

LETTERS

Phase Transition Behavior of Fluorinated Monolayers at the Water–Hexane Interface

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X-ray surface scattering and interfacial tension measurements are used to study the solid-to-gas phase transition in soluble monolayers of $F(CF_2)_8(CH_2)_2OH$ and $F(CF_2)_{10}(CH_2)_2OH$ adsorbed at the water–hexane interface. X-ray reflectivity and diffuse scattering measurements determine the molecular ordering, the presence of domains, and the interfacial coverage of solid domains as a function of temperature. The temperature-dependent coverage can be analyzed by a functional form consistent with a critical transition proposed by theory.

Domain formation in systems with competing interactions has been demonstrated in, for example, Langmuir monolayers of insoluble surfactants at the water–vapor interface, thin ferromagnetic films with easy axis anisotropy, and ferrofluids.^{1–5} Recently, Brewster angle microscopy has been used to observe domain formation in a Gibbs monolayer at the liquid–liquid interface (formed from $F(CF_2)_{10}(CH_2)_2OH$, denoted $FC_{12}OH$, surfactants adsorbed at the water–hexane interface).⁵ Earlier interfacial tension measurements of the $FC_{12}OH$ (water–hexane) system had revealed the presence of a sharp transition with temperature.⁶ Unexpectedly, the Brewster angle microscope observations indicated that the domains were present over a large range of temperatures, appearing at least 12 K below the transition temperature indicated by the interfacial tension measurements.⁵

Our previous X-ray reflectivity measurements from the $FC_{12}OH$ (hexane–water) system demonstrated the presence of an interface partially covered by a solid phase of the $FC_{12}OH$ only very near the phase transition temperature, in contrast with the Brewster angle microscope observations.⁷ Here, we use X-ray reflectivity, X-ray off-specular diffuse scattering, and interfacial tension measurements to study further the solid-to-gas phase

transition in monolayers of $FC_{12}OH$ and, in addition, in Gibbs monolayers of $F(CF_2)_8(CH_2)_2OH$ (denoted $FC_{10}OH$) adsorbed at the water–hexane interface. These new measurements provide evidence for a sharp transition that occurs via a breakup of the monolayer into solid domains at the same temperature as the kink in the interfacial tension data. The diffuse scattering demonstrates that the domains in $FC_{12}OH$ monolayers have a radius of $1.5 \mu m$, in contrast with larger domains (radii greater than $5 \mu m$) observed earlier by Brewster angle microscopy.⁵

It is reasonable to expect that the solid domains at the liquid–liquid interface are stabilized by a balance between the domain line tension and repulsive dipole interactions, similar to domain formation at the liquid–vapor interface.^{1,2} In our system, the repulsive interactions arise from a preferential orientation of the surfactant molecule's dipole moment in the solid monolayer phase. This results in an enhanced interfacial polarization in the region of the domains. Marchenko proposed a correspondence between the critical properties of liquid systems with an interfacial polarization and those of ferromagnetic thin films.⁸ We show that the interfacial coverage of solid domains as a function of temperature near the phase transition can be fit by a functional form consistent with Marchenko's theory.

The liquid samples are stirred and equilibrated in a temperature-controlled, vapor-tight stainless steel sample cell described in detail elsewhere.⁷ Solutions in purified hexane were prepared

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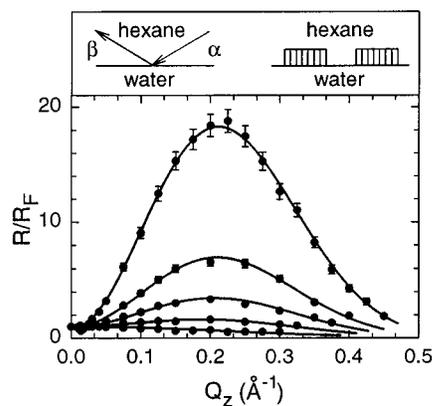


Figure 1. Normalized reflectivity R/R_F vs Q_z for $FC_{10}OH$ monolayers at the water–hexane interface. From the top on down, temperatures are 296, 300.75, 309.55, 319.05, and 329.65 K. Left inset: X-ray scattering geometry. Right inset: cartoon of monolayer domains at water–hexane interface.

well below saturation at room temperature at a molal concentration of 5.0 mmol/kg for $FC_{10}OH$ and 2.0 mmol/kg for $FC_{12}OH$.^{9,10} When the hexane solution is poured on top of the water, the surfactant spontaneously self-assembles into a monolayer at the water–hexane interface. Our interfacial tensions, measured with a Wilhelmy plate¹¹ in the sample cell used for X-ray scattering, are consistent with earlier studies of the tension as a function of temperature.^{6,12}

