Solvent Effect on the Adsorption of 1-Octadecanol at Oil/Water Interface

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In order to study the effect of solvent on the adsorption at interfaces, interfacial tension was measured as a function of temperature and compositon for the systems of water and solutions of 1-octadecanol in cyclohexane, cyclohexene, mesitylene, toluene, and benzene. The interfacial density of 1-octadecanol and the entropy and energy of interface formation were calculated thermodynamically. It was found that cyclohexane causes a significant adsorption of 1-octadecanol and marked decreases in the entropy and energy changes, giving rise to phase transition from expanded to condensed film, while benzene, toluene, and mesitylene cause only a slight adsorption and small decrease in thermodynamic quantities. Cyclohexene was found to give rise to an intermediate adsorptive behavior of 1-octadecanol. The results were interpreted in terms of the mutual solubility between water and solvents and that of 1-octadecanol in the solvents.

The adsorption of various kinds of non-ionic surface active materials at oil/water and air/water interfaces has been investigated by many workers.[1–8] However, their thermodynamic treatment seems insufficient. Recently we have shown that the structure and property of the interface are clarified by applying rigorous thermodynamic treatment to the interfacial tension measured as a function of temperature, pressure, and concentration and evaluating the changes of the thermodynamic quantities associated with adsorption of long chain fatty alcohols at the hexane/water interface.[9–11]

It is evident that the adsorption of surface active substances to the interface is affected not only by temperature, pressure, and concentration but by properties of the solvent. However, the solvent effect on the behavior of the adsorbed film at oil/water interface has hardly been investigated systematically in spite of its importance.[12] The object of the present study is to obtain information on the solvent effect by use of the above treatment for systems consisting of water and the 1-octadecanol solutions in various organic solvents. The organic solvents employed in this work are hydrocarbons of six-membered ring structure differing in degree of saturation and in the side chain: cyclohexane, cyclohexene, benzene, toluene, and mesitylene.

The interfacial tension was measured as a function of temperature and mole fraction under atmospheric pressure. The entropy change, energy change, and the partial molar entropy change were estimated.

Experimental

Materials. 1-Octadecanol was purified by distillation under reduced pressure and triple recrystallization from hexane. Its purity was 99.9% as estimated by gas-liquid chromatography.

Benzene and toluene were purified by shaking with sulfuric acid and refluxing with metallic sodium for 8 h and by distillation under atmospheric pressure. Cyclohexane, cyclohexene, and mesitylene were purified by passing through a column of activated alumina (Woelm neutral activity grade I) and by distillation under atmospheric pressure.

Water was triply distilled, the second and third stages being done from dilute alkaline potassium permanganate solution. Water and each pure organic solvent were saturated mutually before measurements, but it was found to have little influence on the interfacial tension. The purity of water and each organic solvent was checked by the interfacial tension between them before use.

Interfacial Tension Measurements. The pendant drop technique[13,14] was used for the determination of equilibrium interfacial tension with an experimental error of *ca.* 0.05 mN m^{-1}. The values of interfacial tension were calculated by use of Fordham's correction table.[15] Measurements were carried out at fixed concentration and temperature under atmospheric pressure. The temperature was held constant within 0.05 K by circulating thermostated water around the pendant drop cell. The densities of water and pure organic solvents[16–18] were used for calculation of interfacial tension because of their small mutual solubility and low concentrations of solutions.

Results and Discussion

The interfacial tension γ of the system of cyclohexane solution of 1-octadecanol and water is plotted in Fig. 1 against temperature T at a constant mole fraction of 1-octadecanol x_1^0 in the cyclohexane solution, in which the solubility of water is neglected. At lower concentrations γ decreases linearly with increasing T, while at moderately high concentrations γ increases with increase in T. At higher concentrations there exists a point where the γ *vs.* T curve distinctly breaks at a lower temperature. The behavior of this system is very similar to that of hexane solution and water.[11] We conclude that the phase transition occurs from expanded to condensed film at the break point. It is seen that the slope of the γ *vs.* T curve, which is related to the entropy change, becomes larger from negative to positive with increase in concentration.

The interfacial tension, which is the interpolated value at constant temperature given in Fig. 1, is shown as a function of the mole fraction in Fig. 2. The γ *vs.* x_1^0 curve decrease monotonically at higher temperatures, the break point lying at 293.15 K.

