The Formation and Collapse of Mixed Monolayer of Triolein and Tricaprylin

Masayuki NAKAGAKI and Noriaki FUNASAKI*
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606

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The surface pressure-area curves of mixed monolayers of triolein and tricaprylin and the equilibrium spreading pressures of these liquid mixtures were measured at 25 °C. The surface pressures of the monolayers of the pure components, triolein and tricaprylin, did not vary when the monolayer was compressed below its collapse area, but the surface pressure of their mixed monolayers increased with the compression; the surface pressure at a zero area agreed well with the value of the equilibrium spreading pressure. From the two curves, the one representing the relation between the collapse pressure and the composition of the mixed monolayer, and the other representing the relation between the equilibrium spreading pressure and the composition of the liquid mixture, the compositions of the mixed monolayer and the liquid mixture coexisting in the equilibrium were obtained. Consequently, it was found that the component whose collapse pressure was lower was richer in the liquid mixture than in the mixed monolayer, while the other component, whose collapse pressure was higher, was poorer in the liquid mixture than in the mixed monolayer. It was concluded, on the basis of the phase rule and thermodynamics for a plane interface, that triolein and tricaprylin form a regular mixture in the monolayer as well as in a liquid.

Studies of the processes by which a lipid mixture forms a monolayer and a mixed monolayer collapses to deposit a lipid mixture on the water-air interface are important in that the biological membrane contains the lipid mixture as one of its main components. Theoretical and experimental studies have been reported of the collapse pressure of mixed monolayers[1–3] and the equilibrium spreading pressure of mixed crystals.[4]

In a previous paper,[5] the compositions of the monolayer and the solid, which is in equilibrium with the former, have been studied for the binary system of triglyceride and cholesterol, and the miscibility of these components in the monolayer state and the solid state has been discussed on the basis of the two-dimensional phase rule. Moreover, the overcompression of the monolayer has been discussed. The state of the monolayer and the solid in equilibrium could not, however, be explained thoroughly, because these mixtures were solids, so the rate was quite low to arrive at an equilibrium between a monolayer and a solid.

In this paper, the equilibrium spreading pressure and the collapse pressure for the binary system of triolein and tricaprylin were measured, because these substances are liquid at room temperature and are practically insoluble in water.

Experimental

The triolein and tricaprylin were purchased from the Sigma Chemical Company and were stored at −25 °C. The water and chloroform were twice distilled. A mixture of triolein and tricaprylin was produced by evaporating the solvent from a chloroform solution in which the triolein and tricaprylin had been completely mixed. The triolein and tricaprylin were miscible in the liquid state in any proportion examined. When about 20 mg of this liquid mixture was dropped onto a clean aqueous surface with an area of about 60 cm², the surface pressure immediately increased, reaching a constant value after a while. This surface pressure was determined as the equilibrium spreading pressure, F_e, and it was measured at various compositions of mixtures of triolein and tricaprylin. On the other hand, the mixed monolayer of triolein and tricaprylin was spread from their chloroform solution and the pressure-area curve of the mixed monolayer was determined. The surface pressure was measured at 25±0.1 °C using a surface through equipped with a vertical-type surface balance described previously.[6]

Results

Pressure-Area Curve. The surface pressure-area curves of mixed monolayers of triolein and tricaprylin are shown at various mole fractions of tricaprylin, x_c, in Fig. 1. The kink points shown by arrows in this figure indicate that the monolayers begin to collapse at these points. Therefore, the pressures and the areas of these points are the collapse pressure, F_c, and the collapse area, A_c, respectively. At surface pressures lower than the collapse pressure, the pressure-area curves of the monolayers of triolein (shown by open circles in Fig. 1) and tricaprylin (shown by closed circles) were examined to see whether or not they fit the following equation presented by Jura and Harkins:[7]

