

Phase Transition and Domain Formation in the Gibbs Adsorbed Films of Long-Chain Alcohols

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The adsorption behavior of 1,1,2,2-tetrahydroheptafluorodecanol (FC10OH), 1-eicosanol (C20OH), and their mixtures at the hexane solution/water interface is summarized briefly and examined from the viewpoints of interfacial tensions in the presence of domains, domain formation, and the correlation between the phase transition and the miscibility of film forming substances in the adsorbed films. The two-dimensional analogue of the Laplace equation showed that the interfacial tension is always higher in the presence of domains than that in the absence of them. The higher tendency of domain formation of FC10OH compared to C20OH is mainly ascribed to the excess Gibbs energy of mixing of fluorocarbon chains and hydrocarbon solvent being positive and to the interaction energy between domains being more stable against cohesion for FC10OH than for C20OH. The thermodynamic equations derived here suggested the heteroazeotropy in the phase diagram of adsorption and the temperature dependence of interfacial tension at the phase transition points, which are in accord with the experimental findings qualitatively.

Introduction

Adsorption of amphiphiles at oil/water interfaces either from the aqueous solutions or from oil solutions has been extensively studied because it advances fundamental understanding of organization and roles of amphiphile molecules at interfaces. One of the important issues among such studies is a phase transition of adsorbed films, and many papers have been reported on long-chain alcohols,^{1–10} alkyl glycerides,^{11,12} cholesterol,¹³ and some binary combinations of them^{14–16} at oil/water interfaces. Furthermore, there are reports on the cationic surfactant-induced phase transition at the alkane/water interface¹⁷ and on the transition in oil thin films on water surface.^{18,19}

In a series of our studies on adsorption and phase transition of long-chain fluorocarbon alcohols and also their mixtures with hydrocarbon alcohols at the hexane/water interfaces,²⁰ the interfacial tension measurements as a function of temperature, pressure, concentration, and the mixing ratio in the mixture have clearly demonstrated the phase transition of adsorbed films between different states such as gaseous, expanded, and condensed states. Furthermore, the phase diagrams of adsorption have been constructed, which provides the concentration relation between the adsorbed film and bulk solution at fixed interfacial tension, and thus the miscibility of different adsorbed species and information on molecular interaction in the organized assemblies at the interfaces.²¹ Within a thermodynamic framework and within a reproducibility of interfacial tension, the first-order phase transition in the adsorbed film was proved to take place at the break points on the interfacial tension curves and an abrupt change of miscibility accompanied by it was clearly demonstrated.

To obtain further information on the phase transition on a molecular level, structure studies are highly required. Although the adsorbed films targeted here are all buried at oil/water interfaces and thus the available methods are limited, much

efforts have been devoted to, for example, employing Brewster angle microscope,⁶ ellipsometry,¹⁷ neutron scattering,^{22,23} X-ray reflectivity,^{18,24–26} and nonlinear spectroscopic method.²⁷ With the aid of the developments of such structure studies, we also have applied the X-ray reflectivity measurements to the adsorbed films of 1,1,2,2-tetrahydroheptafluorodecanol ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$, denoted by FC10OH, 1-eicosanol ($(\text{CH}_3(\text{CH}_2)_{19}\text{OH}$, denoted by C20OH), and their mixtures at the hexane/water interface.¹⁵ Our results from the X-ray measurements will be summarized briefly in the Results and Discussion section. The important findings among them that still need further consideration are the facts that the adsorbed amphiphile molecules are not dispersed homogeneously but form condensed domains in the dilute gaseous films, that the physical quantities relevant to domains such as size and coverage are different from each other between FC10OH and C20OH, and that their miscibilities are changed drastically at the phase transition.

This report is constructed as follows. In the first part, the adsorption behavior of FC10OH and C20OH is summarized briefly. In the second, we answer the question “is the interfacial tension of the domains the same as or different from that of the surroundings?” by deriving the two-dimensional analogue of the Laplace equation of a spherically curved interface. Furthermore, the domain formation is examined from the viewpoints of line tension^{28,29} at the contact line of the domain and the surrounding, difference in dipole moment density between the inside and outside of domains, mixing of hydrophobic chain in the hydrocarbon solvent, and interaction between domains. In the third, we consider the relation between the phase transition of and the miscibility in the adsorbed films of FC10OH and C20OH mixtures.

