[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Flow Birefringence in Solutions of *n*-Hexadecyltrimethylammonium Bromide[1,2]

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The question of the existence of large asymmetrical particles in detergent-salt solutions and their size and shape has been investigated by the method of flow birefringence. The flow birefringence data, interpreted on the basis of a rigid prolate ellipsoidal model, indicate the existence of elongated micelles whose length increases with increasing salt concentration. The solutions are considerably polydisperse in the range of salt and detergent concentrations studied. Presumably, in high salt concentrations the hydrocarbon tails of the detergent extend radially from the major axis of the ellipsoid ending in the charged heads which make up the surface of the ellipsoid in contact with the water.

The existence of micelles or colloidal aggregates of ions in soap solutions has been recognized for some time. Recently this phenomenon was investigated by Debye[3] and Anacker[4] who studied the light scattering properties of aqueous solutions of the normal alkyl trimethylammonium bromides. These cationic detergent solutions show an increased turbidity above a critical concentration of detergent, this critical concentration depending on the number of carbon atoms in the hydrocarbon tail and the concentration and kind of added electrolytes. Addition of increasing amounts of salts lowers the critical concentration for micelle formation and also increases the micelle molecular weight. Debye outlined a theory for the structure of the micelles to account for these observations using the double-layer, cylindrical model of Harkins and coworkers.[5] The effect of salt on the size and stability of the micelle was considered by Hobbs[6] for the case of dilute salt solutions.

It was further found by Debye and Anacker that, in the presence of high salt concentration, the solutions formed from detergents having long hydrocarbon tails scattered more light in the forward than in the backward direction. From this angular dissymmetry they inferred that the micelles formed from *n*-hexadecyltrimethylammonium bromide were large asymmetrical particles, the data for this dissymmetry being best fitted using a rod as a theoretical model. No dissymmetry was observed in solutions of *n*-tetradecyltrimethylammonium bromide under similar conditions.

The possible existence of such particle asymmetry suggested the use of another technique to shed light on the question of size and shape of soap micelles. Flow birefringence measurements are especially suitable[7] for determining the size of asymmetrical particles which are large enough to be oriented by streaming in a liquid. This technique has been applied here to a study of solutions of the sixteen-carbon detergent whose solutions exhibit flow birefringence at experimentally attainable and feasible velocity gradients.

Experimental

Materials.—*n*-Hexadecyltrimethylammonium bromide was prepared by the reaction of Eastman Kodak Co. cetyl bromide with Eastman Kodak Co. trimethylamine according to the procedure of Scott and Tartar[8] as modified by Anacker[9] and Smudski.[10]

To the cetyl bromide was added a 30% excess of a 25% solution of trimethylamine in methanol. The mixture was refluxed on a steam-bath for one hour using a condenser cooled with ice-water. The resultant solid was recrystallized three times by dissolving in warm methanol and recovering by an ether precipitation with cooling in an ice-bath. The detergent was dried in a vacuum desiccator.

Reagent grade KBr, dried at 115°, was used to control the electrolyte content of the solutions.

Fresh solutions of *n*-hexadecyltrimethylammonium bromide were prepared from weighed amounts of the dry solid. Measured volumes of a stock solution of KBr were added, and the mixtures diluted to 50.0 ml. in volumetric flasks.

Apparatus.—Flow birefringence measurements were made in an apparatus essentially similar to Edsall's.[11] A stainless steel concentric cylinder system was used with the inner cylinder serving as the rotor. The length of the light path through the solution in the rotating cylinder system was 7.01 cm. To have the apparatus adaptable for a variety of investigations three different rotors were constructed to give a range of inter-cylinder gap widths, the largest gap width introducing the least amount of error due to reflection of light from the cylinder walls.

By virtue of the requirement for maintaining laminar flow there is a maximum speed for each rotor beyond which the flow becomes turbulent. Jerrard[12] has recently discussed the question of turbulence and apparatus design in flow birefringence measurements. It has been known[13] that the onset of turbulence very often does not produce any sharp break in the curve of double refraction *vs.* velocity gradient. This is explained by Jerrard as due to the nonlinear character of the velocity across the gap in turbulence in that the gradient is large near the cylinder surfaces and small in the center of the gap. The amount of double refraction obtained would then depend on the alignment of the optical system and in many cases the transition between laminar flow and turbulence would be undetected.

