

X-ray Scattering from *n*-alcohol Monolayers at the Water-hexane Interface

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X-ray scattering during the previous 15 years has radically changed our view of molecular ordering in organic monolayers at the water-vapor interface. A partial motivation for those studies has been to understand molecular ordering in biological membranes. These bilayer lipid membranes exist at *liquid-liquid* interfaces and consist of molecules that are slightly soluble in the surrounding aqueous medium. As a result, biomembranes are believed to be disordered, possibly significantly more so than their counterparts at the water-vapor interface. As one approach to understanding the molecular ordering in organic assemblies at the liquid-liquid interface, we recently pioneered the use of x-ray scattering to study the structure of monolayers at the water-oil interface [1]. Initially, we chose to study fluorinated surfactants at the water-hexane interface partially because of the large electron density contrast. Here, we report studies of *n*-alcohol monolayers at the water-hexane interface. Although this system has much smaller x-ray contrast, it contains surfactants much closer in composition to biological lipids.

Samples are prepared by placing a bulk solution of an *n*-alcohol in hexane on top of bulk water, (the four alcohols used in this study are $\text{CH}_3(\text{CH}_2)_{m-1}\text{OH}$, where $m = 20, 22, 24,$ and 30 , referred to as C_mOH in this article). We study the interface between these two bulk solutions. Previous thermodynamic measurements have shown that the interface undergoes a transition as a function of temperature [2-4]. This is illustrated in Fig. 1, which shows our measurements of interfacial tension γ as a function of temperature for our four systems and for the pure water-hexane interface. The slope, $-\text{d}\gamma/\text{d}T$, is the surface excess entropy. The sharp change in slope reveals an interfacial transition. We have chosen the bulk concentration of C_mOH so that the transition is at a convenient temperature.

X-ray reflectivity from these interfaces is measured with the liquid surface spectrometer at NSLS beamline X19C [5] using techniques specific to the liquid-liquid interface described previously [1, 6]. Figure 2 shows the reflectivity normalized to the Fresnel reflectivity (for an ideal interface without structure), R/R_F , as a function of the wave vector transfer normal to the interface ($Q_z = (4\pi/\lambda) \sin\theta$, where θ is the angle of specular reflection and $\lambda = 0.825 \text{ \AA}$). For each of the four systems

studied, Fig. 2 shows the measured and fitted R/R_F for two temperatures, one far below and the other far above the transition temperature.

The data in Fig. 2 for samples below the transition temperature have an oscillation whose period decreases as the alcohol chain length increases. This indicates that the thickness of the alcohol monolayer increases with chain length, as expected. The lines in Fig. 2 that fit these oscillations are derived from a standard fitting procedure using the Born approximation along with a model for the interfacial profile that consists of 2 or 3 layers sandwiched between bulk water and hexane [7]. The interface between each of these layers and an adjacent layer (or bulk) is roughened by capillary waves with a roughness value calculated from the measured interfacial tensions in Fig. 1. The fitting parameters consist only of the electron density of each layer and the layer's thickness.

One expects that an ordered monolayer will be described by a two layer model: the layer next to bulk water would represent the electron density at the position of the head group (COH), the adjacent layer (next to the bulk hexane) would represent the electron den-

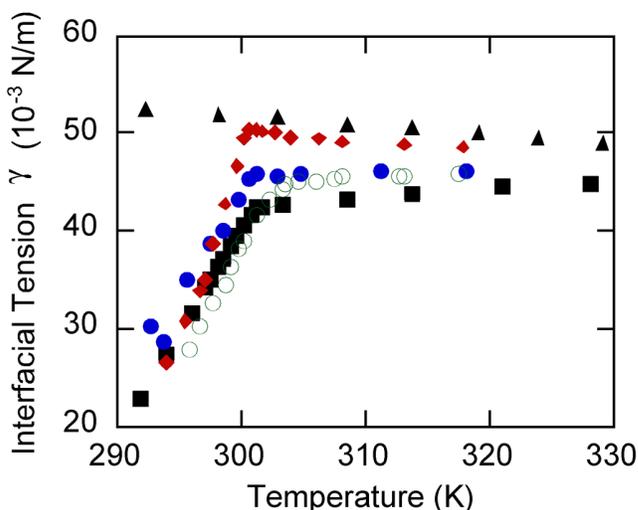


Figure 1. Interfacial tension for $\text{CH}_3(\text{CH}_2)_{m-1}\text{OH}$ monolayers adsorbed at the water-hexane interface: black squares, $m = 20$; blue dots, $m = 22$, open circles, $m = 24$; red diamonds, $m = 30$; black triangles, pure interface.

