

Surface Forces in Adsorbed Multilayers of Water on Quartz

R. M. PASHLEY¹ AND J. A. KITCHENER

Department of Mineral Resources Engineering, Imperial College, London, S.W.7, England

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The adsorption of water vapor on smooth crystalline quartz at pressures close to saturation has been determined by ellipsometry, particular attention being paid to excluding gel layers and contamination. Contrary to some literature reports, such surfaces proved to be perfectly hydrophilic, showing thick adsorption multilayers and zero (or very low) contact angle. Quartz dehydroxylated by heating, or slightly contaminated, or deliberately methylated, showed thinner films and finite contact angles ranging from 20 to 80°. Films on clean quartz at saturation are consistent with calculated electrical double layer repulsion. But below saturation they are much thicker than expected on current theory of DLVO-type forces. Contact angles apparently arise from changes in short-range forces of a "structural" type.

The nature of surface forces acting in thin liquid films has been mainly studied on the one hand from the point of view of colloid stability (and the behavior of wetting films) and on the other from vapor adsorption measurements. The intermediate region of multimolecular adsorption layers requires measurements on smooth solid substrates to avoid the complication of capillary condensation, which would occur near the saturation vapor pressure. The form of the adsorption isotherm of a vapor is related to the contact angle formed by the liquid on the solid; with a finite contact angle, the isotherm is expected to show a definite, limited, thickness at saturation, whereas with zero angle the isotherm is asymptotic to the thickness axis.

Several authors have investigated multilayer adsorption of water on silica (1-4) and glass (5); related measurements on oxidized silicon have also been reported (6). It seems anomalous that measurements

close to saturation on vitreous silica (1-3) indicate that its surface is distinctly hydrophobic, unlike the results obtained on glass, which behaved as a perfectly hydrophilic solid. Recent studies on the cleaning of quartz oscillator plates (7) firmly demonstrate that well-cleaned quartz forms continuous, thick, wetting films when exposed to super-saturated water vapor, whereas microdroplets are formed with only traces of organic impurity on the surface (as proved by Auger electron spectroscopy). Further work on well-characterized, crystalline, quartz surfaces, free from the possibility of gel layers, is obviously needed. As the wetting properties of high energy surfaces are known to be very sensitive to contamination, exceptional cleanliness is required if definitive results are to be obtained.

As in most of the previous measurements, ellipsometry was the method applied in the present work to determine the thickness of water films on smooth, well-characterized, crystalline quartz plates. In addition to rigorously cleaned specimens, heat-dehydroxylated and methylated surfaces were

¹ Present address: Department of Applied Mathematics, Australian National University, Canberra, Australia.

studied. The object of the work was not only to establish the experimental facts but also to examine the applicability of current theories of surface forces in wetting films.

EXPERIMENTAL

Characterisation of Quartz Surfaces

Polishing of quartz. Plates were cut from natural (Brazilian) and synthetic crystalline quartz (supplied by Messrs. Gooch and Housego Ltd.) so that the shortest dimension (~2–3 mm thick) was along the optical axis (i.e., "Z-cut" crystals). The plates were about 1.5 cm². They were polished, on one side only, first with carborundum, then with finer and finer diamond paste. The plates were then polished using "Regipole," a cerium oxide polishing powder (provided by London and Scandinavian Ltd.), in an aqueous slurry on a Pellon pad (Hyprocel Pellon, English Ltd.). Finally, they were polished for long periods with water additions only on the pads. This final procedure has been reported to produce very smooth surfaces, as judged by interferometric techniques (8). Silica surfaces polished by a cerium oxide-based powder (which is a relatively soft material) have been found to show little surface disturbance, as measured by ellipsometry (9). Plates polished by the method described above had scratch-free surfaces but scratches appeared on etching. However, when the plates were then repolished using the cerium oxide powder only and then re-etched no latent scratches were exposed. All the quartz plates used in this study were therefore etched and then repolished using the soft powder.

For accurate ellipsometric measurements of thin water films on quartz it has been shown from a theoretical analysis by one of us (10) that very *smooth* quartz surfaces are required. That such surfaces were, indeed, produced by the polishing process described was shown by replica-transmission electron micrographs and by ellipsometric measurements.