X-ray scattering was measured at beamline X19C at the National Synchrotron Light Source (Brookhaven National Laboratory) with a liquid surface spectrometer and techniques described in detail elsewhere.^{13,14} The X-rays penetrate through the upper bulk phase of hexane solution, then scatter off a nearly planar water–hexane interface. For specular reflection, the incident angle, α , is equal to the scattered angle, β (see Figure 1 inset). Therefore, the wave vector transfer, $Q = k_{\text{scat}} - k_{\text{in}}$, is only in the z -direction normal to the interface, $Q_z = (4\pi/\lambda)\sin(\alpha)$ where the X-ray wavelength $\lambda = 0.825 \pm 0.002 \text{ \AA}$, and $Q_x = Q_y = 0$ where x and y are in the plane of the interface. For off-specular scattering β is varied while α is held fixed, resulting in a nonzero component of the wave vector transfer in the plane of the interface, Q_y .

Figure 1 illustrates R/R_F , X-ray reflectivity measurements normalized by the Fresnel reflectivity, as a function of temperature for the water–hexane interface with $FC_{10}OH$. The peak in R/R_F represents a constructive interference of X-rays reflected from the top and bottom of the monolayer. As shown below, the reduction in amplitude of the peak as the temperature is increased is due to a reduction in the number of surfactant molecules in the monolayer solid phase. This occurs because the monolayer separates into domains of solid phase separated by a monolayer gas phase, with some of the surfactant molecules going into the bulk hexane phase. Similar reflectivity measurements from our group have been previously published for the water–hexane interface with $FC_{12}OH$ monolayers and will be further analyzed here.⁷

Two pieces of evidence indicate that the monolayer separates into domains. First, the value of Q_z ($\approx 0.22 \text{ \AA}^{-1}$) at the maximum in R/R_F and the peak shape in Figure 1 do not change as a function of temperature. Therefore, the thickness of monolayer domains is unchanged with temperature. Second, for the $FC_{12}OH$ system we measured small angle scattering from these monolayer domains (see also ref 15). Figure 2 illustrates this off-specular diffuse scattering obtained by scanning the scattered angle β at fixed incident angle $\alpha = 0.37^\circ$ for a sample near the

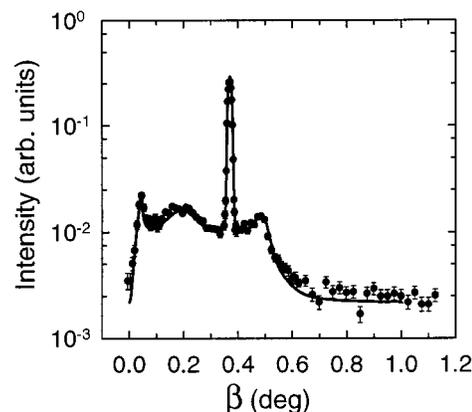


Figure 2. Off-specular diffuse scattering at fixed incident angle $\alpha = 0.37^\circ$ for $FC_{12}OH$ monolayers at the water–hexane interface at $T \approx T_c$ (close to the transition).

solid–gas monolayer transition. The tall peak at $\beta = 0.37^\circ$ is the specular reflection; the narrow peak near $\beta = 0.045^\circ$ is the surface field enhancement peak that indicates the presence of interfacial inhomogeneities.¹⁶ The two small angle scattering peaks in the shoulders of the specular peak provide information about the size and nearest neighbor ordering of the monolayer domains. The fit shown in Figure 2 is the result of a quantitative analysis using a form factor for circular domains and a structure factor with a log-normal distribution for both the domain sizes and separation. This analysis yields a domain radius of $1.5 \mu\text{m}$ and an average distance between domains of $4 \mu\text{m}$. Analysis of similar measurements for temperatures within 2 K of the transition indicate that the mean radius is nearly constant, but the distance between domains increases as the temperature is increased (a detailed discussion will be presented elsewhere¹⁷).

The reflected intensity illustrated in Figure 1 can be interpreted in terms of the interference between X-rays reflected from the top and bottom of the domains and X-rays reflected from the regions between the domains (Figure 1 inset). Using the Born approximation,¹⁸ the normalized reflectivity R/R_F can be written as

$$R/R_F = |c(T)A_1 + (1 - c(T))A_2|^2 \exp[-\sigma^2 Q_z^2] \quad (1)$$

where $A_1 = \Delta\rho_{HL} \exp(-idQ_z) + \Delta\rho_{LW}$, represents the reflection from domains of thickness d , where $\Delta\rho_{uv} = (\rho_v - \rho_u)/(\rho_W - \rho_H)$ is the normalized difference in electron density between the u and v phases (u and v are either H – hexane, L – surfactant layer, or W – water); $A_2 = \Delta\rho_{HW}$, represents the reflection from the regions between the domains (essentially just the pure water–hexane interface); σ is a temperature-dependent interfacial roughness due to capillary waves; the coverage $c(T)$ is the fraction of interface occupied by the solid domains. The electron density for water is $\rho_W \approx 0.334 e^-/\text{\AA}^3$ and that for hexane is $\rho_H/\rho_W = 0.690$. The electron density in the monolayer, ρ_L , is primarily due to the fluorocarbon piece of the surfactant since, as shown elsewhere, these measurements are insensitive to the nonfluorinated region of the molecule.⁷

