Exploring the "friction modifier" phenomenon: nanorheology of n-alkane chains with polar terminus dissolved in n-alkane solvent

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Dilute solutions of two polar end-functionalized linear alkanes (1-hexadecylamine and palmitic acid), each dissolved in tetradecane, were confined between two mica surfaces and investigated using a surface forces apparatus modified to study shear nanorheology. These two solutions showed similar nanorheological properties that differed from those observed for pure n-alkanes. In static measurements, a "hard wall", rather than an oscillatory force, was observed as a function of film thickness. The polar alkane component formed a weakly adsorbed single layer at each mica surface, disrupting the layered structures found in neat n-tetradecane. In dynamic experiments at low shear amplitude, the storage modulus G' exceeded the loss modulus G'' at low frequencies; above some characteristic frequencies G'' increased such that $G' \approx G''$, indicating significantly more energy loss through viscous modes at higher frequency. When the amplitude was varied at fixed frequency, no stick–slip was observed and the limiting value of the shear stress at high effective shear rate was an order of magnitude less than for unfunctionalized n-alkanes at similar loads. Together, these results show that the addition of a small amount of polar alkane component, by disrupting the layered structures that would have been formed in the neat n-alkane, is effective in suppressing static friction and reducing kinetic friction in the boundary lubrication regime.

Keywords: friction modifiers, thin film lubrication, nanorheology, molecular tribology, surface forces apparatus

1. Introduction

In the automotive industry, the precise control of the friction properties of automatic transmission components is one of the most important and challenging tribological issues. Smooth shifting, sufficient torque capacity, anti-shudder protection, and friction durability are key tribological attributes that need to be achieved. All these properties depend to some extent on the actions of lubricants and lubricant additives near sliding surfaces.

Previous studies [1–4] have shown that small amounts of friction modifiers added to automatic transmission fluids play critical roles in controlling the friction between the steel and friction-material interfaces in wet clutches. Friction modifiers are alkane molecules with 10 or more carbon atoms and a complex surface-active group at one end [1] that are added to base oils at low concentration and are observed to lower the friction coefficient. The understanding of the action of friction modifiers at a molecular level is very important in designing more robust materials and systems in automatic transmissions [3,5] as well as in engine oils and numerous other lubrication applications. The focus of our study is to address fundamental questions regarding the behavior of additives with different end-groups: how friction modifier molecules interact with clutch surfaces, how they influence the relationship between frictional force

and sliding velocity (often called the μ–v profile), and what circumstances cause them to be removed from the surface.

Recent analytical developments, such as the surface forces apparatus (SFA), make it possible to study lubrication between well-defined surfaces down to film thicknesses of nanometers, affording a molecular-level study of tribology. The SFA determines the interaction forces between two surfaces as a function of separation from the deflection of a leaf spring supporting one of the surfaces. The separation between the surfaces is measured by multiple beam interferometry [6–8]. Modifications of the instrument allow measurements of both lateral (frictional) and normal (attractive or repulsive) forces between two surfaces that are in relative motion [9–11]. It has been observed that liquids confined in a very narrow gap between two solid surfaces do not behave as bulk liquids under shear [12]. Due to its capacity for constraining the inter-surface separation at close distances while measuring shear forces, the SFA has now become an important tool in tribology.

We have used a surface forces apparatus to investigate the thin-film rheological properties of two functionalized linear alkanes, 1-hexadecylamine and palmitic acid, dissolved in tetradecane. These functionalized alkanes were selected because of their similarity to well-known friction modifiers that are contained in fully-formulated automatic transmission fluids (ATFs) [13,14]. Our intent was to contrast the friction response of molecules that have identical hydrocarbon parts, but different polar head-groups.

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2. Experimental section

The experiments were conducted at the Materials Science and Engineering Department, University of Illinois at Urbana-Champaign, using a surface forces apparatus equipped with a device for oscillatory lateral shearing [9,11]. Using this device, precise measurement and control of shear motions and forces were accomplished through the use of electromechanical transducers (piezoelectric bimorphs), which permitted detailed information about the mechanical responses of liquids to be gathered by means of simple electrical measurements. The surfaces were thin sheets of mica, silvered on one side and glued with their silvered side down onto fused silica discs with 1,5-diphenylcarbazide. The surfaces were mounted in the instrument with the mica surfaces facing each other in a crossed-cylinder geometry that can be thought of as a single asperity contact.

