

## Effect of $\omega$ -Hydrogenation on the Adsorption of Fluorononanol at the Hexane/Water Interface: Temperature Effect on the Adsorption of Fluorononanol

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The interfacial tensions ( $\gamma$ ) of the hexane solutions of 1*H*,1*H*-perfluorononanol (FDFC<sub>9</sub>OH) and its  $\omega$ -hydrogenated analogue 1*H*,1*H*,9*H*-perfluorononanol (HDFC<sub>9</sub>OH) against water were measured as a function of temperature and concentration under atmospheric pressure in order to know the effect of  $\omega$ -dipoles on the adsorption behavior of fluorononanol. The interfacial pressure ( $\pi$ ) versus mean area per adsorbed molecule ( $A$ ) curves consist of two discontinuous changes among three different states: the gaseous, expanded, and condensed states. The  $A$  values at given  $\pi$  in the gaseous and expanded states are larger for HDFC<sub>9</sub>OH than for FDFC<sub>9</sub>OH. The changes in partial molar entropy ( $\bar{s}_1^H - \bar{s}_1^O$ ) and energy ( $\bar{u}_1^H - \bar{u}_1^O$ ) of adsorption were evaluated. Their values are negative, and therefore, the alcohols have a smaller entropy and energy at the interface than in the bulk solution. Furthermore, the  $\bar{u}_1^H - \bar{u}_1^O$  value is more negative for HDFC<sub>9</sub>OH than for FDFC<sub>9</sub>OH in the expanded state and also in the condensed film just above the expanded–condensed phase transition point. This seems to be due to the following: (1) HDFC<sub>9</sub>OH may tilt from interface normal for  $\omega$ -dipoles to interact effectively with water molecules in the interfacial region and to reduce their own repulsive interaction between neighbors arranging parallel in the adsorbed film. This leads to a lower  $\bar{u}_1^H$  value for HDFC<sub>9</sub>OH than for FDFC<sub>9</sub>OH. (2) The contact of  $\omega$ -dipoles with hexane molecules in the bulk solution is energetically unfavorable, and thus, the  $u_1^O$  value of HDFC<sub>9</sub>OH is expected to be larger than that of FDFC<sub>9</sub>OH.

### Introduction

The study on the adsorbed film at the oil/water interface is of great importance from basic scientific as well as industrial viewpoints, because it provides us fundamental and suggestive information about the structures and properties of more complicated molecular organized systems, such as emulsions and biomembranes. We have investigated the adsorption of fluoroalkanol at the hexane/water interface by measuring the interfacial tension and evaluating the interfacial density and thermodynamic quantity change of adsorption.<sup>1–5</sup> In the course of the studies, it was found that the adsorbed films exhibit phase transition between gaseous (or expanded) and condensed states depending on the molecular structure such as the fluorocarbon (FC) chain length and the extent of fluorination of the hydrophobic chain. In addition, the X-ray reflection technique was applied to the adsorbed fluoroalkanol film in order to gain information on the film structure from the molecular level.<sup>6–8</sup> The phase transition observed in the interfacial tension measurement was substantiated by an abrupt change in the interfacial coverage, which is defined as the ratio of the occupied area of the condensed phase to the whole area of the interface, evaluated from the X-ray data analysis.<sup>7,8</sup> Furthermore, it was suggested that the adsorbed film close to the phase transition point is microscopically inhomogeneous with condensed phase domains,

in which the molecules are densely packed, surrounded by a low molecular density region.

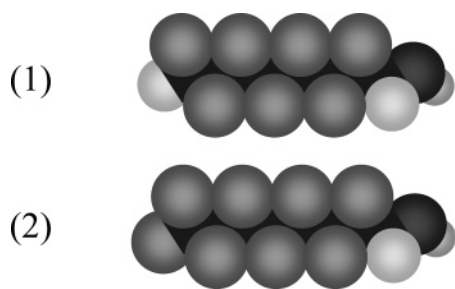
Since one of the most remarkable features of the fluorine atom is its most electronegative effect of all atoms, the substitution of a fluorine atom of a fluorocarbon (FC) chain into a hydrogen atom produces a dipole at the terminal methyl group and thus is expected to affect appreciably the adsorption behavior of FC surface-active substances at interfaces.<sup>9</sup> In our previous study on the adsorption of 1*H*,1*H*,2*H*,2*H*-perfluorooctanol (TFC<sub>8</sub>OH) and its  $\beta$ -fluorinated analogue 1*H*,1*H*-perfluorooctanol (DFC<sub>8</sub>OH) at the hexane/water interface,<sup>5</sup> the substitution of hydrogen atoms at the  $\beta$ -position of the TFC<sub>8</sub>OH molecule into fluorine increases the dipole moment of the hydroxyl group and eventually induces drastic change in the state of the adsorbed film between TFC<sub>8</sub>OH and DFC<sub>8</sub>OH. Furthermore, in the study of the adsorption at the air/water interface and micelle formation of a water-soluble FC surfactant, such as tetraethyleneglycol mono-1,1-dihydrotridecafluoroheptyl ether (pFC<sub>7</sub>E<sub>4</sub>) and its  $\omega$ -hydrogenated analogue tetraethyleneglycol mono-1,1,7-trihydrododecafluoroheptyl ether (FC<sub>7</sub>E<sub>4</sub>), it was found that the substitution of a fluorine atom at the terminal position ( $\omega$ -position) of the FC chain into a hydrogen atom lowers the surface density and increases the critical micelle concentration.<sup>10–14</sup> This is induced by the  $\omega$ -dipole of FC<sub>7</sub>E<sub>4</sub>, which is generated by the hydrogenation of the terminal fluorine of pFC<sub>7</sub>E<sub>4</sub>.

