A possible explanation of immiscibility in silicate melts.

By E. CHRISTIAAN DE WYS, M.A., Ph.D.
International Business Machines Corporation,
Kingston, New York, U.S.A.

[Communicated by the Editor; read 31 March 1960.]

Summary. The problem of silicate immiscibility, of petrological and technological interest, is discussed in terms of the structures of silicate crystals and certain phase diagrams. Physical chemical principles are employed to indicate the author's basis for suspecting that certain structures in the crystalline solid are carried over into the melt and are a major contributory cause of silicate immiscibility. These structures appear to be limited to the neso $(SiO_4)^{4-}$, soro $(Si_2O_7)^{6-}$, cyclo $(Si_3O_9)^{6-}$, and ino $(SiO_3)^{2-}$ types of silicate polymers and do not include the more complex phyllo- and tecto-silicate polymers.

THE following discussion is an attempt to approach the phenomenon of immiscibility in silicate and some borate systems from a chemical crystallographic point of view. In general, previous authors (Warren and Pincus, 1940; and Dietzel, 1937) have suggested that an explanation of the phenomenon of immiscible silicate melts may well lie in considerations of electrostatic share potentials and field strengths of the cations involved in such relationships. Their hypothesis appears to be that the attraction of the silicon ion for all available oxygen in the liquid state is matched or outweighed, in certain instances, by the desire of the cations to become properly coordinated by oxygen ions.

In this present paper it is suggested that consideration of the anionic groups may aid an understanding of the occurrence of immiscible regions. It should be noted that, generally, previous authors did not consider the specific sub-systems involved but rather limited themselves to visualizing actions of the two extreme end-members of a large two-component system, e.g. CaO-SiO_2 rather than the real sub-system involved, $CaSiO_3$–SiO_2 (fig. 1). Since in numerous instances intermediate melting compounds are in a eutectic relationship with SiO_2, it appears to be more in accord with structural realities to consider the actual binary sub-systems showing immiscible relationships.

In order to facilitate an understanding of this particular approach a list of most of the major immiscible and many miscible systems with the network formers SiO_2 and B_2O_3 was prepared. Where feasible,

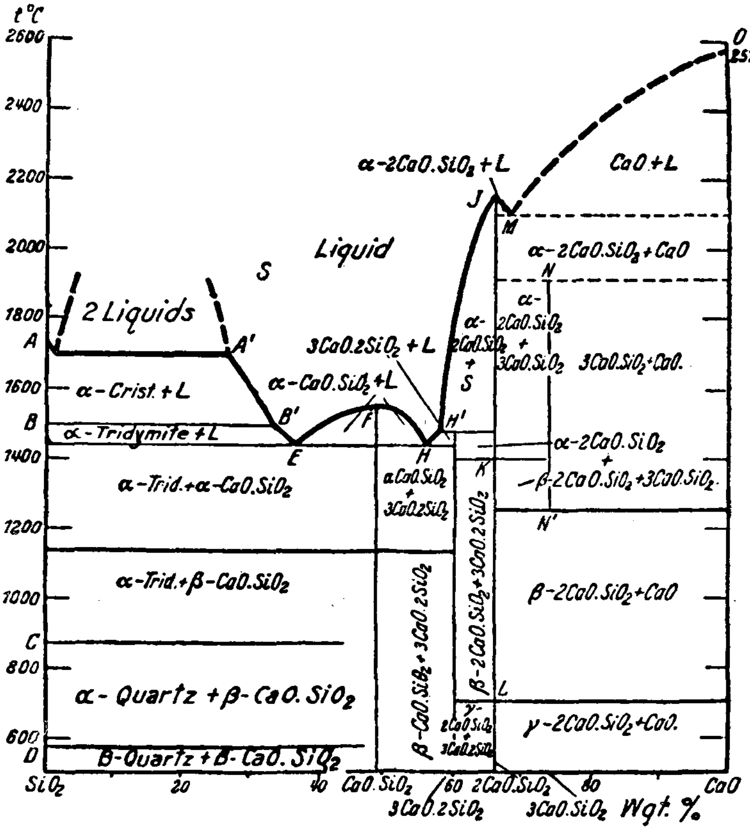

FIG. 1. Binary system silica–calcium oxide, corrected (Rankin and Greig).

systems having a common cation, e.g. Ca^{++}, are listed together, and immiscible systems are shown in heavy type:

