Surface Freezing in Hydrated Alcohol Melts

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(Received 23 September 1997)

Surface freezing in hydrated alcohol melts was studied by surface tension and x-ray methods. An ~2.5 Å swelling of the surface-frozen bilayer is observed at saturated humidity, due to water intercalation into the bilayer. The concomitant upshifts of 2.5 and 3–6 °C, observed in the bulk and surface freezing temperatures, respectively, are traced to the surprising *increase* in hydration upon freezing. For the liquid surface phase, the Gibbs-rule-predicted water depletion at the surface, relative to the bulk, accounts well for the unequal upshifts. It also explains the observed increases in the chain length and temperature ranges over which surface freezing exists. [S0031-9007(97)05229-0]

PACS numbers: 68.10.–m, 61.25.Em, 64.70.Dv

Almost all materials, including metals [1], semiconductors [2], and ice [3], undergo surface melting, i.e., their surfaces melt at a temperature lower than that of the bulk. The notable and, so far, only exceptions are alkanes [4,5] and alcohols [6] which were recently shown to exhibit surface *freezing*, where an ordered phase forms at the liquid surface of the melt at a temperature T_s *above* its bulk-freezing temperature T_b. In alkanes, $\mathrm{CH_3(CH_2)_{n-2}CH_3}$, the van der Waals (vdW) intermolecular interaction induces a single crystalline monolayer at the melt's surface, with temperature and chain length existence ranges of $\Delta T = T_s - T_b \leq 3$ °C and $16 \leq n \leq 50$. However, in alcohols, $\mathrm{CH_3(CH_2)_{n-2}CH_2OH}$ (denoted $\mathrm{C}_n\mathrm{OH}$ hereafter), a crystalline *bilayer*, rather than a monolayer, is formed at T_s, albeit with smaller $\Delta T \leq 1$ °C and $16 \leq n \leq 28$. Since the formation of a bilayer is energetically less favorable than that of a monolayer [7], stabilization by interactions additional to the vdW interaction has to be assumed. The only structural difference between alkanes and alcohols is a replacement of a hydrogen by a hydroxyl group. This makes hydrogen bonding (HB) between the hydroxyl groups of the two layers, both of which reside at the center of the bilayer, the likeliest candidate for the stabilizing interaction. The dependence of surface freezing on the vdW interaction was explored in binary mixtures, where this interaction was tuned by mixing alkanes [8] and alcohols [9] of different lengths. This revealed a rich array of new phenomena, including an increased surface phase stability, indicated by a larger ΔT, new crystalline surface phases, and the suppression of surface freezing in some instances. However, the role, suggested above, of HB and its importance relative to the vdW interaction in stabilizing the crystalline surface phase in alcohols were not studied to date. As concurrent HB and vdW interactions play a crucial role in many biological molecules, nucleic acids being a prominent example [10], such a study is important not only for physics but also for biology and the molecular level study of life processes.

In this paper hydration, recently shown to modify considerably the structure and boundaries of bulk alcohol phases [11], was used to tune the HB component of the interaction in order to elucidate its role in surface freezing. We find a uniform swelling of ~2.5 Å in the surface-frozen bilayer due to water intercalation at its center. More strikingly, a doubling of ΔT and a large increase in the range of chain lengths showing surface freezing are observed. We show that both of these effects can be well accounted for quantitatively by considering the differences in hydration at the surface and in the bulk for the ordered and liquid phases.