Results and Discussion

I. Brief Summary of the Adsorption Behavior of FC10OH and C20OH. The interfacial tensiometry manifested that the adsorbed film of FC10OH at its hexane solution/water interface has three states connected by first-order phase transition.^{5,30} Their existence depends not only on the concentration of FC10OH in

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the hexane solution but also on the temperature and pressure. Furthermore, the X-ray reflectivity studies revealed that the state of the condensed film is very similar to that of solid fluorocarbon with all-trans conformation and the film thickness is around 10.0 ± 1.0 Å and, furthermore, the expanded film is composed of domains of condensed film and low-density gaseous films, and the coverage of the condensed domain is about 50% just above the phase transition point.¹⁵ Only the coherent model could fit the reflectivity data and thus the size of domain may be smaller than about 5 μm.

On the other hand, also the adsorbed film of C20OH exhibited the transition from the expanded to condensed state.¹⁴ However, the X-ray reflectivity experiments revealed that the electron density in the hydrophobic regions in the condensed film is similar to that of liquid alkanol just above the melting point and the film thickness is around 23.0 ± 1.0 Å. Furthermore, although the expanded film may contain the condensed domain, the coverage is less than 7% of surface area even just above the phase transition point.¹⁵ This forms a striking contrast to the domain formation of FC10OH of relatively large size and high coverage up to far from the phase transition temperature.

II. Consideration on Interfacial Tension and Domain Formation. Interfacial Tensions. The synchrotron X-ray reflectivity (XR) studies at the hexane/water interface revealed that adsorbed molecules of FC10OH and C20OH in the so-called expanded film are not homogeneously dispersed but a part of them forms domains with higher surface density and they are dispersed in the adsorbed film with a lower surface density.¹⁵ In that case, the domains are in the condensed state and the surroundings are in the gaseous one. With respect to this situation, our question is “is the interfacial tension of the domains the same as or different from that of the surroundings in this situation?”. We search for the answer for a simple case thermodynamically.

Since a boundary exists between a domain and surrounding at the interface, the nature of interfaces just around the boundary is expected to be different from those far from the boundary. This is similar to the situation that the natures of two bulk phases very near the phase boundary region are different from those far from the boundary region and thus a quantity called interfacial tension γ is introduced. Similarly, a physical quantity describing the nature of the boundary line is reasonably introduced as a line tension τ like γ .^{28,29} Let us assume that there are N_D circular domains, their radii are R , and the interfacial tensions and total areas are γ^I and σ^I for the domains and γ^O and σ^O for the surroundings, respectively. The work term of the system is written by

$$dw = -p dV + \gamma^I d\sigma^I + \gamma^O d\sigma^O + \tau dl \quad (1)$$

where l is the total length of lines. The Helmholtz energy is given by

$$dA = -S dT - p dV + \gamma^I d\sigma^I + \gamma^O d\sigma^O + \tau dl + \sum_i \mu_i dn_i \quad (2)$$

and its Legendre transformation yields

$$d(A + pV) = -S dT + V dp + \gamma^I d\sigma^I + \gamma^O d\sigma^O + \tau dl + \sum_i \mu_i dn_i \quad (3)$$

Therefore, under the equilibrium conditions that temperature, pressure, and total surface area $\sigma = \sigma^I + \sigma^O$ are kept constant for a closed system, eq 3 gives the equation

$$\gamma^O - \gamma^I = \tau/R \quad (4)$$

where the relations $d\sigma^I = N_D 2\pi R dR = -d\sigma^O$ and $dl = N_D 2\pi dR$ were employed. Equation 4 answers the question above; the interfacial tensions are different from each other between the inside and outside of domains, the difference is dependent on the line tension and size of domains, and the difference disappears when two states are separated by a line with a large R . It should be noted that the interfacial tension of the inside is always lower than that of the outside and, thus, the inside has a tendency to expand toward the outside and the outside has a tendency to shrink itself. However, the line tension τ balances the extension and shrink. Since eq 4 is rewritten in terms of the interfacial pressures $\pi^O = \gamma^{\text{pure}} - \gamma^O$ and $\pi^I = \gamma^{\text{pure}} - \gamma^I$, where γ^{pure} is the hexane/water interfacial tension without amphiphiles, as

