

Fluorinated Langmuir Monolayers Are More Viscous than Non-Fluorinated Monolayers

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The surface shear viscosity of the liquid expanded phase in Langmuir monolayers of fluorinated alcohols differs by orders of magnitude from the corresponding surface shear viscosity of Langmuir monolayers of their non-fluorinated counterparts. The line tension between the liquid expanded and the gaseous phase on the other hand is of similar magnitude for both fluorinated and non-fluorinated surfactants. The difference of fluorinated versus non-fluorinated monolayers is measured by active microrheology and by observing the shape relaxation of distorted liquid expanded domains toward a circular shape. Our microrheology measurements are supported by measurements of the relaxation rates of distortions, which in fluorinated liquid expanded phases are proportional to the deviation of the curvature from the mean curvature, whereas they are proportional to the square of the deviation of the curvature from the mean curvature in non-fluorinated monolayers.

Introduction

The shear viscosity η of a fluid is a measure for the rate dependent stress opposing the shearing of a fluid. Microscopically, the shear viscosity arises due to temporal correlations of the transversal flux of momentum. In a fluid, such correlations arise via the specific interactions between the molecules comprising the fluid. Kubo¹ summarized those facts as

$$\eta = \frac{n}{k_B T} \int_0^\infty d\tau \langle J_{xy} J_{xy}(\tau) \rangle \quad (1)$$

where n denotes the density of the fluid, k_B is Boltzmann's constant, T is the temperature, the brackets $\langle \rangle$ denote the equilibrium thermodynamic ensemble average, and

$$J_{xy} = p_x p_y / m \quad (2)$$

is the transversal momentum flux tensor with \mathbf{p} being the momentum and m the mass of the molecules in the fluid. Kubo's formula predicts that, if the microscopic equilibrium momentum flux correlations are the same for the same molecules in different space dimensions, then the viscosities of the liquid in different space dimensions should simply scale with the density of the liquid in d -dimensions. The surface shear viscosity η_s of a fluid monolayer would hence relate to the corresponding three-dimensional bulk shear viscosity η_b via

$$\eta_s = \frac{n_s}{n_b} \eta_b \approx t \eta_b \quad (3)$$

where n_s and n_b denote the areal and volume density of the molecules that roughly relate as $n_s = t n_b$, with t being the

thickness of the monolayer. The interaction of molecules in a monolayer, however, can be very different than in the bulk, and such differences will show up in a violation of eq 3. Equation 3 is a widely used first guess for the surface shear viscosity of monolayers. Here, we show that microscopic interactions between fluorinated alcohols are different in a monolayer as compared to the bulk and that eq 3 is violated.

Experimental Section

Fluorinated alcohol (1*H*,1*H*-perfluoro-1-tetradecanol; 96%) was purchased from Wako Pure Chemical Industries Ltd. and used without further purification. It was spread onto pure water (Millipore Milli-Q at 18 M Ω cm⁻¹) contained in the Teflon trough from the chloroform/ethanol (4:1 in volume ratio) mixed solution (1 mmol L⁻¹), and allowed to evaporate by waiting for 30 min in each measurement.

The surface pressure–area isotherm was monitored with a NIMA 312D trough (Nima Technology Ltd.) at 298.15 K. Surface pressure was measured by using a Wilhelmy plate made from chromatography paper with a compression rate of 4 Å²/min per molecule.

Nickel nanorods used in the surface shear viscosity measurement were synthesized by the electrochemical deposition of nickel into alumina templates.² Small amounts of nickel nanorods were dispersed in chloroform and placed on the air/water surface with the monolayer. Each nickel rod on the surface was visualized using a microscope (Leica) with a 50 \times long working distance objective. An external magnetic field (1 mT) was applied through the home-built electromagnetic coils, and reorientation of rods was recorded by a CCD camera connected to a PC.

Shape relaxation of liquid expanded domains was observed by a fluorescence microscopy combined with optical tweezers. Fluorescence dye (Texas red-DHPE from Molecular Probes) added in the monolayer was excited by a polarized argon ion laser ($\lambda = 488$ nm) to visualize the monolayer. Liquid expanded domains of the fluorinated alcohol were deformed by focusing the IR laser ($\lambda = 1064$ nm) on the surface, and the relaxation of the deformed domain to the circular shape was recorded by a CCD camera.

