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Thermodynamic Study on Penetration of Pentadecanoic Acid Monolayer by Dodecylammonium Chloride

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In order to show that our thermodynamic treatment [*J. Colloid Interface Sci.*, **87**, 333 (1982)] is useful in the study on the monolayer penetration, the surface tension has been measured with the system consisting of pentadecanoic acid monolayer and dodecylammonium chloride solution. Applying the thermodynamic equations to the experimental data, the surface density of dodecylammonium chloride, and entropy and energy of penetration have been estimated numerically. It has been found that the surface density, entropy, and energy all decrease with increasing the concentration of film-forming substance. Therefore, it has been concluded that the penetration of monolayer of this system is caused by the decrease of the energy of penetration which compensates the decrease of the entropy of penetration.

The investigation of monolayer penetration has been made by many workers from the practical and biological points of view.[1-9] Since the penetrated monolayer is a mixed monolayer consisting of film-forming and penetrating molecules, it is also important from the physico-chemical viewpoint to clarify the monolayer penetration. In the previous paper,[10] rigorous thermodynamic equations have been derived for the penetrated monolayer. Application of these equations to experimental data is expected to provide useful information regarding the behavior of film-forming and penetrating molecules in the monolayer state. It seems useful to employ the system consisting of spread monolayer of pentadecanoic acid and adsorbed monolayer of dodecylammonium chloride because they show the phase transitions from an expanded to a condensed state and from a gaseous to an expanded state.

The object of this paper is to measure the surface tension of the pentadecanoic acid monolayer penetrated by dodecylammonium chloride and to evaluate the thermodynamic quantity of penetration with the aid of the thermodynamic equations.

Experimental

Pentadecanoic acid was recrystallized from hexane after fractionation by vacuum distillation, and its purity was checked by gas-liquid chromatography. Dodecylammonium chloride was prepared by the method described previously.[11] Water was distilled from aqueous alkaline permanganate solution after reflux for one day. Hexane used as the spreading solvent was distilled after passing through an activated alumina column.

Surface tension was measured by a Wilhelmy plate technique combined with a Shimadzu recording microbalance. The aqueous solution of dodecylammonium chloride was placed in a glass culture dish of 12 cm diameter, and it was covered doubly so as for the solution not to evaporate and contaminate. On spreading, a micro pipette of 10 μl was used to facilitate the evaporation of hexane. After about half an hour, as the surface tension reached a constant value, the spreading was repeated. This equilibration time varied from 15 min to 2 h as the surface pressure was raised in this experimental range.

Results and Discussion

The surface tension γ of pentadecanoic acid monolayer on the aqueous solution of dodecylammonium chloride was measured as a function of area A per pentadecanoic acid molecule, concentration m_2^{W} of dodecylammonium chloride, and temperatrue T under atmospheric pressure. The variation of the γ *vs.* A curve with m_2^{W} at 293.15 K is shown in Fig. 1. In the absence of dodecylammonium chloride (curve 1), the pentadecanoic acid monolayer is heterogeneous in the range between areas indicated by A and B; gaseous and expanded films coexist in equilibrium.[12] The monolayer becomes the expanded film at the area B and remains homogeneous up to the area C where the monolayer is transformed into the condensed film. Increasing the concentration of dodecylammonium chloride, the homogeneous expanded monolayer region is found to shift to a larger area and broaden significantly. It is also seen that the surface tension decreases greatly with increasing m_2^{W}. Such a behavior can clearly be ascribed to the penetration of penta-

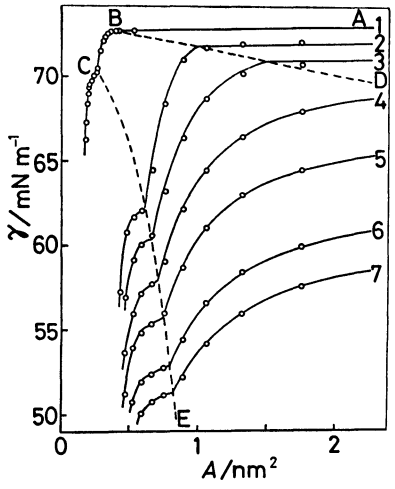

Fig. 1. Surface tension *vs.* area curves of pentadecanoic acid monolayer on dodecylammonium chloride solution at constant concentration at 293.15 K: (1) $m_2^{\mathrm{W}} = 0\ \mathrm{mmol\ kg^{-1}}$; (2) 0.315; (3) 0.714; (4) 1.31; (5) 1.83; (6) 2.62; (7) 3.07.