$$\pi^I - \pi^O = \tau/R \quad (5)$$

it is regarded as a two-dimensional analogue of the Laplace equation for the spherically curved interface having radius R and interfacial tension γ

$$p^I - p^O = 2\gamma/R \quad (6)$$

where p^I and p^O are the inside and outside pressures, respectively.³¹

Now let us examine how large the difference is and whether an experiment can detect the difference or not. From the experimental viewpoint, it is practically impossible to measure γ^O and γ^I separately because the sizes of domains are in micrometers or smaller, and only value accessible is an average one of them, γ , given by

$$\gamma\sigma = \gamma^I\sigma^I + \gamma^O\sigma^O + \tau l \quad (7)$$

Introducing the area fraction $\theta^I = \sigma^I/\sigma$ and employing the relation $l = 2\sigma^I/R$ and the two-dimensional Laplace eq 4 yields

$$\gamma = (\tau/R)(1 - \theta^O) + \gamma^O = (\tau/R)(1 + \theta^I) + \gamma^I \quad (8)$$

Therefore, the domain formation raises the interfacial tension γ through the positive line tension τ . Since it is usual that $R \sim 1$ μm and $\tau \sim 10$ pN, we have $\gamma^O - \gamma^I \sim 10^{-2}$ mN m⁻¹ and $\gamma - \gamma^O \sim 10^{-2}$ mN m⁻¹. This suggests that the difference in the interfacial tensions is comparable to or smaller than an experimental error of interfacial tension measurements and thus the tensiometry itself practically does not catch the domain formation.

Domain Formation. The XR studies elucidated a clear difference in the domain formation between the expanded state with C20OH and the one with FC10OH as follows. In the former it was probable that around 7% is covered by domains of condensed monolayer. However, it is difficult to distinguish between a state with the coverage of 7% and a homogeneous monolayer. Thus, an alternative explanation that the interface is not aggregated into domains is also possible. On the other

hand, the latter was covered by many domains of condensed monolayers separated by regions of gaseous monolayer and the coverage is around 50% near the transition region. These results suggest that C20OH molecules tend to be dispersed molecularly or into quite small domains that cannot be recognized as domains by the XR experiments, while FC10OH molecules have a tendency to gather together to form domains of them.

Why does such a difference arise between C20OH and FC10OH? The most influential may be that mixing of fluorocarbon chains of FC10OH with hydrocarbon chains of hexane accompanies a free energy cost, e.g., the excess Gibbs energy of mixing of *n*-hexane and *n*-perfluorohexane reaches even about 1.3 kJ mol⁻¹, similar in magnitude to the one of hydrocarbon and polar compounds.³² This is more advantageous for FC10OH to form domains than to disperse molecularly at the hexane/water interface. Furthermore, such an immiscible tendency raises the interfacial tension of the fluorocarbon/hydrocarbon interface and thus the line tension τ at the condensed domain/surroundings boundary as follows. τ is very roughly estimated by using the interfacial tension γ^{DS} between the materials forming domain and surrounding it and the length of the contact L by²⁹

$$\tau \approx \gamma^{\text{DS}} L \quad (9)$$

For the domains of FC10OH, γ^{DS} is approximated to be the interfacial tension between perfluorodecane/hexane because the surrounding is in the gaseous state. The rough estimation from the equation

$$\gamma^{\text{DS}} \approx \gamma_{\text{h}} + \gamma_{\text{pd}} - 2\sqrt{\gamma_{\text{h}}\gamma_{\text{pd}}} \quad (10)$$

for nonpolar compounds,³³ where γ_{h} and γ_{pd} are the surface tensions of hexane and perfluorodecane, yields $\gamma \approx 1.5$ mN m⁻¹. The length of extended fluorocarbon chain is $L = 1.3$ nm. Thus, $\tau \sim 2$ pN was obtained, which is on the same order as the one estimated by Schlossman et al.⁹ For C20OH, both hydrophobic parts of domains and surrounding media are hydrocarbon and $\gamma^{\text{DS}} \approx 0$ and thus τ is much smaller than that of FC10OH. Since it is expected from the viewpoint of line tension that the higher τ value is more favorable to the formation of the larger domain than to that of the smaller domain, the calculation here supports our experimental finding from the XR that the FC10OH system forms the larger domains compared to the C20OH system.