Figure 3 shows the γ *vs.* T curves at constant x_1^0 for the system of cyclohexene solution and water. Cyclohexene gives rise to the phase transition of the adsorbed film of 1-octadecanol at very high concentrations and very low temperatures. Comparing cyclohexene and cyclohexane with hexane, we see that the temperature and concentration at which the condensed

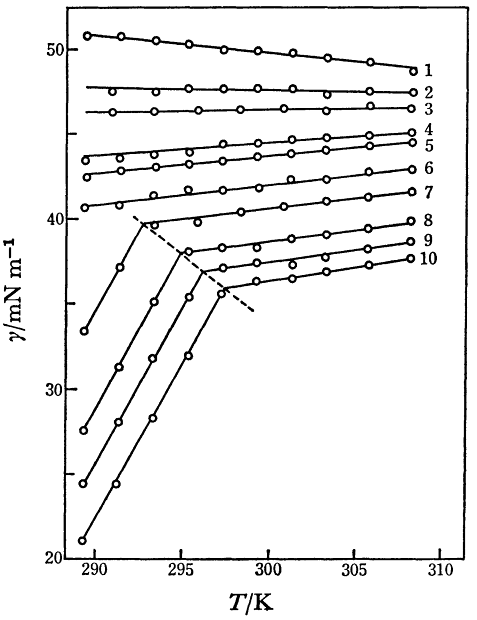

Fig. 1. Interfacial tension *vs.* temperature curves of 1-octadecanol at the cyclohexane/water interface at constant mole fraction: (1) $10^3 x_1^0=0$, (2) 0.138, (3) 0.241, (4) 0.522, (5) 0.734, (6) 1.012, (7) 1.556, (8) 2.065, (9) 2.542, (10) 3.049.

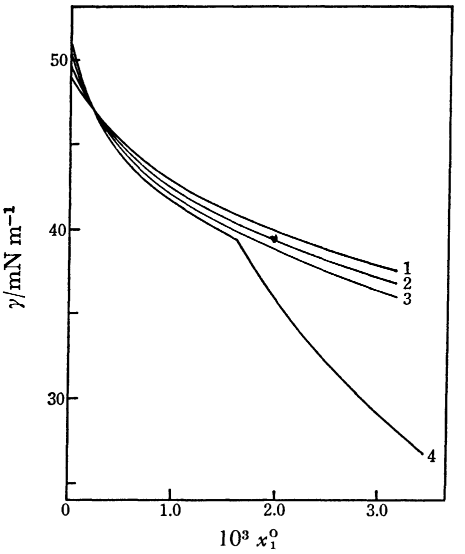

Fig. 2. Interfacial tension *vs.* mole fraction curves of 1-octadecanol at the cyclohexane/water interface at constant temperature: (1) 308.15 K, (2) 303.15 K, (3) 298.15 K, (4) 293.15 K.

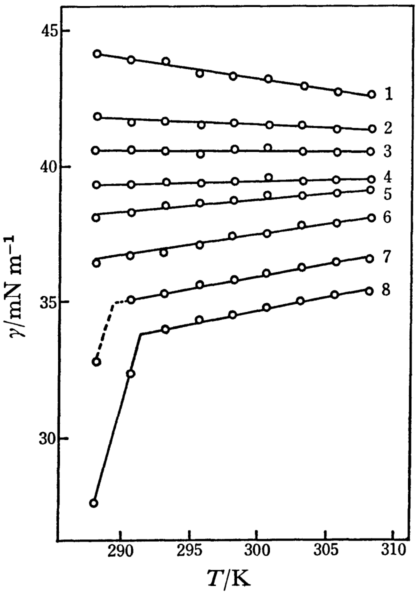

Fig. 3. Interfacial tension *vs.* temperature curves of 1-octadecanol at the cyclohexene/water interface at constant mole fraction: (1) $10^3 x_1^0=0$, (2) 0.165, (3) 0.546, (4) 0.886, (5) 1.240, (6) 2.117, (7) 3.454, (8) 4.733.

