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The Structure of an Electrical Double Layer around a Surfactant Micelle

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Electrophoretic measurements have been made of the micelles of dimethyldodecylamine oxide (DDAO) and *N*-dodecyl-β-aminopropionic acid (DAPA), while changing the pH values of the solutions in the presence of 0.10 M sodium chloride. A picture of the structure of the electrical double layer around the micelle at different pH's was then constructed, according to Stern's theory, by a combination of the zeta potential, ζ, calculated from the electrophoretic mobility and the surface potential, ψ_0, obtained previously from the potentiometric titration. With the micelle of DDAO, the thickness of the immobile part of the double layer depends slightly on the pH of the solution and is estimated to be about 5 Å. With the micelle of DAPA, the estimated thickness of the immobile part seems rather high, especially on the alkaline side of the solution. The ζ/ψ_0 ratio for the micelles of DDAO and DAPA depends on the pH of the solution; in the case of DDAO the value of ζ/ψ_0 increases with a decrease in the surface potential.

The structure of an electrical double layer around a charged surfactant micelle is governed in general by the potential at the surface of the micelle, ψ_0, and the distribution of counter-ions and co-ions in the locality of the charged surface. The thickness of the immobile part of the double layer, the distance from the surface of the micelle to the plane of shear, is related in particular to the zeta potential of the micelle, the potential at the plane of shear, ζ. Several studies have been reported of the ζ-potentials of micelles of ionic surfactants,[1-4] but there has been a lack of studies of the thickness of the immobile layer of micelles.[5]

In the present paper, the ζ-potentials of the micelles of the surfactants, whose surface-charge density depends on the pH of the solution, have been discussed in connection with the surface potentials of the micelles previously evaluated from potentiometric data[6,7] in order to obtain knowledge of the thickness of the immobile layer. Stern's theory[8] is used to construct a picture of the structure of the electrical double layer around the micelle. The surfactants studied are a nonionic-cationic surfactant, dimethyldodecylamine oxide (abbreviated as DDAO), and an amphoteric surfactant, *N*-dodecyl-β-aminopropionic acid (abbreviated as DAPA). The surface-charge densities of the micelles depend on the pH of the solutions. With DDAO, the nonionic and cationic forms related by the equilibrium[6]:

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

[2] T. Nakagawa and H. Inoue, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 636 (1957).

[3] H. W. Hoyer and A. Greenfield, *J. Phys. Chem.*, **61**, 735 (1957).

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

[5] D. Stigter, *J. Colloid Interface Sci.*, **23**, 379 (1967).

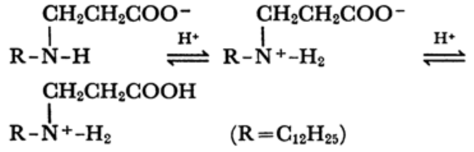
[6] F. Tokiwa and K. Ohki, *J. Phys. Chem.*, **70**, 3437 (1966).

[7] F. Tokiwa and K. Ohki, *ibid.*, **71**, 1824 (1967).

[8] H. R. Kruyt, "Colloid Science," Elsevier Publishing Co., New York (1952).

$$C_{12}H_{25}N(CH_3)_2O \xrightleftharpoons{H^+} C_{12}H_{25}N^+(CH_3)_2OH$$

With DAPA, the anionic and cationic forms are related by the equilibrium[7]:



$$R-\overset{\displaystyle CH_2CH_2COO^-}{\overset{|}{N}}-H \xrightleftharpoons{H^+} R-\overset{\displaystyle CH_2CH_2COO^-}{\overset{|}{N^+}}-H_2 \xrightleftharpoons{H^+} R-\overset{\displaystyle CH_2CH_2COOH}{\overset{|}{N^+}}-H_2 \qquad (R=C_{12}H_{25})$$

Experimental

Materials. The dimethyldodecylamine oxide (DDAO) was prepared by the H_2O_2 oxidation of highly-pure dimethyldodecylamine by the method described in a previous paper.[6] The sample was purified by repeated extraction with petroleum ether and by subsequent recrystallization from a mixture of acetone and benzene. The *N*-dodecyl-β-aminopropionic acid (DAPA) was the same as that used elsewhere.[7] The sodium chloride, hydrochloric acid. and sodium hydroxide were of an analytical reagent grade. The water used in this experiment was distilled and subsequently passed through an ion-exchange column.

