Vapor Adsorption on Mica and Silicon: Entropy Effects, Layering, and Surface Forces

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We have measured the adsorption isotherms of n-pentane, cyclohexane, tetrachloromethane, octamethylcyclotetrasiloxane (OMCTS), and water on muscovite mica and silicon. An angle-averaging, refractive-index-matching ellipsometric technique has been used to avoid problems due to anisotropy and back-reflection in the case of mica. With OMCTS on mica layering effects like those found with simple gases on graphite and single crystals at low temperatures are observed. OMCTS on silicon shows no layering, but the isotherm is qualitatively different from that of the other nonpolar liquids. The water isotherm on the slightly hydrophobic silicon surface is convex upward but smooth and shows only little adsorption (≤1 nm) even at saturation. Up to thicknesses equivalent to about half a statistical monolayer, all other isotherms are smooth and linear, showing the importance of entropy effects at low coverages. The isotherms of the nonpolar liquids except OMCTS on both mica and silicon are very similar when normalized by the molecular diameter. Close to saturation differences in wetting are seen. Cyclohexane and tetrachloromethane wet silicon, and n-pentane wets both mica and silicon. None of the isotherms agrees with the Lifshitz theory of van der Waals forces at separations below 2 nm. The results suggest that structural effects are present in many liquid adsorbed films at room temperature, provided that the substrates are smooth and homogeneous. The absence of layering does not imply agreement with the Lifshitz theory of van der Waals forces.

Introduction

The influence of liquid structure on the interactions between solid surfaces across liquids has been experimentally well-documented in the past 10 years. The monotonically attractive predicted by the Lifshitz theory of van der Waals forces is not found at separations approaching those of molecular dimensions. Instead, oscillatory solvation forces are measured between smooth surfaces in most liquids, from near-spherical, nonpolar molecules such as tetrachloromethane to hydrogen-bonding liquids like methanol and 1,2-ethanediol. Only in the case of water are the solvation (hydration) forces apparently absent under some circumstances, notably between mica surfaces in water at low electrolyte concentrations. Here the forces do superficially resemble a van der Waals attraction, although no quantitative information is available at separations below 2 nm. The experiments are in good qualitative agreement with the predictions of computer simulations of hard-sphere and Lennard-Jones liquids between two walls and the results of integral equation or density-functional theories. Such measurements are only possible for relatively thick films, where the value of II is not too great (typically ≤1000 N m⁻², usually corresponding to thicknesses greater than 10 nm).

The second method is more indirect and is based on determining the vapor adsorption isotherm of the liquid on the solid surface. The thickness of the adsorbed film on the solid surface depends on the "force" between the solid-film interface and the gas-film interface. A repulsive force implies a thickening film with a disjoining pressure defined by

$$
II = \rho_b - \rho_l
$$

where \(\rho_b\) is the pressure in the bubble and \(\rho_l\) is the pressure in the bulk liquid. Experimental setups to measure II have been described by many authors. Such measurements are only possible for relatively thick films, where the value of II is not too great (typically ≤1000 N m⁻², usually corresponding to thicknesses greater than 10 nm).

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$$
II = -\frac{\partial G}{\partial h} = -\left(\frac{kT}{v_m}\right) \ln \left(\frac{p}{p_0}\right)
$$

where \(G\) is the excess free energy of the film due to surface forces, \(h\) is the film thickness, \(p\) is the vapor pressure of the gas in equilibrium with the film, \(p_0\) is the vapor pressure at saturation, and \(v_m\) is the molecular volume of the liquid in the film. Gas adsorption data yield information on the disjoining pressure for very large values of II, hence at relatively small intersurface separations or film thicknesses (≤5–10 nm). To a certain extent these measurements complement the plate–bubble method. Such experiments are in principle capable of yielding the same sort of information as direct force measurements between two solid surfaces.

The adsorption of vapors to solid surfaces is not only a means of measuring the interaction across a thin film. It has been the subject of extensive experimental and theoretical study by physicists, chemical engineers, and physical chemists for diverse reasons. The area is of great fundamental interest to physicists

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because it allows the transition from two-dimensional to three-dimensional phase behavior and the transition from discrete to continuum (bulk) properties to be investigated. Gas adsorption is of practical importance in the study of powders and porous materials, where it is used for surface area determination. The area related to other phenomena like surface melting, wetting, and spreading, all of which ultimately depend on the nature of intermolecular and surface forces.

It has long been recognized that the extent of adsorption of a vapor to a surface depends critically on the strength of the intermolecular interactions between the substrate and the vapor species. This forms the basis for the classification of isotherms by Dash and others. Type I isotherms are found in the case of strong substrate–molecule interactions and are characterized by complete wetting of the substrate by the liquid or adsorption that grows continuously as the vapor pressure approaches saturation. This is equivalent to a disjoining pressure which decreases monotonically with separation, and this is predicted by Lifshitz theory to occur for most common liquids on high-energy surfaces. Intermediate-strength substrate–molecule interactions lead to type II isotherms or incomplete wetting (finite thickness at saturation)—they are found in the case when the liquid subtends a finite contact angle on the solid. Such isotherms are only directly predicted by Lifshitz theory in exceptional cases. Weak interactions lead to no adsorption at any pressure and show type III isotherms, or a negative disjoining pressure at small separations. Older classification schemes like that of Brunauer include many isotherms that show marked effects due to substrate heterogeneity and capillary condensation in porous materials.