For the more advanced understanding of domain formation, a more sophisticated consideration should be introduced. On the thermodynamic equilibrium of monolayer domains, McConnell et al. derived an expression for the edge energy E of a circular and isolated domain with the radius R by assuming that the condensed phase is isotropic and the molecular dipoles are perpendicular to the plane of monolayer (equivalent dipole model). E is given by

$$E = 2\pi R[\tau - (m^2/4\pi\epsilon_0\epsilon)\ln(4R/e^2\Delta)] \quad (11)$$

and thus both the sizes and shapes of domains are affected by a competition between a line tension τ and long-range dipole–dipole repulsion. In eq 11 m (C m⁻¹) is the dipole moment density difference between the domain and the surrounding area, ϵ_0 (C² J⁻¹ m⁻¹) is the permittivity of vacuum, ϵ is the dielectric constant of water, Δ is a closest approach cutoff distance with a order of magnitude of an intermolecular distance.²⁸ Here $R \sim$

μm and $\Delta \sim \text{\AA}$ and thus $4R/e^2\Delta > 1$. Hu et al. have added the entropy of mixing of film forming substances within a domain to eq 11 and derived the mean interaction free energy per molecule in the domain having N molecules μ_{N}^0 as

$$\mu_{\text{N}}^0 = a[4\pi\epsilon_0\epsilon\tau - m^2\ln(4\sqrt{aN}/e^2\Delta\sqrt{\pi})]/2\epsilon_0\epsilon\sqrt{aN\pi} - T\Delta s_{\text{mix}} \quad (12)$$

where a is the apparent cross-sectional area of film forming molecules and $R = \sqrt{(aN/\pi)}$.²⁹ Therefore, the line tension acts to diminish the domain boundary, the dipole moment interaction of almost vertical orientation at the interface is repulsive, and the difference m favors the dispersion of molecules from each other. Although an entropy increase Δs_{mix} is favorable for domain formation, it is negligible for one-component system and even for binary mixtures of FC10OH and C20OH because these two components are completely immiscible in the condensed domain.

The line tension τ appearing in eqs 11 and 12 was already examined above and favors the domain formation for FC10OH. The other important factor is the difference in dipole densities m . When all molecules are almost vertical to the interface plane and their OH groups are invariably toward water phase, the interaction energy w is written by³⁴

$$w(r) = u^2/4\pi\epsilon_0\epsilon r^3 \quad (13)$$

and thus $w > 0$, where r is the distance between the centers of two dipole moments. As already described quantitatively in eq 12, this suggests that the molecular dispersion or dispersion to smaller condensed domains is energetically preferable than the separation into two states. Furthermore, it is reasonably assumed that m is proportional to the difference in interfacial densities between the condensed domain $\Gamma_1^{\text{H,C}}$ and gaseous film surrounding the domains $\Gamma_1^{\text{H,G}}$, $\Delta\mu = \Gamma_1^{\text{H,C}} - \Gamma_1^{\text{H,G}}$, and therefore the larger $\Delta\mu$ is more favorable to the molecular dispersion or dispersion to smaller domains.

$\Delta\mu$ is estimated as follows. Let us assume that both $\Gamma_1^{\text{H,C}}$ and $\Gamma_1^{\text{H,G}}$ do not change appreciably with temperature or with concentration and, thus, the relative proportions of them, θ , is altered with temperature and concentration; the interfacial density experimentally determined $\Gamma_1^{\text{H,exp}}$ is written by

$$\Gamma_1^{\text{H,exp}} = \Gamma_1^{\text{H,C}}\theta^{\text{C}} + \Gamma_1^{\text{H,G}}(1 - \theta^{\text{C}}) \quad (14)$$