The data for the various rotors are summarized in Table I.

For the present investigation the range of velocity gradients necessary to obtain a measurable amount of birefringence required the use of rotor No. 3 with the narrowest gap. Rotor No. 2 also gave a measurable birefringence; however, the velocity gradients were beyond the limits of the region of laminar flow for this rotor for the solvent viscosity used. Glycerol could not be used to increase the viscosity inasmuch as it decreases the micelle size.[14]

The rotor was driven by an auxiliary drive shaft which was geared to both a tachometer generator and a driving motor. The auxiliary shaft was connected to the rotor by a 3.5 inch length of rubber garden hose. In this way the transmission of vibrations from the auxiliary shaft to the cylinder system on the optical bench was essentially eliminated.

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[1] This work was carried out in connection with a project supported by a contract with the Office of Naval Research.

[2] Presented before the Division of Colloid Chemistry at the 119th Meeting of the American Chemical Society, Boston, Mass., April, 1951.

[3] P. Debye, *J. Phys. Colloid Chem.*, **53**, 1 (1949); *Ann. N. Y. Acad. of Sci.*, **51**, 575 (1949).

[4] P. Debye and E. W. Anacker, *J. Phys. Colloid Chem.*, **55**, 644 (1951).

[5] R. H. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys*, **15**, 209 (1947); **16**, 156 (1948).

[6] M. E. Hobbs, *J. Phys. Colloid Chem.*, **55**, 675 (1951).

[7] J. T. Edsall, *Adv. Colloid Sci.*, **1**, 269 (1942).

[8] A. B. Scott and H. V. Tartar, THIS JOURNAL, **65**, 692 (1943).

[9] E. W. Anacker, Ph.D. Thesis, Cornell University, 1949.

[10] P. A. Smudski, Ph.D. Thesis, Cornell University, 1951.

[11] J. T. Edsall, *et al.*, *Rev. Sci. Instruments*, **15**, 243 (1944).

[12] H. G. Jerrard, *J. App. Phys.*, **21**, 1007 (1950).

[13] C. Sadron, *J. phys. radium*, **7**, 263 (1936); Schweiz, *Arch. angew. Wiss. Tech.*, (3-4) **158**, 8 (1937).

[14] R. M. Hagen, Ph.D. Thesis, Cornell University, 1949.

TABLE I

ROTOR DATA

Rotor	Radius,[a] cm.	Gap width, cm.	$\frac{\text{Gradient}}{\text{rotor speed}}$ $\frac{(\text{sec.}^{-1})}{(\text{r.p.m.})}$	Maximum velocity gradient[b] for laminar flow in water at 20° (viscosity = 0.01 poise), (sec.$^{-1}$)
1	2.4706	0.0715	3.67	480 (130 r.p.m.)
2	2.5160	.0261	10.1	6050 (600 r.p.m.)
3	2.5300	.0121	21.9	41,000 (1885 r.p.m.)

[a] The cylinder surfaces were ground by D. W. Mann of Lincoln, Mass. [b] The maximum velocity gradient for the maintenance of laminar flow in a system of our dimensions is given by the formula of Taylor[15] for inner cylinder rotating as

$$G_{\max} = 66\,\frac{\eta}{d^{5/2}} = \frac{2\pi R}{60}\,\frac{N_{\max}}{d}$$

where G = velocity gradient in sec.$^{-1}$
d = gap width in cm.
η = viscosity of medium in poise
R = mean radius of cylinders in cm.
N = speed of rotor in r.p.m.

It is possible to use much higher velocity gradients without causing turbulence if one increases the viscosity by the addition of glycerol to the solutions.

A spoke-marked disc was also mounted on the auxiliary shaft so that the speed could be measured by means of a strobotron.[11] The correct performance of the strobotron circuit was checked occasionally by observing the pattern on another disc mounted on a separate 600 r.p.m. synchronous motor.

