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Miexd Monolayers of Long Normal Chain Fatty Acids with Long Normal Chain Esters. I. Fatty Acids–Ethyl Hexadecanoate System

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Surface pressure-area(π-A) curves of the two-component surface films of long normal chain fatty acids with ethyl hexadecanoate were measured at various compositions and temperatures. It was found that the π-A curves of the mixed monolayers vary characteristically with the number of carbon atoms of the film-forming acid. The two-dimensional phase diagrams of these systems and their partial molar enthalpy changes were obtained by taking advantage of the thermodynamic treatment of multicomponent surface films.[1,2] It was concluded that the chain length of the acid plays an important role in the thermodynamic state of the mixed monolayer.

There have been many studies of mixed monolayers at the air–water interface, aimed at elucidating the effect of the molecular structure on their state and properties.[3–5] But few studies using long normal chain esters have been reported. So we investigated mixed monolayers of long normal chain fatty acids with a long normal chain ester in order to clarify the effect of the chain length of the acid on the thermodynamic state of the two-component monolayers.

In the present study, tridecanoic(C_{13}), tetradecanoic(C_{14}), pentadecanoic(C_{15}), hexadecanoic(C_{16}), heptadecanoic(C_{17}), and octadecanoic(C_{18}) acids were employed as the fatty acids, and ethyl hexadecanoate (EH) was used as the ester. From these experiments, we constructed two-dimensional phase diagrams and calculated the partial molar enthalpy change for the respective systems. Consequently, systematic information concerning the effect of the number of carbon atoms of acid on fatty acid–ester mixed monolayers could be obtained.

Experimental

Long normal chain fatty acids employed in this experiment were obtained from Tokyo Kasei Co., Ltd. and purified by recrystallization from petroleum ether three times. Ethyl hexadecanoate(EH) was synthesized from recrystallized hexadecanoic acid and distilled ethanol by the usual method and purified by distillation. Benzene was used as the spreading solvent. To prevent the ester from hydrolysis, a 0.1 M NaCl solution was used as the substrate; this was prepared from twice distilled water and sodium chloride (Wako super special grade).

The π-A curves were measured by a Wilhelmy type surface balance. The temperature was maintained constant within ±0.2 K during the experiment. The monolayer was compressed continuously with a constant velocity of 2.79×10^{-2} nm^2 molecule^{-1} min^{-1} and the π-A curves were reproducible within ±0.2 mN m^{-1} at the same mean molecular area.

Results and Discussion

Surface pressure-area(π-A) curves were obtained for the C_{13}–EH, C_{14}–EH, C_{15}–EH, C_{16}–EH, C_{17}–EH, and C_{18}–EH systems at various compositions and temperatures. Typical π-A curves are shown in Fig. 1 for the C_{14}–EH system and in Fig. 2 for the C_{18}–EH system, both at 298.15 K.

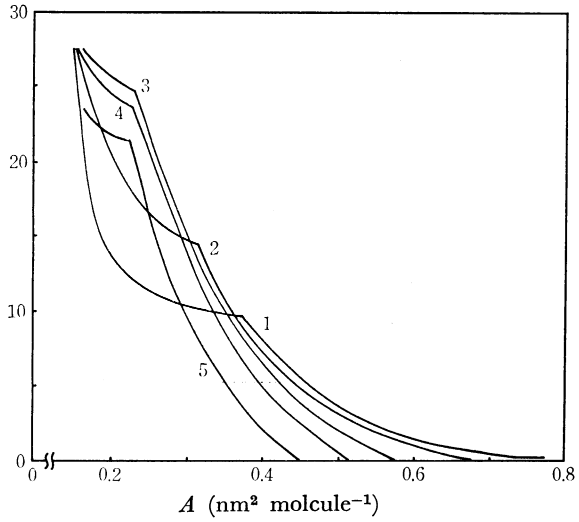

Fig. 1. Surface pressure *vs.* mean area curves of the tetradecanoic acid–ethyl hexadecanoate mixed monolayer at 298.15 K: 1, $x_2^{\pi}=1$ (ethyl hexadecanoate); 2, 0.8; 3, 0.3; 4, 0.15; 5, 0 (tetradecanoic acid).

