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# The Effect of Organic Additives on the Thermodynamic Parameters of Micellization

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The CMC values of dodecylammonium chloride and iodide and of hexadecylammonium chloride were measured in water upon the addition of acetone, 1-propanol, and urea at several temperatures. The effects of the additives were most remarkable on the CMC of hexadecylammonium chloride at 45.0 °C. Urea was less effective on the disruption of micelles than acetone, while the addition of 1-propanol was most effective. The enthalpy of micellization became more negative, while the entropy of micellization became less positive, as the additive concentration increased. We divided the standard free energy of micellization into the hydrophobic term, $\Delta G^\circ_\mathrm{n}$, and the hydrophilic term, $\Delta G^\circ_\mathrm{p}$. The value of $\Delta G^\circ_\mathrm{p}$ became more negative with the additive concentration and contributed to the stabilization of the micelle, while $\Delta G^\circ_\mathrm{n}$ became less negative. Therefore, it was concluded that the disruption of the micelle in the presence of these organic additives results from an increase in the free energy in the hydrophobic group of the surfactant molecule.

It is well known that the addition of a protein denaturant to a surfactant solution brings about the disruption of a micelle. The two phenomena, *i.e.*, protein denaturation and micelle disruption, are qualitatively similar, and so the effects of the organic additives on the micellar properties have received much attention.

On the other hand, the association of the surfactant molecule itself is a significant problem in physical chemistry, apart from biology. In the investigation of the effect of organic additives, nonionic surfactants have often been used;[1–6] there have been fewer systematic studies of ionic surfactant solutions[7–9] because of the complexity of the electrostatic interaction. However, we could previously obtain some significant results in the alkylammonium halide solutions.[10,11]

In the present investigation, our studies were extended to the effect of the additives on the thermodynamic parameters of micellization. Here we reached the significant conclusion that the increase in the CMC in the presence of the organic additives results from the increase in the free energy of the hydrophobic group in the surfactant molecule.

## Experimental

The materials and the experimental procedure were almost the same as those described in previous papers.[10,11] That is, dodecylammonium chloride (DAC), iodide (DAI) and hexadecyammonium chloride (HAC) were used. Their CMC's were measured by the electric conductivity method. The CMC of HAC was not measured in the urea solutions because of the appearance of turbidity.

## Results and Discussion

*The Effect of the Additives on the CMC.* The effect of three organic additives on the micellization of alkylammonium halides was examined. 1-Propanol is a protonic solvent, acetone is aprotic, and urea is well known to be a typical protein denaturant.

The additives affect the micellizations through the breakage of the water structure around the hydrocarbon chain of a surfactant molecule[12] and the modification of the electrostatic interaction.[13] The chloride ion may be a stronger water-structure breaker than the iodide ion, and therefore the water around the hydrocarbon chain may be less ordered and less susceptible to modification by the organic additives in the presence of the chloride ion than in that of the iodide ion. Therefore, the surfactant molecule with a longer hydrocarbon chain or a weaker structure-breaking ion is expected to be more subject to the effect of the additive. The experimental results that the CMC increasing effects of the additives were most remarkable in HAC and less in DAC than in DAI were in accord with these expectations.

Table 1. The effect of propanol on CMC

| Temp. (°C) | CMC × $10^4$ (mole fraction) (CMC/$\mathrm{CMC_0}$) 1-Propanol (mol/1000 g) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 0.659 | 1.318 | 1.977 | 2.636 | 3.294 |
| | | | DAC | | | |
| 25.0 | 2.66 | 1.96 | 1.69 | | 2.12 | 2.74 |
| | (1.00) | (0.74) | (0.64) | | (0.80) | (1.03) |
| 35.0 | 2.79 | 2.14 | 1.92 | | 2.44 | 3.45 |
| | (1.00) | (0.77) | (0.69) | | (0.87) | (1.24) |
| 45.0 | 2.88 | 2.31 | 2.00 | | 3.26 | 5.23 |
| | (1.00) | (0.80) | (0.69) | | (1.13) | (1.82) |
| | | | DAI | | | |
| 25.0 | 1.69 | 1.50 | 1.31 | 2.65 | 3.26 | 4.04 |
| | (1.00) | (0.89) | (0.78) | (1.57) | (1.93) | (2.39) |
| 35.0 | 1.76 | 1.58 | | | 3.36 | |
| | (1.00) | (0.90) | | | (1.91) | |
| 45.0 | 1.96 | 1.64 | 1.60 | 2.77 | 3.71 | 4.60 |
| | (1.00) | (0.84) | (0.82) | (1.41) | (1.89) | (2.34) |
| | | | HAC | | | |
| 25.0 | | | 0.173 | | 0.458 | 0.834 |
| 35.0 | 0.162 | 0.162 | 0.234 | | 0.611 | 1.15 |
| | (1.00) | (1.00) | (1.44) | | (3.77) | (7.10) |
| 45.0 | 0.175 | 0.252 | 0.404 | | 1.02 | 1.63 |
| | (1.00) | (1.44) | (2.31) | | (5.83) | (9.31) |

$\mathrm{CMC_0}$: The CMC in the absence of propanol. The relative CMC is given in the parenthesis under each row.