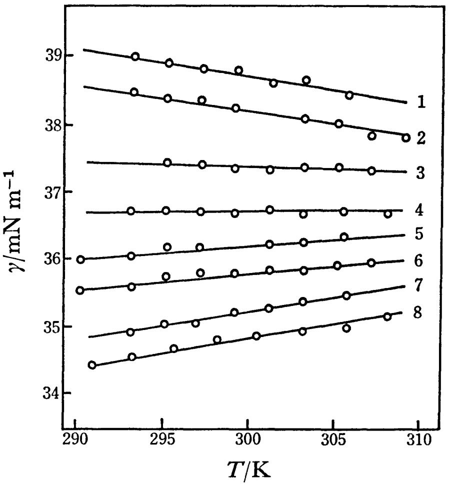

Fig. 4. Interfacial tension *vs.* temperature curves of 1-octadecanol at the mesitylene/water interface at constant mole fraction: (1) $10^3 x_1^0=0$, (2) 0.363, (3) 0.991, (4) 2.002, (5) 2.827, (6) 3.423, (7) 4.247, (8) 4.863.

film is formed becomes lower and higher, respectively, in the order of hexane, cyclohexane, and cyclohexene. It was also found that for the pure cyclohexene/water interface the slope of the γ *vs.* T curve is more gradual and the interfacial tension is smaller than for the pure cyclohexane/water and hexane/water interfaces.

In Fig. 4 γ *vs.* T curve is given for the system of mesitylene solution and water. Comparing Fig. 4 with Figs. 1 and 3 we see that the adsorptive behavior of 1-octadecanol from mesitylene seems similar to that from cyclohexane and cyclohexene at lower concentrations. However, no break point is observed over the whole range measured, the variation of γ with T being very small.

The γ *vs.* T curve for the system of toluene solution and water (Fig. 5) shows the system to behave virtually in the same manner as that of mesitylene, though the interfacial tension is smaller than that of mesitylene.

From the γ *vs.* T curve for the system of benzene solution and water (Fig. 6), we see that the variation of γ with T is steeper than that of toluene and the slope of γ *vs.* T curve is negative over the whole range measured, while the values of γ are smaller than those of toluene.

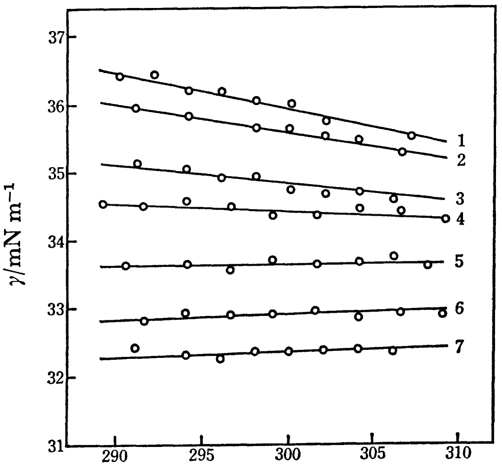

Fig. 5. Interfacial tension *vs.* temperature curves of 1-octadecanol at the toluene/water interface at constant mole fraction: (1) $10^3x_1^0=0$, (2) 0.313, (3) 0.979, (4) 1.864, (5) 2.565, (6) 3.388, (7) 3.897.

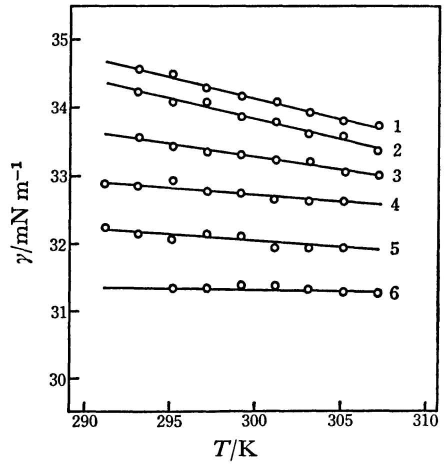

Fig. 6. Interfacial tension *vs.* temperature curves of 1-octadecanol at the benzene/water interface at constant mole fraction: (1) $10^3x_1^0=0$, (2) 0.296, (3) 0.987, (4) 1.571, (5) 2.117, (6) 3.718.

In order to visualize the effect of solvent on the adsorption of 1-octadecanol at the interface, the γ *vs.* x_1^0 curves for the five solvents in the present study and hexane[11] at 293.15 K are compared in Fig. 7. Benzene, toluene, and mesitylene have a similar effect on the adsorption, but their effect differs a great deal from that of hexane and cyclohexane. The effect of cyclohexene seems to be intermediate between that of the two groups of solvents.

