Surfactant-Induced Phases in Water-Supported Alkane Monolayers: II. Structure

Shai Yefet, †§ Eli Sloutskin, †§ Lilach Tamam, †∥ Zvi Sapir, †⊥ Moshe Deutsch, *† and Benjamin M. Ocko*‡

†Physics Department and Institute of Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel
‡Condensed Matter Physics & Materials Sciences Department, Brookhaven National Laboratory, Upton, New York 11973, United States

ABSTRACT: The structure of the Langmuir–Gibbs (LG) films of normal alkanes $C_n$ of length $n = 12−21$ formed at the surface of aqueous solutions of $C_m$TAB surfactants, $m = 14, 16$, and 18, was studied by surface-specific synchrotron X-ray methods. At high temperatures, a laterally disordered monolayer of mixed alkane molecules and surface-adsorbed surfactant tails is found, having thicknesses well below those of the alkanes' and surfactant tails’ extended length. The mixed monolayer undergoes a freezing transition at a temperature $T_s(n,m)$, which forms, for $n \leq m + 1$, a crystalline monolayer of mixed alkane molecules and surfactant tails. For $n \geq m + 2$, a bilayer forms, consisting of an upper pure-alkane, crystalline monolayer and a lower liquidlike monolayer. The crystalline monolayer in both cases consists of hexagonally packed, extended, normal-aligned chains. The hexagonal lattice constant is found to decrease with increasing $n$. The film's structure is discussed in conjunction with their thermodynamic properties presented in an accompanying paper.

INTRODUCTION

When placed on the surface of a dilute surfactant solution, a droplet of alkane wets the surface, forming a monolayer of mixed surfactant tails and alkane molecules, called a Langmuir–Gibbs (LG) film.1–4 This LG film is in equilibrium with the excess alkane molecules residing as macroscopic lenslike droplets on the surface.1,3,4 In a previous paper,5 we explored the phase diagram and thermodynamics of these LG films as a function of the carbon number of the alkane ($n$) and the surfactant’s tail ($m$) for surfactants of the alkyl-trimethylammonium bromide family at a few concentrations. While that study provided a detailed picture of the thermodynamics of these systems and demonstrated the important role played by the interchange energy of the two species in determining the phase diagram, no molecular-resolution structural information was provided by the macroscopic surface tension measurements employed.

We present here a detailed study of the surface-normal and surface-parallel structure of the LG films, both above and below the surface freezing temperature, for the same $n$, $m$, and surfactant concentration ranges over which the thermodynamics of the system was studied. This study confirms the conclusion, drawn in ref 5, that the transition occurring at $T_s$ is a surface freezing (SF) transition from a liquidlike, laterally disordered, monolayer of mixed surfactant tails and alkanes, to an ordered solid phase of closely packed, extended molecules, exhibiting long-range hexagonal lateral order. For alkane lengths, $n$, below the crossover point $n = m + 2$ of the SF line, $T_s(n)$, by the bulk freezing line, $T_b(n)$, the frozen layer is a monolayer of mixed extended alkane molecules and extended surfactant tails. For alkane lengths above the crossover point, the frozen layer is a bilayer, where the upper layer is a crystalline monolayer of pure alkanes, and the lower layer is a disordered, liquidlike layer of surfactant tails. An intermediate structure, where both the lower and upper layers are frozen, was also found.

EXPERIMENTAL SECTION

Materials and Procedures. The further purification of the highest-purity commercially purchased materials, normal-alkanes, $C_nH_{2n+2}$ (denoted hereafter as $C_n$) and alkyltrimethylammonium bromides (denoted as $C_n$TAB), was described in the previous paper.5 Millipore water (18.2 $\Omega$ m) was used throughout. The samples for the X-ray measurements were either 1 mL of surfactant solution spread on a glass slab 3 cm wide by 6 cm long, or a solution-filled shallow KelF (poly(chlorotrifluoroethylene)) trough of 6 cm inner diameter. The sample was placed inside a cell consisting of a cylindrical beryllium shell of 8 cm diameter, 5 cm height, and 0.5 mm wall thickness, sealed at the top and the bottom by copper flanges. The thin beryllium shell provided low X-ray absorption, along with a uniform-temperature environment due to the beryllium’s high thermal conductivity. The temperature of the cell was controlled to $\pm 0.01$ °C by a Lakeshore 340 temperature controller, using flat Minco heaters at the top and bottom of the cell, and 100 $\Omega$ (at 25 °C) TSI thermistors as temperature sensors. A few microliters of freshly sonicated solution of alkane in chloroform (see more detail in ref 5) were deposited on the solution’s surface. After a 5 min wait for the chloroform to evaporate, and moving any excess alkane lenses to the substrate edges.

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to avoid their illumination by, and consequent scattering of, the incident X-ray beam, the cell was sealed and ready for the measurements. Identical results were obtained for alkanes vapor-deposited from above using a hot reservoir of alkanes contained in a copper wick.

X-ray Measurements. The X-ray measurements were carried out using the Brookhaven-Harvard liquid surface diffractometer at beamline X22B, National Synchrotron Light Source, Brookhaven National Laboratory. To reduce beam damage, X-ray exposure times were minimized by using an automatic shutter, which was opened only for counting and kept closed during spectrometer movements, wait times, and so forth. Three surface-specific methods were employed, X-ray reflectivity (XR), grazing incidence diffraction (GID), and Bragg rod (BR) measurements, with the scattering geometry shown in Figure 1. Since these methods are by now well documented in the literature, only a short summary will be given here.

