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Micelle Formation and Surface Adsorption of Octaethylene Glycol Monoalkyl Ether (C_nE_8)

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The surface tension was measured against the concentration of C_nE_8 ($n = 14$, 16, and 18) at temperatures of 298.2, 303.2, 308.2, 313.2, and 318.2 K, from which the critical micelle concentration (CMC) was determined. The CMC decreased with increasing carbon number at lower temperatures, where the decreasing rate became much smaller at higher temperatures. The CMC values were examined by pyrene fluorescence, and the I_1/I_3 ratio of the pyrene spectrum steeply decreased below the CMC, and finally reached a plateau at higher surfactant concentrations. The I_1/I_3 ratios indicate that the microenvironment of pyrene in the micellar region becomes more hydrophobic with increasing the alkyl chain of C_nE_8. The aggregation number by a static light-scattering method increased with increasing the alkyl chain at a definite temperature and with raising the temperature for all of the surfactants. The thermodynamic parameters (ΔG°, ΔH°, $T\Delta S^\circ$) of the micelle formation were calculated from the temperature dependence of CMC and the aggregation number, and the micellization was found to be entropy-driven. The surface excess concentration (Γ) was also determined from the change in the surface tension with the concentration from which the molecular surface area (A) below the CMC was evaluated. The molecular surface areas suggest that longer monoalkyl ethers form a bi-molecular layer with the hydrophobic tail intruding inwards. The positive entropy change (Δs) for the surface adsorption decreased and stayed almost constant with increasing concentration for $C_{14}E_8$ and $C_{16}E_8$, while the change remained almost zero for $C_{18}E_8$ at whole concentrations below the CMC. These results suggest that the non-fully extended alkyl chain in the bulk could not well contribute to a positive entropy change upon adsorption, which results in a smaller decreasing rate in CMC with increasing carbon number of alkylchain for $C_{16}E_8$ and $C_{18}E_8$ compared with the decreasing rate for C_nE_8 with n less than 14.

Many results have been reported in the literature dealing with the critical micelle concentration (CMC) of both ionic and nonionic surfactants as a function of the temperature by using a variety of experimental techniques.[1–3] In general, the dependence of CMC on the temperature for an ionic surfactant shows a U-shaped curve with a minimum around room temperature.[4,5] However, in the case of nonionic surfactants, there are several trends in the CMC dependence on the temperature, i.e., decreasing with increasing temperature,[6] monotonous increasing with increasing temperature,[7] having a maximum at a certain temperature (Λ-shape),[8] and having a minimum similar to ionic surfactants.[9] The thermodynamic parameters of micellization, therefore, have shown various values.

In the surface-adsorption process, nonionic surfactants have also demonstrated a variety of trends of surface excess with the temperature, i.e., increasing with raising the temperature[10,11] or decreasing with raising the temperature.[7,11] Moreover, the entropy change also showed a variety of trends on the concentration, i.e., increasing with increasing concentration[12] or decreasing with increasing concentration.[4] This means that the temperature dependence of the surface excess and the entropy change for a nonionic surfactant are still controversial. These changes can be explained by following three effects accompanied by the adsorption process. First, the systematic orientation of surfactant molecules at an interfacial region gives rise to a decrease in the entropy change. Second, dehydration of the head group and the melting of iceberg water molecules around hydrophobic tail provide a positive entropy change. Third, a thermal solubility increase of the monomer prevents micelle formation. These effects also play an important role in the molecular aggregation in bulk, and lead to a complicated phase behavior of nonionic surfactants.[13] The object of the present investigation is experimentally to determine the thermodynamic parameters of both micellization and surface adsorption of polyethylene glycol n-alkyl ethers with the same ethylene oxide chain, but different long alkyl chains from C14 to C18.

Experimental

Materials. Octaethylene glycol monoalkyl ethers (C_nE_8, $n = 14$, 16, and 18) were purchased from Nikkol Chemical Co., Ltd (>99%), and were used as received, because the gas chromatograph attached for purity certification had only one sharp peak for each surfactant. The purity was further checked by an elemental analysis in percentage: C, 63.60 (63.42); H, 10.95% (11.01) for $C_{14}E_8$, C, 64.65 (64.52); H, 11.11% (11.12) for $C_{16}E_8$, and C, 65.59 (65.49); H, 11.25% (11.33) for $C_{18}E_8$, where the values in parentheses are the calculated ones.