The systems studied were 0.1 wt% solutions of two functionalized linear alkanes with a hydrocarbon part containing 16 carbon atoms, 1-hexadecylamine ($CH_3(CH_2)_{15}NH_2$, Aldrich 99%) and palmitic acid ($CH_3(CH_2)_{14}COOH$, Aldrich 99%), in a linear alkane containing 14 carbon atoms: tetradecane ($CH_3(CH_2)_{12}CH_3$, Aldrich 99%). Both functionalized alkanes were used as received. The tetradecane was dried over molecular sieves (Aldrich, pore size 5 Å) before use. Each functionalized alkane was dissolved in dried tetradecane by agitation in a hot water bath and then in an ultrasonic bath.

The sample solution was injected slowly between the mica surfaces through a flush-cleaned Millex-SR syringe filter (Millipore, pore size 0.5 μm). The experiments were started 30 min–1 h after injecting the solution. The atmosphere in the instrument chamber was kept dry with P_2O_5. All experiments were conducted at $25 \pm 0.2\,°C$.

Force–distance measurement. The interaction force between the two mica surfaces was measured as a function of surface separation as the two surfaces were brought toward each other, brought in contact, and separated. As mentioned above, the distance between the two surfaces (and thus the film thickness) was measured with an accuracy of 1–2 Å by optical interferometry. Zero distance between the surfaces was defined as mica–mica contact in dry air. The force in the direction normal to the surfaces, F, was calculated from the deflection of the leaf-spring (of known stiffness, $k = 927$ N/m) that supported the lower surface. The force was normalized by the geometric-mean radius of curvature of the crossed cylinders, R (typically 1.6–2 cm). The value F/R is proportional to the interaction energy per unit area between two parallel plates (the Derjaguin approximation) [15]. The interaction force measured as a function of distance gives detailed information about adhesion and repulsion between the two surfaces, and the structure, orientation, and rearrangement of confined liquid molecules during loading/unloading cycles can be inferred from the data.

Oscillatory shear experiments. The viscoelastic properties of a confined liquid film can be studied by measuring its response to small-amplitude oscillatory shear, which has been a popular method for characterizing bulk polymers [16]. In our experiments, shear was induced when a sinusoidal voltage output (amplitude A_{in} at the radial frequency ω) from a function generator tended to bend one bimorph (the sender) of the shear device. A lock-in amplifier was used to measure the output signal from the receiver bimorph. This signal had a different amplitude (A_{out}) and was shifted in phase from the input signal by the amount δ:

$$\text{input signal} = A_{in} \sin \omega t, \tag{1}$$

$$\text{output signal} = A_{out} \sin(\omega t + \delta) \tag{2}$$
$$= (A_{out} \cos \delta) \sin \omega t + (A_{out} \sin \delta) \cos \omega t$$
$$\approx G'_{eff} \sin \omega t + G''_{eff} \cos \omega t. \tag{3}$$

In equation (3), the approximation represents a correction for device compliance ("glue correction") calibrated separately in each experiment from the shear of opposed mica sheets in adhesive contact, as described in detail previously [17]. In addition, as discussed previously [17], we indicate that G' and G'' refer to *effective* shear moduli. The complex modulus ($G^* \equiv G'_{eff} + iG''_{eff}$) of the confined film was deduced from the measured amplitudes and phase shift. The quantity $G'(\omega)$ is the storage modulus (or elastic modulus), which is the oscillatory stress that (following Hooke's law of elastic deformation) is in phase with the deformation. The quantity $G''(\omega)$ is the loss modulus, which is the component of the oscillatory stress that (following Newton's law of viscous flow) is in phase with the rate of deformation. In the linear viscoelastic region, the shear amplitude is small enough such that changes in the output signal amplitude, A_{out}, are proportional to changes in the input signal amplitude, A_{in}, for different frequencies ω. Outside the linear viscoelastic region, small changes in A_{in} result in large, disproportionate changes in A_{out}. The film thickness was monitored by optical interferometry before, during, and after the shear experiments. No changes in film thickness were observed during the shear experiments.

