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Mixed Monolayers of Long Normal Chain Fatty Acids with Long Normal Chain Fatty Alcohols

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The mixed monolayers of long normal chain fatty acids with long normal chain fatty alcohols were studied at various compositions and temperatures. The π-A curves of these systems were measured and the two-dimensional phase diagrams were obtained. The partial molar enthalpy change from the expanded to the condensed state was calculated. It was observed that the phase diagram and enthalpy change of these systems are similar to those previously obtained from the mixed monolayers of long normal chain fatty acids. The miscibility of these systems changes with the increase in the difference of the chain length, as in the systems of fatty acids. It was concluded that the monolayer behavior of the mixed system of an acid and an alcohol is analogous to that of the mixed system of the acid and an acid which contains one more carbon atom in a molecule than the corresponding alcohol.

Many workers have extensively studied the monolayers of long normal chain fatty acids.[1–3] Previously we reported some mixed monolayers of these acids and analyzed the phase behavior of the mixed films.[4,5] The thermodynamic treatment of multicomponent surface films was employed.[6,7] It was found that the miscibility of these films varies with the difference of the chain length. But investigations of mixed films of acids with alcohols have been reported much less frequently. The aim of this paper is to clarify the thermodynamic behavior of the mixed film of a fatty acid and an alcohol by taking advantage of the results for mixed films of fatty acids.

Experimental

Tetradecanoic (C_{14}), pentadecanoic (C_{15}), and octadecanoic (C_{18}) acids were employed in this experiment. 1-Tetradecanol ($C_{14}OH$) and 1-hexadecanol ($C_{16}OH$) were used as the long normal chain fatty alcohols. They were purified by fractional distillation and recrystallizations. Benzene, a spreading solvent, was purified carefully by the usual method. The substrate, 0.001 M HCl, was prepared by using twice distilled water and hydrochloric acid (Wako super special grade).

The surface pressure of the monolayers was measured by a Wilhelmy-type surface balance. The temperature was kept constant within ±0.2 °C during the experiment.

Results and Discussion

Typical surface pressure-area curves obtained for the C_{14}–$C_{14}OH$ and C_{14}–$C_{16}OH$ systems at 25 °C are shown in Figs. 1 and 2, respectively. These isotherms are similar to those previously reported for the C_{14}–C_{15} and C_{14}–C_{17} (acid–acid) systems.[4,7] The characteristics of each system may be expressed briefly as follows:

C_{14}–$C_{14}OH$ system (Fig. 1) : the π-A curves of pure tetradecanoic acid and 1-tetradecanol are of the expanded type at 25 °C. When they are mixed, the transition pressure decreases from the value of C_{14} to that of $C_{14}OH$ with increase in the content of the latter. Recently, Roberts, Österlund, and Axberg[8] have claimed that a mixture of 6.12×10^{15} molecules tetradecanoic acid and 1.53×10^{15} molecules 1-hexadecanol spread from petroleum ether together has no transition from the liquid expanded state to the liquid condensed state at 20 °C and pH 2. But in our experimental data at 20 °C and pH 3, the mixed monolayer of the system in which the mole fraction of C_{14} is 0.8 clearly shows a transition at the surface pressure 2.9 dyne/cm.

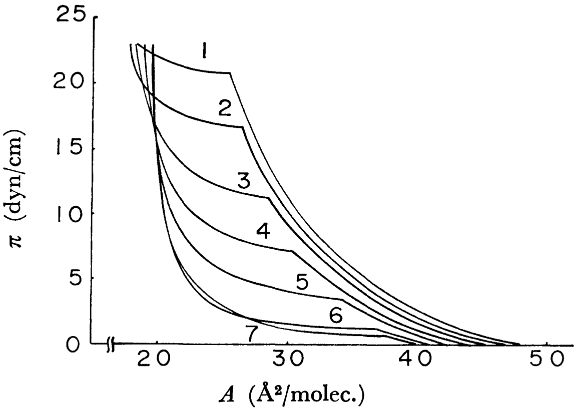

Fig. 1. Surface pressure *vs.* mean area curves of the tetradecanoic acid–1-tetradecanol monolayers at 25 °C: 1, $X_2^\pi=1$(tetradecanoic acid); 2, 0.9; 3, 0.7; 4, 0.5; 5, 0.3; 6, 0.1; 7, 0(1-tetradecanol).

