

Temperature Dependence of the Surface Phase Behavior and Micelle Formation of Some Nonionic Surfactants

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The surface phase behavior and micellar properties of two nonionic surfactants, namely, ethylene glycol mono *n*-dodecyl ether (EGDE) and ethylene glycol mono *n*-tetradecyl ether (EGTE), have been investigated at different temperatures. From the study of film balance and Brewster angle microscopy (BAM), it has been observed that both of the amphiphiles show a first-order phase transition indicating conspicuous cusp points in their respective adsorption isotherms. This is further confirmed by the observation of bright 2-D condensed domains at the solution surfaces just after the appearance of the cusp points in the adsorption isotherms. Each of the above amphiphiles has a definite temperature above which they cannot show any indicative feature of phase transition, even with solutions of concentration above the critical micelle concentration (CMC) of the amphiphiles. These temperatures are found to be 23 and 37 °C for EGDE and EGTE, respectively. The CMC values of the amphiphiles increase with increasing temperature, showing a maximum value at a definite temperature (T_{\max}), and then decrease with further increases in temperature, which is just the opposite trend of the usual behavior of ionic surfactants. Interestingly, T_{\max} values of both of the amphiphiles correspond well to their respective maximum temperature of the appearance of the phase transition in the adsorbed monolayers. The standard thermodynamic parameters for micelle formation were calculated to determine the nature of thermodynamic process involved in micellization. Both enthalpy, ΔH_m° , and entropy, ΔS_m° , terms change their sign from negative to positive and increase monotonically with increasing temperature. The enthalpy term ΔH_m° is found to be zero at T_{\max} , which suggests that micellization is entirely an entropy-driven process at this temperature. A linear relation in the ΔH_m° versus ΔS_m° plots is observed with slopes 304 and 296 for EGDE and EGTE, respectively, having dimensions of the Kelvin temperature. Both of the thermodynamic quantities compensate each other, leading the free energy to be a negative value.

Introduction

Langmuir monolayers at the air–water interface have been a source of fascination since they are the most fundamental state of amphiphilic molecules in 2-D systems. This interest stems in part from their pressure-induced 2-D phase transition leading to an exciting variety of condensed-phase domain formations at the interface. The development of Brewster angle microscopy (BAM)^{1,2} has made it possible to characterize in situ the morphological features of the monolayer just after the phase transition without using any probe impurity.

Quite independently, there has been growing interest in the phase behavior of adsorbed monolayers of water-soluble surfactants at the air–water interface. In this system, the amphiphile molecules undergo spontaneous adsorption from the bulk of the aqueous solution, showing a gradual increase in surface pressure with time. The surface pressure (π)–time (t) isotherm shows a conspicuous cusp point when the pressure attains a definite value, indicating a first-order phase transition. Several research groups including ours have characterized a wide variety of morphological features of adsorbed monolayers that occur just after the appearance of the cusp points in the π – t adsorption isotherms.^{3–11} Since the adsorbed monolayers that result from the sacrifice of the molecules remain in the bulk, the concentration of the molecules and their arrangement in the bulk play

key roles in determining the phase behavior of the adsorbed monolayers. It has been reported that above a definite temperature and below a corresponding bulk concentration no indicative feature of phase transition in the adsorbed monolayer is observed.^{3,11} In a previous paper,¹² we reported that each amphiphile has a definite temperature above which it cannot show any indicative feature of phase transition, regardless of the bulk concentration. Above this temperature, hydrophobic interactions among the alkyl chains make it more favorable for the molecules to remain in the bulk of the solution by forming micelles; there is a gradual trend of decreasing CMC and equilibrium surface pressure at and above the CMC with increasing temperature.

The CMC values of both ionic and nonionic surfactants have been determined as a function of temperature by many workers using a wide variety of experimental techniques.^{13–20} According to the results of ionic surfactants, CMC versus temperature data fit on a U-shaped curve with a minimum around room temperature. However, nonionic surfactants show a gradual trend of decreasing CMC with increasing temperature. However, increases in CMC values with increasing temperature²¹ and the observation of a minimum in the CMC–temperature curve²² have also been reported, in striking contrast to the usual behavior of the nonionic surfactants. We observed that contrary to the usual behavior the CMC values of both EGDE and EGTE increase with increasing temperature, showing a maximum at a definite temperature T_{\max} and then a decrease with further

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increases in temperature. Thus CMC–temperature curves can be represented as Λ -shaped curves, which is just the opposite trend of the behavior of ionic surfactants. The characteristic feature of phase transitions in the adsorbed monolayer is also observed as long as the CMC values show an increasing trend with a rise in temperature.