In this study, we aim at clarifying the effect of  $\omega$ -dipoles on the adsorbed film of fluoroalkanol at the oil/water interface,

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**Figure 1.** Chemical structures of the fluorononanols: (1) HDfC<sub>9</sub>OH; (2) FdFC<sub>9</sub>OH.

because (1) the oil-soluble surface-active substances can form the condensed film in addition to the gaseous and expanded states and therefore the effect of  $\omega$ -dipoles on the molecular orientation in the closely packed state can be examined and (2) the effect of the weak interaction of  $\omega$ -dipoles with oil molecules is also expected to be elucidated in terms of the thermodynamic quantity changes of adsorption. Thus, we employed homologous fluoroalkanols with or without  $\omega$ -dipoles, 1*H*,1*H*,9*H*-perfluorononanol (HDfC<sub>9</sub>OH) and 1*H*,1*H*-perfluorononanol (FdFC<sub>9</sub>OH), shown in Figure 1, as materials and measured the interfacial tension between the hexane solution and water phases as a function of temperature and concentration under atmospheric pressure. The partial molar entropy and energy changes associated with the adsorption of HDfC<sub>9</sub>OH were evaluated and compared to those of FdFC<sub>9</sub>OH in order to see the effect of  $\omega$ -dipoles on the adsorption of HDfC<sub>9</sub>OH.

## Experimental Section

1*H*,1*H*,9*H*-Perfluorononanol (HDfC<sub>9</sub>OH) and 1*H*,1*H*-perfluorononanol (FdFC<sub>9</sub>OH) were purchased from Azmax Co. Ltd. and purified by recrystallization from hexane solution. Their purities were checked by gas-liquid chromatography and by observing no time dependence in the interfacial tension between their hexane solutions and water. Hexane purchased from Aldrich Chemical Co. Ltd. was distilled once, and water, three

times; the second and third stages were done from dilute alkaline permanganate solution.

The interfacial tension ( $\gamma$ ) of the hexane solutions of HDfC<sub>9</sub>OH and FdFC<sub>9</sub>OH against water was measured as a function of temperature ( $T$ ) and the molality of alcohol ( $m_1$ ) (the subscript "1" denotes alcohol) by the pendant drop method based on the drop shape analysis described elsewhere.<sup>15,16</sup> The densities of pure water and hexane were used for the calculation of interfacial tension.<sup>17,18</sup> The error in the  $\gamma$  value was estimated within 0.05 mN m<sup>-1</sup>.