The strength of the substrate–molecule interaction is related to the surface energy of the solid, and high-energy solids such as ionic crystals and metals adsorb strongly and are wetted by most liquids when the surface is truly clean. Low-energy substrates such as organic polymers and surfactant monolayers show intermediate wetting behavior (finite contact angles) and only limited adsorption from vapor. In practice, many high-energy surfaces behave as low- or intermediate-strength substrates due to the presence of adsorbed material on the surface.

There is now a wealth of information on the adsorption of simple gases and hydrocarbons to smooth and homogenous substrates at low temperatures. These experiments have shown that the phase behavior of adsorbed films is complex. Structural effects due to the condensation of successive layers of gas molecules dominate at low temperatures, particularly below the triple point temperature where the adsorbed film is solid like. These layer condensations are first-order phase transitions which terminate at low temperatures, and these are described as discontinuous. The adsorption isotherms show very sharp steps at lower temperatures but these become increasingly rounded with temperature, although structure is usually seen to persist to temperatures above the melting point. Complete wetting is often suppressed in solid films by the effect of the lattice of the underlying substrate, which prevents the adsorbed film from attaining the structure of the bulk crystal. Surface melting of the top layers at temperatures below the melting point may in some cases counteract this effect. A number of two-dimensional phases have been observed in monomolecular layers, in both the solid and the liquid state.

Both lattice gas theories and density-functional models have gone some way toward rationalizing the phase behavior of adsorbed films in such ideal or near-ideal systems. Indeed, most work has been focused on homogeneous crystalline phases like exfoliated graphite. This has focused on the phase behavior of the adsorbed films themselves, often in the solid state. Little attention has been given to the interaction between the vapor and solid across the adsorbed film. This is in stark contrast to the work on adsorption to more heterogeneous substrates, often near room temperature, where the isotherms are smooth. This apparent lack of structure is not surprising (for discussion of a possible exception, see ref 40). The effect of surface heterogeneities would be to smear any layering transitions because they would occur at different pressures at different sites on the surface. Such an effect is responsible for the knee in the familiar BET adsorption isotherm. Even with reasonably homogeneous substrates adsorption of contaminants from the atmosphere would lead to an increased heterogeneity.

Many of these latter investigations have addressed the question of the validity of various theories of intermolecular and surface forces to describe the determined isotherms. When electrostatic contributions such as double-layer forces between the solid surface and the liquid–vapor interface can be safely neglected, as in the case of nonpolar liquids, Lifshitz theory predicts a repulsive pressure across an adsorbed film in most cases. This repulsion will be proportional to $t^2$ in the nonretarded limit (small $t$) and proportional to $t$ in the retarded limit at large thicknesses. This neglects the zero-frequency term which is not retarded but always small for nonpolar systems. The work of Sabisky and Anderson is perhaps the most convincing demonstration of the validity of Lifshitz theory for thin liquid films. This covered the thickness range of 1.2–30 nm, or four or more statistical layers of helium, but the films were obtained by allowing helium to climb up surfaces of alkaline earth fluorides and the liquid film was thus in direct contact with the reservoir of bulk helium. Other claims of agreement are less convincing, particularly in the case of adsorbed films. Good agreement with Lifshitz theory using the plate–bubble technique has been found in a number of systems. Many authors have sought to describe the observed isotherms using so-called potential theories. These assume that van der Waals forces are the dominant forces in the adsorbed layer but rather than considering the film, vapor, and solid as “bulk” media characterized by their dielectric frequency response (as in Lifshitz theory), the interaction between the surface and the adsorbing molecules is evaluated as a sum or integral of many individual interactions. These theories lead to a similar $t^2$ relationship for the pressure across the film (or, equivalently, the chemical potential). Some models use semiempirical exponential and inverse-square contributions to obtain better agreement with experimental observations, and these are sometimes used to fit
adsortion isotherms in much the same way as BET theory is employed.

There has hitherto been a shortage of high-resolution measurements of adsorption isotherms on smooth and homogeneous substrates at room temperature. The extent to which structural effects in adsorbed films are important at higher temperatures is unknown, and few serious quantitative comparisons with Lifshitz theory have been attempted. There is thus a real need for more data on vapor adsorption at room temperature to attempt to increase our knowledge of the interactions in adsorbed films of common liquids.

In this paper we present results of vapor adsorption measurements on muscovite mica and silicon. We have used a novel and very accurate ellipsometric technique to determine the thickness of adsorbed films of cyclohexane, tetrachloromethane, \( n \)-pentane, octamethylcyclotetrasiloxane, and water. Short accounts of some of these experiments have recently appeared elsewhere.\(^{56,47}\) We have compared our results to what is known about adsorption of simple gases on smooth and homogeneous substrates at low temperatures and to previous work with similar liquids on other well-defined substrates at room temperature. We have been particularly concerned with the disjoining pressure of the adsorbed film and with comparing this with theory and previous work. Our results show a number of features previously not seen at room temperature and suggest that many commonly held assumptions need to be critically reviewed. Above all, these measurements open the door to a number of far-reaching investigations of fundamental aspects of the phase behavior and surface forces of adsorbed films.

