

Thermodynamic Study on Phase Transition in Adsorbed Films of Fluoroalkanol at the Hexane/Water Interface. 5. Miscibility in the Adsorbed Film of an Alkanol and Fluoroalkanol Mixture

Takanori Takiue,* Takehiko Matsuo, Norihiro Ikeda,[†] Kinsi Motomura, and Makoto Aratono

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812-8581, Japan

Received: January 6, 1998; In Final Form: May 19, 1998

The miscibility of 1-icosanol ($C_{20}OH$) and 1,1,2,2-tetrahydroheptadecafluorodecanol ($FC_{10}OH$) in the adsorbed film at the hexane/water interface was investigated by evaluating the composition of $FC_{10}OH$ in the adsorbed film X_2^H from the interfacial tension data and drawing the phase diagram of adsorption (PDA). We found that the PDA changes its shape from the positive azeotrope in the expanded state, where the $C_{20}OH$ and $FC_{10}OH$ molecules are miscible at all proportions, to the heteroazeotrope in the condensed state, where they are completely immiscible with each other, as the interfacial tension γ decreases. To examine the deviation from the ideal mixing in the adsorbed film quantitatively, the activity coefficient of component i , f_i^H , and the excess Gibbs energy, $g^{H,E}$, in the expanded state were estimated from the PDA. It was found that the f_i^H value is larger than unity in a whole X_2^H range, and therefore, the corresponding $g^{H,E}$ value is positive at all compositions and increases with decreasing γ . This result shows that the $C_{20}OH$ and $FC_{10}OH$ molecules mix nonideally in the adsorbed film and the mutual interaction between the different kinds of alcohol molecules is very weak compared with that between the same kinds. Furthermore, we estimated the excess area in the adsorbed film $A^{H,E}$ from the dependence of $g^{H,E}$ on γ . The $A^{H,E}$ value was positive, and therefore, the mixing of $C_{20}OH$ and $FC_{10}OH$ molecules in the adsorbed film causes an increase in area A . By comparison of this result with the corresponding volume increase associated with the mixed micelle formation of hydrocarbon and fluorocarbon surfactants, it was suggested that the difference in the geometrical structure between adsorbed films and micelle affects appreciably the molecular packing in them and eventually the molecular interaction between hydrocarbon and fluorocarbon molecules.

Introduction

It is highly important to clarify the miscibility of binary surfactants mixture in the adsorbed film and micelle from the viewpoint of the molecular interaction between them in molecular organized systems.^{1–3} Among our thermodynamic studies on the mixed adsorption from and micelle formation in the aqueous solutions of various combinations of surfactants,⁴ it deserves special mention that the hydrocarbon and fluorocarbon surfactants are miscible at all proportions of the mixture in the adsorbed film at the aqueous solution/oil or air interface but only at limited proportions in the micelle.^{5–7}

However, from our previous study on the adsorption of the 1-icosanol ($C_{20}OH$) and 1,1,2,2-tetrahydroheptadecafluorodecanol ($FC_{10}OH$) mixture from its hexane solution at the solution/water interface,⁸ it was found that γ vs m curves have one or two break points depending on X_2 and it has been proved that the two kinds of phase transitions take place in the adsorbed film and that the $C_{20}OH$ and $FC_{10}OH$ molecules are completely immiscible with each other even in the adsorbed film when it is the condensed one. This has been achieved by measuring the interfacial tension γ as a function of the total molality of their mixture m and the composition of $FC_{10}OH$ X_2 and by

drawing the interfacial pressure π vs area per adsorbed molecule A curves at 298.15 K under atmospheric pressure.

In this paper, the other strategy applicable to the same experimental results is employed to make sure of our previous points on the miscibility of $C_{20}OH$ and $FC_{10}OH$ mixture in the adsorbed film: We evaluate the composition of adsorbed film X_2^H from the interfacial tension data and then draw the phase diagram of adsorption (PDA). Then the activity coefficients of each component in the adsorbed film are estimated from the PDA and used to examine the weak molecular interaction between $C_{20}OH$ and $FC_{10}OH$ molecules in terms of the excess thermodynamic quantities of adsorption.

