Effect of Pressure on the Adsorption of 1-Octadecanol at Oil/Water Interfaces

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In order to investigate the effect of pressure on the adsorption at interfaces, the interfacial tension was measured as a function of pressure and composition for the systems of water and dilute solutions of 1-octadecanol in cyclohexane, benzene, and their equimolar mixture. The interfacial density of 1-octadecanol and the volume of interface formation were evaluated from the experimental data. Under atmospheric pressure, cyclohexane exhibits a significant adsorption of 1-octadecanol and a rapid decrease in the volume of interface formation, giving rise to the phase transition from the expanded to the condensed state in the adsorbed film, while benzene and equimolar mixture display only a small decrease in the thermodynamic quantities on the 1-octadecanol adsorption. Under high pressure, however, all the systems studied cause the phase transition. The effects of pressure and solvent on the phase transition of the adsorbed film were revealed on the basis of the thermodynamic quantities.

The adsorption of long-chain fatty alcohols at interfaces has been studied by many workers.[1–7] However, the pressure effect on the adsorption has hardly been investigated.[8–10] In the previous paper,[10] we clarified that the phase transition of the adsorbed film of 1-octadecanol takes place from an expanded to a condensed state at hexane/water interface and its interfacial tension is altered remarkably by pressure. Further, it was found that the adsorption of 1-octadecanol decreases with an increase in the affinity of oil to water.[7,11]

The object of this paper is to make clear the effect of pressure and solvent on the adsorption of 1-octadecanol, especially on the phase transition of the adsorbed film, at the organic solvent/water interface.

Experimental

Octadecanol was recrystallized five times from hexane after distillation under reduced pressure. Its purity was indicated to be better than 99.5% according to a gas-liquid chromatography test. Cyclohexane and benzene (Nakarai Chemicals Guaranteed Reagent) were refluxed with metallic sodium for 15 h and passed through a column of activated alumina (Woelm neutral activity grade I), and then distilled. Water was triply distilled, the second and third steps being done from dilute alkaline permanganate solution. Purities of organic liquid and water were checked by the equilibrium value of interfacial tension between them. Organic solvent and water were mutually saturated before measurements.

The pendant drop technique described previously[9,12] was used for the determination of interfacial tension. The pendant drops were allowed for about 45 min to attain the thermodynamic equilibrium. Densities of organic liquids, equimolar mixture of them, and water taken from literature[13–15] were used instead of those of mutually saturated oil and water because of so small solubilities. The interfacial tension was measured at 298.15 K with an accuracy of 0.05 mN m^{-1} as functions of pressure up to 150 MPa and mole fraction of 1-octadecanol. Temperature was controlled within 0.05 K at 298.15 K over the whole range of the experiments and pressure was regulated with a precision of 0.25 MPa.

Results and Discussion

The interfacial tension γ of the cyclohexane solution of 1-octadecanol against water was measured as a function of pressure p at a given mole fraction of 1-octadecanol x_1° in the cyclohexane solution. The γ *vs.* p curves at various concentrations are drawn in Fig. 1. In the lower concentration region, γ increases linearly with increasing p and the positive slope of γ *vs.* p curve becomes gradually smaller as the concentration increases. In the higher concentration region, on the other hand, the slope has a large negative value. It is noteworthy that a break point is observed on the γ *vs.* p curve at an intermediate concentration. This behavior resembles that of the system of hexane solution and water.[10] Therefore, we may conclude that the phase transition of the adsorbed film occurs from an expanded to a condensed state at the break point. Figure 2 shows the γ *vs.* p curves at various concentrations for the system of benzene solution and water. It is seen from this figure that the phase transition of the adsorbed film of 1-octadecanol at the benzene/water interface takes place

