The Effect of Organic Additives on the Micelle Formation of Dodecylammonium Halides in Aqueous Solutions

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The critical micelle concentration (CMC) of dodecyl ammonium halides and the degree of dissociation of the micelle (α) of dodecylammonium chloride were determined as functions of the concentrations of the organic additives by measuring the conductivity and the emf of the following cell: calomel/1 M-KCl/sample solution/AgCl, Ag. The CMC was raised more in the presence of acetone and dioxane than in that of acetamide, formamide, urea, and methanol, and was diminished by adding alcohols (C_2—C_4). The effect of the alcohols on CMC decreased in the order of the diminished hydration of the counterion, acetone and dioxane were considered to affect the dodecylammonium iodide solution specifically. The dissociation of the micelle was enhanced in the presence of organic additives. Further, we estimated the solubilized amount of the additives from the degree of dissociation of the micelle and attempted to make quantitative estimation of the increment of CMC produced by organic additives.

The micelle formation in an aqueous solution is known to be affected by organic additives, and there have been many investigations concerning the effects of organic additives on the CMC of anionic[1-4] and cationic[1,5,6] surfactants. Shinoda[7] and Shirahama and Kashiwabe[8] explained the decrease in the CMC in the micellar solutions containing alcohols in terms of the solubilization of alcohol into the micelle. On the other hand, some organic additives gave an increment in CMC, and this cannot be explained by their theories. Emerson and Holtzer[1] found qualitative correlations between the hydrophobic nature of an additive and its micellar breaking-up power, but the correlations are limited.

It is well known that the micellar solutions are influenced by changing the counterion. Schick[2] studied the effect of counterion hydration on the CMC and found that the increment in CMC on urea addition increased in the following order: lithium-, sodium- and tetramethyl ammonium dodecylsulfate. He interpreted this order in terms of the structural concept of water.

At present, however, we have not yet obtained enough knowledge to understand the effects of organic additives on the CMC. Therefore, we attempted to study the effects of aprotic and protonic additives on the micellar solutions of dodecylammonium halides by determining their CMC and the degree of dissociation of their micelles, and tried to estimate the solubilized amount from the degree of dissociation.

Experimental

The dodecylammonium chloride (DACl), -bromide (DABr), and -iodide (DAI) were prepared by the neutralization of dodecylamine (bp 100 °C/5 mmHg) with the corresponding hydrohalic acid and were recrystallized five times from ethanol-ether. The organic additives were distilled before use, but urea and acetamide were of a reagent grade and were used without further purification.

The CMC (C) was determined by the electric-conductivity method. The determination of the activity (a) of the counterion was carried out by using the following cell:

$$\text{Hg, Hg}_2\text{Cl}_2\,|\,1\ \text{M-KCl}\,|\,\text{DACl soln.}\,|\,\text{AgCl, Ag}$$

The degree of dissociation of the micelle (α) was then calculated by using Botré *et al.*'s equation:[9]

$$a = \gamma\{C+\alpha(C_t-C)\} \tag{1}$$

where C_t is the concentration of the surfactant. The Silver-silver chloride electrode prepared by the dry method[10] was calibrated by potassium-chloride solution; its activity coefficient, γ, was estimated by means of this equation:[11]

$$\log \gamma = -\frac{A_0\sqrt{C_l}}{1+B_0\sqrt{C_l}} - D_0C_l \tag{2}$$

where C_l is the concentration of potassium chloride, and where A_0, B_0, and D_0 are constants.

These experiments were carried out at 35.0 °C because of the low solubility of DABr at 25.0 °C.