X-ray Reflectivity. X-ray reflectivity (XR) is the measured fraction, \( R(q_z) \), of the incident X-ray beam’s intensity reflected from the solution surface as a function of the angle of incidence of the incoming beam, \( \alpha \). \( q_z = (4\pi/\lambda)\sin(\alpha) \) is the surface-normal component of the scattering vector \( q = k_{\text{out}} - k_{\text{in}} \) and \( \lambda = 1.5173 \) Å is the wavelength of the X-rays used. In the scattering geometry plot in Figure 1, XR is measured at \( 2\theta = 0^\circ \) and \( \beta = \alpha \). \( R(q_z) \) provides information on the surface-normal structure of the interface. Specifically, the surface normal electron density profile, \( \rho(z) \), is related to \( R(q_z) \) through the Born approximation of a weak reflection by the Master Formula:

\[
R(q_z) = R_0(q_z) \left| \int (\rho(z)) dz \exp(-i q_z z) dz \right|^2
\]

where \( R_0(q_z) \) 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. \( R_0(q_z) \), the Fresnel reflectivity, is the reflectivity from an ideally flat and abrupt interface. The density profile \( \rho(z) \) is extracted from the measured \( R(q_z) \) by constructing a physically motivated model for \( \rho \) and calculating the corresponding analytic \( R(q_z) \) through eq 1. This is then fitted to the measured XR values to yield the model-defining parameter values.

The level of structural detail extractable with confidence from a measured \( R(q_z) \) strongly depends on the extent of modulations appearing in the measured curves, into which the model fit could “lock”, on the \( q_z \)-range of the curve and on the error bars of the measured points (which increase with \( q_z \)). Thus, in modeling the structure it is sometimes necessary to adopt approximations which allow keeping the number of fit parameters low enough to render their refinement independent and confident. Specifically, it was found necessary to approximate the complex Stern–Hehmoltz–Gouy–Chapman ionic double layer of the surfactants’ headgroups by a single uniform slab, as done in previous ellipsometric studies. Thus, for the monolayer phase (liquid and solid), we use a model consisting of two constant-density slabs to represent the LG film. The upper slab represents the mixed monolayer of alkyl tails and alkanes, and the lower slab, the headgroups. For the bilayer phase, two alkyl slabs are used, in addition to the headgroup layer. A very thin low-density slab separating the two alkyl ones was found to be necessary for obtaining a good fit. The underlying bulk is represented by an additional infinite-thickness layer of a constant 0.333 e/Å² electron density. Finally, this so-called “box model” is convoluted with a single Gaussian of adjustable width to account for the surface roughness generated by the thermally-excited capillary waves, present at all liquid surfaces and interfaces. This choice reduces the number of fit parameters, while still allowing excellent fits to be obtained, as shown below. Test fits with a separate roughness at each interface did not improve the fit quality.

Grazing Incidence Diffraction. Grazing incidence diffraction (GID) measures the surface-parallel structure of the LG films. This is done by scanning the detector out of the reflection plane by an angle \( 2\theta \), thus varying the surface-parallel wavevector transfer, \( q_z \),

\[
q_z = (4\pi/\lambda)\sin(\beta/2)
\]

Here, \( \beta \) is the grazing angle of exit of an X-ray diffracted to the detector. To minimize the scattering from the underlying bulk which could overwhelm the weak signal from the thin LG film, the incidence angle is kept at \( \alpha < \alpha_\text{c} \), where \( \alpha_\text{c} \) is the critical angle for total external reflection. At these \( \alpha \) values, only an evanescent wave penetrates below the surface, its intensity decaying exponentially with depth with a decay length of \( \Lambda = 2/(Q^2 - q_z^2)^{1/2} \), where \( Q = (4\pi/\lambda)\sin(\alpha/2) \). In our GID measurements, done at \( q_z/\Lambda < 0.8-0.9 \) with \( q_z \approx 0.022 \) Å⁻¹, the penetration depth is only \( \Lambda \lesssim 100 \) Å, thus reducing bulk scattering.

The GID measurements are carried out using a Soller-slits-preceded linear position sensitive detector, aligned normal to the surface, and scanned over a 0.1 Å⁻¹ \( \leq q_z \leq 1.8 \) Å⁻¹ range. At a given azimuthal angle \( 2\theta \), the intensity integrated over the length of the detector is the GID signal, while the intensity distribution along the detector provides the Bragg rod at this \( q_z \) position.

Bragg Rod Measurement. The Bragg rod (BR) is the surface-normal (i.e., in Figure 1, the \( \beta \)- or \( q_z \)-) distribution of the intensity diffracted by the LG film at a given \( q_z \) position. For \( q_z \) positions not exhibiting a GID peak, only scattering from the underlying bulk is observed. At a position where the GID pattern exhibits a peak, the shape of the BR provides information on the angle of tilt from the normal and its azimuthal direction, the length of the scattering molecules, and their shape, thus allowing their form factor to be determined.

### RESULTS AND DISCUSSION

**Surface-Normal Structure.** The surface-normal structure has been studied by X-ray reflectivity, and the corresponding laterally averaged surface-normal density profiles, \( \langle \rho(z) \rangle \), were extracted by modeling the XR curves by a box model, as discussed above. The main types of \( \langle \rho(z) \rangle \) observed are shown schematically in Figure 2 and discussed in the following subsections.