Table 2. The effect of acetone on CMC

| Temp. (°C) | CMC × $10^4$ (mole fraction) (CMC/CMC$_0$) Acetone (mol/1000 g) 0 | 0.675 | 1.350 | 2.701 | 3.376 |
|---|---|---|---|---|---|
| | DAC | | | | |
| 25.0 | 2.66 | 2.61 | 3.34 | 3.94 | 6.88 |
| | (1.00) | (0.98) | (1.26) | (1.48) | (2.59) |
| 35.0 | 2.79 | 2.95 | 3.59 | 4.88 | 9.17 |
| | (1.00) | (1.06) | (1.29) | (1.75) | (3.29) |
| 45.0 | 2.88 | 3.13 | 3.76 | 5.60 | 9.17 |
| | (1.00) | (1.09) | (1.31) | (1.94) | (3.18) |
| | HAC | | | | |
| 35.0 | 0.162 | 0.228 | 0.392 | 0.830 | |
| | (1.00) | (1.41) | (2.42) | (5.12) | |
| 45.0 | 0.175 | 0.246 | 0.444 | 1.04 | |
| | (1.00) | (1.41) | (2.54) | (5.93) | |

| | Acetone (mol/1000 g) 0 | 0.174 | 0.906 | 1.913 | 2.701 |
|---|---|---|---|---|---|
| | DAI | | | | |
| 25.0 | 1.69 | 1.71 | 2.07 | 2.56 | 3.11 |
| | (1.00) | (1.01) | (1.22) | (1.51) | (1.84) |
| 35.0 | 1.76 | 1.86 | 2.20 | 2.73 | 3.61 |
| | (1.00) | (1.06) | (1.25) | (1.55) | (2.05) |
| 45.0 | 1.96 | 2.04 | 2.45 | 3.07 | 4.25 |
| | (1.00) | (1.04) | (1.25) | (1.57) | (2.17) |

CMC$_0$: The CMC in the absence of acetone.

Table 3. The effect of urea on CMC

| Temp. (°C) | CMC × $10^4$ (mole fraction) (CMC/CMC$_0$) Urea (M) 0 | 1 | 3 | 4.5 | 5 | 6 |
|---|---|---|---|---|---|---|
| | DAC | | | | | |
| 25.0 | 2.66 | 2.96 | 3.88 | | 4.66 | |
| | (1.00) | (1.11) | (1.46) | | (1.75) | |
| 35.0 | 2.79 | 3.06 | 3.88 | | 4.72 | |
| | (1.00) | (1.10) | (1.39) | | (1.69) | |
| 45.0 | 2.88 | 3.15 | 4.17 | | 4.86 | |
| | (1.00) | (1.09) | (1.45) | | (1.69) | |
| | SDS[a] | | | | | |
| 25.0 | 1.30 | 1.37 | 1.78 | 2.12 | | 2.63 |
| | (1.00) | (1.05) | (1.37) | (1.63) | | (2.02) |
| 45.0 | 1.37 | | 1.79 | | | 2.52 |
| | (1.00) | | (1.31) | | | (1.84) |

CMC$_0$: The CMC in the absence of urea. a) From Ref. 12.

The CMC values in Tables 1—3 are seen to increase with the temperature, irrespective of the presence or absence of the additive, and the increment in HAC is remarkable in the presence of additives. The addition of 1-propanol and acetone affects the micellization to a considerable extent, while urea is least effective.

The CMC values of sodium dodecylsulfate (SDS) in the presence of urea reported by Schick[12] are denoted in Table 3 for comparison with our data. The difference between these two sets of data is relatively small. Therefore, in the absence of a strong structure-breaking ion or a strong structure-making ion, the increments in the CMC values on urea addition seem to be determined mainly by its effect on the hydrophobic group of a surfactant molecule.

