Molecular Ordering and Phase Behavior of Surfactants at Water-Oil Interfaces
as Probed by X-ray Surface Scattering

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Abstract

Surfactants have their primary utility, both scientific and industrial, at the liquid-liquid interface. We review recent x-ray surface scattering experiments that probe the molecular ordering and phase behavior of surfactants at the water-oil interface. The presence of the oil modifies the interfacial ordering in a manner that cannot be simply understood from analogies with studies of Langmuir monolayers of surfactants at the water-vapor interface or from the traditional view that the solvent is fully mixed with the interfacial surfactants. These studies explored the role of chain flexibility and headgroup interactions on the ordering of long-chain alkanols and alkanoic acids. Small changes in the surfactant may produce large changes in the interfacial ordering. Interfacial phase transitions as a function of temperature and spatially inhomogeneous phases are observed. Finally, variation of the solvent chain length can alter the fundamental character of the phase transitions and lead to the formation of thick or multilayer interfacial structures.
1. INTRODUCTION

The scientific investigation and industrial utilization of surfactants is an extensive, ongoing enterprise. Techniques such as x-ray and neutron surface scattering and non-linear optics, which are specifically sensitive to surface phenomena, have contributed to this enterprise by determining the ordering and phase behavior of molecules at liquid-vapor interfaces (1-4) and, more recently, at water-oil interfaces (5, 6). In this review, we focus on scattering studies of single interfaces between macroscopically phase separated water and oil phases, as opposed to scattering studies of bulk materials that probe the structure of internal interfaces due to microscopic phase separation, such as those formed by micelles, microemulsions, and vesicles (7). We discuss primarily x-ray surface scattering studies, which have led recently to a new understanding of surfactant ordering at water-oil interfaces.

The surfactants of concern to us consist of polar headgroups (say, alcohol –CH₂OH, or carboxylic acid, –COOH) at the end of a long alkyl or partially fluorinated alkyl chain (CH₃(CH₂)ₘ₋₁ with \( m \) varying from 20 to 30, or CF₃(CF₂)ₘ₋₃(CH₂)₂ with \( m = 10 \) or 12). These surfactants are soluble at low concentrations in hydrocarbon oils, such as alkane liquids (e.g., hexane). If a hexane solution of these surfactants is placed in contact with bulk water, the surfactants will minimize their free energy by partitioning between the bulk hexane and the water-hexane interface. A surfactant that goes to the interface can lower its energy by positioning its polar headgroup in the polar environment of water, which may also allow for hydrogen bonding between its headgroup and water. However, the translational entropy of the surfactant is reduced. Also, water and hexane molecules that were formerly at the interface are displaced in this process.
As more surfactants are adsorbed to the interface, it is sensible to think that interactions between surfactants, such as repulsive steric and attractive van der Waals interactions, become important. However, in an influential textbook, Davies summarized earlier work by stating that “molecules of oil penetrate between the hydrocarbon chains and remove all inter-chain attractions”, thus leading to the widely held views “that the –CH$_2$– groups in the adsorbed film are free to move laterally” and that surfactant monolayers at the water-oil interface are more disordered than the corresponding monolayers at the water-vapor interface (8, 9). Pethica and co-workers discussed similar ideas in their experimental studies of lipids at the water-oil interface (10, 11).

Recent x-ray results have contradicted this point of view, for example, by demonstrating the presence of solid monolayers of close-packed surfactant monolayers at water-oil interfaces (12-14). Interfacial tension measurements provided evidence for condensed monolayers without specifying whether they were solid or liquid (15-20). The formation of a solid monolayer may result from strong interactions between the surfactant chains that overcome the loss of entropy due to conformational degrees of freedom of the chains. Therefore, a prime candidate for the formation of a solid monolayer is a surfactant whose chain is relatively rigid, such as the partially fluorinated alkanol CF$_3$(CF$_2$)$_m$3(CH$_2$)$_2$OH (m = 10 or 12) (12, 13). In this case, little conformational entropy is lost when these chains form a close-packed solid monolayer at the water-hexane interface. Alternatively, we have also observed close-packed, nearly all-trans monolayers at the water-hexane interface of neutral alkanoic acids (CH$_3$(CH$_2$)$_m$2COOH, m = 18, 20, and 30) that have flexible alkyl tails (14). However, it seems that just the van der Waals attractions of the chains alone are not enough to overcome the disordering effect of the tail conformational entropy. This is suggested by observations of monolayers of alkanol surfactants
(CH$_3$(CH$_2$)$_m$OH, $m = 20$ to 30) at the water-hexane interface for which the most stable dense monolayer phase is a liquid (21, 22). Instead, molecular dynamics simulations suggest that an additional attractive interaction (extensive hydrogen bonding of alkanoic acid headgroups to their neighboring headgroups), which is not present in the alkanol monolayers, is responsible for the formation of solid monolayers of the neutral alkanoic acids at the water-hexane interface (14).

These results support the view that the oil solvent has a strong influence on molecular ordering at the interface. Long chain alkanols form solid all-trans monolayers at the water-vapor interface (22-25), though they form liquid monolayers with disordered tails at the water-hexane interface (21, 22). A small amount of hexane penetrating into the region of the monolayer is possible, and our measurements place an upper bound on the amount, but not a lower bound (22). Here, the oil solvent has acted to disorder the monolayer, though perhaps not exactly as envisioned by Davies (8). Surprisingly, even changing the chain length of the alkane solvent (say, from hexane to hexadecane), can greatly alter an adsorbed surfactant layer (26). As shown below, this particular change can alter the interfacial phase of tetracosanol (CH$_3$(CH$_2$)$_{23}$OH) from being a monolayer to a multilayer (26).

In spite of the dissimilarities between surfactant layers at the water-oil interface and the corresponding layers of the same surfactants at the water-vapor interface, a further comparison is useful. Micrometer-scale domains of condensed monolayer phases are observed at both interfaces, and it is likely that long-range dipole interactions stabilize these domains at both interfaces (27-30). The monolayers discussed in this article, at the water-oil interface, are in equilibrium due to the exchange of surfactants between the interface and the bulk oil. Therefore, these monolayers are not easily over-compressed into a metastable or unstable state, as is the
case with monolayers at the water-vapor interface. This has been used to advantage at the water-vapor interface to study domain instabilities (31), but the issue of very long relaxations of internal degrees of freedom in solid monolayers, and their effect on the monolayer phase diagram, has not been fully resolved for Langmuir monolayers (32-34).