Electron micrographs of platinum-shadowed carbon replicas from the polished quartz plates showed no surface roughness to the resolution of the techniques (i.e., about 2–4 nm). Ellipsometric measurements on such surfaces corresponded to a surface roughness of about 0.5 nm. Quartz surfaces produced by the method described were thus sufficiently smooth for the measurement of multimolecular water films.

When the quartz surfaces were mildly etched in dilute hydrofluoric acid the blank ellipsometric measurement did not decrease (as it would if gel layers were being removed), but gradually increased, the increase being due to an increase in surface roughness. However, even after 24 hr etching in 0.5% hydrofluoric acid the surface roughness, as measured by ellipsometry, increased only to about 2nm. This conclusion was substantiated by electron microscopy which indicated that the surface roughness increased only slightly, to about 3nm. Therefore crystalline etched surfaces of quartz could be produced which were still sufficiently smooth for ellipsometric measurement of water films. Apparently the Z-cut plates etched uniformly.

Since the blank ellipsometric measurement could not be further reduced by etching, the blank value was most likely due to a residual slight surface roughness and not to a disturbed or gel layer on crystalline quartz surface.

By using the repeated polishing and etching techniques described, smooth crystalline quartz could be produced which showed no surface disturbance. Such surfaces were used for the ellipsometric measurements of adsorbed water films.

Cleaning of quartz. Because surface cleanliness of the quartz is of fundamental importance for the study of its wetting characteristics, particular attention was given to this problem. A polished plate mildly etched in hydrofluoric acid (followed by minimal water rinsing) showed no trace of Al, Ce, or Fe in ESCA examination and less than 1% of a monolayer of F.

micrographs of platinum-etched replicas from the polished showed no surface roughness. The techniques (i.e., ellipsometry) showed that the surfaces corresponded to a roughness of about 0.5 nm. Quartz surfaces by the method described were sufficiently smooth for the measurement of multilayer water films.

Quartz surfaces were mildly etched with hydrofluoric acid. The blank measurement did not decrease if gel layers were being removed. As the etching gradually increased, the value due to an increase in surface roughness, even after 24 hr etching with hydrofluoric acid, the surface roughness measured by ellipsometry, was about 2 nm. This conclusion was supported by electron microscopy which showed that the surface roughness was slightly, to about 3 nm. Crystalline etched surfaces of quartz were produced which were suitable for ellipsometric measurements of multilayer films. Apparently the etching was uniform.

Blank ellipsometric measurements can be further reduced by etching. The value was most likely due to surface roughness and not to a gel layer on crystalline quartz. Repeated polishing and etching as described, smooth crystalline surfaces were produced which showed no surface roughness. Such surfaces were suitable for ellipsometric measurements of multilayer films.

of quartz. Because surface roughness on quartz is of fundamental importance in the study of its wetting properties, particular attention was given to this problem. A polished plate etched in hydrofluoric acid (followed by repeated rinsing) showed no trace of contamination in ESCA examination and was free of a monolayer of F.

Organic contamination on quartz is difficult to monitor by surface analysis techniques such as Auger and ESCA. A simple method of cleanliness for hydrophobic materials has been described by several workers (7, 11) and has been termed the "steam test"; the cleaned surface is held over warm water and the vapor condensation is observed. On a hydrophilic surface uniform colored fringes are observed, indicating continuous thick wetting films; hydrophobic surfaces (water contact angle $>10^\circ$) give an opaque mist of microdroplets. Gradations of properties between the two extremes correspond to degrees of cleanliness (7). Cleaning studies on quartz oscillator crystals have shown that rigorously cleaned quartz surfaces (i.e., on which no carbon was detectable by Auger analysis) give fringes in the steam test and have a water contact angle of zero (or certainly less than 4°). The steam test is sensitive for fractions of a monolayer of hydrophobic organic contamination.

Using this test, several methods of cleaning quartz and vitreous silica were found to reproducibly give clean, hydrophilic, surfaces, even after initial gross contamination by lipids from the fingers. Only vigorous oxidizing agents or etching reagents were found to be capable of cleaning such contaminated surfaces. Ordinary hot chromic acid was not efficient. Typical successful cleaning processes were: (a) hot, rapidly decomposing ammoniacal hydrogen peroxide solution (100 vol), (b) hot concentrated nitric acid treatment for several hours, and (c) rapid (20 sec) etching in hot 30% sodium hydroxide solution. The first two processes appear to clean primarily by an oxidizing action, whereas the third process probably cleans by rapid removal of the surface layer to which organic contamination is attached (as well as saponification of fats).