Results and Discussion

The Effect of Alcohol on Micelle Formation. The addition of alcohols to the micellar solution is well known to depress the CMC; however, little attention has been paid to the importance of the counterion with respect to the effects of organic additives. The effects of changing the counterion was studied as one of the primary subjects of this investigation. As illustrated in Figs. 1 and 2, the CMC of dodecylammonium halides

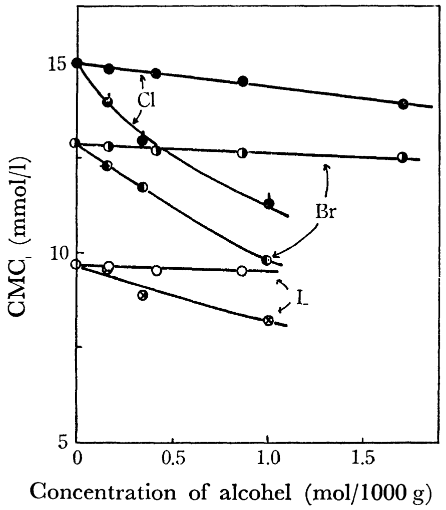

Fig. 1. Effect of ethanol and *n*-propanol on CMC. ●, ◑, ○: ethanol, ●, ◐, ⊗: *n*-propanol

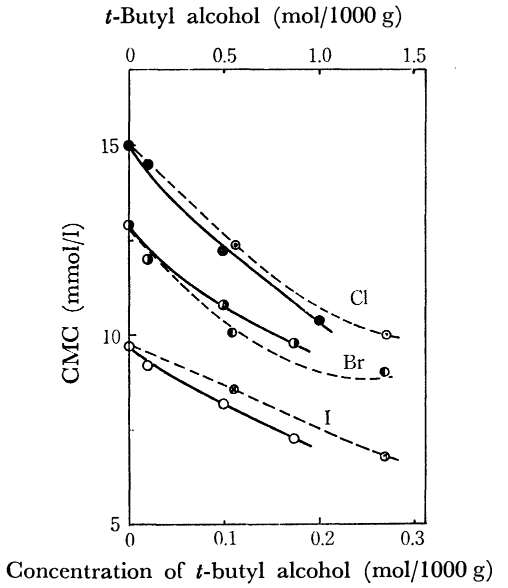

Fig. 2. Effect of butanols on CMC.
——; *t*-butyl alcohol, - - - -: *n*-butanol.

and the effects of alcohols on it decreased in the order of the diminished hydration of the counterion. This order is in line with that of the degree of dissociation of the halide micelles and the salting-out power of the halide anions.[12,13] On the other hand, the depression of the CMC is related to the free energy of the transfer of an alcohol molecule from the water to the micelle phase.[8]

Therefore, the above results suggest that the counterion affects its free energy through the destruction of the water structure around the alcohol molecule and the looseness of the surface charge on a micelle, although the main factor in the depression of the CMC is the carbon number in the alcohol molecule.

The organic additive, in addition to its solubilization effect, modifies the properties of the medium. Figure 3 indicates that the latter effect predominated in the presence of methanol and was influenced almost not at all by changing the counterion.

The Effects of Urea, Formamide, and Acetamide on Micelle Formation. The effect of amide on the CMC has been determined as a function of the amide concentration. The CMC increased with an increase in the urea concentration, and no significant difference in susceptibility to change in the CMC on urea addition was observed at 35.0 °C among the dodecylammonium halides (Fig. 4). It has been reported by Schick, however, that the increment in the CMC of dodecylsulfates at 10—45 °C on urea addition increased in the order of the diminished hydration of the counterion.[2] This may be attributable to the weaker hydration of halide anions compared with that of alkali cations.

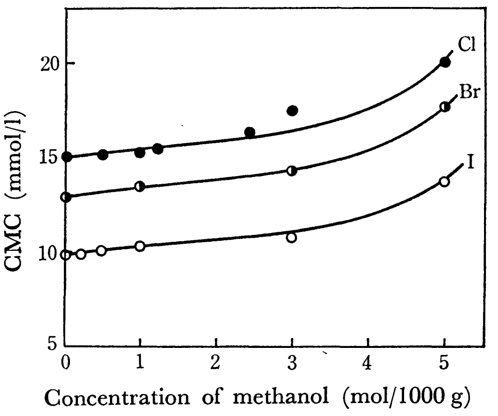

Fig. 3. Effect of methanol on CMC.

