

Effect of Adsorbed Water on Wetting Properties of Borosilicate Glass, Quartz, and Sapphire

MARIANNE K. BERNETT AND W. A. ZISMAN

*Surface Chemistry Branch
Chemistry Division*

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NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

Contact angles of a variety of hydrophobic liquids were measured on clean surfaces of borosilicate glass, quartz, and sapphire at 20°C with the RH at 0.6% and 95%. The adsorption of water molecules at 0.6% RH resulted in the formation of only a fraction of a monolayer; yet, this fraction converted each high-energy solid surface to one having a low critical surface tension of wetting γ_c . The increased amount of water adsorbed at 95% RH to form a film comprising little more than a condensed monolayer further lowered γ_c to a value somewhat above that of bulk water. At each RH investigated the value of γ_c was the same for each of these three solids; hence, γ_c was dependent upon the surface concentration of adsorbed water but was independent of the chemical nature of the solid substrate. The somewhat different values of γ_c obtained on using several different homologous series of hydrophobic liquids are explained in terms of differences in the contribution from nondispersion interfacial forces acting between the water film and the contacting organic-liquid molecules. These results reveal clearly the important influence of only a monolayer of adsorbed water upon the spreading, adhesion, and contact angles of organic liquids resting upon high-energy, hydrophilic, solid surfaces.

To illustrate the effect of the baking pretreatment temperature on the removal of physically adsorbed water, the three specimens were dried at three temperatures: 65°C, 120°C, and 215°C. No significant differences were found on the specimens following baking treatment at the different temperatures.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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EFFECT OF ADSORBED WATER ON WETTING PROPERTIES OF BOROSILICATE GLASS, QUARTZ, AND SAPPHIRE

INTRODUCTION

Shafrin and Zisman (1) have recently described the spreading and equilibrium contact-angle behavior of many pure hydrocarbon and halogenated-hydrocarbon liquids on clean, dry, soda-lime glass at 20°C. They demonstrated that the surface energy γ_s° and the critical surface tension of wetting γ_c of such a glass are greatly decreased by the adsorption of such a minute amount of water as that physically adsorbed at 0.6% RH. This led them to conclude that such a silicate glass is converted into a low-energy surface by the physical adsorption of only one or (at the most) two monolayers of water. However, they pointed out that it is difficult to prepare and maintain soda-lime glass free from any surface accumulation of water-soluble salts, such as alkaline oxides, hydroxides, and carbonates; their assumption, therefore, that under their experimental conditions at 0.6% RH the glass surface was covered with only a monolayer of physically adsorbed water was plausible but by no means certain.

We report here the results of a similar investigation of borosilicate glass, fused quartz, and synthetic α -aluminum oxide (sapphire). These three high-energy, hydrophilic, solid surfaces were chosen because of their importance and because the latter two were known to be free from many problems arising from surface chemical reactions with water beyond the formation of a hydrated surface monolayer.

EXPERIMENTAL MATERIALS AND METHODS

The three solids investigated were (a) borosilicate glass (Corning Pyrex 7740) of composition 80.5% SiO₂, 3.8% Na₂O, 0.4% K₂O, 12.9% B₂O₃, and 2.2% Al₂O₃ (2), (b) ground and polished fused quartz (Type 101) from the Willoughby Quartz Plant, and (c) single-crystal, fused sapphire produced by the Union Carbide Company. The borosilicate and quartz specimens were cut into rectangles 2.5 by 7.5 cm in area and 2 mm in thickness, and the sapphire was used in the original circular shape of 3.75 cm in diameter and 3 mm in thickness.

Each specimen was prepared to have smooth and noncorroded surfaces, free from any adsorbed organic contamination, so that grease-free distilled water spread upon it spontaneously. For cleaning the Pyrex, the method by Tichane (3) was used, which consisted of (a) mild etching for 10 min with a 1% NaOH solution at 95°C, (b) cleaning for 2 min with 5% HCl at 50°C, and (c) final rinsing at room temperature with water which had been triply distilled in an all-quartz still. Quartz specimens were cleaned by (a) immersion for 2 hr in a hot 50-50 vol-% nitric-acid-sulfuric-acid bath, (b) thorough rinsing with distilled water, (c) heating each three times in freshly distilled water to the boiling point, and (d) final rinsing at 20 to 25°C with triply distilled water. Electron micrographs of the clean specimens, using a magnification of 50,000X, showed that even prolonged immersion in the hot acid bath had no evident deleterious effects on the quartz surfaces. The sapphire specimens were immersed in the hot nitric-acid-sulfuric-acid bath for 2 hr and then were rinsed with triply distilled water. The last step in the preparation of all specimens consisted of drying each for 10 min at 120°C in a grease-free oven and then placing it immediately in the controlled humidity chamber for observation of contact angles.