A 115 volt d.c. compound wound, $^3/_{16}$ h.p. motor was rewired to enable separate excitation of armature and field coil. The field coil was activated by means of a 125-volt d.c. source (rectified a.c.), the unregulated voltage being adjusted by means of a rheostat. For armature activation war surplus radar equipment consisting of a 250 volt, G.E. amplidyne generator and a G.E. amplifier was used. The circuit was essentially of the Ward–Lennard type[11] with the amplidyne armature connected to the motor armature and, in addition, contained provision for maintaining the speed constant. With this arrangement, adequate power was obtainable at all speeds for which this cylinder system is normally used, *i.e.*, 100 to 3000 r.p.m.

The speed was varied and maintained constant at any speed setting by means of a closed-loop, feed-back system. This type of speed control uses speed fluctuations as the indicator and is preferable to open-loop systems which use voltage fluctuations as the indicator; *i.e.*, regulation of only the voltage is not sufficient to maintain constant speed by virtue of temperature effects in the resistance and bearings of the motor, etc. At any speed setting the output voltage of the tachometer generator geared to the auxiliary shaft is a direct function of the shaft speed. This voltage was balanced across a variable rheostat fed by a reference source of constant d.c. (a 45-volt B battery). The speed of the motor and drive shaft, for rotation in either direction, could be varied by moving the rheostat setting, after which the tachometer voltage changed as the speed changed. When the desired speed is reached, the tachometer voltage balances the constant input d.c. voltage from the rheostat. If the speed of the auxiliary shaft were then to fluctuate, the tachometer voltage would fluctuate. The resultant unbalance between this voltage and the constant d.c. input was fed into an amplifier which fed the field coils of the amplidyne generator. This, in turn, affected the amplidyne armature in such a way as to transmit more or less voltage to the motor armature to bring the motor back to its original speed. In this manner, speed control was at least of the order of 0.1%, no precession of the strobotron pattern being observed. Also the system showed practically instantaneous response as the motor was brought to any desired speed without any tendency to "hunt."

The optical system mounted on a rigid, vertical optical bench was essentially the same as Edsall's,[11] using a J-25 Western Union concentrated arc lamp[16] (25 watts) at the focal point of a suitable lens, a Farrand interference filter transmitting at 544 mμ, polarizing and analyzing nicol prisms and a mica quarter-wave plate, serving as a Senarmont compensator. A long optical path between the analyzing prism and the telescope served to minimize reflection errors by reducing the intensity of reflected light.

The method of measurement of extinction angle and also the magnitude of the birefringence is described elsewhere.[11] The extinction angle χ is the smaller of the two angles between the cross of isocline and the transmission planes of the nicol prisms. It is also equal to the angle between the stream lines and the optic axis at any point in the flowing liquid. The birefringence ($n_e - n_0$) is expressable in terms of Δ, the angle of rotation (in degrees) of the analyzer of the Senarmont compensator by the relation

$$n_e - n_0 = \frac{\lambda\Delta}{180S}$$

where λ is the wave length of the light in vacuum and S is the length of the light path through the solution. For our system (λ = 544 mμ and S = 7.01 cm.)

$$n_e - n_0 = 4.31 \times 10^{-8}\Delta$$

The alignment of the apparatus was checked with ethyl cinnamate (η = 0.0654 poise at 25.0°). As can be seen from Table I, the viscosity of this material is high enough to assure maintenance of laminar flow at all speeds at which the apparatus is used in the case of rotors No. 2 and 3. For rotor No. 1, the maximum speed of the rotor is 850 r.p.m. for calibration with ethyl cinnamate at this temperature.

Results and Discussion

Effect of Detergent Concentration.—According to Debye and Anacker the angular dissymmetry, I_{40}/I_{140}, for the C_{16} detergent at any particular salt concentration, increases almost linearly with detergent concentration above the critical concentration and then levels off to a constant value, *i.e.*, either the micelles increase in size above the critical concentration and presumably do not attain constant size until a certain detergent concentration is reached or else there is a distribution of micelle sizes above the critical concentration. It was originally planned to study this dependence on concentration which occurs at low detergent concentration. However, even with the narrow gap afforded by rotor No. 3 insufficient orientation was obtained in the region of laminar flow to produce measurable birefringence. Therefore, this investigation was carried out at higher detergent concentrations in the region in which the light scattering data indicate that the dissymmetry is independent of concentration.

