Melting of Short 1-Alcohol Monolayers on Water: Thermodynamics and X-Ray Scattering Studies

B. Berge, O. Konovalov,* J. Lajzerowicz, A. Renault, J. P. Rieu, and M. Vallade

Laboratoire de Spectrométrie Physique (Associé au Centre de la Nationale Recherche Scientifique, URA08), Université Joseph Fourier, Grenoble I, B.P. 87, F-38402 Saint Martin d'Hères, France

J. Als-Nielsen, G. Grübel, and J. F. Legrand†

European Synchrotron Radiation Facility (ESRF), avenue des Martyrs, B.P. 220, 38043 Grenoble, France

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From surface tension measurements we extract the melting entropy Δs_{2D} of fatty-alcohol monolayers on water. Δs_{2D} is found to be $4k_B$/mol lower than in the bulk. Because of the role of the conformational entropy, the melting transition is discontinuous for long chains, but tends to be continuous for molecules shorter than 1-nonanol. For 1-decanol Δs_{2D} is sufficiently small to allow observation of critical fluctuations; the diffraction peak, measured with a high resolution synchrotron experiment, is described by a power-law singularity which broadens as the temperature approaches the melting point.

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After almost a century of studies of Langmuir monolayers on water, an overview of the existing phases appeared recently for the case of fatty acids [1]. The topology of the phase diagram seems not to depend on the chain length, and it has been described by a Landau theory of *weak crystallization* [2]. Up to now, most studies have been concerned with long insoluble molecules [3], although soluble surfactants are also of great importance. In this Letter we study the crystallization of monolayers of short and weakly soluble molecules. Shortening the chains provides a way to decrease the number of conformational degrees of freedom and bring novel features into the phase diagram.

Recently we have shown that short fatty-alcohol monolayers could be studied by placing a drop of alcohol on top of a water surface [4–6]. The drop gets spontaneously surrounded by a monolayer, keeping a finite contact angle at equilibrium (Fig. 1, upper part) [7]. Two different forms of the alcohol are thus in equilibrium: in three dimensions in the bulk of the drop and in two dimensions in the monolayer. The melting point of the monolayer, $T_{m_{2D}}$, is about 15 K above the melting point of the bulk, $T_{m_{3D}}$. Several systems are known to exhibit surface melting at temperatures above the bulk melting, for instance, at the free surface of alkanes and alcohols ($\Delta T \sim 0$–3 K) [8,9] or at the water-alcohol interface (($\Delta T \sim 10$ K) [10].

The crystalline structure of the alcohol monolayer is hexagonal, the long axis of the molecules being vertical on average but with possible instantaneous tilt of a few degrees [6]. In bulk fatty alcohols, a crystalline rotator phase has also been observed just below melting [11]. It can be described as a 3D stacking of monolayers. In the bulk or on the water surface, the layers have a similar crystal structure with almost the same hexagonal lattice spacing. In the bulk another phase transition towards a more ordered structure is reported a few degrees below $T_{m_{3D}}$, while in the monolayer such a phase transition has not been observed so far.

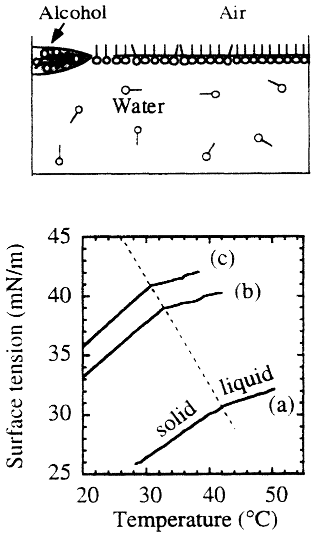

FIG. 1. Upper part: sketch of the system: the monolayer and a reservoir drop are in equilibrium. Lower part: surface tension versus temperature for the dodecanol monolayer in contact with a reservoir drop of : curve *a* pure dodecanol; curve *b* 20% dodecanol in alkane, and curve *c* 10% dodecanol in alkane. The dashed line is the solid-liquid coexistence line.

We present here a thermodynamical analysis of the monolayer melting transition and the results of a high resolution x-ray diffraction study.

Let us first recall that the surface tension has a linear temperature dependence in the solid and liquid phases with positive slopes $(d\sigma/dT)_s$ and $(d\sigma/dT)_l$, respectively [curve *a* of Fig. 1]. If we mix the alcohol with an alkane in the reservoir drop, the surface pressure of the alcohol monolayer decreases [curves *b* and *c* of Fig. 1] [6(a),12].

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Then we can locate the solid-liquid transition line (dashed line in Fig. 1), and it has a negative slope $(d\sigma/dT)_{\mathrm{cl}}$.

