2744 © 1982 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **55**, 2744—2748 (1982) [Vol. 55, No. 9

Temperature Effect on the Adsorption of Ionic Surfactants at Water/Hexane Interface from Micellar Solutions

Michio Yamanaka,* Makoto Aratono, Hidemi Iyota,
Kinsi Motomura, and Ryohei Matuura
Department of Chemistry, Faculty of Science, Kyushu University 33, Higashi-ku, Fukuoka 812

(Received January 16, 1982)

The adsorption behavior of dodecylammonium chloride (DAC) and sodium dodecyl sulfate (SDS) at their aqueous micellar solution/hexane interface has been studied by measuring the interfacial tension as a function of temperature at concentrations around the critical micelle concentration (cmc). The derivative of the interfacial tension with respect to temperature has been observed to change abruptly at the cmc and very little thereafter with increasing concentration in a limited range above the cmc. By applying the thermodynamic treatment of adsorption from micellar solution developed previously to the present experimental results, the entropy changes associated with the adsorption of DAC and SDS from monomeric state and from micellar state and the corresponding energy changes have been calculated. Further, the entropy and energy changes of micelle formation have been obtained from these quantity changes. These values have been compared with those obtained for DAC at water/air interface. It has been observed that the behavior of the micelle in the limited concentration range is controlled solely by temperature and pressure and bears resemblance to that of the adsorbed film at the interface. It has also been observed that the entropy and energy of micelle and adsorbed film are lowered by the hexane existing in the system.

In a recent paper,[1] we have investigated the adsorption of dodecylammonium chloride (DAC) at water/air interface by measuring the surface tension of the solution as a function of temperature at various concentrations around critical micelle concentration (cmc). It has been clarified with the aid of the entropy and energy changes associated with the adsorption of DAC evaluated by applying the thermodynamic treatment of adsorption[2–5] that the thermodynamic properties of the micelle of DAC in the aqueous solution are closely related to those of adsorbed film of DAC at water/air interface. It is now interesting to see if a similar conclusion is obtained at water/oil interface by measurement of the interfacial tension.

The purposes of the present work are to confirm the validity of our thermodynamic treatment of the adsorption from micellar solution[1] and to reveal the difference of the behavior of adsorbed film at water/hexane interface from that of micelle. In order to attain these purposes, we adopt as surfactants DAC and sodium dodecyl sulfate (SDS), of which the adsorbed films at water/hexane interface have well been investigated in the range of concentration below cmc.[3,6] The interfacial tension is measured as a function of temperature at various concentrations around cmc. The thermodynamic quantity changes associated with adsorption from micellar solution are evaluated by applying the thermodynamic equations and compared with corresponding changes of DAC at water/air interface.

Experimental

DAC and SDS were synthesized and purified by the method described in the previous papers.[3,6] Water was distilled three times from alkaline permanganate solution. Hexane was purified by distillation after passing through an activated alumina column.

The equilibrium interfacial tension was measured as a function of temperature at constant total concentration around cmc under atmospheric pressure. The value of the interfacial tension of the system of aqueous SDS solution and hexane was determined by the pendant drop technique[7,8] within the experimental error of 0.05 mN m^{-1}. Since the system of aqueous DAC solution and hexane had a very small interfacial tension (about 2 mN m^{-1}) in the neighborhood of cmc, we adopted the sessile drop technique[8,9] for the determination of the equilibrium interfacial tension.

The sessile drop of hexane made in the DAC solution in the glass cell was allowed to stand for about an hour in order to establish the thermal equilibrium. The enlarged photograph of the sessile drop was taken by the camera and the shape and size of the drop on the photographic film were determined to a precision of μm by Nikon Measurescope. The value of the interfacial tension γ was calculated by the equation

$$\gamma = (1/2)g\Delta d a^2, \tag{1}$$

where g is the acceleration of gravity, Δd the difference in density between aqueous solution and hexane, and a the capillary constant. The value of a^2 is obtained from the experimental values of the radius r of the sessile drop in the equatorial plane and the height h from this plane to the top of the drop:

$$a^2 = r^2 f(h/r),$$

where $f(h/r)$ is a function of h/r. We took the value of $f(h/r)$ from the tables of Tawde and Parvatikar.[10–12] In the case where the value of h/r is too small and deviates from these tables, we calculated it by the equations presented by Blaisdell.[13] The error estimated for the value of the interfacial tension was 0.05 mN m^{-1}.