Electrophoresis. The electrophoretic measurements were carried out in a Tiselius-type cell using a Hitachi Model HTB-2A Tiselius apparatus equipped with a Schlieren optical system. The concentrations of the surfactant in both the upper and lower layers of the cell were taken to be higher than the critical micelle concentration (CMC) in order to avoid the dissociation of the micelle into the monomers at a boundary.[2,4] The concentration of the supporting electrolyte, sodium chloride, was 0.10 м. The pH of solutions was adjusted with hydrochloric acid or sodium hydroxide, and the pH values of all the solutions were rechecked after measurements.

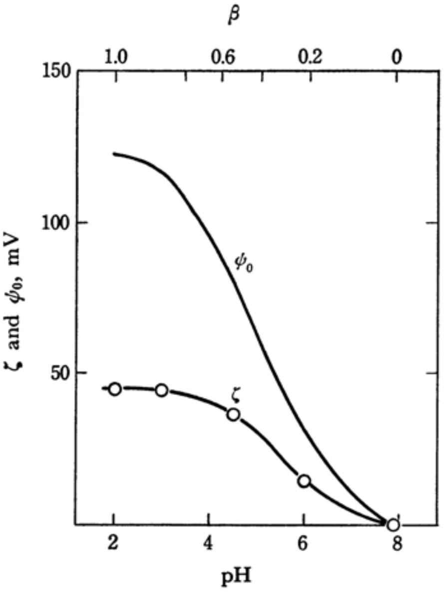


Fig. 1. The values of ζ and ψ_0 for the micelle of DDAO in the presence of 0.10 м NaCl plotted against pH.

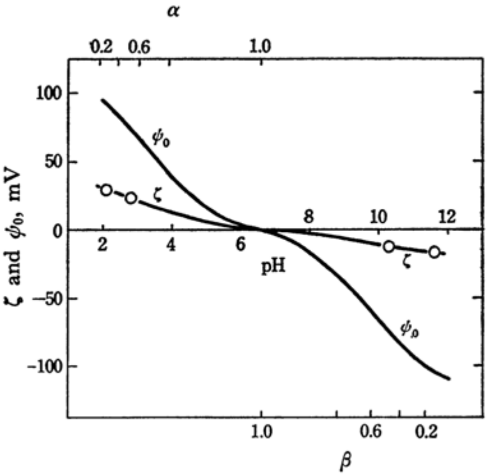


Fig. 2. The values of ζ and ψ_0 for the micelle of DAPA in the presence of 0.10 м NaCl plotted against pH.

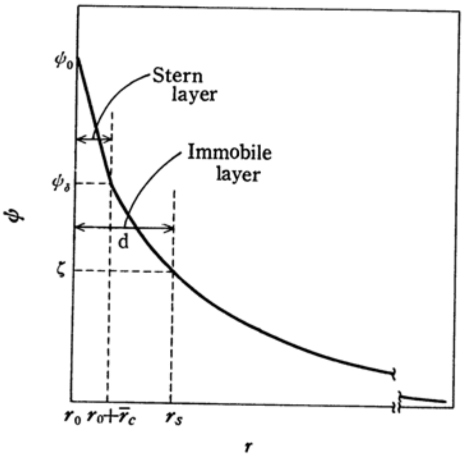


Fig. 3. Schematic representation of the structure of the double layer for the micelle of DDAO at pH 3.0: $\psi_0=117$ mV, $\psi_\delta=73.5$ mV, $\zeta=44.4$ mV, $r_0=29.1$ Å, $\bar{r}_c=1.8$ Å, and $d=5.1$ Å.

Results

In all the systems examined, only one moving boundary was obtained in each of the ascending and descending patterns. The electrophoretic mobility of the micelle, u_M, was calculated from the velocities of the ascending and descending boundaries by applying Dole's theory to the present system.[9,10] The value of u_M was calculated by the equation[2,4]:

$$u_M = X - \frac{Y-X}{(T_M{}^\eta/T_M{}^\alpha)-1} \tag{1}$$

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9) V. P. Dole, *J. Am. Chem. Soc.*, **67**, 1119 (1945).

10) L. G. Longsworth, "Electrophoresis," ed. by M. Bier, Academic Press, New York (1959), p. 91.

