

# Thermodynamic Study on Phase Transition in Adsorbed Film of Fluoroalkanol at the Hexane/Water Interface. 3. Temperature Effect on the Adsorption of 1,1,2,2-Tetrahydroheptadecafluorodecanol

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The interfacial tension  $\gamma$  of a hexane solution of 1,1,2,2-tetrahydroheptadecafluorodecanol  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$  ( $\text{FC}_{10}\text{OH}$ ) against water was measured as a function of temperature  $T$  and molality  $m_1$  under atmospheric pressure. By the calculation of the interfacial density  $\Gamma_1^{\text{H}}$  and then drawing the interfacial pressure  $\pi$  vs area per adsorbed molecule  $A$  curves, it was concluded that two types of first-order phase transitions take place from the gaseous to the expanded state and from the expanded to the condensed one in the adsorbed film of  $\text{FC}_{10}\text{OH}$ . The partial molar entropy  $\bar{s}_1^{\text{H}} - s_1^{\text{O}}$  and energy changes  $\bar{u}_1^{\text{H}} - u_1^{\text{O}}$  associated with the adsorption were estimated and compared with those of 1,1,2,2-tetrahydrohenicosafuorododecanol  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{OH}$  ( $\text{FC}_{12}\text{OH}$ ). It was found that these values of  $\text{FC}_{10}\text{OH}$  are negative and larger than those of  $\text{FC}_{12}\text{OH}$ . It was suggested that, although both  $\bar{s}_1^{\text{H}}$  and  $s_1^{\text{O}}$  values increase, the increment in  $s_1^{\text{O}}$  is larger than that in  $\bar{s}_1^{\text{H}}$  when the fluorocarbon chain is lengthened from  $\text{FC}_{10}\text{OH}$  to  $\text{FC}_{12}\text{OH}$ . Furthermore, it was realized that the energetical stabilization of the  $\text{FC}_{10}\text{OH}$  molecule accompanied by adsorption is less than that of the  $\text{FC}_{12}\text{OH}$  molecule. Furthermore, it was shown that the temperature and pressure dependencies of the  $\pi$  vs  $A$  curve are related to the partial molar entropy and volume changes of adsorption, respectively. By estimation of the temperature and pressure coefficients of  $A$  at constant  $\pi$ , it is found that a temperature increase of only 1 K is sufficient to keep  $\pi$  and  $A$  constant upon a decrease of the pressure by 1 MPa.

## Introduction

The adsorption of long-chain alkanol at the oil/water interface has been studied by many workers through the interfacial tension measurement.<sup>1–11</sup> Recently, the structure of the alcohol monolayer has become apparent by using some new techniques such as Brewster angle microscope,<sup>12,13</sup> X-ray,<sup>14</sup> and neutron reflectometry.<sup>15</sup> Among them, Deutsch et al. have studied the melting of 1-alcohol monolayers adsorbed at the water/air surface by using X-ray reflectivity. They found that the fitted thickness changes drastically at the liquid–solid transition point and the thickness value of the two-dimensional solid phase is smaller than the length of the all-trans molecular chain.<sup>14</sup>

It is of great interest to investigate the adsorption behavior of fluoroalkanol at the hydrocarbon oil/water interface because the mutual interaction between hydrocarbon and fluorocarbon is very weak and they are miscible only in a limited composition range. In our previous papers,<sup>16,17</sup> we have studied the adsorption behavior of 1,1,2,2-tetrahydrohenicosafuorododecanol  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{OH}$  ( $\text{FC}_{12}\text{OH}$ ) at the hexane/water interface by measuring the temperature and pressure dependencies of the interfacial tension and evaluating the entropy  $\Delta s$ , energy  $\Delta u$ , and volume changes  $\Delta v$  associated with the adsorption. It was shown that the  $\Delta s$ ,  $\Delta u$ , and  $\Delta v$  values are diminished by the adsorption of  $\text{FC}_{12}\text{OH}$ . Furthermore, it was found that the first-order phase transition takes place from the gaseous to the condensed state in the adsorbed film.

In this study, we aim at estimating the partial molar entropy and energy changes associated with adsorption and understanding the adsorption behavior of fluoroalkanol, which is generally more hydrophobic and less flexible than a hydrocarbon alcohol,<sup>18</sup> at the hydrocarbon oil/water interface. Therefore, 1,1,2,2-tetrahydroheptadecafluorodecanol  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$  ( $\text{FC}_{10}\text{OH}$ ) was employed as material for the following reasons. First, since we have already studied the adsorption behavior of  $\text{FC}_{10}\text{OH}$  at the hexane/water interface from a volumetric point of view and found the two types of phase transitions from the gaseous to the expanded state and from the expanded to the condensed one in the adsorbed film,<sup>19</sup> the partial molar energy and then the complete set of thermodynamic quantities can be evaluated by measuring the temperature dependence of the interfacial tension and then by combining the entropies evaluated from them with the volumes. These quantities are highly useful for substantiating and understanding the phase transitions. Second, since  $\text{FC}_{10}\text{OH}$  is an analogue of  $\text{FC}_{12}\text{OH}$ , the effect of the fluorocarbon chain length on the adsorption behavior can be examined.

