

Enthalpies of Adsorption and Micelle Formation of Octyl Methyl Sulfoxide

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The surface tension of the aqueous solution of octyl methyl sulfoxide (OMS) was measured as a function of temperature at various molalities below and above the critical micelle concentration. The entropy and enthalpy of adsorption from monomeric and micellar states of surfactant were evaluated by applying the thermodynamic equations to the surface tension measured. The entropy and enthalpy of micelle formation were also evaluated. These thermodynamic quantities were discussed in terms of the orientation of surfactant molecules in the interface and in micelle, the hydration of hydrophilic group of surfactant, and the difference in geometry between the adsorbed film and micelle.

1. Introduction

The enthalpy change accompanied by adsorption at a solid/fluid interface has been measured by calorimetry because the total interfacial area, and thus the total numbers of molecules, participating in the adsorption is generally so large that the heat absorbed or evolved in the process is detected by a calorimeter¹⁾. With respect to the adsorption at a fluid/fluid interface, on the contrary, the total interfacial area participating in the adsorption is usually so small that it is very difficult to detect the heat by a calorimeter even when the enthalpy change per mole of surfactant is comparable with that at the solid/fluid interface.

From this point of view, it is highly useful to evaluate the enthalpy change accompanied with the adsorption at a fluid/fluid interface by the thermodynamic method instead by calorimetry²⁻⁴⁾. In the present paper, the thermodynamic formulation for this purpose is described and then applied to the adsorption of octyl methyl sulfoxide at the air/water interface.

2. Experimental

Octyl methyl sulfoxide was prepared below 0°C by adding *tert*-butyl hypochlorite dropwise to the methanol solution of octyl methyl sulfide⁵⁾, which was distilled under reduced pressure around 75°C. After removing methanol, residual *tert*-butyl hypochlorite, and *tert*-butyl chloride as a by-product, the crude crystal was recrystallized from the mixture of petroleum ether and a slight amount of ethanol and then petroleum ether. The purity was checked by observing no minimum on the surface tension vs. molality curve around the critical micelle concentration⁶⁾. Water was distilled three times from alkaline permanganate solution.

The surface tension was measured within the accuracy of 0.05 mNm⁻¹ by the drop volume method⁷⁾. The temperature of measurement cell was kept constant within 0.01 K by immersing the apparatus in a thermostated water.

3. Thermodynamics

First we summarize the equations developed previ-

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ously to obtain the entropy and enthalpy of adsorption from the aqueous solution to the interface^{2,4)}. The surface tension γ can be written as a function of temperature T , pressure p , and the chemical potential of surfactant μ_1 :

$$d\gamma = -s^H dT + v^H dp - \Gamma_1^H d\mu_1 \quad \dots\dots\dots (1)$$

where s^H , v^H , and Γ_1^H are respectively the surface excess entropy, volume, and number of moles of surfactant per unit surface area and defined with reference to the two dividing planes making the excess numbers of moles of water and air zero.

Substituting the chemical potential of monomeric surfactant μ_1^W given by

$$d\mu_1^W = -s_1 dT + v_1 dp + (RT/m_1^W) dm_1^W \quad \dots\dots\dots (2)$$

for μ_1 in eq. (1), we have

$$d\gamma = -\Delta s(1) dT + \Delta v(1) dp - \Gamma_1^H (RT/m_1^W) dm_1^W \quad \dots (3)$$

where y_i ($y = s, v$) and m_1^W are the partial molar thermodynamic quantity and the molality of monomeric surfactant, respectively. $\Delta s(1)$ and $\Delta v(1)$ are the entropy and volume of adsorption of monomeric surfactant per unit surface area and defined as

$$\Delta y(1) = y^H - \Gamma_1^H y_1, y = s, v \quad \dots\dots\dots (4)$$

From eq. (3), the variation of surface tension with temperature at constant pressure and the total molality m_1 is given by

$$(\partial\gamma/\partial T)_{p, m_1} = -\Delta s(1) - \Gamma_1^H (RT/m_1^W) (\partial m_1^W / \partial T)_{p, m_1} \quad (5)$$

At concentrations below the cmc, the solution is free from micelle, *i.e.*, m_1^W is equal to m_1 , and then eq. (5) is reduced to

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

Since the chemical potentials of components are uniform throughout the system, the Gibbs free energy of adsorption $\Delta g(1)$ is zero and therefore the enthalpy of adsorption $\Delta h(1)$ is given by

$$\Delta h(1) = T\Delta s(1) \quad \dots\dots\dots (7)$$

At concentrations above the cmc, since the m_1^W value is approximately equal to the molality at the cmc C , we obtain

$$T(\partial\gamma/\partial T)_{p, m_1} = -\Delta h(1) - \Gamma_1^H (RT^2/C) (\partial C / \partial T)_p \quad \dots (8)$$

from eqs. (5) and (7). It is noted that the variation of surface tension with temperature is related to the change of monomer concentration as well as the enthalpy of adsorption from monomeric surfactant.