The commercially obtained samples were >99% pure and used as received. About 0.5 g of the material was placed inside a sealed cell, the temperature of which was regulated to better than 0.01 K. Hydration was done by keeping the sample under an atmosphere of saturated water vapor throughout the measurement. A complete restitution of all properties measured on the dry alcohol was observed upon drying the hydrated samples. The structural studies employed x-ray reflectivity (XR), x-ray grazing incidence diffraction (GID), and Bragg rod (BR) measurements at the vapor-melt interface, using the Harvard/BNL Liquid Surface Diffractometer [12] at beam line X22B, NSLS, Brookhaven National Laboratory, with a typical wavelength $\lambda = 1.54$ Å. X-ray reflectivity probes the surface-normal electron density profile [13,14]. The formation of a surface layer of electron density different from the bulk results in the appearance of periodic modulations in the reflectivity curve. The modulation period is inversely proportional to the layer thickness, and its amplitude depends on the electron density difference between the layer and the bulk. GID measurements probe the structure within the surface plane, with sharp diffraction peaks indicating a crystalline structure. BR measurements, i.e., the surface-normal intensity distribution at the diffraction peaks, probe the length and orientation of the molecules within the layer [13]. The surface thermodynamics were probed by surface tension measurements using the Wilhelmy plate method [15]. Neglecting intramolecular energy changes, the excess surface free energy yields a negative slope, $d\gamma(T)/dT = \Delta S = -(S_{\text{surf}} - S_{\text{bulk}})$, for the surface tension curve $\gamma(T)$ when both surface and bulk are liquid. The sharp reduction in the surface entropy, S_{surf}, upon surface freezing changes the slope abruptly from negative to positive at T_s. These measurements allow not only a macroscopic and convenient detection of the occurrence of surface freezing, but also an accurate determination of T_s, T_b, ΔS, and various related thermodynamic quantities. For further details, see [5,15].

Figure 1 shows the XR curves measured for dry and hydrated $C_{28}OH$ at $T_b < T < T_s$. The slight decrease observed in the period of the modulation upon hydration indicates a small increase in the surface bilayer thickness, i.e., swelling. The fits shown employ the matrix method [5], and a five-box model for the electron density profile ρ_e of both dry and hydrated alcohols. The model is convolved with a Gaussian, representing the interface roughness. The five boxes represent (1) the outermost CH_3 terminal group, (2) the $(CH_2)_{n-1}$ chain of the upper layer, (3) the OH head groups region, (4) the $(CH_2)_{n-1}$ chain of the lower layer [same as box (2)], and (5) the innermost CH_3 terminal group [same as box (1)]. An additional box represents the liquid subphase. Note the excellent fits obtained. The corresponding density profiles for $C_{28}OH$ in the inset show an increase of the thickness in the OH headgroup region by ~2.5 Å upon hydration and a slight increase in the roughness of the free surface of the bilayer (the first CH_3 box) by ~0.6 Å.

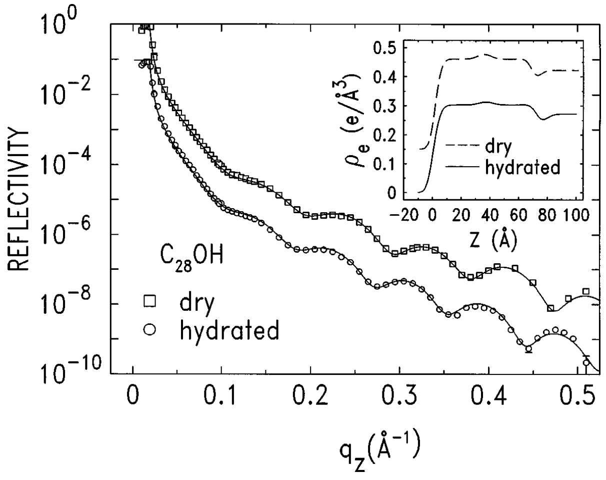

FIG. 1. X-ray reflectivity of surface-frozen $C_{28}OH$ (points), the box-model fits (lines), and the corresponding electron density profiles ρ_e (inset). The shorter modulation period when hydrated indicates a swelling of the surface bilayer.

