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The Formation and Collapse of Mixed Monolayers of 1-Hexadecanol and 1-Octadecanol with Interest in Evaporation Control of Water by Monolayers1)

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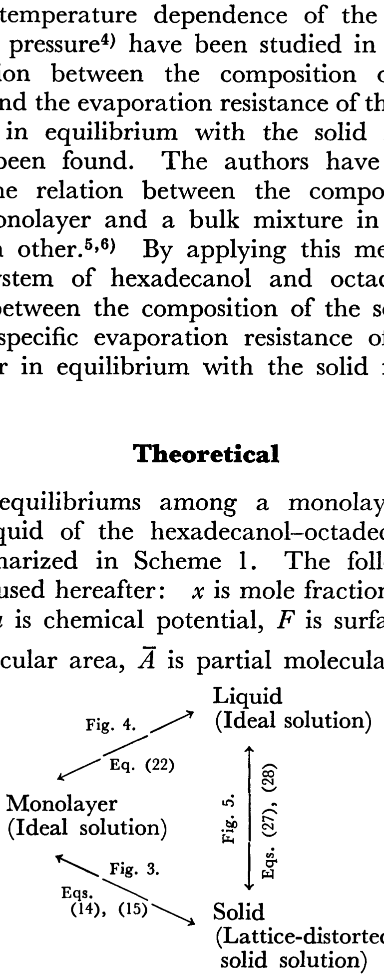
Collapse pressure, equilibrium spreading pressure, and melting points of binary mixtures of hexadecanol and octadecanol were measured in order to study the phase equilibrium among a monolayer, a solid, and a liquid and to apply the result to evaporation control of water by monolayers. Collapse pressure and equilibrium spreading pressure of solid mixtures have a maximum at a given composition, while the equilibrium spreading pressure of a liquid mixture has not a maximum. Melting points have a minimum at a given composition. From thermodynamic analysis of these phase equilibriums, it was concluded that the mixed monolayer and liquid mixture were ideal solutions, while the solid mixture was a lattice-distorted solid solution. That is, when the two components of different molecular volumes form a solid solution, the solid solution has high energy due to the distortion of the crystal lattice and consequently, it becomes easier to spread and the mixed monolayer becomes more stable against collapse. From these results, the relations between the composition of solid solution and the surface pressure, composition, and specific evaporation resistance of the mixed monolayer in equilibrium with the solid solution, were obtained.

It is said that a dusting of powdered solids of the mixed hexadecanol and octadecanol appears to meet best the purpose of the evaporation control of water by monolayers.2) Therefore, the effectiveness of lowering the evaporation rate by these mixed monolayers2,3) and the temperature dependence of the equilibrium spreading pressure4) have been studied in detail. But the relation between the composition of the solid mixture and the evaporation resistance of the monolayer which is in equilibrium with the solid mixture has not yet been found. The authors have shown how to get the relation between the compositions of a mixed monolayer and a bulk mixture in equilibrium with each other.5,6) By applying this method to the binary system of hexadecanol and octadecanol, the relation between the composition of the solid mixture and the specific evaporation resistance of the mixed monolayer in equilibrium with the solid mixture was obtained.

Theoretical

Phase equilibriums among a monolayer, a solid, and a liquid of the hexadecanol–octadecanol system are summarized in Scheme 1. The following notations are used hereafter: x is mole fraction, V is molal volume, μ is chemical potential, F is surface pressure, A is molecular area, $\bar{A}$ is partial molecular area, ΔH_v is molal heat of evaporation, ΔH_m is molal heat of fusion, and n is mole number; the subscripts 1 and 2 indicate the components 1 and 2, the subscripts e and m mean equilibrium and melting, the superscripts m, s, and l mean monolayer, solid, and liquid, and the superscript o means pure substance or standard state. R, T, and N are gas constant, absolute temperature, and Avogadro's number, respectively.



