January, 1991] Bull. Chem. Soc. Jpn., 64, 5—10 (1991)

Temperature Effect on the Adsorption and Micelle Formation of Aqueous Dodecyltrimethylammonium Chloride–Hexane System

Koji Abe,* Ichiro Kajiwara, Norihiro Ikeda,
Makoto Aratono, and Kinsi Motomura
Department of Chemistry, Faculty of Science, Kyushu University 33,
Fukuoka 812
(Received August 9, 1990)

The adsorption at water/hexane interface and micelle formation of dodecyltrimethylammonium chloride (DTAC) were studied by measuring its interfacial tension as a function of temperature under atmospheric pressure at various concentrations around the critical micelle concentration (cmc). By applying the thermodynamic equations developed previously, the entropy and energy changes associated with the adsorption from monomeric and micellar states were estimated and compared with those of the DTAC solution–air system. It was found that the entropy and energy of the adsorbed film of DTAC are remarkably depressed by the coexistent hexane phase. This finding explains the positive entropy change associated with the adsorption of DTAC at water/air interface.

The adsorption and micelle formation of surfactants are affected by the oil phase coexisting with its aqueous solution.[1–5] In our series of the thermodynamic studies, we investigated the effect of hexane on the adsorption and micelle formation of dodecylammonium chloride (DAC) and sodium dodecyl sulfate in terms of entropy, volume, and energy.[6,7] Further the pressure dependence of interfacial tension of dodecyltrimethylammonium chloride (DTAC) solution against oil phase was discussed in terms of volume.[8–10] On the other hand, it was found that the entropy change associated with the adsorption of DTAC from the micellar state is positive at water/air interface while that of DAC is negative at both water/air and water/hexane interfaces. It is now required to examine the temperature dependence of the interfacial tension of the DTAC solution–hexane system.

In the present work, the interfacial tension of the aqueous DTAC solution against hexane is measured as a function of temperature at various concentrations around the critical micelle concentration (cmc). By applying the thermodynamics[11] to experimental results, the entropy and energy changes associated with the adsorption and micelle formation are estimated numerically. The thermodynamic quantities obtained of the DTAC solution–hexane system are compared with those of the DTAC solution–air system.[12]

Experimental

Dodecyltrimethylammonium chloride (DTAC) was synthesized and purified by the method described previously.[8] Water was distilled triply from dilute alkaline permanganate solution. Hexane was purified by distillation.

The equilibrium interfacial tension was measured by the pendant drop technique within an experimental error of 0.05 mN m^{-1} under atmospheric pressure.[13] The temperature was kept constant within 0.01 K.

Results and Discussion

The interfacial tension γ of the aqueous DTAC solution against hexane was measured as a function of temperature T at constant molality m_1 of surfactant under atmospheric pressure. Given in Fig. 1a are the γ