*Thermodynamic Parameters of Micellization.* The standard free energy of micellization can be represented by Eq. (1), and the enthalpy may be calculated from the dependence of the CMC on the temperature by means of Eq. (2):

$$\Delta G^\circ = (1+K_g)RT\ln \mathrm{CMC}\ (\text{mole fraction}) \qquad (1)$$

$$\Delta H^\circ = -(1+K_g)RT^2\frac{\mathrm{d}\ln \mathrm{CMC}}{\mathrm{d}T} \qquad (2)$$

The value of $K_g$ does not change largely with the temperature[14] or with the concentration of the organic additive.[11] The thermodynamic parameters in the present work have been calculated by assuming that $K_g=0.7$.

From the usual relation among thermodynamic functions, the standard entropy of micellization is obtained. In the micellization, the entropy generally has a relatively large positive value, while the enthalpy is small or even negative in an aqueous solution. Shinoda[15] explained these phenomena by taking into account the iceberg formation of the water surrounding a surfactant molecule. Urea is known to denature a protein through the disruption of the iceberg. However, in the present work, acetone, a weaker denaturant, was found to be more effective in the breakage of micelles than urea. Similar phenomena were also suggested by Bruning and Holtzer.[16] A comparison of Fig. 3 with Figs. 1—2 reveals that the effect of urea on the thermodynamic parameters is weaker than those of acetone and 1-propanol and that the enthalpy scarcely changes upon the addition of urea.

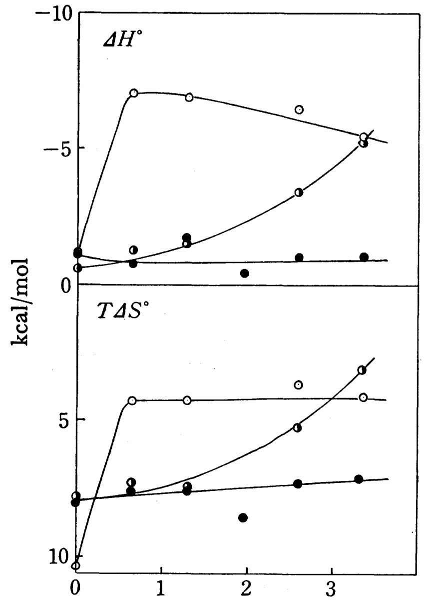

Fig. 1. The effect of 1-propanol on thermodynamic parameters of micellization at 35.0 °C.
—◐—: DAC, —●—: DAI, —○—: HAC.

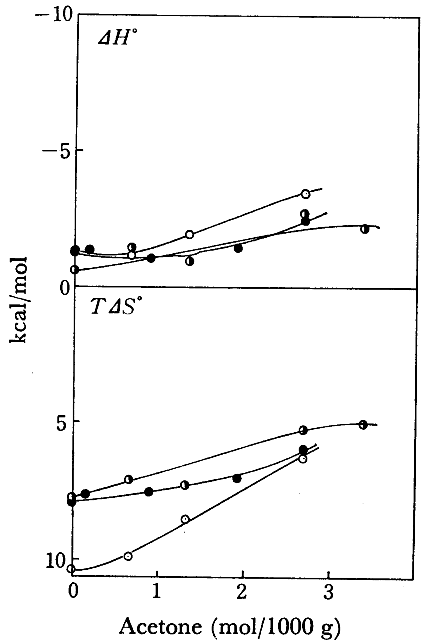

Fig. 2. The effect of acetone on thermodynamic parameters of micellization at 35.0 °C.
Symbols are identical with them in Fig. 1.

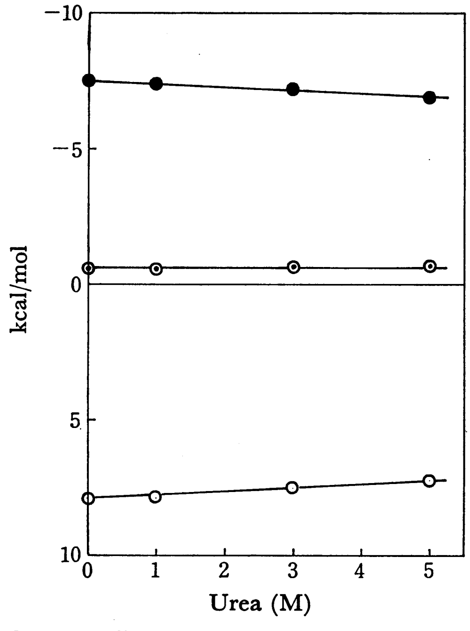

Fig. 3. The effect of urea on thermodynamic parameters of micellization at 35.0 °C.
—●—: $\Delta G^\circ$, —⊙—: $\Delta H^\circ$, —○—: $T\Delta S^\circ$.