where θ^{C} is the fraction of interfacial area occupied by the condensed domain. For FC10OH, since $\theta^{\text{C}} = 0.5$ was obtained from the XR experiment¹⁵ and $\Gamma_1^{\text{H,exp}} = 3.5 \mu\text{mol m}^{-2}$ and $\Gamma_1^{\text{H,C}} = 5.6 \mu\text{mol m}^{-2}$ just above the phase transition point from the interfacial tensiometry,¹⁴ $\Gamma_1^{\text{H,G}} = 1.4 \mu\text{mol m}^{-2}$ is evaluated. For C20OH, on the other hand, $\theta^{\text{C}} = 0.07$, $\Gamma_1^{\text{H,exp}} = 1.8 \mu\text{mol m}^{-2}$, and $\Gamma_1^{\text{H,C}} = 8.1 \mu\text{mol m}^{-2}$ from the experiments gives $\Gamma_1^{\text{H,G}} = 1.3 \mu\text{mol m}^{-2}$, which yields $\Delta\mu = 4.2 \mu\text{mol m}^{-2}$ for FC10OH and $\Delta\mu = 6.8 \mu\text{mol m}^{-2}$ for C20OH, respectively. This result is consistent with the XR observation that the molecular dispersion or dispersion to the smaller domain is more favorable for C20OH.

The remaining factor being influential for domain formation is the stability against cohesion of domains. When two domains of length L and radius R are close each other at the distance D

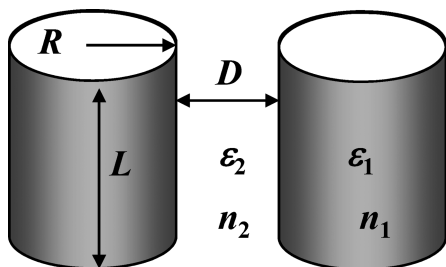


Figure 1. Interaction between two domains. Domains are either hydrocarbon or fluorocarbon but the surrounding is always hydrocarbon in the present situation.

between their surfaces as shown in Figure 1, the van der Waals attraction works and its energy w_v is given by³⁴

$$w_v = -(AL/24D^{3/2})\sqrt{R} \quad (15)$$

Here A is the effective Hamaker constant estimated to be

$$A = (3kT/4)[(\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)]^2 + (3\nu_e/16\sqrt{2})(n_1^2 - n_2^2)/(n_1^2 + n_2^2)^{3/2} \quad (16)$$

where ϵ and n are dielectric constant and refractive index and subscripts 1 and 2 show the inside and outside of domain, respectively. The outside is hexane and the insides for C20OH and FC10OH are reasonably assumed to be eicosane and perfluorodecane, respectively. Thus, $10^{21}A = 3.74$ J and $L = 2.56$ nm are estimated for C20OH and, $10^{21}A = 2.75$ J and $L = 1.29$ nm for FC10OH. The ratio between the van der Waals attractive energy is estimated to be $w_{v,C20OH}/w_{v,FC10OH} = 2.7$. Therefore, from the viewpoint of interaction between domains, the domains of FC10OH are more stable against cohesion than those of C20OH.

The consideration above is summarized as follows. The mixing of fluorocarbon chains of FC10OH with hydrocarbon chains of hexane accompanies a free energy cost and it raises the line tension at the boundary between the condensed domains and the surroundings. These factors are more advantageous for FC10OH molecules to be dispersed as the comparatively larger domains at the hexane/water interface than for C20OH. The difference in dipole moment densities between the inside and outside domains is larger for C20OH than for FC10OH, which is more favorable for C20OH molecules to be dispersed molecularly or into the smaller domains than for FC10OH. Furthermore, the attractive interaction between domains are stronger for C20OH than for FC10OH and thus the domains of FC10OH are expected to be more stable than those of C20OH. All the results are in accord with the experimental findings that C20OH molecules tend to be dispersed molecularly or into quite small domains that can not be recognized as domains by the XR experiments, while FC10OH molecules have a tendency to gather together to form domains of them.