Methods. The surface tension of a surfactant solution was measured by a drop volume method as a function of the temperature at various concentrations under atmospheric pressure. After ca. 80% of the total drop volume was left standing for adsorption equilibrium, the total volume was determined. The temperature was controlled within ±0.01 K by immersing the apparatus in a thermostat. The experimental error for the surface tension was ±0.05 $\mathrm{mN\,m^{-1}}$. Surface-tension measurements of the C_nE_8 solutions were made over the temperature range 298.2–318.2 K. A period of time between 40 min and 1 h was taken for equilibrium readings. This time interval is acceptable for lower surfactant concentrations to reach their equilibrium surface adsorption.

A stock solution of C_nE_8 was introduced stepwise into a saturated solution of pyrene, whose concentration was about 4×10^{-7} $\mathrm{mol\,dm^{-3}}$. The fluorescence-emission spectra were monitored with a fluorescence photometer (Hitachi model 650-60), where the temperature was 298.2 ± 0.3 K. The excitation and emission slit widths were 5 and 1.5 nm, respectively, where the excitation wavelength was 336 nm. The I_1/I_3 ratio of the pyrene fluorescence spectrum was plotted against the C_nE_8 concentrations.

A static light-scattering measurement was made using a laser light-scattering photometer (Otsuka Denshi, SLS 600). The light source was a 5 mW He–Ne laser, and the wavelength was 633 nm. The temperature was controlled within ±0.3 K at 298.2, 308.2, and 318.2 K by circulating thermostated water. The instrument was calibrated using purified benzene. C_nE_8 solutions were filtrated through a membrane filter having a pore size of 0.1 µm (Millex-VV). The specific refractive-index increments of the solutions were measured using a differential refractometer (Otsuka Denshi DRM-1020). The light source was a 20-mW iodine lamp having a wavelength of 632.8 nm.

The cloud points of the surfactant solutions were determined visually by noting the temperature at which turbidity started to be observed, where the surfactant concentration was 100-times the CMC.

Results and Discussion

CMC and Aggregation Number. The surface tensions were plotted against the logarithm of the concentration, as shown in Figs. 1, 2, and 3 for $C_{14}E_8$, $C_{16}E_8$, and $C_{18}E_8$, respectively. Figure 4 illustrates the surface tension change against the logarithm of the C_nE_8 concentration at 298.2 K for comparing these three surfactants; a similar trend was also observed at other temperatures. It is quite interesting that the surface activity at lower concentrations became less for a longer alkyl chain homologue, which suggests that a longer alkyl chain is not fully extended. The critical micelle concentration (CMC) at different temperatures was determined from a sharp break in the above changes; the results are given in Table 1. The CMC values slightly decreased with increasing temperature over the temperature range from 298.2 to 308.2 K, and then remained almost constant for $C_{14}E_8$ and $C_{16}E_8$, while those for $C_{18}E_8$ stayed almost the same at all temperatures. These changes were caused by the fact that increasing dehy-

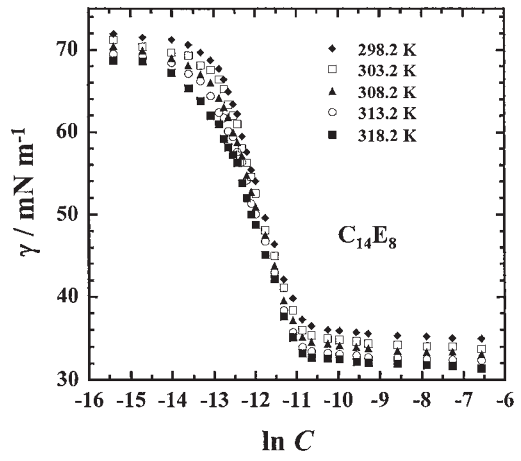

Fig. 1. Change of surface tension with $C_{14}E_8$ concentration.

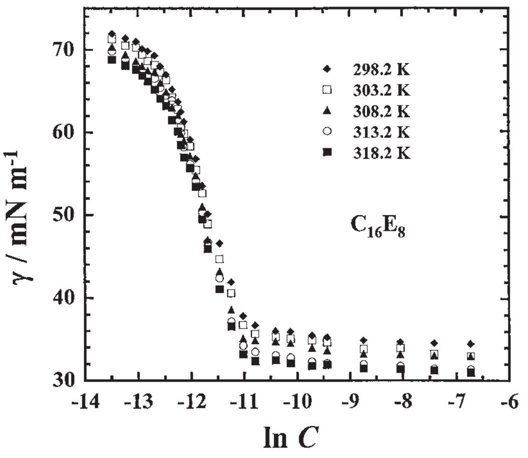

Fig. 2. Change of surface tension with $C_{16}E_8$ concentration.

