Estimation of Micellar Charge from Conductivity Data of Aqueous Detergent Solutions

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(Received July 20, 1961)

The micellar molecular weight and the critical micelle concentration (CMC) are essential quantities in the study of the physicochemical properties of detergents. There are a number of methods for determining the CMC, while only a few methods are available for estimating the micellar molecular weight. This is true because of the complex nature of detergent solution, which contains the single detergent ion and the gegen ion in addition to the micellar aggregate in the concentration above the CMC.

The light scattering method is the most profitable one and is widely employed for the measurement of the micellar molecular weight. It is of interest, however, to estimate the micellar molecular weight from a measurement other than that of light scattering. Some authors have attempted the estimation of micellar size from the measurement of the diffusion coefficient¹⁾, and attempts to determine the micellar charge have also been made by using the data of conductivity²⁾ and cataphoresis³⁾.

Since the measurement of conductivity has widely been employed for study of the solutions of ionic detergent, it is advantageous to estimate the micellar charge or the micellar aggregation number by using the conductivity data if possible. Therefore, we have started to obtain a method for determining the micellar charge based on assumptions somewhat different from those of the early studies²,³⁾.

For simplicity we assume, as did, e.g., Hutchinson²⁾, that above the CMC there is only one kind of micelle, containing a n unit of detergent ion and possessing a charge Z_m, and assume that the concentration of detergent ion in the micellar form is $C-C_m$, where C is the concentration in the gram formula weight per liter and C_m, the critical micelle concentration. It is well known that below the CMC the equivalent conductivity, Λ, of the ionic detergent solution is linear against the ionic strength, I, of the solution:

$$\Lambda=\Lambda_o-\alpha\sqrt{I} \tag{1}$$

$$I=\frac{1}{2}\sum_i C_i Z_i^2 \tag{2}$$

where Λ_o is the equivalent conductivity at infinite dilution, α, a constant for a given detergent, and C_i and Z_i, the concentration and valency of ith ion respectively. Here we assume that in dilute solutions Eq. 1 holds, even in concentrations above the CMC. This involves believing that an abrupt change in conductivity just above the CMC is to be attributed to the presence of the high valent micellar ion, which increases the ionic strength of the detergent solution.

Let us consider an ionic detergent $D_{\nu_d}^{z_d}G_{\nu_g}^{z_g}\rightleftarrows\nu_d D^{z_d\pm}+\nu_g G^{z_g\mp}$, where D and G denote the detergent ion and the gegen ion respectively.

At the CMC,

$$\Lambda_m=\Lambda_o-\alpha\sqrt{I_m} \tag{3}$$

where m refers to the CMC. By comparing Eq. 1 with Eq. 3 we obtain

$$(\Lambda_o-\Lambda/\Lambda_o-\Lambda_m)^2=I/I_m \tag{4}$$

In the concentration above the CMC,

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1) D. Stigter, R. J. Williams and K. J. Mysels, *J. Phys. Chem.*, **59**, 330 (1955); G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc.*, **A168**, 420 (1938); M. E. L. McBain, *J. Phys. Chem.*, **48**, 237 (1944), etc.

2) P. van Rysselberghe, *J. Phys. Chem.*, **48**, 62 (1944); E. Hutchinson, *J. Colloid Sci.*, **9**, 191 (1954).

3) D. Stigter and K. J. Mysels, *J. Phys. Chem.*, **59**, 45 (1955).

the concentration of micelle$=\nu_d(C-C_m)/n$ (5a)

the concentration of the single detergent ion

$$=\nu_d C_m \quad (5b)$$

the concentration of the gegen ion

$$=\nu_g C-(C-C_m)(Z_d-Z_m/n)\times(\nu_d/Z_g) \quad (5c)$$

The ratio of the fixed gegen ion to micelle was taken into account in Eq. 5c.