The densities of pure hexane and water were used instead of those of hexane and aqueous solutions, because the mutual solubility between hexane and water was small and the concentrations of the solution were low. Temperature was kept constant within 0.05 K by circulating thermostated water around the cell.

Results and Discussion

The variation of the interfacial tension γ with temperature T at constant total molality m_1^t of surfactant around cmc under atmospheric pressure is shown in Figs. 1a and 1b for DAC and SDS, respectively. The γ *vs.* T curve of the pure water/hexane interface is

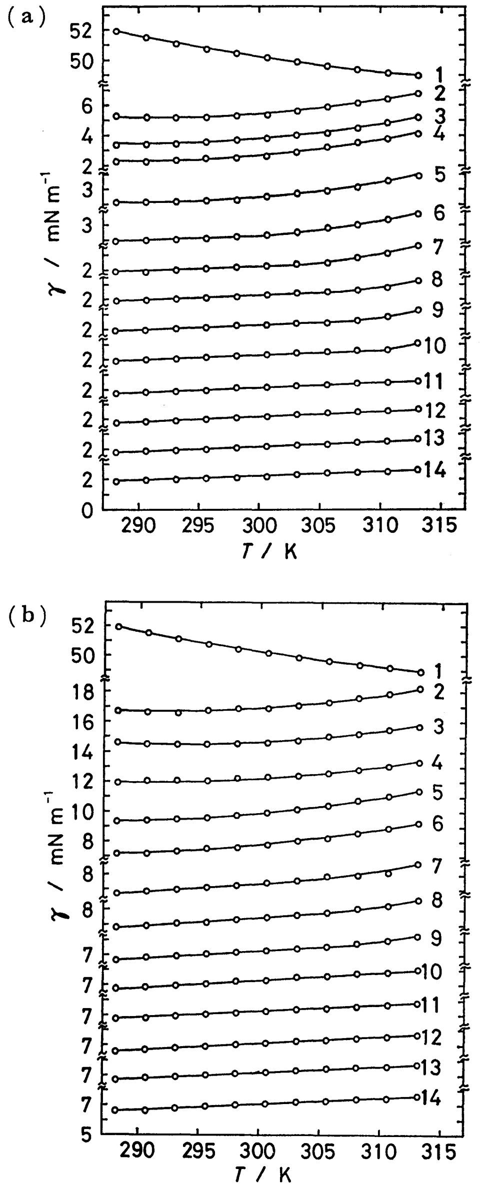

Fig. 1. Interfacial tension *vs.* temperature curves of DAC (a) and SDS (b) at constant total molality under atmospheric pressure.
(a): (1) $m_1^t=0$ mmol kg^{-1}; (2) 11.08; (3) 12.04; (4) 12.51; (5) 12.65; (6) 12.80; (7) 12.98; (8) 13.04; (9) 13.14; (10) 13.29; (11) 15.04; (12) 16.53; (13) 18.03; (14) 20.13. (b): (1) $m_1^t=0$ mmol kg^{-1}; (2) 3.99; (3) 4.59; (4) 5.49; (5) 6.36; (6) 7.20; (7) 7.40; (8) 7.54; (9) 7.67; (10) 7.70; (11) 8.46; (12) 9.97; (13) 11.29; (14) 12.69.