There is a striking dissimilarity between the phase diagrams of, say, long-chain alkanol monolayers at the water-oil and at the water-vapor interfaces. For an interface between water and an oil solution of a single surfactant the interfacial phase is determined by the bulk pressure, temperature, and bulk concentration of the surfactant (15, 35-37). For adequately high temperatures, the interfacial phase appears to be a surfactant gas (22). As the temperature is lowered, a phase transition occurs at which the alkanols form a liquid monolayer phase (22). Depending upon the particular chain length, domains may form en route to this transition (13, 22, 38). If, as Lyklema has suggested, the equation of state is the same for these surfactants at the water-oil and water-vapor interfaces (39), then one might expect that further lowering the temperature would produce a sequence of solid phases, varying in unit cell and tilt angle of the essentially all-trans tailgroup, as is observed for long-chain alkanols at the water-vapor interface when the surface pressure is increased (21, 23-25, 40-45). This is not the case. Instead, before a low enough temperature is reached at which the liquid monolayer might undergo a transition to a solid monolayer, the alkanol will precipitate out of the solution. Also, if the equations of state are the same, one expects the same interfacial monolayer phase for the same interfacial concentration of the surfactant (and temperature and bulk pressure). This is also not the case because the long-chain alkanols at the water-oil interface form only a liquid monolayer phase, while at the water-vapor interface they form a solid monolayer phase under similar conditions. This is true even for the same average interfacial density because the solid phase at the water-
vapor interface will form a spatially inhomogeneous phase in which solid phase domains are separated by interfacial regions of much lower surfactant density (23-25).

In the remainder of this article, we present evidence gathered from x-ray surface scattering, interfacial tension, and Brewster angle microscopy for many of the phenomena mentioned in this introduction.

2. X-RAY SURFACE SCATTERING METHODS

Two x-ray surface scattering techniques have proven useful in the study of surfactant layers at the water-oil interface – x-ray reflectivity and off-specular diffuse scattering (also known as GISAXS, grazing incidence small angle x-ray scattering) (1, 46, 47). X-ray reflectivity probes the variation of electron density with depth into the interface, and by implication the molecular ordering with sub-nanometer resolution at water-oil interfaces. GISAXS can determine the average radius and separation of micrometer-scale domains in surfactant monolayers (38, 47). Both techniques are sensitive to the fraction of the interface covered by the monolayer phase. In addition to the studies of surfactant layers discussed here, these x-ray techniques have been used recently to study other phenomena at the liquid-liquid interface, including the structure of the neat interface (without surfactants) between water and alkane liquids of varying chain lengths (from 6 to 22 carbons long) (48, 49), the neat interface between water and polar oils such as 2-heptanone or nitrobenzene (50, 51), liquid-liquid interfaces between thin wetting films, including protein adsorption at this interface (52-56), the ordering of surfactant mixtures at the water-oil interface (57), phospholipid monolayers at the water-oil interface (58-60), the microemulsion-water interface (61-63), critical phenomena at the liquid-liquid interface (64), the ordering of nanoparticles at the water-oil interface (65, 66), the
ordering of ions at the oil/silica hydrosol (66-69), and ion distributions at the electrified interface between two electrolyte solutions (51, 70, 71).

The scattering geometry for x-ray reflectivity shown in Fig. 1 indicates that x-rays pass through the upper liquid phase on their way to the interface. Significant absorption of the x-rays by the liquid and the need to adjust reflection angles on a scale of millidegrees dictates the use of a synchrotron x-ray source that can provide a highly collimated, intense, and relatively high energy (typically 15 keV or higher) beam of x-rays (72, 73). Reflectivity data are measured as a function of wave vector transfer normal to the interface, $Q_z = (4\pi/\lambda) \sin \alpha$ when the in-plane components of the wave vector are set to zero. The x-ray wavelength $\lambda$ is typically 0.825 Å and the incident and reflected angles are equal for specular reflection ($\beta = \alpha$ in Fig. 1) (12, 22, 73). Specular reflection probes structure normal to the interface, but averaged over the in-plane region of the interface.

X-ray reflectivity $R(Q_z)$ from the water-oil interface can be analyzed to yield the electron density profile by use of the first Born approximation, written as (46)

$$\frac{R(Q_z)}{R_F(Q_z)} \approx \left| \frac{1}{(\rho_W - \rho_O)} \int dz \frac{d\{\rho_e(z)\}_{sy}}{dz} \exp(iQ_z z) \right|^2,$$

where $z$ is in the normal direction, $\{\rho_e(z)\}_{sy}$ is the electron density profile averaged over the surface area of the interface illuminated by the x-rays, $\rho_W$ and $\rho_O$ are the electron densities of bulk water and oil, respectively (e.g., $\rho_W = 0.3337$ e/Å³ and $\rho_{Hexane} = 0.230$ e/Å³ at $T = 20$ °C), the Fresnel reflectivity $R_F(Q_z)$ is calculated for an ideal interface at which the electron density changes abruptly from the value of one bulk phase to the other, and is expressed as (74, 75)
\[ R_f(Q_z) \approx \left| \frac{Q_z - Q_T^z}{Q_z + Q_T^z} \right|^2, \]  

(2)

where \( Q_T^z = \left( Q_z^2 - Q_c^2 \right)^{1/2} \) is the \( z \)-component of the wave vector transfer with respect to the lower phase. Equation (1) is accurate for \( Q_z \geq 3Q_c \), where total reflection of x-rays from the lower phase occurs for \( Q_z \leq Q_c \) and the critical wave vector transfer is \( Q_c = 4\left( \pi r_e (\rho_w - \rho_o) \right)^{1/2} \) (\( \approx 0.012 \text{ Å}^{-1} \) for the water-hexane interface), and \( r_e \) is the classical electron radius. Although Eq.(1) provides insight into the reflection process, the Parratt formalism is an alternative and exact method that is often used to analyze reflectivity measurements (76).

X-ray reflectivity is specifically sensitive to surface or interfacial structure (1). Equation (1) indicates that reflected x-rays are produced when the electron density varies with depth into the interface. X-rays passing through bulk liquid phases do not produce reflections because the value of the electron density, when averaged over the \( x-y \) plane, is constant with depth. Reflected x-rays are produced when incident x-rays encounter the top, or bottom, of a monolayer because the electron density changes with depth in those regions. Likewise, internal structure within the monolayer could produce reflected x-rays. An example of this is the depth at which the headgroups within an ordered surfactant monolayer are bound to the tailgroups. These various reflections will coherently interfere to produce the total x-ray reflectivity. The shape and intensity of the interference fringes produced by the variation of reflectivity with wave vector transfer \( Q_z \) (or, equivalently, incident angle) are analyzed to yield the electron density variation with depth through the interface.

