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Forces between Mica Surfaces across Hydrocarbon Liquids: Effects of Branching and Polydispersity

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ABSTRACT: Results are presented of the forces between molecularly smooth mica surfaces immersed in the saturated branched alkanes 2-methyloctadecane, 2-methylundecane, and 2-methyloctane and various isoparaffin mixtures of known distribution. The effects of water and alcohol on the interactions were also investigated. Previous experiments have demonstrated that the forces across the *unbranched* liquid *n*-alkanes, from hexane to hexadecane, exhibit a decaying oscillatory profile with a periodicity of about 0.4 nm and a range of about 3 nm. In marked contrast to this, experiments now show that the forces across the *branched* liquid isoparaffins, such as 2-methyloctadecane and 2-methylundecane and controlled mixtures of these, are monotonically attractive down to surface separations of 1.5–2.5 nm and monotonically repulsive at smaller separations. Thus, even a single methyl group substituent on the backbone of a relatively long carbon chain suffices to totally eliminate the oscillations that characterize the force profile of the unbranched *n*-alkane. This finding may explain why branched alkanes are better lubricants or lubricant "base oils" than *n*-alkanes. The force profile measured across one such model base oil—a polydisperse mixture of branched alkanes with carbon numbers ranging from C_8 to C_{36}—is similar to that measured across pure (monodisperse) 2-methyloctadecane. The presence of water and alcohols significantly enhances the attraction. The results are discussed in terms of attractive van der Waals forces together with a proposed entropically driven attractive force and short-range repulsive steric forces.

I. Introduction

Spherically shaped molecules in the liquid state order into quasi-discrete layers adjacent to molecularly smooth solid surfaces.[1] The same phenomenon occurs for linear chain molecules, such as *n*-alkanes and poly(dimethylsiloxane)s, where the liquid molecules within the layers orient parallel to the surfaces.[2-5] Such molecular layering leads to a short-range oscillatory variation in the density of the liquid with distance from the surface. This variation is enhanced when a second smooth surface approaches the first and results in an oscillatory force between the two surfaces, which varies with surface separation between attraction and repulsion.[1,4-6] The magnitude of this oscillatory "solvation" or "structural" force can exceed that of the conventional van der Waals force between two surfaces at distances below about 10σ, where σ is the diameter of a spherically shaped molecule or the segment width of a chain molecule. Examples of the latter are the *n*-alkanes from hexane to hexadecane, where $\sigma \approx 0.4$ nm[4] and the 50-segment polymer melt poly(dimethylsiloxane) (PDMS), where $\sigma \approx 0.7$ nm.[5] For both these systems, oscillatory forces dominate the interaction between two molecularly smooth mica surfaces at separations below 3–5 nm. The magnitude of the oscillations becomes negligible at larger distances and, in the case of the *n*-alkanes, the forces approach the monotonically decaying, attractive van der Waals force that is described by the continuum theory of Lifshitz et al.[1]

The origin of the short-range oscillatory forces is now well-understood.[7-9] Indeed, recent theoretical computations of these forces[10] are in very good agreement with the force laws measured between mica surfaces across both an inert nonpolar liquid and across water. Qualitatively, these forces arise from the discrete nature of liquid molecules. A liquid cannot be treated as a structureless continuum once it is confined between two surfaces closer than a few molecular diameters.

The occurrence of an oscillatory force law does, however, require (1) that the interacting surfaces be molecularly smooth (e.g., crystalline surfaces such as mica) and (2) that the liquid molecules themselves be able to order into discrete layers at and between two surfaces. There are indications that the oscillations can be reduced or totally eliminated when the surface roughness is no more than a few angstroms.[11,12] This effect has been studied by coating mica surfaces with surfactant monolayers, thereby creating some degree of surface roughness, and subsequently measuring the forces between two such surfaces in liquids. However, the topography of such surfactant-coated surfaces must first be characterized before the results of such measurements can be unambiguously interpreted in terms of solvation forces.

This paper examines the second of the above two phenomena, that is, the interaction of molecularly smooth surfaces across liquids that are incapable of structuring into well-ordered layers. Recent force measurements with low molecular weight polymer melts[13] indicate that the short-range force depends critically on whether the molecules are branched or unbranched. Unbranched PDMS, for instance, exhibits a short-range oscillatory force profile for separations below a few segment diameters[5] with a periodicity equal to σ, as do liquid *n*-alkanes.[4] However, branched polybutadienes (PB) display only monotonically repulsive short-range force profiles.[13] This very dramatic difference between the force profile across PDMS and PB appears to arise solely from the presence of only 8% randomly substituted butadiene (vinyl) groups along the PB chains. However, the fact that these two polymer systems are chemically and structurally different, and have different degrees of polydispersity, invites further investigation of this interesting and important phenomenon using a well-characterized system.