### Materials and Methods

**Ellipsometry.** With ellipsometry one measures the coefficient of ellipticity \( p \) which is the \( \text{Im} (r) \) at the angle of incidence where \( \text{Re} (r) = 0 \) (the Brewster angle), where \( r = r_p/r_s \) is the ratio of the amplitude reflectivities for \( p \) and \( s \) polarized waves. \( p \) provides the thickness of the absorbed layer \( t \) when that layer is thin and when its dielectric constant (equivalently the refractive index) is known. In particular, \( p \) is given by the expression derived by Drude in a continuum model of the media for small thicknesses

\[
p = \left( \frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right)^{1/2} \frac{(\varepsilon - \varepsilon_1)(\varepsilon - \varepsilon_2)}{\varepsilon} \tag{3}
\]

where \( \varepsilon \) is the dielectric constant of the liquid layer of thickness \( t \) on the substrate of dielectric constant \( \varepsilon_2 \), and light is incident through the vapor of dielectric constant \( \varepsilon_1 \). Note that \( p \) varies linearly with \( t \) for thin films. In analyzing the results the full Drude expression was used since particularly for the case of films on silicon significant nonlinearities occur even for small values of \( t \). Standard values of \( \varepsilon \) taken from the *Handbook of Chemistry and Physics*, 45th ed., were used in the calculations.

While the dielectric constant \( \varepsilon \) of bulk liquids is easily measured, how it varies with thickness as the layer thins to submonolayer equivalent thicknesses has not been extensively studied. However, it is likely that the use of the bulk dielectric constant for such thin films will not lead to seriously misleading thicknesses. The reasoning is as follows: The (relative) dielectric constant of the layer is given by

\[
\varepsilon = \varepsilon_0 + P/E \tag{4}
\]

where \( P \) is the induced polarization per unit volume in the layer by the field \( E \). If the dipole induced in a molecule by the incident electromagnetic wave is not affected by the fields of the induced dipoles on other nearby liquid or substrate molecules, then \( P/E \) will be just \( \varepsilon_0 \), with \( \varepsilon \) the number of molecules with polarizability \( \alpha \) per unit volume. In the bulk liquid, interactions between the molecules modify this to become \( n\alpha/(1 - n\alpha/3) \), the Clausius-Mossoti expression. When \( \varepsilon \) has a value of about 2\( \varepsilon_0 \), typical of most nonpolar liquids, then the interaction term provides a 30% renormalization to \( n\alpha \). A submonolayer layer would thus be expected to be characterized by an effective dielectric constant which is smaller than the bulk by no more than about 15%. Note that this variation in the dielectric constant should occur quite quickly as the coverage \( \theta \) decreases below 1 monolayer, since \( n = \eta /\theta \).

In summary, in the submonolayer region we would expect the ellipticity to follow the above expression, with \( t \) fixed at a monolayer thickness \( d \), but now with a surface coverage dependent \( \varepsilon \) in the expression for \( p \). The latter will be determined by the term \( (\varepsilon - \varepsilon_1) \) at low surface coverage, which will be proportional to \( n = \eta /d \), with \( \eta \) the number of molecules per unit area, i.e., to the surface coverage \( \theta \).

Strachan\(^{48}\) and Shikhunin\(^{49}\) have considered the effects of the coherent scattering by surface molecules spread over a continuum substrate, and derive more rigorously appropriate expressions for the ellipticity in the submonolayer region, through the relation to the bulk properties follows the same argument given above. Experimentally, the only attempt to check the prediction appears to be that of Smith\(^{49}\) in a study of the variation of the ellipticity with the adsorption of fatty acids on the surface of mercury. Within his accuracy of about 20% he finds

\[
p = a\beta d, \quad t < d; \quad p = a\alpha t, \quad t > d \tag{5}
\]

with the proportionality constant \( a \) having the same value in the two regimes. Also, Boinovich and Emelyanenko\(^{50}\) found no change from bulk in very thin layers (1–3 nm) of heptane adsorbed on free glass films.

**Mica as a Substrate.** While mica with its feature of easy preparation of molecularly smooth surfaces has been much used in surface studies, its use as a substrate for ellipsometry measurements has caused difficulties. The top and bottom surfaces of the mica substrate are usually so parallel that severe interference occurs between the light waves reflected from the two surfaces. Interference can be reduced by approximate index matching at the back surface, and we have achieved this easily by using a thick layer of epoxy glue (5 min Araldite) to fix the mica substrate onto a black anodized aluminum holder.