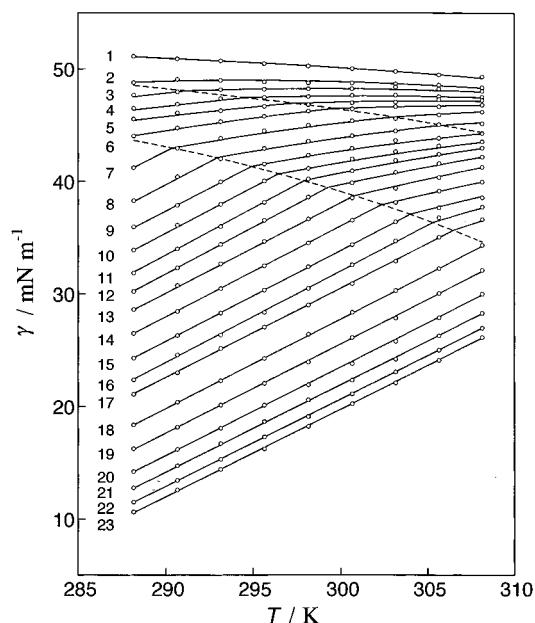
The interfacial tension of a hexane solution of  $\text{FC}_{10}\text{OH}$  against water was measured as a function of temperature and molality under atmospheric pressure. The interfacial density, the partial molar entropy, and energy changes associated with the adsorption were estimated by analyzing the experimental results thermodynamically.

## Experimental Section

1,1,2,2-Tetrahydroheptadecafluorodecanol  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$  ( $\text{FC}_{10}\text{OH}$ ), water, and hexane were purified as described

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**Figure 1.** Interfacial tension vs temperature curves at constant molality ( $m_1$ , mmol kg<sup>-1</sup>) as follows: (1) 0, (2) 0.498, (3) 0.747, (4) 0.995, (5) 1.253, (6) 1.509, (7) 1.985, (8) 2.498, (9) 2.973, (10) 3.485, (11) 3.986, (12) 4.502, (13) 4.950, (14) 5.992, (15) 6.982, (16) 7.974, (17) 9.001, (18) 11.043, (19) 13.001, (20) 14.944, (21) 16.984, (22) 18.859, and (23) 19.811.

previously.<sup>19</sup> Water and hexane were saturated mutually before measuring the interfacial tension.

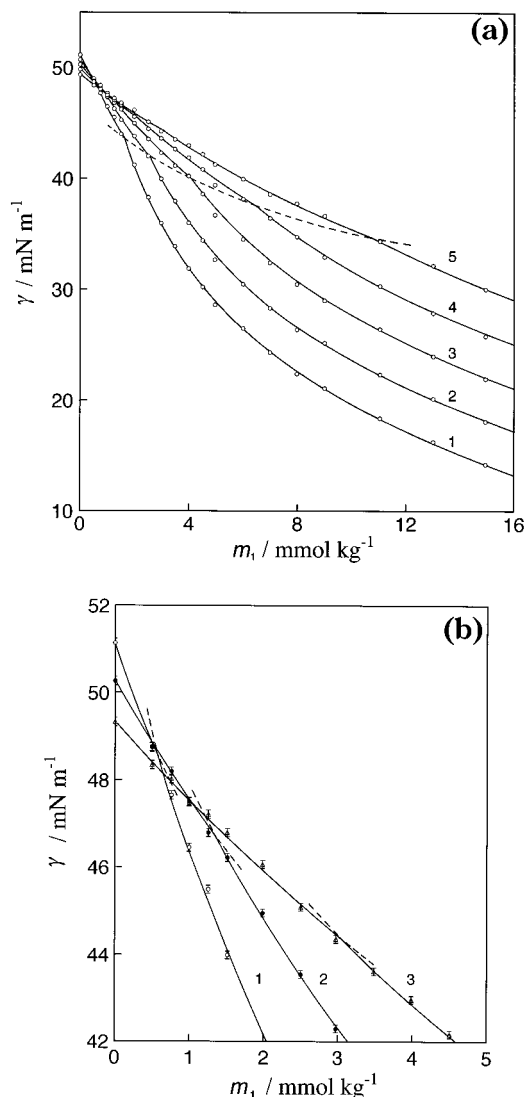
The equilibrium interfacial tension was measured as a function of temperature under atmospheric pressure by the pendant drop technique<sup>6</sup> within an experimental error of 0.05 mN m<sup>-1</sup>. The densities of pure water and hexane<sup>20,21</sup> were used for the calculation of interfacial tension because the hexane solution was very dilute and practically insoluble in water.