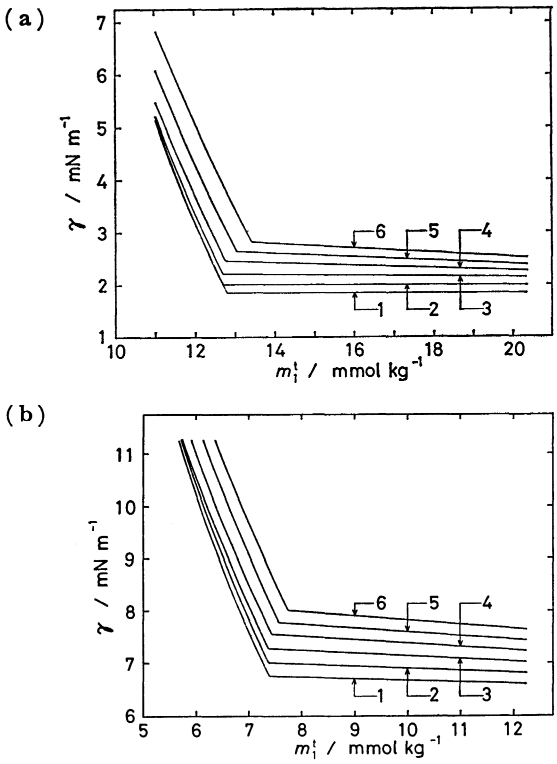

Fig. 2. Interfacial tension *vs.* total molality curves of DAC (a) and SDS (b) at constant temperature under atmospheric pressure.
(a): (1) 288.15 K; (2) 293.15 K; (3) 298.15 K; (4) 303.15 K; (5) 308.15 K; (6) 313.15 K. (b): (1) 288.15 K; (2) 293.15 K; (3) 298.15 K; (4) 303.15 K; (5) 308.15 K; (6) 313.15 K.

included for comparison. These figures seem to resemble each other. The γ *vs.* T curve at a concentration below cmc is slightly concave upward, while at a concentration above cmc γ increases linearly with increasing T in the range of 288.15 K to 313.15 K in contrast with that of the pure water/hexane interface. Examining the γ *vs.* T curve at a concentration near cmc, it is found that the curve consists of linear and curved portions and the linear portion is made longer by the increase of m_1^t. This fact suggests that the values of cmc of DAC and SDS vary with temperature.

The values of the interfacial tension taken from Figs. 1a and 1b are plotted against m_1^t at constant temperature in Figs. 2a and 2b for DAC and SDS, respectively. The γ *vs.* m_1^t curve has a visible break point at a certain concentration which provides the value of cmc. In the concentration range above cmc, γ is observed to decrease linearly and slightly with m_1^t. When we are concerned with a limited range of m_1^t close to the cmc, we may say that γ remains constant.

In Fig. 3, the cmc *vs.* T curves of DAC and SDS obtained from Figs. 2a and 2b are shown together with the curve, for comparison, of the system of aqueous DAC solution and air taken from our previous paper.[1] It is found that the curves are concave upward and have a distinct minimum; the temperature of minimum is near 295 K for the curves of DAC and SDS in this work and near 300 K for the curve of DAC in the previous paper. Further, the value of cmc of DAC measured by the interfacial tension is different from that measured by the surface tension. This fact may be attributable to the difference of the phase coexisting with the DAC solution.

Next, we will consider the derivative of the interfacial tension with respect to temperature at constant concentration under atmospheric pressure. The values of $-\partial\gamma/\partial T$, which are evaluated from Figs. 1a and

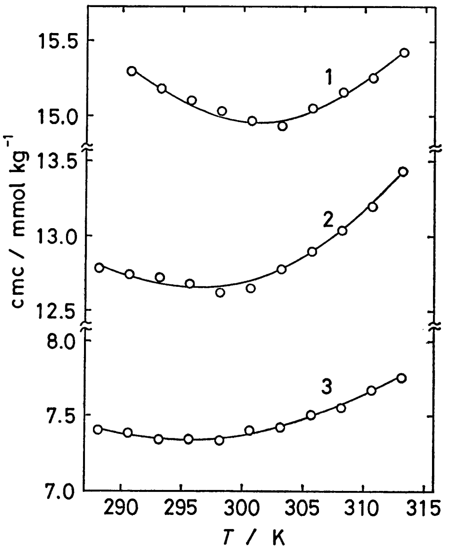

Fig. 3. Critical micelle concentration *vs.* temperature curves under atmospheric pressure.
(1): DAC water/air, (2): DAC water/hexane, (3): SDS water/hexane.

