A Consideration of the Micelle Formation of an Ionic-Nonionic Surfactant through Its Ionization Energy

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It is a widely-accepted concept that the micelle formation of ionic surfactants in aqueous solutions is governed by two factors, the cohesive energy among the hydrocarbon chains and the repulsive electrical energy among the charged heads.[1-3] In previous papers,[3,4] we have discussed the micelle formation of surfactants, such as dimethyldodecylamine oxide[3] and sodium decylbenzene sulfonate,[4] by means of these two factors. With a surfactant whose electrical state depends on the pH of the solution, however, there is yet another way to discuss its micelle formation—through the ionization energies of the micellar and monodispersed species. In the present paper an attempt is made to treat micelle formation in terms of the ionization energy of an ionic-nonionic surfactant. The surfactant studied is dimethyldodecylamine oxide, which can exist in either nonionic or cationic form, depending upon the pH of the solution. These two forms are related by the equation:

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

Figure 1 sets out the relationship between micellization equilibria at $\beta=0$ and $\beta=p$, where β is the degree of ionization of the surfactant. The process 1 represents the micellization in the nonionic form at $\beta=0$. The standard free energy change

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[1] K. Shinoda, "Colloidal Surfactants," Academic Press, New York, N. Y. (1963).

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[3] F. Tokiwa and K. Ohki, *J. Colloid Interface Sci*, **23**, 456 (1967).

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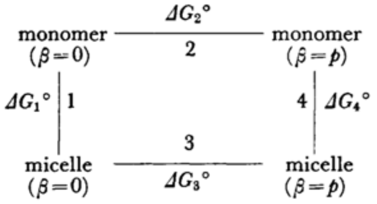

Fig. 1. The diagram of micellization and ionization equilibria.

in micellization per mole, $\Delta G_1°$, is given[5,6] by:

$$\Delta G_1° = \boldsymbol{R}T \ln \mathrm{CMC}_{\beta=0} \tag{1}$$

The process 4 represents the micellization in the cationic form at $\beta=p$, whose free energy change, $\Delta G_4°$, is given by:

$$\Delta G_4° = \boldsymbol{R}T \ln \mathrm{CMC}_{\beta=p} \tag{2}$$

when one assumes that the system is ideal in the presence of excess added salt.[7,8] The processes 2 and 3 represent the ionization of the monomer and micelle, respectively, from $\beta=0$ to $\beta=p$. In the process 2 the free energy change in ionization, $\Delta G_2°$, may be written by:

$$\begin{aligned}\Delta G_2° &= \boldsymbol{R}T\int_{\beta=0}^{\beta=p} \ln K_\mathrm{m}(\beta)\mathrm{d}\beta \\ &= -2.3\boldsymbol{R}T\int_{\beta=0}^{\beta=p} \mathrm{p}K_\mathrm{m}(\beta)\mathrm{d}\beta \end{aligned}\tag{3}$$

where K_m is the ionization constant of the monomer, which, in the present case, is constant independently of β, as may be seen in Fig. 2.[9] Therefore, the right-hand side of Eq. (3) may be reduced to $-2.3\,p\cdot\boldsymbol{R}T\cdot\mathrm{p}K_\mathrm{m}$. In the process 3, the free energy change in ionization, $\Delta G_3°$, may be written by:

$$\begin{aligned}\Delta G_3° &= \boldsymbol{R}T\chi\int_{\beta=0}^{\beta=p} \ln K_\mathrm{M}(\beta)\mathrm{d}\beta \\ &= -2.3\boldsymbol{R}T\chi\int_{\beta=0}^{\beta=p} \mathrm{p}K_\mathrm{M}(\beta)\mathrm{d}\beta \end{aligned}\tag{4}$$

where K_M is the ionization constant of the micelle, which depends on β as is shown in Fig. 2.[9] The χ in Eq. (4) is a correction factor for the ionization energy of the micelle, which may have some relation, for example, with the number of gegenions around the micelle and with the change in micellar-aggregation number with β. In the diagram under consideration, the following energy balance should hold:

$$\Delta G_1° + \Delta G_3° = \Delta G_2° + \Delta G_4° \tag{5}$$

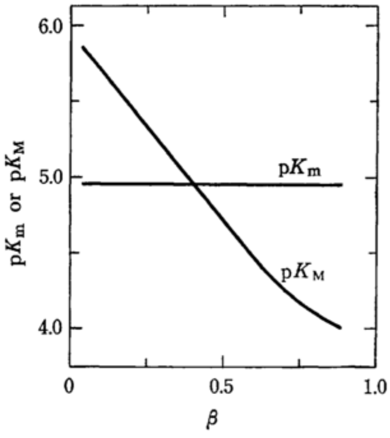

Fig. 2. Values of $\mathrm{p}K_\mathrm{m}$ and $\mathrm{p}K_\mathrm{M}$ as a function of β.