At temperatures well below the phase transition, the monolayer fully covers the interface. Therefore, $c(T) \approx 1$, and the model in eq 1 reduces to a single layer model with a homogeneous monolayer of surfactant sandwiched between bulk water and hexane solution. Analysis of the reflectivity curve for $FC_{10}OH$ at 296 K or for $FC_{12}OH$ at 305 K yields values of the layer thickness, d , in good agreement with the calculated length, d_{calc} , of the fluorinated part of these surfactants,¹⁹ values

TABLE 1: Fit Parameters Described in the Text for the Reflectivity Analysis of Data Taken Far below the Transition Temperature

surfactant	T (K)	d (Å)	d_{calc} (Å)	σ (Å)	ρ_L/ρ_W
FC ₁₀ OH	296	10 ± 1	10.1	3.6 ± 0.3	1.85 ± 0.09
FC ₁₂ OH ^a	305	12.5 ± 0.3	12.3	3.6 ± 0.2	1.90 ± 0.04

^a Data for FC₁₂OH were analyzed in ref 7.

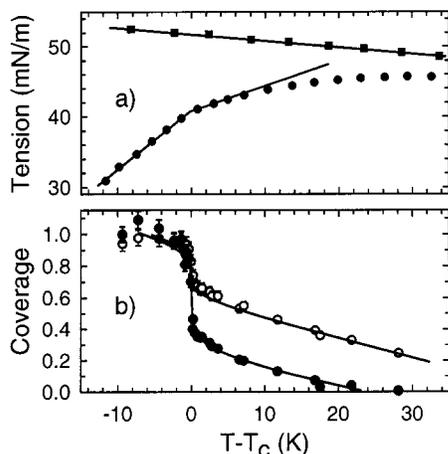


Figure 3. Interfacial tension and coverage vs temperature deviation from the transition temperature for FC₁₀OH monolayers at the water–hexane interface. (a) Tension: monolayer (dots); pure water–hexane interface (squares); lines are a guide to the eye. (b) Coverage: upper line and circles (coherent scattering); lower line and dots (incoherent scattering); $T_c = 300.5$ K.

of the monolayer electron density, ρ_L , in agreement with the density of bulk solid fluoroalkane phases,²⁰ and interfacial roughness, σ , in agreement with the value calculated from our measured values of the interfacial tension (see Table 1).¹⁴ This analysis shows that the monolayer at temperatures well below the phase transition is in a solid phase with the surfactants aligned nearly perpendicular to the interface. A similar phase occurs in monolayers of FC₁₂OH at the water–hexane and water–vapor interfaces.⁷

The solid lines in Figure 1 for the other temperatures are determined by analyzing the reflectivity data using one fitting parameter, the coverage $c(T)$, in eq 1. The success of this one parameter analysis indicates that at these other temperatures the monolayer consists of solid phase domains (whose structure is essentially the same as for the low-temperature homogeneous monolayer) separated by regions of gaseous monolayer. This model is also consistent with the analysis of the diffuse scattering shown in Figure 2. To perform this analysis, the parameters d and ρ_L are taken from the fit to the low-temperature data described above (Table 1). The temperature dependence of the interfacial roughness, σ , is determined by the variation of our measured values of the interfacial tension (see Figures 3a and 4a).¹⁴ In addition to the data shown in Figure 1, R/R_F at four values of Q_z ($= 0.1, 0.15, 0.2,$ and 0.25 \AA^{-1}) was measured for intermediate temperatures. Our measurements indicate that the functional form of the reflectivity is independent of temperature. Therefore, it is possible to determine $c(T)$ from measurements of R/R_F at one value of Q_z for a range of temperatures. Figures 3b and 4b show the coverage $c(T)$ determined by these one parameter fits to the data (at $Q_z = 0.15 \text{ \AA}^{-1}$) for FC₁₀OH and (at $Q_z = 0.1 \text{ \AA}^{-1}$) for FC₁₂OH monolayers. Coverage curves produced from data taken at different values of Q_z are identical (not shown).