The ionic strengths of the solutions above and at the CMC are therefore given as follows:

$$2I=\{C(Z_g+Z_c)+C_m(Z_d-Z_c)\}\nu_d Z_d \quad (6)$$

$$Z_c=\{Z_m{}^2-Z_g(nZ_d-Z_m)\}/nZ_d \quad (7)$$

$$2I_m=(Z_g+Z_d)\nu_d Z_d C_m \quad (8)$$

Substituting Eqs. 6 and 8 into Eq. 4,

$$(\Lambda_o-\Lambda/\Lambda_o-\Lambda_m)^2 =\{(Z_d-Z_c)+(Z_d+Z_c)C/C_m\}/(Z_g+Z_d) \quad (9)$$

The last term on the right hand side of Eq. 7,

$$r=(nZ_d-Z_m)/nZ_d \quad (10)$$

expresses the ratio of the charge of the fixed gegen ion to that of the micelle. If r is zero and, consequently, Z_m is nZ_d, Z_c becomes nZ_d, which is the charge of the micelle having no fixed gegen ions. It may be pointed out here that we shall be able to obtain a similar expression with Eq. 4 for other properties of a detergent solution, e.g.,

$$(\ln f_g/\ln f_{gm})^2=I/I_m \quad (11)$$

where f_g denotes an activity coefficient of the gegen ion. But, unfortunately, we have no exact data on f_g.

Check of the Theory and Discussion

The conductivity data employed in the estimation of the micellar charge were taken from those reports which gave numerical data[4-7], although a number of studies have already been carried out for the conductivities of ionic detergent solutions.

In Figs. 1, 2 and 3, the calculated values of $(\Lambda_o-\Lambda/\Lambda_o-\Lambda_m)^2$ are plotted against C/C_m. The linearity of these lines is satisfactory to some extent above the CMC. The deviation from linearity appearing in higher concentrations probably comes from the assumption of the limiting law as expressed in Eq. 1. This

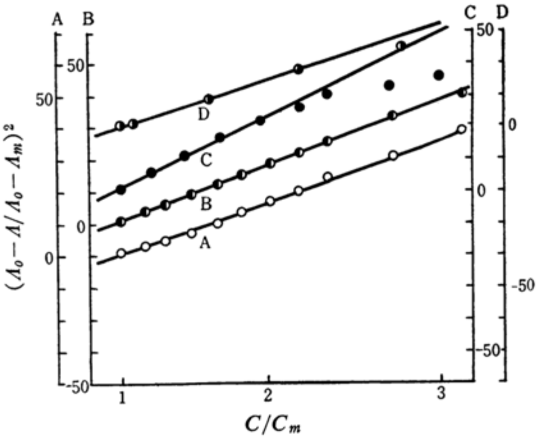

Fig. 1. Test of Eq. 9. A; silver dodecyl sulfate, B; sodium dodecyl sulfate, C; sodium tetradecyl sulfate, D; sodium hexadecyl sulfate.

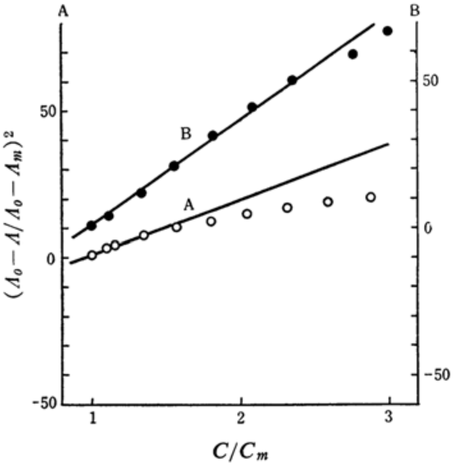

Fig. 2. Test of Eq. 9. A; sodium dodecyl sulfonate, B; sodium tetradecyl sulfonate.

