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## Volume of ionic sites in silicate glasses

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### Abstract

Molar volume data of alkali and alkaline earth silicate glasses have been used to calculate the free volume associated with the bridging and nonbridging oxygen and modifier ions. The free volume associated with the bridging oxygen is constant ( $15.39 \times 10^{-24} \text{ cm}^3$ ) for all modifier ions up to 33.3 mol% modifier oxide. It decreases (in alkali or alkaline earth silicate glasses) with increasing number of nonbridging oxygen ions per structural unit and/or radius of the modifier ion. The nonbridging oxygen ion is associated with a constant free volume ( $6.50 \times 10^{-24} \text{ cm}^3$ ) in all cases. Modifier ions are associated with free volume that increases with increasing number of nonbridging oxygen ions per structural unit and/or radius of the modifier ion. The used model explores the change in the free volume due to changing the concentration of alkali oxides in mixed alkali silicate glasses. The results show that, in such glasses, the free volume related to a certain type of alkali oxide increases with increasing content.

### 1. Introduction

Various physical properties of silicate glasses can be correlated with the concentration of structural units in the glass. Properties such as molar volume [1], refractive index and molar refraction [2, 3], and thermal expansion [4] can be described by additive relations. In these relations a specific factor can be used for each structural unit. The factor depends on the type of property. The obtained factors could successfully be used to calculate the magnitude of those physical properties in binary alkali (or alkaline earth) silicate glasses and mixed alkali and multicomponent silicate glasses. Recently, the refractivity of both the bridging and nonbridging oxygen ions in silicate [5] and aluminosilicate [6] glasses could be calculated by using the factors for molar refraction.

The volumes of voids in the structure are of special importance for the transport properties. The mobility of movable ions is affected to a great extent by the nature of the glass matrix. An 'open matrix', i.e. with high concentration of nonbridging oxygen ions, is characterized by higher electric conductivity than a closed one. The present work presents a trial to calculate the free volume associated with the ions in silicate glasses.

## 2. Procedure

Different spectroscopic techniques have been used to investigate the structure of silicate glasses. NMR and MAS-NMR studies [7–10] indicate that up to about 33 mol% alkali oxide ( $R_2O$ )  $Q_3$  units form at the expense of  $Q_4$  units.  $Q_3$  units are  $SiO_4$  tetrahedra having one nonbridging oxygen ion (NBO) per tetrahedron, where  $Q_4$  units are  $SiO_4$  tetrahedra without NBOs. For 33 mol%  $< R_2O \leq 50$  mol%,  $Q_3$  units convert into  $Q_2$  units. The latter represent  $SiO_4$  tetrahedra with two NBOs for each one. Results of Raman spectroscopy [11] revealed that the conversion process continues, with increasing  $R_2O$  content, from  $Q_2$  to  $Q_1$  (for 50 mol  $< R_2O \leq 60$  mol) and finally from  $Q_1$  to  $Q_0$  (for 60 mol  $< R_2O \leq 66.7$  mol). Here  $Q_1$  and  $Q_0$  refer to  $SiO_4$  tetrahedra having, respectively, three and four NBOs per  $Si^{4+}$  cation. In the light of these findings relations could be predicted to describe the concentration of structural units as a function of modifier oxide concentration in binary alkali or alkaline earth silicate glasses. The relations were modified to calculate the concentration of structural units in mixed alkali silicate glasses [1, 12, 13]. Small deviations from stoichiometry were detected around the border of the above regions [7–10, 14]. It has been shown [1–5] that such deviations would not have a pronounced effect on the present analysis because the predicted relations are approximations to the actual distribution of the  $Q$ -sites in the glass matrix. Similar arguments have also been considered by Peters *et al* [15].