Apparatus and methods used for the contact-angle experiments reported here were essentially the same as those of Shafrin and Zisman (1), i.e., a gas-purification train coupled to a transparent viewing chamber, which was constructed from Pyrex glass components and polytetrafluoroethylene stopcock plugs and sleeves. This equipment could be easily disassembled and acid-cleaned to prevent organic contamination of the specimen chamber. A metered stream of nitrogen gas, carefully freed of organic contaminants in the gas-purification train, was continuously fed to the viewing chamber to provide nitrogen at a constant RH, which could be adjusted from 0.6% to 95%. The many precautions taken to avoid organic contamination of the glass specimen and also the methods of monitoring surface cleanliness and RH have been fully described elsewhere (1).

Since it was necessary to measure contact angles on surfaces coated with a thin film of water, the liquids used for the sessile drops in these measurements had to be chosen so as to be neither hydrolyzable (such as some esters) nor able to spread spontaneously on water, as would be true of hydrogen-bonding liquids, such as glycerol, glycols, formamide, and alcohols. Hence, for this investigation the selection of liquids was limited to hydrocarbons and, for the high-surface tension liquids, almost exclusively to halogenated hydrocarbons. Since the halogenated organic liquids used were available only as commercial preparations, those of unknown purity were redistilled in a molecular still. Only those colorless fractions whose physical constants checked the best available literature values were used for this investigation. The boiling points ($^{\circ}\text{C}/\text{mm Hg}$) and, in some cases, refractive indices (n_D^{20}) of these fractions are given below: α -iodonaphthalene 109/0.6, 1.7015; α -bromonaphthalene 139/16; 1,2,3-tribromopropane 93.5/10.8, 1.5861; 1,1,2-tribromopropane 200/760; 1,3-dibromopropane 68.5/20, 1.5225; 1,2-dibromopropane 141/760; 1,3-diiodopropane 120/20, 1.6358; 1,2,3-tribromobutane 112/19; sym-tetrabromoethane 151/54; 1,2-dibromoethane 131.7/760. These fractions, as well as those compounds which were not redistilled, were subsequently percolated slowly through long adsorption columns of activated alumina and Florisil to remove any polar hydrophilic impurities. Each liquid was used for contact-angle measurements either immediately after such purification or was kept refrigerated in the dark in sealed ampoules until used.

Slowly advancing contact angles (4) of a variety of pure polar and nonpolar liquids were measured with a goniometer telescope (5), which had been modified so that the illuminator and telescope could be moved laterally and independently from the viewing chamber support. The contact angles reported were measured after each solid specimen had been equilibrated for 2 hr at either 0.6% or 95% RH. Each value is the average of contact-angle measurements accurate to ± 2 degree of at least three drops, each on three different solid specimens. All measurements reported were carried out at $20^{\circ} \pm 1^{\circ}\text{C}$.

CRITICAL SURFACE TENSION OF WETTING

Borosilicate Glass (Pyrex)

Table 1 shows that the contact angles of all liquids on Pyrex glass at 0.6% RH were much smaller than at 95% RH; in fact, at 0.6% RH the hydrocarbons either spread spontaneously or exhibited contact angles below 5 degrees, and the same was observed of every polar liquid whose surface tension was below about 42 dynes/cm at 20°C . When the cosine of the contact angle θ was plotted vs the surface tension of the liquid γ_{LV} (Fig. 1a), a short straight line resulted for the polar compounds whose intercept at $\cos \theta = 1$ (or the critical surface tension of wetting γ_c) was about 44 dynes/cm. The value of γ_c for the hydrocarbons could not be determined at 0.6% RH in this manner, since all of them spread; however, γ_c must have been greater than 38.7 dynes/cm, the highest value of γ_{LV} of the hydrocarbon liquids used.

Table 1 reveals that the contact angles of every liquid investigated was larger at 95% than at 0.6% RH. In Fig. 1b are graphs of $\cos \theta$ vs γ_{LV} at 95% RH for all of the

Table 1
Wettability of Glasses at 0.6% RH and 95% RH at 20°C
(Specimens were predried for 10 min at 120°C)

Liquid in Sessile Drops	Surface Tension at 20°C (dynes/cm)	Contact Angles (degrees)					
		0.6% RH			95% RH		
		Pyrex	Quartz	Sapphire	Pyrex	Quartz	Sapphire
Hydrocarbons							
α -Methyl naphthalene	38.7	5	<5	<5	14	6	16
Isopropyl biphenyl	34.8	7	5	<5	8	5	<5
Dicyclohexyl	32.8	spr.*	<5	spr.	28	28	25
p-Octadecyl toluene	31.5	5	9	8	28	16	25
Isopropyl bicyclohexyl	30.9	<5	<5	<5	39	32	35
Squalane	28.6	<5	spr.	<5	22	23	19
n-Hexadecane	27.6	spr.	spr.	spr.	28	28	29
n-Tetradecane	26.7	—	—	—	17	16	17
n-Dodecane	25.4	—	—	—	spr.	<5	<5
n-Decane	23.9	—	—	—	spr.	spr.	spr.
Polar Liquids							
Methylene iodide	50.8	19	22	24	36	37	38
Sym-tetrabromoethane	47.5	8	17	18	33	35	33
Polyphenylthioether MCS 292	46.2	—	—	—	39	37	36
α -Iodonaphthalene	45.9	9	10	10	40	43	43
α -Bromonaphthalene	44.6	9	5	9	36	33	35
1,2,3-Tribromopropane	44.0	8	7	8	28	24	28
o-Dibromobenzene	42.0	<5	5	5	32	28	33
m-Dibromobenzene	40.4	—	—	—	38	33	27
1,3-Diodopropane	40.0	—	—	—	23	25	18
1,2,3-Tribromobutane	39.9	—	—	—	27	18	24
1,3-Dibromopropane	38.9	spr.	spr.	spr.	10	8	6
1,1,2-Tribromopropane	38.9	—	—	—	—	11	9
1,2-Dibromo-1,1-Dichloroethane	38.2	—	—	—	—	9	—
Hexachloropropylene	38.1	—	—	—	—	<5	<5
1,2-Dibromoethane	37.8	—	—	—	—	12	7
Dibromomethane	37.4	—	—	—	—	10	6
Pentachloropropane	36.8	—	—	—	—	7	<5
1,2-Dibromopropane	33.0	—	—	—	—	spr.	—
Bromotrichloromethane	30.3	—	—	—	—	spr.	spr.

