

COORDINATION NUMBER OF MAGNESIUM IONS IN SILICATE GLASSES

AHMAD DIN and M. RASHID SHEIKH

PCSIR Laboratories, Lahore 16

H. W. HENNICKE

Institut für Steine und Erden, Clausthal, West Germany

(Received August 1, 1973)

Abstract. Molar volume and viscosity studies show that Mg^{++} ions possess a coordination number 4 in the silicate glasses $Na_2O \cdot x MeO \cdot 6 - x SiO_2$ at low temperatures and thus exhibit a network former character. At high temperatures the Mg^{++} ions behave just like their counterparts, Ba^{++} , Ca^{++} , Sr^{++} , which exhibit a network modifier tendency.

The density and viscosity measurements on silicate glasses were carried out by various workers for different purposes. Bockris and his coworkers¹ through density and viscosity derivatives showed that magnesium ions are arranged octahedrally in binary silicate glasses. Dietzel² calculated in ternary glasses that magnesium ions despite their smaller ionic radius show no tendency to enter the interstices provided by the silica network. This is in complete contrast to the other ions with larger radii like Ca^{++} , Sr^{++} and Ba^{++} and Pb^{++} which go into the interstices in considerable amounts. Dietzel attributed this anomaly to a different environment of the Mg^{++} as compared to Ca^{++} , Sr^{++} and Ba^{++} ions. Dingwall and Moore³ by their viscosity measurements at the strain point suggested a coordination number 4 for the magnesium ions. The purpose of the present investigation is to provide new data on density and viscosity of glasses both at low and high temperatures and to infer therefrom the configurational arrangements of magnesium ions in ternary silicate glasses at these temperatures.

Experimental

Preparation of Glasses. The sand used for the preparation of glasses had 0.003% iron (Fe_2O_3). Other raw materials were of analytical grade. The melting was done in Pt/10 Rh crucibles at 1420°–1450°C. Some of the barium glasses were melted at 1380°C. The glasses were crushed, remelted and made free of bubbles and seeds. Some of the glasses were chemically analysed. The composition calculated from the batch and that found by the chemical analysis agreed within the limits of experimental error. The composition of the glasses is given in Table 1.

Measurement of Density and Viscosity of Glasses. The density values at room and high temperatures were found by the Archimedes principle. The density at room temperature was obtained by the loss of weight of the glass sample in toluol. At high temperatures the loss of weight of the Pt/10 Rh ball in the glass melt was the basis for the calculation of density of glass. The details of both the methods used are given in a previous work.⁴

The viscosity at high temperature was measured by a rotational viscometer after Dietzel and Bruckner⁵

The strain point at which the viscosity of glass is 10^{13} poise was obtained by the Bollenrath dilatometer after DIN 42324.⁶

Results and Discussion

The molar volume of the different type of glasses of equimolar composition, Na_2O , 0.75; MeO, 5.25; SiO_2 , where MeO = MgO, CaO, SrO and BaO, is plotted against the cations space volume after Biltz,⁷ at 20°C and 1400°C (Fig. 1). At lower temperature and for equimolar composition the Ca^{++} , Sr^{++} and Ba^{++} glasses fall on the same straight-line while the glasses containing Mg^{++} fall out of the straight-line. This is also the case with all the other compositions studied but not shown on the graph. Contrary to this, at 1400°C all the four cations for the equimolar composition fall almost on the same straight-line. According to Biltz the molar volume of a glass or a solution is given by the equation:

$$Vm = K_2 V^+ X + b_2$$

TABLE 1. THE CALCULATED COMPOSITION OF THE TEST GLASSES (mole%).

SiO ₂	MgO	CaO	SrO	BaO	Na ₂ O
85.71	—	—	—	—	14.29
82.14	—	3.57	—	—	14.29
78.57	—	7.14	—	—	14.29
75.00	—	10.71	—	—	14.29
(75.45)	—	(10.79)	—	—	(13.70)
71.43	—	14.29	—	—	14.29
67.85	—	17.86	—	—	14.29
78.57	—	—	7.15	—	14.29
75.00	—	—	10.71	—	14.29
71.43	—	—	14.29	—	14.29
67.85	—	—	17.86	—	14.29
78.57	7.14	—	—	—	14.29
75.00	10.71	—	—	—	14.29
71.43	14.29	—	—	—	14.29
71.40	14.55	—	—	—	14.15
67.85	17.86	—	—	—	14.29
64.28	21.43	—	—	—	14.29
78.57	—	—	—	7.14	14.29
75.00	—	—	—	10.71	14.29
71.43	—	—	—	14.29	14.29
(70.97)	—	—	—	(14.45)	(14.50)
67.85	—	—	—	7.14	14.29
78.57	—	—	—	—	14.29

The figures in brackets are found by chemical analysis.