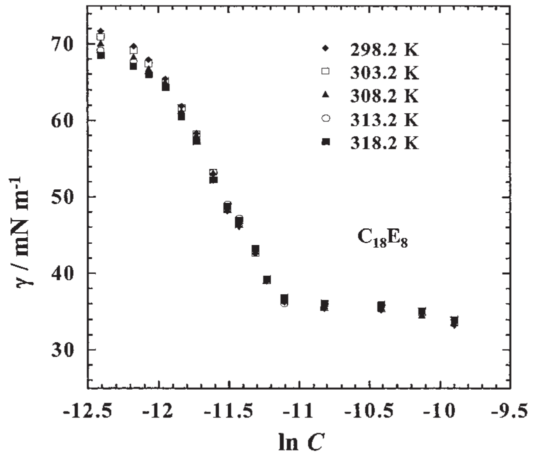

Fig. 3. Change of surface tension with $C_{18}E_8$ concentration.

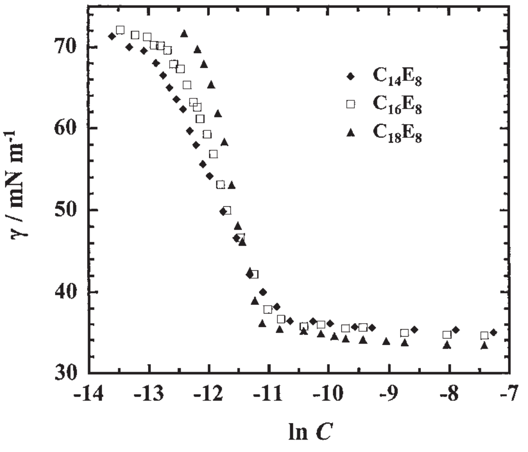

Fig. 4. Change of surface tension with C_nE_8 concentration at 298.2 K.

Table 1. The CMC and the Aggregation Number of C_nE_8 at Several Temperatures

Compound	Temperature K	CMC × 10^5 mol dm^{-3}	Aggregation number /×1000
$C_{14}E_8$	298.2	1.81	1.34
	303.2	1.72	—
	308.2	1.67	1.74
	313.2	1.67	—
	318.2	1.67	3.60
$C_{16}E_8$	298.2	1.60	2.29
	303.2	1.56	—
	308.2	1.49	4.37
	313.2	1.49	—
	318.2	1.49	7.42
$C_{18}E_8$	298.2	1.39	5.27
	303.2	1.34	—
	308.2	1.43	7.82
	313.2	1.46	—
	318.2	1.46	13.9

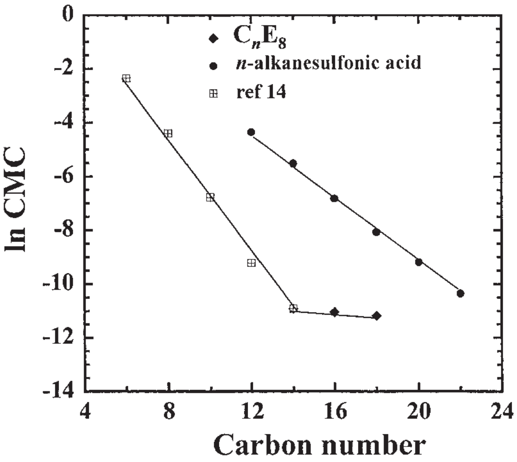

Fig. 5. Dependence of lnCMC on the carbon number of alkyl chain for C_nE_8 at 298.2 K and for n-alkanesulfonic acids at 342.2 K.

dration of the head group with temperature worked more to decrease the CMC than thermal motion to increase the CMC at lower temperatures for the shorter surfactants. On the other hand, increasing hydrophobic dehydration seems to have been compensated by the above increasing thermal motion at higher temperatures, resulting in the stationary values of CMC. At the same time, the CMC change with alkyl chain length was found to be very small, which clearly indicates that the hydrophobic group was not fully extended and did not totally contribute to the micellization of $C_{16}E_8$ and $C_{18}E_8$ (see Fig. 5).