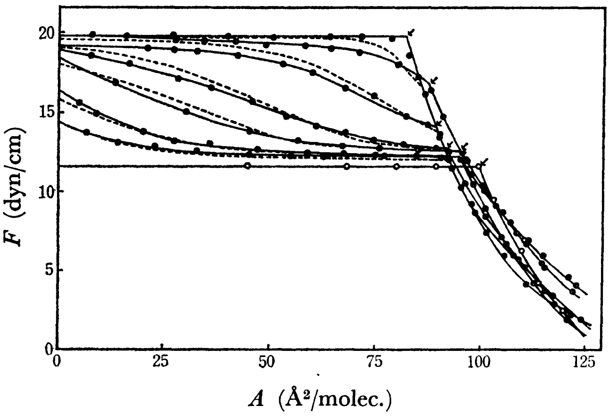

Fig. 1. The pressure-area curves of mixed monolayers of triolein and tricaprylin at various mole fractions of tricaprylin.
x_c, ○: 0, ◓: 0.200, ⦶: 0.309, ◑: 0.520, ⊕: 0.668, ⊖: 0.866, ◐: 0.978, ●: 1.
- - - Theoretical curve from Eq. (3).

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[*] Present address: Kyoto College of Pharmacy, 5-Nakauchi-cho, Misasagi Yamashina, Higashiyama-ku, Kyoto 607,

$$F = -\alpha \log A + \beta A + \gamma \qquad (1)$$

It has been found that these curves can be represented by Eq. (1), with $\alpha=500$ dyn/cm, $\beta=1.57$ dyn molec./cm Å^2, and $\gamma=856.53$ dyn/cm for the triolein monolayer, and with $\alpha=400$ dyn/cm, $\beta=1.290$ dyn molec./cm Å^2, and $\gamma=679.64$ dyn/cm for the tricaprylin monolayer, respectively. It has, therefore, been concluded that the monolayer of each component is in the state of the liquid expanded film. At the area below their collapse areas (shown by arrows), the surface pressure of monolayers of the pure components, triolein and tricaprylin, are kept constant, but those of their mixed monolayers increase with the decrease in the area.

Equilibrium Spreading Pressure and Collapse Pressure. The equilibrium spreading pressure was determined as the time-independent surface pressure exerted when a excess of a liquid mixture of triolein and tricaprylin was dropped onto the clean aqueous surface. In the case of the mixture of triolein and tricaprylin with the molar ratio of 1 : 2, for example, the surface pressure increased rapidly when a drop of the mixture was placed on the surface, thereafter reaching a constant value, as is shown in Fig. 2. Moreover, when the film in this state was compressed to some extent at the time shown by an arrow, the pressure increased slightly, but it returned immediately to its original value. This is the equilibrium spreading pressure, F_e, at the composition of the liquid mixture. Thus, the relation between the equilibrium spreading pressure and the mole fraction of tricaprylin, x_c^b, in the liquid mixture was obtained; it is shown in Fig. 3 by closed circles. The relation between the collapse pressure, F_c, obtained from Fig. 1 and the mole fraction of tricaprylin, x_c^s, in the mixed monolayer is also shown in Fig. 3 by open circles.

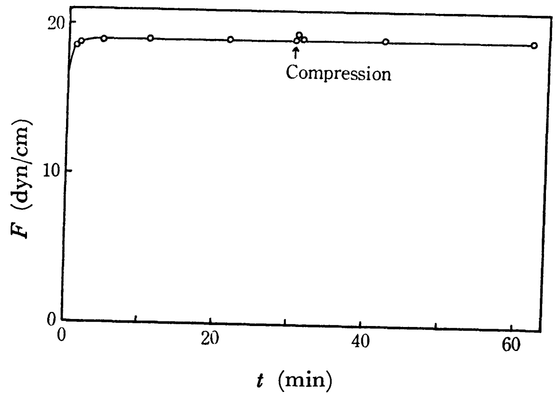


Fig. 2. The change of surface pressure with elapsed time in existence of the liquid mixture of triolein and tricaprylin (1 : 2).

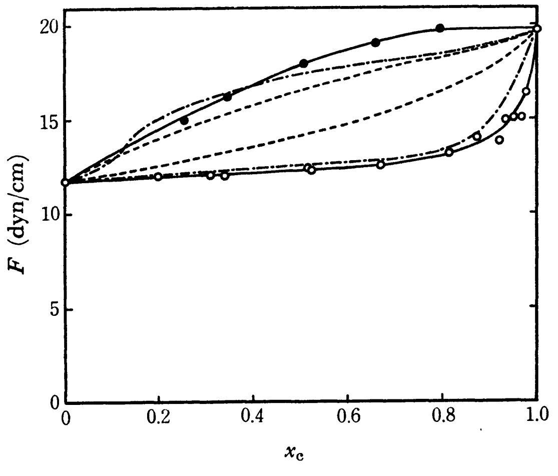


Fig. 3. Equilibrium spreading pressure and collapse pressure for the mixture system of triolein and tricaprylin.