Table II summarizes the flow birefringence data wherein the effects of varying detergent and salt concentrations were studied. The detergent concentration is expressed in units of g./liter and the salt concentration as molarity. Some measurements of the extinction angle, χ, as a function of velocity gradient (in sec.$^{-1}$) are shown in Fig. 1 for KBr concentrations in the range 0.15 to 0.40 *M*. In interpreting the data it should be kept in mind that the inter-cylinder gap is extremely small—0.12 mm.—making accurate alignment of the optical system difficult. Such a small gap usually introduces errors due to reflections of the light from the walls of the cylinders. Using rotor No. 2 of our apparatus (gap width 0.26 mm.) in connection with other studies, we have obtained much better precision in the measurements. This is to be attrib-

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(15) G. I. Taylor, *Phil. Trans Roy. Soc.* (*London*), **A223**, 289 (1923).

(16) J. T. Edsall, G. A. Gilbert and H. A. Scheraga, THIS JOURNAL, to be submitted.

TABLE II

FLOW BIREFRINGENCE RESULTS ON *n*-HEXADECYLTRIMETHYLAMMONIUM BROMIDE IN KBr SOLUTIONS AT 34.0°

KBr concn., M	Detergent concn., g./l.	Range of $G \times 10^{-3}$, sec.$^{-1}$	Range of lengths,[a] Å.	$\left[\frac{\Delta}{G\eta c}\right]_0$
0.15	10.0	6.6–26.3	1200–1770	0.004
		6.6–26.3	1230–1870	.005
		13.2–26.3	1280–1570	.005
.20	5.0	13.2–26.3	1590–1720	.007
		13.2–26.3	1580–1820	.011
		13.2–26.3	1420–1730	.008
		13.2–26.3	1340–1950	.005
	7.0	9.9–26.3	1870–2030	...
		6.6–19.7	1800–2070	...
		6.6–19.7	1570–2180	.009
		13.2–26.3	1620–1970	.009
	10.0	6.6–13.2	1990–2420	...
		9.9–26.3	1570–1920	.012
		6.6–26.3	1550–2380	.008
.25	2.5	13.2–26.3	1670–2120	.002
		13.2–26.3	1530–1820	.007
	3.8	13.2–26.3	1820–2050	...
		6.6–26.3	1560–2380	.007
	5.0	6.6–26.3	1810–2450	.015
		6.6–26.3	1870–2580	.017
		6.6–13.2	1920–2530	...
		6.6–26.3	1670–2390	.016
	7.0	6.6–26.3	1870–2480	.016
		6.6–26.3	1810–2560	.019
.30	5.0	6.6–26.3	2120–2690	.035
		6.6–26.3	1990–2680	.030
.40	5.0	6.6–26.3	2650–3520	.033
		6.6–13.2	3020–3570	...
		19.7–26.3	2850–2980	.040

[a] Lengths were calculated from a prolate ellipsoid model (see equation 1) for the range of G values employed.

uted, in part, to the minimizing of these reflection errors. Nevertheless, while such errors may appear in the data reported here, and hence in the calculated values of the rotary diffusion constant, Θ, it can be seen, by reference to equation (1) below, that the error in the semi-major axis, a, is only $^1/_3$ the error in Θ. Indeed, within the limits used to characterize the lengths in this polydispersed system, it will be seen that these errors in Θ are essentially inconsequential. Δ/c *vs.* G curves are shown in Fig. 2 for these same salt concentrations,[17] c being the detergent concentration. There is very little birefringence at 0.15 M KBr and also at the lowest detergent concentrations in the solutions of higher salt content. The χ and Δ values in these cases, therefore, are subject to larger errors. This should be kept in mind in considering the data of Table II and the corresponding graphs.