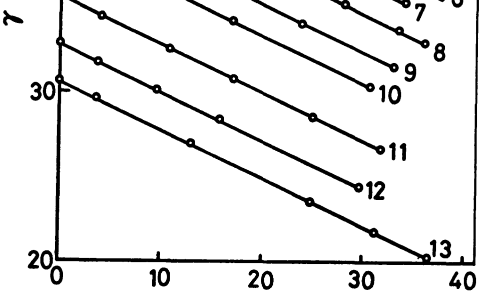

Fig. 1. Interfacial tension *vs.* pressure curves of 1-octadecanol at the cyclohexane/water interface at 298.15 K and constant mole fraction: $10^3\,x_1^{\circ}$ = (1) 0; (2) 0.199; (3) 0.404; (4) 0.910; (5) 1.543; (6) 1.881; (7) 2.030; (8) 2.189; (9) 2.499; (10) 2.729; (11) 3.354; (12) 3.965; (13) 4.560.

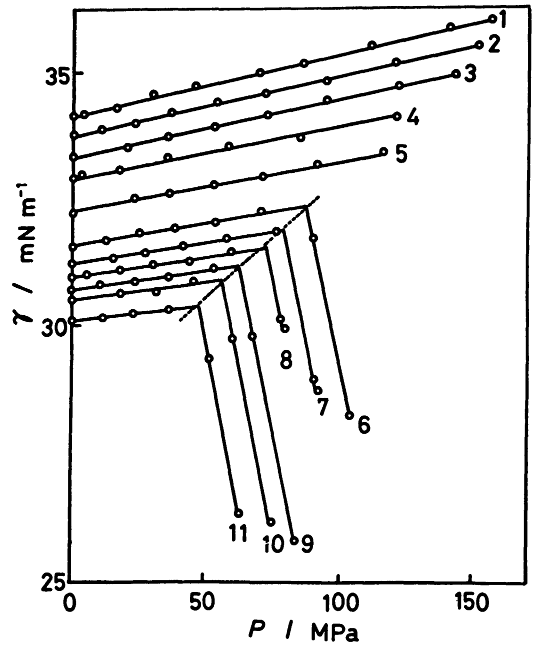

Fig. 2. Interfacial tension *vs.* pressure curves of 1-octadecanol at the benzene/water interface at 298.15 K and constant mole fraction: $10^3 x_1^0$=(1) 0; (2) 0.296; (3) 0.832; (4) 1.159; (5) 1.957; (6) 2.850; (7) 3.236; (8) 3.537; (9) 4.198; (10) 4.613; (11) 5.354.

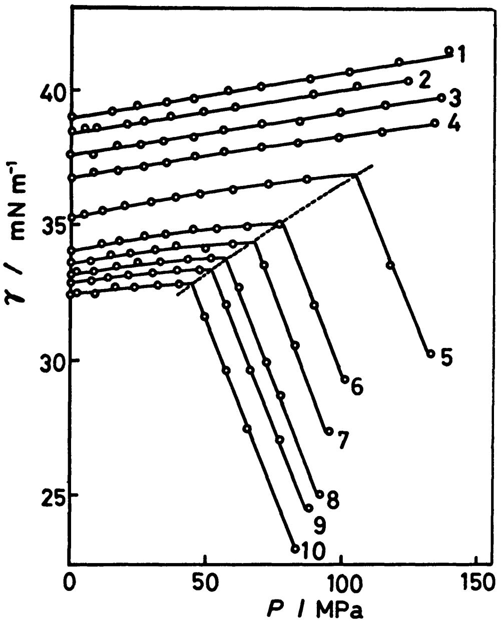

Fig. 3. Interfacial tension *vs.* pressure curves of 1-octadecanol at the X_b^0=0.503/water interface at 298.15 K and constant mole fraction: $10^3 x_1^0$=(1) 0; (2) 0.211; (3) 0.728; (4) 1.103; (5) 2.243; (6) 3.253; (7) 3.749; (8) 4.507; (9) 4.846; (10) 5.471.

only at very high pressure and concentration.

