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Mixed Monolayers of Long Normal-chain Fatty Acids with Long Normal Alkyl Esters. III. Pentadecanoic Acid–Esters System

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The surface pressures of mixed monolayers of pentadecyl acetate, hexadecyl acetate, heptadecyl acetate, and hexadecyl propionate with pentadecanoic acid were measured at various compositions and temperatures. The two-dimensional phase diagram and apparent molar entropy and energy changes were evaluated by means of a previously described thermodynamic treatment. They depend uniquely on the molecular structure of the film-forming substances and on the composition in the mixed monolayer. The phase diagrams of pentadecanoic acid–pentadecyl acetate and pentadecanoic acid–hexadecyl acetate systems are of a complicated type. There are positive and negative regions in the excess apparent molar energy changes. The pentadecanoic acid–heptadecyl acetate and pentadecanoic acid–hexadecyl propionate systems are of the positive azeotropic type. The excess apparent molar energy changes are positive over the whole range of mole fractions.

Previously we have reported unique behavior in the mixed monolayer of the pentadecanoic acid(C_{15})–hexadecyl acetate(HA) system.[1] It has maximum and minimum points in the phase diagram. To investigate this phenomenon in more detail, it is necessary to use esters which have a different chain length of the hydrophobic part from that of HA, such as pentadecyl acetate(PA), heptadecyl acetate(HpA), and hexadecyl propionate(HPr), which has the same chain length as HA, but with a different hydrophilic group. In the present study we have attempted to do experiments with these esters.

Experimental

Pentadecanoic acid(C_{15}) was purified by fractional distillation and recrystallization. Pentadecyl acetate(PA), hexadecyl acetate(HA), heptadecyl acetate(HpA), and hexadecyl propionate(HPr) were synthesized by the usual method[2] and were purified by reduced pressure distillations.

The surface pressure was measured by means of a Wilhelmy-type surface balance. The monolayer was compressed continuously with a constant velocity. The surface pressure-mean area (π-A) curves were reproducible within ± 0.2 mN m^{-1} in the same mean molecular area. Purified benzene was used as the spreading solvent. To prevent the ester from hydrolysis, a 0.1 mol dm^{-3} NaCl solution was used as the substrate; this was prepared from twice-distilled water and sodium chloride (Wako super special grade). The temperature was kept constant within ± 0.1 K during the experiment.

Results and Discussion

Representative π-A curves of the C_{15}–PA, C_{15}–HA,[1] C_{15}–HpA, and C_{15}–HPr systems at 298.2 K are shown in Figs. 1 to 4. These esters and fatty acid spread on the air–water interface formed an expanded monolayer at the experimental temperature. The transition from the liquid expanded to the liquid condensed state was observed for all systems over the whole range of composition. The transition pressure, π^{eq}, corresponds to the surface pressure at the break point of the π-A curve. The variations in π^{eq} with the mole fraction of esters, $x_2^{\pi,e}$, are very different from each other, as is shown in Fig. 5. These curves depend significantly on the chain length and the structure of the hydrophilic group of esters. The

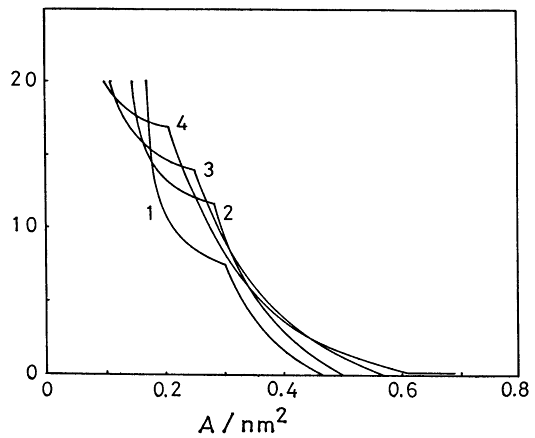

Fig. 1. Surface pressure *vs.* mean area curves of the pentadecanoic acid–pentadecyl acetate mixed monolayer at 298.2 K.
1: $x_2^{\pi}=0$ (pentadecanoic acid), 2: 0.3, 3: 0.7, 4: 1 (pentadecyl acetate).