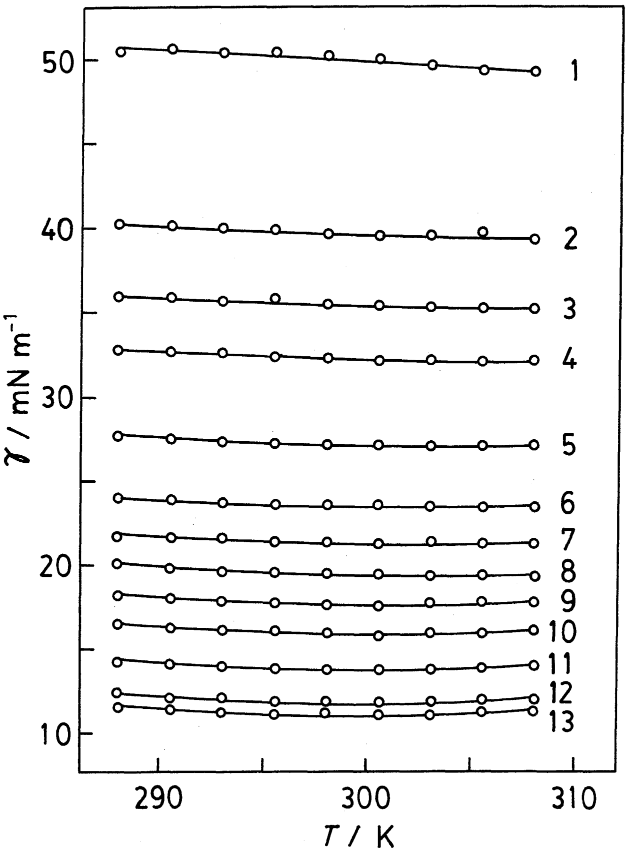

Fig. 1a. Interfacial tension vs. temperature curves at constant molality under atmospheric pressure: (1) m_1=0 mmol kg^{-1}; (2) 1.16; (3) 2.09; (4) 3.02; (5) 5.26; (6) 7.47; (7) 9.08; (8) 10.52; (9) 12.23; (10) 14.10; (11) 16.94; (12) 19.71; (13) 20.62.

vs. T curves at concentrations below the critical micelle concentration (cmc). It is seen that the curve decreases monotonously with increasing temperature at a low concentration while it has the minimum at a higher concentration. In Fig. 1b, a break point is observed on the curve at concentration near the cmc. This finding indicates that micelle formation takes place in the aqueous solution.[11] At a concentration above the cmc, the curve becomes the linear γ vs. T plot with a positive slope.

Picking up the γ values around the cmc at a given temperature from Figs. 1a and 1b, the γ vs. m_1 curves are drawn at constant temperature and illustrated in Fig. 2. It is seen that the curve breaks distinctly at cmc. The values of cmc C are plotted against temperature in Fig. 3; the C vs. T curve shows a shallow minimum and bears a great resemblance in shape to that of the DTAC solution-air (DTAC/A) system.[12] It is noteworthy, however, that the DTAC solution–hexane

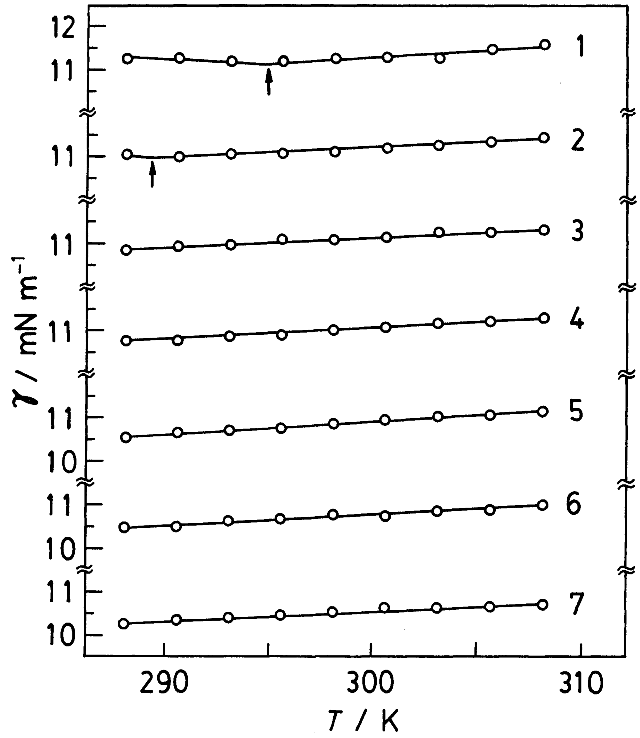

Fig. 1b. Interfacial tension vs. temperature curves at constant molality under atmospheric pressure: (1) m_1=21.32 mmol kg^{-1}; (2) 21.92; (3) 22.92; (4) 25.32; (5) 27.55; (6) 32.02; (7) 43.36.

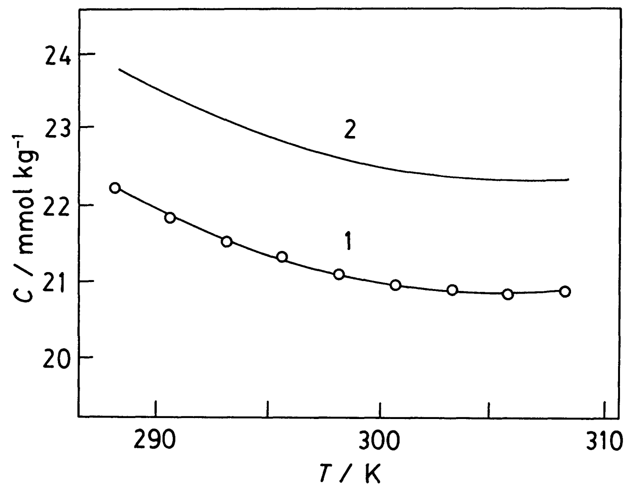

Fig. 3. Critical micelle concentration vs. temperature curves under atmospheric pressure: (1) DTAC/H system; (2) DTAC/A system.

