

## VOLUME-COMPOSITION STUDY OF SILICATE GLASSES

AHMAD DIN, M. RASHID SHEIKH and AZHAR HUSSAIN QURESHI

PCSIR Laboratories, Lahore

(Received January 22, 1972; revised February 21, 1972)

**Abstract.** The density of the ternary and quaternary silicate glasses was measured at room temperature. The density derivative  $V_o$  dependent upon  $R$ , the number of oxygen ions per network former, led to the critical study of the relationship  $V_o = V_o^\circ / 1 - Rx$ . For the same molar composition both  $X$  and  $V_o$  vary as a function of cation radius.

Density of silicate glasses has been measured by various workers for different purposes.<sup>1,2</sup> The results of various measurements differ considerably due to their different cooling rates and the water content of the glasses. From the practically determined density, the factors are given for each glass component to calculate density from composition. These factors, however, are applicable only within definite composition ranges. Stevels<sup>3</sup> has pointed out that the density of glass can be determined irrespective of the measured ranges, from the volume of glass containing one gram atom of  $O^{-2}$ .

Stevels coupled volume of glass containing one gram atom of  $O^{-2}$  and composition as under:

If  $V_o$  and  $V_o^\circ$  be the volume of glass containing one gram atom of  $O^{-2}$  ions and the volume of the oxygen ions contained in volume  $V_o$  of glass respectively, and the volume of the cavities contained in volume  $V_o$  of the glass being  $V_o - V_o^\circ$ , the relative volume of the

cavities is given by 
$$\frac{V_o - V_o^\circ}{V_o} \quad (1)$$

It depends upon the effect of network modifiers on the oxygen ions. The effect of one network modifier on one oxygen ion is called by Stevels as packing coefficient or contraction determining coefficient  $x$ . If  $R$  is the ratio between the number of oxygen ions per network former then effect on all oxygen ions is given by:

$$Rx \quad (2)$$

Equating 1 and 2 
$$Rx = \frac{V_o - V_o^\circ}{V_o} \quad (3)$$

From equation 3 it follows 
$$V_o = \frac{V_o^\circ}{1 - Rx} \quad (4)$$

Where  $R$  is the ratio between the number of oxygen ions and the number of network formers.

In equation (4) the volume  $V_o^\circ$  has been given by Stevels as

$$V_o^\circ = 1.35 NA \frac{4}{3} \pi r^3 = 8.22 \text{ cm}^3$$

Where  $r_o$ , ionic radius;  $NA$ , Avogadro's number; and 1.35, a sterical factor.

$V_o$  can be calculated from density and molar number of oxygen ions. Equation (4) relates the volume of glass  $V_o$  with  $R$ . But in so doing Stevels overlooks the function of network modifiers in his derived equation. Stevels supposes that the network modifiers simply go into the interstices of the network,

and so contribute but little to the volume of glass. In the present study an attempt has been made to show how far in equimolar glass compositions different cations behave differently. These cations not only bring change in the volume of glass,  $V_o$ , but also bring a change in the value of contraction determining coefficient  $x$ . Further the replacement of the smaller cations by bigger cations change the values both  $x$  and  $V_o$ .

## Experimental

*Melting of Glasses.* The glasses were melted in Pt/10 Rh crucibles. The melts were poured on 2 in iron plate, ground and remelted. After getting rid of last traces of seeds, the glasses were stored for further studies.

*Preparation of Sample for Density Measurement.* Samples (2 cm<sup>2</sup>) were cut with a diamond cutter, edges were ground and annealed at the approximate rate of 1°C/min.

*Technique of Density Measurement.* Density measurements were made after the Archimedes principle using toluol as the immersion liquid. The density of the sample was calculated by the loss in weight of the sample in toluol and the density of toluol at room temperature.

## Results and Discussion

The composition of the glasses and the values of experimentally determined density are given in Table 1. As is evident from the results the density of the glasses increases when the amount of network modifiers increase at the expense of silica, and for the same weight per cent compositions, a bigger cation replaces a smaller one.