After each of these processes the plates were thoroughly washed in running distilled water of good quality (see below) and immediately blown dry with a jet of filtered nitrogen (to avoid evaporation and hence

deposition of any contamination present in the washing water).

The water used for washing the plates and as source of vapor for adsorption studies (see later) had to be of such quality that it did not contaminate the cleaned plates. It was prepared by passing once-distilled water through activated charcoal, mixed-bed ion-exchange resin and again through activated charcoal, prior to redistilling it from a Pyrex still fitted with a heated section before the condenser. The condensate was stored in a 20-liter Pyrex vessel from which it was withdrawn at the base. The final distillation and storage system was connected to the air only through an activated charcoal filter, and all the glassware was connected by butt joints of glass held by short lengths of Teflon.

Clean quartz plates which were immersed in the purified water (in a ground-glass sealed vessel) for several days still gave, on drying, excellent fringes in the steam test. The water obtained from the system used was, therefore, sufficiently clean for the experiments reported here on quartz surfaces.

Heat dehydroxylation and methylation of quartz and silica. To dehydroxylate a clean vitreous silica plate, it was held in a silica tube, heated in an electric furnace in air to 875°C for 24 hr. The plate was then allowed to cool while air drawn into the tube was heated to 875°C to prevent entry of aerosol contamination. Advancing and receding water contact angles on the plate were $35-40^\circ$ and about 17° , respectively. The advancing angle agrees with that reported by White (12). The large hysteresis was probably due to surface heterogeneity, i.e., microareas of different silanol density. After 8 weeks the plate was still hydrophobic even though it was left in contact with water vapor in a sealed tube. Heating of the plate to 85°C in contact with water produced a hydrophilic surface, presumably by rehydroxylation. The rate of rehydroxylation was, however, very slow at room temperature. In this experiment, the hydrophobic surface must be due entirely to the loss of

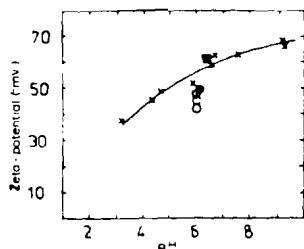


FIG. 1. Influence of heat dehydroxylation on the ζ -potential of quartz in 10^{-2} N KCl. Conditions: (1) Crosses, washed in HCl, stored in Pyrex at pH 6; (2) square, the same, stored in platinum; (3) open circles, as 1, then heated to 1050°C in air, cooled, and rapidly measured; (4) filled circle, as 3, remeasured after 1 week in water.

surface hydroxyl groups and formation of siloxane bridges.

To see whether heat treatment affects the ionization, ground Brazilian quartz ($<30\ \mu\text{m}$) of optical grade was washed in concentrated hydrochloric acid at 60°C for 24 hr to remove surface inorganic contamination and then washed repeatedly in clean water. The final pH value of the suspension was 5.8. One portion of the powder was placed in a platinum crucible (with lid) and heated to 1050°C (in air) and then allowed to slowly cool over 24 hr to 300°C . It was then suspended in 0.01 N KCl solution. The average electrophoretic mobility of the particles was measured immediately and after one week, in a Rank Bros. MK.2 microelectrophoresis apparatus. A second portion of the acid-washed quartz was stored in water in a sealed Pyrex vessel. The ζ -potentials as calculated from the Smoluckowski equation from measured electrophoretic mobilities are given in Fig. 1. From these results it is apparent the ζ -potential on quartz is only slightly affected by loss of surface hydroxyl groups. According to Knozinger (13) there are only about 0.2 – 0.7 OH groups per nm^2 left on silica after heating to 1000°C , compared with an original density of about 4.6 ± 0.2 OH/ nm^2 at room temperature.

Several clean crystalline quartz plates were surface methylated with trimethylchlorosilane following the procedure of

Laskowski and Kitchener (14). The contact angle with water was about 80° and showed very little hysteresis ($\sim 5^{\circ}$).

Water adsorption isotherms on these heat-dehydroxylated and methylated quartz plates were measured by ellipsometry and compared with those obtained on cleaned plates (as reported later).

