The Micelle Formation of Alkylammonium Chloride in 1-Propanol–Water and Acetone–Water Mixtures

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The change in the critical micelle concentrations (CMC) of alkylammonium chlorides (C_{12}—C_{18}) and in the degree of the dissociation of the micelle (α) of dodecylammonium chloride was determined by adding 1-propanol and acetone to water. Both the CMC and the α increased with an additive concentration, each reaching a maximum at a certain concentration (critical composition of solvent for micelle formation, CCSM) and decreasing beyond the CCSM. The increment in the CMC was more influenced by the alkyl-chain length in the surfactant molecule in the presence of 1-propanol than in that of acetone. The effective coefficient of electrical energy (K_g) and the cohesive energy difference per methylene group between the micelle and the monomer states (ω) were calculated from the CMC and the α. The K_g values in both mixed solvents were constant beyond the respective CCSM. The value of ω was less in the presence of 1-propanol than in that of acetone.

It is well known that such factors as additives, temperature, alkyl-chain length, and polar group in a surfactant molecule give rise to considerable changes in the micelle formation.[1–4] Many investigations have been reported into the cooperative effects among these factors; for example, the effects of each alkyl-chain length in a surfactant and an added alcohol molecule,[5] the influence of the temperature[6] and of a change in the counterions[7,8] in the presence of the organic additives, and the effect of the organic additives on the CMC of the surfactant with different ethylene oxide chain lengths.[9,10] These investigations have suggested that the most significant factor in the micelle formation is the interaction between the water and the alkyl-chain in a surfactant molecule. However, there have been few reports about the effect of the alkyl-chain over a wide range of organic additive concentrations. In the present work, the micellar behavior of alkylammonium chlorides (C_{12}–C_{18}) in 1-propanol–water and acetone–water mixtures was studied over the additive concentration range from 0 to about 0.4 in the mole fraction.

Experimental

The alkylammonium chlorides were prepared from vacuum-distilled alkylamines in a manner described previously.[7] They were used after having been recristallized from ethanol-ether several times. The procedures for the measurements of the CMC and of the degree of dissociation of the micelle (α) have been reported previously.[7] The experiments were carried out at 35.0 °C.

Results and Discussion

The Influence of 1-Propanol on the Micelle Formation. The natural logarithms of the CMC in the four surfactant solutions are presented as a function of the mole fraction of 1-propanol in Fig. 1, while the degrees of dissociation of the dodecylammonium chloride micelle are plotted in Fig. 2. The CMC of dodecylammonium chloride (DAC) first decreased, passed through a minimum, and then increased steeply with the 1-propanol concentration until it reached a maximum value at a certain concentration. Similar behavior was observed with regard to the CMC of tetradecyl-(TAC), hexadecyl-(HAC), and octadecylammonium chloride (OAC), although the minimum gradually disappeared as the alkyl-chain length increased. The CMC-decreasing effect can be explained mainly in terms of the solubilization of an additive in a micelle,[5] while the CMC-increasing effect can be explained as being due to the solvent power of the mixture.[10,11] The minimum on the CMC-solvent composition curve is controlled by the competition of the above two effects.

The mole fraction of 1-propanol at which the CMC reaches its maximum— denoted as the critical composition of the solvent for micelle formation (CCSM)[11]

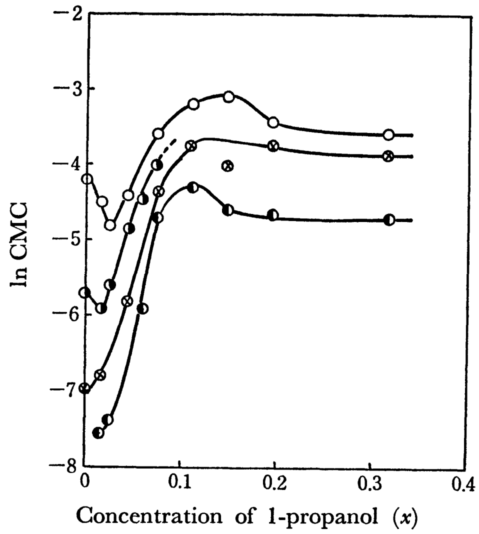

Fig. 1. The Effect of 1-propanol on CMC.
○: DAC, ◑: TAC, ⊗: HAC, ◐: OAC.

