JOURNAL OF MATERIALS SCIENCE 10 (1975) 1291–1299

The wetting of three component silicate glasses on platinum

G. J. COPLEY, A. D. RIVERS
Pilkington Brothers Limited, R & D Laboratories, Lathom, Lancs, UK

Measurements of the contact angles of sessile drops of alkali silicate glasses, containing other oxide additions, on platinum have been used to study the role of the glass composition in the wetting processes. A model has been proposed which relates the degree of wetting to the competition between the substrate metal and cationic and anionic groups in the molten glass for the valency electron of non-bridging oxygen ions. An empirical relationship between equilibrium contact angle and the affinity for oxygen ions of cations in the glass supports this model.

1. Introduction

In a recent paper on the wetting of E-glass on the platinum group metals [1] it was proposed that one of the factors which would govern the propensity of the glass to wet the metal substrate would be the demand by the atoms of the substrate metal to bond with non-bridging oxygen ions in the glass. The degree of wetting would then be determined by the competition for non-bridging oxygen ions from the substrate metal and from the cations in the glass. This model was used qualitatively to explain the observed wetting behaviour of E-glass on platinum, palladium, iridium, rhodium and binary and ternary alloys of these metals.

Other workers have used similar models based upon the strength of the metal oxide bonds and the polarizing power of the metal atoms. Thus Pask *et al.* [2] suggested that the contact angle of glasses on various metals may be related to the polarizing power of the metal while in a later paper [3] they proposed a theory of chemical bonding with a balance of bond energies across the glass/metal interface. Godron [4] considered that polarization may be important and although a trend relating decreasing polarizing power with increasing contact angle was observed the results were not conclusive. Presnov and Nogina [5] adopted a similar approach and suggested criteria for the wetting of oxides by glasses. Visotskis [6] claimed a relationship between contact angle and the radius of alkaline earth metal cations in the glass. Many workers have studied the wetting of the platinum group metals with reference to the metal oxides, their stabilities and the influence of the experimental atmosphere [7-10].

To investigate further the effect on wetting of the cations in the glass, contact angle measurements have been made on silicate glasses on platinum in which the cation content of the glass was varied in a systematic way by the addition of different oxides to a common binary alkali silicate glass. The added cations were selected to have different roles in the base glass (network formers, modifiers or both) and to give a range of cation-oxygen single bond strengths. The equilibrium contact angles of sessile glass drops were measured under constant conditions of temperature, atmosphere and substrate metal so that the comparative wetting behaviour would allow comment to be made on the role of the ions in the glass in the wetting mechanism.

2. Experimental method and results

The experimental method was essentially that described in previous publications, [11, 12] and involved measuring the contact angles of glass sessile drops on platinum substrates.

The glasses used were based upon a binary alkali silicate glass containing a 4:1 mole ratio of SiO_2 to Na_2O. Other oxide additions were made in 5, 10, and 20 mol% proportions to make homogeneous glasses containing CaO, B_2O_3, TiO_2, ZrO_2, ZnO, Al_2O_3 and PbO_2 while maintaining the 4:1 mole ratio of SiO_2 to Na_2O.

Beads were prepared from these glasses by spheroidizing glass chips on a graphite block at