The molar volume ( $V_m$ ) of a glass can be given [12] in the form of an additive relation as

$$V_m = \sum N_u V_u. \quad (1)$$

Here  $N_u$  is the number of the structural unit ( $u$ ) per mole of glass and  $V_u$  is its volume. On the basis of the structural unit distribution in alkali silicate glasses [12], equation (1) can be expressed as

$$V_m = [(1 - 3x)V_4 + 2xV_3]N_A \quad \text{for } (0 < x \leq 0.333) \quad (2)$$

$$V_m = [(2 - 4x)V_3 + (3x - 1)V_2]N_A \quad \text{for } (0.333 < x \leq 0.5) \quad (3)$$

$$V_m = [(3 - 5x)V_2 + (4x - 2)V_1]N_A \quad \text{for } (0.5 < x \leq 0.6) \quad (4)$$

and

$$V_m = [(4 - 6x)V_1 + (5x - 3)V_0]N_A \quad \text{for } (0.6 < x \leq 0.666) \quad (5)$$

where  $x$  is the molar fraction of the alkali oxide and  $N_A$  is Avogadro's number. In these relations  $V_4$ ,  $V_3$ ,  $V_2$ ,  $V_1$  and  $V_0$  are, respectively, the volume of the structural units  $Q_4$ ,  $Q_3$ ,  $Q_2$ ,  $Q_1$  and  $Q_0$ .

In terms of the volumes that the constituting ions occupy in the matrix ( $V_{Si}$ ,  $V_\phi$ ,  $V_R$  and  $V_O$ ), the volumes of the structural units can be given as

$$V_4 = V_{Si} + 2V_\phi \quad (6)$$

$$V_3 = V_{Si} + 1.5V_\phi + (V_O + V_R) \quad (7)$$

$$V_2 = V_{Si} + V_\phi + 2(V_O + V_R) \quad (8)$$

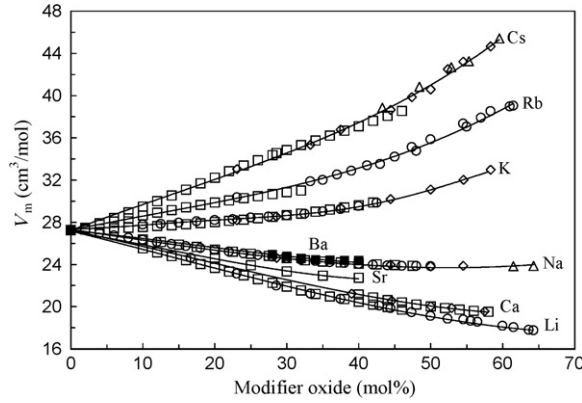
$$V_1 = V_{Si} + 0.5V_\phi + 3(V_O + V_R) \quad (9)$$

and

$$V_0 = V_{Si} + 4(V_O + V_R). \quad (10)$$

Here  $V_{Si}$ ,  $V_\phi$ ,  $V_O$  and  $V_R$  are, respectively, the volumes occupied by  $Si^{4+}$ , bridging oxygen ( $\phi$ ), nonbridging oxygen (O) and alkali ion. The volume occupied by an ion is the volume of ion itself and its associated space (its free volume) in the matrix. These relations can be used to calculate  $V_\phi$  and  $V_O$ . Thus on the basis of equations (1) and (6)–(10) we may write

$$V_m = \sum N_i V_i \quad (11)$$



**Figure 1.** Molar volume  $V_m$  of alkali and alkaline earth silicate glasses as a function of the modifier oxide content. The symbols are determined values based on densities taken from various sources [1, 18–26]. Different symbols refer to different sources. The lines are fitting plots of calculated values obtained from equation (14) and the values given in table 1.

with  $N_i$  being the number of the ion ( $i$ ) per mole of glass and  $V_i$  is the volume occupied by that ion in glass. The last relation can be reformed to

$$V_m = N_{Si} V_{Si} + N_{\phi} V_{\phi} + N_O V_O + N_R V_R \quad (12)$$

where  $N_{Si}$ ,  $N_{\phi}$ ,  $N_O$  and  $N_R$  are, respectively, the number of  $Si^{4+}$ , BO, NBO and alkali ions per mole of glass. The radius of  $Si^{4+}$  ion in oxides is  $0.26 \times 10^{-8}$  cm [16] whereas that of  $O^{2-}$  ion in silicate units is  $1.2 \times 10^{-8}$  cm [17]. Thus the volume of  $Si^{4+}$  ions in vitreous  $SiO_2$  and then in any modified silicate glass is  $\leq 0.5\%$  of the volume of  $O^{2-}$  ions. Therefore, for the first approximation, the first term in equation (12) can be neglected with respect to the other terms. Equation (12) can then be approximated to

