

Effect of Alcohols on the Micelle Formation of Nonionic Surfactants in Aqueous Solutions

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The variation of critical micelle concentrations (CMC) of polyoxyethylene lauryl ethers having various ethylene oxide chain lengths \bar{n} ($\bar{n}=6, 11, 20$, and 31) on addition of short chain alcohols to the surfactant aqueous solutions was determined at 20°C . Thermodynamic quantities of micelle formation in methanol- and ethanol-water mixtures and in pure water were obtained in connection with the heat of micelle formation determined by direct calorimetry. Methanol and ethanol showed a CMC-increasing effect only, whereas the addition of *n*-propanol, *n*-butanol, and *n*-pentanol showed a CMC-decreasing effect. The overall CMC-increasing effect is interpreted as being mainly due to the fact that methanol and ethanol weaken the hydrophobic bond. However, the effect also has a secondary effect of lowering the CMC slightly on the polyoxyethylene portion of a surfactant. Several factors are suggested for explaining this secondary effect. The CMC-decreasing effect is explained by a decrease in the free energy of mixing resulting from the solubilization of alcohol molecules into the micelle.

The mechanism of micellization of nonionic surfactant in aqueous solution is analogous to that of ionic surfactant from the viewpoint that micellization is controlled by two opposing factors, the driving force for association and the factor preventing association.^{1,2} However, detailed studies on the micelle formation of nonionic surfactants are few in number as compared with those of ionic surfactants.

We can gain useful information for clarifying the various factors governing micelle formation from a study of the effect of additives on the critical micelle concentration (CMC) of surfactant. In order to evaluate relative efficacies of protein denaturants weakening hydrophobic interaction, a convenient approach to assess their effects on the CMC of surfactants has been used.^{3,4} Short chain alcohols, urea and guanidine salts are known to be denaturing agents, *viz.*, hydrophobic bond breakers. Their effect on the CMC of nonionic surfactants is of interest in view of protein denaturation.

The effect of alcohols on the CMC of ionic surfactants has been investigated extensively,⁵ but not that of nonionic surfactants.⁶⁻¹⁰ We have studied the effect of methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol on the micelle formation of polyoxyethylene lauryl ethers having various mean ethylene oxide chain lengths. The CMC of polyoxyethylated surfactants in alcohol-water mixtures was determined by the surface tension method. Heats of micelle formation were obtained by direct calorimetric measurements.

Experimental

Materials. The surfactants used (Kao Soap Co., Ltd.) were polyoxyethylene lauryl ethers ($\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{\bar{n}}\text{H}$, $\bar{n}=6, 11, 20, 31$, \bar{n} : the average number of ethylene oxide groups). The average chain lengths of the ethylene oxide adducts were determined from their hydroxyl values. The impurities, potassium acetate and polyethylene glycol, were checked by means of atomic absorption spectrophotometry and paper chromatography and found to be minute. Elementary analysis also showed that the samples were suf-

ficiently pure. All the alcohols were thoroughly purified. Water was redistilled from alkaline permanganate solution and had 1.5×10^{-6} mho/cm specific conductance.

Method. The surface tension measurements were performed at 20°C by the Wilhelmy method with a 22×22 mm glass plate and a Kyowa Electro Surface Balance. Before the measurement the plate was cleaned by heating in a chromic acid mixture for two hours and was washed thoroughly with water. Surfactant solutions were left to stand at the temperature of measurement for a day, preventing evaporation. It took about an hour to obtain equilibrium surface tension after the surfactant solution surface had been cleaned by suction with a fine glass capillary. The CMC was determined from sharp breaks in the surface tension *vs.* logarithm of concentration plots.¹⁰ Precision of the CMC determinations was within $\pm 7\%$. The CMC was also checked by the spectral method,¹¹ good agreement being found between the two methods.

The heats of micelle formation were obtained at 20°C by the heat of dilution method according to Corkill *et al.*¹² with a modified Applied Electric Laboratory Microcalorimeter, Model CM-204S1.

Results and Discussion

Since alcohols are surface active, sharp breaks in the surface tension *vs.* logarithm of the surfactant concentration plots become uncertain with an increase in the concentration of the alcohol. Thus, the surface tension method was used up to *ca.* 8 mol/l alcohol concentration. Within this range well-defined CMC values could be obtained. A small minimum appeared near the CMC in the surface tension *vs.* concentration curve of $\bar{n}=11, 20$ and 31 in water. This may be due to the distribution of the ethylene oxide chain length of a surfactant molecule.¹³ Surfactants used in this study might fall in the category of polydisperse materials defined by Gibbons,¹⁴ but we believe that they have sufficient purity¹⁵ for attaining the aim of the present work, since the appearance of the minimum in the surface tension-concentration curve is not remarkable and analytical result shows sufficient purity.

