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Negative Azeotropic Transformation in Mixed Monolayers of Octadecylammonium Chloride and Tetradecanoic Acid

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The surface pressure of mixed monolayers of octadecylammonium chloride and tetradecanoic acid has been measured as a function of mean area per film molecule at various compositions and temperatures. It has been observed that the transition pressure from expanded to condensed state of either constituent decreases with the addition of the other one. This behavior has been called a negative azeotropy in the two-dimensional state in contrast to the positive azeotropy observed for the ethyl heptadecanoate–tetradecanoic acid system. By applying the thermodynamic treatment, the phase diagram has been constructed and the apparent molar entropy and energy associated with the phase transition have been calculated. The results support the view that the negative azeotropic transformation in the mixed monolayer is brought about by the mutual interaction between octadecylammonium chloride and tetradecanoic acid molecules which is stronger than that between the same kind of molecules.

It has been found useful in clarifying the interaction between film-forming molecules in the monolayer state to analyze the phase transition of mixed monolayers from expanded to condensed states thermodynamically.[1–8] Recently we have shown that a positive azeotropic transformation is observed for the mixed monolayer of slightly different molecules between which the mutual interaction is weaker than that between the same kind of molecules.[6,7] It is now expected for a mixed monolayer of which the constituent molecules interact strongly with each other to exhibit a negative azeotropic transformation. Actually it has been found by Harkins *et al.*[9,10] that the equimolar mixed monolayer of fatty acid and alkylamine has the minimum area per film molecule at a given surface pressure, which can be explained in terms of the decrease of transition pressure by mixing the monolayers.

The object of this paper is to make clear the thermodynamic behavior of the mixed monolayer of tetradecanoic acid and octadecylammonium chloride by measuring the surface pressure as a function of composi tion and temperature.

Experimental

Tetradecanoic acid was purified by vacuum distillation and recrystallization from ether. Octadecylammonium chloride was synthesized from octadecylamine, which was fractionated by vacuum distillation, by the reaction with hydrochloric acid and then recrystallized from ethanol. As a spreading solvent, a mixture of benzene and ethanol (9 to 1 in volume) each purified by ordinary procedures was used. Monolayers were spread on 0.1 M sodium chloride solution which was prepared from twice distilled water and sodium chloride (Wako special grade).

Surface pressure was measured by a Wilhelmy-type surface balance. Temperature was kept constant within 0.1K by circulating thermostated water.

Results and Discussion

The surface pressure, π, of mixed monolayers consisting of octadecylammonium chloride and tetradecanoic acid was measured as a function of the mean area per film molecule, A, at various compositions at a constant temperature. The results at 298.2 K are illustrated in Fig. 1. It is observed that the break point pressure of π *vs.* A curve of either constituent decreases with the addition of the other one and becomes gradually obscure. In Fig. 2, the surface pressure of the break point, referred to as the transition pressure π^{eq}, is plotted against the mole fraction of tetradecanoic acid defined by

$$x_2^{\pi} = n_2/(n_1+n_2), \tag{1}$$

where n_i is the number of moles of film-forming component i. It is clearly seen that the value of π^{eq} of mixed monolayer deviates negatively from a straight line connecting that of the pure monolayers and have a minimum in the vicinity of $x_2^{\pi}=0.5$. This fact indicates that the mixed monolayer is homogeneous in both expanded and condensed states. Such a behavior may be called a negative azeotropic transformation in contrast with the positive azeotropic transformation

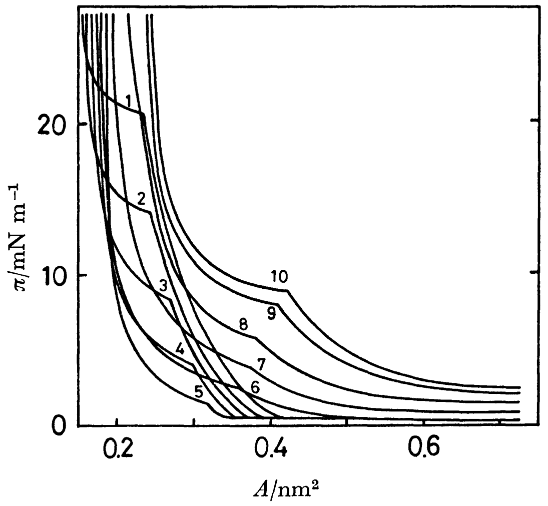

Fig. 1. Surface pressure π *vs.* mean area A curves of octadecylammonium chloride–tetradecanoic acid monolayers at 298.2 K.
(1) $x_2^{\pi}=1$, (2) 0.95, (3) 0.90, (4) 0.85, (5) 0.75, (6) 0.25, (7) 0.20, (8) 0.15, (9) 0.05, (10) 0.

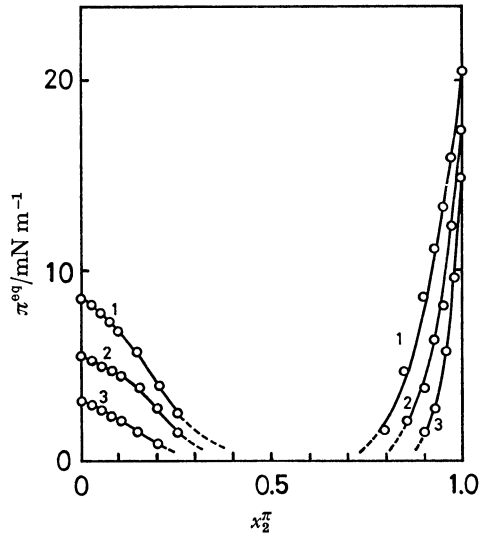

Fig. 2. Transition pressure π^{eq} *vs.* mole fraction of tetradecanoic acid x_2^π curves at constant temperature. (1) 298.2 K, (2) 295.7 K, (3) 293.2 K.

observed for the system of ethyl heptadecanoate and tetradecanoic acid of which the π^{eq} *vs.* x_2^π curve has a maximum.[6] There is a possibility that octadecylammonium chloride and tetradecanoic acid form the one-to-one addition compound in the condensed state. However, this possibility is denied by the fact that each π *vs.* A curves in Fig. 1 does not have more than one break point and the π^{eq} *vs.* x_2^π curves in Fig. 2 behave smoothly.

Measurements were made likewise at 295.7 and 293.2 K. The π^{eq} *vs.* x_2^π curves at these temperatures are shown in Fig. 2. It is found that these curves are similar in shape to each other and shift downward with decreasing temperature. Since the phase transition takes place from the expanded monolayer, of which the concentration is x_2^π, to the condensed monolayer, these curves are referred to as the π^{eq} *vs.* $x_2^{\pi\cdot e}$ curves. Now let us consider to evaluate the composition of condensed monolayer in equilibrium with the expanded monolayer thermodynamically.

According to the thermodynamic treatment,[1,11] the mole fraction of tetradecanoic acid in the condensed monolayer $x_2^{\pi\cdot c}$ is related to $x_2^{\pi\cdot e}$ by the expression

$$x_2{}^{\pi,c} = x_2{}^{\pi,e} + (a^c - a^e)(\partial\pi^{eq}/\partial x_2^{\pi\cdot e})_{T,p}/\{RT/x_1^{\pi\cdot e}x_2^{\pi\cdot e}$$
$$+ (\partial a^e/\partial x_2^{\pi\cdot e})_{T,p,\pi}(\partial\pi^{eq}/\partial x_2^{\pi\cdot e})_{T,p}\int_0^\pi[\partial^2 a^e/(\partial x_2^{\pi\cdot e})^2]_{T,p,\pi}d\pi\}, \tag{2}$$

where a is the mean area per mole of film-forming components and the superscripts e and c represent expanded and condensed states, respectively. By applying Eq. 2 to the experimental results given in Figs. 1 and 2 on the assumption that the value of a^c may be replaced by the corresponding one of octadecanoic acid, the value of $x_2^{\pi\cdot c}$ can be calculated numerically. The π^{eq} *vs.* $x_2^{\pi\cdot c}$ curve obtained at 295.7 K is drawn in Fig. 3 as the curve 1, in which the corresponding π^{eq} *vs.* $x_2^{\pi\cdot e}$ curve taken from Fig. 2 is also depicted as the curve 2. It is found that the areas denoted by the letters e and c are regions in which the expanded and condensed monolayers are stable, respectively, and the area between the curves 1 and 2 is a region in which the expanded and condensed monolayers coexist. Therefore, we may say that Fig. 3 is the phase diagram describing the equilibrium between expanded and condensed monolayers of octadecylammonium chloride–tetradecanoic acid system at 295.7 K.

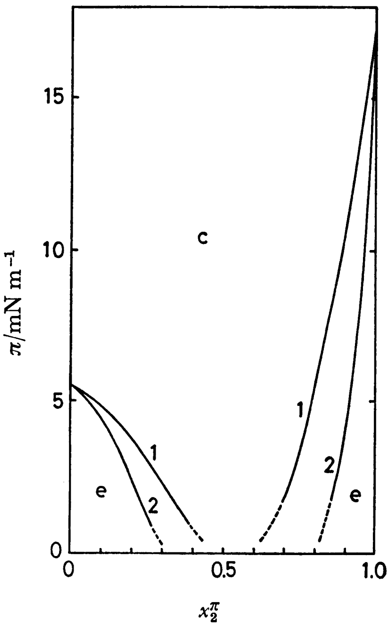

Fig. 3. Phase diagram of octadecylammonium chloride–tetradecanoic acid system at 295.7 K.
(1) π^{eq} *vs.* $x_2^{\pi\cdot c}$ curve, (2) π^{eq}*vs.* $x_2^{\pi\cdot e}$ curve, (c) region of condensed phase, (e) region of expanded phase.

Now we shall consider an apparent molar thermodynamic quantity change Δy^γ associated with the phase transition from expanded to condensed monolayer:

$$\Delta y^\gamma = x_1^{\pi\cdot e}(\bar{y}_1^{\gamma\cdot e} - \bar{y}_1^{\gamma\cdot e}) + x_2{}^{\pi,c}(\bar{y}_2^{\gamma,c} - \bar{y}_2^{\gamma\cdot e}). \tag{3}$$

On the right-hand side of Eq. 3, $\bar{y}_i^\gamma$ is the apparent partial molar quantity defined by

$$\bar{y}_i{}^\gamma = (\partial Y/\partial n_i)_{T,p,\gamma,n_j}\quad i = 1, 2\ (j \neq i), \tag{4}$$

where Y is the thermodynamic quantity inherent in the monolayer and γ the surface tension.[6,12]

The apparent entropy change Δs^γ is related to the derivative of π^{eq} with respect to T at constant $x_2^{\pi\cdot e}$ under atmospheric pressure by

$$\Delta s^\gamma = [a^c - a^e - (x_2^{\pi\cdot e} - x_2^{\pi\cdot e})(\partial a^e/\partial x_2^{\pi\cdot e})_{T,p,\pi}]$$
$$\times [(\partial\pi^{eq}/\partial T)_{p,x_2^{\pi\cdot e}} - (\partial\gamma^\circ/\partial T)_p], \tag{5}$$

where γ° is the surface tension of 0.1 M sodium chloride solution.[6,12] Since $\partial\pi^{eq}/\partial T$ is estimated on the basis of the experimental results shown in Fig. 2 and $\partial\gamma^\circ/\partial T$ on the basis of the value of γ° approximated by that of pure water,[13] we can calculate Δs^γ. In Fig. 4, the value of Δs^γ at 295.7 K is plotted against the mole fraction of tetradecanoic acid in the condensed monolayer. The Δs^γ *vs.* $x_2^{\pi\cdot c}$ curve seems to be approximately linear over the whole range. Taking Eq. 3 into account, therefore, the apparent partial molar entropy

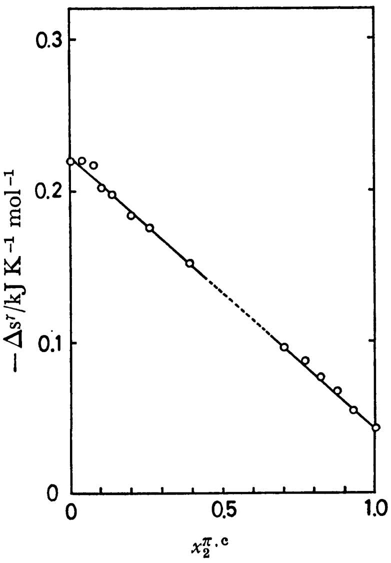

Fig. 4. Apparent molar entropy change Δs^γ *vs.* mole fraction of tetradecanoic acid in condensed monolayer $x_2^{\pi,\mathrm{c}}$ curve for octadecylammonium chloride–tetradecanoic acid system at 295.7 K.

