

The boundary lubrication properties of model esters

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Received 14 November 2000; accepted 28 January 2001

The friction of three chemically distinct esters was measured in order to determine how molecular architecture influences friction. The friction coefficients μ of mica surfaces separated by a thin film (<2 nm) of ω -chlorodecyl benzoate, ω -chlorodecyl pentafluoro benzoate, and ω -chlorodecyl perfluoro hexanoate were measured to be 0.15 ± 0.015 , 0.13 ± 0.012 , and 0.12 ± 0.02 , respectively. The friction coefficients for the esters are lower than the previously measured friction coefficients of simple hydrocarbon liquids such as *n*-tetradecane ($\mu = 0.8$), but are comparable to the friction coefficients of surfactant monolayer coated surfaces ($\mu = 0.001$ – 0.2). The results suggest that the ester molecules adsorb onto the mica surface with the (phenyl or hexyl) carbonyl next to the surface and the hydrocarbon tail pointing away from the surface. Hence, the friction is controlled by the packing density and properties of the hydrocarbon tail. Changes in the chemistry and structure of the carboxylic acid portion of the ester only give rise to small changes in the friction coefficient.

KEY WORDS: lubrication; friction; ester; surface forces apparatus; monolayer

1. Introduction

When two surfaces are rubbed together, some amount of lubrication is generally required to minimize friction and wear [1,2]. Ideally, surfaces are lubricated by a micron thick film of lubricant and the friction is determined by the hydrodynamic properties of the fluid film [1,2]. However, in many applications, the fluid lubricant is pressed out by an applied load, and the surfaces are separated by a lubricant boundary layer that may be only a few molecular dimensions thick [1,2].

A variety of liquid and solid materials have been used through the years to lubricate surfaces. Mineral oils, silicones, polyphenyl ethers, esters, and fluorocarbons are among the types of fluids commonly used as lubricants [3]. Additives are often mixed into lubricants to provide the required performance [4]. For the lubrication of magnetic hard disks, perfluoroethers, dithiocarbaminates, amides, amines, silanes, and esters have been investigated [5–7].

Some of the first detailed experiments on friction were performed in 1690 by Amontons' who found that the friction is proportional to the applied load and independent of the area of contact [8]. In those experiments, Amontons' investigated the sliding of copper, iron, lead, and wood surfaces in the presence of a lubricating layer of pork fat [2,8]. Since pork fat is primarily composed of saturated and unsaturated hexadecyl and octadecyl glycerol esters, one may conclude that Amontons' was one of the first to study the friction of esters.

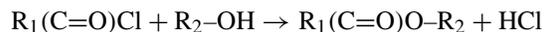
In this paper, the friction of three chemically distinct esters was measured in order to determine how molecular structure influences friction. The friction force of these esters is interesting since these specific chemistries are patented for lubricants for magnetic hard disks [5,6]. All

the esters contain a fluid ω -chlorodecyl tail, but the acid part of the ester has varying structure (linear or cyclic) and degree of fluorination. The results show that the friction coefficients of mica surfaces separated by a thin ester film (<2 nm) are lower than the previously measured friction coefficients of simple hydrocarbon liquids, where the hydrocarbon molecule lays parallel to the mica surface. However, the results are comparable to the value of the friction coefficients measured for adsorbed hydrocarbon monolayers, where the monolayers are oriented perpendicular to the mica surface.

2. Materials and methods

2.1. Synthesis of ω -chlorodecyl esters

The esters were synthesized following standard organic synthesis techniques [9]. Acid chlorides readily react with primary and secondary alcohols to produce esters with high yield, quite often without the need of a solvent. The reaction proceeds via nucleophilic acyl substitution according to



In accordance with this reaction, the esters were synthesized using equimolar amounts of acid chlorides and alcohols. No solvents were used in the reaction. An example of the procedure used to make ω -chlorodecyl pentafluoro benzoate is described below. A similar procedure was used to synthesize the other two esters. All the esters are liquids at room temperature.

