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Contact angle of E and borosilicate glasses in different atmospheres

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The contact angle of E and borosilicate glasses in various atmospheres such as air, steam, glycols, etc, show that the ambient atmosphere significantly affects the wetting behaviour of these glasses with platinum 20% rhodium alloy. The change in the contact angle is attributed to the bond formation between the cations and anions in the substrate, glass and atmosphere. Steam and oxygen which increase the non-bridging oxygens in the glass as well as increase the negativity of the glass surface increase wetting. Glycols and glycerins reduce non-bridging oxygens and increase the surface positivity groups which reduce wetting. As the requirement of oxygen for complete oxidation of atmospheric combustibles increases, the wetting increases and consequently the contact angle decreases.

1. Introduction

The adhesion of a liquid to a solid and the surface forces at the interfaces influence many manufacturing processes. In the glass and ceramics field the production of glass articles, fiberization of glass, enamelling, glass coating, etc, are areas where the adhesion of the glass to the substrate material is of importance.

A liquid, when it comes into contact with a solid, wets the solid. Equilibrium conditions are governed by the three phase equilibrium of surface energies of the solid, liquid and vapour. The Young–Dupre [1, 2] equation using the concept of surface tension describes the equation as:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

where γ_{SV}, γ_{SL} and γ_{LV} are the forces at the solid–vapour, solid–liquid and liquid–vapour interfaces respectively. θ is the contact angle.

When θ is zero, equilibrium conditions cannot exist and the Young–Dupre equation does not apply. At $\theta = 0$ the liquid spreads across the surface as noted by Huntsberger [3]. The use of contact angle to describe the degree of wetting according to Miller [4] is misleading. The contact angle is a consequence of wetting. The relative attraction of solids for a particular liquid can be compared by obtaining the contact angles of the different solids with the same liquid. However, no valid comparison can be made between angles of two liquids with the same solid unless some adjustments are made for the cohesive forces within the liquids. In order to understand the wetting phenomena, other quantities such as the "work of adhesion", the "work of cohesion" and their relationships are more valuable than the contact angle by itself. Despite this, the contact angle is a sensitive physical property and is a function of the temperature, the surface of the solid, its roughness and contaminations, ambient conditions, liquid properties and gravitational forces. There are several reports on this subject [5–10].

The work described here deals with the change of contact angle with temperature and atmosphere. Copley *et al.* [11] have shown the variation of θ with different platinum group metals and alloys at different temperatures. Likewise, Parikh's [12] work demonstrates the change of surface tension with various atmospheres. Since surface tension influences the contact angle, it too varies with the atmosphere.

2. Experimental details

The contact angle is related to the drop shape. Much effort has been directed towards the analysis of the sessile drop profile. Bashforth and Adams

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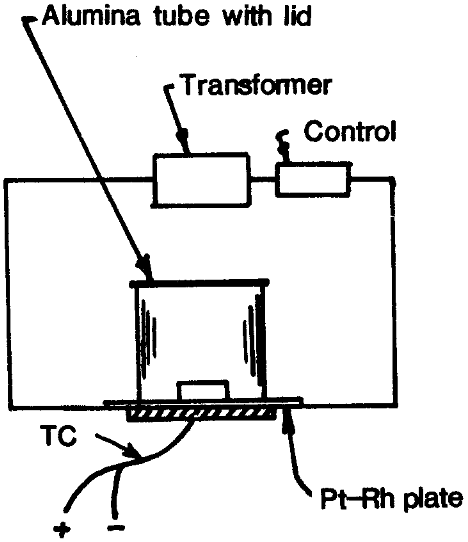

Figure 1 Sketch of experimental set-up.

[13] derived a differential equation for the drop profile and θ. Staicopolus [14], using numerical approximation, obtained a computer solution to this differential equation. In all these calculations, the shape of the sessile drop is important.

In the current experiments, a platinum 20% rhodium plate 100 mm x 100 mm x 3 mm is used as the solid surface and is polished to obtain a mirror-like surface. Electrical current passed through bars at either end heats the plate to the required temperature. A platinum 10% rhodium thermocouple, welded through the bottom surface of the plate close to the top surface (centre) of the plate, measures the plate temperature at the centre. The Pt–Rh plate is thermally insulated. An alumina tube 10 cm diameter with a lid on one end is placed on top of the plate and covers approximately the centre of the plate. An opening on the front side of the tube (12 mm square is used to photograph the drop (Fig. 1). Various atmospheres are introduced into the chamber through a hole in the lid.