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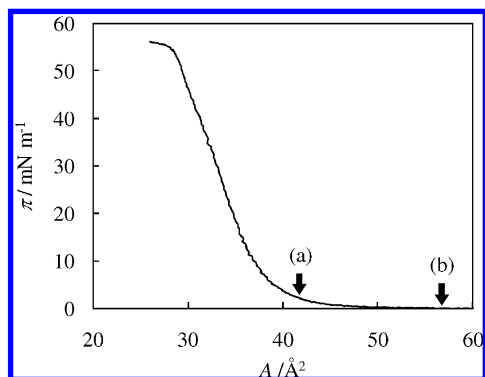


Figure 1. Surface pressure versus area per molecule isotherm. Arrows show the experimental point at which the following measurements are performed: (a) viscosity measurement; (b) shape relaxation measurement.

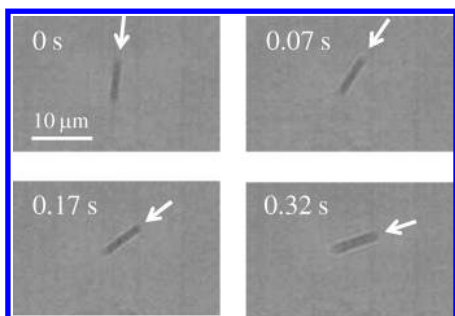


Figure 2. Frame by frame image of the reorientation of a nickel rod in the liquid expanded monolayer.

Experimental Results

Figure 1 shows the surface pressure π versus area per molecule A isotherm of 1H,1H-perfluoro-1-tetradecanol at 298.15 K. The surface pressure is almost zero in the high area region ($A > 50 \text{ Å}^2$), in which the liquid expanded and gaseous phases are coexisting in the monolayer. The surface pressure starts to rise gradually at $A = 50 \text{ Å}^2$ with compression of the monolayer and increases smoothly until the collapse occurs at $A = 28 \text{ Å}^2$ corresponding to the cross-sectional area of the fluorocarbon chain.^{3,4}

We measure the surface shear viscosity of the monolayer by active microrheology.² A nickel rod of length $l = 6 \text{ μm}$ and diameter $d = 200 \text{ nm}$ and magnetic moment⁵ $m = 1.1 \times 10^{-8} \text{ Am}^2$ is immersed into the monolayer at an area per molecule of $A = 42 \text{ Å}^2$ at a surface pressure of 3 mN/m. At this surface density, the monolayer is in the liquid expanded phase. Figure 2 shows transmission microscopy images of the relaxation of the rod orientation when suddenly (at time $t = 0$) applying a magnetic field of $H = 1 \text{ mT}$. The rod initially points into a direction different from the direction of the magnetic field and finally ($t = 0.32 \text{ s}$) adopts the direction of the magnetic field. Theoretically, the reorientation of the nickel rod is described as the balance between the magnetic and viscous torque. This balance gives rise to a differential equation for the angle $\varphi(t)$ between the rod and the magnetic field as a function of time. The solution of this differential equation reads

$$\tan \varphi/2 = \tan \varphi_{t=0}/2 \exp(-t/\tau) \quad (4)$$

where the time constant τ for large surface viscosity $\eta_s \gg \eta_{b,\text{sub}}$ and negligible rod diameter $d \ll l$ reads⁶

$$\tau = \frac{\pi \eta_s l^2}{8 \mu_0 m H} \quad (5)$$

Here, μ_0 is the magnetic permeability of a vacuum, η_s is the surface shear viscosity of the monolayer, and $\eta_{b,\text{sub}}$ is the bulk viscosity of water. Figure 3 shows $\tan \varphi/2$ as determined from the images versus the time together with a fit to eq 4. We find the surface shear viscosity of the liquid expanded phase of the perfluorinated tetradecanol to be $\eta_s = 1.2 \times 10^{-7} \text{ N s/m}$. The corresponding Boussinesq number $B = 28$ is indeed larger than unity.

Additional evidence for this rather large surface shear viscosity $\eta_s \gg \eta_{b,\text{sub}}$ arises when distorting the shape of liquid expanded domains with optical tweezers⁷ and measuring the shape relaxation of the domain. The distortion occurs at an area per molecule of 57 Å^2 where the liquid expanded phase coexists with the gaseous majority phase. The hydrodynamics of unstable or deformed domains has been treated theoretically by Lee et al.,⁸ by Stone and McConnell,⁹ and by Mann et al.¹⁰ In polar coordinates (r, φ) , the dynamics of a slightly deformed domain of radius R is given by

$$r(\varphi, t) = R[1 + \sum \varepsilon_n e^{-\Gamma_n t} \cos(n\varphi)] \quad (6)$$

where ε_n are the Fourier coefficients and Γ_n the relaxation rates of the n th deformation mode. The relaxation rates Γ_n are given by