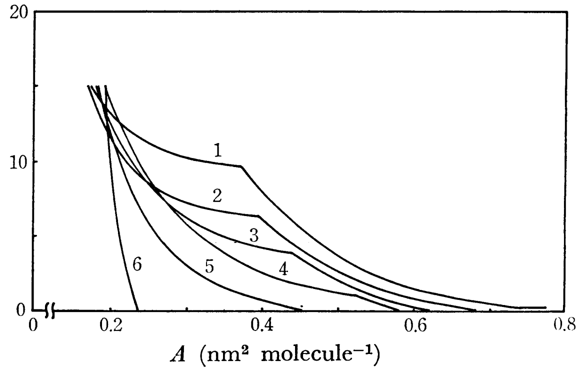

Fig. 2. Surface pressure *vs.* mean area curves of the octadecanoic acid–ethyl hexadecanoate mixed monolayer at 298.15 K: 1, $x_2^{\pi}=1$(ethyl hexadecanoate); 2, 0.9; 3, 0.8; 4, 0.7; 5, 0.5; 6, 0(octadecanoic acid).

For the C_{13}– EH system, the monolayers of pure C_{13} and EH are of the expanded type and a phase transition from liquid expanded to liquid condensed state is found over the whole range of composition at 298.15 and 288.15 K. The π^{eq}-$x_2^{\pi,e}$ curve for this system at 298.15 K is shown in Fig. 3, where π^{eq} is the phase equilibrium surface pressure which corresponds to that of the break point of π-A curve and $x_2^{\pi,e}$ indicates the mole fraction of the EH in the expanded mixed monolayer. It is seen that the curve

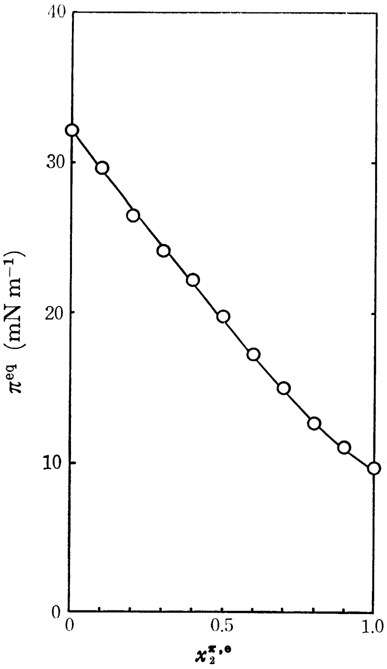

Fig. 3. π^{eq}-$x_2^{\pi,e}$ curves of the tridecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

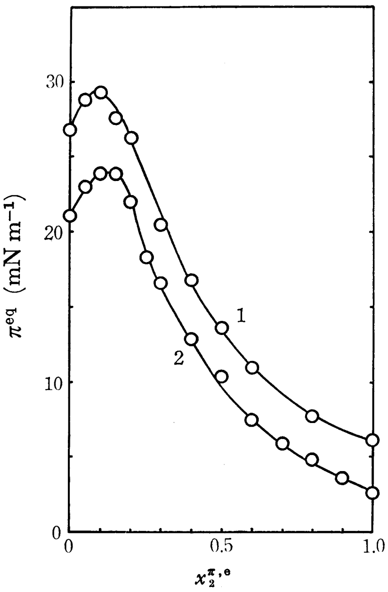

Fig. 4. π^{eq}-$x_2^{\pi,e}$ curves of the tridecanoic acid-ethyl hexadecanoate mixed monolayer at 293.15 and 288.15 K: 1, 293.15 K; 2, 288.15 K.

is of the simple, monotonous type. When the temperature is lowered, the shape of the π^{eq}-$x_2^{\pi,e}$ curve changes; it is noteworthy that at 293.15 and 288.15 K a maximum appears on the curve, as is shown in Fig. 4.