**The Bare Surface of the Solution.** The measured, Fresnel-normalized, reflectivity curves (symbols) of the surfaces of the surfactant solutions before deposition of the alkane are shown in Figure 3. For a simple liquid, for example, water, or simple organic liquids, a monotonically decreasing \( R/R_0 \) is observed with increasing \( q_z \). The modulated \( R/R_0 \) observed here, showing a dip separating two higher-intensity regions, is akin to the Kiessig fringes of conventional optics. The modulations indicate, therefore, the presence of a surface layer, denoted hereafter as the “bare” surface layer (shown in Figure 2a), of an electron density differing from that of the underlying bulk, and of a thickness inversely proportional to the dip’s \( q_z \) position. The dip’s position is observed to decrease with...
the surfactant’s length, indicating that the thickness of the surface layer increases with \( m \). The two CTAB curves in Figure 3a, measured for 60\% (□) and 100\% (▽) of the critical micelle concentration (cmc), show that an increase in the surfactant’s bulk concentration also shifts the dip to a lower \( q \) value, indicating a corresponding increase in the alkyl layer thickness. This is a consequence of the change in the surface coverage by the surfactants upon increasing the bulk concentration.\(^{19,20}\)

Following previous studies,\(^4\) we use a two-slab model to obtain the density profiles \( \rho(z) \) from the measured \( R/R_F \), as discussed in the Experimental Section, and shown in Figure 2a above. The water-adjacent slab represents the layer of the headgroups, and the air-adjacent slab represents the layer of alkyl tails. Good agreement is obtained in the fits (lines) with the measured curves (symbols) for all three surfactants in Figure 3a. The corresponding density profiles, shown in Figure 3b, exhibit for the headgroup slab an average thickness of 6.6 ± 0.5 Å, and a slightly increased electron density, ~0.36 e Å\(^{-3}\), as compared to 0.33 e Å\(^{-3}\) for water. The significantly lower density obtained for the alkyl chains’ slab, ~0.27 e Å\(^{-3}\), agrees well with 0.266 e Å\(^{-3}\) calculated from the known 30 Å\(^3\) volume\(^{22}\) and the eight electrons of a CH\(_2\) group.

The alkyl slab thickness values obtained from the fit (Table 1 and Figure 3c) are about 1−1.5 Å lower than those inferred\(^22\) from sum frequency measurements.\(^23\) However, as discussed above, the thickness is concentration dependent. Our lower concentrations, as compared with those of the sum frequency study, yield, therefore, lower thickness values. These values are

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) Measured (symbols) and model-fitted (lines) Fresnel-normalized X-ray reflectivity curves from the bare solution surface before alkane deposition for STAB, CTAB, and TTAB at a bulk concentration of ~60% of the cmc. For CTAB, the reflectivity curve at 100% of the cmc is also shown in blue inverted triangles. Curves are shifted from each other vertically by a decade for clarity. (b) The surface-normal electron density profiles obtained from the fits are shown in the same color and line type as the lines in (a). Curves are shifted from each other vertically by 0.08 e Å\(^{-3}\). (c) Fit-derived thicknesses, listed in Table 1 (symbols), and their linear fits (lines) for the bare (solid line) and alkane-wetted liquid (dashed line) surface layers, at a bulk concentration of ~60% of the cmc. The red triangle represents the bare CTAB surface at ~100% of the cmc.

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**Table 1. Alkyl Slab Thickness, \( d \), and Densities of Alkyl, \( \rho_t \), and Headgroup, \( \rho_h \), Slabs, Obtained from Fits to the Measured XR Curves for the Alkane-Free Surface (bare) and the Alkane-Wet Surface in Its Liquid Phase (liquid)**

<table>
<thead>
<tr>
<th>surfactant</th>
<th>( l_t ) Å</th>
<th>( c ), mM</th>
<th>cmc, mM</th>
<th>( d ), Å</th>
<th>( \rho_t ), e Å(^{-3})</th>
<th>( \rho_h ), e Å(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTAB</td>
<td>19.2</td>
<td>3.5(3)</td>
<td>7.4(7)</td>
<td>0.26(1)</td>
<td>0.37(1)</td>
<td></td>
</tr>
<tr>
<td>CTAB</td>
<td>21.7</td>
<td>0.6</td>
<td>0.93(5)</td>
<td>9.9(10)</td>
<td>0.28(1)</td>
<td>0.38(1)</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.93</td>
<td>15.9(9)</td>
<td>0.30(2)</td>
<td>0.41(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STAB</td>
<td>24.7</td>
<td>0.16</td>
<td>0.32(4)</td>
<td>12.0(8)</td>
<td>0.28(1)</td>
<td>0.36(1)</td>
</tr>
<tr>
<td>TTAB</td>
<td>2</td>
<td>9.3(6)</td>
<td></td>
<td></td>
<td>0.26(1)</td>
<td>0.37(1)</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.6</td>
<td>11.7(8)</td>
<td>0.27(1)</td>
<td>0.37(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STAB</td>
<td>0.16</td>
<td>14.3(11)</td>
<td>0.28(2)</td>
<td>0.37(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Surfactant concentration, \( c \), critical micelle concentration cmc (at 20 °C, obtained from the linear fits in Figure 8b in Ref 5.), and literature values for the surfactants’ extended tail lengths, \( l_t \),\(^{22}\) are also listed. The liquid-phase quantities are the same for all alkanes measured for a given surfactant, as discussed in the text and shown in Figure 7.

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**Figure 2.** Laterally-averaged, surface-normal density profiles found in this study. The cartoons show the arrangements and conformations of the headgroups, tails (C\(_m\) alkyl groups of the surfactant molecules), and alkanes (C\(_n\)) in each density profile. The bulk contains solvated surfactant molecules which coexist with the surface adsorbed ones.
all much lower than the extended lengths of the tails of the CTAB molecules even for a maximal surface coverage, achieved at the cmc (0.93 mM for CTAB). Our d values support therefore previous neutron reflection, ellipsometry, and sum frequency measurements which conclude that the layer of surfactant tails is liquidlike and consists of flexible tails containing gauche segments rather than extended ones. This conclusion is further supported by the absence of any diffraction peaks in the GID scans we measured for this layer, indicating the absence of surface-parallel order.

The alkyl layer thickness should depend in principle on the surface coverage by, and thus on the bulk concentration of, the surfactant. In our case, the maximum coverage is determined by the cross section of the headgroup, which is significantly larger than that of the alkyl tail. Thus, the identical headgroups of the surfactants studied here should yield a roughly equal coverage for all three surfactants at concentrations which are an equal fraction of their respective cmc’s. This is the case for three of the solutions in Table 1, where concentrations of ~60% of the respective cmc’s were used. Dividing the alkyl slab thickness d in Table 1 by the number of methyls + methylenes residing in this layer, m, yields an average effective height of 0.6 Å (±15%) per carbon within the “bare” layer. This height and the known volume of a methylene group in the liquid phase, 30 Å³/CH₂, yield, in turn, a surface area per surfactant molecule of ~50 Å², which corresponds to a coverage of Π ≈ 3.3 μmol/m². This value agrees with previous surface tension and neutron reflection measurements for the 0.6 mM CTAB solution and, within ≤20%, with the values obtained in ref 5 for STAB and TTAB from the measured γ(c) curves.

The Liquid Phase of the LG Film. Alkane droplets were placed on the bare surfactant-decorated water surface, at a temperature above the corresponding surface freezing temperature, T_fs listed in Table 1 of ref 5. At this T > T_fs, they form at the surface a monolayer of mixed surfactant tails and alkane molecules, coexisting with 3D alkane lenses. The R/Rₙ curves measured here for such films are shown in Figure 4. Fits to the same two-slab model discussed in the previous section are shown in solid lines in this figure, and the refined parameters are listed in Table 1 under “liquid”. The general shape of the corresponding density profiles is shown in Figure 2b. For each surfactant, the dip in the R/Rₙ curve is observed to shift from its position for the bare surface to a lower q₀, indicating that the mixed monolayer is thinner than the monolayer of pure surfactants’ tails. However, the alkane-independent dip positions for each surfactant also show that the increase in thickness is independent of the alkane length, n. Moreover, the increase, ~1.8 Å, is also independent of the surfactant length m, as demonstrated in Figure 3c by the dashed black line, denoted “liquid”, being almost parallel to the solid blue line, denoted “bare”. The fitted electron densities, ρₑ of the liquid slab in Table 1 coincide with those of the bare surfactant layer, indicating that the mixed layer is also a liquid film. Indeed, no GID peaks were found for the mixed layer at T > T_fs.

Bare and Liquid Surface Layer Thicknesses. To understand why the bare and mixed surface layers have different thicknesses, it is important to note that while both layers are liquidlike, their thicknesses are determined by different effects. For the bare layer, the areal density of the surfactant molecules is determined by the bulk surfactant concentration through the adsorption thermodynamics. As the fitted ρₑ values in Table 1 show, for this adsorption-determined area per molecule, the layer thickness is set by the system to a value such that the resultant electron density of the film coincides (within the measurement error) with that of the bulk liquid alkane.

The mixed layer’s thickness is determined very differently. Here the droplets constitute a macroscopic reservoir of alkane (oil) molecules. Spreading, or otherwise, of these droplets on the surfactant-decorated surface depends on the initial spreading coefficient, Sᵣ = γₐw − (γₐw + γ₀w), where γₐw, γ₀w and γₚ are the interfacial tensions of the air/water, oil/water, and air/oil, respectively, and the overbar indicates the absence of oil. If Sᵣ > 0, the free energy of the alkane-covered surface is lower than that of the air/water interface and spreading occurs. If Sᵣ < 0, the opposite is true and the droplet remains condensed and does not spread. The later is the situation for all alkanes of n ≥ 7 on pure water. Adding a surfactant to the water at the concentrations used here switches the sign of Sᵣ from negative to positive, and a spreading of alkane across the interface is induced.

The equilibrium layer thickness is determined by the minimum of the system’s free energy. In addition to the relevant surface tensions, this free energy includes also a term accounting for the long-range dispersive forces acting across the film’s two interfaces. The free energy is well approximated in our D range by F(D) = (γ₀w + γₚw) − A_H(12πD⁴), where D is the film’s total thickness (see Figure 2) and A_H is the Hamaker constant of the air/alkane/water interface, which is positive for all alkanes studied here. This approximation for F(D) must, however, break down as D → 0, since without an alkane film F(D) → γₚw. For our positive A_H, the dispersive term causes F(D) to decrease with decreasing D, that is, pushes for a thinner wetting layer. However, since Sᵣ > 0, γₚw is larger than (γ₀w + γₚw). Thus, to reach γₚw at D = 0, F(D) must switch from a decreasing to an increasing function at some nonzero D, thus forming a minimum at some value D_eq ≠ 0, which is the equilibrium thickness of the wetting film. This wetting scenario
is called pseudopartial wetting. The microscopic wetting film thus formed coexists at the interface with the macroscopic alkane droplets. This is the mixed layer detected in our measurements shown in Figure 4.

The following conclusions emerge from the discussion above. First, for the bare monolayer, the roughly equal 0.6 cmc bulk concentrations yield an equal areal density of surfactant molecules for the different surfactants studied here. Consequently, the equal (liquid) density requirement leads to a bare layer thickness which increases linearly with \( m \) (Figure 3c). Second, the liquid layer thickness favored by \( F(D) \) is obviously greater than that of the bare one. Thus, the positive spreading coefficient drives sufficient molecules from the droplets into the bare layer to achieve the thermodynamically favored equilibrium thickness. Space filling considerations require that, for a given bare layer, the same amount of \( \text{CH}_3 \) groups is drawn from the droplets in forming the mixed layer, regardless of the length of the alkane molecules in the droplets. This is the reason for the equal dip positions, and hence equal layer thicknesses, observed in Figure 4 for all liquid layers originating in the same surfactant, regardless of the alkane length forming the droplets. This conclusion of an equal density of \( \text{CH}_2 \) groups’ incorporation into the mixed layer implies that the number of alkane molecules incorporated scales inversely with the molecular length \( n_f \) supporting a similar conclusion of earlier, mostly macroscopic, studies.

In the following, we show that the mole fraction of the surfactants’ alky tails, \( \phi \), a quantity used in the thermodynamic calculations of ref 5, can be obtained from the ratio of the bare and alkane-wetted liquid surface layer thicknesses. Using the lengths presented in Table 1, we find that the ratio is equal to 0.80 \( \pm \) 0.1, 0.85 \( \pm \) 0.10, and 0.84 \( \pm \) 0.10 for TTAB, CTAB, and STAB, respectively. In calculating \( \phi \) from this ratio, the exact chain lengths and the density differences between the terminal \( \text{CH}_3 \) and \( \text{CH}_2 \) moieties should be taken into account, a small overall effect due to the low abundance of \( \text{CH}_3 \) groups. Also, this calculation is based on an assumption that the surface adsorption of the surfactant does not change upon alkane deposition. This assumption is consistent with an absence of any significant variation in headgroup slab’s thickness and density between the bare surfactant monolayer and the alkane-comprising liquid monolayer, in agreement with earlier studies.

In addition, we neglect here the difference between mole and volume fractions, which is in any case very small for these chain lengths, well below the sensitivity of thermodynamic calculations to the precise value of \( \phi \). Therefore, in this limit, \( \phi \) is equal to the slab thickness ratio. Based on this analysis, we have set \( \phi = 0.8 \) for all \( n \) and \( m \) in the thermodynamic calculations in ref 5. Also, with the molecular area of \( A = 19.9 \text{ Å}^2 \), derived below from GID for the solid phase, the analysis above implies that for the liquid phase \( A \approx 19.9/0.8 = 25 \text{ Å}^2 \), 19.9/0.85 = 23.4 \text{ Å}^2 \), and 19.9/0.84 = 23.7 \text{ Å}^2 \), for TTAB, CTAB, and STAB, respectively, which are used in ref 5.

Solid Surface Layer. Plots of the measured XR for \( T < T_s \) for a range of alkane lengths are shown in Figures 5a and 6a for CTAB and STAB, respectively, with the top curve in each figure showing, for comparison, the \( n \)-independent XR curve measured for the mixed liquid surface phase above \( T_s \) for that surfactant. Even without detailed modeling, one can see that for the frozen monolayer the first and second dips in \( R/R_s \) shift to \( q_x \) values lower than those of the liquid monolayer, indicating the formation of a thicker layer. The sharpness of the second dip implies a uniform-thickness layer. These characteristics prevail up to \( n \leq m + 1 \), while for \( n \geq m + 2 \), a more complex XR curve is obtained. Here, shorter-period modulations, showing two periodicities, are observed in \( R/R_s \). These indicate an overall thicker surface film, consisting of two different-thickness layers.

To gain quantitative understanding, the \( T < T_s \)-measured \( R/R_s \) for \( n \leq m + 1 \) were fitted by the same model used for the liquid phase at \( T > T_s \) discussed above. The resultant best fits are shown in solid lines in Figures 5a and 6a, with the corresponding density profiles shown in Figures 5b and 6b. For both surfactants, for \( n \leq m + 1 \), we obtain a monolayer of \( n \)-dependent thickness, corresponding roughly to the extended length of the alkane, and having a density \( \rho = 0.31 \text{ e/Å}^3 \), equal to that of solid alkane. These properties prove the \( T < T_s \).
monolayer to be a solid, as shown in Figure 2c. For \( n \geq m + 2 \), a bilayer structure is observed. The upper layer’s thickness equals the extended alkane molecule’s length, and its density—that of a solid alkane. The lower layer is thinner and has a density of a liquid alkane. Thus, the bilayer consists of an upper solid monolayer supported on a lower liquid one, as shown schematically in Figure 2d.

As mentioned above, for all bilayers, a thin depletion slab had to be used between the upper solid layer and the lower liquidlike layer to obtain a good fit. Following work by Ocko et al.,\(^3\) we suggest that this depletion slab originates in the lower-density methyl groups terminating both upper and lower layers, and is similar to that found between two basal planes of a 3D alkane crystal.\(^3\) X-ray reflectivity lacks the sensitivity to independently refine both width, \( \delta_w \), and density, \( \rho_{dep} \), of a deeply-buried thin slab. Only their product can be confidently determined from model fits.\(^5,30\) We refine therefore \( \Phi = \delta_w \rho_w \) where \( \delta \rho = \rho_w - \rho_{dep} \) and \( \rho_w \) is the average of the densities on both sides of the slab. Our bilayer \( R/R_0 \) could be fit well for any \( 0.1 \text{ Å} \leq \delta_w \leq 2 \text{ Å} \), with the fitted \( R/R_0 \)’s and density profiles practically coinciding with those shown in Figures 5 and 6. The fits yield of course different \( \rho_{dep} \) for different \( \delta_w \), but a narrowly distributed \( \Phi = (0.48 \pm 0.05) \text{ e/Å}^2 \). This \( \Phi \) agrees to within 20% with \( \Phi = 0.58 \text{ and } 0.56 \text{ e/Å}^2 \) obtained for crystalline alkanes and lipid bilayers,\(^30-32\) respectively, and thus supports the identification suggested here for this slab.

The XR curve of C\(_{10}\) on STAB in Figure 6a deserves additional discussion. Based on present, and previous,\(^4\) results, the two carbon difference between \( n \) and \( m \) should have resulted in this \( R/R_0 \) being that of a bilayer. In fact, however, while it does exhibit the shorter-period modulations of a bilayer, it lacks some of the other characteristics of bilayer XR curves shown in Figures 5a and 6a, for example, the sharp dip at \( q \approx 0.24 \text{ Å}^{-1} \). The model fits reveals that a bilayer density profile where both the top and bottom layer are solid (see Figure 6b) fits this XR curve well. This could imply either a uniform solid bilayer or a coexistence of domains of a solid monolayer phase with domains of a “normal” bilayer phase, where the bottom layer is liquid and top layer is solid. As XR averages over a macroscopic surface area, these two possible structures can yield (for certain range of relative domain abundances) very similar results that cannot be distinguished. We note that two-phase coexistence regions involving a solid monolayer, a solid bilayer, and a liquid phase were very recently observed in macroscopic optical measurements on a system very similar to ours.\(^3\) This point deserves further detailed study, perhaps by methods like GISAXS (grazing incidence small-angle X-ray scattering) and GTSAXS (grazing transmission small-angle X-ray scattering), which could resolve the domain structure of the surface film.

The thickness values of the surface layers supported on the surfactant solutions studied here are shown in Figure 7. These are the thicknesses denoted by \( d \) and \( D \) in Figure 2. For the monolayer phase, \( n \leq m + 1 \), as well as for the upper layer of the bilayer phase, the layer thickness \( d \) derived from the fits agrees with the calculated extended length of the alkane molecules,\(^9,21,34,35\) \( L_n = 1.27(n - 1) + 1.5 \text{ Å} \), shown in solid lines in Figure 7. This and the electron density (0.31 ± 0.01) e/Å\(^2\), which is equal to that of bulk solid alkanes, show that the monolayer is a solid consisting of a mixture of surface-normal-oriented, closely packed, extended alkane molecules and surfactant tails. This conclusion is supported by our GID measurements discussed below, which clearly demonstrate that the monolayer phase has a lateral hexagonal crystalline order.

The measured layer thickness \( d \) of the solid monolayer phase for STAB solutions is shown in Figure 7c to deviate systematically and increasingly above the alkane’s length \( L_n \) with decreasing \( n \). The deviation can be rationalized by taking into account the fact that the monolayer is a mixture of alkanes and surfactant tails, and thus, if both are fully extended and surface-normal, the expected mixed monolayer’s thickness is simply a concentration-weighted average, \( d_{avg} \), of the lengths of the shorter alkanes and the longer surfactant tails. This can be expressed in the following equation:

\[
d_{avg} = L_n + x_n(L_{18} - L_n) \tag{3}
\]

Here \( L_{18} \) is the length of the STAB molecule’s tail, taken to be equal to the length of an octadecane molecule, \( L_n \) is the length of the extended C\(_n\) molecule, and \( x_n \) is the concentration of the surfactant tails in the solid monolayer phase. \( x_n \) is obtained from the fit of the theory, discussed in ref 5, to the measured surface transition temperatures, \( T_m \) as shown in Figure 6c of ref 5. For mixtures with a carbon number mismatch of \( \Delta n \leq 2 \), the difference between \( d_{avg} \) and \( L_n \) is less than the measurement error; hence, the fitted monolayer thickness agrees well with \( L_n \). \( d_{avg} \) as calculated from eq 3, is shown in a dashed red line in Figure 7c, and observed to agree well with the experimental values, thus supporting the interpretation above.
The effect discussed in the previous paragraph is more difficult to observe for CTAB solutions. Note that for STAB the largest \( n \) where \( d \) shows a visible, out-of-error-bar, deviation from \( L_\alpha \) in Figure 7c is \( n = 14 \), that is, four carbons less than the STAB’s alkyl tail length. Moreover, the deviation for that \( n \) is still less than two error bars, \( 2\sigma \). Correspondingly, for CTAB such a (minimal) deviation is expected to show up only at \( n = 12 \). Indeed, the dashed line in Figure 7b, calculated from eq 3, agrees within \( 1\sigma \) with the measured values for \( n > 12 \), and even for \( n = 12 \), the shortest alkane measured, the deviation is still well within \( 2\sigma \).

The bilayer phase has, for each \( n \), a top layer of a density equal to that of the corresponding monolayer phase, 0.31 e/Å\(^2\). However, here, for all surfactants, the top layer’s thickness agrees closely with the calculated extended lengths of the alkanes studied. This supports the identification of this layer as a solid layer consisting of pure alkanes only. For the bottom layer, the liquidlike densities, \((0.28 \pm 0.01)\) e/Å\(^2\), and thicknesses, obtained from the fits, are close to those of the corresponding liquid monolayer phases (Table 1), leading to the conclusion that this layer is liquidlike. The GID results discussed next strongly support these conclusions. Finally, no systematic variations with \( m \), \( n \), or phase (bare, liquid, and solid) were observed in the surface roughness width refined from the reflectivity fits. The average value of all fits, \((3.7 \pm 0.3)\) Å, agrees well with the value expected from capillary wave theory.\(^{10,18}\)

**Surface Parallel Structure.** Only the surface-frozen phase below \( T_s \) exhibits GID peaks, indicating that above \( T_s \) the surface has no long-range lateral order, while below \( T_s \) such order exists. For the surface-frozen phase a single GID peak was found for all surfactant/alkanes combinations studied here, implying a hexagonal packing, in line with the similar packing found for the surface-frozen phases of molten alkanes\(^2\) and alcohols\(^3\) and for the highly-condensed phases of Langmuir films comprising surface-normal-aligned, end-functionalized alkane molecules.\(^{15,38}\) The GID peak measured for the surface-frozen phase of \( C_{20}/\text{CTAB} \) combination is shown in Figure 8a. The measured peak positions for all alkanes/surfactants combinations have an average value of \( qz = \{(1.515 \pm 0.01)\} \) Å\(^{-1}\), corresponding to a hexagonal lattice constant of \( a = 4\pi/(\sqrt{3}qz) = (4.789 \pm 0.035)\) Å and a molecular area of \( A = \sqrt{3}a^2/2 = (19.9 \pm 0.3)\) Å\(^2\)/molecule, in good agreement with the corresponding value for surface frozen layers in alkane melts.\(^6,36\) The full width at half-maximum (fwhm) of a GID peak, \( \Delta q_{\text{fwhm}} \) and the resolution width of our experimental setup, \( \Delta q_{\text{res}} \), yield through the Debye–Scherrer formula\(^{39}\) \( \xi \approx 0.9 \times 2\pi/[(\Delta q_{\text{fwhm}})^2 - \Delta q_{\text{res}}^2]^{1/2} \), an estimate for the average crystalline coherence length \( \xi \) within the film. We obtain \( \xi_{\text{CTAB}} = (420 \pm 50)\) Å and \( \xi_{\text{STAB}} = (330 \pm 50)\) Å for the average of all films supported on CTAB and STAB solutions, respectively. These two values agree, within their combined error bars, with each other. Similar few-hundred-angstrom crystalline coherence lengths were found to be typical of surface-frozen rotator phases in previously studied Langmuir–Gibbs films\(^4\) and for some Langmuir films on water\(^{15}\) and mercury.\(^{58,40}\)

The Bragg rod corresponding to the typical GID peak shown in Figure 8 extends along the \( q_x \) axis (Figure 8b) and peaks at \( q_q \approx 0 \) Å\(^{-1}\) (Figure 8c). These properties demonstrate, respectively, that the GID peak originates in a quasi-2D surface layer, rather than a 3D crystal,\(^7\) and that the diffracting molecules are surface-normal oriented. The length extracted from the GID model fit, \((24.3 \pm 0.8)\) Å, is smaller than, but close to, the extended length of a single \( C_{16} \) molecule, 25.6 Å, calculated from \( L_\alpha \) above. The slight difference in these values may result from a small fraction of chain-end gauche conformations within the layer. The Bragg rod characteristics found here for this particular surface-frozen layer hold for all surfactant/alkane combinations studied. Specifically, Bragg rods always correspond to a single molecular layer, where the molecules are closely packed, extended, and oriented along the surface normal. This result is not surprising for alkane/surfactant combination satisfying \( n \geq m + 1 \), where the XR measurements discussed above find a single surface-frozen monolayer. For \( n \geq m + 2 \), where XR reveals a bilayer, the BRs, like that in Figure 8c, demonstrate that only one of the layers is ordered laterally. Were both upper and lower layers laterally ordered and in registration, a BR corresponding to twice the extended molecular length would have resulted. Such a calculated BR, shown in a dash line in Figure 8c, clearly disagrees with the measured BR. The single ordered layer is, for all \( n \), the pure alkane upper monolayer whose XR-derived thickness is identical with that derived from the BR fit. The thinner, lower layer does not exhibit long-range lateral order and is therefore liquidlike, consisting of flexible tails containing gauche conformations and/or tilted surfactant tails.

Based on the packing arrangement discussed above, the observed coherence lengths, and the Bragg rod results, we conclude that the surface-frozen monolayers, that is, the mixed alkane/surfactant layer in the monolayer phase and the upper, pure alkane monolayer in the bilayer phase, are highly likely to be in a rotator phase, same as the surface-frozen monolayer on alkane melts.\(^9\)

To get a measure of the elastic properties of these films, we measured the temperature dependence of the lattice constant \( a \) of the hexagonal packing in surface-frozen films of \( C_{16}/\text{CTAB} \) and \( C_{15}/\text{STAB} \). These are shown in Figure 9a. The linear thermal expansion coefficients \( \epsilon_{\text{T1}} = (\Delta a/\Delta T)/a \) obtained for

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**Figure 8.** GID and BR for the surface-frozen phase of \( C_{20} \) on a 0.6 mM CTAB solution. (a) Measured, background-subtracted GID peak (points), fitted by a single Gaussian (line). (b) Equal-intensity contour plot of the Bragg rod corresponding to the GID peak in (a). (c) Measured (points) and model-fitted (solid line) Bragg rod. The Bragg rod calculated for two solid layers in registration is also shown (dash line).
the two films coincide to within their combined error bars. They are very close to the $\alpha_{2D}$ values obtained for other van der Waals dominated quasi-2D structures, like $6.5 \times 10^{-4}$ and $5 \times 10^{-4}$ K$^{-1}$ for mercury-supported monolayers of standing-up alcohol\textsuperscript{10} and fatty acid\textsuperscript{41} molecules, respectively, and $3 \times 10^{-4}$ K$^{-1}$ measured normal to the alkyl chains for mercury-supported monolayers of lying-down diacid molecules.\textsuperscript{42} The surface-frozen monolayer of a C\textsubscript{20} alkane melt, the only one for which $\alpha_{2D}$ was measured,\textsuperscript{43} exhibits, surprisingly, a higher expansion coefficient of $(9 \pm 0.05) \times 10^{-4}$ K$^{-1}$. While the reason for this 30% difference is not clear, we note that this value is still of the same order of magnitude as those found here.

The $\alpha$ values obtained for the frozen phase of all CTAB and STAB solutions, interpolated to $T = 25$ °C using $\alpha_{2D}$ in Figure 9a, and then averaged for each $n$, are plotted in Figure 9b and c. A clear decreasing trend is observed in these values (black circles). A linear fit to these values yields the lateral expansion coefficient due to chain length variation, $\delta = (da/dn)/a$. The negative values indicate a small decrease in the lattice constants of $(1.6 \pm 0.1) \times 10^{-2}$ and $(1.1 \pm 0.2) \times 10^{-2}$ Å as $n$ is increased by unity for CTAB- and STAB-solution-supported surface-frozen films, respectively. Within the scatter of the data points, no difference could be discerned between monolayer and bilayer phases for any surfactant. The contraction of the lattice constant with increasing alkane length is likely due to the increase in the van der Waals attraction between the alkane molecules as their lengths increase. $\alpha_{2D}$ measurements for surface-frozen monolayers on alkane melts, highly challenging because of the small variation of $\alpha_{2D}$ over the small $\leq 3$ °C temperature range of existence of surface freezing here, were carried out to date for C\textsubscript{20} only.\textsuperscript{45} Thus, it is not clear whether the $n$-dependent contraction observed here exists in those monolayers as well, and whether its magnitude differs in the three different surface phases exhibited by these monolayers as $n$ is varied from 15 to 50.\textsuperscript{9} Such measurements are clearly desirable.

A comparison of the contraction found here for LG films to the bulk alkane behavior is complicated by the rich $(n, T)$ phase diagram of alkanes in the $T$-region just below their bulk freezing $T_{fi}$. In particular, the bulk phase closest in structure to our surface-frozen LG films is the $R_{II}$ rotator phase, which exhibits hexagonal packing of molecules with their long axis aligned normal to the basal planes of the alkane crystal, and their backbone planes are free to rotate around that axis. However, this phase appears in the bulk only for alkane lengths $n = 22$–26, outside the $n$-range studied for our LG films.\textsuperscript{44} Within that $n$-range, however, no change exceeding the error bars was found in the hexagonal lattice constant, indicating that no lattice contraction occurs with increasing $n$ in the bulk $R_{II}$ rotator phase. Lower-$T_{fi}$ fully-crystalline, rhombohedral phases of alkanes also show no $n$-dependent contraction of the hexagonal lattice spacing.\textsuperscript{45–47} Thus, the contraction with $n$ may be a unique feature of our LG films.

## SUMMARY AND CONCLUSIONS

We presented here a detailed study by X-ray methods of the surface parallel and surface normal structure of the “bare” surfactant solution, and the Langmuir–Gibbs film formed at the solution’s surface when placing on it a macroscopic droplet of liquid alkane, resulting in pseudopartial wetting.\textsuperscript{2,26} After depositing the droplet, we find above the surface-freezing temperature $T_{fi}$ a mixed monolayer of alkanes and surfactant tails, exhibiting no lateral long-range order. Surface freezing at $T_{fi}$ yields two different structures: for $n \leq m + 1$, the mixed monolayer simply freezes, while for $n \geq m + 2$, the mixed monolayer phase separates vertically, forming a frozen upper monolayer of pure alkanes and a lower liquidlike monolayer of surfactants alkyl tails. The frozen layers in both cases comprise fully extended, surface-normal-aligned alkane molecules, packed in a hexagonal crystalline structure of a lattice constant which decreases with increasing alkane length, a behavior observed here, to our knowledge, for the first time for any type of interfacially frozen monolayers. No further structural transitions were found in these layers beyond the freezing of the liquid LG film. The layer thicknesses in the bare and liquid surface phases depends on the surfactant’s tail length, but is independent of the alkane length, an effect rationalized by the requirements of space filling, and the $n$-independent cohesive energy of the liquid layer. The linear thermal expansion coefficients of the frozen monolayer phase were also determined for both CTAB and STAB and were found to coincide with each other. The values obtained are similar to those of standing-up phases of mercury-supported Langmuir films of alcohol and fatty acid molecules, and close to those of surface-frozen monolayers of alkane melts.

The results derived here from the structural X-ray measurements, and those derived in the accompanying paper\textsuperscript{5} from surface tension measurements, agree well with, and support, each other, forming a full picture of the thermodynamics, phase diagram, and structure of the Langmuir–Gibbs films studied here. Nevertheless, a few puzzles still remain. One is the nature of the transition observed in the slope of $\gamma(T)$ at a temperature denoted as $T_{n}$, which yields an $n$-dependent line closely parallel to, but a few degrees below, the $T_{fi}(n)$ line. The surfactant
concentration dependence should also be explored well beyond the two concentrations measured here for STAB and TTAB. Also, the important surfactant-length dependence of the interchange energy $\omega$ was measured here only for CTAB and STAB, which are too few and too closely spaced to yield insight into, and the elucidation of, this dependence and its origin. Measurements for additional C$_n$TAB surfactants are clearly indicated.

We hope that the detailed experimental results presented in this and the accompanying paper will stimulate further work, in particular theoretical and simulational, on the molecular-level origin and nature of the surfactant-induced surface freezing effect.

**AUTHOR INFORMATION**

*Corresponding Authors*
*E-mail: deutsch@mail.biu.ac.il.*
*E-mail: ocko@bnl.gov.*

**Present Addresses**
*Z.S.: Intel (Israel) Ltd., Kiryat Gat, Israel.*

**Author Contributions**
*S.Y. and E.S. contributed equally to this work.*

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