## Results and Discussion

The interfacial tension  $\gamma$  of the hexane solution of FC<sub>10</sub>OH against water is drawn as a function of temperature  $T$  under atmospheric pressure in Figure 1. The  $\gamma$  value of pure hexane/water interface decreases slightly, while that of the solution increases, with increasing temperature. Furthermore, the dependence of  $\gamma$  on  $T$  becomes large with increasing concentration and is almost constant at high concentrations. It is noted that the  $\gamma$  vs  $T$  curve in the intermediate concentration region has one or two break points at which the curve changes its slope abruptly. In Figure 2a, the  $\gamma$  values read from Figure 1 at a given temperature were plotted against molality  $m_1$  and the  $\gamma$  vs  $m_1$  curves are magnified in a low concentration region in Figure 2b. It is seen from Figure 2b that the extrapolation of the  $\gamma$  vs  $m_1$  curve from high concentrations to zero does not give the  $\gamma$  value at the pure hexane/water interface. Therefore, it was hypothesized that two break points exist on the  $\gamma$  vs  $m_1$  curves at all temperatures. The  $\gamma$  value of the break point decreases and the corresponding  $m_1$  value increases with increasing temperature as shown by the dash lines. Taking into account our previous results,<sup>19</sup> these breaks suggest the phase transition in the adsorbed film of FC<sub>10</sub>OH at the hexane/water interface.

Now we evaluate the interfacial density  $\Gamma_1^H$  by applying the equation

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



**Figure 2.** (a) Interfacial tension vs molality curves at constant temperature ( $T$ , K) as follows: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15, and (5) 308.15. (b) Interfacial tension vs molality curves at constant temperature ( $T$ , K) as follows: (1) 288.15, (2) 298.15, and (3) 308.15.

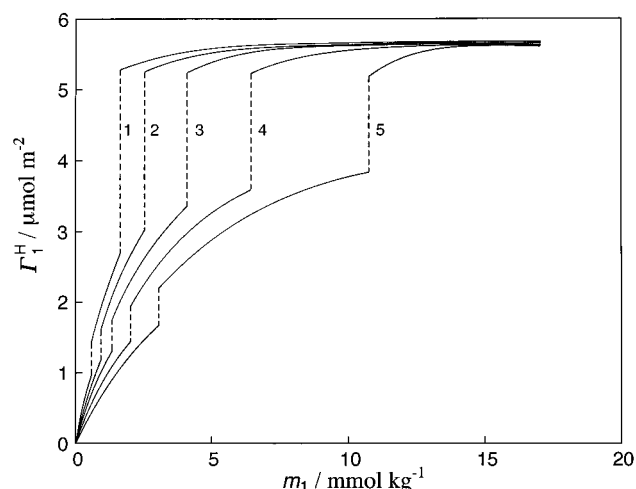
to the  $\gamma$  vs  $m_1$  curves in Figure 2. The results are shown in the form of the  $\Gamma_1^H$  vs  $m_1$  curves at various temperatures in Figure 3. It is seen that the  $\Gamma_1^H$  value increases with increasing  $m_1$  and changes discontinuously at the concentrations corresponding to the break points on the  $\gamma$  vs  $m_1$  curves. To make clear the state of the adsorbed film, we calculated the interfacial pressure  $\pi$  and the mean area per adsorbed molecule  $A$  by the equations

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

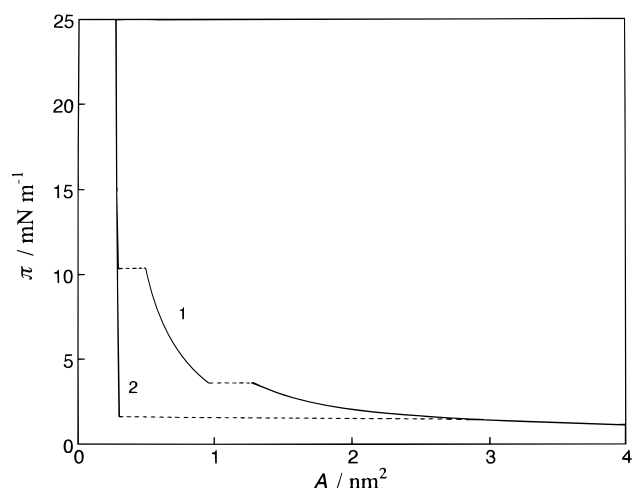
and

$$A = \frac{1}{N_A \Gamma_1^H} \quad (3)$$

where  $\gamma^0$  is the interfacial tension of the pure hexane/water interface and  $N_A$  is Avogadro's number. In Figure 4, the  $\pi$  vs  $A$  curve of FC<sub>10</sub>OH is compared with the corresponding curve of 1,1,2,2-tetrahydrohenicosafuorodecanol (FC<sub>12</sub>OH) at 298.15 K. It is seen that the curve of FC<sub>10</sub>OH consists of the three parts connected by the discontinuous changes, while that of



**Figure 3.** Interfacial density vs molality curves at constant temperature ( $T$ , K) as follows: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15, and (5) 308.15.