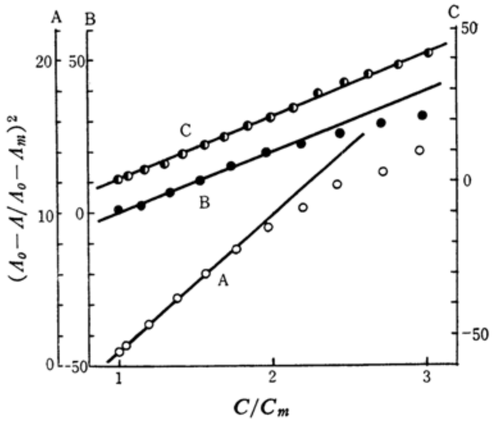

Fig. 3. Test of Eq. 9. A; trimethyl dodecylammonium sulfate, B; dodecylammonium chloride, C; trimethyl octadecylammonium chloride.

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[5] K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, *J. Am. Chem. Soc.*, 61, 549 (1939).

[6] G. L. Brown, P. F. Griezer and C. A. Kraus, ibid., 71, 95 (1949).

[7] J. F, Voekes and H. V. Tartar, *J. Phys. Chem.*, 59, 1190 (1955).

TABLE I. MICELLAR CHARGES OBTAINED FROM CONDUCTIVITY DATA AND MICELLAR AGGREGATE NUMBERS OBTAINED FROM LIGHT SCATTERING DATA

Detergent	CMC, mol./l.	Temp.	Z_c	Ref.	Temp.	n_l	Ref.	r
SDS	6.4×10^{-3}	40	37	4)	23	40	9)	0.04
STS	3×10^{-3}	40	49	4)	23	43	8)	
SHS	5.76×10^{-4}	40	29	4)				
AgDS	6.4×10^{-3}	40	33	4)				
SDS*	1.26×10^{-2}	40	37	5)	40	45	9)	0.09
STS*	2.7×10^{-3}	40	70	5)	60	80	8)	0.06
DAC	1.48×10^{-2}	25	39	6)		55	10)	0.15
TMOAC	3.4×10^{-4}	25	42	6)				
TMDAS	1.64×10^{-2}	25	25	7)	23	65	8)	0.38

SDS: Sodium dodecyl sulfate; STS: Sodium tetradecyl sulfate; SHS: Sodium hexadecyl sulfate; AgDS: Silver dodecyl sulfate; SDS*: Sodium dodecyl sulfonate; STS*: Sodium tetradecyl sulfonate; DAC: Dodecylammonium chloride; TMOAC: Trimethyl octadecylammonium chloride; TMDAS: Trimethyl dodecylammonium sulfate.

agrees well with the result that the reduced concentration, C/C_m at which the deviations are observed to begin becomes lower as the CMC of the detergent solution increases. The value of Z_c may be obtained from the slope of each linear portion according to Eq. 9.

Table I shows the value of Z_c and r, together with the value of n_l, the micellar aggregation number observed by means of the light scattering technique[8-10]. r was calculated from Eqs. 7 and 10 by using the value of n_l in place of n in these equations. As is seen in this table, the values of the Z_c of anionic detergent are almost the same as those of n_l. This would suggest that the micellar aggregate of the anionic detergent ion behaves as if it were *a* polyvalent ion with few fixed gegen ions.

Thus, Z_c gives approximately the micellar aggregation number; we can therefore estimate the micellar aggregation number from the conductivity data as described in the present study. We were unable to obtain a linear portion near the CMC in the plot, $(\Lambda_o-\Lambda/\Lambda_o-\Lambda_m)^2$ vs. C/C_m, for sodium decyl sulfonate. This probably comes from the fact that the CMC of sodium decyl sulfonate is relatively high, 6.25×10^{-2} mol./l., where the limiting law does not hold any more. The values of r for cationic detergents are somewhat higher than those for anionic detergents. This agrees with the conclusion obtained by Hartley[11].

Summary

An equation relating the micellar charge to the conductivity data was derived for the ionic detergent solutions. It was found that the calculated values of the micellar charge were approximately the same as the micellar aggregation number observed by means of the light scattering technique. The ratio of the fixed gegen ion to the micelle was also estimated.

The authors wish to express their thanks to Professor Ryohei Matuura of this department for his kind advice and discussion in the course of this study.

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