$CaSiO_3$–SiO_2
$CaMgSi_2O_6$–SiO_2
$CaAl_2Si_2O_8$–SiO_2
CaB_2O_4–B_2O_3
PbB_4O_7–B_2O_3
$PbSiO_3$–SiO_2
Fe_2SiO_4–SiO_2
Zn_2SiO_4–SiO_2
Mg_2SiO_4–SiO_2
$Mg_2B_2O_5$–B_2O_3
MnO–Mn_2SiO_4–$MnSiO_3$–SiO_2
MnB_6O_{10}–B_2O_3
$SrSiO_3$–SiO_2
$BaSi_2O_5$–SiO_2
$Na_2Si_2O_5$–SiO_2
$Na_2B_8O_{13}$–B_2O_3
$Li_2Si_2O_5$–SiO_2
$Li_2B_{10}O_{16}$–B_2O_3
$K_2Si_4O_9$–SiO_2
$K_2Al_2Si_6O_{13}$–SiO_2
$K_2B_{10}O_{16}$–B_2O_3
B_2O_3–SiO_2
Al_2O_3–SiO_2
GeO_2–SiO_2

From this list it will be observed that the cations Pb^{++}, Mn^{++}, and Ca^{++} form a miscible as well as an immiscible system with such similar network formers as SiO_2 and B_2O_3.

The field strength of an ion is $Z/(Ra+Rx)^2$, where Z is its valence and Ra is the radius of the anion, Rx of the cation. It has been suggested by previous authors that cations with high field strength lead to immiscibility, but Mn^{++} with a field strength as high as 0·48 does not form an immiscible relationship with B_2O_3 while Pb^{++} with a field strength of only 0·34 does; further, the oxides of boron, germanium, and aluminium with ionic field strengths of 1·65, 1·75, and 0·84 respectively, do not show immiscible relationships with the network former SiO_2.

The electrostatic share potential is defined as $q = Z/CN$, where CN is the coordination number of the ion, and it has been suggested that a high share potential leads to immiscibility. When in sixfold coordination, Ca^{++}, Mg^{++}, and Pb^{++} have a similar electrostatic share potential of 0·333, but again immiscibility with a network former does not always result. For example, MnO–B_2O_3 shows no immiscibility while PbO–B_2O_3 does; again B^{+++}, Ge^{+++}, and Al^{+++} with share potentials of 1, 1, and 0·50 to 0·75 show no immiscibility.

To obtain a more consistent picture of immiscibility, an analysis of the significance of the morphology of the liquidus would be helpful. In the analysis of a liquidus slope, which usually indicates the effect of the colligative property called freezing-point lowering (ΔT_f), it is helpful to consider the equation $\Delta T_f = RT_f T_l\, a/\gamma \Delta H_f$, where ΔH_f is the latent heat of fusion of the primary phase, R the molar gas constant, T_l the liquidus temperature of the primary phase region, T_f the melting-point of the pure primary phase, a the activity of a particular component of a solution, and γ the activity coefficient.

The presence of a liquid miscibility gap, characterized by a horizontal discontinuity in the liquidus curve, indicates a region where a positive deviation from Raoult's law $P_a/P_{\dot{a}} = a/\gamma$ exists (P_a is the partial vapour pressure of constituent a, $P_{\dot{a}}$ the vapour pressure of the pure constituent a). The interpretation of such a liquidus shape has usually been that association, resulting from dipole formation, has taken place. In general such dipoles are due to structural distortions and orientation of specific units in the liquid in response to some field of force. It is known that the magnitude of the induced dipole is related not only to the polarizability of the unit but also to the concentration of such structures in the liquid and to the magnitude of the forces inducing this phenomenon. The relationships of some of the above factors are given by the Debye equation:

$$P = (4\pi nM/3\rho)(\alpha_0 + u^2/3KT),$$

where P is the polarization of the structure, n the number of polarizable structures per unit volume, M the mass of the structure, ρ the density of the structure, α_0 the distortion effect factor, $u^2/3KT$ the orientation effect factor (u, being the dipole moment, $= \alpha F$, where α is the polarizability and F is the intensity of applied field), and K is Boltzman's constant.

At this point one ought to consider what types of liquid structures are associating and thus causing a decrease in ΔT_f, and this involves some general considerations concerning the structure of silicate melts, a matter on which there is at present no general agreement. In a later paper we hope to discuss our viewpoint in more detail and to present new experimental data.