The comparison in Fig. 2 of the fit results for all dry and hydrated alcohols studied demonstrates the systematic swelling of the bilayer's OH region by 2.4–2.7 Å. Direct integration over the density profiles yields an increase of ~14 electrons upon hydration in a molecular area of $A \approx 19.5$ Å^2 [4,6]. This is somewhat more than, but not too far from, the 10 electrons of a single water molecule, indicating the intercalation of approximately one water molecule in between each pair of upper and lower alcohol molecules in the bilayer. This approximately 1:2 water-to-alcohol ratio is close to that of the hydrated bulk [11]. The swelling at the surface is, however, consistently ~0.5 Å higher than that in the corresponding bulk rotator phases. This is not unreasonable, considering the somewhat different energetics of the surface and the bulk. The fits also indicate a small, consistent increase, ~0.5 Å, in the capillary-wave-induced surface roughness σ, barely outside the experimental error. This must result from wavelengths in the capillary-wave spectrum below the cutoff imposed by the intermolecular distance, since the only other contribution is proportional to $\gamma^{-1/2}$ [16] and the measured γ is virtually unchanged by hydration. The increase in the below-cutoff contribution implies an increase in the static or dynamic up-down disorder of adjacent individual molecules in the layer, with no near-neighbor correlations. The GID and BR measurements indicate the same in-plane hexagonal packing for both dry and hydrated alcohols. The lattice parameter and tilt orientation (next-nearest neighbor) remain the same, and only a slight decrease of 1–2° is observed in the molecular tilt in the tilted phases ($n \geq 24$). Consequently, the true swelling for these lengths is 0.2–0.6 Å less than that obtained from the XR measurements.

The most dramatic effect of hydration is the large, and unequal, changes in T_b and T_s, $\delta T_b = T_b^{\text{wet}} - T_b^{\text{dry}}$ and $\delta T_s = T_s^{\text{wet}} - T_s^{\text{dry}}$. Unlike other impurities [8,9], hydration *increases* these temperatures showing the water to have a stabilizing effect. Our $\delta T_b \approx 2.5$ °C, shown

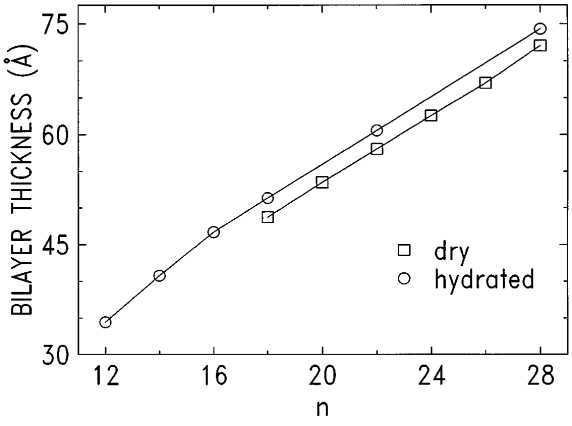

FIG. 2. The surface bilayer thickness, refined from the reflectivity fits. A uniform ~2.5 Å swelling is observed.

in Fig. 3(a), is approximately constant with n and agrees closely with previous measurements [11]. δT_s, however, decreases from ~6 to ~3 °C with n and is larger than δT_b for all n. This approximately doubles the existence range, $\Delta T = T_s^j - T_b^j$ (where $j = wet$ or dry), of the surface bilayer, from ≤ 1 to ~2 °C, as shown in Fig. 3(b). The surface-freezing effect vanishes for $n = 30$ for both dry and hydrated alcohols [17]. The low-n limit, however, is considerably extended upon hydration, increasing by 50% the n range showing surface freezing. We now show that δT_s, δT_b, and the low-n limit extension can all be accounted for quantitatively, based on the entropy-of-mixing of water and alcohol and on the surprising *increase* in water solubility from an H_2O:alcohol molecular ratio of $\leq$1:4 for the molten phase [18] to ~1:2 for the ordered rotator phase [11].

Equating the chemical potentials of the rotator (r) and the liquid (l) bulk (b) [surface (s)] hydrated alcohol phases at T_b (T_s) yields for the temperature upshift δT_b (δT_s) [11] the following:

$$\delta T_i = k_B T_i \ln[(1 - \phi_i^l)/(1 - \phi_i^r)]/\Delta S_i\,, \qquad (1)$$

