

A Viscometric Study of the Micelles of Sodium Dodecyl Sulfate in Dilute Solutions

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The viscosities of solutions of sodium dodecyl sulfate of concentrations up to 0.8 percent in distilled water and in 0.01- to 0.12-*M* sodium chloride have been measured. By introducing the concept of a monomer saturation concentration it is possible to determine the intrinsic viscosity of the micelles at each concentration of sodium chloride. A method for the experimental determination of the monomer saturation concentration is presented. The dependence of the intrinsic viscosity on the salt concentration is discussed in terms of electroviscous and hydration effects. The data indicate the presence of spherical micelles in the solutions investigated.

1. Introduction

Since the early experiments of Krafft [1]¹ and McBain [2] on soap solutions, and the subsequent interpretation of their results in terms of the existence of micelles in such solutions, many researches [3, 4] have been undertaken to investigate the size and shape of these particles. It is now generally assumed that there are at least two types of micelles. In the concentration range between the onset of micelle formation (about 0.1 to 0.25 percent by weight) and about 1 to 2 percent, a small, highly charged and highly conducting micelle is thought to exist. This type of micelle has been discussed at some length by Hartley [5, 6]. He considered them as spheres, but there has been no general agreement on their shape. A large micelle, having a structure discernible by X-ray diffraction, exists at higher concentrations (about 10 percent or greater). They have been discussed and investigated by McBain [2], Hess [7], Philippoff [8], and others [9]. Harkins [10] and his coworkers interpret their later X-ray diffraction data for concentrated solutions in terms of cylindrical micelles. Brady [11], however, utilizing a treatment considered by Corrin [12], interprets his data for concentrated sodium dodecyl sulfate solutions in terms of a radial distribution of spherical micelles. Recent light-scattering investigations by Debye [13] indicate that in the presence of high concentrations of electrolyte, the micelles of hexadecyl trimethyl ammonium bromide are rod-like.

The purpose of this research was to investigate the viscometric behavior of dilute solutions of a pure, well-defined detergent, sodium dodecyl sulfate. Detergent concentrations up to 0.8 percent by weight were used. Distilled water and 0.01 to 0.12 *M* sodium chloride solutions were used as solvents.

2. Materials

The sodium dodecyl sulfate was synthesized, as described by Shedlovsky [14], from a vacuum-distilled sample of *n*-dodecyl alcohol. The chlorosulfonic acid used in the synthesis was distilled immediately before use. All other reagents used in the synthesis and subsequent purification conformed with Ameri-

can Chemical Society specifications. Prior to making up solutions for the measurements, the detergent was extracted with diethyl ether for about 8 hr in a Soxhlet extractor.

After a measurement, the detergent was recovered from solution in the following manner: The solution was evaporated to dryness and the residue taken up in ethyl alcohol. The alcohol solution was filtered and evaporated to dryness. This residue was then taken up in water and crystallized. Finally, the crystals were extracted with ether.

3. Experimental Details

3.1. Viscosity

a. Efflux Times

The efflux times of all solutions were determined in modified Ostwald viscometers, which gave flow times of approximately 200 sec for water at 23° C. Absolute viscosities were calculated by means of the standard two-constant equation

$$\eta = A\rho t_c + \frac{B\rho}{t_c} \quad (1)$$

The constants *A* and *B* were determined from experiments with distilled water at three temperatures. The absolute viscosity of water at 20° C was taken to be 1.002 centipoise [15]. ρ is the density of the solution. t_c is the efflux time corrected for surface-tension effects and for variations in the filling temperature. The surface-tension correction, arising from the difference of shape of the meniscus of the solution in the upper and lower bulbs of the viscometer, is treated as a time-averaged head correction. The filling-temperature correction is also treated as a head correction. The equation for t_c then takes the form

$$t_c = t_o \left(1 + \frac{\Delta h_\gamma}{h} + \frac{\Delta h_f}{h} \right),$$

where t_o is the observed efflux time. Δh_γ and Δh_f represent the change in the effective head arising from surface tension effects and variations in filling temperature respectively. h is the mean

¹ Figures in brackets indicate literature references at the end of this paper.

head during a run in the absence of such corrections. In the viscometers used $\Delta h_r/h$ is about 1.4 percent for a liquid of $\gamma=70$ dynes/cm. $\Delta h_r/h$ exceeds 1 part per 10 thousand only when the difference between the filling and measuring temperatures is 5 deg or more. The calibration of capillary viscometers has been discussed fully by Barr [16].

