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ORIGINAL CONTRIBUTION

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Thermodynamic study on the adsorption and micelle formation of long chain alkyltrimethylammonium chlorides

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Abstract The surface tension of aqueous solutions of tetradecyltrimethylammonium chloride (TTAC) and decyltrimethylammonium chloride (DeTAC) were measured as a function of temperature at concentrations below and above the critical micelle concentration under atmospheric pressure. The entropy and energy of adsorption from the monomeric state and from the micellar state and also the entropy and energy of micelle formation for TTAC were evaluated and compared with those of dodecyltrimethylammonium chloride (DTAC). The values of $\Delta_W^M s$ and $\Delta_W^M u$ for TTAC and DTAC systems show that the micelle formation is driven by the entropy at low temperatures and by the energy at high temperatures.

Key words Surface tension – adsorption – micelle – entropy – energy

Introduction

The thermodynamic quantities obtained by a surface tension measurement have been shown to provide very useful information that clarify the behavior of adsorption and micelle formation of surfactants [1–9]. We have studied the effect of the chemical structure of the surfactant molecule on the thermodynamic quantity associated with the adsorption and the micelle formation. To study a contribution from a polar head group to the thermodynamic quantities, we have studied the successive *N*-methylation of dodecylammonium chloride (DAC) systematically [6]. It was concluded that the change in the molecular geometry and in the hydrophilicity of the polar head group of dodecylammonium chloride affects the adsorbed film at a plane interface more significantly than the micelles with a spherical structure.

There are many reports on the measurement of the critical micelle concentration (cmc) and the results have been related to the change of standard Gibbs' energy of micellization [10–14]. However, it has been shown to be more interesting and useful to discuss the micelle formation by use of the excess thermodynamic quantities. In this paper we investigate the thermodynamic quantity changes associated with the adsorption and the micelle formation of long chain alkyltrimethylammonium chlorides. We have chosen tetradecyltrimethylammonium chloride (TTAC), dodecyltrimethylammonium chloride (DTAC), and decyltrimethylammonium chloride (DeTAC), because of their preferable experimental conditions (e.g., cmc, krafft point, etc.). The surface tension of the aqueous solutions of TTAC and DeTAC was measured as a function of temperature at fixed concentrations under atmospheric pressure. The thermodynamic quantity changes of TTAC and DeTAC were evaluated by applying the rigorous thermodynamic equations. Combining these results with that of DTAC [5, 6], we can understand the variations in the adsorption and micelle formation for these surfactants.

Experimental

TTAC and DTAC were synthesized according to the method previously described [15] and recrystallized five times from a mixture of ethanol and ethyl acetate. Their purities were confirmed by the absence of a minimum on the surface tension vs concentration isotherms. Water was distilled three times from an alkaline permanganate solution. The surface tension was measured within the error of $0.05\,\mathrm{mN\,m^{-1}}$ by use of the drop volume technique described previously [16]. The temperature was controlled within 0.05 K by using the measuring cell in a thermostated water bath.

Results and discussion

The surface tension γ was measured as a function of temperature T at various molalities m_1 of surfactant in the aqueous solution under atmospheric pressure. The surface tension vs temperature curves of the aqueous solutions of TTAC are shown in Fig. 1. The value of γ decreases with an increase in temperature and the curves at low concentrations were slightly concave upwards. At higher concentrations, however, the surface tension value decreases linearly with increasing temperature. Thus the γ vs T curve at an intermediate concentration has a break point indicated by an arrow in Fig. 1b; the break corresponds to the critical micelle concentration at the temperature. Figure 2 show the γ vs T curves of the aqueous solutions of DeTAC. Because of the difficulty in determining the break points in γ vs T curves, we calculated the temperatures of the break points from the curves 1 and 3 in Fig. 4, namely the result of the γ vs m_1 curves.

The γ vs m_1 curves of TTAC and DeTAC are shown together with those of DTAC at 298.15 K in Fig. 3; all the curves possess a sharp break point and its molality is referred to as the critical micelle concentration cmc. The value of cmc increases approximately exponentially with a decrease in carbon number in the alkyl chain in a well-known manner [10–14, 17–19]. The values of cmc C described in the concentration unit of $\mathrm{mmol\,kg^{-1}}$ are plotted against T in Fig. 4. We notice that the temperature dependence of C increases with a decrease in carbon number in the alkyl chain. Furthermore, Fig. 3 shows that the surface tension at the cmc slightly increases upon decreasing the carbon number.

Let us now apply the thermodynamic equations described by the excess thermodynamic quantities [1] to these results. The surface excess number of moles of surfactant Γ_1^{H} is defined with reference to the two dividing plane surfaces, which make the surface excess numbers of moles of air and water to be zero, and evaluated by applying the relation

$$\Gamma_1^{\mathrm{H}} = -(m_1/2RT)(\partial\gamma/\partial m_1)_{T,p} \tag{1}$$

to the γ vs m_1 curves in Fig. 3. The result is shown as Γ_1^{H} vs m_1 plot at 298.15 K under atmospheric pressure in Fig. 5a. The surface pressure π vs the mean area per adsorbed molecule A curve are shown in Fig. 5b, where the values of π and A are calculated by using the equations

$$\pi = \gamma^0 - \gamma\,, \tag{2}$$

$$A = 1/N_{\mathrm{A}}\Gamma_1^{\mathrm{H}}\,, \tag{3}$$

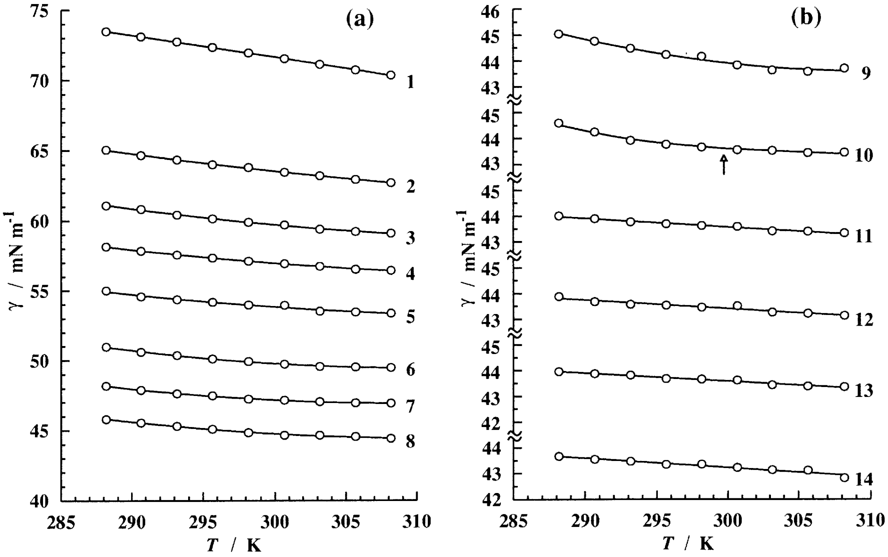

Fig. 1 Surface tension vs temperature curves of TTAC at constant concentration: (1) $m_1 = 0$; (2) 0.09; (3) 1.50; (4) 1.96; (5) 2.61; (6) 3.49; (7) 4.32; (8) 5.00; (9) 5.24; (10) 5.40; (11) 5.78; (12) 5.95; (13) 6.72; (14) $7.02\,\mathrm{mmol\,kg^{-1}}$

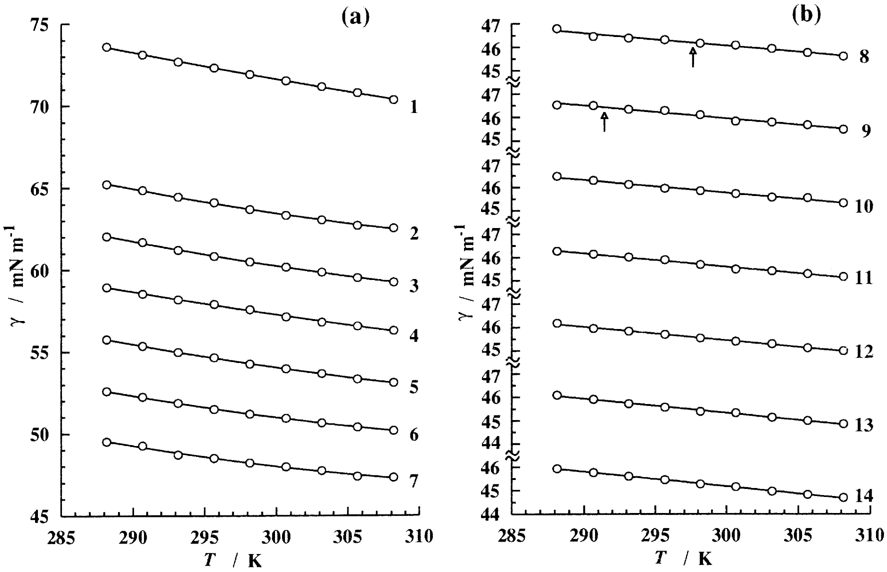

Fig. 2 Surface tension vs temperature curves of DeTAC at constant concentration: (1) $m_1 = 0$; (2) 14.98; (3) 23.05; (4) 32.54; (5) 45.04; (6) 59.94; (7) 79.40; (8) 96.85; (9) 99.14; (10) 101.24; (11) 107.77; (12) 119.60; (13) 124.52; (14) 145.95 mmol kg^{-1}

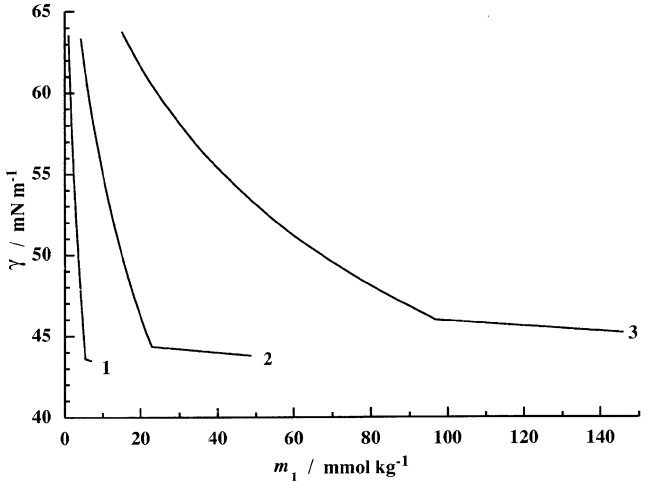

Fig. 3 Surface tension vs concentration curves at 298.15 K: (1) TTAC; (2) DTAC; (3) DeTAC

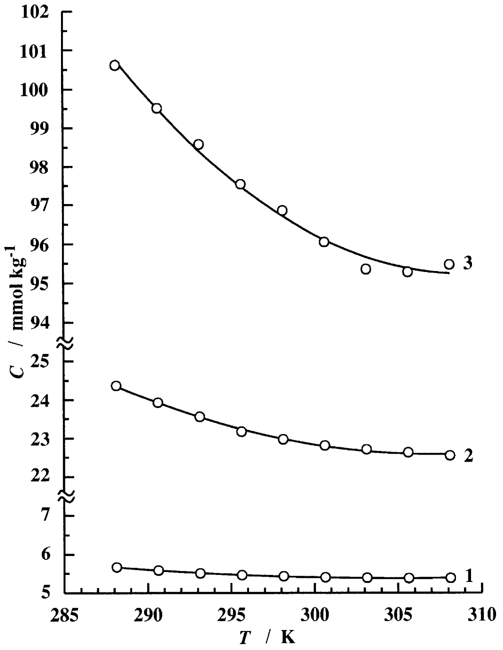

Fig. 4 Critical micelle concentration vs temperature curves: (1) TTAC; (2) DTAC; (3) DeTAC

respectively, where γ^0 is the surface tension of the pure water/air interface and N_A is Avogadro's constant. It is seen that TTAC forms the most condensed film among the three. Taking account of the generally observed fact that the smallest value of A (≈ 0.5 nm^2) is much larger than the closest average area expected from the geometry of the molecules [19, 20], we may say that a surfactant–water interaction is rather influential than a surfactant–surfactant interaction in adsorption behavior in these adsorbed films.

We have demonstrated that the temperature dependence of surface tension of aqueous micellar solution is the one of the useful quantities to clarify the structure and properties of adsorbed films and micelles [1–9]. The temperature derivative of the surface tension of aqueous TTAC solution obtained from Fig. 1 is illustrated against molality m_1 at constant temperature in Fig. 6. The value of $\partial\gamma/\partial T$ highly depends on concentration and temperature at a concentration below the cmc, although it is almost

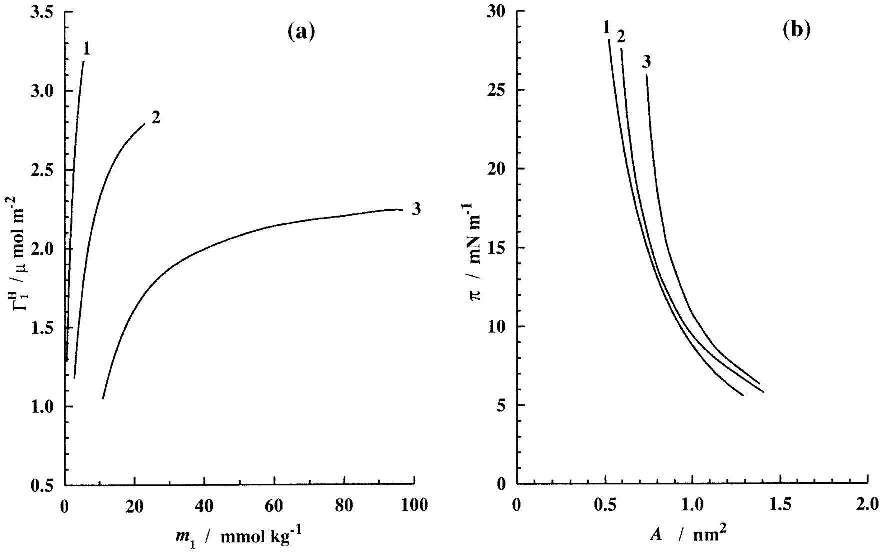

Fig. 5 (a) Surface excess number of moles vs concentration curves and (b) Surface pressure vs area per molecule curves at 298.15 K: (1) TTAC; (2) DTAC; (3) DeTAC

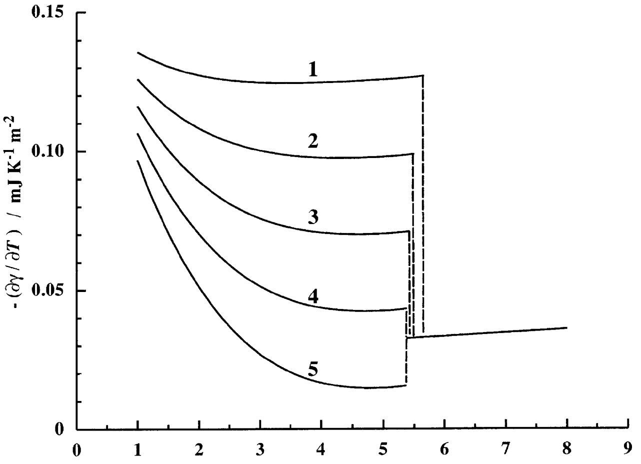

Fig. 6 Derivative of surface tension with respect to temperature vs concentration curves of TTAC at constant temperature: (1) T = 288.15 K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15

independent of them at a concentration above the cmc. Thus, the $-(\partial\gamma/\partial T)$ vs m_1 curves change discontinuously at the cmc for TTAC. Although the $\partial\gamma/\partial T$ values were estimated for the DeTAC system, the values seem not to be accurate enough to calculate the entropy change especially at concentrations around cmc because of a relatively large ambiguity in determining cmc and then break points on the γ vs T curves. Therefore the results of entropy and energy change of the DeTAC system will be excluded from the following discussion.

At a concentration below the cmc, the entropy change associated with the adsorption of surfactant from the monomeric state in the aqueous solution $\Delta s(1)$ is defined by [1]

$$\Delta s(1) = \Gamma_1^H[(s^H/\Gamma_1^H) - s_1] \;, \tag{4}$$

where s^H and s_1 are the surface excess entropy per unit area and the partial molar entropy of the monomeric surfactant in aqueous solution, respectively. At concentrations above the cmc, the entropy change associated with the adsorption of surfactant from the micellar state $\Delta s(\mathrm{M})$ is defined by

$$\Delta s(\mathrm{M}) = \Gamma_1^H[(s^H/\Gamma_1^H) - (s^M/N_1^M)] \;, \tag{5}$$

where N_1^M and s^M are the excess number of surfactant ions in the micelle particle and the excess molar entropy of micelle particle, respectively. They are defined with respect to the spherical dividing surface making the excess number of moles of water to be zero. Here $\Delta s(1)$ and $\Delta s(\mathrm{M})$ are evaluated from the derivative of surface tension with respect to temperature

$$\Delta s(1) = -(\partial\gamma/\gamma T)_{p,m_1}, \quad m_1 < C \;, \tag{6}$$

$$\Delta s(\mathrm{M}) = -(\partial\gamma/\partial T)_{p,m_1}, \quad m_1 \geq C \;. \tag{7}$$

According to Eqs. (6) and (7), and the results given in Fig. 6, we note the value of $\Delta s(1)$ of TTAC decreases with an increase in bulk concentration and reaches a constant value below the cmc at a given temperature. From Eq. (5) and $\Delta s(\mathrm{M})$ in Fig. 6, it may be approximately concluded that the dependence of the entropy of surfactant on temperature and concentration in the adsorbed film is similar to that in the micelle although it is different from that in the aqueous solution judging from Eq. (4) and $\Delta s(1)$ in Fig. 6.

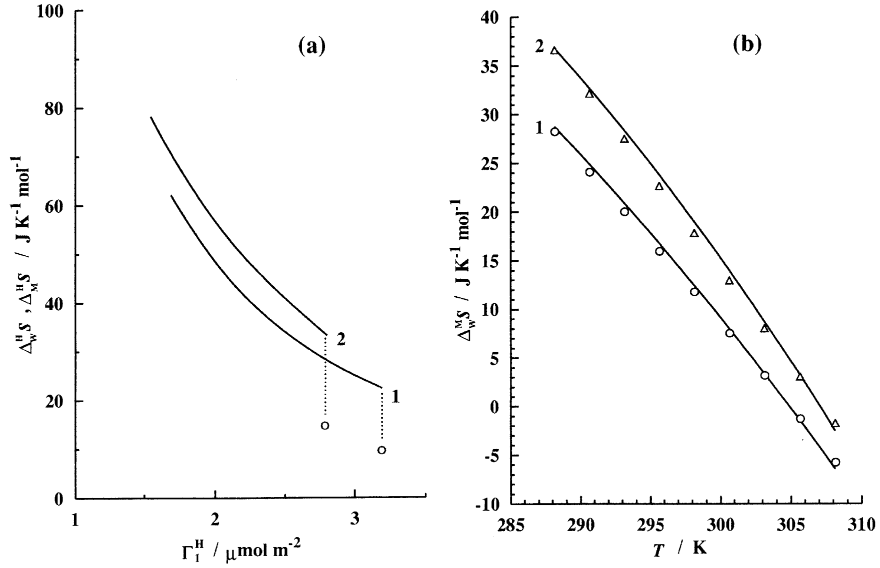

Fig. 7 (a) Entropy of adsorption vs surface excess number of moles at 298.15 K: (—) $\Delta^{\mathrm{H}}_{\mathrm{W}}s$; (○) $\Delta^{\mathrm{H}}_{\mathrm{M}}s$ and (b) entropy of micelle formation vs temperature curves: (○, △) Eq. (10); (—) Eq. (11), (1) TTAC, (2) DTAC

Now let us define the entropy of adsorption per mole of surfactant from the monomeric state in the aqueous solution $\Delta^{\mathrm{H}}_{\mathrm{W}}s$ and that from the micellar state $\Delta^{\mathrm{H}}_{\mathrm{M}}s$ by [21]

$$\Delta^{\mathrm{H}}_{\mathrm{W}}s = \Delta s(1) / \Gamma^{\mathrm{H}}_{1} , \tag{8}$$

$$\Delta^{\mathrm{H}}_{\mathrm{M}}s = \Delta s(\mathrm{M}) / \Gamma^{\mathrm{H}}_{1} . \tag{9}$$

Furthermore, the entropy of micelle formation at the cmc is defined by [1, 21]

$$\begin{aligned} \Delta^{\mathrm{M}}_{\mathrm{W}}s &= \Delta^{\mathrm{H}}_{\mathrm{W}}s - \Delta^{\mathrm{H}}_{\mathrm{M}}s \\ &= (s^{\mathrm{M}}/N^{\mathrm{M}}_{1}) - s_1 . \end{aligned} \tag{10}$$

The values of $\Delta^{\mathrm{H}}_{\mathrm{W}}s$ and $\Delta^{\mathrm{H}}_{\mathrm{M}}s$ for TTAC are plotted against Γ^{H}_{1} together with those of DTAC in Fig. 7a. First we note that the values of $\Delta^{\mathrm{H}}_{\mathrm{M}}s$ are positive. This means that the entropy in the monolayer state is greater than that in the micellar state. It may be explained that this behavior is partly responsible for the difference in the hydration of the hydrophilic group of surfactant molecules between the adsorbed film at a plane interface and the spherical micelle [9].

With respect to the entropy of micelle formation in the solution shown in Fig. 7b, it is seen that the values of $\Delta^{\mathrm{M}}_{\mathrm{W}}s$ for these alkyltrimethylammonium chlorides are positive below the temperature of the minima of the cmc vs T curves (about 305 K for TTAC and about 308 K for DTAC). This implies that the entropy in the micellar state is greater than that in the monomeric state. Furthermore, it is noted that the values of $\Delta^{\mathrm{M}}_{\mathrm{W}}s$ decrease with an increase in temperature. Taking advantage of the second expression in Eq. (10), this result may demonstrate that the s_1 value increases significantly due to dehydration of water molecules around hydrocarbon chain with an increase in temperature [6]. Another interesting point about the entropy is that the incorporation of methylene groups into the hydrocarbon chain, i.e. from DTAC to TTAC, has a very similar influence in magnitude on the value of $\Delta^{\mathrm{H}}_{\mathrm{W}}s$ at the cmc and that of $\Delta^{\mathrm{M}}_{\mathrm{W}}s$ (about 9 J K^{-1} mol^{-1}). This is in contrast to the case of the N-methylation of the head group of DAC, that is from DAC to DTAC; the difference in $\Delta^{\mathrm{M}}_{\mathrm{W}}s$ is about 10 J K^{-1} mol^{-1} while that in $\Delta^{\mathrm{H}}_{\mathrm{W}}s$ is about 40 J K^{-1} mol^{-1} at 298.15 K [6].

In Fig. 7b, the value of $\Delta^{\mathrm{M}}_{\mathrm{W}}s$ obtained by applying

$$\Delta^{\mathrm{M}}_{\mathrm{W}}s = -(2RT/C)(\partial C/\partial T)_p \tag{11}$$

to the C vs T curves are also shown by solid lines. The good agreement between the symbol and the solid line indicates that the micelle formation of TTAC and DTAC can be treated approximately like the appearance of a macroscopic bulk phase in the range of concentration near the cmc [1].

Finally, let us consider the energy changes associated with the adsorption of surfactant from the monomeric state $\Delta u(1)$ and that from the micellar state $\Delta u(\mathrm{M})$ defined, respectively, by [6]

$$\Delta u(1) = \gamma + T\Delta s(1) - p\Delta v(1) , \tag{12}$$

$$\Delta u(M) = \gamma + T\Delta s(\mathrm{M}) - p\Delta v(\mathrm{M}) , \tag{13}$$

where $\Delta v(1)$ and $\Delta v(\mathrm{M})$ are the corresponding volume changes. Since the $p\Delta v$ terms are negligibly small compared with the other terms under atmospheric pressure

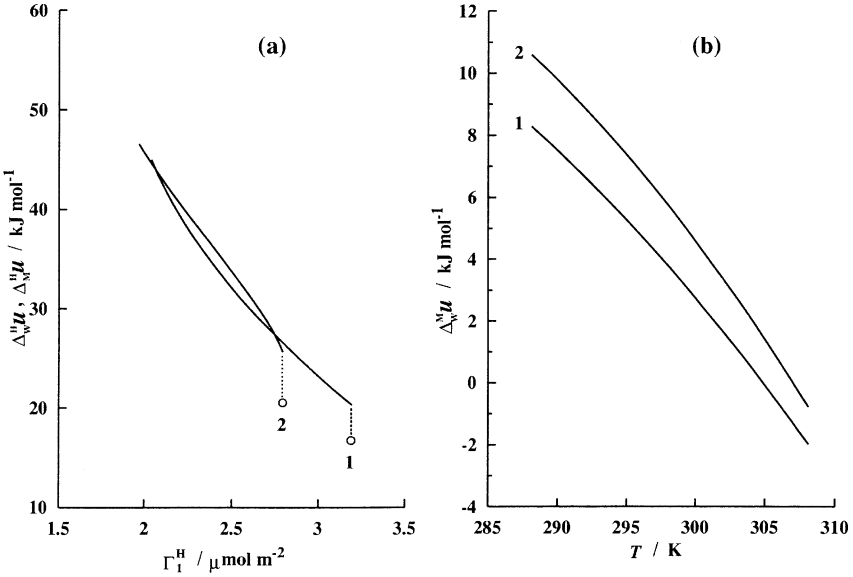

Fig. 8 (a) Energy of adsorption vs concentration curves at 298.15 K: (—) $\Delta_W^H u$; (○) $\Delta_M^H u$ and (b) Energy of micelle formation vs temperature curves: (1) TTAC; (2) DTAC

[16], we calculate the energy of adsorption per mole of surfactant $\Delta_W^H u$ and $\Delta_M^H u$ without $p\Delta v$ terms by using [21]

$$\Delta_W^H u = \Delta u(1)/\Gamma_1^H , \quad (14)$$

$$\Delta_M^H u = \Delta u(\mathrm{M})/\Gamma_1^H . \quad (15)$$

Then the energy of micelle formation at the cmc is evaluated through [6]

$$\Delta_W^M u = \Delta_W^H u - \Delta_M^H u. \quad (16)$$

In Fig. 8a, $\Delta_W^H u$ and $\Delta_M^H u$ are plotted against Γ_1^H at 298.15 K. It is noteworthy that the curves of $\Delta_W^H u$ are very close to each other. Therefore it is said that the difference in the energy of surfactant between the adsorbed film and the aqueous solution is similar to each other for TTAC and DTAC at a given surface density of the surfactant.

Figure 8b shows that the values of $\Delta_W^M u$ decrease significantly from positive to negative with an increase in temperature. This is probably responsible for an increase in u_1 value caused by dehydration around hydrocarbon chain with increasing temperature [6]. Considering the experimental findings given in Figs. 7b and 8b, it is said that the micelle formation is driven by entropy at low temperatures and by energy at high temperatures for the TTAC and DTAC systems.

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