Now it is of great interest to investigate the adsorption of 1-octadecanol from the equimolar mixture of cyclohexane and benzene. Given in Fig. 3 is the γ *vs.* p curve at X_b^0=0.503, where X_b^0 is the composition of mixed solvent defined by

$$X_b^0 = x_b^0/(x_c^0 + x_b^0), \tag{1}$$

x_c^0 and x_b^0 being the mole fraction of cyclohexane and benzene, respectively. The behavior of 1-octadecanol in this interface seems to be akin to that in the benzene/water interface rather than in the cyclohexane/water interface, although the γ *vs.* p curve is slightly convex upward at higher concentrations. From Figs. 1 to 3, it is evident that higher pressure makes smaller the concentration of 1-octadecanol at which the phase transition takes place.

The adsorption behavior of 1-octadecanol is compared among the systems of cyclohexane, benzene, and their mixture in Figs. 4a and 4b where the value of interfacial tension taken up from Figs. 1 to 3 is plotted against the concentration at 0.1 and 80 MPa; the γ *vs.* x_1^0 curve at 80 MPa is not drawn for the system of cyclohexane because the cyclohexane solution freezes above about

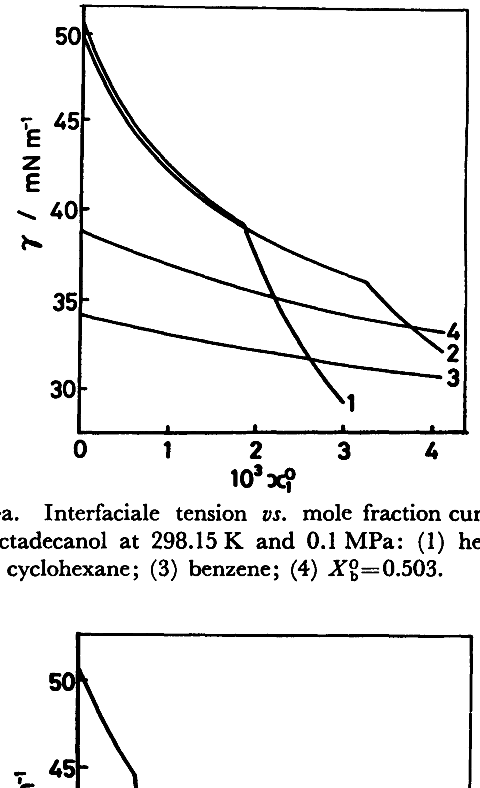

Fig. 4a. Interfaciale tension *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 0.1 MPa: (1) hexane; (2) cyclohexane; (3) benzene; (4) X_b^0=0.503.

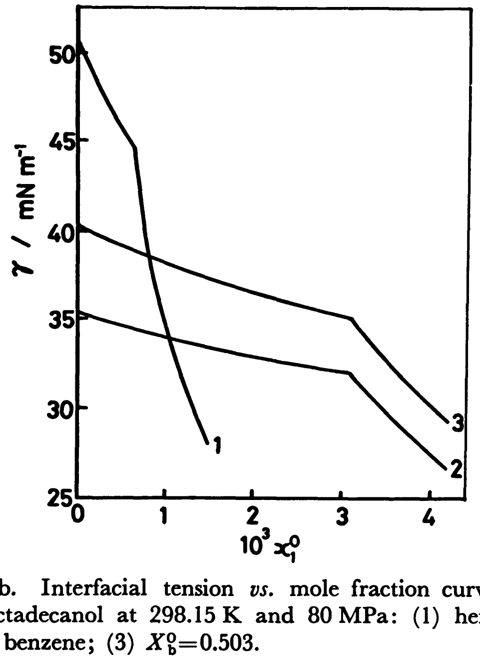

Fig. 4b. Interfacial tension *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 80 MPa: (1) hexane; (2) benzene; (3) X_b^0=0.503.

40 MPa. The results for the hexane system[10] are also shown for comparison. It may be supposed from Fig. 4a that the 1-octadecanol molecule is adsorbed remarkably at the cyclohexane/water interface as at the hexane/water interface whereas it is not done so much at the benzene/water interface, and its adsorption from the mixed solvent is intermediate between the adsorptions from the pure solvents. At 80 MPa, on the other hand, the γ *vs.* x_1^o curves are characterized by the break point.