●: $F_e - x_c^b$, ○: $F_c - x_c^s$.

--- Curve calculated from Eq. (10) and Eq. (11) with $B^b=B^s=0$. —·—·- Curve calculated from Eq. (10) and Eq. (11) with $B^b=0.78$ kcal/mol and $B^s=1.13$ kcal/mol.

For the monolayers of both the pure components, triolein and tricaprylin, the collapse pressure was in good agreement with the equilibrium spreading pressure. For mixtures, however, the equilibrium spreading pressure varied continuously with the composition of the liquid mixtures, while the collapse pressure also varied with the composition of the mixed monolayer. The two curves, $F_e - x_c^b$ and $F_c - x_c^s$, did not agreed with each other, suggesting that the compositions of the liquid droplet and the monolayer are different from each other.

Discussion

Equilibrium Spreading Pressure and Collapse Pressure. Figure 3 shows the relation between the composition of a liquid mixture and that of the mixed monolayer coexisting at a given surface pressure. If a horizontal line is drawn at a given surface pressure in Fig. 3, the intersections of this line with the curve of the equilibrium spreading pressure (drawn through closed circles) and with the curve of the collapse pressure (drawn through open circles) give the mole fractions of tricaprylin in the liquid mixture and the mixed monolayer respectively. Therefore, it is found that tricaprylin, whose equilibrium spreading pressure is higher, is richer in the mixed monolayer than in the liquid mixture, while triolein, whose equilibrium spreading pressure is lower, is richer in the liquid mixture than in the mixed monolayer.

The facts in Fig. 3 show that both the equilibrium spreading pressure and the collapse pressure vary continuously, meaning that these components are miscible both in a liquid and in a monolayer. This can be concluded from the following. According to the phase rule for a plane interface,[8] the number of degrees of freedom for the surface phase, ω, is given by the Eq. (2):

$$\omega = c - \varphi - (\psi - s) + 2 \qquad (2)$$

where c is the number of components, φ is the number of the bulk phases, ψ is the number of the interface phases, and s is the number of types of interfaces. When G, W and L designate air, water, and the liquid mixture of triolein and tricaprylin respectively, $c=4$, $\varphi=3$(G,W,L), $s=3$ (G/W, G/L, L/W), and $\psi=3$ (one phase at each interface). Then, ω is equal to the 3 from Eq. (2). As the temperature and pressure are constant under the experimental conditions used in this study, it may be concluded that one more freedom is left. Therefore, the surface pressure can be varied continuously while the compositions of the liquid mixture and the mixed monolayer are fixed for each value of the surface pressure. This is the case when triolein and tricaprylin are miscible both in a liquid and in a monolayer. On the other hand, when both components are immiscible in either the liquid state or the monolayer state, the equilibrium spreading pressure or the collapse pressure must take a constant value, independent of the composition of the liquid mixture or of the mixed monolayer. This has been described in detail in a previous paper.[5]

The Pressure-Area Curve of the Monolayer in Equilibrium with Liquid Droplets. The interrelation between the pressure-area curve (Fig. 1) and the curves of the equilibrium spreading pressure and collapse pressure (Fig. 3) is illustrated schematically in Fig. 4. The left figure (a) of Fig. 4 corresponds to Fig. 3, while the NKLMP and NHIJP curves represent the equilibrium spreading pressure and the collapse pressure respectively. The right figure (b) of Fig. 4 corresponds to Fig. 1, while the BCDE curve represents the pressure-area curve of the mixed monolayer, whose mole fraction is x_2. In Fig. 4(b), the relation between the collapse pressure, F_c, and the collapse area, A_c, is given by the chained line, which is so drawn that it passes through the kink-points indicated by arrows in Fig. 1.