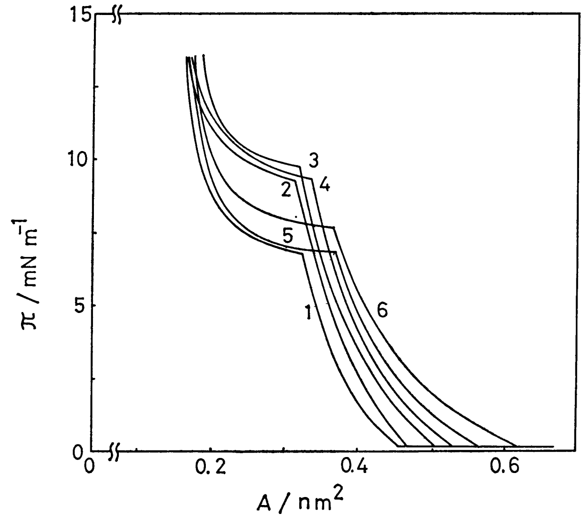

Fig. 2. Surface pressure *vs.* mean area curves of the pentadecanoic acid–hexadecyl acetate mixed monolayer at 298.2 K.
1: $x_2^{\pi}=0$ (pentadecanoic acid), 2: 0.2, 3: 0.3, 4: 0.4, 5: 0.8, 6: 1 (hexadecyl acetate).

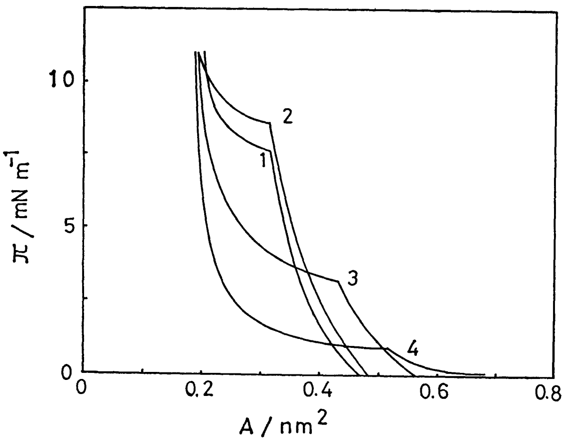

Fig. 3. Surface pressure *vs.* mean area curves of the pentadecanoic acid–heptadecyl acetate mixed monolayer at 298.2 K.
1: $x_2^\pi=0$ (pentadecanoic acid), 2: 0.2, 3: 0.7, 4: 1 (heptadecyl acetate).

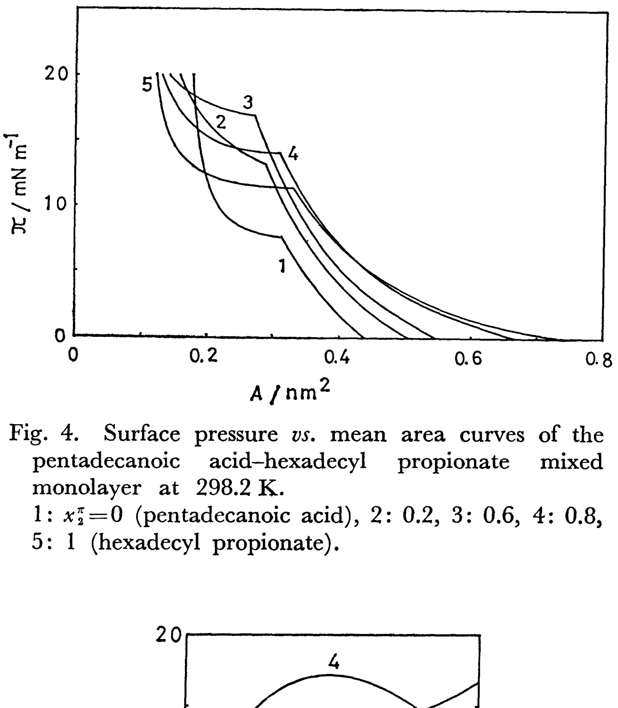

Fig. 4. Surface pressure *vs.* mean area curves of the pentadecanoic acid–hexadecyl propionate mixed monolayer at 298.2 K.
1: $x_2^\pi=0$ (pentadecanoic acid), 2: 0.2, 3: 0.6, 4: 0.8, 5: 1 (hexadecyl propionate).

