The Surface Tension of Aqueous Solutions Saturated with Triacetin-Tributyrin Mixtures

Noriaki FUNASAKI and Sakae HADA

Kyoto College of Pharmacy, Yamashina, Kyoto 607

(Received March 12, 1976)

The surface tension of aqueous solutions saturated with triacetin–tributyrin mixtures was measured in order to study the phase equilibria among an adsorbed monolayer (m), an aqueous solution (w), and an oily mixture (l). The variation in the surface tension, γ, of saturated aqueous solutions with an increase in the number of moles, m_t, of the added mixtures depended on the mole fractions, x_2, of tributyrin in the mixtures; the γ value remained unchanged in the case of $x_2=0.0027$, decreased in the case of $x_2>0.0027$, and increased in the case of $x_2<0.0027$. The results of the theoretical analysis of the γ *vs.* m_t curves gave the mole fractions, $x_2{}^1$, of tributyrin in the oily mixtures. The $x_2{}^1$ values thus evaluated agreed with those determined gas-chromatographically. It was found that all of the γ *vs.* $x_2{}^m$, γ *vs.* $x_2{}^1$, and γ *vs.* $x_2{}^w$ curves have a minimum, at which the γ values are identical and at which $x_2{}^m=x_2{}^1>x_2{}^w$. The characteristics of these curves were explained thermodynamically on the basis of the assumption that triacetin and tributyrin form a regular mixture in a monolayer as well as in a liquid.

The overcompression and the dissolution of a spread monolayer often make it impossible to study the equilibrium state between the spread monolayer and the bulk of the film-forming substance on an aqueous surface.[1–4] When a film-forming substance is soluble in the underlying water, the equilibria among the adsorbed monolayer, the bulk, and the saturated aqueous solution are easily established.

Hence, the present authors measured the surface tension of aqueous solutions saturated with triacetin–tributyrin mixtures and discussed thermodynamically the results of the adsorbed monolayer-bulk equilibrium in comparison with those of the spread monolayer-bulk equilibrium.[2–6]

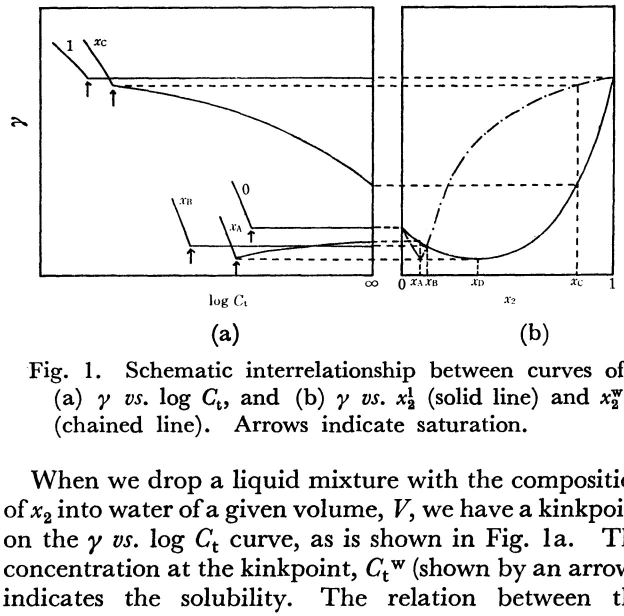
Theoretical

We consider a system composed of a liquid mixture of Component 1 and 2 (oily phase) and an aqueous solution (aqueous phase) in equilibrium with each other. The notations used hereafter are summarized in Table 1. The superscripts, w, l, and m mean the aqueous phase, the oily phase, and an adsorbed monolayer at the air-water interface. The superscript o means the pure substance or the standard state. The subscripts 1 and 2 mean triacetin and tributyrin, and the subscript t means the sum of the parts of triacetin and tributyrin.

