Light scattering studies of several cationic detergents
by Edwin H Eylar

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

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LIGHT SCATTERING STUDIES OF SEVERAL CATIONIC DETERGENTS

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I. ABSTRACT

Aqueous solutions of various dodecylalkyl-, dodecyldialkyl-, dodecyltrialkylammonium chlorides and dodecyltrimethylammonium halides were examined by light scattering methods in an attempt to gain further insight into the phenomenon of micelle formation. Molecular weights of micelles formed by these surface active agents and their critical concentrations were measured. Micelle size was found to be influenced both by the nature of the gegen ion and the makeup of the substituent groups on the nitrogen atom. Dodecylmethylammonium chloride micelles (the largest) were found to have a molecular weight of approximately 74,600 while dodecyltrimethylammonium chloride micelles were found to have molecular weights in the neighborhood of 9,300.

II. INTRODUCTION

McBain (20) in 1913 concluded that certain abnormal properties exhibited by soaps in solution could best be explained by assuming that the long-chain ions of the soap* came together to form large colloidal aggregations, which were later termed micelles. Solutions of surface active agents have been studied quite extensively by osmotic pressure, ultracentrifuge, diffusion, X-ray, conductivity, and light scattering methods in order to determine structure, shape, weight, and other characteristics of their micelles. Since light scattering was used in this investigation, a brief review of the theory follows (2,4,8,9).

The turbidity T of a scattering medium is defined by

$$T = -\frac{1}{I}\frac{dI}{dL}$$

Integration gives

$$I = I_0 e^{-TL}$$

I_0 is the intensity of the incident light and I is the intensity of the light after passing through L cm. of the medium.

According to electromagnetic theory, the intensity of light scattered from a small, isolated, isotropic, dielectric

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*McBain studied compounds like potassium stearate, which is properly designated a "soap." However, the compounds considered in this study should not, according to the commonly accepted nomenclature, be termed soaps but shall be referred to throughout this thesis as "detergents" or "surfactants."

particle--when excited by unpolarized light of intensity I_o--is

$$I = \frac{8\pi^4(1+\cos^2\theta)\alpha^2}{r^2\lambda^4} I_o$$

α is the polarizability of the scattering center.

λ is the wave length of the incident and scattered light "in vacuo."

r is the distance from the scattering particle to the point of observation.

θ is the angle between the incident beam and the direction in which the scattering is observed.

An expression for the turbidity of an ideal gas consisting of n independent molecules (scattering centers) per cubic centimeter can be calculated. Consider a small volume of gas with the shape of a disk. The faces of the disk are perpendicular to the direction of propagation of the incident light. The disk volume is AdL where A is face area and dL is disk thickness. The intensity I_θ of the scattered light at a distance r from the disk ($r \gg A^{\frac{1}{2}}$), and at an angle θ with the incident beam is

$$I_\theta = \frac{8\pi^4(1+\cos^2\theta)\alpha^2}{r^2\lambda^4} I_o nAdL$$

Now consider a sphere of radius r with the disk of gas at its center ($r \gg A^{\frac{1}{2}}$) and a small zone of this sphere whose defining planes are $\perp$ to the axis of propagation of the inci-

dent light. The angle between any radius vector to the zone and the axis of propagation of the incident light is θ. The width of the zone is $rd\theta$ and its area approximately $2\pi r^2 \sin\theta \, d\theta$. The energy radiated each second through the zone in the form of scattered light is

$$dE = \frac{8\pi^4(1+\cos^2\theta)\alpha^2}{r^2 \lambda^4} I_0 nAdL 2\pi r^2 \sin\theta \, d\theta$$

The total energy radiated each second through the sphere due to scattering of the incident light by the gas molecules within the disk is

$$E = \int_0^{\pi} \frac{16\pi^5 n \alpha^2 A I_0 dL}{\lambda^4} \sin\theta \, (1+\cos^2\theta) d\theta$$

$$\frac{8\pi}{3} \left(\frac{2\pi}{\lambda}\right)^4 n\alpha^2 A I_0 dL$$

The decrease in intensity, dI, of the primary beam, with intensity $= I_0$, due to scattering by the gas molecules in the disk is $-E/A$. Hence

$$T = -\frac{1}{I_0}\frac{dI}{dL} \quad \frac{8\pi}{3}\left(\frac{2\pi}{\lambda}\right)^4 n\alpha^2$$

According to electromagnetic theory the polarizability of an ideal gas is related to the refractive index, μ, by

$$\alpha^2 = \frac{(\mu-1)^2}{4\pi^2 n^2}$$

so that

$$T = \text{turbidity of an ideal gas} = \frac{32\pi^3(\mu-1)^2}{3\lambda^4 n}$$

Thus far only scattering from a dilute gas has been considered. However, the application to solutions is easily made with the aid of simplifying assumptions already proposed, i.e., that the molecules are isotropic; that they are small compared to λ; that solute molecules are randomly distributed in solution (hence solution is very dilute); and that the light scattered from the solute molecules is given as the difference between total scattering and light scattered from solvent molecules. The polarizability, α, in this case is given by:

$$\frac{\mu_o(\mu-\mu_o)}{2\pi n} = \alpha$$

or

$$\alpha = \frac{\mu_o(\mu-\mu_o)}{2\pi \frac{CN}{M}} = \frac{\mu_o}{2\pi}\left(\frac{\mu-\mu_o}{C}\right)\frac{M}{N}$$

and

$$\alpha^2 = \frac{\mu_o^2\left(\frac{\mu-\mu_o}{C}\right)^2 M^2}{4\pi^2 N^2}$$

Therefore, for a solution at low concentration

$$T = \frac{32\pi^3\mu_o^2\left(\frac{\mu-\mu_o}{C}\right)^2}{3N\lambda^4} CM$$

where μ = refractive index of solution,

μ_o = refractive index of solvent,

C = concentration of solute in g./cc.,

N = Avogadro's number,

M = molecular weight of solute particle.

An expression more accurate at higher concentrations was derived by Einstein. He was able to relate osmotic pressure ρ and turbidity T:

$$\tau = \frac{32\pi^3\mu_o^2\left(C\frac{\partial u}{\partial C}\right)^2}{3N\lambda^4 C\frac{\partial}{\partial C}\left(\frac{\rho}{RT}\right)}$$

For most solutions $\frac{\partial u}{\partial C}$ is practically constant at low concentration, and can be replaced by $\frac{\mu-\mu_o}{C}$. A general expression for the osmotic pressure in terms of concentration is a power series expansion in terms of C:

$$\frac{\rho}{RTC} = \frac{1}{M} + BC + CC^2 + DC^3 + \cdots\cdots$$

where B is called the interaction constant and is a function of the solvent and solute pair, but is independent of the molecular weight of the solute. Only the B term need be considered in dilute solution. Hence

$$\frac{\partial}{\partial C}\left(\frac{\rho}{RT}\right) = \frac{1}{M} + 2BC$$

and

$$\frac{HC}{T} = \frac{1}{M} + 2BC$$

where

$$H = \frac{32\,\pi^3 \mu_o^2 \left(\frac{\mu-\mu_o}{C}\right)^2}{3N\,\lambda^4}$$

When HC/T is plotted against C, a straight line is usually obtained where M, the molecular weight, is equal to the reciprocal of the HC/T intercept. For particles exhibiting anisotropy a depolarization correction must be made.* Debye and others have developed formulas from which shape of particles with dimensions greater than 1/20 λ can be determined by measuring the angular dissymmetry of the scattered light.

The purpose of this investigation was to determine molecular weights of micelles of several series of detergents in the hope that a correlation of the data might reveal information concerning the structure of the cationic micelles. A survey of the literature shows that much disagreement exists among investigators regarding micelle shape and size. Hartley supported the view that only spherical micelles are likely (13). McBain (19) has cited evidence for two micelle structures, spherical and lamellar. He also gives evidence that some micelles contain thick layers of immobilized water. A review of micelle literature may be found in a recent paper (1949) by Debye (5).

Light scattering methods have proven valuable in studies

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*If a scattering particle is isotropic the light scattered at 90° is linearly polarized. If depolarization is observed it means that the particles are not isotropic. Cabannes and Debye have indicated the appropriate correction to be made.

involving large molecules. If the solution contains particles of different weights, light scattering gives a weight-average molecular weight. In the present investigation quaternary ammonium salts were used. No complications because of hydrolysis were apparent. In all cases the intensity of the scattered light was measured. Transmission data have been used by some investigators.