The index matching, however, cannot be perfect, since mica is optically anisotropic. With the approximation \( \varepsilon_1 = \varepsilon_2 = \varepsilon_3 \), it is best to choose \( \varepsilon_1 \) to be at the Brewster angle for a thin anisotropic layer on the isotropic medium \( \varepsilon_0 \); see Lekner.\(^{52}\) Measurements and calculations by one of us\(^{53}\) show that the residual signal, which has interference effects as the angle of incidence is varied, is shifted as a whole to larger values of \( \text{Im} (r) \) by an amount calculated for a thin film on an equivalent isotropic substrate, as shown in Figure 1. A measure of the angle-averaged ellipticity signal thus removes the residual interference effects and leaves a signal that can be easily interpreted in terms of the adsorbed layer thickness. A variation in the angle of incidence of about \( 5^\circ \) will typically provide between 5 and 10 interference oscillations for a typical mica substrate of about 100-µm thickness, and so we perform the appropriate angle averaging by using a lens to provide this range of angles in converging incident light beam, followed by a second lens after the sample to focus the light beam onto the detector. One of the authors\(^{54}\) studied drops spreading on mica using an imaging ellipsometer, and there the objective lens provided the simplifying angle averaging so that mica interference effects were also not important there.

We have found that the ellipticity signal from clean mica depends also upon the rotational orientation of the anisotropic mica cleavage surface relative to the plane of incidence. Mica

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\(^{56}\) Beaglehole, D. *Phys. Rev.* 1938, 100B, 163.


\(^{52}\) Lekner, J. *Theory of Reflection;* Martinus Nijhoff: Amsterdam, 1987, p 144.

\(^{53}\) Beaglehole, D. *Unpublished results.*

The angle average between top and bottom is just that calculated with the usual angle of incidence varies from $\rho \cdot \tau$. Figure 1. Locus of $e_0/e_\perp$ for an anisotropic substrate of $e_\perp = 2.47, e_\parallel = 2.53$, and $d = 100 \mu m$ with approximate index matching $\epsilon = 2.50$. The angle of incidence varies from $52^\circ$ to $63^\circ$. (top) No layer; (bottom) with surface layer $\epsilon = 2.0$ and $t = 5.0 \mu m$. The upward displacement of the angle average between top and bottom is just that calculated with the usual $\rho \cdot \tau$ relationship.

in fact is monoclinic. It cleaves in the 001 plane; the optic axis lies in the 010 plane, inclined at about $15^\circ$ to the 010 normal; and $e_\perp \sim 2.47, e_\parallel \sim 2.56, \epsilon_2 \sim 2.59$, where $\beta$ and $\gamma$ directions are 010, 100, respectively, and $\alpha$ lies in the 010 plane. The theoretical description of this ellipticity from such an anisotropic crystal remains a challenge for the theoretician. We observe that the smallest signal is obtained when the mica optic axis lies in the $p$ direction (in the plane of incidence), and we have used this orientation in all our measurements.

Silicon as a Substrate. Silicon is weakly absorbing to visible light, having a dielectric constant for 600-nm radiation $\epsilon = 15 + 0.156i$. The absorption obviates any back-reflection problems. For a perfect surface it would also yield an ellipticity of about $10^{-3}$. The large value for the real part of the dielectric constant gives a strong dependence of ellipticity upon adsorbed gas layer thickness.

Wafers for the electronics industry have a high-quality finish, with typically a few angstrom root-mean-square surface roughness on the short scale. In the study here we used a wafer cut normal to the [111] direction. The nature of the surface depends upon the chemical treatment. We washed the substrate in a dilute HF/HNO$_3$ wash and then placed the substrate in boiling HNO$_3$ for 5 min, a procedure which leads to a thin well-formed SiO$_2$ layer on the surface.$^{34}$ The resulting surface is moderately hydrophilic (the contact angle of water was not measured but should be similar to the angle measured on heat-dehydroxylated quartz, i.e. 20-45$^\circ$) and the ellipticity signal (in the absence of adsorbed gases) was about $3 \times 10^{-2}$, corresponding to an oxide layer of 3 nm.

Adsorption Techniques. In earlier experiments we noticed that thick layers tend to adsorb onto metal surfaces in the measuring cell, and it is essential to prevent these from draining onto the substrate. The mica surface was therefore mounted clear of the support, and the support was isolated from the metal sealing cap and glass walls by a Teflon stopper; see Figure 2. The temperature of the cell was kept below that of the plumbing and the surrounding room, by completely enclosing the cell in a secondary enclosure through which temperature-controlled water ($\pm 5$ mK) flowed continuously.

The gas-handling system is shown schematically in Figure 2. We used Datametrics capacitance pressure gauges, matched in sensitivity to the vapor pressure of the gas, and Nupro ultra-high-vacuum valves. The system was heated to 80$^\circ$C, and checked to be leak tight using a helium leak detector, and also by monitoring the residual leakage rate when the valves were closed.

The liquids were stored over Union Carbide 4A molecular sieves zeolite pellets to remove any residual water. The liquid was placed in the reservoir in an atmosphere of pure nitrogen. Residual water vapor in the cell was pumped by a liquid nitrogen trap, which was then closed off for the experiment. The reservoir liquid was frozen to liquid nitrogen temperature, and the whole system was pumped hard to remove the background nitrogen atmosphere.