The CMC values of C_nE_8, whose carbon number is from 6 to 14 (Ref. 14), are plotted together with the present experimental values in Fig. 5, where the CMC values in the reference were determined by a surface-tension method, and are interpolated or extrapolated ones with regards to the number of ethylene oxides using the reference data. From the figure, the CMC value of $C_{14}E_8$ is just on a line for the relationship between the logarithm of CMC and the carbon number for the shorter homologues. On the other hand, the linear relationship observed from 6 to 14 is not applicable to the CMC's of $C_{16}E_8$ and $C_{18}E_8$. This might be caused by the fact that the longer alkyl chain was not fully extended. A similar behavior has been observed, where the logarithm of the partition coefficient of fatty acids between aqueous solution and organic solvent linearly increased from C7 up to C14, while the logarithm values for C16 to C18 deviated downwards from the linearity.[15] The above observations strongly suggest that a transition in the shape of a long alkyl chain from a fully extended to a looped state at a certain chain length is highly possible, as the result of an intramolecular hydrophobic interaction. Such a hydrophobic interaction would reduce the hydrophobic effects of an individual molecule for transfer into an organic medium or for dimerization.[15] These phenomena are discussed again latter.

The CMC dependence of C_nE_8 was also compared with those of n-alkanesulfonic acid, whose carbon number changed from 12 to 22 (Fig. 5). The result showed that a linear relationship was maintained up to 22 carbon atoms for the n-alkanesulfonic acids at 342.2 K.[16] This was due to a long-range electrostatic repulsive force between ionic head groups of n-alkanesulfonic acid. Therefore, lnCMC was able to linearly decrease up to carbon numbers of 22. From the linear relationship between lnCMC and the carbon number of alkyl chain, the contribution of CH_2 group to ΔG° of micellization could be obtained.[17,18] This is mentioned later.

The CMC values were examined by the pyrene fluorescence spectrum (I_1/I_3) in Fig. 6, where the CMC values from surface tension are shown by dashed lines. The I_1/I_3 ratio slowly decreased below the CMC and then rapidly above it for $C_{14}E_8$, while it sharply decreased for $C_{16}E_8$ and $C_{18}E_8$ with increasing the concentration, even at concentrations below the CMC. This fact suggests that there exists a weak association among C_nE_8 monomers or a looped alkyl chain of the monomers, at concentrations below the CMC for $C_{16}E_8$ and $C_{18}E_8$. The ratio gradually decreased above the CMC, and finally reached a plateau at higher surfactant concentrations for C_nE_8. This behavior can suggest the following two possibilities: (i) pyrene is associated with a looped alkyl chain or with some kind of premicellar aggregates of C_nE_8 at lower concentrations than the CMC, and the aggregates grow in size with increasing concentrations

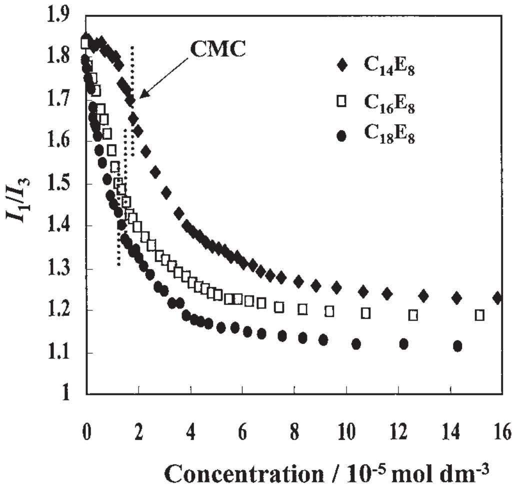

Fig. 6. I_1/I_3 ratio of pyrene fluorescence with C_nE_8 concentration at 298.2 K.

and (ii) a few surfactant molecules may self-associate with pyrene into small aggregates that are not formed in the absence of pyrene, where pyrene acts as a trigger for their formation. Moreover, the I_1/I_3 ratio at the plateau region decreases more with a longer alkyl chain surfactant, which indicates that the solubilized pyrene resides in a more hydrophobic environment as the aggregate size increases and that the dielectric constant of the hydrophobic micellar region decreases with increasing alkyl chain length.

The static-light scattering method is most commonly used to determine the molecular weight of macromolecules or micelles. This method is very useful for a micellar system whose micelles are monodisperse or polydisperse in size and have a clear CMC. The scattered light intensity at 90° from solutions above the CMC was analyzed by the Debye equation,

$$\frac{K(C-\mathrm{CMC})}{R_{90}-R_{90}^{0}} = \frac{1}{M} + 2B(C-\mathrm{CMC}), \tag{1}$$

where K is the optical constant, C is the total surfactant concentration (g/cm^3), R_{90}^0 is the reduced intensity (R_{90}) at the CMC, M is the weight-average molecular weight of micelles, and B is the second virial coefficient. The optical constant is given by

$$K = \frac{4\pi^2 \bar{n}_0^2(\partial\bar{n}/\partial C)^2}{N_\mathrm{A}\lambda^4} \tag{2}$$