A water bath whose temperature was maintained at 23.00° C was used for all measurements of efflux time and density. The reproducibility of the temperature setting of the bath from day to day was well within 0.003° C. During the course of any single measurement the mean temperature of the bath did not vary by more than 0.0015° C.

Timing was accomplished manually with a 60-cycle synchronous clock powered by an amplified constant-frequency 60-cycle signal. The average deviation from the mean of five determinations on the same solution was rarely more than 0.03 sec.

b. Surface Tension

The surface tension of each solution was determined with a conventional ring-type interfacial tensiometer. An accuracy of 1 dyne/cm was sufficient for the purposes of this research.

c. Density

All density measurements were made in picnometers similar to those described by Wright and Tartar [17]. The modified picnometers used by the authors held approximately 50 g of solution, thus making it a simple task to obtain densities with a precision of 2 parts per 100 thousand. Examination of these data shows that the densities of the solutions as a function of concentration above the region of micelle formation are best represented by straight lines of equal slopes. Below this region, not enough data were obtained to define the shape of the curve.

Table 1 lists the experimentally determined viscosities and densities.

3.2 Determination of the Monomer Saturation Concentration

Modern treatments of the problem of the viscosity of suspensions of large particles lead to an expression of the following type

$$\frac{(\eta_{rel}-1)}{\varphi} = K + D\varphi \quad (2)$$

K is a constant related to the shape of the particles. It is equal to 2.5 for spheres. D is a constant related to those interactions in the suspension that give rise to disturbing hydrodynamic effects. φ is the volume fraction of the suspended particles, and η_{rel} is the viscosity of the solution relative to the viscosity of the suspending medium. It is usually more convenient to express the concentration of suspended particles in grams per deciliter of solution rather than in volume fractions. In

this case

$$\frac{(\eta_{rel}-1)}{c} = [\eta] + D'c, \quad (3)$$

where $[\eta]$ is the intrinsic viscosity and has the units deciliters per gram. It is related to K by the expression

$$[\eta] = \frac{K}{100d} \quad (4)$$

d is the density of the suspended particles.

If one wishes to apply eq 3 to the viscosity of detergent solutions with the hope of determining the intrinsic viscosity of the micelles, two problems must be considered. The first is that c must refer to the concentration of micelles, rather than to total detergent in solution. Second, η_{rel} is then the viscosity of the micelle solution relative to that of some arbitrary concentration of detergent, above which

TABLE 1. Viscosity of sodium dodecyl sulfate in water and sodium chloride solutions (23°C)