To make ω -chlorodecyl pentafluoro benzoate, 20.9 g (0.108 moles) of 10-chlorodecanol (Aldrich) was added dropwise to 25 g (0.108 moles) pentafluorobenzoyl chloride

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(Aldrich™). The 250 ml reaction flask was placed in a water bath and continually stirred. The mixture was maintained at room temperature. A reflux condenser was connected to the reaction flask to minimize possible reactant loss. A gas, which was acidic to pH paper, was evolved. The reactant mixture was left to stir overnight. After 24 h, the water bath was heated to 70 °C and continually stirred for 2.5 h. The product was allowed to cool to room temperature and air was bubbled through the liquid for 1 h to dispel residual dissolved HCl gas. An infrared spectrum of the liquid product showed no –OH peaks present, indicating complete reaction of the 10-chlorodecanol. The refractive index was measured to be 1.4582. The ¹H nuclear magnetic resonance spectrum showed the product to be better than 95% pure.

2.2. Surface forces measurements

A surface forces apparatus (SFA) with a lateral sliding attachment was used to measure the shear forces [10,11].¹ The lateral sliding attachment slides two surfaces past each other. The technique generally uses mica surfaces which were cleaved to obtain molecularly smooth surfaces. The back side of each mica sheet was silvered to allow interferometry measurements and glued onto silica support disks. One disk was mounted onto a rigid steel plate which was connected through two vertical double-cantilever springs to a translation stage. A variable speed motor driven micrometer pressed against the translation stage, regulating motion. One of the vertical springs contained an attached semiconductor strain gauge which was connected to a chart recorder which recorded the lateral force. Another disk was mounted onto horizontal double-cantilever springs which measured the normal force. The spring constants of the normal and lateral force measuring springs were 100 ± 10 N/m and $3 \times 10^3 \pm 3 \times 10^2$ N/m, respectively.

Besides measuring the shear and normal forces, the SFA simultaneously measures the surface separation and contact area via observation of the optical interferometric fringes. Typical values of the sliding velocity v , applied normal load L , contact area A and lateral force F in this study were $1 \mu\text{m/s}$, $0\text{--}100$ mN, $0\text{--}10^{-3}$ cm², and $0\text{--}200$ mN, respectively. The velocity and applied load have an estimated relative standard uncertainty of $\pm 5\%$ of the measured values, whereas the friction force and contact area have an estimated relative standard uncertainty of less than $\pm 10\%$ of the measured values. The surface separation can be measured to ± 0.1 nm.

The surfaces were placed inside the SFA chamber which was then purged with dry nitrogen. A small container filled with P₂O₅ was placed in the chamber of the SFA to extract residual moisture from the atmosphere. Initial mica/mica

contact measurements were made in dry air. A small droplet of the liquid ester was placed between the surfaces and the friction, load, and surface separation was simultaneously measured. Sliding was maintained in one direction until a steady friction was observed. The direction was reversed and the steady state friction was again measured. The load was then increased gradually and the friction and surface separation were measured after each increase. All experiments were carried out at a temperature of 23 ± 1 °C and a sliding velocity of $1 \mu\text{m/s}$. At least three repeat measurements were performed for each ester.

3. Results

The surface tension of the bulk liquids was measured by the Wilhelmy plate method [12]. The results are given in table 1, and show that increasing fluorination of the ester decreases the measured surface tension.

SFA force–distance profile measurements of all of the esters showed a monotonically repulsive force as the mica surfaces were brought together, indicating that the surfaces were non-adhering in the presence of the esters.