In this paper, it will be shown that two factors must be taken into consideration to account for the existence of a phase transition in the adsorbed monolayer. These are (1) the effect of temperature on the equilibrium surface pressure attainable at and above the CMC and the critical surface pressure necessary for the appearance of the phase transition and (2) the variation in the micellar properties of the surfactants in the bulk with temperature and its effect on the 2-D surface concentration of the molecules at the interface. Keeping these views in mind, we endeavor to present a detail account of the dependence of the phase behavior of the surfactants on their micellar properties to gain new insight into the domain-formation mechanism. For this purpose, we study the adsorption kinetics and surface morphology of the amphiphiles over a wide range of temperature. To investigate the effect of micelle formation on the adsorption kinetics and surface morphology of the amphiphiles, we study the effect of temperature on the critical micelle concentration and the equilibrium surface pressure at and above the CMC values. This approach also includes the nature of thermodynamic quantity changes associated with micelle formation. We used Muller's²³ treatment to explain the observed behavior of the surfactants. According to this treatment, when CMC* is the minimum value at temperature T^* , as in the case of an ionic surfactant, the CMC value at other temperatures T can be given by

$$\ln(\text{CMC}/\text{CMC}^*) = [\Delta C_p / (1 + \alpha)R] \{ [1 - (T^*/T)] + \ln(T^*/T) \} \quad (1)$$

where ΔC_p is the heat capacity change, R is the gas constant, and α is the counterion binding capability of a micelle that is defined as the ratio of the number of surfactant ions to the number of its counterions in a micelle.

We observed that eq 1 can fairly be applied in the case of nonionic surfactants that show a maximum CMC over a particular temperature range of the form

$$\ln(\text{CMC}/\text{CMC}_{\max}) = [\Delta C_p / R] \{ [1 - (T_{\max}/T)] + \ln(T_{\max}/T) \} \quad (2)$$

where CMC_{\max} is the maximum value at T_{\max} . The data treatment was performed similarly to that described by Muller. When $\ln(\text{CMC})$ is plotted against $[1 - (T_{\max}/T)] + \ln(T_{\max}/T)$, the slope gives $\Delta C_p/R$, and the intercept gives $\ln \text{CMC}_{\max}$. The values of the enthalpy and entropy changes of micellization are calculated by the following expressions:

$$\Delta H_m^\circ = \Delta C_p(T - T_{\max}) \quad (3)$$

$$\Delta S_m^\circ = \Delta S_{\max}^\circ + \Delta C_p \ln(T/T_{\max}) \quad (4)$$

where

$$\Delta S_{\max}^\circ = -\Delta G_{\max}^\circ/T_{\max} = -R \ln(\text{CMC}_{\max}) \quad (5)$$

Experimental Section

The amphiphiles EGDE ($\text{CH}_3(\text{CH}_2)_{11}\text{OCH}_2\text{CH}_2\text{OH}$) and EGTE ($\text{CH}_3(\text{CH}_2)_{13}\text{OCH}_2\text{CH}_2\text{OH}$) were supplied by Nikko

Chemicals Co. Ltd., Tokyo, Japan, with a purity of $>99\%$ and were used as received. The experimental setup for the adsorption kinetics and surface morphology study was equipped with a home-built, 2-mm-thick Langmuir trough above which a Brewster angle microscope (BAM) was mounted. Surface pressure was measured by the Wilhelmy method using a small rectangular glass plate. The BAM is composed of a 20-mW He–Ne laser, a Glan–Thompson polarizer, an analyzer, a zooming microscope with a CCD camera of high sensitivity, a TV monitor, and a video recording system. Recorded images were treated with image-processing software to maximize the contrast and to correct the distortion of the images caused by the oblique glancing of the microscope. Details of the instrumentation may be found elsewhere.²⁴

The experiments were carried out by pouring a definite amount of aqueous solution into the trough. To attain equilibrium with the desired experimental temperature, the solution was allowed to stand for about 25 min before starting the experiments. The molecules that were already adsorbed at the solution surface during this span of time were removed by sweeping the surface with the movable Teflon barriers. Under these conditions, the surface concentration of the amphiphile molecules can be considered to be zero (i.e., $\pi = 0$ at $t = 0$). The increase in surface pressure was then followed with time, and simultaneously, the surface of the aqueous solution was observed by BAM.

For CMC measurements, the surface tensions of the aqueous solutions of different concentrations were measured by a surface tensiometer (Krüss K 10) equipped with a platinum plate. The solutions were transferred into a vessel that was thermostated by circulating water of the desired temperature. The surface tension measurements were started with a dilute solution, and subsequent concentrated solutions were made adding a previously prepared stock solution to the vessel. The establishment of equilibrium was checked by taking a series of readings after 15-min intervals until no significant change occurred. To eliminate evaporation losses beyond 25 °C, the vessel was covered with a lid. The accuracy of these measurements was within ± 0.1 mN/m. Ultrapure water of resistivity 18 M Ω cm (Elgastat UHQ-PS) was used throughout the present study.