It is now appropriate to estimate the interfacial density of 1-octadecanol Γ_1^H and the volume of interface formation Δv defined on the basis of the Hansen convention. Since the system under consideration satisfies the conditions that the two phases are actually immiscible and that the surfactant is soluble only in one of the phases, we have the following equations:[16,17]

$$\Gamma_1^H = -(x_1^o/RT)(\partial\gamma/\partial x_1^o)_{T,p} \tag{2}$$

and

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

where the ideality of the alcohol solution is assumed.

For the system in which the solvent of the oil phase is a mixture, Eqs. 2 and 3 are replaced by the equations[18]

$$\Gamma_1^H = -(x_1^o/RT)(\partial\gamma/\partial x_1^o)_{T,p,X_b^o}, \tag{4}$$

and

$$\Delta v = (\partial\gamma/\partial p)_{T,x_1^o,X_b^o}, \tag{5}$$

where the two dividing planes are chosen so as to satisfy the relations

$$\Gamma_w^H = 0, \tag{6}$$

and

$$\Gamma_b^H + \Gamma_c^H = 0. \tag{7}$$

The value of Γ_b^H is estimated by

$$\Gamma_b^H = -X_b^o X_c^o(\partial\gamma/\partial X_b^o)_{T,p,x_1^o}/ RT[1+(\partial \ln f_b^o/\partial \ln X_b^o)_{T,p,x_1^o}], \tag{8}$$

where f_b^o is the activity coefficient of solvent b in the oil phase.

Applying Eqs. 2 and 4 to the γ *vs.* x_1^o curves in Figs. 4a and 4b, the value of Γ_1^H was evaluated at 0.1 and 80 MPa as a function of x_1^o. The results are illustrated in Figs. 5a and 5b, respectively. It is seen at 0.1 MPa that the Γ_1^H value of the cyclohexane system, like that of the hexane system changes discontinuously at the point of phase transition from a relatively small value of the expanded film to a very large one of the condensed film. For the benzene system, the adsorbed film remains in an expanded state of which the Γ_1^H value is significantly small. The value of the $X_b^o=0.503$ system seems to be close to that of the benzene system. On the other hand, it is found at 80 MPa that the phase transition takes place for the benzene and $X_b^o=0.503$ systems and the Γ_1^H values of condensed films are about the same irrespective of the solvent. Therefore, it may be said that the affinity of benzene molecules to water molecules affects the adsorption of 1-octadecanol in the expanded state but not in the condensed state. This can be ascribed to the intermolecular interaction between octadecanol molecules in the condensed film which is strong enough to disregard a difference in that between octadecanol and organic solvent and between organic solvent and water.

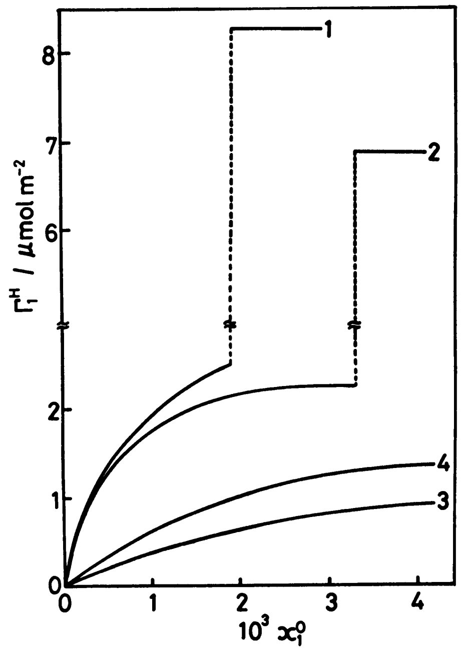

Fig. 5a. Interfacial density *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 0.1 MPa: (1) hexane; (2) cyclohexane; (3) benzene; (4) $X_b^o=0.503$.