Scheme 1. Summarized relationship among three phases of a monolayer, a solid, and a liquid for the binary mixture of hexadecanol and octadecanol.

Equilibrium between a Monolayer and a Solid. It is known that the distortion energy of a crystal lattice due to the differences of size and shape of molecules contributes greatly to the heat of mixing of solids and, consequently, that it often makes the formation of a solid solution difficult.7) According to Scott,7,8) this distortion energy, ΔE_D, is given by the following equation:

$$\Delta E_\mathrm{D} = \frac{2\delta_1\delta_2(V_1V_2)^{1/2}(V_1-V_2)^2}{x_1^\mathrm{s}V_1^2+x_2^\mathrm{s}V_2^2}\,x_1^\mathrm{s}x_2^\mathrm{s}\,, \tag{1}$$

where δ is the solubility parameter:

$$\delta = \left(\frac{\Delta H_\mathrm{v}-RT}{V}\right)^{1/2}. \tag{2}$$

In order to simplify this equation, ω is defined as

$$\omega = 2\delta_1\delta_2(V_1V_2)^{1/2}(V_1-V_2)^2. \tag{3}$$

Assuming that the entropy of mixing ΔS and the enthalpy of mixing ΔH may be written as

$$\Delta S = -R(x_1^\mathrm{s}\ln x_1^\mathrm{s}+x_2^\mathrm{s}\ln x_2^\mathrm{s}) \tag{4}$$

and

$$\Delta H = \Delta E_\mathrm{D}\,, \tag{5}$$

and from the definitions of Gibbs free energy G and chemical potential μ:

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

and

$$\mu_1^\mathrm{s} - \mu_1^\mathrm{0s} = \left[\frac{\partial(n_1+n_2)\Delta G}{\partial n_1}\right]_{T,P,n_2}, \tag{7}$$

we obtain μ_1^s for component 1:

$$\mu_1^\mathrm{s} = \mu_1^\mathrm{0s} + RT\ln x_1^\mathrm{s} + \frac{\omega(x_2^\mathrm{s}V_2)^2}{(x_1^\mathrm{s}V_1^2+x_2^\mathrm{s}V_2^2)^2}. \tag{8}$$

Similarly, we obtain μ_2^s for component 2:

$$\mu_2^s = \mu_2^{0s} + RT\ln x_2^s + \frac{\omega(x_1^s V_1)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2}, \tag{9}$$

where μ^{os} is the chemical potential in the pure solid. Assuming that a mixed monolayer is considered as an ideal solution, in the equilibrium state of a monolayer and a solid, the following equations

$$\mu_1^{0s} + RT\ln x_1^s + \frac{\omega(x_2^s V_2)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} = \mu_1^{0m} + RT\ln x_1^m + NF\bar{A}_1 \tag{10}$$

and

$$\mu_2^{0s} + RT\ln x_2^s + \frac{\omega(x_1^s V_1)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} = \mu_2^{0m} + RT\ln x_2^m + NF\bar{A}_2 \tag{11}$$

can be established,[5,6] where μ^{om} is the standard chemical potential in the monolayer. For the one-component systems,

$$\mu_1^{0s} = \mu_1^{0m} + NF_{1e}A_{1e} \tag{12}$$

and

$$\mu_2^{0s} = \mu_2^{0m} + NF_{2e}A_{2e} \tag{13}$$

are derived from Eqs. (10) and (11). Substituting Eqs. (12) and (13) for Eqs. (10) and (11), we obtain the following equations:

$$RT\ln x_1^s + \frac{\omega(x_2^s V_2)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} + NF_{1e}A_{1e} = RT\ln x_1^m + NF\bar{A}_1 \tag{14}$$

and

$$RT\ln x_2^s + \frac{\omega(x_1^s V_1)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} + NF_{2e}A_{2e} = RT\ln x_2^m + NF\bar{A}_2. \tag{15}$$