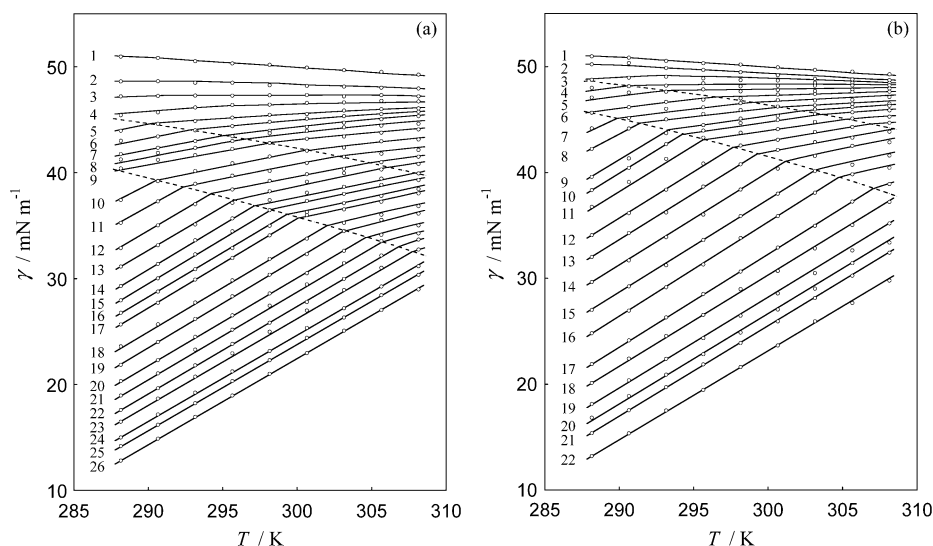
## Results and Discussion

Figure 2 shows the temperature dependence of the interfacial tension of the HDfC<sub>9</sub>OH (Figure 2a) and FdFC<sub>9</sub>OH (Figure 2b) systems. In both systems, the  $\gamma$  value decreases slightly with increasing  $T$  at low concentrations and increases greatly at high concentrations. In the middle  $m_1$  range, the  $\gamma$  versus  $T$  curves show one or two break points, at which the slope of the curves changes abruptly. The  $\gamma$  values read from Figure 2 at 298.15 K were plotted against  $m_1$  in Figure 3. The  $\gamma$  value decreases with increasing  $m_1$ , and the curves show two break points shown by arrows. These break points are attributable to the phase transitions in the adsorbed film of fluorononanols at the hexane/water interface. In Figure 4 are shown the temperature dependence of the equilibrium interfacial tension ( $\gamma^{\text{eq}}$ ) and molality ( $m_1^{\text{eq}}$ ) at the transition points. The  $\gamma^{\text{eq}}$  value decreases with increasing temperature, and the corresponding  $m_1^{\text{eq}}$  value increases. It is noted that the  $\gamma^{\text{eq}}$  value of HDfC<sub>9</sub>OH is lower and the  $m_1^{\text{eq}}$  value higher than those of FdFC<sub>9</sub>OH.

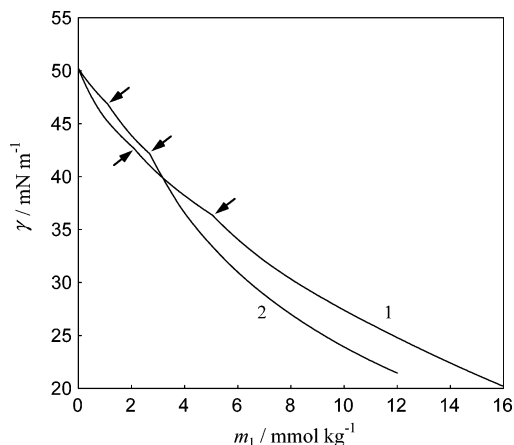
To assign the state of the adsorbed film, first, the interfacial density of alcohol ( $\Gamma_1^{\text{H}}$ ) was calculated by applying the equation

$$\Gamma_1^{\text{H}} = -(m_1/RT)(\partial\gamma/\partial m_1)_{T,p} \quad (1)$$

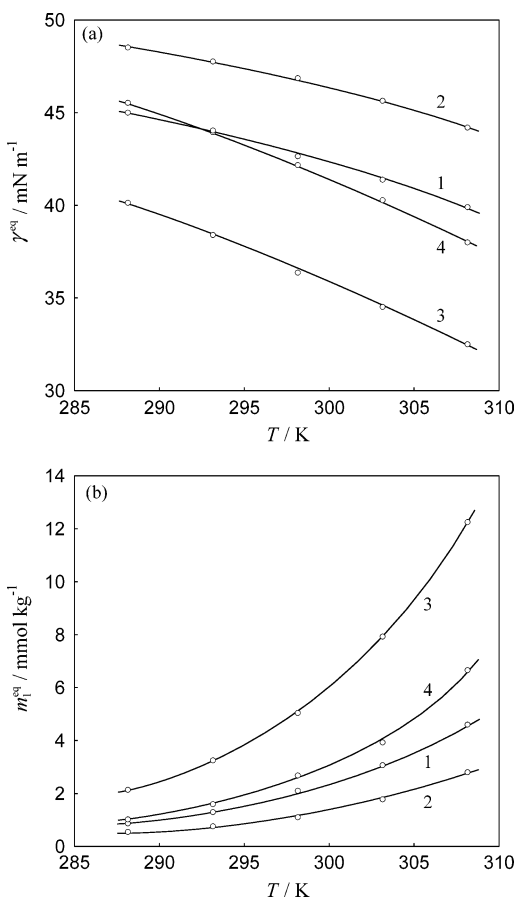
to the  $\gamma$  versus  $m_1$  curves in Figure 3. The results are shown as the  $\Gamma_1^{\text{H}}$  versus  $m_1$  curves in Figure 5. The  $\Gamma_1^{\text{H}}$  value increases with  $m_1$  and changes discontinuously at the phase transition points. Then, the interfacial pressure ( $\pi$ ) and the mean area per