Let us now estimate the interfacial density of 1-octadecanol Γ_1^H which is calculated by applying the following equation to the γ *vs.* x_1^0 curve:

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

where the solution is assumed to be ideal.[10] The values of $\partial\gamma/\partial x_1^0$ are obtained by fitting the γ *vs.* x_1^0 data to the polynomial

$$\gamma = c_3x_1^{03} + c_2x_1^{02} + c_1x_1^0 + c_0 \qquad (2)$$

for cyclohexane and cyclohexene and to the function

$$\gamma = A\exp(Bx_1^0) + C \qquad (3)$$

for benzene, toluene, and mesitylene by means of the least square method, where c_3, c_2, c_1, c_0, A, B, and C are constants.

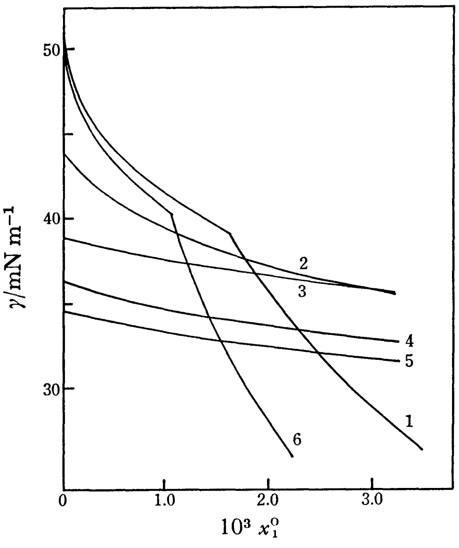

Fig. 7. Interfacial tension *vs.* mole fraction curves at 293.15 K: (1) cyclohexane, (2) cyclohexene, (3) mesitylene, (4) toluene, (5) benzene, (6) hexane.

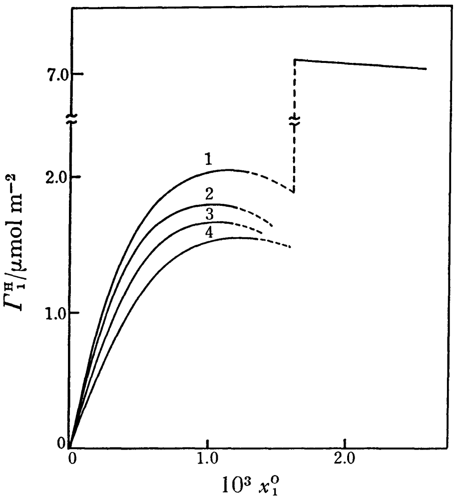

Fig. 8. Interfacial density *vs.* mole fraction curves of 1-octadecanol at the cyclohexane/water interface at constant temperature: (1) 293.15 K, (2) 298.15 K, (3) 303.15 K, (4) 308.15 K.

The value of Γ_1^H calculated at constant temperature for the system of cyclohexane solution and water is plotted against x_1^0 in Fig. 8. Γ_1^H becomes smaller with rise in T. The Γ_1^H *vs.* x_1^0 curves seem to have maximums. The abnormal behavior may be due to the assumption of the ideal solution for Eq. 1. Practically alcohol molecules are known to undergo strong autoassociation in nonpolar solvents.[19] It is obvious that the discontinuity on the Γ_1^H *vs.* x_1^0 curve at 293.15 K corresponds to the first-order phase transition from expanded to condensed film.

In a similar manner we can calculate the values of Γ_1^H for the systems of cyclohexene, mesitylene, toluene, and benzene. For the sake of comparison the Γ_1^H *vs.* x_1^0 curves at 303.15 K are given for the five organic

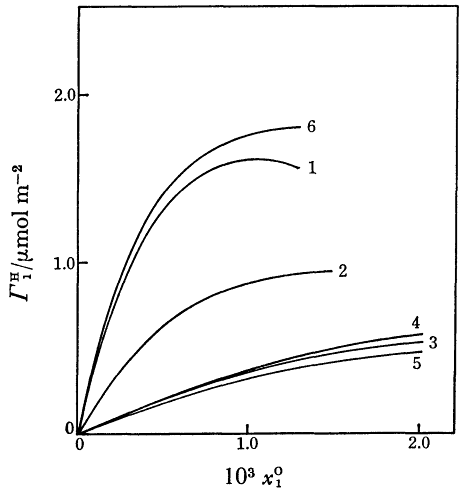

Fig. 9. Interfacial density *vs.* mole fraction curves at 303.15 K: (1) cyclohexane, (2) cyclohexene, (3) mesitylene, (4) toluene, (5) benzene, (6) hexane.