Now let us derive the equations to estimate the entropy and enthalpy of adsorption from micellar state³⁾. This is accomplished by substituting the chemical potential of surfactant in the micellar state, instead of that in the monomeric state μ_1^W , for μ_1 in eq. (1). Introducing the excess number of molecules of surfactant in the micelle N_1^M and taking into account that monomeric surfactants are in equilibrium with surfactants in the micellar state, the chemical potential of micelle particle μ^M is given by

$$\mu^M = N_1^M \mu_1^W \quad \dots\dots\dots (9)$$

Furthermore, it has been shown that the thermodynamic properties of micellar solution is described by using the excess thermodynamic quantities in a way similar to those of adsorbed film and the micelle formation is treated as an appearance of a new macroscopic phase³⁾. Therefore, the chemical potential of micelle particle μ^M is assumed to be a function of only temperature and pressure within a limited concentration around the cmc and written by

$$d\mu^M = -s^M dT + v^M dp \quad \dots\dots\dots (10)$$

where $y^{(M)}$ is the excess thermodynamic quantity of micelle particle.

Substituting eqs. (9) and (10) into eq. (1), we have

$$d\gamma = -\Delta s(M) dT + \Delta v(M) dp \quad \dots\dots\dots (11)$$

where Δy^M is the thermodynamic quantity of adsorption of surfactant from the micellar state per unit surface area defined by

$$\Delta y(M) = y^H - \Gamma_1^H (y^M / N_1^M) \quad \dots\dots\dots (12)$$

Therefore the temperature dependence of surface tension gives $\Delta s(M)$ at concentration above the cmc:

$$(\partial\gamma/\partial T)_{p, m_1} = -\Delta s(M) \quad \dots\dots\dots (13)$$

and the corresponding enthalpy is given by

$$\Delta h(M) = T\Delta s(M) \quad \dots\dots\dots (14)$$

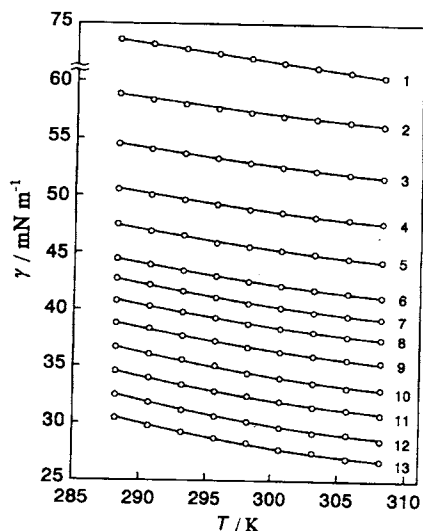


Fig.1 (a) Surface tension vs. temperature curves at constant molality below the critical micelle concentration. (1) $m_1 = 0$ mmol kg⁻¹, (2) 1.66, (3) 2.69, (4) 4.08, (5) 5.51, (6) 7.33, (7) 8.62, (8) 10.23, (9) 12.22, (10) 14.53, (11) 17.42, (12) 20.85, (13) 24.35.

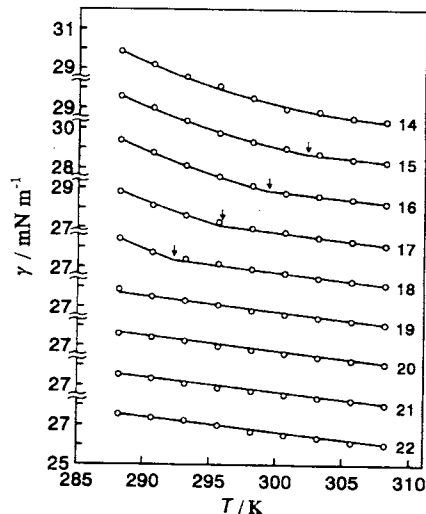


Fig.1 (b) Surface tension vs. temperature curves at constant molality around and above the critical micelle concentration. (14) $m_1 = 25.84$ mmol kg⁻¹, (15) 26.47, (16) 27.02, (17) 27.93, (18) 29.15, (19) 31.02, (20) 33.78, (21) 44.16, (22) 55.18.

