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Effect of Adsorbed Water Upon the Spreading of Organic Liquids on Soda-Lime Glass

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
MEASUREMENT OF CONTACT ANGLES IN CONTROLLED ATMOSPHERES	2
PROCEDURE USED FOR CLEANING THE GLASS SPECIMENS	4
EXPERIMENTAL MATERIALS	5
SPREADING BEHAVIOR OF HYDROCARBONS AND HALOCARBONS ON GLASS	5
Hexadecane	7
Squalane	8
Dicyclohexyl	8
Other Hydrocarbons	9
Halocarbons	9
SPREADING BEHAVIOR OF HYDROPHILIC LIQUIDS ON MOIST GLASS	11
MECHANISM OF THE EFFECT OF RAPID CHANGES IN RH ON SPREADING UPON GLASS	12
ORIGIN OF AN ANNULAR WATER RING AROUND AN ORGANIC LENS	12
EFFECT OF RH ON THE CRITICAL SURFACE TENSION OF GLASS	13
ADDITIONAL REMARKS	16
REFERENCES	18

ABSTRACT

The spreading behavior and equilibrium contact angle (θ) of selected, pure, organic liquids on clean soda-lime glass surfaces were observed in equipment specifically designed to purify and control the atmosphere at relative humidities varying from 1 to 95%. Increasing relative humidity was found to increase θ for many nonhydrophilic liquids on glass; no comparable effects occurred in identical experiments on a nonadsorptive low-surface-energy solid (polytetrafluoroethylene). Rapid and reversible changes in θ following large changes in relative humidity revealed that the spreading behavior was essentially controlled by the adsorption or desorption of water molecules from the areas of the glass surface immediately adjacent to the periphery of the organic liquid drop.

The decrease in the wettability of the glass with increasing relative humidity resulted from the physical adsorption of a surface layer of water molecules sufficient to convert the normally high-energy surface of glass into one that behaves as a low-energy surface, i.e., a surface with a low critical surface tension for spreading (γ_c) toward the nonhydrophilic liquids. Thus, as the thickness of the adsorbed film of water increased, soda-lime glass behaved like a low-energy surface having a γ_c which decreased from about 46 dynes/cm at 1% RH to 30 dynes/cm at 95% RH. Additional increases in the thickness of the adsorbed layer to that of a duplex water film depressed γ_c further. The agreement of these results with the spreading behavior of the same liquids on bulk water supports this conclusion.

These results can be related to the effect of adsorbed water on the spreading or adhesion of resins to glass and other hydrophilic solids and to the problem of developing better adhesives for dental fillings.

PROBLEM STATUS

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

AUTHORIZATION

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EFFECT OF ADSORBED WATER UPON THE SPREADING OF ORGANIC LIQUIDS ON SODA-LIME GLASS

INTRODUCTION

Little information is available in the literature on the effect of the thickness of an adsorbed water film upon the ability of organic liquids to spread on a hydrophilic solid surface. Fox, Hare, and Zisman (1,2) reported that at 20°C and 50% relative humidity (RH) pure, high-boiling, aliphatic, naphthenic, and aromatic liquid hydrocarbons spread spontaneously with a zero contact angle on polished clean quartz and synthetic sapphire (α -alumina). Such solid surfaces at this temperature and RH under equilibrium conditions are coated with only one monolayer of physically adsorbed water (3). In marked contrast to the above observations, these organic liquids are not able to spread upon such solids coated with a duplex water film (hundreds of molecules thick) nor can they do so upon the clean surface of bulk water. The latter observation exemplifies the well-known generalization of Harkins and Feldman (4) that the initial spreading coefficients of high-boiling paraffinic and aromatic hydrocarbon liquids are always negative on bulk water at 20°C; their conclusions have been confirmed by others (5-8). Zisman (9) has recently pointed out that all of the above facts indicate that as a physically adsorbed film of water on hydrophilic solids like glass becomes more than one or two molecules thick, there must result a significant decrease in the spreading coefficient of each higher liquid alkane (such as hexadecane) and of white mineral oil as well as an accompanying increase in the equilibrium contact angles.

A scattering of observations reported in the journals are in accord with the preceding conclusion. Thus, Bartell and Bristol (10) showed that the advancing contact angle of pure acetylene tetrabromide (or sym-tetrabromoethane) on borosilicate glass and also that on quartz was larger the higher the RH. Cottington, Levine, and Zisman (11) found that the equilibrium contact angles of methylene iodide on quartz, borosilicate, and soda-lime glass also increased with increasing RH. Timmons and Zisman (12) recently reported that the contact angle of methylene iodide on clean polished platinum decreased considerably with RH and suggested that it and the n-alkyl halides would spread spontaneously if the platinum surface were entirely free of adsorbed water. Bowden and Throssel (13) and Vernon, Macaulay, Bowden, and Throssel (14) had shown previously that platinum foil which was clean and free of hygroscopic contamination was covered with not more than a monolayer or two of adsorbed water vapor; therefore, we can reason from Timmons and Zisman's results (12) that only one or two adsorbed monolayers of water have a large effect in increasing the contact angle of methylene iodide on platinum.

In the present report are results of an investigation of the extent to which water adsorbed on a silicate glass surface affects the spreading and the equilibrium contact angle of various pure organic liquids. Of especial interest is the effect of the transition of the physically adsorbed water film from a polymolecular to a monomolecular film. Work on other hydrophilic solids will be reported later.

Note: This report incorporates material presented in part at the 151st Annual Meeting, American Chemical Society, Division of Colloid and Surface Chemistry, Pittsburgh, Pennsylvania, March 23, 1966, and in part at the Symposium on Surface Chemistry of Glass, 68th Annual Meeting, American Ceramic Society, Washington, D.C., May 11, 1966.

MEASUREMENT OF CONTACT ANGLES IN CONTROLLED ATMOSPHERES

Our experimental approach was to observe directly the spreading behavior and the equilibrium contact angle at 20°C of various pure organic liquids on a horizontal plane sheet of clean glass coated with water films of various thicknesses under conditions of controlled RH such as to preclude any surface contamination by organic material. The physically adsorbed water layer was varied in thickness from that of a bulk liquid, through that of a "duplex" polymolecular film which exhibited interference colors, and finally to that of a monolayer at less than 1% RH. For this purpose an enclosed, compact, readily disassembled chamber made of Pyrex (borosilicate glass) was constructed so that the interior could be acid-cleaned and thoroughly washed before each experiment; thus, residual vapors or adsorbed films from one experiment could not contaminate clean surfaces introduced for a subsequent experiment. Grease and other organic materials were avoided by using carefully cleaned poly(tetrafluoroethylene) for stop-cock plugs and sleeves to seal the standard taper joints in the gas-purification train which delivered the purified gas to the specimen viewing chamber.

The specimen chamber is shown in cross section in Fig. 1, the upper view corresponding to the chamber as used for the measurement of the contact angle (θ) and the lower view as used for the measurement of RH. Important characteristics of this chamber are: it was made of transparent glass which was relatively free of optical distortion, it was kept free of internal sources of organic contamination, it was readily assembled and disassembled, and it was easily acid-cleaned and washed. The female 45/50 section of a Pyrex standard-taper joint provided a suitable chamber and a reasonably gastight fit to the fritted glass disk element of the 45/35 lower male section of a commercial chromatographic adsorption column. The other open end of the female joint was fitted with a slip-on glass cap (made from a Petri dish of appropriate size) provided with a small hole to permit delivery of the sessile drop of liquid to the surface of the solid specimen. When not in use the hole was closed with a clean poly(tetrafluoroethylene) stopper. The slip fit between the cap and the viewing chamber served as an exit for the gas and as a mechanical baffle to minimize the entry of room air against the slight positive pressure of the humidified gas in the chamber.