**Figure 2.** (a) Interfacial tension vs temperature curves of HDfC<sub>9</sub>OH at constant molality:  $m_1$  = (1) 0, (2) 0.2500, (3) 0.5000, (4) 0.7499, (5) 1.000, (6) 1.250, (7) 1.500, (8) 1.750, (9) 1.997, (10) 2.500, (11) 3.000, (12) 3.496, (13) 4.000, (14) 4.501, (15) 5.000, (16) 5.500, (17) 6.000, (18) 6.999, (19) 8.002, (20) 9.000, (21) 10.00, (22) 11.00, (23) 12.00, (24) 13.00, (25) 14.00, and (26) 15.50 mmol kg<sup>-1</sup>. (b) Interfacial tension vs temperature curves of FdFC<sub>9</sub>OH at constant molality:  $m_1$  = (1) 0, (2) 0.2000, (3) 0.4000, (4) 0.5999, (5) 0.8001, (6) 0.9999, (7) 1.200, (8) 1.400, (9) 1.600, (10) 1.800, (11) 2.000, (12) 2.500, (13) 3.001, (14) 3.500, (15) 4.000, (16) 5.000, (17) 6.000, (18) 7.000, (19) 7.999, (20) 9.001, (21) 9.998, and (22) 12.00 mmol kg<sup>-1</sup>.



**Figure 3.** Interfacial tension vs molality curves at 298.15 K: (1) HDFC<sub>9</sub>OH; (2) FDFC<sub>9</sub>OH.



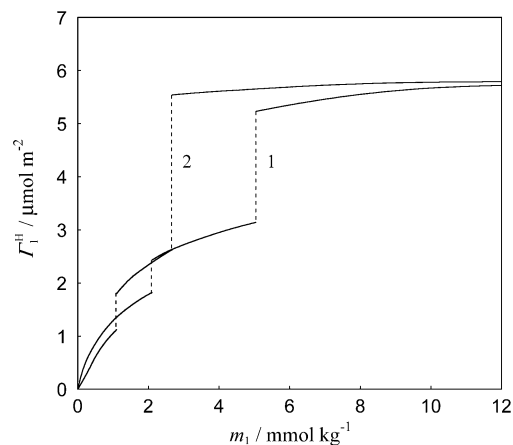
**Figure 4.** (a) Equilibrium interfacial tension vs temperature curves: (1) gaseous–expanded transition for HDFC<sub>9</sub>OH; (2) gaseous–expanded transition for FDFC<sub>9</sub>OH; (3) expanded–condensed transition for HDFC<sub>9</sub>OH; (4) expanded–condensed transition for FDFC<sub>9</sub>OH. (b) Equilibrium molality vs temperature curves: (1) gaseous–expanded transition for HDFC<sub>9</sub>OH; (2) gaseous–expanded transition for FDFC<sub>9</sub>OH; (3) expanded–condensed transition for HDFC<sub>9</sub>OH; (4) expanded–condensed transition for FDFC<sub>9</sub>OH.

