Mixed Monolayers of Long Normal Chain Fatty Acids with Long Normal Chain Esters. II. Fatty Acids–Hexadecyl Acetate System

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In order to clarify the effect of molecular structure on states and properties of mixed monolayers, surface pressure-area(π-A) curves of the two-component surface films of long normal chain fatty acids with hexadecyl acetate were measured at various compositions and temperatures. By use of thermodynamic analysis, the phase diagrams and partial molar enthalpy changes were calculated. For four systems studied in the present paper it was found that the diagram and enthalpy change vary characteristically with the number of carbon atoms of acids, but the dependence on the chain length of acid in fatty acid–hexadecyl acetate systems was very different from that in fatty acid–ethyl hexadecanoate systems.

In our previous studies of fatty acid–fatty acid,[1,2] fatty acid–fatty alcohol,[3] and fatty acid–fatty ester[4] systems, it was found that the interaction, the miscibility, the state, and the thermodynamic quantities in mixed monolayers change successively with increase in the chain length of the film-forming acid. The present work has been undertaken to investigate the difference between fatty acid–hexadecyl acetate and fatty acid–ethyl hexadecanoate[4] systems, in order to elucidate the effect of molecular structure on mixing.

Experimental

The long normal chain fatty acids employed in this experiment were tetradecanoic(C_{14}), pentadecanoic(C_{15}), hexadecanoic(C_{16}), and octadecanoic(C_{18}) acids. They were purified by repeated recrystallization. Hexadecyl acetate (HA) was synthesized from distilled acetic acid and 1-hexadecanol of Tokyo Kasei Co., Ltd., and purified by distillation.

Experimental conditions were the same as described in the previous paper.[4]

Results and Discussion

Surface pressure-area(π-A) curves obtained for C_{14}–HA, C_{15}–HA, C_{16}–HA, and C_{18}–HA systems at 298.15 K are shown in Figs. 1 to 4. It was observed that in the C_{14}–HA system (Fig. 1) there is a maximum equilibrium surface pressure, similar to the C_{14}–EH system[4] at $x_2^{\pi,e}=0.05$, where $x_2^{\pi,e}$ is the mole fraction of the second component(HA) in the expanded monolayer and EH indicates ethyl hexadecanoate, as described in the previous paper.[4] In the C_{15}–HA system (Fig. 2) there is a unique result: *i.e.*, the curve has a maximum and a minimum point at $x_2^{\pi,e}=0.3$ and 0.87, respectively. This phenomenon is peculiar to the C_{15}–HA system and we have not observed it in any other systems until now. In the C_{16}–HA(Fig. 3) and C_{18}–HA(Fig. 4) systems the equilibrium surface pressure, π^{eq}, decreases monotonously with the decrease of $x_2^{\pi,e}$, but the extent of decreasing is larger in the C_{18}–HA system than in the C_{16}–HA system.

In the preceding papers[5,6] the thermodynamic equations of multicomponent monolayers were derived. Taking advantage of them (Eqs. 38, 42, and 43 in Ref. 6), we obtained the two-dimensional phase diagram and partial molar enthalpy change associated with the phase transition from an expanded to a condensed state. The diagrams of the C_{14}–HA, C_{15}–HA, C_{16}–HA, and C_{18}–HA systems are shown in Figs. 5 to 8, respectively.

The C_{14}–HA system (Fig. 5) has a maximum point in the phase diagram which is analogous to the C_{14}–EH system,[4] but the composition of the maximum

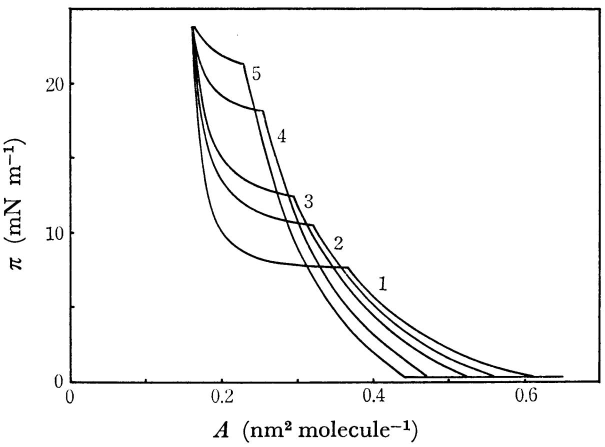

Fig. 1. Surface pressure *vs.* mean area curves of the tetradecanoic acid–hexadecyl acetate mixed monolayer at 298.15 K: 1, $x_2^{\pi}=1$(hexadecyl acetate); 2, 0.7; 3, 0.6; 4, 0.3; 5, 0(tetradecanoic acid).