When the mixed monolayer at the mole fraction of x_2 is compressed along the BC curve, the monoalyer starts collapsing at the C point. At this point, it may be seen from Fig. 4(a) that the mixed monolayer at the mole fraction of x_2 coexists with a trace of the liquid mixture at the mole fraction of x_2^{K}. If the surface pressure is now increased further, the concentration of the 2 component (more stable against collapse) in the monolayer is increased by separating the liquid mixture further. At a certain point, *e.g.*, D in Fig. 4(b), the mixed monolayer of the composition of x_2^{I} and the liquid mixture of the composition of x_2^{L} coexist at the molar ratio of $(x_2-x_2^{\mathrm{L}})$ to $(x_2^{\mathrm{I}}-x_2)$, as may easily be seen from Fig. 4(a). Finally, at the E point in Fig. 4(b), the liquid mixture of the composition of x_2 coexists with a trace of the mixed monolayer of the composition of x_2^{J}, as may be seen in Fig. 4(a). Since the area occupied by the liquid mixture is negligible, the mean molecular area at the E point, A^{E}, is obviously zero and the surface pressure in this state is the equilibrium spreading pressure of the liquid mixture whose composition is x_2.

Now, the CDE curve of Fig. 4(b) can be drawn theoretically as follows by calculating the area, A^{D}, corresponding to the point, D, at which the mixed monolayer of the surface pressure, F^{D}, coexists with the liquid mixture. The area actually occupied by one molecule in the monolayer is A^{G}, but only a fraction, $(x_2-x_2^{\mathrm{L}})/(x_2^{\mathrm{I}}-x_2^{\mathrm{L}})$, of the initially-spread molecules remains in the monolayer. Since the area occupied by the liquid deposit can be neglected, the area divided by the total number of initially-spread molecules, A^{D}, is given by the following Eq. (3):

$$A^{\mathrm{D}} = \frac{x_2-x_2^{\mathrm{L}}}{x_2^{\mathrm{I}}-x_2^{\mathrm{L}}}\times A^{\mathrm{G}} \tag{3}$$

The relation between the values of A^{D} calculated from Eq. (3) and various surface pressure values is shown by dotted lines in Fig. 1 as a function of the x_2 parameter, which is the mole fraction of the 2 component in the initially-spread monolayer. The calculated curves (dotted lines) are in good agreement with the curves obtained experimentally (solid lines).

Thermodynamic Treatment. The equilibrium between the mixed monolayer and the liquid mixture will be discussed here thermodynamically. Because the chemical potentials of the components, 1 and 2, in the liquid mixture are equal to those in the mixed monolayer in the equilibrium, the following two equations can be written according to Joos[9]:

$$\mu_1^{\mathrm{ob}} + kT\ln \gamma_1^{\mathrm{b}}x_1^{\mathrm{b}} = \mu_1^{\mathrm{os}} + kT\ln \gamma_1^{\mathrm{s}}x_1^{\mathrm{s}} + F\bar{A}_1 \tag{4}$$

$$\mu_2^{\mathrm{ob}} + kT\ln \gamma_2^{\mathrm{b}}x_2^{\mathrm{b}} = \mu_2^{\mathrm{os}} + kT\ln \gamma_2^{\mathrm{s}}x_2^{\mathrm{s}} + F\bar{A}_2 \tag{5}$$

where μ^0 is the standard chemical potential, γ is the activity coefficient, x is the mole fraction, and $\bar{A}$ is the partial molecular area. The superscripts, b and s, indicate the liquid mixture and the mixed monolayer respectively, while the subscripts, 1 and 2, indicate the components, 1 and 2 respectively. For one-component systems,

$$\mu_1^{\mathrm{ob}} = \mu_1^{\mathrm{os}} + F_{1\mathrm{c}}A_{1\mathrm{c}} \tag{6}$$

is derived for the 1 component from Eq. (4), with $x_1^{\mathrm{b}}=x_1^{\mathrm{s}}=1$, and $\gamma_1^{\mathrm{b}}=\gamma_1^{\mathrm{s}}=1$, while

$$\mu_2^{\mathrm{ob}} = \mu_2^{\mathrm{os}} + F_{2\mathrm{c}}A_{2\mathrm{c}} \tag{7}$$

is derived for the 2 component from Eq. (5). Assuming that the theory of regular solution applies to both the liquid mixture and the mixed monolayer, the activity coefficients can be replaced by using the following equations, which contain the B^{b} and B^{s} constants:

$$kT\ln \gamma_1^{\mathrm{b}} = B^{\mathrm{b}}(x_2^{\mathrm{b}})^2, \qquad kT\ln \gamma_1^{\mathrm{s}} = B^{\mathrm{s}}(x_2^{\mathrm{s}})^2 \tag{8}$$

$$kT\ln \gamma_2^{\mathrm{b}} = B^{\mathrm{b}}(x_1^{\mathrm{b}})^2, \qquad kT\ln \gamma_2^{\mathrm{s}} = B^{\mathrm{s}}(x_1^{\mathrm{s}})^2 \tag{9}$$