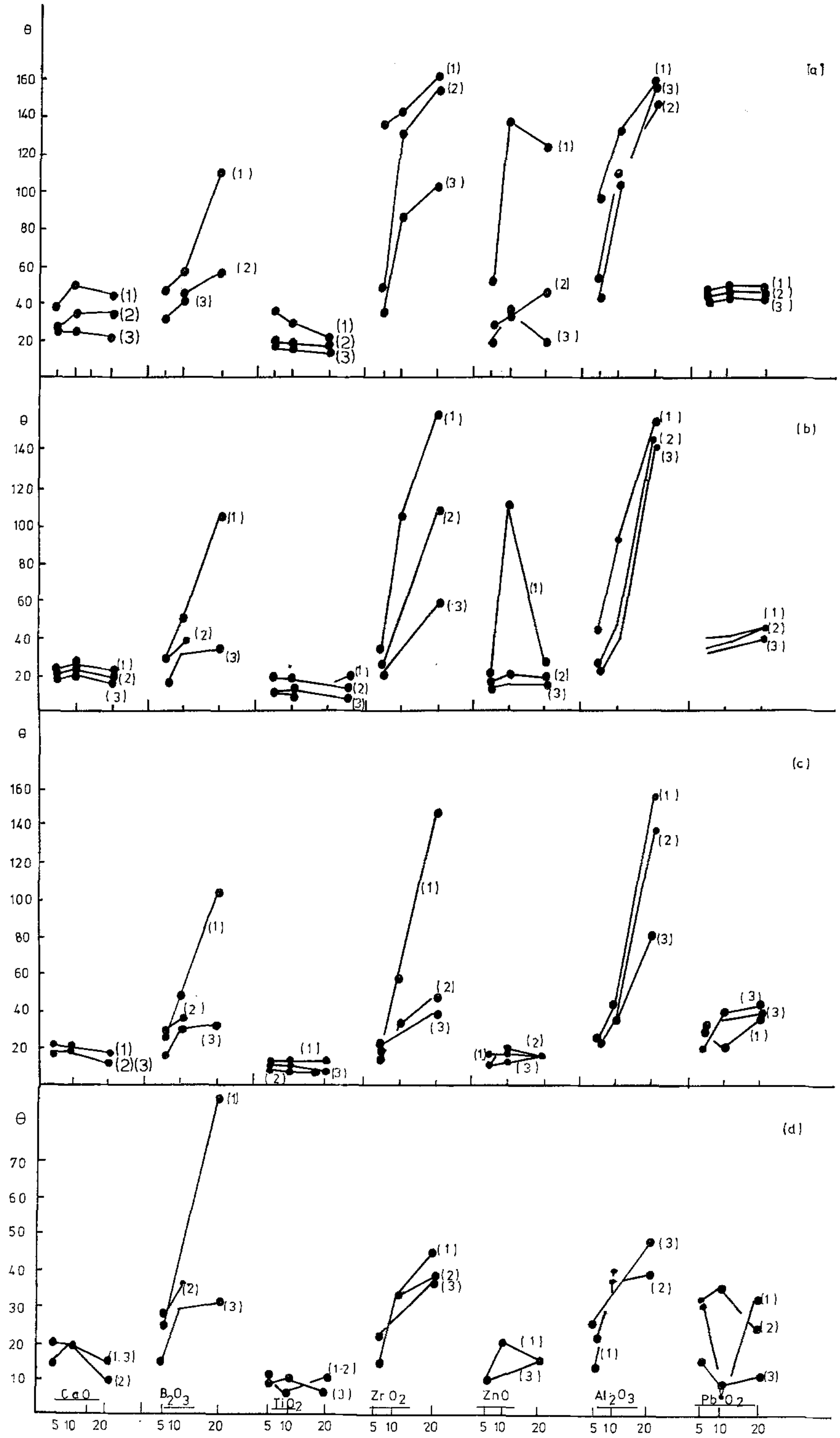


Figure 1 Contact angles and compositions of the experimental glasses at 1273 K (curve 1), 1378 K (curve 2), and 1453 K (curve 3). Contact angles measured at (a) 1 min, (b) 10 min, (c) 100 min, and (d) at equilibrium.

1573 K; the beads had a nominal diameter of 1 mm. The platinum substrates were prepared by metallographic grinding, polishing and degreasing techniques. The substrates were held in the furnace at temperature for 15 min before the glass beads were placed on them.

Sessile drop experiments were performed in air at 1283, 1378, 1418 and 1453 K. The beads were observed and photographed in profile until "equilibrium" conditions were achieved. Contact angles were subsequently determined from the photographs; a typical curve showing the variation of contact angle with time is shown in Fig. 2 of the preceding article in this journal.

The glasses had a wide range of viscosity–temperature characteristics and in certain cases, with the most viscous glasses at the lower temperatures, the experiments had to be performed over a period of many hours to achieve "equilibrium" conditions or until no further change could be detected in the contact angle within the time scale of the experiments.

The contact angles for each of the glasses at 1273, 1378 and 1453 K at 1, 10 and 100 min and at equilibrium, are depicted in Fig. 1 and tabulated in Table I.