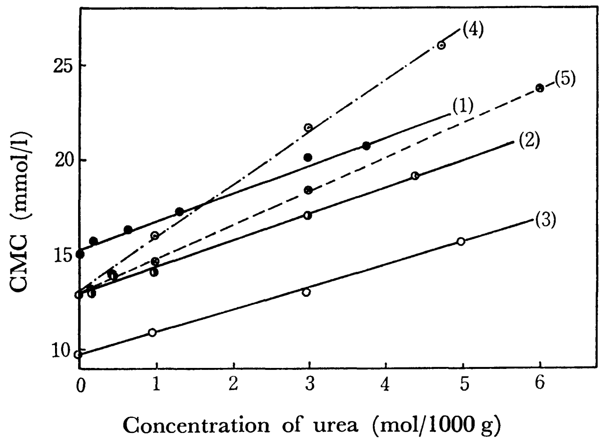

Fig. 4. Effect of amides on CMC.
(1): DACl——urea, (2): DABr——urca, (3): DAI ——urea, (4): DABr——acetamide, (5): DABr——formamide.

On the other hand, the order of effectiveness in breaking up the micelle was: acetamide>formamide>urea. Urea raises the dielectric constant of water,[14] acetamide lowers it,[14] and formamide may raise it because of its high dielectric constant. Acetamide, furthermore, has a stronger hydrophobic character. The lowering of the dielectric constant and the hydrophobic character are considered to break up the micelle through an increment in the electrostatic repulsion on the micelle surface and a reduction of the interfacial energy between the hydrocarbon chain of single ions and water. Therefore, the above result may be attributable to these two effects. In all the micellar solutions containing alcohols except for methanol, however, the solubilization effect is more significant than these effects.

The Effect of Acetone and Dioxane on Micelle Formation. The alcohols and amides described above were protonic additives; the effects of aprotic solvent—acetone and dioxane—were also studied.

As is shown in Figs. 5 and 6, the addition of acetone or dioxane into the dodecylammonium halide solutions resulted in the increment of CMC, the effect of this on the DAI solution was different, however. In the presence of dioxane, the DAI solution became yellowish and precipitation resulted from the addition of many dioxane. It is known that a complex results from the interaction between acetone and the iodine ion.[15] Accordingly, the addition of the aprotic solvents is considered to affect the DAI solution specifically.

In summary, the CMC of dodecylammonium halide was raised more in the presence of aprotic solvents

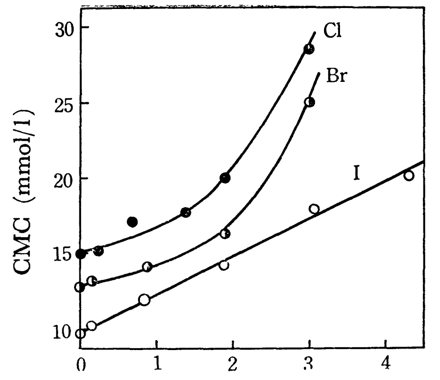

Fig. 5. Effect of acetone on CMC.

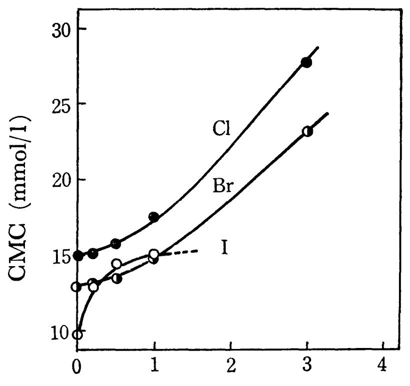

Fig. 6. Effect of dioxane on CMC.

than in that of amides and was depressed by the addition of alcohols; a change in the counterion was more effective on the reduction of the CMC than on its increment.

The Influence of Organic Additives on the Degree of Dissociation of Micelle. The dissociation of an electrolyte is depressed by adding salts or by lowering the dielectric constant of the medium; that of a micelle is also depressed by added salts. Therefore, a micelle may be expected to be less dissociative in the presence of an organic additive with a low dielectric constant. Figure 7, however, shows the opposite results. A sodium tetradecyl sulfate (STS) solution containing dioxane[16] and sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide in a 3 M urea solution[17] also gave the same results.