For the C_{14}–EH system, as can be seen from Fig. 1, the π^{eq}-$x_2^{\pi,e}$ curve has a maximum even at 298.15 K. The shape of the curve is similar at 293.15 and 288.15 K to that at 298.15 K, although the equilibrium surface pressure decreases gradually as the temperature is lowered, as shown in Fig. 5. We see that the composition of the maximum point is almost independent of temperature.

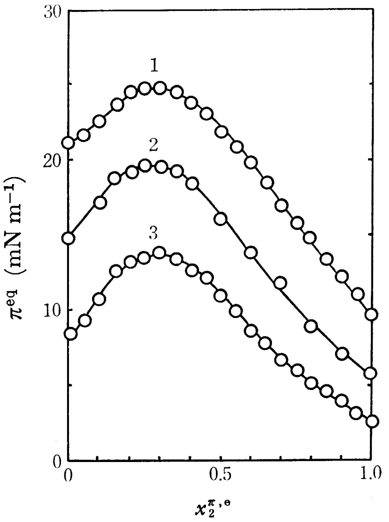

Fig. 5. π^{eq}-$x_2^{\pi,e}$ curves of the tetradecanoic acid-ethyl hexadecanoate mixed monolayer at several temperatures: 1, 298.15 K; 2, 293.15 K; 3, 288.15 K.

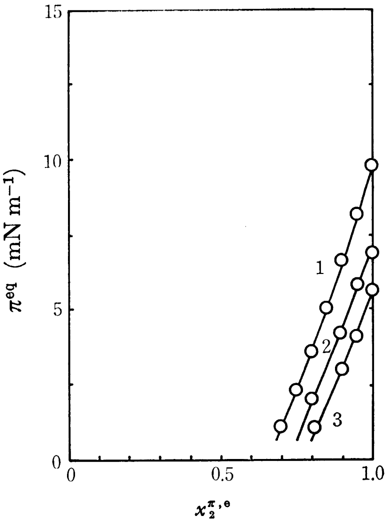

Fig. 6. π^{eq}-$x_2^{\pi,e}$ curves of the octadecanoic acid-ethyl hexadecanoate mixed monolayer at several temperatures: 1, 298.15 K; 2, 293.15 K; 3, 288.15 K.

For the C_{15}–EH and C_{16}–EH systems, the π^{eq}-$x_2^{\pi,e}$ curve is similar to that for the C_{14}–EH system, except that the maximum point shifts to the right along the $x_2^{\pi,e}$ axis; that is, the composition of the maximum becomes richer in EH as the carbon number of the fatty acid increases.

Figure 2 represents π-A isotherms of the C_{18}–EH system at 298.15 K. The π-A curve of this system is very different from the curves of the above-mentioned lower fatty acids–EH systems, in that the phase transition takes place only in a limited range of compositions. This difference may be caused by the fact that pure shorter-chain fatty acids give rise to the expanded film, while long-chain fatty acids form the condensed film at 298.15 K. The π^{eq}-$x_2^{\pi,e}$ curves for the C_{18}–EH system at various temperatures are shown in Fig. 6. It is found that the π^{eq} decreases monotonously with the decrease of $x_2^{\pi,e}$, and the lowering

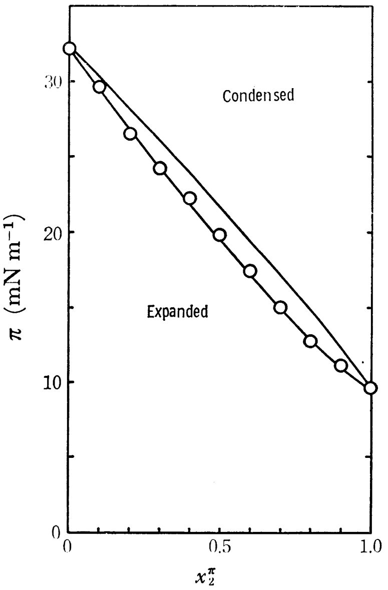

Fig. 7. Phase diagram of the tridecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