Comparatively little work has been done concerning micelle structure of quaternary ammonium salts. Dodecylammonium chloride and several alkyltrimethylammonium bromides have received nearly all the attention (5,6). Solutions of these salts show abrupt changes in turbidity at the critical concentration (the point at which micelles begin to form in relatively great numbers). When inorganic salts were added containing the anion in common with that of the detergent, the critical concentration decreased and the molecular weight of the micelles increased. The kind or charge of the cation of the added inorganic salt appeared inconsequential. This, of course, is not surprising since positively charged particles would be repelled from the micelle while the anion would be attracted. These experimental results are in agreement with theoretical expectations since the free energy of formation of the micelle would be decreased by the presence of gegen ions, i.e., less work would be required to bring long chain ions together. The effect within limits becomes more pronounced with further inorganic salt ad-

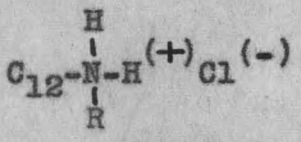
dition.

According to the literature cited above, detergent ions are held together in the micelle by van der Waal's forces between neighboring hydrocarbon chains. The micelle size is limited by the repulsion of the positively charged monomer heads. The micelle should increase in size up to the point where the energy liberated by the system, when long chains come together, is balanced by the work required to overcome repulsive forces between the polar heads. Debye (5) and others have considered quantitatively the energetics of a micelle system, and have shown that a micelle with hydrocarbon chains aligned and the polar ends oriented toward the water phase is feasible. A variety of configurations for such an aggregate is possible; the most probable include a sphere in which hydrocarbon tails occupy the interior, a disk sandwich two molecules thick, and a rod of circular cross-section and a radius equal to the length of the organic ion.

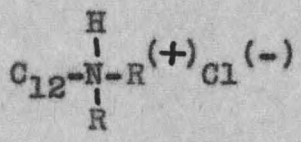
Hydrocarbon chains of twelve carbons were selected in this study because previous work (3) with a series of alkylammonium bromides indicated that good results could be expected with them.

III. PREPARATION OF DETERGENTS (17)

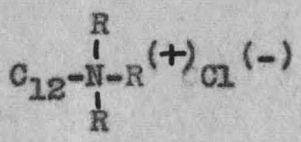
The compounds of this study comprise four series with general formulae:



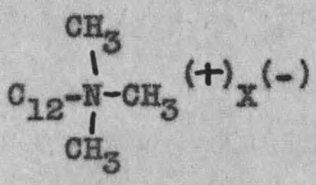
(I)



(II)



(III)

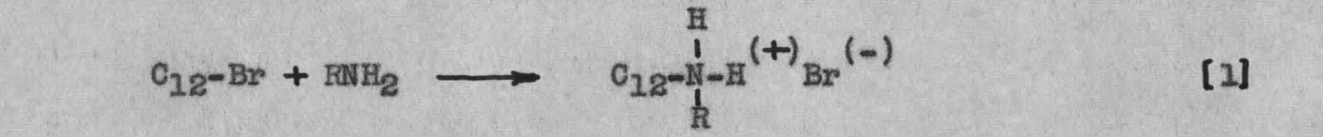


(IV)

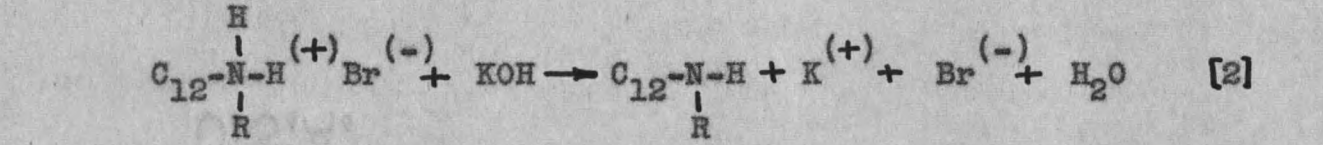
where R = hydrogen (in (I) only), methyl, ethyl, n-propyl, or n-butyl and X = iodide, bromide, or chloride.

1. Series (I)

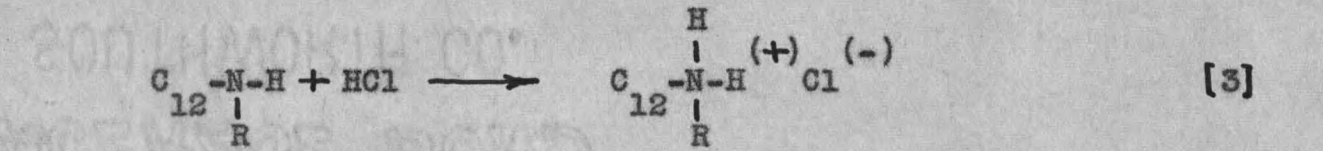
The main reactions for preparation are:



[1]



[2]



[3]

The general procedure for preparation of this series went as follows. Dodecyl bromide, alkyl amine, and ethyl alcohol

(absolute), in the mole ratio of 1:2:3, were heated 12-16 hours in a sealed glass tube at 130°-140° centigrade. It is important to have enough ethyl alcohol present so that formation of a dodecylalkylammonium bromide precipitate, which might decompose at this temperature, is prevented. After the mixture had been heated, ethyl ether was added. This caused the dodecylalkylammonium bromide to crystallize out of solution. The ether mixture was filtered and the crystalline precipitate collected. The precipitate was then dissolved in ethyl alcohol. Concentrated potassium hydroxide, when added to the alcoholic solution, produced two immiscible layers. The amine layer was separated from the aqueous layer, dried over sodium, and vacuum distilled. The fraction of the distillate containing the dodecylalkylamine was collected. The amines were colorless, odorless liquids. Hydrochloric acid in one-half mole excess was added to alcoholic solutions of the amines to give the dodecylalkylammonium chlorides. Repeated precipitation and solvation with ethyl ether and ethyl alcohol respectively gave white, flaky crystals of the necessary purity. Before storing over P_2O_5, the detergents were vacuum desiccated.

However, the yield was diminished because of the side reactions:

$$C_{12}\text{-}\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{N}}\text{-}H^{(+)}\,Br^{(-)} \rightleftharpoons H^{(+)} + Br^{(-)} + C_{12}\text{-}\overset{\overset{H}{|}}{N}\text{-}R \qquad [4]$$

$$C_{12}\text{-}\overset{H}{\underset{|}{N}}\text{-}R + C_{12}\text{-}Br \longrightarrow C_{12}\text{-}\overset{H}{\underset{C_{12}}{\overset{|}{\underset{|}{N}}}}\text{-}R^{(+)}\ Br^{(-)} \qquad [5]$$

The produce of reaction [5] is easily separated from the monododecylalkyl amine because of the great difference in boiling points. No attempt was made to prepare the didodecylamine chloride salts.

Dodecyl bromide was preferred as a starting material to dodecyl iodide because of expense, and preferred to dodecyl chloride because the reaction rate constant for reaction [1] was found to increase with increasing molecular weight of dodecyl halide. Prolonged heating increased the yield of the didodecyl salt, and correspondingly decreased the monododecyl salt yield. An increase in temperature over a long period of time caused decomposition. However, a good yield could be obtained with very little decomposition by heating the reactants in a closed tube from one to two hours at 190°-200°C.

2. Series (II)

The main reactions (1) for preparation and general experimental procedure are similar to those for Series (I). However, the occurrence of a side reaction corresponding to reaction [5] to form a trialkyldodecyl salt is not so likely. Therefore, the starting materials were usually heated from 180°-190°C. in a closed tube for four to five hours. Ethyl alcohol (absolute)

was used as solvent. Enough ethyl alcohol must be present to prevent any crystallization, since decomposition would occur at high temperatures. If crystallization cannot be practically prevented, or if decomposition occurs in solution, then the reaction should be carried out at a temperature below the decomposition point of the desired product. However, at lower temperatures the reaction rate is much slower.

In preparing the compounds of this series, in distinction to those of Series (I), excess dodecyl bromide (as well as excess dialkyl amine) could be eliminated easily in the vacuum distillation. Also, the compounds of Series (I) were more easily purified than dodecyldipropyl- and dodecyldibutylammonium chloride. In fact, the latter two detergents could not be sufficiently purified to justify study by light scattering methods. Although the apparently pure amines were prepared, it is thought decomposition occurred due to the high temperature at which the closed tube reaction was carried out. It is felt that the difficulties could have been overcome by preparation at lower temperatures.