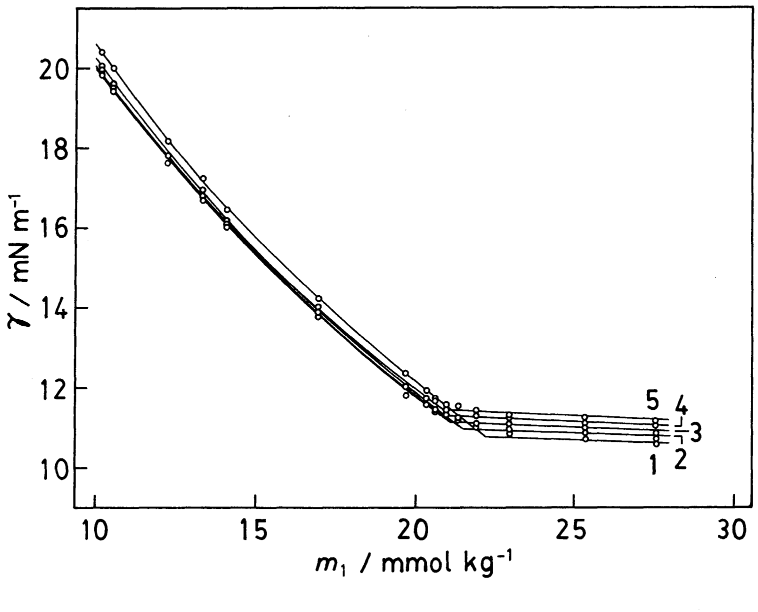

Fig. 2. Interfacial tension vs. molality curves at constant temperature under atmospheric pressure: (1) T=288.15 K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

(DTAC/H) system has a C value smaller than the DTAC/A system. The similar observation has been reported on the aqueous surfactant solution–oil systems and explained by the solubilization of oil.[1,3–5]

To examine more closely the influence of hexane on interfacial and micellar properties of the aqueous DTAC solution, let us evaluate the interfacial density and the thermodynamic quantities associated with adsorption and micelle formation of surfactant. Assuming the aqueous solution of DTAC to be a dilute ideal solution, the interfacial density Γ_1^H of surfactant is calculated by applying the relation

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

to the γ vs. m_1 curve and is shown as a function of m_1 at constant T in Fig. 4. The interfacial pressure π vs. area per surfactant molecule A curve is useful to consider the state of adsorbed film. Here π and A are defined by

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

and

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

where γ^0 is the interfacial tension of the DTAC/A and DTAC/H systems without surfactant and N_A is Avogadro's number. The π vs. A curve is depicted at 298.15 K and compared with corresponding curve of the DTAC/A system in Fig. 5. It is obvious that the adsorbed film of the DTAC/H system is more expanded than that of the DTAC/A system.

It has been demonstrated that the thermodynamic treatment of the adsorption of surfactant from its micellar solution is useful.[6–12,14–16] According to the thermodynamics, the entropy change associated with the adsorption of surfactant from its monomeric state, $\Delta s(1)$, and that from its micellar state, $\Delta s(\mathrm{M})$, are evaluated respectively by the equations

$$\Delta s(1) = \Gamma_1^H(s^H/\Gamma_1^H - s_1^W) \tag{4}$$

$$= -(\partial\gamma/\partial T)_{p,m_1}, \quad m_1<C \tag{5}$$

and

$$\Delta s(\mathrm{M}) = \Gamma_1^H(s^H/\Gamma_1^H - s^M/N_1^M) \tag{6}$$

$$= -(\partial\gamma/\partial T)_{p,m_1}, \quad m_1\geqq C, \tag{7}$$

where s^H, s^M, s_1^W, and N_1^M are the interfacial excess entropy per unit area, the molar entropy of micelle, the

