Thermodynamic Study on the Adsorption of 1-Octadecanol at Hexane/Water Interface

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The interfacial tension γ between water and hexane solution of 1-octadecanol has been measured as functions of temperature T, pressure p, and mole fraction of 1-octadecanol in hexane x_1^0 by the pendant drop method. The curves of γ *vs.* T, γ *vs.* p, and γ *vs.* x_1^0 show noticeable break points. Calculated thermodynamic quantities such as energy changes, entropy changes, and volume changes associated with the adsorption show the points of discontinuity at a certain temperature, pressure, and composition, corresponding to the above breaking points. It has been clarified that the first order phase transition between the expanded and condensed states takes place at the interface like that of monomolecular films spread on water surfaces. The expanded state is characterized by a relatively high energy, high entropy, and large volume, while the condensed state by low energy, low entropy, and small volume.

In a previous paper, the structure and properties of adsorbed films of 1-tetradecanol at the hexane/water interface were clarified by applying the thermodynamic treatment developed previously.[1,2] As an extension of the work, the adsorbed films of 1-octadecanol at the same interface was studied, and it was expected that a longer chain alcohol exhibits a phase transition from an analogy with the insoluble monolayer spread on water surface. There has been little data to suggest the phase transition at the liquid/liquid interface, and, in particular, the analysis appears to be insufficiently rigorous thermodynamically.[4–10] The major purpose of this work was to confirm that the phase transition really takes place in the adsorbed film and to clarify the type of the phase transition thermodynamically.

Experimental

1-Octadecanol used was purified by distillation and the purity checked by gas-liquid chromatography; only one peak was obtained. Water distilled three times from $KMnO_4$ solution was used as the aqueous phase. Hexane was dehydrated and the impurities removed by passing hexane through an activated alumina column. Interfacial tension measurements were performed by the pendant drop method, the detailed descriptions of which have been previously reported.[2,3]

Results

To calculate the entropy change Δs, the volume change Δv of the interface formation, and the interfacial density of 1-octadecanol Γ_1^H, data of the variations of interfacial tension with temperature T, pressure p, and mole fraction of 1-octadecanol in hexane x_1^0 are required. The interfacial tension was measured at 293.15, 295.65, 298.15, 300.65, and 303.15 K over the pressure range from 0.1 to 150 MPa, and concentration up to 2.3×10^{-3} mol fraction. In Figs. 1 and 2 the interfacial tension is plotted against the pressure at constant concentration and at constant temperature, 303.15 and 298.15 K. It is seen that the interfacial tension increases linearly with increasing pressure at low concentration, like the case of the 1-tetradecanol solution.[2] At an intermediate concentration, however, it decreases abruptly at a certain pressure which is dependent on the concentration of 1-octadecanol in hexane. The broken lines in Figs. 1 and 2 are obtained by connecting these break points. This behavior was not observed for 1-tetradecanol over the same range of temperature, pressure, and concentration.[2] At a high concentration, the interfacial tension decreases with the increase in pressure up to a point at which the crystallization of 1-octadecanol solution starts. It is clearly demonstrated in the Figures that the break point is affected by temperature. Figure 3 showes the variation of interfacial tension γ with temperature T at constant concentration, and pressure of 0.1 MPa. At low concentration a linear relation is obtained between γ and T and the slope varies from negative to positive with the increase in concentration in a similar manner to that of 1-tetradecanol. At high concentration, however, the γ *vs.* T curve has a break point. It is found that the decrease in

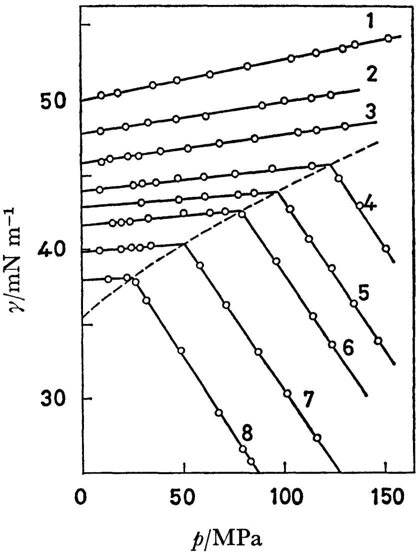

Fig. 1. Interfacial tension *vs.* pressure curves at constant mole fraction of octadecanol in hexane at 303.15 K. 1: $x_1^0=0$, 2: 1.04×10^{-4}, 3: 3.08×10^{-4}, 4: 6.31×10^{-4}, 5: 8.82×10^{-4}, 6: 1.08×10^{-3}, 7: 1.60×10^{-3}, 8: 2.38×10^{-3}.

