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Shear response of Langmuir monolayers of heneicosanoic (C_{21}) acid studied using a torsion pendulum

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We have studied the shear relaxation of heneicosanoic (C_{21}) acid monolayers on the surface of water at different temperatures and pressures, in the CS, L_2'', L_2', and S phases. A torsion pendulum was displaced from its equilibrium position by an angle $\theta(0)$ and the relaxation $\theta(t)$ was measured. Only the CS phase sustains a static shear (~160 dyn/cm) at the time scales studied ($\approx 10^3$ s). The data fit well to a stretched exponential form $\theta(t)=\theta(\infty)+\{\theta(0)-\theta(\infty)\}\exp\{-(t/\tau)^n\}$. We find that $k\tau^n/n$ is independent of the torsion constant k; this implies that the viscosity is time dependent. $k\tau^n/n$ is a strong function of pressure and temperature. At phase boundaries there is a discontinuity in either $k\tau^n/n$ or its slope. [S1063-651X(96)09407-X]

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I. INTRODUCTION

X-ray diffraction studies of Langmuir monolayers of fatty acids with different chain lengths have revealed that all the phases observed in these monolayers show some degree of order and that two of the phases may have long-range order [1–5]. It has also been reported that certain phases of heneicosanoic acid monolayers develop surface tension anisotropy when uniaxially compressed [6]. From this it was concluded that the phases which show surface tension anisotropy are solid phases and those which do not are mesophases. However, this does not provide quantitative information about the shear modulus or viscosity, nor does it yield any qualitative insight about the interactions at the molecular level.

To determine the viscosity and/or shear modulus of Langmuir monolayers we chose to study heneicosanoic (C_{21}) acid using a torsion pendulum. In an overdamped decay, the time dependence of the rotor angle potentially yields information on the molecular interactions involved; e.g., if the decay fits to a single exponential then it is usually assumed that only one type of molecular interaction dominates the decay. Historically, an activation energy has been deduced from the viscosity [7,8] and some specific molecular interaction can often be associated with the activation energy. Similarly, if the data fit a functional form with two time constants (i.e., sum of two exponentials) then we might conclude that there are two dominant decay processes. In our experiments we find that the functional form of the decay angle cannot be adequately described as the sum of one or two exponentials.

II. EXPERIMENTAL DETAILS

To minimize the anisotropy created by uniaxial compression we used a centrosymmetric trough. This instrument uses twelve radially symmetric ''fingers,'' holding an elastic band that acts as a barrier for the monolayer [9] (see Fig. 1). The fingers move in or out synchronously, driven by an electric motor. The resulting 12-sided polygon approximates a circle. Since the compression is approximately a shape-conserving operation in this geometry, a macroscopic surface tension anisotropy is suppressed; in the limit that the inner radius is much smaller than the outer radius, the compression is essentially hydrostatic (isotropic).

To measure the surface tension we used a capillary wave probe. Capillary waves are generated on the surface of the film by applying an alternating voltage to a horizontal blade kept just above the water surface [10]. At a fixed horizontal distance from the blade, the motion of the surface is detected by reflecting a laser beam from the surface of the water and processing the resulting interferometric response. The amplitude of the interference pattern contains the necessary information about the phase and amplitude of the capillary wave, which in turn can be related to the capillary wavelength (from which we obtain the surface tension) and the attenuation. This technique is discussed in detail elsewhere [11].

