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Adsorption of Dodecyltrimethylammonium Chloride from the Micellar Solution at Water/Air Interface

Makoto ARATONO,* Toru OKAMOTO, and Kinsi MOTOMURA
Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812

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The surface tension of the aqueous solution of dodecyltrimethylammonium chloride (DTAC) was measured as a function of temperature under atmospheric pressure at concentrations below and above the critical micelle concentration. The thermodynamic quantity changes associated with the adsorption of DTAC from its monomeric and micellar states were evaluated and proved to satisfy the thermodynamic relation derived on the assumption that the micelle formation can be treated as the appearance of a macroscopic bulk phase in the solution. Further their values were compared with those of the aqueous solution of dodecylammonium chloride and the influence of the chemical structure of the head group on the adsorption and micelle formation were discussed from the thermodynamic viewpoint.

It has been observed in the previous papers[1,2] that the entropy changes associated with surface adsorption and micelle formation of surfactant at concentrations around the critical micelle concentration (cmc) in its aqueous solution have negative values for dodecylammonium chloride and positive ones for 2-(octylsulfinyl)ethanol. Further the micelle has been proved to be treated thermodynamically as a macroscopic bulk phase in the solution when the thermodynamic quantities of micelle are replaced by the excess one with reference to the dividing surface chosen so that the excess number of moles of water equals zero. This treatment has been supported by measurements of the temperature and pressure dependence of interfacial tension of the aqueous solution of surfactant against oil.[3–6]

It is now interesting to investigate what influence the chemical structure of the polar head group of surfactant has on the thermodynamic quantity changes associated with adsorption and micelle formation. In this paper we are concerned with the adsorption of dodecyltrimethylammonium chloride (DTAC) at its aqueous solution/air interface at concentrations below and above the critical micelle concentration (cmc). The surface tension is measured as a function of temperature at fixed concentrations under atmospheric pressure and the thermodynamic quantity changes are evaluated by applying thermodynamic equations. The results are compared with those of dodecylammonium chloride (DAC).

Experimental

Dodecyltrimethylammonium chloride was synthesized and purified according to the method described previously[7] and its purity was checked by observing no minimum on the surface tension vs. concentration curve. Water was triply distilled from alkaline permanganate solution. The surface tension was measured by the drop volume technique described previously[8] and reproducible within 0.05 mN m^{-1}. The temperature was kept constant within 0.05 K by immersing the measuring cell in a thermostated water bath.

Results and Discussion

The surface tension γ was measured as a function of temperature under atmospheric pressure at various molalities m_1 of dodecyltrimethylammonium chloride in the aqueous solution. The surface tension vs. temperature curves are shown in Figs. 1a and 1b. It is seen that the value of γ decreases with increasing temperature and the curves at low concentrations are concave upward. At high concentrations, however, the curves seem to be linear. Therefore, it is expected that a break point will be observed on a surface tension vs. temperature curve at an intermediate concentration. Actually the curve 2 in Fig. 1b is found to have a break point, of which the concentration can be proved to be the critical micelle concentration.

Figure 2 illustrates the γ vs. m_1 curve depicted by picking up the γ values at a given temperature in Fig. 1. The sharp break is observed on the curve and its molality is referred to as the critical micelle concentration. The cmc values are shown as a function of temperature in Fig. 3 together with those of DAC. It is seen that the values depend remarkably on temperature and the cmc vs. T curve has a minimum. Comparing this curve with that of DAC, we notice that the chemical structure of the head group of surfactant has a considerable influence on the cmc value and temperature dependence of cmc. Making reference to our previous paper,[1] we also notice that the surface tension of DTAC at the cmc is considerably different from that of DAC.