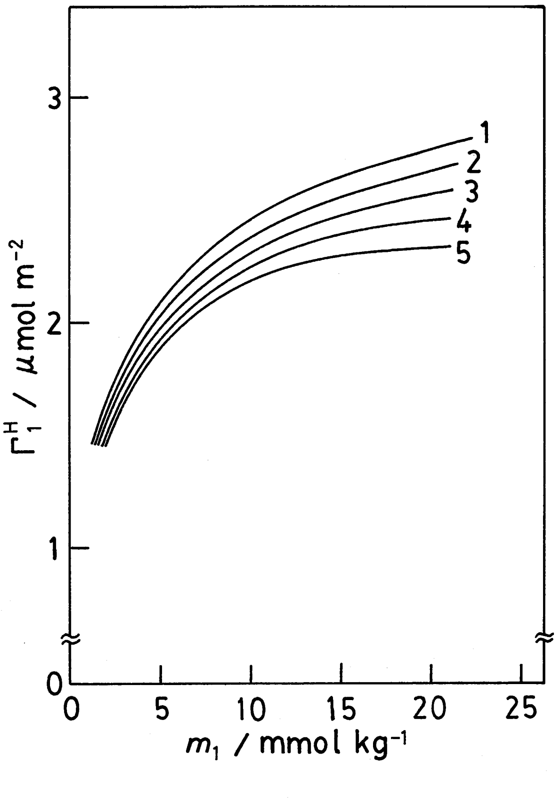

Fig. 4. Interfacial density vs. molality curves at constant temperature under atmospheric pressure: (1) T=288.15 K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

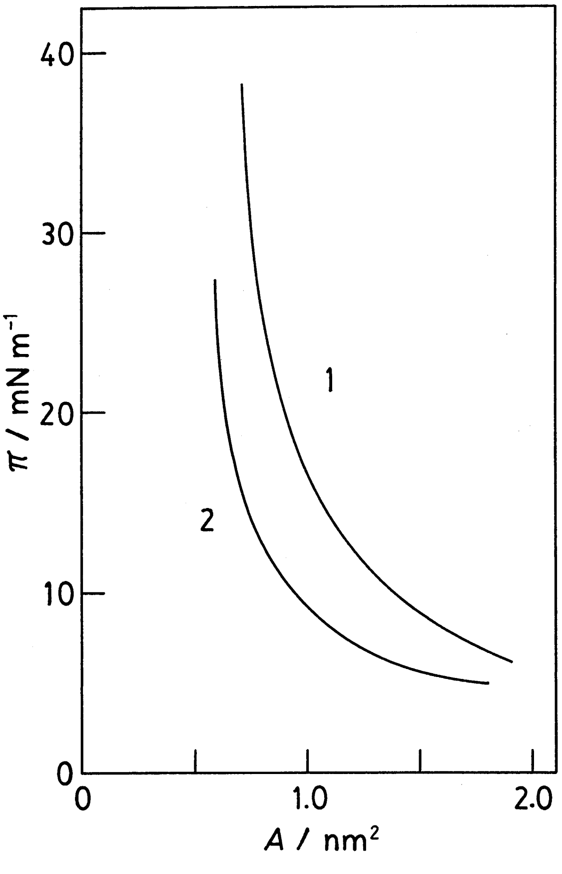

Fig. 5. Interfacial pressure vs. area per molecule curves at 298.15 K under atmospheric pressure: (1) DTAC/H system; (2) DTAC/A system.

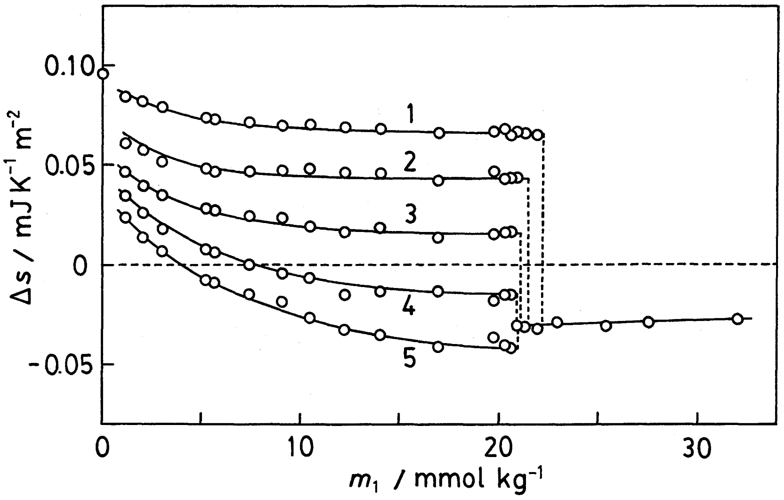

Fig. 6. Entropy change associated with adsorption vs. molality curves at constant temperature under atmospheric pressure: (1) T=288.15 K; (2) 293.15; (3) 298.15; (4) 303.15; (5) 308.15.