III. Consideration on Phase Transition of Adsorbed Films of Mixtures of Fluorocarbon and Hydrocarbon Alcohols. It has been reported that three kinds of phase transition are observed among the expanded state (E), the condensed state of C20OH (C_H), and the condensed state of FC10OH (C_F) in the adsorbed films of binary mixtures of FC10OH and C20OH at the hexane solution/water interface.¹⁴ They are the transition from E to C_H at lower X_2 , the one from E to C_F at higher X_2 , and the one from C_F to C_H after the transition from E to C_F (two-

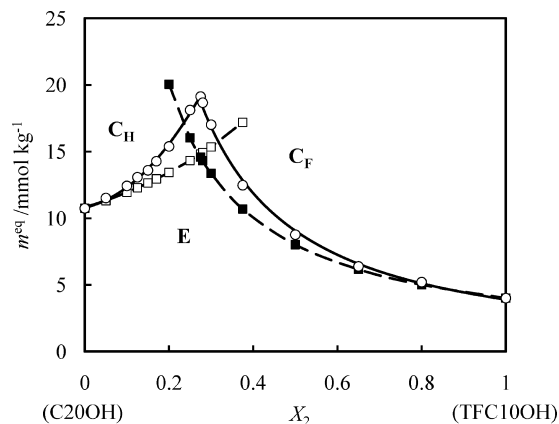


Figure 2. Total molality vs bulk composition curves at the phase transition points: (O) m^{eq} vs X_2 , (□) $m_1^{eq,0}/X_1$ vs X_2 , (■) $m_2^{eq,0}/X_2$ vs X_2 .

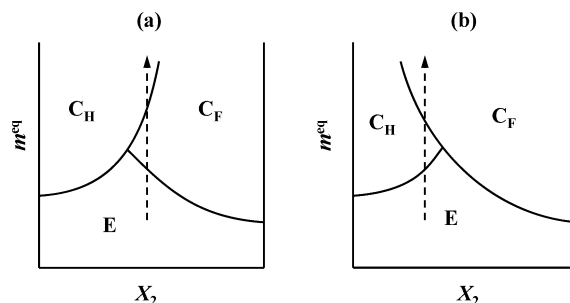


Figure 3. Total molality vs bulk composition curves at the phase transition points: (a) $[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{C_H,C_F}^{eq} > 0$ and $E \rightarrow C_F \rightarrow C_H$, and (b) $[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{C_H,C_F}^{eq} < 0$ and $E \rightarrow C_H \rightarrow C_F$.

step transition) within a limited X_2 range when the total concentration of alcohols $m = m_1 + m_2$ increases at fixed the bulk composition $X_2 = m_2/m$. Here m_1 and m_2 are the molalities of C20OH and FC10OH in the hexane solution, respectively.

One important finding is that the two branches of the equilibrium molality m^{eq} vs X_2 curve extrapolated from the lower and higher X_2 cross at a point and form a cusp as shown in Figure 2. The point is called as the heteroazeotropic one and two different condensed states coexist at the point. To examine this feature, let us calculate two curves corresponding to the two branches in an ideal case; two components are completely immiscible in the condensed states (C_H and C_F), and the transition from the expanded to the condensed states occurs at molalities $m^{eq,id}$ that contain the equal amount of $m_1^{eq,0}$ and $m_2^{eq,0}$ in the mixed solution. Thus, the branches are estimated by $m^{eq,id} = m_1^{eq,0}/X_1$ for C_H at lower X_2 and $m^{eq,id} = m_2^{eq,0}/X_2$ for C_F at higher X_2 , respectively, and displayed in Figure 2. It is clearly shown that, although the two branches locate at lower concentrations compared to the m^{eq} vs X_2 curves, they meet at a X_2 very near the X_2 of heteroazeotropic point. Therefore, complete immiscibility in the condensed states is probably assured from this estimation. The higher m^{eq} than $m^{eq,id}$ suggests that the two components are rather immiscible compared to an ideal mixing but still miscible at all compositions in the expanded state,¹⁴ while they are completely immiscible in the condensed state.

The other important finding is that the sequence of the two-step transition was $E \rightarrow C_F \rightarrow C_H$ and the sequence $E \rightarrow C_H \rightarrow C_F$ was never observed when m is increased at a given X_2 . This seems to be self-explanatory from the fact that FC10OH changes its state from E to C_F at a lower concentration than C20OH. Examining the correlation between the variation of γ^{eq} with m^{eq} , T^{eq} , and X_2^{eq} and the thermodynamic quantities such as interfacial

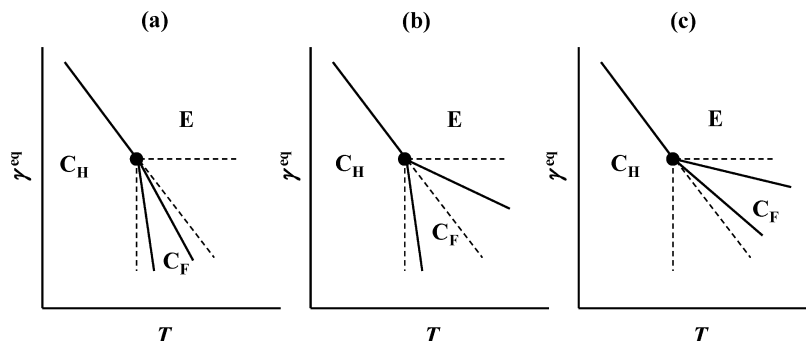


Figure 4. Interfacial tension vs temperature curves at the phase transition points: (a) $|[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_H}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_F}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{C_H,C_F}^{\text{eq}}|$; (b) $|[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_F}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_H}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{C_H,C_F}^{\text{eq}}|$; (c) $|[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_F}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{C_H,C_F}^{\text{eq}}| < |[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_H}^{\text{eq}}|$.

densities Γ^H and entropy of adsorption Δs , however, it is demonstrated that the sequence $E \rightarrow C_F \rightarrow C_H$ is not necessary but observable when some conditions are fulfilled. The differentials of the interfacial tensions of α and β states are written by

$$d\gamma^\alpha = -\Delta s^\alpha dT + \Delta v^\alpha dp - RT(\Gamma^{H,\alpha}/m) dm - RT(\Gamma^{H,\alpha}/X_1X_2)(X_2^{H,\alpha} - X_2) dX_2 \quad (17)$$

and

$$d\gamma^\beta = -\Delta s^\beta dT + \Delta v^\beta dp - RT(\Gamma^{H,\beta}/m) dm - RT(\Gamma^{H,\beta}/X_1X_2)(X_2^{H,\beta} - X_2) dX_2 \quad (18)$$

respectively. Here the superscript β refers to the one having the higher total surface density, $\Gamma^{H,\beta} > \Gamma^{H,\alpha}$. When the α and β states are in equilibrium with each other, eqs 17 and 18 hold at the same time. Thus, we have the equation describing how m^{eq} changes with X_2 at constant T and p as

$$[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{\alpha,\beta}^{\text{eq}} = [X_2 - (\Gamma^{H,\beta}X_2^{H,\beta} - \Gamma^{H,\alpha}X_2^{H,\alpha})/(\Gamma^{H,\beta} - \Gamma^{H,\alpha})] \quad (19)$$

and the one describing how the interfacial tension γ^{eq} changes with T at constant X_2 and p as

$$[(\partial\gamma/\partial T)_{p,X_2}]_{\alpha,\beta}^{\text{eq}} = -(\Gamma^{H,\beta}\Delta s^\alpha - \Gamma^{H,\alpha}\Delta s^\beta)/(\Gamma^{H,\beta} - \Gamma^{H,\alpha}) \quad (20)$$

where the values of the right-hand side are also the ones at the phase transition point.

The left-hand side of eq 19 could be generally either positive or negative. For the C20OH and FC10OH mixtures, however, it was demonstrated from the phase diagram of adsorption that they do not mix in the condensed states. Therefore, when the adsorbed film transforms its state from the expanded (E) to the condensed state of C20OH (C_H), we have $X_1^{H,C_H} = 1$, $X_2^{H,C_H} = 0$, and $\Gamma^{H,C_H} > \Gamma^{H,E}$ and thus

$$[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{E,C_H}^{\text{eq}} = [X_2 + \Gamma^{H,E}X_2^{H,E}/(\Gamma^{H,C_H} - \Gamma^{H,E})] > 0 \quad (21)$$

On the other hand, for the transition from the expanded (E) to the condensed states of FC10OH (C_F), $X_2^{H,C_F} = 1$, $X_1^{H,C_F} = 0$, and $\Gamma^{H,C_F} > \Gamma^{H,E}$ and thus

$$[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{E,C_F}^{\text{eq}} = [X_2 - \Gamma^{H,C_F}/(\Gamma^{H,C_F} - \Gamma^{H,E})] < 0 \quad (22)$$