where $i = b, s$, and $\phi_i^{l,r}$ and ΔS_i are the water molar concentrations at the indicated phase and the entropy change at the transition, respectively. From our γ measurements, $\Delta S_s = (d\gamma/dT)_{\rm exp} = -0.37 + 0.11n$ mN m^{-1} K^{-1} for both wet and dry alcohols and [11] $\Delta S_b \approx \Delta S_s$. The bulk water concentration in the melt, $\phi_b^l = 0.663 - 0.1911 \ln(n)$, is a convenient *ad hoc* functional fit to the only extant such data [18] which, however, extends up to $n = 17$ only. The calculated bulk δT_b [solid line in Fig. 3(a)] required only a slight adjustment of ϕ_b^r, from the nominal 1/3 (the 1:2 ratio discussed above) to 0.28 to reach the excellent agreement with experiment seen in the figure. Consider now δT_s. Since the difference in hydration between the solid and the liquid phases determines δT_i, the measured $\delta T_s > \delta T_b$ indicates a larger hydration difference for the surface than for the bulk. The x-ray measurements, however, show a roughly equal hydration for the solid bulk and surface, $\phi_b^r \approx \phi_s^r \approx 1/3$. The *liquid* surface must, therefore, have a lower hydration than the liquid bulk. This bulk/surface hydration difference can be obtained from Gibbs' rule [19], $x_s^l/x_b^l = [(1 - x_s^l)/(1 - x_b^l)]^{1/r} \exp[-A_w(\gamma_w - \gamma_a)/k_B T]$, which applies in our low concentration and low heat-of-mixing case, having unequal sized molecules. $A_w \approx 11.6$ Å^2 is the molecular area of water, $r = (1.27/1.9) \times n$ is the alcohol/water length ratio, and x denotes volume fractions. Indeed, given the much higher surface tension of water, $\gamma_w \approx 72$ mN/m, as compared to alcohols, $\gamma_a \approx 27$ mN/m, Gibbs rule yields a ϕ_s^l varying from ~0.068 for $n = 10$ to ~0.01 for $n = 28$, about threefold lower than the corresponding bulk concentrations, ϕ_b^l. Using Gibbs rule for x_s^l, Eq. (1) yields the solid line in Fig. 3(a) for the surface with $\phi_s^r = 0.29$, slightly higher than, but close to, the bulk ϕ_b^r above, and the nominal ~1/3. The agreement of the calculated δT_i curves with the measured data is remarkable, particularly since virtually no adjustable parameters are involved. The different δT_i for the surface and the bulk leads to a considerable increase in ΔT upon hydration, as shown in Fig. 3(b). The solid line marked "dry" is a fit to $\Delta T = a/n - b/n^3$ ($a = 41.5$, $b = 10\,299$, $c = 2.8$), an empirical form shown to apply in alkanes [5,15]. This was also used to obtain the dry T_s for $n = 10, 12, 14$, which are not measurable and which are used in calculating the δT_s points for these n in Fig. 3(a). The "wet" solid line, $\Delta T^{\rm wet} = (T_s^{\rm dry} + \delta T_s) - (T_b^{\rm dry} + \delta T_b) = \Delta T^{\rm dry} + (\delta T_s - \delta T_b)$, uses the calculated δT_i in Fig. 3(a) and the dry solid line $\Delta T^{\rm dry}$. The excellent agreement for both curves with the measurements strongly supports the suggested hydration-difference mechanism.