At any temperature the Gibbs adsorption equation [13] describes the equilibrium of the monolayer with the 3D reservoir drop by

$$(d\sigma/dT) = (s_{3\mathrm{D}} - s_{2\mathrm{D}})/a, \quad (1)$$

where σ is the surface tension, and s and a are the entropy and area per molecule. 2D and 3D refer to the monolayer and drop phases, respectively. The quantity in Eq. (1) is often referred to as the entropy of interface formation [10,14]. Applying (1) to both sides of the monolayer transition leads to

$$\begin{aligned}\Delta s_{2\mathrm{D}} &\equiv (s_{2\mathrm{D}})_l - (s_{2\mathrm{D}})_s \\ &= a_s(d\sigma/dT)_s - a_l(d\sigma/dT)_l. \end{aligned} \quad (2)$$

The 2D equivalent of the usual Clapeyron relation can be written for the monolayer

$$(d\sigma/dT)_{\mathrm{cl}} = \frac{\Delta s_{2\mathrm{D}}}{a_s - a_l}, \quad (3)$$

where s and l refer to the solid (rotator) and liquid phases. Finally, in eliminating entropies from (2) and (3) one gets

$$\frac{a_l}{a_s} = \frac{(d\sigma/dT)_s - (d\sigma/dT)_{\mathrm{cl}}}{(d\sigma/dT)_l - (d\sigma/dT)_{\mathrm{cl}}}. \quad (4)$$

X-ray data yield $a_s = 21.5$ Å^2/mol independent of chain length. Equation (4) thus allows the calculation of a_l from thermodynamic data, without any approximation. Equation (3) then gives $\Delta s_{2\mathrm{D}}$. Figure 2 shows the results for the entropy of melting $\Delta s_{2\mathrm{D}}$ [Fig. 2(a)] and the area per molecule in the liquid phase a_l [Fig. 2(b)] as a function of the chain length n (number of carbon atoms). Good linear estimates are $\Delta s_{2\mathrm{D}} \cong 1.0 \times (n - 8.2)k_B$ and $a_l \cong a_s + (n - 8.1)$ Å^2/mol, shown in Fig. 2 as dashed lines. Also shown is $\Delta s_{3\mathrm{D}} = (s_{3\mathrm{D}})_l - (s_{3\mathrm{D}})_s$, the entropy of melting of the 3D rotator phase [15]. Finally, with a_s and a_l determined previously we can use Eq.(1) to compare 3D and 2D entropies in a given phase:

$$\begin{aligned}(s_{3\mathrm{D}})_l - (s_{2\mathrm{D}})_l &\cong (2.0 \pm 0.5)k_B, \\ (s_{3\mathrm{D}})_s - (s_{2\mathrm{D}})_s &\cong (-2.1 \pm 0.7)k_B \end{aligned} \quad (5)$$

independent of n. To obtain the latter one we have used values of $\Delta s_{3\mathrm{D}}$, measured at $T_{m_{3\mathrm{D}}}$[15].

It has to be recalled that the entropy of a "fully melted" chain with equal probability for each bond to be in *trans* or gauche configurations is about $(n - 2)k_B$, also shown as a dashed line in Fig. 2(a). This quantity overestimates $\Delta s_{3\mathrm{D}}$ only slightly, as shown on Fig. 2(a). On the contrary, it is larger than $\Delta s_{2\mathrm{D}}$ by about $6k_B$, although it accounts for the observed linear dependence with the correct slope. Clearly part of the entropy change is missing in the monolayer transition, as if the melting involved only a portion of the chain (about n-6 carbon atoms [16]). This is confirmed by the results given above in Eq. (5). $(s_{3\mathrm{D}})_l > (s_{2\mathrm{D}})_l$ implies that the molecules are more ordered in the 2D liquid than in the 3D liquid: This mainly originates from the well-known orienting effect of the water-air interface. In contrast $(s_{3\mathrm{D}})_s < (s_{2\mathrm{D}})_s$, indicating that the 2D rotator crystal is more disordered than the corresponding 3D phase. This result confirms that the stability of this phase is increased in the monolayer compared to bulk. In Eq. (5) both relations contribute to make the melting entropy lower in 2D than in 3D. It should be challenging to know if computer simulations can reproduce these phenomena [17].