Experimental Section

The purification procedures of the materials used in this study and the method of interfacial tension measurement were mentioned in our previous paper.⁸

Results and Discussion

The interfacial tension γ of the hexane solution of 1-icosanol ($C_{20}OH$) and 1,1,2,2-tetrahydroheptadecafluorodecanol ($FC_{10}OH$) mixture against water was measured as a function of total molality m and composition of $FC_{10}OH$ X_2 at 298.15 K under atmospheric pressure in our previous study.⁸ The results were shown as the γ vs m curves at constant X_2 in ref 8. We have found that the γ vs m curve has one or two break points which correspond to the phase transitions from the expanded to the

* To whom correspondence should be addressed. E-mail: t.taksc@mbbox.nc.kyushu-u.ac.jp.

[†] Present address: Department of Environmental Science, Faculty of Human Environmental Science, Fukuoka Women's University, Fukuoka 813-8529, Japan.

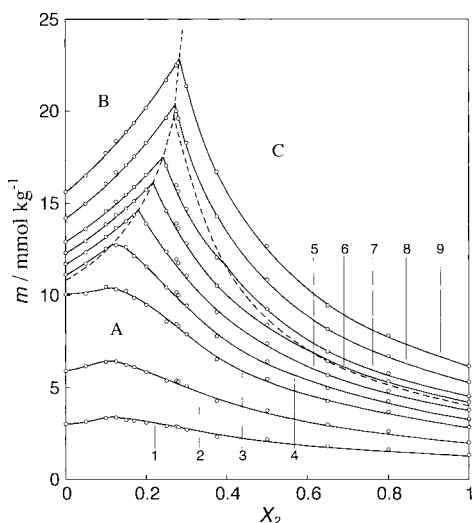


Figure 1. Total molality vs composition curves at constant interfacial tension: (1) $\gamma = 47 \text{ mN m}^{-1}$, (2) 45, (3) 43, (4) 42, (5) 41, (6) 40, (7) 39, (8) 37, (9) 35; (---) m^{eq} vs X_2 curve.

condensed state (the first break point) and from the FC₁₀OH condensed to the C₂₀OH condensed one (the second) in the adsorbed film. From these curves, we read the m values at a given γ and plotted them against X_2 in Figure 1. The total molality at the phase transition point m^{eq} vs X_2 curve is also shown in this figure. According to our previous results, there are three different states (shown by A–C) divided by the m^{eq} vs X_2 curve; the regions A–C have been found to correspond to the expanded, C₂₀OH condensed, and FC₁₀OH condensed states, respectively. It is seen from this figure that the curve at a high γ (expanded state) has a rounded maximum and that at

a low γ (condensed state) attains a sharp-pointed maximum. Furthermore, some of the curves at an intermediate γ have one or two break points on the m^{eq} vs X_2 curve. This result suggests that the miscibility of C₂₀OH and FC₁₀OH in the adsorbed film is quite different in the three states depending on the bulk composition and total molality.

Phase Diagrams of Adsorption. In order to make clear the miscibility of alcohols in the adsorbed film, we first evaluated the composition of FC₁₀OH in the adsorbed film X_2^{H} defined by

$$X_2^{\text{H}} = \Gamma_2^{\text{H}} / \Gamma^{\text{H}} \quad (1)$$

where Γ^{H} and Γ_2^{H} are the total interfacial density of C₂₀OH and FC₁₀OH and the interfacial density of FC₁₀OH, respectively, which are defined with reference to the two dividing planes making the excess numbers of moles of water and hexane zero simultaneously.^{4,9} The X_2^{H} value is calculated by applying the equation

$$X_2^{\text{H}} = X_2 - (X_1 X_2 / m) (\partial m / \partial X_2)_{T,p,\gamma} \quad (2)$$

to the m vs X_2 curves.⁴ In Figure 2 are drawn the m vs X_2^{H} curves together with the m vs X_2 curves at a given γ . The m^{eq} vs X_2 curve is also shown in this figure. These figures give the quantitative relation between the bulk composition X_2 and the film one X_2^{H} and have been employed to visualize the miscibility of surface-active substances in the adsorbed film as the phase diagram (phase diagram of adsorption; PDA).^{4–7,10–12} Let us look at the PDA at various interfacial tensions.