Accordingly, this paper looks at the interactions of mica across three branched paraffins, 2-methyloctadecane, 2-methylundecane, and 2-methyloctane, and compares the results with those previously obtained for *n*-alkanes.[4] In order to examine the effects of polydispersity on the range and strength of the interactions, various controlled mix-

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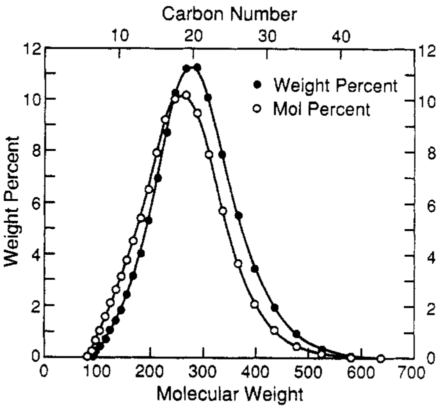

Figure 1. Mole percent and weight percent distribution of the white oil used in this series of experiments, which is mainly composed of branched alkanes (see Materials section).

tures of these pure liquids were studied and a highly polydisperse mixture of isoparaffins was also investigated.

Theoretically, one expects there to be a repulsion between two surfaces in a polymer melt if the molecules are pinned to the surfaces,[14] but no *long-range* force is expected in a melt between two inert walls.[14,15] Apart from the fundamental interest of these forces, this type of system is germane to a fuller understanding of lubrication since branched hydrocarbon liquids are commonly employed as the main constituents of lubricants or "lube oils", while branched polymer melts are used as bases for paints.

Finally, the effect of water in both the mono- and polydisperse oils was also studied since previous investigations have shown that trace amounts of water strongly affect the interaction forces, especially between hydrophilic surfaces such as mica that are "water-wet" in oil.[16]

II. Experimental Techniques and Materials

Techniques. The general experimental methods and conditions are not new and have been described in detail previously.[6,17] Briefly, two thin sheets of molecularly smooth mica are mounted as cross cylinders of radii $R \approx 1$ cm into an apparatus described in ref 6 and 17. The shortest distance between the two curved surfaces D is measured by an optical interferometric technique with a resolution of ~0.1 nm. The force between the surfaces is measured by monitoring the deflection of a "force-measuring" spring on which the lower sheet is mounted. In the present experiments the single-cantilever force-measuring spring of ref 17 was replaced by a variable-stiffness double-cantilever spring described in ref 6.

Materials. The branched alkanes 2-methyloctadecane, 2-methylundecane, 2-methyloctane, and 2-methylpentacosane were obtained from Wylie Organics (98–99% pure) and were further purified by distillation under pure, dry nitrogen gas and then stored over P_2O_5 before use.

"White oil" was a specially prepared research sample supplied by Exxon Chemical Co. It is a colorless liquid composed mainly of saturated branched alkanes and is used as a model base oil for lubricants. Its composition has been characterized by gel-phase chromatography (GPC), gas chromatography (GC), carbon NMR, and vapor-phase osmometry (VPO). These analyses show that there is an average of about 22 carbons per molecule; the mole percent and weight percent distributions are shown in Figure 1. There is an average of one branched methyl group per molecule, of which about 20% are located in the C_2 position, 15% are in the C_3 position, and the rest are internal methyl branches. One to two percent of the oil is unbranched n-alkanes, and 0.3–1% is branched alcohols (C_6–C_{11}). There is no other type of polar molecule, nor are there any aromatics, olefins, or surfactants. The white oil was centrifuged at 7000 rpm for 30 min in order to remove particulates and subsequently stored over P_2O_5 prior to the experiment.

Experimental Procedure. All experiments were performed with a macroscopic droplet of the liquid injected between the mica surfaces. Before injecting the liquid, the inside of the apparatus was dried by placing a receptable of P_2O_5 inside the main chamber and continuously purging it with dry N_2 for several hours. After injection and during the course of an experimental run, the N_2 flow was stopped but the P_2O_5 remained inside the air-tight chamber. To study the effects of water, the P_2O_5 in the receptable was replaced by water or a saturated salt solution, and the water was allowed to diffuse into the liquid via its vapor, as previously described.[4,5,13,16] All measurements were made at 22 °C.

