Anomalous Melting Properties of Some Classical Monolayer Systems

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(Received 5 July 1983)

The responses to shear stress of monomolecular films of fatty alcohols, $C_nH_{2n+1}OH$, spread on water have been studied for $n = 20$, 21, and 22. A compression-induced melting transition has been observed for the first time.

PACS numbers: 64.70.Dv, 46.60.Bd, 62.10.+s, 68.15.+e

We have recently pioneered the development[1] and application[2] of a sensitive balance for making shear modulus measurements on two-dimensional (2D) "floating" solid films. In the absence of x-ray diffraction data, we use the presence of an observable static shear modulus as the operational definition of a solid. In the past, it has been traditional to identify a certain class of kinks in the Π-A diagram as indicative of a liquid-solid transition. Here Π, the 2D analog of pressure, is defined as the change in surface tension caused by the absorbed monolayer and it is determined as a function of the areal density, A (square angstroms per molecule). In some cases measurements of the surface viscosity have been made which show a significant rise in the high-density phase. However, in view of a bewildering array of possible 2D liquid-crystal-like phases,[3,4] which, like their 3D counterparts, might have high viscosities, the inference that high viscosity signals a liquid/solid transition must be rejected.

Our apparatus has the distinct feature of being completely centrosymmetric. The aqueous substrate is contained in a Teflon cup, the interior of which is a truncated cone. The force transducer is a Teflon annulus mounted so that its axis coincides with the cup axis. The annulus is fastened to a light coil former with a $2\frac{1}{2}$-turn coil which is, in turn, suspended by two fine wires between the poles of a magnet. The film is compressed by withdrawing water from the bottom as the cup is raised to keep the annulus in contact with the surface. Surface pressure is measured by monitoring the phase velocity of driven capillary waves.[5]

The shear response usually displays a viscoelastic behavior[6] and may be studied in several ways. A step-function current may be applied to the coil. Depending on the viscosity, the coil will exhibit either damped oscillatory motion or a monotonic creep toward an equilibrium position. The time-dependent motion in either case is recorded by reflecting a laser beam from a mirror (mounted on the coil former) to a position-sensing photodiode. Alternatively, for a stiff film, the cup may be rotated through a small angle and the time-dependent rotation of the transducer recorded as before. If the stress does not relax to the base line, then a static modulus exists and, by definition, the film is solid. Typical plots of the time-dependent relaxation have been reported elsewhere[7] and will not be reproduced here.

For the case of an oscillatory ringdown, the frequency and decay time involve, through the differential equation governing the rotor, the dynamic shear modulus of the film,

$$\mu(\omega) = \mu'(\omega) + i\mu''(\omega). \qquad (1)$$

For the case of a monotonic response, analysis[1,8] requires a specific form for the time-dependent shear modulus, $\mu(t)$; our data were well represented by

$$\mu(t) = \mu_\infty\{1 - A[1 - \exp(-t/\tau_1)] - B[1 - \exp(-t/\tau_2)]\}, \qquad (2)$$

where μ_∞ is the instantaneous (or infinite-fre-

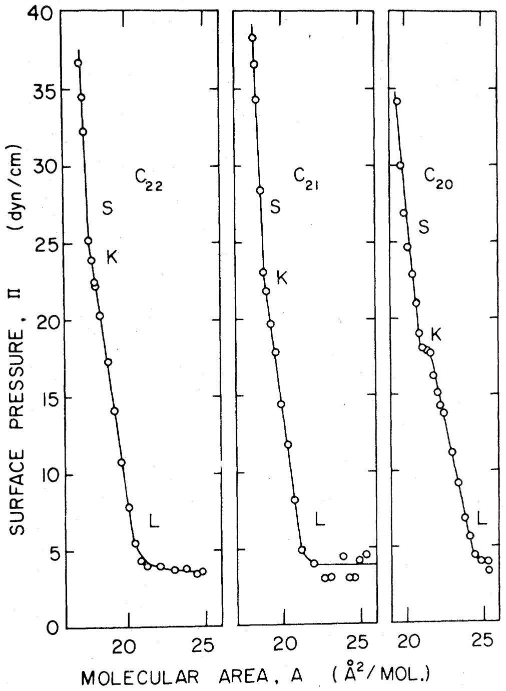

FIG. 1. Plots of the surface pressure Π vs molecular area A for long-chain fatty alcohols of the form $C_nH_{2n+1}OH$ for $n = 20$, 21, and 22.