*Spr. indicates that the liquid spreads spontaneously; i.e., the contact angle is zero.

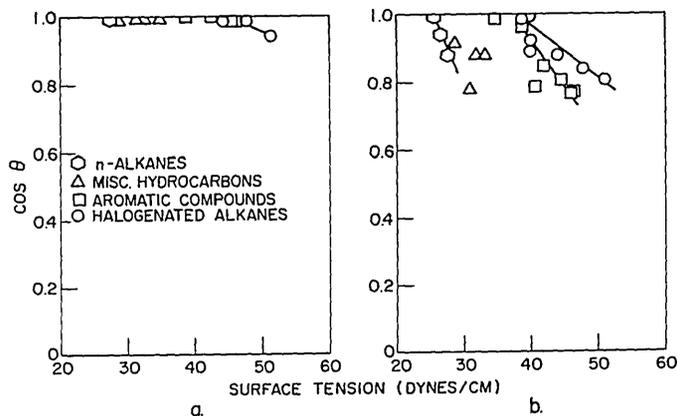


Fig. 1 - Comparison of the wettability of borosilicate glass (a) at 0.6% RH and (b) at 95% RH

organic liquids. Three distinct straight lines were obtained: one for the homologous family of the *n*-alkanes whose intercept was at 26 dynes/cm, another for the various aromatic compounds, and a third for the halogenated *n*-alkanes. The graphs of the latter two families of compounds showed more scattering of the graphical points from the straight line drawn, which is not surprising since these compounds were not homologs. Although the slopes of these two graphs were different, the straight line for the halogenated alkanes intercepted the $\cos \theta = 1$ axis at 37 dynes/cm, and the line for the aromatics intercepted the axis at 36 dynes/cm.

Quartz

Wettability data for quartz are listed in Table 1 and graphed in Figs. 2a and 2b. Just as in the experiments with Pyrex, the hydrocarbon liquids either spread spontaneously on quartz or exhibited values of $\theta < 5$ degrees at RH of 0.6%, and the halogenated hydrocarbon liquids exhibited nonzero values of θ when γ_{LV} at 20°C exceeded about 42 dynes/cm. Again, as with the borosilicate glass, the contact angles of the liquids on the quartz surface were greater at 95% RH than at 0.6% RH, and we found three well-defined straight lines: one for the *n*-alkanes, one for aromatics, and one for halogenated alkanes. Figure 2b reveals that the value of γ_c derived from the wetting behavior of the *n*-alkanes was 25.5 dynes/cm, and the value derived from the wetting of the halogenated hydrocarbons was 37 dynes/cm. These values of γ_c are the same (within the experimental error) as the above-mentioned results obtained with Pyrex.

Sapphire

Table 1 and Fig. 3 give the contact angles obtained with the same group of liquids on sapphire surfaces at 0.6% and 95% RH. The results were very much like those observed with Pyrex and quartz surfaces. Thus, all of the hydrocarbons spread at 0.6% RH, but the halogenated hydrocarbon liquids spread only when the liquid surface tension was below 44 dynes/cm. Well-defined values of γ_c were again obtained at 95% RH: 25.5 dynes/cm for the *n*-alkanes, 36 dynes/cm for the hydrogen-bonding aromatics, and 37 dynes/cm for the halogenated *n*-alkanes.