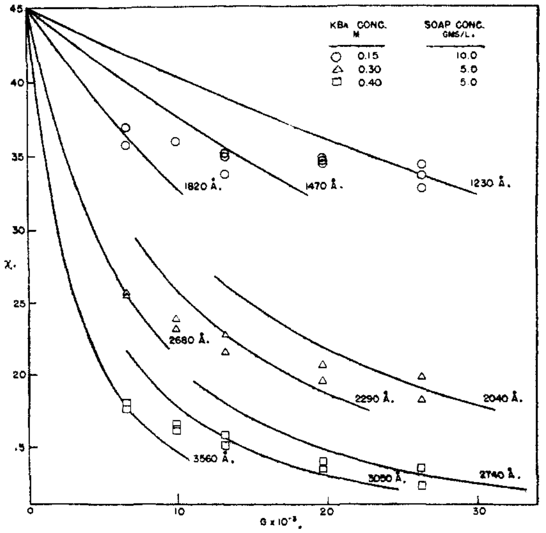

Fig. 1.—Behavior of extinction angle as a function of velocity gradient for several salt and detergent concentrations. Theoretical curves, for monodispersed particles of the lengths indicated, are shown. Increasing the salt concentration decreases the values of the observed extinction angles, indicating increasing particle length.

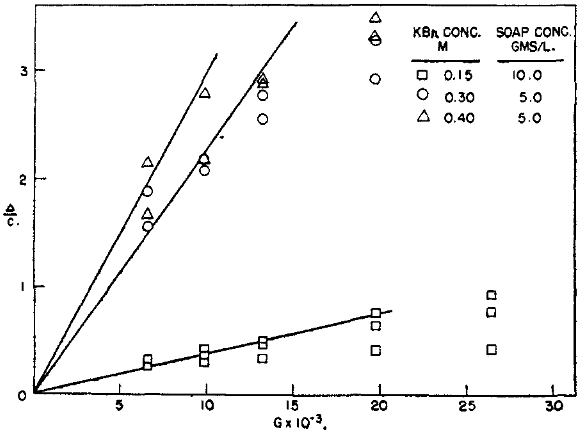

Fig. 2.—Δ/c *vs.* G data for several salt and detergent concentrations. Lines are drawn for initial linear portion of curves, with departure from linearity illustrated at the higher gradients. Increasing the salt concentration increases the initial slope of the curves.

The sign of the birefringence, $n_e - n_0$, was positive.

In all of these studies the solvent was water plus the KBr concentration indicated, all measurements being carried out at 34.0° to obtain a sufficiently high detergent solubility. The viscosity of water at this temperature is 0.00737 poise.

The curves in Fig. 1 are theoretical ones based on the orientation theory of Peterlin and Stuart[18] for monodisperse solute particles assumed to be rigid ellipsoids of revolution. The solutions of their equations were obtained with a mechanical computer[19] for a wide range of values of the parameter α ($\alpha = G/\Theta$ where G is the velocity gradient across the gap between the cylinders and Θ is the rotary diffusion constant of the asymmetrical solute particle). For a monodisperse system, a knowledge of the experimental χ *vs.* G curve enables one to determine Θ by comparison with the theoretical χ *vs.* α curve if one knows the axial ratio of the particles, which is usually obtained from viscosity measurements using Simha's theory for

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(17) The significance of the Δ measurements for obtaining information about the optical properties of the detergent micelles will be discussed in a forthcoming paper.

(18) A. Peterlin and H. A. Stuart, *Hand. u. Jahrb. d. Chem. Physik*, Bd. 8, Abt. IB (1943).

(19) H. A. Scheraga, J. T. Edsall and J. O. Gadd, *J. Chem. Phys.*, 19, 1101 (1951).

rigid particles.[20] However, in the present study we have assumed that the semi-minor axis of the ellipsoid is 24 Å., the length of a monomer chain.[4] Θ depends on the dimensions of the particle according to the relations of Perrin.[21] For example, for an elongated prolate ellipsoid ($a > 5b$)

$$\Theta = \frac{3kT}{16\pi\eta a^3}\left(-1 + 2\ln\frac{2a}{b}\right) \quad (1)$$

where a and b are the semi-major and semi-minor axes, respectively, and η is the viscosity of the solvent. Thus the length of the semi-major axis, a, can be calculated from the experimentally determined values of Θ.

For a given salt concentration there is a slight dependence of the observed χ *vs.* G curve on detergent concentration. This is similar to the situation found, for example, in the study of flow birefringence in solutions of human fibrinogen[22] and has been attributed to solute–solute interaction at the higher solute concentrations. This interaction is in the direction of apparently increasing particle length and may possibly indicate the formation of longer aggregates at high detergent concentrations.

