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Electrophoretic Behavior of Micelles of a Polyether-sulfate Type Surfactant

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The electrophoretic properties of the micelle of sodium dodecyltrioxyethylene sulfate have been studied in the presence of various types of inorganic z_+-z_- electrolytes and in the presence of organic electrolytes (RNH_3Cl and RCOONa) of various sizes. The effect of the type of electrolytes on the zeta potential of the micelle, ζ, is similar in tendency to the effect to be expected on the basis of the Gouy-Chapman equation for spherical colloid particles. The valence of counter-ions has a considerable effect on ζ, but that of the co-ions has only a slight effect. With respect to the size of ions, counter-ions (RNH^+) appreciably influence the potential of the micelle, whereas co-ions ($RCOO^-$) influence the potential almost not at all. The value of ζ slightly increases, and then steeply decreases, with an increase in the size of the cations through a maximum value.

In a previous work[1] studies have been made of the effects of small electrolyte ions and long-chain alkyl ions on the surface potential of the micelle, ψ_0, of dimethyldodecylamine oxide by means of potentiometric titrations. The results have shown that the effect of small ions on ψ_0 is in accord with the effect predicted on the basis of the Gouy-Chapman equation for spherical colloid particles, while the effect of long-chain alkyl ions is directly related to their charge properties.

In the present work the zeta potential of the micelle, ζ, of sodium dodecyltrioxyethylene sulfate (SDPS-3), $C_{12}H_{25}O(CH_2CH_2O)_3SO_3Na$, has been studied by electrophoretic measurements in the presence of various electrolytes in order to learn the effect of the type of electrolytes on ζ. The reason for the choice of SDPS-3 was that the surfactant is dissolved in water in the presence of any types of electrolytes used and is, therefore, fit for the purposes of the present experiment. Further, the effect of the size of cationic and anionic ions on ζ has also been examined using a series of alkylamine hydrochlorides or sodium alkanoates.

Experimental

Materials. Sodium dodecyltrioxyethylene sulfate (SDPS-3) was synthesized by the sulfation of dodecyl trioxyethylene ether by the procedure described in a previous paper.[2] The dodecyl trioxyethylene ether, $C_{12}H_{25}O(CH_2CH_2O)_3H$, was prepared from dodecyl alcohol of a high purity by the addition of ethylene oxide and was pruified by fractional distillation to remove polyethylene glycol and higher and lower homologues. The number of oxyethylene units per molecule for the distilled ether was found, from its hydroxyl value, to be 3.05. The sample of SDPS-3 was purified by the ion-exchange method of Ginn and Church.[3] All of the inorganic electrolytes used in this experiment were of a guaranteed reagent grade. The short-chain alkylamine hydrochlorides and sodium alkanoates, which had been obtained from the Tokyo Kasei Kogyo Co., were also of a guaranteed reagent grade.

Electrophoresis. The electrophoretic measurements were carried out at 25°C with a Tiselius-type apparatus, Hitachi Model HTB-2A. The concentrations of SDPS-3 in both the upper and lower layers of the cell were taken to be higher than the critical micelle concentration in order to avoid the dissociation of the micelle into the monomers at the moving boundary;[4,5] the concentrations were taken to be 0.2 g/100 m*l* in the upper layer and 1.0 g/100 m*l* in the lower layer. An electrolyte was then added to give the solution an ionic strength of 0.10. The electrophoretic mobility of the micelle, U_M, was calculated from the velocities of the

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[1] F. Tokiwa and K. Ohki, *J. Colloid and Interface Sci.*, **27**, 247 (1968).

[2] F. Tokiwa and K. Ohki, *J. Phys. Chem.*, **71**, 1343 (1967).

TABLE 1. ELECTROPHORETIC DATA FOR SDPS-3 MICELLES IN THE PRESENCE OF VARIOUS TYPES OF ELECTROLYTES AT AN IONIC STRENGTH OF 0.10 AT 25°C

Type of electrolyte	Electrolyte	pH	$-U_M$[a) $\times 10^4$ cm^2/V·sec	$-\zeta$ mV	$-\sigma_s \times 10^{-4}$ esu/cm^2
1-1	NaCl	6.2	2.86	52	1.8
1-2	Na_2SO_4	6.3	2.92	53	1.6
1-3	Na_3PO_4	11.6	3.14	57	1.6
2-1	$MgCl_2$	6.2	1.62	29.6	1.15
2-2	$MgSO_4$	6.2	1.80	32.9	1.18
3-1	$AlCl_3$	3.2[b)	0.71	13.0	0.42
3-2	$Al_2(SO_4)_3$	3.4[b)	0.76	13.9	0.44[c)

a) The average value of three measurements.
b) At this pH the ion present in the solution is considered to be Al^{3+}.
c) Estimated from the σ_s *vs.* ζ curves for 3-1 and 3-3 electrolytes.

ascending and descending boundaries, V_a and V_d, by the equation[4,6]:

$$U_M = V_d\tau^\beta - \frac{V_a\tau^\alpha - V_d\tau^\beta}{(T_M{}^\beta/T_M{}^\alpha) - 1} \qquad (1)$$

where T_M is the transference number of the micelle, τ is the specific conductance of the solution, and where α and β superscripts refer to the upper and lower layers respectively.