Equilibrium between a Monolayer and a Liquid. Assuming that both the monolayer and the liquid are ideal solutions, in equilibrium with each other, the following equations

$$\mu_1^{01} + RT\ln x_1^1 = \mu_1^{0m} + RT\ln x_1^m + NF\bar{A}_1 \tag{16}$$

and

$$\mu_2^{01} + RT\ln x_2^1 = \mu_2^{0m} + RT\ln x_2^m + NF\bar{A}_2 \tag{17}$$

can be established.[5,6] For the one-component systems,

$$\mu_1^{01} = \mu_1^{0m} + NF_{1e}A_{1e} \tag{18}$$

and

$$\mu_2^{01} = \mu_2^{0m} + NF_{2e}A_{2e} \tag{19}$$

are derived from Eqs. (16) and (17). Substituting Eqs. (18) and (19) for Eqs. (16) and (17), we obtain the following equations:

$$RT\ln x_1^1 + NF_{1e}A_{1e} = RT\ln x_1^m + NF\bar{A}_1 \tag{20}$$

and

$$RT\ln x_2^1 + NF_{2e}A_{2e} = RT\ln x_2^m + NF\bar{A}_2. \tag{21}$$

Substituting Eqs. (20) and (21) for the following equation:

$$x_1^1 + x_2^1 = 1,$$

we obtain Eq. (22):

$$x_1^m e^{(F\bar{A}_1 - F_{1e}A_{1e}/kT)} + x_2^m e^{(F\bar{A}_2 - F_{2e}A_{2e}/kT)} = 1. \tag{22}$$

Equilibrium between a Solid and a Liquid. In the equilibrium state of a solid and a liquid, from Eqs. (10), (11), (16), and (17), we obtain Eqs. (23) and (24):

$$\mu_1^{0s} + RT\ln x_1^s + \frac{\omega(x_2^s V_2)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} = \mu_1^{01} + RT\ln x_1^1 \tag{23}$$

and

$$\mu_2^{0s} + RT\ln x_2^s + \frac{\omega(x_1^s V_1)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} = \mu_2^{01} + RT\ln x_2^1. \tag{24}$$

Assuming that ΔC_p is independent of temperature, the following equations

$$\mu_1^{01} - \mu_1^{0s} = \Delta H_{1m}\left(1 - \frac{T}{T_{1m}}\right) - \Delta C_{1p}(T_{1m} - T) + T\Delta C_{1p}\ln\frac{T_{1m}}{T} \tag{25}$$

and

$$\mu_2^{01} - \mu_2^{0s} = \Delta H_{2m}\left(1 - \frac{T}{T_{2m}}\right) - \Delta C_{2p}(T_{2m} - T) + T\Delta C_{2p}\ln\frac{T_{2m}}{T} \tag{26}$$

are derived for the one-component systems.[9] Substituting Eqs. (25) and (26) for Eqs. (23) and (24), we obtain Eqs. (27) and (28):

$$\Delta H_{1m}\left(1 - \frac{T}{T_{1m}}\right) - \Delta C_{1p}(T_{1m} - T) + T\Delta C_{1p}\ln\frac{T_{1m}}{T} + RT\ln x_1^1 = RT\ln x_1^s + \frac{\omega(x_2^s V_2)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2} \tag{27}$$

and

$$\Delta H_{2m}\left(1 - \frac{T}{T_{2m}}\right) - \Delta C_{2p}(T_{2m} - T) + T\Delta C_{2p}\ln\frac{T_{2m}}{T} + RT\ln x_2^1 = RT\ln x_2^s + \frac{\omega(x_1^s V_1)^2}{(x_1^s V_1^2 + x_2^s V_2^2)^2}, \tag{28}$$

where ΔC_p is the differences in the molal heat capacities between the liquid and the solid.