CMC in alcohol-water mixtures are shown in Figs. 1, 4, and 5 as a function of alcohol concentrations. Methanol and ethanol show only a CMC-increasing

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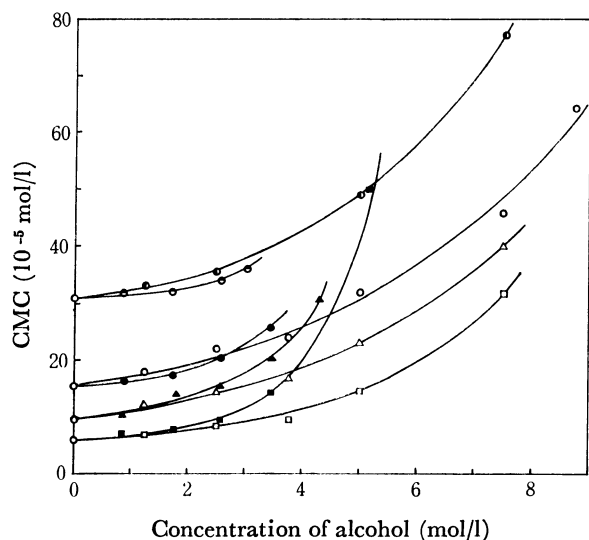


Fig. 1. The CMC's of $\bar{n}=6, 11, 20$ and 31 surfactants in methanol- and ethanol-water mixtures at 20°C .

□: methanol, $\bar{n}=6$ ■: ethanol, $\bar{n}=6$
 △: methanol, $\bar{n}=11$ ▲: ethanol, $\bar{n}=11$
 ○: methanol, $\bar{n}=20$ ●: ethanol, $\bar{n}=20$
 ●: methanol, $\bar{n}=31$ ●: ethanol, $\bar{n}=31$

effect (Fig. 1). *n*-Propanol shows a CMC-decreasing effect in the low concentration range for all \bar{n} 's and a CMC-increasing effect at higher concentration for $\bar{n}=6$ and 11 (Figs. 4 and 5), while *n*-butanol and *n*-pentanol show a CMC-decreasing effect (Figs. 4 and 5). However, the CMC-increasing tendency may be expected to appear in excess of the decreasing effects by more addition of these alcohols to the surfactant solutions in analogy with *n*-propanol. These results are in line with those for ionic surfactants.¹⁶⁾

The CMC-increasing effect of methanol and ethanol is attributable to the increasing solvent power of these alcohol-water mixtures, if we neglect the solubilization of alcohols into the palisade layer of the micelle. At low concentrations of alcohols, ethanol behaves almost the same as methanol with respect to the efficiency of the CMC-increasing effect. With increasing concentrations, however, ethanol becomes much more effective than methanol.

In order to clarify the above behavior, the heats of micellization in methanol- and ethanol-water mixtures

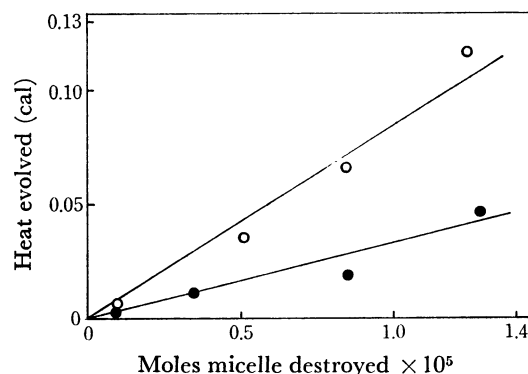


Fig. 2. The plots of heat evolved against moles of $\bar{n}=31$ surfactant demicellized at 20°C in water (○) and 0.87 M ethanol (●).