TABLE I Contact angles for three-component glasses at (a) 1273, (b) 1378 and (c) 1453 K measured at 1, 10 and 100 min, and equilibrium

	Contact angle (degrees)								
	(a)			(b)			(c)		
	Oxide addition to 80:20 SiO_2:Na_2O glass (wt %)								
Time (min)	5	10	20	5	10	20	5	10	20
	CaO								
1	37	49	44	26	36	36	24	24	22
10	19	24	20	17	19	15	20	20	16
100	15	20	15	16	18	10	20	20	16
Equilibrium	16	20	15	15	19	10	20	20	15
	B_2O_3								
1	46	57	110	31	42	—	28	43	56
10	28	48	105	27	36	—	17	31	33
100	25	47	103	27	35	—	15	30	32
Equilibrium	24	47	87	27	35	—	15	29	31
	TiO_2								
1	36	29	20	19	17	17	16	15	14
10	18	18	12	10	9	19	10	11	6
100	12	12	12	10	6	6	9	10	6
Equilibrium	11	6	11	10	5	5	9	10	5
	Zr_2O_3								
1	136	143	162	49	131	155	35	87	104
10	33	103	161	20	52	108	22	31	48
100	18	56	147	14	33	47	22	27	38
Equilibrium	14	33	44	12	33	38	22	27	37
	ZnO								
1	52	137	124	36	34	46	19	36	19
10	20	111	27	15	19	17	13	16	15
100	16	17	15	10	20	15	10	11	14
Equilibrium	16	8	15	10	20	15	10	11	15
	Al_2O_3								
1	97	133	160	52	110	148	42	102	157
10	44	92	158	23	47	146	25	39	143
100	22	43	156	22	36	137	25	34	80
Equilibrium	15	39	—	21	37	38	25	35	48
	PbO_2								
1	43	47	42	44	46	44	40	44	38
10	32	34	40	33	37	43	39	39	43
100	30	20	37	32	36	42	21	38	38
Equilibrium	15	9	11	32	35	24	15	9	11

The ionic additions had various effects on the equilibrium contact angles. In summary the addition of calcium oxide, zinc oxide and lead oxide increased the contact angle (in comparison with the binary sodium silicate glass); boron oxide, zirconium oxide and aluminium oxide markedly increased the contact angle; titanium oxide markedly reduced the contact angle (increased the degree of wetting).

3. Discussion

In the earlier paper on the wetting of E-glass on platinum group metals [1] it was proposed that the propensity to wet was determined by the demand by the metal atoms in the substrate surface to form chemical bonds with the non-bridging oxygen ions in the glass. According to this model the degree of wetting would be governed by the competition for non-bridging oxygen ions between the cations present in the glass and the platinum substrate atoms.

In the present experiments the demand by the valency electrons of the platinum atoms to form bonding orbitals with the valency electrons of the non-bridging oxygen ions in the glass is assumed to be a constant factor. The ability to form bonds will then depend upon the availability and polarizability of the bonding electrons of the oxygen ions and this will vary with the ionic field strength of the cations present in the glass and their role in the silicate network. The degree of interaction will be reflected in the equilibrium contact angle.

The structure of the alkali silicate glasses used in these experiments will consist of a continuous, but irregular, three dimensional network of SiO_4-tetrahedra with the alkali cations in interstitial sites in the network. The added cations will enter either interstitial sites (Ca^{2+} Zr^{4+}); substitutional sites replacing silicon ions (Ti^{4+}, B^{3+}); or both interstitial and substitutional sites (Al^{3+} Pb^{2+}) according to their role as network former or modifiers.

During the "melting" of the silicate glasses some Si–O bonds will be broken resulting in the formation of two types of ionic group one group having an overall negative charge due to an excess of O^- ions, the other a positive charge due to the high positive charge on the silicon ion and a deficiency of oxygen ions. The two groups are represented schematically in Fig. 2.

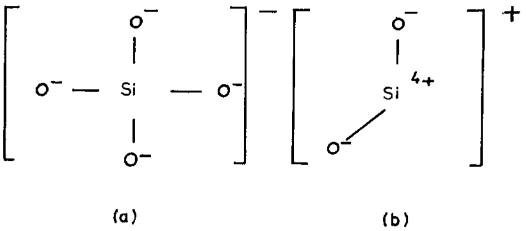


Figure 2 Ionic groups formed on "melting" a binary sodium silicate glass: (a) an anionic group $(I)^-$ and (b) a cationic group $(II)^+$ with an excess and a deficiency of non-bridging oxygen ions respectively.