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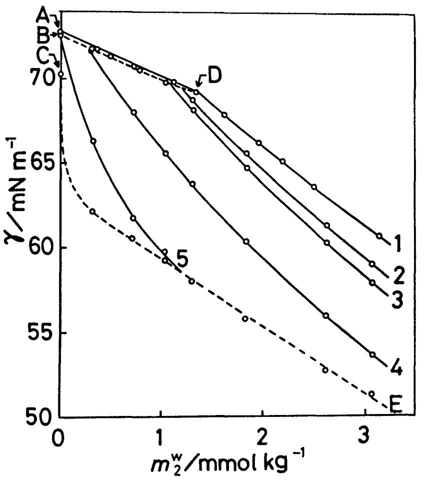

Fig. 2. Surface tension *vs.* molality curves at constant area at 293.15 K: (1) $A=\infty$ nm^2; (2) 3.00; (3) 2.00; (4) 1.00; (5) 0.70.

decanoic acid monolayer by dodecylammonium chloride molecules.

It has been shown previously[13)] that the adsorbed film of dodecylammonium chloride at air/water interface transfers from a gaseous to an expanded phase at 1.38 mmol kg^{-1}. To specify the state of the penetrated monolayer, it may be necessary to recognize how the transition point between two phases on the γ *vs.* m_2^W curve varies with A. The variation of γ *vs.* m_2^W curve with A is shown in Fig. 2, where the curve of the condensed film is excluded because of its uncertainty. The break point, denoted by D, on the curve 1 represents the phase transition of dodecylammonium chloride film from the gaseous to the expanded state. On the other hand, the point B on the ordinate represents the corresponding phase transition of pentadecanoic acid monolayer. Therefore, the broken line BD is the equilibrium γ *vs.* m_2^W curve between gaseous and expanded phases. Moreover, the broken line CE is proved to be the equilibrium γ *vs.* m_2^W curve between expanded and condensed phases. Comparing Fig. 1 with Fig. 2, we notice that the penetrated monolayer behaves as the expanded film in the area DBCE on Fig. 1 and the gaseous film is never realized at concentrations larger than 1.38 mmol kg^{-1}.

Let the penetrated monolayer be an expanded film at the area A. When the concentration m_2^W is larger than 1.38 mmol kg^{-1}, the monolayer is homogeneous in the area range from A to infinity. In this instance we can use Eq. [10] of Ref. 10, referred to as Eq. (Ref. 10, 10), to calculate the surface density Γ_2^H of dodecylammonium chloride:

$$\Gamma_2^H = \Gamma_2^H(0) - [1/A(\partial\mu_2/\partial m_2^W)]\int_A^\infty (\partial\Pi/\partial m_2^W)_{T,p,A}\mathrm{d}A, \qquad (1)$$

where $\Gamma_2^H(0)$ is the value of Γ_2^H at $A=\infty$, μ_2 the chemical potential of dodecylammonium chloride, and Π the surface pressure defined as the difference between the surface tension of a subsolution and that of a monolayer on the subsolution by Eq. (Ref. 10, 8). On the solution of the concentration $m_2^W<1.38$ mmol kg^{-1}, on the other hand, the monolayer is attended by the phase transition from gaseous to expanded film, the value of Γ_2^H being not calculated by Eq. 1. Evidently Eq. (Ref. 10, 40) is applicable to the calculation of Γ_2^H at the area A^e of the expanded film which is in equilibrium with the gaseous film. Integrating Eq. (Ref. 10, 9) from A to A^e and combining the resulting equation with Eq. (Ref. 10, 40), we can obtain the expression

$$\Gamma_2^H = \Gamma_2^H(0) - [1/A(\partial\mu_2/\partial m_2^W)]\left[\int_A^{A^e} (\partial\Pi/\partial m_2^W)_{T,p,A}\mathrm{d}A + \int_{A^e}^{A^g} (\partial\Pi^{eq}/\partial m_2^W)_{T,p}\mathrm{d}A + \int_{A^g}^{\infty} (\partial\Pi/\partial m_2^W)_{T,p,A}\mathrm{d}A\right], \qquad (2)$$

where A^g is the area of the gaseous film in equilibrium with the expanded film and Π^{eq} the equilibrium surface pressure.