An example of such interference fringes is shown in Figure 2A which illustrates x-ray reflectivity data for alkanols \( \text{CH}_3(\text{CH}_2)_m\text{OH} \) with \( m = 20, 22, 24, \) and 30 (22). These data are analyzed by fitting to a model of the electron density profile that consists of two or three slabs,
each of constant electron density, sandwiched between bulk water and bulk hexane solution. The slabs are ordered water–1–2–3–hexane. Slab 1 represents the headgroup region (–CH₂OH), slabs 2 and 3 represent the tailgroup region (–(CH₂)m-2CH₃). The interface is roughened by capillary waves whose amplitude is determined by the interfacial tension, which is measured separately using the Wilhelmy plate method. Since x-ray reflectivity measures the electron density profile as a function of z, but averaged over the x-y plane, the effect of capillary waves on the reflectivity can be modeled by a smooth crossover in the electron density from one slab to its neighboring layer or bulk phase. A general formula for the electron density gradient normal to a surface with M slabs is (77)

\[
\frac{d\langle \rho_e(z) \rangle_{xy}}{dz} = \sum_{i=0}^{M} (\rho_i - \rho_{i+1}) \frac{1}{(2\pi\sigma_{i+1}^2)^{1/2}} e^{-(z-D_i)^2/2\sigma_{i+1}^2},
\]

where \( \rho_o \) is the electron density of the water, \( \rho_{M+1} \) is the density of the upper oil phase, and the Gaussian functions provide a smooth crossover between slabs \( i \) and \( i+1 \) with an interfacial width \( \sigma_{i+1} \) (the same value of \( \sigma_{i+1} \) is used for all \( i \) to model the effect of capillary waves). If \( L_i \) is the thickness of the \( i \)th slab, then \( D_i = \sum_{j=1}^{i} L_j \) is the distance from the surface of the water to the interface between the \( i \)th and \( (i+1) \)th slabs.

3. TAILGROUP EFFECTS

Figure 2B illustrates the electron density profiles that yield the best fits to the data shown in Fig. 2A (22). A quantitative analysis of the fitting supports the following conclusions that specify the disordered nature of these \( n \)-alkanol (CH₃(CH₂)m-1OH) monolayers. The average area per alkanol at the water-hexane interface is 23±1 Å², larger than the close-packed area of 18.7 Å². The tailgroup is disordered with progressively more disorder when proceeding from the headgroup to the terminal methyl group. This conclusion is based upon numerical comparison of
the electron density profile with values of the electron densities of bulk phases and the molecular ordering in the bulk phases as determined by diffraction or spectroscopy. The ordering in the region of the tailgroup adjacent to the headgroup (with an electron density of \( 0.317 \text{ e}^{-} \text{Å}^{-3} \)) is similar to the structure of \( \alpha \) (rotator) bulk phases of alkyl chains. Ordering in the rest of the tailgroup (with an electron density of \( 0.267 \text{ e}^{-} \text{Å}^{-3} \) over more than half of the alkyl chain) is similar to the conformation of liquid alkyl chains just above the freezing point of bulk alkanes. These experiments place an upper limit on the amount of hexane mixed into the region of the tailgroup (1 hexane for every 5 or 6 alkanols). Also, the headgroup region contains a small fraction of water (approximately 1 water for every 3 alkanols). These last two conclusions are based upon the number of electrons measured in the slabs that correspond to the interfacial depth of the tailgroups and headgroups as well as consideration of the volume occupied by alkanols.

The disordered nature of these long, flexible alkyl tails is not surprising when the gain in conformational entropy of the tailgroups is considered. However, similar molecular ordering of these alkanols has not been observed at the water-vapor interface. Instead, only solid monolayer phases of close-packed, essentially all-trans tailgroups were observed at this interface (22-25, 41). The presence of the hexane has produced a large change in the monolayer, but not because of a large fraction of hexane intercalated into the monolayer as proposed by Davies.

Alternatively, x-ray reflectivity experiments of surfactants with rigid-rod tailgroups indicate that the surfactants form close-packed monolayers that fully exclude hexane. Measurements of the interface between hexane solutions of \( \text{CF}_3(\text{CF}_2)_{m-3}(\text{CH}_2)_2\text{OH} \) (total carbon number \( m = 10 \) or 12) and water demonstrate the presence of a surfactant monolayer that can be described by a single slab (in this case, the much greater electron density of the fluorinated part of the tailgroup and the shorter chain renders these reflectivity measurements insensitive to the
headgroup) (12, 13, 38, 57). The electron density $\rho_e = 0.635 \pm 0.01 \text{ e}^{-\text{Å}^3}$ that corresponds to the fluorinated part of the tailgroup of a monolayer of CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$OH at the water-hexane interface ($T = 32 \, ^\circ\text{C}$) lies between the known densities of the monoclinic crystal phase and the rhombohedral rotator solid phase of bulk fluoroalkanes (e.g., for $n$-C$_{20}$F$_{42}$) (78). The measured thickness of this slab, $1.25 \pm 0.03 \, \text{nm}$, corresponds precisely to the calculated length of the fluorinated part of the tailgroup, which is $1.27 \, \text{nm}$. These measurements exclude the possibility that this monolayer could be in a liquid monolayer phase or could have any substantial concentration of hexane in the monolayer.

These measurements suggest that surfactants with rigid-rod tailgroups whose shape allows them to close-pack will do so at the water-oil interface, thereby excluding the oil from the interfacial layer, even if the surfactants are soluble in the oil. Conversely, soluble surfactants with flexible tailgroups can form loosely packed liquid monolayer phases with disordered tailgroups. However, they can also form solid close-packed monolayer phases, as will be demonstrated next.

4. HEADGROUP EFFECTS

$N$-alkanol and $n$-alkanoic acids differ slightly in their chemical composition. When adsorbed to pH 2 water the alkanoic acid headgroup is neutral, as is the alkanol headgroup. Nevertheless, the x-ray reflectivity measurements shown in Figure 3A from monolayers of CH$_3$(CH$_2$)$_{29}$OH and CH$_3$(CH$_2$)$_{28}$COOH at the water-hexane interface exhibit oscillations of very different amplitude (14). The alkanoic acid tailgroup can be described by a single slab of electron density $0.317 \pm 0.003 \text{ e}^{-\text{Å}^3}$ that is comparable to the density in the $\alpha$ rotator solid phases of long chain alkanes, in contrast to the alkanol molecules which exhibit liquid-like chain
disorder at the interface (79). The CH$_3$(CH$_2$)$_{28}$COOH layer is slightly thicker than the CH$_3$(CH$_2$)$_{29}$OH layer as indicated by the interference minima appearing at slightly smaller $Q_z$.

The area per molecule of 19 ± 1 Å$^2$ determined by the reflectivity measurements is also consistent with a close-packed solid monolayer. We have also measured solid monolayer ordering for shorter alkanoic acids with 18 and 20 carbons (unpublished). Analysis of the reflectivity is consistent with the molecular dynamics (MD) simulation shown in Figure 3B, including the slight tilt of the molecules.

The MD simulation also indicates the presence of hydrogen bonded headgroups arranged in rows (Fig. 3B) (14). Since literature values lead to an estimate of approximately five gauche conformations in the disordered portion of the CH$_3$(CH$_2$)$_{29}$OH tailgroup (22, 80), the attractive energy gained by hydrogen bonding of the alkanoic acid headgroups (~5 kcal/mol per bond) is comparable to the conformational free energy lost (~0.6 kcal/mol per gauche conformation) when a disordered tail becomes all-trans. This demonstrates the plausibility of a model in which the presence of the attractive hydrogen bonding brings the alkanoic acid surfactants closer together while ordering what would otherwise be a partially disordered tailgroup. The chain ordering is more favorable when hydrogen bonds link a row of head groups (as for CH$_3$(CH$_2$)$_{28}$COOH), rather than just bonding isolated pairs (or triplets) of head groups (as observed in the MD simulation of CH$_3$(CH$_2$)$_{29}$OH, not shown) because the ratio of total hydrogen bonding energy to total conformational free energy is greater. We have also shown that the effect of hydrogen bonding on these monolayers can be considered in terms of an elastic free energy that describes the stretching of the alkyl tail from the shorter, disordered CH$_3$(CH$_2$)$_{29}$OH to the longer all-trans CH$_3$(CH$_2$)$_{28}$COOH (14).
5. PHASE TRANSITIONS AND INHOMOGENEOUS PHASES

Interfacial tension measurements as a function of temperature, bulk pressure, and composition can be used to determine the interfacial phase diagram of water-oil-surfactant systems (15, 35-37). Examples of the tension as a function of temperature $\gamma(T)$ are shown in panels A and B of Fig. 4. The slope of the tension curve $\gamma(T)$ determines the interfacial excess entropy per unit area, $S^\sigma_a = -\left(\frac{\partial \gamma}{\partial T}\right)_{p,c}$, which is the excess entropy of molecules at the interface over their entropy in the bulk (39). The location of the slope discontinuity in the tension curves in Fig. 4 identifies the location of a phase transition whose temperature can be tuned by varying the surfactant concentration and the bulk pressure (though changes in pressure on the order of MPa are required for a noticeable effect (15)). The close proximity in temperature of the phase transitions in Fig. 4A is due to a judicious choice of bulk concentration.

At temperatures below the transition temperature, the large positive slope in $\gamma(T)$ indicates that the entropy of molecules at the interface is much smaller than in the bulk. Above the transition the excess interfacial entropy is either slightly negative or slightly positive. Therefore, with increasing temperature the interface undergoes an order-disorder transition. X-ray reflectivity measurements reveal an abrupt reduction in surfactant adsorption at the phase transition. Presumably, surfactants that leave the interface are solvated in the oil phase. The surfactants are vaporized (or sublimated) from the lower temperature liquid (or solid) monolayer into the dilute oil solution. At high temperatures the interfacial surfactant density is very low and the behavior of the interface approaches that of the neat water-hexane interface, for which $\gamma(T)$ has a slightly negative slope. Some interfacial tension measurements suggest that the change in slope from slightly positive to slightly negative (e.g., for CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$OH, denoted
FC10 in Fig. 4B) occurs via a second phase transition (19), rather than just a crossover, though structural measurements such as x-ray scattering have not been able to confirm this. However, tension measurements as a function of bulk pressure provide clear evidence for the existence of two phase transitions (17).

As an example, consider the phase transition that occurs for monolayers of CH₃(CH₂)ₘ₋₁OH (m = 20, 22) at the water-hexane interface (Fig. 4A) (22). In this case, x-ray reflectivity below the transition is essentially unchanged with temperature, except for the effect of interfacial roughness that varies with temperature because the tension is temperature dependent. At the transition, the reflectivity curve changes abruptly (over ~ 0.02°C) to that of an interface without a monolayer, though there is evidence that a small number of surfactant molecules are still at the interface. The latter, indirect conclusion is based upon the measurement of a larger interfacial width than expected from a neat water-hexane interface. Figure 4C illustrates the domain coverage of the interface, which is the fraction of interface covered by surfactant domains. The coverage changes abruptly at the transition from 1, which indicates an interface fully covered by the monolayer, to nearly 0. This first order transition occurs between a condensed liquid monolayer phase and a dilute gaseous monolayer.

Increasing the chain length of CH₃(CH₂)ₘ₋₁OH to m = 24 or 30, or changing the surfactant to CF₃(CF₂)ₘ₋₃(CH₂)₂OH (m = 10 or 12) alters the character of the phase transition (Figs. 4D and 4E) (13, 22). The most thoroughly investigated system is CF₃(CF₂)₉(CH₂)₂OH, which has been studied with GISAXS and Brewster angle microscopy, as well as x-ray reflectivity (12, 13, 30, 38). The interfacial coverage for CF₃(CF₂)₉(CH₂)₂OH at the water-hexane interface is qualitatively similar to that shown in Fig. 4C for CH₃(CH₂)₁₉OH except that the crossover at the transition is rounded with a width of ~2°C (Fig. 4E). GISAXS measurements in Fig. 5A reveal
that in the transition region the interface is in a domain phase that consists of solid monolayer
domains separated by dilute gaseous regions (of nearly pure water-hexane interface) (38). The
two peaks adjacent to the specular peak represent small angle scattering from the interfacial
domains. Under the assumption that the domains are circular, further analysis reveals that the
average domain radius is ~1.5 μm (Fig. 5B) and the average domain separation varies from 2 μm
at the lowest temperatures (when the radius is 1 μm and the domains fill the interface) to ~8 μm
very close to the transition (Fig. 5C). The domain phase near the transition is reproducible upon
heating or cooling through the transition, without any measurable hysteresis.

The constancy of the domain size under conditions at which the interfacial concentration
of surfactants changes by a factor of 20 indicates that domains are created or annihilated upon
cooling or heating. Thus, the surfactants at the interface can exchange with those in the bulk to
allow full equilibration of these systems. Above the transition region all evidence of domains
disappears. Brewster angle microscope images provided further evidence for domains in this
system, although the domain size was below the optical resolution (~10 μm) of the microscope
(30).

In a slightly shorter fluorinated surfactant, CF₃(CF₂)₇(CH₂)₂OH, the domain phase persists
over a much larger range of temperature. Fig. 4E shows that although the coverage changes
abruptly at the transition, it changes by only ~30%. Above the transition the coverage further
decreases gradually over tens of °C. All of the x-ray reflectivity curves throughout this range of
temperatures exhibit the same interference pattern, differing only in the amplitude of the
interference fringe (57). Therefore, the thickness of the monolayer is unchanged, but its average
electron density changes with temperature. The coverage shown in Fig. 4E is produced by
assuming that the domains have the same molecular ordering as the low temperature phase that
fully covers the interface. Fig. 4E also demonstrates that the domain coverage produced by this analysis agrees with values of the thermodynamic coverage derived from interfacial tension measurements as a function of both surfactant concentration and temperature (57).

It could be argued that the reflectivity data is equally well explained by a homogeneously covered interface in which the CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$OH molecules are progressively displaced from their neighbors with increasing temperature. Although this model could be objected to on purely physical grounds, the x-ray reflectivity provides further justification for the presence of domains. The analysis of reflectivity from inhomogeneous phases requires consideration of the x-ray coherence, that is, whether x-rays reflected from different positions on the interface will add coherently or incoherently. The results for the coverage, above the phase transition, differ by more than a factor of two when analyzed using coherent or incoherent reflections (13). Agreement with the thermodynamic coverage occurs only for coherent reflections, suggesting that the domain size is smaller than the ~5 µm coherence length (22). This is consistent with the domain size measured for the slightly longer CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$OH (30). Similar considerations have also been documented for the hydrocarbon surfactants CH$_3$(CH$_2$)$_{m-1}$OH ($m = 24, 30$) that exhibit rounding of the coverage near the transition (Fig. 4C) (22).

The Gibbs phase rule indicates that these interfaces with domains are not coexistence regions of two interfacial phases, but rather are a single inhomogeneous phase. As shown elsewhere, this is a consequence of our observations that the domains are observed over a range of temperatures, that the domains are in equilibrium, and that the role of impurities seems to be negligible (22). The thermodynamic variance $w$ of this system is given by

$$w = 2 + (c - r) - \phi - (\psi - s),$$

where $c=3$ is the number of components (water, hexane, and surfactant), $r = 0$ is the number of chemical reactions, $\phi=2$ is the number of bulk phases, $s = 1$ is
the number of types of interfaces, and $\psi$ is the number of interface phases (81). This expression for the variance is appropriate for systems in which the interface phases are contiguous (so, only the liquid-liquid interface is considered) and the interface is flat.

For one interfacial phase ($\psi = 1$, $v = 3$), the state of the interface is determined by specifying three intensive thermodynamic variables, such as temperature, bulk pressure, and surfactant concentration. If there are two interfacial phases ($\psi = 2$, $v = 2$), then they can co-exist at only one temperature for a given bulk pressure and alkanol concentration. If the presence of domains indicates a coexistence between two phases, then that coexistence can occur at only one temperature. However, domains are observed over a range of temperatures for a given bulk pressure and concentration. An alternative explanation is that the interface is in a single spatially inhomogeneous phase. In this case, the interfacial concentration of surfactants is not isotropic, but varies within the interface due to the presence of domains. As discussed elsewhere, it is unlikely that the presence of impurities or non-equilibrium effects could invalidate this application of the phase rule (22).

Spatially inhomogeneous phases have been shown theoretically to be the result of competing interactions in both 2- and 3-dimensional systems (82, 83). In the case of monolayers of polar molecules, the van der Waals forces act as a short range attractive interaction and the dipoles of the surfactants produce a long range repulsive interaction. Extensive theoretical work in a variety of areas of condensed matter has demonstrated that such competing interactions can stabilize single phases whose order parameter (i.e., the interfacial density in the case of surfactant monolayers) varies spatially throughout the phase. Andelman and coworkers introduced the idea that a sufficiently strong repulsive interaction produces inhomogeneous phases of organic monolayers in the region of the phase diagram that would otherwise be
occupied by the liquid-gas critical point (83). A phase diagram for 3-dimensional systems as a function of chemical potential \( \mu \), the inverse of the amplitude of attractive interactions \( \varepsilon^{-1} \), and the amplitude of the repulsive interactions was recently suggested by Archer and Wilding (84). Figure 6 shows a cut through this phase diagram for fixed amplitude of repulsive interactions.

Application of the theoretical development of inhomogeneous phases to our experimental results is not without difficulties. Our earliest application involved a scaling theory of a critical phase transition developed by Marchenko for magnetic systems (82). Marchenko’s prediction for the interfacial polarization can be rewritten in terms of domain coverage of a surfactant system as

\[
C(T) - C(T_c) = b \, \text{sign}(T_c - T)\left[\ln\left(\frac{T_c}{|T_c - T|}\right)\right]^{-a} \quad \text{for } T \to T_c, \tag{4}
\]

where \( T_c \) is the phase transition temperature, \( C(T_c) \) is the domain coverage at the transition, and \( a \) and \( b \) are positive constants related to scaling parameters in the theory (13, 22). The theory cannot predict the constants \( a \) and \( b \), so we investigated the variation of these parameters obtained by fitting our data (the lines in Figs. 4C, D, and E are fits to Eq.(4)). Although the functional form in Eq.(4) allows the data to be fit, the six systems we have studied did not produce an understanding of the variation of these parameters with system (22). Also, the Marchenko theory describes a critical transition, whereas the x-ray data, particularly for \( \text{CH}_3(\text{CH}_2)_{19}\text{OH} \) and \( \text{CH}_3(\text{CH}_2)_{21}\text{OH} \), indicate that the transition is first order (Fig. 4C).

Further insight may be provided by comparison of our data with the phase diagram in Fig. 6. Although Fig. 6 was suggested for 3-dimensional systems, we use it as a guide to the behavior of a monolayer. The surfactant chemical potential of the dilute oil solution is

\[
\mu = \mu^\circ + RT \ln c, \quad \text{where } c \text{ is the bulk concentration. Therefore, increasing the temperature is}
\]
equivalent to lowering the chemical potential. As discussed, the coverage curve for FC12
(CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$OH) shown in Fig. 4E indicates a transition from a condensed low-temperature
monolayer phase through a region of an inhomogeneous phase that covers a small range in
temperature (~2°C) to a region of a gas phase. This may be equivalent to path B indicated in Fig.
6. The slightly shorter surfactant FC10 (CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$OH, see Fig. 4E) undergoes a transition
from a condensed monolayer phase at low temperatures to an inhomogeneous phase that persists
over tens of degrees Celsius. Since FC10 is shorter than FC12, but otherwise similar in
composition, the attractive van der Waals forces will be smaller and the appropriate path through
the phase diagram should be at larger $\varepsilon^{-1}$. These results are consistent with path C indicated in
Fig. 6. Although these results are suggestive, a difficulty persists. The low temperature phases
measured for FC10 and FC12 are solid phases, not liquid as discussed by the theory. Whether
this theory will apply to these pseudo-2-dimensional solid phases that may not exhibit long-range
positional order is unclear. Also unclear is the exact nature of the spatial and orientational
correlations in these systems.

The application of the theory in Fig. 6 to the case of CH$_3$(CH$_2$)$_{m-1}$OH surfactants, which
exhibit a liquid monolayer phase, is problematic. As illustrated in Fig. 4C, C20 and C22
(CH$_3$(CH$_2$)$_{19}$OH and CH$_3$(CH$_2$)$_{21}$OH) undergo a first order phase transition from a liquid to gas
monolayer, similar to path A in Fig. 6. Since we expect the longer alkanols C24 and C30
(CH$_3$(CH$_2$)$_{23}$OH and CH$_3$(CH$_2$)$_{29}$OH) to have greater van der Waals attraction the path through
the phase diagram should be at smaller $\varepsilon^{-1}$, that is, a path to the left of path A. This would
indicate that longer alkanols should also just exhibit a simple liquid-gas transition. However, the
temperature variation of the coverage for C24 and C30 (Fig. 4D) indicates partial coverage of the
interface for a few degrees both above and below an abrupt change in coverage. It is not clear
whether this sequence of coverage is due to pre-transition effects on either side of the transition or if it represents a monolayer phase sequence of (i) homogeneous liquid to inhomogeneous phase I, (ii) inhomogeneous phase I to inhomogeneous phase II, and (iii) inhomogeneous phase II to homogeneous gas. If interpreted as three transitions, then the coverage changes continuously at transitions (i) and (iii), but abruptly at (ii). Of equal importance, the variation of interfacial tension with temperature exhibits one kink, which indicates a first order phase transition (say, transition (ii)), though smaller changes in the slope within a few degrees of this transition may indicate the presence of transitions (i) and (iii). Transitions between inhomogeneous phases are predicted to occur in the region labeled “inhomogeneous phases” in Fig. 6. It is possible that accounting for the conformational degrees of freedom of these molecules will allow for agreement between theory and experiment, however, the phase sequence of the hydrocarbon alkanols is still an open issue.

6. SOLVENT EFFECTS ON ORDERING AND MULTI-LAYERING TRANSITIONS

Two important features of surfactant ordering at the water-alkane interface depend upon the relative chain lengths of the alkane solvent and the surfactant (26). First, there is a strong dependence of the structure of the adsorbed layer on the length of the alkane used for the solvent. Second, the nature of the adsorption, or vaporization, transition, changes dramatically when the alkanol chain is only six to eight carbons longer than the solvent alkane chain.

To characterize these features, interfacial tension data were used to calculate $\Delta S^\sigma_a$, which is the change in interfacial excess entropy per unit area at the phase transition (i.e., the transition indicated by the kink in curves similar to those shown in Fig. 4A). Figure 7 illustrates $\Delta S^\sigma_a$ vs. $r$, where $r = m/m_o$ is the ratio of the alkanol surfactant carbon number $m$ to the alkane solvent.
carbon number \(m_0\), and \(\Delta S_\sigma^a\) was determined from tension measurements of a water interface with either a hexane solution or a hexadecane solution of hydrocarbon alkanols (26). For a given solvent, \(\Delta S_\sigma^a\) approaches zero as the chain length of the surfactant is reduced to within approximately six carbons of the solvent chain length. Consistent with this, for a given alkanol chain length the value of \(\Delta S_\sigma^a\) is smaller at the water-hexadecane than at the water-hexane interface.

The difference in \(\Delta S_\sigma^a\) for \(\text{CH}_3(\text{CH}_2)_{29}\text{OH}\) at the two interfaces indicates that \(\text{CH}_3(\text{CH}_2)_{29}\text{OH}\) is either more ordered in bulk hexadecane than in bulk hexane or less ordered in the low temperature interfacial phase at the water-hexadecane interface than at the low temperature water-hexane interface, or possibly both. One might expect some small difference in the bulk ordering of \(\text{CH}_3(\text{CH}_2)_{29}\text{OH}\) because bulk hexadecane is closer to its freezing point (18 °C) than hexane (-95 °C). However, x-ray reflectivity measurements reveal a large difference in the ordering of \(\text{CH}_3(\text{CH}_2)_{29}\text{OH}\) monolayers in the low temperature phase (26). At the water-hexane interface, as previously discussed, the portion of the tailgroup near the headgroup is ordered like a rotator alkane phase, but becomes progressively more disordered further from the headgroup until the ordering is liquid-like in the half of the chain that includes the terminal methyl group. At the water-hexadecane interface, reflectivity measurements indicate that the entire tailgroup of \(\text{CH}_3(\text{CH}_2)_{29}\text{OH}\) is disordered.

A more striking effect is produced when \(\Delta S_\sigma^a\) approaches zero. Panel A in Fig. 8 illustrates the difference between the reflectivity for \(\text{CH}_3(\text{CH}_2)_{23}\text{OH}\) at the water-hexane (\(\Delta S_\sigma^a = 2.4 \pm 0.1 \text{ mJ m}^{-2} \text{K}^{-1}\)) and water-hexadecane (\(\Delta S_\sigma^a = 0.26 \pm 0.05 \text{ mJ m}^{-2} \text{K}^{-1}\)) interfaces and Fig. 8B displays the electron density profiles for these interfaces (26). The unusual form of the
reflectivity from CH$_3$(CH$_2$)$_{23}$OH at the water-hexadecane interface cannot be fit with a monolayer. Instead, a bi-molecular layer is formed at the water-hexadecane interface, as illustrated in Fig. 8B. The average electron density of the first layer (0.323 e$^-$/Å$^3$) corresponds to a rotator solid phase, but the electron density of the second layer is much smaller (0.247 e$^-$/Å$^3$) indicating that this layer is very disordered. It is possible that the second layer is only a partial layer, but these measurements cannot determine that. Similarly, the other system that we measured with a very low $\Delta S^\sigma_a$ (= 0.16 ± 0.02 mJ m$^{-2}$ K$^{-1}$), CH$_3$(CH$_2$)$_{11}$OH at the water-hexane interface, exhibits interfacial multilayering of three or four-molecular layers. In this case, the layers are also progressively more disordered starting from the layer closest to water. These results suggest that a layer by layer wetting transition is approached as $\Delta S^\sigma_a$ approaches zero (26).

7. CONCLUSIONS

The recent application of x-ray surface scattering to study the molecular ordering and phase behavior of surfactants at the interface between water and an oil solution of surfactants has led to a greatly revised understanding of these important interfacial structures. X-ray reflectivity provides information on the molecular ordering of the surfactants with sub-nanometer spatial resolution as a function of depth into the interface. Off-specular diffuse scattering probes the in-plane structure of inhomogeneous phases. Together, these techniques have demonstrated that neither studies of Langmuir monolayers of surfactants at the water-vapor interface nor the traditional view of liquid-liquid interfaces espoused by Davies provide a good guide to these interfaces.
The studies presented here have begun to address a number of fundamental issues of surfactant ordering at the water-oil interface. The role of tailgroup flexibility on surfactant ordering was studied by examining fluorocarbon alkanols with rigid rod tails and hydrocarbon alkanols with flexible tails. The result that the fluorocarbon alkanols formed ordered solid phases and the hydrocarbon alkanols formed disordered liquid phases was not surprising, except possibly in light of corresponding experiments at the water-vapor interface in which both types of molecules form solid phases. The importance of complex interactions was revealed by the study of hydrocarbon alkanoic acids, which formed an ordered solid phase at the water-hexane interface. This phase was most likely driven to its ordered state by hydrogen bonding between the acid headgroups whose attractive interaction overcame the disordered effect of the long flexible tailgroups.

Variation of the oil solvent can also affect surfactant ordering, as demonstrated by many studies of interfacial tension (e.g., see (37, 85)). Evidence from computer simulations, theoretical modeling, and interfacial tension measurements indicate that steric matching of the solvent chain length with some aspect of the surfactant architecture can alter the interfacial ordering (86-88). Here, we have demonstrated that increasing the length of the alkane solvent molecules to be closer to, but not matching, the length of the alkanol surfactants leads to a markedly different ordering of the interfacial molecules. As a critical chain length difference of approximately 6 carbons is approached, the interfacial monolayer is converted to a multilayer.

In addition to this observation of surfactant multilayers at the water-oil interface, a number of other observations indicate the importance of multilayer or thicker structures at the water-oil interface. For example, multilayering of lipids at the water-alkane interface is known to produce macroscopically thick layers and vesicle budding (89) (see Ref. (90) for a review and
references on the formation of thick films of amphiphiles at liquid-liquid interfaces). A 60 Å thick multilayer of hexadecylphosphorylcholine at the water-hexadecane interface has been measured recently by neutron reflectivity (91). And, macroscopically thick layers are formed at the interface between crude oil and water, the so-called rag layer (92).

Surfactants at water-oil interfaces demonstrate a rich phase structure consisting of homogeneous and inhomogeneous phases made up of liquid, solid, and gas monolayer regions. X-ray studies have probed these transitions as a function of temperature, which allows for variation of the surfactant chemical potential. A satisfactory correspondence between these experimental results and theory does not exist. It might be expected that such spatially inhomogeneous phases could also exist at the internal surfactant interfaces in water-in-oil or oil-in-water emulsions, as well as at other internal interfaces, but the authors are not aware of such observations.

Although these x-ray measurements carried out during the past decade have revealed new features of surfactant ordering at the water-oil interface, much remains to be understood. This includes understanding the complex interactions that determine the molecular ordering and phase behavior of the interface, as well as extending these studies to other types of surfactants, such as ionic surfactants and surfactants of a variety of architectures that raise interesting scientific questions and are important for many industrial applications.

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9. FIGURE CAPTIONS

Figure 1. X-ray scattering geometry from the interface between water and an oil solution of surfactants. The x-rays pass through the upper hexane solution, then reflect off the surfactant monolayer at the interface. X-ray reflectivity is measured with $\alpha = \beta$ (equal incident and reflection angles). The wave vector transfer for reflectivity, $Q_z = (4\pi/\lambda) \sin \alpha$, is normal to the interface, indicating that reflectivity probes structure normal to the interface. Off-specular diffuse scattering is measured by fixing $\alpha$ and scanning $\beta$, leading to a non-zero in-plane component of the wave vector transfer and a sensitivity to in-plane structure.

Figure 2. (A) X-ray reflectivity (normalized to the Fresnel reflectivity) as a function of the wave vector transfer normal to the interface for $n$-alkanol monolayers at the water-hexane interface. At the chosen temperatures the monolayers are in a condensed (liquid) monolayer phase ("Cm" refers to $\text{CH}_3(\text{CH}_2)_{m-1}\text{OH}$); C20 - 19.4°C; C22 - 21.6°C; C24 - 21.93°C; C30 - 24.1°C (black) & 24.5°C (blue) (see Fig. 4 for alkanol concentrations in hexane). Curves have been offset for clarity. Lines are fits described in the text. Two slab models are used for C20 and C22; three slab models are used for C24 and C30. (B) Electron density profiles for alkanol monolayers at the water-hexane interface determined from the data shown in panel (A) (the profile for C30 at 24.5°C is shown). Profiles for the three shorter alkanols have been offset for clarity. The alkyl chains in the monolayer at the water-hexane interface are progressively disordered from a relatively ordered region near the water to a disordered liquid-like region adjacent to bulk hexane. Hexane is mixed with the monolayer alkyl chain and water is mixed with the headgroup region. In the cartoon the long molecules represent the $\text{CH}_3(\text{CH}_2)_{29}\text{OH}$. 


surfactants and the short molecules represent hexane (for illustrative purposes only). Adapted with permission (22).

Figure 3  (A) Comparison of reflectivity data for triacontanol \((\text{CH}_3(\text{CH}_2)_{29}\text{OH}), \text{denoted C}_{30}\text{OH in figure})\) and triacontanoic acid \((\text{CH}_3(\text{CH}_2)_{29}\text{OOH}, \text{denoted C}_{30}\text{OOH in figure})\) monolayers at the water-hexane interface. Chains are disordered for triacontanol monolayers, but ordered for triacontanoic acid monolayers. Reprinted with permission (93).

(B) Molecular dynamics simulation of a triacontanoic acid monolayer at the water-hexane interface. Color scheme: H – white, C – blue, O – red, except that head groups of triacontanoic acid in the middle panel are yellow. Middle panel illustrates the ordered all-trans alkyl tails (this side view of the interface shows, from bottom to top, water/triacontanoic acid/hexane). The right panel, with hexane, water molecules, and most of the surfactant tail removed, illustrates nearly parallel rows of hydrogen bonds between adjacent –COOH head groups (bottom view of interface). The simulation cell size was 54.3 Å x 57.2 Å x 92.0 Å (normal to the interface) and contained 2720 water molecules, 475 hexane molecules, and 136 triacontanoic acid molecules. Reprinted with permission (14).

Figure 4  (A) Interfacial tension as a function of temperature for hydrocarbon alkanols at the water-hexane interface. “Cm” refers to \(\text{CH}_3(\text{CH}_2)_{m-1}\text{OH}\). For comparison, the pure water-hexane interface is shown by the black squares. C20 – 15 mmol/kg (black dots); C22 – 7 mmol/kg (green); C24 – 3 mmol/kg (red, displaced down by 5 mN/m for visual clarity); C30 – 0.7 mmol/kg (blue). (B) Interfacial tension as a function of temperature for fluorocarbon alkanols at the water-hexane interface, “FCm” refers to \(\text{CF}_3(\text{CF}_2)_{m-1}(\text{CH}_2)_{2}\text{OH}\). Black squares represent the pure water-hexane interface. Lines are a guide to the eye. FC10 – 5.0 mmol/kg (blue); FC12 – 2.0 mmol/kg (red). (C) – (E) Domain coverage (fraction of the interface covered
by surfactant domains) as a function of temperature determined from x-ray reflectivity measurements. Labeling similar to panels (A) – (B). Lines are a theoretical fit (13, 22, 82). Open squares in panel E represent the thermodynamic coverage determined from interfacial tension measurements (57).

Figure 5 (A) Off-specular diffuse scattering (or GISAXS) from the interface between water and a 2 mmol/kg solution of CF$_3$(CF$_2$)$_9$(CH$_2$)$_2$OH in hexane measured upon cooling through the phase transition. Curves displaced for clarity. Similar data (not shown) is measured upon heating through the transition. The transition temperature is between the two highest temperatures, i.e. 39.58 °C and 40.19 °C. Above the transition, the interface is nearly free of surfactants. Surfactant domains are present below the transition. The large peaks at $\beta = 0.37^\circ$ at all temperatures are the specular reflectivity. The small peaks at $\beta = 0.045^\circ$ are due to a surface field enhancement affect that indicates the presence of interfacial inhomogeneities. Additional scattering and peaks above the background observed at 40.19 °C represent small angle scattering from interfacial domains. (B) Mean radius of domains, assumed to be circular, and (C) mean separation between domain centers determined from off-specular diffuse scattering data taken while heating (red) and cooling (black) through the transition. The vertical lines in panels (B) and (C) illustrate the polydispersity in radius and separation. Adapted with permission (38).

Figure 6  Phase diagram suggested by Archer and Wilding for 3-dimensional inhomogeneous phases (84). Paths A – D through first order transitions in this phase diagram are discussed in the text. Adapted with permission (84).

Figure 7  Change in interfacial excess entropy per unit area across the transition $\Delta S^\sigma_a$ versus $r$ for solutions in hexane (blue) and in hexadecane (black), where $r = m/m_o$ is the
ratio of the alkanol carbon number $m$ to the alkane solvent carbon number $m_o$. Symbols are labeled with the carbon number of the alkanol surfactant. Adapted with permission (26).

Figure 8  Studies of the interface between water and a hexane or hexadecane solution of CH$_3$(CH$_2$)$_{23}$OH at temperatures well below the phase transition. (A) X-ray reflectivity (normalized to the Fresnel reflectivity) as a function of the wave vector transfer from CH$_3$(CH$_2$)$_{23}$OH in the low temperature phase at the water-hexane ($T = 21.9$ °C, blue) and water-hexadecane ($T = 50.8$ °C, black) interfaces. Solid blue line is a three slab model of a monolayer; solid black line is a two slab model of a bilayer.  B) Electron density profiles; $z << 0$ is bulk hexane (blue) or hexadecane (black) in the low temperature region from the fits in panel (A). CH$_3$(CH$_2$)$_{23}$OH forms a monolayer at the water-hexane interface and a bilayer at the water-hexadecane interface. Reprinted with permission (26).
10. FIGURES

Figure 1
Figure 2
Figure 3
Figure 4

Interfacial Tension $\gamma$ ($10^{-3}$ N/m)

Temperature (°C)

Coverage

Figure 4
Figure 5

A

Intensity (arb. units)

\(10^{-4}\)

\(10^{-2}\)

\(10^0\)

\(10^2\)

\(10^4\)

\(\beta\) (degrees)

30.01 °C

37.02 °C

38.03 °C

38.85 °C

39.27 °C

39.58 °C

40.19 °C

B

Mean Radius (µm)

37

38

39

Temperature (°C)

Heating

Cooling

C

Mean Separation (µm)
Figure 6
Figure 7

\[ \Delta S^\sigma (\text{mJ/m}^2\text{K}) \]

\[ r = \text{alkanol C#/alkane C#} \]

- hexadecane
- hexane
- C30
- C24
- C22
- C20
- C18
- C12
Figure 8