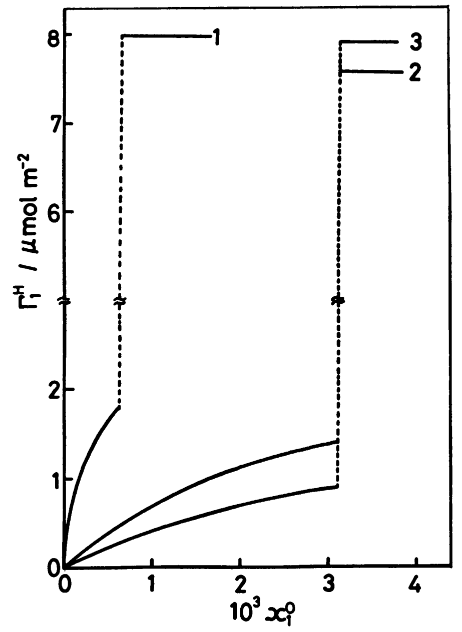

Fig. 5b. Interfacial density *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 80 MPa: (1) hexane; (2) benzene; (3) $X_b^o=0.503$.

The application of Eqs. 3 and 5 to the γ *vs.* p curves in Figs. 1 to 3 enables us to calculate the value of Δv. The variation in Δv with x_1^o at 0.1 and 80 MPa is shown in Figs. 6a and 6b. Under atmospheric pressure the Δv value for the cyclohexane system decreases rapidly with an increase in x_1^o from the positive value of the pure

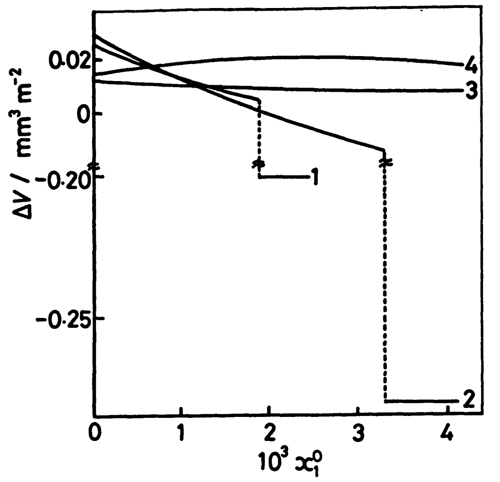

Fig. 6a. Volume change *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 0.1 MPa: (1) hexane; (2) cyclohexane; (3) benzene; (4) $X^0_b=0.503$.

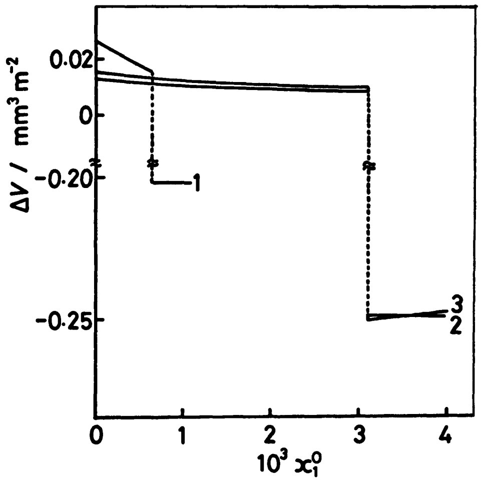

Fig. 6b. Volume change *vs.* mole fraction curves of 1-octadecanol at 298.15 K and 80 MPa: (1) hexane; (2) benzene; (3) $X^0_b=0.503$.

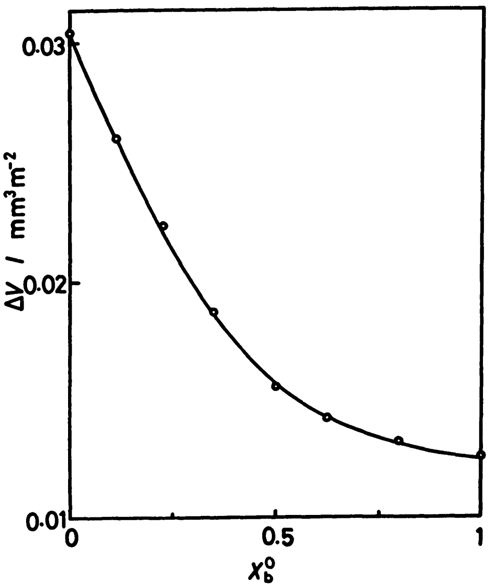

Fig. 7. Volume change *vs.* composition curve for $x^0_1=0$ at 298.15 K and 0.1 MPa.