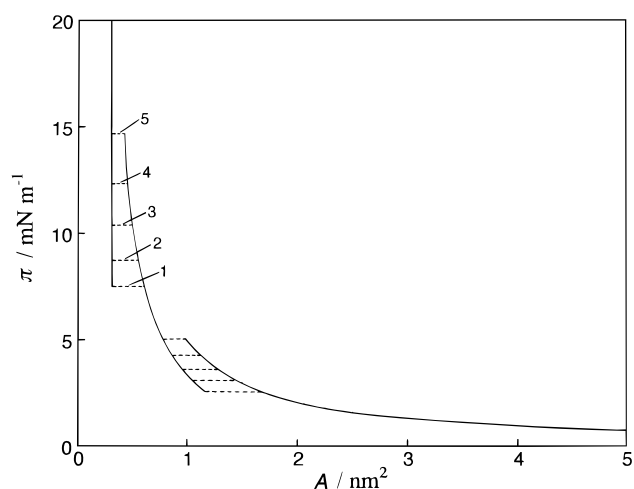


**Figure 4.** Interfacial pressure vs mean area per molecule curves at 298.15 K: (1)  $\text{FC}_{10}\text{OH}$ ; (2)  $\text{FC}_{12}\text{OH}$ .

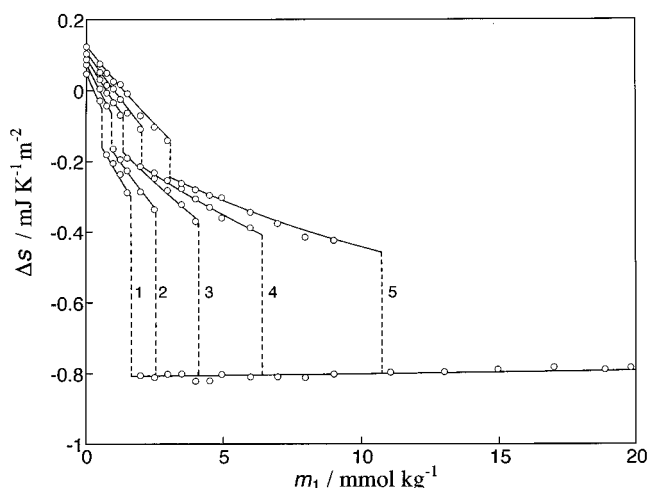
$\text{FC}_{12}\text{OH}$  consists of the two parts only. Taking account of the previous finding that the adsorbed film of  $\text{FC}_{12}\text{OH}$  exhibits the phase transition from the gaseous to the condensed state,<sup>16,17</sup> it is concluded that the two types of phase transitions take place from the gaseous to the expanded state and from the expanded to the condensed one in the adsorbed film of  $\text{FC}_{10}\text{OH}$ . Furthermore, it is noted that both  $A$  values of  $\text{FC}_{10}\text{OH}$  and  $\text{FC}_{12}\text{OH}$  of the condensed state are very close to the cross sectional area of fluorocarbon chain of ca.  $0.3 \text{ nm}^2$ .

The  $\pi$  vs  $A$  curves of  $\text{FC}_{10}\text{OH}$  at various temperatures are shown in Figure 5. It is seen that the interfacial pressure and the mean area at the transition point increase and decrease, respectively, with increasing temperature owing to a balance between the thermal motion and mutual interaction of  $\text{FC}_{10}\text{OH}$  molecules. However, we note that the  $A$  value at a given  $\pi$  does not appear to depend appreciably on temperature in the three states of adsorbed film. This is in contrast to our previous finding that the  $A$  value strongly depends on pressure in the expanded state (Figure 4 in ref 19). We will discuss this difference between the pressure and temperature dependencies later.

Next, let us consider the adsorption behavior of  $\text{FC}_{10}\text{OH}$  from the viewpoint of entropy. The entropy change associated with the adsorption  $\Delta s$  is evaluated by applying the equation



**Figure 5.** Interfacial pressure vs mean area per molecule curves at constant temperature ( $T$ , K) as follows: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15, and (5) 308.15.



**Figure 6.** Entropy change associated with the adsorption vs molality curves at constant temperature ( $T$ , K) as follows: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15, and (5) 308.15.