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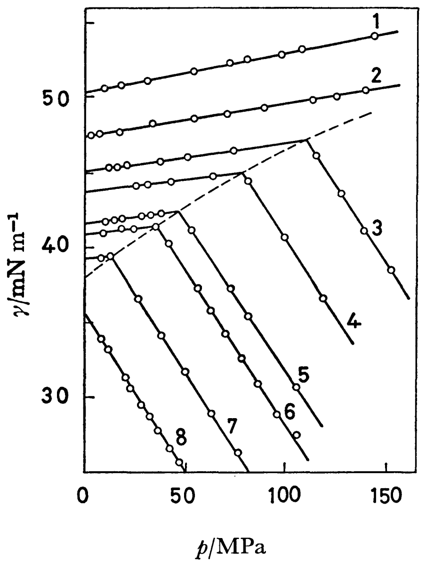

Fig. 2. Interfacial tension *vs.* pressure curves at constant concentration at 298.15 K. 1: $x_1^0=0$, 2: 1.46×10^{-4}, 3: 4.16×10^{-4}, 4: 6.18×10^{-4}, 5: 9.49×10^{-4}, 6: 1.13×10^{-3}, 7: 1.58×10^{-3}, 8: 2.21×10^{-3}.

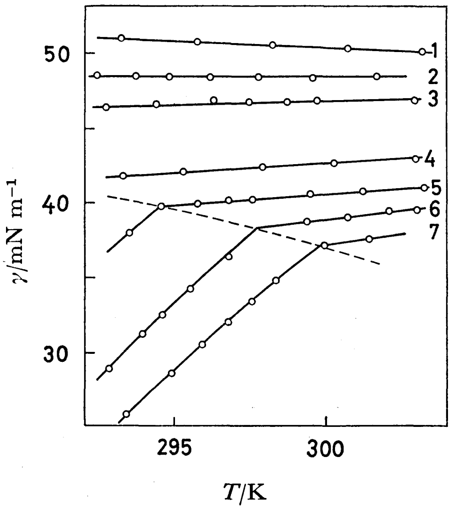

Fig. 3. Interfacial tension *vs.* temperature curves at constant concentration under 0.1 MPa. 1: $x_1^0=0$; 2: 1.33×10^{-4}, 3: 2.55×10^{-4}, 4: 8.05×10^{-4}, 5: 1.26×10^{-3}, 6: 1.68×10^{-3}, 7: 2.32×10^{-3}.

temperature and increase in concentration gives rise to the break in the curve. At any pressure similar figures as that in Fig. 3 can be drawn with the aid of the above γ *vs.* p curves. No striking difference was observed, but the temperature of the break point increase with the increase in pressure.

The interfacial tension γ can be plotted as a function of the concentration x_1^0 of 1-octadecanol in hexane at any temperature and pressure. In order to show that the break points in the γ *vs.* p curves clearly reflect those in the γ *vs.* x_1^0 curves, the behavior is illustrated in Fig. 4 at the temperatures of 293.15, 298.15, and 303.15 K at a constant pressure of 80 MPa.

At 0.1 MPa, the γ *vs.* x_1^0 curve breaks only at low temperature, and at 150 MPa, it breaks in a lower concentration range. It seems appropriate to show the behavior of the break point in figures at 80 MPa, and in the following section the data at 80 MPa will be used for the thermodynamic discussion.

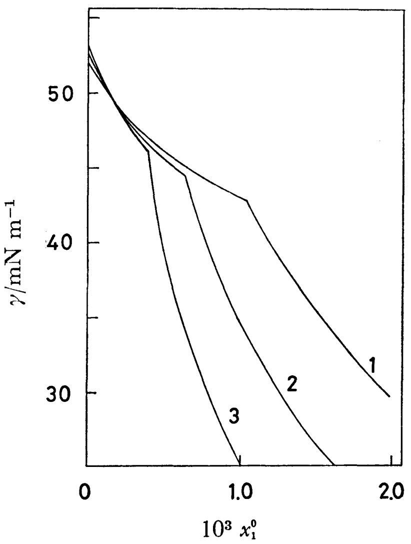

Fig. 4. Interfacial tension *vs.* concentration curves at constant temperature under 80 MPa. 1: 303.15 K, 2: 298.15 K, 3: 293.15 K.