To support the flat glass specimen, a quartz shelf was so placed in the chamber that the upper surface of the specimen lay approximately along the axis of the viewing chamber; this minimized distortion caused by the curvature of the walls of the cylindrical

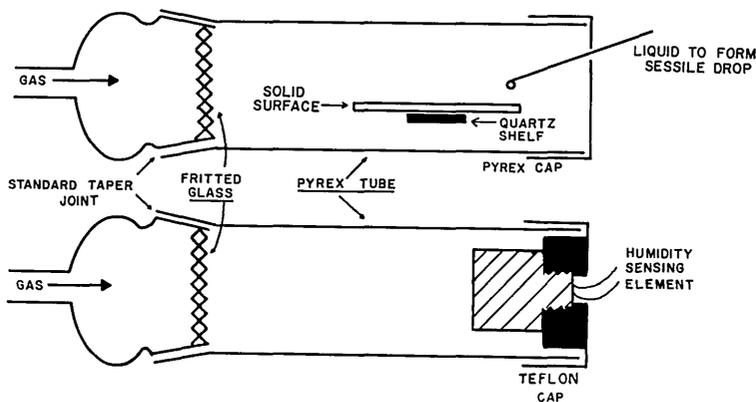


Fig. 1 - Cross section of the transparent viewing chamber as used for measuring contact angles (upper view) and monitoring RH (lower view)

chamber. Measurements of the contact angle were made on a sessile drop of the liquid equilibrated with the atmosphere in the viewing chamber. The drop was illuminated from behind so that its profile could be viewed with a horizontal telescope fitted with a Ramsden eyepiece; two independently rotatable crosshairs attached to a pointer and to the 0-to-180° axis of a protractor head, respectively, permitted direct measurement of the contact angle. Since the viewing chamber was attached to a rigid, all-glass system, the position of the glass specimen was essentially fixed; therefore, it was necessary to modify the telescope-goniometer used in the past (15,16) so that all required motions horizontally and vertically transverse to the optical axis were incorporated in the mounting of the optical elements. This was done by mechanically divorcing the specimen support (the support for the viewing chamber) from the optical bench carrying the illuminator and telescope and by mounting the optical bench on a lateral-motion carriage with horizontal scale to permit the alignment of the optical axis with the opposite sides of the sessile drop. Thus, accurate measurements could be made both on the contact angle and the drop diameter in the focal plane of the telescope.

Each sessile drop of organic liquid was built up by the addition of successive small increments so the measurements could be made on θ , the slowly advancing contact angle (16); for the purposes of this investigation the receding contact angle held only minor interest (16,17). Measurements were readily made on drop diameters and contact angles in excess of 5°. For smaller contact angles, oblique illumination and viewing were required to establish that a stable position was reached by the outer edge of the drop. Finally, when spontaneous spreading occurred (i.e., $\theta = 0$), we merely recorded the speed of drop expansion and whether interference colors appeared. The wall curvature of the viewing chamber did not cause an error in the measurement of the contact angle, for the value of θ so obtained with sym-tetrabromoethane on poly(tetrafluoroethylene) was 79° ± 1°, in good agreement with previously published results (16).

A metered stream of nitrogen gas which had been freed of organic contaminants by passage through a series of long columns of Drierite, coconut charcoal, and activated chromatographic alumina was continuously delivered to the viewing chamber. A Teflon stopcock permitted the purified gas to pass through (or around) a gas-washing bottle containing sufficient distilled water or aqueous solution of calcium chloride to provide the desired RH. Fitted to the gas inlet of the viewing chamber was a fritted glass disk (coarse porosity; nominal maximum pore size 40 to 60 microns) which removed particulate matter and provided a uniform distribution of the flowing gas. Since the viewing chamber was only 1-1/2 in. in diameter and 6 in. in length, a flow of 100 ml/min was sufficient to replace the total volume of gas every 2 minutes and to raise the RH from 1% to 95% within 10 minutes. Variations in θ with time were eliminated after 1 hour of equilibration at low RH or 2 hours at high RH.

Both the viewing chamber and the fritted glass orifice were freshly cleaned in acid, rinsed with distilled water, and dried for each organic liquid investigated. During successive relative humidity measurements on a single, high-boiling, organic liquid, only the viewing chamber was recleaned. The incoming gas stream was monitored for organic impurities by placing a small, freshly flamed platinum foil in the gas stream for a period of time and then determining its water contact angle. The effect was to accumulate on the platinum surface any contamination which streamed by the specimen during that time. Since each spreading experiment or contact angle measurement was completed in from 2 to 4 hours, the absence of any significant hydrophobic contamination on the platinum foil exposed to the nitrogen stream for that same time provided a sensitive check on the freedom of the gas stream from organic material. Additionally, the value of θ for a drop equilibrated on a glass surface for 2 hours in a gas-swept system was the same as that obtained in the same time in a static, closed, clean system containing air in equilibrium with activated adsorbent alumina. Since introducing a drop of water to monitor the rate of contamination of the platinum control surface would alter the RH of the chamber, and introducing a drop of the organic liquid on the glass specimen would

result in contaminating the atmosphere as well as the platinum surface, these two types of measurements were never made simultaneously.

Measurements of θ and RH at the same time were also impossible, because the humidity sensor was fabricated from polymeric material which could not be cleaned for each experiment. Therefore, equilibrium conditions were first established in the gas stream with the humidity sensor operating in a dummy viewing chamber in place (Fig. 1, lower view). Next, the chamber and glass frit were replaced with essentially identical freshly cleaned components, then the glass specimen was mounted on the freshly flamed quartz shelf, and finally the chamber was closed with the glass cap and Teflon stopper. After equilibrium conditions had been established and contact angle measurements were completed, the humidity sensor was returned to the system and the RH was measured again. Thus, by monitoring the RH before and after but not during the measurement of θ , contamination by vapor-phase transfer of material from the humidity sensor was avoided.

An Aminco-Dunmore Electric Hygrometer with narrow-range high-sensitivity elements was used to measure the RH from 1.6% to 98.5%. The minimum RH attained in the chamber was lower than could be detected with this hygrometer. Activated alumina (the final adsorbent in the gas purification train) reportedly leaves only 0.005 mg of residual water per liter of dried air at 25°C (18), which corresponds to 0.02% RH. An independent determination of the minimum RH with a Moisture Monitor (Consolidated Electroynamics Corp., Type 26-302) to sample the gas just before it reached the viewing chamber indicated 0.6% RH. Unfortunately, this instrument could not be used in the viewing chamber as arranged for contact angle measurements; however, its use established that the minimum RH achieved in these experiments (to be referred to as 1%) could not be below 0.6%.

PROCEDURE USED FOR CLEANING THE GLASS SPECIMENS

Soda-lime microscope slides were investigated first because (a) they were readily obtainable with flat, polished, and reproducible surfaces, (b) reliable information was available concerning the effects of various cleaning techniques on them (19), and (c) preliminary measurements indicated that the contact angles of various organic liquids upon them were reproducible. A method of cleaning the glass slides was sought which would remove gross organic contamination without brushing or other mechanical assistance, would leave no organic or inorganic film (from either the original contamination or from the cleaning agent), and would have a negligible effect in reacting with, eroding, or otherwise altering the glass surface. After many methods were investigated, the procedure adopted was as follows: After a 1-minute brushing with a Tide solution at room temperature to remove gross dirt, the glass slide was rinsed briefly with flowing, grease-free tap water, followed by singly distilled water. The slide was then immersed for 10 minutes at 80°C in an 0.5 wt-% solution of "technically pure" tetrasodium ethylene diamine tetraacetate dihydrate (Na_4EDTA) available commercially as Sequestrene Na_4 from Geigy Industrial Chemicals. Next, the slide was copiously flushed with singly distilled grease-free water followed by triply distilled water from a quartz still in order to prevent the adsorption of metallic ions. The resulting dripping-wet slide was mounted on the flamed quartz shelf in the viewing chamber, or on acid-cleaned glass supports in a grease-free drying oven at 120°C for 10 minutes prior to transfer to the controlled atmosphere in the viewing chamber. Effective degreasing was obtained with the Na_4EDTA ; this material had also been shown by the electron micrograph studies of Tichane and Carrier (19) to produce an essentially smooth surface on soda-lime glass when immersed in a hot, dilute solution for a short time. The 10-minute treatment adopted here was more than double the time required to obtain reproducibly grease-free surfaces. Although it was not determined directly if any sequestering agent remained chelated to the glass surface after the extensive rinsing treatment, the results of wetting experiments on glass surfaces cleaned by this method did not differ from those on glass cleaned only by Tide solution.