for polarized incident light of wavelength λ, where $\bar{n}_0$ is the solvent refractive index, $\partial\bar{n}/\partial C$ is the refractive-index increment of the solution, and N_A is Avogadro's number. The intercept values of the plots on the ordinate were determined by a linear-regression analysis. The aggregation number of micelles (n) was obtained by the equation $n = M/W$, where W is the molecular weight of $\mathrm{C}_n\mathrm{E}_8$. The thus-obtained aggregation numbers are given in Table 1. The aggregation number increased with increasing alkyl chain length at a definite temperature and with raising temperature for all of the surfactants. The increase in the aggregation number with temperature means an approach of the aggregates to a separate phase at the cloud point. The cloud point was determined to be 346, 341, and 336 K for $\mathrm{C}_{14}\mathrm{E}_8$, $\mathrm{C}_{16}\mathrm{E}_8$, and $\mathrm{C}_{18}\mathrm{E}_8$, respectively. Decreasing the cloud point of $\mathrm{C}_n\mathrm{E}_8$ with increasing carbon number corresponds to an easing of the phase separation with increasing aggregation number. It clearly indicates that the hydrophobicity of alkyl chain plays an important role in the micellar size.

The temperature dependence of the aggregation number is more pronounced for a longer alkyl chain than for a shorter one. This means that the hydrophobic group has a larger effect than the hydrophilic group on the micelle aggregation number.

Thermodynamics of Micellization. Based on the mass-action model of micelle formation, the following equilibrium can be given for monodisperse micelle formation of a nonionic surfactant:[5]

$$n\mathrm{S} \overset{K_n}{\rightleftharpoons} \mathrm{M}_n, \tag{3}$$

where S and M_n are the monomer and micelle of the aggregation number (n), respectively. From Eq. 3, the micellization constant (K_n) is given as

$$K_n = \frac{n-2}{(2n^3-n^2)(cmc)^{n-1}}, \tag{4}$$

where the Philips definition of CMC was employed.[5,19] The important implication of Eq. 4 is that the micellization constant (K_n) can be estimated in terms of the CMC value and the aggregation number of micelles.

The standard Gibbs energy change per mole of the surfactant then follows from the micellization constant,

$$\Delta G^\circ = RT\ln\mathrm{CMC} + (RT/n)\ln(2n^2) \quad \text{for} \quad n > 50. \tag{5}$$

The corresponding enthalpy (ΔH°) and entropy (ΔS°) changes are given, respectively, as

$$\frac{\Delta H^\circ}{T^2} = -\frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right)_P, \tag{6}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T. \tag{7}$$

Since the temperature dependence of two micellization parameters (CMC, n) had already been obtained (Table 1), it became possible to evaluate the thermodynamic variables: ΔG°, ΔH°, and ΔS° (Figs. 7a–7c). According to their values, they are more dependent on the temperature for $\mathrm{C}_{14}\mathrm{E}_8$ and $\mathrm{C}_{16}\mathrm{E}_8$ than for $\mathrm{C}_{18}\mathrm{E}_8$; in addition, the micellization was found to be entropy-driven over the examined temperature range. This fact originates from the small temperature dependence of the CMC's; also, the contribution of the temperature dependence of the aggregation number (see the second term of Eq. 5) is negligibly small compared with that of the CMC change, even for a very large aggregation number. A small enthalpy change means that during the micellization the attractive interaction among the hydrophobic chains is opposed by the steric hindrance of the bulky oxyethylene chains, which are associated with many water molecules.

On the other hand, the contribution to the ΔG° per methylene group ($-\mathrm{CH_2}-$) of the present surfactants is an important parameter to see the hydrophobicity of the inner micelles. This can be determined by the slope of ln CMC against the number of carbon atoms in an alkyl chain. As for an ionic surfactant, the following equation can be used:[18]

$$\left[\frac{\Delta(\Delta G^\circ)}{\Delta n_\mathrm{c}}\right] = \left(1+\frac{m}{n}\right)RT\left[\frac{\Delta(\ln\mathrm{CMC})}{\Delta n_\mathrm{c}}\right]_{T,P} - \frac{RT}{n}\left[\frac{\Delta(\ln[\mathrm{M}_n])}{\Delta n_\mathrm{c}}\right]_{T,P}. \tag{8}$$

The results are $-1.10RT$ ($T = 298.2$ K) and $-1.08RT$ ($T = 303.2$ K) for $\mathrm{C}_n\mathrm{E}_8$ and n-alkanesulfonic acids, respectively, where 0.67 was used for the degree of counterion binding to the micelle (m/n) for n-alkanesulfonic acids.[17] This means that a micellar core of $\mathrm{C}_n\mathrm{E}_8$ is almost the same in hydrophobicity as that of n-alkanesulfonic acids.