ELLIPSOMETRIC TECHNIQUE

A manual ellipsometer was constructed in the Department from precision components which were mounted on a large rigid metal base plate such that a fixed angle of incidence of 60° was obtained on a vertically held sample. The ellipsometer was housed in a constant temperature room ($25.0 \pm 0.1^{\circ}\text{C}$). Its precision was carefully tested with an evaporated gold specimen. The errors in measurement of the ellipsometric parameters were approximately: $\Delta = \pm 0.2^{\circ}$ and $\psi = \pm 0.05^{\circ}$. For a 5-nm water film on quartz this would correspond to ± 0.2 nm.

The sample was enclosed in a special cell constructed of Pyrex glass and Teflon with windows of polished vitreous silica.

A sample holder was constructed of Teflon so that the reflecting surface of the sample rested on three Teflon spikes which defined its position. The holder was positioned into the cell (which could then be sealed) by locating it on three glass spikes. The cell itself was also positioned in the ellipsometer by three glass spikes. With this arrangement, the cell and holder could be dismantled and cleaned (e.g., by 20 sec washing in hot 30% sodium hydroxide solution, followed by rinsing) and then replaced such that the position of the reflecting surface (and hence the ellipsometer alignment) was not significantly affected. The Teflon holder was cleaned by boiling it in concentrated sodium hydroxide solution for 24 hr (15) followed by several hours boiling in clean water. The quartz plates were usually cleaned by rapid etching in sodium hydroxide as this method was found to be the most convenient.

and Kitchener (14). The contact angle was about 80° and showed hysteresis ($\sim 5^\circ$). Adsorption isotherms on these silylated and methylated quartz were measured by ellipsometry and those obtained on cleaned quartz are reported later).

ELLIPSOMETRIC TECHNIQUE

The ellipsometer was constructed in part from precision components mounted on a large rigid metal base which had a fixed angle of incidence obtained on a vertically mounted ellipsometer was housed in a temperature room ($25.0 \pm 0.1^\circ\text{C}$). It was carefully tested with an optical specimen. The errors in the ellipsometric parameters are approximately: $\Delta = \pm 0.2^\circ$ and $\psi = \pm 0.2^\circ$ and a 5-nm water film on quartz correspond to ± 0.2 nm.

The sample was enclosed in a special cell made of glass and Teflon. The quartz was vitreous silica. The cell was constructed of Teflon. The surface of the sample was silylated with Teflon spikes which were positioned on three glass spikes. The holder was positioned in the cell which could then be heated on three glass spikes. The sample was also positioned in the cell by three glass spikes. With this arrangement the cell and holder could be cleaned (e.g., by 20 sec of 30% sodium hydroxide solution by rinsing) and then replaced in the position of the reflecting surface of the ellipsometer alignment) without being affected. The Teflon was cleaned by boiling it in concentrated sodium hydroxide solution for 24 hr. The quartz plates were usually cleaned by several hours boiling in sodium hydroxide solution. The quartz plates were usually cleaned by acid etching in sodium hydroxide solution. This method was found to be the most

The partial pressure of water vapor inside the cell was controlled by enclosing various concentrations of sodium chloride solution, for which relative vapor pressures have been accurately measured (16). The solutions were made up in distilled water from salt which had been heated to 600°C in air in a tube furnace and cooled under nitrogen filtered through activated charcoal. Saturated vapor pressure was obtained with distilled water. There was no liquid contact between the sample and the solution since the sample was held in an all-Teflon holder which was, of course, not wetted by the solutions.

The cell was thermally insulated inside a cardboard box packed with cotton wool and the variation in temperature inside the cell monitored by a quartz oscillator thermometer was typically about 0.05°C over a period of 12 hr. Temperature differences between different positions inside the insulated glass cell (e.g., between the solution immediately below the sample, 1–2 cm away, and the sample itself) should therefore be no more than about 0.02°C , which corresponds to a difference in relative vapor pressure of about 0.001.

Both the sample cell and solution and the sample itself were allowed to come to thermal equilibrium in the constant temperature room before sealing the sample in the cell. The sample was always stored in a sealed vessel containing filtered nitrogen.)