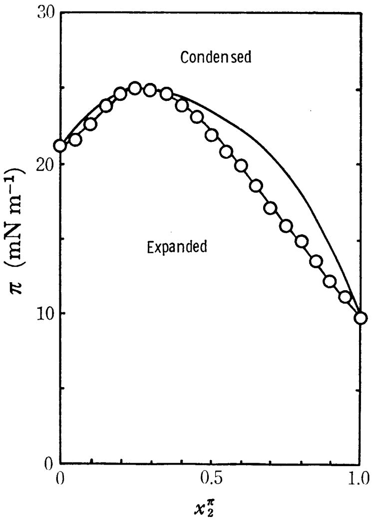

Fig. 8. Phase diagram of the tetradecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

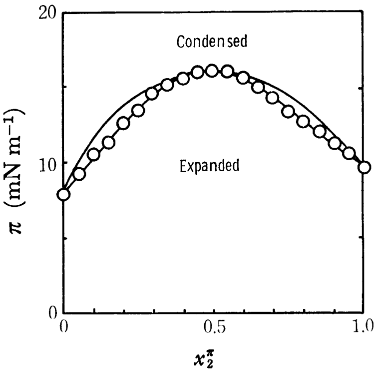

Fig. 9. Phase diagram of the pentadecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

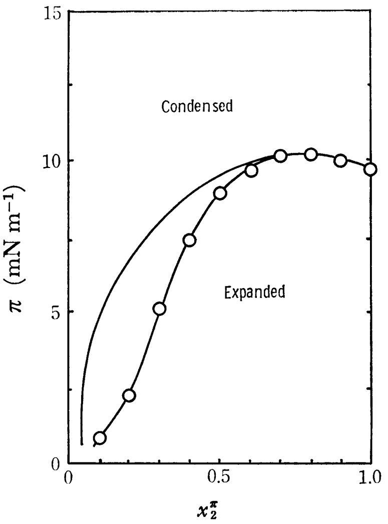

Fig. 10. Phase diagram of the hexadecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

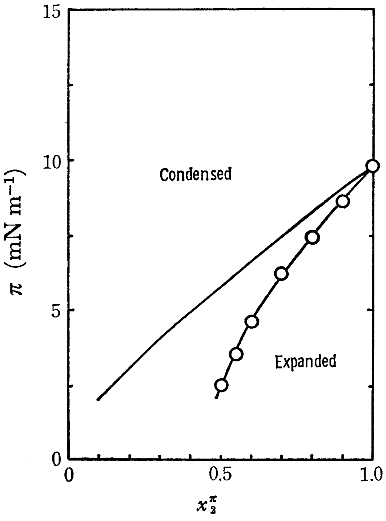

Fig. 11. Phase diagram of the heptadecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

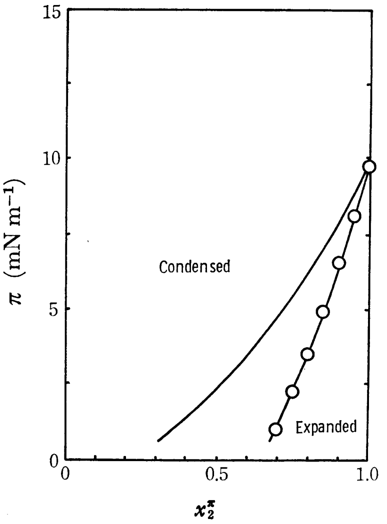

Fig. 12. Phase diagram of the octadecanoic acid-ethyl hexadecanoate mixed monolayer at 298.15 K.