EXPERIMENTAL MATERIALS

"Precision Grade," soda-lime glass microscope slides obtained from the A.S. Aloe Company were used. These slides were made from exceptionally hard noncorrosive glass qualifying under the Federal Specification GG-S-446a of October 1956, which requires corrosion-resistant glass meeting specific boiling and solubility tests. No analysis was made of the glass composition, but it is presumed to be about the same as the composition for a corrosion-resistant slide given by Tichane and Wilson (20) in weight percent as 73% SiO₂, 14.5% Na₂O, 7% CaO, 4% MgO, and 1.5% Al₂O₃.

The 0.005-in. platinum foil used to monitor atmospheric cleanliness was a 99.9% pure grade free of scratches which was produced by the Baker Platinum Works; it was degreased by being flamed to a dull red heat for a few seconds in a small gas burner immediately prior to use. The poly(tetrafluoroethylene) used for comparison measurements was a pure specimen (21) whose smooth glossy surface was washed with aqueous Tide solution and rinsed well with distilled water before each use (22).

Each of the organic liquids from the sources indicated below was finally purified just before each experiment by slow percolation through a long column of the adsorbents specified below until no spreading of a drop of the liquid occurred on the clean surface of water adjusted to either an acidic or alkaline pH (6). Silica gel and alumina were used to purify the following liquids: n-hexadecane (Humphrey-Wilkinson Co.; ASTM normal cetane), sec-p-octadecyl toluene (prepared by Dr. Hennion of the University of Notre Dame, b.p. 207-209°C at 2 mm Hg; $n_D^{20} = 1.4846$), mono-isopropyl bicyclohexyl (Monsanto Chemical Company; research sample; 62% meta and 38% para isomers; density 0.885 g/cc at 25°C; $n_D^{20} = 1.4807$), and monoisopropyl biphenyl (Monsanto Chemical Company; research sample; 62% meta and 38% para isomers; density 0.9844 g/cc at 25°C; $n_D^{20} = 1.5835$). Silica gel, fuller's earth, and alumina were used for purifying dicyclohexyl (Monsanto Chemical Company; b.p. 239.0-239.6°C; $n_D^{20} = 1.4790$). Florisil and alumina were used for α -methyl-naphthalene (Reilly Tar and Chemical Co.; density 1.0208 g/cc at 25°C; $n_D^{20} = 1.6163$; only one component shown by thin-layer chromatography). The same adsorbents were used for the fraction of squalane (Robeco Chemical Co.) distilling from a Podbelniak Still at 70-80°C/2 μ Hg ($n_D^{20} = 1.4525$) (23). Silica gel, potassium carbonate, and alumina were used for sym-tetrabromoethane (Eastman Organic Chemicals; reagent grade; density 2.965 g/cc at 20°C), and activated carbon (DARCO Grade X) was added for the adsorption treatment of methylene iodide (Fisher Chemical Co.; "purified" grade).

Column chromatography was also used to purify each of the following liquids, after which it was spread on the surface of water lightly dusted with talc to see if spreading would occur as a duplex film without the formation of a monolayer in advance of the spreading lens. Silica gel and alumina were used for purifying formamide (Eastman Chemical Co.; reagent grade), ethylene glycol (Jefferson Chemical Co.; research sample), and propylene carbonate (Eastman Chemical Co.; practical grade; density 1.198 g/cc at 25°C). Alumina alone was used for purifying hexachloropropylene (Hooker Electrochemical Company; research sample). Florisil alone was used to purify glycerol (Wallace and Tiernan) and thiodiglycol (prepared at NRL). Alumina and florisil were used for bis(2-ethylhexyl)sebacate (prepared and characterized (24) by J. G. O' Rear of NRL), and alumina and fuller's earth were used for bis(2-ethylhexyl)ortho-phthalate (Carbon and Carbide Company; Plexol Plasticizer DOP).

SPREADING BEHAVIOR OF HYDROCARBONS AND HALOCARBONS ON GLASS

Tables 1 and 2 summarize the results of our observations on the spreading and contact angles exhibited by the organic liquids investigated. These liquids were divided into two groups accordingly as they had negative initial spreading coefficients and formed

nonspreading lenses on the surface of bulk water (Table 1) or had positive initial spreading coefficients and spread spontaneously over the surface of bulk water (Table 2). The liquids are listed in the second column of each table in the order of decreasing surface tension (γ_{LV}). In the remaining columns are given the values of θ observed for each liquid on the indicated surfaces.

Of the nine liquids listed in Table 1, the last seven are hydrocarbons of several structural types. When each of these seven hydrocarbons was placed on the surface of a very thin but visible layer (duplex film) of distilled water coating a clean glass slide, a nonspreading lens similar to that observed on bulk water was formed. The presence of the solid substrate provided sufficient mechanical support for the organic lens to eliminate the usual concave interface and make possible a measurement of θ for the organic

Table 1
Spreading Behavior on Glass of Pure Liquids Having
Negative Spreading Coefficients on Bulk Water
(All data at 20°C)

Liquid Sessile Drop	Surface Tension (γ_{LV}) (dynes/cm)	Contact Angle (θ) or Spreading Behavior of Drop			
		On Duplex Water Film	On Glass Equilibrated at		
			95% RH	63-53% RH	1% RH
Methylene iodide	50.8	37°	36°	31°	13°
Tetrabromoethane	47.5	31°	36°	9°	9°
1-Methylnaphthalene	38.7	22°	7°	—	< 5°
iso-Propyl biphenyl	34.8	19°	16°	—	< 5°
Dicyclohexyl	32.8	31°	21°	21°	Spread
p-Octadecyl toluene	31.5	29°	17°	—	< 5°
iso-Propyl bicyclohexyl	30.9	33°	13°	—	< 5°
Squalane	28.5	24°	Spread	—	Spread
n-Hexadecane	27.6	23°	Spread	Spread	Spread

Table 2
Spreading Behavior on Glass of Pure Liquids Having
Positive Spreading Coefficients on Bulk Water
(All data at 20°C)

Liquid Sessile Drop	Surface Tension (γ_{LV}) (dynes/cm)	Contact Angle (θ) or Spreading Behavior of Drop on Glass Equilibrated at	
		95% RH	1% RH
Water	72.8	Spread	—
Formamide	58.2	Spread	—
Thiodiglycol	54.0	Spread	Spread
Ethylene glycol	47.7	Spread	—
Propylene carbonate	41.1	Spread	Spread
Tricresyl phosphate	40.9	6°	14°
Hexachloropropylene	38.1	Spread	Spread
bis(2-Ethylhexyl) phthalate	31.3	23°	—
bis(2-Ethylhexyl) sebacate	31.1	17°	—
Pentaerythritol tetracaprate	30.4	8°	—

lens on the water surface (third column). Observed values ranged from 19° to 33° ; however, the following experimental difficulties made these measurements less meaningful than comparable ones on lenses placed in direct contact with solid surfaces.