$$V_m \approx N_{\phi} V_{\phi} + N_O V_O + N_R V_R. \quad (12a)$$

Equations (7)–(10) show that  $N_O = N_{R+}$  and equation (12a) can be rewritten as

$$V_m \approx N_{\phi} V_{\phi} + N_O (V_O + V_R). \quad (12b)$$

A nonbridging oxygen ion is always bound to an alkali ion (or a half alkaline earth ion) and therefore the term between brackets can be looked as an undividable quantity that can be assigned by  $V_B$ . Thus

$$V_B = V_O + V_R. \quad (13)$$

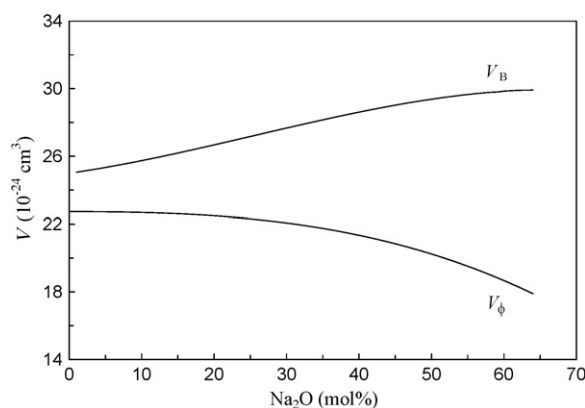
It follows that

$$V_m = N_{\phi} V_{\phi} + N_O V_B. \quad (14)$$

Equation (14) can be solved simultaneously for two values of  $V_m$  close to each other to get  $V_{\phi}$  and  $V_B$ .

### 3. Results

Figure 1 shows the molar volume of alkali and alkaline earth silicate glasses as a function of the modifier oxide concentration. The symbols represent determined  $V_m$  values, i.e. obtained



**Figure 2.** Dependence of  $V_\phi$  and  $V_B$  on the alkali oxide content in  $\text{Na}_2\text{O}$ – $\text{SiO}_2$  glasses.  $V_\phi$  and  $V_B$  were calculated from equation (14) and values obtained from the fitting equation of the experimental  $V_m$  data for  $\text{Na}_2\text{O}$ – $\text{SiO}_2$  glasses in figure 1.

from determined densities given by various investigators [1, 18–26]. In this respect,  $V_m$  has been obtained from the relation

$$V_m = M/D \quad (15)$$

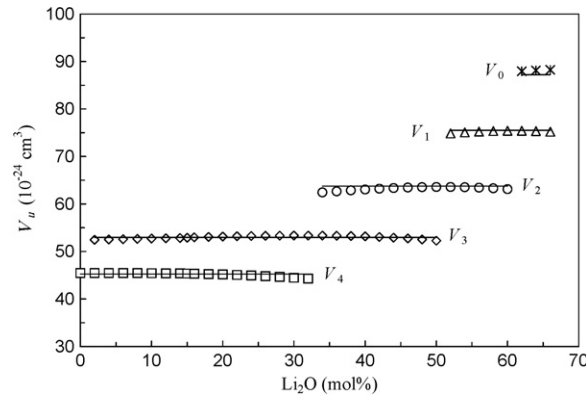
where  $M$  is the relative molecular mass of glass and  $D$  is its density. From figure 1 it is deduced that in each type of alkali and alkaline earth silicate glass, at any concentration of the modifier oxide,  $V_m$  increases with increasing size of the modifier ion.