The increase in density is explained on the basis that when the oxides of the network modifiers,  $Me_nO$  are introduced, the cations go into the cavities of the silica network while oxygen ions add to the packing of glass structure. The greater the addition of the cations the greater the filling of the cavities and hence an increase in density. Because of the increased mass per unit volume when a smaller cation is replaced by a bigger one, there also results an increase in density in the latter case.

Figure 1 shows a relationship between  $R$  and composition  $x_1$ . It is evident that  $R$  increases with pro-

TABLE 1. DEPENDENCE OF DENSITY AND VOLUME OF GLASS CONTAINING ONE GRAM ATOM O<sup>-2</sup> (V<sub>O</sub>) ON COMPOSITION.

SiO <sub>2</sub> (%)		MgO(%)		NaO <sub>2</sub> (%)		BaO(%)		SrO(%)		CaO(%)		Density (g)	Volume of glass containing 1 g-atom O <sup>-2</sup> (V <sub>O</sub> )
Mole	Wt	Mole	Wt	Mole	Wt	Mole	Wt	Mole	Wt	Mole	Wt		
78.57	80.09	7.14	4.85	14.29	15.04	—	—	—	—	—	—	2.3897	13.8632
75.00	77.39	10.71	7.37	14.29	15.23	—	—	—	—	—	—	2.4137	13.8208
71.43	74.62	14.29	9.95	14.29	15.42	—	—	—	—	—	—	2.4331	13.8069
67.85	71.78	17.86	12.59	14.29	15.61	—	—	—	—	—	—	2.4534	14.1208
78.57	75.72	—	—	14.29	14.22	—	—	7.14	10.05	—	—	2.5103	13.9813
75.00	77.15	—	—	14.29	14.00	—	—	10.71	14.84	—	—	2.6050	14.0354
71.43	66.74	—	—	14.29	13.79	—	—	14.29	19.54	—	—	2.6976	14.1124
67.85	62.42	—	—	14.29	13.58	—	—	17.86	23.99	—	—	3.8280	14.4951
78.57	78.57	—	—	14.29	14.76	—	—	—	—	7.14	6.6	2.4348	13.8785
75.00	75.17	—	—	14.29	14.79	—	—	—	—	10.71	10.02	2.4845	13.7209
71.43	71.77	—	—	14.29	14.83	—	—	—	—	14.29	13.39	2.5290	13.7982
67.85	68.34	—	—	14.29	14.86	—	—	—	—	17.86	16.78	2.5758	14.1396
78.57	70.34	—	—	14.29	13.23	7.14	16.32	—	—	—	—	2.6708	14.1296
75.00	64.05	—	—	14.29	12.60	10.71	23.05	—	—	—	—	2.8462	14.2104
71.43	58.52	—	—	14.29	12.03	14.29	29.71	—	—	—	—	3.0116	14.3496
67.85	52.94	—	—	14.29	11.55	17.86	35.53	—	—	—	—	3.1806	14.8196
<i>Four Component Glasses</i>													
74.83	75.00	—	—	14.48	15.00	—	—	—	—	10.68	10.00	2.4841	13.7770
75.86	75.00	—	—	14.68	15.00	0.78	2.00	—	—	8.66	8.00	2.4966	13.7893
76.91	75.00	—	—	14.88	15.00	1.60	4.00	—	—	6.59	6.00	2.5103	13.8405
78.00	75.00	—	—	15.09	15.00	2.44	6.00	—	—	4.45	4.00	2.5205	13.8941
79.12	75.00	—	—	15.31	15.00	3.30	8.00	—	—	2.25	2.00	2.5308	13.9477
80.27	75.00	—	—	15.53	15.00	4.19	10.00	—	—	—	—	2.5411	14.0043

gressive replacement of SiO<sub>2</sub> by oxides. Every oxide addition breaks bridged oxygen ions of the network. The cations mostly go into the interstices and the oxygen ions find place in the network as nonbridged oxygen ions, the charge being balanced by the cations going into the nearly interstices. This enhances the oxygen ions of the network with the decreased amount of the network formers. Therefore, the value of *R*, the ratio between the oxygen ions per network former, also increases.

