January, 1985] Bull. Chem. Soc. Jpn., 58, 247—251 (1985)

A Thermodynamic Study on Micellization of Nonionic Surfactant in Water and in Water-Ethanol Mixture by Gel Filtration

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(Received July 13, 1984)

Micellization of hexa(oxyethylene) dodecyl ether ($C_{12}E_6$) was studied in water and in ethanol-water mixtures at different temperatures by gel filtration on Sphacryl S-200. Standard enthalpies and entropies of micellization were determined from variation of critical micelle concentration(cmc) with temperature. Compensation plots were obtained, slopes for alcohol-water mixtures being indentical with that for pure water. Therefore, the micelle formation in water and ethanol-water mixtures has been explained in terms of its bulk structure. Gel fitration of $C_{12}E_6$ micelle with addition of a large amount of ethanol has led to a finding that the micelle size gradually becomes small with increasing ethanol content until micelles disappear above 35%v/v.

Thermodynamic studies on micellization are based on the assumption that monomer concentration is constant above cmc. However, any of the general methods, *e.g.*, the surface tension[1-3] and dye methods,[4,5] cannot verify the constancy of monomer concentration above cmc. We previously reported[6] that gel filtration of aqueous nonionic surfactant gave more reasonable cmcs than other methods, pointing out that monomer concentration became nearly constant at high concentrations of nonionic surfactant. Therefore, this method is effective for obtaining useful thermodynamic information regarding micellization.

In this research, we investigated the effect of temperature on the cmc of hexa(oxyethylene) dodecyl ether ($C_{12}E_6$) in water and in water–ethanol mixture by means of gel filtration for the purpose of elucidating thermodynamically the effect of ethanol on the micellization and the process of destruction of micelles by added ethanol.

Experimental

Materials. Hexa(oxyethylene) dodecyl ether,$H(OCH_2CH_2)_6OC_{12}H_{25}$ ($C_{12}E_6$), was supplied from Nikko Chemical Co., Ltd. Sephacryl S-200 and Sephadex LH-60 used for gel filtration were purchased from Pharmacia Fine Chemicals. Distilled water was used after degassing *in vacuo*.

Gel Filtration. Sephacryl S-200 was mainly used because this gel hardly shrinks by added ethanol. The gel column was jacketed and maintained at a constant temperature within 0.1 °C. Tail analysis was carried out as previously reported.[6] Retention volumes of micelles (V_m) and monomer (V_f) and monomer concentration (C_f) were measured by the same method as described in our previous paper.[6]

Results and Discussion

Thermodynamic Studies on Micellization in Water. The effect of temperature (0—30 °C) on the behavior of $C_{12}E_6$ micelle in water was studied. Monomer concentrations measured on solutions in the range 4×10^{-5}—2×10^{-2} M (1 M=1 mol dm^{-3}) were plotted against total concentration (C_t) of $C_{12}E_6$ (Fig. 1). The monomer concentration increases toward a limiting concentration with increase in C_t at each temperature. The limiting concentration corresponding to cmc increases with lowering temperature. The plots, in Fig. 2, against temperature of ratio V_m/V_f obtained by gel filtration of 5×10^{-3} M $C_{12}E_6$ solution indicate that the hydrated micellar size increases with increase in temperature, in accord with Suzuki.[7] On the basis of the cmcs obtained by this tail analysis at various temperatures (Fig. 1), the standard free energy (ΔG°_m), standard enthalpy (ΔH°_m), and standard entropy (ΔS°_m) of micellization