3. Series (III)

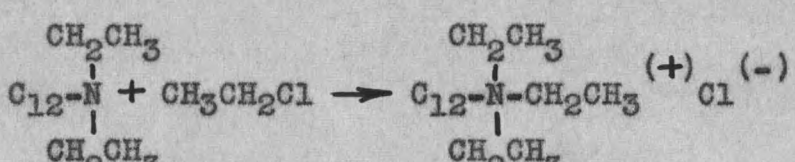
The main reaction is:

$$C_{12}\text{-}Cl + NR_3 \longrightarrow C_{12}\text{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}\text{-}R^{(+)}\,Cl^{(-)} \qquad [6]$$

The detergents of this series were easily prepared by mix-

ing EtOH (absolute), dodecyl chloride, and trialkyl amine in the mole ratio 2:1:2. The trimethyl salt (23) was obtained by refluxing appropriate reagents for two hours in a dry-ice cooled system. Refluxing for a week produced very little dodecyltriethyl or dodecyltripropyl salt. Yet heating the reagents in a closed tube for one hour at 160°-170°C. or for 24-28 hours at 90°-100°C. gave almost quantitative yields. Since the end product of reaction [6] is the desired salt, the closed tube mixture was directly purified. Crystallization occurred when ethyl ether was added to the alcoholic mixture. A check on purity at this point revealed a product of only slight contamination. Subsequent purification of the trialkylammonium salts with ethyl alcohol and ether, alcohol and benzene, or ethyl acetate and dry ice resulted in considerable decomposition. Finally, the triethyl salt was purified only after several careful recrystallizations wherein the temperature never exceeded fifty degrees. The purification of the tripropyl and tributyl salts was not completed because these compounds were found to be too insoluble in water for light scattering work.

An attempt to prepare triethyldodecylammonium chloride according to the method of Kraft (18) for dodecyltriethylammonium iodide was unsuccessful. The reaction,



[7]

did not occur to great extent. This further illustrates the relative reactivity between alkyl chlorides, bromides, and iodides since alkyl iodides seem to react easily. Probably the dodecyltripropyl and dodecyltributyl salts could have been purified by very careful recrystallizations at low temperature. A possible decomposition reaction could be:

$$C_{12}\text{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}\text{-}R^{(+)}\,Cl^{(-)} \longrightarrow C_{10}\text{-}\overset{\overset{H}{|}}{C}=CH_2 + \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{HN}}\text{-}R^{(+)}\,Cl^{(-)} \qquad [8]$$

An onion-like odor, characteristic of alkenes, was noticed in some cases, viz., tripropyl, dibutyl, dipropyl. Also, the per cent chloride increased with each crystallization, thereby indicating decomposition.

4. Series (IV)

Either dodecyltrimethylammonium bromide or dodecyltrimethylammonium chloride was dissolved in 90 per cent ethyl alcohol, treated with moist Ag_2O in slight mole equivalent excess. The resulting mixture was stirred intermittently over a two-hour period and filtered through a sintered glass, fine filter to get rid of AgBr. The filtrate was neutralized with the desired acid, i.e., HCl or HI, and evaporated. Originally trimethyldodecylammonium bromide and chloride were made and purified by the methods given under Series (III). Hence, the chloride salt was produced by two independent methods. Only the chloride salt exhibited observable deliquescence.

5. General Remarks

Halogen determination in all cases offered the most convenient method for determining purity. A modified Volhard procedure was developed. A sample of detergent, equivalent to 15 to 25 cc. 0.1N $AgNO_3$, was weighed out. 10-15 cc. of water, 3-5 cc. of dilute HNO_3, and sufficient EtOH to produce a clear solution (usually 5-10 cc.) were added. After a 3-5 cc. excess of $AgNO_3$, ferric ammonium sulfate indicator, and 10-15 cc. of nitrobenzene were added, the solution was mixed vigorously to effect adsorption of nitrobenzene by AgCl. Then KSCN was titrated into the mixture to the first perceptible color change (clear to faint orange). With this method no foaming occurs, nitrobenzene is not emulsified, and the end point is sharp and stable. Also, far less time is required for an analysis than with methods using gravimetric analysis. For bromide and iodide salts, nitrobenzene is not needed.

Dodecylammonium chloride was obtained by treating dodecyl amine with concentrated hydrochloric acid according to the method of Ralston and Hoerr (22).

Detergents insoluble in water at room temperature were crystallized from EtOH by the addition of H_2O as well as ether. All were dried over P_4O_{10} before physical constants were measured. Results are tabulated in Table I. Melting points were obscured by decomposition, but the decomposition points were reproducible within $\pm 7^{\circ}C$. Only those Kraft points above $30^{\circ}C$.

TABLE I

Physical Constants of Synthesized Products and Reagents

COMPOUND	% Halogen, theoretical	% Halogen, experimental	Boiling Point in Degrees C.	Pressure in mm. of Mercury	Decomposition Pt. in $^{o}\pm7^{o}$C.	Kraft Point in ^{o}C.
1. Dodecyl chloride			134-136	15		
2. Dodecylammonium chloride	16.06	16.03			139	
3. Dodecyltrimethylamm. chlor.	13.47	13.51			151	
4. Dodecyldiethylamm. chloride	12.83	12.81			73	
5. Dodecylmethylamm. chloride	15.07	15.09			82	
6. Dodecylethylamm. chloride	14.23	14.26			99	35
7. Dodecylpropylamm. chloride	13.47	13.50			87	45
8. Dodecylbutylamm. chloride	12.79	12.77			92	63
9. Dodecyltrimethylamm. bromide	12.95	12.92			147	
10. Dodecyltrimethylamm. iodide	35.76	35.72			125	43
11. Dodecylmethyl amine			113-116	7-8		
12. Dodecylethyl amine			121-124 or 142-144	5 or 15		
13. Dodecylpropyl amine			146-149	11-12		
14. Dodecylbutyl amine			155-156	10-11		
15. Dodecyldimethyl amine			124-127	6-10		
16. Dodecyldiethyl amine			132-134	5-7		
17. Dodecyldipropyl amine			164-167	11-12		
18. Dodecyldibutyl amine			170-172	6-9		

are recorded.

6. Reagents

Purity and not yield was the main criterion in preparing the detergents. Dodecyl chloride was prepared from dodecyl alcohol using Lucas Reagent. Yield was 65 per cent theoretical. Dodecyl bromide and some dodecyl chloride were obtained from Columbia Chemical Company and were fractionally distilled using a column of 25 theoretical plates and a reflux ratio of 1:25. Dodecyl chloride fractions were collected at 134-136°C. at 15 mm. of mercury, and dodecyl bromide fractions at 147-149°C. at 15 mm. of mercury.

The amines (best grade Eastman Kodak) were distilled or vacuum distilled depending on boiling points. Methyl, dimethyl, and ethyl amine were obtained as aqueous solutions. They were easily separated from the H_2O by distillation into a tube cooled by dry ice. However, the 40 per cent aqueous methyl amine solution, when added directly to the dodecyl amine-alcohol mixture and maintained at 225°C. in a closed tube, gave a good yield of dodecyl methyl amine.

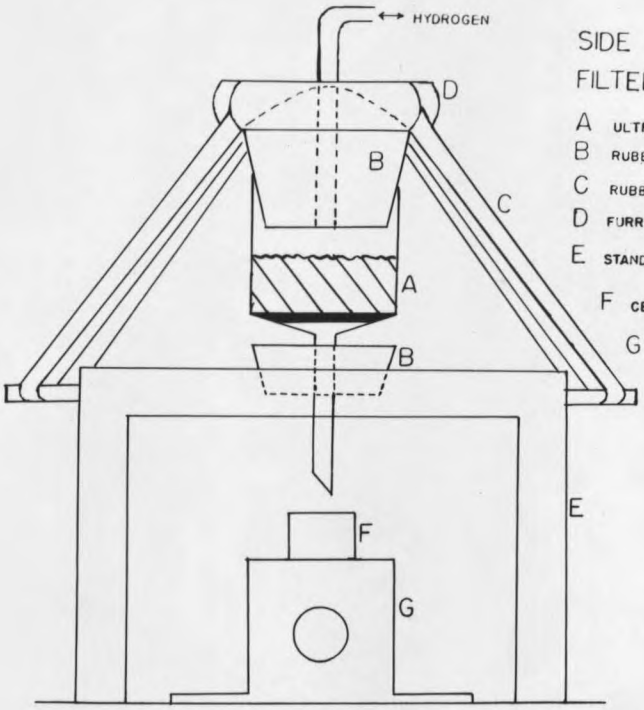
The absolute alcohol and USP ether were freshly distilled before use. Dodecyl amine (best grade Matheson), hydrochloric acid, hydriodic acid, and hydrofluoric acid, all USP, were not further purified. Bureau of Standards sucrose (Standard Sample 17) was not further purified. Raffanose pentahydrate d(+), CP, was obtained from the Pfanstiehl Chemical Company and further purified by several recrystallizations from fresh, doubly-dis-

tilled water to eliminate sucrose (16). The purified raffanose pentahydrate was dried at 75°C. under moderate vacuum.