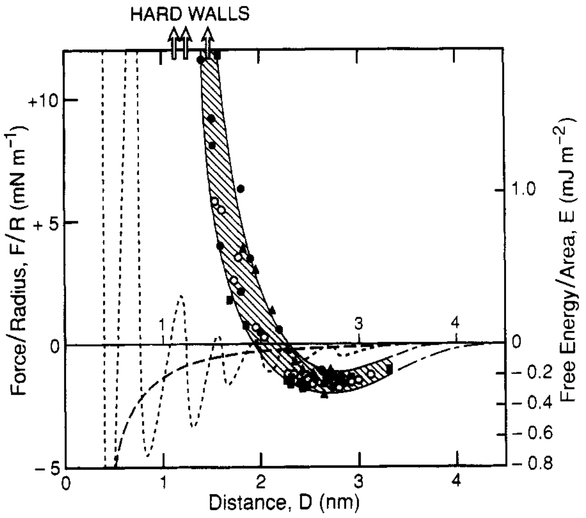

Figure 2. Force F as a function of distance D between two curved mica surfaces of radius R in 2-methyloctadecane liquid at 22 °C obtained from three different experiments. Full points, totally dry liquid (in equilibrium with P_2O_5-dried atmosphere); open circles, N_2-dried atmosphere. Dashed curve: conventional monotonic van der Waals force curve, as expected from the Lifshitz theory.[1] Dotted curve: previously measured force between mica surfaces in the unbranched liquids n-tetradecane and n-hexadecane.[4] The arrows at the top indicate the (off-scale) positions of the effectively "incompressible hard wall" that could not be surmounted even at compressive forces of $F/R > 1000$ mN/m. The right-hand ordinate gives the corresponding free energy per unit area, E, between two flat surfaces based on the Derjaguin approximation, eq 2. Note that these, and subsequent force curves, all show the *equilibrium* force laws, which often required some tens of seconds to a few minutes.

III. Results

2-Methyl-C_{18}. The force–distance profile of two mica surfaces across the dry and purified monodisperse 2-methyloctadecane is presented in Figure 2. The force curves of n-tetradecane and n-hexadecane and the Lifshitz prediction for the continuum van der Waals force law are also shown on the same graph for comparison. Clearly, the very forms of the force curves for the branched and unbranched liquids are markedly different.

At large surface separations, beyond 6 nm, the force across 2-methyloctadecane is monotonically attractive and is as expected if only van der Waals forces are operating. This was ascertained from the measured distance D_J at which the two surfaces jumped toward each other, from which the Hamaker constant A can be deduced via the relation[17]

$$A = 3KD_J^3/R \qquad (1)$$

where R is the radius of the curved surfaces and K is the spring constant. From these jump measurements we obtained $A = 7.7 \times 10^{-21}$ J. The theoretical value may be readily calculated from the standard equation (ref 1, eq 11.14), which is based on the Lifshitz theory and is expressed in terms of the refractive indices of mica and 2-methyloctadecane (1.60 and 1.438, respectively) and the UV absorption frequency ($\nu = 2.9 \times 10^{15}$ s^{-1}). From this, we obtain $A = 8.1 \times 10^{-21}$ J. The experimental and theoretical values are clearly in excellent agreement. Hence, it may be concluded that at separations beyond the adhesive minimum, the forces are well described by the Lifshitz theory of van der Waals forces.

The attractive force increases monotonically with decreasing separation, i.e., becomes more negative, reaching a shallow adhesive minimum at a surface separation of about 2.5 nm (Figure 2). Below this there is a steep monotonic repulsion, which becomes an effectively insurmountable "hard wall" at $D \approx 1.2$–1.5 nm, even at F/R values as high as 1000 mN/m (corresponding to compressive pressures of about 100 atm.). The shaded region of the curve in Figure 2 represents the small degree of scatter in the data obtained from three independent experiments. The most remarkable features of the force law are the absence of oscillations and the deep adhesive minimum at $D = 2.5$ nm, which, when compared with the theoretical van der Waals force curve, is a factor of 5–10 times stronger. Clearly, somewhere between $D = 6$ and 2.5–3.5 nm a different type of force has come into play, resulting in a much stronger attraction than can be attributed to the action of van der Waals forces alone.

It was also noted that the depth of the adhesive well exhibited a small dependence on the time the mica surfaces remained in contact there: the longer the time in "contact" at $D \approx 2.5$ nm the larger the pull-off force required to separate the mice surfaces. However, after 1–3 min in contact, the adhesion would reach a plateau and did not increase further. This maximum adhesion was interpreted as the "equilibrium" value, and these are the values plotted in Figure 2. Similar effects were observed with some of the other liquids, especially with the mixtures, as described below. Also of interest is the fact that the adhesive minimum is quite broad. The origins of the extra attraction, the shallow and time-dependent adhesive minimum, and the steep repulsion at smaller separations are considered in the Discussion section.

Finally, it should be stated that the measured force curves were always reversible and reproducible, even after 2 days. In particular, the reversibility of the forces measured on either approach or separation over a very large range of F/R is a clear indication of the absence of any oscillatory component.

The unbranched *n*-alkanes, on the other hand, display typical oscillatory force characteristics at surface separations less than 3–4 nm.[4] As the surface separation decreases, the force oscillates between successive maxima and minima with a spacing of 0.40–0.45 nm (i.e., the width of an *n*-alkane chain) between each oscillation. An oscillatory force profile is not predicted by continuum theories such as the Lifshitz theory but is expected from theories and computer simulations that take into account the discrete size of the intervening liquid molecules.[3,7-10] 2-Methyloctadecane does *not* show these oscillations, but it is interesting to note that for both the branched and unbranched liquids the forces begin to deviate significantly from the Lifshitz prediction at surface separations below about 4 nm, i.e., below about 10 molecular chain widths.