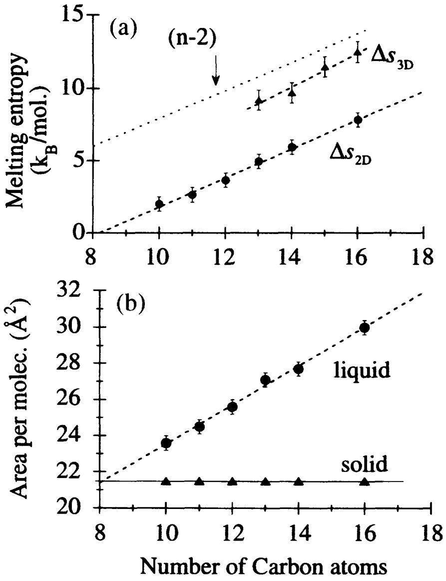

FIG. 2. (a) Calculated values of the monolayer entropy of melting $\Delta s_{2\mathrm{D}}$ (closed circles) as a function of the chain length n. Also reported are the values of $\Delta s_{3\mathrm{D}}$, the melting entropy of the bulk rotator phase (triangles from [15]). (b) Area per molecule a_l in the 2D liquid (closed circles) and a_s in the solid (triangles, from x-ray data [6(b)]).

Independent of the interpretation, $\Delta s_{2\mathrm{D}}$ and $a_l - a_s$ both indicate that the first-order character of the transition is expected to vanish for $n < 9$. The next part shows fluctuation effects which are precursor of the change in the order of the phase transition.

We have performed x-ray grazing incidence diffraction from monolayers of 1-decanol ($n = 10$; $T_{m_{2\mathrm{D}}} = 14.3 \pm 0.3$ °C) and 1-dodecanol ($n = 12$; $T_{m_{2\mathrm{D}}} = 38.5 \pm 0.5$ °C). The experiment was conducted on the BL9-Troika line at ESRF. In the undulator beam a flat diamond monochromator (1.3776 Å) deflects the beam at an angle of 0.85 times the critical angle for total reflection on water. The trough has been described elsewhere [6(b)].

We just recall that it is able to rotate around the vertical axis, with oscillations of 60° amplitude with a period of 50 s. This was necessary to smooth the grain crystalline texture [6(b)]. After diffraction by the sample, the beam was analyzed by a $\langle 111 \rangle$ germanium crystal, achieving an excellent resolution (FWHM ~ 0.0008 Å^{-1}, about 10 times less than in previous works [18]). This was made possible by the high brilliance of the source. Far from any phase transition [see Fig. 3(a)] the width of the peak is limited by the instrument resolution, meaning a coherence length of at least a few μm. In Fig. 3(a) the background has been materialized by a dashed line in order to emphasize the presence of side tails in the diffraction peaks. We checked that these tails do not come from the apparatus function and are real features of the monolayer diffraction. We must add that a search for higher order reflections was unsuccessful, leading to upper bounds for their intensities: $I_{\langle 11 \rangle}/I_{\langle 10 \rangle} < 0.005$ and $I_{\langle 20 \rangle}/I_{\langle 10 \rangle} < 0.003$. For decanol, when the transition is approached the shape changes: Figure 3 shows the temperature evolution of the raw diffraction data. The use of the high resolution setup reveals a clear broadening starting a few degrees below $T_{m_{2D}}$. In previous experiments with lower resolution only the intensity decrease was observed [5]. We now analyze this broadening in more detail.

In two dimensions, it is known [19] that Bragg peaks are replaced by power-law singularities. These are expected to be isotropic around the singularity, due to their multiphonon origin, so the scattering function is given by $S(\mathbf{Q}) \propto |\mathbf{Q} - \mathbf{G}|^{-(2-\eta)}$, where $\mathbf{G}$ is a vector of the reciprocal lattice and [20]

$$\eta = (k_B T / 4\pi\mu)\mathbf{G}^2 \qquad (6)$$

in the limit where the ratio of the Lamé coeficients $\mu/\lambda \ll 1$. In order to fit our data, we numerically integrated $S(\mathbf{Q})$ along a circle in the reciprocal space (2D powder averaging) and then convoluted with the experimental resolution function. The circular integration was realized with a variable mesh to ensure good accuracy even when the integration path grazes the singularity. The free parameters were the position, amplitude, and power-law exponent η of the peak, plus a linear background. Note that only one parameter, η, determines the width of the peak. The resulting fits are the continuous line in Fig. 3. The agreement between the fit and the experiment is reasonably good. A Lorentzian line shape does not fit the data, even at low temperatures, as the parameter χ^2 (goodness of fit) increases by a factor ~ 3. A sum of two Lorentzian would fit a little better than the power law (χ^2 decreased by $\sim 10\%$) but with two additional free parameters without clear physical basis. Figure 4 shows the temperature dependence of the hexagonal lattice parameter deduced from peak positions, and of the exponent η, for decanol. Figure 4(a) shows a progressive change in the thermal expansion which is always large ($>10^{-3}$ K^{-1}). We see in Fig. 4(b) that far from the transition η is about zero, the value expected at low temperatures, meaning that the "tails" observed in Fig. 3(a) come from a $|\mathbf{Q} - \mathbf{G}|^{-2}$ singularity. One point leads to the unphysical value $\eta \sim -0.5$ but with the biggest error bar. The peak broadening appears as an increase of η with temperature up to $\eta(T_{m_{2D}}) \approx 0.6 \pm 0.15$. We have made the same analysis for dodecanol without detecting any peak broadening up to 0.25 °C below $T_{m_{2D}}$: The fit led in this case to a constant low value $\eta < 0.2$. This confirms that the pretransitional broadening in decanol really comes from critical fluctuations related to the weakness of the first order character of the transition.