IV. APPARATUS

A detailed description of a similar light scattering instrument has been given elsewhere (6). The essential features of this simple fluorimeter type instrument are illustrated in Figure 1. The light source is a 100 watt, low pressure mercury arc (GE AH-4). A ballast lamp serves to stabilize the output of the source. The incident light passes through a lens system, which produces a parallel beam, and a monochromatizing filter (4358 Å) before entering the rectangular scattering cell. Light scattered perpendicular to the primary beam is reflected by a mirror to a multiplier photo tube (RCA 1P21). The intensity of the scattered beam is proportional to the deflection of the needle of a sensitive galvanometer connected directly to the multiplier photo tube. Because of the high sensitivity of the 1P21, light shielding is essential. Hence, the pathway from the mirror to the 1P21 is regulated by a shutter. The entire chamber containing the cell is blackened to keep reflections at a minimum. A light trap prevents the transmitted light from causing spurious readings. A tight-fitting lid, forming the top of the instrument, provides access to the chamber. A single cell of fused pyrex glass, approximately 7½ cm. high and of square cross-section about 3.6 sq. cm., was used for solution investigations.

The most practical voltage for operation was about 90-100 volts per dynode stage of the 1P21 tube. At this voltage, sen-



SIDE VIEW
FILTER APPARATUS

A ULTRA FINE FILTER
B RUBBER STOPPER
C RUBBER TUBING
D FURROWED TOP
E STAND
F CELL
G CELL HOLDER

FIG. 3

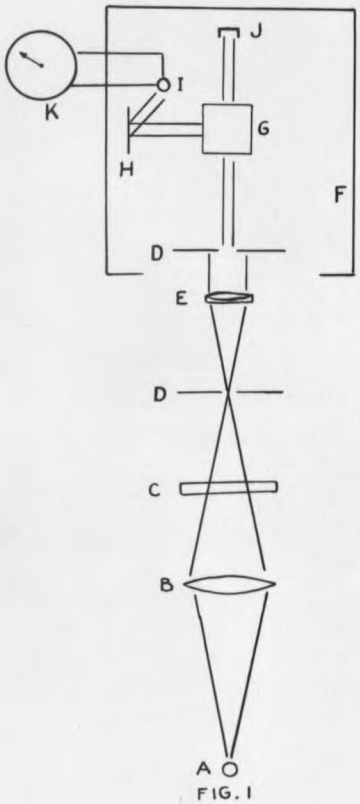


FIG. 1

SCHEMATIC VIEW OF
90° LIGHT SCATTERING

A AH-4 LAMP
B CONDENSING LENS
C FILTER
D DIAPHRAGM
E COLLIMATING LENS
F CHAMBER
G CELL
H MIRROR
I IP21 TUBE
J LIGHT TRAP
K AMMETER

TOP VIEW

DIFFERENTIAL
REFRACTOMETER
SYSTEM

A AH-4 LAMP
B PINHOLE
C FILTER
D SLIT
E SIMPLE LENS
F CELL
G CROSS HAIRS
AND EYEPIECE

FIG. 2

sitivity is sufficient to minimize error in galvanometer readings, yet not so great as to cause noticeable photo tube deterioration with time or to diminish stability of readings. At any voltage, sensitivity will decrease somewhat during the duration (usually about two hours) of operation. However, the initial sensitivity is regained when the instrument is not used for about five hours. Before each trial, when using the standard, the needle deflection of the galvanometer was always approximately 35 per cent of the full scale reading. The power supply circuit for the photo tube is that recommended by RCA. It employs a full-wave rectifier with voltage divider for supplying DC voltages to the 1P21 in applications critical as to hum modulation.

Refractive index relations were conveniently determined with a differential refractometer (8) schematically shown in Figure 2 (not drawn to scale). The light beam, originating from a mercury vapor arc (GE AH-4), passes through in succession a pinhole, monochromatizing filter, a slit, a simple lens, the cell, another simple lens, and finally, the eyepiece. The slit is located at the focal plane of the first lens; the cross hairs of the eyepiece at the focal plane of the second. The eyepiece is of the filar micrometer type. The distance from cell to cross hairs is approximately 110 cm.

The refractometer consists of two compartments separated by a glass barrier. To prevent evaporation a metal top is

placed over the cell. Contact with the outer sides prevents difficulties due to capillary action.

V. EXPERIMENTAL METHODS

Solutions were studied in the following manner. Samples of the surfactants were weighed out to the closest milligram, placed in 25 cc. pyrex volumetric flasks, and dissolved in water. The solutions were diluted almost to 25 cc., placed in a constant temperature atmosphere and, finally, diluted exactly to 25 cc. Each solution was filtered through a pyrex, ultrafine, fritted glass funnel directly into the light scattering cell. Pressure filtration was used to avoid foaming. Hydrogen gas was used as the source of pressure--from 2 lbs./sq. inch for most detergent solutions to 10 lbs./sq. inch for concentrated sucrose and raffanose solutions. Figure 3 illustrates the set-up. A furrowed cap was glued to the top of the large rubber stopper, which fitted snugly into the filter funnel. Hydrogen gas passed directly to the solution from a tank through an opening in the cap and rubber stopper. After filtration, the cell was placed in the cell holder with the same orientation each time. Two ball bearings, projecting from two sides within the cell holder, kept the cell in the same position each time. All experimental work was done at 30°C. unless otherwise stated.

Rarely after filtration of a detergent solution would bubbles form (between the scattering cell-liquid interface) or sudsing occur. Bubbles were easily removed with a stirring rod or by physical agitation. It was necessary to do this to pre-

vent reflections from the meniscus, and diffractions and reflections due to bubbles.

Measurements at elevated temperatures were carried out by heating the immediate surroundings to the desired temperature. The solutions were made up at the elevated temperatures. Before and after scattering readings were made, the temperature of the solution was taken. The difference was usually 1°-2°C. A more desirable procedure for elevated temperature studies would have been to make turbidity measurements using a cell with a surrounding chamber heated by resistance wires.

Light scattering readings were taken immediately following filtration. The intensity of the light scattered from a solution was compared with the intensity of light scattered from a polished lucite block (2). Readings on the standard were made just before and after those made on a solution. Only 90° scattering was measured. Ten solutions required about two hours for a complete run.

Reference was made to the lucite block for two reasons:

(a) Standardization of the light scattering instrument essentially means in this study determining the "effective" turbidity of the lucite block. Hence comparison of galvanometer readings of a solution with the lucite block gave directly the turbidity of the solution.

(b) A decrease in intensity of the light source with time, and a decrease in sensitivity of the 1P21 tube.

The light scattering instrument was standardized in the following manner. Scattering measurements with aqueous solutions of purified sucrose and water (solvent) were made. The galvanometer deflection due to water, divided by the deflection due to lucite block, was subtracted from the deflection due to the solution divided by block deflection. This gave KT. K is the reciprocal turbidity (effective) of the lucite block, and T is the solution turbidity minus water turbidity. As previously stated, the galvanometer deflections are proportional to light striking the 1P21 tube, i.e., the light scattered at 90° to the incident beam. Since $HC/T=(1/M)+BC$, extrapolation of the HC/T vs. C plot to zero concentration yields 1/M.

$$\left(\frac{HC}{T}\right)_{C=0} = \frac{1}{M}, \text{ or } K\left(\frac{HC}{KT}\right)_{C=0} = \frac{1}{M}$$

$$\frac{1}{342.3} = K\left(\frac{HC}{KT}\right)_{C=0}$$

and

$$K = \frac{1}{H\left(\frac{C}{KT}\right)_{C=0} 342.3}$$

Only two unknowns need to be determined. $(C/KT)_{C=0}$ is obtained from a curve of (C/KT) vs. C (g/cc.). (See Figure 4.) H was determined using the relations

$$H = \frac{32\,\pi^3 \mu_o^2}{3N\,\lambda^4}\left(\frac{\mu-\mu_o}{C}\right)^2$$

$(\mu-\mu_o)/C$ was obtained from differential refractometer data. The differential refractometer was standardized with sucrose, using blue light (4358 Å). Sucrose solutions were prepared where both weight per cent solute and grams per cc. were recorded. The scale deflection of each solution, minus deflection due to water, was referred to as ΔR. According to McCartney (21), the relation $(\mu-\mu_o)_{5893} = 14.51\ C_w \times 10^{-4}$ at 20°C. holds for sucrose for the sodium D line. Refractive index of solution and water are designated μ and μ_o respectively. C_w is concentration in weight per cent sucrose. From the Cauchy formula, $\mu = A + (B/\lambda^2)$, $(\mu-\mu_o)$ at $\lambda =$ 4358 Å can be calculated. Since $\mu = A' + B'/\lambda^2$, and $\mu_o = A'' + B''/\lambda^2$

therefore $\mu-\mu_o = A + B/\lambda^2$, in which $A = A'-A''$ and $B = B'-B''$.