The micellization for the present three surfactants was confirmed by the solubilization of butylbenzene into the micelle, where the maximum additive concentration started to steeply increase with increasing concentration above the CMC obtained by the surface tension.[20] Therefore, the CMC mentioned above is quite similar to the conventional one, above which surfactant molecules start to aggregate, although the aggregation numbers are very large.

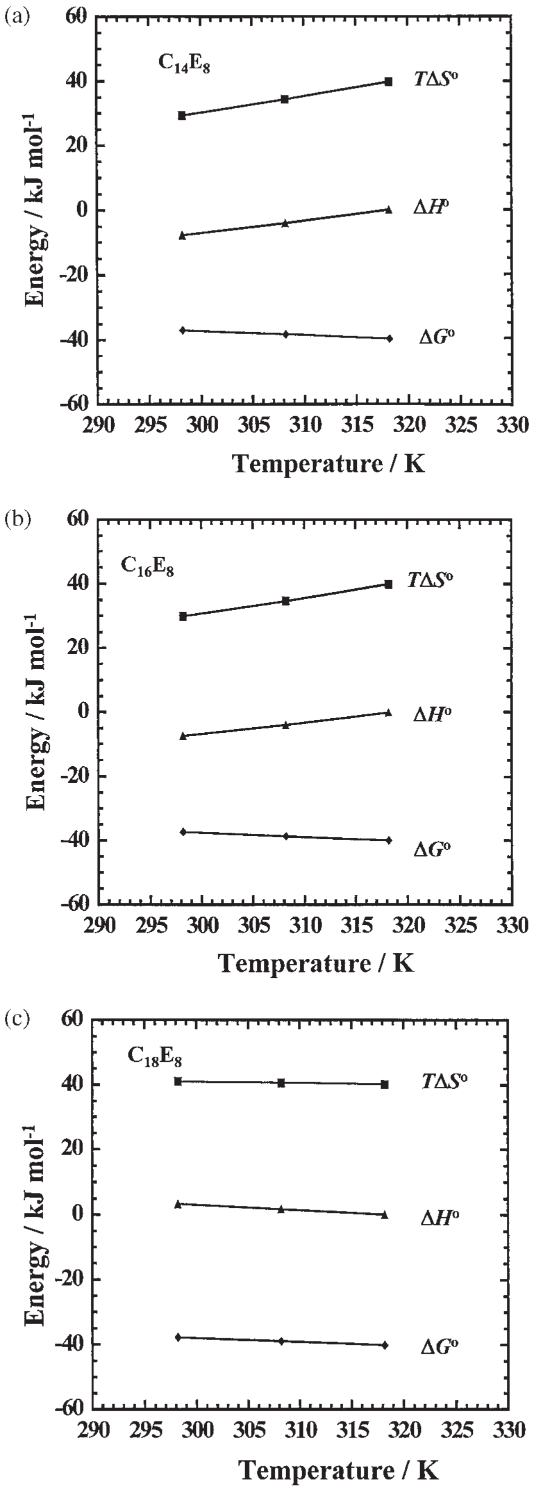

Fig. 7. Changes of ΔG°, ΔH°, and $T\Delta S^\circ$ of micellization with temperature for $C_{14}E_8$ (a), $C_{16}E_8$ (b), and $C_{18}E_8$ (c).

Surface Properties. Figures 1, 2, and 3 illustrate the surface tension vs logarithm of concentration plot for C_nE_8. These results indicate that the temperature dependence of the surface activity is more prominent for a shorter alkyl chain than for a longer one.

The surface tension (γ) is a function of temperature (T), pressure (P), and chemical potential (μ_i) of component i (the Gibbs–Duhem equation for interface). However, as for a system of two phases (air and solution) and three components (surfactant, water, and air), it becomes trivariant under equilibrium according to the phase rule. Then, we have the following Gibbs equation for the surface tension:[5,21]

$$d\gamma = -s^s dT + \tau^d dP - \Gamma d\mu, \tag{9}$$

where s^s, τ^d, and Γ are the excess entropy per unit area at the interfacial layer, the thickness between the two dividing surfaces, and the surface excess of surfactant per unit area, respectively. At constant temperature and pressure, the surface excess of the surfactant (Γ) becomes a function of the surfactant concentration,

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right)_{T,P}, \tag{10}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature, and C is the surfactant concentration. The surface tension versus the logarithm of the concentration below the CMC was analyzed by dividing the plot into two parts. The surface tensions at higher concentrations were analyzed by a linear equation, while those at lower concentrations were done by the second-order equation against the concentration; the slope of the equations was used to determine the surface excess by Eq. 10.