$$\Gamma_n = \begin{cases} n \frac{\lambda_n}{2(\eta_{s,\text{LE}} + \eta_{s,\text{g}})R} & \text{for } \eta_{s,\text{LE}}, \eta_{s,\text{g}} \gg \eta_{b,\text{sub}}R \\ n^2 \frac{4(n^2 - 1)\lambda_n}{(4n^2 - 1)\eta_{b,\text{sub}}\pi R^2} & \text{for } \eta_{s,\text{LE}}, \eta_{s,\text{g}} \ll \eta_{b,\text{sub}}R \end{cases} \quad (7)$$

with $\eta_{s,\text{LE}}$ being the surface viscosity of the liquid expanded domain and $\eta_{s,\text{g}}$ the surface viscosity of the gaseous surroundings. The line tension λ_n is a mode dependent line tension that is renormalized by electrostatic interactions. If these electrostatic interactions are weak, there is little mode dependence of the line tension. For our fluorinated surfactants, the dominating mode dependency is given by the hydrodynamics. Electrostatic effects can be neglected if there is little mode dependency of the line tension, $d \ln \lambda_n / d n \ll 1$.

The experiments are performed in the coexistence region between liquid expanded (LE) and gaseous phase (G) at a

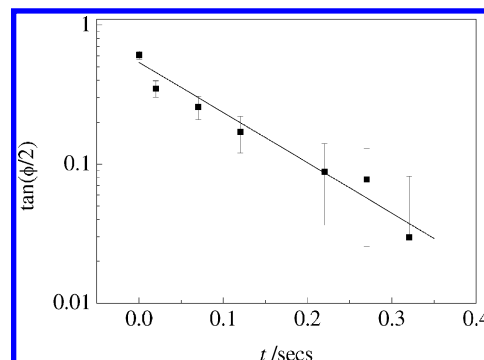


Figure 3. $\tan(\varphi/2)$ versus time plot. The slope of the fit line corresponds to the time coefficient $\tau = 0.12 \text{ s}$.



Figure 4. Fluorescence microscopy images of the shape relaxation of the deformed domain. Fits by eq 6 are added as white lines.

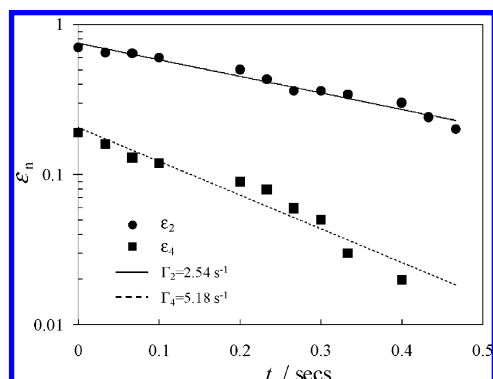


Figure 5. Second and fourth Fourier coefficients versus time plots. Lines indicate the exponential decay of both coefficients with $\Gamma_2 = 2.54 \text{ s}^{-1}$ and $\Gamma_4 = 5.18 \text{ s}^{-1}$.

temperature of 25 °C on pure water ($\eta_{\text{b,sub}} = 0.725 \times 10^{-3} \text{ N s/m}^2$). In Figure 4, an LE-domain of radius $R = 11.0 \mu\text{m}$ is deformed ($t = -0.067 \text{ s}$) by the tweezers (white cross) when flowing through the laser focus. After the domain has passed the laser focus ($t = 0 \text{ s}$), its shape relaxes back to a circle ($0 \text{ s} < t < 0.46 \text{ s}$). We have fitted the shape with eq 6. The resulting fits to the domain shapes are depicted as white lines in Figure 4. Two Fourier coefficients $\varepsilon_n(t) = \varepsilon_n e^{-\Gamma_n t}$ ($n = 2, 4$) of the fit are depicted in Figure 5. Both Fourier components decay exponentially as predicted by eq 6. The ratio of both rates corresponds to the ratio of the mode numbers $n/n' = 2/4$ as predicted by eq 7a, showing that $\eta_{\text{s,LE}} > \eta_{\text{b,sub}} R \approx 10^{-8} \text{ N s/m}$, in correspondence with what was measured with the active microrheology. Furthermore, it shows that the line tension does not depend on the mode n such that electrostatic effects are negligible. Using the liquid expanded viscosity $\eta_{\text{s,LE}} = 1.2 \times 10^{-7} \text{ N s/m}$ from the active microrheology measurement together with eq 7a for the domain mode relaxation rate allows us to also determine the line tension between the liquid expanded and the gaseous phase. The lever rule states that intensive thermodynamic properties should not change as we change the area fractions of the LE and gaseous phase. Hence, we imply that the surface shear viscosity of the LE phase is similar at the surface coverages of 42 and $57 \text{ Å}^2/\text{molecule}$. We find a line tension via eq 7a of $\lambda = 3.2 \text{ pN}$. This value is comparable to line tensions of $\lambda \approx 1 \text{ pN}$ obtained for hydrocarbon surfactants.¹¹