Stern[18] derived the following equation concerning adsorption on the double layer;

$$\frac{n}{N-n} = \frac{AM}{1000} C_i \exp(-\Delta G/kT) \tag{3}$$

where n and N are number of adsorbed molecules on the surface and its maximum number, A is a constant, M is the molecular weight of the solvent, C_i is the concentration of the adsorbate, and ΔG is the free energy of transfer from a bulk solution to the surface.

If a micelle consists of N monomers and N' organic additives and n counterions, n/N may be equal to $1-\alpha$, and when the micelle is large, Stern's equation can be applied to its surface. Thus, we obtain:

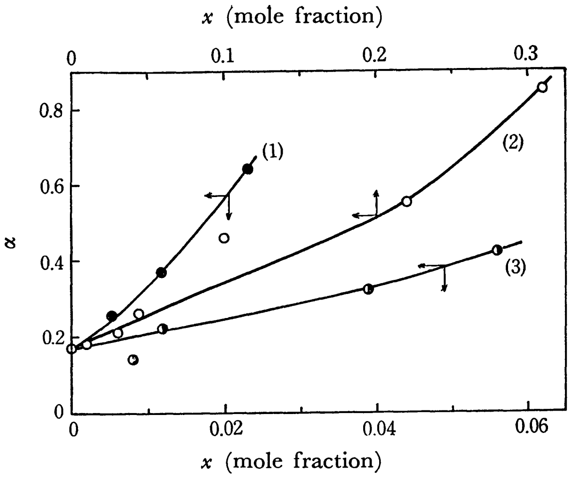

Fig. 7. Effect of organic additives on α in DACl solutions.
1): *n*-propanol, 2): methanol, 3): acetone.

$$\frac{1-\alpha}{\alpha} = \frac{AM}{1000} C_i \exp(-\Delta G/kT) \tag{4}$$

As ΔG consists of the electrostatic energy, $\Delta G_{\text{elec.}}$, and the chemical energy, $\Delta G_{\text{chem.}}$, Equation (4) becomes:

$$\frac{\alpha}{1-\alpha} = \frac{1000}{AMC_i} \exp(\Delta G_{\text{elec.}} + \Delta G_{\text{chem.}}) \tag{5}$$

The electrostatic energy is given by:

$$\Delta G_{\text{elec.}} = -kT \ln \frac{2000\pi\sigma^2}{DNkTC_i} \tag{6}$$

$$\sigma = x_s \sigma_1 \tag{7}$$

where σ_1 and σ are the charge densities of the micelle containing no and $1-x_s$ organic additives, x_s is the mole fraction of the surfactant in the micelle, and D is the dielectric constant of the solvent. Further, we assume the following two equations;

$$M = M_1(1-x) + xM_2 \tag{8}$$

$$\Delta G_{\text{chem.}} \approx \Delta G_{\text{sol.}} = -\Delta G_2 x - \Delta G_1(1-x) \tag{9}$$

where $\Delta G_{\text{sol.}}$ is the desolvation energy, ΔG_1 and ΔG_2 are solvation energies of water and the organic additive respectively, and x is the mole fraction of the organic additive. Equation (5) can then be rewritten as:

$$\ln\frac{\alpha}{1-\alpha} = \ln\frac{1000}{AM_1C_i} - \ln\left\{1+\left(\frac{M_2}{M_1}-1\right)x\right\} - \ln\frac{2000\pi\sigma_1^2}{D_1NkTC_i} - 2\ln x_s + \ln\frac{D}{D_1} - \frac{\Delta G_1}{kT} + \frac{\Delta G_1-\Delta G_2}{kT}x \tag{10-a}$$

When the micellar solution does not contain the organic additive, (10-a) becomes (10-b):

$$\ln\frac{\alpha_1}{1-\alpha_1} = \ln\frac{1000}{AM_1C_i} - \ln\frac{2000\pi\sigma_1^2}{D_1NkTC_i} - \frac{\Delta G_1}{kT} \tag{10-b}$$