Now we can calculate the value of Γ_2^H from the experimental data. Inspecting Fig. 3 which is made from Fig. 2, it is seen that the slope of Π *vs.* m_2^W curve decreases markedly with increasing A. This is clearly shown in Fig. 4 where $\partial\Pi/\partial m_2^W$ is plotted against A. Furthermore, the slope of Π^{eq} *vs.* m_2^W curve (broken line BD in Fig. 3) is found to be negligibly small. In the case of the system under consideration, it might be possible to assume that the values of $\partial\Pi/\partial m_2^W$ at large areas give negligible contributions to the integrals of Eqs. 1 and 2, and these equations are replaced by the approximation

$$\Gamma_2^H = \Gamma_2^H(0) - (m_2^W/2ART)\int_A^{A'} (\partial\Pi/\partial m_2^W)_{T,p,A}\mathrm{d}A, \qquad (3)$$

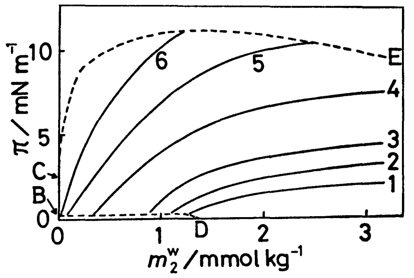

Fig. 3. Surface pressure *vs.* molality curves at constant area at 293.15 K: (1) $A=3.00$ nm^2; (2) 2.00; (3) 1.50; (4) 1.00; (5) 0.80; (6) 0.70.

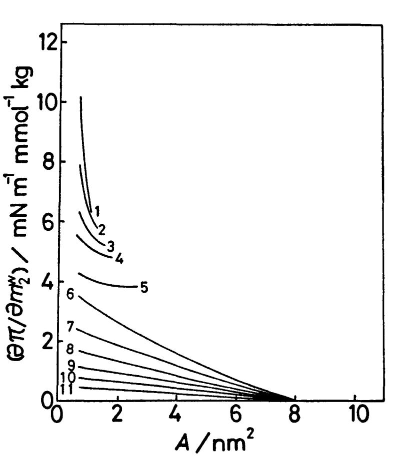

Fig. 4. $(\partial\Pi/\partial m_2^W)$ *vs.* A curves at constant m_2^W at 293.15 K: (1) $m_2^W=0.4$ mmol kg^{-1}; (2) 0.6; (3) 0.8; (4) 1.0; (5) 1.2; (6) 1.4; (7) 1.6; (8) 1.8; (9) 2.0; (10) 2.4; (11) 3.0.

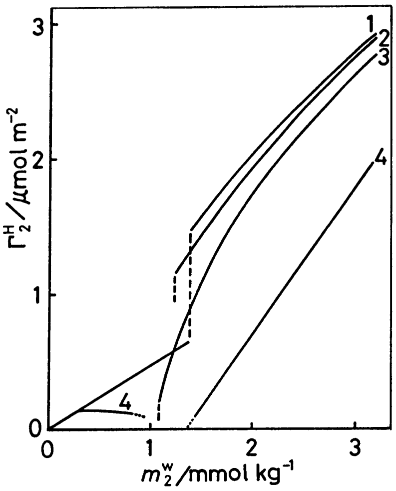

Fig. 5. Surface density of dodecylammonium chloride *vs.* molality curves at constant area at 293.15 K: (1) $A=\infty$ nm^2; (2) 3.00; (3) 2.00; (4) 1.00.

where A' is taken as the area extrapolated to $\partial\Pi/\partial m_2^{\mathrm{w}}=0$ when $m_2^{\mathrm{w}}>1.38$ mmol kg^{-1} and as A^{e} when $m_2^{\mathrm{w}}<1.38$ mmol kg^{-1}. We have also assumed that the dodecylammonium chloride solution behaves ideally. The calculation of Γ_2^{H} was performed on a FACOM OS IV computer. The values calculated at several areas at 293.15 K are plotted against m_2^{w} in Fig. 5. The curve at $A=\infty$ is the $\Gamma_2^{\mathrm{H}}(0)$ *vs.* m_2^{w} curve and accordingly its discontinuous change displays the phase transition between gaseous and expanded phases.13) It is observed from Fig. 5 that the value of Γ_2^{H} decreases with decrease in A. At first glance this looks like a strange result. Adding the surface density of pentadecanoic acid Γ_1^{I} to Γ_2^{H}, however, the sum is undoubtedly larger than the value of $\Gamma_2^{\mathrm{H}}(0)$. Therefore, we may conclude that the present result is reasonable and the adsorption of dodecylammonium chloride is enhanced by the presence of pentadecanoic acid monolayer. Here, attention should be called to the fact that Γ_2^{H} has a negative value at a concentration around 1 mmol kg^{-1}. It might be said that Eq. 3 is a poor approximation of Eq. 2 at this concentration because of a considerable contribution of the term involving $\partial\Pi^{\mathrm{eq}}/\partial m_2^{\mathrm{w}}$ which is positive. In order to shed light on this point, it will be required to measure the surface pressure accurately at large areas.