Results and Discussion

Adsorption Kinetics and Surface Morphology. With time, the spontaneous adsorption of the molecules of both EGDE and EGTE at the solution surface results in a gradual increase in surface pressure. When the surface pressure attains a definite value at a definite temperature, the π – t adsorption isotherms show a conspicuous cusp point followed by a pronounced plateau region. Such a feature is characteristic of a first-order phase transition from a lower-density liquid expanded (LE) phase to a higher-density liquid condensed (LC) phase.^{4–11} The phase transition starts when the surface pressure attains a certain critical value at a definite temperature. After the plateau region, the surface pressure experiences a second rise in the values that lead to the global equilibrium. Figure 1 shows the π – t adsorption isotherms of EGDE and EGTE at different temperatures. For EGDE, the curves for 10, 15, 20, and 23 °C were taken using 1.3×10^{-5} , 2.0×10^{-5} , 2.5×10^{-5} and 3×10^{-5} M solutions, respectively. We chose the concentrations at different temperatures arbitrarily, considering the fact that condensed domains are observed at the solution surfaces during the experiments when the aforementioned concentrations correspond to the temperatures of the experiments. For example,

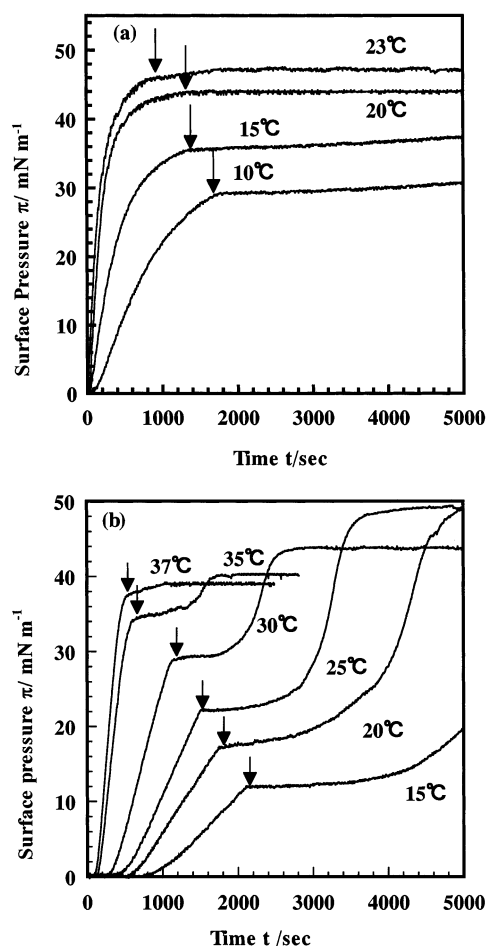


Figure 1. (a) π - t adsorption kinetics of aqueous solutions of EGDE at different temperatures with different concentrations: 10 °C, 1.3×10^{-5} M; 15 °C, 2.0×10^{-5} M; 20 °C, 2.5×10^{-5} M; and 23 °C, 3.0×10^{-5} M. (b) π - t adsorption kinetics of a 1.0×10^{-5} M aqueous solution of EGTE at different temperatures. The arrows in the isotherms indicate the positions of the appearance of the phase transitions in the adsorbed monolayers.

TABLE 1: Experimental and Calculated CMC Values of EGDE and EGTE at Different Temperatures

EGDE (CMC $\times 10^5$ /M)			EGTE (CMC $\times 10^6$ /M)		
temp/°C	exptl	calcd	temp/°C	exptl	calcd
10	1.75	1.92	15	1.65	1.69
15	2.40	2.41	20	2.00	2.15
20	2.74	2.73	25	2.40	2.57
25	2.75	2.76	30	2.85	2.88
30	2.45	2.51	35	3.30	3.04
35	2.32	2.10	40	3.08	3.02
T_{\max} (23)	2.85	2.78	45	2.85	2.85
			T_{\max} (37)	3.35	3.15

at 10 °C, the system can attain the necessary surface pressure for the LE-LC phase transition when the bulk concentration is 1.3×10^{-5} M. This concentration is not sufficient for the formation of condensed domains at higher temperatures (i.e., a higher concentration of the solution is necessary to attain the surface pressure for the occurrence of the phase transition). However, for EGTE, we used a 1.0×10^{-5} M solution for all of the adsorption isotherms whereas the CMC values of amphiphiles lie within 1.6×10^{-6} to 3.4×10^{-6} M over the temperature range (Table 1). We chose this higher concentration of the solution to reduce the time of the experiments. It is clear in Figure 1b that the π - t isotherms of EGTE show a pronounced

plateau region at almost zero surface pressure that decreases with the increasing temperature of the experiments. In light of dynamic surface tension measurements and fluorescence observations, this feature has been characterized as a transient surface adsorption during the gas-liquid expanded (G-LE) phase transition.²⁵