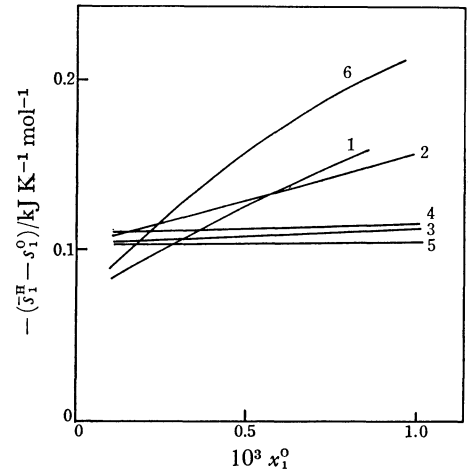

Fig. 11. Partial molar entropy change of 1-octadecanol *vs.* mole fraction curves at 303.15 K: (1) cyclohexane, (2) cyclohexene, (3) mesitylene, (4) toluene, (5) benzene, (6) hexane.

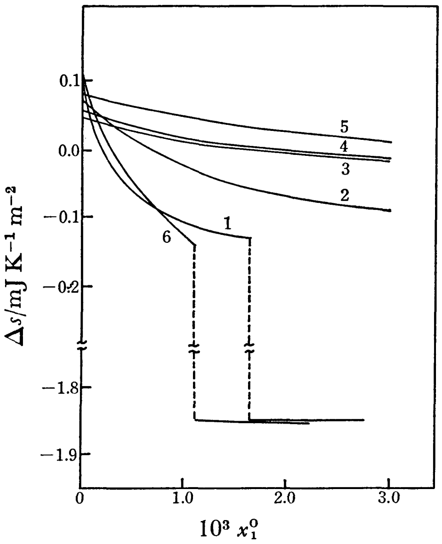

Fig. 10. Entropy of interface formation *vs.* mole fraction curves at 293.15 K: (1) cyclohexane, (2) cyclohexene, (3) mesitylene, (4) toluene, (5) benzene, (6) hexane.

solvents and hexane in Fig. 9. The value of Γ^{H}_{1} is remarkably large for cyclohexane and hexane while benzene and its derivatives give very small values. As expected, cyclohexene has an intermediate value. This suggests that the affinity of aromatic solvent molecules to water molecules is strong enough to reduce the adsorption of 1-octadecanol.

Next let us consider the entropy of interface formation, Δs. It is related to the slope of γ *vs.* T curve by[10)]

$$\Delta s = -(\partial\gamma/\partial T)_{p,x_1^{o}}. \tag{4}$$

By estimating $\partial\gamma/\partial T$ graphically from the γ *vs.* T curve, the values of Δs are obtained which are given against x_1^{o} at 293.15 K in Fig. 10. It is thought that the dependence of Δs on T is negligibly small since the γ *vs.* T curves are approximately linear. We find that in the cases of hexane and cyclohexane Δs decreases rapidly with increasing x_1^{o} from the positive value of pure interface to a negative value in a low concentration region. On the other hand, the extent of variation of Δs for mesitylene, toluene, and benzene is very small as compared with that for the above two solvents, the value of Δs becoming small in the order mesitylene, toluene, and benzene. It is clear that the formation of pure interface causes increase in the entropy of the whole system but the adsorption of 1-octadecanol diminishes it.

Comparing Figs. 9 and 10, we see that the value of Δs decreases as the value of Γ^{H}_{1} increases, indicating that the adsorption of 1-octadecanol to the interface is characterized by a negative change in entropy. The discontinuity in the Δs *vs.* x_1^{o} curve for cyclohexane also indicates first-order phase transition from the expanded to the condensed film. The negative large value of entropy suggests that the freedom of motion of 1-octadecanol molecules is restrained a great deal in the condensed state.