Figure 2 depicts the values of V<sub>O</sub>, the glass contain 1 g-atom oxygen ions, as a function of *R*. Contrary to the findings and formulae of Stevels and parallel to that of Coenen<sup>4</sup> on binary borates there exists no linear relationship between these two quantities. For the same value of *R*, V<sub>O</sub> increases with the cation size, the fact strengthens the hypothesis that bigger cations of the network modifiers stretch out the silica framework, while smaller cations due to their high field strength cause a contraction of the same. Peculiar is the behaviour of the calcium and magnesium system of glasses. Although the cation radius of Mg<sup>++</sup> ions is far below than those of Ca<sup>++</sup> ions yet for the same molar composition the values of V<sub>O</sub> found in Mg<sup>++</sup> system are higher compared to those in calcium system. Hennicke and Din<sup>5</sup> have shown that for these composition ranges Mg<sup>++</sup> ions occur in glasses in tetrahedral configuration. This type of configuration where Mg<sup>++</sup> ions come in coordination No. 4 are more voluminous than those where these exist in coordination No. 6.

TABLE 2. CONTRACTION DETERMINING COEFFICIENT X AS A FUNCTION OF CATION RADIUS AND COMPOSITION.

x	X=x·12·16	Crystal radius of cation (Å)	Cation type
0.1793	2.1803	0.65	Mg <sup>++</sup>
0.1739	2.1146	"	"
0.1693	2.0587	"	"
0.1693	2.0587	"	"
0.1815	2.2070	"	"
0.1778	2.1620	1.13	Sr <sup>++</sup>
0.1739	2.1146	"	"
0.1750	2.1280	"	"
0.1796	2.1838	"	"
0.1720	2.0915	0.99	Ca <sup>++</sup>
0.1691	2.0526	"	"
0.1691	2.0563	"	"
0.1842	2.2399	"	"
0.1809	2.1997	1.35	Ba <sup>++</sup>
0.1782	2.1669	"	"
0.1803	2.1924	"	"
0.13813	1.67-6	"	"
0.17484	2.1260	0.99	Ca <sup>++</sup>
0.17656	2.1469	1.35	Ba <sup>++</sup>
		0.99	Ca <sup>++</sup>
0.17911	2.1779	1.35	Ba <sup>++</sup>
		0.99	Ca <sup>++</sup>
0.18170	2.2094	1.35	Ba <sup>++</sup>
		0.99	Ca <sup>++</sup>
0.18439	2.2421	1.35	Ba <sup>++</sup>

The plot between  $\text{MenO}(\%)$  replacing  $\text{SiO}_2$  and  $V_o$  is given in Fig. 3.  $V_o$  increases proportionally as  $\text{MenO}$  content is increased. Every oxide addition causes a breakage of bridged oxygen ions and produces additional nonbridged oxygen ions leading to a fluffy type of structure and hence to volume increases. For the same molar composition, the values of  $V_o$  increase with the cation size because of the reasons discussed under Fig. 2.

The increase in  $V_o$  as shown in Fig. 4 for ternary and quaternary glasses where  $\text{Ca}^{++}$  ions are progressively replaced by  $\text{Ba}^{++}$  ions is explained on the basis that  $\text{Ba}^{++}$  ions, due to their size, stretch out the  $\text{SiO}_2$  framework more than do the  $\text{Ca}^{++}$  ions, with their higher field strength, resulting in a contraction effect on the network. Secondly, the  $(\%)$  cations going down into the cavities is proportional to their size.<sup>6</sup> According to this, the  $\text{Ba}^{++}$  ions, as compared

with  $\text{Ca}^{++}$  ions, remain outside the cavities and cause an additional volume increase.