Discussion

Bevengnu et al.¹¹ have shown that the surface shear viscosities of the liquid expanded phase of hydrocarbon surfactants are smaller than $\eta_{\text{s,LE}} < 10^{-9} \text{ N s/m}$. In succession, several groups have tried to quantify the surface shear viscosity^{12–20} of the liquid expanded phase. Microscopic techniques are limited by the microscopic resolution $\Delta x \approx 0.5 \mu\text{m}$. Microscopic rheology therefore is limited by the fact that $\eta_{\text{s,LE}} < \eta_{\text{b,sub}} \Delta x$ and surface viscous effects amount only to a tiny fraction of the dominating viscous dissipation to the water. Accurate measurements of the deviation of the viscous loss from that of an incompressible nonviscous surface together with an equally accurate theory of those deviations are needed to obtain meaningful values of the LE surface shear viscosity. More realistic values of the surface

shear viscosity have been obtained for lipid membranes in the liquid expanded phase using techniques capable of resolving the motion of submicrometer particles in the membrane. Translational diffusion constants of lipids in mixtures of phospholipids and cholesterol measured with fluorescence correlation spectroscopy²¹ and diffusion NMR²² report diffusion constants D of the lipids of $0.1 \times 10^{-8} \text{ cm}^2/\text{s} < D < 20 \times 10^{-8} \text{ cm}^2/\text{s}$. If we assume that those lipids diffuse as individuals without forming larger complexes and neglect the noncontinuous structure of the membrane on the molecular scale, we may fit those single lipid translational diffusion constants using classical formulas of Saffman and Delbrück.²³ We assume the hydrodynamic membrane radius of the lipid is of the order of 5 Å . Under these circumstances, the lipid diffusion constants correspond to surface viscosities of $3 \times 10^{-8} \text{ N s/m} > \eta_{\text{s,LE}} > 1 \times 10^{-10} \text{ N s/m}$. Hence, the surface shear viscosity of a perfluorinated surfactant is larger than the surface shear viscosity of a hydrocarbon surfactant by a factor of $1000 > \eta_{\text{s,LE}}^{\text{F}}/\eta_{\text{s,LE}}^{\text{H}} > 100$, while the ratio of the bulk viscosities²⁴ is $\eta_{\text{bulk}}^{\text{F}}/\eta_{\text{bulk}}^{\text{H}} \approx 4$.

The persistence length L_p measures the distance over which the direction of a chain segment persists, in the time or ensemble average, owing to limited flexibility of the chain. The hydrophobic perfluorinated chains are shorter²⁵ (1.8 nm) than the persistence length of $L_p = 2.8 \text{ nm}$, while hydrocarbon chains of the corresponding hydrocarbon surfactants are longer than the persistence length. Hence, fluorocarbon chains are rigid, while hydrocarbons are flexible. The chain conformation of hydrocarbons is disordered in the liquid expanded phase and the bulk. In the liquid condensed phase, they are orientationally ordered. The rigidity of the fluorocarbon chains leads to a surface induced orientational order in both the liquid expanded and the liquid condensed phases. It is the surface ordering that renders interactions between molecules very different at the surface as compared to the bulk. LC and LE phases are much more similar for the fluorocarbons than for the hydrocarbons. This also shows up in the pressure–area isotherms with a pressure that smoothly increases upon compression of the monolayer. In the hydrocarbons, the transition from the liquid expanded to the liquid condensed phase shows up in discontinuities of the slope of the isotherm. Differences in order between the liquid expanded and the liquid condensed phases of the hydrocarbon chains at the surface are hence much more pronounced than in the fluorocarbons. This might explain why the surface viscosity of the LE phase of fluorocarbons has similar values to the surface viscosity of a LC phase of hydrocarbon surfactants and very different values than the rough estimate given by eq 3.

Conclusions

The interactions of fluorocarbon surfactants in Langmuir monolayers significantly differ from the interactions of the same molecules in the bulk. The difference of interactions manifests in the macroscopic transport properties: The surface shear viscosity of 1H,1H-perfluoro-1-tetradecanol is larger by a factor of 100–1000 than the usual estimate that one obtains by multiplying the bulk viscosity by the monolayer thickness. Macroscopic equilibrium properties like the line tension between

the gaseous and liquid expanded phase seem to be less affected by the difference of interaction. Both findings emphasize that the dynamics is richer than the equilibrium statics of a system.

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