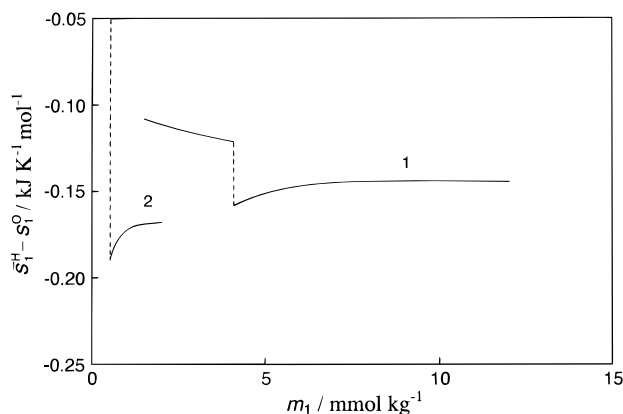
$$\Delta s = -(\partial\gamma/\partial T)_{p,m_1} \quad (4)$$

to the  $\gamma$  vs  $T$  curves in Figure 1. The  $\Delta s$  values obtained are plotted against  $m_1$  in Figure 6. It is seen that the  $\Delta s$  value decreases with increasing adsorption and changes discontinuously at the phase-transition points. The  $\Delta s$  value decreases from the positive to the negative value in the gaseous state and becomes more negative in the expanded state. In the condensed state, it is largely negative and hardly depends on temperature and molality. Therefore, it is said that the adsorption of  $\text{FC}_{10}\text{OH}$  at the hexane/water interface diminishes the  $\Delta s$  value.

To obtain further insight into the adsorption behavior of fluoroalkanol at the hexane/water interface, it is informative to estimate the partial molar entropy change of alcohol associated with the adsorption  $\bar{s}_1^H - s_1^O$  and to compare the values between  $\text{FC}_{10}\text{OH}$  and  $\text{FC}_{12}\text{OH}$ . The  $\bar{s}_1^H - s_1^O$  value is estimated by the following equation<sup>22</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 the alcohol in the hexane solution,  $\bar{s}_1^H$  the mean partial molar entropy inherent in the interface, and  $a_1$  the partial molar area of the alcohol



**Figure 7.** Partial molar entropy change of adsorption vs molality curves at 298.15 K: (1) FC<sub>10</sub>OH; (2) FC<sub>12</sub>OH.

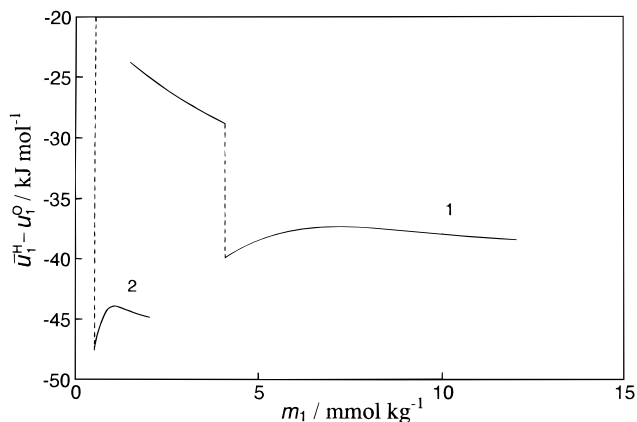
molecule, respectively. Here, it should be noted that there are some possibilities of assigning values to  $a_1$ , since  $a_1$  cannot be determined experimentally. One of them is  $a_1 = 0.3 \text{ nm}^2$ , being close to the cross sectional area of fluorocarbon chain, and another is  $a_1 = 1/\Gamma_1^H$ . However, we found that the difference in  $a_1$  value does not change appreciably the  $\bar{s}_1^H - s_1^O$  value in the expanded and condensed states within experimental error. Therefore, the  $a_1$  value is assumed to be  $0.3 \text{ nm}^2$  in this study because the contribution of water and hexane molecules to the  $\Delta s$  value is not taken into account when  $a_1 = 1/\Gamma_1^H$  is employed.<sup>22</sup>

In Figure 7 are shown the  $\bar{s}_1^H - s_1^O$  vs  $m_1$  curves for the expanded and the condensed states of FC<sub>10</sub>OH and for the condensed state of FC<sub>12</sub>OH at 298.15 K. It is found that the  $\bar{s}_1^H - s_1^O$  value is negative and changes discontinuously at the phase-transition point. Therefore, it is realized that the FC<sub>10</sub>-OH molecule has a smaller entropy at the interface than in the hexane solution owing to the orientation of FC<sub>10</sub>OH molecule at the hexane/water interface. Figure 7 also demonstrates the effect of fluorocarbon chain length of the fluoroalkanol molecule on the  $\bar{s}_1^H - s_1^O$  value. It is found that the  $\bar{s}_1^H - s_1^O$  value of the condensed state of FC<sub>12</sub>OH is smaller than that of FC<sub>10</sub>OH. Furthermore, it has been known that the mixing of fluorocarbon and hydrocarbon molecules is generally accompanied by the positive excess volume and entropy.<sup>23</sup> These suggest two possibilities when the fluorocarbon chain is lengthened from FC<sub>10</sub>OH to FC<sub>12</sub>OH. The first is that although both  $\bar{s}_1^H$  and  $s_1^O$  values increase, the increment in  $s_1^O$  is larger than that in  $\bar{s}_1^H$ . And the second is that although the  $s_1^O$  value increases,  $\bar{s}_1^H$  decreases. Taking account of our previous finding<sup>17</sup> that the increase in the partial molar volume of alcohol accompanied by the increase in the fluorocarbon chain length is larger in the hexane solution than in the interface because the fluoroalkanol molecules mix with hexane in the bulk solution, the first seems to be more probable.