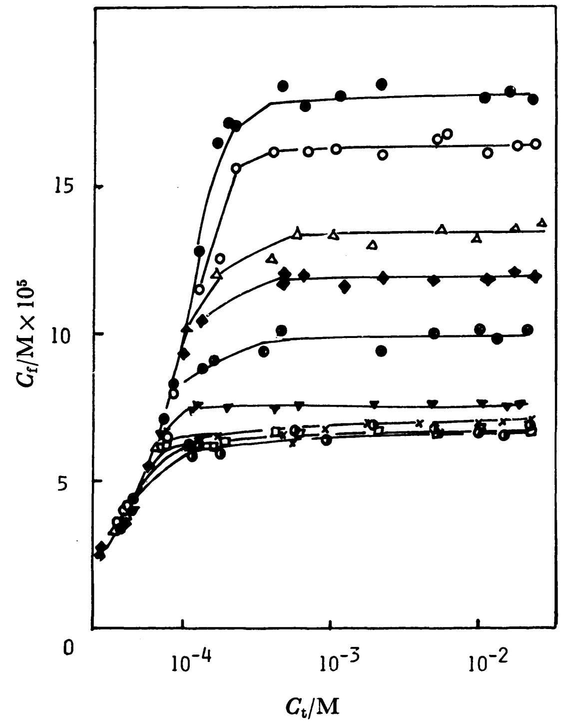

Fig. 1. Plots of Monomer Concentration, C_f, against Total Concentration, C_t.
●: 0 °C, ○: 2 °C, △: 5 °C, ◆: 10 °C, ⊗: 15 °C, ▼: 20 °C, ×: 25 °C, ◑: 27 °C, □: 30 °C.

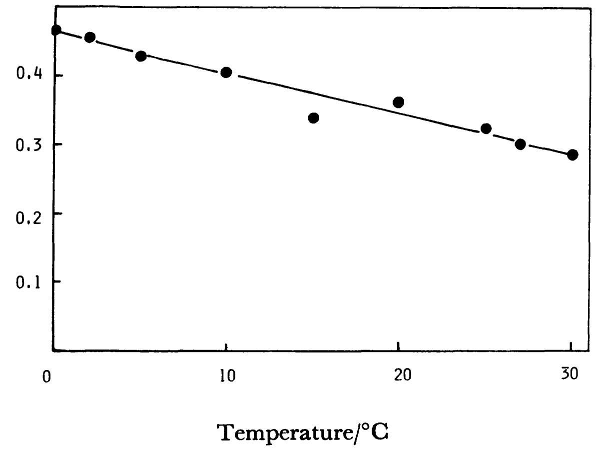

Fig. 2. Plots of V_m/V_f against Temperature.

were determined by use of the phase separation model. The standard free energy is obtained by

$$\Delta G^\circ_m \approx RT \ln \text{cmc}, \tag{1}$$

where cmc is expressed in mole fraction. The standard enthalpy of micellization can be obtained by

$$\Delta H^\circ_m = -RT^2[\mathrm{d}(\ln \text{cmc})/\mathrm{d}T]. \tag{2}$$

However, since ΔH°_m is dependent on temperature, values of ΔH°_m were obtained by fitting a quardratic function of the form[8]

$$\ln \text{cmc} = a/T^2 + b/T + c \tag{3}$$

to observed data and applying subsequently Eq. 2; values of ΔH°_m were calculated with a computer. Standard entropies of micellization were calculated from values of ΔH°_m and ΔG°_m by

$$\Delta S^\circ_m = (\Delta H^\circ_m - \Delta G^\circ_m)/T. \tag{4}$$

As shown in Table 1, the large positive entropy is responsible for the negative free energy of micellization since the enthalpy change is positive. This is caused by release of the ordered water from around the hydrocarbon chain on micellization.[14]

Table 1. Values of thermodynamic parameters (cmc/M, ΔG°_m and ΔH°_m/kcal mol^{-1}, ΔS°_m/cal deg^{-1}) for $C_{12}E_6$ in water at various temperatures

T/°C	cmc	ΔG°_m	ΔH°_m	ΔS°_m
0	1.80×10^{-4}	−6.86	+9.68	+60.6
2	1.64×10^{-4}	−6.96	+9.18	+58.7
5	1.35×10^{-4}	−7.14	+8.45	+56.1
10	1.19×10^{-4}	−7.34	+7.26	+51.6
15	9.89×10^{-5}	−7.58	+6.11	+47.5
20	7.51×10^{-5}	−7.87	+5.00	+43.9
25	6.99×10^{-5}	−8.04	+3.93	+40.2
27	6.74×10^{-5}	−8.12	+3.51	+38.8
30	6.69×10^{-5}	−8.20	+2.89	+36.6