TABLE 1. LIST OF NOTATIONS

γ: surface tension of an aqueous solution
F: surface pressure on an aqueous surface
V: total volume of water in the system
C: concentration of an aqueous solution
C_i^{ow}: solubility of a pure liquid, i, in water
Γ: adsorption amount at the air-water interface
$\bar{A}_i$: partial molecular area of Component i
μ_i: chemical potential of Component i
B: constant representing the intermolecular interaction
m: moles of triglyceride
R: gas constant
k: Boltzmann constant
T: absolute temperature
N: Avogadro number
$C_t=(m_1+m_2)/V$
$x_2{}^1=m_2{}^1/(m_1{}^1+m_2{}^1)$
$x_2{}^m=\Gamma_2/(\Gamma_1+\Gamma_2)$
$x_2{}^w=C_2{}^w/(C_1{}^w+C_2{}^w)$

Surface Tension of Saturated Aqueous Solutions. Although the following consideration is entirely general, we illustrate the γ *vs.* log C_t curves for triacetin–tributyrin mixtures in Fig. 1a. We consider the interrelation between the curves of γ *vs.* log C_t and γ *vs.* $x_2{}^1$ in the presence of both aqueous and oily phases.



(a) (b)

Fig. 1. Schematic interrelationship between curves of (a) γ *vs.* log C_t, and (b) γ *vs.* x_2^1 (solid line) and x_2^w (chained line). Arrows indicate saturation.

When we drop a liquid mixture with the composition of x_2 into water of a given volume, V, we have a kinkpoint on the γ *vs.* log C_t curve, as is shown in Fig. 1a. The concentration at the kinkpoint, $C_t{}^w$ (shown by an arrow), indicates the solubility. The relation between the surface tension and the mole fraction of Component 2 in the aqueous solution, $x_2{}^w$ (equal to the value of the dropped-in liquid mixture, x_2) at the kinkpoint is shown by a chained line in Fig. 1b. When we drop in an infinite amount of a liquid mixture, though, we can neglect the amount dissolved into the water. Thus, we can obtain the relation between the surface tension at $C_t \rightarrow \infty$ and the mole fraction of Component 2 in the oily phase, $x_2{}^1$ (equal to the value of the dropped-in liquid mixture, x_2), as is shown by a solid line in Fig. 1b. This relation can also be obtained through the simultaneous determination of the surface tension of the aqueous solution and the composition of the oily mixture in equilibrium with the former.

As is shown in Fig. 1a, the surface tension of the aqueous solution saturated with the pure substance, 1 (Curve 0) or 2 (Curve 1), remains unchanged regardless of the presence of an excess of the substance. In particular, the liquid mixture with the composition, x_B, at which the solid and chained lines in Fig. 1b intersect each other, behaves as if it were a pure substance in this respect (Curve x_B). On the other hand, as the dropped-in amount of a liquid mixture at $x_2 < x_B$ increases, the surface tension passes through a minimum (*e.g.*, Curve x_A). When a liquid mixture at $x_2 > x_B$ is dropped in, the surface tension gradually decreases with an increase in the C_t (*e.g.*, Curve x_C). In the case of mixtures, a variation in the surface tension of aqueous solutions with an increase in C_t results from the simultaneous variation of the compositions in the aqueous and oily phases.

We can obtain the relation between x_2^{w} and x_2^{l} at an equilibrium state from Fig. 1b. If a horizontal line is drawn at a given surface tension in Fig. 1b, the points of the intersection of this line with a solid and a chained line give the mole fractions of Component 2 in the oily and aqueous phases respectively. For example, it is found that the aqueous solution with the composition of x_A is in equilibrium with the oily mixture with the composition of x_D.

When we drop a mixture with the composition of x_2 into water above its solubility, we can calculate the γ *vs.* log C_t relation, using the experimental values of γ, C_1^{w}, and C_2^{w} of the aqueous solution in equilibrium with the oily mixture with the composition of x_2^{l}. The total moles of Components 1 and 2 can be given by the following equations:

$$C_t x_1 V = C_1^{w} V + m^{l} x_1^{l} \tag{1}$$

$$C_t x_2 V = C_2^{w} V + m^{l} x_2^{l} \tag{2}$$

Eliminating m^{l}, the total moles of the oily mixtures, from Eqs. 1 and 2, we obtain Eq. 3:

$$C_t = \frac{C_1^{w} x_2^{l} - C_2^{w} x_1^{l}}{x_1 x_2^{l} - x_2 x_1^{l}} \tag{3}$$

Using Eq. 3, we can calculate a C_t value at a given surface tension for the saturated aqueous solution.