Table 1. The critical compositions of solvent for the micelle formation

Surfactants	Mole fractions 1-Propanol	Acetone
D A C	0.12	0.10
H A C	0.12	0.11
O A C	0.11	0.15
S T S[a]	0.11	0.14
POE D E[b]	0.11	—

a) From Ref. 11. b) From Ref. 12.

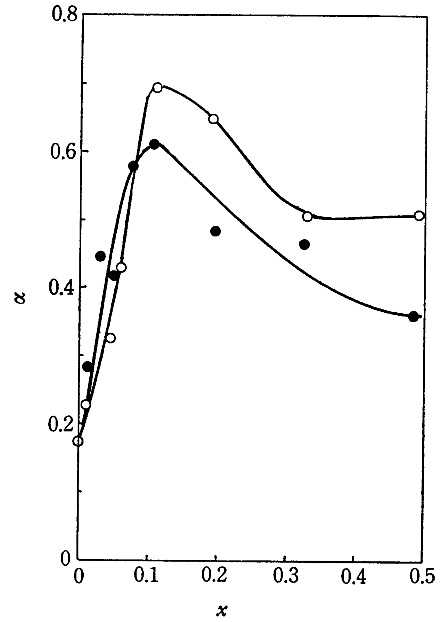

Fig. 2. The dependence of α on the additive concentration.
○: Acetone, ●: 1-Propanol.

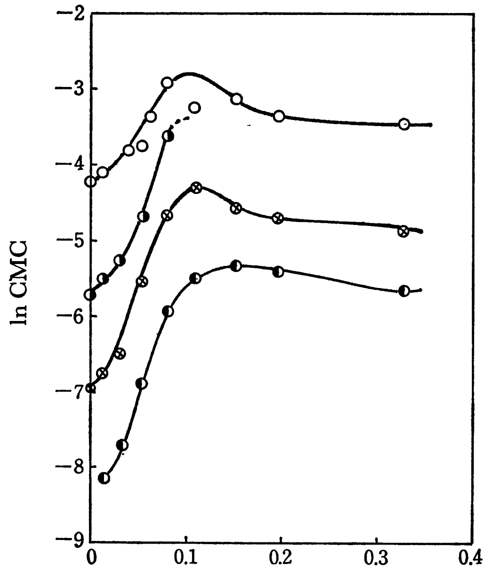

Fig. 3. The effect of acetone on CMC.
Symbols are identical with them in Fig. 1.

—is given in Table 1, together with the data for sodium tetradecyl sulfate (STS)[11] and polyoxyethylene dodecyl ether (POEDE).[12] The values of the CCSM were almost independent of the alkyl-chain length in the surfactant molecule and also of its head group. Also, the α increased with the 1-propanol concentration, reached a maximum at the same concentration as the CCSM, and decreased beyond it.

The Influence of Acetone on the Micelle Formation. The behavior of the alkylammonium chloride solutions containing acetone (Fig. 2, 3) was essentially the same as that of solutions in the presence of 1-propanol. However, both the solubilization effect and the solvent effect were less in the former mixed solvent than in the latter. There was no minimum in the values of the CMC as a function of the acetone concentration, and the increments in the CMC with acetone and the influence of the alkyl-chain length on their increments were less than in the presence of 1-propanol. The differences among the maximum CMC's of the alkylammonium chlorides were larger in the presence of acetone than in that of 1-propanol.

The CCSM in the acetone–water systems depended on the nature of the surfactants, but the values were scattered in the neighbourhood of 0.1—0.15. The heat of mixing in acetone–water systems has a minimum at 0.15,[13] and the viscosity and the tracer-diffusion coefficient of acetone have thier maximum and minimum, respectively, at about 0.2,[14,15] In the system of 1-propanol–water, the activity coefficient of 1-propanol changes rapidly in the neighbourhood of 0.1.[16] These authors, however, have avoided a detailed discussions concerning the structure change in the solutions. Any detailed discussion of the relation among these experimental facts must wait until details of the structure changes in the aqueous solutions become apparent. In the present paper, we will describe only the experimental fact; further investigation will be reported later.