3. Experimental results

The two functionalized alkanes were selected with the expectation that they would attach to the mica surface to form a single layer thick film with a structure analogous to surfactant monolayers physisorbed onto solid surfaces from aqueous solutions. Their ability to adsorb weakly to mica from tetradecane was confirmed by studying mica sheets (ca. 2×4 cm) that had been exposed to the sample solutions for 1 h, withdrawn, and rinsed briefly (a few seconds) by dipping into water. The resulting surfaces were not wetted by water and hence were found to be hydrophobic, although native cleaved mica is hydrophilic. The palmitic acid formed a layer that was less stable in water than the
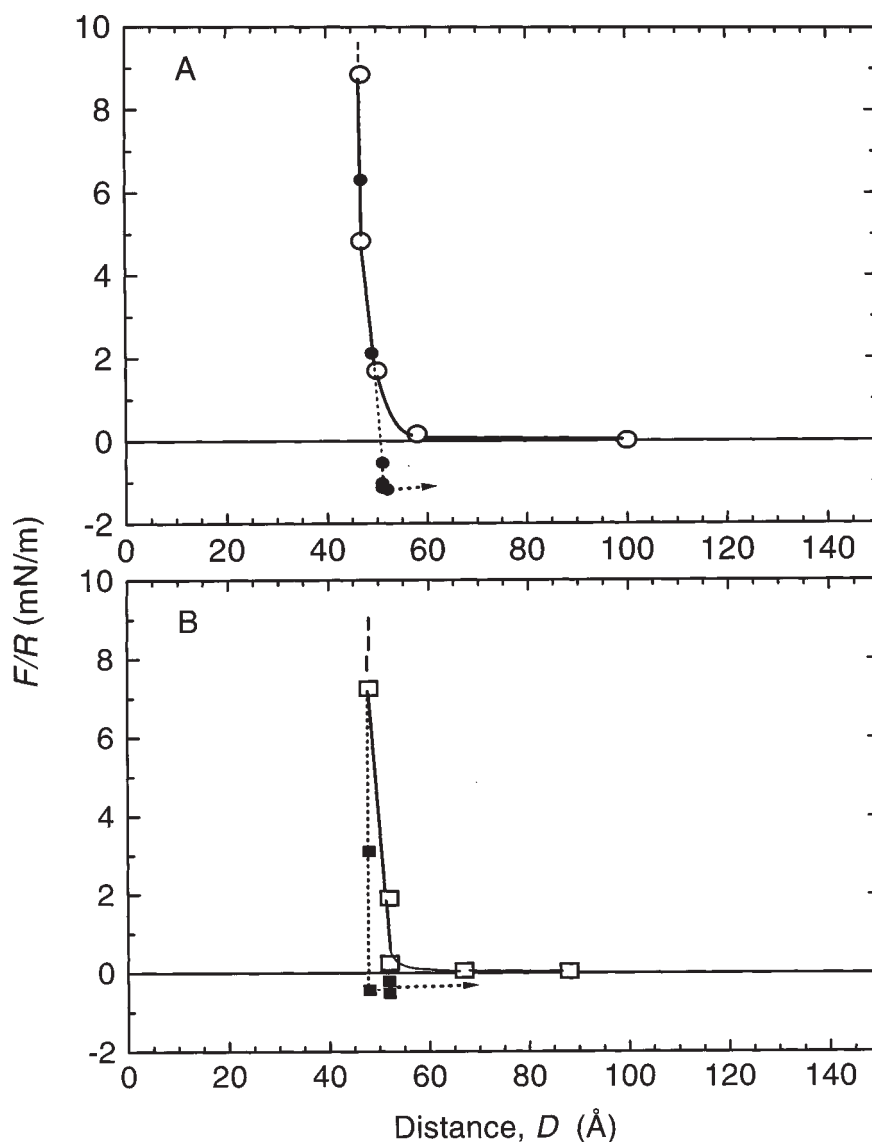
Figure 1. The normalized static force vs. film thickness for (A) 0.1 wt% 1-hexadecylamine and (B) 0.1 wt% palmitic acid in tetradecane confined between two mica surfaces. The force (F) needed to bring opposed surfaces to a given distance (D) is normalized by the mean radius of curvature of the opposed mica surfaces (R). Open symbols denote forces measured upon bringing the surface closer together, and filled symbols the forces measured upon separation. The arrows indicate instabilities (outward jumps) at the points where dF/dD exceeds the spring constant of the spring supporting one of the surfaces.

amine, since the mica sheet had spots where it was wetted by water. The contact angle of water droplets placed on the layers decayed by about 10° over a period of 30–60 s from an initial value around 90° for 1-hexadecylamine and 80° for palmitic acid, which is an indication that the layer was not close-packed and was only weakly adsorbed to the surface, as expected. In experiments still underway, we are exploring the extent to which this difference in effectiveness of surface protection may also manifest itself as a difference in wear rate.

Figure 1(A) shows the interaction force measured as a function of surface separation for 0.1 wt% 1-hexadecylamine in tetradecane, i.e., the static force required to bring the opposed mica surfaces to a given separation. As mentioned in the previous section, the separation D be-

tween the mica plates is defined to be zero at mica–mica contact. As the two surfaces were brought together from a large separation, a strong repulsive force was detected at a separation of 47 Å. The two surfaces could not be brought closer together, even when the force was increased beyond the values shown in figure 1(A). The observation of a "hard wall" repulsion at such large separation supports the assumption (based on the adsorption of a hydrophobic layer on mica pieces withdrawn from the solutions, as described above) that a single layer was formed on each mica surface and could not be removed from the gap between them as the confinement was increased. When the two mica surfaces were separated, a modest attractive force was observed, as shown by the minimum in the plot (at $D \approx 50$ Å). As the two surfaces receded further, no interaction force was ob-

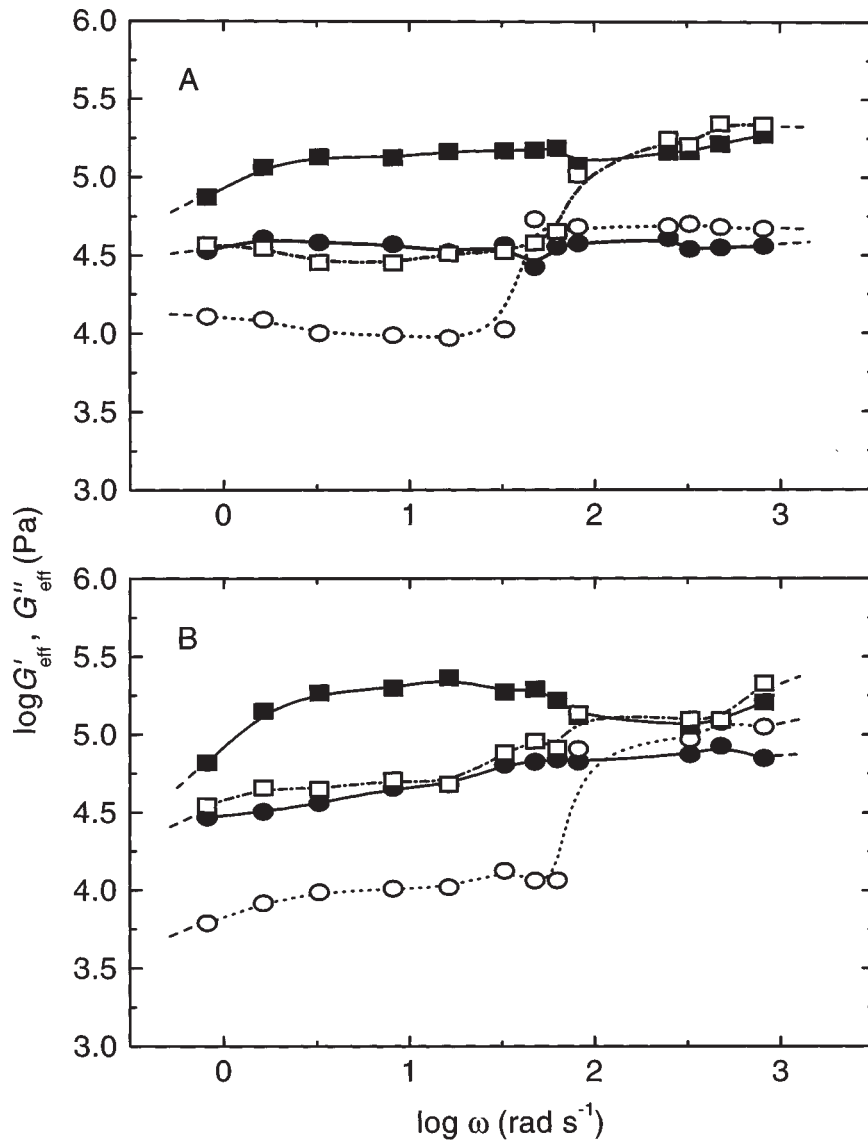Figure 2. Log–log plot of effective storage and loss shear moduli, G'_{eff} and G''_{eff}, as a function of angular frequency, ω, for (A) 0.1 wt% 1-hexade-cylamine and (B) 0.1 wt% palmitic acid in tetradecane. Filled symbols denote storage moduli, G'_{eff}, and open symbols denote loss moduli, G''_{eff}. The measurements were done at two mean normal pressures, 1.1 MPa (circles) and 3.3 MPa (squares).

served after jumping out of contact. Almost identical inter-actions were observed for 0.1 wt% palmitic acid in tetrade-cane confined between two mica surfaces (figure 1(B)). The hard-wall separation for palmitic acid was measured to be 48 Å (the same as for 1-hexadecylamine within ex-perimental uncertainty). Upon separation of the surfaces, we observed that it was easy to damage the palmitic acid layers (material was pulled out and gathered in the contact zone) unless the separation was done very carefully.

The hard-wall repulsion and weak adhesion measured in our systems resemble the forces measured between loose-packed surfactant layers (formed separately by self-assembly from aqueous solution) across linear alkanes [18]. In contrast, for linear alkanes confined between close-packed single layers, oscillatory forces were observed with peak magnitudes of F/R much smaller than the hard-wall magnitudes in figure 1 [18–20]. The absence of an oscilla-tory force in our systems is consistent with the indication from the contact angle experiment that the structure of the adsorbed single layers is loose-packed, rough, or patchy. The fully extended chain length of the tail portion of these functionalized alkanes is approximately 20–22 Å [20], and it has been shown that dry single layers of various surfac-tants with hydrocarbon chains containing 16 carbon atoms have thicknesses around 18–20 Å [21,22]. Since this is less than half the hard-wall thickness measured in our sys-tem, the layers are likely separated by an additional thin layer of solution that could not be squeezed out by apply-ing a large pressure. This layer probably consists of both functionalized alkane and tetradecane that can penetrate to some extent into the hydrocarbon part of the adsorbed lay-ers. The similar force–distance relations observed for both samples suggest that the layer structures formed were sim-ilar for both samples, with the headgroup adsorbed on the
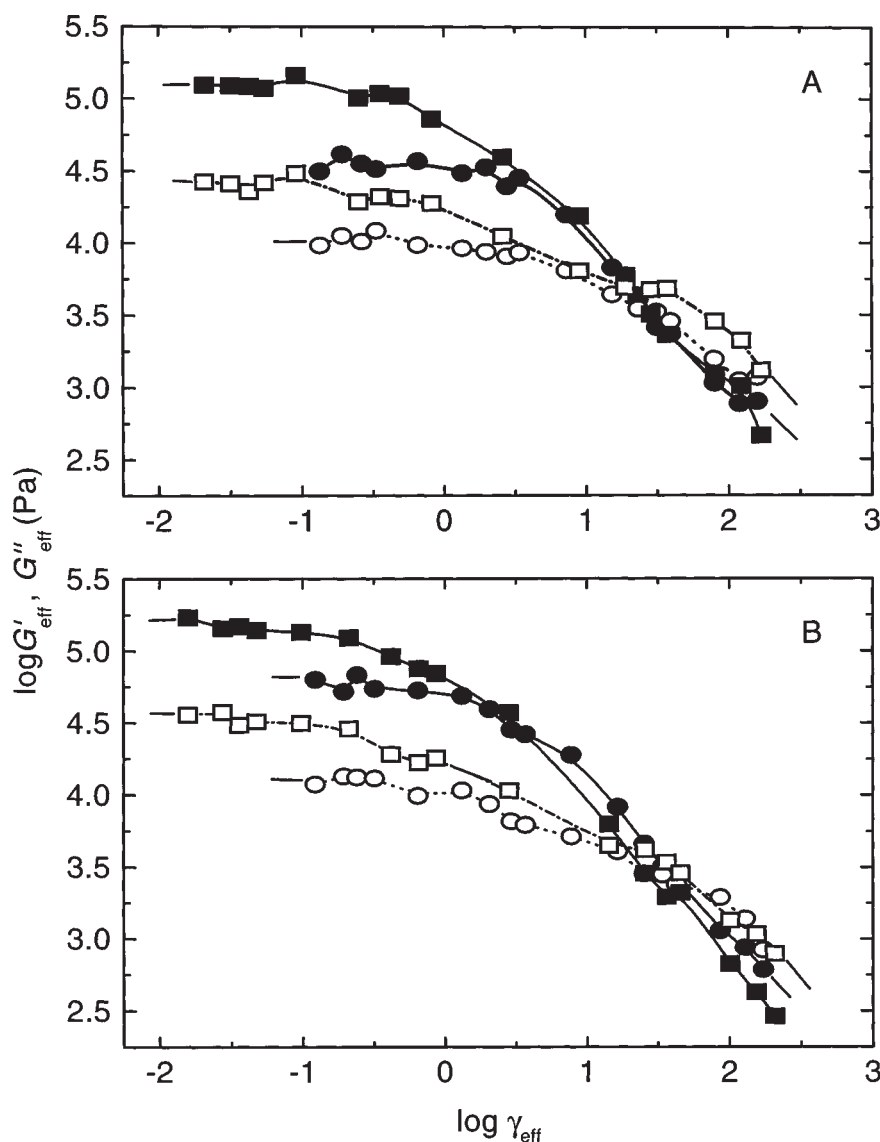
Figure 3. Log–log plot of effective storage and loss shear moduli, G'_{eff} and G''_{eff}, as a function of effective strain, γ_{eff}, for (A) 0.1 wt% 1-hexadecylamine and (B) 0.1 wt% palmitic acid in tetradecane. The strain is defined as shear amplitude divided by film thickness (see text). The measurements were made at a fixed frequency, 16 rad s^{-1}, at pressures of 1.1 and 3.3 MPa. The symbols are the same as in figure 2.

mica surface and the alkyl chain sticking out into the solution.

Concerning the rheology of these layers, we first consider the linear viscoelastic response. Figure 2(A) shows the frequency dependence of the storage and loss moduli for the 1-hexadecylamine/tetradecane system at normal pressures of 1.1 and 3.3 MPa. The thickness of the intervening film confined between the layers, in which it is likely that the dissipation occurs, was calculated from the total hardwall separation of 48 and 47 Å at 1.1 and 3.3 MPa, respectively, by subtracting twice the adsorbed layer thickness (ca. 18 Å). The resulting film thicknesses of 12 and 11 Å were used in the calculations of shear moduli, strain, and strain rate. In doing so, we assumed that all shear occurred in the fluid confined between the monolayers, with no slip (i.e., zero velocity) at the monolayer surface. (If portions of the monolayer were deformed under shear, the strain and strain rate would each decrease slightly from the values reported here and the shear moduli would increase proportionately.)

The normal pressure was calculated as the normal load (W) divided by the area of contact (the crossed cylinders became flattened at their tips as the normal load was raised, forming locally-flat circular plates). If one assumes the Hertzian (non-adhesive) contact, the pressure was zero at the circle periphery and $(3/2)W$ at the center [23]. In the oscillatory shear experiments presented in figure 2, the shear amplitude was kept constant at a low level (a few Å) relative to the film thickness and the frequency was varied. Note that the linearity of the response at small shear amplitude was confirmed directly by the additional data presented in figures 3(A) and (B).

In figure 2(A) (the 1-hexadecylamine/tetradecane system), one observes that $G'_{eff} \gg G''_{eff}$ at $\omega < 30$ rad s^{-1},
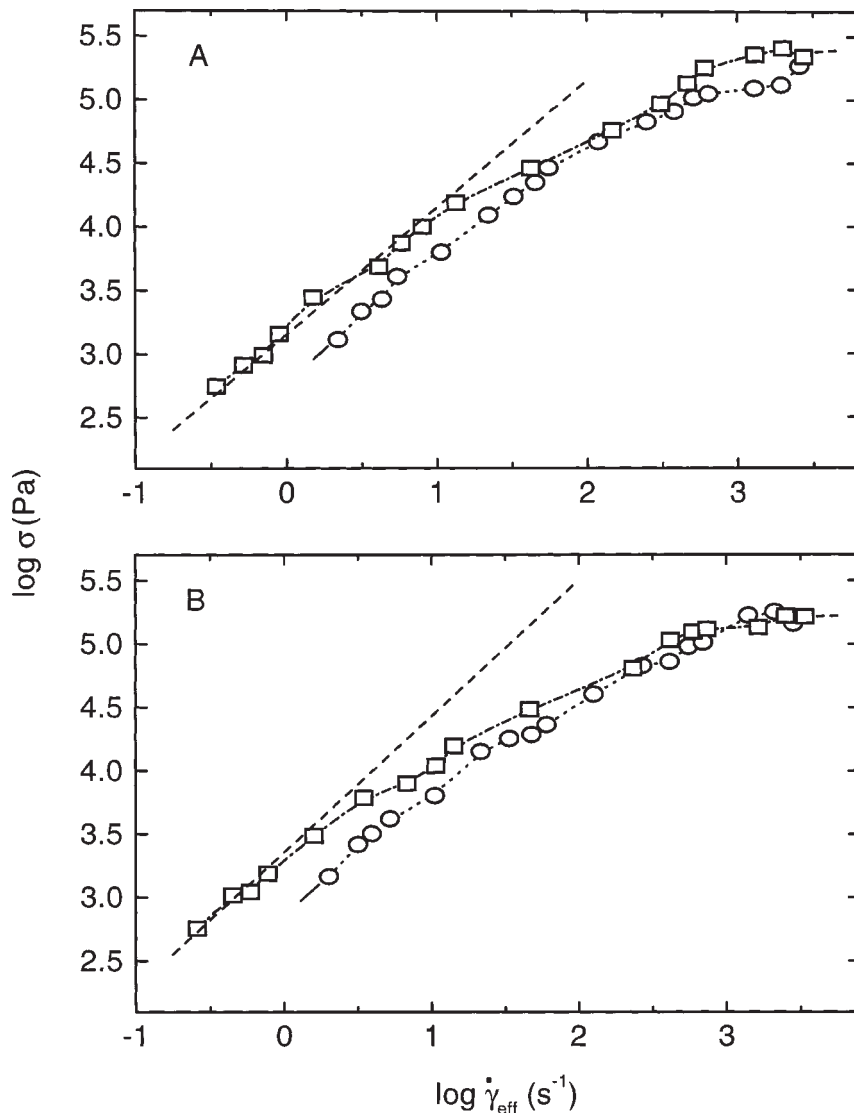
Figure 4. Log–log plot of viscous shear stress and effective shear rate for (A) 0.1 wt% 1-hexadecylamine and (B) 0.1 wt% palmitic acid in tetradecane. In both systems, the viscous shear stress saturates at ~ 0.2 MPa at $\dot{\gamma} > 10^3$ s^{-1} and displays larger load dependence at low shear rate than at high. The measurements were done at two mean normal pressures, 1.1 MPa (circles) and 3.3 MPa (squares). Dashed lines indicate the Newtonian regime of constant effective viscosity.

indicating a predominantly elastic response. At higher frequency we saw little change in this elastic response (the modulus in the solid-like region was comparable to that of slightly entangled bulk polymer chains above their glass transition temperature [24]) but a significant augmentation of the dissipative response, indicating significantly more energy lost in viscous modes over this range of higher frequency.

This separation of frequency response into two regimes appeared equally markedly at an increased normal load. The moduli increased by a factor of approximately 3 with a three-fold increase in the normal pressure (figure 2(A)). Based on experience with other systems we speculate that elastic responses may be associated with enhanced tendency towards wear, but this possibility remains to be explored in future work. The onset of these dissipative modes is expected to depend on hydrocarbon chain length and on

surface packing fraction, but this aspect also remains to be explored.

As shown in figure 2(B), very similar results were obtained for the linear viscoelastic response of palmitic acid/tetradecane as a function of frequency and pressure. The thickness of the film confined between the layers was calculated to be 11 and 9 Å at 1.1 and 3.3 MPa, respectively. As for the 1-hexadecylamine system, the data split into two distinct regions: one above and one below $\omega \approx 30$ rad s^{-1}. We attribute the similar results to similar arrangement of these functionalized molecules on the solid surfaces. The different head-groups did not cause any significant difference in the friction responses (nor in the interaction forces shown in figure 1); the near-identical responses indicate that these properties were dominated instead by the hydrocarbon tails and the additional confined solution. In the palmitic acid/tetradecane system (fig-

ure 2(B)), the pressure dependence was more pronounced than in 1-hexadecylamine/tetradecane at low frequencies (an increase in moduli by a factor 4–5) and less obvious at higher frequencies (increase by a factor 2).

Figures 3(A) and (B) contrast the linear viscoelastic responses with those obtained at higher shear amplitudes – shear amplitudes whose magnitude exceeded the film thickness. These measurements were made at a fixed frequency, 16 rad s^{-1}. The shear amplitude was normalized by the film thickness (12 and 11 Å in figure 3(A) and, similarly, 11 and 9 Å in figure 3(B), at pressures of 1.1 and 3.3 MPa, respectively) to produce a dimensionless measure of deformation, the *effective strain*, which is the abscissa in figures 3(A) and (B). As the strain amplitude was raised from 0.3 to 1900 Å, the effective strain varied from 0.02 to approximately 160. In measurements of the bulk rheology of lubricants, the strains customarily investigated are on the order of unity or less. The strains reported here are evidently much larger than is possible to study in a bulk measurement. Such large strains could be found in a sliding wet-clutch interface.

With increasing strain, one observes that the shear moduli decreased by two orders of magnitude, with onset of nonlinear response when the shear amplitude exceeded approximately one-third of the film thickness. In addition, the viscoelastic response changed from being predominantly elastic to having comparable elastic and viscous components, indicating a progressive breakup of elasticity with increasing strain. The smooth decrease of the shear moduli with increasing strain contrasts with the stick–slip response that is commonly observed for thin films of single-component liquids, including tetradecane [25]. The adsorbed layers formed by these model friction modifiers thus do affect the shear response in the desired direction, within our experimental condition.

Alternatively, the data can be presented as functions of *effective shear rate*. It is established from prior work that at large shear rates such data superpose regardless of whether the frequency is kept constant and the amplitude varied, or vice versa [12]. This has been interpreted [12] to indicate that an experiment performed with sinusoidal oscillations of huge amplitude is really more like a steady-flow experiment, with shear rate averaged over a cycle. In other words, data at high effective strain rate are essentially like a non-Newtonian flow plot.

In figure 4, we observe the transition from Newtonian to strongly non-Newtonian response. At low shear rate the relationship between viscous stress and effective shear rate is linear. It follows that on log–log scales the slope of stress versus shear rate equals unity (indicated in the figures) in the regime where the effective viscosity is a constant. The effective viscosity (η_{eff}) refers to the flow of the confined fluid at this temperature, film thickness, and pressure. At higher shear rates, the viscosity decreases with increasing shear rate (shear thinning), which has commonly been described by a power law behavior, $\eta_{\text{eff}} \sim \dot{\gamma}^{-a}$. Otherwise stated, the viscous shear stress (σ) would level off

as $\sigma_{\text{eff}} \propto \dot{\gamma}^{1-a}$. It was initially observed that $a \approx 2/3$ for molecularly-thin films [12,26], but later experiments found that $a \to 1$ with further increases of sliding velocity [27,28]. When $a = 1$, the viscous stress ceases to depend on the shear rate.

Such behavior has been reported previously for single-component fluids. The relatively low magnitude of the limiting shear stress, $\sigma \approx 0.2$ MPa at $\dot{\gamma} > 10^3$ s^{-1}, is significantly lower than what has been observed for single-component fluids, including tetradecane, in a hard-wall regime of film thickness [25]. The increase in shear stress with increasing shear rate at constant load indicates that the friction coefficient (defined as the frictional force divided by normal force) increases with sliding speed in these conditions, even while the solutions exhibited shear thinning. We anticipate that the relatively low limiting stress will be associated with favorable wear rates.

4. Discussion and conclusions

Our study of the microscopic actions of adsorbed functionalized alkanes has found that they behave differently from confined unfunctionalized alkanes. Tetradecane solutions of these molecules formed single layers spontaneously on mica surfaces due to weak adsorption of the polar functional group. Additional solution was confined between these adsorbed layers. Under shear, the confined film showed a predominantly solid-like response at low frequencies and shear rates and a more dissipative response at higher frequencies and shear rates. At present, it is unclear why the viscous losses in the linear response presented such strong dependence on frequency. Further studies, in which the chain length of the functionalized alkane is varied, will be instructive in this regard. The friction properties appeared to be the result of the adsorbed layers, i.e., a covering of the surfaces with hydrocarbon chains (selected to have the same length in both systems), and did not depend on the type of polar head group. The interaction forces observed for these two systems were clearly different from those observed for the pure solvent, tetradecane. It is well known that in pure linear alkanes such as tetradecane between mica surfaces, an oscillatory force is observed in confined films thinner than 30 Å [20]. Clearly, addition of a small amount of functionalized alkane molecules disrupts the layered structures that would have been formed by tetradecane alone. The structure formed is able to support a considerable normal load. However, on separation, also without prior strong compression, it was occasionally possible to damage the palmitic acid layers and these might thus be less strongly associated with the polar surface. The weak adhesion observed is similar in magnitude to what has been observed in other systems of loose-packed surfactant layers interacting across alkanes [18,25].

The smooth decrease of the shear moduli with increasing strain, and the relatively low limiting shear stress, contrast with the stick–slip response and high stress that is characteristic of molecularly-thin single-component liquids (or dry

layers). This suggests the effectiveness of these friction modifiers in impeding a static friction response. A more detailed study of the transition from solid-like to liquid-like friction response may help lead to an understanding of friction-induced vibrations. We expect that the smooth transitions that were observed in this study, which contrast with the abrupt "stick–slip" responses observed for single-component alkane fluids under similar loads, will result in less friction-induced vibration. In addition, we anticipate that the relatively low limiting shear stress in these systems will be associated with favorable wear rates, thus suggesting another mechanism for the efficacy of friction modifiers.

Acknowledgement

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