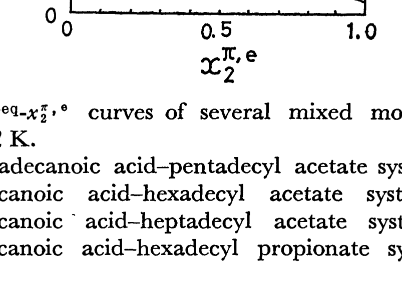

Fig. 5. π^{eq}-$x_2^{\pi,\mathrm{e}}$ curves of several mixed monolayers at 298.2 K.
1: Pentadecanoic acid–pentadecyl acetate system, 2: pentadecanoic acid–hexadecyl acetate system, 3: pentadecanoic acid–heptadecyl acetate system, 4: pentadecanoic acid–hexadecyl propionate system.

hydrophilic group of PA, HA, and HpA is the same, that is, acetoxyl group (CH_3COO–), but the carbon number of the hydrophobic group is different in each. On the other hand, the hydrophilic group of HPr is different from that of HA, while the chain length is the same. In the C_{15}–PA system, π^{eq} increases gently with an increase in the mole fraction of the ester in the expanded state, $x_2^{\pi,\mathrm{e}}$. There are maximum and minimum points in the C_{15}–HA system, as has previously been mentioned.[1] For the C_{15}–HpA system, a small maximum was observed, while the C_{15}–HPr system has a large maximum.

Recently thermodynamic equations of a multicomponent mixed monolayer in which the contribution of water is incorporated were derived by Motomura.[3–6] When two components are miscible in both the expanded and condensed states, the following equations (Eqs. 209, 201, and 205 in Ref. 6) have been reported:

$$\begin{aligned} x_2^{\pi,\mathrm{c}} = x_2^{\pi,\mathrm{e}} &+ (a^{\mathrm{c}}-a^{\mathrm{e}})(\partial\pi^{\mathrm{eq}}/\partial x_2^{\pi,\mathrm{e}})_{T,p} \\ &/\{RT/x_1^{\pi,\mathrm{e}}x_2^{\pi,\mathrm{e}}+(\partial a^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}(\partial\pi^{\mathrm{eq}}/\partial x_2^{\pi,\mathrm{e}})_{T,p} \\ &+\int_0^{\pi}[\partial^2 a^{\mathrm{e}}/(\partial x_2^{\pi,\mathrm{e}})^2]_{T,p,\pi}\mathrm{d}\pi\}, \end{aligned} \tag{1}$$

$$\begin{aligned} \Delta s^{r} = &[a^{\mathrm{c}}-a^{\mathrm{e}}-(x_2^{\pi,\mathrm{c}}-x_2^{\pi,\mathrm{e}})(\partial a^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}] \\ &\times[(\partial\pi^{\mathrm{eq}}/\partial T)_{p,x_2^{\pi,\mathrm{e}}}-(\partial\gamma^{\circ}/\partial T)_p], \end{aligned} \tag{2}$$

and;

$$\begin{aligned} \Delta u^{r} = &-(\pi^{\mathrm{eq}}-\gamma^{\circ})[a^{\mathrm{c}}-a^{\mathrm{e}}-(x_2^{\pi,\mathrm{c}}-x_2^{\pi,\mathrm{e}})(\partial a^{\mathrm{e}}/\partial x_2^{\pi,\mathrm{e}})_{T,p,\pi}] \\ &+\Delta T s^{r}, \end{aligned} \tag{3}$$

where x_2^π is the mole fraction of the second component (ester) in the mixed monolayer; a is the mean area per mole of film-forming components; π^{eq} is the phase-equilibrium surface pressure, which corresponds to that of the break point of the π-A curve; the superscripts c and e represent the condensed and expanded states respectively; Δs^r and Δu^r are the apparent molar entropy and energy changes, and γ° is the surface tension of water.

Now we can obtain two curves; one is the experimental π^{eq}—$x_2^{\pi,\mathrm{e}}$ curve, and the other is the π^{eq}—$x_2^{\pi,\mathrm{c}}$ curve calculated using Eq. 1. A two-dimensional phase diagram is constructed by means of these two curves. The diagrams of the C_{15}–PA, C_{15}–HA, C_{15}–HpA, and C_{15}–HPr systems at 298.2 K are shown in Figs. 6 to 9. For all systems, two components are miscible in the expanded as well as the condensed states. At the maximum and minimum points, the mole fractions of the expanded($x_2^{\pi,\mathrm{e}}$) and condensed ($x_2^{\pi,\mathrm{c}}$) phases are equal. According to the previously presented classification of phase diagrams,[7,8] the C_{15}–PA and C_{15}–HA systems are of a complicated type, while the C_{15}–HpA and C_{15}–HPr systems are of a positive azeotropic type.