Generally the hydrocarbon lenses drifted slowly over the water-covered glass surface. If this water layer was allowed to thin by evaporation, drifting ceased when interference colors became visible in some area of the water film, not necessarily immediately adjacent to the drop of hydrocarbon. Frequently, the water layer "piled up" at the periphery of the hydrocarbon lens into a visible annular ring which persisted even after the remainder of the glass surface was so denuded of bulk water that the interference colors disappeared. No difference was apparent in the annular rings around liquids which were denser than water. It appeared that the water layer was concentrated at the periphery of the oil lens rather than beneath it. This annular ring, the cause of which will be discussed later, partially obscured the drop profile with its meniscus and made it difficult to measure θ .

Hexadecane

Hexadecane has the highest surface tension of any unbranched aliphatic hydrocarbon that is a liquid at 20°C . When placed in contact with horizontal, heat-dried, glass surfaces previously allowed to equilibrate at 20°C at 1, 15, 52, 94, or 98.5% RH, hexadecane spread rapidly; a 0.003-ml drop doubled its initial diameter within the first 6 minutes, and interference colors developed after 30 minutes. When the hexadecane drop was placed on a glass slide equilibrated at 1% RH and the ambient RH was subsequently slowly raised, the rate of spreading decreased; spreading ceased even before interference colors developed in the oil layer. When the drop of hexadecane was subjected to a rapidly increasing RH, the initial rate of spreading remained comparable to that observed under equilibrium conditions until the RH had reached about 50% (roughly equivalent to a 5-minute exposure to the rapidly increasing RH); thereafter the rate of spreading decreased. After some 45 minutes when the RH had reached 92%, no further spreading was observed, although the drop diameter had only increased 2-1/2-fold. Interference colors were never observed in the oil film.

The above-mentioned change in the spreading of hexadecane as a function of increasing RH led to observation of the changes occurring in spreading when the amount of water present in the system was progressively decreased. Therefore a glass slide was covered with a thin visible layer of water (a duplex film) and was inserted in the viewing chamber which had previously been flushed with nitrogen at 1% RH. Hexadecane formed a nonspreading lens on the resulting surface with an initial contact angle of 23° , which was expected because of the nonspreading of hexadecane on bulk water. The initial contact angle remained constant and the drop remained nonspreading until the water film had evaporated, interference colors had disappeared over most of the surface, and very little liquid could be seen under 10X magnification in the annular ring surrounding the hexadecane lens. But as the last of this annular layer evaporated, the hexadecane contact angle decreased rapidly, the diameter of the liquid lens doubled within less than 1 minute, quintupled in diameter in the next 6 minutes, and continued to spread.

Thus, the transition of hexadecane from spreading to nonspreading occurred when the glass surface had become coated by a water film which was thicker than that developed on equilibration at 98.5% RH (i.e., probably not more than a few molecules thick) but definitely thinner than that required for the appearance of interference colors (hundreds of molecules thick).

Squalane

Squalane (2,6,10,15,19,23-hexamethyltetracosane) has a surface tension only 0.9 dyne/cm greater than hexadecane at 20°C, and it, too, spread on glass equilibrated at 1, 95, and 98.5% RH; however, squalane spread more slowly than hexadecane because of its nearly sevenfold greater viscosity (26.8 centistokes at 25°C as compared with 4.0 centistokes (23)). The initial contact angle of 24° exhibited by squalane on a duplex water film (Table 1) reduced to 17° upon 24 hours' exposure to an organic-free nitrogen stream of 90% RH; subsequent further reduction of the RH to 1% and the resulting evaporation of water until the water film exhibited interference colors caused a rapid decrease in θ until it became too low to be measured by low-magnification profile techniques and the drop diameter tripled within 30 minutes. The transition from nonspreading to spreading of squalane occurred, as in the case of hexadecane, when the layer of adsorbed water was too thin to cause interference colors but was thicker than that formed on equilibration of originally dry glass at 98.5% RH.

Dicyclohexyl

Although the surface tension of dicyclohexyl is only 5 dynes/cm above that of hexadecane at 20°C, they spread differently. In Fig. 2 is plotted the contact angle of dicyclohexyl in contact with the glass surface after the standard 2-hour equilibration at the indicated RH. From 1% to 29% RH a drop of dicyclohexyl spread rapidly with a contact angle of less than 1°. The volatility of the dicyclohexyl in the flowing gas stream was sufficient to prevent measuring the slowly advancing contact angle to determine if θ was zero instead of 1°. However, on glass which had been equilibrated at any RH from 53% to 98.5%, the dicyclohexyl drop was nonspreading and θ was 21°. When the glass was coated with a thin but visible layer (duplex film) of water, θ was even higher (31°). Thus, there was a two-step change in θ with increasing thickness of the adsorbed water film.

When a drop of dicyclohexyl was placed on glass covered with a visible water layer and was then exposed to a nitrogen gas flow of 1% RH in order to observe the effect of evaporating the film of water, an annular ring of water first formed around the oil lens,

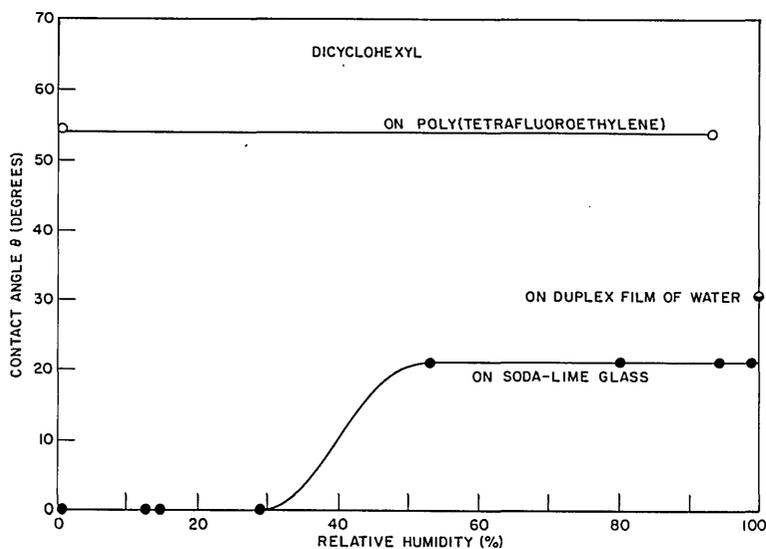


Fig. 2 - The effect of RH on the contact angle of dicyclohexyl on different surfaces

and the remaining water film evaporated uniformly while exhibiting broad interference bands. As long as this water annulus remained, θ was 31° . As had been observed with hexadecane, the contact angle of the dicyclohexyl decreased abruptly a few seconds after the annular ring of water had evaporated; during the first few seconds θ decreased to 10° , after which it decreased much more slowly. Only after 20 minutes had θ become too small to measure. Thus, the two-step change in θ observed with decreasing water-layer thickness paralleled that mentioned for increasing thickness.

The same set of experiments was conducted with the hydrophilic glass surface replaced by the hydrophobic surface of smooth clean poly(tetrafluoroethylene). A contact angle of 54° was found on the poly(tetrafluoroethylene) equilibrated at any RH from 1% to 95% (Fig. 2). These results with poly(tetrafluoroethylene) eliminated moisture effects on the surface tension of the organic liquid alone as the source of the changes in spreading of dicyclohexyl with the RH. Because the changes with RH occurred only on substrates capable of adsorbing water, and in view of the rapidity with which changes in θ occurred on glass, it is concluded that the water adsorbed on the glass at the periphery of the dicyclohexyl lens had caused the retraction which exposed fresh solid surface at the new periphery and allowed the process to be repeated.

Other Hydrocarbons

The remaining hydrocarbons in Table 1 all exhibited nonzero contact angles on soda-lime glass at low RH and larger values at higher RH. When the thickness of the water layer on the glass increased to that of a duplex film, θ increased further. Conversely, if the water from the duplex layer was allowed to evaporate, θ remained large until the water layer developed interference colors; then θ decreased as evaporation thinned the water layer and the lens spread, but θ did not decrease to zero, i.e., the drop did not spread indefinitely.