A fresh cleave of the mica surface was performed directly before mounting the substrate into the cell. The cell was then immediately pumped hard and liquid nitrogen trapped, and the background mica ellipticity was determined. Some vapor was then leaked into the cell, and the ellipticity recorded once equilibrium in both pressure and ellipticity was obtained, usually after a few seconds. A continuous recording of ellipticity versus pressure could be obtained on an $X$-$Y$ recorder, leaking the gas in slowly. With this speedy response it was easy to cycle from low to high pressure quickly, thus monitoring the background mica value for contamination, and checking for pressure drifts. Near saturation with the high vapor pressure liquids the pressure in the cell would occasionally develop thermomolecular pressure oscillations, with the ellipticity following the pressure variations.

The ellipticity was measured with a sensitivity of $10^{-4}$, which corresponds to a thickness sensitivity of about 0.005 nm for liquids on mica and 0.002 nm for liquids on silicon. The data shown below are representative values read from the continuous experimental curves.

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Vapor Adsorption on Mica and Silicon

Figure 3. Ellipsometrically determined thickness $t$ of adsorbed films on silicon as a function of the relative vapor pressure $p/p_0$ at 18 °C of water (filled triangles), cyclohexane (open diamonds), tetrachloromethane (open squares), $n$-pentane (open triangles), and octamethylcyclosiloxane (OMCTS) (filled squares).

Figure 4. Ellipsometrically determined thickness $t$ of adsorbed films on mica as a function of the relative vapor pressure $p/p_0$ at 18 °C of water (filled triangles), cyclohexane (open diamonds), tetrachloromethane (open squares), $n$-pentane (open triangles), and OMCTS (filled squares).

Figure 5. Thickness of adsorbed films on mica and silicon for liquids that appear to wet the substrate for $p/p_0 \geq 0.9$. The experimental points are $n$-pentane on silicon (filled diamonds) and mica (open diamonds), cyclohexane on silicon (open squares), and tetrachloromethane on silicon (filled squares).

Figure 6. Thickness of adsorbed films of OMCTS on mica, showing three different measurements with three different mica sheets (open symbols) and OMCTS on silicon (filled squares). Note the shape of the isotherms and the sudden increase in adsorption at $p/p_0 = 0.8$ for the isotherms on mica.

Results

The adsorption isotherms measured on silicon at 18.1 °C are shown in Figure 3 for film thicknesses below 5 nm. Water shows very limited adsorption, as expected from the slight hydrophobicity of the silica-like surface of the silicon wafer. The amount of adsorption at saturation is about half that obtained by Gee et al. in a recent study of water vapor adsorption on heat-dehydroxylated quartz. Cyclohexane, tetrachloromethane, and $n$-pentane all appear to wet the silicon substrate (see below), and the two first isotherms are almost indistinguishable at vapor pressures below 0.9. Note the linear regime that extends to $p/p_0$ about 0.3, where the adsorbed amount equals about half the thickness of a statistical monolayer. OMCTS does not wet silicon and the shape of the isotherm is convex with respect to the pressure axis at low pressures, with an inflection point at $p/p_0 = 0.5$, instead of concave as for the other liquids (except water). (In this paper we use "wetting" to indicate the growth of layers to thicknesses greater than 5 nm or so, since there seems to be a clear distinction between liquids limiting at around 2 nm and those growing considerably thicker.)

The adsorption isotherms for the same liquids on mica at 18.1 °C are shown in Figure 4. Cyclohexane, tetrachloromethane, and $n$-pentane show very similar adsorption, and the linear regime persists to $p/p_0 = 0.4$, or to slightly higher pressures than on silicon. Water shows less adsorption at lower relative vapor pressures, but the adsorption close to saturation ($p/p_0 = 0.99$) is very similar to that of cyclohexane and tetrachloromethane. The greater adsorption compared to that on silicon is to be expected from the small contact angle of water on mica (∼7°). The OMCTS isotherm is very obviously different from those of the other liquids—note in particular the sudden increase in adsorption at $p/p_0 = 0.8$, the pronounced convex shape, and the absence of any substantial linear region at low pressures. The overall shape of the isotherm is similar to that of the same liquid on silicon. Only $n$-pentane wets mica and the adsorption near saturation is large, of the order of 20 nm.

Figure 5 shows the film thickness as a function of the relative vapor pressures for the wetting systems at higher relative vapor pressures ($n$-pentane, tetrachloromethane, and cyclohexane on silicon and $n$-pentane on mica).

Figure 6 presents data from three different experiments with OMCTS using different mica sheets. The variability of the isotherms gives an idea of the typical differences found from experiment to experiment with all vapors. The shape is the same.
in all cases as is the sharp increase in adsorption at around \( p/p_\text{b} \approx 0.8 \). For comparison, the adsorption isotherm of OMCTS on silicon is also shown. Adsorption data as a function of temperature below and above the melting point of bulk OMCTS (\( \approx \) triple point temperature, 18.4 °C) are shown in Figure 7. There is no qualitative change in the isotherm at the melting point, as expected, but the sudden increase in adsorption at \( p/p_\text{b} \approx 0.8 \) shifts to higher pressures with decreasing temperature. The total film thickness at saturation increases with temperature.