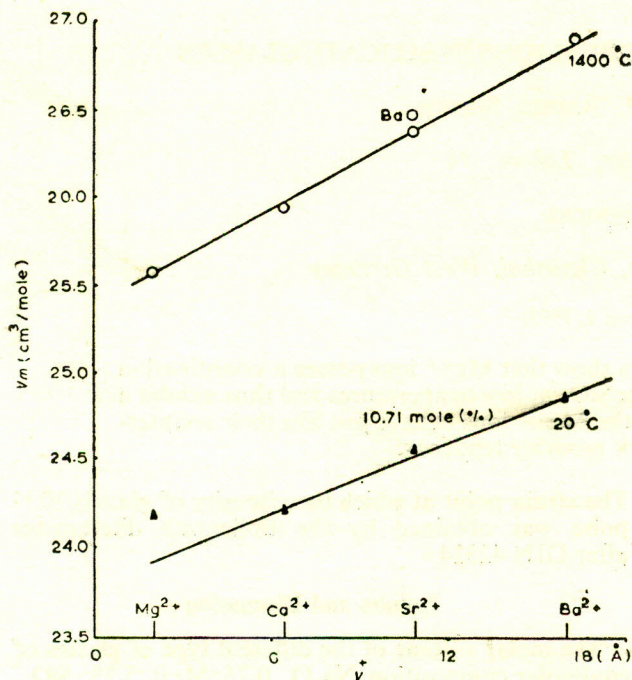


Fig. 1. Cations space requirements and molar volume of the glasses $\text{Na}_2\text{O}, 0.75/\text{CaO}, 5.5/\text{SiO}_2$ at 20° and 1400°C

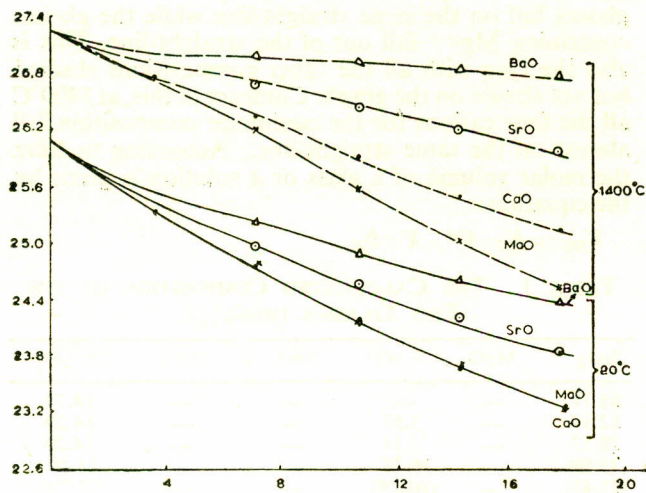


Fig. 2. Molar volume vs MeO of $\text{Na}_2\text{O} \times \text{MeO} (6-X) \text{SiO}_2$ glasses.

where K_2 is a constant; X , mol fraction of cation; b_2 volume of the matrix, and V^+ cations space volume.

From the above equation it is evident that in binary silicate glasses molar volume is proportional to the cation space requirements. The studied glasses have a constant content of Na_2O . Only alkaline earth oxides replace silica and hence these behave just like binary silicate glasses and the above equation is applicable in this case too.

From the foregoing equation and the results for low temperatures it may be concluded that except for the glasses containing Mg^{++} the other glasses containing Ca^{++} , Sr^{++} and Ba^{++} have the same configuration of

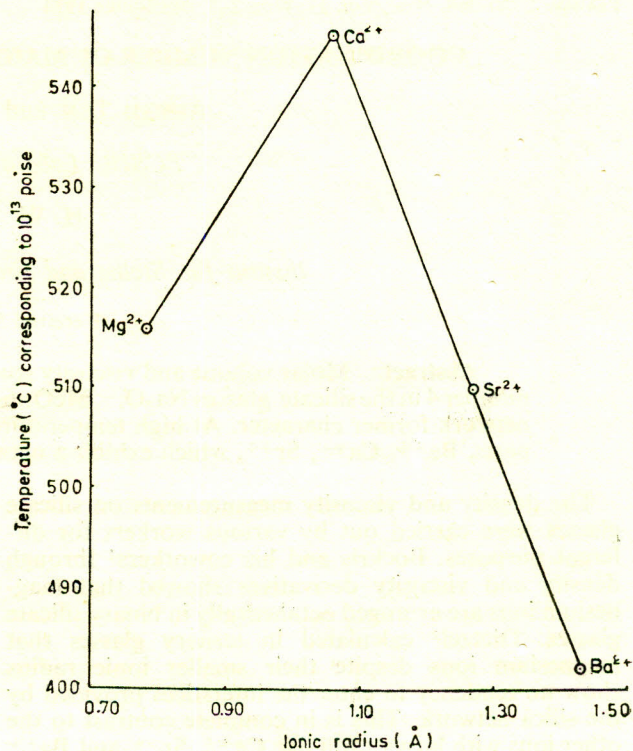


Fig. 3. Temperature ($^\circ\text{C}$) vs ionic radii of the glasses $\text{Na}_2\text{O}.075 \text{MeO} 5.25 \text{SiO}_2$.

the silicate matrix or that of the silicate network. Mg^{++} containing glasses at lower temperatures have acquired a configuration which results in a voluminous type of the structure.