sity in the tail group region ($(\text{CH}_2)_m$). A two layer model provides a good fit to the data for C_{20}OH , C_{22}OH , and C_{24}OH , but can only fit the first two oscillation peaks for C_{30}OH (also note that a one layer model cannot fit the data). An example of the real space electron density profile for the two layer model is shown in Fig. 3. Although this profile is derived from fits to the C_{30}OH data, it is qualitatively similar to the fits for the shorter chain alcohol monolayers. This two layer profile has the following features. (1) The sum of the thickness of the two layers is equal to the calculated length of an all-trans (i.e., a straight) alcohol molecule for all four systems. However, the thickness of the head group is much larger and the tail group much smaller than expected from molecular dimensions. (2) The electron density in the head group region is higher than that of water, as expected for well-packed alcohol molecules. (3) The tail group electron density is close to the density for *liquid* bulk alkanes of a similar chain length, indicating a large disorder in the tail group. It is hard to reconcile these features of the model into a coherent physical

picture. Fortunately, the C_{30}OH data resolves this problem.

The longer length of C_{30}OH allowed us to measure a third oscillation in the reflectivity. The complete set of C_{30}OH data cannot be fit with the two layer model. Instead, fitting requires three layers. The fit in Fig. 2d is a three layer fit and the three layer profile is shown in Fig. 3. This exhibits a narrow peak for the head group region, though still wider than expected for close-packed head groups all arranged in a single plane [8]. The tail group region is modeled by two layers. The layer next to the head group has an electron density (normalized to bulk water) of 0.94, very close to the value measured for close-packed methylene chains (0.95 to 1) [9]. The layer closest to the hexane has a lower electron density, similar to the value expected for liquid alkanes of a similar length [9].

Further analysis of the head group region indicates the existence of 15 ± 5 electrons more than expected per alcohol molecule. This can be explained if water molecules exist at the same interfacial height as the head groups with a hydration ratio as large as 3 (H_2O): 2 (C_mOH). The necessity for some disorder along the interfacial normal of the head groups to accommodate the hydrated H_2O is consistent with the slightly larger than expected width for the head group region.

Although the three layer model introduces a slightly artificial electron density change in the middle of the tail group, it is important to realize that the absolute spatial resolution is approximately $\pi/Q_{z,\text{max}} \approx 7$ Å. Therefore, it is unjustified to introduce an atomic scale electron density profile to analyze these data. The three layer model captures the essential structural features of our data. For the tail group, this analysis indicates that the region of the tail group near the head group is ordered (and nearly close-packed) and the end of the tail group near the hexane is disordered. We could not measure to large enough Q_z to record a third oscillation for the shorter alcohols. However, given the problems with interpretation of the two layer model for the shorter alcohols, it is likely that the three layer model is also appropriate for these data.

The high temperature data in Fig. 2 are featureless and indicate that most of the C_mOH molecules have desorbed from the interface into the bulk hexane. The lines (Fig. 2) through these data are from a one parameter fit to a model of a simple interface between two bulk media (i.e., no layers), with

