Shear Viscosity of Langmuir Monolayers in the Low-Density Limit

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We have measured the shear viscosity in the liquid phase of several Langmuir monolayers with an accuracy better than 30%. The method is based on the optical monitoring of the Brownian diffusion of submicron latex spheres floating at the air-water interface. The values are between 1 and $10^{-10}$ N s m$^{-1}$, which is 10 to 100 times lower than previous data on similar systems. For $N$-palmitoyl-6-$n$-penicillanic acid and $L$-α-dipalmitoylphosphatidylcholine, the variation of the shear viscosity with surface density agrees with a classical free area model, whereas for pentadecanoic acid we observe a compensation effect.

Important phenomena, such as the fusion of vesicles, the breakdown of foams and emulsions, and the opening of transitory pores in membranes, are governed by the viscoelastic properties of ultrathin films of amphiphilic molecules. Two distinct viscosity coefficients are involved, one for compression and one for in-plane shear (we neglect here the transverse shear viscosity which is significant only in solidlike films) [1]. Langmuir monolayers of insoluble organic surfactants spread at liquid-air interfaces provide a convenient model of such fluid films because their density can be varied over the entire range from gaseous up to solid crystalline [2]. In addition, their surface rheology can be studied by a variety of experimental techniques. The compression viscosity for monolayers of short chain amphiphiles has been investigated by surface light scattering. It is typically $10^{-5}$ N s m$^{-1}$ at high densities (e.g., in the partially ordered $L_1$ phase) and $10^{-7}$ N s m$^{-1}$ at low densities (the isotropic fluid denoted $L_2$ phase) [3,4]. The shear viscosity is much less known because most of the measurements thus far have been based on macroscopic mechanical techniques such as the torsion pendulum or the oscillating magnetized rod. Values of the order of $10^{-5}$ N s m$^{-1}$ have been reported in the $L_2$ phase but only an upper limit of $10^{-7}$ N s m$^{-1}$ in the $L_1$ phase [5,6]. Ingenious optical methods based on the observation of the motion of $L_2$ domains in the $L_1$ phase have also been tried because they are less perturbative. However, the reported data are widely scattered. Wurlitzer et al. have found $10^{-7}$ N s m$^{-1}$ by measuring the drag force acting on a translating $L_2$ domain with an optical tweezer setup [7]. In separate experiments, Klingler et al. [8] and Schwartz et al. [9] have reached the very different conclusion that the shear viscosity was probably less than $10^{-9}$ N s m$^{-1}$. Another drawback of these optical approaches is that they measure the shear viscosity at a single value of the surface density in the $L_1$ phase, corresponding to the $L_1$-$L_2$ coexistence region.

In this Letter, we present the first quantitative measurements of the shear surface viscosity in the entire $L_1$ phase, and for three different amphiphiles. The experimental method is based on the optical tracking of the Brownian motion of submicron latex particles floating at the air-water interface. It is well suited to low density phases and yields the viscosity with an accuracy of 30%. We also report two distinct behaviors of the shear viscosity versus monolayer density depending on the structure of the amphiphiles.