These equations substantiate the experimental finding that m^{eq} from E to C_H is increased at the lower X_2 but m^{eq} from E to C_F is decreased at the higher X_2 with increasing X_2 , respectively, as shown in Figure 2. The value of $[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{\alpha,\beta}^{\text{eq}}$ could be either positive or negative also for the transition between C_H and C_F , and thus both the sequences (a) $E \rightarrow C_F \rightarrow C_H$ and (b) $E \rightarrow C_H \rightarrow C_F$ are probable as schematically shown in Figure 3. Employing the observation of $X_2^{H,C_F} = 1$ and $X_2^{H,C_H} = 0$, however, eq 19 is reduced to

$$[(X_1X_2/m)(\partial m/\partial X_2)_{T,p}]_{C_H,C_F}^{\text{eq}} = [X_2 + \Gamma^{H,C_F}/(\Gamma^{H,C_H} - \Gamma^{H,C_F})] > 0 \quad (23)$$

This claims that the transition should take place from C_F to C_H like the case (a) in Figure 3. Again the experimental result is coincident with this view.

The variation of γ^{eq} with T is given by eq 20 and rewritten as

$$[(\partial\gamma/\partial T)_{p,X_2}]_{\alpha,\beta}^{\text{eq}} = -(\Delta s^\beta/\Gamma^{H,\beta} - \Delta s^\alpha/\Gamma^{H,\alpha})/(1/\Gamma^{H,\beta} - 1/\Gamma^{H,\alpha}) \quad (24)$$

It should be noted here that Δs and Γ^H are the entropy of adsorption and adsorption amount per unit interfacial area, respectively, and thus $\Delta s/\Gamma^H$ is an average entropy change per unit adsorption. Therefore, when α is the expanded phase (E) like a two-dimensional liquid and β is either the condensed one of C_H or that of C_F like a two-dimensional solid, the inequality $\Delta s^\beta/\Gamma^{H,\beta} < \Delta s^\alpha/\Gamma^{H,\alpha}$ holds generally and thus we have $[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_H}^{\text{eq}} < 0$ and $[(\partial\gamma/\partial T)_{p,X_2}]_{E,C_F}^{\text{eq}} < 0$; the interfacial tension at the phase transition point should decrease with increasing temperature. On the other hand, when both α and β are the condensed phases, the sign of $[(\partial\gamma/\partial T)_{p,X_2}]_{\alpha,\beta}^{\text{eq}}$ depends on the magnitude of $\Delta s/\Gamma^H$ for the C_H and C_F phases. Our previous experiments showed that $\Gamma^{H,C_H} > \Gamma^{H,C_F}$, $\Delta s^{C_H} < \Delta s^{C_F}$ and $\Delta s^{C_H}/\Gamma^{H,C_H} < \Delta s^{C_F}/\Gamma^{H,C_F}$. This yields again $[(\partial\gamma/\partial T)_{p,X_2}]_{C_H,C_F}^{\text{eq}} < 0$. Taking account that three kinds of $[(\partial\gamma/\partial T)_{p,X_2}]_{\alpha,\beta}^{\text{eq}}$ are all negative and the transition takes place from E to C_F to C_H as increasing m at

a given X_2 , there are three possible situations depending on the magnitude of $[(\partial\gamma/\partial T)_{p,X_2}]_{\alpha,\beta}^{\text{eq}}$ as given in Figure 4. The experiments demonstrated case (b). This implies that the average entropy change per unit adsorption $\Delta s/\Gamma^{\text{H}}$ is negative and in the order of $\Delta s^{\text{C}_\text{H}}/\Gamma^{\text{H,C}_\text{H}} < \Delta s^{\text{C}_\text{F}}/\Gamma^{\text{H,C}_\text{F}} < \Delta s^{\text{E}}/\Gamma^{\text{H,E}}$.

Let us summarize the results in subsection III. On the basis of information from the phase diagram of adsorption that C20OH and FC10OH molecules are completely immiscible in the condensed states and hard to be mixed even in the expanded state, the variation of m^{eq} with X_2 as well as that of γ^{eq} with T could be suggested from the thermodynamic considerations in this paper. The suggestions were significantly consistent with the experimental observations. These corroborate that our experiments, the formulation of thermodynamic equations, and the construction of phase diagram of adsorption have been correctly performed and are beneficial to clarifying adsorption phenomena at oil/water interfaces.

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