are compared. The examples of measured heat of micellization are shown in Fig. 2 with $\bar{n}=31$, in water and in 0.86 M ethanol. The abscissa represents the amount of micelle destroyed on dilution and the ordinate the observed heat change. The plot is almost linear and crosses close to the origin. Hence, within experimental error the assumption of Corkill *et al.*¹²⁾ is satisfied, *viz.* the heats of dilution of monomers and micelles are negligibly small as compared to the heat of micellization which is independent of concentration. The slope (Fig. 2) is the heat of micelle formation and equal to the standard enthalpy ΔH_m^0 with an opposite sign to that of the observed heat change.¹²⁾ The standard enthalpy ΔH_m^0 in conjunction with the standard free energy of micellization ΔG_m^0 gives the standard entropy ΔS_m^0 . We take the pseudo-phase separation approach and get the following equations:^{17,18)}

$$\Delta G_m^0 = RT \ln X_c \quad (1)$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (2)$$

where X_c is CMC expressed in mole fraction, since the CMC is small enough to replace activity by mole fraction. The solubilization of methanol and ethanol is considered to be negligible. Thus, the micelles in these short chain alcohol-water systems are single-component ones. The standard enthalpy ΔH_m^0 can be obtained in the above way (Fig. 2), and Eqs. (1)

TABLE 1. THERMODYNAMIC QUANTITIES OF MICELLE FORMATION FOR SURFACTANTS OF $\bar{n}=6$ AND 31 IN PURE WATER, METHANOL- AND ETHANOL-WATER MIXTURES AT 20°C

Additive	$\bar{n}=6$			$\bar{n}=31$		
	ΔH_m^0 kcal/mol	ΔS_m^0 e.u./mol	$\Delta G_m^0 \pm 0.06$ kcal/mol	ΔH_m^0 kcal/mol	ΔS_m^0 e.u./mol	$\Delta G_m^0 \pm 0.06$ kcal/mol
in water	7.8 ± 1.6	54 ± 5	-7.99	7.8 ± 1.6	51 ± 5	-7.03
1.25 M MeOH	4.5 ± 0.9	42 ± 3	-7.88	5.0 ± 1.0	41 ± 3	-6.95
3.75 M MeOH	3.0 ± 0.6	36 ± 3	-7.65	2.7 ± 0.5	33 ± 2	-6.83
7.50 M MeOH	-0.4 ± 0.1	22 ± 1	-6.91	-0.1 ± 0.1	22 ± 1	-6.40
0.43 M EtOH	4.1 ± 0.9	41 ± 3	-7.92	5.3 ± 1.1	42 ± 4	-7.01
0.86 M EtOH	2.2 ± 0.5	34 ± 3	-7.86	3.3 ± 0.7	35 ± 3	-6.99
2.58 M EtOH	0.6 ± 0.1	28 ± 1	-7.66	0.5 ± 0.1	25 ± 1	-6.91
5.16 M EtOH	-3.7 ± 0.8	10 ± 3	-6.62			

and (2) are valid for these systems, regarding the alcohol-water mixtures as solvents.

The values of ΔH_m^0 and ΔS_m^0 for representative methanol- and ethanol-water mixtures of $\bar{n}=6$ and 31 together with those in water are given in Table 1.

For the results in water, the large positive entropy ΔS_m^0 is responsible for the negative free energy ΔG_m^0 for micelle formation, since the enthalpy ΔH_m^0 is positive. Several causes for the positive entropy can be considered. Current views¹⁸⁻²⁸ are as follows. The ordered water around the hydrocarbon chains is released on micellization, contributing to the positive entropy. The gain in the conformational entropy of hydrocarbon chains may also give a positive value. Contribution of the change in solvation of hydrophilic chains is complicated. Desolvation of polyethylene oxide chains, which gives rise to a positive entropy change, has been proposed.²¹⁻²⁴ Elworthy and Florence^{25,26} suggested that the mesh of polyethylene oxide chains in the micellar state can trap more solvent than the single chains in monomer, leading to a negative change. The negative contribution of the decrease of the configurational entropy of the flexible hydrophilic chains on micellization is also involved.

Studies on the dependence of ΔS_m^0 on the ethylene oxide content with the same hydrocarbon chains might elucidate the contribution of polyoxyethylene chains to ΔS_m^0 . We have obtained the following data of ΔS_m^0 for various values of \bar{n} in aqueous solution at 20 °C.