Discussion

Over the range of experimental conditions, the interfacial tension varies almost linearly with temperature and pressure, apart from the characteristic break points observed. It is conceivable that the phase transition in the interfacial film causes an abrupt change in the curves. Lutton *et al.*[8] also observed that the γ *vs.* T curve exhibits a break point for the system of triglyceride oil solutions of propylene glycol monoester and monoglyceride and water. They suggested that the behavior observed could be accounted for in terms of a melting of the surfactant monolayer adsorbed at the interface. Hutchinson[4-6] studied the adsorption of myristic acid at the cyclohexane/water interface and observed that the interfacial pressure *vs.* area per molecule curve displayed a transition. He assumed that the transition takes place between the liquid expanded and the liquid condensed films. A similar observation for 1-octadecanol in the cyclohexane/mercury system was made by Ambawani *et al.*[9] In order to understand the mechanism, it is necessary to analyze the experimental results thermodynamically.

For the system under consideration, it may be assumed that the mutual solubility of hexane and water is in fact negligible and 1-octadecanol is soluble only in hexane. In comformity with this view, the thermodynamic treatment applied to the adsorption of 1-tetradecanol at the hexane/water interface is applied in this study.[2] Since the measurements were made on the solution of solute mole fraction below 2.3×10^{-3}, the solution was regarded as an ideal one. The interfacial density of 1-octadecanol is given by the equation

$$\Gamma_1^{\mathrm{H}} = -(x_1^0/RT)(\partial\gamma/\partial x_1^0)_{T,p}\,. \qquad (1)$$

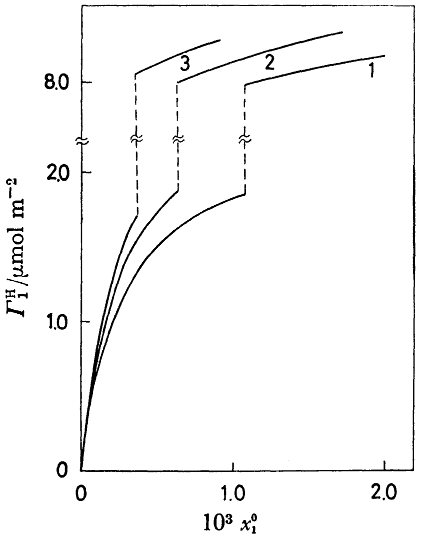

Fig. 5. Interfacial density *vs.* concentration curves at constant temperature under 80 MPa. 1: 303.15 K, 2: 298.15 K, 3: 293.15 K.

Figure 5 shows Γ_1^H as a function of x_1^0 at various temperatures and at 80 MPa. The discontinuous change on the Γ_1^H *vs.* x_1^0 curve indicate a phase transition in the adsorbed film of 1-octadecanol.

To further elucidate the adsorption, the relationships between the interfacial pressure π and the area per molecule A are given in Fig. 6 at three temperatures at 80 MPa, and in Fig. 7 at four pressures at 303.15 K. The isothermal and isobaric π *vs.* A curves show typical phase transition between the expanded and condensed films. Further, the intermediate region between both states become narrow with increasing temperature at constant pressure or with decreasing pressure at constant temperature. This behavior is comparable with that of the myristic acid monomolecular film spread at the air/water interface.[11]

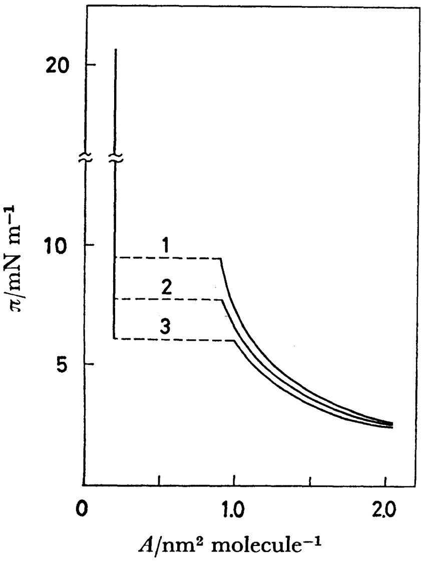

Fig. 6. Interfacial pressure *vs.* area curves at constant temperature under 80 MPa. 1: 303.15 K, 2: 298.15 K, 3: 293.15 K.

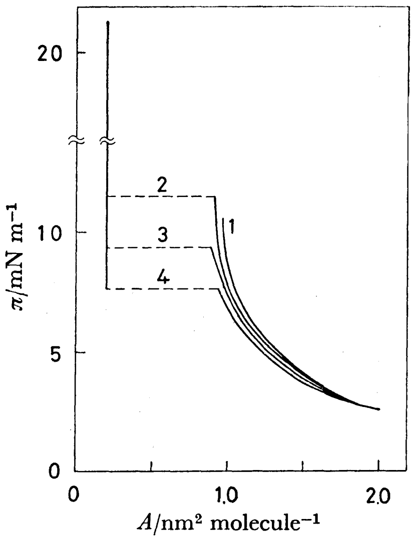

Fig. 7. Interfacial pressure *vs.* area curves at constant pressure at 303.15 K. 1: 0.1 MPa, 2: 40 MPa, 3: 80 MPa, 4: 120 MPa.