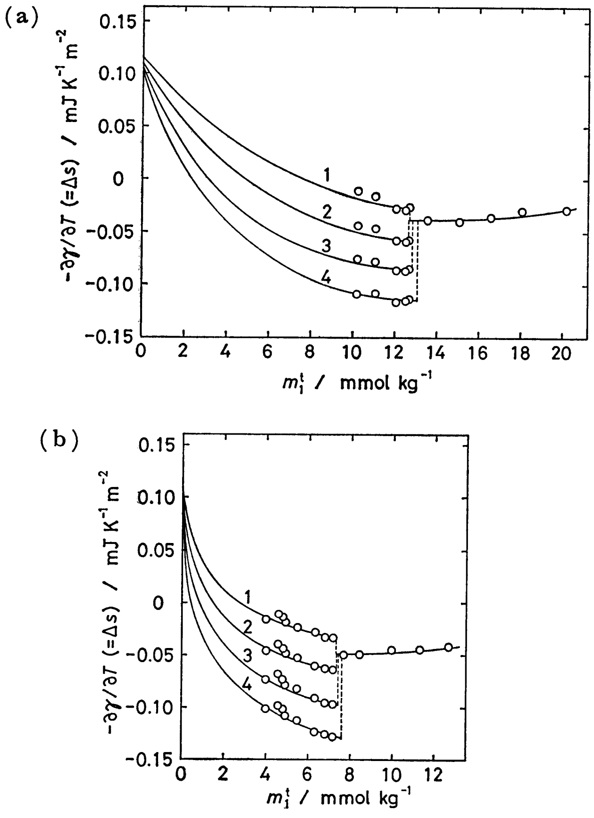

Fig. 4. Derivative of interfacial tension with respect to temperature *vs.* total molality curves of DAC (a) and SDS (b) at constant temperature under atmospheric pressure.
(a): (1) 293.15 K; (2) 298.15 K; (3) 303.15 K; (4) 308.15 K. (b): (1) 293.15 K; (2) 298.15 K; (3) 303.15 K; (4) 308.15 K.

1b, are plotted against m_1^t in Figs. 4a and 4b for DAC and SDS, respectively. It is seen clearly that $-\partial\gamma/\partial T$ varies discontinuously at the cmc. Above cmc it has a negative and almost constant value in the limited range of concentration near cmc. The same observation has been obtained with the adsorption of DAC at water/air interface.[1] The constancy of $-\partial\gamma/\partial T$ and γ in the limited range of m_1^t suggests that the concentration of monomeric surfactant is not varied significantly by m_1^t and the behavior of the micelle in this concentration range is controlled solely by temperature and pressure.

According to our thermodynamic treatment of the adsorption from micellar solution developed previously,[1] we can evaluate the two types of the thermodynamic quantity changes denoted by $\Delta y(1)$ and $\Delta y(\mathrm{M})$, which are associated with the adsorption of surfactant from its monomeric state and micellar state, respectively. Let us assume that the surfactant is a strong electrolyte and that the behavior of micelle is described by using thermodynamic properties of an imaginary micelle particle which contains the surrounding counterions so as to satisfy the condition of electroneutrality. Since the total differential of its chemical potential μ^{M} is expressed as a function of T and p:

$$d\mu^{\mathrm{M}} = -s^{\mathrm{M}}dT + v^{\mathrm{M}}dp, \tag{2}$$

where s^{M} and v^{M} are the molar entropy and volume of micelle, respectively, $\Delta y(1)$ and $\Delta y(\mathrm{M})$ are defined by the equations

$$\Delta y(1) = y^{\mathrm{H}} - \Gamma_1^{\mathrm{H}} y_1^{\mathrm{W}}, \tag{3}$$

and

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

where Γ_1^{H} is the interfacial density of surfactant, y^{H} the interfacial excess quantity per unit area, y_1^{W} the partial molar quantity of surfactant in the solution, and N_1^{M} the number of surfactant ions in the micelle.