In binary sodium silicate glass the positively charged alkali cations will tend to be located in the cationic group, where their positive charge can be screened by the excess of non-bridging oxygen ions. Overall electrical neutrality is maintained by the balance of the charge on these groups.

When the molten glass is brought into contact with the platinum metal surface, the valency electrons of the platinum atoms seek to form bonding orbitals with the oxygen ions; this demand can best be satisfied by the anionic groups. The glass immediately in contact with the platinum might then be expected to contain an excess of the anionic groups, while an excess of the cationic groups, would form an electrical double layer in the glass more remote from the metal surface. Indirect evidence for such a composition gradient may be reflected in the detailed shape of glass beads wetted onto platinum previously reported [11]. Attention was drawn to the micro- and macro-contact angles of binary sodium silicate glass beads on platinum. The inflection in the shape of the bead near its periphery would be consistent with the proposed surface layer as depicted in Fig. 3.

The platinum atoms have high-energy d-state electrons and the surface energy of the platinum will be reduced if spreading of the glass occurs and d-bonds form between the platinum atoms and the O^- ions in the glass. However, the cationic groups $(II)^+$ in the glass and the added cation Na^+, Ca^{2+} etc will also be competing for non-bridging oxygen ion neighbours. The degree of wetting will thus be governed by the relative strengths of (1) the platinum-oxygen d-bonds and (2) the cation–oxygen bonds.

Compositional changes, made by adding cations to the glass, will influence the wetting by changing the relative ionic field strengths of the cationic $(II)^+$ and anionic $(I)^-$ groups. Thus additions which increase the negativity of the anionic groups or decrease the positivity of the

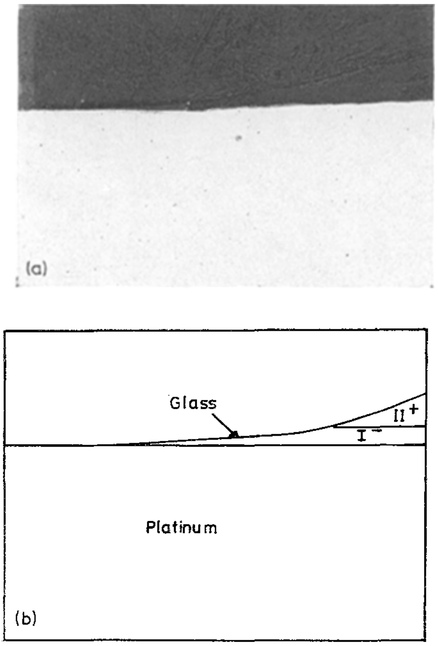


Figure 3 (a) Photomicrograph of the micro- and macro-contact angles of an alkali silicate glass bead on platinum, × 550. (b) Schematic representation of a postulated double layer. I^- designates an excess of anionic groups; I^+ designates an excess of cationic groups.

cationic groups (or do both) will make available more of the charge on the non-bridging oxygen ions for bonding with platinum atoms and hence will allow more wetting. Conversely, additions which decrease the negativity of the anion groups or increase the positivity of the cation groups (or do both) will discourage wetting by using the charge on the oxygen ions to screen the cations in the glass.

In these experiments, cations with a range of ionic field strengths and different roles in the silicate network were added to a basic binary alkali silicate glass. The ionic additions caused different degrees of wetting determined by measurement of the equilibrium contact angles. The influence each cation had in determining the amount of charge on the non-bridging oxygen ions which is available to form bonding orbitals with the platinum atoms may be considered in terms of their contribution to the relative strength of the charges on the anionic and cationic groups.

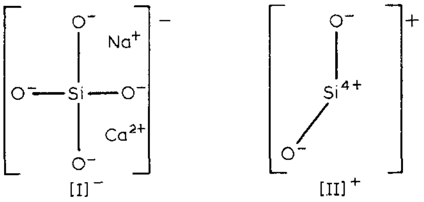
Of the added ions sodium, calcium and probably zirconium and zinc enter the silicate lattice in interstitial sites (zirconium may also under some circumstances enter substitutional sites); boron and probably titanium enter substitutional sites, effectively replacing silicon atoms; aluminium and lead will enter both substitutional and interstitial sites [13].