Brenner and Leal [10] have shown that the Brownian diffusion of a solid sphere of radius $R$, and confined at the interface between two immiscible fluids, can still be described by the classical Einstein formalism $D = kT/\eta R$. The friction factor $f$ is a complicated non-linear function of the contact angle of the particle and the two liquid viscosities. Only its functional form could be given in the original paper. Their theory has been later extended by Danov et al. [11] to the case of viscous monolayers at water-air interfaces. Although the boundary conditions for the Navier-Stokes equations contain second-order derivatives of the velocity, for which no analytical solutions are known, it was shown that the drag coefficient can be computed numerically by taking a specific bicylindrical coordinate system of revolution. At fixed contact angle, $f$ increases approximately linearly to the bulk water viscosity $\eta_w$ times the reduced parameter $E = \eta_s/\eta_w R$, where $\eta_s$ is the monolayer viscosity. For a half-immersed particle of micron size, $E$ changes from 0 to 10 for $\eta_s$ values between 0 (no monolayer) and $5 \times 10^{-9}$ N s m$^{-1}$ and the corresponding friction factor ranges from 3 to 13. An additional simplification is that $f$ varies only weakly with $\theta$, especially at large $E$: It changes by less than 5% for contact angles between 20° and 90°. Danov’s calculations can be compared to earlier predictions by Saffman and Delbrück [12] and by Hughes, Pailthorpe, and White [13] for a cylinder of radius $R$ and length $L$ floating in a membrane surrounded by fluids. In their case, $f$ takes a comparable value of 16 when $E = 10$ and the cylinder length equals the membrane thickness. It can also be noted that the value of 3 obtained when $E = 0$ was already known in the literature and is exactly half that for a sphere diffusing in bulk.
Experimentally, we have selected polystyrene spheres with a diameter of 0.4 μm (Interfacial Dynamics Corp., Batch 2-63-46.186), which are large enough to be easily detected under an optical microscope. The beads were thoroughly cleaned with mixed-bed ion exchange resins (BioRad AG 501-X8) (30% v/v) to remove the soluble surfactants which could adsorb at the air-water interface and perturb the measurements. Small aliquots (3 μl) of the final bead-methanol suspension (C = 1 g/l) were spread on ultrapure water (Elga Maxima, resistivity \(2 \times 10^{14} \Omega \cdot \text{cm}\)) in a temperature-controlled Teflon Langmuir trough of dimensions 100 × 30 × 3 mm\(^3\). A glass window in its bottom allows optical observations of the interface with an inverted microscope (Reichert-Jung MeF 3) at 400× magnification. After evaporation of the methanol, most of the beads were well separated and at arbitrary positions on the water surface. The macroscopic drifts were efficiently minimized by limiting the effective monolayer area with the help of a stainless steel collar as in [8]. Because of their small size, the beads were observed to undergo vigorous random Brownian motion in the plane of the air-water interface. The beads motion was recorded over a period of 10 sec at 25 frames per second. The procedure was repeated 5 times at different positions in the monolayer and the mean square displacements (MSD) between all possible pairs of beads in each sequence were then calculated and plotted as a function of time. Trajectories which differ in their MSD along two arbitrary orthogonal directions by more than 10% were not analyzed because it indicates that local inhomogeneous drifts are superimposed on the Brownian diffusion.

Langmuir films were spread from chloroform solutions (analytical grade Chromanorm, Prolabo) of three different amphiphiles. The first two, namely, pentadecanoic acid (PDA, Fluka) and L-α-dipalmitoylphosphatidylcholine (DPPC, Sigma) were purchased commercially whereas N-palmitoyl-6-α--penicillanic acid (PPA) was synthesized in the laboratory. All had purity > 99%. After approximately 15 min to allow solvent evaporation, the monolayer surface pressure was measured as a function of the molecular surface density by using a \(\mu\)-balance from Riegler&Kirstein (Wilhelmy plate method) with a relative accuracy of 0.1 mN m\(^{-1}\). The phase diagrams were further determined by using the preferential partitioning of a fluorescent marker (4-hexadecylamino-7-nitrobenz-2-oxa-1,3-diazole, Molecular Probes) to visualize the transition between the \(L_1\) phase and the \(L_1-L_2\) coexistence region. All bead diffusion experiments were performed exclusively in the homogeneous \(L_1\) phase. The phase that we have worked in can be identified as an isotropic liquid by the following arguments.

1. It is the first phase that appears upon compressing the gas phase and the transition is first order. In the two-phase coexistence region, foam structures typical of a dispersion of gas in a continuum liquid phase (or vice versa depending on the respective proportion of the two components) have been observed by fluorescence microscopy for each one of the three compounds. At extremely low liquid content, the liquid regions take a circular droplet shape, as expected for an isotropic fluid [14].

2. Fatty acids and phospholipids analogous to PDA and DPPC compounds have been extensively studied in the literature and no x-ray Bragg diffraction peaks have ever been reported in this range of low surface densities. The Bragg peaks start to be observed when the surface density is roughly 2 times higher (see, for example, [15,16] for myristic acid and L-α-dimyristoylphosphatidylcholine that have phase diagrams similar to PDA and DPPC, respectively).