The Δ and ψ values (measured by the ellipsometer) for the system investigated were calculated (by computer) for various water film thicknesses from the Drude equations (17) (Fig. 2). The values calculated for films of slightly different assumed refractive index are also given for comparison. It can be concluded from Fig. 2 that, for the level of accuracy of ψ values obtained here, the refractive index of a very thin film on quartz (i.e., < 20 nm) is not precisely determinable. Hall (3) reached a similar conclusion. In this work, therefore, the water films were assumed to have the normal bulk refractive index.

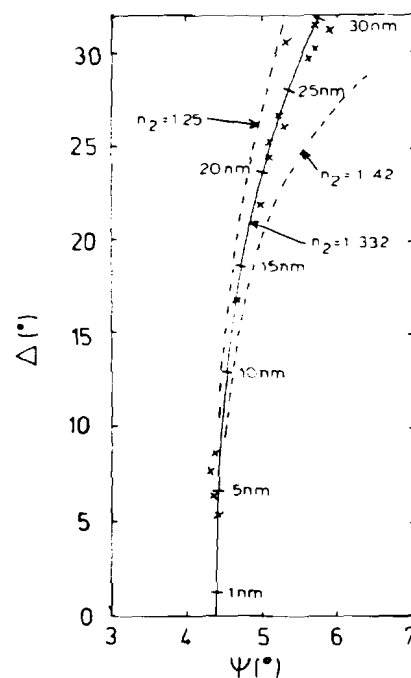


FIG. 2. Theoretically calculated $\Delta - \psi$ lines for films of refractive index 1.25, 1.332, and 1.42 on quartz, and experimental points obtained with adsorbed water (crosses). Calibration marks on the line for 1.332 show the dependence on film thickness.

From Fig. 2 the thickness of water films on quartz can be read off directly from measured values of Δ and ψ . Some typical experimental values are also plotted on Fig. 2 for comparison. The experimental measurements Δ and ψ values agree closely with the theoretically calculated values for water films up to at least 30 nm, and the smallness of the "blank" confirms that the prepared quartz surfaces were free from abnormalities.

ADSORPTION RESULTS

Clean Quartz

Colored interference fringes were seen on clean quartz plates about 4 hr after sealing in the cleaned cell with high quality water. (The cell and sample were equilibrated for 24 hr in the constant temperature room before sealing.) Ellipsometric measurements indicated that these water films were about

150 nm thick. Such films were generally stable for up to 3 days. In certain cases the film thickness fell off rapidly to about 10 nm; but this was only when the cell became obviously contaminated (e.g., showing a positive result in the bubble persistence test of the water in the cell and mist on the sample in the steam test). Similarly, if either the water or the plate were already contaminated according to these tests when the experiment was set up, thick films were not observed.

Numerous experiments proved that it was very difficult to both obtain and maintain clean conditions inside the cell for several days. Only with great care and attention to cleanliness of all the components, and with careful assembly, could stable thick films be reproducibly obtained.

The measured equilibrium water film thicknesses produced on clean quartz plates sealed with salt solutions, at various relative vapor pressures, are given in Fig. 3, curve A. In order to reach equilibrium thicknesses the sample was left sealed for 3–5 days at each vapor pressure, the thickness being monitored ellipsometrically. Equilibrium was reproducible from either side.

The curve obtained is characteristic for a perfectly hydrophilic solid with a continu-

ous transition between thin and thick water films.

To demonstrate the liability of silica to contamination, a quartz plate which after cleaning gave colored fringes in the steam test was held in running London tap water for about 30 sec and then blown dry with nitrogen and enclosed in the cell with water. A finite equilibrium film thickness of about 5 nm was measured at saturated vapor pressure. This plate subsequently gave an opaque mist in the steam test and was therefore obviously contaminated.

Dehydroxylated and Methylated Quartz

A clean quartz plate was heated to 850°C for several hours in air and slowly cooled in a nitrogen atmosphere. It was then sealed in the cell with various relative vapor pressures. The corresponding water film thicknesses measured are given in Fig. 3, curve B. The behavior of this surface is that expected for a hydrophobic solid; at saturated vapor pressure it carries a water film of limited thickness, namely, 7 nm.

After the surface had been exposed to undersaturated water vapor for several days, the film thickness was remeasured in saturated vapor, and a value of 11 nm was obtained. The surface appears to rehydroxylate slowly when in contact with only an adsorbed layer. The advancing water contact angle on this plate was about 20°, which is substantially lower than that of a freshly dehydroxylated plate (i.e., ~40°).