Figure 2a shows the PDA at 45 mN m^{−1} at which the adsorbed film takes an expanded state at all compositions. It is seen that the m vs X_2 and X_2^{H} curves have a rounded

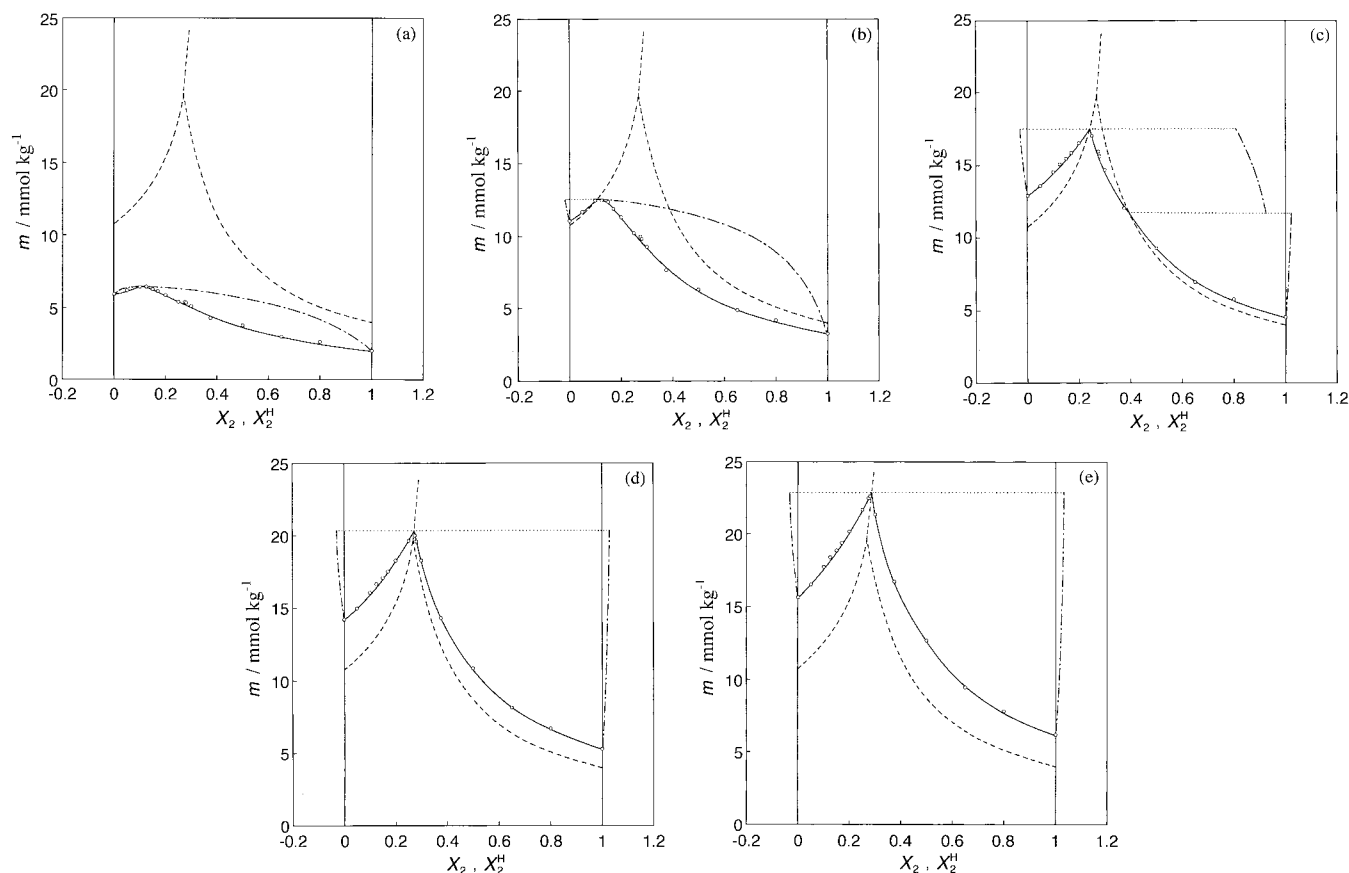


Figure 2. Phase diagram of adsorption at constant interfacial tension: (a) $\gamma = 45 \text{ mN m}^{-1}$, (b) 42.1, (c) 39, (d) 37, (e) 35; (—) m vs X_2 , (---) m vs X_2^{H} , (— · —) m^{eq} vs X_2 curve.