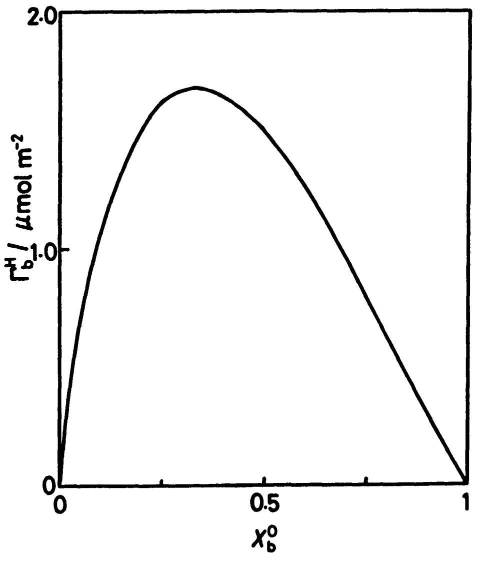

Fig. 8. Interfacial density *vs.* composition curve for $x^0_1=0$ at 298.15 K and 0.1 MPa.

interface to a large negative value of the condensed film, while the Δv values for benzene and $X^0_b=0.503$ systems vary slightly. At 80 MPa, the Δv *vs.* x^0_1 curves of the benzene and $X^0_b=0.503$ systems are quite similar in shape. It is observed that Δv has a large negative value for all the condensed films. This can be accounted for by a negative value of the partial molar volume change associated with the transfer of octadecanol molecules from the solution to the interface.[9,10] The similarity between the adsorption of 1-octadecanol from the mixture and that from benzene is presumed to be accounted for by a large concentration of benzene in the interfacial region. In Figs. 7 and 8, the values of Δv and Γ^H_b evaluated for $x^0_1=0$ are plotted against X^0_b at 298.15 K and 0.1 MPa.[19] It is seen from Fig. 7 that the Δv *vs.* X^0_b curve deviates greatly from the straight line connecting the values of the pure cyclohexane and benzene systems and the value of Δv at $X^0_b=0.503$ is not so different from that at $X^0_b=1$. Further, Fig. 8 shows that the value of Γ^H_b is remarkably large at the maximum. These results support the above presumption.

In order to visualize the effect of pressure on the adsorbed film of 1-octadecanol at the oil/water interfaces, let us draw its surface pressure *vs.* area curves. Since the interfacial pressure and the area per 1-octadecanol molecule are defined, respectively, by

$$\pi = \gamma^0 - \gamma, \tag{9}$$

and

$$A = 1/N_A\Gamma^H_1, \tag{10}$$

where γ^0 is the interfacial tension of pure interface and N_A is Avogadro number, the curves are obtained by making use of Figs. 4 and 5. The results are depicted in Figs. 9a and 9b. It is seen that the pressure makes the adsorbed film of 1-octadecanol condensed while the affinity of oil to water does it expanded. It should be

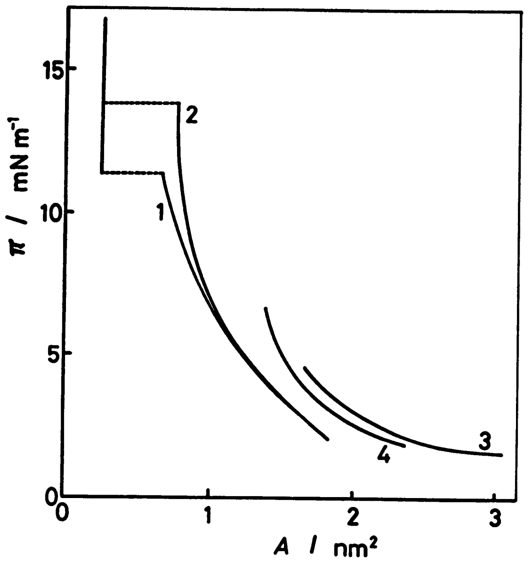

Fig. 9a. Interfacial pressure *vs.* area curves of 1-octadecanol at 298.15 K and 0.1 MPa: (1) hexane; (2) cyclohexane; (3) benzene; (4) $X_b^0=0.503$.