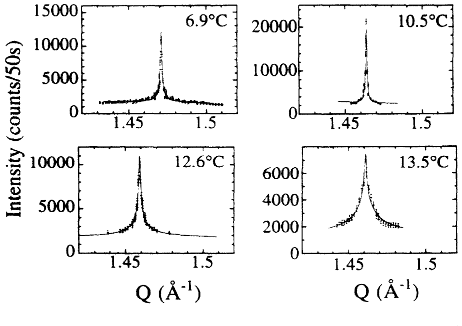

FIG. 3. Temperature evolution of the high resolution x-ray diffraction for the decanol ($T_{m_{2D}} = 14.3$ °C). The crosses are the measurements, and the lines are the fit of a power law with 2D-powder averaging (see text).

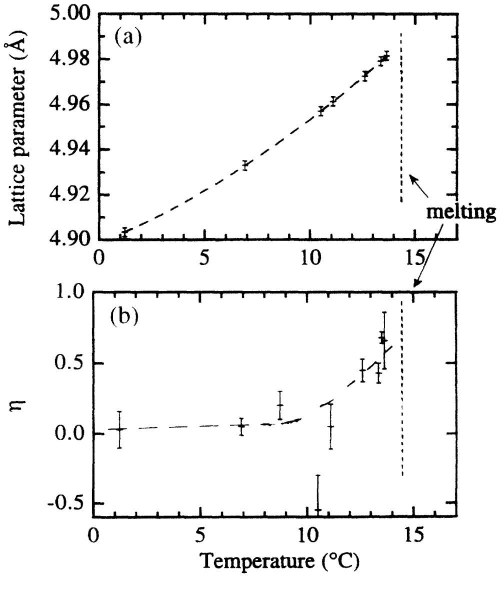

FIG. 4. Results of the fit for decanol versus temperature. (a) Hexagonal lattice parameter. (b) Exponent η; the dashed line is a guide for eyes. The error bars correspond to 10 times the standard errors produced by the fit and should be viewed only as relative quantities.

The observed temperature dependence of η, with the use of Eq. (6), indicates the decrease of the shear modulus μ near $T_{m_{2D}}$. One then finds that $\mu > 0.5$ N/m for $T \leq T_{m_{2D}} - 4$ K and decreases to $\mu(T_{m_{2D}}) \sim (0.1 \pm 0.02)$ N/m. This last value exceeds that expected for the crystal-hexatic continuous transition [20] $\mu_c = 4\pi k_B T_m / a_0^2 \approx 0.2$ N/m in the Halperin-Nelson scenario. Although this result is somewhat surprising one must note that this theory cannot be strictly applicable to the present case, since the transition is (weakly) first order. Let us also recall that, among the various observations [21] of an algebraic decay of position-position correlations near the 2D melting, some of them also show values of μ smaller than μ_c.

To summarize, we have observed that the 2D melting entropy of 1-alcohol monolayers shows a linear decrease with the chain length, so that for $n < 9$ the transition would be continuous. In decanol monolayers ($n = 10$) the transition is only weakly first order, and we have shown that critical fluctuations just below 2D melting can be observed by high resolution x-ray diffraction, revealing a marked softening of the shear elastic constant. We note that evidence of critical fluctuations was also observed in this system above $T_{m_{2D}}$ by ellipsometry [4]. Experiments on shorter alcohols, for which the transition is expected to be continuous, are clearly of great interest, although they present special difficulties.

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*Permanent address: Institute of Crystallography, Russian Academy of Science, Leninsky Prospect 59 117333 Moscow, Russia.

†Present address: Laboratoire de Spectrométrie Physique, Université J. Fourier, Grenoble I, B.P. 87, F-38402 Saint Martin d'Hères, France.

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