A schematic diagram of our torsion pendulum is shown in Fig. 1. The torsion pendulum itself is constructed from components which were originally part of an induction galvanometer. The moving coil (to which the rotor is attached), is suspended between the poles of a permanent magnet. The static flux density is approximately 8.0 kG. Field coils,

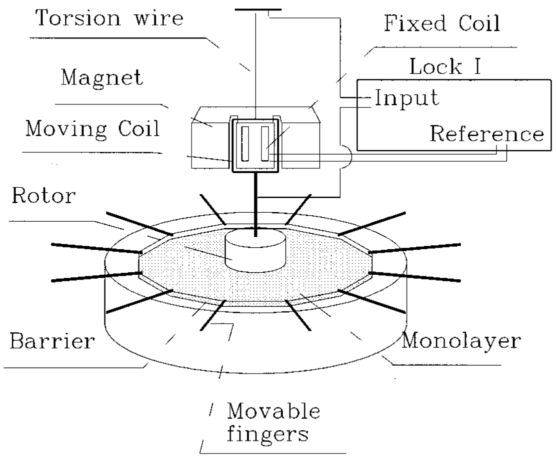

FIG. 1. Schematic diagram of the centrosymmetric trough and the torsion pendulum. The area is controlled by an elastic band (which plays the role of barrier in a conventional trough) and radially movable fingers (which support the band).

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through which a high-frequency alternating component of magnetic flux can be superimposed on the static field, are attached to the permanent magnet. The (saturated) solid iron flux paths are not efficient for coupling the high-frequency component of the flux. Conversely, magnetic materials used for high-frequency applications generally have permeabilities which are too large for the relatively high level of steady flux from the permanent magnet. For this reason, iron powder–resin compacts were inserted into each pole piece as well as the core [12].

The torsion wire is used as one of the electrical leads to the moving coil. The other electrical lead is placed in a cup of mercury. This prevents any misalignment of the movable coil which, in turn, would displace the rotor from the vertical. The deflection of the movable coil is measured as follows. When it is parallel to the alternating field, the signal picked up from the high-frequency coil is zero. When the coil makes a nonzero angle with the field, a high-frequency voltage is induced in the coil. For the small angular displacements (~mRad) employed here the magnitude of this signal is directly proportional to the angle of deflection. This signal is fed to a lock-in amplifier.

To measure the shear modulus and viscosity of the monolayer the rotor is turned through an initial angle $\theta(0)$ by passing a direct current through it. This is done at low pressures where the film has a negligible effect on the rotor. The film is then compressed to the desired pressure. The current through the coil is then switched off. If the film has a finite static shear modulus then the angle between the magnet and the coil will be nonzero even when the initial decay has stopped. This static shear modulus is calculated using the expression [13]

$$k\theta(\infty)+\left\{\frac{4\pi(r_0 r_i)^2}{r_0^2-r_i^2}\right\}[\theta(\infty)-\theta(0)]\mu=0. \tag{1}$$

Here k is the torsion constant, r_i is the rotor radius, r_0 is the outer radius of the film (defined by the position of the elastic band), and μ is the shear modulus.

The temperature was kept constant within ±0.1 °C by circulating water underneath the trough and above the lid. The pressure was constant within ±0.1 dyn/cm except for the high-pressure CS and S phases where the pressure was accurate within ±1 dyn/cm.

III. RESULTS AND DISCUSSION

The experiments to be discussed here involve heneicosanoic (C_{21}) acid monolayers in the temperature range 2–10 °C and at pressures between 10 and 35 dyn/cm. Figure 2 shows pressure vs area isotherms for various temperatures. The relevant phases are identified by CS, L_2'', L_2', and S.

The static shear modulus (μ) was found using Eq. (1). For all the phases studied here with the exception of the CS phase, the value of μ was zero within the experimental limits. In CS phase μ was found to be =160 (±50) dyn/cm. This value is an average value in the CS phase over all the pressures and temperatures studied. The large error bar stems from the fact that there is a large uncertainty in the value of $\theta(\infty)$ because decay is very slow. Since μ is directly proportional to $\theta(\infty)$ these errors are reflected in μ. These errors make it impossible for us to measure a significant pressure or temperature dependence.