Entropy and volume changes of interface formation are given by the equations

$$\Delta s = -(\partial\gamma/\partial T)_{p,x_1^0} \tag{2}$$

and

$$\Delta v = (\partial\gamma/\partial p)_{T,x_1^0}. \tag{3}$$

In Figs. 8 and 9, the values of Δs and Δv are plotted as functions of concentration at 293.15, 298.15, and 303.15 K and at a constant pressure 80 MPa. In the expanded state, Δs and Δv are independent of temperature and pressure within the precision of the observations. Both the positive values of Δs and Δv for the system of pure hexane and water indicate that the contact between hexane and water causes increases in entropy and volume. With increasing concentration both values decreases gradually. This means that the adsorption of 1-octadecanol at the interface makes a negative contribution to Δs and Δv and that the partial molar entropy and volume of the adsorption are negative, as in the case of

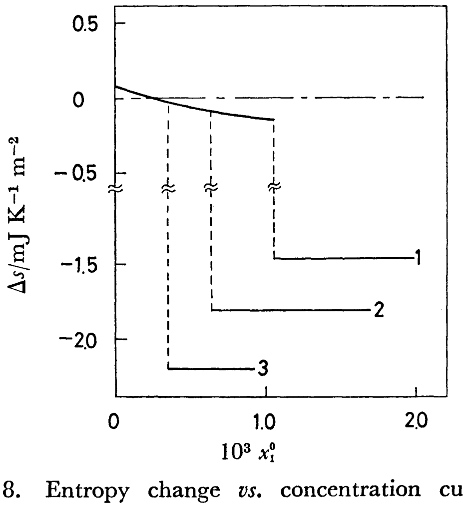

Fig. 8. Entropy change *vs.* concentration curves at constant temperature under 80 MPa. 1: 303.15 K, 2: 298.15 K, 3: 293.15 K.

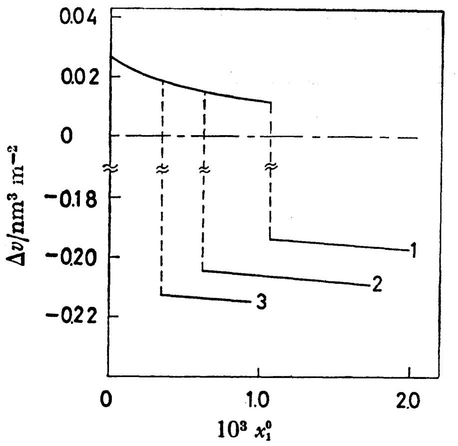

Fig. 9. Volume change *vs.* concentration curves at constant temperature under 80 MPa. 1: 303.15 K, 2: 298.15 K, 3: 293.15 K.

1-tetradecanol. In the condensed state, on the other hand, it is apparent that both Δs and Δv are dependent on temperature and are characterized by remarkably negative values.

The striking discontinuities in the Δs *vs.* x_1^0 and Δv *vs.* x_1^0 curves indicate that the break points in the γ *vs.* T and γ *vs.* p curves are the first order phase transition points, and at these points the expanded and condensed films coexist. With reference then to the gas-liquid equilibrium, the expanded state is favored by relatively high entropy and large volume and the condensed state by low entropy and small volume. Thus the increase in pressure and the decrease in temperature favor the condensed state.

It has been known that the differentials of interfacial tension in the condensed and expanded phases are expressed respectively as

$$\mathrm{d}\gamma = -\Delta s^c \mathrm{d}T + \Delta v^c \mathrm{d}p - \Gamma_1^{\mathrm{H}.c}(\partial\mu/\partial x_1^0)\mathrm{d}x_1^0 \tag{4}$$

and

$$\mathrm{d}\gamma = -\Delta s^e \mathrm{d}T + \Delta v^e \mathrm{d}p - \Gamma_1^{\mathrm{H}.e}(\partial\mu/\partial x_1^0)\mathrm{d}x_1^0, \tag{5}$$

where the condensed and expanded states are denoted by the superscript *c* and *e*, respectively. From these equations, it may be seen that