c	Density	η_{rel}^1	η_{rel}^2	c_m^1	η_{rel}^3	$\frac{\eta_{rel}-1}{c}$
Water						
g/100 ml	g/cm ³	cp	cp	g/100 ml		
0.00	0.99754	0.9323	-----	-----	-----	-----
.10	0.99773	9388	-----	-----	-----	-----
.20	0.99790	9398	-----	-----	-----	-----
.281*	-----	-----	0.9434	0.00	1.0000	0 [0.085]
.30	0.99806	9442	0.9446	.019	1.0013	.068
.40	0.99821	9520	9514	.119	1.0085	.071
.50	0.99835	9594	9598	.219	1.0174	.079
.60	0.99849	9689	9690	.319	1.0271	.085
0.01 N NaCl						
0.00	0.99799	0.9323	-----	-----	-----	-----
.05	0.99809	9350	-----	-----	-----	-----
.10	0.99818	9351	-----	-----	-----	-----
.20	0.99834	9394	-----	-----	-----	-----
.204*	-----	-----	0.9395	0.00	1.0000	0 [0.048]
.30	0.99846	9441	9441	.096	1.0049	.051
.40	0.99858	9503	9495	.198	1.0106	.054
.50	0.99872	9552	9554	.298	1.0169	.057
.60	0.99888	9614	9619	.398	1.0238	.060
.70	0.99901	9681	9687	.496	1.0311	.063
0.02 N NaCl						
0.00	0.99838	0.9329	-----	-----	-----	-----
.05	0.99847	9360	-----	-----	-----	-----
.10	0.99854	9367	-----	-----	-----	-----
.15	0.99862	9385	-----	-----	-----	-----
.161*	-----	-----	0.9391	0.00	1.0000	0 [0.045]
.20	0.99868	9400	9408	.059	1.0018	.046
.25	0.99880	9427	9431	.089	1.0043	.048
.30	0.99883	9457	9453	.139	1.0066	.047
.40	0.99897	9505	9500	.239	1.0116	.049
.50	0.99912	9550	9549	.339	1.0168	.050
.60	0.99924	9601	9603	.439	1.0226	.051
.80	0.99965	9728	9722	.639	1.0352	.055
0.03 N NaCl						
0.00	0.99880	0.9339	-----	-----	-----	-----
.05	0.99891	9362	-----	-----	-----	-----
.10	0.99900	9370	-----	-----	-----	-----
.136*	-----	-----	0.9386	0.00	1.0000	0 [0.041]
.15	0.99905	9395	9392	.014	1.0006	.043
.20	0.99911	9416	9411	.064	1.0027	.042
.25	0.99920	9451	9452	.114	1.0049	.043
.30	0.99924	9462	9452	.164	1.0070	.043
.40	0.99942	9498	9496	.264	1.0117	.044
.50	0.99954	9539	9542	.364	1.0166	.046
.60	0.99965	9589	9590	.464	1.0217	.047
.80	0.99999	9692	9692	.664	1.0328	.049

See footnotes at end of table.

TABLE I. Viscosity of sodium dodecyl sulfate in water and sodium chloride solutions (23°C)—Continued

c	Density	η_{raw}^1	η_{curve}^2	c_m^3	η_{rel}^4	$\frac{\eta_{rel}-1}{c_m}$
0.04 N NaCl						
0.00	0.99921	0.9349	-----	-----	-----	-----
.05	.99932	.9360	-----	-----	-----	-----
.10	.99938	.9378	-----	-----	-----	-----
.119*	-----	-----	0.9384	0.00	1.0000	[0.039]
.15	.99947	.9399	.9396	.031	1.0012	.039
.20	.99953	.9415	.9414	.081	1.0032	.040
.25	.99961	.9433	.9433	.131	1.0052	.040
.30	.99967	.9452	.9453	.181	1.0074	.041
.40	.99980	.9502	.9494	.281	1.0117	.042
.50	.99993	.9541	.9539	.381	1.0165	.043
.60	1.00005	.9579	.9585	.481	1.0214	.044
.80	1.00037	.9683	.9683	.681	1.0319	.047
0.05 N NaCl						
0.00	0.99963	0.9357	-----	-----	-----	-----
.05	.99969	.9371	-----	-----	-----	-----
.10	.99976	.9381	-----	-----	-----	-----
.106*	-----	-----	0.9386	0.00	1.0000	[0.038]
.15	.99989	.9400	.9401	.044	1.0018	.038
.20	1.00000	.9422	.9420	.094	1.0036	.038
.25	1.00005	.9438	.9439	.144	1.0056	.039
.30	1.00011	.9456	.9459	.194	1.0078	.040
.40	1.00024	.9504	.9500	.294	1.0121	.041
.50	1.00049	.9545	.9542	.394	1.0166	.042
.60	1.00053	.9588	.9586	.494	1.0213	.043
.80	1.00033	.9673	.9674	.694	1.0307	.044
0.08 N NaCl						
0.00	1.00094	0.9380	-----	-----	-----	-----
.05	1.00094	.9391	-----	-----	-----	-----
.083*	-----	-----	0.9408	0.00	1.0000	[0.037]
.10	1.00102	.9466	.9414	.017	1.0006	.035
.15	1.00110	.9439	.9432	.067	1.0026	.039
.20	1.00114	.9451	.9450	.117	1.0045	.038
.25	1.00124	.9473	.9469	.167	1.0065	.039
.30	1.00129	.9497	.9488	.217	1.0085	.039
.40	1.00142	.9532	.9527	.317	1.0126	.040
.50	1.00159	.9568	.9567	.417	1.0169	.041
.60	1.00170	.9607	.9609	.517	1.0214	.041
.80	1.00198	.9695	.9695	.717	1.0305	.043
0.12 N NaCl						
0.00	1.00245	0.9407	-----	-----	-----	-----
.065*	-----	-----	0.9422	0.00	1.0000	[0.035]
.10	1.00259	.9433	.9433	.035	1.0012	.034
.15	1.00288	.9467	.9450	.085	1.0030	.035
.20	1.00279	.9466	.9468	.135	1.0049	.036
.40	1.00306	.9553	.9541	.335	1.0128	.038
.60	1.00328	.9620	.9620	.535	1.0210	.039
.80	1.00355	.9701	.9701	.735	1.0296	.040