The similarity of all the isotherms, on both silicon and mica, becomes readily apparent when the results are plotted on the same graph. By normalizing the film thicknesses by some quantity related to the mean molecular diameter of the molecules, the isotherms become virtually indistinguishable in many cases. In Figure 8 the measured film thicknesses have been normalized by the cube root of the molecular volume, which should give a good relative measure of the mean molecular diameter. With these units, one statistical monolayer corresponds to a normalized thickness of approximately 0.12. As can be seen, only the OMCTS isotherms are very clearly different from the others at low relative vapor pressures. The water isotherm on mica shows less adsorption at low pressures.

**Discussion**

The most striking features of the measured isotherms are (i) the very different shape of the OMCTS isotherms and in particular the structure shown by the isotherms of this substance on mica, (ii) the overall similarity of all the other isotherms below film thicknesses of 2 nm (except, to some extent, water on both mica and silicon), including the linear regime at low pressures on both mica and silicon, and (iii) the sharp distinction in wetting behavior on both mica and silicon between liquids of very similar properties.

We will discuss each of these points in turn and then turn our attention to comparisons with Lifshitz theory. We also discuss possible implications of the two main problems in vapor adsorption studies—temperature control and adsorption of contaminants.

**Layering: Structural Effects.** The convex (upward) shape of the OMCTS isotherms and the sharp increase in adsorption at \( p/p_\text{b} \approx 0.8 \) (on mica) are evidence of molecular layering in the adsorbed film. Such layering is commonly seen even in liquid films (above the triple point temperature of the bulk liquid) of simple hydrocarbons and inert gases on graphite. The very rounded shape of the isotherm suggests that the film is far above the roughening temperature, where the layering transitions are continuous. The similarity in shape of the OMCTS isotherm on silicon suggests that there are remnants of layering effects on this substrate too. The greater surface roughness and/or some slight surface heterogeneity related to the occurrence of silanol groups on the silica-like surface may be responsible for the absence of any distinct steps in the adsorption isotherm. It is even possible that surface heterogeneity of the mica substrate is responsible for the very smooth appearance of the first layer condensation. Any surface heterogeneities would have less influence as the second layer condenses because the surface is already covered by OMCTS molecules. The fact that the isotherms are plotted as a function of the relative vapor pressure does, however, expand the features at lower pressure compared to those at higher pressures. This expansion would be even more noticeable if the results were plotted as a function of chemical potential (\( kT \ln (p/p_\text{b}) \)). If we assume that the adsorption is governed by van der Waals interactions that decay as \( r^{-\alpha} \) (that this is reasonable is clear from results discussed below), we can give roughly equal space to each layer by plotting the film thickness as a function of \( \mu - \mu_\text{b} \)^{1/3} (cf. ref 25) to obtain the isotherms shown in Figure 9. As can be seen, the 0-1 and 1-2 transitions are now seen to be much closer in shape, although the second one still appears to be slightly sharper than the first (compare the slopes of the isotherms in the vicinity of the transitions). The fact that the 0-1 transition is less sharp than the 1-2 may be indicative of a higher critical temperature for the second layering transition, as predicted by lattice gas theories and seen previously in some experiments. For comparison, the results of using the same “linearization” for cyclohexane on mica and OMCTS on silicon are also shown (these isotherms have been displaced for clarity). These isotherms are qualitatively different and appear completely smooth.

The shift in the 1-2 transition toward lower pressures (and chemical potentials) with increasing temperatures is characteristic of a liquid whose wetting of the substrate increases with temperature. Such a shift has been observed with gases adsorbed on graphite. The maximum adsorption of OMCTS is also seen to increase with temperature (see Figures 6 and 9). As expected, the isotherms show a smooth evolution with temperature that is not affected by the bulk triple point. Disregarding any significant decrease in adsorption at still lower temperatures, a hypothetical isotherm at temperatures far below the triple point temperature, where the layering transitions are first-order, might appear as the dotted line in Figure 7.

The other liquids show no sign of layering effects. It is likely that the convex shape of the water isotherm on silicon is related...
to surface heterogeneities (silanol) groups would have a larger affinity for water than other sites) rather than layering, given that the isotherm on mica (which has no surface hydroxyl groups) appears completely smooth. The other liquids are all much further above their respective triple point temperatures than OMCTS; cyclohexane, where $T_s$ is 5.4 °C, is closest. A liquid–vapor interface is rough due to capillary waves, and the density profile is believed to decay from liquid to vapor over a length of some two molecular diameters. In a thin film of a few molecular layers on a solid surface the potential of the solid substrate may have the effect of increasing order in the adsorbed film and thereby layering is commonly seen to persist above the melting point. The higher the temperature above the melting point, the less the ordering effect of the solid substrate. Layering in OMCTS compared to the other liquids is also favored because its polarizability and consequently attraction for the substrate are larger.