The calculated surface excess (Γ) of C_nE_8 is shown as a function of the concentration at different temperatures in Figs. 8a–8c. These figures indicate that the surface excess increased with increasing concentration at lower concentrations, and then reached a maximum plateau at around a half CMC. Furthermore, the surface excess decreased with increasing temperature due to an increase in the thermal motion of the molecules. The systematic increase in Γ with the alkylchain length indicates that the surface adsorption takes place with the alkyl chain fully elongated instead of looped. That is, the attractive interaction of hydrophobic alkyl chains became stronger for the elongated state than for the looped one. The surface excess value of $C_{14}E_8$ in this study was smaller than a reference value obtained by the Wilhelmy method.[22] Tajima et al. also found the dissimilarity of the surface excess value due to different methods.[23]

From the surface excess, the molecular surface area (A) at the surface layer can be calculated by

$$A = 1/N_A\Gamma, \tag{11}$$

where N_A is Avogadro's number. The results are shown in Fig. 9. The molecular surface area increased with increasing temperature and with decreasing carbon number of C_nE_8, as is usually observed. This result indicates that a longer alkyl chain becomes more closely packed than a shorter one by a stronger attractive interaction between the hydrophobic chains. The important finding is that the molecular surface area is less than the cross-sectional area of the alkyl chain for $C_{16}E_8$ and $C_{18}E_8$. Such small molecular surface areas strongly suggest that the molecules form bi-lamellar aggregates with the hydrophobic tails contacted with one another while intruding inward, where a layer of water molecules with a certain width lies between the air/solution interface and a plane made of upper head groups of the bi-lamellar aggregates.[24]

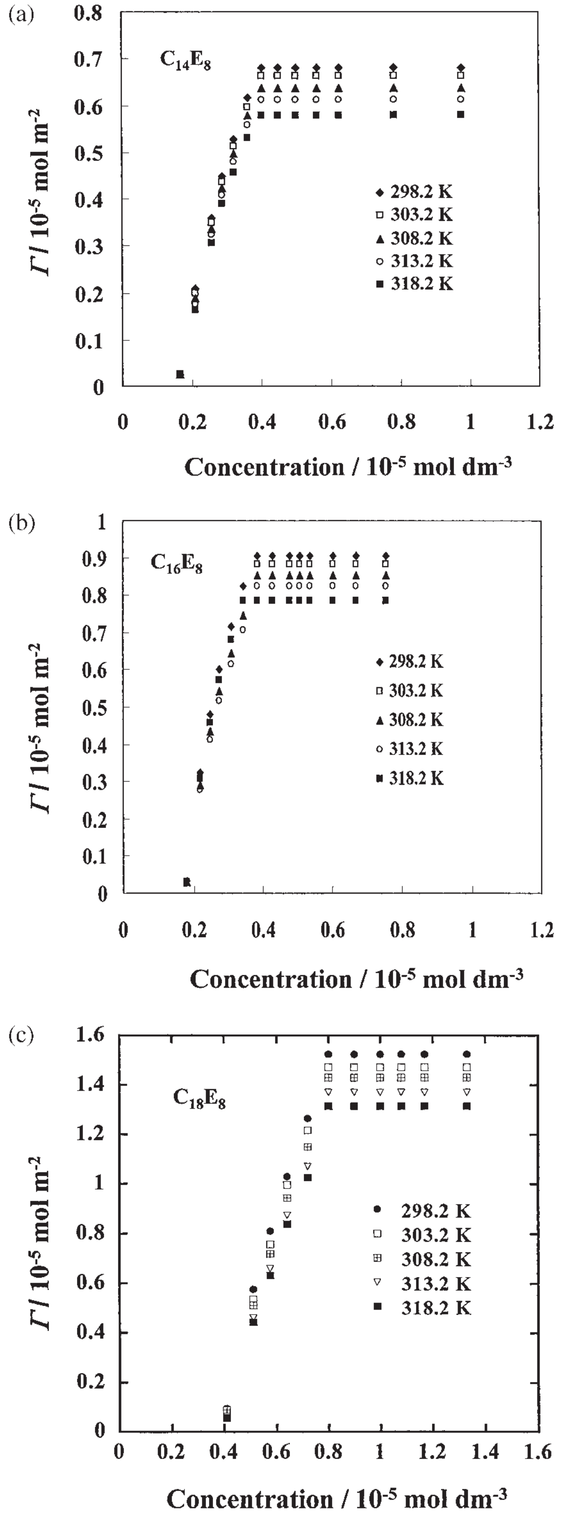

Fig. 8. Change of surface excess with concentration for $C_{14}E_8$ (a), $C_{16}E_8$ (b), and $C_{18}E_8$ (c).