¹ η_{raw} —experimental viscosity, in centipoise.
² η_{curve} —viscosity taken from best smooth curve representing the dependence of η_{raw} on concentration.
³ c_m —(total concentration of detergent)—(monomer saturation concentration).
⁴ η_{rel} —viscosity of solution/viscosity at monomer saturation concentration, both values being obtained from a smooth curve (see footnote 2).
⁵ * indicates monomer saturation concentration.
⁶ [] denotes the intrinsic viscosity in deciliters per gram.

it can be safely assumed that essentially all added detergent becomes micelles. This concentration shall be referred to as the monomer saturation concentration and is given the symbol c_m . The concentration of detergent present as micelles c_m , at a total detergent concentration c , is then very nearly $c - c_m$. Consideration of the equilibrium between detergent molecules or ions and their micelles [3, 18] shows that the concentration range in which the fraction of added detergent going into micelles changes from 0 to 1 depends on n , the number of detergent molecules per micelle. For n less than 100, as previous investigations [18] have indicated for sodium dodecyl

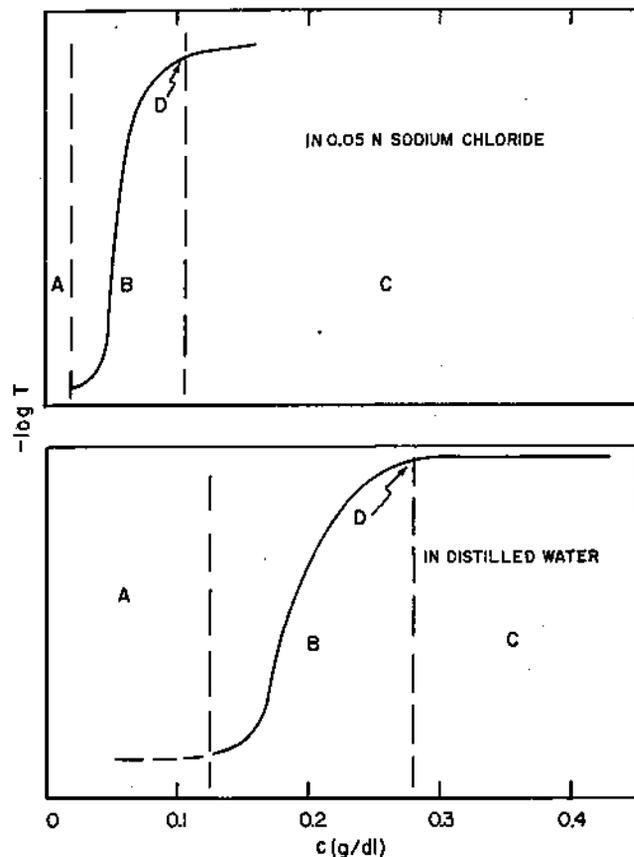


FIGURE 1. Typical plots of the absorbance ($-\log T$) versus concentration of sodium dodecyl sulfate.

The concentration of toluidene blue is 0.001 g/dl. The point D occurs at the monomer saturation concentration.

sulfate, the monomer saturation concentration cannot be identified with the critical micelle concentration as defined by Debye [18]. Further, as a number of the published experimental methods for the determination of the critical micelle concentration yield results indicative of the concentration at which micelles begin to form (that is, even below Debye's critical micelle concentration), this identification would be less justified.