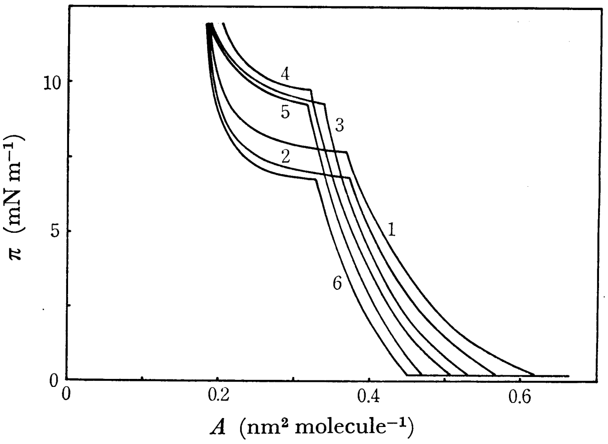

Fig. 2. Surface pressure *vs.* mean area curves of the pentadecanoic acid–hexadecyl acetate mixed monolayer at 298.15 K: 1, $x_2^{\pi}=1$(hexadecyl acetate); 2, 0.8; 3, 0.4; 4, 0.3; 5, 0.2; 6, 0(pentadecanoic acid).

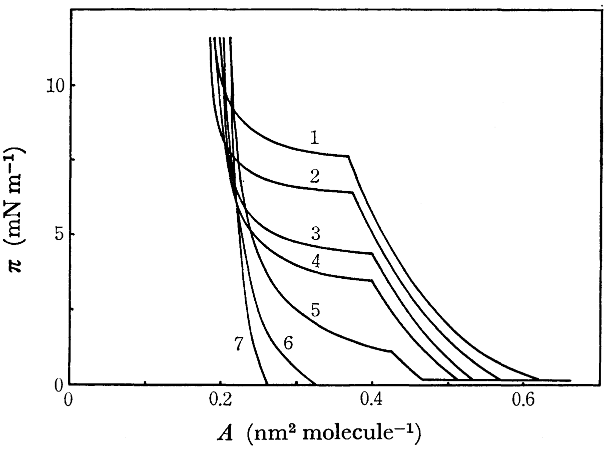

Fig. 3. Surface pressure *vs.* mean area curves of the hexadecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K: 1, $x_2^\pi=1$(hexadecyl acetate); 2, 0.9; 3, 0.7; 4, 0.5; 5, 0.2; 6, 0.1; 7, 0(hexadecanoic acid).

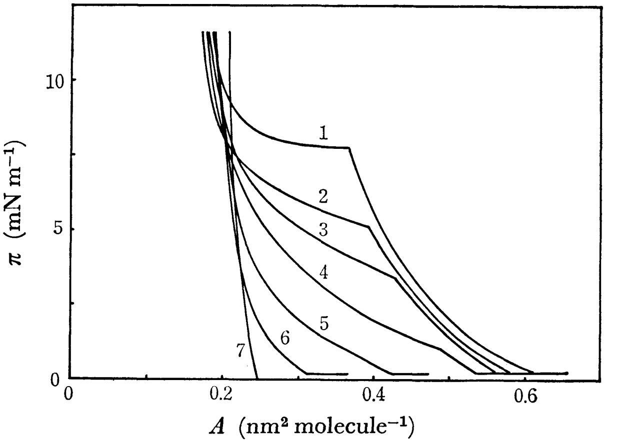

Fig. 4. Surface pressure *vs.* mean area curves of the octadecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K: 1, $x_2^\pi=1$(hexadecyl acetate); 2, 0.95; 3, 0.9; 4, 0.8; 5, 0.7; 6, 0.6; 7, 0(octadecanoic acid).