In Fig. 5, the contraction determining coefficient  $x$  is plotted against the mole  $(\%)$   $\text{MenO}$  substituting  $\text{SiO}_2$  in glasses  $\text{Na}_2\text{O} \times \text{MenO} \cdot 6 \times \text{SiO}_2$  as given in Table 2. It is noticed that up to about 15 mole  $(\%)$  substitution of  $\text{MenO}$  for  $\text{SiO}_2$ , there occurs a gradual decrease in the value of  $x$ . Replacements beyond 15 mole  $(\%)$  bring about an increase in contraction determining coefficient  $x$ . Moreover  $x$  increases with the increasing cation radius. Similar results are evident from the study of Figs. 6 and 7 where  $x$  and  $V_o$  are plotted respectively against cation radii for different composition ranges. The foregoing facts indicate that  $x$  is definitely related with the compactness of the  $\text{SiO}_2$  network. Since bigger cations, as discussed earlier, for the same molar composition, cause greater modification of the network and vice versa, hence both the values of  $x$  and  $V_o$  increase. This negates Stevels hypothesis that the value of  $x$  remains constant for all types of glasses.

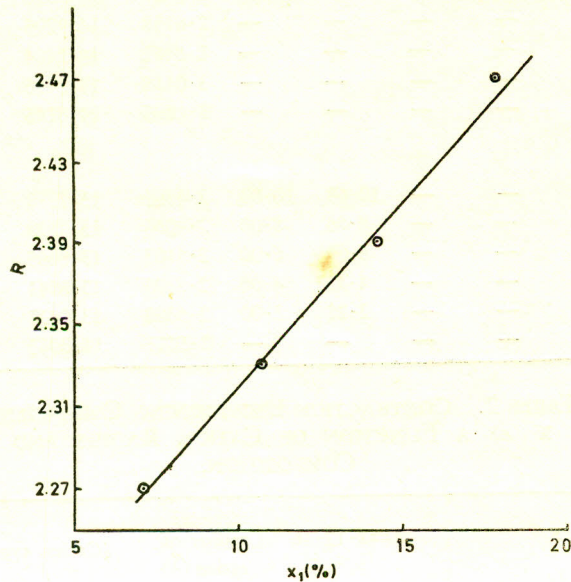


Fig. 1. Relationship between  $R$  and the molar composition of the glasses  $\text{Na}_2\text{O} \cdot X \text{MenO} \cdot 6 - X \text{SiO}_2$ .

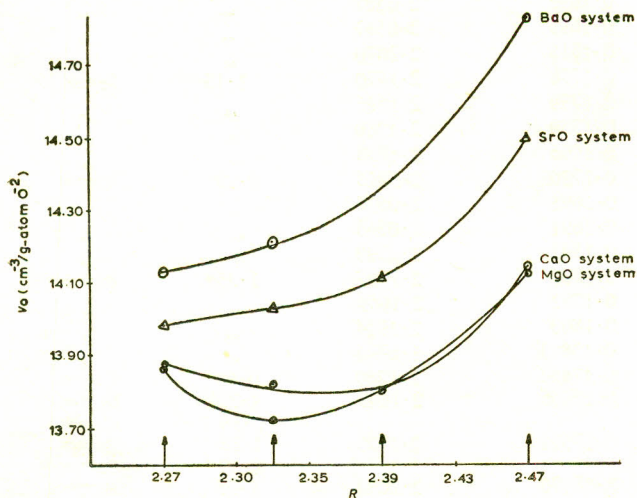


Fig. 2. Relationship between volume of glass containing one gram atom of oxygen ions  $V_o$  and number of oxygen ions per network former.