The added cations will be situated preferentially in the negatively charged anionic group $(I)^-$ if they go into interstitial sites (thereby being screened by the valency electrons of the excess non-bridging oxygen ions). The cations will enter both the anionic $(I)^-$ and cationic $(II)^+$ groups if they go into substitutional sites replacing silicon. In both cases the added ions will change the balance of charge between the anionic and cationic groups.

An interstitial cation will add its competition for the valency electrons of the non-bridging oxygen to the anionic group thereby reducing the overall positive charge and reducing wetting. A substitutional cation will increase or decrease the positivity of the cationic group according to whether its field strength is greater or less than the ionic field strength of the silicon ion. The role of each added cation and its influence on wetting may, therefore, be summarized in a qualitative way.

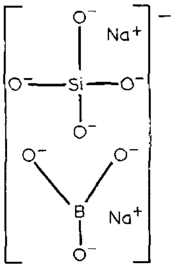
Of the interstitial cation additions the sodium ion has the smallest ionic field strength. The non-bridging oxygens will, therefore, in the basic binary glass, be relatively polarisable and the valency electrons will be available to form d-bonds with the platinum atoms and a low contact angle will result. The observed contact angle is low, being about 10°.

The calcium and zinc ions have slightly higher ionic field strengths than sodium and their charge will be added to the competition for oxygen valency electrons in the anionic group $(I)^-$ thus reducing the negativity of the group and slightly reducing the wetting when compared with the binary alkali silicate glass.

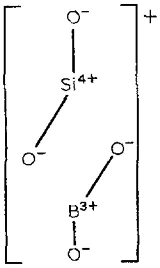


The observed contact angle is 15° for the glass containing 20% calcium oxide and 12° for the glass containing 20% zinc oxide.

Boric oxide will form a network of boron and oxygen atoms arranged in nearly planar triangles interlocking the silicate network. Effectively the boron ions will be in substitutional sites and the ionic groups may be represented as follows:



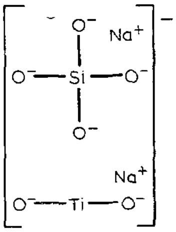
[I]$^-$



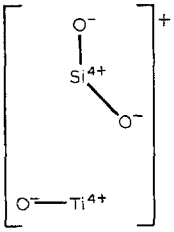
[II]$^+$

The boron ion has a higher positive charge than the silicon ion thus the substitution of boron for silicon will reduce the negativity of the anionic group (I)$^-$ and increase the positivity of the cationic group (II)$^+$. Both factors will reduce the charge of the valency electrons of the non-bridging oxygen ions available for bonding to the platinum and a marked reduction in the amount of wetting would be expected. The observed contact angle of the 20% boric oxide glass is 31°.

The titanium ion has a field strength lower than silicon and hence a substitution of titanium for silicon will have the opposite effect to that of boron, increasing the negativity of the anionic group (I)$^-$ and decreasing the positivity of the cationic group (II)$^+$. Both factors will increase the wetting.



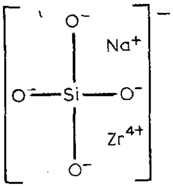
[I]$^-$



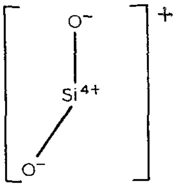
[II]$^+$

The observed equilibrium contact angle for the titanium containing glass is very low, being 5°.

The zirconium ion enters silicate networks either interstitially or substitutionally. The marked decrease of wetting in the zirconia containing glass suggests that the important contribution to the wetting behaviour is from the interstitial ions which would markedly reduce the negativity of the anionic group.



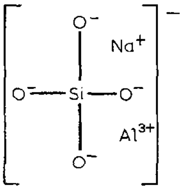
[I]$^-$



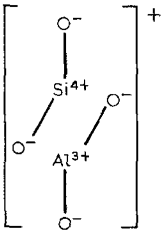
[II]$^+$

The observed contact equilibrium contact angle for the 20% zirconia-containing glass is high, being 37°.

Aluminium and lead ions can both enter the silicate lattice in either substitutional or interstitial sites. In the case of aluminium, the ion has a lower ionic field strength than the silicon ion and hence, when replacing silicon in substitutional sites, will lower the positivity of the cationic group.