In order to ascertain whether the hard wall at 1.2–1.5 nm represented a truly infinite barrier or whether it simply could not be surmounted in these experiments, two experiments were carried out where the mica surfaces were first brought into molecular contact in vapor and kept there while the 2-methyloctadecane was injected. It was found that the surfaces remained at this position and were not separated by the liquid (similar findings were obtained with *n*-alkanes and polybutadienes[4,13]). On mechanically separating the surfaces from molecular contact, a strongly adhesive force was measured, corresponding to $F/R = -14$ mN/m. This indicates that the final equilibrium adhesion, or potential energy minimum, is actually at $D = 0$, but the force barrier required to achieve this minimum on approach of two surfaces was too large to be overcome in these experiments.

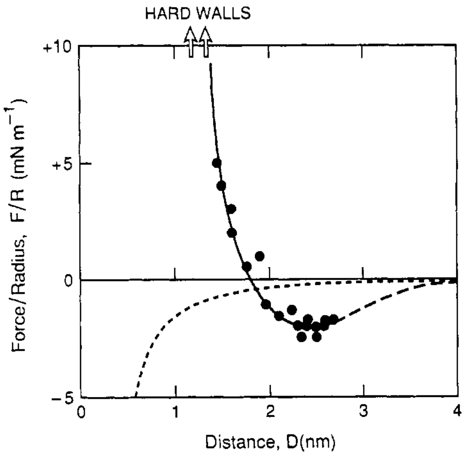

Figure 3. Forces between mica surfaces in 2-methylundecane obtained from two different experiments in totally dry liquid (i.e., with the liquid in equilibrium with a P_2O_5-dried atmosphere). Notations are the same as for Figure 2. Dashed curve: conventional monotonic van der Waals force curve, as expected from the Lifshitz theory.

The introduction of saturated water vapor into the chamber altered the force–distance behavior of the mica/2-methyloctadecane system shown in Figure 2. The main consequence of the presence of water was an increase in the adhesion at the minimum, which also moved farther in, and it was now possible to surmount the force barrier and bring the surfaces into molecular contact at $D = 0$. On separation from molecular contact the value of F/R was −470 mN/m, which corresponds to an interfacial energy of $\gamma = F/4\pi R = 37$ mJ/m^2.[1] This is close to that expected for two curved surfaces in adhesive contact due to the Laplace pressure of the microscopic oil–water annulus holding them together.[1,4,16] Nonetheless, the effects of water are far less dramatic than those previously observed with the unbranched *n*-alkanes.[4]

2-Methyl-C_{11} and 2-Methyl-C_8. Figures 3 and 4 show the results obtained with two branched alkanes of lower molecular weight. As we go from 2-methyl-C_{18} through 2-methyl-C_{11} to 2-methyl-C_8 there are two obvious trends: (i) the force curves move further in, for example, the positions of the adhesive minima and the repulsive hard walls are closer in as we go from Figure 2 through Figure 4, and (ii) there is a progressive increase in the depths of the adhesive wells, which, in all cases, exceeds the conventional van der Waals force. The results with 2-methyloctadecane and 2-methylundecane are qualitatively very similar, with no sign of any oscillations, while with 2-methyloctane one oscillation of periodicity 0.4 nm was measured. This force curve is very similar to that previously measured by Christenson on the isooctane 2,2,4-trimethylpentane, where only one oscillation peak of comparable height and depth was observed (ref 18, Figure 3). As in all these experiments, the introduction of water into the liquid via the vapor resulted in an increased adhesion, with the water easily displacing the hydrocarbon liquid and with the surfaces coming into strong adhesive contact at $D = 0$. We return to a consideration of these results in the Discussion section.

White Oil: A Polydisperse Mixture of Branched Hydrocarbons. Figure 5 shows the reversible force–dis-

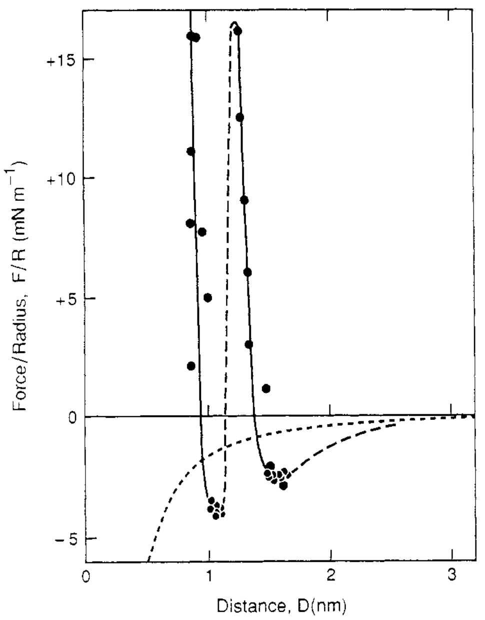

Figure 4. Forces between mica surfaces in dry 2-methyloctane liquid obtained from two different experiments. Notations are the same as for Figure 2. Dashed curve: conventional monotonic van der Waals force curve, as expected from the Lifshitz theory.