By contrast, the forces measured between two mica surfaces in cyclohexane, tetrachloromethane, and OMCTS are virtually identical when normalized by the mean molecular diameter. In this case the important factor is the hard-core repulsion between the individual molecules and the molecules and the surface, and this is much less dependent on temperature than the smoothness of a liquid–vapor interface. The solvation forces in both OMCTS and cyclohexane have been shown to be virtually independent of temperature in the range 14–30 °C.58

**Similarity of Isotherms.** The adsorption laws for all films on uniform surfaces should tend to Henry's law in the limit of low pressures. If the adsorbing species are sufficiently far apart, only the substrate–molecule interaction is important and the behavior is dominated by entropy effects related to the coverage of the surface. Both the BET and Langmuir isotherms tend to Henry's law at low pressures. Our isotherms show linear behavior up to unusually high degrees of coverage, up to almost 1/2 monolayer in the case of cyclohexane, n-pentane, and tetrachloromethane on mica and slightly less for the same liquids on silicon. The presence of surface heterogeneities normally acts to reduce the linearity, particularly at very low pressures where the most energetic sites are covered very quickly. Typically, linear behavior is normally seen only up to about 1/10-monolayer coverage. Our results are thus evidence of good substrate homogeneity (note the exception of water on silicon, discussed above). Even in the case of water on mica intermolecular interactions are obviously not of major importance in the submonolayer regime. (Note that we have argued earlier that a nonlinearity of less than 15% might be expected between $p$ and $t$, occurring in the vicinity of $t \sim d$. The observed linearity in the experimental curves extends to about 0.4d.)

The similarity of the isotherms of pentane, cyclohexane, and tetrachloromethane on both mica and silicon as well as water on mica extends to larger thicknesses (see Figure 8). In the case of the nonpolar liquids the interactions would be expected to be very similar on both substrates. That the water isotherm on mica is as close as it is to the other liquids is perhaps more surprising. The adsorption of water in terms of molecular layers, however, is larger than the other nonwetting liquids—possibly a reflection of increasing cooperativity due to hydrogen bonding once the water film is thicker than a few molecular layers.

**Wetting Isotherms and Lifshitz Theory.** If the disjoining pressure of the films is calculated using eq 2 and the results are compared with the predictions of the Lifshitz theory of van der Waals forces, the results appear as in Figures 10 and 11. Note that the calculations are straightforward for $\mu$ and are expected to be quite accurate as the dielectric data used have previously been shown to yield values in good agreement with experimental results for benzene and water.

Disjoining pressure of adsorbed films on mica surfaces plotted on a logarithmic scale. Symbols show experimental points (squares, pentane; triangles, water; diamonds, cyclohexane); the solid line is the prediction of the Lifshitz theory of van der Waals forces for $n$-pentane. The dashed line shows the total disjoining pressure from the van der Waals interaction and an extra contribution caused by the dissolution of 1/4-monolayer of soluble material in mica, assuming the solute behaves ideally and has the same molecular volume as pentane (see text). The Lifshitz interaction for cyclohexane is almost the same as for pentane, and that for water is only slightly smaller at a given separation, but has the same shape.

Vapor Adsorption on Mica and Silicon

Figure 9. Adsorption isotherms of OMCTS on mica (11 open diamonds), 14 (filled diamonds), 19 (open squares), and 24 °C (filled squares), cyclohexane on mica at 18 °C (filled triangles), and OMCTS on silicon at 18 °C (open triangles) plotted as a function of $(\mu - \mu_0)^{-1/3}$. This gives equal weight to the different layers of OMCTS on mica on the assumption that the adsorption is governed by some van der Waals-like potential decaying as $t^{1/3}$. The points for cyclohexane on mica and OMCTS on silicon have been displaced by 0.01 to the right for the sake of clarity.

Figure 10. Disjoining pressure of adsorbed films on mica surfaces plotted on a logarithmic scale. Symbols show experimental points (squares, pentane; triangles, water; diamonds, cyclohexane); the solid line is the prediction of the Lifshitz theory of van der Waals forces for $n$-pentane. The dashed line shows the total disjoining pressure from the van der Waals interaction and an extra contribution caused by the dissolution of 1/4-monolayer of soluble material in mica, assuming the solute behaves ideally and has the same molecular volume as pentane (see text). The Lifshitz interaction for cyclohexane is almost the same as for pentane, and that for water is only slightly smaller at a given separation, but has the same shape.

appearance of the theoretical curves. The nonwetting liquids (including OMCTS) all show similar behavior on mica—the experimental points cross the Lifshitz force at submonolayer thicknesses and then show considerably greater than expected film thicknesses until adsorption levels off at or close to saturation. Pentane wets mica and the films grow to very large thicknesses—in excess of 20 nm at saturation. On silicon only water and OMCTS appear to show thicknesses below about 5 nm close to saturation, whereas the isotherms of pentane, cyclohexane, and tetrachloromethane are very similar and grow to large thicknesses (≈10 nm).

The disagreement with Lifshitz theory for the thin films of the nonwetting liquids is not surprising. Lifshitz theory is a continuum theory and uses bulk dielectric data to predict the behavior of thin films on substrates. It is clearly of questionable validity in films of only a few molecular diameters. Theoretically, wetting behavior is expected for all studied liquids on both mica and silicon. The fact that no liquids except n-pentane wet mica, is however, in accord with the observations that these liquids all show small but distinct contact angles on mica. Even if Lifshitz theory is accepted as being valid for thick films, this does not imply that it can correctly predict wetting or the lack thereof.