In the first place, the entropy changes, $\Delta s(1)$ and $\Delta s(\mathrm{M})$, can be calculated by applying the following equations to the present experimental results:

$$\Delta s(\mathrm{M}) = -(\partial\gamma/\partial T)_{p,m_1^t}, \tag{5}$$

and

$$\Delta s(1) = -(\partial\gamma/\partial T)_{p,m_1^t} - 2(RT/\mathrm{cmc})\Gamma_1^{\mathrm{H}}(\partial\mathrm{cmc}/\partial T)_p, \tag{6}$$

where it is presumed that the micellar solution behaves ideally and the concentration of monomeric surfactant is equal to the value of cmc. On the other hand, in the case where the system is free from micelle, $\Delta s(1)$ is provided directly by the equation

$$\Delta s(1) = -(\partial\gamma/\partial T)_{p,m_1^t}. \tag{7}$$

Thus, it is evident from Eqs. 5 and 7 that the value of $-\partial\gamma/\partial T$ in Figs. 4a and 4b provides $\Delta s(\mathrm{M})$ at the concentration above cmc and $\Delta s(1)$ at the concentration below cmc. Therefore, the discontinuous change in $-\partial\gamma/\partial T$ at the cmc corresponds to the difference between $\Delta s(1)$ and $\Delta s(\mathrm{M})$ and its value is related to the temperature dependence of cmc by the equation

$$\Delta s(1) - \Delta s(\mathrm{M}) = -2(RT/\mathrm{cmc})\Gamma_1^{\mathrm{H}}(\partial\mathrm{cmc}/\partial T)_p \text{ at cmc.} \tag{8}$$

The right side of Eq. 8 is calculated easily, since the value of Γ_1^{H} is estimated by applying the equation

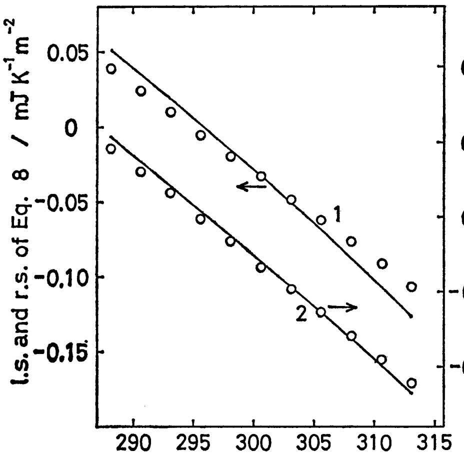

Fig. 5. Comparison between left side ($\Delta s(1)-\Delta s(\mathrm{M})$) and right side ($-2(RT/\mathrm{cmc})\Gamma_1^{\mathrm{H}}(\partial\mathrm{cmc}/\partial T)_p$) of Eq. 8. Left side ○ and right side ——; (1) DAC; (2) SDS.

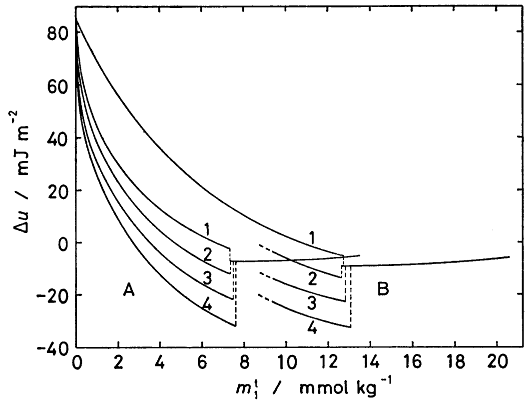

Fig. 6. Energy change associated with adsorption *vs.* total molality curves of DAC and SDS at constant temperature under atmospheric pressure.
(A): SDS; (B): DAC; (1) 293.15 K; (2) 298.15 K; (3) 303.15 K; (4) 308.15 K.

$$\Gamma_1^{\mathrm{H}} = -(m_1^t/2RT)(\partial\gamma/\partial m_1^t)_{T,p}, \tag{9}$$

to the γ *vs.* m_1^t curves in Figs. 2a and 2b, and the values of cmc and $\partial\mathrm{cmc}/\partial T$ are obtained from the cmc *vs.* T curves in Fig. 3. The left side of Eq. 8 is evaluated by extrapolating the values of $\Delta s(1)$ and $\Delta s(\mathrm{M})$ to the cmc. Both sides of Eq. 8 are compared in Fig. 5. They seem to be in fair agreement with each other. A similar result has been obtained for the system of aqueous solution of DAC and air.[1] This fact indicates that Eq. 2 is a useful approximation for the behavior of micelle in a limited concentration range near the cmc.