Structural considerations concerning silicate melts. In general, the fusion of silicates is accompanied by negligible increases in volume. If one assumes that the volume of the quenched glass is not very different from that of the liquid, the slight change in volume between a solid and its melt is exemplified by the following data from Huckel (1951), where the volumes of some glasses and crystals are presented, extrapolated to absolute zero:

	Na_2SiO_3	$Na_2Si_2O_5$	$CaSiO_3$	$BaSiO_3$
Crystal	46·7	73·0	40·0	48·2
Glass	47·7	73·1	40·0	48·3

These and other data considered below suggest that the arrangement of structural units in a liquid, in the neighbourhood of the liquidus at least, must be somewhat related to that in the crystalline solid from which it originated. Further, the latent heat of fusion is much smaller (by a factor of 30 to 40) than the latent heat of vaporization. It would appear from this that the forces between structural units decrease only very slightly in the process of melting, in agreement with the observation that the volume increase is slight. Again, the specific heat of condensed bodies is only very slightly effected by melting, being somewhat greater just above the melting-point than just below it. This could well indicate that the character of thermal motion near the point of stable nucleation remains fundamentally the same as in crystalline materials, small vibratory movements about ionic equilibrium positions. This viewpoint is in agreement with the preceding since the slight increase of distance between structural entities cannot effect materially the binding forces nor the character of their vibratory motion.

Simple thermodynamic calculations, based on the fundamental equations $\Delta G = \Delta H_f - T\Delta S$ and $\Delta S = \Delta H_f/T$ (since $\Delta G = 0$ under equilibrium conditions at constant pressure), indicate that the change in entropy for silicates is slight for transitions across the liquidus (ΔG is the change in free energy, ΔH_f the heat of fusion, T the temperature in °K., ΔS the change in entropy). Again this would indicate that the change in the degree of structural order or disorder on melting is small.

Consideration of the relation of thermal expansion and composition to the structure of glasses (Blau, 1951) tends to indicate that the silicate anionic group configuration in glass is reminiscent of that of the crystalline solid; and thermodynamic evaluation of the silicate system (de Wys, 1955) $CaAl_2Si_2O_8$-$Ca_2MgSi_2O_7$ tends to support the above viewpoint. Again, Lark-Horowitz and Miller (1936) found a similar X-ray diffraction pattern for the melt and the crystal phase, while Randall, Rooksby, and Cooper (1930) investigated wollastonite and borax glasses which showed the X-ray diffraction interference bands of $CaSiO_3$ and $Na_2O.2B_2O_3$ in broad, indistinct rings. In the literature one may readily find illustrations where electroconductivity measurements (Bockris, 1948) and viscosity (Preston, 1942) data tend to support the above viewpoint in respect to the structure of silicate melts.

It would appear that an ion-pair with a small negative electrostatic potential would suffer greater separation than an ion pair with a larger negative electrostatic potential. In considering this potential energy per pair of ions in a crystalline structure, the energy, U, may be related to the coulomb ionic effect and the repulsive potential. The increase of lattice stability due to polarization also comes into consideration. A formula simplifying some of the above relationships may be written as:

$$U = (AZ_1Z_2e^2/r^2)+(B/r^n)-(ZeU_p/r^2),$$

where the first term is the Coulomb potential, the second the repulsive potential, and the last the effect of the polarization, with $U_p = \alpha F$ as was indicated by the Debye equation. Obviously then, besides the effect of electrostatic share potential, the polarizing power and polarizability of the ions concerned must be considered. Goldschmidt (1926) has proposed using the quantity Ze/r^2 as a measure of ionic polarizing power. Polarizability of an anion, however, appears to increase with ionic radius. Finally, the presence of a resonance phenomenon apparently increases significantly the stability of an ion-pair. Since the radius of Si^{4+} is considerably smaller than those of the other ions considered (Mg, Li, Zn, Fe, Mn, Na, Ca, Sr, Pb, K, Ba) and its valence is higher, it is to be expected that the Coulomb term would indicate greater ion-pair stability for a Si–O configuration than any of the other cation–O bonds.

The electrostatic share potentials, q, for some of the ions are included in table I. Clearly the potential for Si–O is far greater than those for the other ions listed; this again indicates a greater stability for the Si–O pair than for the other cation–O bonds. When these cations are reduced to 'rambling' units in a melt it seems likely that the stability differences will be even more pronounced.

The polarizing powers, Ze/R^2, of various cations, after Goldschmidt (1926), are also included in table I. Again, the value for Si^{4+} is much higher than for the other cations, suggesting that the Si–O pair should be more stable by virtue of the polarization effect term of the potential energy of ion pairs.

TABLE I. Physical constants for various ions. C.N., coordination number; q, electrostatic share potential; Ze/R^2, polarizing power; e.n.d., electronegativity difference between the cation and oxygen.