The method devised for estimating the monomer saturation concentration is based on the experiments of Corrin and Harkins [20] and Michaelis [19]. Michaelis observed that the absorption of toluidene blue at $630 m\mu$ is markedly affected by the presence of colloidal materials, among these being the micelles of sodium oleate and Aerosol 22. Typical plots of absorbance ($-\log T$), at constant concentration of toluidene blue, as a function of concentration of sodium dodecyl sulfate are shown in figure 1. The absorbance in region A, in which no micelles are present, is sensibly a constant. In region B, the absorbance undergoes a marked change. In region C, in which micelles are known to be present, the absorbance is once more almost constant.

That region B is the region of micelle formation is evident from the following considerations. Let N_0 be the number of dye molecules per unit volume of

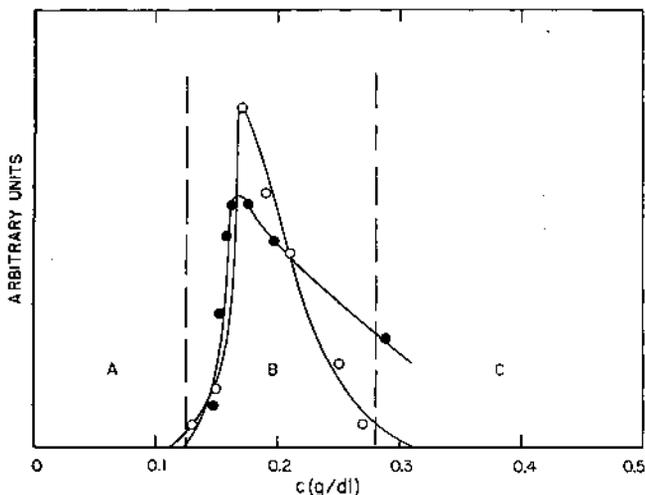


FIGURE 2. $\Delta(c_m/c)/\Delta c$ versus c as obtained from calculations of Debye for the case $n=65$, and the observed $\Delta(-\log T)/\Delta c$ versus c .

Hollow circles represent $\Delta(-\log T)/\Delta c$ versus concentration of sodium dodecyl sulfate in distilled water. Black circles indicate $\Delta(c_m/c)/\Delta c$ versus c .

solution, N_m/N_0 the fraction of dye molecules associated with micelles, and N_1/N_0 the fraction not associated with micelles. Assuming that an equilibrium exists between dye molecules associated with micelles and those not, N_m/N_0 should be a function of c_m/c . The observed behavior of the absorbance during a dilution, at constant dye concentration, can then be represented by an equation of the form

$$-\log T = k \frac{N_1}{N_0} + k' \frac{N_m}{N_0} \quad (5)$$

When $N_m/N_0=0$, $-\log T=k$ (region A). When $N_m/N_0=1$, $-\log T=k'$ (region C). Region B is then that in which N_m/N_0 goes from 0 to 1, this change arising from the rapid change of c_m/c in the region of micelle formation.

Figure 2 shows a plot of $\Delta(c_m/c)/\Delta c$ versus c as obtained from calculations of Debye [18] for the case $n=65$, and the observed $\Delta(-\log T)/\Delta c$ versus c . The similarity in the general nature of the curves strongly indicates that a close relationship exists between the observed absorbance and c_m/c .

All of the transmission data were obtained with a Coleman model No. 2 Universal Spectrophotometer set at 630 $m\mu$. A known volume of detergent solution of concentration about twice the critical micelle concentration, and containing 0.001 g/dl of toluidene blue was placed in a Nessler tube, which fit into the cell carriage of the spectrophotometer. Dilutions were made by adding known volumes of distilled water or the appropriate sodium chloride solution; they too contained 0.001 g/dl of toluidene blue. After each addition of diluent the solution was stirred and a transmission measurement made.