The substitution of these relations into Eqs. (4) and (5) yields:

$$kT\ln x_1^{\mathrm{b}} + B^{\mathrm{b}}(x_2^{\mathrm{b}})^2 + F_{1\mathrm{c}}A_{1\mathrm{c}} = kT\ln x_1^{\mathrm{s}} + B^{\mathrm{s}}(x_2^{\mathrm{s}})^2 + F\bar{A}_1 \tag{10}$$

and:

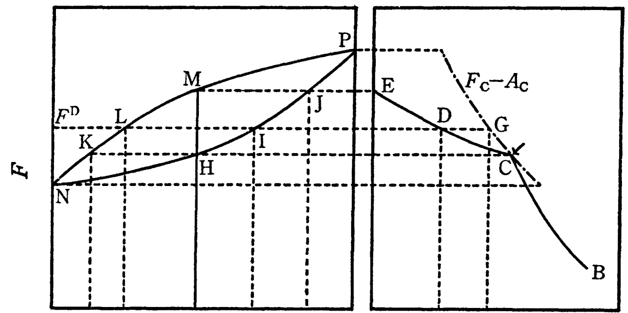
$$kT\ln x_2^{\mathrm{b}} + B^{\mathrm{b}}(x_1^{\mathrm{b}})^2 + F_{2\mathrm{c}}A_{2\mathrm{c}} = kT\ln x_2^{\mathrm{s}} + B^{\mathrm{s}}(x_1^{\mathrm{s}})^2 + F\bar{A}_2 \tag{11}$$

Therefore, the relation between x^{s} and x^{b} can be obtained by solving Eqs. (10) and (11) simultaneously, if the value of the partial molecular area, $\bar{A}$, is known as a function of the surface pressure, F, and if the values of the parameters, B, are assumed properly. If the values of the parameters, B^{b} and B^{s}, are assumed properly, the only unknown quantities in Eqs. (10) and (11) are x^{s} and x^{b} at a given surface pressure. The values of the partial molecular area, $\bar{A}$, should be obtained by drawing a tangent on the curve representing the relation between the mean area, A, and the mole fraction, x^{s}, of the monolayer at a given surface pressure. When A

was plotted against x^s on the basis of the data given in Fig. 1, a linear relationship between them was found to hold within the limits of experimental error. It was, therefore, concluded that the partial molecular area, $\bar{A}$, is equal to the molecular area of the pure component. For triolein, whose collapse pressure is relatively low, the following equation, previously presented, was used to obtain the value of the molecular area, by extrapolation, for a surface pressure higher than its collapse pressure:

$$F = -500 \log A + 1.547 A + 856.53. \qquad (12)$$

When both B^b and B^s are set equal to zero, the values of x^s and x^b, as calculated from Eqs. (10) and (11), are as shown by dotted lines in Fig. 3. In this case, $\gamma_1{}^s$, $\gamma_1{}^b$, $\gamma_2{}^s$, and $\gamma_2{}^b$ are all equal to one, according to Eqs. (8) and (9): their solutions are ideal both in the liquid mixture and in the mixed monolayer. They are considerably different from the experimental values. Next, when x^s and x^b are calculated from Eqs. (10) and (11) with B^b=0.78 kcal/mol and B^s=1.13 kcal/mol, the calculated results are as shown by chained lines in Fig. 3. These chained lines are fairly closed to the experimentally-found values. Therefore, it may be concluded that the mixture of triolein and tricaprylin can be treated like the regular solutions both in the liquid and in the monolayer states.



(a) (b)

Fig. 4(a). The curve of equilibrium spreading pressure, NKLMP, and the curve of collapse pressure, NHIJP.
(b). Pressure-area curve, BCDE.
—·—·— Collapse pressure-collapse area curve.

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