It should also be noted that the data cannot be fitted by a theoretical curve for a monodisperse system. While we assume here that the particles are rigid this is not necessarily so. If the particles were not rigid, one might expect a distortion of the micelle with increasing gradient giving an apparently longer particle. Actually the flattening of the χ *vs.* G curve indicates, if anything, a shortening of the length with gradient. This could possibly be attributed to a splitting or bending of the micelle at these rates of shear. However, we are inclined to attribute this shape of the curve to the presence in solution of a range of particle sizes. If such were the case, then the observed data are those to be expected according to Sadron's treatment[23] of a polydispersed system wherein, qualitatively, the longer particles are oriented at the lower gradients and the shorter ones at the higher gradients. Similar results were obtained by von Muralt and Edsall[24] for solutions of myosin, a protein exhibiting extreme heterogeneity in length, and also by Foster and Lepow[25] for solutions of starch amyloses. In the case of the amyloses it was concluded that the elongation of coiled molecules rather than simple orientation was the predominant effect. In our case, the behavior of the Δ/c *vs.* G curves, in tending toward a saturation value, seems compatible with a process of orientation of rigid particles. Also, even in solutions at rest where there is no hydrodynamic distortion, the light scattering results indicate the presence of asymmetric, rod-like structures.

For various types of distributions of particle sizes one can compute,[26] using Sadron's equations, the expected χ *vs.* G curve. Rather than attempt such a calculation in this unfractionated system, it is more instructive to show the limits of size instead of trying to carry out a complete analysis of the distribution. Thus the curves in Fig. 1 are theoretical ones for monodispersed particles of the sizes indicated. A "mean" length is also indicated wherein this mean is approximately the median of all the lengths measured. This is a sufficiently good quantity to characterize the distribution for our purposes. It does not appear advisable, in the present case, to extrapolate the lengths to zero micelle concentration at each salt concentration. It is not completely accurate to give a lower size limit to the distribution since smaller particles than this limit could exist in solution without being oriented at the gradients used here. If it were not for the requirement of maintaining laminar flow, higher velocity gradients could have been employed to obtain orientation of shorter particles. Similarly, the upper limit could conceivably be extended to longer lengths if precise measurements could have been made at χ values close to 45° where the birefringence is extremely small. If the assumption is made that the distribution of particle lengths is Gaussian then the most probable length of the distribution is shorter than the "mean" length defined here[26] and is equal to or slightly less than the lower size limits shown in Fig. 1.

A disc model (oblate ellipsoid) has not been considered here inasmuch as it is ruled out as a possibility by the light scattering data of Debye and Anacker.[4] Using a disc model compatible with their observed values for angular dissymmetry they calculate a molecular weight which is much higher than the observed value. Considering the sphere, the rod, and the disc models, only the rod model is feasible to account for both their dissymmetry and molecular weight data.

Effect of Salt Concentration.—On the basis of these results, it appears that at salt concentrations of 0.15, 0.20, 0.25, 0.30 and 0.40 M the system is extremely polydispersed and the mean lengths are 1470, 1750, 1960, 2290 and 3050 Å. These results are shown in Fig. 3. The extrapolation may be of somewhat dubious validity since it

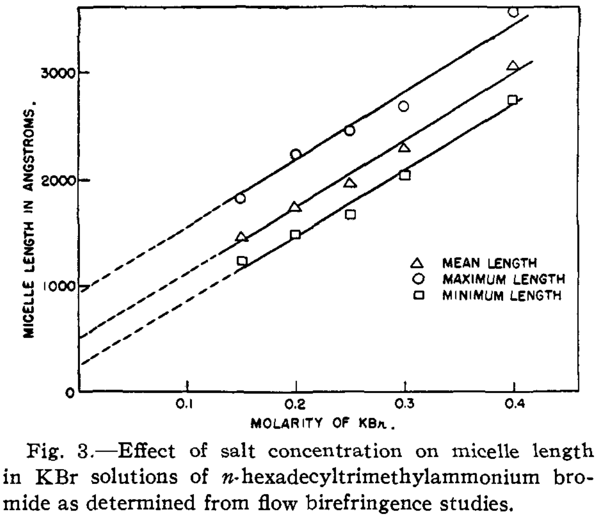

Fig. 3.—Effect of salt concentration on micelle length in KBr solutions of n-hexadecyltrimethylammonium bromide as determined from flow birefringence studies.