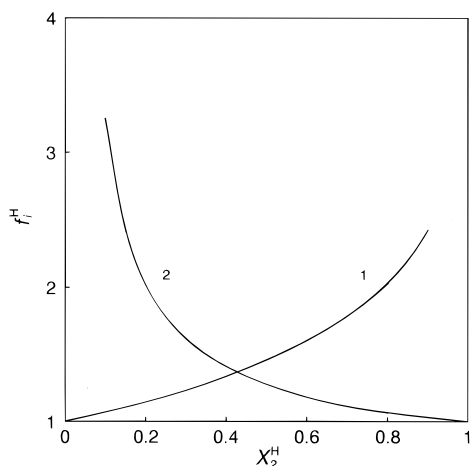


Figure 3. Activity coefficient vs composition curves at 45 mN m⁻¹: (1) f_1^H vs X_2^H ; (2) f_2^H vs X_2^H .

maximum at about $X_2 = 0.1$ and these two curves touch each other at this point. Therefore, it is said that the C₂₀OH and FC₁₀OH mixture forms a positive azeotrope in the expanded film; the adsorbed film is richer in C₂₀OH molecules below and in FC₁₀OH molecules above the positive azeotropic point than the bulk solution. Since our previous studies have proved that the m vs X_2^H curve representing the ideal mixing in the adsorbed film is given by the straight line connecting the m values of individual pure components for the nonionic–nonionic mixture,¹⁰ the m vs X_2^H curve of C₂₀OH and FC₁₀OH mixture deviates positively from the ideal mixing line and, therefore, the C₂₀OH and FC₁₀OH molecules mix nonideally in the expanded state.

As the interfacial tension decreases, the positive-azeotropic point approaches gradually the m^{eq} vs X_2 curve and touches it at 42.1 mN m⁻¹ (Figure 2b). Then the m vs X_2 curve breaks on the m^{eq} vs X_2 curve. It is seen that the C₂₀OH condensed state appears in a composition below the break point and the X_2^H value of this state is nearly zero or even slightly negative; this condensed film is constructed from C₂₀OH molecules, and FC₁₀OH molecules are expelled from the interfacial region. This forms a striking contrast with the expanded film, where C₂₀OH and FC₁₀OH molecules are miscible at all proportions.

At 39 mN m⁻¹ (Figure 2c), the m vs X_2 curve shows another break at a composition larger than the maximum of the m^{eq} vs X_2 curve. At X_2 above this break point, it is found that the FC₁₀OH condensed state appears and the X_2^H value is nearly 1; the FC₁₀OH condensed film is constructed by only FC₁₀OH molecules, and C₂₀OH is expelled from the interfacial region. The results confirm our previous finding that the condensed films are constructed from only individual components and the expanded film is constructed from the C₂₀OH and FC₁₀OH mixture.⁸

Decreasing further the interfacial tension down to 37 mN m⁻¹ (Figure 2d), the adsorbed film takes a condensed state in a whole composition range. It is clearly seen from this PDA that the mixture forms a heterogeneous azeotrope (heteroazeotrope) in the adsorbed film and there are two different condensed films depending on the bulk composition; one is constructed from only C₂₀OH molecules at compositions below, and the other, from only FC₁₀OH above the heteroazeotropic point. Furthermore, it is noted that these two condensed films coexist in the adsorbed film at the heteroazeotropic point. If we summarize the points of these PDAs, the positive azeotrope in the expanded state, where C₂₀OH and FC₁₀OH molecules are miscible at all

proportions, is transformed to the heteroazeotrope in the condensed state, where they are practically immiscible with each other, as the interfacial tension decreases.