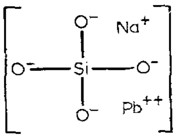
[I]$^-$



[II]$^+$

In interstitial sites aluminium will strongly reduce the negativity of the anionic group since its ionic field strength is much larger than the sodium ion. Apparently the second of these effects is of overriding importance since aluminium additions markedly increase the equilibrium contact angle.

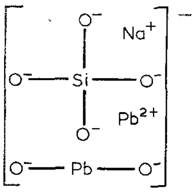
In the case of lead it is possible that the first additions enter the lattice in interstitial sites while at larger concentrations the lead ions occupy both interstitial and substitutional sites. With the reasoning used above, the first additions in interstitial sites would reduce the negativity of the anionic group and hence would reduce the wetting.



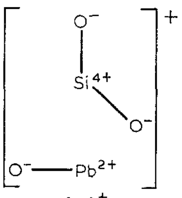
[I]$^-$

The equilibrium contact angle for the 5% lead oxide glass is 15° compared with 10° for the basic glass.

If the lead ions enter both substitutional and interstitial sites at larger concentrations, the negativity of the anionic group would be increased and the positivity of the cationic group decreased since lead has a lower field strength than silicon.



$[\mathrm{I}]^-$

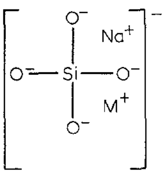


$[\mathrm{II}]^+$

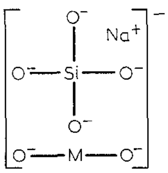
Both changes would contribute to the observed increased wetting. The equilibrium contact angle for the 20% lead oxide glass is 11°.

The proposed model in which the propensity to wet is related to the demand by the d-electrons of the platinum atoms to form bonding orbitals with the valency electrons of the non-bridging oxygen ions in the glass, and in which the degree of wetting is related to the competition for these electrons between the platinum atoms and the cations and cationic group in the glass, helps to explain and predict the wetting behaviour of the various glasses. Abundant data are available for the single bond strengths of all the cations used in the experiments; these values are shown in Table II. It should be possible using these values to relate the degree of wetting expressed as the equilibrium contact angle to the relative strengths of the cation–oxygen bonds since we have assumed in the foregoing arguments that, to a first approximation, $\theta_\theta = f(E_{\mathrm{Pt-O}} - E_{\mathrm{i-O}})$. Where θ_θ is the degree of wetting expressed as a function of θ, $E_{\mathrm{i-O}}$ is the single bond strength between the cations in the glass and oxygen and $E_{\mathrm{Pt-O}}$ is the single bond strength between the platinum atom and oxygen. If it is assumed that $E_{\mathrm{Pt-O}}$ is constant with the different glasses then θ_θ may be expressed as the sum of a function of all the cation-oxygen bond strengths, thus $\theta_\theta = \sum_i f(E_{\mathrm{i-O}})$.

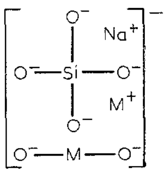
Three different cases may then be distinguished, namely the added cations entering (1) interstitial sites only, (2) substitutional sites only, and (3) both interstitial and substitutional sites. The three cases may be represented schematically as follows:



(i)



(ii)



(iii)

In case 1 it is assumed that $\sum_i f(E_{\mathrm{i-O}})$ is the arithmetic sum of the bond energies of silicon, sodium and the added cation M, thus

$$\theta_\theta = \sum_i f(E_{\mathrm{i-O}}) = f(E_{\mathrm{Si-O}} + E_{\mathrm{Na-O}} + E_{\mathrm{M-O}})\,. \qquad (1)$$

In case 2 the net effect on the availability of oxygen valency electrons will be determined by the weighted mean of the bond energies $E_{\mathrm{Si-O}}$ with $E_{\mathrm{M-O}}$ with the arithmetic addition of $E_{\mathrm{Na-O}}$; thus

$$\theta_\theta = f(x E_{\mathrm{Si-O}} + y E_{\mathrm{M-O}} + E_{\mathrm{Na-O}})$$

where x and y are the mole fractional concentrations of Si–O and M–O bonds. Assuming a 2:1 ratio of silicon to added cations for the 80:20 binary glass with a 20 mol% addition

$$\theta_\theta = f\left(\frac{2E_{\mathrm{Si-O}}}{3} + \frac{E_{\mathrm{M-O}}}{3} + E_{\mathrm{Na-O}}\right)\cdot \qquad (2)$$