By comparing eq. (8) with eq. (13), we note that the temperature dependence of the cmc is related to the difference between the values of $\Delta h(1)$ and $\Delta h(M)$:

$$\Delta h(1) - \Delta h(M) = \Gamma_1^H (RT^2/C) (\partial C / \partial T)_p \quad \text{..... (15)}$$

4. Results and discussion

The surface tension has been measured as a function of temperature at 40 different molalities. **Fig.1** shows part of the γ vs. T curves obtained. It is seen that the surface tension decreases with increasing temperature at all concentrations. Looking more closely at the experimental results, we note that the curve is concave upward at low m_1 , linear at a high m_1 , and has a break point at a limited concentration range, respectively. In **Fig.2** are shown the γ vs. m_1 curves obtained by picking the γ values at a given temperature in **Fig.1**. The surface tension decreases with increasing molality and the curve has a definite break at a molality which we referred to as the critical micelle concentration (cmc).

The enthalpies of adsorption are calculated by substituting the values of $\Delta s(1)$ and $\Delta s(M)$, which are re-

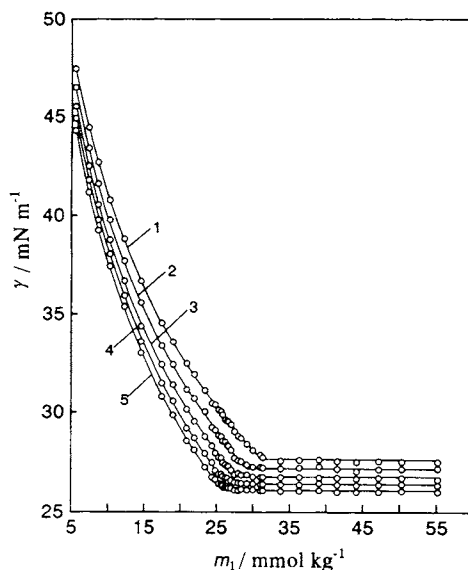


Fig.2 Surface tension vs. molality curves at constant temperature. (1) $T = 288.15$ K, (2) 293.15, (3) 298.15, (4) 303.15, (5) 308.15.

spectively estimated by applying eqs. (6) and (13) to the γ vs. T curves in **Fig.1**, into eqs. (7) and (14) and

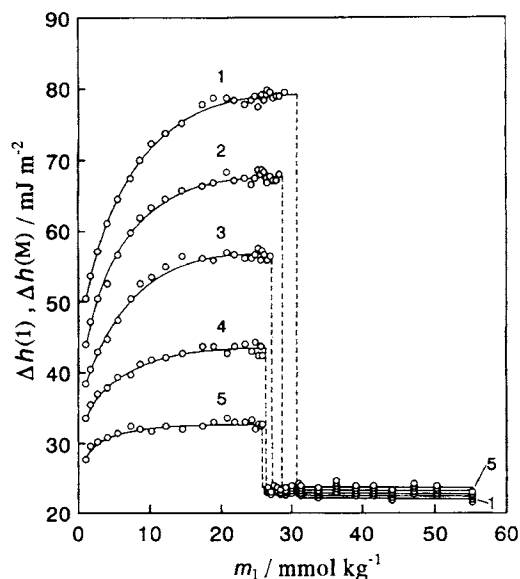


Fig.3 Enthalpy of adsorption per unit surface area vs. molality curves at constant temperature. (1) $T = 288.15$ K, (2) 293.15 , (3) 298.15 , (4) 303.15 , (5) 308.15 .

plotted against molality at constant temperatures in **Fig.3**. At a concentration below the cmc, the value is the enthalpy of adsorption at the air/solution interface from monomeric surfactant $\Delta h(1)$. It is noted that the $\Delta h(1)$ value increases with increasing concentration, namely with increasing surface density of surfactant, and depends strongly on temperature. This means that the adsorption process of OMS is endothermic. Furthermore, taking eq. (7) into account, the corresponding entropy is also increased by increasing adsorption. Since amphiphile molecules are generally forced to orient strongly in the interfacial region, it is usual that the entropy decreases with increasing adsorption. For the present case, therefore, it is probable that the increase in enthalpy and entropy is attributable to the decrease of hydration around the hydrophilic group due to adsorption although the surfactant molecules orient at the interface. This is consistent with the fact that the higher the temperature is, the smaller the increase in enthalpy and entropy is.