Here we briefly mention again the second break point observed on the γ vs m curves at $X_2 = 0.275$ and 0.280 (Figure 1 in ref 8). Looking at the PDAs at $\gamma = 37$ and 35 mN m⁻¹ (Figure 2d,e), it is seen that the heteroazeotropic point sits below $X_2 = 0.275$ at 37 mN m⁻¹ and above 0.280 at 35 mN m⁻¹. Therefore, it is realized that the adsorbed films at these X_2 at a concentration between the first and the second break points is constructed from only FC₁₀OH molecules and those above the second break point from only C₂₀OH molecules. This is totally consistent with our conclusion that the second break on the γ vs m curve corresponds to the phase transition from the C₂₀OH condensed to the FC₁₀OH condensed state.

Excess Thermodynamic Quantities of Adsorption. Next, let us examine the deviation from the ideal mixing in the adsorbed film quantitatively. The chemical potential of component i in the adsorbed film is given by

$$\mu_i^H = \mu_i^{H,0} + RT \ln f_i^H X_i^H \quad i = 1, 2 \quad (3)$$

where $\mu_i^{H,0}$ is the chemical potential in the pure adsorbed film at given T , p , and γ and f_i^H is the activity coefficient defined as $f_i^H \rightarrow 1$ when $X_i^H \rightarrow 1$.^{11,12} The corresponding chemical potential in the bulk solution is given by

$$\mu_i = \mu_i^\ominus + RT \ln X_i m \quad i = 1, 2 \quad (4)$$

where μ_i^\ominus is the standard chemical potential and the solution is assumed to be ideal dilute. Using the equilibrium conditions

$$\mu_i^H = \mu_i \quad (5)$$

and

$$\mu_i^{H,0} = \mu_i^0 \quad (6)$$

we obtain from eqs 3–6

$$X_i^H f_i^H = X_i m / m_i^0 \quad i = 1, 2 \quad (7)$$

where m_i^0 is the molality of component i in the pure system at the given γ . It is noted that eq 7 describes the shape of PDA and proves that the ideal mixing ($f_i^H = 1$) is given by the straight line

$$m = m_1^0 + (m_2^0 - m_1^0)X_2^H \quad (8)$$

Now the excess Gibbs energy $g^{H,E}$ is defined in terms of the excess chemical potential of the component i , $\mu_i^{H,E}$, by

$$g^{H,E} = X_1^H \mu_1^{H,E} + X_2^H \mu_2^{H,E} \quad (9)$$

and then given by

$$g^{H,E} = RT(X_1^H \ln f_1^H + X_2^H \ln f_2^H) \quad (10)$$

At first we estimated the f_i^H value by applying eq 7 to the PDAs and then calculated the $g^{H,E}$ by using eq 10. Because the condensed films are constructed from only individual alcohols and therefore the activity coefficients are unity and infinity, we consider here the f_i^H and $g^{H,E}$ values in the expanded state. The f_i^H vs X_2^H curves at $\gamma = 45$ mN m⁻¹ are illustrated in Figure 3. It is seen that the f_i^H values are larger

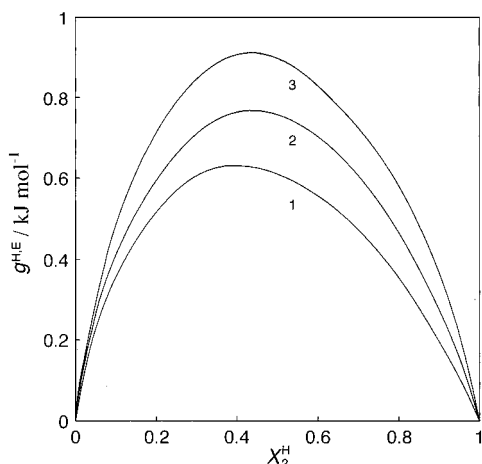


Figure 4. Excess Gibbs energy vs composition curves at constant interfacial tension: (1) $\gamma = 47 \text{ mN m}^{-1}$; (2) 45; (3) 43.