Experimental

Materials. The 1-hexadecanol and 1-octadecanol used are supplied by Nihon Yushi Company. The composition of hexadecanol (abbreviated as $C_{16}OH$) was $C_{18}OH$ 0.6%, $C_{16}OH$ 99.0%, and $C_{14}OH$ 0.4% and that of octadecanol was $C_{20}OH$ 1.0%, $C_{18}OH$ 98.7%, and $C_{16}OH$ 0.3%. The melting points of hexadecanol and octadecanol were 50.0—50.5 °C (literature value[10,11] 49.3 °C) and 58.5—59.0 °C (literature value[10] 58.0 °C), respectively. The solid mixture was prepared by the methods of fusion and solution (*n*-hexane as solvent; details have been reported previously[5,6]) and used later than one month after the preparation. The water and *n*-hexane of analytical grade used were distilled twice.

Measurement of Surface Pressure. The surface pressure was measured at 20±0.1 °C using a surface trough equipped with a vertical-type surface balance described previously.[5,6] The pressure-area curve was drawn by measuring the surface pressure of the monolayer which had been compressed at nearly constant speed independently of the area and the composition of mixed monolayers. The equilibrium spreading pressure was determined as an unvaried surface pressure exerted after the solid mixture (prepared by the solution method) had been placed onto the aqueous surface. Details

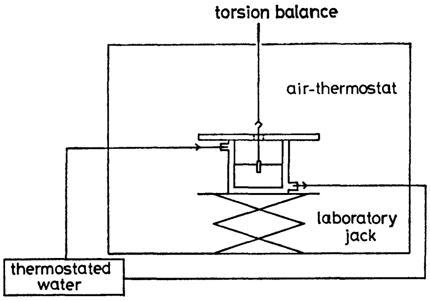


Fig. 1. The apparatus for measuring surface pressure at 65 °C.

have been described previously.[5,6]

The equilibrium spreading pressure at 65±0.2 °C was measured by means of the same surface balance in a thermostated glass cell (Fig. 1).

Measurement of Melting Points. The initial and final melting points of solid mixtures (prepared by the methods of solution and fusion) were measured with a Yanagimoto-melting point apparatus, SR-50, equipped with a polarization microscope.

Results

Collapse Pressure and Equilibrium Spreading Pressure. Figure 2 shows the pressure-area curve of a hexadecanol monolayer at 20 °C. The collapse pressure, F_c, was determined as the surface pressure unvaring with the area after the monolayer began to collapse. The collapse pressures of mixed monolayers of hexadecanol and octadecanol were likewise determined. The open circles in Fig. 3 show the relation between the collapse pressure and the mole fraction of hexadecanol in mixed monolayer, x^m_{16}. The closed circles in Fig. 3 show the relation between the equilibrium spreading pressure, F_e, and the mole fraction of hexadecanol in the solid mixture, x^s_{16}. The values of F_c and F_e have a maximum, at which F_c and F_e are 44.0 and x^m_{16} and x^s_{16} are 0.56 dyn/cm. The collapse pressure of hexadecanol, F_{16c}, was equal to the equilibrium spreading pressure, F_{16e}, while the collapse pressure of octadecanol, F_{18c}, was higher than the equilibrium spreading pressure, F_{18e}. This means that the octadecanol monolayer tends to be overcompressed. Therefore, it is suspected that the collapse pressure of octadecanol-rich mixed monolayer is also higher than the equilibrium value.

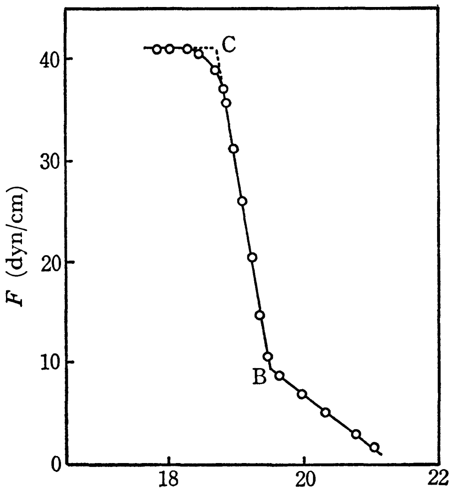


Fig. 2. The pressure-area curve of a hexadecanol monolayer at 20 °C.

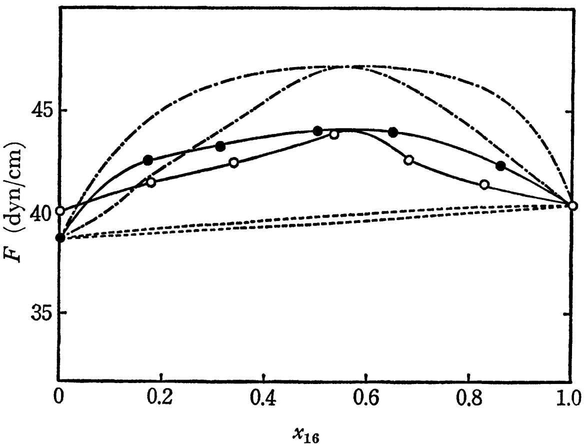


Fig. 3. Equilibrium spreading pressure and collapse pressure for the binary mixture of hexadecanol and octadecanol at 20 °C.
●: $F_e-x^s_{16}$, ○: $F_c-x^m_{16}$. —·— Curve calculated from the Eqs. (14) and (15). ---- Curve calculated from the Eqs. (32) and (33).

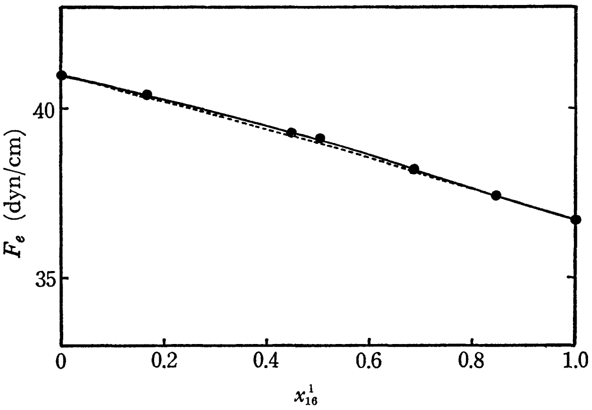


Fig. 4. Equilibrium spreading pressure for the binary system of hexadecanol and octadecanol at 65 °C.
●: $F_e-x^l_{16}$. ---- Curve calculated from the Eq. (22).

Since the value of the equilibrium spreading pressure varies greatly near the melting point,[4,11] the equilibrium spreading pressure of liquid was measured at 65 °C somewhat higher than the melting points of the mixtures. The closed circles in Fig. 4 show the relation between the equilibrium spreading pressure at 65 °C and the mole fraction of hexadecanol in the liquid mixture, x^l_{16}. In this case, it was found that the equilibrium spreading pressure did not have a maximum. The measurement of the collapse pressure at 65 °C was very hard because of the dissolution of the monolayers and the evaporation of the underlying water.

Phase Diagram of Solid-Liquid Equilibrium. The open and closed circles in Fig. 5 are initial and final

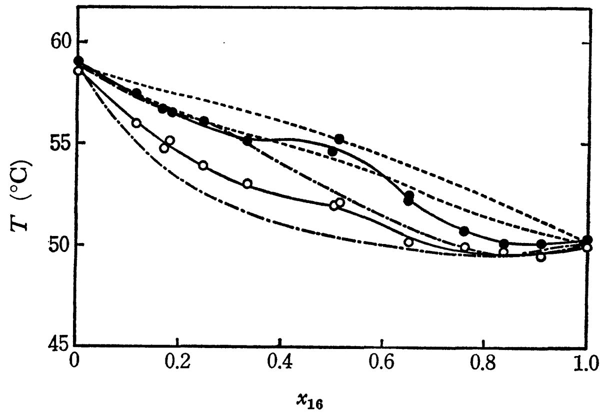


Fig. 5. The initial and final melting points for the binary system of hexadecanol and octadecanol.
○: Initial melting point, ●: final melting point.
—·— Curve calculated from the Eqs. (27) and (28).
----- Curve calculated from the Eqs. (27) and (28) with $\omega=0$.

melting points of the solid mixtures, respectively. It was found that mixtures of hexadecanol and octadecanol form a complete series of solid solutions and the melting points have a minimum near $x_{16}=0.84$.

Discussion

Phase Equilibriums among a Monolayer, a Solid, and a Liquid. Equilibrium between a Monolayer and a Solid: The numerical values of ΔH_v, V_1/V_2, F_e, A_e, and $\bar{A}$ are necessary for calculating x^m and x^s at a given surface pressure from Eqs. (14) and (15). From Figs. 2 and 3, we obtain $F_{16_e}=40.8$ dyn/cm, $F_{18_e}=38.7$ dyn/cm, $A_{16_e}=18.70$ Å^2/molec, and $A_{18_e}=18.76$ Å^2/molec. $\bar{A}$ was assumed to be equal to the molecular area, A, calculated from the state equation of the solid film using Fig. 2 (straight line BC):

$$A = -0.0265F + 19.78 \quad (\text{Å}^2/\text{molec}). \tag{29}$$

ΔH_v was calculated from the experimental results of Davies and Kybett:[12]

$$\Delta H_{16v} = 47.6 - 0.0642T \quad (\text{kcal/mol}) \tag{30}$$

and

$$\Delta H_{18v} = 52.8 - 0.0716T \quad (\text{kcal/mol}) \tag{31}$$

with $T=293.15$ K. For the ratio of molar volumes, V_{18}/V_{16}, 1.118, which is the value of supercooled liquid at 20 °C,[10] was used.

Substituting these numerical values and solving the simultaneous equation of Eqs. (14) and (15) numerically, we obtain x_{16}^m and x_{16}^s at a given surface pressure. These calculated results are shown by the chained lines in Fig. 3. In addition, assuming that the solid solution is ideal *viz.*, $\omega=0$, we obtain from Eqs. (14) and (15) the following equations:

$$x_1^m \, e^{(F\bar{A}_1-F_{1e}A_{1e})/kT} + x_2^m \, e^{(F\bar{A}_2-F_{2e}A_{2e})/kT} = 1 \tag{32}$$

and

$$x_1^s = x_1^m \, e^{(F\bar{A}_1-F_{1e}A_{1e})/kT}. \tag{33}$$

We can calculate x_{16}^m and x_{16}^s at a given surface pressure from Eqs. (32) and (33). These calculated results are shown by the dotted lines in Fig. 3. The values calculated as an ideal solid solution are very different from the experimental values, while the values calculated as a lattice-distorted solid solution explain the features of the experimental values well. It is, however, found that ΔE_D of Eq. (1) is slightly too large.

Equilibrium between a Monolayer and a Liquid: From the experimental results of Fig. 4, we obtain $F_{16_e}=36.7$ dyn/cm and $F_{18_e}=41.0$ dyn/cm. The values of A_{16_e}, A_{18_e}, $\bar{A}_{16}$, and $\bar{A}_{18}$ at 65 °C are set equal to 24.8 Å^2/molec, the value of which is extrapolated from the data of Boyd and Schubert.[11] Substituting these values in Eqs. (22) and (20), we can calculate x_{16}^m and x_{16}^l at a given surface pressure. This result is shown by the dotted line in Fig. 4 and is in close agreement with the experimental values.

Equilibrium between a Solid and a Liquid: T_{16_m} and T_{18_m} are 323.20 K and 331.70 K (our values). According to Davies,[12]

$$\Delta H_{16m} = 3.6 + 0.0316T \quad (\text{kcal/mol}),$$

$$\Delta H_{18m} = 5.7 + 0.0362T \quad (\text{kcal/mol}),$$

$$\Delta C_{16p} = 0.0316 \quad (\text{kcal/mol·deg}),$$

and

$$\Delta C_{18p} = 0.0362 \quad (\text{kcal/mol·deg}).$$

Substituting these values for Eqs. (27) and (28), we can solve these equations numerically as a simultaneous equation. These results are shown by the chained lines in Fig. 5. Moreover, the values which are calculated from Eqs. (27) and (28) with $\omega=0$, *viz.*, as ideal solid solution, are also shown by the dotted lines in Fig. 5. The experimental values are different from the dotted lines, while they have the same tendency as the chained lines. It is, however, found that ΔE_D of Eq. (1) is slightly too large.

From the above thermodynamic treatment of phase equilibriums among a monolayer, a solid, and a liquid for the binary system of hexadecanol and octadecanol, it is concluded that a monolayer and a liquid are ideal solutions and a solid is a lattice-distorted solution, as is shown in Scheme 1. In other words, when the two components consisting of different molecular volumes form a solid solutions, the solid solution has a high energy due to the distortion of the crystal lattice; consequently, it becomes easier to spread and easier to melt and the mixed monolayer becomes more stable against collapse. These are found from the comparison of the solid lines with the dotted lines in Figs. 3 and 5.

Application to Evaporation Control of Water by Monolayers. In view of the effectiveness of lowering evaporation rate, spreading rate, and economic reasons, it is said that dusting of powdered solids of the mixed hexadecanol and octadecanol appears to meet best the purpose of evaporation control of water by monolayers.[2]

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 hexadecanol in the solid solution and the mixed monolayer, respectively. Therefore, if the composition of the solid solution is given, the equilibrium spreading pressure and the composition of the mixed monolayer in equilibrium are determined.

The specific evaporation resistance of the mixed monolayer, representing the effectiveness of lowering evaporation rate, can be calculated as a function of the surface pressure and the composition of mixed monolayer from the following equations:[2,3]

$$\ln r = \frac{FA^{\neq}}{kT} + \frac{mE^{\neq}{}_{\mathrm{CH_2}}}{RT} + \text{constant} \qquad (34)$$

and

$$\ln r = x_1^{\mathrm{m}} \ln r_1 + x_2^{\mathrm{m}} \ln r_2 \,. \qquad (35)$$

Figure 6 shows the relation between the specific resistance and the mole fraction of hexadecanol in solid solution calculated from the data of Fig. 3, using Eqs. (34) and (35). The mixed monolayer tends to be slightly overcompressed in the region where the mole fraction of octadecanol is large. It seems likely that the dotted line through the open circles represents the relation between r and x_{16}^{s} at equilibrium. As the result, it may be concluded that the lowering of the evaporation rate of water is expected to be more effective when a solid mixture contains more octadecanol. It is also seen from Fig. 6 that the effect remains almost unchanged when the solid mixture is varied over the compositions between 0.3 and 0.7.

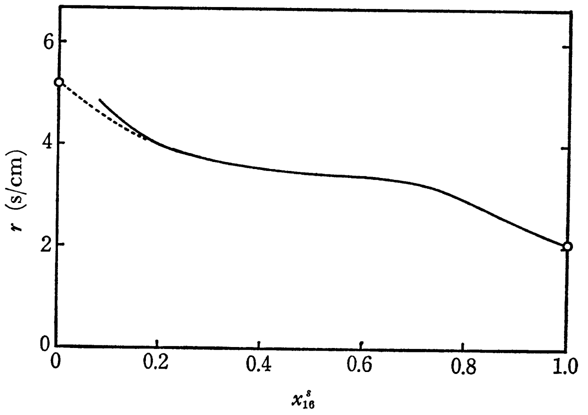


Fig. 6. The relation between the specific evaporation resistance and the mole fraction of hexadecanol in solid solution which is in equilibrium with the mixed monolayer of hexadecanol and octadecanol.

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