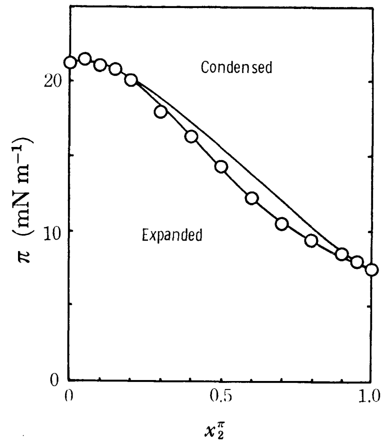

Fig. 5. Phase diagram of the tetradecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K.

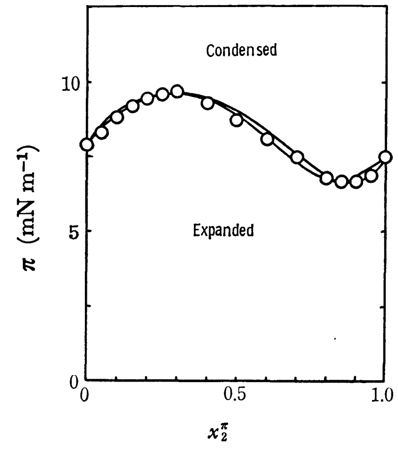

Fig. 6. Phase diagram of the pentadecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K.

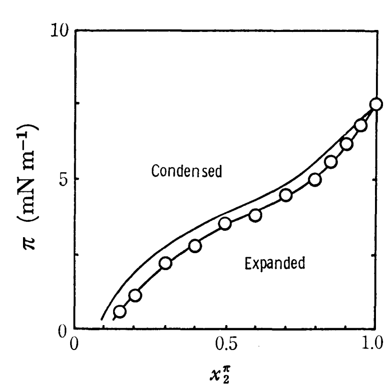

Fig. 7. Phase diagram of the hexadecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K.

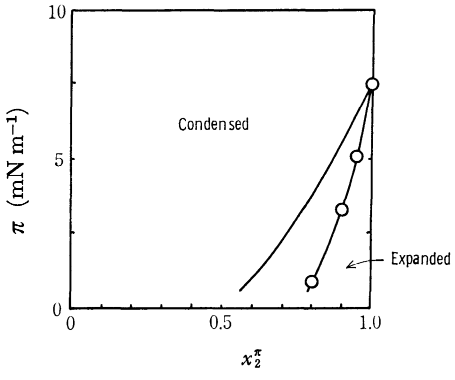

Fig. 8. Phase diagram of the octadecanoic acid-hexadecyl acetate mixed monolayer at 298.15 K.

point in the former system is $x_2^{\pi,e}=0.05$ while that in the latter system $x_2^{\pi,e}=0.3$. From the molecular structural point of view, the hydrocarbon chain of HA is longer than that of EH. It seems that C_{14} and HA are less miscible with each other than C_{14} and EH in mixed monolayer, and so in the C_{14}–HA system the composition of maximum point shifts towards the acid side more than that in the C_{14}–EH system. By using ethyl heptadecanoate, which has the same hydrocarbon chain length as HA, we investigated the mixed monolayer with C_{14}; it was found that in the C_{14}–ethyl heptadecanoate system there existed a maximum at $x_2^{\pi,e}=0.2$.[7]

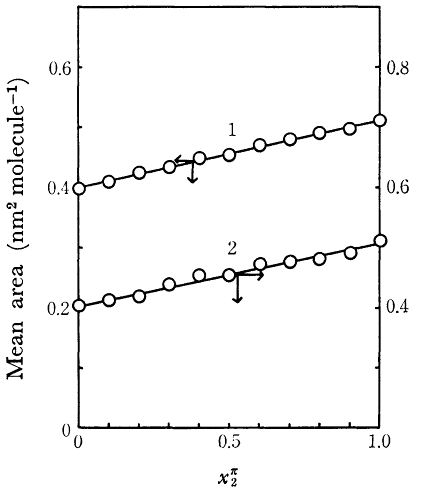

Fig. 9. Additivity of area at 2 mN m^{-1} for C_{14}–HA and C_{15}–HA systems at 298.15 K: 1, C_{14}–HA; 2, C_{15}–HA.