It is also useful to discuss the adsorption behavior of FC<sub>10</sub>-OH from the viewpoint of energy. The partial molar energy change of adsorption,  $\bar{u}_1^H - u_1^O$ , was calculated by using the following equation,

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

The  $\bar{u}_1^H - u_1^O$  vs  $m_1$  curve of FC<sub>10</sub>OH is illustrated together with the curve of FC<sub>12</sub>OH at 298.15 K under atmospheric pressure in Figure 8. The negative value of  $\bar{u}_1^H - u_1^O$  substantiates that the adsorption of FC<sub>10</sub>OH is caused by a decrease in energy that exceeds the decrease in entropy. Furthermore, it is



**Figure 8.** Partial molar energy change of adsorption vs molality curves at 298.15 K: (1) FC<sub>10</sub>OH; (2) FC<sub>12</sub>OH.

found that the  $\bar{u}_1^H - u_1^O$  value of FC<sub>10</sub>OH is larger than that of FC<sub>12</sub>OH, and therefore, the energetical stabilization of the FC<sub>10</sub>-OH molecule accompanied by the adsorption from the hexane solution is less than that of FC<sub>12</sub>OH molecule.

Now, we will prove that the experimental finding in Figure 5 that the  $\pi$  vs  $A$  curve does not depend appreciably on temperature is associated with a decrease in partial molar entropy accompanied by adsorption. The total differential of the interfacial tension  $\gamma$  of the hexane solution/water interface is

$$d\gamma = -\Delta s dT + \Delta v dp - \Gamma_1^H(\partial\mu_1/\partial m_1)_{T,p} dm_1 \quad (7)$$

where  $\Delta v$  and  $\mu_1$  represent the volume change associated with adsorption and the chemical potential of alcohol in the hexane solution, respectively.

For the hexane/water interface without alcohol, we have

$$d\gamma^0 = -\Delta s^0 dT + \Delta v^0 dp \quad (8)$$

where  $\Delta s^0$  and  $\Delta v^0$  are the entropy and volume of interface formation, respectively. From eqs 7 and 8, the total differential of interfacial pressure  $\pi$  is expressed by

$$d\pi = -(\Delta s^0 - \Delta s) dT + (\Delta v^0 - \Delta v) dp + \Gamma_1^H(\partial\mu_1/\partial m_1)_{T,p} dm_1 \quad (9)$$

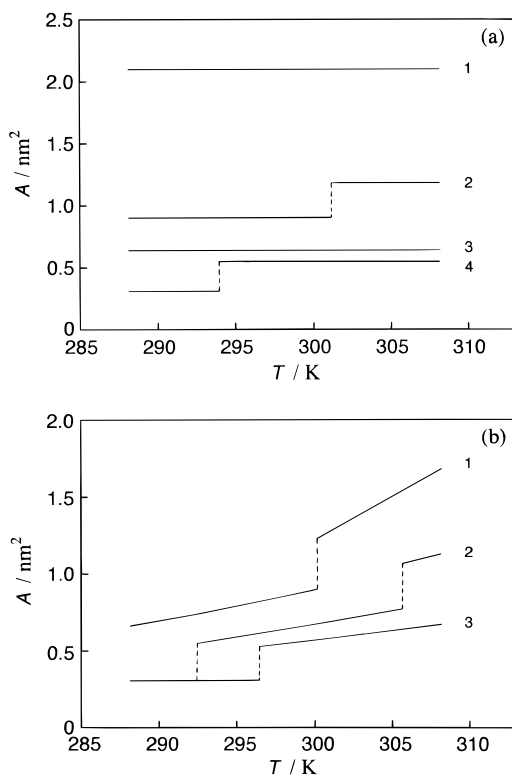
Since the area per adsorbed molecule  $A$  is also a function of  $T$ ,  $p$ , and  $m_1$ ,

$$dA = (\partial A/\partial T)_{p,m_1} dT + (\partial A/\partial p)_{T,m_1} dp + (\partial A/\partial m_1)_{T,p} dm_1 \quad (10)$$