This acquiring of the voluminous type of the structure by the magnesium containing glasses in the presence of an alkali oxide can also be seen if the molar volume is plotted against the molar percentage of MeO (MgO , CaO , SrO), when these replace SiO_2 in the glasses $\text{Na}_2\text{O} \times \text{MeO} 6-X \text{SiO}_2$. The results for low as well as for high temperatures are shown in Fig. 2. As is visible from the results of Fig. 2, for equimolar composition and cations types as mentioned under Fig. 1, at low temperatures the molar volume is proportional to the cation size. Mg^{++} containing glasses show an exception to this rule. Although the size of Mg ions is far less than that of the calcium ions yet glasses containing Ca^{++} as well as Mg^{++} ions show almost the same molar volumes. The Mg ions in the glasses studied might have acquired a tetrahedral configuration as in the case of spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$. In spinel type structure the measured volume is greater than that of the calculated volume if Mg ions are taken in octahedral coordination.⁸ If the molar volume is calculated taking Mg^{++} ions in tetrahedral coordination then the calculated and the measured volume tally with each other. This shows that Mg ions when present in tetrahedral coordination, show higher volumes than expected.

At 1400°C the glasses irrespective of the nature of the cations have the molar volume proportional to the cation sizes. This indicates that at higher temperatures Mg ions behave just like their counterparts (Ca^{++} ,

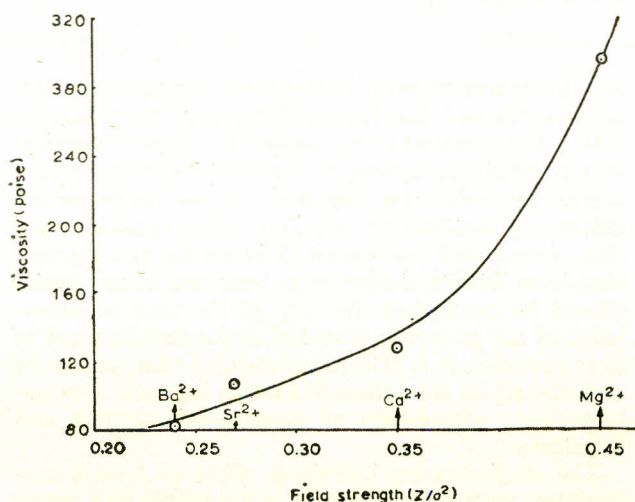


Fig. 4. Dependence of viscosity of the glasses Na₂O 0.75 MeO 5.25 SiO₂ on field strength.

Sr²⁺ and Ba²⁺) and show a pure network modifier character.

The results of the viscosity values at the strain point corresponding to 10¹³ poise are given in Fig. 3. In the glasses containing Ca²⁺, Sr²⁺ and Ba²⁺ ions the viscosity increases as the cation radius decreases or the bond strength increases. Here also the magnesium containing glasses are an exception and show low viscosity values relative to the calcium containing glass for equimolar compositions. This reflects that viscosity is not only a function of the ionic radius or the bond strength of the individual cations but is also dependent upon coordinational and sterical arrangements in the glass structure. As stated earlier the Mg ions lead to a voluminous type of the structure than do the calcium containing glasses at the low temperature. A voluminous type of the structure results in the

lowering of viscosity values when the Mg ions are present in the tetrahedral coordinations in the glasses studied. Dingwall and Moore³ also suggested a coordination number 4 for the Mg ions present in the quaternary glass compositions.³

In the case of glasses containing Ca²⁺, Ba²⁺ and Sr²⁺ ions no such rearrangements as stated above takes place and the factor controlling the viscosity is the field strength of the cation to hold together the various silicate structural units together.⁹ The higher the field strength, the higher the viscosity rule applied in this case. The results of viscosity measurements at 1400°C are shown in Fig. 4. As is visible from the results, viscosity for the same molar composition of the glasses increases as the field strength increases. In this case the power of the cation to hold together the various structure units of the silicate structure only matters. Mg ions do not make an exception at high temperatures, it suggests an almost simple network modifier character of the Mg ions at 1400°C.

References

1. J.W. Tomlinson, M.S.R. Heynes and J.O'M. Bockris, *Trans. Faraday Soc.*, **54**, 1822 (1958).
2. A. Dietzel, *Naturwiss.*, **31**, 110 (1943).
3. A.G.F. Dingwall, and H. Moore, *J. Soc., Glass Technol.*, **37**, 316 (1953).
4. A.D. Sheikh, Ph.D. thesis, submitted to Technical University, Clausthal, 1968.
5. A. Dietzel and R. Bruckner, *Chem. Ber.*, **28**, 455 (1955).
6. DIN 42324. Pruffung von Glas. Bestimmung der Transformations Temperature, December (1960).
7. W. Biltz, *Vosstanov. Leipzig.* (1934).
8. E.F. Reibling, *J. Chem. Phys.*, **44**, 2857 (1966).
9. J.O'M. J.W. Tomlinson and J.L. White Bockris, *Trans. Faraday Soc.*, **52**, 299 (1956).