TABLE I Glass composition

	Glass A (wt %)	Glass B (wt %)
SiO_2	55	64
Al_2O_3	14	6
B_2O_3	8	4
Fe_2O_3	0.4	0.2
CaO	18	6
MgO	4	3
Na_2O	0.3	15
K_2O	0.3	1
F_2	0.2	0.9

0.1 g glass is placed at the centre of the plate. The atmosphere inside the chamber is purged with the gas that makes up the atmosphere for that test. Gas flow is maintained until the experiments are concluded. The plate temperature is then raised to the required value and maintained there for 15 min before the drop is photographed. Separate experiments earlier showed that the drop attains a steady shape in 10 min at 1040° C. Above that, less time is required. Glass compositions are given in Table I.

The contact angle is directly measured from the photograph and averaged with that calculated from

$$\tan\frac{\theta}{2} = \frac{2h}{d} \qquad (2)$$

where h is the height of the drop at the centre of d, and d is the diameter of the drop. We assumed the drops to be a segment of a sphere.

3. Results and discussion

The contact angle from Figs. 2 and 3 decreases with increase in temperature. In the case of glycol [15] and glycerin, θ did not show any significant

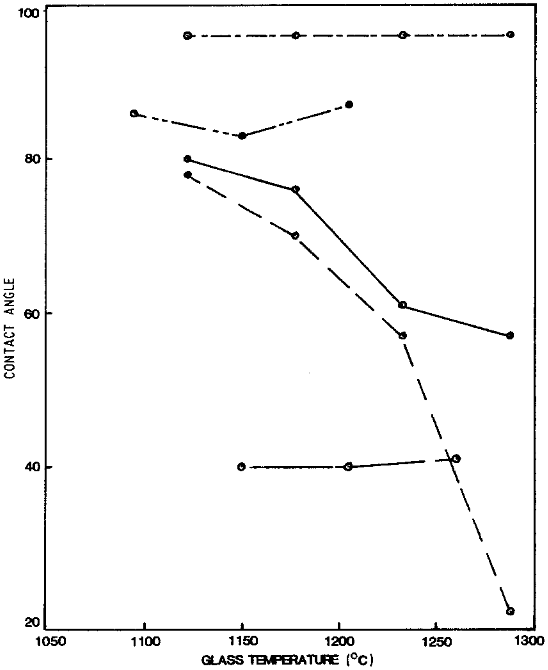

Figure 2 Contact angle of glass A (E) at various temperatures and atmospheres. ⊙——⊙ air; ⊙— — —⊙ steam; ⊙— - —⊙ glycol; ⊙- — -⊙ oxygen; ⊙— - - —⊙ glycerin.

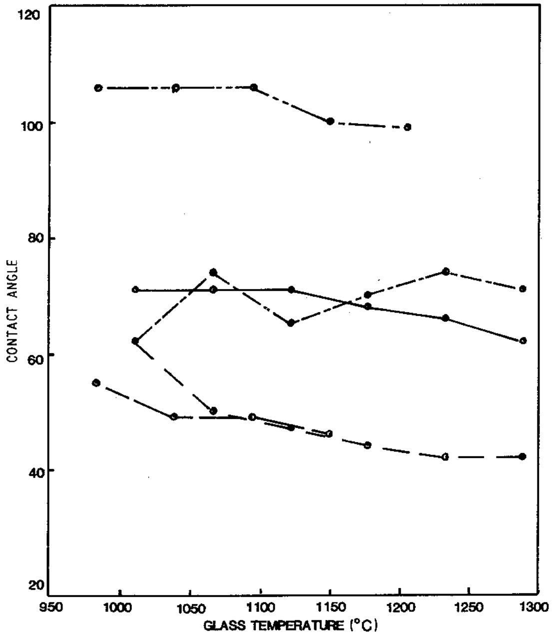

Figure 3 Contact angle of glass B at various temperatures and atmospheres. ⊙——⊙ air; ⊙— — —⊙ steam; ⊙— - —⊙ glycol; ⊙- — -⊙ oxygen; ⊙— - - —⊙ glycerin.

change. Beyond 1150°C glycerin ignited and, hence, no readings were taken.