TABLE 1. SURFACE PRESSURE AND COMPOSITION AT MAXIMUM POINT

System	298.15 K		293.15 K		288.15 K	
	$(\pi^{eq})_{max}$	$(x_2^\pi)_{max}$	$(\pi^{eq})_{max}$	$(x_2^\pi)_{max}$	$(\pi^{eq})_{max}$	$(x_2^\pi)_{max}$
C_{13}-EH	—	—	29.3	0.1	23.9	0.12
C_{14}-EH	24.8	0.3	19.7	0.3	13.7	0.3
C_{15}-EH	16.1	0.5	11.1	0.5	6.7	0.5
C_{16}-EH	10.2	0.8	—	—	—	—

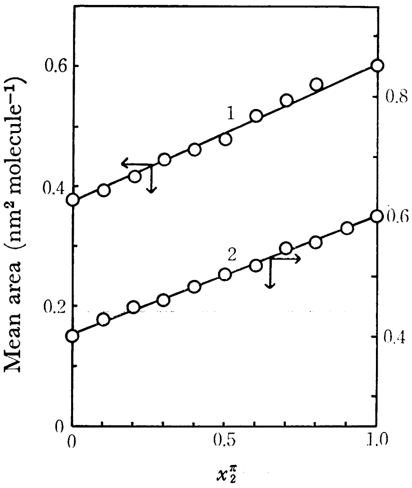

Fig. 13. Additivity of area at 2 mN m^{-1} for C_{14}–EH and C_{15}–EH systems at 298.15 K : 1, C_{14}–EH; 2, C_{15}–EH.

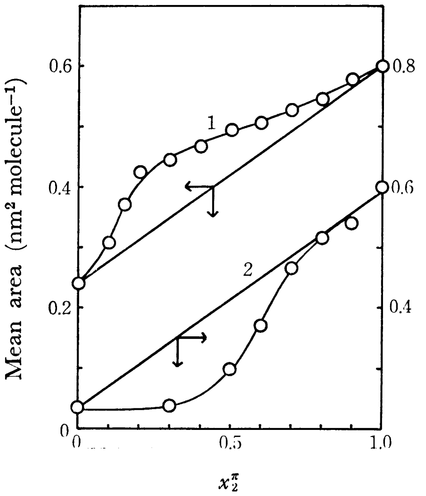

Fig. 14. Additivity of area at 2 mN m^{-1} for C_{16}–EH and C_{18}–EH systems at 298.15 K : 1, C_{16}–EH; 2, C_{18}–EH.

of temperature causes the parallel decrease in π^{eq} of this mixed monolayer. The π^{eq} disappears finally at a certain $x_2^{\pi,e}$, below which the phase transition from the expanded to the condensed film is not observed any more.

For the C_{17}–EH system we have a π^{eq}-$x_2^{\pi,e}$ curve similar to that for the C_{18}– EH system, although the phase transition region is a little wider for the former than for the latter.

Now the entire phase diagram can be constructed for each system by using thermodynamic equations previously described.[1,2] In Figs. 7 to 12 are shown the two-dimensional phase diagrams for C_{13}–EH to C_{18}–EH systems, respectively, at 298.15 K. The experimental points are indicated by open circles which give the π^{eq}-$x_2^{\pi,e}$ curve and the corresponding π^{eq}-$x_2^{\pi,c}$ curve calculated is shown by the solid line, where $x_2^{\pi,c}$ indicates the mole fraction of the EH in the condensed mixed monolayer.

The phase diagram for the C_{13}–EH system (Fig. 7) at 298.15 K is of an ideally mixing type; tow components form a continuous series of mixtures in the condensed as well as in the expanded phase. For C_{14}–EH, C_{15}–EH, and C_{16}–EH systems, a maximum appears on the phase diagram (Figs. 8, 9, and 10), where the composition of the expanded phase is equal to that of the condensed one. Therefore, this maximum may be called a two-dimensional positive azeotropic point. At this point the phase transition pressure $(\pi^{eq})_{max}$ decreases, while the mole fraction of ester $(x_2^\pi)_{max}$ increases, with increase in the number of carbon atoms of fatty acid, as shown in Table 1. The positive azeotropy suggests that there are mutual interactions between two components in the mixed monolayer which are weaker than the interactions between the pure component molecules themselves.