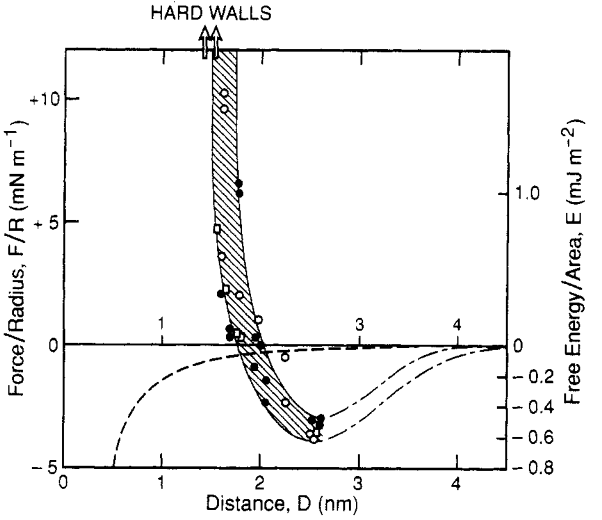

Figure 5. Force as a function of distance between mica surfaces in white oil at 22 °C, as obtained from two different experiments. Full points, totally dry liquid (in equilibrium with P_2O_5-dried atmosphere); open points, N_2-dried atmosphere. The other notations are the same as for Figure 2. Note that the scales and axes of this figure and Figure 2 are identical, allowing a direct comparison between the two sets of results, which shows them to be quite similar.

tance profile of the mica/white oil system. It is very similar to that of the mica/2-methyloctadecane system of Figure 2. The dry mica/white oil system also exhibits a monotonic van der Waals like attraction at surface separations of 4.5 nm and beyond, where from the measured inward jumps, a value of $A = 3.5 \times 10^{-21}$ J was deduced. This compares with the theoretical value (based on the measured refractive index of 1.467 for white oil) of $A = 5.2 \times 10^{-21}$ J, which is about 50% higher than the measured value. Again there is an adhesive minimum at 2.5 nm, as in the mica/2-methyloctadecane system. However, the adhesive minimum is about twice as deep and is now more than an order of magnitude stronger than anything that could be expected from van der Waals forces. The position of the hard wall is also about the same as in the mica/2-methyloctadecane system.

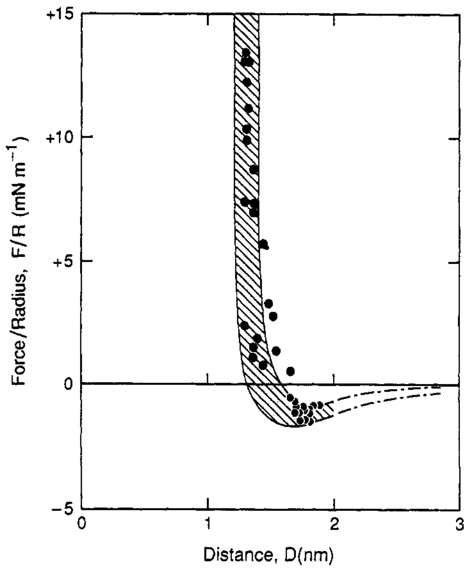

Figure 6. Forces as a function of distance between mica surfaces in a 1:1 mixture of pure 2-methyl-C_{18} and 2-methyl-C_{11} (black points). Experiments with two other mixtures were also carried out: a 1:4 mixture of 2-methyl-C_{18} and 2-methyl-C_{11} and a 1:3 mixture of 2-methyl-C_{25} and 2-methyl-C_8. In both these cases the force curves were slightly closer in than for the 1:1 2-methyl-C_{18}:2-methyl-C_{11} mixture, but all the data fell within the shaded band shown. The slightly shorter range of the interactions with the mixtures compared to those of the pure liquids is consistent with previous experiments using other two-component miscible mixtures.[26]

As in the case of 2-methyloctadecane, when white oil was injected with the surfaces in contact, it did not work itself in between them, and the adhesion force needed to separate the surfaces was as strong as for the 2-methyloctadecane system.

The presence of water vapor had a much more pronounced effect on the mica/white oil system than that observed with mica/2-methyloctadecane but was not as dramatic as that previously observed with *n*-alkanes and other organic liquids.[4,5,16] The time taken for the effect of water to manifest itself was also far quicker than with 2-methyloctadecane. At 75% relative humidity the surfaces jumped in from $D = 5.3$ nm (as expected if only van der Waals forces were operating at this separation), but the jump was now straight into adhesive contact at $D = 0$. The subsequent pull-off force corresponded to a value of γ of 40 mJ/m^2, as measured for 2-methyloctadecane under similar conditions.

Two-Component Mixtures of Pure Branched Alkanes. The enhanced attraction measured with the white oil was initially believed to arise from its polydispersity, which could have given rise to an additional attractive "depletion" force.[19,20] Such forces occur when noninteracting polymers in a solvent becomes excluded from between two approaching surfaces, and it was considered as a likely explanation for the greater adhesion obtained with the white oil where the lower molecular weight components were effectively acting as a "solvent" for the higher molecular weight components. Accordingly (after the suggestion of one of the referees), it was decided to test this hypothesis by performing experiments with isoparaffin mixtures. Figure 6 shows the results obtained with various two-component mixtures of pure branched alkanes of known composition, including one with a 1:3 ratio of 2-methyl-C_{25} and 2-methyl-C_8. The force curves were generally slightly closer in than, or intermediate between, those of the two pure components, but there was definitely no indication of any enhanced attraction. The results