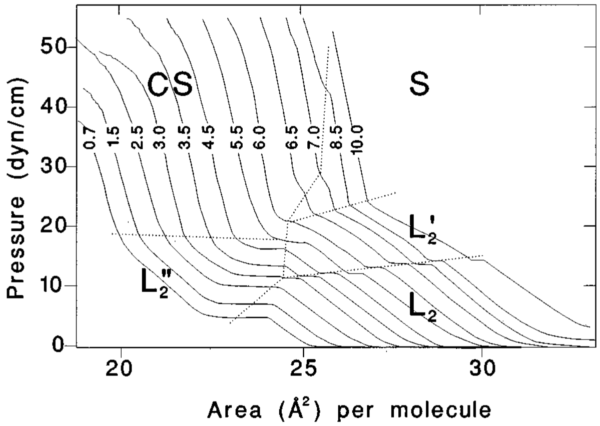

FIG. 2. The isotherms of C_{21} acid monolayers. The area values correspond to the first isotherm; the rest have been shifted horizontally for clarity. The dotted lines are drawn to guide the eye. (From Ref. [1].)

If there is only one dominant time constant responsible for the decay of mechanical shear then we would expect the angle as a function of time to be given by

$$\theta(t)=\theta(\infty)+\{\theta(0)-\theta(\infty)\}\exp(-t/\tau). \tag{2a}$$

Similarly, if there are two such times governing the decay, then the equation would be as follows:

$$\theta(t)=\theta(\infty)+\{\theta(0)-\theta(\infty)\}[A\ \exp(-t/\tau_1)+(1-A)\exp(-t/\tau_2)]. \tag{2b}$$

Here A and $1-A$ are the relative ''strengths'' of the two contributions and τ_1 and τ_2 are the corresponding time constants, $\theta(0)$ is the initial angle to which the rotor is displaced, and $\theta(\infty)$ is the final angle of the rotor (after the initial decay has stopped). However, we found (see Fig. 3; data in the CS phase at 2 °C) that a stretched exponential, i.e., a function of the form

$$\theta(t)=\theta(\infty)+\{\theta(0)-\theta(\infty)\}\exp\{-(t/\tau)^n\}, \tag{3}$$

where τ is an effective relaxation time and $0<n<1$ fits much better than the two-exponential form, while having fewer parameters.

Stretched exponentials have been observed in many systems dating back to the middle of the 19th century [14–17]. Though various theoretical models have been proposed [18–21], there is no consensus about the physics responsible for this behavior. One popular model assumes the presence of an ''energy landscape'' involving a large number of metastable ''ground states'' with similar energies. This picture is expected to be true for complex biological molecules [22]. Whether the various configurations of a Langmuir monolayer involving a 21-carbon organic acid can provide the necessary landscape is an open question.

Since the viscosity of the monolayer varies by four orders of magnitude, in the temperature and pressure range studied, it is not possible to use the same torsion wire for all the

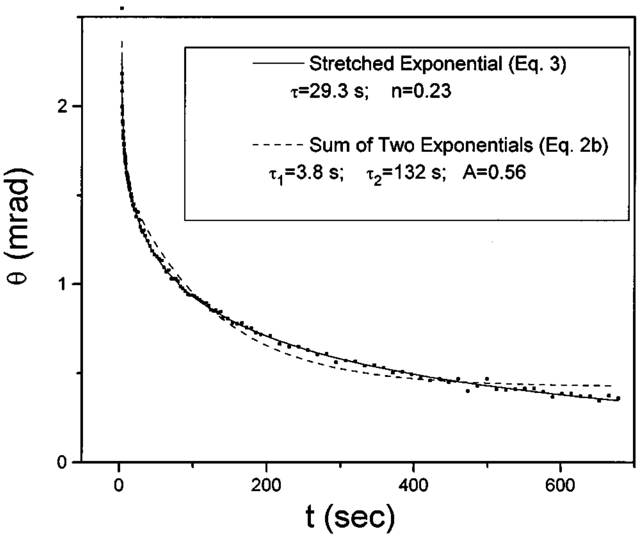

FIG. 3. The rotor angle as a function of time in the CS phase ($T=2$ °C, $\Pi=39.2$ dyn/cm) showing the best fits to a stretched exponential and to a sum of two exponentials.

phases. A typical wire (with torsion constant $k=25$ erg) used in the L_2 phase would yield $\tau\approx 10$ s. If the same wire were used for the CS phase where the monolayer has a large viscosity, the relaxation time would be $>10^6$ s. This can be avoided by using a wire with higher k. However, to compare the results one must then find a quantity that is independent of the value of k used. We now show that $k\tau^n/n$ may be such an ''intrinsic'' quantity.