#### 4. Discussion

$V_m$  values obtained from the fitting plots of the experimental data (figure 1) were treated by equation (14). For the sake of clarity the fitting plots of the experimental data are not presented in figure 1, since they are very close to the solid lines shown in the figure. Figure 2 shows, as an example, the change of  $V_\phi$  and  $V_B$  with the alkali oxide content in  $\text{Na}_2\text{O}$ – $\text{SiO}_2$  glasses. The features observed in figure 2 are characteristic for all the studied glasses. There is an increase in  $V_B$  with increasing  $\text{Na}_2\text{O}$  content whereas  $V_\phi$  decreases. Up to 64 mol%  $\text{Na}_2\text{O}$  the increase in  $V_B$  is about 19% and  $V_\phi$  decreases by about 27%. This reveals that when increasing the modifier oxide content the volume of the binding ( $\text{O}-\text{R}^+$ ) or ( $\text{O}-0.5\text{R}^{2+}$ ) increases at the expense of that of  $\phi$ . In other words, the space associated with a nonbridging oxygen ion increases at the expense of that associated with a bridging one.

In spite of the change in  $V_\phi$  and  $V_B$  it is found that the volumes of the structural units (as obtained from equations (6)–(10)) are constant (figure 3). This is consistent with the results of previous studies. The solid lines in figure 3 represent  $V_u$  values in  $\text{Li}_2\text{O}$ – $\text{SiO}_2$  glasses obtained from analysing the density data [12]. Similar results were found for the refractive index of silicate glasses. It has been indicated [2] that factors ( $f_{\text{Si}}$ ,  $f_\phi$ ,  $f_{\text{O}}$  and  $f_{\text{R}}$ ) with which the ions contribute to the refractive index in an alkali silicate glass vary from one composition region to another but they remain the same in any one of the regions. In addition, the factor  $f_u$  for a structural unit is constant. The constancy of  $V_u$  values (figure 3) implies that the change in the volume of bridging oxygen ions ( $\Delta V_\phi$ ) in a unit might equal and oppose the change in the volume of nonbridging oxygen bindings ( $\Delta V_B$ ). From equations (6)–(10) it can be concluded that

$$n_\phi \Delta V_\phi = -n_{\text{O}} \Delta V_B \quad (16)$$



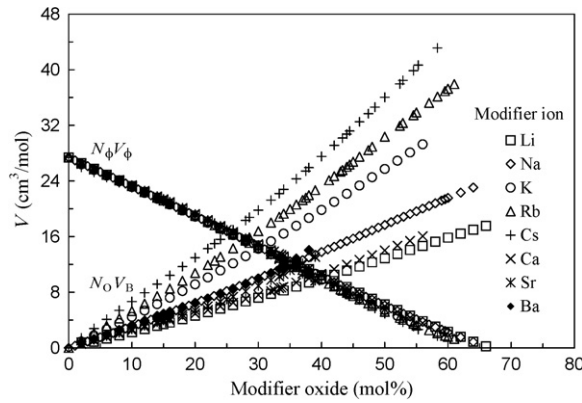
**Figure 3.** Volumes of the structural units in  $\text{Li}_2\text{O-SiO}_2$  glasses as a function of  $\text{Li}_2\text{O}$  content. The symbols represent values obtained from equations (6)–(10) and  $V_\phi$  and  $V_B$  calculated from equation (14). The lines denote  $V_u$  values obtained from analysing the density data of  $\text{Li}_2\text{O-SiO}_2$  glasses [1].

**Table 1.** Volume of the bridging oxygen ion ( $V_\phi$ ) and nonbridging oxygen binding ( $V_B = V_O + V_{R^+}$  or  $V_O + 0.5V_{R^{2+}}$ ) in silicate glasses.  $V_\phi$  and  $V_B$  are given in ( $10^{-24} \text{ cm}^3$ ).

Type of glass	Composition region							
	$0 < x \leq 0.333$		$0.333 < x \leq 0.5$		$0.5 < x \leq 0.6$		$0.6 < x \leq 0.666$	
	$V_\phi$	$V_B$	$V_\phi$	$V_B$	$V_\phi$	$V_B$	$V_\phi$	$V_B$
$\text{Li}_2\text{O-SiO}_2$	22.63	19.10	21.52	20.80	19.90	21.75	18.50	21.80
$\text{Na}_2\text{O-SiO}_2$	22.63	26.24	21.11	28.76	19.36	29.68	18.08	29.91
$\text{K}_2\text{O-SiO}_2$	22.63	37.86	19.84	41.47	16.67	43.19	—	—
$\text{Rb}_2\text{O-SiO}_2$	22.63	44.98	20.20	48.71	14.88	51.17	10.12	51.63
$\text{Cs}_2\text{O-SiO}_2$	22.63	54.01	20.20	57.72	13.75	60.75	—	—
$\text{CaO-SiO}_2$	22.63	20.97	21.60	22.40	18.90	23.70	—	—
$\text{SrO-SiO}_2$	22.63	23.32	21.30	25.17	—	—	—	—
$\text{BaO-SiO}_2$	22.63	27.16	20.85	29.50	—	—	—	—