From (10-a) and (10-b), we obtain:

$$\ln\frac{\alpha}{1-\alpha} = \ln\frac{\alpha_1}{1-\alpha_1} - \ln\left\{1+\left(\frac{M_2}{M_1}-1\right)x\right\} - 2\ln x_s + \ln\frac{D}{D_1} + \frac{\Delta G_1-\Delta G_2}{kT}x \tag{10}$$

Accordingly, by measuring α and α_1, we can calculate the solubilized amount of the organic additive, x_m

$(=1-x_s)$. The amount of the organic additive in the micelle phase was less than 5% of its amount in the bulk phase; therefore, the value of x was regarded as the total of the added amount. For the values of $(\Delta G_1-\Delta G_2)/kT$, those of hydrochloric acid or sodium hydroxide[19] were used as an expedient; that is, 4.65, 6.28, 7.19, and 14.8 were used for the systems of DACl-methanol, -propanol, -acetone, and STS-dioxane respectively.

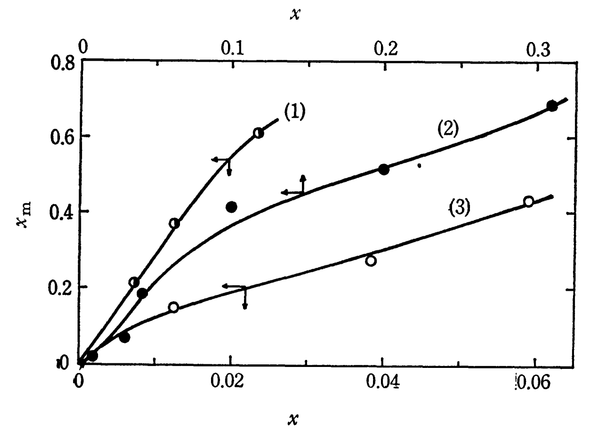

Fig. 8. Solubilization of organic additives in DACl solutions.
1): *n*-propanol 2): methanol, 3): acetone.

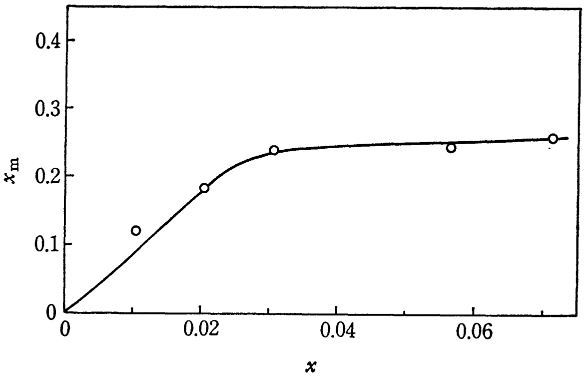

Fig. 9. Solubilization of dioxane in sodium tetradecylsulfate solution*.
*; x_m was calculated from α in Ref 14.

As is shown in Figs. 8 and 9, x_m increases with the concentration of the additives and attains a large value in high concentrations. The large value of the solubilized amount can be explained by considering that the large micelle to which Equation (1) can be applied does not exist in high concentrations of the additive. The aggregate, however, changes continuously from the micelle to the oligomer with the concentration of the additive; therefore, it is difficult to divide the micelles into two regions, so we call them all "micelles". According to Uehara *et al.*, however, the CMC and the aggregation number of SDS could be determined in high methanol concentrations.[4]

The Dependence of the CMC on the Concentration of Organic Additives. We attempted to estimate the dependence of the CMC on the additive concentration from the degree of dissociation of a micelle.

In a micellar solution the chemical potential of the surfactant ion in the bulk solution is equal to that in the micelle phase. Therefore,

$$\mu_b^\circ + kT\ln Cf = \mu_m^\circ + kT\ln x_s f_s + e\psi \tag{11}$$

$$e\psi = kT\ln\frac{2000\pi\sigma^2}{DNkTC_i} \tag{12}$$

where μ_b° and μ_m° are the standard chemical potentials of the surfactant ion in the bulk solution and in the micelle phase respectively, f and f_s are the activity coefficients of the surfactant ions in the bulk solution and in the micelle phase respectively, and $e\psi$ is the electrostatic work. In the absence of added salt, C_i is equal to C; therefore, from Eqs. (7), (11), and (12) we obtain

$$2\ln Cf = \frac{\mu_m^\circ-\mu_b^\circ}{kT} + \ln\frac{2000\pi\sigma_1{}^2x_s{}^2}{DNkT} + \ln x_s + \ln f_s \tag{13-a}$$