Let us now proceed to evaluate the entropy of penetration Δs. Since the pure pentadecanoic acid monolayer carries out the phase transition, Eq. (Ref. 10, 45) can be used when the concentration of dodecylammonium chloride is higher than 1.38 mmol kg^{-1}:

$$\Delta s = \Delta s(0) - (1/A)\left[\int_{A}^{A_0^{\mathrm{g}}}(\partial(\Pi-\Pi_0^{\mathrm{eq}})/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A + \int_{A_0^{\mathrm{g}}}^{\infty}(\partial(\Pi-\Pi_0)/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A\right], \tag{4}$$

where A^{g} is the area of the aqueous phase of the pure pentadecanoic acid monolayer in equilibrium with the expanded phase and Π_0 the surface pressure of the pure monolayer. At concentration lower than 1.38 mmol kg^{-1}, we must use the extended equation of Eq. 4:

$$\Delta s = \Delta s(0) - (1/A)\left[\int_{A}^{A^{\mathrm{e}}}(\partial(\Pi-\Pi_0^{\mathrm{eq}})/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A + \int_{A^{\mathrm{e}}}^{A_0^{\mathrm{g}}}(\partial(\Pi^{\mathrm{eq}}-\Pi_0^{\mathrm{eq}})/\partial T)_{p,m_2^{\mathrm{w}}}\mathrm{d}A + \int_{A_0^{\mathrm{g}}}^{A^{\mathrm{g}}}(\partial(\Pi^{\mathrm{eq}}-\Pi_0)/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A + \int_{A^{\mathrm{g}}}^{\infty}(\partial(\Pi-\Pi_0)/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A\right], \tag{5}$$

where we have assumed $A^{\mathrm{e}}<A_0^{\mathrm{g}}<A^{\mathrm{g}}$.

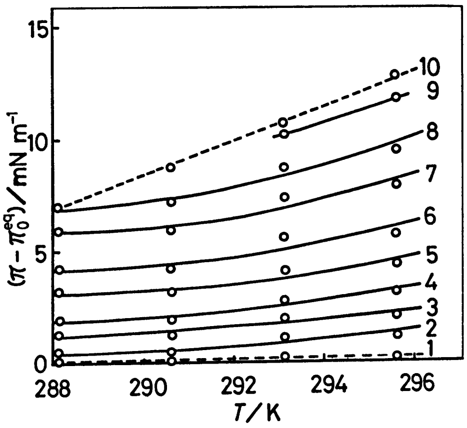

Fig. 6. Surface pressure difference *vs.* temperature curves at constant area at $m_2^{\mathrm{w}}=1.00$ mmol kg^{-1}: (1) $A^{\mathrm{e}}<A<A_0^{\mathrm{g}}$; (2) $A=1.50$ nm^2; (3) 1.30; (4) 1.15; (5) 1.00; (6) 0.90; (7) 0.80; (8) 0.75; (9) 0.70; (10) $A^{\mathrm{c}}<A<A^{\mathrm{e}}$.

Further measurements of the surface tension were made at 288.15, 290.65, and 295.65 K. In Fig. 6, the results at $m_2^{\mathrm{w}}=1.00$ mmol kg^{-1} are depicted in the form of $\Pi-\Pi_0^{\mathrm{eq}}$ *vs.* T plot. It appears that the values of $\Pi-\Pi_0^{\mathrm{eq}}$ show some scatter. This might be attributable partly to a small change of the surface tension with temperature and partly to the difficulty of measuring the equilibrium surface tension. It is found by drawing a smooth curve that the slope of the curve decreases with increase in A. At the areas between A^{e} and A_0^{g}, the value of $\Pi^{\mathrm{eq}}-\Pi_0^{\mathrm{eq}}$ seems to be nearly independent of T. Therefore, Eqs. 4 and 5 may be approximated by the expression