The lowering of contact angle with increase in temperature is expected with the change in surface energies. With glass A, in air (12% r.h.) and in steam, the contact angle reduces with rise in temperature. In air, θ drops quickly at first and, then the graph tends to flatten at 1265°C. On the other hand, the initial reduction in θ with steam is gradual, with the slope being steep after 1232°C. In general, the contact angle is smaller in steam than in air. In the case of glass B, the contact angle decreases with temperature, but the change is small.

The wetting of glasses with platinum–rhodium substrate depends on the relative strength and stability at various temperatures of the platinum–rhodium–oxygen bond, glass cation–oxygen/hydroxyl bond and the cation/anion (in ambient atmosphere)–glass and substrate bonds.

According to Copley *et al.* [11] silicate glasses when melted, form into two types of ionic group, one group having excessive positive charge due to oxygen deficiency and the other having excessive oxygen and is consequently negatively charged. They represent the group as in Fig. 4.

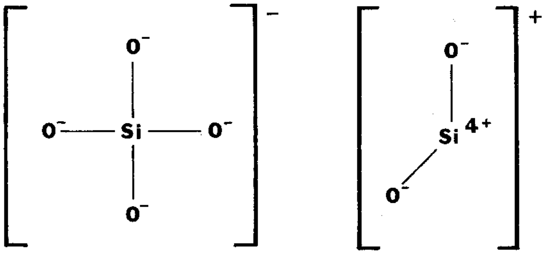

Figure 4 Anionic and cationic groups in silicate glass.

When glass is in contact with platinum, the valence electrons of platinum attempt to bond with oxygen ions of the anionic group of the glass. However, the cations in the glass also compete for the non-bridging oxygens. The relative strengths of the cation–oxygen bond and the platinum–oxygen bond determine which gets the non-bridging oxygen. The resultant change that occurs in the negativity of the anionic group determines the degree of wetting and consequently the contact angle.

The ionic field strengths of the cation, including platinum in this case, influence the change in negativity of the anionic group. As an example, if Na^+ is replaced by Ca^{2+}, the greater ionic field strength of the Ca^{2+} reduces the negativity of the anionic group and, hence, the glass with Ca^{2+} wets the metal less than the glass with Na^+. A reduction in the positivity of the cationic group or a decrease in the negativity of the anionic group decreases wetting.

Paul and Douglas [16] defined autoionization in silica and boric acid as

$$2\,SiO_2 \rightleftharpoons SiO^+_{3/2} + SiO^-_{5/2} \qquad (3)$$

$$B_2O_3 \rightleftharpoons BO^+ + BO_2^- \qquad (4)$$

The existence of the above charges on the surfaces of glasses A and B influence their wetting characteristics. In a steam atmosphere the sodium (glass B) at the surface is removed as NaOH. More non-bridging oxygens are now available for platinum. The positivity of the charges is also reduced by OH^- associating with the $SiO^+_{3/2}$ group. The net effect is for the glasses to wet the substrate. In an oxygen atmosphere the positivity is reduced and the negativity increased by the transformation of $SiO^+_{3/2}$ groups to $SiO^-_{5/2}$ groups which results in increased non-bridging oxygen available for platinum and hence increased wetting. The degree of wetting in air depends on the relative humidity of the air.

Glycerols and glycerins atmospheres decrease wetting in comparison to air, steam or oxygen atmospheres. In both cases the contact angle does not change much with temperature. During the breakdown of the organic compounds on the glass surface at the temperatures of the experiment, it appears that bonding takes place with oxygen available at the surface. As a result, the positivity of the group increases as well, as no oxygens are available for bonding with platinum. Under these conditions some Si–O–Si bonds may also form. In addition, these compounds keep moisture away from the glass surface, thus avoiding the wetting influence due to moisture. The net effect is a drastic reduction in wetting and consequently high contact angles.

Glass A wets the metal (80% Pt, 20% Rh) plate more and has a lower contact angle than glass B. The lower SiO_2 content of glass A gives more oxygen available for bonding with platinum.