Therefore:

$$\Delta G_4° = \Delta G_1° - \Delta G_2° + \Delta G_3° \tag{6}$$

Table 1 gives the values of χ, which were calculated to satisfy Eq. (6) from the observed values of CMC at different pH values in the presence of 0.10 M NaCl. (The addition of excess salt is required if one is to use Eq. (2) and also obtain a constant value of χ at a constant ionic strength.) The correction factor, χ, is nearly equal to 0.86 and is independent of the pH (or β) value except at a low pH. Thus, the CMC value at a certain degree of ionization, p, may be estimated by the equation:

$$\begin{aligned}\log \mathrm{CMC}_{\beta=p} &= \log \mathrm{CMC}_{\beta=0} \\ &\quad + p\cdot\mathrm{p}K_\mathrm{m} - 0.86\int_{\beta=0}^{\beta=p} \mathrm{p}K_\mathrm{M}(\beta)\mathrm{d}\beta \end{aligned}\tag{7}$$

In Fig. 3 the CMC values obtained from Eq. (7) are plotted against pH in comparison with those experimentally obtained in the presence of 0.10 M NaCl. The similar plots in the absence of added

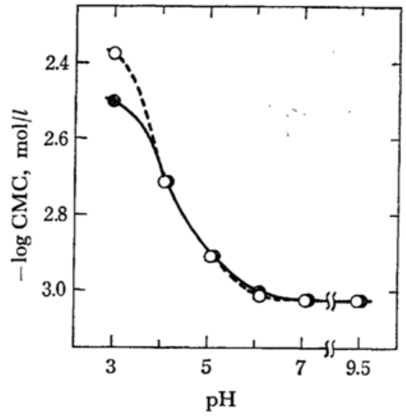

Fig. 3. The CMC *vs.* pH plots obtained from Eq. (7) (○) and from the experiment (◍) in the presence of 0.10 M NaCl.

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Table 1. Variations of $\mathrm{CMC_{obs}}$, $\Delta G_4°$, $(\Delta G_1°-\Delta G_2°+\Delta G_3°)$ and χ with pH

pH	β	$\mathrm{CMC_{obs}}$ mol/$l\times 10^3$	$-\Delta G_4°$ kcal/mol	$-(\Delta G_1°-\Delta G_2°+\Delta G_3°)$ kcal/mol	χ
3.0	0.91	3.16	5.77	$0.36+6.02\chi$	0.89
4.1	0.65	1.94	6.06	$2.13+4.54\chi$	0.86
5.1	0.41	1.24	6.33	$3.73+3.03\chi$	0.86
6.1	0.19	1.00	6.45	$5.18+1.50\chi$	0.85
7.1	0.052	0.95	6.48	$6.13+0.41\chi$	0.86
9.5	0.00	0.95	6.48	$6.48+0.00$	—

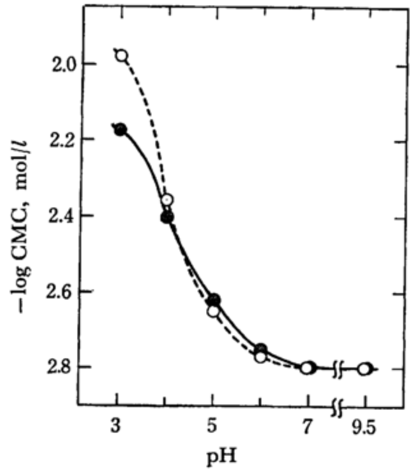

Fig. 4. The CMC *vs.* pH plots obtained from Eq. (7) (○) and from the experiment (●) in the absence of added salt.

salt, obtained by Eq. (7), are shown in Fig. 4. The discrepancy in the calculated CMC values from the observed values at low pH values in the absence of added salt is somewhat larger than that in the presence of excess added salt. Probably, the assumption described in Eq. (2) is no longer reasonable in the absence of added salt, especially in the lower pH region.

From the preceding considerations, it can be said, in conclusion, that the CMC of a surfactant whose ionized state depends on the pH of the solution can be estimated by using the ionization constants of the monomer and micelle of the surfactant. At any degree of ionization, p, the CMC can be expressed by Eq. (7) as long as Eq. (2) is valid.

Experimental

The CMC values at different pH values were determined by the solubilization method using an oil soluble dye, Yellow-OB, as a solubilizate.[9,10] The ionization constants of the monomer and micelle were obtained from the potentiometric titration of the surfactant, the details of which have been presented in a previous paper.[9]

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10) F. Tokiwa, This Bulletin, **36**, 222 (1963).