Next, let us evaluate the energy changes, $\Delta u(1)$ and $\Delta u(\mathrm{M})$, by the use of the relations

$$\Delta u(1) = \gamma + T\Delta s(1) - p\Delta v(1), \tag{10}$$

and

$$\Delta u(\mathrm{M}) = \gamma + T\Delta s(\mathrm{M}) - p\Delta v(\mathrm{M}). \tag{11}$$

Since the terms of $p\Delta v(1)$ and $p\Delta v(\mathrm{M})$ on the right sides of these equations are usually negligible compared with the other terms under atmospheric pressure,[3,6,14] the numerical values of $\Delta u(1)$ and $\Delta u(\mathrm{M})$ can be obtained by making use of Figs. 2a, 2b, 4a, and 4b. They are plotted against m_1^t in Fig. 6 for both DAC and SDS. It is apparent that the values of $\Delta u(1)$ and $\Delta u(\mathrm{M})$ depend on m_1^t in a similar manner as the corresponding entropy changes in Figs. 4a and 4b.

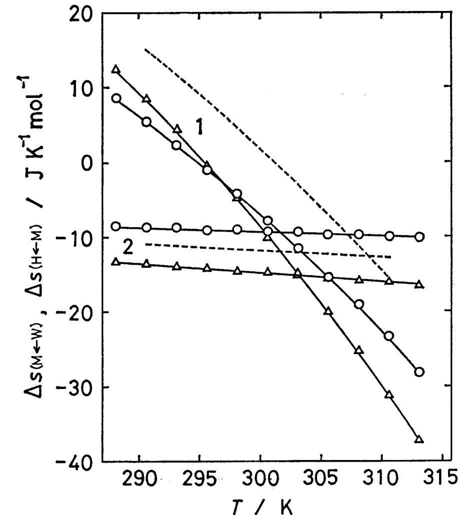

Fig. 7. Entropy change of micelle formation (Δs(M←W)) *vs.* temperature curves and entropy change associated with adsorption from micellar state (Δs(H←M)) *vs.* temperature curves under atmospheric pressure.
(1): Δs(M←W), (2): Δs(H←M), ○: DAC water/hexane, △: SDS water/hexane, - - - -: DAC water/air.

Now, it is instructive to look more closely at the behavior of DAC and SDS molecules in the adsorbed film and micelle. In order to do this, it is convenient to introduce the thermodynamic quantity changes per mole of surfactant, which are defined by the equations

$$\Delta y(\mathrm{H}\leftarrow\mathrm{M}) = y^{\mathrm{H}}/\Gamma_1^{\mathrm{H}} - y^{\mathrm{M}}/N_1^{\mathrm{M}} = \Delta y(\mathrm{M})/\Gamma_1^{\mathrm{H}}, \tag{12}$$

and

$$\Delta y(\mathrm{M}\leftarrow\mathrm{W}) = y^{\mathrm{M}}/N_1^{\mathrm{M}} - y_1^{\mathrm{W}} = [\Delta y(1) - \Delta y(\mathrm{M})]/\Gamma_1^{\mathrm{H}}, \tag{13}$$

where Eqs. 3 and 4 have been used.

In Fig. 7, the entropy changes, Δs(H←M) and Δs(M←W), which are obtained from Figs. 4a, 4b, and 5, are plotted against temperature. Included in this figure for comparison are those obtained for the system of DAC solution and air.[1] Their values are found to be fairly different between DAC and SDS and between the water/hexane and water/air interfaces. It is also seen that the value of Δs(H←M) is negative and slightly dependent on T while the value of Δs(M←W) decreases from a positive value to a negative one with increasing T.