According to Hallwachs (15)

$$(\mu-\mu_o)_{4861} - (\mu-\mu_o)_{6563} = .0124\ (\mu-\mu_o)_{5893}$$

Utilization of these two relationships enables one to get the following:

$$(\mu-\mu_o)^{20°}_{4358} = 1.016\ (\mu-\mu_o)^{20°}_{5893}$$

However, measurements were generally made at 30°C.

Hallwachs found for sucrose solutions that

$$\left[\frac{d(\mu-\mu_o)}{dt}\right]^{17.8°}_{5893} = -(\mu-\mu_o)_{5893} \times 9.5 \times 10^{-4}$$

For a 10° increase in temperature the decrease in $(\mu-\mu_o)_{5893}$

would be approximately .0095 $(\mu-\mu_o)_{5893}$.

If we assume $(\mu-\mu_o)_{4358}$ to decrease in a similar manner

$$(\mu-\mu_o)^{30^\circ}_{4358} = (\mu-\mu_o)^{20^\circ}_{4358} - .0095\ (\mu-\mu_o)^{20^\circ}_{4358}$$

$$= (\mu-\mu_o)^{20^\circ}_{4358}\ (1 - .0095)$$

$$= 1.016\ (\mu-\mu_o)^{20^\circ}_{5893}\ (.9905)$$

$$= 1.016\ (14.51\ C_w \times 10^{-4})\ (.9905)$$

$$= 14.60 \times 10^{-4}\ C_w$$

When ΔR was plotted against C_w, the least squares slope $\Delta R/C_w = 14.72$, or $C_w = \Delta R/14.72$.

Therefore $$(\mu-\mu_o)^{30^\circ}_{4358} = 9.913\ \Delta R \times 10^{-5}$$

where ΔR refers to the reading given by the refractometer for pure solvent minus the reading for the solution. This is the working equation for the differential refractometer.

To obtain H for any solution, $\Delta R/C$ only need be determined since $(\mu-\mu_o)/C = 9.913 \times 10^{-5}(\Delta R/C)$ where C = g/cc.

For sucrose:

$$\frac{\Delta R}{C} = \frac{\Delta R\ 100}{C_w\ \rho}$$ where ρ = density of a 1% sucrose solution at 30°C. Therefore

$$\frac{\Delta R}{C} = \frac{14.72 \times 100}{9.995 \times 10^{-3}} = 1.474 \times 10^3$$

and $$\left(\frac{u-u_o}{C}\right)^2 = (9.913 \times 1.474 \times 10^{-2})^2 = .02135$$

From the Lange Handbook (6th edition), at 30°C., for H_2O,

λ =	5893	4861	4340
μAIR =	1.3320	1.3360	1.3392

μVAC = μAIR x 1.000294

By using the empirical Cauchy formula again, constants A and B can be calculated:

μ_{4358} for H_2O, 30°C. = 1.3395

Therefore, for sucrose, λ = 4385, temp. = 30°C, and $H = 5.832 \times 10^{-6}$.

In Figure 4, (C/KT) vs. C is plotted for sucrose, and extrapolation to C = 0 gives $(C/KT)_{C=0} = 0.566$. From the sucrose determination, then, $K = 8.89 \times 10^2$.

Standardization of the light scattering instrument with raffanose pentahydrate was done in the same manner as with sucrose. For raffanose $\cdot 5H_2O$ at 30°C., $H = 5.832 \times 10^{-6}$. From Figure 4, where C = 0, C/KT = 0.431. The average K is 8.66×10^2.

In order to calculate molecular weights of micelles, certain assumptions must be made. Unlike the sugar molecules, micelles carry a charge. Doty and Steiner (10) have discussed scattering due to colloidal electrolytes. At the critical concentration the concentration of micelles is extremely small (ideally zero), and interaction negligible. Hence molecular weights should be determined by extrapolation to the critical concentration C_c and not to zero concentration (5). For all

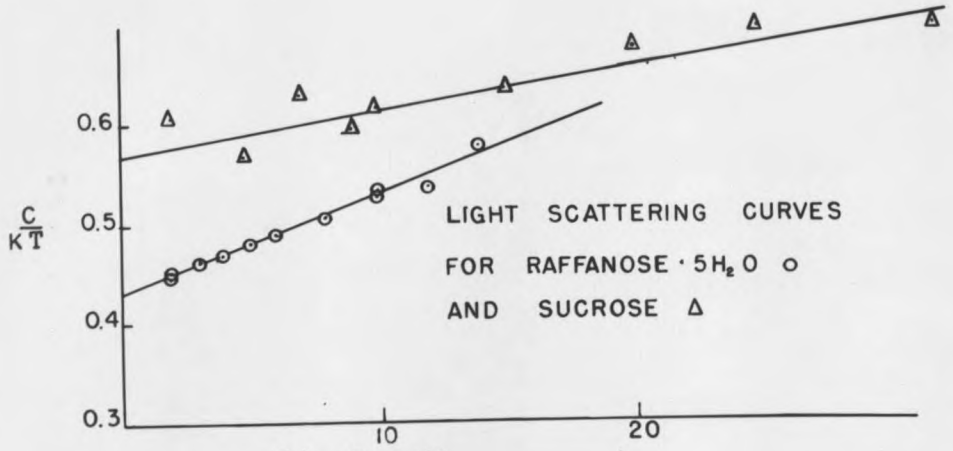


figure 4

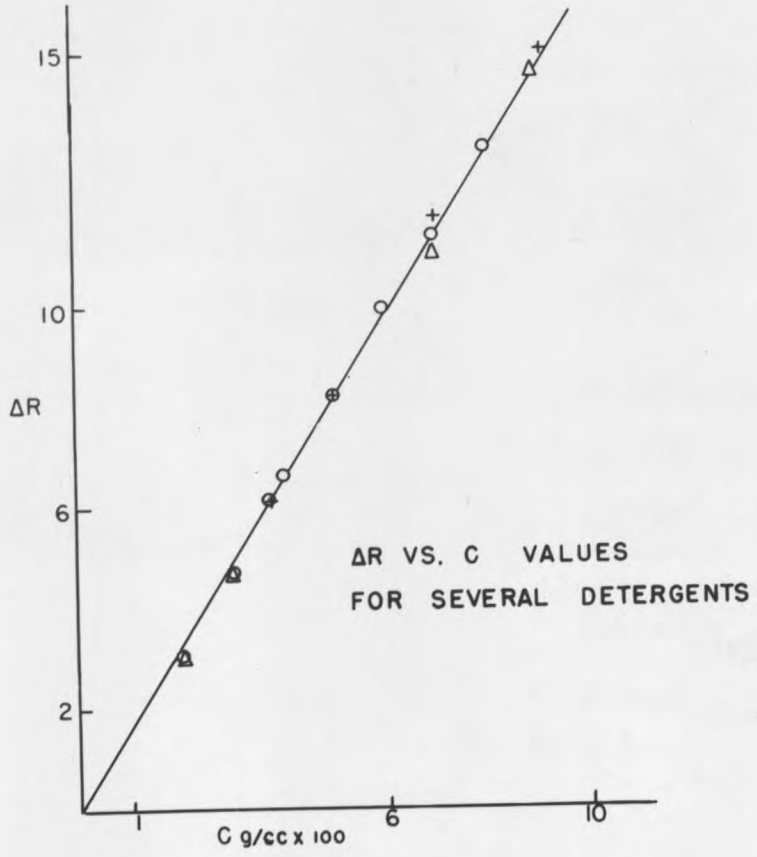


figure 5

practical purposes it can be assumed that the surfactant ions are unassociated up to the critical concentration, and above this concentration all added detergent molecules aggregate to form micelles. Hence H $(\frac{C-C_o}{T})$ rather than H (C/T) values should be plotted as a function of C. Debye (3) has shown that a high concentration of charge exists at the ends of the micelle, presumably near the nitrogen atom, and the existence of a highly charged species in solution without attraction of gegen ions would be very unlikely. We will assume that the over-all micelle charge is very close to zero, that our solute is the micelles, and our solvent is the solution at the critical concentration.