adsorbed molecule ( $A$ ) values are evaluated by using the equations

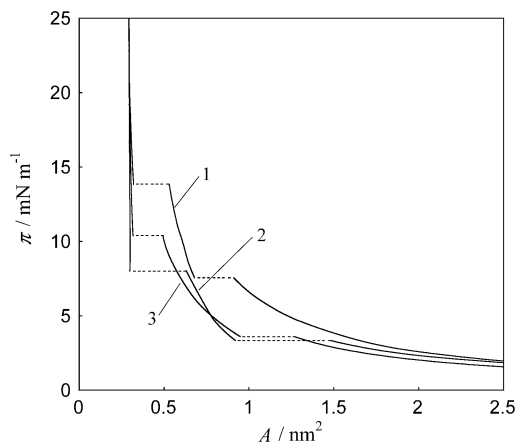
$$\pi = \gamma^0 - \gamma \quad (2)$$

and

$$A = 1/N_A \Gamma_1^H \quad (3)$$

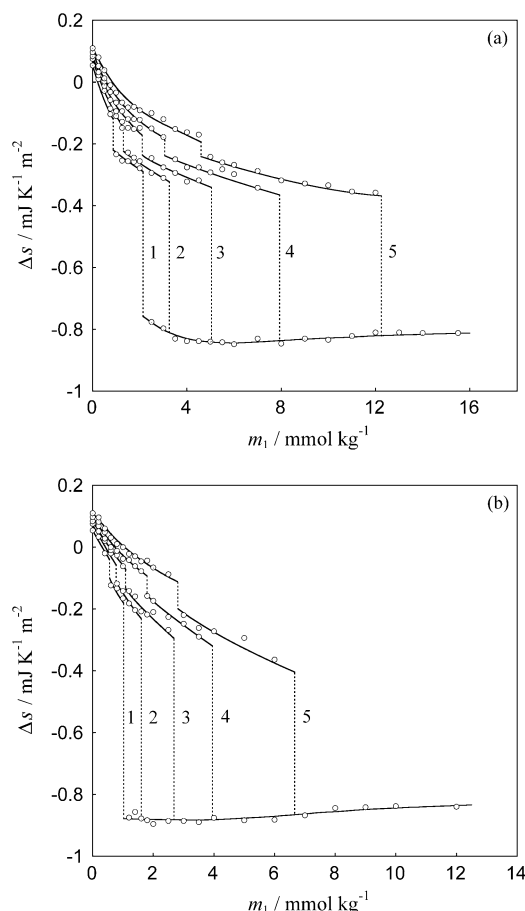


**Figure 5.** Interfacial density vs molality curves at 298.15 K: (1) HDFC<sub>9</sub>OH; (2) FDFC<sub>9</sub>OH.



**Figure 6.** Interfacial pressure vs mean area per adsorbed molecule curves at 298.15 K: (1) HDFC<sub>9</sub>OH; (2) FDFC<sub>9</sub>OH; (3) TFC<sub>10</sub>OH.

respectively, where  $\gamma^0$  is the interfacial tension between the pure hexane/water interface and  $N_A$  is Avogadro's number. Figure 6 shows the  $\pi$  versus  $A$  curves of both systems together with the curve obtained for the 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (TFC<sub>10</sub>OH) system for comparison. It is realized that the curves exhibit two discontinuous changes among three different states; the two types of phase transitions occur in the adsorbed film of fluorononanol. The  $A$  value in the almost vertical region is around 0.3 nm<sup>2</sup> which is very close to the cross-sectional area of the FC chain. Thus, this region corresponds to the condensed state in which the alcohol molecules are closely packed with each other. Taking account of our previous conclusion that the adsorbed film of TFC<sub>10</sub>OH shows two types of phase transitions from the gaseous to the expanded state and from the expanded to the condensed state,<sup>2,4</sup> the adsorbed films with middle and large  $A$  values are assigned to the expanded and gaseous states, respectively. It seems that the  $A$  values at given  $\pi$  in the expanded and gaseous states are larger for HDFC<sub>9</sub>OH than for FDFC<sub>9</sub>OH, and the interfacial pressure ( $\pi^{\text{eq}}$ ) at the transition points is larger, while the area ( $A^{\text{eq}}$ ) is smaller for HDFC<sub>9</sub>OH than for FDFC<sub>9</sub>OH. These differences rely on two factors induced by the substitution of a fluorine atom at the  $\omega$ -position of a FDFC<sub>9</sub>OH molecule into a hydrogen atom. One is the repulsive interaction of  $\omega$ -dipoles arranging parallel with each other in the adsorbed HDFC<sub>9</sub>OH film.<sup>19</sup> Another is the weaker dispersion interaction between the HDFC<sub>9</sub>OH molecules compared to that between the FDFC<sub>9</sub>OH ones because of the lower molecular weight of HDFC<sub>9</sub>OH.



**Figure 7.** Entropy change associated with adsorption vs molality curves at constant temperature:  $T = (1) 288.15$ ,  $(2) 293.15$ ,  $(3) 298.15$ ,  $(4) 303.15$ , and  $(5) 308.15$  K: (a) HDfC<sub>9</sub>OH; (b) FDFC<sub>9</sub>OH.

Now let us discuss the adsorption behavior of fluorononanol from the viewpoints of entropy and energy. The entropy change associated with adsorption ( $\Delta s$ ) was evaluated by applying the equation

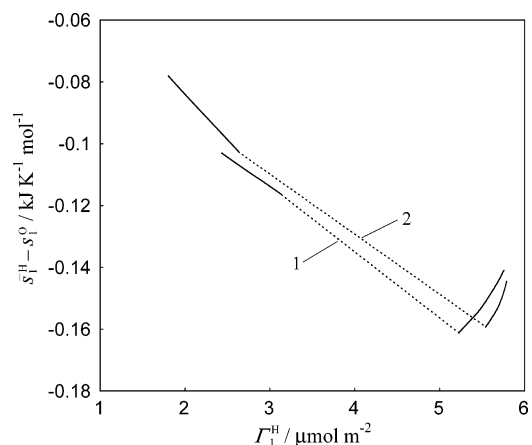
$$\Delta s = -(\partial\gamma/\partial T)_{p,m_1} \quad (4)$$

to the  $\gamma$  versus  $T$  curves in Figure 2. The results are shown as the  $\Delta s$  versus  $m_1$  curves at constant temperature in Figure 7. The essential feature of the curves is the same in both systems: the  $\Delta s$  value decreases from positive to negative with increasing adsorption and changes discontinuously at the phase transition points. The condensed state is characterized by a large negative  $\Delta s$  value.