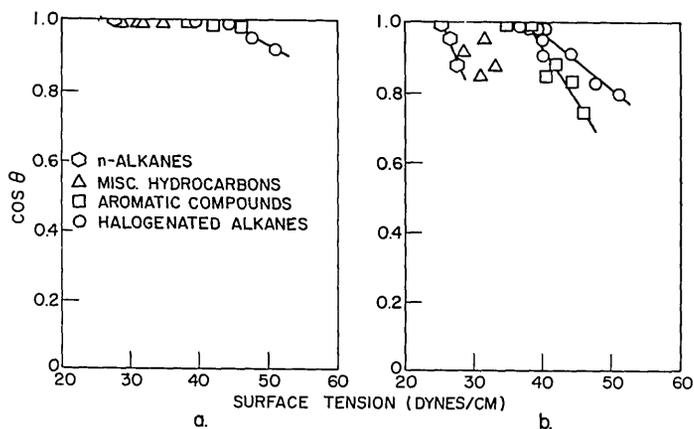


Fig. 2 - Comparison of the wettability of quartz (a) at 0.6% RH and (b) at 95% RH

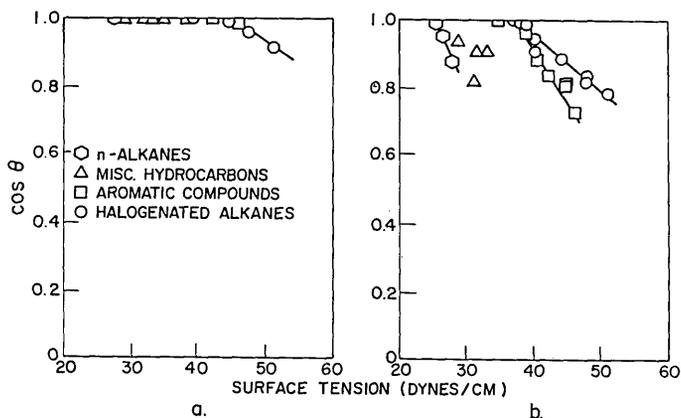


Fig. 3 - Comparison of the wettability of sapphire (a) at 0.6% RH and (b) at 95% RH

Comparison to γ_c on Bulk Water

From much past experience (4) we would expect γ_c for any given solid or liquid surface to be the same for all series of homologous liquids, provided the interaction between the liquid and the solid surface arises from London dispersion forces only. However, if the interaction includes a significant contribution from nondispersion forces of adhesion, such as those causing hydrogen bonding, γ_c should be displaced toward higher values, the amount of displacement being a measure of the contribution of such nondispersion interfacial forces.

Pomerantz, Clinton, and Zisman (6) recently measured the extent to which the unsaturated bonds in the aromatic hydrocarbon ring make such compounds more hydrophilic than the analogous alkanes containing the same number of carbon atoms; thus, the benzene ring had to lie adsorbed flat on the surface of bulk water, and a hydrogen-bonding contribution resulted from the interaction of the resonating double bonds with the water molecules. In the investigation reported here, a water monolayer was always present on the solid substrate; hence, the adhesional wetting energies for an homologous series of

aromatic liquids should result in a higher γ_c than those of a series of n-alkanes. Our experimental results confirm this conclusion, as shown in Figs. 1b, 2b, and 3b; we, therefore, are in agreement with the similar conclusion reached by Shafrin and Zisman (1) relative to soda-lime glass.

However, the effect of aromaticity cannot be defined by one definite quantity for all aromatic compounds, since the nondispersion forces depend on several factors, such as the number of single rings present in the molecule, the number of condensed rings, and the steric configuration of the molecule and its constituents which control the ability of the aromatic ring to orient itself to provide optimum area of contact with the solid substrate. This last effect is evidenced in the present investigation, for example, by the lower contact angles of o-dibromobenzene on Pyrex and quartz as compared to those of m-dibromobenzene, even though the ortho isomer has a higher value γ_{LV} (Table 1) and would otherwise be expected to show the higher value.

Shafrin and Zisman (7) have determined the critical surface tension of spreading on bulk water by plotting the initial spreading coefficient on water of each organic liquid of a given series S_{ba} (where b denotes the respective organic liquid and a denotes the substrate water) vs its surface tension γ_{LV} ; the intercept at $S_{ba} = 0$ of these straight lines was then taken to be γ_c for this system. The value of 21.7 dynes/cm at 20°C was thus calculated from the spreading of the members of the pure n-alkane series of liquids. A higher value of $\gamma_c = 25$ dynes/cm for water was obtained from the spreading of the n-alkenes, and a still higher value of $\gamma_c = 30$ dynes/cm resulted for the n-alkyl benzene series, when S_{ba} was plotted vs the number of carbon atoms in the alkyl chain.

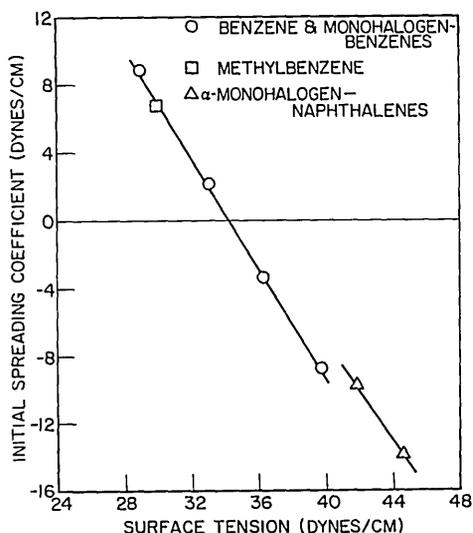


Fig. 4 - Initial spreading coefficients of halogenated aromatics vs their surface tensions at 20°C

Figure 4 shows a plot of S_{ba} vs γ_{LV} of several series of related halogenated aromatic liquids on water; the values of S_{ba} are those from publications of Harkins and coworkers (8,9) and are listed in Table 2. The intercept at $S_{ba} = 0$ for the halogenated benzenes leads to a γ_c value of 34 dynes/cm. Not enough points are available for the naphthalenes to define a corresponding γ_c ; however, indications are that γ_c falls very close to that of the benzenes. Figure 5 is a plot of S_{ba} vs γ_{LV} of several brominated n-alkanes; a straight line drawn through these points intercepts $S_{ba} = 0$ at γ_c of 36 dynes/cm.

If we now compare the intercepts in Figs. 4 and 5 at $S_{ba} = 0$, which correspond to the value of γ_c of bulk water for series of liquids of various molecular configurations, with the values of γ_c obtained in our study on moist, high-energy, hydrophilic solids for the same series of organic liquids, we find a good correlation (Table 3). In each case γ_c had the lowest value for the nonhydrogen-bonding, non-ionic liquids (the n-alkanes). Also, γ_c for each series of organic liquids had a higher value on the high-energy solid surfaces covered with the condensed monomolecular layer of water adsorbed at 95% RH than on bulk water.

Since we were successful in determining γ_c relative to water for several halogenated aromatic and n-alkane series, we thought it of interest to calculate some additional surface chemical properties for these same series. The concepts of these properties and the appropriate equations had been developed by Pomerantz, Clinton and Zisman (6).

Table 2
Surface Chemical Properties of Aromatics and Brominated n-Alkanes
with Respect to Bulk Water (All data was taken at 20°C)*

Liquid	γ_b (dynes/cm)	F_{ba} (dynes/cm)	γ_{ab} (dynes/cm)	W_{ba} (ergs/cm ²)	σ_b (Å ²)	ω_{ba} (cal/g-mole)
Benzene	28.9	8.9	35.0	66.7	34.2	3280
Methylbenzene	29.9	6.8	36.1	66.6	38.8	3740
Chlorobenzene	33.1	2.3	37.4	68.6	38.5	3800
Bromobenzene	36.3	-3.3	39.8	69.3	42.0	4190
Iodobenzene	39.7	-8.8	41.9	70.6	45.5	4620
Bromoethane	24.2	17.4	31.2	65.8	21.5	2030
1,2-Dibromo- ethane	37.2	-2.5	37.5	73.1	28.7	3020
1,2,3-Tribromo- propane	44.0	-11.1	39.9	76.9	44.8	4960
1,1,2,2-Tetra- bromoethane	47.5	-15.7	41.0	79.3	43.7	4990

*Concepts and equations as developed in Ref. 6:

γ_b = Surface tension of the organic liquid

Film pressure $F_{ba} = S_{ba}$ (Initial spreading coefficient); a = water

Interfacial tension from $\gamma_{ab} = (\gamma_a - \gamma_b) - F_{ba}$

Reversible work of adhesion from $W_{ba} = 2\gamma_b + F_{ba}$

σ_b = area occupied at the organic liquid/water interface by each molecule of organic liquid (from molecular models)

Reversible work of adhesion per adsorbed molecule of organic liquid from

$$\omega_{ba} = \frac{W_{ba} \sigma_b (6.02 \times 10^{23})}{4.18 \times 10^7} \quad \text{cal/g-mole.}$$

Table 2 lists the initial film pressure F_{ba} (where $F_{ba} = S_{ba}$), the initial interfacial tension γ_{ab} , the initial reversible work of adhesion W_{ba} , the area occupied by each molecule of organic liquid at the organic liquid/water interface σ_b (as calculated from the molecular ball models), and the initial reversible work of adhesion per adsorbed molecule of organic liquid ω_{ba} . When σ_{ba} of the bromoethanes is plotted vs the number (N) of substituted bromine atoms per molecule (Fig. 6), a linear relation is obtained which shows that the value of ω_{ba} contributed by each bromine atom substituted on such a molecule is about 990 cal/g-mole. Nearly the same value, 910 cal/g-mole, is also obtained when a bromine atom is substituted on a benzene molecule (Table 2).

Unfortunately, no data are available on homologous families of chloro- or iodo-substituted ethanes which would permit calculation of the contribution of a chlorine or an iodine atom to the reversible work of adhesion. However, since ω_{ba} per bromine

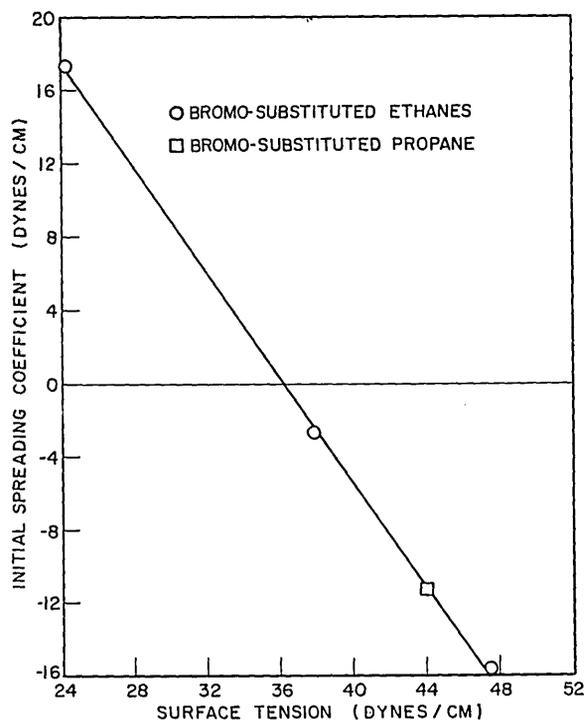
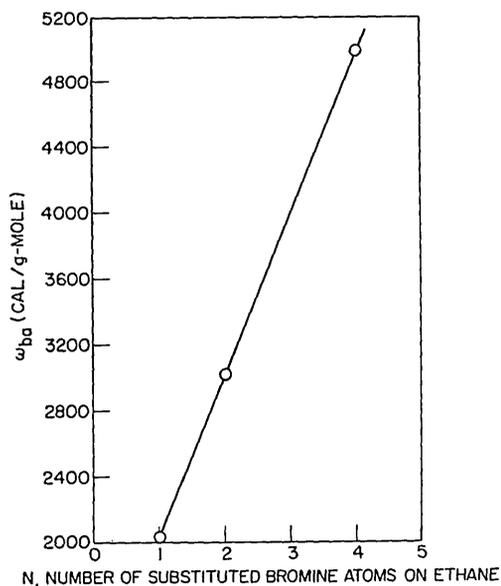


Fig. 5 - Initial spreading coefficients of bromo-substituted alkanes vs their surface tensions at 20°C

Fig. 6 - Contribution of bromine atoms to ω_{ba}



atom calculated from the difference for bromobenzene and benzene in Table 2 of between 910 and 990 cal/g-mole agrees well with the results from the homologous series of bromoethanes of Fig. 6, we can assume that the values of ω_{ab} of about 500 cal/g-mole for a chlorine atom and about 1350 cal/g-mole for an iodine atom, as calculated for substituted benzenes (Table 2), are good estimates and should agree with results that would be obtained for a series of chloroethanes or a series of iodoethanes.

EFFECT OF VARYING PRETREATMENT TEMPERATURE

The results on the Pyrex, quartz, and sapphire surfaces discussed above were obtained after exposing each clean specimen to a drying temperature of 120°C for 10 min

Table 3
Comparison of γ_c for Surfaces of Bulk Water (Calc.) and of
High-Energy Glasses Equilibrated at 95% RH

Series of Liquids	Critical Surface Tension of Wetting (dynes/cm)	
	Bulk Water	Glasses at 95% RH
n-Alkanes	22*	25.5-26
Halogenated Aromatics	34†	36-37
Halogenated n-Alkanes	36‡	37

*From Ref. 7.

†From Fig. 4.

‡From Fig. 5.

prior to subjecting it to the humid nitrogen atmosphere at 20°C. These conditions had originally been chosen to assure adequate removal of physically adsorbed water without causing excessive exposure of the surface to organic contamination. It has been known for many years that exposure of various types of glasses to increasing temperatures will remove successively decreasing amounts of adsorbed water on any one specimen (10, 11). Garbe and Christians (12) found that on heating the specimen to 380°C *in vacuo* water vapor evolved from three zones in the glass — the surface, a thin region below the surface, and the interior. Approximately the same percentages were given off from each zone by soda-lime and borosilicate glass. Garbe, Klopfer, and Schmidt (13) also investigated the adsorption of water vapor on a borosilicate glass at different temperatures, after first degassing it at 10⁻⁹ torr and 380°C. On subsequent exposure to a temperature of 25°C and a water vapor pressure of 10⁻⁶ torr, the water adsorbed was about 0.1% of that required to form a monolayer; at higher temperatures the amount adsorbed was even less.

Numerous investigations have been carried out on the removal of water from silica. Taylor, Hockey, and Pethica (14) suggested that dehydration of silica in air above 300°C in the presence of some water vapor produced a lower-energy surface, because the remaining surface hydroxyls had rearranged so as to participate in the maximum permissible interhydroxyl hydrogen bonding. Essentially similar results were found by Asher, Goodman, and Gregg (15). In their recent investigation of porous Vycor sheets (96% SiO₂), Low and Ramasubramanian (16) found that all physically adsorbed water could be removed from this porous glass at room temperature, whereas Elmer, Chapman, and Nordberg (17) had concluded that physically adsorbed water was present up to temperatures of 200°C. Young (18) found that physical adsorption of hydroxyl groups on silica could occur only on sites where hydroxyl groups were chemisorbed, which had to be below 400°C. When Garbe and Christian (12) exposed silica to air after first degassing it at 1000°C *in vacuo* they found that the water vapor released by reevacuating the silica and rebaking it to 480°C corresponded to one monolayer only. Thompson (19) later suggested that the changes which occur on heating silica *in vacuo* may be the following: at 26°C, physically adsorbed water is removed from the exterior surface; further heating to 200°C expels the water from the capillaries in the surface. Water adsorption on alumina surfaces was investigated recently by Hardie and Petch (20), who found that heating to 170°C *in vacuo* was sufficient to drive off initial moisture and leave about a 20% monolayer coverage; heating to about 350°C left only a 1% coverage.

Although these previous investigations were made on different types of glasses, and most of them involved a preliminary degassing at low pressures, they all agreed on the

effect of temperature: temperatures in excess of 200°C were not necessary to remove physically adsorbed water; temperatures in excess of 400°C should be avoided if subsequent water-vapor adsorption is desired, since they tend to cause irreversible removal of chemisorbed hydroxyl groups, which are necessary to serve as sites for such adsorption.

In view of the importance revealed in the literature of effects at high temperature, we decided to dry our specimens at two other temperatures (besides the 120°C value producing the results given in Table 1) before exposure to nitrogen at the desired RH: (a) a mild baking treatment at 65°C, well below the boiling point of water to preclude any possible corrosion of the surface, and (b) a more severe baking at 215°C to assure removal of all physically adsorbed water (16, 17). If subsequent contact angles measured on specimens prepared at 215°C were significantly lower than those prepared at 120°C or 65°C, it would indicate that physically adsorbed water had still remained on the solid surface after drying it at the lower temperatures. Table 4 compares the contact angles measured in nitrogen at 0.6% RH and 20°C after the specimens had been dried under one of the following conditions: 20 min at 65°C, 10 min at 120°C, or 10 min at 215°C. The results show that except for slightly lower contact angles exhibited at 215°C by methylene iodide on all three glasses and by tetrabromoethane on quartz and sapphire no significant differences were found on the specimens following baking treatments at the different temperatures. These few lower values are not sufficient to affect the general conclusions that the drying temperature of 120°C originally employed was adequately high.

Table 4
Comparison of Contact Angles at 0.6% RH and 20°C on Glasses
After They Had Been Predried at Different Temperatures

Liquid	Surface Tension at 20°C (dynes/cm)	Contact Angle (degrees)								
		Pyrex Dried at			Quartz Dried at			Sapphire Dried at		
		65°C	120°C	215°C	65°C	120°C	215°C	65°C	120°C	215°C
Hydrocarbons										
Dicyclohexyl	32.8	spr.*	spr.	spr.	<5	<5	spr.	<5	spr.	spr.
Hexadecane	27.6	spr.	spr.	spr.	spr.	spr.	spr.	spr.	spr.	spr.
Polar Liquids										
Methylene iodide	50.8	19	19	16	23	22	15	24	24	16
Sym-tetrabromoethane	47.5	12	8	10	12	17	9	12	18	12
Polyphenylthioether MCS 292	46.2	—	—	—	9	—	6	12	—	8
α -Iodonaphthalene	45.9	9	9	7	8	10	8	10	10	6
α -Bromonaphthalene	44.6	9	9	5	5	5	5	9	9	5
1,2,3-Tribromopropane	44.0	8	8	8	9	7	7	7	8	8

*Spr. indicates that the liquid spreads spontaneously; i.e., $\theta = 0$.

Table 5
Comparison of Contact Angles at 95% RH and 20°C on Glasses
After They Had Been Predried at Different Temperatures

Liquid	Surface Tension at 20°C (dynes/cm)	Contact Angle (degrees)								
		Pyrex Dried at			Quartz Dried at			Sapphire Dried at		
		65°C	120°C	215°C	65°C	120°C	215°C	65°C	120°C	215°C
Hydrocarbons										
Dicyclohexyl	32.8	27	28	27	24	28	27	26	25	25
n-Hexadecane	27.6	34	28	32	33	28	27	33	29	28
Polar Liquids										
Methylene iodide	50.8	38	36	38	38	37	35	38	38	35
Sym-tetrabromoethane	47.5	34	33	32	32	35	28	35	33	32
Polyphenylthioether MCS 292	46.2	—	39	—	—	37	—	—	36	36
α -Iodonaphthalene	45.9	44	40	42	42	43	38	42	43	40
α -Bromonaphthalene	44.6	40	36	36	34	33	31	36	35	31

Table 5 compares the wettability of each type of solid surface after the three different baking pretreatments at 95% RH. Evidently there were no significant differences attributable to insufficient drying or to subsequent variations in water-vapor adsorption. It is therefore concluded that any drying temperature from 65° to 215°C is sufficient to drive off all of the physically adsorbed water molecules. Thus, the contact angles observed at 0.6% and 95% RH necessarily must be caused only by the thin film of water molecules adsorbed at 20°C from the humid nitrogen atmosphere in which the solid had been immersed.