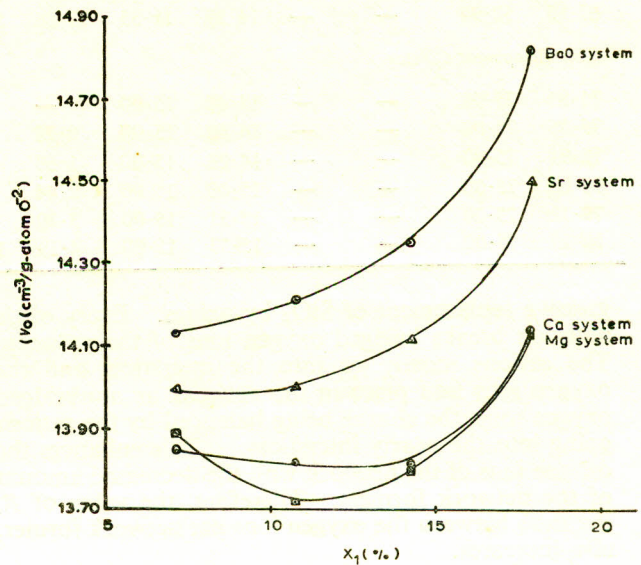


Fig. 3. Composition ( $X_1$ ) dependence on  $V_o$  for different systems of glasses  $\text{Na}_2\text{O} \cdot X \text{MenO} \cdot 6 - X \text{SiO}_2$ . Where  $\text{MenO} = \text{MgO}, \text{CaO}, \text{SrO}$  and  $\text{BaO}$ .

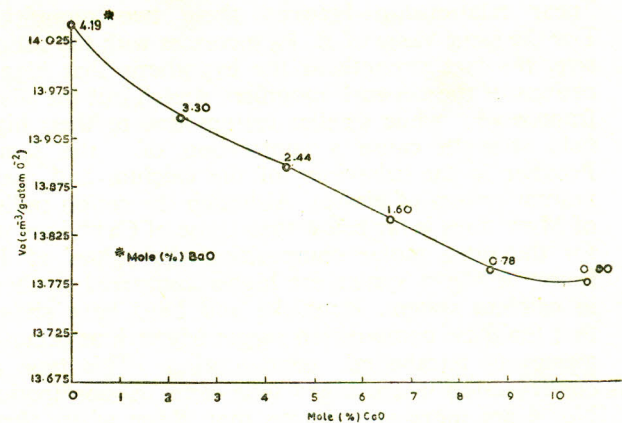


Fig. 4. Relationship between  $V_o$  and composition as calcium ions are replaced by barium ion on mole  $(\%)$  basis.

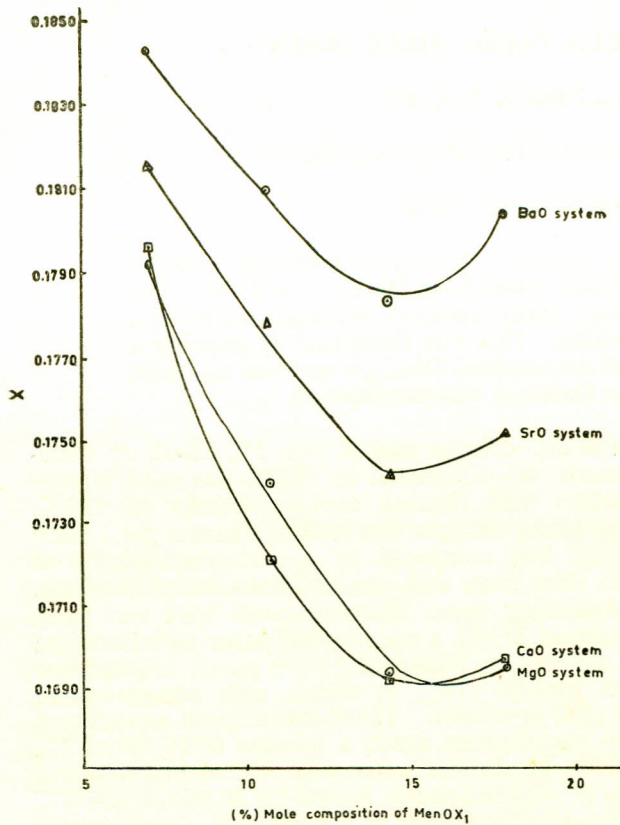


Fig. 5. Contraction determining coefficient  $X$  vs mole composition.