Therefore, acetone and 1-propanol seem to affect the micellization through other mechanisms, in addition to the disruption of iceberg; for example, the preferential solvation of the hydrocarbon chain by the additives or the more appropriate solubility parameter of the mixed solvent.

The effects of additives on the enthalpy and the entropy were remarkable in the HAC solution; the difference between their effects in the DAC and DAI solutions was small at low concentrations of the additives. These results suggest that their effects are operative primarily on the hydrophobic group of the surfactant, while only secondarily on the hydrophilic group.

Furthermore, the entalpy is more negative, and the entropy is less positive, in the presence of additives; therefore, the contribution of the enthalpy to the micellization becomes increasingly important with the additive concentrations, in contrast to the predominance of entropy in the aqueous solutions. Such more negative enthalpy in the presence of organic additives has also been observed in other systems.[2–5] We consider these phenomena to result from the decrease in the highly ordered structure through hydrogen bonding in an aqueous solution. Further investigations, however, will be required before a detailed discussion can be done.

*The Hydrophobic and the Hydrophilic Terms in the Free Energy.* It is possible to divide the standard free energy of micellization in the DAC solution, $\Delta G_{DAC}^\circ$, into two components, one due to the hydrophobic group of the surfactant molecule, $\Delta G_n^\circ$, and the other, due to the hydrophilic group, $\Delta G_p^\circ$. We will represent the standard free energy of micellization in the HAC solutions as $\Delta G_{HAC}^\circ$ and will assume the following equation, similar equations have been used by some other authors:[4,5,9)]

$$\Delta G_n^\circ = 3(\Delta G_{HAC}^\circ - \Delta G_{DAC}^\circ) \tag{3}$$

$$\Delta G_p^\circ = \Delta G_{DAC}^\circ - \Delta G_n^\circ \tag{4}$$

Such a division may give further detailed knowledge about the effects of additives. The variations in $\Delta G_n^\circ$ and $\Delta G_p^\circ$ with additive concentrations are represented in Figs. 4—5. The value of $\Delta G_n^\circ$ becomes less negative as the additive concentration increases, while $\Delta G_p^\circ$, surprisingly, becomes more negative. Consequently, we reach the significant conclusion that the increase in $\Delta G_{DAC}^\circ$ in the presence of organic additives should be ascribed to the increase in $\Delta G_n^\circ$. The stabilization of the micelles at the lower concentrations of additives is explained by the more negative $\Delta G_p^\circ$. A similar calculation made with the HAC solutions gave values of $\Delta G_p^\circ$ identical with those in the DAC solution, but the values of $\Delta G_n^\circ$ were more negative.

On the other hand, a comparison between Figs. 4

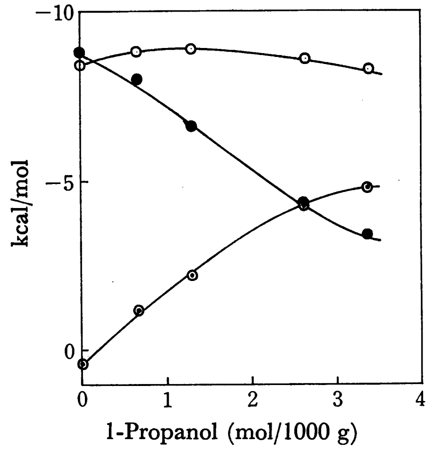

Fig. 4. The effect of 1-propanol on free energy of micellization of DAC at 35.0 °C.
—●—: $\Delta G_n^\circ$, —⊙—: $\Delta G_p^\circ$, —○—: $\Delta G_{DAC}^\circ$.

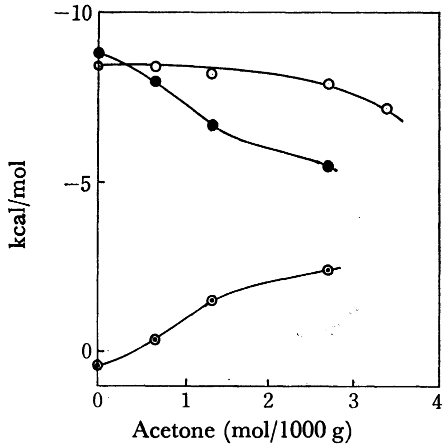

Fig. 5. The effect of acetone on free energy of micellization of DAC at 35.0 °C.
Symbols are identical with them in Fig. 4.

and 5 suggests that 1-propanol increases $-\Delta G_p^\circ$ more than acetone does. According to a previous paper,[10] propanol is more solubilized in the DAC micelle than is acetone. The increase in the solubilizate may produce the decrease in the surface-charge density of the micelle. Therefore, the fact reported above can be explained by the difference in their solubilized amounts.

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