DISCUSSION

This investigation demonstrates that (a) the clean, smooth surfaces of borosilicate glass, fused quartz, and fused synthetic sapphire (α -aluminum oxide) had each been converted to a surface of much lower γ_c , and therefore lower surface energy, by the adsorption of water molecules, and (b) the resulting critical surface tensions of wetting were nearly identical at a given RH for all three types of high-energy, hydrophilic, nonmetallic surfaces. A fourth such high-energy solid, soda-lime glass, studied earlier by Shafrin and Zisman (1), can also be included in the same generalization, since their results were essentially the same as those presented here. Since all four types of solid surfaces were exposed to the same controlled RH and temperature, the conversion from high to low γ_c (and therefore lower surface energy γ_{S^0}) must be the result of the physical adsorption of only a monolayer of water molecules onto each surface. We can conclude that the critical surface tension and also the surface energy of clean, high-energy, hydrophilic solids (like a borosilicate glass, fused quartz, and crystalline α -alumina) after exposure to a humid atmosphere is dependent upon the surface concentration of water adsorbed on that surface, but that it is independent of the chemical nature of the underlying solid. At

20°C and the low RH of 0.6%, there cannot be as much as a close-packed monolayer of water physically adsorbed on each of these types of solid surfaces; yet, it drastically decreased γ_c . Additional water-vapor adsorption in going from 0.6% RH to 95% RH formed little more than one condensed monolayer and caused a further decrease in γ_c . This further reduction in γ_c was highly significant experimentally, although it was much smaller; thus, γ_c at 0.6% RH was 45 dynes/cm and at 95% RH it was 25 dynes/cm.

Armstrong, Chaklader, and Clarke (21) and Ritter and Burton (22) have recently measured the contact angles of pure liquid nickel and its alloys with titanium, chromium, and zirconium at 1500°C and 10^{-5} torr on a solid sapphire surface approximately coincident with the 10 $\bar{1}2$ plane. From these data Eberhart (23) has calculated the value of γ_c of sapphire at 1500°C and 10^{-5} torr as 1050 ± 100 dynes/cm. Investigations carried out during the last few years (24-28) on the effect of temperature on contact angles (where temperature changes were no greater than 150°C) indicated only slight variations in the contact angle with temperature. At present, no information on large-temperature variations has been published. If we extrapolate from the currently available data to much larger temperature changes, we estimate γ_c of sapphire at 20°C in vacuum to be not greatly different from γ_c at 1500°C; even if we assume that γ_c changes 0.1 dyne/cm for every 1°C (corresponding to the temperature coefficient for the free surface energy γ_{S^0} (29)), γ_c at 20°C in vacuum would be about 1200 ± 100 dynes/cm. Our present data thus show there was a drastic decrease in γ_c to about 45 dynes/cm when only a fractional monolayer of water had physically adsorbed on the sapphire surface.

Hardie and Petch (20) recently studied the lowering of the surface energy of α -alumina (having a surface area of 41.2 m²/g) as the result of water-vapor adsorption. By assuming from crack-propagation techniques the free surface-energy value of α -alumina at 20°C to be 1900 erg/cm², they calculated the lowering of surface energy to be 354 ± 8 erg/cm² at $p/p_0 = 0.3$ (30% RH) and about 480 erg/cm² in saturated water vapor $p/p_0 = 1.00$. This small additional lowering of surface energy is, therefore, qualitatively in agreement with our findings of a decrease in γ_c of about 20 dynes/cm — from 45 dynes/cm at 0.6% RH down to 25 dynes/cm at 95% RH.

Since four chemically different solid surfaces were affected in the same manner by a monolayer of adsorbed water with regard to the surface energy of wetting, we can make the reasonable extrapolation that other high-energy hydrophilic surfaces, such as metals and metal oxides, will also be affected similarly.

A monolayer of adsorbed water thus exerts an important influence upon the spreading and adhesion of organic liquids on high-energy solids. Unless the solid surface is completely free of adsorbed water molecules, spontaneous spreading of many organic liquids will be impeded; consequently, there will be decreased adhesion of the liquid to the solid. It should also be noted that the frequently used assumption that adsorbed water lowers the surface energy and so assists in crack propagation is given much reinforcement by our conclusions.

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13. ABSTRACT <p>Contact angles of a variety of hydrophobic liquids were measured on clean surfaces of borosilicate glass, quartz, and sapphire at 20°C with the RH at 0.6% and 95%. The adsorption of water molecules at 0.6% RH resulted in the formation of only a fraction of a monolayer; yet, this fraction converted each high-energy solid surface to one having a low critical surface tension of wetting γ_c. The increased amount of water adsorbed at 95% RH to form a film comprising little more than a condensed monolayer further lowered γ_c to a value somewhat above that of bulk water. At each RH investigated the value of γ_c was the same for each of these three solids; hence, γ_c was dependent upon the surface concentration of adsorbed water but was independent of the chemical nature of the solid substrate. The somewhat different values of γ_c obtained on using several different homologous series of hydrophobic liquids are explained in terms of differences in the contribution from nondispersion interfacial forces acting between the water film and the contacting organic-liquid molecules. These results reveal clearly the important influence of only a monolayer of adsorbed water upon the spreading, adhesion, and contact angles of organic liquids resting upon high-energy, hydrophilic, solid surfaces.</p> <p>To illustrate the effect of the baking pretreatment temperature on the removal of physically adsorbed water, the three specimens were dried at three temperatures: 65°C, 120°C, and 215°C. No significant differences were found on the specimens following baking treatment at the different temperatures.</p>			

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