partial molar entropy of surfactant in the solution, and the number of surfactant ion in the micelle particle, respectively. Here, Eqs. 6 and 7 were derived on the assumption that the micelle formation can be treated thermodynamically like the appearance of a new macroscopic phase when its thermodynamic quantities are given by the excess thermodynamic quantities similar to those used for the adsorbed film. In Fig. 6, the entropy changes evaluated are plotted against molality at various temperatures. The value of $\Delta s(1)$ is found to decrease with increasing concentration and temperature. On the other hand, the value of $\Delta s(M)$ exhibits little dependence on m_1 and T. These results indicate that the temperature dependence of entropy of the adsorbed film is similar to that of the micelle through markedly different from that of the aqueous solution. Now it is important to note that the $\Delta s(M)$ value of the DTAC/H system is negative while that of the DTAC/A system is positive. In Fig. 7, the $\Delta s/\Gamma_1^H$ vs. m_1 curve is drawn together with that of the DTAC/A system[12] at 298.15 K.

Here, let us consider the difference between the entropies in the solution and micelle at the cmc. The entropy of micelle formation at the cmc is defined by

$$\Delta_W^M s = s^M/N_1^M - s_1^W \tag{8}$$

and evaluated by use of the relation

$$\Delta_W^M s = [\Delta s(1) - \Delta s(M)]/\Gamma_1^H. \tag{9}$$

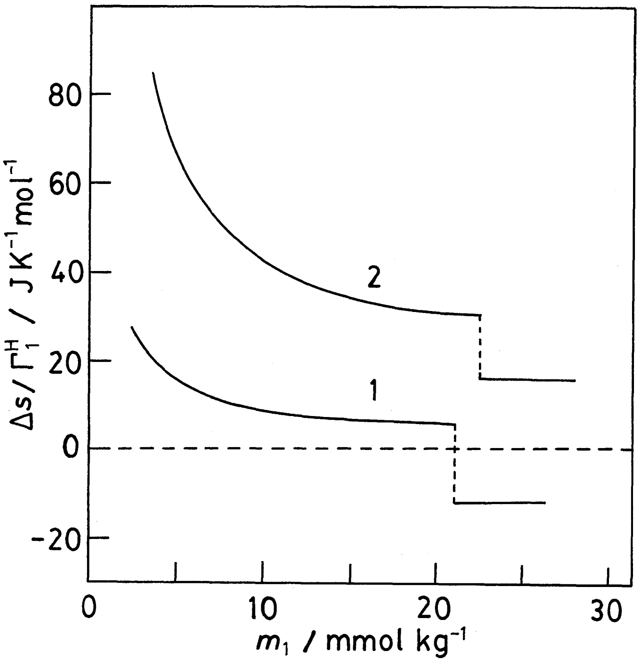

Fig. 7. Entropy change associated with adsorption per mole of surfactant vs. molality curves at 298.15 K under atmospheric pressure: (1) DTAC/H system; (2) DTAC/A system.

The $\Delta_W^M s$ value is plotted against T in Fig. 8. It is alternatively evaluated by applying the equation

$$\Delta_W^M s = -(2RT/C)(\partial C/\partial T)_p \tag{10}$$

to the C vs. T curve drawn in Fig. 3. The comparison between them are also made in Fig. 8; the agreement is satisfactory. This proves that the assumption described above is probable at a concentration near the cmc. Furthermore, the $\Delta_W^M s$ vs. T curve of the DTAC/H system is compared with the curve of the DTAC/A system in Fig. 8. Both the curves seem to be close to each other. Thus, it is found that the micelle formation of DTAC in the DTAC/H system is similar to that in the DTAC/A system. This finding tells us that the difference in $\Delta s(M)$ between the DTAC/H and