Halocarbons

The two halocarbon liquids investigated were chosen because of their high surface tensions and lack of hydrophilic substituents. As would be expected from their negative initial spreading coefficients (4), drops of methylene iodide and tetrabromoethane were nonspreading even after floating for 15 minutes on the clean surface of water. Since there was no radial motion in a layer of grease-free talc dusted lightly over the surrounding water surface, no molecules were escaping from the liquid lens by edge diffusion (6). These two halocarbons also formed nonspreading lenses of high contact angle when placed on a duplex film of water covering a soda-lime glass slide (Table 1). As both tetrabromoethane and methylene iodide are denser than water, it is possible that each liquid lens sank through the water layer to displace it from the glass surface. Thus, the apparent contact angle may not have corresponded to conditions at the water/organic liquid interface. Moreover, the meniscus of the displaced water layer may have obscured or distorted the view of the interface. For these reasons, the highest value of θ observed on the water-wetted glass was reported, since the primary effect of the meniscus should be to obscure the limb of the drop closest to the point of the triple interface and, in the case of $\theta < 90^\circ$, to make the apparent angle lower than the actual angle.

This investigation also has confirmed our previous reports (11,12) of the effect of RH on the methylene iodide contact angle on siliceous surfaces and on platinum. Figure 3 represents the contact angle of a drop of methylene iodide on soda-lime glass which had been equilibrated previously for 2 hours or more at the indicated RH. Each graphical point represents the average value of θ for several drops of liquid on a single glass slide; multiple symbols at a given RH represent results on independently prepared and measured glass slides. At a low RH the variation in average θ for different glass slides

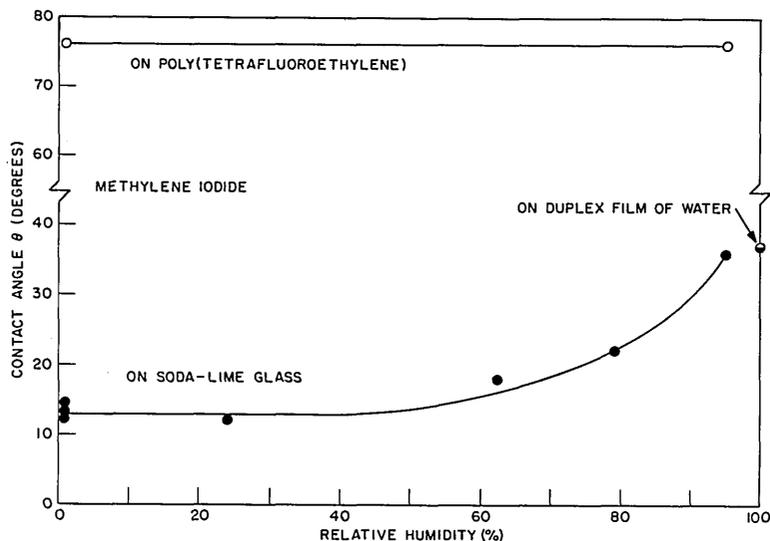


Fig. 3 - The effect of RH on the contact angle of methylene iodide on different surfaces

was the same as that for different drops on a single slide ($\pm 1\text{-}1/2^\circ$); at a high RH variations as large as $\pm 3^\circ$ were observed on a single slide. Note that values of θ above 90% RH became comparable to those obtained in the presence of a duplex film of water (half-shaded circle). The above experiments were repeated under identical conditions except that a smooth, clean, static-free surface of poly(tetrafluoroethylene) was substituted for glass. Poly(tetrafluoroethylene) does not adsorb significant amounts of water at these temperatures. Moreover, since poly(tetrafluoroethylene) has the low critical surface tension of 18.5 dynes/cm (16), the contact angle of methylene iodide on it is much larger than that on glass. Since $\cos \theta$ decreases approximately rectilinearly as the liquid surface tension rises, the identical values of θ observed on poly(tetrafluoroethylene) (open circles in Fig. 3) at 1% and 95% RH prove that dissolved water in the organic liquid cannot be the cause of the observed changes in θ with RH shown in the lower curve.

Measurements were also made of the effect of rapid changes in RH on the contact angle of a drop of methylene iodide previously placed on a glass and on a poly(tetrafluoroethylene) surface. No change in θ was observed on the latter surface. However, on raising the RH, each drop of methylene iodide on glass retracted, and θ increased to values only slightly lower at any given RH than those obtained on glass surfaces initially equilibrated at that same RH. The reverse effect was noted when the RH was rapidly decreased: θ for methylene iodide decreased, and the drop spread over progressively larger areas of the surface.

Similar measurements on drops of tetrabromoethane revealed that θ was essentially constant on soda-lime glass equilibrated at different values of the RH in the range of about 1% to 65%; but at higher RH values, θ increased rapidly with the RH (see Fig. 4). The variation in the values of θ from site to site on any one glass slide did not increase at the higher RH values, but the variation from one slide to another increased significantly. The highest value of θ observed on glass free of visible water was greater than that apparent in the presence of a visible film of water (half-filled circle in Fig. 4); the difference may not be significant, however, due to the obscuring effect of the water meniscus as mentioned earlier. Differences in RH had no effect on the spreading behavior of the tetrabromoethane on a poly(tetrafluoroethylene) surface.

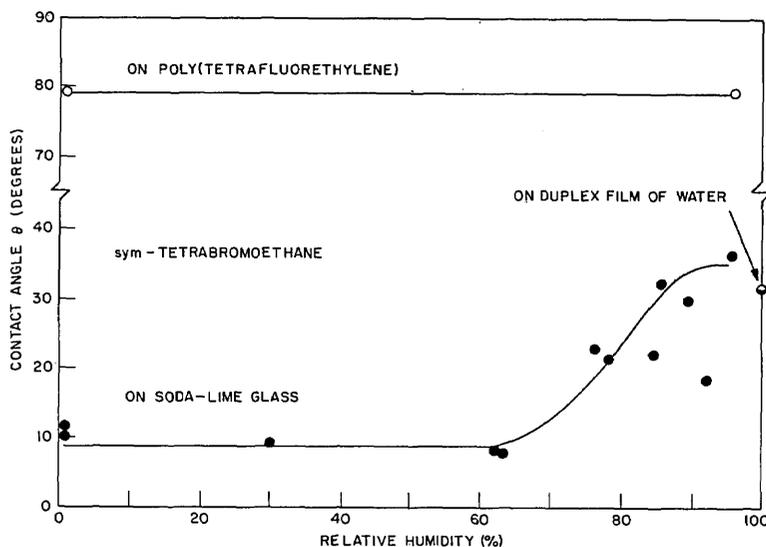


Fig. 4 - The effect of RH on the contact angle of sym-tetrabromoethane on different surfaces

Remarkable alterations in the contact angle of tetrabromoethane on glass were observed when making large and sudden changes in RH by breathing moist air on the sessile drop. A drop of tetrabromoethane having an initial diameter of 8 mm and contact angle of 10° at 55% RH contracted promptly to a diameter of 2 mm when exposed to a sudden rise in RH. A subsequent decrease in RH caused the diameter to expand to nearly its original value. This procedure could be repeated as many as twenty times on the same drop without any detectable change in the results except that the diameter of the drop in its most extended condition decreased slightly with repeated expansions, so that after twenty cycles the diameter was 6 mm instead of the initial 8 mm. The effect of cycling the RH on θ and on drop diameter is shown schematically in Fig. 5.

Changing the RH had no effect on θ or the drop diameter of tetrabromoethane in contact with poly(tetrafluoroethylene). Similar behavior on rapidly cycling the RH was observed with dicyclohexyl and methylene iodide, namely, a corresponding cycling of drop diameter when in contact with a hydrophilic solid (glass) and no effect when in contact with a nonhydrophilic solid (poly(tetrafluoroethylene)).