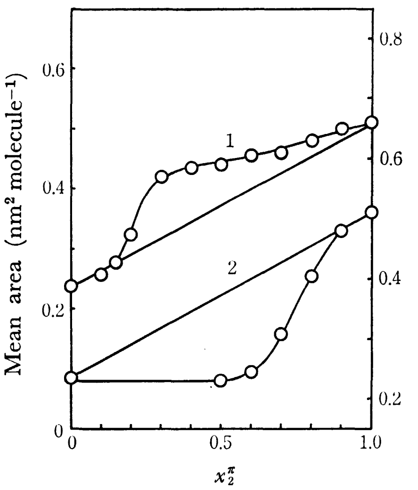

Fig. 10. Additivity of area at 2 mN m^{-1} for C_{16}–HA and C_{18}–HA systems at 298.15 K: 1, C_{16}–HA; 2, C_{18}–HA.

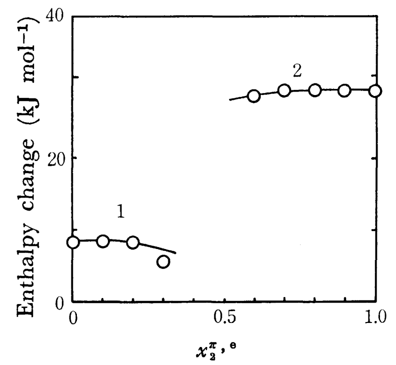

Fig. 11. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the tetradecanoic acid–hexadecyl acetate at 293.15 K: 1, tetradecanoic acid; 2, hexadecyl acetate.

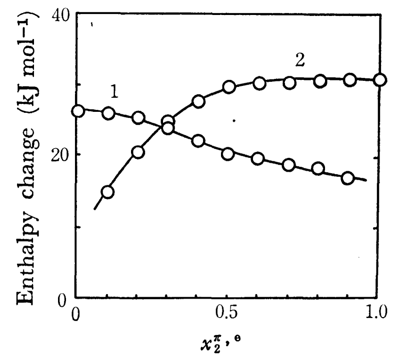

Fig. 12. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the pentadecanoic acid–hexadecyl acetate at 295.65 K: 1, pentadecanoic acid; 2, hexadecyl acetate.

The diagram of the C_{15}–HA system at 298.15 K is shown in Fig. 6. There exist maximum and minimum points in this diagram at $x_2^{\pi,e}=0.3$ and 0.87, respectively. This is particularly surprising from the thermodynamic point of view and we have not observed such a result in any other system. This phase diagram shows that in the C_{15} rich region the excess free energy of the monolayer in the expanded state ($G^{E,e}$) is smaller than that in the condensed state ($G^{E,c}$), and in the HA rich region the $G^{E,e}$ is larger than $G^{E,c}$ at relatively high pressures.[8] According to thermodynamic analysis,[7] it is easily understandable that in a positive azeotrope system, which has a maximum point in the phase diagram, the mutual interaction between film-forming substances in the mixed monolayer is weaker than the interaction between the pure component molecules themselves. In other words, in the C_{15} rich region C_{15} and HA are likely to be located apart from each other, since the hydrophilic group of HA is so different from that of C_{15} that C_{15} and HA are difficult to pack together. It is thus more stable as the expanded state in this region than as the condensed state. But in the HA rich region, it seems that C_{15} and HA are likely to pack together owing to the ease of packing of C_{15} and HA. In this way it is seen that the thermodynamic state of the monolayer is very much influenced by the molecular structure of the components. This is also revealed by the difference in phase diagrams between the C_{15}–HA(Fig. 6) and C_{15}–EH[4] systems.

Figure 7 represents the phase diagram of the C_{16}–HA system. This is also very different from that of the C_{16}–EH system.[4] π^{eq} decreases gradually with the decrease of $x_2^{\pi,e}$. It seems that the interaction between C_{16} and HA is complicated. In the C_{18}–HA system (Fig. 8), the diagram is analogous to that of the C_{18}–EH system.[4] But the π^{eq} decreases more rapidly with the decrease of $x_2^{\pi,e}$ than that of the C_{18}–EH system. This indicates that in the mixed monolayer HA is more condensed than EH. This can also be seen from the result of mean area *vs.* mole fraction curves (Fig. 10) and the partial molar enthalpy changes (Fig. 14).