In contrast to this positive azeotropy, we have observed negative azeotropy in C_{14}–D,L-α-dipalmitoyl lecithin(DPL), EH–DPL, hexadecyl acetate(HA)–DPL, 1-monopalmitin–DPL, and EH–HA systems; these results will be reported in a separate paper.

For C_{17}–EH and C_{18}–EH systems at 298.15 K the phase transition from expanded to condensed states appears only in a limited range of composition, and so the phase diagram is incomplete, as shown in Figs. 11 and 12. Because of the strong condensing effect of longer chain fatty acids, C_{17} or C_{18}, the phase transition pressure decreases remarkably with increase in the amount of the fatty acid, resulting finally in the disappearance of the expanded phase at a certain composition of the mixed monolayer.

The situation of the interaction and miscibility of two components in the mixed monolayer may also be obtained from mean molecular area A_m at constant surface pressure *vs.* mole fraction x_2^π relations. The A_m-x_2^π curves were obtained for the C_{13}–EH, C_{14}–EH, C_{15}–EH, C_{16}–EH, C_{17}–EH, and C_{18}–EH systems at 2 mN m^{-1}. Several examples are shown in Figs. 13 and 14. From these results, it is found that at 2 mN m^{-1} the simple additivity is nearly established for the C_{13}–EH, C_{14}–EH, and C_{15}–EH systems, but the curves of the C_{16}–EH, C_{17}–EH, and C_{18}–EH systems

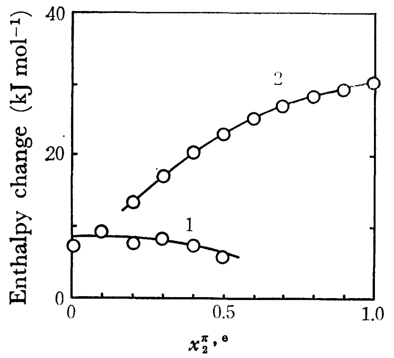

Fig. 15. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the tetradecanoic acid–ethyl hexadecanoate at 293.15 K: 1, tetradecanoic acid; 2, ethyl hexadecanoate.

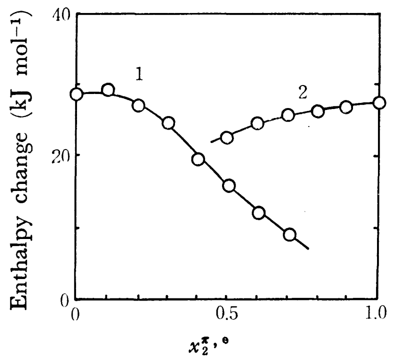

Fig. 16. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the pentadecanoic acid–ethyl hexadecanoate at 293.15 K: 1, pentadecanoic acid; 2, ethyl hexadecanoate.

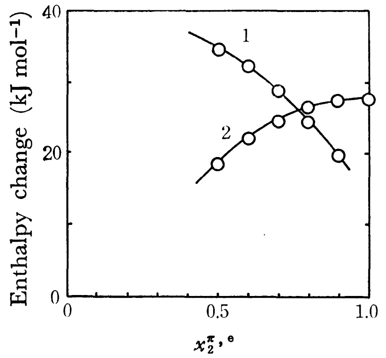

Fig. 17. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the hexadecanoic acid–ethyl hexadecanoate at 293.15 K: 1, hexadecanoic acid; 2, ethyl hexadecanoate.