Condensed-phase domains observed by BAM further confirm the existence of the first-order phase transition in the adsorbed layers of the amphiphiles. As a representative example, some BAM images of EGDE and EGTE are presented in Figure 2. At 10 °C, the domains of EGDE are of a fingering pattern (image A). With increasing temperature, the number of fingers in a domain increases, and narrowing of the fingers is found to occur (image B). However, EGTE shows a wide variety of textures in the condensed domains at different temperatures (Figure 2, images C-F). At 15 °C, the shape of the domains is found to be circular with internal stripes (image C). A maximum of three stripes are observed in a fully developed domain at this temperature. The number of stripes in a domain is found to decrease with an increase in temperature (image D). At 25 °C, they lose their striped texture, showing uniform brightness over all the domains (image E). The domains are found to be circular up to 27 °C. Above this temperature, the domains are of a fingering pattern (image F). At a definite temperature, the shape of a condensed domain is governed by the balance between the dipole-dipole repulsion of the molecules and the line tension of the condensed phase. Since the hydrophobic alkyl chain of EGTE is longer than that of EGDE by two $-\text{CH}_2-$ units, it is expected that the former should experience a higher line tension than the latter. Thus, a higher line tension in the case of EGTE monolayers gives circular domains at higher temperature compared to those of EGDE. Details of the morphological feature of the amphiphiles may be found elsewhere.¹²

Thermodynamic Behavior of Micelle Formation and Its Dependence on Surface Morphology. Figure 3 shows the decrease in surface tension γ with the increasing bulk concentrations of EGDE and EGTE at different temperatures. The curves show a distinct break point at the CMC. Table 1 shows the experimental CMC values along with the values calculated by the use of eq 2. The calculated CMC values are found to be in good agreement with the experimental values. This agreement between the experimental and calculated values provides a good degree of applicability of Muller's treatment²³ to nonionic surfactants.

At a definite temperature, the CMC value of an amphiphile is governed by the balanced interaction of the van der Waal forces between the hydrophobic alkyl groups that tend to stabilize the micelles and the opposing hydration of the headgroups that tends to break up the micelles. The CMC values of nonionic surfactants are found to decrease gradually with increasing temperature. Contrary to the usual behavior of nonionic surfactants, the CMC values of both EGDE and EGTE increase with increasing temperature until they attain a maximum at their respective T_{\max} values. Maximum CMC values are observed at 23 and 37 °C for EGDE and EGTE, respectively. Two opposing thermally controlled effects are to be considered to explain the temperature dependence of CMC: (1) an increase in the dehydration of the headgroup that results in an increase in the hydrophobic character of the molecules with increasing temperature and (2) an increase in the thermal solubility of the

TABLE 2: Thermodynamic Parameters of Micellization for EGDE and EGTE at Different Temperatures^a

temp/°C	EGDE				EGTE			
	ΔH_m° (kJ mole ⁻¹)		ΔS_m° (JK ⁻¹ mole ⁻¹)		ΔH_m° (kJ mole ⁻¹)		ΔS_m° (JK ⁻¹ mole ⁻¹)	
	eq 3	eq 6	eq 4	eq 7	eq 3	eq 6	eq 4	eq 7
10	-39.7	-43.4	-50	-46				
15	-24.5	-29.6	3	19	-39.9	-45.8	-27	-17
20	-9.2	-13.0	56	75	-30.8	-35.1	3	20
25	6.1	2.1	107	128	-21.7	-27.0	34	45
30	21.4	15.5	158	170	-12.7	-17.7	64	80
35	36.7	33.3	208	225	-3.6	-8.7	94	110
40					5.4	3.3	123	150
45					14.5	16.8	184	190

^a ΔH_m° values are in kJ mole⁻¹, and ΔS_m° values are in J K⁻¹ mole⁻¹. CMC values were taken in mole fraction units for the calculations.