The apparent molar entropy change of these systems was evaluated by means of Eq. 2. They are shown in Fig. 10. In the C_{15}–PA system, Δs^r decreases gently with an increase in $x_2^{\pi,\mathrm{c}}$. The Δs^r of the C_{15}–HA system has a small minimum. The value for the C_{15}–HpA system increases gradually with an increase in $x_2^{\pi,\mathrm{c}}$. The C_{15}–HPr system has an obvious minimum. In this way, the apparent molar entropy changes of these systems depend also uniquely on the chain length and structure of the hydrophilic group of esters.

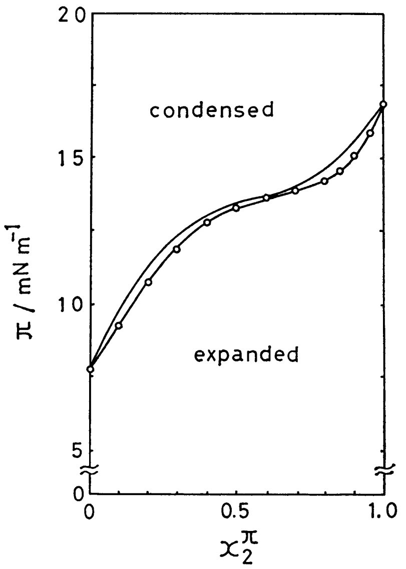

Fig. 6. Phase diagram of the pentadecanoic acid-pentadecyl acetate mixed monolayer at 298.2 K.

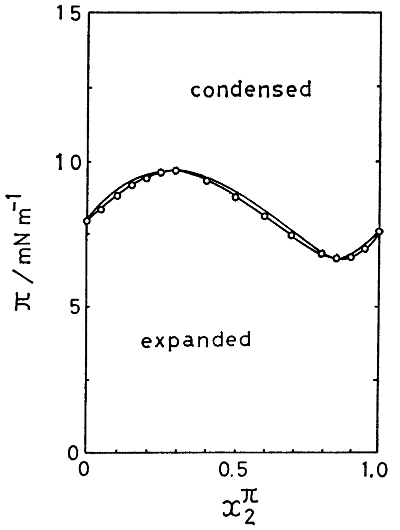

Fig. 7. Phase diagram of the pentadecanoic acid-hexadecyl acetate mixed monolayer at 298.2 K.

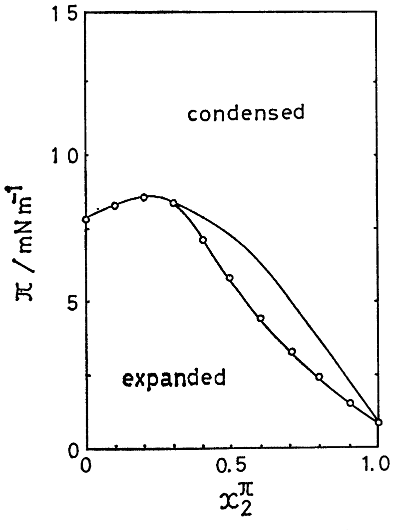

Fig. 8. Phase diagram of the pentadecanoic acid-heptadecyl acetate mixed monolayer at 298.2 K.

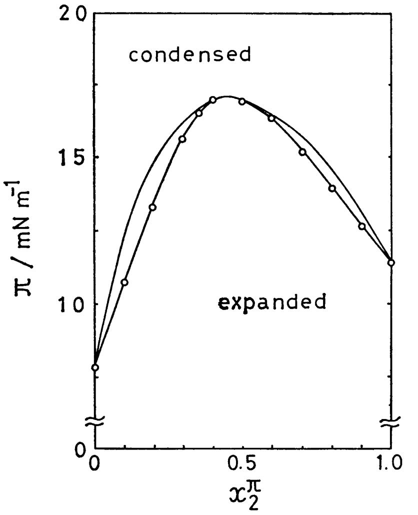

Fig. 9. Phase diagram of the pentadecanoic aicd-hexadecyl propionate mixed monolayer at 298.2 K.