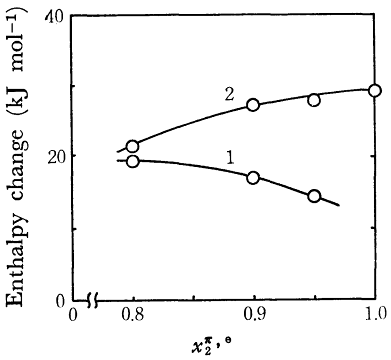

Fig. 18. Partial molar enthalpy change of the phase transition, $-(\bar{h}_i^c-\bar{h}_i^e)$ *vs.* mole fraction in the expanded monolayer, $x_2^{\pi,e}$, curves of the octadecanoic acid–ethyl hexadecanoate at 295.65 K: 1, octadecanoic acid; 2, ethyl hexadecanoate.

evidently deviate from this rule. Judging from this fact and the appearance of phase transition, it is concluded that in the former group the miscibility of two components is quite good, but in the latter group it gradually decreases with an increase in the difference of carbon number between the two components.

By the use of a thermodynamic treatment (Eqs. 38, 42, and 43 in Ref. 2), the partial molar enthalpy change accompanying the phase transition form the expanded to the condensed state was calculated for the C_{14}–EH, C_{15}–EH, C_{16}–EH, and C_{18}–EH systems; the results are shown in Figs. 15 to 18. It is difficult to make such a calculation over the whole range of composition with sufficient accuracy, and so in these figures data are shown for some limited ranges.

In the C_{14}–EH system (Fig. 15), the partial molar enthalpy change of C_{14} is small and decreases slightly, while that of EH is large and increases considerably, with increase of the composition of EH. The value of EH in the pure monolayer is larger than that of EH in the mixed monolayer. This shows that EH is more condensed in the mixed monolayer than in the pure monolayer.

In the C_{15}–EH system (Fig. 16), the partial molar enthalpy change of C_{15} decreases but the value of EH increases with the increase of $x_2^{\pi,e}$ to almost the same extent. This indicates that both C_{15} and EH are more condensed in the mixed monolayer than in the pure monolayer, respectively. In other words, the mixed monolayer of C_{15} and EH at relatively high pressure is less stable in the condensed state than in the expanded state and needs less heat for the transition from the condensed to expanded state than does the monolayer of pure components. On the contrary, in the system of negative azeotropy, such as EH–HA, EH–DPL, and so on, the monolayer is more stable in the condensed state than in the expanded state at relatively high pressure and needs much heat for the transition from the condensed to expanded state than does the monolayer of pure components.

In the C_{16}–EH system(Fig. 17), the partial molar enthalpy change of C_{16} decreases more than that of C_{15} in the C_{15}–EH system and the value of EH increases more than that of EH in the C_{15}–EH system, with increase of $x_2^{\pi,e}$. The tendency is much more pronounced in the C_{18}–EH system (Fig. 18). From these results it is seen that the partial molar enthalpy changes of acids and EH vary more rapidly with increase of the chain length of the acid. From Figs. 15 to 17, it was found that the values of partial molar enthalpy change of acids and EH are quite close to each other at the composition of the maximum point.

In conclusion, the chain length of the acid plays an important role in the thermodynamic state of the mixed monolayer. Taking advantage of the thermodynamic treatment it is seen that the C_{13}–EH system has a cigar type phase diagram at 298.15 K, while it comes to have a maximum point when the temperature is lowered. C_{14}–EH, C_{15}–EH, and C_{16}–EH systems have maximum points in their phase diagrams at 298.15 K. They correspond to the positive azeotrope in the three-dimensional phase diagram. This result suggests that there are mutual interactions between two components in the mixed monolayer which are weaker than the interactions between the pure component molecules themselves. The composition of the maximum point gradually shifts towards the ester side, with increase of the number of carbon atoms of acids. Finally it disappears in the C_{17}–EH and C_{18}–EH systems. It was found that the miscibility, phase diagram, and the partial molar enthalpy change of these systems change successively with the difference of the chain length.

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