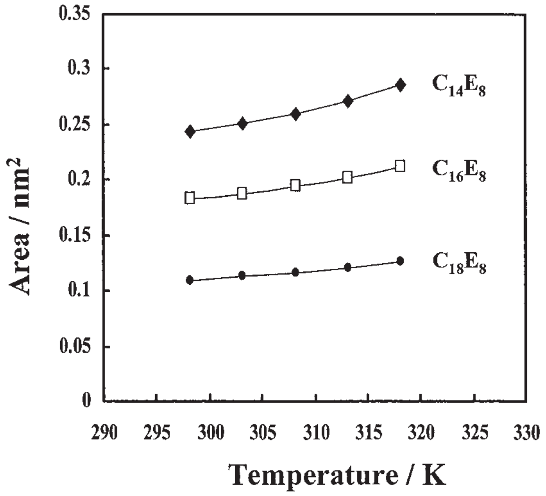

Fig. 9. Temperature dependence of molecular surface area of C_nE_8 just below the CMC.

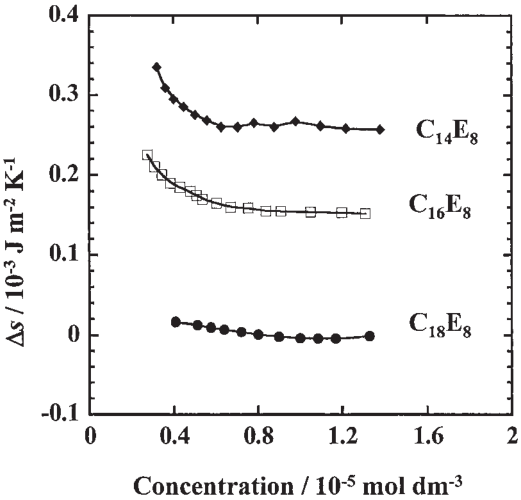

Fig. 10. Entropy changes for surface adsorption with concentration over the whole temperature range studied.

The chemical potential of the surfactant is also a function of the temperature, pressure, and concentration,

$$d\mu = -s\mathrm{d}T + v\mathrm{d}P + \left(\frac{\partial \mu}{\partial C}\right)_{T,P} \mathrm{d}C, \tag{12}$$

where s and v are the partial molar entropy and volume, respectively. After introducing Eq. 12 into Eq. 9, the following equation is obtained:

$$\Delta s = s^{\mathrm{s}} - \Gamma s = -\left(\frac{\partial \gamma}{\partial T}\right)_{P,C}. \tag{13}$$

The thus-obtained results are shown in Fig. 10. It can be seen from Fig. 10 that the entropy change of adsorption or surface condensation decreased with increasing concentration of C_nE_8. In addition, the entropy changes of C_nE_8 adsorption were all positive, except for $C_{18}E_8$ at higher concentrations. This means that the melting of iceberg water molecules around long alkyl chain with a positive entropy change on the adsorption still contributed more than the concentration and the orientation of molecules in the surface layer by adsorption with a negative entropy change. Decreasing entropy change with increasing concentration of C_nE_8 means that the C_nE_8 molecules became more ordered, or more restricted, with increasing adsorbed amount. The positive entropy changes decreased with increasing alkyl chain length of C_nE_8, which also suggests that the alkyl chain is not fully extended in a monomeric state but is fully extended in bi-lamellar aggregates, and therefore can not perfectly contribute to the positive entropy change at adsorption.

Conclusion

The CMC dependence on the carbon number of a long alkyl chain was very small, which means that a long alkyl chain in the monomeric state can not totally contribute to the micellization. The alkyl chains are as closely packed in $C_{14}E_8$ micelles as they are in ionic micelles, judging from the Gibbs energy change of transfer per CH_2 group from aqueous bulk to micelle interior. C_nE_8 with a longer alkyl chain is less surface active at concentrations far below the cmc, which suggests that the longer alkyl chain does not fully contribute to the adsorption by its hydrophobicity, too. Two possibilities are suggested: 1) a longer alkyl chain is not fully extended, but is folded or looped in the bulk, 2) very weak inter-molecular association takes place among hydrophobic alkyl chains of the molecules. According to the molecular surface area in the adsorbed state, bi-lamellar aggregates are formed for longer C_nE_8 with hydrophobic tails in contact with one another and intruding inward.

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