At a concentration above the cmc, the value in **Fig. 3** is the enthalpy of adsorption at the air/solution interface from micellar state of surfactant $\Delta h(M)$. Since

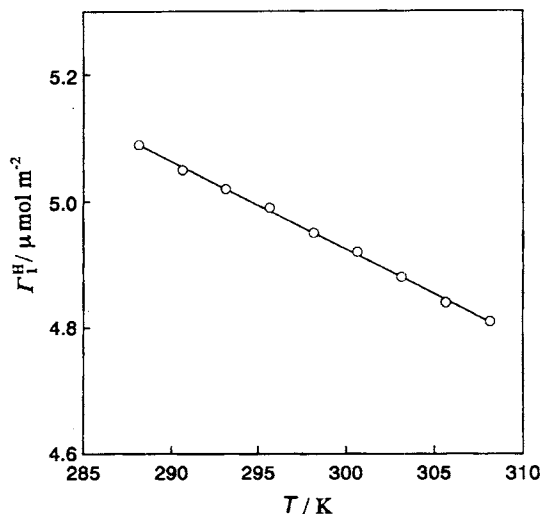


Fig.4 Surface density at the cmc vs. temperature curve.

the $\Delta h(M)$ value is positive, the adsorption from micellar state also accompanies the increase in the enthalpy and entropy. It may be said, therefore, that the hydrophilic group is less hydrated in the adsorbed film than in the micelle. This is probable because the adsorbed film and micelle are respectively plane and spherical in their shape and thus the hydrophilic group is more compactly packed in the former than in the latter. Furthermore it is seen that the $\Delta h(M)$ value does not change so much with temperature. Therefore it is concluded that the temperature dependence of micro circumstances in the adsorbed film is not very different from that in the micelle.

Here let us focus on the quantities at the cmc. It is useful to introduce the enthalpy of adsorption per mole of surfactant from the monomeric state $\Delta_w^H h$ and that from the micellar state $\Delta_M^H h$ instead of the corresponding enthalpies of adsorption per unit surface area. The $\Delta_w^H h$ and $\Delta_M^H h$ are calculated from $\Delta h(1)$ and $\Delta h(M)$ through the equations

$$\Delta_w^H h = \Delta h(1) / \Gamma_1^H \quad \dots\dots\dots (16)$$

and

$$\Delta_M^H h = \Delta h(M) / \Gamma_1^H \quad \dots\dots\dots (17)$$

respectively, where the surface density of surfactant is evaluated by applying the equation

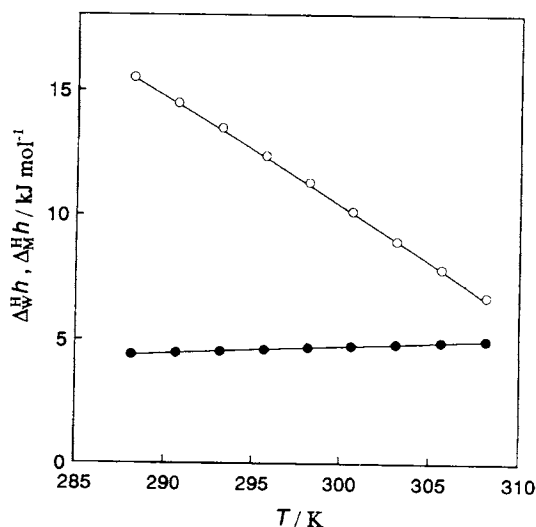


Fig.5 Enthalpy of adsorption per mole of surfactant at the cmc vs. temperature curves. (○) $\Delta_w^H h$, (●) $\Delta_M^H h$.

$$\Gamma_1^H = -(m_1 / RT) (\partial \gamma / \partial m_1)_{T,p} \quad \dots\dots\dots (18)$$

to the γ vs. m_1 curves given in **Fig.2**, and given in **Fig. 4** as a function of temperature at the cmc. The $\Delta_w^H h$ and $\Delta_M^H h$ values at the cmc are plotted against temperature in **Fig.5**. It is seen that the $\Delta_w^H h$ value decreases steeply and the $\Delta_M^H h$ value increases slightly with increasing temperature. It means that the difference in state between the bulk solution and surface becomes rapidly smaller and that between the surface and micelle slowly larger with increasing temperature from the view point of enthalpy.