The beads were incorporated in the most expanded state of the monolayer, which was then slowly compressed to the desired final surface density. Typical bead density was 1/400μm\(^2\). This is low enough to make long-range hydrodynamic interactions negligible. The small size of the beads also precludes possible deformations of the interface by gravity, which could have led to spurious capillary interactions. Their contact angle with water was measured by observing optically the penetration depth of large polystyrene spheres (6 to 10 μm) localized at the meniscus of a sessile drop on a silanized glass plate. It was found to be 50° ± 5° for pure water and 30° ± 5° for an interface saturated with PDA.

In Fig. 1, we show the results of a calibration experiment in which the beads diffuse at a free water surface, with no monolayer present. The linear variation predicted by the Stokes-Einstein relationship \(\langle R^2 \rangle = 4Dt\) is observed for time intervals not exceeding 5% of the total duration of the experiment. For longer intervals, the behavior appears much more erratic. This is due to the difference in the number of data points which can be used for the averaging. The first point is calculated using 250 relative bead positions, whereas the last one corresponds to a single event. The initial linear slope yields \(D = 1.33 ± 0.02 \mu m^2 s^{-1}\). Significant variability in the shape of the curve was observed between different pairs of beads in the same sample and also from sample to sample. Therefore we have averaged all results first on a per sample basis and then over all different samples, giving them the same statistical weight. This double averaging yields a final value \(D = 1.26 ± 0.19 \mu m^2 s^{-1}\) for the diffusion coefficient of the 0.4 μm beads at the water surface [17]. Using the Danov calculations, we obtain 1.24 \(\cdot\) \(10^{-3}\) N s m\(^{-2}\) for the viscosity of the aqueous subphase at 22°C (using \(\theta = 50°\) and \(R = 0.2 \mu m\)). All of our data are normalized to this reference value [18].

The diffusion experiments on three different Langmuir films were then performed at several surface densities within the \(L_1\) phase. The results are plotted in Fig. 2 and the inset shows the generic phase diagram obtained from the surface pressure isotherm measurements. The \(A_T\) value at which the homogeneous \(L_1\) phase is replaced by a biphasic \(L_1-L_2\) coexistence region is 27 and 48.5 Å\(^2\) for
PDA and PPA, respectively, at 22 °C and 70 Å² for DPPC at 26 °C. The corresponding surface pressures (plateau values) \( \Pi \) are 3.5, 15, and 13 mN/m. The variation of \( D \) with \( A \) in the \( L_1 \) phase is strikingly different for the three samples. For DPPC and PPA, \( D \) decreases linearly by 16% upon a 10 Å² reduction in the mean monolayer area. For PDA, the decrease is at most 2% per 10 Å². Considering the error bars, it can be said that \( D \) remains constant as the surface density of the PDA monolayer is decreased by a factor of 1.5.

According to the free area model, the viscosity dependence on the area per molecule is phenomenologically described by

\[
\ln \eta_S = \ln \eta_0 + B \frac{A_{L_2}}{A - A_{L_2}}.
\]  

To check our results against this model, the data of Fig. 2 have been converted into surface viscosities \( \eta_S \) by using the master curve given by Danov and taking 50° for the contact angle. The influence of the monolayer compressibility does not need to be taken into account because the density variations induced by the sphere motion are a negligible fraction of the mean film density (the ratio is \( 10^{-7} \)).

The dependence of \( \eta_S \) versus \( A_{L_2}/(A - A_{L_2}) \) has been plotted in semilog scales in Fig. 3. The values of the surface viscosities in the \( L_1 \) phase for all three compounds fall in the range of 1 to 11 × 10^{-10} N s m^{-1}. Such values are clearly beyond reach for the macroscopic mechanical methods that have a 10^{-7} N s m^{-1} sensitivity limit. On the other hand, the measured data are in line with the estimate of 8 × 10^{-10} N s m^{-1} proposed by Stone [19] for PDA in the \( L_1-L_2 \) biphasic region. His single result was based on a fit between the profiles measured for pressure-driven flows inside a canal viscometer [9] and exact representations of the monolayer and subphase velocity fields. The new set of data is much more precise since the earlier determination by the fit method cannot yield the surface viscosity to better than a factor of 5 when the surface viscosity is small. It also agrees with the results of Klingler and McConnell for the Brownian diffusion of \( L_2 \) domains in the \( L_1 \) phase of DPPC [8]. Although these authors were under the impression that the influence of the monolayer viscosity on the diffusion properties was negligible, their estimate of 0.025–0.1 for \( E = \eta_S/(\eta_w R) \) suggests that