The temperature derivative of surface tension obtained from Fig. 1 is plotted against molality at constant temperature in Fig. 4. It is seen that the value of $\partial\gamma/\partial T$ depends on temperature remarkably at concentrations below the cmc, while it is independent of temperature at concentrations above the cmc. Accordingly, the $-\partial\gamma/\partial T$ vs. m_1 curve is observed to vary discontinuously at the cmc. This observation supports the view that the micelle formation of DTAC is treated thermodynamically as if a macroscopic

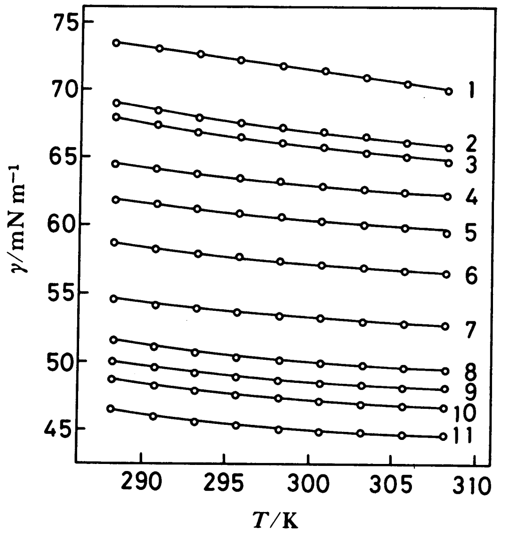

Fig. 1a. Surface tension vs. temperature curves at constant concentration under atmospheric pressure: (1) m_1=0 mmol kg^{-1}; (2) 2.18; (3) 2.76; (4) 4.18; (5) 5.83; (6) 7.76; (7) 11.32; (8) 14.59; (9) 16.45; (10) 18.32; (11) 21.57.

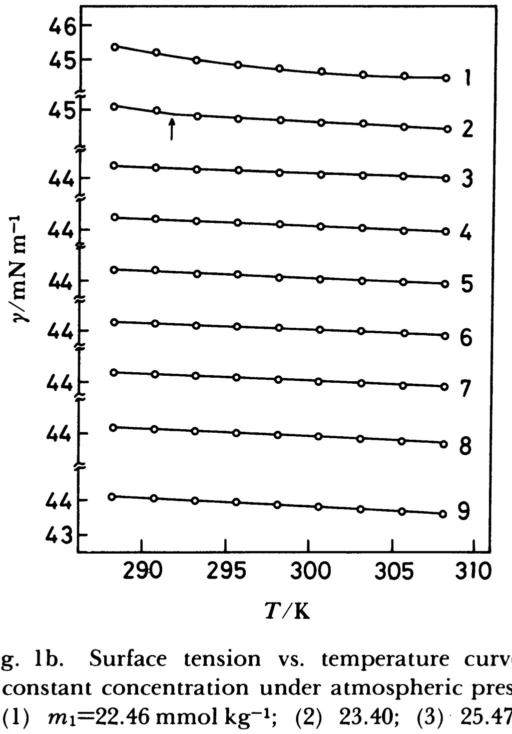

Fig. 1b. Surface tension vs. temperature curves at constant concentration under atmospheric pressure: (1) m_1=22.46 mmol kg^{-1}; (2) 23.40; (3) 25.47; (4) 27.76; (5) 28.50; (6) 29.43; (7) 31.70; (8) 37.29; (9) 48.76.

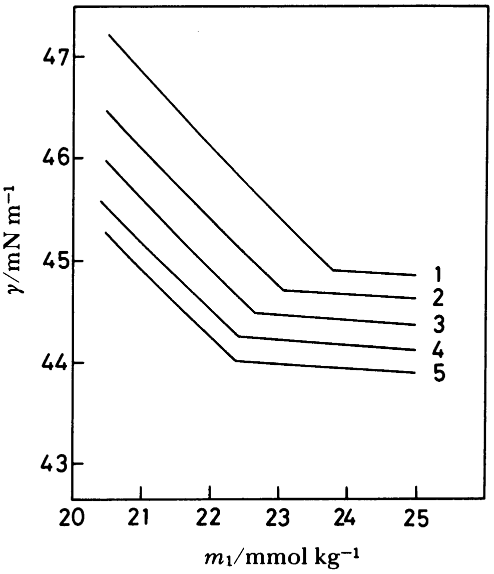

Fig. 2. Surface tension vs. concentration curves at constant temperature under atmospheric pressure: (1) 288.15 K; (2) 293.15 K; (3) 298.15 K; (4) 303.15 K; (5) 308.15 K.