The identification of the concentration at point D of figure 1 with the monomer saturation concentration would appear to be justified in the light of the following qualitative considerations. As dilution oc-

curs in region C, the absorbance decreases slightly indicating a slight decrease in the ratio N_m/N_0 . This is associated with the decrease in c_m/c that occurs simply as a dilution effect in the region well above micelle formation. However, at point D, c_m/c begins to decrease much faster than can be attributed to dilution only. This must then correspond to the upper limit of the region of micelle formation. If the region of micelle formation is defined as being that in which the fraction of added detergent going into micelles goes from 0 to 1, then it is apparent that D is at the monomer saturation concentration. The point D, at each sodium chloride concentration, was visually estimated from a plot similar to those shown in figure 1. It was taken as that concentration at which, on dilution, the curve begins to deviate from linearity. Choosing a monomer saturation concentration significantly lower than D results in reduced specific viscosity, $(\eta_{rel}-1)/c$, versus concentration of micelle curves that deviate markedly from linearity at low concentrations. Choosing a monomer saturation concentration moderately higher than D causes a negligible change in the intrinsic viscosity. The critical micelle concentrations of sodium dodecyl sulfate as obtained by Corrin and Harkins [20] at various sodium chloride concentrations fall approximately in the center of the regions of micelle formation as determined by this method. The estimated monomer saturation concentrations C_s are indicated in table 1.

4. Discussion

The viscosities of sodium dodecyl sulfate solutions relative to the monomer saturation concentration (η_{rel}) are shown graphically in figure 3. It is to be observed that, at least up to 0.12 N , the presence of added neutral electrolyte lowers the relative viscosity curve, the effect becoming smaller with each addition. The reduced specific viscosities, $\eta_{rel}-1/C_m$, are shown in figure 4. The intrinsic viscosity of the micelles in water is 0.065 dl/g. However, in solvents of increasing salt concentration, it decreases to a limiting value of slightly less than 0.035 dl/g. This trend is shown in figure 5.

The existence of a charge on the kinetic units in these solutions eliminates the possibility of interpreting these data solely as a decrease in the axial ratio of the micelles. The viscosity of dilute solutions of charged spheres has been treated by Smoluchowski [21] and Krasny-Ergen [22]. Both arrived at substantially the same equation, which predicts that the electroviscous effect can be vanishingly small by the addition of neutral electrolyte to the solution. The contribution of the electroviscous effect is such as to increase the relative viscosity of the solutions, thus resulting in a larger intrinsic viscosity than would be measured in the absence of any charge effects. Figures 3, 4, and 5 can be satisfactorily interpreted from this point of view, the limiting value of the intrinsic viscosity being that for the micelle when the electroviscous effect has become negligibly small.

It is also possible to interpret such data, at least qualitatively, from the point of view of a desolvation

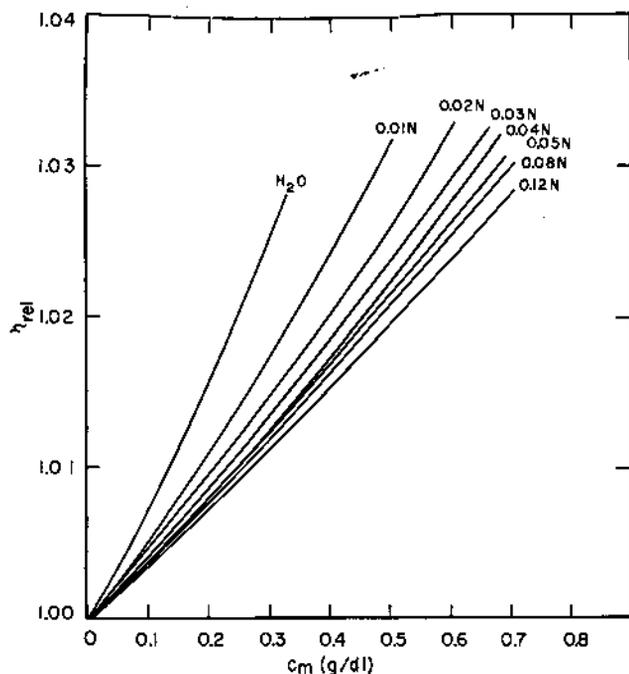


FIGURE 3. Relative viscosities of solutions of sodium dodecyl sulfate in distilled water and aqueous sodium chloride as a function of c_m .

