromide for all detergents except HTPAB. The results obtained are in good agreement with the results obtained in other laboratories for the same or similar compounds except for TPB in 0.05 N sodium bromide. The micellar molecular weight obtained for this compound in salt solution is approximately twice that obtained for TTMAB and more than twice that obtained for TTPAB. No satisfactory explanation has been found for this difference.

The number of unneutralized charges on each micelle was calculated and found to be about ten charges for all micelles in water. Charge calculations in 0.05 N sodium bromide solution were considered to be generally dubious since frequently relatively large errors were likely in the determination of the slopes of the $H(C-C_0)/(\tau-\tau_0)$ vs. $(C-C_0)$ plots. In addition the charges per micelle were found to be higher in salt solution than in water for TPB and TTPAB which seems preposterous.

It was observed that the slopes of the $(S-S_0)$ vs. $(C-C_0)$ plots increased with increase in detergent concentration for all detergents in aqueous solution. This was taken to indicate that a micelle can be considered as a microphase and solubilization an extraction process. Increase in the concentration of charged micelles is equivalent to the addition of salt and results in a progressive salting out of the
solubilizate with a corresponding enhancement of the efficiency of the extraction process.

No increase in solubilizing power was observed for TTPAB relative to TPB or TTMAB despite the greater bulk of the charged head in TTPAB and therefore hoped for greater void space inside the micelle. This, in conjunction with the decrease in surface tension with time, suggests that the tri-propyl head group does not occupy a particularly larger area than a trimethyl or pyridinium group and that in addition the long propyl chains possibly extend down between the tetradecyl chains thereby actually reducing the void space in the TTPAB micelle relative to the void space in the micelles of the other two compounds.

In aqueous solution it was possible to compare solubilizing efficiency directly on the basis of the similarity of the micellar molecular weights and the results of the solubilization determinations. However, in salt solution rather wide differences in micellar molecular weights were observed and direct comparison of solubilizing power was not possible. The criterion of benzene molecules to detergent monomers in the micelle was used. On this basis TTPAB appears to be a more efficient solubilizer in 0.05 N sodium bromide. Comparison with the results in water would make it seem that this could be so only if the TTPAB micelle could
swell to a greater extent than could the micelles of TPB or TTMAB and could thus accommodate more benzene.

This suggests that an interesting experiment would be the measurement of the interfacial tension between a solution of TTPAB in 0.05 N sodium bromide and a benzene layer and comparison of these results with surface tension results in 0.05 N sodium bromide of the type presented in this work. The interfacial tension measurements would be difficult experimentally and possibly could not be done using the ring method used here. Also the adsorption equations necessary to interpret the results are much more complicated than the ones presented here but are available in the references given in the introductory chapter. Area per molecule calculations from the two types of experiments could possibly be used to determine if swelling of the TTPAB micelle actually takes place.

The ratio of benzene molecules to detergent monomers per micelle was the same within the limits of experimental error for TTMAB and TPB in 0.05 N sodium bromide despite the nearly twofold difference in micellar molecular weights. This led to the conclusion that formation of large micelles by the break-up of smaller ones would not enhance the solubilizing power of a detergent and could not explain the curvature of the solubilization curves in water.
The solubilization data for LPB do not contribute materially to the present work. The proposed project of correlating changes in solubilizing efficiency with chain length was abandoned. The results were presented primarily so that they would be available to other workers in this field of endeavor.

Indications were found that the formation of emulsions when aqueous solutions of detergents were shaken with large quantities of benzene was due to the presence of trace impurities.

Experimental manipulation of solutions containing solubilized benzene was difficult because of the observed rapid loss of benzene when the detergent solutions were exposed to air.
SELECTED BIBLIOGRAPHY


VITA

Raymond Leslie Venable was born near Carthage, Arkansas on August 27, 1935. His elementary education was obtained in the elementary schools of Bunn, Arkansas and Plain Dealing, Louisiana. He was graduated with honors from Plain Dealing High School in May, 1952, and received the American Legion award for outstanding seniors.

In June, 1952, he entered Southern State College, Magnolia, Arkansas. On December 21, 1953, he married Glendene Zumwalt of Blevins, Arkansas. He received, with honors, the degree of Bachelor of Science in May, 1955.

He entered the Graduate School of Louisiana State University in September, 1955. On May 18, 1957, a daughter, Francilda Ann, was born. In May, 1958, he became a member of Phi Lambda Upsilon, national honor fraternity for chemists and chemical engineers.

On May 12, 1958, he entered the Exploration and Production Research Division of the Research and Technical Department of Texaco, Inc., at the Bellaire, Texas laboratories. On July 7, 1959 a second daughter, Brenda Faye, was born and on October 22, 1960 a third daughter, Ramona Lynn, was born.
He re-entered the Graduate School of Louisiana State University in February, 1961. In May, 1962 he became a member of the Society of the Sigma Xi. He is now a candidate for the degree of Doctor of Philosophy.
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Title of Thesis: Solubilization and Related Phenomena in Quaternary Ammonium Halides

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