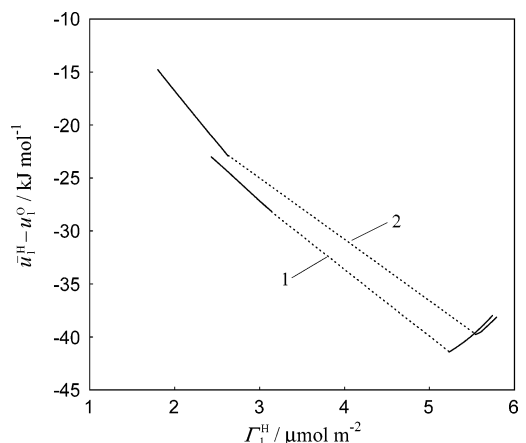
The negative contribution of alcohol to the  $\Delta s$  value is examined by evaluating the partial molar entropy change of adsorption ( $\bar{s}_1^H - s_1^O$ ). Here, the superscripts “H” and “O” represent the adsorbed film and hexane phase, respectively. The value is estimated by using the relation<sup>20</sup>

$$\bar{s}_1^H - s_1^O = [\Delta s + (1 - \Gamma_1^H a_1)(\partial\gamma/\partial T)_{p,\Gamma_1^H}]/\Gamma_1^H, \quad (5)$$

where  $s_1^O$  is the partial molar entropy of alcohol in the hexane solution,  $\bar{s}_1^H$  is the mean partial molar entropy inherent in the interface, and  $a_1$  is the partial molar area of the alcohol. Here, we employed  $0.3 \text{ nm}^2$  for the  $a_1$  value in this study.<sup>4</sup> In Figure 8, the  $\bar{s}_1^H - s_1^O$  values at 298.15 K are plotted against  $\Gamma_1^H$  for the expanded and condensed states. It is realized that the  $\bar{s}_1^H - s_1^O$  value is negative and therefore the fluorononanol has a smaller



**Figure 8.** Partial molar entropy change of adsorption vs interfacial density curves at 298.15 K: (1) HDfC<sub>9</sub>OH; (2) FDFC<sub>9</sub>OH.



**Figure 9.** Partial molar energy change of adsorption vs interfacial density curves at 298.15 K: (1) HDfC<sub>9</sub>OH; (2) FDFC<sub>9</sub>OH.

entropy in the adsorbed film than in the bulk solution because of the restricted orientation of molecules at the interface. Furthermore, the discontinuous change in the  $\bar{s}_1^H - s_1^O$  value at the expanded–condensed transition point, which gives a partial molar entropy change between the expanded and condensed states,  $\bar{s}_1^{H,e} - \bar{s}_1^{H,c}$ , is larger for FDFC<sub>9</sub>OH than for HDfC<sub>9</sub>OH. The difference in  $\bar{s}_1^{H,e} - \bar{s}_1^{H,c}$  values may come from the larger  $\bar{s}_1^{H,e}$  value of FDFC<sub>9</sub>OH due to the larger entropy of mixing of fluorononanol without  $\omega$ -dipoles with hexane molecules in the expanded state and smaller the  $\bar{s}_1^{H,c}$  value of FDFC<sub>9</sub>OH due to the stronger dispersion interaction between the FDFC<sub>9</sub>OH molecules in the condensed state than between the HDfC<sub>9</sub>OH molecules.

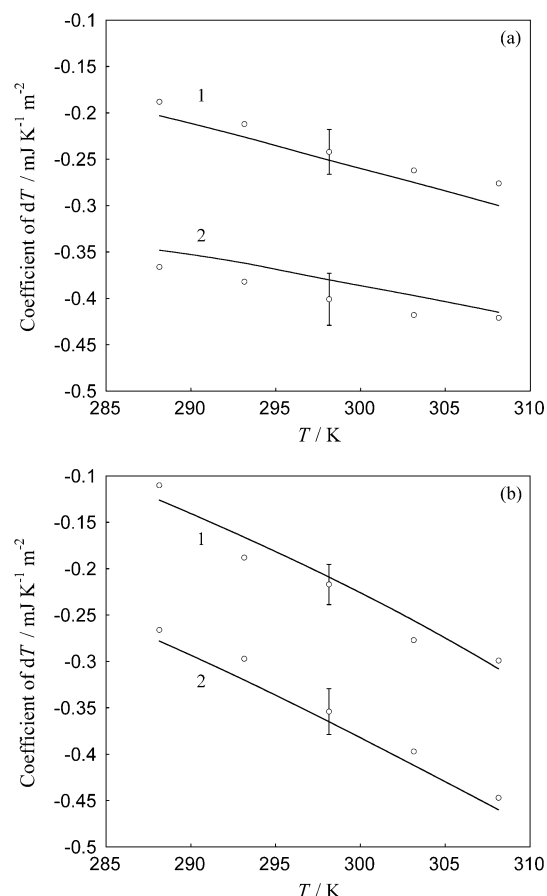
The partial molar energy change of adsorption ( $\bar{u}_1^H - u_1^O$ ) was calculated by using the following equation