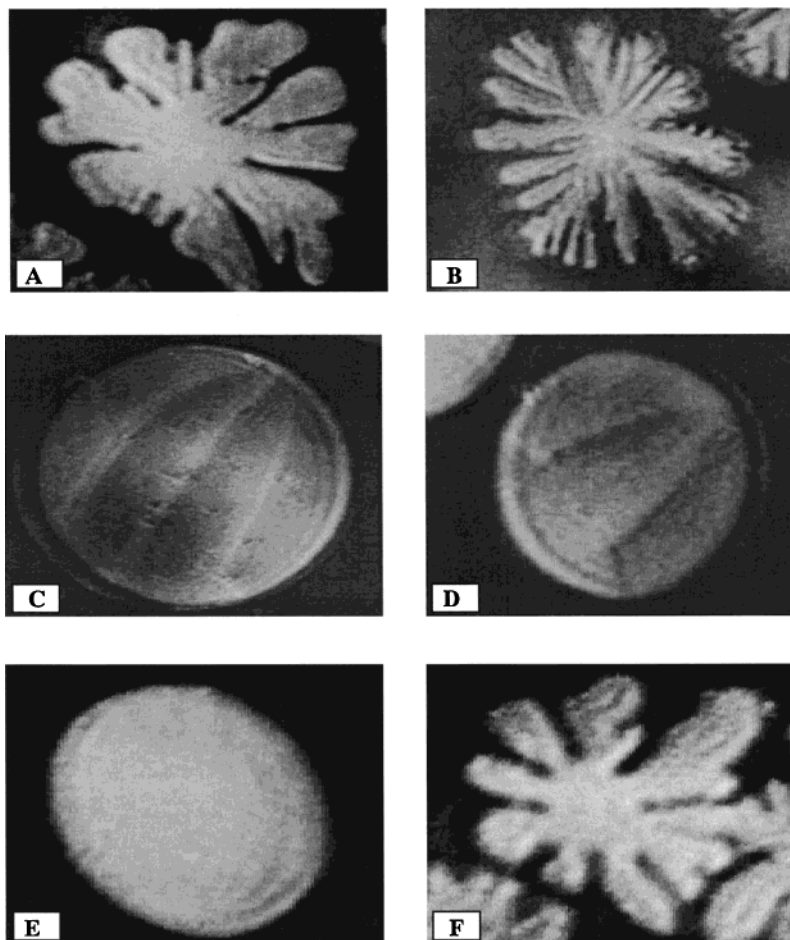


Figure 2. BAM images of condensed-phase domains of adsorbed monolayers of EGDE (A, 10 °C; B, 15 °C) and EGTE (C, 15 °C; D, 20 °C; E, 25 °C; and F, 30 °C) observed after the appearance of phase transitions.

molecules with increasing temperature. Crook et al.²¹ reported that the increase in the CMC of nonionic surfactants is the result of the predominance of the thermal solubility over the dehydration effect of the hydrophilic headgroup with increasing temperature. Below T_{\max} , the increase in the CMC values of the amphiphiles is the result of the dominating effect of the thermal solubility of the molecules over dehydration in this temperature range. Above T_{\max} , the CMC values start to decrease. This is because high temperature induces the dehydration around the hydrophilic headgroup that probably outweighs the thermal solubility of the molecules and conveniently provides the amphiphile molecules to accumulate to form micelles in the bulk.

Figure 4 shows the $\ln(\text{CMC})$ versus $\{[1 - (T_{\max}/T)] + \ln(T_{\max}/T)\}$ plots of the amphiphiles. The ΔC_p values obtained

from the slopes of the plots are 3.05 kJ K⁻¹ mol⁻¹ and 1.81 kJ K⁻¹ mol⁻¹ for EGDE and EGTE, respectively. The estimated uncertainties are found to be ± 0.02 kJ K⁻¹ mol⁻¹, leading to uncertainties of ± 0.3 kJ mol⁻¹ in ΔH_m° and ± 1.0 J K⁻¹ mol⁻¹ in ΔS_m° . A major contribution to ΔC_p in micellization is derived from the removal of hydrocarbon chains from water, and the associated ΔC_p values are found to be negative. However, the ΔC_p values in this case are found to be positive. This is probably due to the crowding of a substantial number of water molecules around the headgroups of the amphiphiles, which outweighs the effect of the breakdown of the water structure upon micellization within the studied temperature range. Table 2 shows the thermodynamic parameters of micellization at different temperatures. To compare the thermodynamic quantities obtained from eqs 3 and 4, the enthalpy and entropy of

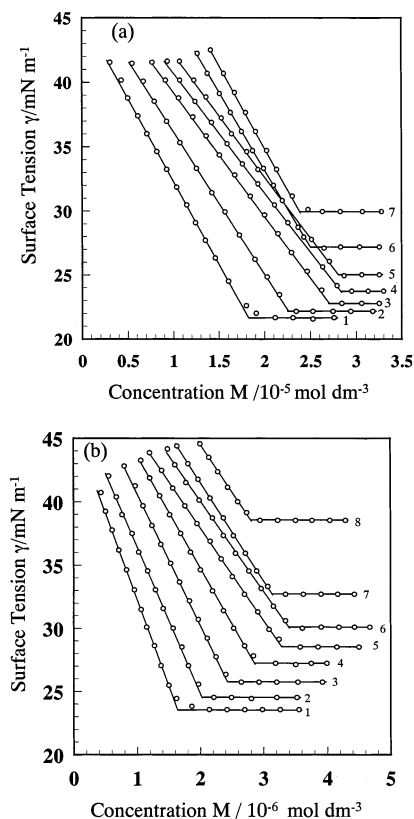


Figure 3. Surface tension vs concentration (M) curves for (a) EGDE (1, 10 °C; 2, 15 °C; 3, 20 °C; 4, 23 °C; 5, 25 °C; 6, 30 °C; and 7, 35 °C) and (b) EGTE (1, 15 °C; 2, 20 °C; 3, 25 °C; 4, 30 °C; 5, 35 °C; 6, 37 °C; 7, 40 °C; and 8, 45 °C).