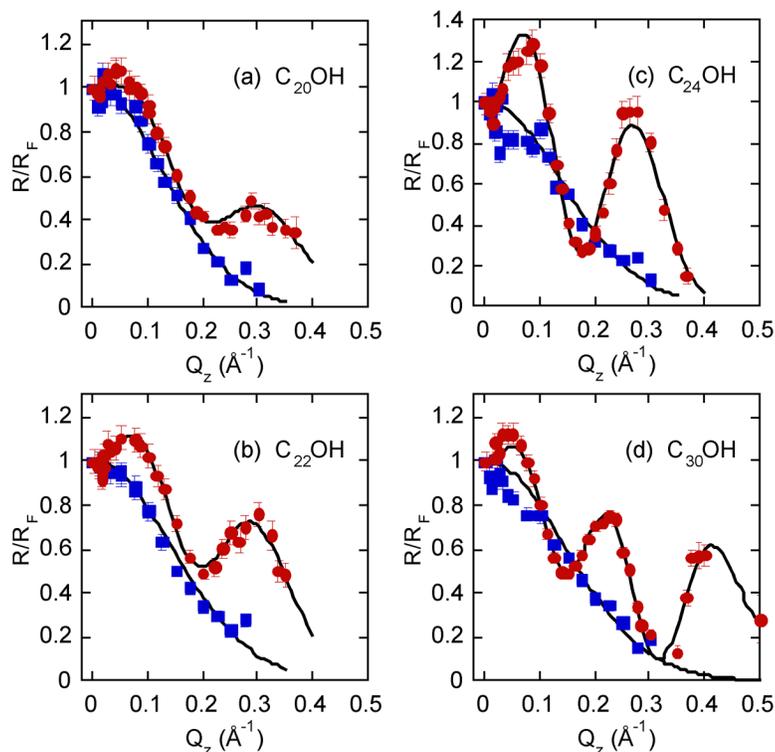


Figure 2. X-ray reflectivity normalized by the Fresnel reflectivity versus wave vector transfer normal to the interface for $\text{CH}_3(\text{CH}_2)_{m-1}\text{OH}$ monolayers adsorbed at the water-hexane interface. Red dots are for temperatures far below the transition T , blue squares are for T much greater than the transition T . (a) $m = 20$ (dots, $T = 292.4$ K; squares, $T = 318.6$ K), (b) $m = 22$ (dots, $T = 294.8$ K; squares, $T = 318.8$ K), (c) $m = 24$ (dots, $T = 295.8$ K; squares, $T = 318.4$ K), (d) $m = 30$ (dots, $T = 297.7$ K; squares, $T = 318.2$ K). Lines are fits described in the text.

the interfacial width (or roughness) as the only fit parameter. The width is approximately $5.0 \pm 0.2 \text{ \AA}$ for all four systems and is much larger than the expected value of $\approx 3.6 \text{ \AA}$ from capillary wave theory. It is known that the measured interfacial width of the water-hexane interface is the same as the prediction of the capillary wave theory [10]. This indicates that the larger interfacial width is due to the low density of $C_m\text{OH}$ molecules that remain at the interface. It is interesting to note that the measured interfacial width is similar to the value measured between bulk docosane ($C_{22}H_{46}$) and water [11]. The large width at the water-docosane interface is believed to be due to an intrinsic width from the bulk correlation length of the flexible docosane. A similar effect may be present in the high temperature phase of our systems.

Figure 4 shows R/R_F measured at $Q_z = 0.175 \text{ \AA}^{-1}$ as a function of temperature for the $C_{24}\text{OH}$ system. The monolayer transition occurs at the minimum of the “V” in this curve. Significant off-specular diffuse scattering (not shown) in a region near the transition temperature

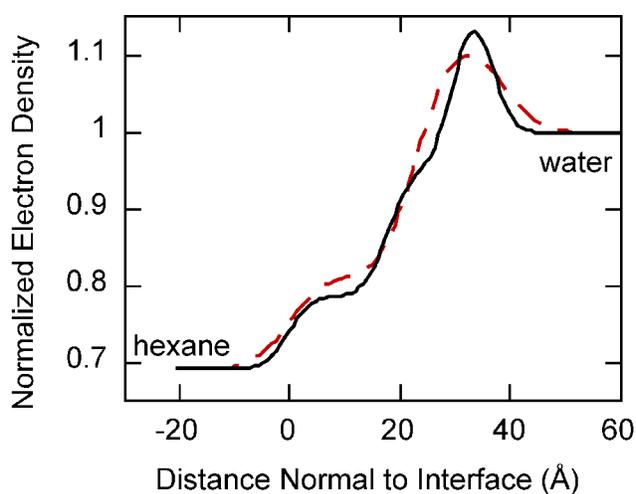


Figure 3. Electron density (normalized to the density for bulk water) as a function of the distance normal to the interface (dashed line – two layer model, solid line – three layer model). This profile is determined by fitting to the data for the $\text{CH}_3(\text{CH}_2)_{29}\text{OH}$ monolayers. The bulk water phase occurs at distances greater than $\sim +45 \text{ \AA}$; the bulk hexane phase for distances more negative than $\sim -10 \text{ \AA}$.