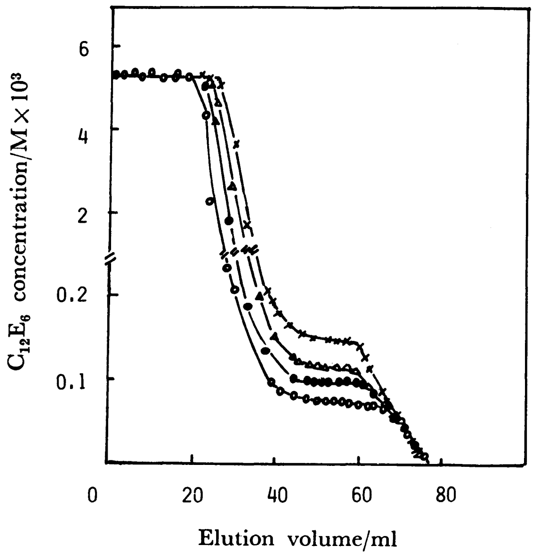

Fig. 3. Tail Analysis of Micellar $C_{12}E_6$ Solution on Sephacryl S-200.
○: without ethanol, ●: 5 % v/v ethanol, △: 10 % v/v ethnol, ×: 15 % v/v ethanol. $C_{12}E_6$ concentration, 5 mM.

The Effect of Added Ethanol on Micellization. Figure 3 shows a tail analysis of aqueous $C_{12}E_6$ solution in the presence of ethanol using a column of Sephacryl S-200 at 25 °C. The retention volume of micelle and the monomer concentration increase with increase in ethanol content, indicating that the micelle becomes progressively unstable with decrease in its size. As the ethanol concentration rose to 20, 25, and 30%v/v, as shown in Fig. 4a, it became difficult to observe the presence of micelles from the tail part of $C_{12}E_6$ elution curve. Based on the finding from the elution curves of propyl p-hydroxybenzoate that the propyl ester is solubilized into $C_{12}E_6$ micelle in water,[9] a similar analysis was made on the system of $C_{12}E_6$–propyl p-hydroxybenzoate in ethanol–water mixtures (Fig. 5). The result suggested that micelles might be present even in 30%v/v ethanol. However, since Sephacryl S-200 can be used only for fractionation of substances with molecular weights 5000—250000, it seems difficult to distinguish clearly between micelles and monomer in higher concentrations than 30%v/v ethanol. When Sephadex LH gel was used (Fig. 4b) which can fractionate substances with molecular weights ranging from 500 to 10000 and is less influenced by organic additive, it could differentiate clearly the micelle and monomer even in 30%v/v ethanol. However, it seems likely that micelles are scarcely present above 35%v/v ethanol. The above results directly

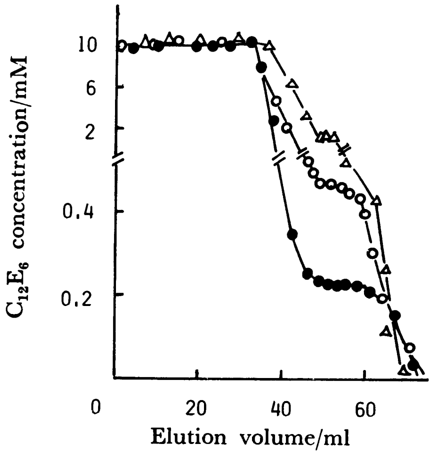

Fig. 4a. Tail Analysis for Elution Curves of 10 mM $C_{12}E_6$ in Ethanol-Water Mixtures on Sephacryl S-200 at 25 °C.
●: 20% v/v ethanol, ○: 25% v/v ethanol, △: 30% v/v ethanol.

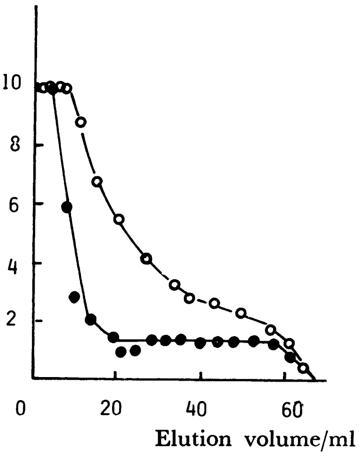

Fig. 4b. Tail Analysis for Elution Curves of 10 mM $C_{12}E_6$ in Ethanol-Water Mixtures on Sephadex LH-60 at 25 °C.
●: 30% v/v ethanol, ○: 35% v/v ethanol.