A clean quartz plate was methylated by the method of Laskowski and Kitchener (14). The water film thicknesses measured for equilibrium at two relative vapor pressures are given in Fig. 3, curve D. These thicknesses are, however, only approximate values because the blank value on the dry methylated plate, even after benzene washing and heating to 320°C (for 15 hr) in a nitrogen atmosphere, was not negligible. It corresponded to 2.6 nm if calculated as water. The water film thicknesses shown were estimated by subtracting this blank

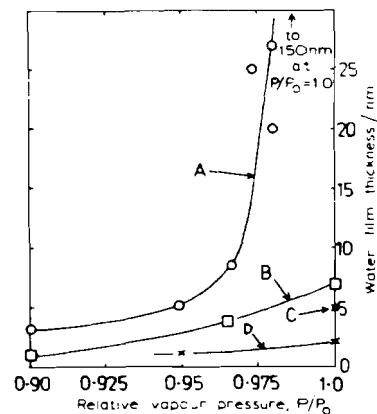


FIG. 3. Water adsorption isotherms determined on crystalline quartz plates at 25°C. (A) Clean, hydroxylated quartz. (B) Heat dehydroxylated at 850°C. (C) Slightly contaminated by hydrophobic material. (D) Methylated quartz.

tween thin and thick water films present on the surface. Evidently the "blank" corresponds to a much thicker film than would be expected from a close-packed layer of methyl groups obtained by reaction of surface hydroxyl groups with trimethylchlorosilane. A likely explanation may be as follows. Since the latter reagent was not specially purified before use it is possible that silicone resin (formed by hydrolysis of dimethyldichlorosilane, which might well be present as an impurity in the reagent) was also deposited on the quartz surface. However, the cause of this relatively large blank value was not investigated further.

1 and Methylated Quartz

The freshly methylated plate had an advancing water contact angle of about 80° , with little hysteresis ($\sim 5^\circ$). The contact angle dropped to 70° after several days in the presence of saturated water vapor. These observations agree with those reported by Laskowski and Kitchener.

Methylated plates are clearly more hydrophobic than heat dehydroxylated plates. The finite water film thickness at saturated vapor pressure was correspondingly lower. Previous published work on supposedly clean vitreous silica yielded intercepts ranging from about 4 to 8 nm for the equilibrium thickness at saturation. Such results correspond approximately to what has now been observed with contaminated, dehydroxylated, or methylated quartz.

Vitreous silica appears to behave in a very similar way to crystalline quartz; when they are both sufficiently well cleaned, both form colored fringes in the steam test.

DISCUSSION

Validity of the Experimental Results

From the temperature control in the cell it follows that with water the relative vapor pressure cannot have exceeded $P/P_0 = 1.001$. It was found that nucleation of microdroplets on a typical hydrophobic surface (e.g., treated quartz of water contact angle 20 to 40°) did not occur under

these conditions. Similarly, it is very unlikely that the thick water films observed on clean quartz (which were obtained under the same conditions as were thin films on hydrophobic samples) could have been formed via supersaturation (i.e., by passing through a region of negative disjoining pressure). That this did not occur is further substantiated by the observation that a clean quartz plate inserted while warmer than the vapor source water still formed thick water films after a few hours. Furthermore, water films of up to 30 nm were measured on plates in equilibrium with salt solutions of relative vapor pressure substantially less than 1.0 (e.g., 0.98).

That these very thick films measured by ellipsometry did not consist of microdroplets of water can be shown by several observations:

(a) The presence of microdroplets on the reflecting surface would drastically reduce the absolute reflected intensity—which was not observed.

(b) If droplets were formed there should be no limit to their size—hence the film thickness at saturation should increase beyond the observed 150 nm. Actually, this limiting value is that expected for the case of a water film supported on a vertical plate (see later).

(c) From observations by naked eye with a clean plate, highly reflecting, uniform, fringes are observed. Therefore, very thick continuous films were certainly present.

The thick wetting films observed on clean crystalline quartz could not have been due to gel layers formed on the surface of the quartz. This is proved by the ellipsometric measurements on bare quartz substrates which indicated the equivalent of only a very thin (i.e., 0.5 nm or less) low refractive index layer—most likely due to a residual slight surface roughness.