The mean area *vs.* mole fraction curves of the mixed monolayers at 2 mN m^{-1} are shown in Figs. 9 and 10. In C_{14}–HA and C_{15}–HA systems (Fig. 9) the additivity rule is approximately established under these conditions. Owing to this result and the phase dia-

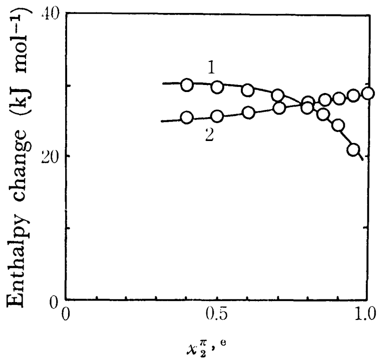

Fig. 13. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^{c}-\bar{h}_i^{e})$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the hexadecanoic acid–hexadecyl acetate at 298.15 K: 1, hexadecanoic acid; 2, hexadecyl acetate.

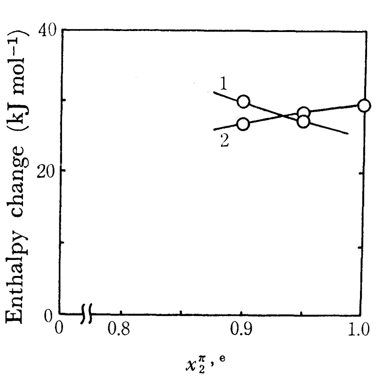

Fig. 14. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^{c}-\bar{h}_i^{e})$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the octadecanoic acid–hexadecyl acetate at 298.15 K: 1, octadecanoic acid; 2, hexadecyl acetate.

grams (Figs. 5 and 6), it may be said that these systems are nearly ideal at low surface pressures, but deviate appreciably from ideal behaviors as the pressure increases. In the C_{16}–HA system (Fig. 10) there is a considerable positive deviation from the additivity rule, similar to that of the C_{16}–EH system.[4] The C_{18}–HA system shows a considerable negative deviation in the expanded state, as shown by the solid line (Fig. 10), and the deviation is larger in the C_{18}–HA system than in the C_{18}–EH system.[4]

The partial molar enthalpy change was obtained from the thermodynamic analysis(Eqs. 38, 42, and 43 in Ref. 6), and they are shown in Figs. 11 to 14. In the C_{14}–HA system (Fig. 11), the enthalpy change of C_{14} gradually decreases, and that of HA slightly increases, with increase of $x_2^{\pi,e}$. Although the C_{15}–HA system has maximum and minimum points in the phase diagram, the nature of the enthalpy change, as shown in Fig. 12, is very similar to that of the C_{15}–EH system[4] which has only one maximum point in the phase diagram. The partial molar enthalpy change of C_{15} decreases, and that of HA increases considerably, with increase of $x_2^{\pi,e}$. In the C_{16}–HA system (Fig. 13), the enthalpy change of C_{16} also decreases, and the value of HA increases, with increases of $x_2^{\pi,e}$. This system shows the same tendency as the C_{16}–EH system[4] but the degree of variation of the partial molar enthalpy change is larger in the C_{16}–EH system than in the C_{16}–HA system. The characteristics of the enthalpy change of the C_{18}–HA system(Fig. 14) are similar to those of the C_{15}–HA and C_{16}–HA systems.

In conclusion, it was found that the phase diagram and partial molar enthalpy change vary with the chain length of the film-forming acid. There exists a maximum point in the C_{14}–HA system and this result is analogous to that of the C_{14}–EH system. However, in the C_{15}–HA system there is not only a maximum point but also a minimum point. This phenomenon was not observed in the C_{15}–EH or other systems, but is peculiar to the C_{15}–HA system. The C_{16}–HA system is also very different from the C_{16}–EH system. But the C_{18}–HA system is similar to the C_{18}–EH system. In this way, it is seen that the state of mixed monolayers is very much influenced by the molecular structure of film-forming components, especially by the chain length of the acid and the structure of the hydrophilic group of the ester. It seems that the structure effect is larger in mixed monolayers as the difference of the chain length between acid and ester becomes smaller.

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