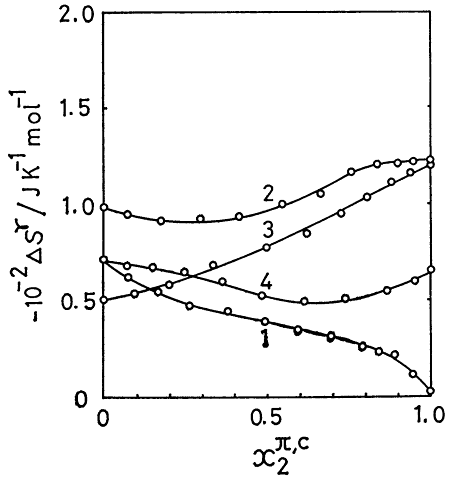

Fig. 10. Δs^r *vs.* $x_2^{\pi,c}$ curves of several mixed monolayers.
1: Pentadecanoic acid-pentadecyl acetate system at 298.2 K, 2: pentadecanoic acid-hexadecyl acetate system at 295.7 K, 3: pentadecanoic acid-heptadecyl acetate system at 299.7 K, 4: pentadecanoic acid-hexadecyl propionate system at 298.2 K.

The excess apparent molar energy change is defined by $\Delta u^r - \overline{(\Delta u^r)}$, where $\overline{(\Delta u^r)}$ is the composition average of Δu^r. From Eq. 3 and the above definition, we can now calculate the excess apparent molar energy changes. They are given in Fig. 11. It is interesting that there are positive and negative regions in the energy change. This is why C_{15}–PA and C_{15}–HA systems show complicated phase diagrams. They indicate the following facts: (1) in the positive region, there are mutual interactions between the two components in the mixed monolayer which are weaker than the interactions between the pure component molecules themselves, and (2) in the negative region, there are mutual interactions between the two components in the mixed monolayer which are stronger than the interactions between the pure component molecules themselves. Upon comparing the C_{15}–PA,

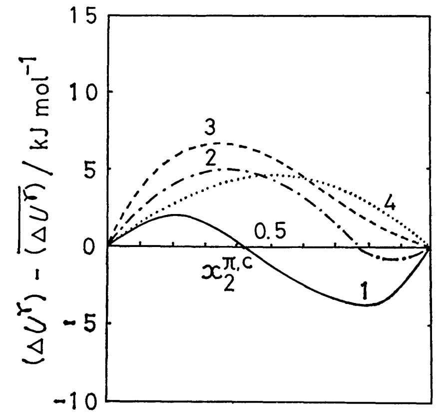

Fig.11. $(\Delta u^r)-\overline{(\Delta u^r)}$ *vs.* $x_2^{\pi,c}$ curves of several mixed monolayers.
1: Pentadecanoic acid-pentadecyl acetate system at 298.2 K, 2: pentadecanoic acid–hexadecyl acetate system at 295.7 K, 3: pentadecanoic acid–heptadecyl acetate system at 299.7 K, 4: pentadecanoic acid–hexadecyl propionate system at 298.2 K.

C_{15}–HA, and C_{15}–HpA systems, we find that the positive region increases with an increase in the chain length of the esters until, in the C_{15}–HpA system, the energy change is positive over the whole range of $x_2^{\pi,c}$. In these C_{15}–PA, C_{15}–HA, and C_{15}–HpA systems, the hydrophilic group of the esters is the same, but the chain length of the esters is different in each. Therefore, the above results show the following facts: (1) interactions between two components in the mixed monolayer decrease with an increase in the difference in chain length between the two components, and (2) in the low $x_2^{\pi,c}$ region, the contribution of the hydrophilic-hydrophilic steric hindrance becomes relatively large. The excess apparent molar energy change of the C_{15}–HPr system is positive over the whole range of $x_2^{\pi,c}$. This also indicate the weaker interactions. This is why C_{15}–HPr system shows a positive azeotropic transformation in mixed monolayers.[5,8,9] HPr has a propyl group(C_3H_8–) in its hydrophilic part, but PA, HA, and HpA have a methyl group(CH_3–) in their hydrophilic parts. The steric hindrance of the propyl group is much larger than that of the methyl group. Therefore, the steric hindrance of the propyl group may be supposed to play an important role in the positive azeotropic transformation.

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