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FIG. 1. (a) Superposition of two snapshots of 0.4-μm polystyrene beads diffusing at the air-water interface. The arrows indicate the direction of motion. Bar length is 10 μm. (b) Relative mean square displacement \( \langle (R_1 - R_2)^2 \rangle \) for one pair of beads. X and Y are two arbitrary orthogonal directions. The variation is linear at short times (see inset) and becomes erratic at long times.

FIG. 2. Diffusion coefficient versus molecular area \( A \) for 0.4-μm spheres in Langmuir monolayers of PDA (○), DPPC (△), and PPA (□). Temperature is 22 °C for PDA and PPA and 26 °C for DPPC. Subphase pH is 2. The inset shows the generic surface pressure isotherm. The homogeneous \( L_1 \) phase exists for \( A > A_T \). The plateau region corresponds to the biphasic \( L_1-L_2 \) region of the phase diagram.

\[
\ln \eta_S = \ln \eta_0 + B \frac{A_{L_2}}{A - A_{L_2}}.
\]
The surface viscosity was between 0.25 and $1 \times 10^{-10}$ N m$^{-1}$ s$^{-1}$.

The finding that the PPA and DPPC data are fitted reasonably well with linear curves indicates that the surface viscosity is mainly governed by the monolayer packing density and geometrical free area. Interestingly, the two slopes are identical despite the fact that DPPC is bicaudal whereas PPA is monocaudal. The bulky DPPC and PPA head groups (according to molecular models their cross section is 54 and 42 Å$^2$, respectively) limits the contribution of the leaner (19 Å$^2$) hydrocarbon chains to the surface viscosity. On the other hand, the nature of the polar heads influences the absolute $\eta_S$ values: they differ by a factor of 5 between DPPC and PPA.

The observation that $\eta_S$ for PDA is independent of the free area is unexpected. This behavior suggests an antagonistic effect which lowers the hydrodynamic friction as the packing density increases. We suspect this to be the consequence of the increase in chain elongation and decrease in chain tilt. Similar pressure-induced effects have been reported in solidlike phases with long-range positional ordering [6,20]. For instance, the surface viscosity drops by a factor of 8 as the molecular tilt decreases to zero in the $L_2$ phase of eicosanol. The hydrocarbon chain tilt cannot be directly measured in the $L_1$ phase but it is clear that the large variations in surface density induce changes in chain ordering which are even more prominent than in the condensed phases.

In conclusion, the present work provides quantitative data of the shear viscosity for monomolecular films in the liquid-expanded $L_1$ phase. The range of values is between $10^{-10}$ N m$^{-1}$ s$^{-1}$ and $10^{-9}$ N m$^{-1}$ s$^{-1}$ for the three amphiphiles studied. This is 2 orders of magnitude smaller that what has been reported in the literature. Two different dependencies of the shear viscosity versus surface density have been observed depending on the respective head group and tail cross sections of the molecules.

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[17] The variability between different measurements limits the accuracy to 20%. This is in agreement with statistical theory [H. Qian, M. P. Sheetz, and E. L. Elson, Biophys. J. 15, 2841 (1994]], considering that for each MSD curve we have applied the linear fit to the first 14 time steps out of 250.
[18] This value is 30% higher than the bulk viscosity of water. We have checked that it is not due to a contamination of the interface by surfactants leaching out from the beads. We have also eliminated the possibility of hydrodynamic coupling between the latex beads by repeating the experiments at lower bead densities. Subtle hydrodynamic effects at the bead surface (slip/no-slip, extra dissipation due to the displacement of the three-phase contact line, etc.) may need further consideration in the theoretical models. We have alleviated this problem by performing relative measurements.