	Ca^{2+}	Mg^{2+}	Mn^{2+}	Pb^{2+}	Fe^{2+}	Zn^{2+}	Sr^{2+}	Ba^{2+}	Na^{+}	K^{+}	Li^{+}	Si^{4+}
C.N.	8 or 6	6 or 4	6	6	6	4	8	8	8	8 or 12	6	4
q	0·25–0·33	0·33–0·5	0·33	0·33	0·33	0·50	0·25	0·25	0·125	0·125–0·08	—	1·00
Ze/R^2	1·78	3·27	—	—	—	—	1·24	0·98	1·04	0·57	1·64	26·30
e.n.d.	2·5	2·3	—	2·9	—	2·0	2·5	2·6	2·6	2·7	2·5	1·7

It is known that when the electronegativity difference between two atoms is small, both ionic and covalent types of bonding may contribute to the resultant ion-pair configurations, and resonance between the two types of bonds is superimposed on the resonance associated with the normal homopolar bond and thus increases the bond energy. The electronegativity differences between the various cations and oxygen (table I) indicate that the resonance contribution to the Si–O bond is likely to be more significant than to the other cation–O bonds.

From all of the considerations stated above, it would appear that on the basis of chemical crystallographic theory and other data, the particular predominant type of silicate anionic structure would tend to be preserved in the liquid state in preference to any other cation-oxygen grouping. In general, then, all of the considerations taken into account seem to indicate that the liquid, at least immediately above the liquidus, shows some type of a structural memory of the crystalline state and that such a structural resemblance would be especially pronounced in silicate melts.

General hypothesis of immiscibility. With this in mind, it appeared fruitful to reconsider some of the systems characterized by the presence or absence of a miscibility gap. Considerations of the significantly lower bond strength of the cations and the observation that a particular cation could partake in an immiscible as well as a miscible relationship with the same network former, tended to emphasize the need for recognizing the role enacted by the anionic structures.

Analyses of the immiscible systems in terms of the anionic groups indicate that only those compounds that have the following type of complexes enter into an immiscible relationship with a framework-type liquid such as SiO_2: neso, $(SiO_4)^{4-}$; soro, $(Si_2O_7)^{6-}$; cyclo, $(Si_3O_9)^{6-}$, $(Si_4O_{12})^{8-}$, and $(Si_6O_{18})^{12-}$; ino, $(SiO_3)^{2-}$ or $(Si_4O_{12})^{6-}$.

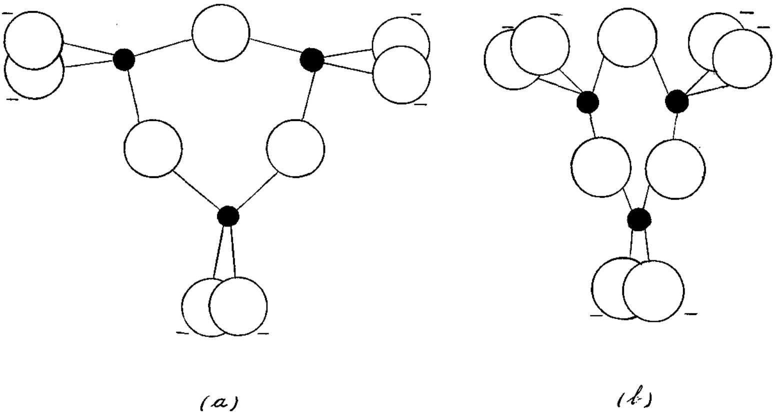

FIG. 2. Diagram showing a non-deformed (*a*) and deformed (*b*) ionic group $Si_3O_9{}^{6-}$.

The miscible systems showed only phyllo- or tecto-types of complexes such as: phyllo, $(Si_2O_5)^{2-}$; and tecto, $(Al_2Si_6O_{12})^{2-}$, $(Al_2Si_2O_8)^{2-}$, and SiO_2 (the $(AlO_4)^{5-}$ complex is considered simply a part of the SiO_2 network).

It would appear, therefore, that only those complexes with two or more non-bridging polarizable oxygen ions per network-forming ion tend to pronounced associative phenomena in a binary solution. As an example the behaviour of the silicate complex $Si_3O_9{}^{6-}$, which if the dominant structure in a particular crystalline compound would be present in the liquid, may be visualized in a compressive or non-compressive force field as shown in fig. 2.