$$\Delta s = \Delta s(0) - (1/A)\int_{A}^{A'}(\partial(\Pi-\Pi_0^{\mathrm{eq}})/\partial T)_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A, \tag{6}$$

which corresponds to Eq. 3 for Γ_2^{H}. By applying Eq. 6 to the experimental data, the value of Δs was computed. The variation of the Δs *vs.* m_2^{w} curve with A at 293.15 K is shown in Fig. 7. The curve at $A=\infty$ represents the $\Delta s(0)$ *vs.* m_2^{w} curve which has the small, although definite, discontinuous change corresponding to the change of the $\Gamma_2^{\mathrm{H}}(0)$ *vs.* m_2^{w} curve. As the area is reduced, the curve is found to shift significantly to a negative value of Δs. It is also seen that the value of Δs decreases remarkably with increasing m_2^{w}. These facts indicate that the entropy of penetrated monolayer is smaller than that of spread

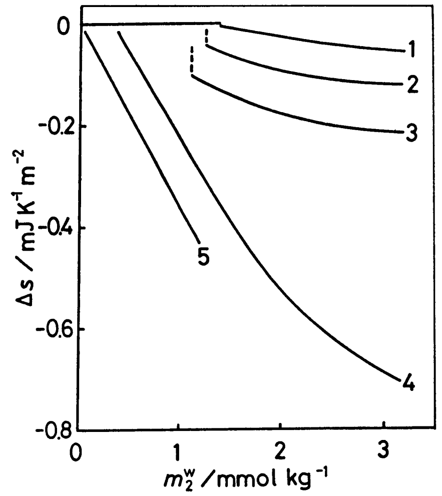

Fig. 7. Entropy of penetration *vs.* molality curves at constant area at 293.15 K: (1) $A=\infty$ nm^2; (2) 3.00; (3) 2.00; (4) 1.00; (5) 0.70.

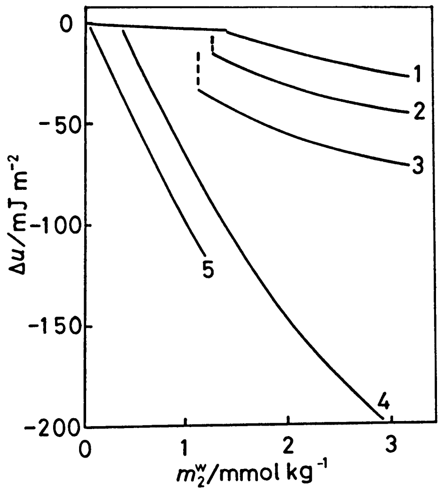

Fig. 8. Energy of penetration *vs.* molality curves at constant area at 293.15 K: (1) $A=\infty$ nm^2; (2) 3.00; (3) 2.00; (4) 1.00; (5) 0.70.

film of pentadecanoic acid and decreases with increase in the total surface density. Therefore it is proved that the penetration is an unfavorable process from the viewpoint of entropy. We may also say that the film-forming and penetrating molecules are forced to take highly restricted conformation in the penetrated monolayer.

Further, we can evaluate the energy of penetration Δu. Evidently an equation similar to Eqs. 3 and 6 is expected to hold. Taking account of Eqs. (Ref. 10, 27) and (Ref. 10, 46), it may be written in the form

$$\Delta u = \Delta u(0) + (1/A)\int_{A}^{A'} (\partial[(\Pi-\Pi_0^{\mathrm{eq}})/T]/\partial(1/T))_{p,A,m_2^{\mathrm{w}}}\mathrm{d}A. \qquad (7)$$

Now we can use Eq. 7 to calculate the value of Δu from the experimental data. The value obtained at 293.15 K is plotted against m_2^{w} at constant A in Fig. 8. Comparing Fig. 8 with Fig. 7, the variation of Δu with m_2^{w} and A is observed to be quite similar to that of Δs. It is clear that the penetration by dodecylammonium chloride diminishes the energy of pentadecanoic acid monolayer. Therefore, we may conclude that the penetration is brought about by the energy decrease which results predominantly from the mutual interaction between pentadecanoic acid and dodecylammonium chloride. This is in harmony with the observation that the mixed monolayer of tetradecanoic acid and octadecylammonium chloride shows a negative azeotropic transformation between expanded and condensed films.[14]

The above thermodynamic analysis of experimental results demonstrates that the equations derived by us[10] are useful to make clear the penetration of monolayers.

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