It is therefore concluded that the thick films observed on clean quartz are equilibrium adsorption layers. The origin of the surface forces responsible must now be considered.

Theories of Surface Forces

In discussing the forces operating in thin water films, Derjaguin and Churaev (18) analyzed previous data in terms of the total "disjoining pressure," π defined as $-(\partial G/\partial h)$, which can be evaluated from the equation

$$\pi = -(RT/V_m) \ln (P/P_0). \quad [1]$$

Here V_m is the molar volume of the liquid, T is the temperature and R is the molar gas constant, G is the free energy of a film of thickness h . π simply measures the change of chemical potential of water in the adsorbed state; no structural theory is involved at this stage. It was then assumed that π contains three main, independent, components:

$$\pi = \pi_{vdw} + \pi_{el} + \pi_s \quad [2]$$

where π_{vdw} is the macroscopic van der Waals pressure, π_{el} is the electrical double layer pressure, and π_s is a "structural" component.

Whereas the first two can be calculated approximately, as in conventional DLVO theory, at present π_s can be evaluated only

by subtraction of π_{vdw} and π_{el} from the measured total π .

Using Eq. [1], the corresponding π values have been calculated for the measured isotherms and are plotted in Fig. 4 as a function of film thickness. π_{vdw} was calculated, over the range shown, using the nonretarded Hamaker equation with a constant $A = -1.12 \times 10^{-20}$ J (curve E); this component is small but positive. π_{el} was calculated—for want of a better theory—by using Langmuir's approximation for thin films of very dilute electrolyte on surfaces of high potential (18, 19) (Curve D). [Constant potential heterocoagulation theory was not used because, for the interaction of one high and one low potential plane (of same sign), it predicts attraction for relatively thick films at low ionic strength; this is physically unreasonable (20).]

Comparison of Theory and Experiment

From Fig. 4 it is apparent that both clean quartz and dehydroxylated quartz form substantially thicker films than would be expected from DLVO type theory (e.g., for $P/P_0 \leq 0.999$). For dehydroxylated quartz near the saturation vapor pressure ($\pi = 0$)

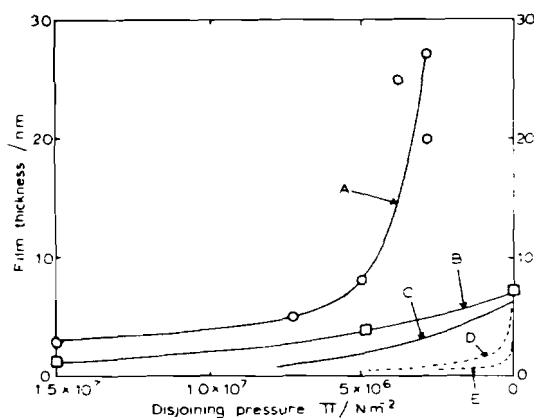


FIG. 4. Disjoining pressures as a function of film thickness for hydrophilic and hydrophobic surfaces, calculated from the isotherm data and compared with theoretical values for electrical double layer (D) and dispersion forces (E). (A) Present results for clean quartz. (B) Present results for heat-dehydroxylated quartz. (C) Results of Derjaguin and Zorin for vitreous silica. (D) Disjoining pressure calculated from electrical double-layer theory (π_{el}) with Langmuir's equation. (E) Disjoining pressure due to dispersion forces (π_{vdw}), calculated with nonretarded Hamaker constant.

of π_{vdw} and π_{el} from the π . The corresponding π values plotted in Fig. 4 as a function of thickness. π_{vdw} was calculated, shown, using the nonretarded van der Waals theory with a constant $A = -1.12 \times 10^{-20}$ erg cm (see E); this component is small compared to π_{el} was calculated—for want of a better theory—by using Langmuir's theory for thin films of very dilute electrolyte on surfaces of high potential (see D). [Constant potential theory was not used because of the interaction of one high and one low potential plane (of same sign), it is not a good approximation for relatively thick films; this is physically un-

the water film thickness was found to be insensitive to relative pressure, whereas DLVO theory predicts that the water film thickness should increase steeply. The π_{vdw} and π_{el} theories should apply to both fully hydroxylated and heat dehydroxylated quartz surfaces since removal of, say, half a monolayer of OH groups will not significantly affect π_{vdw} and the surface potential (and hence π_{el}) for the two types of surface were found to be nearly the same.