The decrease in entropy leads us to expect a more regular conformation of 1-octadecanol in the interfacial region, which can be clarified by estimating the change in partial molar entropy of 1-octadecanol. The partial molar entropy change can be calculated from experimental data with the aid of

$$\bar{s}^{H}_{1} - s^{o}_{1} = -\,[(\partial\gamma/\partial T)_{p,x_1^{o}} - (1-\Gamma^{H}_{1}\bar{a}_1)(\partial\gamma/\partial T)_{p,\Gamma^{H}_{1}}]/\Gamma^{H}_{1}, \tag{5}$$

where $\bar{a}_1$ is the partial molar area of 1-octadecanol.[10)] In Fig. 11 the values of $\bar{s}^{H}_{1}-s^{o}_{1}$ are given against x_1^{o} at 303.15 K for the low concentration region where the solutions are supposed to be ideal. It is of great significance that the value of the partial molar entropy change is definitely negative over the whole range of concentration and becomes more negative as the concentration increases. This indicates that the molecules of 1-octadecanol are compelled to take a more restricted conformation in the interface than in the bulk solution. The dependence of the partial molar entropy change on the bulk concentration seems to

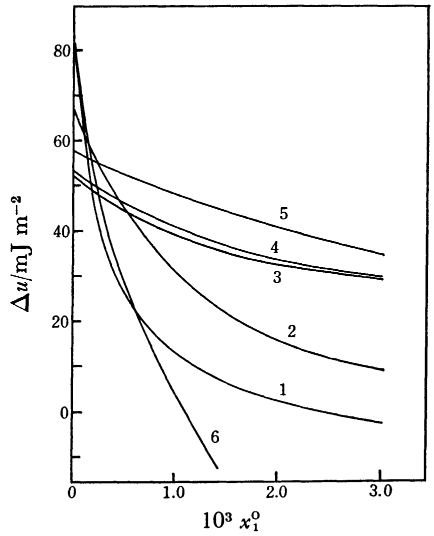

Fig. 12. Energy of interface formation *vs.* mole fraction curves at 303.15 K: (1) cyclohexane, (2) cyclohexene, (3) mesitylene, (4) toluene, (5) benzene, (6) hexane.

differ among the solvents. However, the difference is not so remarkable when the difference in the values of Γ_1^H shown in Fig. 9 is taken into consideration.

Let us calculate the energy of interface formation, Δu. We have the thermodynamic relation[9)]

$$\Delta u = \gamma + T\Delta s - p\Delta v, \qquad (6)$$

where Δv is the volume of interface formation. Since the term $p\Delta v$ is negligibly small as compared with the other terms on the right side of Eq. 6,[10)] the value of Δu is determined by the values of γ and Δs. In Fig. 12 Δu is given against x_1^0 at 303.15 K for all the solvents. The values of Δu decrease steeply with x_1^0 for cyclohexane and hexane and decrease gradually for mesitylene, toluene, and benzene. Such a behavior is qualitatively similar to that of the Δs *vs.* x_1^0 curves (Fig. 10) except for the discontinuous changes of Δs attributable to the phase transition observed at 293.15 K. This indicates that the decrease in Δu by the adsorption of 1-octadecanol overcomes the disadvantage brought about by the decrease in Δs irrespective of the solvent.

The interfacial tension between organic liquid and water is related to their mutual solubility.[20)] Thus, the small value of the interfacial tension between benzene and water is accounted for by the large affinity which the π electron system on the benzene ring possesses for water. When hydrophobic side chains are introduced in benzene molecule, interfacial tension increases and the entropy and energy of interface formation decrease. However, in spite of such a difference among benzene, toluene and mesitylene, the adsorptive behavior of 1-octadecanol at the interfaces between these solvents and water is very similar. The appreciable affinity of the aromaticity of the solvents for water plays a dominant role in the adsorption of 1-octadecanol.

On the other hand, the adsorption from the saturated hydrocarbons like cyclohexane and hexane is in striking contrast to that from the above aromatic solvents. It is characterized by the large value of Γ_1^H, the significant dependence of Δs and Δu on the concentration, and the phase transition from expanded to condensed film. Such a behavior is understandable on the basis of the low mutual solubility of saturated hydrocarbon and water, the high affinity of hydroxyl group of 1-octadecanol for water, and the strong lateral force between 1-octadecanol molecules. In terms of the solubilities of 1-octadecanol in cyclohexane and hexane, which are 1.81 and 0.47 in weight percent at 303.15 K, respectively, the slight difference in the adsorptive behavior between cyclohexane and hexane is also interpreted. For cyclohexene, we can expect an intermediate behavior between cyclohexane and benzene, which has been confirmed experimentally.

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