Copley *et al.* [11] suggested equations for the degree of wetting (θ_0) for three different cases that occur with the addition of a cation. In the first case it is assumed that all cations added occupy interstitial sites and that $\Sigma_i f(E_{i\text{-O}})$ is the arithmetic sum of the bond energies of silicon, sodium and the cations that are added. Then

$$\theta_0 = \sum_i f(E_{i\text{-O}}) = f(E_{\text{Si-O}} + E_{\text{Na-O}} + E_{\text{M-O}}) \qquad (5)$$

In the second case, if the added cations occupy substitutional sites only, then the equation becomes

$$\theta_0 = f(XE_{\text{Si-O}} + YE_{\text{M-O}} + E_{\text{Na-O}}) \qquad (6)$$

where X and Y are mole fractional concentrations of Si–O and M–O bonds. In the third case where the added cations occupy both substitutional and interstitial sites the equation is

$$\theta_0 = f(XE_{\text{Si-O}} + YE_{\text{M-O}} + E_{\text{Na-O}} + E_{\text{M-O}}) \qquad (7)$$

which includes the bond energies of the mole fraction that occupies substitutional sites and those that occupy interstitial sites. In the glasses considered here, M includes Al, B, Ca and Mg. Table II [11] is used for calculation of bond energies. $E_{\text{Pt-O}}$ is taken as constant for both glasses. The greater the θ_0 value, the higher is the contact angle. If all aluminium is assumed to be in interstitial sites, θ_0 for glass B (144.5) is slightly higher than glass A (143.5) and vice versa if all aluminium is assumed to be in substitutional sites. The experimental values of θ in air show glass A to have higher values than glass B at lower temperatures (1100 to 1200° C). In the neighbourhood of 1200° C and above both glasses have similar values. However, glass A values are consistently lower than glass B, although the values of both glasses are within each others limits of experimental error. The experimental values are the average of six readings taken from three different samples of the same glass.

TABLE II Single bond strength of cations with oxygen

M in MO_x	Role in network*	Single bond strength $E_{\text{M-O}}$ (kcal)
Na	I	20
Ca	I	32
Al	I	60
Al	S	100
Si	S	106
B	S	119

*I = interstitial site.
S = substitutional site.

The chances of volatilization of some of the glass constituents are high, especially at higher temperatures and humid atmospheres. However, such volatilization did not change the values of contact angle (± 2°) measured at intervals of 10 min.

Fig. 5 shows the net oxygen that is required for complete oxidation of the constituents of the ambient atmosphere or the amount of oxygen that is available in the atmosphere against the contact angle. The value assigned to each atmosphere is given in Table III. As the amount of oxygen required for complete oxidation increases, the contact angle of the glass increases. When excess oxygen is available from the ambient atmosphere the contact angle is low. This follows the reasonings expressed earlier in this paper. The changes in equilibria of these reactions at the temperature of the experiment cause the changes in contact angle for the same atmosphere at different temperatures.

TABLE III Oxygen requirement or availability

Atmosphere	Oxygen required or available (as O^-)
Steam	0
Oxygen	−2
Ethylene glycol	5
Glycerin	7
Diethylene glycol	10

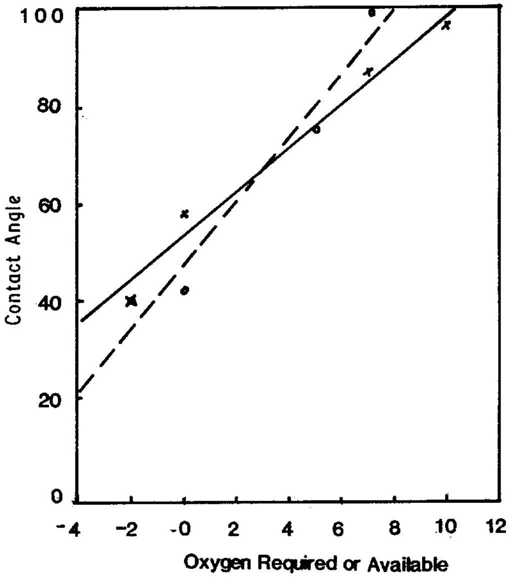

Figure 5 Oxygen requirement or availability in atmosphere as a function of contact angle. X glass A; ● glass B.

4. Conclusion

Contact angles in all cases considered here reduce or remain constant with increase in temperature. The relative stability of the substrate–oxygen bond, glass cations–oxygen/hydroxyl bond and the ambient atmospheric cation/anion–oxygen bonds at various temperatures determine the degree of wetting and contact angle.

The degree of wetting increases with increase in the humidity of the ambient atmosphere. Moisture increases the negativity of the ionic group and makes it possible for platinum to bond with the non-bridging oxygen of the glass. Oxygen atmosphere also increases wetting, but glycerin and glycols decrease wetting considerably and consequently have high contact angles. The absence of moisture and oxygen, possible the bond formation of carbon with $Si{-}O^-$ and formation of Si–O–Si bonds contribute to the high contact angle.

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