In each solvent, the viscosities are relative to the monomer saturation concentration.

process [23]. Such an approach is particularly appropriate to the consideration of aqueous solutions of micelles that have a lyophilic surface. Experiments of McBain [24] have shown that potassium laurate molecules are hydrated to the extent of about 10 molecules of water per soap molecule. Presumably then the micelle, too, could be hydrated. If the micelle is hydrated, thus increasing its kinetic volume and intrinsic viscosity, then the addition of neutral electrolyte would tend to dehydrate the micelle until some limiting volume is reached corresponding to a dehydrated micelle.

From either the charge or solvation considerations, the limiting value of the intrinsic viscosity, as the electrolyte concentration is increased, should be determined by the nature of the micelle exclusive of such effects. It remains to consider the significance of a limiting value of the intrinsic viscosity of slightly less than 0.035 dl/g.

From eq 4, it is seen that the intrinsic viscosity of rigid, noninteracting spheres whose density is unity, is equal to 0.025 dl/g. Since most of the volume of any shape of micelle proposed for sodium dodecyl sulfate is occupied by dodecyl chains in a liquid-like array, it is reasonable to assume that the density of the micelle should be fairly close to that of liquid dodecane, approximately 0.75 at 20° C. Substitution of this value for d in eq 4 gives $[\eta]=0.033$ dl/g for spherical micelles. This is to be compared with the limiting value of 0.035 dl/g that has been obtained in these experiments.

Admittedly this close agreement between the observed and theoretical intrinsic viscosity rests on

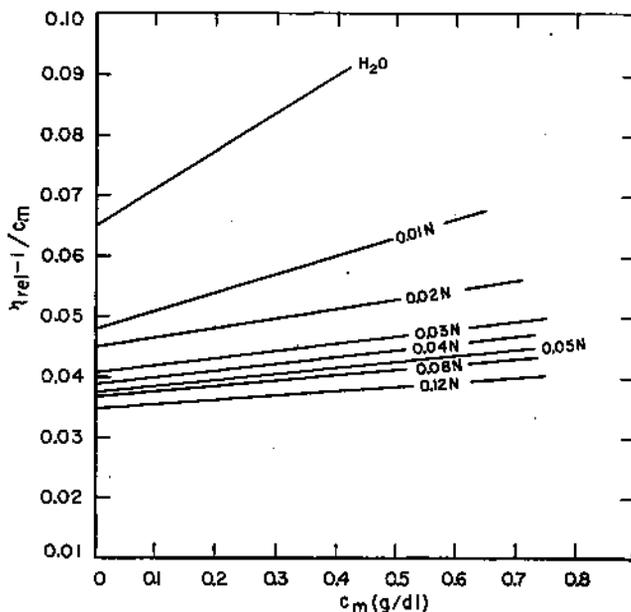


FIGURE 4. Reduced specific viscosities of sodium dodecyl sulfate solutions as a function of c_m .

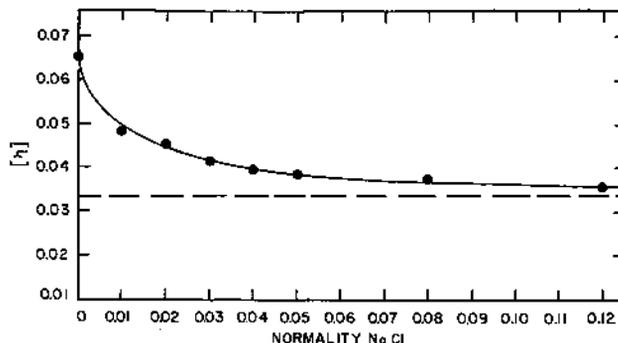


FIGURE 5. Dependence of the intrinsic viscosity of sodium dodecyl sulfate micelles on concentration of sodium chloride.

The broken line represents the calculated limiting value for spherical micelles, 0.033 dl/g.

the assumption that the density of the micelles is 0.75. However, additional evidence for the existence of spherical micelles in these solutions is to be obtained from the data. Previous work [18, 13] has indicated that as electrolyte is added to micellar solutions, not only does the region of micelle formation shift to lower concentrations, but the molecular weight of the micelles increases. If this actually occurs, and the micelles herein considered are rods or cylinders having a constant thickness as has been proposed for other detergents, then the axial ratio of the micelles must increase with increasing salt concentration. Such behavior would be evidenced by a corresponding increase in the intrinsic viscosity. This has not been observed.