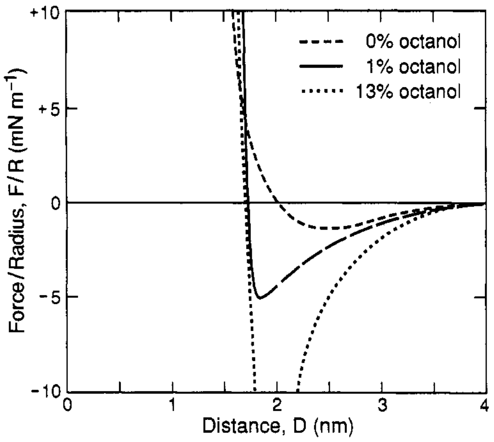

Figure 7. Forces between mica surfaces in 2-methyloctadecane containing 1% by weight octanol (solid line) where the adhesive minimum was $F/R = -4.9 \pm 0.4$ mN/m and with 13% octanol (dotted line) where the adhesive minimum was approximately $F/R \approx -25$ mN/m. For comparison, the dashed curve shows the result of Figure 2 for pure 2-methyloctadecane.

strongly suggest that at least for the system of branched alkanes, polydispersity of homologous components has a small effect on the forces as long as the average molecular weight remains roughly the same.

Effects of Small Amounts of Water and Alcohol. It is well established that even trace amounts of water can have a very dramatic effect on enhancing the attractive forces between mica and various colloidal surfaces in nonpolar liquids,[1,5] especially in hydrocarbon liquids (this work and ref 4, 16, 21). The origin of this phenomenon is still not understood, but it does not appear to be restricted to water alone, since methanol has also been found to dramatically increase the adhesion of mice surfaces in hydrocarbon liquids.[21] The question arose whether longer chained alcohols could also produce such effects; for example, whether the small quantity C_{6-11} alcohols present in the white oil could account for the enhanced attraction observed in that system.

To test this possibility, an experiment was carried out with 2-methyloctadecane containing 1% octanol. The results (Figure 7) show that while octanol does not have an effect nearly as dramatic as those of water or methanol previously observed in hydrocarbon liquids,[21] it nevertheless enhanced the adhesion by a factor of about 3 compared to that in pure 2-methyloctadecane. The results of another experiment with 2-methyloctadecane containing 13% octanol showed an even larger increase in the adhesion, by a factor of about 20. In both cases, however, the position of the steric hard wall was the same as in the pure liquid (within ±0.3 nm). It appears that the presence of as little as 1% octanol is sufficient to account for a 2-fold increase in the attraction. Therefore, it is tentatively concluded here that it is the presence of alcohol in white oil, rather than the polydispersity of the liquid, that is responsible for the enhanced adhesion measured in white oil.

An indication of any possible enhancement of the conventional van der Waals force is a change in the refractive index of the thin layers of liquid immediately adjacent to the surfaces. For the 2-methyloctadecane/13% octanol system (Figure 7), where the extra attraction was particularly pronounced, a value of 1.443 was obtained, by means of the optical FECO technique,[17] for the refractive index of the 1.52-nm-thick hard-wall layer. The bulk value for the liquid, as measured with an Abbé refractometer, is 1.438. The excellent agreement of the two values rules out the possibility that the large adhesive forces are due to an enhanced van der Waals force.

IV. Discussion and Conclusions

The force–distance profiles of the branched saturated alkane liquids, 2-methyloctadecane, 2-methylundecane, and white oil, between two molecularly smooth mica surfaces exhibit a monotonic attraction, reaching an adhesive minimum at a surface separation of 2.0–2.5 nm. There is a steep monotonic repulsion at smaller distances, which prevents the mica surfaces from coming into contact. In contrast to this, the force–distance profiles of the unbranched n-alkanes, or low molecular weight branched alkanes, are dominated by short-range oscillations. It may at first appear surprising that two liquids as chemically similar as 2-methyloctadecane and, for example, tetradecane and hexadecane can display such different force–distance characteristics (Figure 2). However, consideration of the physical mechanism from which oscillatory forces arise elucidates the reasons for the differences.

Short-range oscillatory forces arise whenever the geometry and structure of liquid molecules allow them to order into discrete layers between two molecularly smooth solid surfaces at small separations. The force required to bring the surfaces closer together increases with decreasing separation until some maximum force is attained that is sufficient to squeeze out one of the liquid layers. At this point, the free energy of the system is at a potential maximum. As the liquid layer slides out from between the surfaces, the energy of the system falls into a potential minimum. The force must now be increased again in order to remove the next layer of liquid molecules. Hence the cycle is repeated, with the force oscillating between maxima and minima, until no liquid remains between the two surfaces. Clearly, liquids consisting of asymmetric, branched molecules, as investigated here, and the polybutadienes investigated in ref 13 are unable to order into distinct layers that can be easily slid out when compressed between two surfaces. Consequently, no oscillatory force can arise. It does appear, however, that the carbon chain must be long enough to possess a certain degree of flexibility to smooth out the discreetness of the liquid layers between the two molecularly smooth surfaces. 2-Methyloctane obviously is not a long enough molecule and its flexibility is somewhat restricted compared to that of the other molecules investigated here. Hence, oscillations (at least one) are observed with this liquid.