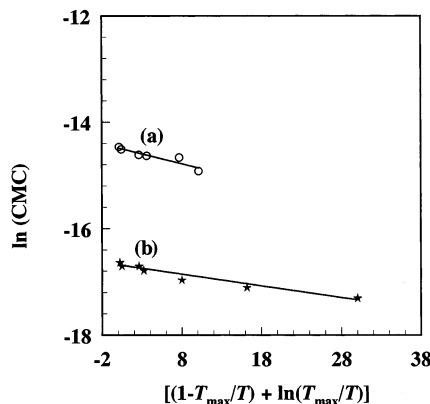


Figure 4. $\ln \text{CMC}$ vs $[1 - (T_{\text{max}}/T)] + \ln(T_{\text{max}}/T)$ plots for (a) EGDE and (b) EGTE used to calculate ΔC_p and CMC_{max} of the amphiphiles. The CMC values used are in mol fraction units.

micellization have also been calculated using the following well-known relations:

$$\Delta H_m^\circ = -RT^2 \delta \ln(\text{CMC})/\delta T \quad (6)$$

and

$$\Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ)/T \quad (7)$$

where

$$\Delta G_m^\circ = RT \ln(\text{CMC}) \quad (8)$$

Taking the mole fraction of CMC, $\ln(\text{CMC})$ values were plotted against T to calculate ΔH_m° . The plot was found to be

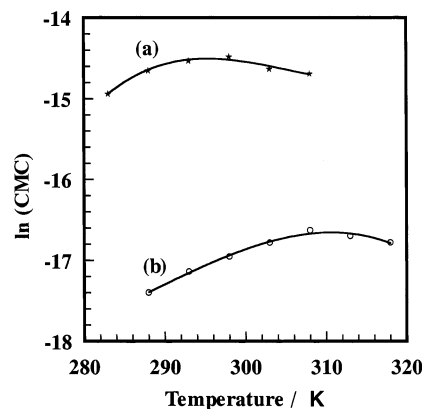


Figure 5. $\ln \text{CMC}$ vs temperature curves for (a) EGDE and (b) EGTE. The CMC values were taken in mol fraction units.

curvilinear (Figure 5). A tangent was drawn through the required point of the curve, and the slope of the tangent was taken to be $\delta \ln(\text{CMC})/\delta T$ at that temperature and was used to calculate ΔH_m° . The thermodynamic parameters calculated using the above equations are found to be in good agreement with those calculated using eqs 3 and 4. At any given temperature, both the ΔH_m° and ΔS_m° values of EGTE are found to be lower than those of EGDE. This suggests that the enthalpy term for EGTE is more effective in contributing to the free-energy term being negative compared to that for EGDE. Lower values of the ΔS_m° terms for EGTE compared to those for EGDE are probably a result of the organization of a greater number of EGTE molecules from randomly oriented monomers to well-organized micelle structures. It is shown that the enthalpy terms of both of the surfactants increase monotonically and change from negative to positive as the temperature increases. Thus, we expect the value of the enthalpy change to be zero at T_{max} , which is consistent with eq 3. Therefore, micelle formation can be considered to be an entirely entropy-driven process at this temperature. Such results have been observed previously for ionic surfactants.^{26–31} Upon micellization, the destruction of the orderly arrangement of water molecules or so-called “iceberg” around the monomeric units of amphiphiles gives a positive entropy change. However, the destruction of higher degree of hydrogen bonding in the icebergs around the alkyl chains gives a positive enthalpy change. Despite this micellization-favoring phenomenon, at lower temperatures, both the entropy and enthalpy changes are negative. A negative ΔH_m° can occur when a substantial number of water molecules surrounding the small hydrophilic headgroups become more important than the destruction of icebergs at lower temperatures. However, a negative entropy change can occur if the ordering of the randomly oriented amphiphile molecules from the solvated form into a micelle structure is more pronounced than the disordering effect due to the destruction of icebergs around the alkyl chains. At the same time, the motion of the water molecules bound to hydrophilic heads becomes more restricted, contributing to the decrease in entropy. For both amphiphiles, entropy and enthalpy terms are found to compensate each other. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term, is more effective (as observed at lower temperatures) at giving a large, negative free-energy term and vice versa. The enthalpy and entropy terms calculated using eqs 3 and 4, respectively, are plotted in Figure 6. The entropy–enthalpy compensation plots are found to be linear for both of the amphiphiles. The slopes of the plots having the dimension of Kelvin are found to be 304 and 296 for EGDE and EGTE, respectively. These values lie within the suggested literature