Results and Discussion

The Effect of the Type of Electrolytes. Table 1 summarizes the electrophoretic mobilities, U_M, of SDPS-3 micelles in the presence of various types of inorganic electrolytes at an ionic strength of 0.10. The zeta potential of the micelle, ζ, can be evaluated from U_M by the numerical computation developed by Wiersema *et al.*[7] on the assumptions that, for example, the interaction between micellar particles is negligible, that the micelle may be treated as a rigid sphere, and that the charge of the micelle is uniformly distributed on the surface. This numerical computation is rather elaborate. However, the relation between ζ and U_M becomes linear when the value of U_M is small; the Henry equation[8] may then be used to evaluate the zeta potential:

$$\zeta = \frac{6\pi\eta}{D\cdot f(\kappa r_0)} U_M \qquad (2)$$

where $f(\kappa r_0)$ is Henry's function; κ, the Debye-Hückel parameter; r_0, the radius of the micelle, and η and D, the viscosity and dielectric constant of the medium respectively. The values of ζ obtained from U_M in terms of Eq. (2), assuming that the radius of the micelle is 25 Å in the present case, are also given in Table 1. In the solutions of $MgCl_2$, $MgSO_4$, $AlCl_3$, and $Al_2(SO_4)_3$, the ζ values obtained by Eq. (2) are reliable since the values of U_M are small. In the solutions of NaCl, Na_2SO_4, and Na_3PO_4, on the other hand, the values of U_M are relatively high. In these cases, the use of Eq. (2) will introduce errors into the calculated ζ values. For example, the errors in ζ compared with the numerical calculation are about 9%, 3%, and 1% for the values in the solutions of NaCl, Na_2SO_4, and Na_3PO_4 respectively, when $\zeta = 51$ mV and when $\kappa r_0 = 2.5$ (at a radius of 25 Å and an ionic strength of 0.10).[*1] Henry's approximation (Eq. (2)) is better for 1-2 and 1-3 electrolytes than it is for the 1-1 type; it also happens to be more accurate than Overbeek's approximation.[7,9]

It may be seen in Table 1 that the difference in U_M or ζ among chlorides, sulfates, and phosphates is relatively small (*e.g.*, compare NaCl with Na_2SO_4 and Na_3PO_4), while the difference among sodium, magnesium, and aluminium salts is considerable (*e.g.*, compare NaCl with $MgCl_2$ and $AlCl_3$). Namely, the valence of anions (co-ions) has only a slight influence on U_M or ζ, but the valence of cations (counter-ions) has a considerable influence. These results are similar to those obtained in the previous work studying the effect of electrolyte ions on the surface potential of the micelle, ψ_0, of dimethyldodecylamine oxide.[1]

The surface charge density of the micelle at the plane of shear, σ_s, is given by the equation[10]:

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3) M. E. Ginn and C. L. Church, *Anal. Chem.*, **31**, 551 (1955).

4) F. Tokiwa and K. Ohki, *Kolloid-Z. u. Z. Polymere*, **223**, 38 (1968).

5) T. Nakagawa and H. Inoue, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 636 (1957).

6) F. Tokiwa and K. Ohki, This Bulletin, **41**, 2828 (1968).

7) P. H. Wiersema, A. L. Loeb and J. Th. G. Overbeek, *J. Colloid and Interface Sci.*, **22**, 78 (1966).

8) D. C. Henry, *Proc. Roy. Soc.*, **A133**, 106 (1931).

[*1] Estimated from Fig. 7 in Ref. 7.

9) J. Th. G. Overbeek, *Advan. Colloid Sci.*, **3**, 97 (1950).

10) A. E. Loeb, P. H. Wiersema and J. Th. G. Overbeek, "The Electrical Double Layer Around a Spherical Colloid Particle," M. I. T. Press, Cambridge, Massachusetts (1961).

$$\sigma_s = -\frac{D}{4\pi}\left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_{r=r_s} \tag{3}$$

where ψ is the electrical potential at a certain distance, r, from the center of the particle and where the subscript s denotes values at the plane of shear. To obtain the quantity of $(\mathrm{d}\psi/\mathrm{d}r)_{r=r_s}$ in Eq. (3), we must solve the Poisson-Boltzmann equation for negatively-charged, spherical particles. Loeb *et al.* have solved the equation exactly under different conditions; the results are tabulated in Ref. 10. The results are given as functions of the "reduced distance" ($q_0 \equiv \kappa r_s/\lambda$, where $\lambda^2 = (z_+ + z_-)/2z_+$), the "reduced potential" ($y_0 \equiv e\zeta/\boldsymbol{k}T$), and the valence of positive and negative ions (z_+ and z_-). With the aid of the $I(q_0, y_0, z_+, z_-)$ tables of Loeb *et al.*, Eq. (3) may be rewritten:

$$\sigma_s = \frac{D}{4\pi}\cdot\frac{kT\kappa}{e\lambda}I(q_0, y_0, z_+, z_-) \tag{4}$$

If the values of q_0 and of z_+ and z_- are given, we can obtain the relation between σ_s and y_0, or that between σ_s and ζ, from Eq. (4). Figure 1 shows the relation between σ_s and ζ for negatively-charged, spherical particles with r_s of 25 Å in aqueous solutions of various types of electrolytes at an ionic strength of 0.10.