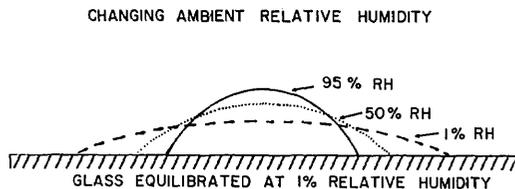


Fig. 5 - The effect of cycling the RH shown schematically (magnified vertically) for a nonhydrophilic organic liquid in contact with a hydrophilic solid

SPREADING BEHAVIOR OF HYDROPHILIC LIQUIDS ON MOIST GLASS

Tri-ortho-cresyl phosphate contains a hydrophilic polar group, and as would be expected a drop spread spontaneously on bulk water. When placed on a duplex film of water covering a soda-lime glass slide, a drop of the triester exhibited an initial contact angle of 15° which decreased rapidly in the first several minutes; thereafter, the lens diameter decreased continuously. However, a constant and reproducible contact angle of 14° was

exhibited by the triester in contact with the soda-lime glass slide equilibrated at 1% RH. No measurements were made at intermediate RH values in the present work, but Fox, Hare, and Zisman had reported (1) autophobic behavior and a 14° equilibrium contact angle of the same triester on fused silica at 50% RH. When a drop of the triester was placed on soda-lime glass equilibrated at 96% RH, the contact angle was lower initially than that at 1% RH and it continued to decrease slowly as the drop spread out over the glass surface.

Bernard and Hirtz (25) have reported a slow decrease with time of the contact angle of tri-ortho-cresyl phosphate on quartz surfaces and have attributed this to the replacement of a film of water, initially present, by the ester. Schrader and Lerner (26) recently interpreted the results of their studies on isotopically tagged tricresyl phosphate interacting either with Pyrex or fused silica as indicating the hydrolysis of the ester by water molecules adsorbed at the surface to produce free H_3PO_4 and cresol.

The hydrolysis and subsequent adsorption of the hydrolytic fragments to form an autophobic monolayer on the glass surface also accounts for the appreciable contact angles observed at 95% RH for the remaining esters in Table 2. Indeed, the strong likelihood of hydrolysis makes studies of the spreading behavior of esters in general potentially less useful than those of liquids which are not so susceptible to hydrolysis.

In order to check the spreading behavior on glass of polar hydrophilic liquids which do not hydrolyze, observations were made on the following liquids in contact with soda-lime glass surfaces equilibrated at 95% RH: formamide, thiodiglycol, ethylene glycol, and propylene carbonate. Complete and rapid spreading was observed in each case as might be expected because of their large positive initial spreading coefficients on bulk water (4).

MECHANISM OF THE EFFECT OF RAPID CHANGES IN RH ON SPREADING UPON GLASS

The rapid, reproducible, and reversible changes in θ of organic liquids on glass surfaces with changes in RH shown schematically in Fig. 5 are indicative of the mechanism involved. It has been established experimentally that these changes occur on hydrophilic surfaces and not on hydrophobic surfaces, that they cannot arise from alterations in the surface tension of the organic liquid, and that they occur more rapidly than is consistent with a mechanism of alteration of the liquid/glass interface by adsorption of water molecules migrating through the organic liquid. It is concluded, therefore, that the important changes caused by altering the RH take place at the periphery of the drop, i.e., at the line defining the triple interface. After an increase in RH, (a) water molecules from the atmosphere adsorb on the glass surface immediately adjacent to the organic liquid, (b) this water migrates laterally along the glass surface and displaces the organic liquid from a small peripheral area, (c) the newly exposed area adsorbs water molecules from the atmosphere, and (d) the sequence repeats rapidly until an equilibrium is reached. During reduction of the RH the process reverses; it is the loss of water molecules adsorbed just at the edge of the organic liquid which permits the drop to spread.

ORIGIN OF AN ANNULAR WATER RING AROUND AN ORGANIC LENS

An explanation is needed for the previously described appearance and persistence of the aqueous annulus around the lens of organic liquid. The film of water originally spread upon the glass slide had a level upper surface; upon the addition of the drop of organic liquid, a meniscus was formed with the organic lens. Subsequently the stream of dry nitrogen caused the film of water to evaporate everywhere except in the annulus-shaped

ring surrounding the lens. This aqueous annulus had a wedge-shaped vertical cross section. The outer lower edge of the annulus approached the level of the supporting glass slide as evaporation progressed and the outer diameter of the annulus decreased. As the inner diameter was defined by the unchanged size of the organic lens which it enclosed, it remained constant. Under equilibrium conditions there is a thermodynamic necessity for a constant contact angle between the organic liquid and the water so long as any bulk water is present. But since the organic liquid is not hydrophilic, it will not displace adsorbed water from the glass. Hence, as long as a water film more than a few molecules thick is present, the oil lens will not displace the water and the lens will appear to float on a thin layer of water.

An additional influence on the aqueous annular ring arises from local variations in the rate of evaporation of the water, since the water closest to the organic lens appears to evaporate more slowly than that at a distance from that lens. The effect cannot result from evaporation retardation due to the presence of an organic liquid monolayer floating on the water surface, because no organic substance used in these experiments is able to spread on water to form a film which has significant ability to retard water evaporation. This leaves the difference in heat conductivities of water and the organic liquids as the source of the differences in evaporation rates. The surface of the water is cooled by evaporation. Where the surface is adjacent to more water, this heat loss can be compensated by thermal conduction through the water phase. Where the surface of the water is close to the mass of the organic liquid, however, any evaporative heat loss is less rapidly compensated because of the lower thermal conductivity of the organic liquids; hence, the water surface becomes cooler, resulting in a thermal retardation of evaporation. Such effects could become significant in the system employed here, where the evaporation is facilitated by the use of a continuous stream of freshly dried gas.

EFFECT OF RH ON THE CRITICAL SURFACE TENSION OF GLASS

Among the nine hydrocarbon and halocarbon liquids investigated (Table 1) the lower the liquid surface tension, the lower the contact angle and the more the spreading. Since the glass behaved as if it had a critical surface tension of wetting (γ_c) (16), a plot was made of the cosine of the equilibrium contact angle (θ) observed at 95% RH against the surface tension (γ_{LV}) of the organic liquid. The result (Fig. 6B) is a good straight line which fitted all graphical points except 1-methylnaphthalene; from the intercept on the line $\cos \theta = 1$, $\gamma_c = 30$ dynes/cm. The exceptional behavior of the 1-methylnaphthalene is understandable, because it can adsorb with the aromatic ring horizontal in the water surface; as shown in Ref. 8, this compound would therefore be expected to have some hydrogen-bonding ability. When the system was equilibrated at 1% RH, the data points for the identical liquids (Fig. 6A) were on, or very close to, the line $\cos \theta = 1$, except for methylene iodide. Measurements of θ were obviously needed for other pure liquids free of hydrophilic groups with surface tensions over 40 to 45 dynes/cm; however, such liquids are rare, because liquids with higher surface tensions than 45 dynes/cm usually contain one or more hydrophilic, hydrogen-bonding groups, such liquids including water, glycerol, glycol, thiodiglycol, and formamide. These liquids could not be used for the plot in Fig. 6A, because they spread spontaneously on water-coated surfaces. However, if a straight line is fitted to the graphical points for the halocarbons and is made parallel to the graph in Fig. 6B for 95% RH, the intercept on the line $\cos \theta = 1$ in Fig. 6A is 46 dynes/cm; it will be assumed that this is a fair estimate of the value of γ_c for glass at 95% RH. It is remarkable that the increase in the amount of adsorbed water caused by raising the RH from 1% to 95% caused such a decrease in γ_c , namely, from 46 to 30 dynes/cm.