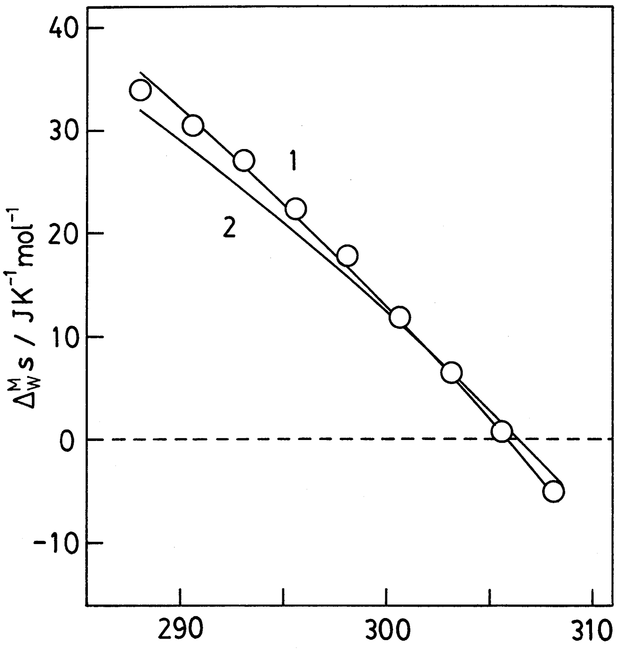

Fig. 8. Entropy of micelle formation vs. temperature curves under atmospheric pressure: (O) Eq. 9; (—) Eq. 10; (1) DTAC/H system; (2) DTAC/A system.

DTAC/A systems stems from the difference in s^H. Therefore, remembering the results given in Fig. 7, we can conclude that the DTAC molecules adsorbed at water/hexane interface are forced to have a fairly restricted conformation as compared with those at water/air interface. The corresponding results of DAC support this view.[17]

The energy change associated with the adsorption of surfactant from its monomeric state, $\Delta u(1)$, and that from its micellar state, $\Delta u(\mathrm{M})$, are obtained respectively by the equations

$$\Delta u(1) = \gamma + T\Delta s(1) - p\Delta v(1) \qquad (11)$$

and

$$\Delta u(\mathrm{M}) = \gamma + T\Delta s(\mathrm{M}) - p\Delta v(\mathrm{M}), \qquad (12)$$

where $\Delta v(1)$ and $\Delta v(\mathrm{M})$ are the corresponding volume changes. The Δu value was estimated numerically by making use of γ and Δs values given in Figs. 1 and 6 since the $p\Delta v$ terms are negligibly small compared with other terms under atmospheric pressure.[7–10] The results are shown in the form of $\Delta u/\Gamma_1^H$ vs. m_1 curve at 298.15 K in Fig. 9, where for comparison the curve of the DTAC/A system is also depicted. Further, the plot of the energy of micelle formation $\Delta_W^M u$ defined by a similar equation to Eq. 8 against T are compared between the DTAC/H and DTAC/A systems at the cmc in Fig. 10. Taking into account that the $\Delta_W^M u$ vs. T curves of both systems are quite similar to each other, the u^H value of the DTAC/A is said to be significantly larger than that of the DTAC/H system. It is clear that this large u^H value is closely related to the large s^H value cited above. In the case of DAC, an analogous

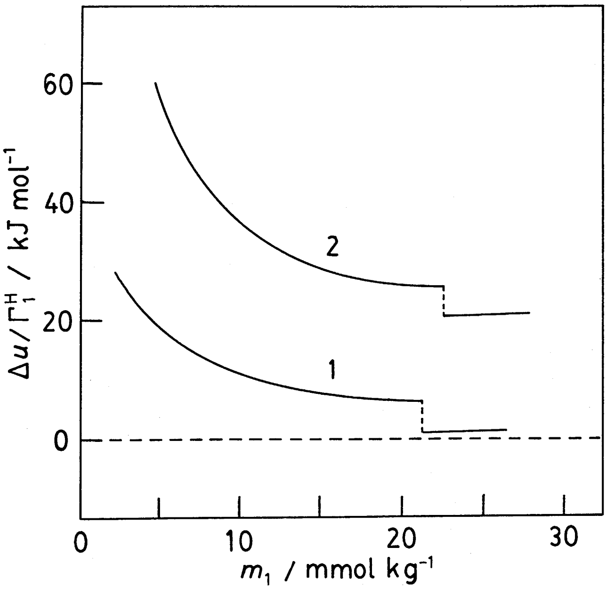

Fig. 9. Energy change associated with adsorption per mole of surfactant vs. molality curves at 298.15 K under atmospheric pressure: (1) DTAC/H system; (2) DTAC/A system.