A least squares method has been employed in which C_o, M, and the slope of the H $\frac{C-C_o}{T}$ vs. C curve are simultaneously obtained (2). The best straight line is represented by $\frac{H(C-C_o)}{T} = A+SC$ where A=intercept and S is the slope. If

$$f_i = \frac{H(C_i-C_o)}{T_i} - A - SC_i$$

then

$$\sum f_i^2 = \sum_1^n \left[\frac{H(C_i-C_o)}{T_i} - A - SC_i \right]^2$$

for n experimental points. By determining $\frac{\partial \sum f_i^2}{\partial C_o}$, $\frac{\partial \sum f_i^2}{\partial A}$,

and $\frac{\partial \sum f_i^2}{\partial S}$ and setting them equal to zero, we get three equations which may be solved simultaneously for C_o, A, and S. Experimental points, above the critical concentration, that exhibit non-anomalous behavior (taken from observation of a T vs. C curve) are chosen for the calculation. Since

$$\frac{1}{M} = \left[\frac{H(C-C_o)}{T}\right]_{C=0} = A + SC_o ,$$

$$M = \frac{1}{A + SC_o}$$

VI. RESULTS

When light scattering theory was discussed it was pointed out that $(\mu-\mu_o)/C$ was assumed to be constant. Figure 5 is a plot of ΔR vs. C for a number of surfactants used in this study. The break in the refractive index plot of soap solutions found by some investigators (14) was not observed in this work. The slope, 0.163, represented in Figure 5 is an average slope obtained by least squares using points obtained from measurements of several surfactants. The error introduced in using this slope in calculation of H for all surfactants appears to be quite small for the chloride salts, but is not justified for the bromide and, perhaps, iodide salt since an error of about 20% is possible (3). By substituting $\Delta R/C$ in the working equation for the differential refractometer, H for the surfactants was determined as 7.164×10^{-6} at 30°C.

For higher temperatures, other considerations were involved. Corrections were made for the expansion of the glass volumetric flasks. Actually, density of water data could have been used to correct for concentration changes. The error involved can safely be assumed to be less than 0.1 per cent (22). To calculate the change in H with temperature, the change in $(\mu-\mu_o)/C$ would have to be determined. This might have been done by using a cell for the differential refractometer which would keep the cell contents at any high temperature desired. A hollow chamber within the cell holder, to allow continuous

flow of heated solution, or an insulated cell jacket could have been constructed. With the present differential refractometer, measurements can only be made at room temperature.

The Lorenz-Lorentz equation could be applied to calculate $(\mu-\mu_0)/C$ at higher temperature. This would entail other difficulties (3). Furthermore, the necessary density data were lacking. To consider H constant with temperature should introduce error within 1 per cent at 30°C., 2 per cent at 50°C., and 3 per cent at 60°C. For all calculations with detergents, $H = 7.164 \times 10^{-6}$.

The KT vs. C curves (Figure 8) strikingly illustrate the change that takes place in soap solutions at the critical concentration. Conductivity and density vs. concentration curves also show abrupt changes at the critical concentration. In all cases, except dodecyltrimethylammonium chloride, scattering below the critical concentrations was insignificant. For this detergent, reproducible scattering below the critical concentration occurred, although not shown in Figure 8. This suggests, more dramatically than in the case of the other surfactants, that micelles do exist below the critical concentration in small numbers. The abnormal rise in this case could be due to a slight amount of impurity which is solubilized in the micelle. It should be remembered, however, that the critical concentration is not a point, but a range.