Although the structure of branched chain molecules confined between two surfaces is likely to be more isotropic and random than that of unbranched molecules, as discussed above, there will still be a tendency for the branched molecules to orient parallel to a surface.[2,13,22] Now, any appreciably aligned molecule near a surface loses some entropy,[22] which corresponds to a gain of about kT in free energy per molecule relative to a molecule far from the surface. If two such surfaces are far apart, each has its own independent layer of aligned molecules with a corresponding increase in the total free energy of the system of $2kT$ due to each layer. When the surfaces are brought close enough together so that the two aligned layers overlap, the surfaces share each others aligned layers. The total loss of entropy due to alignment is now no longer the sum of that for each separate layer but is somewhat less. Thus, the free energy of the system is lowered when the surfaces are broght together. This results in an additional attractive short-range force between the surfaces, whose range would be expected to be comparable to the length (or twice the length) of the liquid molecules between the surfaces, i.e., about 2.5–5.0 nm. Furthermore, as in the case of the entropically enhanced surface energy of polymer melts,[22] the magnitude of the energy gained should be of the order of the orientational free energy of the aligned molecules, i.e., of the order of kT per affected molecule.

The above argument can be applied to 2-methyloctadecane, for example, whose projected area is close to 1 nm^2. One would expect a decrease of about $E = 8$ mJ/m^2 at 22 °C in the maximum additional interfacial free energy per unit area, if *all* the molecules were to be removed from between the surfaces, i.e., if the surfaces come into contact at $D = 0$. In the present case, only a small fraction, perhaps 5–10%, of the molecules can be expected to be so affected at $D = 2.5$ nm. This would result in an energy decrease closer to $E \approx 0.5$ mJ/m^2. Now, the Derjaguin approximation[1,23] relates the free energy per unit area, E, between two flat plates to the force, F, between two curved surfaces of radious R by

$$F/R = 2\pi E \qquad (2)$$

Thus the above energy corresponds to a value for F/R of about 3 mN/m (mJ/m^2), which is close to the values that were measured for the adhesive forces in the present set of experiments (cf. Figures 2–6).

The magnitude and range of the extra attraction observed in the branched alkane systems are roughly comparable to the entropy of alignment of chainlike molecules. This interpretation is also consistent with the trends observed as a function of molecular weight. With decreasing molecular weight, one would expect (i) the strength of the attraction to increase since E will increase as the surface area per molecule decreases and (ii) the range of the interaction to decrease. Both of these effects were observed in the present study. Furthermore, if the results are extrapolated to higher molecular weights, i.e., higher segment numbers, we would expect that the additional attractive component should disappear, leaving only the van der Waals attraction and short-range stabilizing steric repulsion. This is precisely what has been predicted theoretically for the equilibrium interaction of two inert surfaces in high molecular weight polymer melts.[14,15]

With regard to the above model, mention may also be made of recent experiments performed in this laboratory of the forces between various *surfactant-coated* mica surfaces across both 2-methyloctadecane and white oil. No oscillations were observed in these experiments and the depths of the adhesive minima, while less than observed in the present work, were still far greater than could be explained from theories of van der Waals forces. It appears that once the solid surfaces are modified so as to reduce their molecular smoothness, the aligned layers adjacent to each surface are disrupted to some extent. This reduces the loss of entropy at the isolated surfaces and, consequently, reduces the strength of the extra entropic attraction between them. A comprehensive report of this study will be published. These findings using different surfaces are important because they indicate the generality of this extra attraction (proposed here to be an attractive "entropic orientational" force) in certain anisotropic liquids composed of chainlike or orientable molecules. This force may be thought of as being analogous to the final adhesive minimum at contact, characteristic of oscillatory forces. It is related to the density entropy of the molecules (a scalar quantity) rather than to the orientational entropy[15,22] (a vector quantity) as proposed here. The force may also be conceptually similar to the hydrophobic interaction, which is also believed to be due to entropic orientational effects.[24]

Our model for the orientational forces would suggest that they should be associated with conformational changes of the anisotropic liquid molecules between the two surfaces as they approach each other. It is therefore not surprising that small time-dependent effects associated with the adhesion minima were observed in these studies; viz., it was necessary for the surfaces to be close together for about 1 min in order for the adhesion to reach its maximum equilibrium value. This further supports the idea that conformational, i.e., entropic, rearrangements of molecules are involved in determinin these short-range interactions.