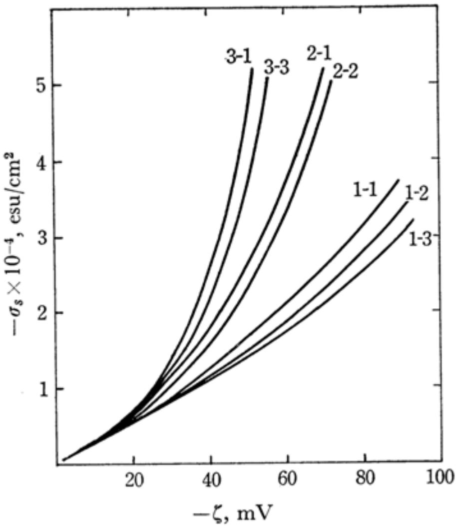

Fig. 1. The σ_s *vs.* ζ curves for a negatively charged, spherical particle with r_s of 25 Å in aqueous solutions of various z_+-z_- electrolytes at an ionic strength of 0.10.

As may be seen in Fig. 1, the relation of σ_s to ζ depends on the type of added electrolytes, especially on the valence of the cationic ions, which may be related to the results given in Table 1. We can now obtain the values of σ_s from ζ for the micelle of SDPS-3 using the curves shown in Fig. 1. The values of σ_s thus obtained are given in Table 1. It may be seen that the values of σ_s are also considerably influenced by the valence of the cations rather than by that of the anions. This implies that the valence of the counter-ions primarily governs the effective charge of the micelle, which must then be reflected to σ_s.

The Effect of the Size of Electrolytes. In Fig. 2 the values of U_M for SDPS-3 in the presence of alkylamine hydrochlorides ($C_nH_{2n+1}NH_3Cl$) or sodium alkanoates ($C_nH_{2n+1}COONa$) are plotted against the alkyl chain length, n. The value of U_M is dependent on the size of the cations and is almost independent of the size of the anions. With the cations, the maximum value appears around $n=3$. It is of interest to note that the value of U_M in the presence of HCOONa is somewhat higher than the value observed in the presence of NaCl or NH_4Cl, even though the same value is to be expected for these three 1-1 electrolytes according to the Gouy-Chapman equation. The reason for this is not clear at present. However, it could be explained by the difference in steric effect between $HCOO^-$ and Cl^- anions or by the effect of the hydration of the anions.

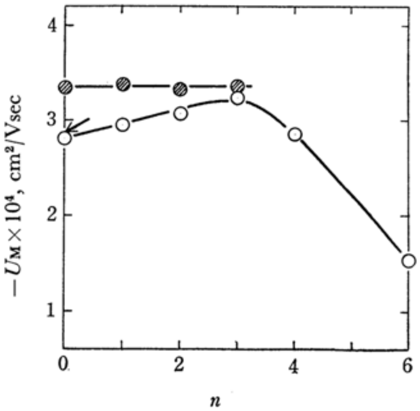

Fig. 2. The values of U_M for SDPS-3 in the presence of $C_nH_{2n+1}NH_3Cl$ (○) or $C_nH_{2n+1}COONa$ (●) at an ionic strength of 0.10 plotted against n. The arrow indicates the value in 0.10M NaCl.

In the general treatment of the distribution of ions in an electrical double layer based on the Boltzmann equation, electrolyte ions are assumed to be point charges instead of ions of a finite volume. A number of authors have attempted to introduce the ionic volume correction into the double-layer theory by rewriting the Boltzmann equation with some form of space restriction factor.[11] Thus, Haydon and Taylor[12] have derived relationships

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11) D. A. Haydon, "Recent Progress in Surface Science," ed. by J. F. Danielli *et al.*, Academic Press, New York (1964), p. 97.

12) D. A. Haydon and F. H. Taylor, *Phil. Trans.*, **A253**, 255 (1960).

corresponding to the Gouy-Chapman equation for symmetrical electrolytes, corrected for the finite ionic volumes. According to their results, the surface potential increases with an increase in the size of the counter-ion when the surface charge density, the radius of the co-ion, and the concentration of the electrolyte are kept constant. With alkylamine hydrochlorides, the initial increase in U_M with an increase in n may be explained by the above result, although the effect is not as large as that to be expected from the calculation of Haydon and Taylor. The steep decrease in U_M after passing through a maximum value may be attributed to a direct influence of added alkylamine hydrochloride with a relatively large alkyl group. Probably, the SDPS-3 surfactant forms a complex with the alkylamine hydrochloride by the partial neutralization of the micellar charge. The fact that SDPS-3 is precipitated in the presence of octylamine hydrochloride supports this complex formation. With sodium alkanoates, the finding that the value of U_M is almost independent of n may be accounted for by the slight effect of anions on the potential of the micelle, as has been described above.

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