the temperature coefficient of  $A$  at constant  $p$  and  $\pi$  is obtained by eliminating  $dm_1$  from eqs 9 and 10,

$$\begin{aligned} (\partial A/\partial T)_{p,\pi} &= -[(\Delta s - \Delta s^0)/\Gamma_1^H(\partial\mu_1/\partial m_1)_{T,p}](\partial A/\partial m_1)_{T,p} + \\ &\quad (\partial A/\partial T)_{p,m_1} \\ &\approx -(m_1/RT)(\bar{s}_1^H - s_1^O)(\partial A/\partial m_1)_{T,p} + (\partial A/\partial T)_{p,m_1} \end{aligned} \quad (11)$$

where we assumed that the contribution of solvent molecules to  $\Delta s$  does not change appreciably from the entropy of pure hexane/water interface formation  $\Delta s^0$ ,  $\Delta s - \Delta s^0 \approx \Gamma_1^H(\bar{s}_1^H - s_1^O)$ , and that the hexane solution is an ideal dilute one. It is noted that  $(\partial A/\partial T)_{p,\pi}$  consists of two contributions; one is closely related to the partial molar entropy change of adsorption,  $\bar{s}_1^H -$



**Figure 9.** (a) Mean area per molecule vs temperature curves at constant interfacial pressure ( $\pi$ , mN m<sup>-1</sup>) as follows: (1) 2.0, (2) 4.0, (3) 7.0, and (4) 9.0. (b) Mean area per molecule vs temperature curves at constant molality ( $m_1$ , mmol kg<sup>-1</sup>) as follows: (1) 1.5, (2) 2.5, and (3) 3.5.

**TABLE 1: Estimation of R.S. Value of Eq 11 at 2.5 mmol kg<sup>-1</sup> and 298.15 K ( $\pi = 7.0$  mN m<sup>-1</sup>)**

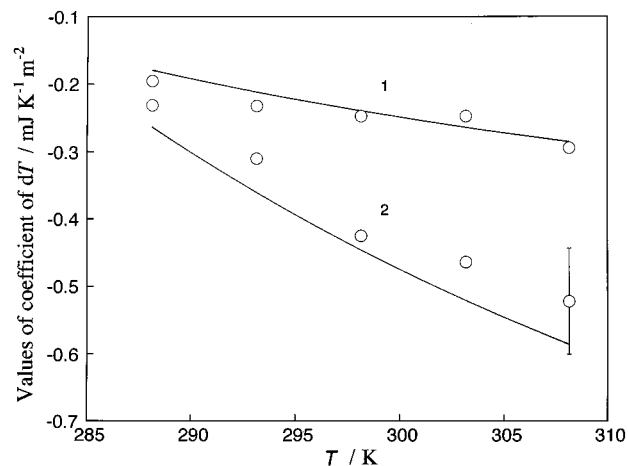
$\bar{s}_1^H - s_1^O$ /kJ K <sup>-1</sup> mol <sup>-1</sup>	-0.11
$(\partial A/\partial m_1)_{T,p}$ /nm <sup>2</sup> mmol <sup>-1</sup> kg	-0.15
$(\partial A/\partial T)_{p,m_1}$ /nm <sup>2</sup> K <sup>-1</sup>	$1.8 \times 10^{-2}$
R.S./nm <sup>2</sup> K <sup>-1</sup>	$1.0 \times 10^{-3}$

$s_1^O$ , and another is the change in  $A$  with temperature at constant bulk concentration.

The  $A$  vs  $T$  curves are shown at a given  $\pi$  in Figure 9a and at a given  $m_1$  in Figure 9b under atmospheric pressure. In the condensed state, it is seen that  $(\partial A/\partial T)_{p,m_1}$  is almost zero. And  $(\partial A/\partial m_1)_{T,p} = -(\partial \Gamma_1^H/\partial m_1)_{T,p}/N_A(\Gamma_1^H)^2$  is expected to be also very small from Figure 3. This substantiates that  $(\partial A/\partial T)_{p,\pi}$  is almost zero even when the partial molar entropy change is largely negative (Figure 7). On the other hand,  $(\partial A/\partial T)_{p,m_1}$  increases with increasing temperature in the expanded state. Then the right-hand side (R.S.) of eq 11 was estimated in the expanded state at  $m_1 = 2.5$  mmol kg<sup>-1</sup> and 298.15 K ( $\pi = 7.0$  mN m<sup>-1</sup>). The result is shown in Table 1 together with the  $\bar{s}_1^H - s_1^O$ ,  $(\partial A/\partial m_1)_{T,p}$ , and  $(\partial A/\partial T)_{p,m_1}$  values. It is seen that the R.S. value is slightly positive and  $\Delta A/\Delta T \approx 0.02$  nm<sup>2</sup> K<sup>-1</sup> for  $\Delta T = 20$  K; the decrease in  $\bar{s}_1^H - s_1^O$  compensates for the increase in  $(\partial A/\partial T)_{p,m_1}$ . This is why the dependence of the  $\pi$  vs  $A$  curve on  $T$  is very small, although the surface density depends strongly on  $T$  at a given  $m_1$  in the temperature range in this study.