When the micellar solutions do not contain organic additives, (13-a) becomes:

$$2\ln C_1f_1 = \frac{\mu_m^\circ-\mu_b^\circ}{kT} + \ln\frac{2000\pi\sigma_1{}^2}{D_1NkT} \tag{13-b}$$

Therefore, we obtain:

$$2\ln C/C_1 + 2\ln f/f_1 = 3\ln x_s - \ln D/D_1 + \ln f_s \tag{13}$$

If the following equation is assumed as a first approximation:

$$\ln f_s - 2\ln f/f_1 = k_i x \tag{14}$$

where k_i is a constant, we obtain:

$$2\ln C/C_1 = 3\ln x_s - \ln D/D_1 + k_i x \tag{15}$$

As the x_s value is obtained from Eq. (10), Equation (15) finally becomes:

$$\ln\frac{C}{C_1} = \frac{3}{4}\left[\ln\frac{\alpha_1}{1-\alpha_1} - \ln\frac{\alpha}{1-\alpha} - \ln\left\{1+\left(\frac{M_2}{M_1}-1\right)x\right\} + \frac{\Delta G_1-\Delta G_2}{kT}x\right] + \frac{1}{4}\ln\frac{D}{D_1} + \frac{1}{2}k_i x \tag{16}$$

Here, k_i was taken as fitting with the experimental values. Figures 10 and 11 show the comparison between the theoretical and the experimental values. It is seen that the agreement between the experimental

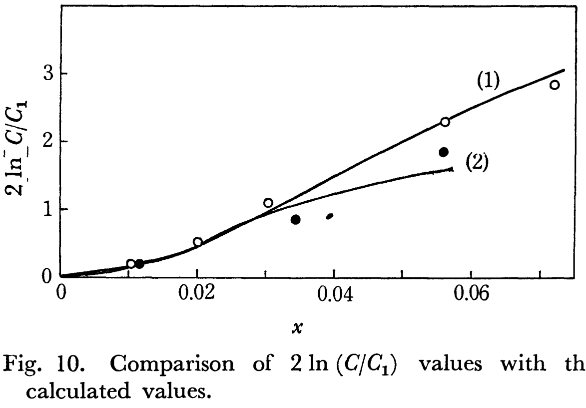

Fig. 10. Comparison of $2\ln(C/C_1)$ values with the calculated values.
(1) Sodium tetradecyl sulfate—dioxane, $k_i=52.3$, (2): DACl—acetone, $k_i=54$. The solid lines are the calculated values.

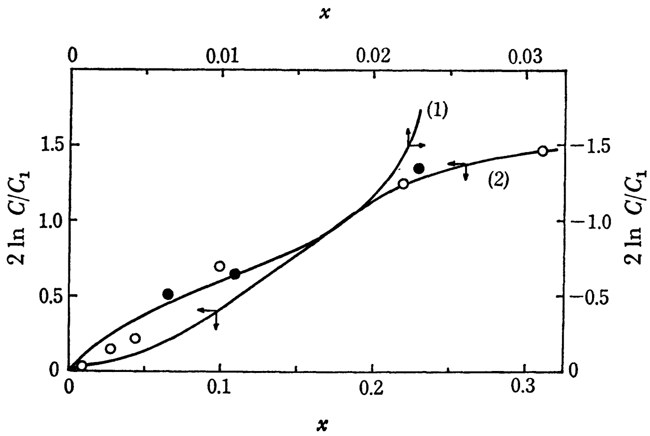

Fig. 11. Comparison of 2 ln (C/C_1) values with the calculated values in DACl solutions.

1) *n*-propanol, k_i=59, 2) methanol, k_i=15.2 The solid lines are the calculated values.

and theoretical curves is rather good in spite of some approximations.

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