In case 3 using similar arguments;

$$\theta_\theta = f\left(\frac{2E_{\mathrm{Si-O}}}{3} + \frac{E_{\mathrm{M-O}}}{3} + E_{\mathrm{Na-O}} + E_{\mathrm{M-O}}\right)\cdot \qquad (3)$$

Using the single bond strengths from Table II

TABLE II Single bond strengths of the added cations with oxygen

M in MO$_x$	Role in network*	Single bond strength $E_{\mathrm{M-O}}$ (kcal)
Na	I	20
Ca	I	32
Zr	I	61
Zn	I	36
Pb	I	36
Pb	S	73
Al	I	60
Al	S	100
Si	S	106
Ti	S	73
B	S	119

*I = occupying an interstitial site.
S = occupying a substitutional site.

in these equations, a figure is obtained which is a measure of the affinity for oxygen of the ionic groups in the glass. The higher the affinity then the less oxygen valency electrons will be available for bonding with the platinum surface atoms and the less will be the degree of wetting, θ_θ.

TABLE III Empirical values for the affinity for oxygen of the cationic groups in the experimental glasses and the equilibrium contact angles observed at 1453 K

Added cation M	Role in glass	Affinity for oxygen	Equilibrium contact angle (degrees)
Na	I	126	10
Ca	I	158	15
Zr	I	187	37
Zn	I	162	15
Pb	I	162	15
Pb	I + S	150	11
Al	I + S	183	48
Ti	S	114	6
B	S	130	31

The data are summarized in Table III with the equilibrium contact angle for each glass. For the purposes of comparison the results from the glasses with the higher ionic additions are used and, for the purposes of interpretation, the higher temperature results are taken since these are the most likely to be equilibrium angles despite the variation of viscosity from glass to glass.

The empirical relationship between the degree of wetting expressed as the measured equilibrium contact angle θ, and the "affinity for oxygen" figures derived from the bond strengths of silicon, sodium and the added cations with oxygen ions is plotted in Fig. 4. As can be seen in the figure, the contact angle increased (wetting is decreased) as the demand for oxygen bonding by the cations in the glass increased – most of the elemental additions falling on a smooth curve. This regular behaviour supports the view that the wetting mechanism is a competition for the valency electrons of the non-bridging oxygen ions. Boron and aluminium are notable exceptions to this behaviour; however, both these elements, while strong glass formers, are trivalent and it is unlikely that their occupancy of the silicate network would lend itself to the simple arithmetical treatment of oxygen bond strengths used in the above analysis.

The effect on the equilibrium contact angles of adding a third component to an alkali silicate glass is reminiscent of the treatment used by many workers to describe phase separation in