The curves in Figures 3b and 4b indicate a sharp change in coverage at a transition temperature $T = 300.5 \pm 0.2$ K for

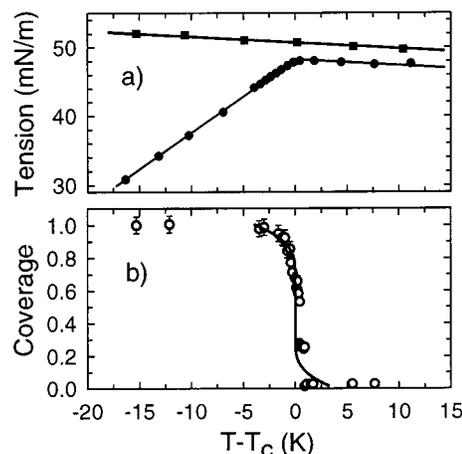


Figure 4. Interfacial tension and coverage vs temperature deviation from the transition temperature for FC₁₂OH monolayers at the water–hexane interface. (a) Tension: monolayer (dots); pure water–hexane interface (squares); lines are a guide to the eye. (b) Coverage: circles; line described in text; $T_c = 313.5$ K.

FC₁₀OH and $T = 313.5 \pm 0.2$ K for FC₁₂OH. These transition temperatures correlate very well with the location of slope discontinuities in the interfacial tension (see Figures 3a and 4a).²¹ Above the transition in the FC₁₀OH monolayer the coverage decays gradually over a range of 30 K while the coverage for the FC₁₂OH system decays rapidly over a range of 2 K. A similar distinction of a gradual versus rapid change is evident in the slope of the interfacial tension curves for these two systems. Previous thermodynamic measurements of the interfacial adsorption are consistent with this analysis.^{6,12}

It is important to note that eq 1 assumes that X-rays reflected from the solid and gas domains interfere coherently. The X-ray spatial coherence length projected onto the sample interface is 5 to 10 μm , consistent with coherent scattering from the small domains in the FC₁₂OH monolayers. However, we were unable to measure the small angle scattering peaks in the off-specular diffuse scattering from the FC₁₀OH (water–hexane) interface. If domains in FC₁₀OH monolayers were a factor of 5–10 times smaller or larger than the FC₁₂OH domains, our measurements would not detect these peaks (due to the limited resolution of the diffuse scattering measurements). For domains of diameter larger than approximately 10 μm , eq 1 must be modified to account for the incoherent interference of X-rays reflected from the solid and gas domains. Our present measurements do not provide any guidance as to the domain size or distribution in the FC₁₀OH monolayers, so we present in Figure 3b the analysis assuming either coherent or incoherent scattering.

Marchenko proposed that a critical transition will occur in a monolayer of polar surfactants at a liquid interface.⁸ He predicted the behavior of the interfacial polarization near this transition, which we write in terms of the coverage as

$$c(T) - c(T_c) = b \text{sign}(T_c - T) [\ln(T_c/|T_c - T|)]^{-a} \quad (2)$$

where $T \rightarrow T_c$, T_c is the critical transition temperature, a and b are positive constants related to unspecified scaling parameters in the theory.⁸ The coverage curves in Figures 3 and 4 can be fit using the parameters in eq 2. For the FC₁₂OH monolayer, the fit parameters are $c(T_c) = 0.5 \pm 0.02$, $b = 1.9 \pm 0.2$, and $a = 0.9 \pm 0.1$. For the FC₁₀OH monolayer, the parameters depend on whether these data are analyzed using coherent or incoherent scattering. For coherent scattering, the parameters are $c(T_c) = 0.77 \pm 0.02$, $b = 2.1 \pm 0.2$, and $a = 1.6 \pm 0.1$; for

incoherent scattering, $c(T_c) = 0.6 \pm 0.02$, $b = 1.6 \pm 0.2$, and $a = 1.0 \pm 0.1$. From the lines in Figures 3b and 4b, it is seen that our data near T_c are well represented by the temperature dependence in eq 2. It is our understanding that these data represent the first experimental test of the temperature dependence in eq 2.

The theoretical parameters a and b derived from the incoherent scattering analysis for FC₁₀OH monolayers are similar to those from the FC₁₂OH monolayers. Although the relationship of these parameters to the molecular properties of our two systems is currently unknown, it is reasonable to expect that they would be similar for systems of similar chemical composition as used here. This suggests that the incoherent analysis is preferred and that large domains exist in the FC₁₀OH monolayers. We plan to extend these studies to other surfactant systems to probe further the meaning of these theoretical parameters.

In summary, we have shown that FC₁₀OH and FC₁₂OH monolayers at the water–hexane interface undergo a solid-to-gas phase transition in which the lower temperature solid monolayer breaks into domains at the same temperature as the kink in the interfacial tension curve. The discrepancies between these measurements and earlier Brewster angle microscopy measurements⁵ may be due to a higher level of impurities in the earlier samples, though this issue remains to be resolved. X-ray reflectivity and diffuse scattering were used to determine the phase structure, the presence of domains, and the interfacial coverage of solid domains as a function of temperature. The dependence of the coverage on temperature near the phase transition is consistent with a critical transition theory of monolayer domains stabilized by a balance of the line tension and dipole interactions.⁸

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