\bar{n}	6	11	20	31
ΔS_m^0 (e.u./mol)	54	54	50	51

It is seen that no essential difference of ΔS_m^0 in water exists among the surfactants having various oxyethylene chain lengths, so that we can consider that the contribution of polyoxyethylene chains is secondary. Thus, the large positive entropy ΔS_m^0 in water is considered to be primarily due to the loss of iceberg structure during the course of micellization. We see that the addition of methanol and ethanol to the surfactant aqueous solutions reduces the entropy ΔS_m^0 , and the effectiveness of reducing ΔS_m^0 of ethanol becomes greater than that of methanol. At least qualitatively these alcohols primarily weaken the hydrophobic interactions, the important driving force for micellization, although other effects may also be involved.²⁹

The difference in the effect of alcohol on ΔS_m^0 among various ethylene oxide chain lengths is ambiguous, but the effect on ΔG_m^0 displays the difference. In water and at constant concentrations of methanol and ethanol, ΔG_m^0 vs. \bar{n} plots are almost linear. Thus, the gradient of the ΔG_m^0 vs. \bar{n} plots is the free energy increment of the hydrophilic part of a surfactant in the process of micellization. The gradient $\Delta(\Delta G_m^0)/\Delta\bar{n}$ is plotted against the alcohol concentration in the solvent (Fig. 3). With increasing concentration of alcohols, the parameter $\Delta(\Delta G_m^0)/\Delta\bar{n}$ decreases rapidly, the rate being greater for ethanol than methanol. Alcohols might reduce the hydration of polyoxyethylene chains through the hydrogen bonding with water, but the interaction of alcohols with water is complicated.^{30,31} According

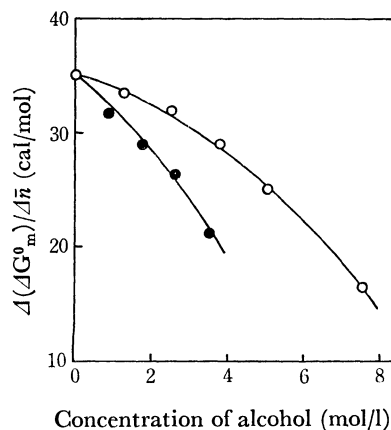


Fig. 3. $\Delta(\Delta G_m^0)/\Delta\bar{n}$ vs. methanol (●) and ethanol (○) concentration plots.

to Ray and Nemethy,⁸ it is probable that alcohols have a solvent effect on the ethylene groups in the oxyethylene chains as well as the hydrocarbon chains of surfactants, since the ethylene groups may also be expected to increase the structural order in the surrounding water.

The CMC-increasing effect of methanol and ethanol is considered to contain two opposing factors: the primary effect on the hydrocarbon part, in which the alcohols weaken the hydrophobic bond, and lead to increasing the CMC; a secondary effect on the polyoxyethylene chains, which is a small effect of CMC-decreasing. The overall effect of methanol and ethanol is inclined towards raising the CMC.

Alcohols which have longer hydrocarbon chains than ethanol show a CMC-decreasing effect. The results are shown in Figs. 4 and 5 with $\bar{n}=6$ and 31, respectively. A similar behavior was obtained for $\bar{n}=11$ and 20. At low concentrations of alcohols, the CMC-decreasing effects are attributable to the penetration of alcohols into the palisade layer of the micelle, forming

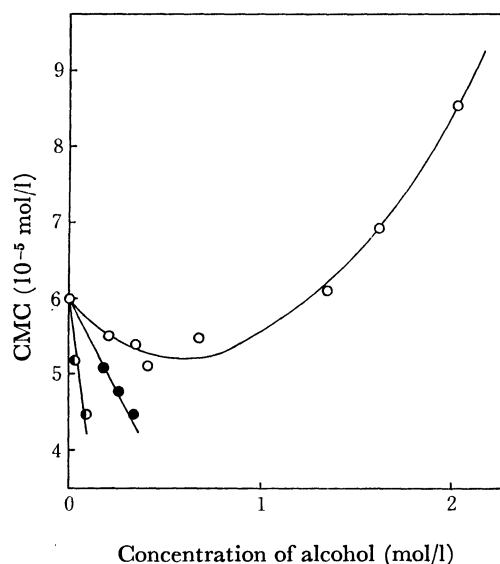


Fig. 4. The CMC's of $\bar{n}=6$ surfactant as a function of the concentrations of *n*-propanol (○), *n*-butanol (●) and *n*-pentanol (◐) at 20 °C.