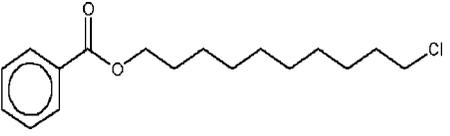
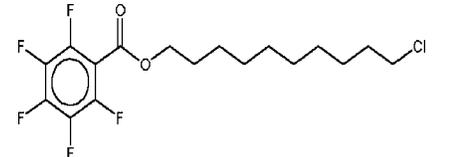
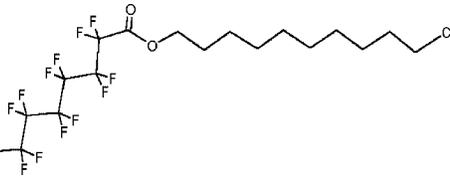
Figure 1 shows the decrease in surface separation with increasing load for ω -chlorodecyl benzoate. The step-like decrease in the surface separation with load indicates ordering or layering of the molecules in the thin film. The change in separation at the step was 0.45 ± 0.1 nm. During the transition, it is possible for part of the surface to be at one surface separation and another part of the surface to be at another surface separation. As shown in figure 1, the transition in going from 0.75 to 0.4 nm showed this behavior. For ω -chlorodecyl pentafluoro benzoate, the surface separation quickly decreased to 0.8 nm at low loads and remained at 0.8 ± 0.1 nm for loads up to 80 mN. Hence, between 30 and 70 mN, the surface separation for both esters was 0.8 ± 0.15 nm.

Figure 2 shows the friction forces measured between mica surfaces separated by thin films of ω -chlorodecyl benzoate (solid circles) and ω -chlorodecyl pentafluoro benzoate (open circles). For both liquids, the friction increases monotonically with load. The slope of the force versus load plot gives the friction coefficient $\mu \equiv \partial F / \partial L$. The data for each ester are surprisingly similar. Three repeat measurements for each ester at different mica surface positions show that the friction coefficient for ω -chlorodecyl benzoate is slightly higher ($\mu = 0.15 \pm 0.015$) whereas the friction coefficient for ω -chlorodecyl pentafluoro benzoate is 0.13 ± 0.012 . In both cases, the sliding is “smooth” and no stick/slip or intermittent sliding is observed.

Due to the elastic behavior of the epoxy attaching the mica to the silica disks, the contact area increased as the load increased. Even at low loads ($6 \text{ mN} < L < 12 \text{ mN}$), a significant contact area (contact area = $0.001\text{--}0.002 \text{ mm}^2$) was sometimes measured. Although the values of the contact area measured were dependent upon the specific experiment, the contact area typically varied from 0.001 to 0.015 mm^2

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1

Ester, surface tension, γ_{LV}	Chemical structure
ω -chlorodecyl benzoate, $\gamma_{LV} = 38.7 \pm 1$ mN/m	
ω -chlorodecyl pentafluoro benzoate, $\gamma_{LV} = 33.7 \pm 1$ mN/m	
ω -chlorodecyl perfluoro hexanoate, $\gamma_{LV} = 16.6 \pm 1$ mN/m	

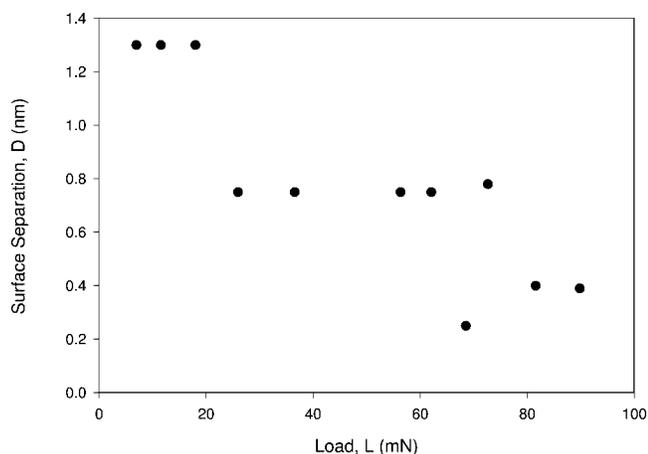


Figure 1. Measured surface separation as a function of applied load for a thin film of ω -chlorodecyl benzoate between mica surfaces. The surface separation is measured to ± 0.1 nm.

for loads corresponding to 6 to 82 mN. The corresponding contact pressures were calculated to be 3 to 6 MPa. The mean radius of curvature of the mica surfaces is estimated to be 1.5 ± 0.5 cm.

Previous measurements have shown that stopping the sliding during the friction measurement can give an indication of the physical state of the intervening film [13]. If the friction decreases to zero, then the intervening film behaves like a liquid. If the friction does not fall, then the intervening film behaves like a solid. This was investigated for ω -chlorodecyl pentafluoro benzoate. On stopping sliding for 20 s at a load of 110 mN, there was 25–35% decrease in the friction force followed by a friction “spike” on start of the sliding. This shows there is some ability for stress to relax, but, since the friction did not decrease to zero, the intervening material was not completely fluid.

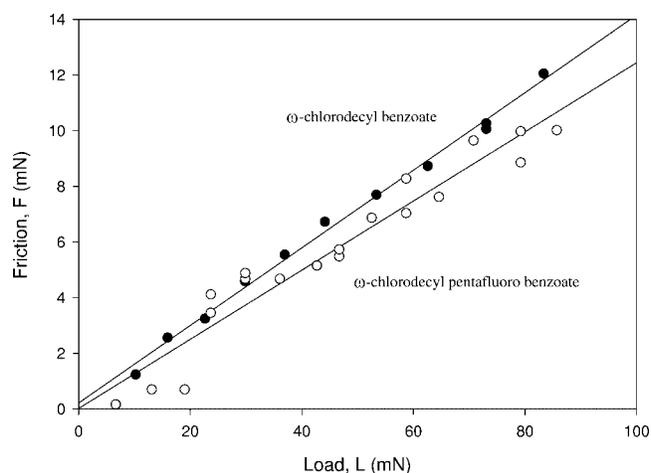


Figure 2. Measured friction forces F between two mica surfaces separated by a thin (< 2 nm) film of ω -chlorodecyl benzoate (\bullet) and ω -chlorodecyl pentafluoro benzoate (\circ) as a function of load L . The solid lines are linear regression fits to the data. The slope, $\partial F / \partial L$, gives the friction coefficient. The friction coefficients were measured to be 0.15 ± 0.015 and 0.13 ± 0.012 , for ω -chlorodecyl benzoate and ω -chlorodecyl pentafluoro benzoate, respectively. The friction force is measured to $\pm 10\%$.

In contrast to ω -chlorodecyl benzoate and ω -chlorodecyl pentafluoro benzoate, ω -chlorodecyl perfluoro hexanoate did exhibit stick–slip motion at $v = 1 \mu\text{m/s}$. The static friction was generally 10% greater than the kinetic friction. Figure 3 shows the kinetic friction force of a thin film of ω -chlorodecyl perfluoro hexanoate between mica surfaces. The friction increases monotonically with load, giving $\mu = 0.12 \pm 0.02$. A plot of the surface separation versus load is shown in the inset for ω -chlorodecyl perfluoro hexanoate between mica surfaces. The surface separation quickly decreases with load until a separation of 0.7 ± 0.1 nm is reached whereupon no further decrease in surface separation is measured for applied loads up to 100 mN.

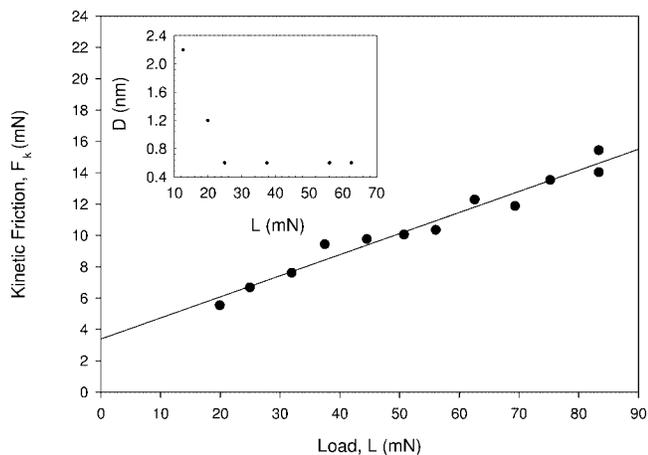


Figure 3. Measured friction force between two mica surfaces separated by a thin (<2 nm) film of ω -chlorodecyl perfluoro hexanoate. The solid line is a linear regression fit to the data. The friction coefficient is measured to be 0.12 ± 0.02 . The friction force is measured to $\pm 10\%$. The inset shows the surface separation, measured to ± 0.1 nm, as a function of applied load for a thin film of ω -chlorodecyl perfluoro hexanoate between mica surfaces.

4. Discussion

The friction of three chemically distinct esters was measured in order to determine how molecular structure influences friction. The friction coefficients of the three liquid esters, ω -chlorodecyl benzoate, ω -chlorodecyl pentafluoro benzoate, and ω -chlorodecyl perfluoro hexanoate were measured to be 0.15 ± 0.015 , 0.13 ± 0.012 , and 0.12 ± 0.015 , respectively. Surprisingly, the friction coefficients are quite similar even though the esters are chemically and structurally quite different. The values of the friction coefficients of the esters are, however, lower than the values of the friction coefficients of simple hydrocarbon liquids. For example, friction coefficients of 0.8 and 0.3 have been measured for *n*-tetradecane and 2-methyloctadecane, respectively [13]. Polymeric materials can give even lower friction coefficients [14,15].

The reason the friction coefficients of the esters are lower than the friction coefficients of simple hydrocarbon liquids is likely due to differences in the orientation of the molecules between the surfaces. As seen in figure 4(a), tetradecane and similar short chain hydrocarbon molecules tend to lie parallel to the mica surface when confined. For Langmuir–Blodgett monolayers adsorbed on mica, the head group is attached to the mica surface and the hydrocarbon tail is oriented away from the surface, as shown in figure 4(b).

It has been observed that for self-assembled monolayers such as cetyl pyridinium chloride adsorbed on mica [16] and decyl imidazole-2-thiones adsorbed on gold [17], adsorption occurs with the ring structure laying flat against the surface and the hydrocarbon tail extending away from the surface. If the esters have the same orientation, then the (phenyl or hexyl) carbonyl group is adsorbed onto the mica surface and the alcohol portion of the ester, the ω -chlorodecyl tail, is

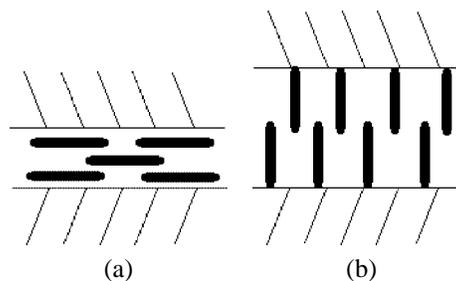


Figure 4. Schematic diagram of the orientation of tetradecane (shown in (a)) and Langmuir–Blodgett monolayers (shown in (b)) adsorbed on solid surfaces. It is proposed that the orientation of the tail of the ester is similar to (b).

oriented away from the surface. In this conformation, the hydrocarbon tails touch and slide past each other, as shown in figure 4(b). This would explain why the measured friction is so similar.

Slight variations in the value of the friction coefficient are expected due to the differences in adsorption and packing density. With decreasing molecular packing density, monolayers go from being solid-like to amorphous to liquid-like [18]. The state of the monolayers will affect the amount of interdigitation and hence the coefficient of friction. The measured friction coefficients of surfactant monolayer coated surfaces vary from 0.001 to 0.2 [18–20]. The range of friction coefficients measured here, 0.15 ± 0.015 to 0.12 ± 0.02 , is at the high end of the measurements for surfactant coated surfaces.

For low loads (<20 mN), the surface separation was greater than 1.3 nm, and hence the boundary lubrication regime may not apply. Between loads of 30 and 70 mN, the surface separation for all esters was between 0.6 and 0.8 nm. Since the surface separation was measured from mica/mica contact in air, the film thickness was more likely 1.2–1.7 nm as 0.3–0.5 nm of material is often displaced from mica surfaces when placed in an organic or aqueous solvent. This implies that the film thickness is 0.6–0.9 nm per surface, consistent with the thickness expected for a monolayer containing a decyl tail with the orientation of the tail perpendicular to the mica surface.

In general, molecules that pack more efficiently show stick–slip behavior. For example, a thin film of *n*-tetradecane between mica surfaces will show stick–slip behavior, whereas a branched hydrocarbon such as 2-methyloctadecane will not. For the esters described here, only ω -chlorodecyl perfluoro hexanoate demonstrated stick–slip behavior. This was the only ester that contained two alkyl groups. The other two esters, ω -chlorodecyl benzoate and ω -chlorodecyl pentafluoro benzoate contain a benzyl group and an alkyl chain. Assuming no overlap of the benzyl groups on the surface, the packing density of the benzene ring may be less than the packing density of the perfluoro hexanoate group. The greater degree of packing of the perfluoro hexanoate group will give rise to more closely packed hydrocarbon tails giving less interdigitation and lower friction. The higher degree of packing of

the ω -chlorodecyl perfluoro hexanoate is also supported by surface tension measurements where a low value of the surface tension is measured, demonstrating the ability of the fluorinated alkyl chains to pack at the air/water interface.

Esters are often used for friction modifiers in metalworking. On base metals, esters are known to react with the surface [1]. Hydrolysis of the ester leads to the formation of a small amount of a fatty acid soap film that reacts with the metal. In the SFA experiments, the velocity is low (1 $\mu\text{m/s}$) and the ester most likely stays intact during the measurement. However, if the (phenyl or hexyl) carbonyl is indeed adsorbed onto the surface with the hydrocarbon tail oriented perpendicular to the surface, then the friction is determined by the hydrocarbon tail, as in metalworking.

Although the determination of the structure of the adsorbed ester will require more study, it is possible for both the ester linkage and the (phenyl or hexyl) group to be adsorbed to the mica surface. Since the ester linkage is polar, it will likely have a strong adsorption to the mica surface. The specific structure and packing may also be influenced by the hydrophobic chain, as has been observed for the fat soluble vitamins A, E, and K₁. These materials have a ring-type structure at one end of the molecule and an organic alkyl group at the other end of the molecule. They form stable monolayers on water [16]. The pressure–area behavior of the expanded monolayer appears to be governed by the character of the hydrophobic chain [16], in agreement with the experiments described here. Future studies will investigate the packing of the esters at interfaces by IR and pressure–area isotherm measurements.

5. Conclusions

The friction coefficients of mica surfaces separated by thin films (<2 nm) of ω -chlorodecyl benzoate, ω -chlorodecyl pentafluoro benzoate, and ω -chlorodecyl perfluoro hexanoate were measured to be 0.15 ± 0.015 , 0.13 ± 0.012 , and 0.12 ± 0.02 , respectively. The friction coefficients for the esters are lower than the previously measured friction coefficients of simple hydrocarbon liquids such as *n*-tetradecane which has a friction coefficient of 0.8. The measured friction coefficients of surfactant monolayer coated surfaces have been measured to vary from 0.001 to 0.2. The results indicate that the ester molecules adsorb onto the mica surface with the acid part of the ester next to the surface and the hydrocarbon tail pointing away from the surface. Hence, the friction is dictated by the packing density and properties

of the hydrocarbon tail. Changes in the chemistry and structure of the carboxylic acid portion of the ester give rise to only small changes in the friction coefficient.

Acknowledgement

I would like to thank Dave Vanderah, Joe Ritter, and Gil Johnson for their assistance in the chemical synthesis and characterization of the esters.

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