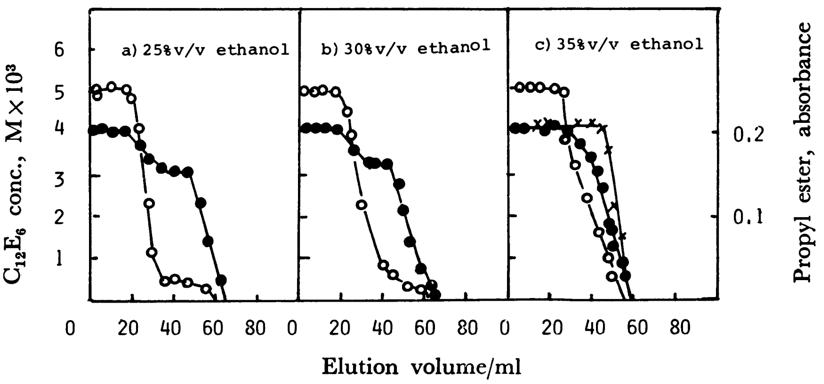

Fig. 5. Tail Analysis for Elution Curves of 0.278 mM Propyl *p*-hydroxybenzoate and 5 mM $C_{12}E_6$ in Ethanol-Water Mixtures on Sephacryl S-200 at 25 °C.
○: $C_{12}E_6$, ●: propyl *p*-hydroxybenzoate absorbance, ×: propyl *p*-hydroxybenzoate absorbance without $C_{12}E_6$

demonstrated that no micelles having a limiting size disappear suddenly with increasing ethanol content, whereas the micelle size becomes gradually small with micelles slowly disappearing. Deguchi *et al.*10) assumed on the basis of charge-transfer interaction that the concentration of ethanol required for the destruction of $C_{12}E_7$ micelle is in the range 30—35%v/v, in consistency with the present result.

Figure 6 is a plot of C_f obtained by the gel filtration on Sephacryl S-200 against C_t at 2, 5, 10, and 15% v/v at 25 °C. Since the value of C_f increased toward a limiting concentration with increase in C_t at each ethanol content, it was also possible in the presence of ethanol to estimate cmc and to discuss the micellization thermodynamically. A general expression11) for the solvent effect on nonionic surfactant micelle formation is

$$RT \ln [\mathrm{cmc}]/[\mathrm{cmc}]_o = -(\mu_2^{so}-\mu_2^{so'}) + RT \ln X + RT \ln f, \qquad (5)$$

where $[\mathrm{cmc}]_0$ is the cmc without organic additive, μ_2^{so} and $\mu_2^{so'}$ are the standard chemical potentials of the surfactant in bulk solutions of water and water–organic additive mixture, respectively, and X and f are the mole fraction and the activity coefficient of surfactant in the mixed micelle, respectively, both of which become unity when the solvent is pure water. The cmc-lowering effect of a solubilizate is explained in terms of mixed entropy and the reduction of activity on adding solubilizates.11,12) If the organic additive is not solubilized into the micellar phase, the solvent effect on micellization may be due mainly to the contribution of $-(\mu_2^{so}-\mu_2^{so'})$. In this experiment, $\ln[\mathrm{cmc}]/[\mathrm{cmc}]_0$ increased with in-

Table 2. Values of thermodynamic parameters (cmc/M, ΔG_m° and ΔH_m°/kcal mol^{-1}, ΔS_m°/cal deg^{-1}) for $C_{12}E_6$ in water-ethanol mixture at various temperatures