A typical T vs. C curve, viz., for an uncharged polymer

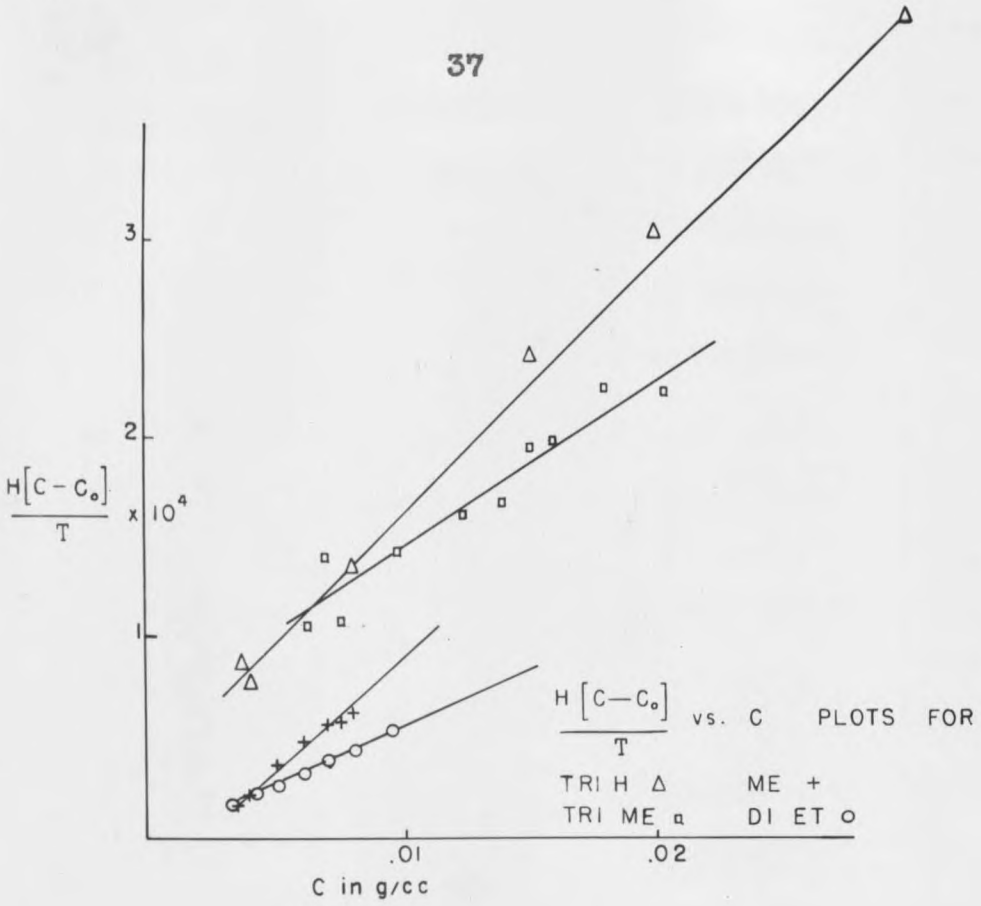


figure 6

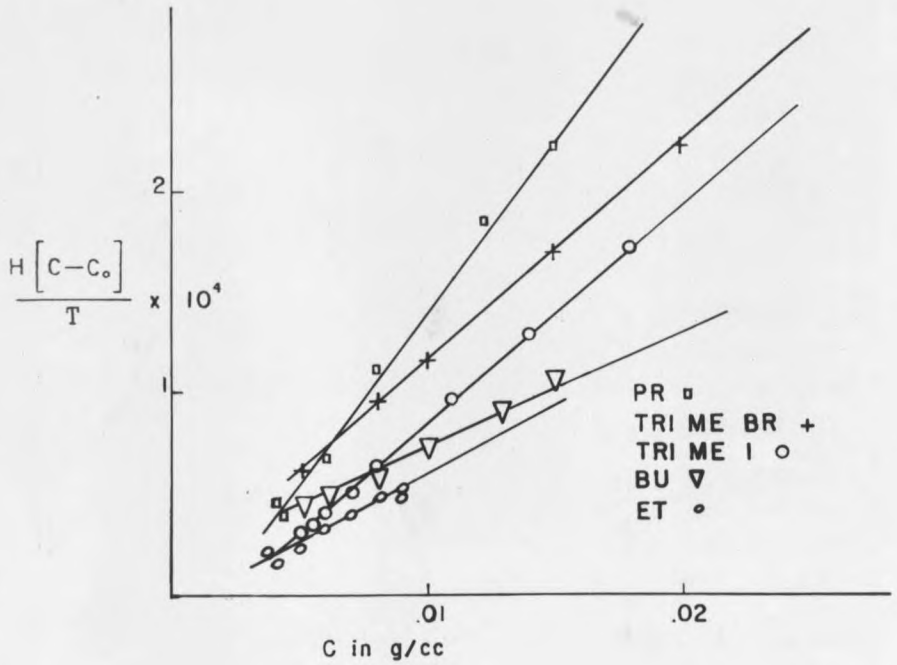


figure 7

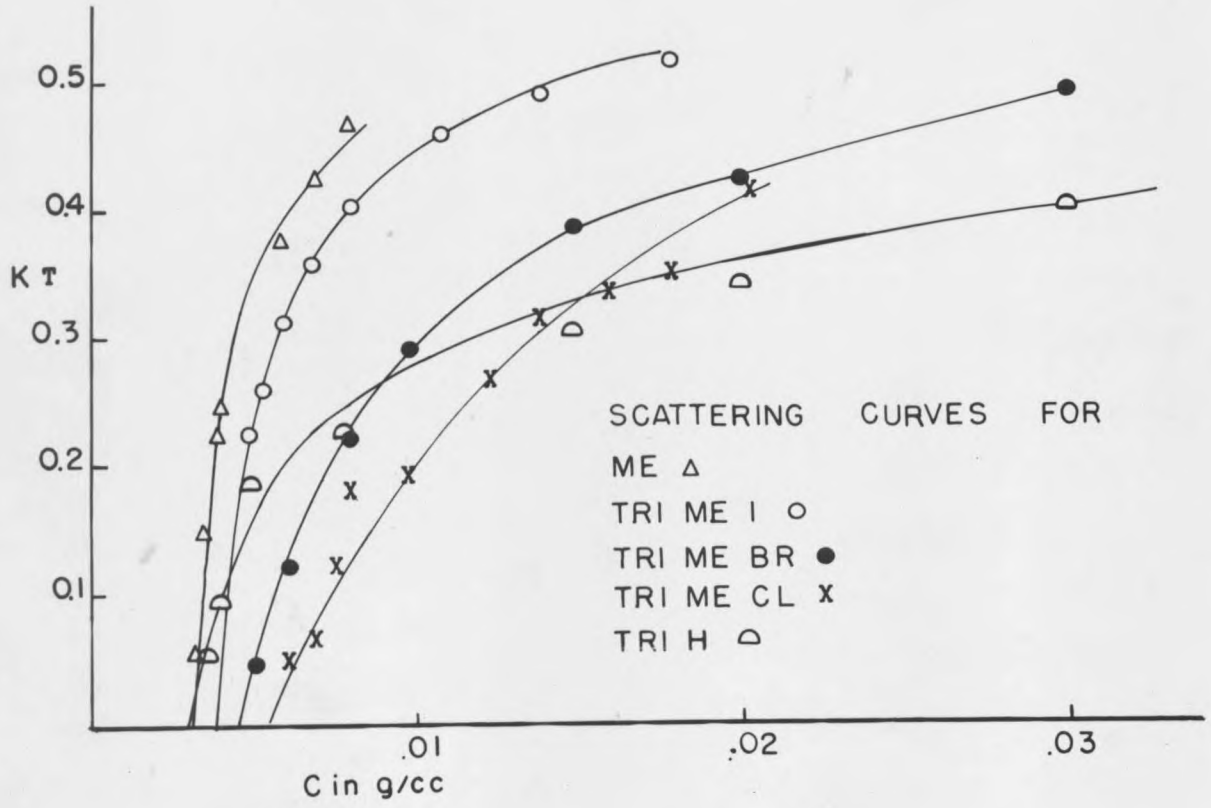

0.5
0.4
K T
0.3
0.2
0.1
.01
.02
.03
C in g/cc
SCATTERING CURVES FOR
ME △
TRI ME I ○
TRI ME BR ●
TRI ME CL X
TRI H ⌓

figure 8

smaller than one-twentieth the wave length of incident light, is similar to that for dodecyltrimethylammonium bromide and chloride except that it goes through the origin. The leveling off at higher concentrations is due to the ordering of solute molecules, which results in interference effects. The turbidity vs. concentration plots bring out quite clearly which points can be employed in the least squares method of determining critical concentration and molecular weight. Any anomalies are also clearly indicated. From Figure 8 the desired range of points to be used in the molecular weight calculations is suggested. It is clear that near the critical concentrations, the error in a particular value of "T" is greater than at higher concentrations. Since the equation used for calculations has an $\frac{H(C-C_0)}{T}$ term, points very close to the critical concentration should be avoided, and furthermore, we would expect these points to show greatest displacement from the least squares curve for $\frac{H(C-C_0)}{T}$ vs. C.

Perhaps a better way of weighting the points for least squares calculation would have been to use

$$f_i = H(C_i-C_0) - AT_i - SC_iT_i$$

At higher concentrations, the micelles may not act independently of one another and, therefore, assumptions made in deriving the light scattering equation would not hold. It is desirable then

to use intermediate points.

In the case of the methyl, ethyl and diethyl salts, the KT vs. C curve did not level off but instead rose sharply at concentrations about 0.01 g/cc. Only those points below this concentration were used in calculating molecular weights.

The ethyl, propyl and butyl salts were run at 37°, 50°, and 65°C., respectively. The only other detergent observed at a temperature greater than 30°C. was trimethyl iodide salt at 45°C. These higher temperatures were used because of the limited solubility of the detergents at lower temperatures.

$\frac{H(C-C_o)}{T}$ vs. C plots, Figures 6 and 7, represent the best straight lines obtainable from the experimental data. Table II gives the calculated results.

Molecular weights for detergents studied by Anacker (3), who reported values of 12,300 and 15,500 for dodecylammonium chloride and dodecyltrimethylammonium bromide respectively, are in fair agreement with the corresponding values obtained in this study. In the case of the dodecylalkylammonium chlorides and trimethylammonium iodide, standardization of the results to 30°C. was done by calculating the rate of change of molecular weight with temperature for dodecyltrimethylammonium bromide using Anacker's data, assuming the same rate held for these materials. These approximations are rough. Time did not permit an individual study of these salts with temperature change.

TABLE II
Calculated Results

DETERGENT	C_o (g/cc.)	Slope x 10^3	Molecular Weight*
Dodecylmethylammonium chloride	.00314	11.69	74,600
Dodecylethylammonium chloride	.00304		71,900
Dodecylpropylammonium chloride	.00301		36,000
Dodecylbutylammonium chloride	.00279		28,900
Dodecyldiethylammonium chloride	.00336	5.96	52,300
Dodecyltrihydrogenamm. chloride	.00290	13.13	14,400
Dodecyltrimethylamm. chloride	.00544	8.31	9,300
Dodecyltrimethylammonium bromide	.00453	10.62	17,200
Dodecyltrimethylammonium iodide	.00347		58,700
Dodecylethylamm. chlor. at 38°C.	.00309	6.22	65,900
Dodecylpropylamm. chlor. at 48°C.	.00346	16.73	31,900
Dodecylbutylamm. chlor. at 65°C.	.00440	5.63	28,300
Dodecyltrimethylamm. iod. at 46°C.	.00382	10.60	49,400

*At 30°C. unless otherwise specified.

VII. DISCUSSION

Although no measurements were attempted, dissymmetry and depolarization of the scattered light have been assumed to be negligible. The relatively small values of the molecular weights support the assumption.

According to the experimental results, micelle weights are strongly dependent upon the make-up of the substituent groups present on the nitrogen. The author at this time is unable to present a complete and fully consistent explanation of the observed phenomena. The following considerations may be of some limited value.

The equilibrium size of the micelle is determined by the interplay of two forces. The short range van der Waal's forces hold the long hydrocarbon tails of the surfactant ions together in the micelle. Energy is released when a number of hydro-carbon tails are removed from the surrounding water and brought into contact with each other in the micelle. The energy given up is roughly proportional to the number of ions which aggregate. On the other hand, long range coulombic forces must be overcome when charged ends of the hydrocarbon chains are brought together in the outer surface of the micelle. This process requires the expenditure of energy. The larger the micelle the greater will be the electrical work required to bring an additional long-chain ion into the micelle.