indicates the presence of inhomogeneities, probably domains, in this monolayer. To extract the fraction of interface covered by domains as a function of temperature the reflectivity must be interpreted as due to reflection from a domain filled interface. Domains that are much smaller than the projection of the x-ray spa-

tial coherence length onto the interface will produce reflectivity through a coherent addition of the x-ray wave field scattered from domains and from the region between the domains. Likewise, an incoherent addition will occur for domains much larger than the in-plane x-ray coherence length. A detailed analysis reveals that the temperature behavior of R/R_F cannot be explained by incoherent addition of the x-ray wave field and, therefore, the monolayer domains must be on the order of a few micrometers in size or smaller. A similar conclusion is valid for the $C_{30}\text{OH}$ system, but no conclusion regarding domain sizes can be drawn for the two shorter chain systems. Figure 5 shows the monolayer coverage as a function of temperature through the phase transition. The lines in Figures 4 and 5 are fits to a theory for this transition based upon a balance of domain line tension and in-plane dipolar energies [12, 13].

In summary, we have shown that the structure of adsorbed monolayers of hydrogenated *n*-alcohol surfactants can be studied at the water-hexane interface. These surfactants are soluble in the hexane and self-

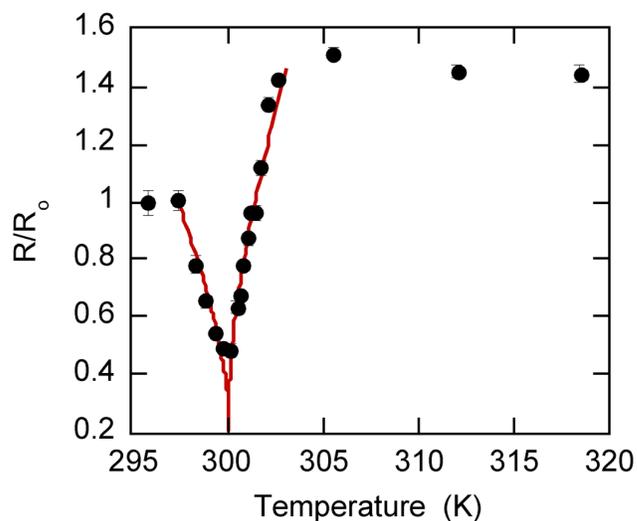


Figure 4. R/R_0 measured at $Q_z = 0.175 \text{ \AA}^{-1}$ as a function of temperature for the $C_{24}\text{OH}$ system. R_0 is the reflectivity at $T = 295.8 \text{ K}$. The line is a fit discussed in the text.

assemble into a monolayer under the right conditions. Our studies show a distinctive type of disorder in this monolayer. The monolayer thickness is the same as a molecular length, indicating that the molecules are oriented nearly perpendicular to the interface and are nearly all-trans. Penetration of hydration water mol-

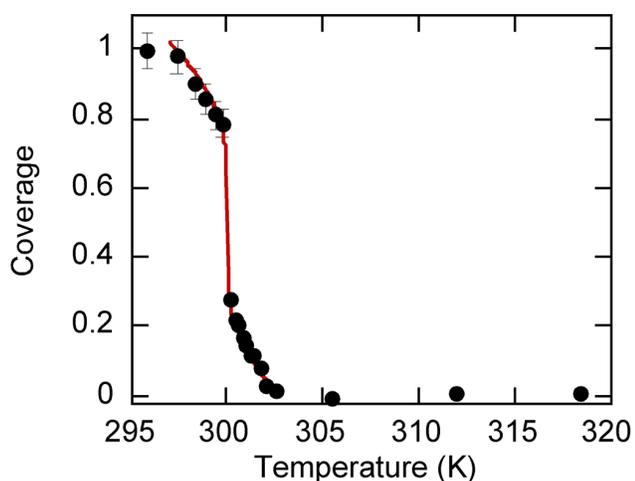


Figure 5. Fraction of interface covered by the monolayer (coverage) as a function of temperature through the phase transition for the $C_{24}OH$ system. The line is a fit discussed in the text.

ecules into the region of the head group must be accompanied by head group disorder along the interfacial normal. The region of the tail group next to the head group is nearly close-packed while the region adjacent to the hexane is more disordered. This disorder is in sharp contrast to the very ordered, close-packed monolayers formed by fluorinated alcohol surfactants at the water-hexane interface [1].

Acknowledgements

These studies were supported by the NSF Division of Materials Research. Research carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886.

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