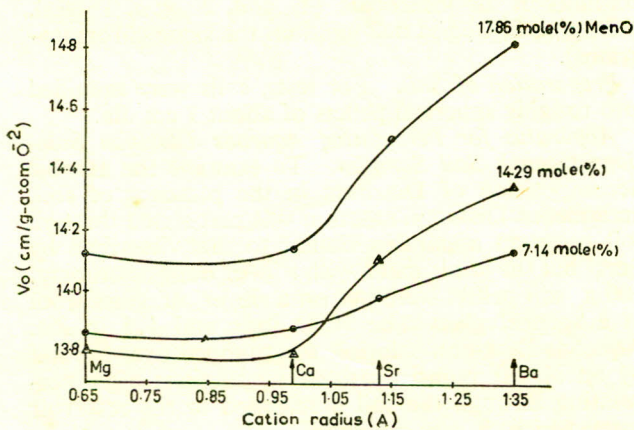


Fig. 7. Dependence of  $V_o$  on radius for different composition of glasses  $Na_2O \cdot x \cdot MenO \cdot (6-x) \cdot SiO_2$ .

The results of Fig. 8 for ternary and quaternary glasses when  $Ca^{++}$  ions are replaced by  $Ba^{++}$  ions also strengthen the results discussed earlier that bigger cations either for the same molar composition or

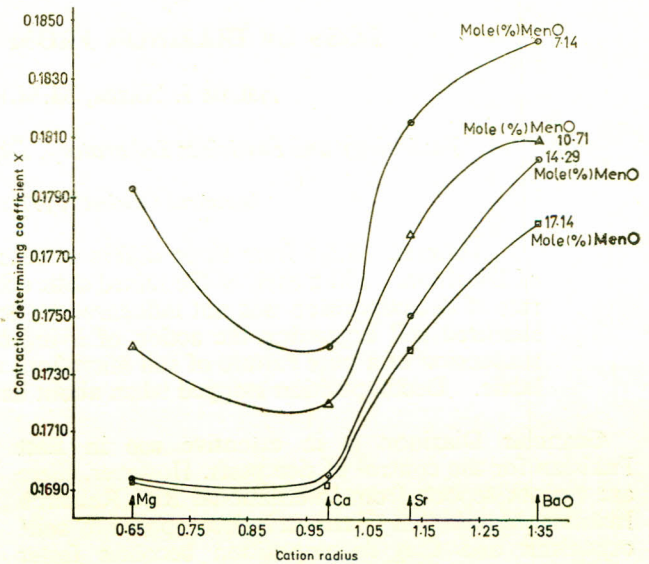


Fig. 6. Dependence of contraction determining coefficient on cation radius and composition in glasses  $Na_2O \cdot MenO \cdot (6-x) \cdot SiO_2$ .  $MenO$  =  $MgO$ ,  $CaO$ ,  $SrO$  and  $BaO$ .

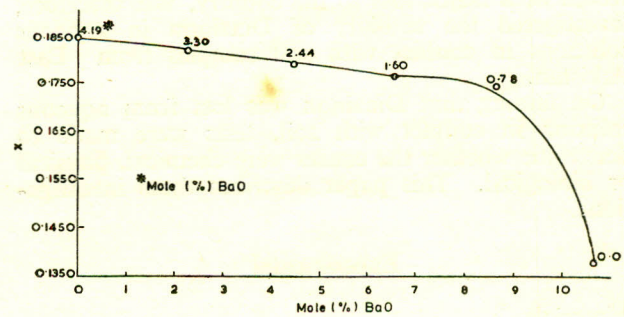


Fig. 8. Replacement of  $Ca^{++}$  by  $Ba^{++}$  and the resultant change in contraction determining coefficient  $X$ .

replacing the smaller ones increase the values of the contraction determining coefficient  $x$ .

References

1. G. Gehlhoff and M. Thomas, *Z. Techn. Physik.*, **7**, 106 (1926).
2. M.L. Huggins, *J. Opt. Soc. Am.*, **30**, 420 (1940).
3. J.M. Stevels, *Progress in the Theory of the Physical Properties of Glass* (Elsevier, Amsterdam, 1948), p. 20.
4. M. Coenen, *Glastech. Ber.*, **35**, 14(1962).
5. H.W. Hennicke and A.D. Sheikh, *Proceedings of the Eighth International Congress on Glass*, London (1968).
6. A. Dietzel, *Naturwissens-Chaften*, **31**, 110 (1943).