where  $n_\phi$  is the number of bridging oxygen ions per structural unit and  $n_O$  is the number of nonbridging oxygen ions in the same unit. Equation (16) reveals that  $\Delta V_\phi = 0$  in  $Q_4$  and  $\Delta V_B = 0$  in  $Q_0$ . The same can be deduced from figure 2, at the beginning of the plot for  $V_\phi$  and at the end of the plot for  $V_B$ , respectively.

An alternative point of view in estimating  $V_m$  of a glass is to assume constant values of  $V_\phi$  and  $V_B$  in each composition region. Starting from the mean values of  $V_\phi$  and  $V_B$  in the different composition regions it was possible to get values that verify the above assumption. The estimated constant values of  $V_\phi$  and  $V_B$  (table 1) are very close to their mean values in the concerned composition region. The solid lines in figure 1 represent the fitting plots of  $V_m$  as calculated from equation (14) and the values given in table 1. The agreement between the experimental and the calculated  $V_m$  values indicates that  $V_\phi$  and  $V_B$  can be approximated to constant values in each composition region and this leads to a high degree of accuracy in calculating  $V_m$ . It is worthy to mention that the volume of a structural unit can be predicted from the values in table 1 in the regions where the unit appears. For example,  $Q_3$  exists in the regions  $0 < x \leq 0.333$  and  $0.333 \leq x < 0.5$ . By using equation (7) and the values in table 1,



**Figure 4.** Contribution of both the bridging oxygen ions ( $N_\phi V_\phi$ ) and nonbridging oxygen bindings ( $N_O V_B$ ) in alkali and alkaline earth silicate glasses as a function of the modifier oxide content.

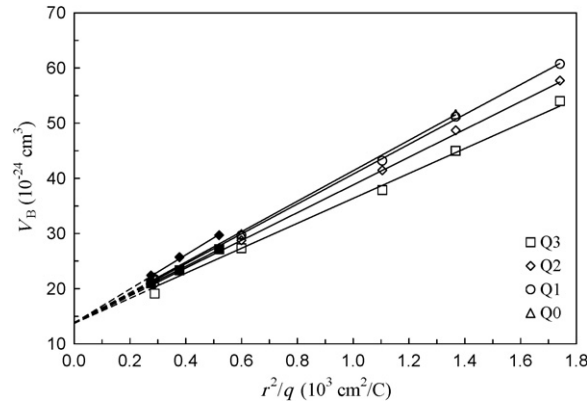
for  $\text{Li}_2\text{O-SiO}_2$  glasses as an example, one gets  $V_3 = 53.045 \times 10^{-24} \text{ cm}^3$  for  $0 < x \leq 0.333$  and  $53.08 \times 10^{-24} \text{ cm}^3$  for  $0.333 \leq x < 0.5$ . These values agree well with those presented in figure 3.

In figure 4 is shown the entire contribution of both the bridging and nonbridging oxygen ions in the glasses investigated. As the modifier oxide content increases the total contribution of bridging oxygen ions ( $N_\phi V_\phi$ ) decreases, whereas that of the nonbridging oxygen bindings ( $N_O V_B$ ) increases. The decrease in  $N_\phi V_\phi$  is related to the decrease in the  $\text{SiO}_2$  content. Up to 33 mol% of the modifier oxide, the values of  $N_\phi V_\phi$  are mostly the same for all types of modifier ions. This behaviour reveals that  $V_\phi$  is not affected by the type of modifier ion up to one nonbridging oxygen ion per  $\text{SiO}_4$  tetrahedron. This is in consistence with the data in table 1. Above this concentration  $N_\phi V_\phi$  varies slightly with the type of modifier oxide. On the other hand,  $N_O V_B$  increases when increasing the modifier oxide content. There is a marked difference between the values from one type of modifier to another. From figure 4 it is concluded that  $V_m$  of a glass decreases with increasing modifier oxide concentration ( $C$  mol%) for  $|d(N_\phi V_\phi)/dC| > d(N_O V_B)/dC$  and vice versa.