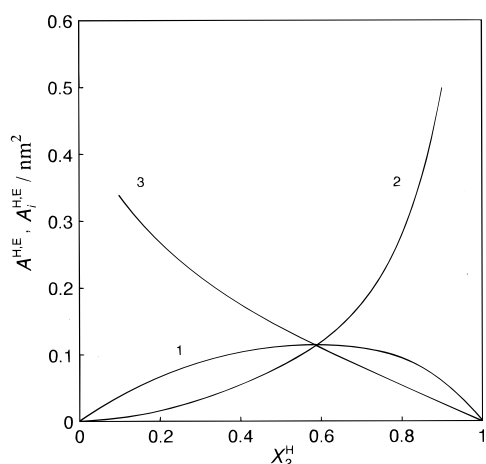


Figure 5. Excess area vs composition curves at 45 mN m^{-1} : (1) $A^{\text{H,E}}$ vs X_2^{H} ; (2) $A_1^{\text{H,E}}$ vs X_2^{H} ; (3) $A_2^{\text{H,E}}$ vs X_2^{H} .

than unity and increased by adding the other component at all compositions. In Figure 4 are shown the $g^{\text{H,E}}$ vs X_2^{H} curves at $\gamma = 47, 45$, and 43 mN m^{-1} ; the $g^{\text{H,E}}$ value is positive over the whole X_2^{H} range. Therefore it is said that the C_{20}OH and FC_{10}OH molecules mix nonideally in the adsorbed film and the mutual interaction between the different kinds of alcohol molecules is very weak compared with that between the same kind.

Figure 4 also demonstrates that the $g^{\text{H,E}}$ value increases with decreasing γ . Let us show that this observation proves the weak mutual interaction between hydrocarbon and fluorocarbon chains. Since μ_i^{H} is a function of T, p, γ , and X_2^{H} as expressed by eq 3, $g^{\text{H,E}}$ is also a function of these variables. Then we have¹⁶

$$(\partial g^{\text{H,E}} / \partial \gamma)_{T,p,X_2^{\text{H}}} = -RT[X_1^{\text{H}} \partial \ln f_1^{\text{H}} / \partial \gamma]_{T,p,X_2^{\text{H}}} + X_2^{\text{H}} (\partial \ln f_2^{\text{H}} / \partial \gamma)_{T,p,X_2^{\text{H}}} \quad (11)$$

On the other hand, the fundamental equation describing the adsorption of the nonionic–nonionic compounds mixture is expressed as⁴

$$d\gamma = -s^{\text{H}} dT + v^{\text{H}} dp - \Gamma_1^{\text{H}} d\mu_1 - \Gamma_2^{\text{H}} d\mu_2 \quad (12)$$

where Γ_i^{H} is the interfacial density of component i . Substituting the chemical potentials and $g^{\text{H,E}}$ respectively defined by eqs

3 and 9 into eq 12 and differentiating the resulting equation with respect to γ at constant T, p , and X_2^{H} , we obtain

$$A = X_1^{\text{H}} A_1^0 + X_2^{\text{H}} A_2^0 - (1/N_A)(\partial g^{\text{H,E}} / \partial \gamma)_{T,p,X_2^{\text{H}}} \quad (13)$$

where the mean area per adsorbed molecule for the pure system defined by

$$A_i^0 = -(1/N_A)(\partial \mu_i^{\text{H,0}} / \partial \gamma)_{T,p} \quad (14)$$

and the corresponding one for the mixed system

$$A = 1/N_A \Gamma^{\text{H}} \quad (15)$$

are introduced. Since the equation

$$A = X_1^{\text{H}} A_1^0 + X_2^{\text{H}} A_2^0 \quad (16)$$

holds for the ideal mixing, the excess area in the adsorbed film $A^{\text{H,E}}$ is defined by

$$A^{\text{H,E}} = A - (X_1^{\text{H}} A_1^0 + X_2^{\text{H}} A_2^0) \quad (17)$$

and evaluated numerically by using

$$A^{\text{H,E}} = -(1/N_A)(\partial g^{\text{H,E}} / \partial \gamma)_{T,p,X_2^{\text{H}}} \quad (18)$$

Considering the relation $A = X_1^{\text{H}} A_1 + X_2^{\text{H}} A_2$ and introducing the excess partial molar area of the component i $A_i^{\text{H,E}}$ defined by

$$A_i^{\text{H,E}} = A_i - A_i^0 \quad (19)$$

we obtained the following equation:

$$A_i^{\text{H,E}} = A^{\text{H,E}} - X_j^{\text{H}} (\partial A^{\text{H,E}} / \partial X_j^{\text{H}})_{T,p,\gamma} \quad (i, j = 1, 2; i \neq j) \quad (20)$$