$$\bar{u}_1^H - u_1^O = \gamma a_1 + T(\bar{s}_1^H - s_1^O) - p(\bar{v}_1^H - v_1^O) \quad (6)$$

$$\approx \gamma a_1 + T(\bar{s}_1^H - s_1^O) \quad (7)$$

where it is assumed that the contribution of the last term in eq 6 to the  $\bar{u}_1^H - u_1^O$  value is negligibly small under atmospheric pressure. The  $\bar{u}_1^H - u_1^O$  versus  $\Gamma_1^H$  curves at 298.15 K are illustrated in Figure 9. The  $\bar{u}_1^H - u_1^O$  value is negative, and thus, the adsorption of fluorononanol is caused by a reduction of energy that overcomes a decrease in entropy. It is found that the  $\bar{u}_1^H - u_1^O$  value of HDfC<sub>9</sub>OH is smaller than that of FDFC<sub>9</sub>OH at given  $\Gamma_1^H$  in the expanded state; the energetical stabili-





**Figure 10.** Values of the coefficients of  $dT$  of eqs (○) 8 and (—) 9 vs temperature curves for (a) HDfC<sub>9</sub>OH and (b) FDFC<sub>9</sub>OH: (1) gaseous–expanded transition; (2) expanded–condensed transition.

zation by the adsorption of HDfC<sub>9</sub>OH molecules from the hexane solution is larger than that of FDFC<sub>9</sub>OH molecules. Furthermore, it is noted that the  $\bar{u}_1^H - u_1^O$  value of HDfC<sub>9</sub>OH in the condensed state just above the phase transition point is largely negative. Taking note of the difference in the  $\pi$  versus  $A$  curves obtained, the above results are explained by two factors: (1) HDfC<sub>9</sub>OH tends to tilt from interface normal for  $\omega$ -dipoles to interact effectively with water molecules in the interfacial region and to reduce the repulsive force acting between neighbors. This leads to a lower  $\bar{u}_1^H$  value for HDfC<sub>9</sub>OH than for FDFC<sub>9</sub>OH. (2) The contact of  $\omega$ -dipoles with hexane molecules in the bulk solution is energetically unfavorable, and therefore, the  $u_1^O$  value of HDfC<sub>9</sub>OH is expected to be larger than that of the FDFC<sub>9</sub>OH system.

The  $\bar{u}_1^H - u_1^O$  values of both alcohols are almost equal to each other at the saturated interfacial density. The X-ray reflectivity study on the adsorbed film of 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (TFC<sub>10</sub>OH), which does not have an  $\omega$ -dipole, at the hexane/water interface shows that the TFC<sub>10</sub>OH molecules stand almost upright in the condensed state which is regarded as a two-dimensional solid state in terms of the electron density value of the adsorbed film.<sup>7,8</sup> Therefore, the HDfC<sub>9</sub>OH molecules as well as the FDFC<sub>9</sub>OH ones would orient nearly perpendicular to the interface in the saturated  $\Gamma_1^H$  region.

However, HDfC<sub>9</sub>OH has a smaller interfacial density in the condensed films and clearly different values of thermodynamic quantities related to the adsorption compared to FDFC<sub>9</sub>OH as mentioned above. Thus, in the next paper,<sup>21</sup> we will discuss the effect of  $\omega$ -dipoles on the molecular orientation at the

interface from the viewpoint of volume through the measurement of the pressure dependence of interfacial tension.

Finally, let us examine the phase transition found in this study. When the two states  $\alpha$  and  $\beta$  coexist at the interface, the equilibrium interfacial tension ( $\gamma^{\text{eq}}$ ) is given by<sup>4,22</sup>

$$d\gamma^{\text{eq}} = -[(\Delta s^\beta/\Gamma_1^{H,\beta} - \Delta s^\alpha/\Gamma_1^{H,\alpha})/(1/\Gamma_1^{H,\beta} - 1/\Gamma_1^{H,\alpha})] dT + [(\Delta v^\beta/\Gamma_1^{H,\beta} - \Delta v^\alpha/\Gamma_1^{H,\alpha})/(1/\Gamma_1^{H,\beta} - 1/\Gamma_1^{H,\alpha})] dp \quad (8)$$

Since the  $\gamma^{\text{eq}}$  value is a function of temperature and pressure, we have

$$d\gamma^{\text{eq}} = (\partial\gamma^{\text{eq}}/\partial T)_p dT + (\partial\gamma^{\text{eq}}/\partial p)_T dp \quad (9)$$

Therefore, the coefficients of  $dT$  of eqs 8 and 9 are evaluated separately by using the  $\Gamma_1^H$  and  $\Delta s$  values in Figures 5 and 7 and by the slope of the  $\gamma^{\text{eq}}$  versus  $T$  curve in Figure 4, respectively. The results are shown in Figure 10 for both alcohol systems. It is realized that the agreement of both coefficients is good enough to claim that the two types of phase transitions take place in the adsorbed films of fluorononanol.