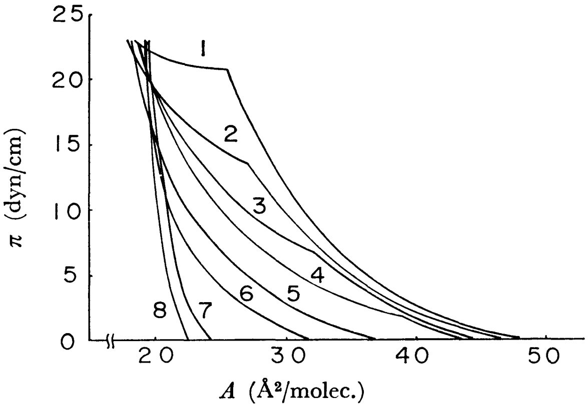

Fig. 2. Surface pressure *vs.* mean area curves of the tetradecanoic acid–1-hexadecanol mixed monolayers at 25 °C: 1, $X_2^\pi=1$(tetradecanoic acid); 2, 0.9; 3, 0.8; 4, 0.7; 5, 0.6, 6, 0.5; 7, 0.3; 8, 0(1-hexadecanol).

C_{14}–$C_{16}OH$ system (Fig. 2) : the pure $C_{16}OH$ forms a stable condensed film. The mixtures of the acid and alcohol with molar ratios from 9:1 to 7:3 give expanded monolayers which have transition pressures. On the other hand, in mixtures less than 3 : 2 in the molar ratio, the monolayers are considerably condensed and the transition pressure disappears.

When a binary condensed monolayer is in equilibrium with a binary expanded monolayer, the variation of the equilibrium surface pressure π^{eq} with mole fraction of component 2 in the expanded monolayer $X_2^{\pi,e}$ is related to thermodynamic quantities of the monolayers.[6] According to Eq. 38 in the preceding paper,[6]

$$X_2^{\pi,c} = X_2^{\pi,e} + [(A^c - A^e)X_1^{\pi,e}X_2^{\pi,e}/kT] \times (\partial\pi^{eq}/X_2^{\pi,e})_{T,p}, \qquad (1)$$

where the mean area per molecule A has been used with superscripts c and e indicating condensed and expanded films, respectively. We can calculate the numerical values of $X_2^{\pi,c}$, the mole fraction of component 2 in the condensed film, from the dependence of π^{eq} on $X_2^{\pi,e}$. The results evaluated for the C_{14}–$C_{14}OH$ and C_{14}–$C_{16}OH$ systems at 25 °C are shown in Figs. 3 and 4.

The C_{14}–$C_{14}OH$ system (Fig. 3) gives a typical pattern of a simple mixed system in which the two components are miscible in all compositions. This behavior is identical with that of the C_{14}–C_{15} system previously obtained at 20 °C.[7] In the C_{14}–$C_{16}OH$ system, as shown in Fig. 4, the situation of miscibility is somewhat different from the C_{14}–$C_{14}OH$ system. The expanded phase disappeared in the monolayers in which the mole fractions of tetradecanoic acid are below 0.65. A similar phase diagram has been observed for the C_{14}–C_{17}[7] and C_{14}–$C_{14}OH$ systems at 20 °C. We consider that, in this region, the mixed film changes from the expanded to the condensed state in the process of compression at low surface pressures. This shows that the miscibility of the two components at the same temperature gradually decreases with increase in the difference of carbon number between the two film components. When the surface pressure reaches 20.8 dyne/cm, the transition pressure of the pure tetradecanoic acid monolayer at 25 °C, the mixed film perfectly changes into the condensed film.

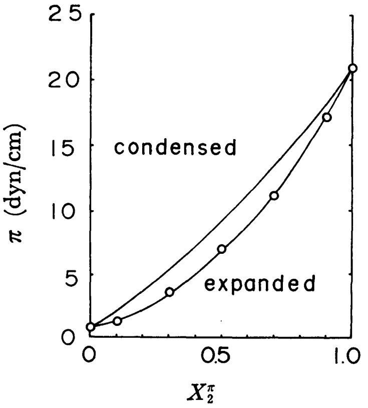

Fig. 3. Phase diagram of the tetradecanoic acid-1-tetradecanol mixed monolayer at 25 °C.

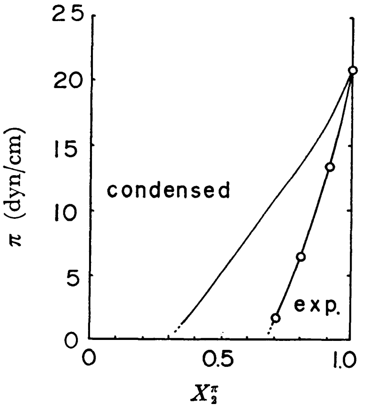

Fig. 4. Phase diagram of the tetradecanoic acid-1-hexadecanol mixed monolayer at 25 °C.

Phase diagrams of the C_{15}–$C_{14}OH$ and C_{15}–$C_{16}OH$ systems are also shown in Figs. 5 and 6. The appearance of these phase diagrams corresponds to that of the C_{14}–$C_{14}OH$ and C_{14}–$C_{16}OH$ systems, respectively. In the C_{15}–$C_{14}OH$ system, as shown in Fig. 5, the transition range is somewhat smaller in composition than that in the C_{14}–$C_{14}OH$ system. This indicates that the miscibility of the C_{15}–$C_{14}OH$ system is likely to be more ideal than that of the latter.[7] This is also applicable to the C_{15}–$C_{16}OH$ system (Fig. 6) as compared with the C_{14}–$C_{16}OH$ system. According to these results, we would conclude that the monolayer of a long normal chain fatty alcohol is analogous to that of a fatty acid which has one more carbon atom than the corresponding alcohol molecule.

The π^{eq}-$X_2^{\pi,e}$ curves obtained for the $C_{14}OH$–$C_{16}OH$ and C_{18}–$C_{14}OH$ systems at 30 °C are shown in Figs. 7 and 8. The two-dimensional phase diagram for the $C_{14}OH$–$C_{16}OH$ system (Fig. 7) seems to be the same type as that of the C_{14}–$C_{16}OH$ and C_{15}–$C_{16}OH$ systems.

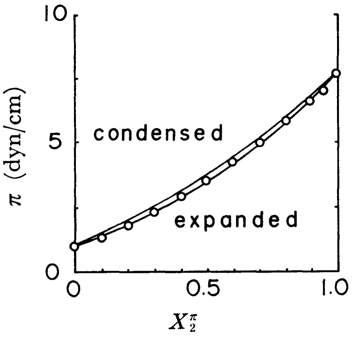

Fig. 5. Phase diagram of the pentadecanoic acid-1-tetradecanol mixed monolayer at 25 °C.

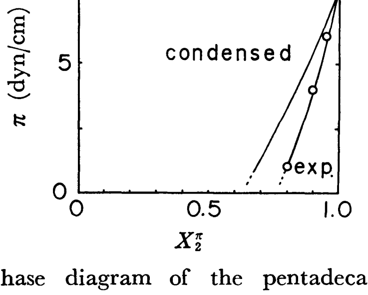

Fig. 6. Phase diagram of the pentadecanoic acid-1-hexadecanol mixed monolayer at 25 °C.

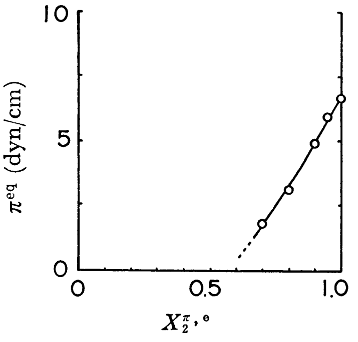

Fig. 7. π^{eq}-$X_2^{\pi,e}$ curve of the 1-tetradecanol-1-hexadecanol mixed monolayer at 30 °C.

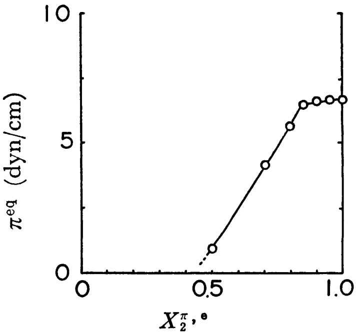

Fig. 8. π^{eq}-$X_2^{\pi,e}$ curve of the octadecanoic acid-1-tetradecanol mixed monolayer at 30 °C.

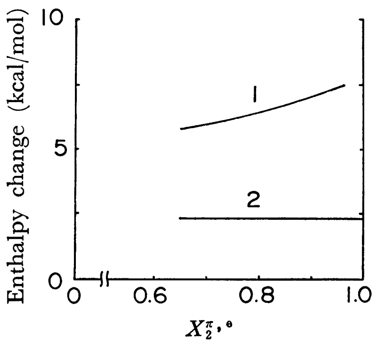

Fig. 9. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $X_2^{\pi,e}$, curves of the tetradecanoic acid-1-tetradecanol at 20 °C: 1, 1-tetradecanol; 2, tetradecanoic acid.

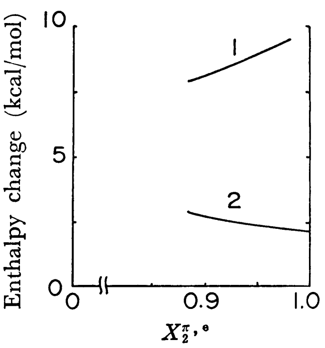

Fig. 10. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $X_2^{\pi,e}$, curves of the tetradecanoic acid-1-hexadecanol at 20 °C: 1, 1-hexadecanol; 2, tetradecanoic acid.

In the C_{18}–$C_{14}OH$ system (Fig. 8), the π^{eq}-$X_2^{\pi,e}$ curve is complicated because of the presence of the break point. However, by the analysis of the fatty acid's phase diagram,[7)] it was found that this system is similar to the C_{14}–C_{19} system.

From the variation of the transition pressure with temperature, we can calculate the thermodynamic quantities such as the partial molar entropy and enthalpy of the transfer from expanded to condensed phase. We have reported the following expression (Eq. 42 in Ref. 6):

$$\bar{s}_i^c - \bar{s}_i^e = (\bar{s}_i^{\pi,c} - \bar{s}_i^{\pi,e}) + (a^e - \bar{a}_i^e)(\partial\pi^e/\partial T)_{p,x_w^e,x_2^{\pi,e}} - (\bar{a}_i^c - \bar{a}_i^e)(\partial\gamma^0/\partial T)_p,\ i = 1,\ 2 \tag{2}$$

where $\bar{a}_i$ is the partial molar area of component i in the monolayer $\partial\pi^e/\partial T$ is the variation of surface pressure with respect to temperature at a given state of the expanded monolayer, γ^0 is the surface tension of water, and the subscript w represents water. In the above equation, $\bar{s}_i^\pi$ is the partial molar entropy of component i in the equilibrium monolayer, and $\bar{s}_i^c - \bar{s}_i^e$ is the thermodynamically well-defined partial molar change in entropy at the phase transition from the expanded to the condensed state.[5,6)] The corresponding enthalpy change can be evaluated by the following expression, which has been obtained as Eq. 43 in Ref. 6:

$$\bar{h}_i^c - \bar{h}_i^e = T(\bar{s}_i^c - \bar{s}_i^e). \tag{3}$$

We have assumed that $\bar{A}_1^e = \bar{A}_2^e = 20$ Å^2/molec. and $\bar{A}_1^c = \bar{A}_2^c = 18$ Å^2/molec.; then we can calculate the values of $\bar{s}_i^c - \bar{s}_i^e$ from Eq. 2. $\bar{h}_i^c - \bar{h}_i^e$ can also be evaluated from Eq. 3.

The calculated values for the C_{14}–$C_{14}OH$ and C_{14}–$C_{16}OH$ systems at 20 °C are shown in Figs. 9 and 10. In the former system (Fig. 9), the enthalpy change of the tetradecanoic acid has a nearly constant value independent of $X_2^{\pi,e}$ in the range of the composition shown. The partial molar enthalpy change of the tetradecanoic acid, 2.2 kcal/mol, is fully acceptable in comparison with that of a mixed film of long normal chain fatty acids.[7)] On the other hand, the partial molar enthalpy change of the 1-tetradecanol decreases slightly with decreasing $X_2^{\pi,e}$. The enthalpy change of 1-tetradecanol is larger than that of tetradecanoic acid at the same composition. This indicates that this alcohol is less stable in the expanded state and needs much more heat for the transition from the liquid condensed to the expanded state. This agrees with the experimental result that the transition pressure is elevated by the addition of tetradecanoic acid. In the case of the C_{14}–$C_{16}OH$ system (Fig. 10), the change of partial molar enthalpy of the tetradecanoic acid decreases, while that of the 1-hexadecanol increases, with increasing $X_2^{\pi,e}$, in the range of the composition shown in the figure. The pattern of these two curves is identical with that of the C_{14}–C_{17} system,[7)] but the slope of these curves is smaller than that of the latter. This is related to the miscibility of the two components. Taking advantage of the results for C_{14}–C_{15}, C_{14}–C_{17}, and C_{14}–C_{19} systems,[7)] it seems that the more ideal the miscibility, the smaller the inclination is.

In conclusion, mixed monolayers of long normal chain fatty acids with long normal chain fatty alcohols have the same behavior as that of mixed monolayers of fatty acids. That is to say, the acids and alcohols are miscible with each other in the expanded as well as in the condensed state. And the miscibility of two components gradually decreases with an increase in the difference of carbon number between the two components. Finally, we conclude that the monolayer of the alcohol is analogous to that of a fatty acid which contains one more carbon atom in the molecule than the corresponding alcohol.

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