$$(\partial\gamma^{\mathrm{eq}}/\partial T)_p = -(\Delta s^c/\Gamma_1^{\mathrm{H}.c} - \Delta s^e/\Gamma_1^{\mathrm{H}.e})/(1/\Gamma_1^{\mathrm{H}.c} - 1/\Gamma_1^{\mathrm{H}.e}) \tag{6}$$

and

$$(\partial\gamma^{\mathrm{eq}}/\partial p)_T = (\Delta v^c/\Gamma_1^{\mathrm{H}.c} - \Delta v^e/\Gamma_1^{\mathrm{H}.e})/(1/\Gamma_1^{\mathrm{H}.c} - 1/\Gamma_1^{\mathrm{H}.e}). \tag{7}$$

The left-hand sides of these equations can be easily obtained as the slopes of the broken lines of Figs. 2 and 3, and the right-hand side may be calculated by the quantities derived above. The values of both sides of Eq. 6 at 298.15 K and at 80 MPa are 0.37 and 0.45 mJ K^{-1} m^{-2}, and those of Eq. 7 are 0.71 and 0.81 mm^3 m^{-2}, respectively. Taking into account the precision of the right hand sides of equations, the agreement is not unsatisfactory. Then this fact supports that the phase transition in the adsorbed film of 1-octadecanol is the first order phase transition.

The energy change associated with the adsorption may be obtained at any temperature, pressure, and composition with the aid of the relation

$$\Delta u = \gamma + T\Delta s - p\Delta v. \tag{8}$$

TABLE 1. COMPARISON OF THERMODYNAMIC QUANTITIES AT 303.15 K AND 80 MPa

$10^3 x_1^0$	State of film	γ / mJ m^{-2}	$T\Delta s$ / mJ m^{-2}	$p\Delta v$ / mJ m^{-2}	Δu / mJ m^{-2}
0.0	*e*	52.02	27.3	2.10	77.2
0.2	*e*	48.74	6.6	1.66	53.8
0.4	*e*	46.63	−9.1	1.40	36.1
0.6	*e*	45.15	−21.2	1.22	22.7
0.8	*e*	43.96	−30.9	1.08	12.0
1.0	*e*	42.95	−39.1	0.97	2.9
1.2	*c*	39.92	−452	−15.7	−395
1.4	*c*	36.88	−455	−15.8	−402
1.6	*c*	34.18	−455	−15.8	−405
1.8	*c*	31.87	−455	−15.9	−407
2.0	*c*	29.81	−457	−16.0	−411

In Table 1, values of Δu, γ, $T\Delta s$, and $p\Delta v$ at 303.15 K and at 80 MPa are given. It is seen that in the expanded state the values of Δu decrease with increase in concentration in a similar way as in the case of 1-tetradecanol.[2] In the condensed state the adsorption of 1-octadecanol remarkably lowers the hexane/water interface energy.

All work prior to this has been carried out without taking into account the effect of pressure on interfacial tension provided that it has no pronounced effect on the properties of the condensed phase. For the system investigated in this study, the term $p\Delta v$ makes a relatively smaller contribution to Δu than $T\Delta s$ as shown in Table 1, and in fact has only a negligible contribution at atmospheric pressure. But it is important to investigate the effect of pressure on interfacial tension which will provide important data concerning the volumetric properties of the interface as discussed above.

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References

1) K. Motomura, *J. Colloid Interface Sci.*, **64**, 348 (1978).
2) K. Motomura, N. Matubayasi, M. Aratono, and R. Matuura, *J. Colloid Interface Sci.*, **64**, 356 (1978).
3) N. Matubayasi, K. Motomura, S. Kaneshina, M. Nakamura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **50**, 523 (1977).
4) E. Hutchinson, *J. Colloid Interface Sci.*, **3**, 219 (1948).
5) E. Hutchinson, *J. Colloid Interface Sci.*, **3**, 235 (1948).
6) E. Hutchinson and D. Randall, *J. Colloid Interface Sci.*, **7**, 151 (1952).
7) C. E. Stauffer, *J. Colloid Interface Sci.*, **27**, 625 (1968).
8) E. S. Lutton, C. E. Stauffer, J. B. Martin, and A. J. Fehl, *J. Colloid Interface Sci.*, **30**, 283 (1969).
9) D. S. Ambawani, R. A. Jao, and T. Fort, Jr., *J. Colloid Interface Sci.*, **42**, 8 (1973).
10) M. Lin, *C. R. Acad. Sci. Ser. B*, **281**, 619 (1975).
11) N. K. Adam, "The Physics and Chemistry of Surface," Oxford University Press, (1938).