In conclusion, it is necessary to point out that the assignment of spherical shape to the micelles of sodium dodecyl sulfate has been made on the basis of viscometric data. It is possible that other experimental techniques may favor a different inter-

pretation. Further, the interpretation presented here does not imply the micelles of all detergents are spherical. The molecules of sodium dodecyl sulfate have a very simple structure and shape. However, different detergent molecules may find it sterically or energetically impossible to agglomerate into spherical clusters. It must also be remembered that the data considered in this paper were all obtained from solutions no more concentrated than 0.8 percent in detergent and 0.12 *N* in sodium chloride. An extension of these results to systems having significantly higher concentrations of either would probably be unjustified. Factors other than those considered here would surely come into play. It might, for instance, be energetically more favorable for a large number of small, spherical micelles, close enough for their gegenion clouds to overlap, to coalesce with the formation of a few larger micelles which would probably not be spherical. However, Brady [11] is able to interpret his X-ray diffraction data for 14.71 and 29.42 percent sodium dodecyl sulfate solutions by utilizing the concept of small, spherical micelles.

5. References

- [1] F. Krafft, Ber. deut. Chem. Ges. **29**, 1328 (1896).
- [2] J. W. McBain, in Colloid Chemistry, edited by J. Alexander, **5**, p. 102 (Reinhold Publishing Corp., New York, N. Y., 1944).
- [3] A. E. Alexander and P. Johnson, Colloid Science, **II**, p. 669 (Oxford University Press, London, 1949).
- [4] J. W. McBain, Colloid Science, p. 255 (D. C. Heath & Co., Boston, 1950).
- [5] G. S. Hartley, Aqueous Solutions of Paraffin-Chain Salts, (Hermann et Cie, Paris, 1936).
- [6] G. S. Hartley, B. Collie, and C. S. Somis, Trans. Faraday Soc. **32**, 795 (1936).
- [7] K. Hess, Fette u. Seifen, **49**, 81 (1942); K. Hess and J. Gundermann, Ber. deut. Chem. Ges. **70**, 1800 (1937).
- [8] W. Philippoff, Kolloid-Z. **96**, 255 (1941); J. Colloid Sci. **5**, 169 (1950).
- [9] H. Kiessig, Kolloid-Z. **96**, 252 (1941); J. Stauff, Kolloid-Z. **89**, 224 (1939); **96**, 244 (1941); S. S. Marsden and J. W. McBain, J. Phys. & Colloid Chem. **52**, 110 (1948); W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. **68**, 220 (1946).
- [10] W. D. Harkins, J. Chem. Phys. **16**, 156 (1948); R. W. Mattoon, R. S. Stearns, and W. D. Harkins, J. Chem. Phys. **16**, 644 (1948).
- [11] G. W. Brady, J. Chem. Phys. **19**, 1547 (1951).
- [12] M. L. Corrin, J. Chem. Phys. **16**, 844 (1948).
- [13] P. Debye and E. W. Anacker, J. Phys. & Colloid Chem. **55**, 644 (1951).
- [14] L. Shedlovsky, Ann. N. Y. Acad. Sci. **46**, Art. 6, 427 (1946).
- [15] J. F. Swindells, J. R. Coe and T. B. Godfrey, J. Research NBS **48**, 1 (1952) RP2279.
- [16] G. Barr, A Monograph of Viscometry (Oxford University Press, London, 1931).
- [17] K. A. Wright and H. V. Tartar, J. Am. Chem. Soc. **61**, 544 (1939).
- [18] P. Debye, Ann. N. Y. Acad. Sci. **51**, Art. 4, 575 (1949).
- [19] L. Michaelis, J. Phys. & Colloid Chem. **54**, 1 (1950).
- [20] M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc. **69**, 683 (1947).
- [21] M. von Smoluchowski, Kolloid-Z. **18**, 194 (1916).
- [22] W. Krasny-Ergen, Kolloid-Z. **74**, 172 (1936).
- [23] H. R. Kruyt, Colloid Science, **II**, p. 209, (Elsevier Publishing Co., New York, N. Y., 1949).
- [24] J. W. McBain, J. Kawakami, and H. P. Luca, J. Am. Chem. Soc. **55**, 2762, 2763 (1933).

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