The corresponding energy changes, Δu(H←M) and Δu(M←W), obtained from Fig. 6 and the previous paper,[1] are shown in Fig. 8. It is noteworthy that the Δu(H←M) has nearly equal negative values for DAC and SDS at water/hexane interface and has a positive value for DAC at water/air interface. It is also seen that Δu(H←M), likely Δs(H←M), depends slightly on T. These facts indicate that the tempera-

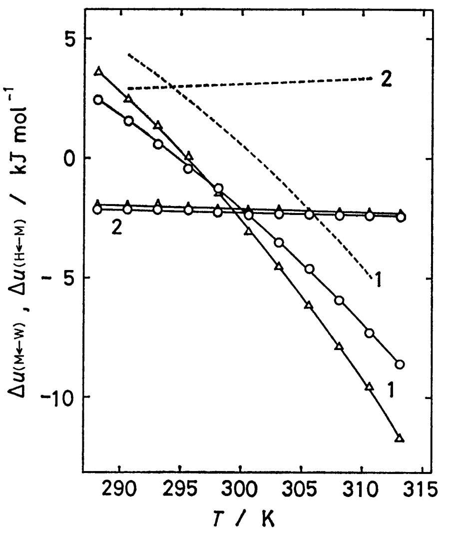

Fig. 8. Energy change of micelle formation (Δu(M←W)) *vs.* temperature curves and energy change associated with adsorption from micellar state (Δu(H←M)) *vs.* temperature curves under atmospheric pressure.
(1): Δu(M←W), (2): Δu(H←M), ○: DAC water/hexane, △: SDS water/hexane, ----: DACwater/air.

ture dependence of energy and entropy of the micelle bears resemblance to that of the adsorbed film. The resemblance of the behavior between the adsorbed film and the micelle will be further confirmed by evaluating the corresponding volume changes from the pressure dependence of the interfacial tension, which will be reported in the near future.[14)]

Finally, let us examine the temperature dependence of Δu(M←W) and Δs(M←W). According to Eq. 13, they may be respectively referred to as the energy and entropy changes of micelle formation. As can be seen in Figs. 7 and 8, the values of Δu(M←W) and Δs(M←W) vary with temperature in a similar manner. It is also seen that the temperature dependence of Δu(M←W) and Δs(M←W) of DAC at water/hexane interface is smaller than that of SDS. This result may be attributable to the difference in charge and size of the ionic head group and counterion of surfactant between DAC and SDS. Furthermore, we notice that the values of Δu(M←W) and Δs(M←W) for the aqueous DAC solution–hexane system are fairly smaller than those for the aqueous DAC solution–air system. We may conclude that such a behavior results from the lowering of the energy and entropy of micelle of DAC by the solubilization of hexane into the micelle.

The present work was supported by a Grant-in-Aid for Scientific Research No. 547009 from the Ministry of Education, Science and Culture.

References

1) K. Motomura, S. Iwanaga, M. Yamanaka, M. Aratono, and R. Matuura, *J. Colloid Interface Sci.*, **86**, 151 (1982).
2) K. Motomura, *J. Colloid Interface Sci.*, **64**, 348 (1978).
3) K. Motomura, M. Aratono, N. Matubayasi, and R. Matuura, *J. Colloid Interface Sci.*, **67**, 247 (1978).
4) K. Motomura, S. Iwanaga, Y. Hayami, S. Uryu, and R. Matuura, *J. Colloid Interface Sci.*, **80**, 32 (1981).
5) K. Motomura, *Adv. Colloid Interface Sci.*, **12**, 1 (1980).
6) M. Aratono, M. Yamanaka, N. Matubayasi, K. Motomura, and R. Matuura, *J. Colloid Interface Sci.*, **74**, 489 (1980).
7) N. Matubayasi, K. Motomura, S. Kaneshina, M. Nakamura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **50**, 523 (1977).
8) J. F. Padday, "Surface and Colloid Science," ed by E. Matijević, Wiley, New York (1969), Vol. 1, p. 101.
9) J. F. Padday, *Phil. Trans. R. Soc. London, A*, **269**, 265 (1971).
10) N. R. Tawde and K. G. Parvatikar, *Indian J. Phys.*, **25**, 473 (1951).
11) N. R. Tawde and K. G. Parvatikar, *Indian J. Phys.*, **28**, 345 (1954).
12) K. G. Parvatikar, *Indian J. Phys.*, **32**, 174 (1958).
13) B. E. Blaisdell, *J. Math. Phys.*, **19**, 186 (1940).
14) M. Yamanaka, M. Aratono, K. Motomura, and R. Matuura, unpublished data.