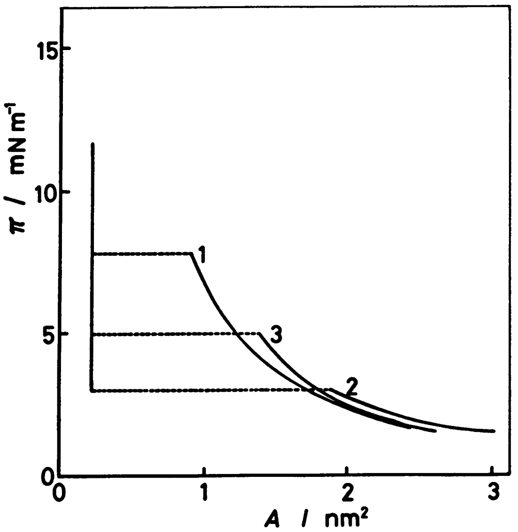

Fig. 9b. Interfacial pressure *vs.* area curves of 1-octadecanol at 298.15 K and 80 MPa: (1) hexane; (2) benzene; (3) $X_b^0=0.503$.

noted that the adsorption behavior of 1-octadecanol at the oil mixture/water interface is affected similarly by pressure.

In conclusion, we can say that the pressure has a significant effect on the phase transition of the adsorbed film to transform the expanded state produced by the affinity of benzene molecules to water molecules into the condensed one.

References

1) E. Hutchinson, *J. Colloid Interface Sci.*, **3**, 219 (1948).

2) E. Hutchinson and D. Randall, *J. Colloid Interface Sci.*, **7**, 151 (1952).

3) J. J. Jasper and B. L. Houseman, *J. Phys. Chem.* **67**, 1548 (1963).

4) E. S. Lutton, C. E. Stauffer, J. B. Martin, and A. J. Fehl, *J. Colloid Interface Sci.*, **30**, 283 (1969).

5) R. Aveyard, B. J. Briscoe, and J. Chapman, *J. Colloid Interface Sci.*, **44**, 282 (1973).

6) R. Vochten, and G. Petre, *J. Colloid Interface Sci.*, **42**, 320 (1973).

7) T. Ikenaga, N. Matubayasi, M. Aratono, and K. Motomura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **53**, 653 (1980).

8) M. Lin, *C. R. Acad. Sci., Ser. B*, **281**, 619 (1975).

9) K. Motomura, N. Matubayasi, M. Aratono, and R. Matuura, *J. Colloid Interface Sci.*, **64**, 356 (1978).

10) N. Matubayasi, K. Motomura, M. Aratono, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **51**, 2800 (1978).

11) K. Motomura, H. Iyota, M. Aratono, M. Yamanaka, and R. Matuura, *J. Colloid Interface Sci.*, **93**, 264 (1983).

12) N. Matubayasi, K. Motomura, S. Kaneshina, M. Nakamura, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **50**, 523 (1977).

13) G. S. Kell and E. Whally, *Phil. Trans. R. Soc. London, Ser. A*, **258**, 565 (1965).

14) T. Grindly, and J. E. Lind, Jr., *J. Chem. Phys.*, **54**, 3983 (1971).

15) H. Kashiwagi, T. Fukunaga, Y. Tanaka, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jpn.*, **49**, 70 (1979).

16) K. Motomura, *J. Colloid Interface Sci.*, **64**, 348 (1978).

17) K. Motomura, *Adv. Colloid Interface Sci.*, **12**, 1 (1980).

18) K. Motomura, M. Aratono, H. Iyota, and R. Matuura, to be submitted.

19) H. Iyota, M. Aratono, K. Motomura, and R. Matuura, to be submitted.