It is worthwhile to note that the enthalpy of micelle formation defined by

$$\Delta_w^M h = h^M / N_1^M - h_l \quad \dots\dots\dots (19)$$

is calculated by the enthalpies given in **Fig.5** through

$$\Delta_w^M h = \Delta_w^H h - \Delta_M^H h \quad \dots\dots\dots (20)$$

and also by the temperature dependence of cmc given in **Fig.6** through eq. (15). The results obtained by the two independent ways are shown in **Fig.7** and in fair agreement with each other. This means that the micelle formation is reasonably treated as an appearance of a new macroscopic phase and the chemical potential of

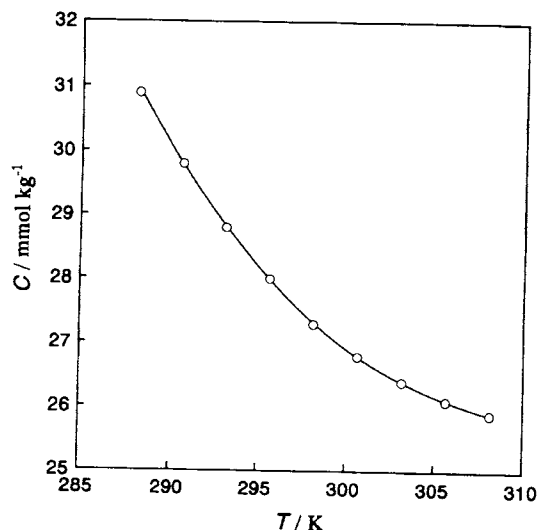


Fig.6 Critical micelle concentration vs. temperature curve.

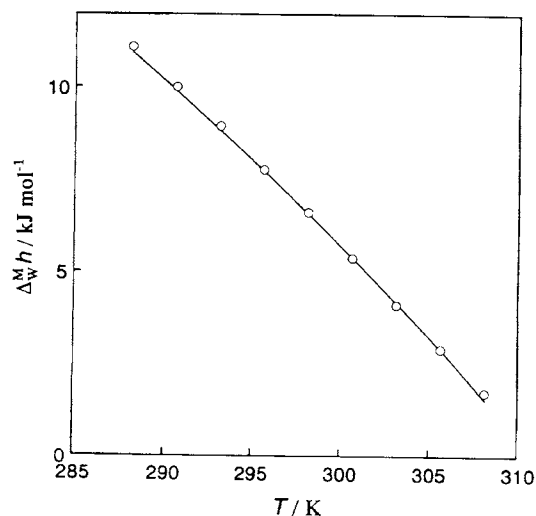


Fig.7 Enthalpy of micelle formation vs. temperature curve. (○) eq. (19), (—) $-(RT^2/C) (\partial C / \partial T)_p$.

micelle is approximately given by eq. (10) in terms of the excess thermodynamic quantities. The results in **Fig.7** show that the micelle formation accompanies the positive enthalpy and entropy changes probably mainly due to the dehydration around the hydrophilic group in the micellization process.

The enthalpy change accompanied by micelle formation has been directly measured by a calorimeter⁸⁾ be-

cause the total number of surfactant molecules participating in the micelle formation is large enough for the total enthalpy change to be detected; the enthalpy of mixing of 10ml of water and pure surfactant at the concentration above the cmc is estimated to be order of J. With respect to the enthalpy change accompanied by adsorption at a fluid/fluid interface, however, there has been no report on the measurement by a calorimeter. This is probably due to the fact that the total number of surfactant molecules participating in the adsorption is so small that the total enthalpy change to be detected is extremely small; taking the results in Fig.3 into account, the total enthalpy change accompanied by adsorption is estimated to be order of μJ for the 1cm^2 interface. Therefore the indirect method given in this paper, that is, the measurement of surface tension as a function of temperature and surfactant concentration and the thermodynamic analysis of them, is highly useful to estimate the enthalpy of adsorption.

For the measurement of extremely small heat flow, some devices have been developed and the identification limit of a calorimeter has been improved in recent years⁹⁾. The value of $\Delta_w^M h$ measured by using isothermal titration calorimeter TAM2277 will be reported and compared with the one obtained by using the thermodynamic method described here in the near future. Also the measurements of enthalpy of adsorption at a fluid/fluid interface is now undertaken by means of the calorimeter.

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要 旨

非イオン性界面活性剤であるオクチルメチルスルホキンド水溶液の表面張力を、濃度一定下で温度の関数として測定した。熱力学を適用することにより、モノマーおよびミセル状態からの界面の吸着のエントロピーとエンタルピー、ミセル形成のエンタルピーが計算された。これらの熱力学量が界面とミセルにおける分子の配向状態、活性剤の親水基の水和、ミセルと吸着膜の幾何学的形状の相違などにより議論された。