Conversely, we can also obtain the expression for x_2^{l} from Eq. 3:

$$x_2^{l} = \frac{C_t x_2 - C_2^{w}}{C_t - C_1^{w} - C_2^{w}} \tag{4}$$

Hence, we can calculate an x_2^{l} value (the composition of the oily mixture) at a given surface tension from Eq. 4, using the γ *vs.* log C_t relation.

Equilibria among Aqueous, Oily, and Surface Phases. Assuming that triacetin and tributyrin form a regular solution in an oily mixture as well as in an adsorbed monolayer, and that they behave as a dilute solution in an aqueous solution, we can express the chemical potentials, μ_i, of Component i (i=1 or 2) in the oily mixture, the adsorbed monolayer, and the aqueous solution as follows:

$$\mu_i^{l} = \mu_i^{ol} + RT \ln x_i^{l} + B^{l}(1 - x_i^{l})^2 \tag{5}$$

$$\mu_i^{m} = \mu_i^{om} + RT \ln x_i^{m} + B^{m}(1 - x_i^{m})^2 + NF\bar{A}_i \tag{6}$$

$$\mu_i^{w} = \mu_i^{ow} + RT \ln C_i^{w} \tag{7}$$

where μ_i^{ol} is the chemical potential of the pure liquid, i; μ_i^{om} and μ_i^{ow} are the standard chemical potentials, and $\bar{A}_i$ is the partial molecular area of Component i. Equation 6 has also been used for a spread monolayer.[3-6)]

Equilibrium between Aqueous and Oily Phases. From the equality of the chemical potential in the phase equilibria, we can obtain:

$$\mu_1^{ow} + RT \ln C_1^{w} = \mu_1^{ol} + RT \ln x_1^{l} + B^{l}(x_2^{l})^2 \tag{8}$$

$$\mu_2^{ow} + RT \ln C_2^{w} = \mu_2^{ol} + RT \ln x_2^{l} + B^{l}(x_1^{l})^2 \tag{9}$$

using Eqs. 5 and 7. When x_i^{l} is equal to 1, we obtain from Eqs. 8 and 9:

$$\mu_1^{ow} + RT \ln C_1^{ow} = \mu_1^{ol} \tag{10}$$

$$\mu_2^{ow} + RT \ln C_2^{ow} = \mu_2^{ol} \tag{11}$$

where C_i^{ow} represents the solubility of the pure liquid, i, in water. Using Eqs. 8—11, we obtain Eqs. 12—14:

$$C_1^{w} = C_1^{ow} x_1^{l} \exp\left[\frac{B^{l}}{RT}(x_2^{l})^2\right] \tag{12}$$

$$C_2^{w} = C_2^{ow} x_2^{l} \exp\left[\frac{B^{l}}{RT}(x_1^{l})^2\right] \tag{13}$$

$$C_t^{w} = C_1^{ow} x_1^{l} \exp\left[\frac{B^{l}}{RT}(x_2^{l})^2\right] + C_2^{ow} x_2^{l} \exp\left[\frac{B^{l}}{RT}(x_1^{l})^2\right] \tag{14}$$

If the B^{l} value is assumed appropriately, we can calculate the C_t^{w} *vs.* x_2^{l} curve from Eq. 14, and also the C_t^{w} *vs.* x_2^{w} curve from Eqs. 12 and 13.

Equilibrium between Oily and Surface Phases. In the equilibrium state of the two phases, we can obtain from Eqs. 5 and 6 the following equations:

$$\mu_1^{ol} + RT \ln x_1^{l} + B^{l}(x_2^{l})^2 = \mu_1^{om} + RT \ln x_1^{m} + B^{m}(x_2^{m})^2 + NF\bar{A}_1 \tag{15}$$

$$\mu_2^{ol} + RT \ln x_2^{l} + B^{l}(x_1^{l})^2 = \mu_2^{om} + RT \ln x_2^{m} + B^{m}(x_1^{m})^2 + NF\bar{A}_2 \tag{16}$$