T	5%v/v Ethanol				10%v/v Ethanol				15%v/v Ethanol			
°C	cmc	ΔG_m°	ΔH_m°	ΔS_m°	cmc	ΔG_m°	ΔH_m°	ΔS_m°	cmc	ΔG_m°	ΔH_m°	ΔS_m°
0	1.80×10^{-4}	−6.85	+5.55	+45.0	1.55×10^{-4}	−6.90	+5.41	+45.0	1.50×10^{-4}	−6.90	+7.90	+54.0
5	1.23×10^{-4}	−7.17	+3.94	+39.9	1.31×10^{-4}	−7.12	+3.88	+40.0	1.30×10^{-4}	−7.10	+5.22	+44.3
10	1.15×10^{-4}	−7.34	+2.27	+33.9	1.21×10^{-4}	−7.29	+2.34	+34.0	1.20×10^{-4}	−7.27	+2.53	+34.5
15	1.10×10^{-4}	−7.49	+0.68	+28.0	1.13×10^{-4}	−7.46	+0.85	+28.9	1.07×10^{-4}	−7.47	−0.07	+26.0
20	1.05×10^{-4}	−7.65	−0.86	+23.0	1.13×10^{-4}	−7.59	−0.58	+23.0	1.19×10^{-4}	−7.54	−2.58	+16.9
25	9.43×10^{-5}	−7.84	−2.34	+18.0	1.16×10^{-4}	−7.70	−1.97	+19.0	1.38×10^{-4}	−7.58	−5.01	+8.6

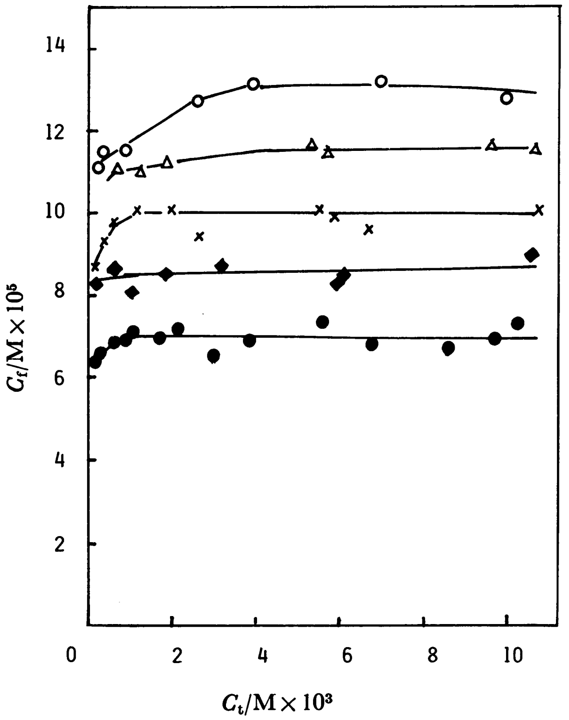

Fig. 6. Plots of Monomer Concentration, C_f, against Total Concentration, C_t in the presence of ethanol. ●: without ethnol, ◆: 2% v/v ethanol, ×: 5% v/v ethanol, △: 10% v/v ethanol, ○: 15% v/v ethanol.

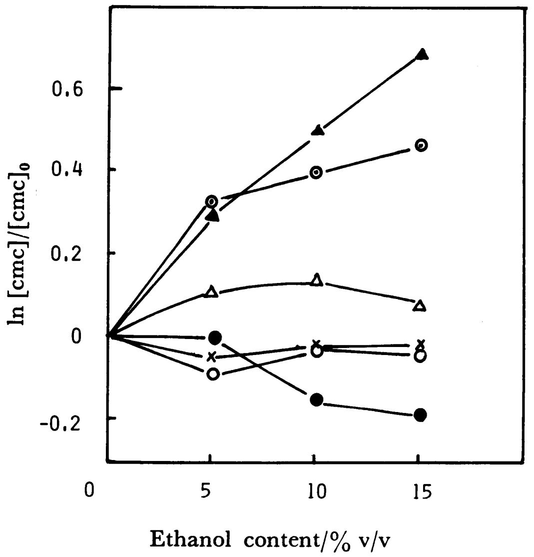

Fig. 7. Plots of ln[cmc]/[cmc]$_0$ against Ethanol Content. ●: 0 °C, ○: 5 °C, ×: 10 °C, △: 15 °C, ⊙: 20 °C, ▲: 25 °C.