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[20] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

[21] F. Perrin, *J. phys. radium*, [7] **5**, 497 (1934).

[22] J. T. Edsall, J. F. Foster and I. H. Scheinberg, THIS JOURNAL, **69**, 2731 (1947).

[23] C. Sadron, *J. phys. radium*, [7] **9**, 381 (1938).

[24] A. L. von Muralt and J. T. Edsall, *J. Biol. Chem.*, **84**, 315, 351 (1930).

[25] J. F. Foster and I. H. Lepow, THIS JOURNAL, **70**, 4169 (1948).

[26] H. A. Scheraga, *J. Chem. Phys.*, **19**, 983 (1951).

is quite conceivable that at salt concentrations lower than 0.15 M, where accurate measurements could not be made, the curves could show downward curvature indicating the presence of much smaller micelles in the absence of salt. For particles even of the size indicated by the linear extrapolation it would be almost impossible by measurements of this kind to distinguish an asymmetrical micelle from a spherical one. The degree of polydispersity could conceivably decrease at lower salt concentration.

The effect of salt on $[\Delta/G\eta c]_0$, the initial slope of the Δ/c *vs.* G curve, can also be seen by reference to the last column of Table II. The increase in these values with increasing KBr concentration is probably a reflection, primarily, of the dependence of $n_e - n_0$ on the orientation factor[19] in that the long particles formed in 0.40 M KBr would be more readily oriented at these gradients than the short ones formed in 0.15 M KBr.[17]

The behavior of soap molecules in dilute salt solutions has been explained by Hobbs[6] on the basis of Debye's theory of the soap micelle. Hobbs finds, in agreement with Anacker and the results reported here, that the micelle size increases with increasing κ where κ is the reciprocal of the ion atmosphere thickness of the Debye–Hückel theory.

It thus appears that there may be two possible extreme configurations for the micelles, namely, the relatively small ones formed at low salt concentrations (double layer, cylindrical model—or "sandwich") and the large ones formed at high salt concentrations (rod model).

The dimensions of the small micelles are such that they are practically indistinguishable from spheres from the point of view of an experiment which measures a long dimension. Debye has suggested magnetic birefringence studies on these small micelles since a cylindrical one would exhibit anisotropy in its magnetic permeability whereas a spherical one would presumably be isotropic. Experimentally one does not find a long dimension for micelles at low salt concentrations. In the absence of such a long dimension, light scattering or flow birefringence are not of much help in determining size and shape.

In his theory for small micelles Debye[3] showed that relatively high energies would be involved if one tried to change the micelle size by more than two or three monomers. Hence, the small micelles should have a narrow distribution of sizes. If the salt concentration is increased the charged end-groups become shielded so that it does not require as much work to be done to bring up more molecules. This would increase the mean micelle size and would probably make for a high degree of polydispersity which has been observed in the flow birefringence measurements.

For the sixteen-carbon detergent at high salt concentrations we have the other extreme model, *i.e.*, one with a long dimension on the basis of light scattering and flow birefringence evidence.

It appears, therefore, taking the C_{16} detergent as an example, that the addition of salt increases the micelle size and, at some intermediate salt concentration, there is a micellar rearrangement from the "sandwich" form with rounded ends to the rod model. At present, it has not been possible to devise an experiment to shed light on the changes assumed to take place in this transition region. The qualitative, more so than the quantitative, aspect of these results should be emphasized wherein it is shown that in the presence of salt this detergent shows a distribution of sizes, the existence of large asymmetrical particles and an increase in particle size with increasing salt concentration.

Thus these large asymmetries fit the picture[4] of a C_{16} micelle in the presence of high salt concentration as being a rod from whose axis the hydrocarbon tails are projected radially, ending in polar heads which make up the surface of the rod at the micelle–water interface.

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