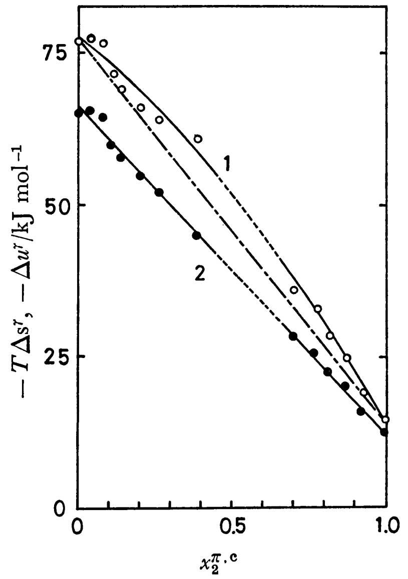

Fig. 5. Δu^γ *vs.* $x_2^{\pi,\mathrm{c}}$ curve (1) and $T\Delta s^\gamma$ *vs.* $x_2^{\pi,\mathrm{c}}$ curve (2) at 295.7 K for octadecylammonium chloride–tetradecanoic acid system.

changes of octadecylammonium chloride and tetradecanoic acid are given by intercepts of the straight line on the ordinates. This dependence of Δs^γ on $x_2^{\pi,\mathrm{c}}$ is quite similar to that of the system of pentadecanoic and tetradecanoic acids which is known to form an ideal mixed monolayer.[2] Furthermore, an analogous Δs^γ *vs.* $x_2^{\pi,\mathrm{c}}$ curve is observed for the mixed monolayer of ethyl heptadecanoate and tetradecanoic acid which exhibits the positive azeotropic transformation.[6] This fact indicates that the apparent molar entropy change associated with the phase transition has an ideal value even when the mixed monolayer behaves nonideally. This means that the apparent molar entropy change is of limited significance in the azeotropic transformation. Therefore, the azeotropic behavior of octadecylammonium chloride–tetradecanoic acid system should be explained in terms of other thermodynamic quantity changes.

Next let us consider the apparent molar internal energy change associated with the phase transition Δu^γ which is given by the relation

$$\begin{aligned}\Delta u^\gamma = & -(\pi^{\mathrm{eq}}-\gamma^\circ)[a^\mathrm{c}-a^\mathrm{e}-(x_2^{\pi,\mathrm{e}}-x_2^{\pi,\mathrm{e}})(\partial a^\mathrm{e}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}] \\ & -p\Delta v^\gamma - T\Delta s^\gamma, \end{aligned} \tag{6}$$

where Δv^γ is the apparent molar volume change.[6] Taking into account that the $p\Delta v^\gamma$ term on the right-hand side of Eq. 6 is negligibly small compared with other terms under atmospheric pressure,[6,14] the value of Δu^γ can be evaluated by making use of the above experimental results. In Fig. 5, the Δu^γ *vs.* $x_2^{\pi,\mathrm{c}}$ curve is drawn. The curve is found to show a remarkable deviation from the straight line connecting the value of Δu^γ for the pure components as compared with the $T\Delta s^\gamma$ *vs.* $x_2^{\pi,\mathrm{c}}$ curve also depicted in Fig. 5. Here we notice that the value of Δu^γ is smaller than an ideal one for the system of octadecylammonium chloride and tetradecanoic acid, while it was larger for the system of ethyl heptadecanoate and tetradecanoic acid.[6]

In order to examine the connection of the azeotropic transformation with the interaction between film-forming molecules, it is appropriate to look closely at partial molar energies of the film-forming components. Taking account of Eq. 3, the apparent partial molar energy of component i is given by the intercept of tangent to the Δu^γ *vs.* $x_2^{\pi,\mathrm{c}}$ curve on the ordinate specified by $x_1^{\pi,\mathrm{c}}=1$. As seen in the previous paper,[6] the positive azeotropy of ethyl heptadecanoate–tetradecanoic acid system is characterized by the decrease of $\bar{u}_1^{\gamma,\mathrm{c}}-\bar{u}_1^{\gamma,\mathrm{e}}$ with increase in $x_1^{\pi,\mathrm{c}}$. For the octadecylammonium chloride–tetradecanoic acid system, however, we can see from Fig. 5 that the value of $\bar{u}_1^{\gamma,\mathrm{c}}-\bar{u}_1^{\gamma,\mathrm{e}}$ increases with increasing $x_1^{\pi,\mathrm{c}}$. This fact indicates that the mutual interaction between octadecylammonium chloride and tetradecanoic acid molecules in the mixed monolayer is stronger than the interactions between the same kind of constituent molecules. This finding is very reasonable.

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