creasing ethanol content at room temperature and hardly varied with ethanol content at low temperatures (Fig. 7). Therefore, the cmc-increasing effect of ethanol at room temperature is attributable to the increasing solvent power of these alcohol–water mixtures. It is of interest that the added ethanol hardly affects the micellization at low temperatures. This phenomenon may be explained as follows: the cmc-increasing effect attributable to the increasing solvent power of water–alcohol mixture would be compensated by the cmc-decreasing effect resulting from the solubilization of ethanol into $C_{12}E_6$ micelle. However, Nishikido *et al.*[13] reported that the solubilization of ethanol in nonionic micelle was negligible. We also investigated this system thermodynamically. Table 2 shows ΔG_m°, ΔH_m°, and ΔS_m° for the micellization in ethanol–water mixtures. The added ethanol caused a decrease in ΔH_m° and the micelle formation became exothermic in the neighborhood of room temperature as the content of ethanol increased (Table 2), while the micelle formation in water was endothermic as shown in Table 1. The entropy of micellization which has a large positive value in water, became small as the ethanol content increased (Table 2). Therefore, the cmc-increasing effect of ethanol at room temperature is ascribed to the weakness of the hydrophobic bond.[14] However, at low temperatures, the micellization in the presence of ethanol is responsible for the positive entropy. This indicates that the added ethanol might hardly destroy the structure of water at low temperatures.

Linear correlation between enthalpy and entropy changes has been observed for solution processes in aqueous media. This correlation is called the compensation phenomenon.[15–18] According to Lumry[15] the slope of compensation line has the dimension of temperature, T_c, in the range 220—290 K in

TABLE 3. T_c VALUES FOR MICELLIZATION IN DIFFERENT SYSTEMS

System	T_c/K	Reference
$C_{12}E_6$ in water	284 (r=1.000)	Present study
$C_{12}E_6$ in aqueous 5%v/v ethanol	289 (r=1.000)	Present study
$C_{12}E_6$ in aqueous 10%v/v ethanol	278 (r=0.999)	Present study
$C_{12}E_6$ in aqueous 15%v/v ethanol	280 (r=0.999)	Present study
Ionic surfactant in water (sodium dodecyl sulfate and cetyltrimethylammonium bromide)	283	8
Alkyltrimethylammonium bromide	313	19

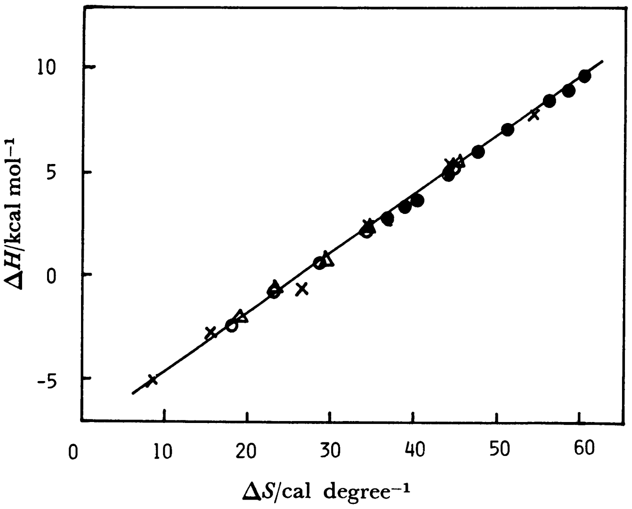

Fig. 8. Compensation plots of $C_{12}E_6$ Micellization. ●: without ethanol, ○: 5% v/v ethanol, △: 10% v/v ethanol, ×: 15% v/v ethanol.

aqueous media. Krishnan and Friedman[18] suggested that the entropy-enthalpy compensation was also observed in hydrophobic interactions. Sigh *et al.*[8] and Aoki *et al.*[19] found that their compensation plots obtained for the micellization of ionic surfactants in aqueous media were in accordance with Lumry's law.[15] Figure 8 shows compensation plots for nonionic surfactant micelle in water and in alcohol-water mixture. The compensation temperature of $C_{12}E_6$ micelle in water is 284 K, equal to that of ionic surfactant.[8] The compensation temperatures for alcohol-water mixtures are also in fair agreement with Lumry's law[15] (Table 3). Therefore, it is assumed that the micellization of $C_{12}E_6$ in water is related closely to the bulk structural property and proceeds even in the presence of ethanol essentially in a process similar to that in water.

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