quency) shear modulus, and the remaining parameters describe two (independent) internal relaxation processes of strengths A and B and relaxation time constants τ_1 and τ_2, respectively. Note that the static (or zero-frequency) shear modulus is given by $\mu_0 \equiv \mu_\infty(1-A-B)$. The parameters are extracted from least-squares fits to the observed time-dependent annulus response.

Figure 1 shows the Π-A relations for several long-chain fatty alcohols $C_nH_{2n+1}OH$ with $n = 20$, 21, and 22. All measurements were made between 24.6 and 24.8 °C. Figures 2–4 show the pressure dependence of various shear parameters for the same compounds.

Note that the Π-A curves show kinks at pressures of approximately 17.5, 23, and 25 dyn/cm for $n = 20$, 21, and 22, respectively. For the case of $n = 20$, there is a drastic reduction in slope near the kink. The same behavior (for $n = 20$) was observed by Harkins and Copeland[9] and also, at reduced temperatures, for $n = 18$ and 19.

The damping for $n = 20$ was such that both the dynamic and static methods could be conveniently applied; Fig. 2(b) shows a plot of $\mu'(\omega)$ and $\mu''(\omega)$ at the rotor ringdown frequency of ~1 Hz. Note that both quantities *fall* with increasing Π and that above a pressure of about 17.5 dyn/cm, μ' and μ'' abruptly become pressure independent. The data of Fig. 2(a) show that both μ_0 and μ_∞ fall, to a value below our sensitivity, with Π greater than 12 dyn/cm. Taken together these two data sets suggest that, for $n = 20$, the kink signals compression-induced *melting* rather than freezing and that the Harkins L phase[9] is most likely a solid. This is to be contrasted with our earlier work[2] on stearyl alcohol ($n = 18$) where a solid phase exists above the kink (albeit one with an exceedingly small shear modulus).

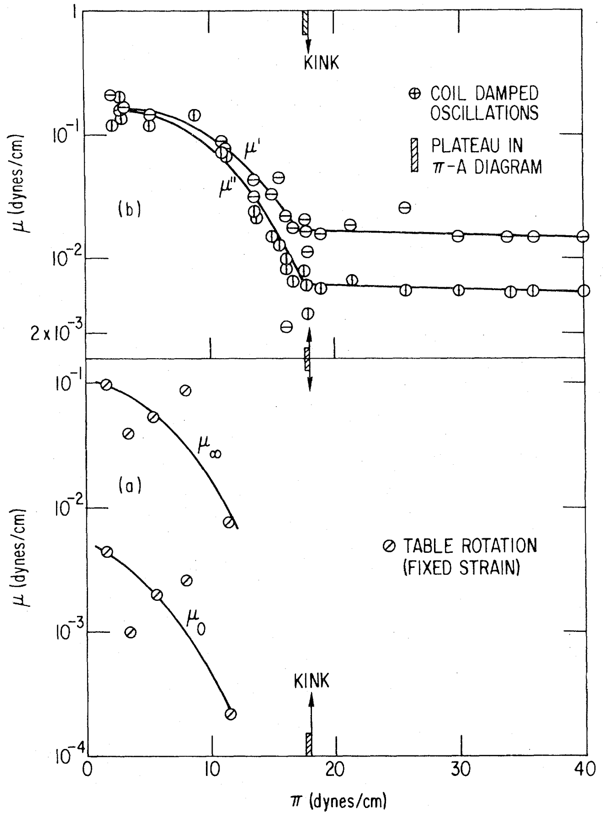

FIG. 2. (a) The parameters μ_0 and μ_∞ resulting from the time-dependent behavior of the rotor following trough rotation for the compound $C_{20}H_{41}OH$. (b) The pressure dependence of the in-phase (μ') and out-of-phase (μ'') components of the dynamic shear modulus resulting from the ringdown behavior of the rotor (near its natural frequency of ~1 Hz) following a step rotation for the compound $C_{20}H_{41}OH$.