Consider the equation of motion for the rotor

$$I\frac{d^2\theta}{dt^2}=-k\theta-\eta\frac{d\theta}{dt},$$

where I is the moment of inertia of the rotor, k is the torsion constant of the wire, and η is an effective damping factor. Since the pressure and temperature range and the torsion constant k were all chosen to yield an overdamped decay, the decay was monotonic and slow. For a typical data set ranging from $t=0$ to $t^{\sim}\ 10^3$ the magnitude of $(I\ d^2\theta/dt^2)/\kappa\theta$ calculated from raw data is less than 0.01 after the first 0.5 s. The ratio drops to less than 0.001 after the first 3 s. This can be verified using, for example, the data in Fig. 3, with $I=143.6\ \mathrm{g\,cm}^2$ and $k=21\,482$ erg. Hence the term $I\ d^2\theta/dt^2$ can be neglected. Then, if we substitute $\theta(t)=\theta(0)\exp\{-(t/\tau)^n\}$ we get $k\theta=\eta\theta(n/\tau^n)t^{n-1}$, which yields,

$$\eta=(k\tau^n/n)t^{n-1}. \tag{4}$$

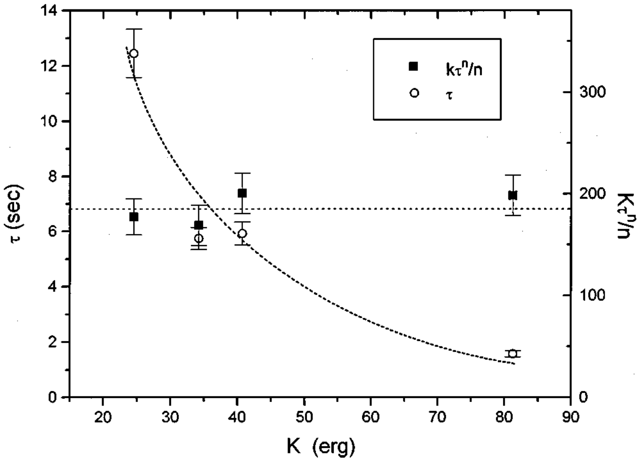

FIG. 4. The quantity $k\tau^n/n$ (■) and τ (○) as a function of k, the torsion constant. The dotted lines are drawn to guide the eye.

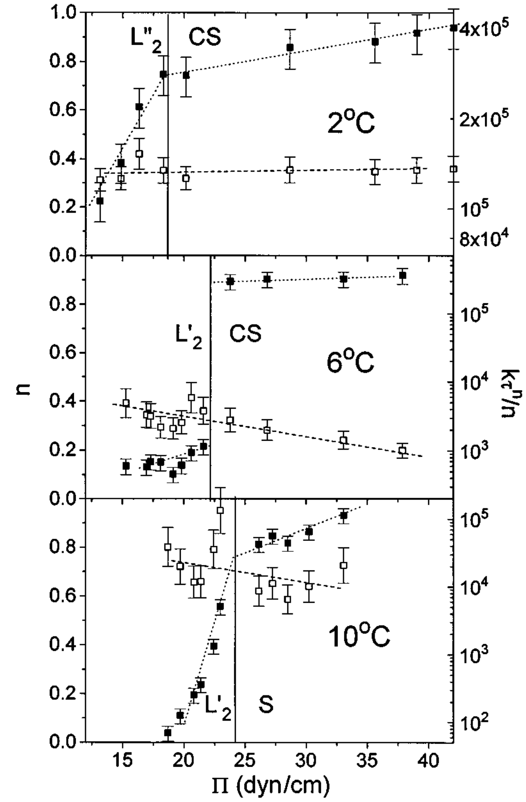

FIG. 5. Stretched exponential parameters $k\tau^n/n$ (■) and n (□) as a function of pressure at 2, 6, and 10 °C. The vertical lines indicate the phase boundaries. The dotted lines are drawn to guide the eye.