In addition, it was found from the present experiment that the solubilities of these surfactants were less in acetone than in 1-propanol.

The Determination of K_g and ω. The CMC is expressed by this equation:[17]

$$\ln \mathrm{CMC} = -\frac{m\omega}{(1+K_g)kT} + \frac{K_g}{1+K_g}\ln\frac{2000\,\pi\sigma^2}{DNkT} + \frac{\ln(1000/Nv)-1}{1+K_g} \tag{1}$$

where m is the carbon number in a surfactant molecule, ω is the cohesive energy difference per methylene group between a micelle and a monomer states, K_g is the effective coefficient of the electrical energy, σ is the charge density, D is the dielectric constant of the solution, N is the Avogadro number, k is the Boltzmann constant, and T is the absolute temperature of the solution. As the second and the third terms on the right-hand side of this equation are almost independent of m,[17] the differentiation of Eq. (1) with respect to m gives the following equation:

$$\frac{\mathrm{d}\ln \mathrm{CMC}}{\mathrm{d}m} = -\frac{\omega}{(1+K_g)kT} \tag{2}$$

The values of $-\mathrm{d}\ln \mathrm{CMC}/\mathrm{d}m$ are plottedas functions of the additive concentrations in Fig. 4. It was found that $-\mathrm{d}\ln \mathrm{CMC}/\mathrm{d}m$ decreased rapidly with an increase in the concentration of the additives and reached constant values at the CCSM. The decreasing effect by the addition of 1-propanol was more than that by the acetone addition. In order to discuss these results in detail, we need to know the value of ω. We therefore attempted to determine K_g, and then ω was calculated from Eq. (2).

We define K_g as follows:

$$K_g = \psi/\psi_0 \tag{3}$$

where ψ is the effective potential at the micelle surface

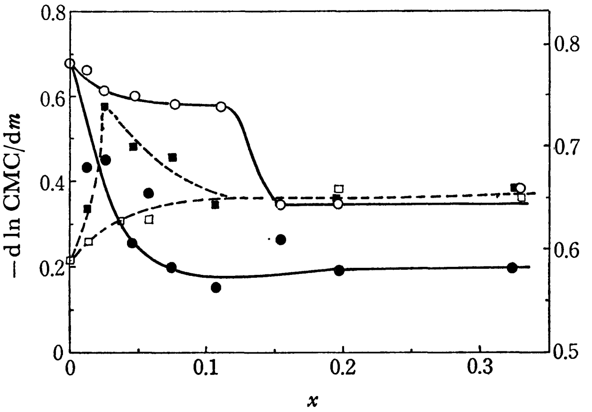

Fig. 4. The dependence of $-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}m$ and K_g on the additive concentrations.
○,□: Acetone, ●,■: 1-Propanol.
——: $-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}m$, ----: K_g.

and where ψ_0 is the hypothetical potential when a counterion is not adsorbed on the micelle surface when the other conditions are constant. These potentials are given by the following two equations:

$$\psi = \frac{kT}{e}\ln\frac{2000\pi\sigma^2}{DNkTC_i} \tag{4-1}$$

$$\psi_0 = \frac{kT}{e}\ln\frac{2000\pi\sigma_0{}^2}{DNkTC_i} \tag{4-2}$$

where σ and σ_0 are the surface-charge densities of the micelle and of the hypothetical micelle, e is the electric elementary quantum, and C_i is the molarity of the couterion. By combining Eqs. (3) with (4—1) and (4—2), the following equation is obtained:

$$\frac{\psi_0-\psi}{\psi} = \frac{1}{K_g} - 1 = \frac{2kT}{e\psi}\ln\frac{\sigma_0}{\sigma} \tag{5}$$