Furthermore, the pressure coefficient of  $A$  at constant  $T$  and  $\pi$  is given by using the following relation,

$$(\partial A/\partial p)_{T,\pi} \approx (m_1/RT)(\bar{v}_1^H - v_1^O)(\partial A/\partial m_1)_{T,p} + (\partial A/\partial p)_{T,m_1} \quad (12)$$



**Figure 10.** Values of coefficient of  $dT$  of eqs 13 and 14 vs temperature curve: (○) eq 13; (—) eq 14; (1) gaseous  $\leftrightarrow$  expanded, (2) expanded  $\leftrightarrow$  condensed.

**TABLE 2: Estimation of R.S. Value of Eq 12 at 1.3 mmol kg<sup>-1</sup> and 0.1 MPa ( $\pi = 3.0$  mN m<sup>-1</sup>)**

$\bar{v}_1^H - v_1^O$ /cm <sup>3</sup> mol <sup>-1</sup>	-3.3
$(\partial A/\partial m_1)_{T,p}$ /nm <sup>2</sup> mmol <sup>-1</sup> kg	-0.80
$(\partial A/\partial p)_{T,m_1}$ /nm <sup>2</sup> MPa <sup>-1</sup>	0
R.S./nm <sup>2</sup> MPa <sup>-1</sup>	$1.4 \times 10^{-3}$

which relate  $(\partial A/\partial p)_{T,\pi}$  to the partial molar volume change of adsorption,  $\bar{v}_1^H - v_1^O$ , and the pressure coefficient at constant  $T$  and bulk concentration. The R.S. value of eq 12 was calculated for the expanded film at  $m_1 = 1.3$  mmol kg<sup>-1</sup> and 0.1 MPa ( $\pi = 3.0$  mN m<sup>-1</sup>) and listed in Table 2. It is seen that the R.S. value is small and positive but  $\Delta A/\Delta p \approx 0.2$  nm<sup>2</sup> MPa<sup>-1</sup> for  $\Delta p \approx 150$  MPa; the pressure dependence of the  $\pi$  vs  $A$  curve is visualized in the experimental pressure region.<sup>19</sup> Furthermore, it is found that the ratio  $(\partial A/\partial T)_{p,\pi}/(\partial A/\partial p)_{T,\pi} = -(\partial p/\partial T)_{A,\pi}$  is about 0.7 MPa K<sup>-1</sup>, of which the absolute value is very close to that of the thermal pressure coefficient of liquid.<sup>24</sup> Therefore, it is found that a temperature increase of only 1 K is sufficient to keep  $\pi$  and  $A$  values constant upon decreasing the pressure by 1 MPa.

Finally, we examined the order of the phase transition found in this study. When the two states  $\alpha$  and  $\beta$  coexist in the interface, the equilibrium interfacial tension is given by

$$d\gamma^{\text{eq}} = -[(\Delta s^\beta/\Gamma_1^{\text{H},\beta} - \Delta s^\alpha/\Gamma_1^{\text{H},\alpha})/(1/\Gamma_1^{\text{H},\beta} - 1/\Gamma_1^{\text{H},\alpha})] dT + [(\Delta v^\beta/\Gamma_1^{\text{H},\beta} - \Delta v^\alpha/\Gamma_1^{\text{H},\alpha})/(1/\Gamma_1^{\text{H},\beta} - 1/\Gamma_1^{\text{H},\alpha})] dp \quad (13)$$

As is shown from the experimental results given in Figure 1,  $\gamma^{\text{eq}}$  is also determined solely by pressure and temperature:

$$d\gamma^{\text{eq}} = (\partial \gamma^{\text{eq}}/\partial T)_p dT + (\partial \gamma^{\text{eq}}/\partial p)_T dp \quad (14)$$

The coefficients of  $dT$  of eqs 13 and 14 were calculated separately in a similar manner described previously<sup>16</sup> and compared in Figure 10. It is seen that the agreement is fairly good for the two types of phase transitions by taking account of the experimental error; the two types of first-order phase transitions take place in the adsorbed film of FC<sub>10</sub>OH at the hexane/water interface. Recently, these two types of phase transitions were further confirmed by investigating the adsorption behavior of a mixed FC<sub>10</sub>OH–FC<sub>12</sub>OH system. The phase transitions and miscibility of fluoroalkanols of this mixed system will be discussed in near future.<sup>25</sup>

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