The closeness of the value of γ_c of 30 dynes/cm for a glass surface at high RH to that of 30 to 31 dynes/cm characteristic of smooth solids contaminated with a condensed

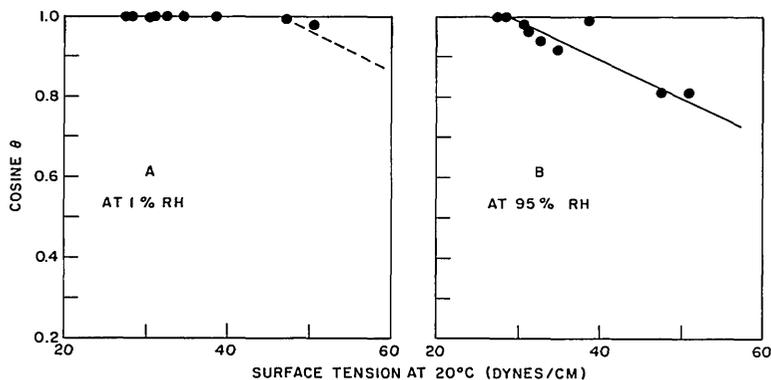


Fig. 6 - Comparison of the wettability by selected hydrocarbon and halocarbon liquids of soda-lime glass surfaces at two different RH values

film of an aliphatic hydrocarbon (27) could imply that our results arise from contamination of the glass surface by adsorbed aliphatic materials. Only two potential sources of such contamination in our experimental system deserve serious consideration: (a) the atmosphere to which the freshly cleaned glass surface was exposed during equilibration in the apparatus, and (b) volatile impurities left in the lens of organic liquid after final purification. Source (a) can be eliminated because of the ability of the glass surface to be completely wet with water ($\theta = 0$) even after a 2-hour exposure to the controlled atmosphere in our apparatus and also because of our periodic monitoring of the incoming gas stream with a flame-cleaned platinum foil to detect adsorbed organic films. Source (b) can also be eliminated, for the following reasons: Although the observed increase in θ with increased RH might be explained on the basis that hydrophilic organic contamination was accumulating on the glass surface to make it less wettable by liquids of higher surface tension, the reversibility of the RH effects on θ as the RH was decreased cannot be so explained. The volatile contaminants coming from the organic liquid lens could not be hydrophilic, because it is seen from Table 1 that a drop of the organic liquid did not spread when placed on the clean surface of water in a hydrophil trough; it is well known (6) that such a spreading test is extremely sensitive to the presence of hydrophilic organic impurities. Furthermore, the contaminant deposited on the glass would not be expected to be the same from each of nine structurally different and carefully purified organic liquids. A nonhydrophilic contaminant would be more readily adsorbed by a glass surface equilibrated at 1% RH than at 95% RH, and the value of θ observed at 1% RH would be greater than at 95% RH. However, this was not true in any of our experiments. Therefore, it is concluded that the results observed were not caused by organic contamination of the glass surface while in the glass system used.

Soda-lime glass is a hard high-melting solid bound together with strong ionic forces; thus it would be expected to have a high surface energy (1,16). Although the critical surface tension of wetting (γ_c) is always less than the free surface energy (γ_{S^0}), it would likewise be expected that γ_c of dry glass would be high. As is true of most solids, neither the surface tension nor the free surface energy of glass at ordinary temperatures is readily (or reliably) measured. Some of the experimental approaches tried in the past include microhardness measurements (28), comparisons of tensile strength in air vs in water (29), and the energy changes involved in crack propagation (30). The resulting room temperature values of surface energies or tensions have ranged around 200 to 400 ergs/cm². Values of the surface tension of around 330 dynes/cm at 900°C were obtained by Davis and Bartell (31) using the pendant drop method on solidified drops of glass, and Parikh (29) obtained around 280 dynes/cm at between 500 and 700°C by

fiber elongation methods. In the latter measurements on commercial soda-lime glass, the presence of water vapor was effective in lowering the measured surface tension even at such high temperatures. Recently Bryant (32) has reported that the energy required for cleavage of mica in an ultrahigh vacuum or in helium, argon, or nitrogen atmospheres is 30 times greater than in air or water vapor atmospheres, which also demonstrates a high sensitivity of fracture strength and the surface energy to the adsorption of water vapor.

Olsen and Osteraas plotted literature data on the contact angles in evacuated systems of the liquid alkali metals, mercury, and indium and reported (33) that a plot of $\cos \theta$ vs the surface tension of the liquid metal was a straight line from which the value of γ_c of 75 ± 10 dynes/cm could be obtained. Presumably, this value is for glass coated with the water vapor adsorbed from an atmosphere whose partial water vapor pressure was of the order of 10^{-5} mm Hg.

There is ample testimony in the literature to the extremes required to desorb water from glass surfaces. Only recently Dettre and Johnson (34) reported a 40° advancing contact angle for methylene iodide on a soda-lime glass heated to 550°C and then kept at 165°C for several days in an attempt to eliminate physically adsorbed water. From sorption studies on porous Vycor glass, Kershaw and Panckhurst (35) concluded that much water remained on the surface after prolonged heating to 450°C in oxygen. Debye and van Beek (36) postulated that heating glass to a temperature somewhat below the softening point is required to destroy the water layer which normally covers an ordinary glass surface. Despite the apparent necessity for vigorous and prolonged heating to remove water from glass, the possibility remains that the film of water physically adsorbed on glass at ordinary temperature is removable by relatively mild treatment. Unfortunately, the successful removal of this water cannot be differentiated from water eliminated through the condensation of surface silanol groups or through the gradual expulsion of water dissolved or occluded in the interior of the glass (36-38). The latter two mechanisms could explain the necessity reported in the past for extreme heating of glass to remove the last traces of water.

The reversibility of the contact angles and spreading properties of the various hydrocarbon and halocarbon liquids on glass following cycling of the RH indicates that in our experiments there was present an outer layer of physically adsorbed water which was readily removed. The conversion of the glass surface from one of high energy to one of much lower energy is believed the result primarily of the adsorption of an initial layer of chemically bound water; additional water adsorbed on top of that surface is physically adsorbed, and it is that layer whose variation in thickness is responsible for the sensitivity to RH observed in the contact angle behavior on glass of the liquids of Table 1. Our experiments have revealed that the spreadability of such liquids on glass is very limited in the presence of water physically adsorbed on the accessible glass surface. Since such limitation at high RH is caused by the presence of one or more condensed monolayers of physically bound water on the surface of the glass, the effect on θ at 95% RH or higher of changing the chemical composition of the underlying glass would be expected to be minor. The results reported here on γ_c for a moist soda-lime glass should be representative of the results to be obtained at high RH using a composition such as borosilicate glass or E-glass. However, values of γ_c for RH below 50% and especially around 1% or less may well vary with the chemical composition of the glass.

Johnson and Dettre (39) and Shafrin and Zisman (40) demonstrated recently by different methods that the clean surface of bulk water is a low-energy surface with respect to the spreading of nonhydrogen-bonding liquids, such as the alkanes. The latter reported that $\gamma_c = 22.0$ dynes/cm at 20°C . This result is to be compared with the conclusion reported here that $\gamma_c = 30$ dynes/cm for glass coated with a physically adsorbed condensed film of water at 95% RH. A comparison of these two results, the one for bulk water and the other for glass coated with the water adsorbed at 95% RH, is very revealing.