Table 1. Electrical properties for the micelle of DDAO in the presence of 0.10 M NaCl

pH	β	$r_0\times10^8$ cm	n	$u_M\times10^4$ $\mathrm{cm^2/V\cdot sec}$	ζ mV	ψ_0 mV	ψ_δ mV	ζ/ψ_0	$d\times10^8$ cm
2.0	1.00	29.5	134	2.55	44.7	122	74.1	0.366	5.2
3.0	0.91	29.1	129	2.54	44.4	117	73.5	0.380	5.1
4.5	0.55	25.4	85.9	2.06	36.3	81.9	59.1	0.443	5.0
6.0	0.21	22.2	67.0	0.81	14.4	30.9	22.2	0.466	4.7
7.9	0.0	22.1	66.5	0	0	0	0	—	—

Table 2. Electrical properties for the micelle of DAPA in the presence of 0.10 M NaCl

pH	α and β	$u_M\times10^4$, $\mathrm{cm^2/V\cdot sec}$	ζ mV	ψ_0 mV	ψ_δ mV	ζ/ψ_0	$d\times10^8$ cm
2.1	$\alpha=0.27$ $(\beta=1.00)$	1.67	29.5	93.0	56.1	0.317	6.0
2.8	$\alpha=0.54$ $(\beta=1.00)$	1.30	22.9	71.4	48.0	0.321	6.9
10.3	$\beta=0.48$ $(\alpha=1.00)$	-0.71	-12.5	-75.0	-44.2	0.167	11.4
11.6	$\beta=0.01$ $(\alpha=1.00)$	-0.93	-16.4	-105	-46.5	0.157	9.2

Assuming $r_0=25$Å and $n=100$.

The details of Eq. (1) and its derivation are described in the Appendix. Tables 1 and 2 give the values of u_M for DDAO and DAPA respectively, calculated in terms of Eq. (1).

On several simplifying assumptions,[1,5,11] the relation between ζ and u_M may be written in the form[12]:

$$\zeta = 6\pi\eta u_M/D\cdot f(\kappa r_0) \tag{2}$$

where $f(\kappa r_0)$ is Henry's function;[14] r_0, the radius of the micelle; κ, the inverse Debye radius, and η and D, the viscosity and the dielectric constant of the medium respetively. The ζ-potentials of the micelles of DDAO and DAPA as calculated by Eq. (1) are plotted in Figs. 1 and 2 respectively, together with the surface potentials of the micelles, ψ_0,[6,7] as a function of the pH of the solutions. In calculating Eq. (2), the r_0 values for DDAO were estimated from the potentiometric data reported previously,[15] and the value for DAPA was assumed to be 25 Å.

Discussion

A schematic representation of the structure of a double layer around a micellar particle according to Stern's model is given in Fig. 3 as a simple illustration. The surface potential, ψ_0, is divided into one potential, ψ_δ, over the diffuse part of the double layer and another, $\psi_0-\psi_\delta$, over the molecular condenser, as is shown in Fig. 3, where ψ_δ is a potential at the surface of the Stern layer.[8]

For the Stern layer, the equation for a spherical condenser may be used to obtain the value of ψ_δ from ψ_0. If one assumes that the Stern layer is the adsorbed monolayer of counter-ions,[16,17] and that, hence, the thickness of the layer is equal to the radius of the counter-ions, $\bar{r}_c$, the value of ψ_δ may be estimated by the equation:

$$\psi_\delta = \psi_0 - \frac{Q}{D}\left(\frac{1}{r_0} - \frac{1}{r_0+\bar{r}_c}\right) \tag{3}$$

where Q is the net charge of the micelle, which is given by $\varepsilon n\beta$ for DDAO and by $\varepsilon n(\beta-\alpha)$ for DAPA, where ε is the elementary charge; n, the number of molecules per micelle; α, the degree of ionization of the carboxyl group, and β, the degree of the protonation of the nitrogen atom. The counter-ion for DDAO is Cl^-, and that for DAPA is Cl^- on the acid side and Na^+ on the alkaline side. A reasonable value of $\bar{r}_c$ is 1.84 Å for Cl^- and 2.17 Å for Na^+.[18] The ψ_δ values for the DDAO micelle at different pH's, as calculated by Eq. (3), are given in Table 1, together with the values of ψ_0, r_0 and n which have previously been obtained from potentiometric titration data in previous works.[6,15] Table 2 also gives the rough ψ_δ values for the DAPA micelle estimated by assuming that $n=100$.

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[11] D. J. Shaw, "Introduction to Colloid and Surface Chemistry," Butterworth & Co., London (1966).

[12] Recently Wiersema *et al.*[13] have reported a more strict method of calculating the ζ-potential of a spherical colloidal particle by using an electronic computer. In the present case, however, the difference between the values obtained from Eq. (2) and their calculated values is not significant since the ζ-potentials are relatively low.

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

[14] D. C. Henry, *Proc. Roy. Soc.*, **A133**, 106 (1931).

[15] F. Tokiwa and K. Ohki, *J. Colloid Interface Sci.*, **24**, 219 (1967).

[16] M. Nagasawa and A. Holtzer, *J. Am. Chem. Soc.*, **86**, 531 (1964); M. Nagasawa, T. Murase and K. Kondo, *J. Phys. Chem.*, **69**, 4005 (1955).

[17] J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y. (1961), p. 85.

[18] C. B. Monk, "Electrolytic Dissociation," Academic Press, New York, N. Y. (1961), p. 271.

For the diffuse layer, a potential, ψ, at a certain distance from the center of a particle, r, may be calculated by Gouy-Chapman's equation for a spherical double layer. With $1/m$ valent electrolyte, Gouy-Chapman's equation is written in the form[19]:

$$r^{-2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)=\frac{4\pi\varepsilon n_0}{D}\left[\exp\left(\frac{\varepsilon\psi}{\boldsymbol{k}T}\right)-\exp\left(-\frac{\varepsilon\psi}{\boldsymbol{k}T}\right)\right] \tag{4}$$

where n_0 is the concentration (number/cm^3) of positive or negative ions in the bulk of the solution. For the sake of convenience, by introducing a dimensionless "reduced potential" y $(=\varepsilon\psi/\boldsymbol{k}T)$ and a "reduced distance" $q(=\kappa r)$ into Eq. (4), we obtain[19]:

$$q^{-2}\frac{\mathrm{d}}{\mathrm{d}q}\left(q^2\frac{\mathrm{d}y}{\mathrm{d}q}\right)=\frac{1}{2}(\mathrm{e}^{y}-\mathrm{e}^{-y}) \tag{5}$$

The solutions of Eq. (5) under different boundary conditions, y_0 and q_0, and using an electronic computer have been given by Loeb *et al.*[19] and are tabulated in Ref. 19. In the present case, y_0 and q_0 are written:

$$y_0=\varepsilon\psi_\delta/\boldsymbol{k}T, \quad \text{and} \quad q_0=\kappa(r_0+\bar{r}_c)$$

Thus, we can construct ψ *vs.* r curves, an example of which for the micelle of DDAO is given in Fig. 3.

The thickness of the immobile part of the double layer, $d(=r_s-r_0)$, may be obtained from the ζ-potential and the ψ *vs.* r curve. The d values for the DDAO micelle at different pH's are given in Table 1; about 5 Å, they depend slightly on the pH of the solution. The thickness obtained here is comparable to that obtained by Stigter for the micelle of sodium dodecyl sulfate (4—5 Å) from the viscosity and the diffusion data.[5] It is of interest to calculate the ratio of ζ to ψ_0 from the present data. The ζ/ψ_0 ratio has been discussed by Davies and Rideal.[20] According to their calculation, the tendency is for ζ/ψ_0 to increase as the surface potential is lowered. The results obtained here agree in tendency with their calculations.

Table 2 gives the rough values of the thickness of the immobile layer for the DAPA micelle. The thickness is roughly 6—7 Å on the acid side and 9—11 Å on the alkaline side, thicker than that for DDAO. The ζ/ψ_0 ratios for DAPA are lower than those for DDAO, especially on the alkaline side. The reason for this is not clear; however, the results probably have some relation with the configuration of charged groups[21] at the surface of the micelle. The charged groups would be located relatively inside the surface of the micell.