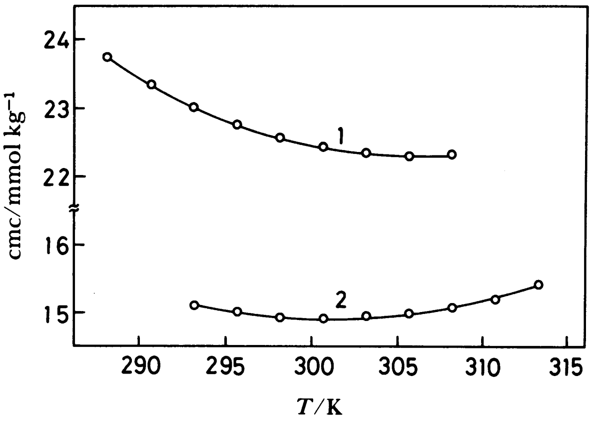

Fig. 3. Critical micelle concentration vs. temperature curves under atmospheric pressure: (1) DTAC; (2) DAC.

phase appears in the solution at the cmc.

It has been shown that the temperature dependence of surface tension of an aqueous micellar solution provides useful information upon the structures and properties of adsorbed films and micelles.[1-3] According to the thermodynamics of the adsorption of surfactant from its micellar solution,[1] the derivative of surface tension with respect to temperature under atmospheric pressure at a concentration below the cmc is related to the entropy change associated with the adsorption of surfactant from the aqueous solution $\Delta s(1)$:

$$(\partial\gamma/\partial T)_{p,m_1} = -\Delta s(1), m_1 < \text{cmc}, \tag{1}$$

while the derivative at a concentration above the cmc is related to the entropy change associated with the adsorption of surfactant from the micellar state $\Delta s(\text{M})$:

$$(\partial\gamma/\partial T)_{p,m_1} = -\Delta s(\text{M}), m_1 \geqq \text{cmc}, \tag{2}$$

on the assumption that the micelle formation may be treated thermodynamically like an appearance of a

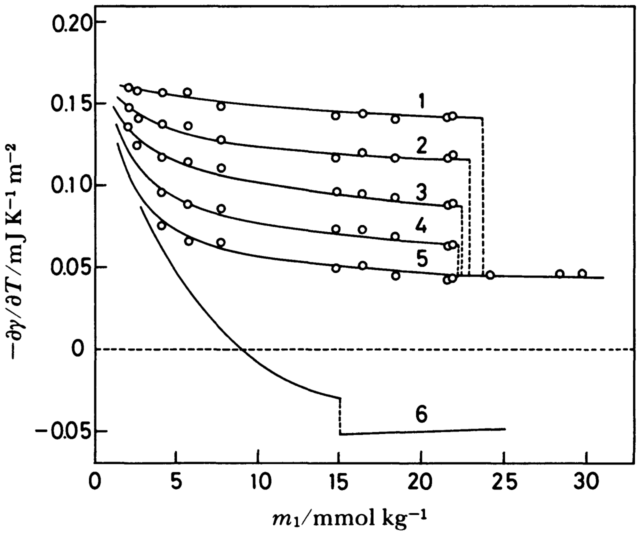

Fig. 4. Derivative of surface tension with respect to temperature vs. concentration curves under atmospheric pressure: (1) 288.15 K; (2) 293.15 K; (3) 298.15 K; (4) 303.15 K; (5) 308.15 K; (6) 298.15 K (DAC).