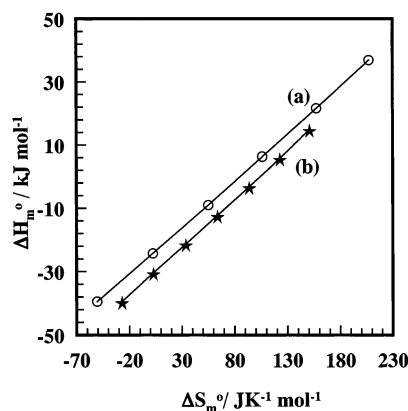


Figure 6. Enthalpy–entropy compensation plots for (a) EGDE and (b) EGTE.

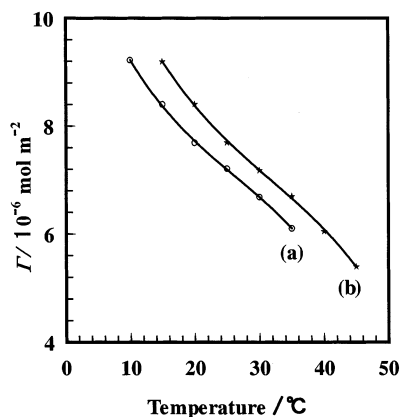


Figure 7. Dependence of the surface excess concentration on temperature for (a) EGDE and (b) EGTE.

value for water, 250–315 K,³² which further supports the degree of successful application of Muller's treatment in the case of EGDE and EGTE. Such enthalpy–entropy compensation effects have been previously observed for many physicochemical processes including micelle and monolayer formation.^{31,33–35}

Now, let us consider the effect of temperature on the surface excess concentration (Γ) of the adsorbed molecules. Taking the logarithm of the bulk concentration ($\log C$) below CMC used in Figure 3, the γ values are plotted against $\log C$ (not shown) to calculate the Γ values of the amphiphiles from the relation $d\gamma = -2.303RT d \log C$. Figure 7 shows the Γ values of the amphiphiles at different temperatures. The Γ values decrease as the temperature increases, which is in line with the increase in the equilibrium surface tension with increasing temperature (Figure 3). This suggests that the coherence of the adsorbed molecules to form condensed domains becomes more difficult as the temperature increases.

We are particularly interested in finding out how the surface morphology of the adsorbed monolayers is influenced by the tendency of surfactants to form micelles in the bulk. This phenomenon is particularly important from the following points of view: First, the condensed domains are observed as long as the CMC values increase with increasing temperature. Second, the critical surface pressure necessary for the phase transition increases with increasing temperature and coincides with the equilibrium surface pressure at T_{\max} , the temperature at which the CMC is maximized (Figure 8), and finally, above T_{\max} , the CMC values start to decrease (Table 1) whereas the equilibrium surface pressure at \geq CMC remains far below the hypothetical surface pressure necessary for the phase transition, showing a preferential tendency of the molecules to remain in the bulk.

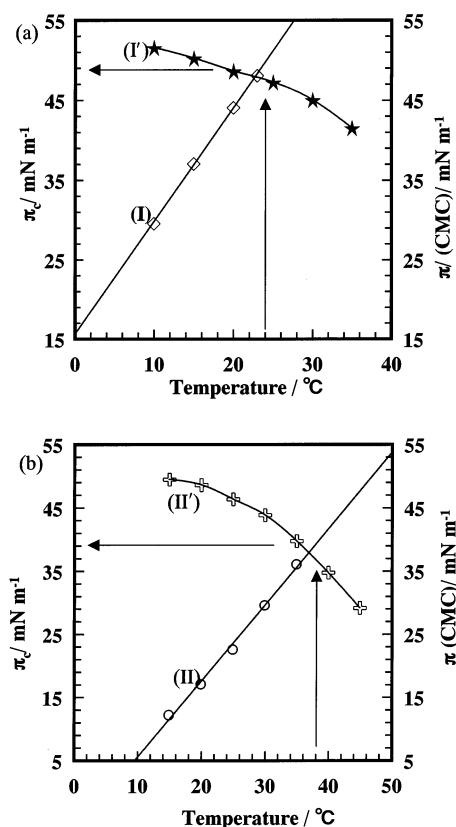


Figure 8. Dependence of the critical surface pressure π_c necessary for the phase transitions (I, II) and the equilibrium surface pressure $\pi(\text{CMC})$ attainable at and above CMC (I', II') for EGDE (a) and EGTE (b) on temperature. The arrows in each of the plots indicate the hypothetical critical surface pressure necessary for the phase transition above T_{\max} for the respective amphiphiles.