Figure 3(a) shows the data for μ_0 and μ_∞ for the case $n = 21$. Note that the magnitudes for μ_∞ and μ_0 differ by a factor of approximately 100. Thus our films are exceedingly viscoelastic. What is unique, however, is that both moduli fall to a value below our detection sensitivity for an intermediate range of pressures. If the static

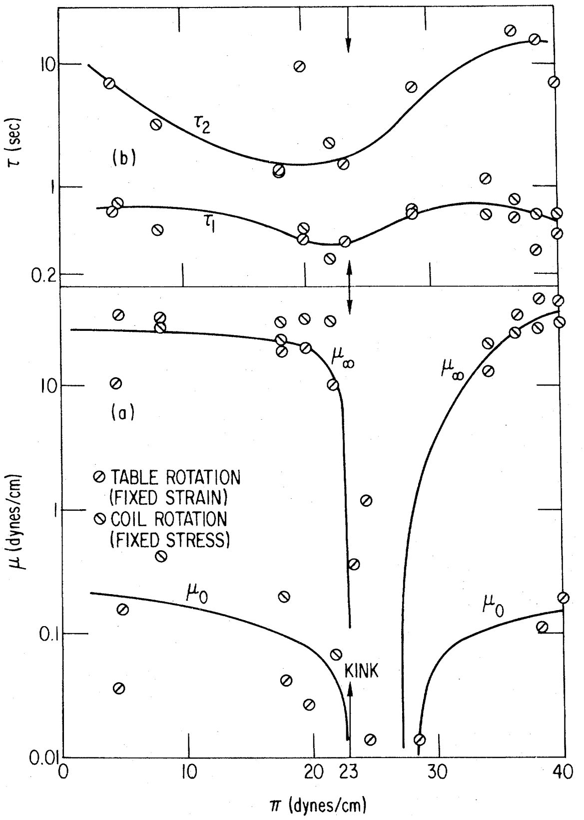

FIG. 3. The pressure dependence of μ_0 and μ_∞ for the compound $C_{21}H_{43}OH$. Data shown are deduced from both coil-rotation and trough-rotation experiments. (b) The pressure dependence of τ_1 and τ_2 for the compound $C_{21}H_{43}OH$. Data shown are deduced from both coil-rotation and trough-rotation experiments.