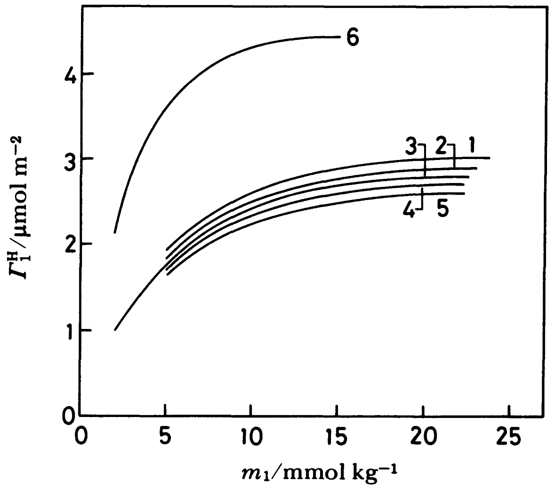

Fig. 5. Surface excess number of moles vs. concentration curves at constant temperature under atmospheric pressure: (1) 288.15 K; (2) 293.15 K; (3) 298.15 K; (4) 303.15 K; (5) 308.15 K; (6) 298.15 K (DAC).

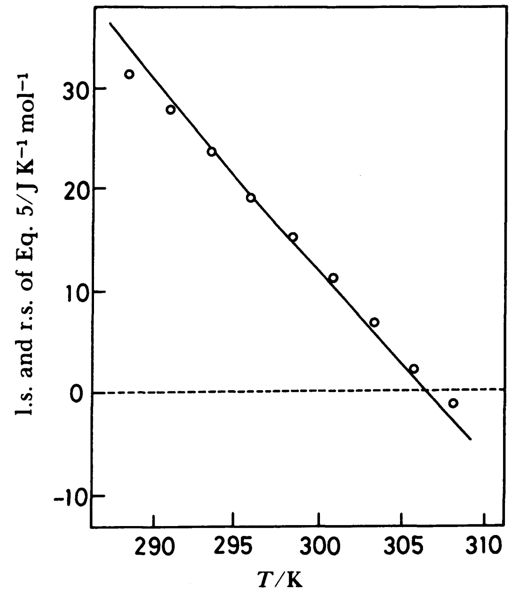

Fig. 6. Comparison between the left and the right side of Eq. 5: (O) left side; (—) right side.

new macroscopic phase and the behavior of micelle is determined only by temperature and pressure in a limited concentration range. Here $\Delta s(1)$ and $\Delta s(\mathrm{M})$ are respectively defined by

$$\Delta s(1) = \Gamma_1^{\mathrm{H}}(s^{\mathrm{H}}/\Gamma_1^{\mathrm{H}} - s_1) \tag{3}$$

and

$$\Delta s(\mathrm{M}) = \Gamma_1^{\mathrm{H}}(s^{\mathrm{H}}/\Gamma_1^{\mathrm{H}} - s^{\mathrm{M}}/N_1^{\mathrm{M}}), \tag{4}$$

where Γ_1^{H} and s^{H} are the surface excess number of moles of surfactant and surface excess entropy with reference to the two dividing planes making the surface excess numbers of moles of air and water to be zero,[8,9] respectively, N_1^{M} and s^{M} are the number of surfactant ions in the micelle and the molar entropy of micelle defined with respect to the spherical dividing surface making the excess number of moles of water to be zero,[1] respectively, and s_1 is the partial molar entropy of monomeric surfactant in the solution.

Comparing the above equations with the results given in Fig. 4, it is found that $\Delta s(1)$ and $\Delta s(\mathrm{M})$ have positive values and accordingly the excess entropy of adsorbed film per mole of surfactant is larger than the partial molar entropy of monomeric surfactant and the excess entropy of micelle per mole of surfactant. This behavior is slightly different from that of DAC (curve 6). Further it is seen that the value of $\Delta s(1)$ decreases with increasing the concentration and depends on temperature remarkably, while that of $\Delta s(\mathrm{M})$ is almost independent of the concentration and temperature. On the other hand the discontinuous change of the $-\partial\gamma/\partial T$ vs. m_1 curve at the cmc, $\Delta s(1)-\Delta s(\mathrm{M})$, is correlated to the derivative of cmc with respect to T by the expression:[1]

$$[\Delta s(1) - \Delta s(\mathrm{M})]/\Gamma_1^{\mathrm{H}} = -(2RT/\mathrm{cmc})(\partial\mathrm{cmc}/\partial T)_p. \tag{5}$$