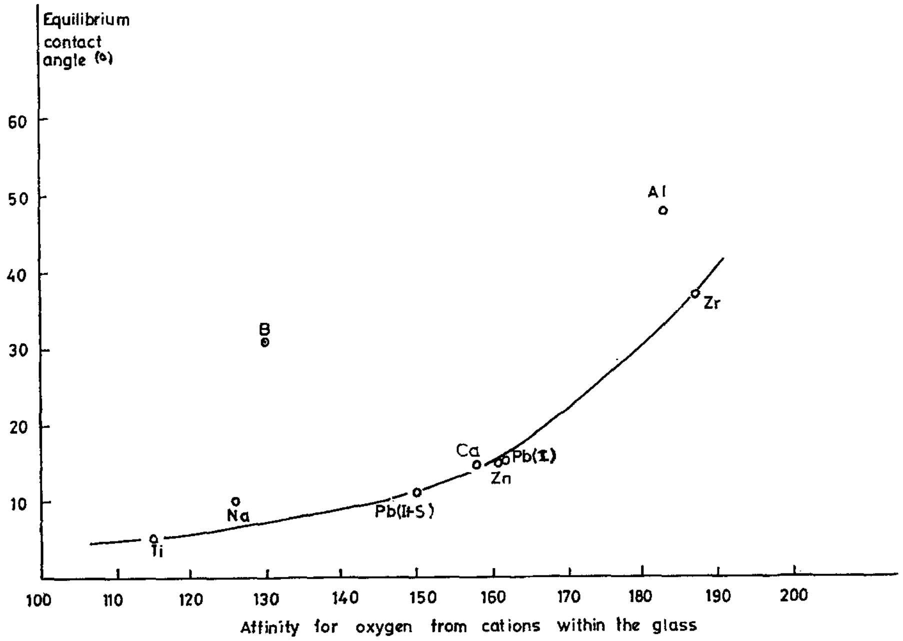


Figure 4 Empirical relationship between equilibrium contact angle and the affinity for oxygen from cations within the glass.

glasses in which parameters such as the miscibility temperatures are related to the ionic field strength of the constituent ions [14, 15]. The factors which govern the energy of an interface between the separated components in a molten glass and those at the interface between a molten glass and a metal are similar and it is instructive to regard a wetting system with a low contact angle as a homogeneous solid solution, while a non-wetting configuration maybe regarded as a phase separated system. Indeed there are many fruitful parallels to be drawn between the extensive studies of phase separation and the problems of controlling wetting at glass-metal interfaces.

4. Conclusions

The propensity for alkali silicate glasses to wet platinum has been regarded as originating in the demand by the platinum atoms to form bonds with the non-bridging oxygen ions in the molten glass. The formation of a double layer in the glass may account for the inflected shape of glass beads on platinum and the formation of micro- and macro-wetting angles. The degree of wetting has been related to the competition for the valency electrons of non-bridging oxygen ions between the substrate metal and cationic and anionic groups in the molten glass. Third element additions influence the wetting behaviour by changing the balance in the competition for oxygen ions. The influence of several cations of different field strengths, entering different sites in the silicate structure suggests that cations which increase the negativity of anionic groups in the glass will increase the degree of wetting by making available valency electrons from the non-bridging oxygen ions to form d-bonds with the platinum atoms. Conversely, cations which decrease the negativity of anionic groups decrease the degree of wetting by more tightly binding the oxygen valency electrons.

Acknowledgement

The authors wish to thank Dr D. S. Oliver, Director of Research and Development, and the Directors of Pilkington Brothers Ltd for their permission to publish this paper.

References

1. G. J. COPLEY, A. D. RIVERS and R. SMITH, *J. Mater. Sci.* **10** (1975) 1285.
2. V. F. ZACKAY, D. W. MITCHELL, S. P. MITOFF and J. A. PASK, *J. Amer. Ceram. Soc.* **36** (3) (1953) 84.
3. M. L. VOLPE, R. M. FULRATH and J. A. PASK, *ibid* **42** (2) (1959) 102.
4. Y. GODRON, *Silicates Industrials* (1959) 539.
5. V. A. PRESNOV and S. S. NOGINA, *Tekk. Inst. Tomsk., V.V., Kuibyshera* **36** (1958) 241.
6. K. K. VISOTSKIS, *Zhurnal Prikladnoi Khimii* **39** (1966) 1645.
7. R. KATZSCHMANN, *Silik Tech.* **18** (7) (1967) 211.
8. G. SELMAN, M. R. SPENDER and A. S. DARLING, *Plat. Mats. Rev.* **9** (3) (1965) 92.
9. J. A. PASK, "*Mod. Aspects Vitreous State*", Vol. 3 (Butterworths, London, 1964) pp. 1-28.
10. M. G. CHERNIAK and G. G. NAIDUS, *J. Tech. Phys. Acad. Sci. UdSSR* **27** (1958) 2268.
11. G. J. COPLEY, A. D. RIVERS and R. SMITH, *Glass Tech.* **13** (2) (1972) 50.
12. *Idem*, *J. Mater. Sci.* **8** (1973) 1049.
13. W. W. WEYL and E. C. MARBOE, "The Constitution of Glasses" Vol. 11 Part 1 & 2 (Interscience, New York, London, Sydney, 1964).
14. E. M. LEVIN, *J. Amer. Ceram. Soc.* **50** (1967) 29.
15. M. TASHIRO, 8th International Congress on Glass London (1968) p. 113.

Received 4 December 1974 and accepted 17 January 1975.