In other words, a time-dependent effective damping constant η results in a stretched exponential form. Though the exact time dependence is not understood, it seems likely that a distribution of damping processes operating on different time scales would yield some kind of time dependence for the effective damping coefficient. Since $0<n<1$, η decreases as time goes on. This is plausible if as the time increases, the damping processes with smaller time scales ''die out.'' Nevertheless, we have succeeded in isolating a wire-independent quantity, namely, $k\tau^n/n$ (when $n=1$, this reduces to $k\tau$, as expected for a simple exponential response). Figure 4 shows the graph of $k\tau^n/n$ and τ as a function of the torsion constant k in the L_2' phase at 8 °C. Note that the value of k changes by a factor of 4 and τ varies by a factor for 10, yet $k\tau^n/n$ remains essentially constant. The four points shown are averages of three data sets each for a given torsion constant.

The reproducibility of the data was checked in the L_2' phase of 6 °C using the same wire. The value of $k\tau^n/n$ was reproducible on average within ±10%. In most of the cases the crucial data near the phase boundaries were taken using two different torsion constants, and we find that the data overlap. Figure 5 shows the wire-independent quantity $k\tau^n/n$ and the exponent n as a function of pressure at 2, 6, and 10 °C. The data reported here are all restricted to the high-pressure and intermediate-pressure phases only. This is because, in a low-pressure phase such as the L_2 phase, the response of the torsion pendulum is of the same order as that of surfactant free water; i.e., a torsion constant of approximately 1 erg leads to a relaxation time of order 1 s. We are then no longer in the overdamped regime (where we can safely neglect the term involving $I\ d^2\theta/dt^2$). At 2 °C there is a transition from the L_2'' phase to the CS phase. This transition is known to be second order [1]. The isotherm (Fig. 2) shows a ‘‘rounded kink’’ for this transition. The plot of $k\tau^n/n$ also shows a change of slope at the transition point. At 6 °C there is a transition from the L_2' phase to the CS phase. This is a first order transition [1]. Correspondingly, $k\tau^n/n$ shows a discontinuity. This is by far the most dramatic jump observed for the quantity $k\tau^n/n$, where it changes from $\approx 10^2$ to $\approx 10^5$. The 10 °C data show an apparently second-order phase transition from the L_2' phase to the S phase [1]. The slope of $k\tau^n/n$ changes substantially at the phase transition. When these three graphs are taken together, we see that $k\tau^n/n$ always decreases as the temperature is increased. Considering that $k\tau^n/n$ is the magnitude of the effective damping of the film, these graphs give us a qualitative picture of the damping as a function of pressure and temperature. At the phase transitions the behavior as a function of pressure reflects the order of the transition through the corresponding kinks and the discontinuities. It is difficult to discern any pattern in the behavior of the exponent n as a function of temperature and pressure, although we can see a trend of higher values of n for higher temperature. The case $n=1$ implies simple exponential decay with one time constant. The other extreme, $n=0$, implies an ideal solid. The higher the temperature, the more the film resembles a simple ‘‘fluidlike’’ system with only one dominant decay mechanism. At this stage we do not have a clear picture as to what the quantity $k\tau^n/n$ and the exponent n mean physically. However, in view of Eq. 4, and the fact that the quantity $k\tau^n/n$ is found to be a constant, we are led to conclude that the effective damping factor η is time dependent. The origin of this time dependence is not understood at present; hopefully our data can provide insight into the molecular relaxation mechanisms involved.

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