Clearly, the large difference between the adsorption isotherms on the two types of surface must be due primarily to the loss of short-range interaction between surface hydroxyl groups and adjacent water layers. Since the refractive index of very thin water layers could not be measured by ellipsometry, it was not possible to determine the kind of structure present in such films on the hydrophobic quartz. However, it is known that heat dehydroxylation does not remove all surface hydroxyl groups (13) and it is therefore likely that the thin film is composed of clusters of water molecules grouped around the remaining isolated silanol groups (21, 22). Interpretation of the adsorption data in terms of a homogeneous medium subject to a disjoining pressure leads to difficulties. If it is assumed, with Derjaguin and Churaev (18), that there is a uniform "α-film" on (hydrophobic) quartz and that deviations from π_{vdw} and π_{el} are caused by a "structural" component, π_s , it can be seen from Fig. 4 that π_s would have a strongly positive contribution at $P/P_0 \approx 0.999$ then become strongly negative at $P/P_0 \approx 0.999$ to account for a finite intercept on the thickness axis. Since it is necessary to invoke this rather complex scheme it can be concluded only that the disjoining pressure concept is not useful for such thin films.

For the thicker water films on clean quartz the disjoining pressure concept should be of more value, but a major discrepancy arises. The observation that over most of the range studied the water films were substantially thicker than expected from theory needs

to be explained. Only for the case of the thickest films reported do the results obtained here agree roughly with theory. The limiting thickness observed of about 150 nm at saturated vapor pressure can be explained by the fact that the film was about 1 cm above the level of the reservoir of water. Using the simple relation

$$\pi = h\rho g \quad [3]$$

the disjoining pressure in such a film can be calculated. From Langmuir's equation the film thickness giving an equal value for π_{el} is readily calculated. For $h = 1$ cm, the thickness required was, in fact, found to be about 150 nm. Thus, these very thick films are controlled by long-range double-layer repulsion.

That the thinner films on clean quartz (at $P/P_0 < 0.98$) are not explained by the theory might be due to invalidity of the model used. In the theory used by Langmuir it is assumed that the quartz-water interface has a constant potential independent of film thickness. This is probably not true for thin films. The surface charge may be expected to vary with film thickness because the hydrogen ion concentration in the thin film would also change. However, application of a dissociation model of this kind greatly increases the complexity of electrical double layer calculations (23). In the Langmuir model it is also assumed that the potential gradient at the air/water interface is zero (i.e., that there is no charge at this interface). This is also likely to be inaccurate since there is some evidence for preferential adsorption of hydroxyl ions at the air/water interface (24). In the Langmuir treatment it is also assumed that the film is in contact with bulk electrolyte, whereas for a thin film condensed on a plate this is not the case; here equilibrium is possible only through vapor transfer.

For the case of thin water films on clean, fully hydroxylated, quartz there must be an extra interaction (π_s) between silanol groups and adjacent water layers which is not in-

Theory and Experiment

It is apparent that both clean and hydroxylated quartz form substrates that would be expected to follow DLVO theory (e.g., for fully hydroxylated quartz at zero relative pressure ($\pi = 0$))



Disjoining pressure calculated for electrical double layer (D) on hydrophilic and hydrophobic surfaces. Disjoining pressure due to dis-

cluded in π_{vdw} and π_{el} theory. However, this interaction, although possibly relatively strong, should operate only over short-ranges. e.g., about 10 nm.

CONCLUSIONS

(1) Polished crystalline quartz (and vitreous silica) surfaces are remarkably difficult to clean and to keep clean. Once clean, however, the surface is definitely hydrophilic with a zero (or very low) water contact angle.

(2) Such surfaces show a water adsorption isotherm corresponding to a perfectly hydrophilic solid. However, substantially thicker films were measured than expected from current theory.

(3) Quartz surfaces which have been heat dehydroxylated, methylated or contaminated by hydrophobic materials show large contact angles with water (20 to 80°) and thin equilibrium water films (<10 nm) in saturated water vapor. Adsorption isotherm results on such quartz surfaces resemble those reported on supposedly clean vitreous silica by Derjaguin and Zorin and by Hall.

(4) Changes in short-range interactions are responsible for the difference in wetting properties between fully hydroxylated (hydrophilic) and dehydroxylated (hydrophobic) quartz.

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