Using Eqs. 15 and 16, as has been shown previously,[5)] we can obtain the following equations:

$$x_1^{l} \exp\left[B^{l} \quad (x_2^{l})^2\right] = x_1^{m} \exp\left[\frac{B^{m}}{RT}(x_2^{m})^2 + \frac{F\bar{A}_1 - F_{1e}A_{1e}}{kT}\right] \tag{17}$$

$$x_2^{l} \exp\left[\frac{B^{l}}{RT}(x_1^{l})^2\right] = x_2^{m} \exp\left[\frac{B^{m}}{RT}(x_1^{m})^2 + \frac{F\bar{A}_2 - F_{2e}A_{2e}}{kT}\right] \tag{18}$$

where F_{ie} and A_{ie} are the surface pressure and the molecular area at the interface between the air and an aqueous solution saturated with a pure substance, i. We can obtain the F *vs.* x_i^{l} and F *vs.* x_i^{m} relations by solving Eqs. 17 and 18 simultaneously if the $\bar{A}$ value is found and if the B^{l} and B^{m} values are assumed appropriately.

Equilibrium between Aqueous and Surface Phases. We can calculate the F *vs.* x_i^{w} curve using Eqs. 12, 13, 17, and 18 if the B^{l} and B^{m} values are assumed appropriately.

Experimental

Materials. The triacetin and tributyrin used were obtained from Nakarai Chemicals.[7] The ion-exchanged water was twice distilled before use.

Measurement. A triacetin–tributyrin mixture was dropped into water of a given volume with a weight-pippete and the surface tension of the aqueous solution was measured at 37±0.2 °C by means of the Wilhelmy method.[7] The concentration, C, was expressed on a solute mole/water volume basis. When the amount of the oily mixture was relatively great, we measured the surface tension of the aqueous solution separated from the oily mixture.

The composition of the oily mixture separated from the aqueous solution was determined with a Shimadzu gas chromatograph, GC-3BT. The water content in the oily mixtures was found to be negligibly small.

Results

Figure 2 shows the plots of the surface tension of aqueous solutions, γ, against the logarithm of the total concentration, C_t, when a triacetin–tributyrin mixture with the composition of x_2 was dropped into the water. The kinkpoints (indicated by arrows) on the γ *vs.* log C_t curves indicate saturation.

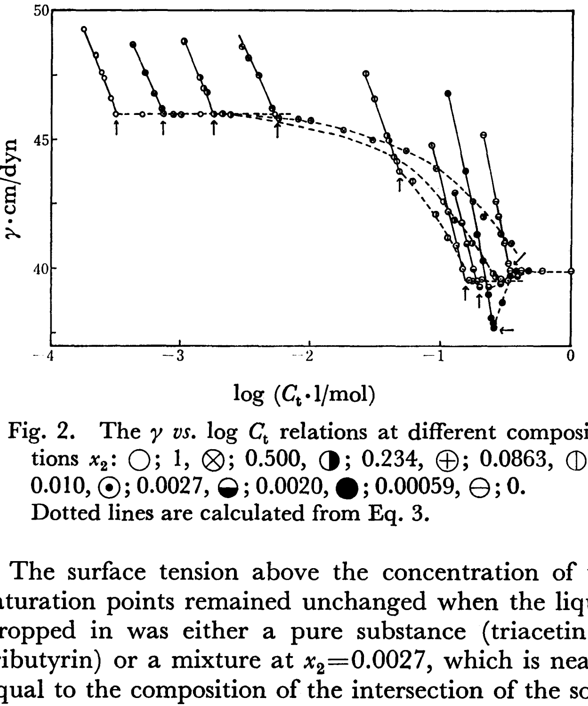


Fig. 2. The γ *vs.* log C_t relations at different compositions x_2: ○; 1, ⊗; 0.500, ◑; 0.234, ⊕; 0.0863, ⦶; 0.010, ⊙; 0.0027, ◒; 0.0020, ●; 0.00059, ⊖; 0.
Dotted lines are calculated from Eq. 3.

The surface tension above the concentration of the saturation points remained unchanged when the liquid dropped in was either a pure substance (triacetin or tributyrin) or a mixture at $x_2=0.0027$, which is nearly equal to the composition of the intersection of the solid lines in Fig. 4 to be described below. On the other hand, the γ value increased in the case of mixtures at $x_2<0.0027$, but decreased in the case of mixtures at $x_2>0.0027$, with an increase in the C_t.

Figure 3 shows the relation between the surface tension and the logarithm of the total concentration of triacetin, C_1, when triacetin was dropped into tributyrin solutions with the concentration of C_2. The kinkpoints (shown by arrows) indicate the saturation.

The open circles in Fig. 4 show the relation between the surface tension and the mole fraction of tributyrin in an aqueous solution, x_2^w. Furthermore, the closed circles in Fig. 4 show the relation between the surface tension of the aqueous solutions and the mole fraction of tributyrin in the oily phase (in equilibrium with the

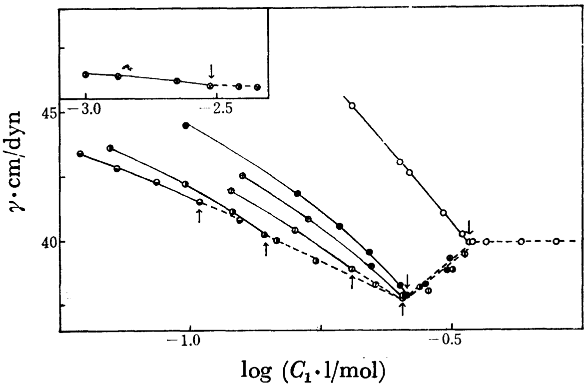


Fig. 3. The γ *vs.* log C_1 relations at different concentrations of tributyrin C_2 (mol/l) × 10^4: ⊗; 3.94, ◒; 3.31, ◑; 3.02, ⦶; 1.89, ⊕; 1.46, ●; 1.13, ○; 0.
Dotted lines are calculated from Eq. 22.

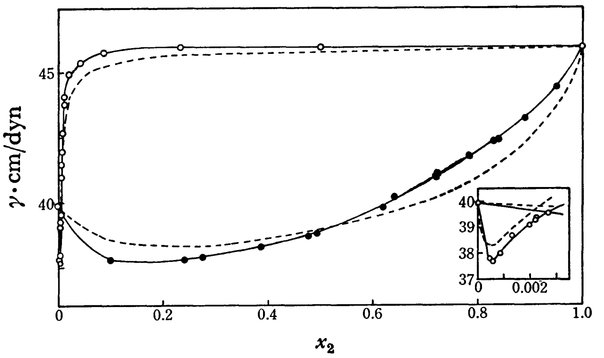


Fig. 4. The curves of γ *vs.* x_2^1 (closed circles) and γ *vs.* x_2^w (open circles) with partial expansion of tributyrin-poor region as an insert. Dotted lines are calculated from Eqs. 12, 13, 17, and 18 with $B^1=0.5RT$ and $B^m=-1.9RT$.

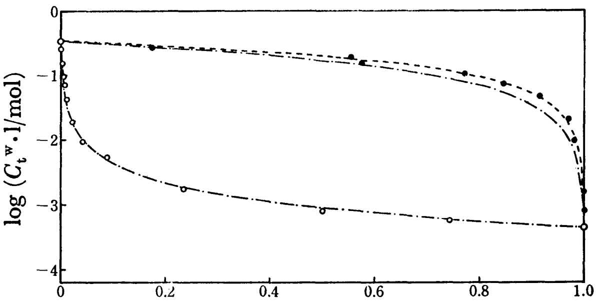


Fig. 5. The plots of log C_t^w *vs.* x_2^w (open circles) and *vs.* x_2^1 (closed circles). Chained and dotted lines are calculated from Eqs. 12—14 with $B^1=0$ and $B^1=0.5RT$.

former), x_2^1, which was determined gas-chromatographically.

The open circles in Fig. 5 show the log C_t^w *vs.* x_2^w relation obtained from the kinkpoints (indicated by arrows) in Figs. 2 and 3. In addition, the closed circles in Fig. 5 show the log C_t^w *vs.* x_2^1 curve determined from the x_2^1 *vs.* x_2^w relation, which was obtained from the intersections of the horizontal line with the γ *vs.* x_2^w and γ *vs.* x_2^1 curves in Fig. 4.

We can write the Gibbs adsorption equation in aqueous solutions of Components 1 and 2 as:[8)]

$$-\mathrm{d}\gamma = \Gamma_1 RT \,\mathrm{dln}\, C_1^{\mathrm{w}} + \Gamma_2 RT \,\mathrm{dln}\, C_2^{\mathrm{w}} \tag{19}$$

In the case of a constant $C_1^{\mathrm{w}}/C_2^{\mathrm{w}}$ ratio, Eq. 19 is reduced to:

$$-\mathrm{d}\gamma = (\Gamma_1+\Gamma_2) RT \,\mathrm{dln}\, C_{\mathrm{t}}^{\mathrm{w}} \tag{20}$$

Hence, we can obtain the γ *vs.* $(\Gamma_1+\Gamma_2)$ relation for the adsorbed monolayers in equilibrium with oily mixtures; the respective values of γ and $(\Gamma_1+\Gamma_2)$ are evaluated at the kinkpoints in Fig. 2.

On the other hand, in the case of a constant C_2^{w}, Eq. 19 is reduced to:

$$-\mathrm{d}\gamma = \Gamma_1 RT \,\mathrm{dln}\, C_1^{\mathrm{w}} \tag{21}$$

Hence, we can obtain the γ *vs.* Γ_1 relation for the adsorbed monolayers in equilibrium with oily mixtures; the respective values of γ and Γ_1 are evaluated at the kinkpoints in Fig. 3.

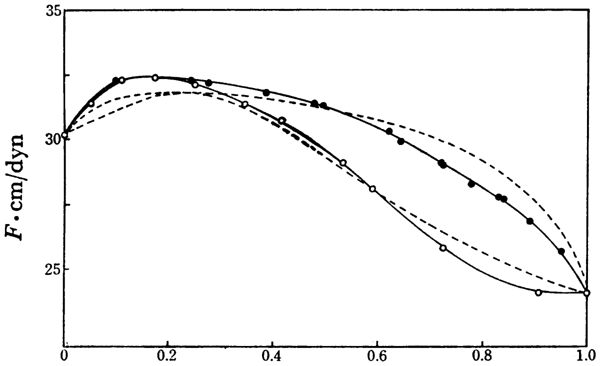


Fig. 6. The plots of F *vs.* x_2^1 (closed circles) and *vs.* x_2^{m} (open circles). Dotted lines are calculated from Eqs. 17 and 18 with $B^1=0.5RT$ and $B^{\mathrm{m}}=-1.9RT$.

Thus, we can obtain the relation between the surface pressure, F, and the mole fraction, x_2^{m}, of tributyrin in an adsorbed monolayer from the combination of the γ *vs.* $(\Gamma_1+\Gamma_2)$ and γ *vs.* Γ_1 relations. This result, shown by open circles in Fig. 6, is found to be similar to that for the spread mixed monolayers of 1-hexadecanol and 1-octadecanol.[4)] The upper and lower curves in Fig. 6 correspond to the curves of the equilibrium-spreading pressure and the collapse pressure respectively.

Discussion

Surface Tensions of Saturated Aqueous Solutions. We can calculate a C_{t} value by substituting into Eq. 3 the values of C_1^{w} and $C_2^{\circ\mathrm{w}}$ (determined from the kinkpoints in Figs. 2 and 3) and x_2^1 (obtained from the upper solid curve in Fig. 6) at a given surface tension when a liquid mixture with the composition of x_2 is dropped in and when the aqueous and oily phases coexist in equilibrium. The γ *vs.* log C_{t} curves thus obtained are shown by dotted lines in Fig. 2. Similarly, when we drop triacetin into a tributyrin solution with the concentration of C_2, we can calculate the C_1 value by means of the following equation:

$$C_1 = C_1^{\mathrm{w}} + \frac{(C_2-C_2^{\mathrm{w}})}{x_2^1} \times x_1^1 \tag{22}$$

Here, the experimental values of C_1^{w}, C_2^{w}, and x_2^1 at a given surface tension are substituted into Eq. 22. The γ *vs.* log C_1 curves thus obtained are shown by dotted lines in Fig. 3. The dotted lines in Figs. 2 and 3 were found to be in good agreement with the experimental results.

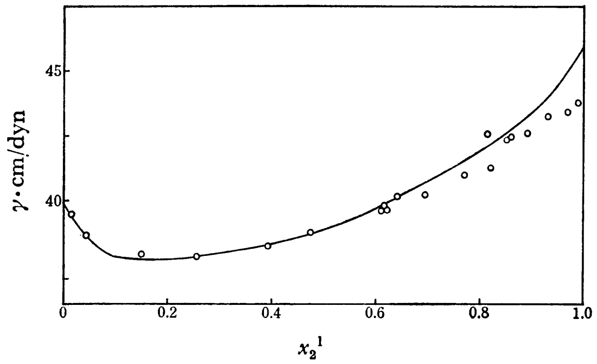


Fig. 7. The γ *vs.* x_2^1 relation in which a solid line is etermined gas-chromatographically and open circles are calculated from Eq. 4.

Conversely, we can calculate an x_2^1 value at a given surface tension by using Eq. 4 and the experimental results of the γ *vs.* log C_{t} curves in Fig. 2. The results thus calculated are plotted by open circles in Fig. 7. The solid line is drawn through the x_2^1 values determined gas-chromatographically. Thus, it was found that we can evaluate the composition of oily mixtures from the concentration dependence of the surface tension of aqueous solutions saturated with oily mixtures.

Equilibria among Aqueous, Oily, and Surface Phases. Assuming that $B^1=0.5RT$, we can calculate the log $C_{\mathrm{t}}^{\mathrm{w}}$ *vs.* x_2^{w} (lower curve) and log $C_{\mathrm{t}}^{\mathrm{w}}$ *vs.* x_2^1 (upper curve) relations from Eqs. 12—14. These relations, shown by dotted lines in Fig. 5, agree well with the experimental results. The chained lines in Fig. 5 show the relations calculated from Eqs. 12—14 with $B^1=0$, *viz.*, as an ideal solution in the oily mixture. It should be noted that the B^1 value has little effect on the log $C_{\mathrm{t}}^{\mathrm{w}}$ *vs.* x_2^{w} relation.

Furthermore, assuming that $B^1=0.5RT$ and $B^{\mathrm{m}}=-1.9RT$, we can calculate the F *vs.* x_2^{m} (lower curve) and F *vs.* x_2^1 (upper curve) relations from Eqs. 17 and 18. These relations are shown by dotted lines in Fig. 6. In the above calculation, we used the values of $F_{1\mathrm{e}}=30.19$ dyn/cm, $F_{2\mathrm{e}}=24.12$ dyn/cm, $A_{1\mathrm{e}}=41.6$ Å²/molec, $A_{2\mathrm{e}}=81.3$ Å²/molec, $C_1^{\circ\mathrm{w}}=0.343$ mol/l, and $C_2^{\circ\mathrm{w}}=4.41\times10^{-4}$ mol/l and assumed that the $\bar{A}$ value is equal to the molecular area in an adsorbed monolayer of the pure substance.

The dotted lines in Fig. 4 are reproduced from the dotted lines in Figs. 5 and 6.

The dotted lines in Figs. 4, 5, and 6 represent fairly well the trend of the experimental results; this means that the above thermodynamic treatment is approximately valid.

References

1) G. L. Gaines, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces," Interscience Publishers, New York (1966), pp. 144—155.

2) M. Nakagaki, N. Funasaki, and K. Fujita, *Nippon Kagaku Zasshi*, **93**, 243 (1972).

3) M. Nakagaki and N. Funasaki, *Bull. Chem. Soc., Jpn.*, **47**, 2094 (1974).

4) N. Funasaki and M. Nakagaki, *Bull. Chem. Soc. Jpn.*, **48**, 2727 (1975).

5) M. Nakagaki and N. Funasaki, *Bull. Chem. Soc. Jpn.*, **47**, 2482 (1974).

6) N. Funasaki, *Nippon Kagaku Kaishi*, **1975**, 1841.

7) N. Funasaki, S. Hada, and K. Suzuki, *Chem. Pharm. Bull.*, **24**, 731 (1976).

8) R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, "Surface Tension and Adsorption," Longmans, London (1966), p. 86.