Then the $A^{\text{H,E}}$ and $A_i^{\text{H,E}}$ values were estimated by using eqs 18 and 20 at $\gamma = 45 \text{ mN m}^{-1}$ and shown in Figure 5. It is seen that the $A^{\text{H,E}}$ value is positive in a whole composition range and about 0.1 nm^2 at the maximum. Furthermore, the $A_i^{\text{H,E}}$ values increase with increasing the fraction of the other component in the adsorbed film. Taking account of the fact that the cross-sectional areas of hydrocarbon and fluorocarbon chains are about 0.2 and 0.3 nm^2 , respectively, we realize that the mixing of C_{20}OH and FC_{10}OH in the adsorbed film causes a great increase in A value. This supports strongly the weak mutual interaction between the hydrocarbon and fluorocarbon alcohols.

With respect to the mixed micelle formation of hydrocarbon and fluorocarbon surfactants in the aqueous solution, it has been known that the mixing of these surfactants causes an increase of a few percent of their molar volume.^{14,15} So the present finding suggests that the difference in the geometrical structure between adsorbed films and micelle affects appreciably the molecular packing in them and eventually molecular interactions such as the van der Waals one between hydrocarbon and fluorocarbon molecules.

Conclusion

By analyzing the same experimental data given in our previous study by means of the different thermodynamic strategy, we obtained the following results:

(1) The composition of adsorbed film could be calculated from the interfacial tension data, and the phase diagram of

adsorption (PDA) was drawn. PDA gives the quantitative relation of the compositions between the adsorbed film and the bulk solution.

(2) The excess Gibbs energy and area in the adsorbed film were evaluated from the PDA, and the miscibilities of C₂₀OH and FC₁₀OH in the adsorbed film were elucidated more quantitatively on the basis of the excess quantities.

Acknowledgment. This work was supported in part by The Grant for Physics and Chemistry Research from Shiseido Co., Ltd., and in part by the Kurata Foundation.

References and Notes

- (1) *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series 311; American Chemical Society: Washington, DC, 1986.
- (2) *Mixed Surfactant Systems*; Holland, P. M., Rubingh, D. N., Eds.; ACS Symposium Series 501; American Chemical Society: Washington, DC, 1992.
- (3) *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Surfactant Science Series 46; Marcel Dekker: New York, 1993.
- (4) Motomura, K.; Aratono, M. In *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Marcel Dekker: New York, 1993; Vol. 46, p 99.
- (5) Aratono, M.; Ikeguchi, M.; Takiue, T.; Ikeda, N.; Motomura, K. *J. Colloid Interface Sci.* **1995**, *174*, 156.
- (6) Matsuki, H.; Ikeda, N.; Aratono, M.; Kaneshina, S.; Motomura, K. *J. Colloid Interface Sci.* **1992**, *150*, 331.
- (7) Matsuki, H.; Ikeda, N.; Aratono, M.; Kaneshina, S.; Motomura, K. *J. Colloid Interface Sci.* **1992**, *154*, 454.
- (8) Takiue, T.; Matsuo, T.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Phys. Chem. B*, in press.
- (9) Motomura, K. *J. Colloid Interface Sci.* **1978**, *64*, 348.
- (10) Todoroki, N.; Tanaka, F.; Ikeda, N.; Aratono, M.; Motomura, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 351.
- (11) Iyota, H.; Aratono, M.; Motomura, K. *J. Colloid Interface Sci.* **1996**, *178*, 53.
- (12) Aratono, M.; Villeneuve, M.; Takiue, T.; Ikeda, N.; Iyota, H. *J. Colloid Interface Sci.* **1998**, *200*, 161.
- (13) Iyota, H.; Tomimitsu, T.; Motomura, K.; Aratono, M. *Langmuir*, in press.
- (14) Funasaki, N.; Hada, S. *J. Phys. Chem.* **1982**, *86*, 2504.
- (15) Harada, S.; Sahara, H. *Chem. Lett.* **1984**, 1199.