When the initial chains come together, the energy released

is greater than the energy required to bring the polar heads together. Since the energy released is negative by convention, the total energy of the micelle, i.e., the algebraic sum of the energy gained by bringing N hydrocarbon tails together and the electrical work which must be done, will reach a minimum value which is negative. At this minimum, the value of the corresponding N represents the number of molecules making up the micelle of most stable configuration. At this point $dW/dN = 0$, in which W is equal to the total energy of the micelle.

Any factor which will modify the forces involved will affect the equilibrium size of the micelle. The adsorption on, or close approach to, the surface of the micelle of oppositely charged gegen ions will screen the action of the charges on the micelle and will reduce the electrical work required to bring additional long-chain ions into the aggregate. Hence in the presence of added electrolyte, the equilibrium size of the micelle will be larger than when no additional electrolyte is present.

Any factor which will increase the distance between the nitrogen atoms in the surface of the micelle will decrease the surface charge density and should also decrease the electrical work necessary to bring a new molecule into the micelle. Thus the size of the micelle should increase. However, separation of the polar heads will result in some separation of the hydrocarbon tails, which in turn would tend to decrease the micelle

size. These two effects then partially cancel each other. Let us examine the following table with the above considerations in mind.

Consider dodecylammonium chloride as a member of each of the three horizontal rows. In the top row we notice a marked increase in the aggregation number when one of the hydrogen atoms on the nitrogen is replaced by an alkyl radical. Since the nitrogen atom is smaller than a carbon atom, and bonds tetrahedrally--or approximately so--to four other atoms or groups, it is unlikely that the nitrogen atoms in adjacent chains are forced apart by the replacement. Hence the size increase cannot be due to a reduction in the electrical work required to form a micelle from independent ions. The alkyl radical, if it does anything, forces the counter ion away from the nitrogen atom and thus should tend to make the aggregation number fall instead of rise. This may be the explanation for the observed decrease from the second member on. The reason for the big difference in aggregation number between dodecylammonium chloride and dodecylmethylammonium chloride is not evident.

In the second horizontal row there is an increase in micellar weight as we go from left to right. A possible explanation of this increase is the forcing apart of nitrogen atoms in adjacent heads.

In the bottom horizontal row we might explain an increase in micelle size as we go from dodecylammonium chloride to do-

decyltrimethylammonium chloride again as involving an increase in the distance between adjacent nitrogen atoms. The nitrogen atoms for the trimethyl micelle are farther apart than for any other and, if the distance between nitrogen atoms were the only factor to be considered, we would expect this micelle to be the largest of any considered. An increased distance of closest approach of the gegen ion to the nitrogen atom and some separation of the hydrocarbon tails may be the primary factors determining the small size.

TABLE III
Comparison Between Surfactants at 30°C.

Trihydrogen MW = 14,400 N = 65	Methyl MW = 74,600 N = 317	Ethyl MW = 71,900 N = 288	Propyl MW = 36,000 N = 137	Butyl MW = 28,900 N = 96
Trihydrogen MW = 14,400 N = 65		Diethyl MW = 52,300 N = 188		
Trihydrogen MW = 14,400 N = 65	Trimethyl MW = 9,300 N = 35			

The observed fall of aggregation number as we descend the third vertical column, assuming trimethyl and triethyl to be approximately the same size, would lead us to conclude that in

this series, progressive forcing back of the gegen ion from the nitrogen atom was the controlling factor. This may also be the case in the second vertical column.

Another factor which should be considered is the "effective" dielectric constant in the region of the charge on the nitrogen atom. Since coulombic repulsion between like charges varies inversely as the dielectric constant surrounding the charges, we would expect two charged monomer heads to repel each other with much greater force where alkyl groups surround the nitrogen atom than where they do not. We would therefore expect micelle size to decrease as the number of alkyl groups around the nitrogen atom increases. Indeed, the results show that the molecular weight of the micelle decreases in the series alkyl→dialkyl→trialkyl. Also, as the aliphatic chain is lengthened the molecular weight decreases. This effect is most pronounced in the case of trialkyl salts, and, together with gegen ion hindrance, explains the low value of their micelle size.

Another effect worth mentioning, but of lesser importance, is the van der Waal attraction between alkyl groups around a nitrogen atom and alkyl groups of an adjacent monomer head. This would cause a small negative contribution to the total energy of the system and tend to increase molecular weight.

An interesting comparison can be made between the trihydrogen and trialkyl salts where gegen ion and alkyl group hin-

drances are at a minimum and maximum respectively. Since their molecular weights are of nearly the same order of magnitude, it can be deduced that the two steric effects are of nearly the same order of magnitude. Furthermore, when an alkyl group is removed from the trialkyl or added to the trihydrogen salt to give dialkyl and alkyl salts respectively: in the first instance the gegen ion effect is enhanced while the alkyl hindrance effect changes little; in the case of the trihydrogen and ethyl, the greater change is in the alkyl hindrance. In both cases one effect is enhanced and micelles of much larger molecular weight can be expected. This is evident in Table III, where trimethyl, MW = 9,300 → diethyl, MW = 52,300; and trihydrogen, MW = 14,400 → ethyl, MW = 71,900. The large jump in molecular weight observed from dodecylammonium chloride to dodecylalkylammonium chloride may be due to a decrease in the "effective dielectric constant." This would mean that in the case of trihydrogen, although the gegen ion can approach closely, the effective dielectric constant surrounding the nitrogen atom would be greater than in the case of ethyl, or even diethyl; and so shielding by the gegen ion would be greater in cases where alkyl groups surround the nitrogen atom.

No attempt was made to determine the shape of the micelles, but it is evident from simple calculation that the micelles are probably not spherical under the conditions of this study. A spherical micelle would have a diameter no greater than twice

the length of the dodecyl chain, or $2 \times 1.26 \times 10^{-8} \times 12$ cm. Its volume would be $4/3\ \pi (2 \times 1.26 \times 10^{-8} \times 12)^3$ cm^3. Assuming a density of unity (more likely near 0.8), the molecular weight would be $1 \times 4/3\ \pi (2 \times 1.26 \times 10^{-8} \times 12)^3 \times 6 \times 10^{23}$, or about 8,700. The trimethyl salt is the only surfactant reported here whose molecular weight is in this range.

In the above discussion molecular weight is correlated with micelle structure. A correlation could be made of micelle structure and critical concentration. Perhaps future knowledge of critical concentration and molecular weight relationship will illuminate micelle structure.

Table III shows that a direct increase in critical concentration occurs in dodecyltrimethylammonium halides with progression from iodide to chloride anions. One might expect that the neutralizing effect of the gegen ion depends on the distance of approach of the monomer head and the gegen ion. This is apparently a function of the size of the ion. However, the "size" of the ion includes the ionic radius plus the adsorbed water. From heat of solution data, and as a consequence of the Debye-Hückel theory, the chloride ion is hydrated the most and the iodide ion the least. Hydration would tend to screen the ionic field by alignment of the water mo ecules along the lines of force, thereby increasing the dielectric constant. According to ionic conductance data, at infinite dilution the relative size of the ions in solution can be obtained, showing the

bromide ion to be slightly larger than the iodide and chloride ions, which are about the same size. In view of this, the experimental results reported here are surprising, and their interpretation imposes a formidable challenge.

VIII. BRIEF SUMMARY

Related detergents were prepared by modification of standard methods, and a relatively simple and rapid method for halogen analysis was devised.

The light scattering instrument was standardized with sucrose and raffanose with fair agreement.

Critical concentrations and molecular weights of micelles were determined for nine detergents. Rough theoretical correlation was attempted in strictly qualitative terms. There was considerable speculation concerning the relation between molecular weight and micelle structure. Factors tending to increase molecular weight were thought to be:

a. closeness of approach of the gegen ion to the monomer head,
b. increased separation of polar heads by the introduction of groups around the nitrogen atom,
c. some van der Waal attraction between alkyl groups of adjacent molecules.

Factors tending to decrease molecular weight were thought to be:

a. hindrance of the gegen ion,
b. close approach of the charged monomer heads,
c. increase in alkyl groups around the nitrogen atom, thereby lowering the "effective" dielectric constant surrounding the charge,
d. separation of the hydrocarbon tails due to bulkiness

of alkyl groups around the nitrogen atom.

The influence of the gegen ion on the equilibrium size of the micelle was clearly demonstrated. The effect of the iodide ion compared to the bromide and chloride ions appeared to be out of proportion in view of the relative size of the hydrated ions estimated from conductivity data. However, the size of the micelle did not seem to vary as the size of the ion. The size of the micelle did vary inversely as the degree of hydration of the ion, but this may be fortuitous.

IX. ACKNOWLEDGEMENTS

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