The increase in  $N_O V_B$  (for a certain modifier concentration) from  $\text{Li}_2\text{O-SiO}_2$  to  $\text{Cs}_2\text{O-SiO}_2$  reveals that the volume  $V_B$  becomes greater with lowering the field strength of the modifier ion. Figure 5 represents the dependence of the volume  $V_B$  in various structural units on the reciprocal of the field strength. The latter is expressed as  $q/r^2$ , where  $q$  is the charge of modifier ion and  $r$  is its radius. As shown, there is a linear increase in  $V_B$  in all cases. Any of the lines can be expressed as

$$V_B = s(r^2/q) + 13.737 \times 10^{-24} \text{ (cm}^3\text{)}, \quad (17)$$

where  $s$  is the slope of the straight line. All the lines intersect the vertical axis at nearly the same point,  $(13.737 \pm 0.064) (10^{-24} \text{ cm}^3)$ . According to equation (13) this value corresponds, theoretically, to  $V_B$  for  $V_R = 0$ , i.e.  $V_O$ . It seems therefore that  $V_O$  has a constant value and the increase in  $V_B$  with increasing  $V_R$  is then related to the size of the alkali ion. A greater alkali ion size means lower field strength and weaker bond with the nonbridging oxygen and this leads to a greater  $V_B$  value. With reference to the size of the  $\text{O}^{2-}$  ion in silicate units ( $7.24 \times 10^{-24} \text{ cm}^3$ ) it is concluded that, on average, each NBO is associated with a space of  $6.50 \times 10^{-24} \text{ cm}^3$ . As shown in table 1, up to 33 mol% of modifier oxide  $V_\phi$  has a constant value ( $22.63 \times 10^{-24} \text{ cm}^3$ ). By neglecting the volume of  $\text{Si}^{4+}$  ion it is concluded that, in this region, the average associated space is  $15.39 \times 10^{-24} \text{ cm}^3$  per bridging oxygen ion. These results



**Figure 5.** Dependence of the volume of nonbridging oxygen binding  $V_B$  in various structural units on the reciprocal of the field strength of the modifier ion. Open symbols represent  $V_B$  in alkali silicate glasses and the filled symbols are for alkaline earth silicate glasses. The lines are guides for the eyes.

**Table 2.** Volume of space associated with an alkali ion or a half alkaline earth ion in binary silicate glasses.

Modifier ion	Composition region			
	$0 < x \leq 0.333$	$0.333 < x \leq 0.5$	$0.5 < x \leq 0.6$	$0.6 < x \leq 0.666$
	$V_{Sp} (10^{-24} \text{ cm}^3)$	$V_{Sp} (10^{-24} \text{ cm}^3)$	$V_{Sp} (10^{-24} \text{ cm}^3)$	$V_{Sp} (10^{-24} \text{ cm}^3)$
Li	4.05	5.75	6.69	6.75
Na	8.56	11.08	12.00	12.23
K	14.27	17.88	19.60	—
Rb	17.66	21.39	23.85	24.31
Cs	20.77	24.48	27.51	—
Ca	5.49	6.92	—	—
Sr	6.80	8.65	—	—
Ba	8.93	11.27	—	—

reveal that the associated space of a bridging oxygen ion is greater than that for a nonbridging one. Such a difference might be related to the electrostatic interaction between the nonbridging oxygen ions and modifier ions.