## Conclusions

The effect of  $\omega$ -hydrogenation on the adsorption of fluorononanol at the hexane/water interface was examined by evaluating the partial molar entropy and energy changes associated with adsorption and comparing the values between the two alcohols, 1*H*,1*H*-perfluorononanol (FDFC<sub>9</sub>OH) and its  $\omega$ -hydrogenated analogue 1*H*,1*H*,9*H*-perfluorononanol (HDFC<sub>9</sub>OH). The energy change is more negative for HDfC<sub>9</sub>OH than for FDFC<sub>9</sub>OH in the condensed film just above the expanded–condensed phase transition point as well as in the expanded state. This would rely on the following:

(1) HDfC<sub>9</sub>OH tends to tilt from interface normal for  $\omega$ -dipoles to interact effectively with water molecules in the interfacial region and to reduce the repulsive interaction between neighbors arranging parallel in the adsorbed film. This leads to a lower energy value for HDfC<sub>9</sub>OH than for FDFC<sub>9</sub>OH in the adsorbed film.

(2) HDfC<sub>9</sub>OH molecules are energetically unstable in the hexane solution compared to FDFC<sub>9</sub>OH ones because of the hydrophilic nature of the  $\omega$ -dipole, and therefore, the partial molar energy of HDfC<sub>9</sub>OH is expected to be larger than that of FDFC<sub>9</sub>OH.

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## References and Notes

- (1) Hayami, Y.; Uemura, A.; Ikeda, N.; Aratono, M.; Motomura, K. *J. Colloid Interface Sci.* **1995**, *172*, 142.
- (2) Takiue, T.; Yanata, A.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Phys. Chem.* **1996**, *100*, 13743.
- (3) Takiue, T.; Yanata, A.; Ikeda, N.; Hayami, Y.; Motomura, K.; Aratono, M. *J. Phys. Chem.* **1996**, *100*, 20122.
- (4) Takiue, T.; Uemura, A.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Phys. Chem. B* **1998**, *102*, 3724.
- (5) Takiue, T.; Sugino, K.; Higashi, T.; Toyomasu, T.; Hayami, Y.; Ikeda, N.; Aratono, M. *Langmuir* **2001**, *17*, 8098.
- (6) Zhang, Z.; Mitrovic, D. M.; Williams, S. M.; Huang, Z.; Schlossman, M. L. *J. Chem. Phys.* **1999**, *110*, 7421.
- (7) Tikhonov, A. M.; Li, M.; Schlossman, M. L. *J. Phys. Chem. B* **2001**, *105*, 8065.
- (8) Pingali, S. V.; Takiue, T.; Luo, G.; Tikhonov, A. M.; Ikeda, N.; Aratono, M.; Schlossman, M. L. *J. Phys. Chem. B* **2005**, *109*, 1210.

- (9) *Fluorinated Surfactants*; Kissa, E., Ed.; Marcel Dekker: New York, 1994; Chapter 3.
- (10) Matsukubo, T.; Matsubara, M.; Takiue, T.; Aratono, M. Unpublished data.
- (11) Downer, A.; Eastoe, J.; Pitt, A. R.; Penfold, J.; Heeman, R. K. *Colloids Surf., A* **1999**, *156*, 33.
- (12) Downer, A.; Eastoe, J.; Pitt, A. R.; Simister, E. A.; Penfold, J. *Langmuir* **1999**, *15*, 7591.
- (13) Eastoe, J.; Paul, A.; Rankin, A.; Wat, R.; Penfold, J.; Webster, J. R. P. *Langmuir* **2001**, *17*, 7873.
- (14) Ravey, J. C.; Stebe, M. J. *Colloids Surf., A* **1994**, *84*, 11.
- (15) Sakamoto, H.; Murao, A.; Hayami, Y. *J. Inst. Image Inf. Television Eng.* **2002**, *56*, 1643.
- (16) Murakami, R.; Sakamoto, H.; Hayami, Y.; Matsubara, H.; Takiue, T.; Aratono, M. *J. Phys. Chem. B*, submitted for publication, 2005.
- (17) Kell, G. S.; Whally, E. *Philos. Trans. R. Soc. London, Ser. A* **1965**, *258*, 565.
- (18) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6814.
- (19) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992; Chapter 4.
- (20) Motomura, K. *J. Colloid Interface Sci.* **1978**, *64*, 348.
- (21) Takiue, T.; Hirose, D.; Murakami, D.; Sakamoto, H.; Matsubara, H.; Aratono, M. *J. Phys. Chem. B*, submitted for publication, 2005.
- (22) Matubayasi, N.; Motomura, K.; Aratono, M.; Matuura, R. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2800.