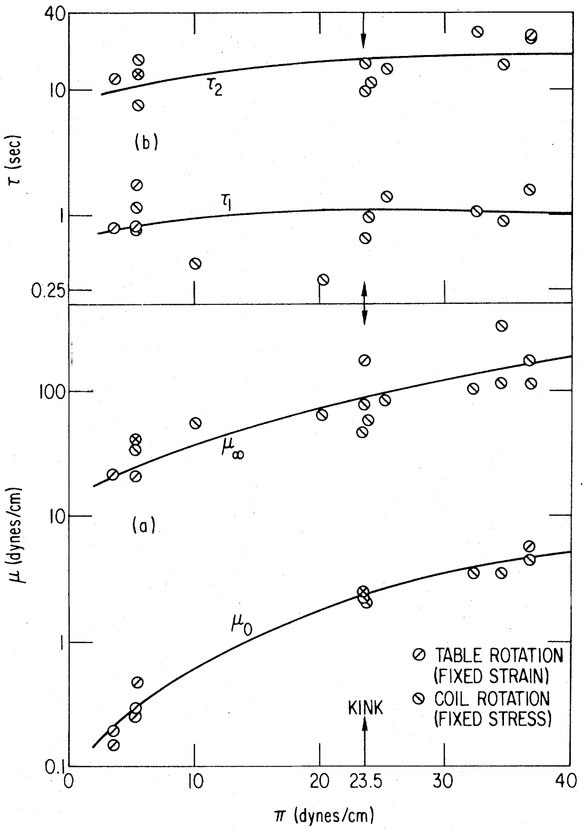

FIG. 4. The same as Fig. 3 for the compound $C_{22}H_{45}OH$.

modulus (μ_0) is in fact zero for this interval, we have observed a reentrant behavior: solid-(anisotropic?) liquid-solid. The low-pressure side of this interval coincides with the Π-A kink position of Fig. 1 (and, as for $n = 20$, corresponds to compression-induced melting). On the other hand, the high-pressure side of the interval, presumably marking an independent line of phase transitions in Π-T space, does not appear to contribute an observable anomaly to the Π-A diagram, although the Ehrenfest criteria would require it.[10] Thus higher-resolution Π-A studies would be desirable. If the higher-pressure side of the window of vanishingly small shear modulus is, in fact, a phase transition, it suggests that the phase diagrams of monolayer systems may be considerably richer than has been previously suspected and that shear studies are a powerful (and possibly necessary) probe.

Little can be said concerning the data on the relaxation times, τ_1 and τ_2 [Fig. 3(b)]; we offer the data for completeness only.

Finally, in Fig. 4, we examine the case of $n = 22$. Here the moduli show a monotic behavior, i.e., no melting/freezing transitions (the relaxation times are essentially constant). The break in the Π-A curve at 25 dyn/cm must then correspond to a solid-solid transition!

In conclusion we have demonstrated that (1) the conventional phase assignments in the long-chain fatty alcohols $C_nH_{2n+1}OH$ appear to be largely in error, (2) compression-induced melting and even reentry likely exist, and (3) additional phase boundaries appear to be present which have gone undetected in Π-A studies.

This work was supported primarily by the U.S. Department of Energy; some support was received from the National Science Foundation under Grant No. DMR 81-07385.

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[9] W. D. Harkins and L. E. Copeland, J. Chem. Phys. **10**, 272 (1942). The most complete work was for $n = 18$; a detailed study of the Π-A diagram for various temperatures revealed that there was a range of temperatures extending from about 7.5 to 11 °C where Π was essentially constant for a finite change in area, indicative of a first-order transition. Above and below this interval only kinks were observed implying second-order transitions. From surface viscosity measurements, L. Fourt and W. D. Harkins, J. Chem. Phys. **42**, 897 (1938), discovered a triple point at 7.5 °C where the pressure of the third phase boundary increased much more rapidly with temperature. {The spontaneous change from first order to second order on the lower branch would be a tricritical point [L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980), p. 493].} A triple (or bicritical) point, involving the junction of two lines of second-order and one line of first-order transitions, is one of the allowed classes considered by Lifshitz (Ref. 3). {We are unaware of a generalization of Lifshitz's analysis based on modern ideas where topological order is considered, except for absorbed monolayers on crystalline solid surfaces [see for example J. M. Shick, Prog. Surf. Sci. **11**, 245 (1981)].} The phases I, II, and III of the Lifshitz classification would (Fig. 4 of that work) be the S, LS, and L phases of Harkins and Boyd. Since the I (or S) phase is always the most symmetric, the II (or LS) and III (or L) phases must be anisotropic; i.e., they *cannot* be 2D isotropic liquids, although a 2D tilted liquid-crystal-like phase is not forbidden.

[10] It is also possible that the kink does not appear in the Π-A diagram if the phase transition is of the dislocation-mediated type. This is because the slope in the Π-A diagram does not represent a true "lattice compressibility" if the vacancies are not conserved. See D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979), footnote 37.