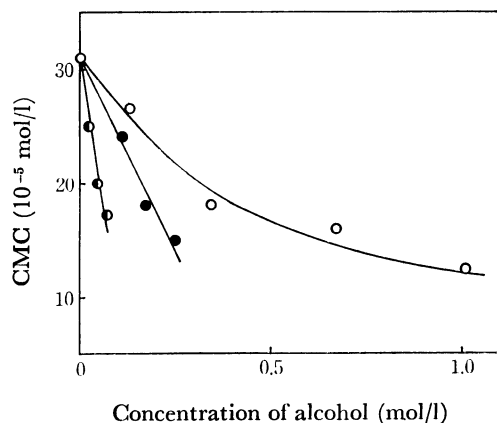


Fig. 5. The CMC's of $\bar{n}=31$ surfactant as a function of the concentrations of n -propanol (\circ), n -butanol (\bullet) and n -pentanol (\circ) at 20 °C.

a mixed micelle.¹⁶⁾ At higher concentrations of n -propanol, the CMC-increasing effect overcomes the decreasing effect. This is due to the solvent effect as in the case of methanol and ethanol, although it is not seen in the case of n -butanol and n -pentanol. The CMC initially decreases linearly with alcohol concentration, which resembles closely the case of ionic surfactants (Figs. 4 and 5). The CMC-decreasing effects of alcohols have been explained by Shinoda in the case of ionic surfactants.¹⁶⁾ His view is herewith applied to the case of nonionic surfactants.

We take the phase separation model, equating the chemical potential of the surfactant molecule in the micelle phase to that in the bulk phase, assuming that the standard chemical potentials in water and alcohol-water system are approximately the same if the concentration of alcohols added is sufficiently low. We then have

$$\frac{X_c'}{X_c} = 1 - x; \quad x \ll 1 \quad (3)$$

where x is the mole fraction of alcohol in the mixed micelle, and X_c and X_c' are the CMC in the mole fraction unit in water and in the mixed solvent, respectively. Alcohols are considered to undergo partition between the micellar and bulk phase. The partition law is as follows.

$$\frac{X_a}{x} = K \exp\left(-\frac{m'\omega}{kT}\right); \quad X_a \ll 1 \quad (4)$$

where K is a constant, m' the number of carbon atoms in an alcohol, and ω the free energy change per methylene group transferred from water into the micelle phase. Near the CMC, the amount of solubilized alcohol is negligible. Thus, X_a can be put equal to the mole fraction of alcohol in the aqueous surfactant solution.

From Eqs. (3) and (4) we get

$$\begin{aligned} \ln \frac{X_c - X_c'}{X_a} &= \ln X_c + \frac{m'\omega}{kT} - \ln K \\ &= \ln X_c + 1.1m' - \ln K \end{aligned} \quad (5)$$

where the value of ω is adopted to be $1.1 kT$.^{32,33)}

This gives the relation between the logarithm of the

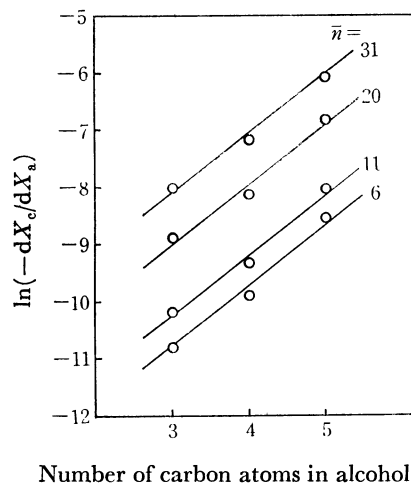


Fig. 6. The logarithm of the rate of change of the CMC with alcohol concentration, $\ln(-dX_c/dX_a)$ vs. the number of carbon atoms in alcohol, m' .

rate of change of CMC with alcohol concentration, $\ln(-dX_c/dX_a)$, and the number of carbon atoms in alcohol, m' . The former, obtained from experimental data is plotted against the latter in Fig. 6. The values of the gradients of these plots are close to 1.1, the experimental data fitting Eq. (5) fairly well. The value of K obtained for each \bar{n} is:

\bar{n}	6	11	20	41
K	1.57	1.51	0.64	0.55

It can be seen from Eq. (4) that x is inversely proportional to K when m' and X_a are fixed. We see that the surfactant with a larger oxyethylene chain length has a greater mole fraction of alcohol in mixed micelle. It seems that the surfactant solution with larger \bar{n} solubilizes the alcohols to a greater extent. The result for n -propanol reflects the situation. At higher concentrations of alcohol, the CMC-increasing effect overcomes the CMC-decreasing effect on account of the increase of non-solubilized alcohol. It is seen that the CMC-increasing effect of n -propanol is more enhanced for the smaller \bar{n} , the CMC-decreasing effect prevailing for the larger \bar{n} (Figs. 4 and 5). The results indicate that the CMC-decreasing effect (solubilization effect) increases with the increase of oxyethylene chain length. This conclusion agrees with Cohen's result in the case of n -heptanol.³⁴⁾

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