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Appendix

An initially sharp boundary between two solutions containing n ion species will generally split, upon the passage of an electric current, into $n-1$ separate boundaries, each moving at a different rate. According to Dole,[9,10] the following polynomials can be derived for each moving boundary:

$$\sum_j\frac{T_j^{\alpha}}{u_j-X_k}=0, \qquad \sum_j\frac{T_j^{\eta}}{u_j-Y_k}=0 \tag{A1}$$

$$k=1,2,3,\cdots,n-1$$

where:

$$\begin{array}{ll} X_1=V^{\alpha\beta}\sigma^{\beta} & Y_1=V^{\alpha\beta}\sigma^{\alpha} \\ X_2=V^{\beta\gamma}\sigma^{\gamma} & Y_2=V^{\beta\gamma}\sigma^{\beta} \\ \cdots\cdots & \cdots\cdots \\ X_{n-1}=V^{\zeta\eta}\sigma^{\eta} & Y_{n-1}=V^{\zeta\eta}\sigma^{\zeta} \end{array}$$

Here T_j and u_j are the transference number and the mobility of j ion species respectively, σ is the specific conductance of the solution, and V is the boundary velocity. The superscripts α, $\beta,\cdots$, η refer to the α, $\beta,\cdots,\eta$ phases, and $\alpha\beta$, $\beta\gamma,\cdots$, $\zeta\eta$ refer to $\alpha\beta,\beta\gamma,\cdots$, $\zeta\eta$ boundaries, respectively. Since the total of each transference number must be unity, *i. e.*, $\sum_j T_j^{\alpha}=1$, and $\sum_j T_j^{\eta}=1$, the solutions of Eq. (A1) become:

$$T_j^{\alpha}=\frac{(u_j-X_1)(u_j-X_2)\cdots(u_j-X_{n-1})}{(u_j-u_1)(u_j-u_2)\cdots(u_j-u_n)} \tag{A2}$$

$$T_j^{\eta}=\frac{(u_j-Y_1)(u_j-Y_2)\cdots(u_j-Y_{n-1})}{(u_j-u_1)(u_j-u_2)\cdots(u_j-u_n)} \tag{A3}$$

The denominators of Eqs. (A2) and (A3) are identical and may be eliminated to give:

$$\frac{T_j^{\alpha}}{T_j^{\eta}}=\frac{(u_j-X_1)(u_j-X_2)\cdots(u_j-X_{n-1})}{(u_j-Y_1)(u_j-Y_2)\cdots(u_j-Y_{n-1})} \tag{A4}$$

In the present system, the ionic species are surfactant monomer (m) and micelle (M) ions, and positive and negative electrolyte ions (Na$^+$ and Cl$^-$). However, since the concentrations of m ions can be assumed to be equal in the initial two phases, we can expect two boundaries to appear, one of which is stationary; in fact, we have experimentally obtained only one moving boundary. Thus, the experession of Eq. (A4) for micelles is simplified to:

$$T_M^{\alpha}/T_M^{\eta}=(u_M-X)/(u_M-Y) \tag{A5}$$

or:

$$u_M=X-\frac{Y-X}{(T_M^{\eta}/T_M^{\alpha})-1} \tag{A6}$$

The X and Y in Eq. (A6) are written in the following forms when an apparatus of the Tiselius type is used.

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[19] A. L. 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).

[20] J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York (1961), p. 140.

[21] K. Durham, Proc. 3rd Intern. Congr. Surface Activity, Collogne, 1960, B/1/3, p. 130.

$$X = V_d\sigma^\eta, \quad \text{and} \quad Y = V_a\sigma^\alpha$$

where V_d and V_a are the velocities of the descending and ascending boundaries respectively. The $T_M{}^\eta/T_M{}^\alpha$ ratio is given by:

$$T_M{}^\eta/T_M{}^\alpha = (C_M{}^\eta/\sigma^\eta)/(C_M{}^\alpha/\sigma^\alpha)$$

where $C_M{}^\alpha$ and $C_M{}^\eta$ are the concentrations of M ions in the upper and lower layers in the cell respectively; they are given by:

$$C_M{}^\alpha = (C - \mathrm{CMC})_\alpha, \text{ and } C_M{}^\eta = (C - \mathrm{CMC})_\eta$$

The values of $C_M{}^\alpha$ and $C_M{}^\eta$ are known, and V_a, V_d, σ^α, and σ^η are all determinable. The u_M values given in Tables 1 and 2 are thus obtained from Eq. (A6).