As σ/σ_0 is corresponds to α, Eq. (5) can be modified as follows:

$$K_g = \frac{e\psi/kT}{e\psi/kT-2\ln\alpha} \tag{6}$$

On the other hand, according to a previous paper,[7] we have:

$$\frac{1-\alpha}{\alpha} = \frac{AMC_i}{1000}\exp\left(-\Delta G/kT\right) \tag{7}$$

where ΔG is the effective potential energy, M is the molecular weight of the solvent, and A is a constant. If ΔG can be given solely by an electrical term, we have the following equation:

$$\frac{\Delta G}{kT} = -\frac{e\psi'}{kT} = -\ln\frac{2000\pi\sigma'^2}{DNkTC_i} \tag{8}$$

where ψ' and σ' are the potential and the charge density at a micelle surface in this case. Combining Eq. (7) with Eq. (8), we obtain:

$$\frac{e\psi'}{kT} = \ln\frac{1000}{AMC_i} + \ln\frac{1-\alpha}{\alpha} \tag{9}$$

As ψ' is considered to be nearly equal to ψ, the introduction of Eq. (9) into Eq. (6) gives the following equation:

$$K_g = \frac{\ln 1000/AMC_i+\ln(1-\alpha)/\alpha}{\ln 1000/AMC_i+\ln(1-\alpha)/\alpha^3} \tag{10}$$

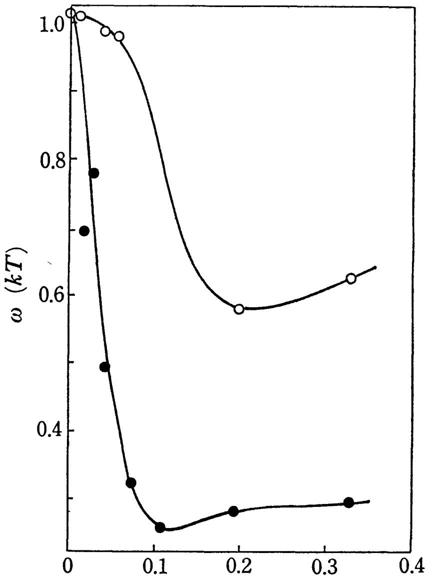

Fig. 5. The dependence of ω on the additive concentration.
○: Acetone, ●: 1-Propanol.

The concentration of the counterion, C_i, is equal to the CMC in the absence of an added electrolyte. Consequently, Eq. (10) becomes Eq. (11):

$$K_g = \frac{\ln(1-\alpha)/\alpha-\ln\mathrm{CMC}+\ln 1000/AM}{\ln(1-\alpha)/\alpha^3-\ln\mathrm{CMC}+\ln 1000/AM} \tag{11}$$

The value of A is unknown, but it can be determined as follows. According to many papers published, ω in an aqueous solution is given as 1.08 kT. The value of $-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}m$ in the absence of an organic additive is given as 0.68 from Fig. 4. We can then obtain 0.59 as K_g from these two values and Eq. (2). Introducing 15×10^{-3} M, 0.18, 0.59, and 18 for the CMC, α, $K_{,g}$ and M respectively in the aqueous solution into Eq. (11) gives 121 as A. Then, Eq. (11) may be rewritten as follows:

$$K_g = \frac{\ln(1-\alpha)/\alpha-\ln\mathrm{CMC}+\ln 1000/121M}{\ln(1-\alpha)/\alpha^3-\ln\mathrm{CMC}+\ln 1000/121M} \tag{12}$$

The values of K_g calculated from Eq. (12) are shown in Fig. 4. Beyond the CCSM, they were almost constant. The values of ω calculated from Eq. (2) by using K_g and $-\mathrm{d}\ln\mathrm{CMC}/\mathrm{d}m$ are plotted in Fig. 5, which shows that ω decreased more rapidly in the presence of 1-propanol than in that of acetone and that the final value in the former solution was about one-half of that in the latter solution. These results suggest that the hydrophobic interaction in these micelle formation was less on the addition of 1-propanol than on that of acetone. However, we must note that the factors attributable to the decrease in ω are probably complicated; not only the hydrophobic interaction but also other factors, for example, the solubility parameters of the mixed solvents,[18] must be considered.

Fianlly, let us mention that the value of α calculated from Botré's equation[19] is not correct. Indeed, the decrease in the surfactant-ion concentration has been considered above CMC.[20,21] However, the results determined on the basis of α are not unlike, for the divergence seems not be large when the experimental error of the determination of α is taken into consideration. Therefore, we believe that the qualitative behavior described above remains valid.

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