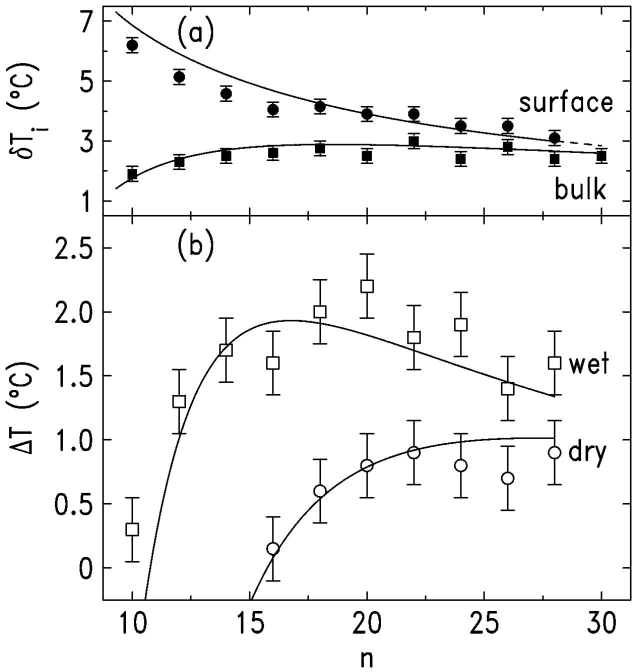

FIG. 3. The measured (points) and calculated (lines) (a) upshift, δT_i, in the surface- and bulk-freezing temperatures upon hydration, and (b) temperature range of existence of the surface freezing. Both lines in (a) and the wet line in (b) are calculated with virtually no adjustable parameters. The effect vanishes for $n = 30$, hence no points are shown for this n.

Another dramatic effect of hydration is observed on the low-n limit for the occurrence of surface freezing. In Fig. 3(b) the dry ΔT curve goes negative for $n < 16$, indicating a preemption of surface freezing by bulk freezing, i.e., $T_s < T_b$. Upon hydration, however, the unequal upshifts of the two temperatures reverse this relation; ΔT becomes positive and surface freezing occurs even for chain lengths as short as $n = 10$. As the good agreement between the solid line and the measured wet ΔT in Fig. 3(b) demonstrates for this n range, the calculations presented above predict this effect, and accurately estimate the ΔT ranges observed. The n-range increase of the surface-freezing effect has, thus, the same origin as the increase in ΔT.

Unlike the low-n limit, the vanishing of the effect at $n = 30$ is not influenced by hydration. This can be understood by considering the relative importance of the intrachain entropy and the interchain, water-enhanced, hydrogen bonds at both limits of n. The former, which tends to inhibit surface ordering, increases with chain length and temperature and is not expected to change significantly with hydration. The latter interaction concerns only the head group. Hence, it is strongly influenced by hydration but is chain length independent [20]. Thus, the influence of hydration should be most significant for short chains where the conformational entropy is small, and the behavior is dominated by the balance between interchain and head-group interactions. The large-n limit, on the other hand, is dominated by the balance between intrachain conformational entropy and the interchain vdW interaction. It should have, therefore, only a marginal dependence on changes in the head-group interactions induced by hydration. These two expectations are indeed in line with the observations. The gradual reduction with n of the increase in ΔT^{wet} and its convergence towards ΔT^{dry}, observed in Fig. 3(b), also support a diminishing of the relative importance of the HB as compared to the interchain vdW interaction and the conformational entropy. In fact, as indicated by the near convergence at $n = 30$ of δT_s and δT_b in Fig. 3(a), if the surface freezing was to continue beyond $n = 28$, it would have soon reached the limit of $\delta T_s \approx \delta T_b$. This, in turn, would have caused the hydration-induced increase in ΔT to vanish. These are all clear indications of the fast decrease of the importance of HB with n in the surface layer, from near dominance at $n \approx 10$ to near insignificance at $n \approx 28$.

In conclusion, the water intercalation into the surface-frozen alcohol bilayer, revealed in the XR measurements, increases the bilayer's stability by enhancing the HB. This is reflected in the large *up*shift in T_s and T_b. The different hydration of the liquid surface and bulk, calculated from Gibbs' rule, accounts quantitatively for the observed increase in ΔT and the appearance of surface freezing for $10 \leq n \leq 14$. The decrease in the HB dominance with increasing n is reflected in the reduction of the ΔT enhancement with n, and the lack of change in the upper-n limit of surface freezing at $n = 30$ upon hydration, in contrast with the considerable reduction observed in the lower-n limit. Additional work, now in progress, indicates that an even wider interaction tunability range is possible by a judicious choice of the architecture and properties of additive molecules.

Contributions by J. Patel and T. Peterson, and support by the Israel Science Foundation, Jerusalem (M. D.) and the Petroleum Research Fund, administered by The American Chemical Society (X. Z. W.), are gratefully acknowledged. B. N. L. is supported by DOE Contract No. DE-AC02-76CH00016.

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