From this schematic diagram it would appear that on deformation of such a complex containing six non-bridging oxygen ions a structural dipole would be formed with resultant associative effects. Considering, for example, the system $CaSiO_3$–SiO_2 rather than the general binary CaO–SiO_2 it becomes evident that in the crystalline mixture, below the eutectic horizontal, units with cyclo-structures of the type $Si_3O_9^{6-}$ are in equilibrium with the tecto-type SiO_2 compound. It would appear that if such ring structures were caught, in a state of liquid equilibrium, inside a compressing, thermally oscillating SiO_2 framework, the existence of which has been reasonably well established, the formation of induced dipoles with resultant association and thus positive deviation from Raoult's Law would result. In essence this is what we would like to suggest as a possible explanation of the immiscibility observed.

In the system $CaSiO_3$–SiO_2 a liquid corresponding to the composition on the high SiO_2 side of the two-liquid region shown in fig. 1 was apparently so viscous that it pulled away from the crucible walls on cooling and remained as a rigid amorphous cylinder. A liquid of the composition on the high $CaSiO_3$ side, however, formed a more fluid spheroid at the bottom of the crucible. It would appear that some significant structural difference may thus exist between the two. One may speculate, with Warren, that on the SiO_2 side, the SiO_2 network remains sufficiently intact to withstand, to a large extent, the collapsing thermal forces. An increase of the number of $Si_3O_9^{6-}$ complexes and their orientability would result, as is indicated by Debye's formula, in an increased dipolar strength, which is represented by the higher temperatures needed to overcome the increased association effects. On the $CaSiO_3$ side, the framework, and thus the intensity of the applied field as indicated by the Debye equation, is apparently rapidly breaking down so that even a continued increase of cyclo complexes is insufficient to preserve continued immiscibility. The downward slope of the line separating the two liquid and the one liquid phase region, as shown in fig. 1, is the result. The peak of the miscibility gap apparently represents the combined optimum effects of network rigidity and $Si_3O_9^{6-}$ concentration.

A similar point of view may be readily developed for borate compounds forming a miscible or immiscible relationship with B_2O_3.

We now seem to have an explanation of the apparent contradiction observed when only cations are considered. For example, $CaSiO_3$ is a cyclo-compound, $CaMgSi_2O_6$ and CaB_2O_4, also having an immiscible relationship with SiO_2, are known to be ino types of compounds while, in contrast, $CaAl_2Si_2O_8$ is a tecto type of compound, which would explain why it forms a miscible system with SiO_2.

Greig (1927) stated that: 'The similarity in chemical behaviour of calcium, strontium and barium, together with the fact that the liquidus of silica rises very steeply from the eutectic tridymite–$BaSi_2O_5$ suggested that baria, like magnesia, lime and strontia would be only partially miscible with silica.' It is, of course, well known that the system $BaO-SiO_2$ does not show any miscibility gap. In considering the actual sub-system $BaSi_2O_5-SiO_2$ no such a gap would be expected according to the point of view suggested in this paper since $BaSi_2O_5$ is a phyllo-silicate and thus has less than two non-bridging oxygens per Si ion.

Conclusions. On the basis of crystal chemical considerations the author suggests that the structure of the anionic groups appears to be the main determinant of the occurrence or absence of immiscibility although consideration of field strength and electro-static share potential may have some practical validity.

References.

BLAU (H. H.), 1951. Trans. Soc. Glass Tech., vol. 35, p. 307.

BOCKRIS (J. O. M.), KITCHENER (J. A.), IGNOTOWICZ (S.), and TOMLINSON (J. W.), 1948. Discuss. Faraday Soc., (4), 265–281.

DE WYS (E. C.), 1955. Ph.D. dissertation, Ohio State University.

DIETZEL (A.), 1937. Naturwiss., vol. 29, p. 537.

GOLDSCHMIDT (V. M.), 1926. Skr. Norske Vidensk. Akad. Kl., No. 2.

GREIG (J. W.), 1927. Amer. Journ. Sci., ser. 5, vol. 13, p. 1.

HUCKEL (W.), 1951. Structural Chemistry of Inorganic Compounds (Elsevier), p. 780.

LARK-HOROWITZ (K.) and MILLER (E. P.), 1936. Strukturberichte, vol. 4, p. 92; Physical Rev., ser. 2, vol. 4, p. 48.

MARTIN (A. E.) and DERGE (G.), 1943. Trans. Amer. Inst. Min. Met. Eng., vol. 154, p. 104.

PRESTON (E.), 1942. Journ. Soc. Glass Tech., vol. 26, p. 82.

RANSDALL (J. T.), ROOKSBY (H. P.), and COOPER (B. S.), 1930. Nature, vol. 125, p. 458.

WARREN (B.), and PINCUS (A. G.), 1940. Journ. Amer. Ceram. Soc., vol. 10, p. 301.