The left side of Eq. 5 is numerically evaluated at the cmc by using the values of $\Delta s(1)$ and $\Delta s(\mathrm{M})$ given in Fig. 4 and the values of Γ_1^{H} which are calculated by applying the relation

$$\Gamma_1^{\mathrm{H}} = -(m_1/2RT)(\partial\gamma/\partial m_1)_{T,p} \tag{6}$$

to the γ vs. m_1 curves and shown in Fig. 5 at constant temperature under atmospheric pressure. The right side is calculated by the temperature dependence of the cmc values shown in Fig. 3. In Fig. 6, the values of the left side are plotted by circles and those of the right side are drawn by the full line. The values of both sides are in fair agreement with each other within the experimental error. Therefore, we can say that the present results concerning DTAC support the view that the micelle formation is treated like an appearance of a macroscopic phase in the solution in a limited concentration range.

It is now required to examine an effect of the head group of surfactant on the thermodynamic states of adsorbed film and micelle. This can be done by comparing the results of the DTAC system with those of the DAC system obtained in our previous paper.[1] Comparison between their temperature dependences of cmcs are made in Fig. 3. Looking at Fig. 4, the entropy change associated with the adsorption is found to be affected considerably by the difference in the head group. Since $\Delta s(1)/\Gamma_1^{\mathrm{H}}$ gives the difference of the mean partial molar entropy of surfactant in the adsorbed film $\bar{s}_1^{\mathrm{H}}$ from s_1 approximately at a large value of Γ_1^{H},[2] the $\bar{s}_1^{\mathrm{H}}$ value of DTAC may be said to be larger than that of DAC. This seems to be related to the fact that DTAC has fairly smaller Γ_1^{H} values than DAC as shown in Fig. 5. Further, it is noted that the $\Delta s(\mathrm{M})$ value of DTAC is positive, while that of DAC is negative. Taking into account that $\Delta s(\mathrm{M})/\Gamma_1^{\mathrm{H}}$ is approximately equal in magnitude to $\bar{s}_1^{\mathrm{H}}-\bar{s}_1^{\mathrm{M}}$,[2] where $\bar{s}_1^{\mathrm{M}}$ is the mean partial molar entropy of surfactant in the micelle, the value of $\bar{s}_1^{\mathrm{H}}$ may be concluded to be larger than that of $\bar{s}_1^{\mathrm{M}}$ in the case of DTAC in contrast with the case of DAC. Moreover, it is interesting that the corresponding entropy changes of 2-(octylsulfinyl)ethanol, which is a nonionic surfactant, behave similarly. These results indicate that the size and shape of the head group have a great influence on the packing of the surfactant molecules in the adsorbed film, the aggregation number of micelle,[10] and the distribution of counter ions.

Now we can obtain the thermodynamic quantities of micelle formation from the values of $\Delta s(1)$ and $\Delta s(\mathrm{M})$ at the cmc, because the adsorbed film, the micelle, and the monomeric surfactant in the solution are in equilibrium with each other when the adsorption takes place from the micellar solution. From Eqs. 3 and 4, we have

$$[\Delta s(1) - \Delta s(\mathrm{M})]/\Gamma_1^{\mathrm{H}} = s^{\mathrm{M}}/N_1^{\mathrm{M}} - s_1. \tag{7}$$

The entropy change defined by the right side is referred to as the entropy of micelle formation $\Delta_{\mathrm{W}}^{\mathrm{M}}s$.[11] The values of $\Delta_{\mathrm{W}}^{\mathrm{M}}s$ evaluated by using the results in Figs. 4 and 5 are plotted against temperature with those of DAC in Fig. 7. It can be seen that the $\Delta_{\mathrm{W}}^{\mathrm{M}}s$ values of both systems decrease similarly with temperature and change their signs at high temperatures. Therefore we may say that the partial molar entropy of surfactant in the micelle is larger than that of monomeric surfactant at low temperature and is smaller at high temperature. Comparing the values of $\Delta_{\mathrm{W}}^{\mathrm{M}}s$ of DTAC with those of DAC, it is probable that the mean partial molar entropy of DTAC in the micelle is larger than that of DAC in conformity with the observation that the mean partial molar entropy of DTAC in the adsorbed film is larger than that of DAC.

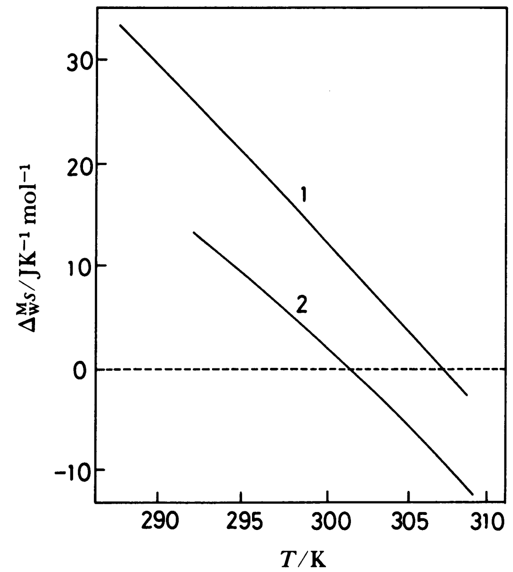

Fig. 7. Entropy change of micelle formation vs. temperature curves under atmospheric pressure: (1) DTAC; (2) DAC.

Finally let us consider the micelle formation from an energetic point of view. The energy change associated with the adsorption of surfactant from the monomeric state $\Delta u(1)$ and that from the micellar state $\Delta u(\mathrm{M})$ are evaluated respectively by use of the relations

$$\Delta u(1) = \gamma + T\Delta s(1) - p\Delta v(1) \tag{8}$$

and

$$\Delta u(\mathrm{M}) = \gamma + T\Delta s(\mathrm{M}) - p\Delta v(\mathrm{M}), \tag{9}$$

where $\Delta v(1)$ and $\Delta v(\mathrm{M})$ are the corresponding volume changes, respectively. The $\Delta u(1)$ and $\Delta u(\mathrm{M})$ values obtained by disregarding the pv terms on the right side[8] are illustrated in Fig. 8 at 298.15 K under atmospheric pressure. It is seen that $\Delta u(1)$ decreases with increasing concentration and is changed discontinuously at the cmc to $\Delta u(\mathrm{M})$ which is nearly constant for both surfactant systems. Comparing the $\Delta u(\mathrm{M})$ values of DTAC and DAC, though the $\Delta s(\mathrm{M})$ values of DTAC and DAC are opposite in sign as shown in Fig. 4, they are found to be positive, which suggests that the energy of the adsorbed state is larger than that of the micellar state for the two systems. It is further found that the $\Delta u(1)$ and $\Delta u(\mathrm{M})$ values of

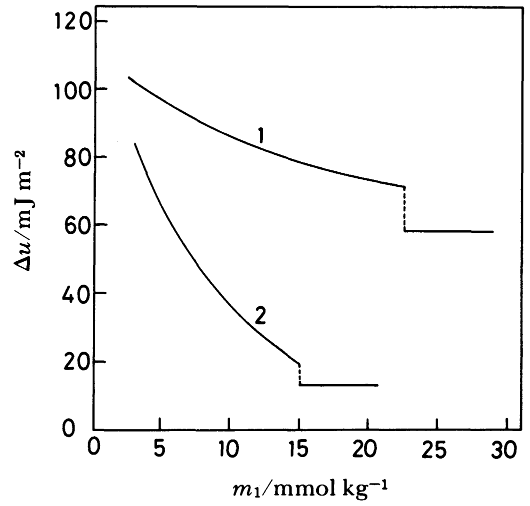

Fig. 8. Energy change associated with the adsorption vs. concentration curves at 298.15 K under atmospheric pressure: (1) DTAC; (2) DAC.

DTAC are larger than those of DAC. These results indicate that the energy states of the adsorbed film and micelle of surfactant are affected appreciably by the chemical structure of its head group. Further information regarding the effect of the head group will be obtained by investigating the systems of alkyldimethylammonium chloride and alkylmonomethylammonium chloride.

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