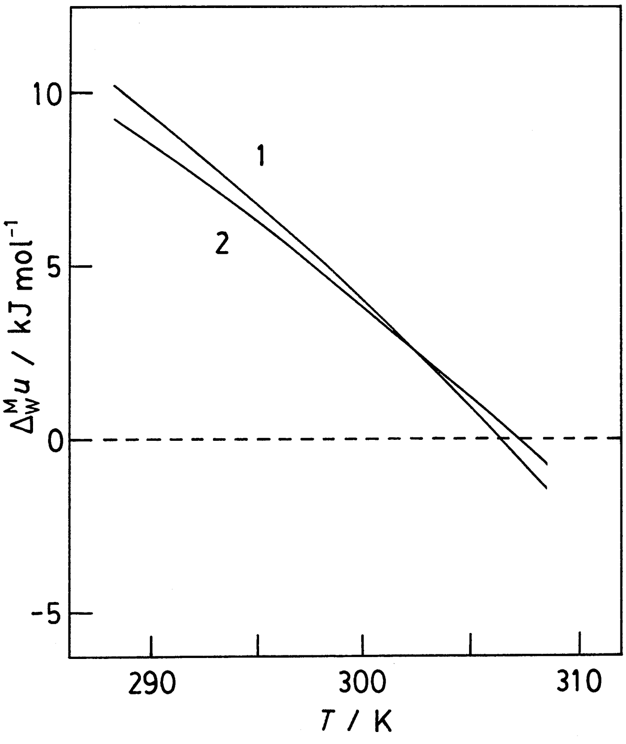

Fig. 10. Energy of micelle formation vs. temperature curves under atmospheric pressure: (1) DTAC/H system; (2) DTAC/A system.

behavior is obtained. These results indicate that the adsorption of surfactant at the interfaces is remarkably affected by the air phase coexisting with its aqueous solution.

References

1) A. W. Ralston and D. N. Eggenberger, *J. Phys. Chem.*, **70**, 983 (1948).

2) N. D. Weiner, H. C. Parreira, and G. Zografi, *J. Pharm. Sci.*, **55**, 187 (1966).

3) S. J. Rehfeld, *J. Phys. Chem.*, **71**, 739 (1967).

4) B. R. Vijayendran and T. P. Brush, *J. Colloid Interface Sci.*, **68**, 383 (1979).

5) D. S. Murphy and M. J. Rosen, *J. Phys. Chem.*, **92**, 2870 (1988).

6) M. Yamanaka, N. Aratono, H. Iyota, K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **55**, 2744 (1982).

7) M. Yamanaka, H. Iyota, M. Aratono, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **94**, 451 (1983).

8) M. Yamanaka, M. Aratono, K. Motomura, and R. Matuura, *Colloid Polym. Sci.*, **262**, 338 (1984).

9) M. Yamanaka, M. Aratono, and K. Motomura, *Bull. Chem. Soc. Jpn.*, **59**, 2695 (1986).

10) M. Yamanaka, M. Aratono, Y. Hayami, and K. Motomura, *Colloid Polym. Sci.*, **268**, 70 (1990).

11) K. Motomura, S. Iwanaga, M. Yamanaka, M. Aratono, and R. Matuura, *J. Colloid Interface Sci.*, **86**, 151 (1982).

12) M. Aratono, T. Okamoto, and K. Motomura, *Bull. Chem. Soc. Jpn.*, **60**, 2361 (1987).

13) N. Matubayasi, K. Motomura, S. Kaneshina, M. Nakamura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **50**, 523 (1977).

14) K. Motomura, S. Iwanaga, S. Uryu, H. Matsukiyo, M. Yamanaka, and R. Matuura, *Colloids Surf.*, **9**, 19 (1984).

15) M. Aratono, T. Okamoto, N. Ikeda, and K. Motomura, *Bull. Chem. Soc. Jpn.*, **61**, 2773 (1988).

16) K. Motomura, I. Kajiwara, N. Ikeda, and M. Aratono, *Colloids Surf.*, **38**, 61 (1989).

17) K. Motomura, S. Iwanaga, Y. Hayami, S. Uryu, and R. Matuura, *J. Colloid Interface Sci.*, **80**, 32 (1981).