These phenomena collectively govern the morphological features of the molecules adsorbed at the solution surfaces, which can be made clear by considering the following example: a Brewster angle microscopic study reveals that the condensed domains in the monolayers of EGDE exist up to 23 °C. Above this temperature, for example, at 24 °C, the monolayer cannot show any characteristic feature of phase transition even with a 4.0×10^{-5} M solution of EGDE (data are not shown) whereas the CMC value of the amphiphile is around 2.75×10^{-5} M (Table 1) at this temperature. Figure 8a shows that at 24 °C the EGDE monolayer should attain a surface pressure of 49 mN/m for the phase transition whereas the maximum possible equilibrium surface pressure attainable at and above CMC is around 47 mN/m, which is less than the surface pressure necessary for the phase transition by 2 mN/m at this temperature. This result suggests that a phase transition is not possible in the EGDE monolayers at ≥ 24 °C. Again, Table 1 shows that above T_{\max} the CMC values start to decrease gradually with increasing temperature, indicating a higher degree of stability of the micelle. Therefore, molecules prefer forming micelles in the bulk to adsorbing at the surface when the temperature exceeds T_{\max} . As a result, the system cannot acquire the surface pressure necessary for the phase transition because of the lower surface concentration of the adsorbed molecules. Again, condensed domain formation is possible only when the line tension dominates the kinetic energy of the molecules. With increasing temperature, the line tension decreases while the kinetic energy of the molecules increases. As the temperature increases, the kinetic energy starts to exert its influence and finally dominates when the temperature exceeds T_{\max} . This renders the possibility of condensed domain

formation unfavorable. Again, increased molecular motion and chain flexibility with increasing temperature result in a poorer packing of the molecules in the adsorbed monolayers; consequently, the area per molecule increases. Therefore, the predominance of the kinetic energy of the molecules over the line tension at and above this temperature is not favorable for the molecules to form condensed domains. None of these effects allow the molecules to form condensed domains in the adsorbed monolayers of EGDE when the temperature is ≥ 24 °C. Similar phenomena are found to hold in the case of EGTE, as shown in Figure 8b where a phase transition and subsequent condensed domain formation are possible up to 37 °C. Therefore, we expect that the phase transition in adsorbed layers is a function of both the surface concentration and the state of molecular arrangement in the bulk. If the experimental conditions are more favorable for micellization in the bulk than for adsorption at the surface, then the system cannot acquire the necessary surface pressure for the phase transition because of the low 2-D surface concentration of the amphiphiles.

Conclusions

We have discussed the dependence of the phase behavior of the adsorbed monolayers of EGDE and EGTE on their micellization in the bulk. Both of the amphiphiles undergo a first-order phase transition in the adsorbed monolayers at the air–water interface. A phase transition, and therefore condensed domain formation, is possible as long as the CMC values increase with increasing temperature. Contrary to the usual behavior of nonionic surfactants, the CMC values of both EGDE and EGTE increase with increasing temperature up to their respective T_{\max} values and then decrease gradually with further increases in temperature. We applied Muller's treatment to explain the temperature dependence of the micellization of the amphiphiles. The calculated CMC values are found to be in good agreement with the experimental CMC values. It is interesting that the T_{\max} values of the amphiphiles correspond well to their respective maximum temperatures of formation of condensed domains in the adsorbed monolayers. The values of ΔH_m° in both cases change from negative to positive, showing that $\Delta H_m^\circ = 0$ corresponds to the maximum temperature of CMC at T_{\max} . The values of ΔS_m° also change from negative to positive with increasing temperature. In both cases, an enthalpy–entropy compensation effect is observed; when the enthalpy term contributes less to the free energy, its counterpart, the entropy term, is more effective at contributing to the negative value of the free energy and vice versa. At T_{\max} , the critical surface pressure necessary for the phase transition and the equilibrium surface pressure become equal. Above this temperature, the system needs a still-higher value of surface pressure for the phase transition to occur, but because of the surface-concentration limit, the equilibrium surface pressure at \geq CMC cannot reach the critical surface pressure when the temperature exceeds T_{\max} . When the temperature is increased above T_{\max} , the CMC values start to decrease, and the molecules prefer forming micelles to adsorbing at the surface. This results in a considerable decrease in the 2-D surface concentration of the amphiphiles because of the increase in chain flexibility with

increasing temperature. Consequently, the system cannot acquire the necessary surface pressure for the phase transition because of the low 2-D surface concentration. At the same time, an increase in molecular motion with increasing temperature causes a poorer packing of the molecules in adsorbed layers. As a result, the area per molecule increases, and the van der Waals interactions between the alkyl chains cannot conveniently accumulate molecules to form condensed domains in the adsorbed monolayer.

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