To relate the data discussed above, a plot of γ_c vs RH was made. Because $RH = p/p_0$ (where p is the partial vapor pressure of the water in the atmosphere and p_0 is the vapor pressure at saturation), we have chosen to plot γ_c vs p/p_0 . The range of values of p/p_0 to be considered here is great; hence p/p_0 is plotted on a logarithmic scale in Fig. 7. At $p/p_0 = 1$ the value of γ_c of 22.0 dynes/cm for bulk water (40) is used. The value of $\gamma_c = 75$ dynes/cm obtained by Olsen and Osteraas (33) for liquid metals on glass can also be plotted here (filled circle in Fig. 7). To do so we have assumed that p/p_0 for the water vapor is about 10^{-5} . The resulting graph in Fig. 7 fits a straight line very well. Because γ_c for bulk water is about 8 dynes/cm less than for the adsorbed water at 98.5% RH, we conclude that the local field of force emanating from the surface of bulk water is weaker than that from the surface of glass coated with only one or two monolayers of adsorbed water. In other words, the surface field of force of dry glass is not suppressed completely by the contributions to that field resulting from the first several monolayers of water adsorbed on it. After many additional monolayers of water have been adsorbed on the glass, the surface field of force gradually approaches that of bulk water. Our presently available data do not allow us to estimate the thickness of the water layer needed to make the surface of glass behave like bulk water.

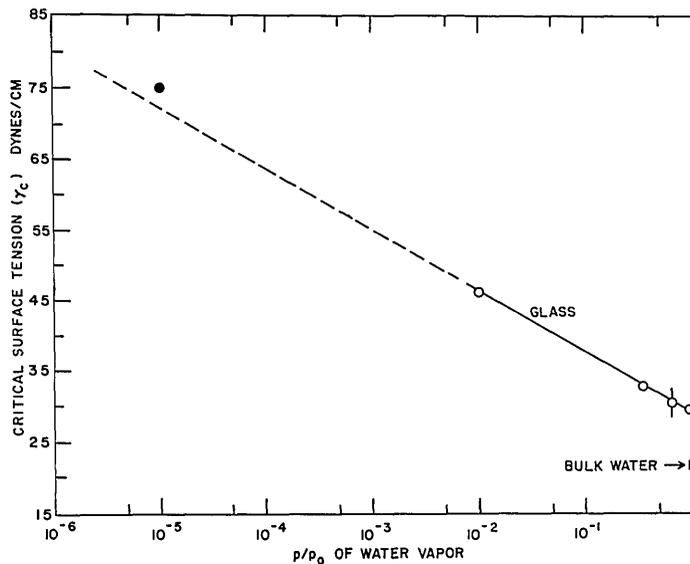


Fig. 7 - The effect of the partial pressure of water vapor on the critical surface tension of soda-lime glass

ADDITIONAL REMARKS

The results reported here explain why many pure hydrocarbon and halogenated hydrocarbon liquids, excluding the autophobic liquids (1,2), are not able to spread spontaneously on such high-energy surfaces as clean, dry, silicate glasses. We have demonstrated that the effect on γ_c of even minute amounts of adsorbed water is so great that even at less than 1% RH, glass behaves like a low-energy surface toward these liquids.

In view of the impracticality of attempting to remove all physically adsorbed water from glass, the existence of a critical surface tension of glass of 30 dynes/cm at ordinary relative humidities and temperatures is of interest in relation to many technological

and scientific problems. For example, it follows that spontaneous spreading on glass at 20°C and ordinary relative humidities by any nonhydrophilic liquid whose surface tension is more than 30 dynes/cm cannot occur; hence, there is much difficulty in impregnating glass fibers with such a polymeric hydrocarbon liquid (9).

There are two possible approaches to making such a liquid spread spontaneously on glass: (a) to modify the organic liquid, and (b) to alter the surface properties of the glass. Approach (a) would comprise either lowering the surface tension of the liquid with a surface-active additive or incorporating a water-displacing agent (41-43) to remove as much as possible of the physically adsorbed water and thus raise γ_c above the surface tension of the organic liquid. Some water-displacing agents perform both functions; however, the properties of such materials may be of minor benefit under many conditions encountered in practice. In approach (b) a glass "finish" or "conditioning" agent could be used to coat the clean glass surface, displace some or all of the adsorbed water, and raise γ_c of the surface. In general, however, the chemical constitution of conventional glass finishes will not result in a surface with a value of γ_c high enough to permit the majority of organic liquid resins to spread spontaneously (9). In order to raise γ_c , one might incorporate halogen atoms other than fluorine (9) in the outermost structure of the adsorbed molecules of finish. From the results presented above, it can be inferred that it would be advantageous to use liquid resins able either to completely displace water surface-chemically or else to react with or absorb the water. Many resins now in use either dissolve or react with adsorbed water to some extent. However, from existing information on the water susceptibility of glass resin-reinforced plastic systems, it appears that the additional use of an appropriately designed and applied chemisorbed glass finish would be most advantageous.

The results with soda-lime glass surfaces reported here may prove representative of the general wetting behavior of a larger variety of glasses or other hydrophilic, high-energy, solid surfaces. Further research is planned on the value of γ_c under various conditions of RH of other glasses, various hydrophilic minerals, and certain metal oxides. Such data would be helpful in describing more quantitatively the effect of adsorbed water on adhesion. In addition, it would be helpful to use a glass (unlike soda-lime glass) which is readily kept free from the surface accumulation of water-soluble salts such as alkaline oxides, hydroxides, and carbonates.

A similar sensitivity to adsorbed water on the part of the natural mineral constituents of teeth, as for example, the calcium hydroxyl apatite in dental enamel and dentine may have particular significance in the development of more effective dental adhesives (44). It appears impossible to remove the adsorbed moisture from the surface of a tooth cavity during dental treatment, and any adhesive used in filling the cavity must necessarily be applied in a highly humid atmosphere. The application of a finish comparable to that used on glass fiber surfaces is made difficult by the restriction to materials which would not be toxic, be corrosive, or generate objectionable products of reaction. These considerations need not eliminate the possibility of using a chemisorbed film of organic material tolerable to the body, and there are possibilities being investigated for developing finishes which are specifically suitable to such dental applications. The greatest advantage would come from the use of a chemisorbed finish on which the resin itself could adsorb or react in a way as to minimize the possibility of detachment during prolonged exposure to water environment.

Finally, since the surface tension of water at 20°C is 72.8 dynes/cm and γ_c for glass at 95% RH is 30 dynes/cm, it might be wondered why water is not autophobic (2) on glass. The reason is simply that the value of 30 dynes/cm describes γ_c for the glass only with respect to spreading on it of liquids free of hydrophilic groups. When a drop of water is placed on the glass surface, the physically adsorbed water molecules reorient, and consequently γ_c rises greatly.

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13. ABSTRACT The spreading behavior and equilibrium contact angle (θ) of selected, pure, or-organic liquids on clean soda-lime glass surfaces were observed in equipment specifically designed to purify and control the atmosphere at relative humidities varying from 1 to 95%. Increasing relative humidity was found to increase θ for many non-hydrophilic liquids on glass; no comparable effects occurred in identical experiments on a nonadsorptive low-surface-energy solid (polytetrafluoroethylene). Rapid and reversible changes in θ following large changes in relative humidity revealed that the spreading behavior was essentially controlled by the adsorption or desorption of water molecules from the areas of the glass surface immediately adjacent to the periphery of the organic liquid drop. The decrease in the wettability of the glass with increasing relative humidity resulted from the physical adsorption of a surface layer of water molecules sufficient to convert the normally high-energy surface of glass into one that behaves as a low-energy surface, i.e., a surface with a low critical surface tension for spreading (γ_c) toward the nonhydrophilic liquids. Thus, as the thickness of the adsorbed film of water increased, soda-lime glass behaved like a low-energy surface having a γ_c which decreased from about 46 dynes/cm at 1% RH to 30 dynes/cm at 95% RH. Additional increases in the thickness of the adsorbed layer to that of a duplex water (over)			

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film depressed γ_c further. The agreement of these results with the spreading behavior of the same liquids on bulk water supports this conclusion.

These results can be related to the effect of adsorbed water on the spreading or adhesion of resins to glass and other hydrophilic solids and to the problem of developing better adhesives for dental fillings.