The positive disjoining pressure calculated assumes that the film will thicken because the free energy decreases monotonically from its value at zero film thicknesses $\sigma_0$ to the value at effectively infinite thicknesses $\sigma_{SL} + \sigma_{LV}$. If, however, the system has an energy minimum at some small thickness, where the theory does not hold, this would prevent further thickening and the result is nonwetting, as observed. Such a situation would conceivably lead to hysteresis in the behavior of the films. If the film were thinned from large thicknesses down to contact, it might be possible to access the regime that is inaccessible on thickening.

The behavior on silicon is also in qualitative agreement with contact angle data. The nonwetting liquids are OMCTS and water, and water has a rather high contact angle on the hydrophobic silica-like surface. The wetting liquids all show similar S-shaped curves on the log-log plot of Figure 11 and much larger than predicted film thicknesses, as for n-pentane on mica.

The fact that some of the liquids wet the substrate and others with very similar properties do not warrants careful consideration. The wetting films are of such thicknesses that one might expect Lifshitz theory to hold. There are a number of previous investigations showing that Lifshitz theory provides an accurate representation on the behavior of thicker films. Examples include the work of Sabisky and Anderson on helium films on alkaline earth fluorides, the work of Blake on decane films on alumina, and various Soviet studies of films on glass and polished steel. None of these, however, has involved actual vapor adsorption measurements. Most work showing good agreement with Lifshitz theory for solid—liquid—vapor systems has been carried out with the bubble—plate method. Gee et al. unfortunately did not provide any meaningful comparison for large film thicknesses in their recent publications on adsorption of alkanes and alcohols to silica. We note also that the work of Blake on vapour adsorption of n-decane (film thicknesses $\leq 5$ nm) appears to show exactly the same deviation from Lifshitz theory as that observed by us. A recent study by Tidwell et al. using X-ray techniques finds good agreement with the Lifshitz theory for cyclohexane on silicon. Their measurement was made at 30 °C which, other than their technique, appears to be the major difference with our study.

**Effect of Surface Contamination.** The thick-film region presents two very great experimental problems. The first is temperature uniformity and control, and close to saturation temperature gradients of a few hundreds of a degree can lead to substantial differences between actual and measured relative vapour pressure. We do not believe that this is a serious concern in our system. The second problem is related to the occurrence of adsorbed species other than the vapor under investigation. Any high-energy surface that is handled in an atmosphere will adsorb molecules to the surface. Particularly mica has a very high surface energy, but on cleavage in air at normal pressures it is rapidly coated with an adsorbed layer that reduces its surface energy considerably. This has been amply discussed in various papers on direct force measurements between mica surfaces. The precise chemical composition of the adsorbed material is not known, but it is certainly composed mainly of water vapor and carbon dioxide. There are definite indications that some water-soluble compound, possibly a potassium salt, also forms on the surface through the slow leaching process. There is thus no doubt that the mica substrate is covered by some adsorbrates which are not removed under vacuum. Freshly cleaved mica is wetted by water, but an instant of exposure is sufficient to give a small contact angle. Small variations in the amount and composition of adsorbed material may be responsible for the variability of the isotherms from sample to sample. The adsorption of spurious contaminants during an experiment (e.g., pump oil from the vacuum system) would invariably lead to hysteresis in the measured isotherms, and this was never observed in our experiments.

The effect of thin (subnanometer) adsorbed layers on the calculated van der Waals forces would be marginal in all but the thinnest films. Dissolution of any adsorbed species in the liquid films would, however, lead to an additional disjoining pressure due to the reduction in chemical potential of the adsorbed liquid. This can be a large effect close to saturation. It has been shown that the very thick wetting films of water found on hydrophilic quartz and silica can be quantitatively accounted for by the dissolution of soluble species in the water films. A similar calculation for our wetting isotherms shows that such an effect would lead to isotherms similar to those observed on both mica and silicon. As can be seen in Figure 10, a quantity of soluble material equal to 1/4 monolayer is sufficient to give a good fit to the pentane isotherm on mica. Slightly smaller quantities are required to fit (approximate) the silicon isotherms (see Figure 11). The deviations for films ≥10 nm may be explained by gravitational thinning.
Gallosilicate Zeolite Catalysts: Structural Features of [Si,Ga]-ZSM-5

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A series of gallosilicates with the ZSM-5 structure was synthesized in an alkaline medium using tetrapropylammonium bromide (TPABr) as a template, and characterized by XRD, IR, TGA, SEM, MAS NMR, and chemical analysis. The results clearly demonstrate that the number of defects, the strength of interaction between the template molecules and the framework, the distribution of particle sizes, and the size of the crystallites, as well as the content of template, water molecules, and sodium cations, are all correlated with the gallium content.

Introduction

Isomorphous substitution of Si atoms in zeolitic frameworks by heteroatoms such as Al, B, Fe, Ge, Ti, and Ga is of considerable importance in view of the interesting adsorptive and catalytic properties of the products in reactions such as: