

Freezing transition of Langmuir-Gibbs alkane films on water

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Abstract

We show that adding CTAB (CTAB, hexadecyltrimethylammonium bromide) in sub-millimolar bulk concentrations to water reduces its surface tension (ST) to a level where spontaneous surface spreading of a monolayer of medium-sized alkane (C_nH_{2n+2} , $12 \leq n \leq 17$) occurs. ST and X-ray reflectivity (XR) measurements are used to show that the quasi two-dimensional (2D) liquid monolayer can be driven through a reversible surface freezing phase transition upon cooling. Grazing incidence diffraction (GID) shows that the frozen monolayer is crystalline, hexagonally packed, with surface-normal molecules, and a crystalline coherence length of at least a few hundred Å, very similar to the structure of surface-frozen (SF) monolayers at the surface of similar-length alkane melts. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Linear-chain hydrocarbons (alkanes, $H(CH_2)_nH$, denoted C_n) are important building blocks of many organic molecules [1,2]. In spite of their simple structure, and simple van der Waals (vdW) interactions, their bulk phase diagram is rich. Moreover, their melts exhibit a remarkable effect, surface freezing, whereby an ordered solid monolayer forms at the surface of the melt a few degrees *above* their bulk melting temperature. Similar effects have been found also in alkanes on solid substrates [3]. Recent liquid–liquid interface studies show that while no interfacial freezing occurs at the alkane–water interface [4], adding C_{16} TAB to the water at millimolar bulk concentrations induces freezing at the interface [5,6]. We show here that spreading of monolayers of relatively long alkanes becomes possible at the free surface of the same C_{16} TAB–water solution. Moreover, upon cooling, a freezing effect akin to the SF in alkane melts is observed.

Langmuir monolayers on water, consisting of insoluble amphiphilic molecules, exhibit rich quasi-2D array of ordered phases [7]. By contrast, surface-adsorbed films of almost all *soluble* surfactants (Gibbs monolayers), do not exhibit ordered

phases [8]. Alkanes with $n > 7$ do not spread on water. However, recent studies [8,9] demonstrate that pseudo-partial wetting of the surface of an aqueous subphase by a film of longer alkanes can be induced on subphases containing ionic surfactants at millimolar concentrations. The resultant liquid alkane surface layer is stabilized by an interplay between the dispersion

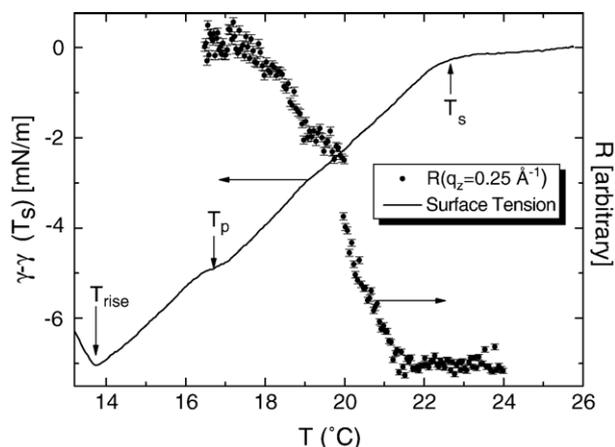


Fig. 1. Temperature dependence of the ST and the XR at a fixed $q_z = 0.25 \text{ \AA}^{-1}$. The change in both the ST slope and the XR intensity at $T = T_s$ indicate the onset of the LG film crystallization. Possible interpretations of T_p and T_{rise} are discussed in the text.

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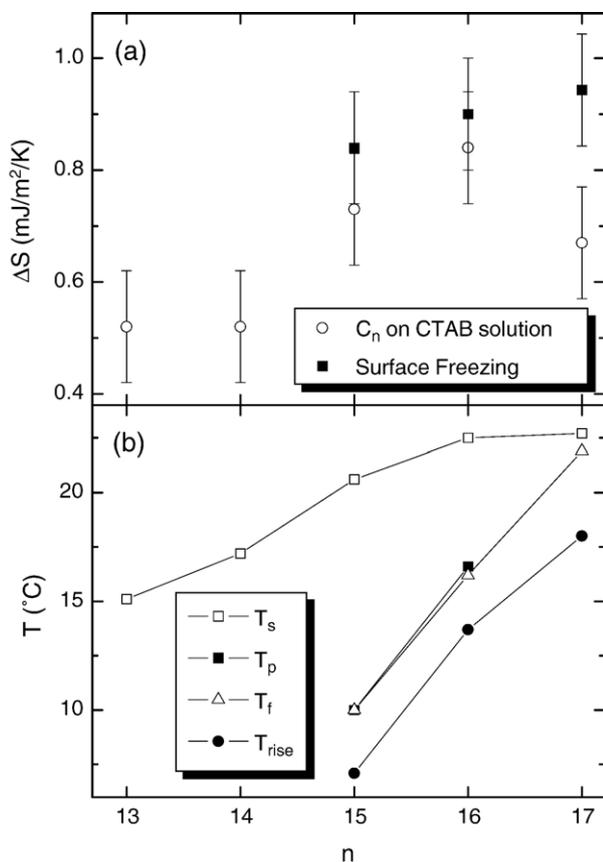


Fig. 2. (a) Measured entropy loss upon SF in alkane melts and in LG films on an aqueous CTAB solution. (b) The phase diagram of C_n LG films on 0.6 mM aqueous CTAB solution. T_s , T_p and T_{rise} are defined in the text. T_f are the bulk alkane freezing temperatures, shown here to coincide with T_p .

(Casimir) forces and the interfacial tensions [9,10,11]. The water soluble C_{16} TAB surfactant is of particular interest. As it Gibbs-adsorbs from the bulk onto the surface, its C_{16} alkyl tail sticks out of the solution's surface, and can mix well into the alkane layer. Thus, the mixed alkane-CTAB layer can be regarded as a Langmuir–Gibbs (LG) film. These films were shown recently to undergo a freezing transition [8,9]. However, the sum-frequency generation and ellipsometry measurements used were unable to resolve the film's structure, detect possible in-plane order, and determine its lateral range. We employed XR, GID [12], and ST [13] measurements to show that the LG alkane film can be temperature-driven through a freezing transition, below which a quasi-2D long-range crystalline in-plane order is established.

2. Experimental

The alkanes and the CTAB surfactant, >99% pure, were purchased from Sigma–Aldrich–Fluka. Alkanes were passed twice through an active alumina column. CTAB was recrystallized twice from an acetone–methanol solution. Millipore water (18.2 M Ω cm) was used throughout. An 0.6 mM aqueous CTAB solution was used as the subphase in the measurements reported here. The alkane was dissolved in chloroform (Aldrich, 99+%) at a 1:10 v/v ratio, and 1–4 μ L were used for spreading of each film, well in excess of the amount required for a monolayer. The excess alkane coalesced into tiny droplets, which, however, covered only a negligible surface area. No variations were observed in the measured results after the first 10–15 min, nor upon changing the alkane concentration of the spreading solution or the exact amount deposited. The Wilhelmy method [13] was employed to measure the ST, $\gamma(T)$, using a platinum plate attached to an electronic balance.

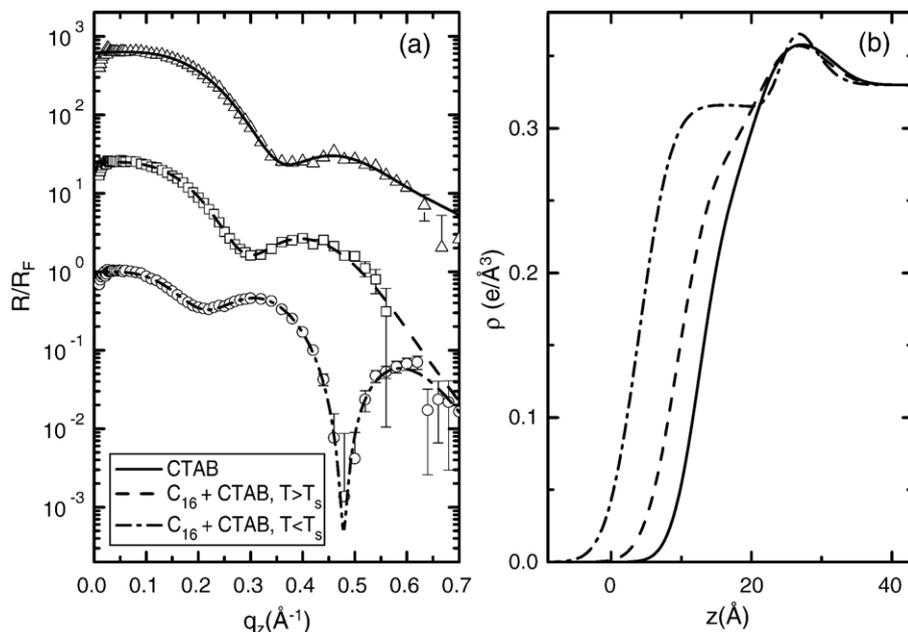


Fig. 3. (a) Measured (symbols) Fresnel-normalized XR curves of the bare surface of a 0.6 mM CTAB solution, and of the same surface covered by a C_{16} LG film in its liquid and frozen phases. The reflectivity curves are shifted vertically from each other for clarity. Lines are model fits, with the corresponding density profiles shown in (b), using the same line-coding.

The absolute accuracy in the temperature and ST values were ± 0.5 °C and ± 1 mN/m, respectively, with the precision being at least one order of magnitude better. The X-ray measurements were carried out at beamline X22B, National Synchrotron Light Source, Brookhaven National Laboratory, using X-rays with a wavelength $\lambda = 1.52$ Å. The sample was an LG film at the surface of a 50 mm diameter, 1 mm deep, CTAB solution puddle, residing on a thick glass substrate, enclosed in a temperature-controlled (< 0.01 C) cell. Three types of measurements were carried out: XR, which probes the surface-normal density profile and surface roughness, GID, which probes the in-plane order, and BR, the surface-normal intensity distribution at the position of a GID peak, which probes the molecular length and tilt. For further experimental details see Refs. [1,14].

3. Thermodynamics

The static ST, γ , is the free energy excess of the surface over the bulk. Upon cooling, as the surface freezes at $T = T_s$, a surface entropy loss results, causing a slope change in $\gamma(T)$ [2]: $\Delta S = d\gamma(T < T_s)/dT - d\gamma(T > T_s)/dT$. This is indeed observed in the measured $\gamma(T)$ in Fig. 1 (C_{16} over a 0.6 mM CTAB solution). The slope change at T_s is the onset of freezing of the LG film at the surface. The features observed at the temperatures denoted as T_p and T_{rise} are discussed below. The linearity of $\gamma(T)$ above and below T_s down to T_p indicates that no further transitions occur in the film over this T -range. Qualitatively similar $\gamma(T)$ curves were obtained for other alkanes in the range $13 \leq n \leq 17$.

Fig. 2(a) shows ΔS , as calculated from the slope change in $\gamma(T)$, versus the chain length. For $n > 15$, these values agree reasonably well with those measured for SF in alkane melts [1,2]. The large error bars reflect possible incomplete coverage of the surface by the LG monolayer. The excess alkane droplets, which cover part of the surface, may cause the systematic, though slight, decrease of the LG films' ΔS relative to those of the melts. So would a larger concentration of defects in the monolayer's structure. The reasonable agreement, in spite of the differences between the systems, implies that the thermodynamics of both are similar. As shown elsewhere [1,2], for alkyl chain molecules ΔS is mostly determined by the molecules' internal degrees of freedom: $\Delta S \approx k_B (n - 3) \ln 3$, where k_B is the Boltzmann constant. The loss of entropy for many other phase transitions (e.g. orientational transitions of alkanes or CTAB molecules) involves less degrees of freedom and can be readily ruled out on the basis of the high ΔS values observed. T_s , T_p and T_{rise} increase almost linearly with the chain length n of the alkane, as shown in Fig. 2(b). The values of T_s are in good agreement with those determined by ellipsometry [8]. The published [15] T_f (shifted by a constant 0.3 °C, due to the different temperature sensors) coincide with the present T_p , suggesting T_p to mark the freezing of the excess alkane droplets. It is possible that the shapes and the volumes of these droplets change upon freezing, so that additional cooling is required to bring the monolayer's pressure to the same value as that before the droplets froze. This could explain the short and slightly sloped plateau observed in $\gamma(T)$ at T_p . The γ increase at T_{rise} is

more of a mystery. One possible explanation is that it is caused by a dewetting transition. Since the entropy of the 3D solid is slightly lower than that of the 2D monolayer [1,2], at a low enough temperature, the free energy gain due to wetting of the CTAB solution by the alkane may be overcome by gain upon formation of 3D crystallites. The monolayer molecules adjacent to the 3D islands would then coalesce into the islands, barring part of the CTAB solution's surface, and thus increasing the average ST of the system. The balance between the increase in the surface energy by the increase in the monolayer-free surface and the decrease in the total free energy due to the 3D coalescence will determine at each temperature the area of the exposed surface, and thus $\gamma(T)$. This, in turn, will result in an increase in $\gamma(T)$ with decreasing T , as observed, in Fig. 1(a).

The interpretations of T_p and T_{rise} given above, while plausible and appealing, are not without problems. For example, the entropy loss occurring upon freezing of the 3D droplets at T_p should have caused a slope change in $\gamma(T < T_p)$. This is not observed. Moreover, one could argue that surface dewetting should occur at surface pressures [16] close to zero. By contrast, T_{rise} is observed to occur at the lowest $\gamma(T)$, i.e. at the largest surface pressure observed. While counter arguments to these

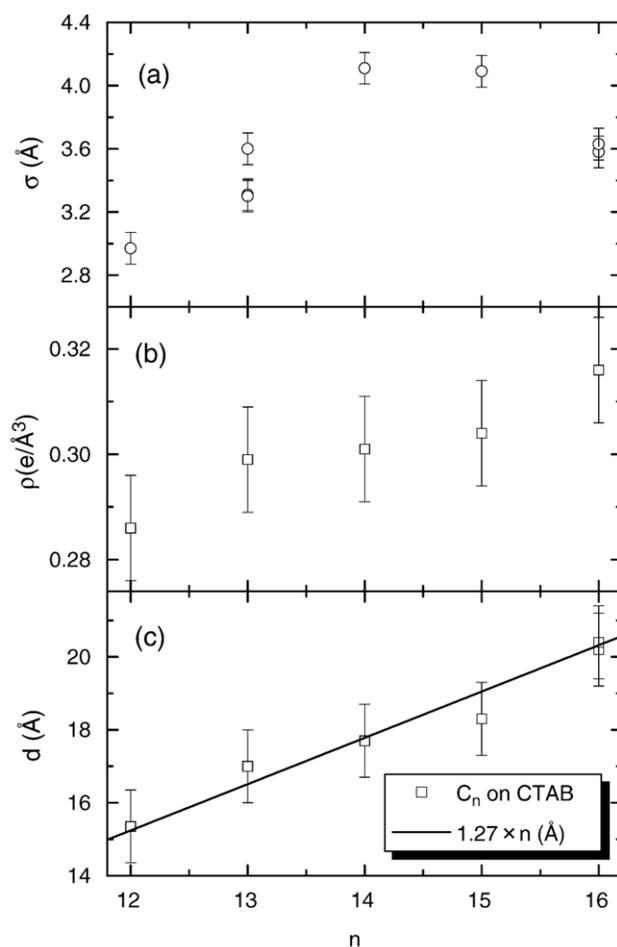


Fig. 4. The parameter values obtained from the XR fits at $T < T_s$. (a) Layer–vapour interface roughness, (b) electron density of the hydrocarbon top box, and (c) thickness of the hydrocarbon top box (squares) and the calculated length of the fully extended C_n molecule (line). Note the good agreement.

objections could be offered, the foregoing discussion demonstrates that a complete elucidation of the nature of T_p and T_{rise} would require further work.

Fig. 3(a) shows the measured XR curves normalized to that of an ideally flat and smooth surface (Fresnel reflectivity, R_F) [1,12]. These were measured as function of the surface-normal wavevector transfer, $q_z = (4\pi/\lambda)\sin\alpha$, where α is the X-rays' grazing angle of incidence onto the surface. The XR modulation period, Δq_z , is inversely related to the monolayer's thickness: $d = 2\pi/\Delta q_z$. Thus, the Gibbs-adsorbed surface layer of the bare CTAB solution is the thinnest, and the frozen LG film is the thickest, among the three films. When cooling an LG film, the decrease in Δq_z at T_s results in a significant increase in the XR signal at $q_z = 0.25 \text{ \AA}^{-1}$. This increase, marking the onset of SF, is clearly observed in Fig. 1, where an XR temperature scan at a fixed $q_z = 0.25 \text{ \AA}^{-1}$ is shown. The transition is possibly smeared out by the high scan rate of the temperature, $0.2 \text{ }^\circ\text{C}/\text{min}$.

The XR curves were analyzed quantitatively using the Master formula [12]:

$$R(q_z)/R_F(q_z) = |(\rho_b)^{-1} \int [d\rho(z)/dz] \exp(-iq_z z) dz|^2, \quad (1)$$

where ρ_b is the bulk electron density, and $\rho(z)$ is the electron density at a depth z below the surface, averaged over a surface-parallel plane. A two-box model was employed for $\rho(z)$, consisting of two constant-density slabs above a third, infinitely-thick, slab, representing the bulk, with all the interfaces roughened by Gaussian functions. The upper and lower boxes represent the layers of the cetyl alkyl tails and the trimethylammonium (TA) bromide headgroups, respectively. The parameter values of this model were obtained by fitting its R/R_F , calculated from Eq. (1), to the measured values [1]. The fits, and the corresponding $\rho(z)$, are shown in Fig. 3. The fits are

very good. The Gibbs film of the bare CTAB solution (solid line) exhibits a broad peak due to the headgroups at $z \approx 20 \text{ \AA}$. This corresponds to the double layer of the TA^+ and Br^- ions. Above that layer resides the cetyl alkyl tails' layer, for which the fit yields a thickness of $d = 8 \text{ \AA}$. Since the fully extended length of the cetyl tail is over 20 \AA , we conclude that the tails are strongly disordered. As discussed in Section 1, this is indeed expected for Gibbs films, which are usually disordered and liquid-like. The cross-sectional area of the TA moiety is significantly higher than that of the cetyl tail [17], preventing close approach, and dense packing, of the tails. Upon alkane deposition on the surface, a pseudo-partial wetting occurs, and a liquid LG film is formed. The corresponding profile (shown in dashed line) has the same headgroup structure as the bare CTAB's Gibbs film, while the upper alkyl/alkane slab is now thicker, and its density higher. The headgroup layer's "bump" remains unchanged upon surface wetting by the alkane film, indicating that no significant changes occur in the TA^+ ion packing and/or in the Br^- counterion surface concentration and z -distribution. The thickness of the alkyl/alkane layer indicates that it is liquid. Its higher density is due to the alkane molecules intercalating between the wider-spaced alkyl chains of the CTA^+ ions.

Finally, the fitted profile at $T < T_s$ clearly exhibits an alkyl layer of thickness of 20.4 \AA which corresponds very well to the calculated length of the C_{16} molecule. This, and the high $\rho(z) = 0.318 \text{ e/\AA}^3$ obtained, indicate a layer of close-packed, extended molecules [1]. The GID results discussed below confirm that this layer is indeed crystalline. Interestingly, the "bump" in Fig. 3 (dash-dot line), corresponding to the headgroups' slab, is now sharper than that above T_s . This implies the occurrence of structural changes within the ionic double layer formed by the headgroups. While this effect

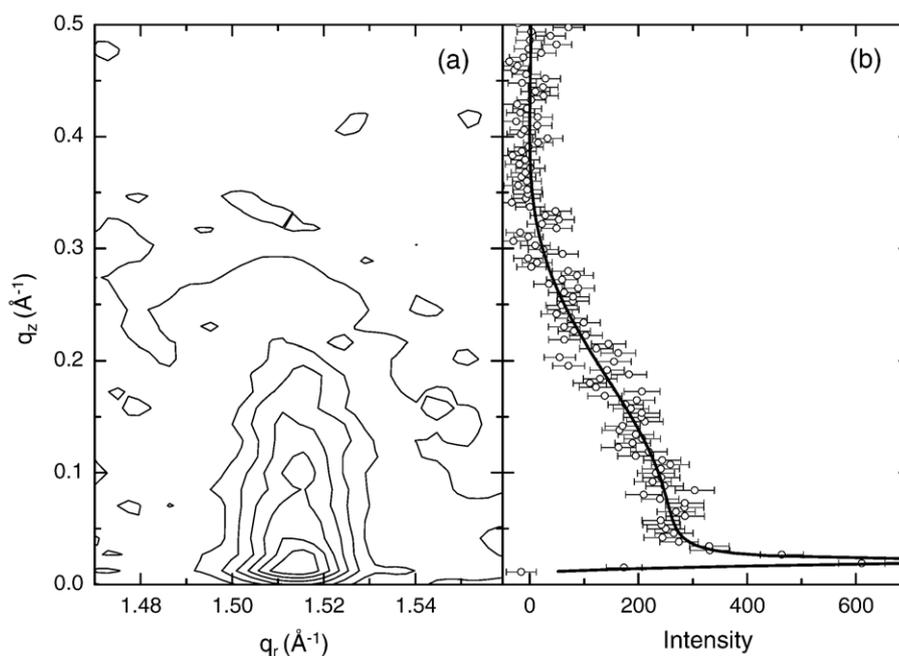


Fig. 5. (a) A contour map of the single GID peak, obtained for a surface-frozen C_{16} LG monolayer on the surface of a 0.6 mM CTAB solution. $q_r = (4\pi/\lambda)\sin\theta$ is the surface-parallel wavevector transfer, and θ is half the diffraction angle. The BR scan is shown in (b), fitted (solid line) by the model used in earlier studies [1].

appears to be real, further work is required to elucidate its nature, and the details of the structural changes involved.

All alkanes studied here, $12 \leq n \leq 17$, exhibit qualitatively similar features. The fit parameter values for $T < T_s$ are plotted in Fig. 4(a)–(c). While for $T > T_s$ did not show any systematic variation with n , the frozen monolayer follows closely the length variation of the extended molecule, as shown in Fig. 4(a)–(c). The mismatch between the lengths of the fully extended alkane and the cetyl tail of the surfactant results in a reduced density of the hydrocarbon slab for short alkanes (see Fig. 4(b)). The highest density is obtained for C_{16} , and equals the density of close-packed crystalline bulk alkanes [1]. The shortest alkane measured (C_{12}) exhibits an electron density of $\sim 0.285 \text{ e}/\text{\AA}^3$, still higher than that of the molten alkane, $\sim 0.26 \text{ e}/\text{\AA}^3$.

Fig. 5(a) shows the contour map of the single GID peak found for the SF phase of the C_{16} monolayer. Similar GIDs were found for the other C_n studied here. The BR, obtained by integrating the intensity over the surface-parallel direction, is shown in Fig. 5(b). It exhibits a Vineyard peak at $q_z = q_c$, which is the fingerprint of diffraction from a quasi-2D structure [18]. The fit (solid line) uses the model employed earlier for the SF monolayers of alkane melts [1]. The molecular lengths obtained were consistent with the hydrocarbon layer thicknesses obtained from the XR curves discussed above. The GID and BR patterns reveal a hexagonal, untilted molecular packing. The peak position, $q_r = 1.516 \text{ \AA}^{-1}$ yields a lattice plane spacing of 4.144 \AA , a unit cell of $4.785 \times 4.785 \sqrt{3} \text{ \AA}^2$, and, with two molecules per cell, an area of $19.83 \text{ \AA}^2/\text{molecule}$. These results agree very well with the structure observed for the untilted surface-frozen monolayers of alkane melts with molecular lengths of $16 \leq n \leq 30$, which are 2D rotator phases [1]. The q_r width of the GID peak is resolution limited, indicating a crystalline coherence length of at least a few hundreds of \AA . The length (20.3 \AA in Fig. 4(c)), molecular area (19.83 \AA^2), and number of electrons (130) of C_{16} yield an electron density of $\rho = 0.322 \text{ e}/\text{\AA}^3$ for the ordered monolayer, which coincides, within the error bar, with the value shown in Fig. 4(b), obtained from the XR fit. This indicates a close to complete coverage of the surface by the frozen LG film. Finally, the absence of any additional peaks in the GID pattern, and/or modulations in the BR curve, imply that the CTA^+ cations or the BR^- anions do not form an ordered structure, either commensurate or incommensurate with that of the alkane LG film.

4. Conclusion

We have shown here, using ST and X-ray scattering methods, that sub-millimolar bulk concentration of a surfactant, CTAB, in water can induce spreading of a long-chain alkane monolayer on the surface of the aqueous surfactant solution. The monolayer exhibits a freezing transition, resulting in a

hexagonally packed crystalline monolayer of the same structure as that found for surface-frozen layers of alkane melts of similar lengths. However, while no SF was observed in alkane melts of $n < 15$, here we find freezing for $n = 13$ and 14 as well. Ellipsometry has revealed similar transitions for $n = 11$ and 12 [8] at temperatures currently inaccessible with our X-ray sample cell. Further studies, using alkanes of other chain lengths and different surfactants, may uncover new quasi-2D phases, determine T -, n -, and CTAB-concentration dependent trends, and help elucidating the physics and chemistry underlying the formation and phase behaviour of these films. Such studies are currently under way in our laboratory.

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