The repulsive hard walls at very small surface separations seen in this study (Figures 2–6) have also been observed in previous investigations of both alkanes and polymer melts.[4,5,13,18] They almost certainly arise because the first one or two layers adjacent to the mica surfaces are more strongly held than the molecules that reside further out. Consequently, a very large force, unattainable in the present experiments, is necessary to bring the mica surfaces from a large separation into molecular contact (at $D = 0$). In the present experiments the hard walls occurred at surface separations of 0.8–1.7 nm (increasing with increasing molecular weight). This corresponds to between one and two monolayers aligned parallel to each surface, which is in keeping with previous studies of the adsorption from solution of large alkane molecules onto solid surfaces.[2]

Another important feature of the present work is the difference between the depths of the adhesive minima of 2-methyloctadecane and white oil (which has an average molecular weight similar to that of 2-methyloctadecane). The force of adhesion across either liquid, as discussed above, is already far greater than expected if only van der Waals forces are operating, but in addition to this, the adhesive minimum for the white oil was sigificantly deeper than that measured for 2-methyloctadecane (cf. Figures 2 and 5). Now the main differences between these liquids is that white oil is a polydisperse mixture of branched alkanes whereas 2-methyloctadecane is a monodisperse liquid. Initially, it appeared reasonable that the difference in the adhesive minima could be accounted for in terms of the relative polydispersities of the two liquids: in a polydisperse liquid the larger molecular species are the most constrained when the two surfaces are forced into close proximity. Thus, as the distance between the two surfaces is reduced, the larger molecules are forced out from between the two surfaces while the smaller molecules remain in gap. This results in a concentration gradient of the larger molecules in the thin film between the surfaces relative to the bulk liquid which gives rise to an additional entropic or osmotic pressure between the surfaces. It is an attractive force, since it induces the migration of the smaller molecules out from between the surfaces in order to dilute the larger molecules in the bulk liquid. This type of attractive force is known as a "depletion force" and was first proposed for the case of nonadsorbing polymers in solution.[19] It has been measured recently between lipid bilayers across aqueous solutions of nonadsorbing sugars and polymers.[20]

However, the present experiments with the two-component isoparaffin mixtures of similar average molecular weight do not seem to support the simple explanation of depletion attraction, though it cannot be ruled out totally as partially contributing to the enhanced attraction in the complex polydisperse white oil. Nonetheless, it still remains that the similarities of the various force curves measured in both the pure liquids and the mixtures strongly suggest that polydispersity does not have a large effect on the forces as long as the average molecular weights of the samples are similar.

On the other hand, the results with two-component 2-methyl-C_n/octanol mixtures do indicate that even small

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amounts of alcohol (<1%) dissolved in the nonpolar hydrocarbon liquid can more than double the strength of the adhesion force. It is therefore concluded that the polarity of the alcohols present in the white oil is most likely the reason for the extra adhesion. This is consistent with previous findings that trace amounts of both water and methanol can drastically increase the adhesion of mica and other hydrophilic surfaces immersed in various hydrocarbon liquids.[1,4,16,21] The origin of this extra attraction is, however, still not understood.

In the light of the results presented here, it is somewhat clearer as to why isoparaffins, and other branched chain molecules, make good lubricating oils. Branching of hydrocarbon chains, even when limited to only one methyl group, eliminates the layered structure common to symmetric liquids constrained between two surfaces. This prevents the surfaces from coming into contact by the progressive sliding out of molecular layers or from coming into adhesive minima at discrete molecular separations, at which positions there are strong frictional forces on shearing one surface relative to the other.[25] The monotonic repulsion, observed at small surface separations when 2-methyloctadecane, 2-methylundecane, or white oil are the intervening liquids, acts as a soft cushion, which prevents the surfaces from coming too close together thereby averting high friction and surface damage.

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Registry No. 2-Methyloctadecane, 1560-88-9; 2-methylundecane, 7045-71-8; 2-methyloctane, 7732-18-5; 1-octanol, 111-87-5.

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Improved Hole Drift Mobility in Excimer-Free Polymers Containing a Dimeric Carbazole Unit

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ABSTRACT: Hole drift mobility of a series of homo- and copolymers containing a dimeric carbazole unit, 1,2-*trans*-bis(9*H*-carbazol-9-yl)cyclobutane (DCZB), was measured. The hole drift mobility of the polymer containing only the DCZB group as the functional group is more than 10 times higher than that of poly(9-vinylcarbazole) (PVK) or poly(9-ethyl-3-vinylcarbazole) (P3VK). Comparison of their photophysical properties indicated that the high hole drift mobility of the DCZB polymers was brought about by the reduction of the concentration of trapping sites (excimer-forming sites (EFS)). The concentration is much smaller in the DCZB polymers than in PVK or P3VK. This was further confirmed by the temperature and electric field dependence of the mobility.

Introduction

Interest in charge transport in amorphous organic materials has been increasing in connection with their potential applications as photoreceptor materials in electrophotographic processes such as photocopying and laser printing. Recently, photoreceptors with layered structure consisting of a charge-transport layer (CTL) and a charge-generation layer (CGL) have been most commonly used. High efficiency of charge transport in CTL is strongly desired to improve the overall sensitivity of the photoreceptor. There are several scientific publications concerning charge transport in organic films.[1-20] However, the detailed mechanism of the charge transport has not been fully understood.[10] For example, there is no widely accepted explanation for the origin of temperature and field dependence of charge mobility or for the relationship

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