Furthermore, from equations (13) and (17) it appears that

$$V_R = s(r^2/q). \tag{17a}$$

This is the volume related to the modifier ion, i.e. the size of the ion itself and its associated space. Then the volume of the latter ( $V_{Sp}$ ) can be obtained as

$$V_{Sp} = (V_B - 13.737 \times 10^{-24}) - V_{R^+} \tag{18}$$

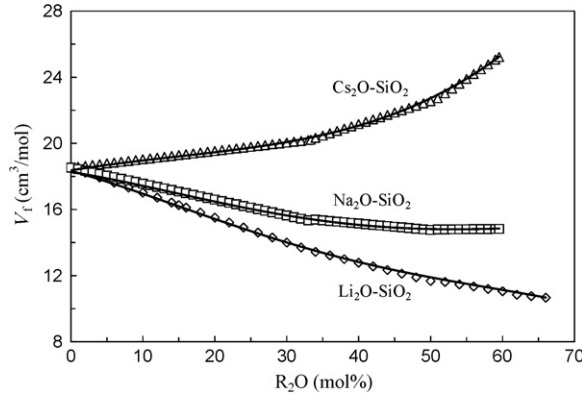
for alkali ions, and

$$V_{Sp} = (V_B - 13.737 \times 10^{-24}) - 0.5V_{R^{2+}} \tag{18a}$$

for alkaline earth ions. Here  $V_{R^+}$  is the size of the alkali ion and  $V_{R^{2+}}$  is that of the alkaline earth ion as obtained from the radii. Values of  $V_{Sp}$  are given in table 2.

The obtained volumes can be used to calculate the free volume ( $V_f$ ) of the studied glasses. This might represent a test of the validity of the model and the obtained results. The free volume





**Figure 6.** Free volume of  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$  and  $\text{Cs}_2\text{O-SiO}_2$  glasses as a function of the alkali oxide content. The symbols represent data obtained from the fitting plots of the experimental  $V_m$  values in figure 1 and equation (19). The lines are fitting plots of calculated values obtained from equation (20) and the data given in tables 1 and 2.

can be obtained from the molar volume and the volume of the ions in glass. It is given as

$$V_f = V_m - \sum N_i v_i \quad (19)$$

where  $N_i$  is the number of the ion ( $i$ ) per mole of glass and  $v_i$  is the size as obtained from its radius. On the other hand,  $V_f$  can be calculated using the volume of spaces associated with ions in the glass. For alkali silicate glasses  $V_f$  may be expressed as

$$V_f = N_\phi (V_\phi - 7.24 \times 10^{-24}) + N_O \times 6.5 \times 10^{-24} + N_R V_{Sp} \quad (\text{cm}^3) \quad (20)$$

where

$$N_\phi = 2N_4 + 1.5N_3 + N_2 + 0.5N_1, \quad (21)$$

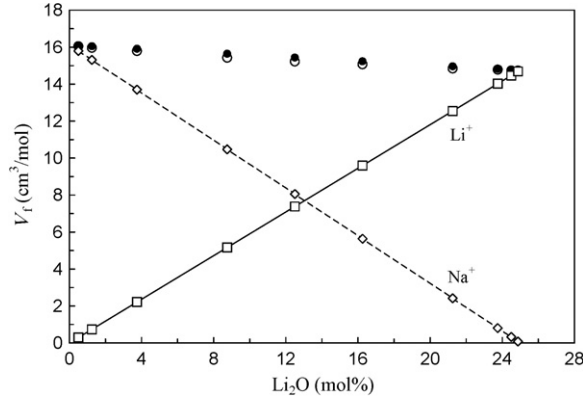
$$N_O = N_3 + 2N_2 + 3N_1 + 4N_0. \quad (22)$$

and

$$N_R = 2xN_A. \quad (23)$$

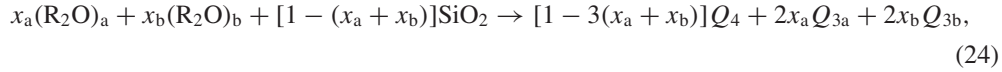
In these relations  $N_4$ ,  $N_3$ ,  $N_2$ ,  $N_1$  and  $N_0$  are, respectively the numbers of the structural units  $Q_4$ ,  $Q_3$ ,  $Q_2$ ,  $Q_1$  and  $Q_0$  per mole of glass.  $N_4-N_0$  can be obtained from equations (2)–(5). It is noteworthy that both  $V_\phi$  and  $V_{Sp}$  vary with the glass composition, tables 1 and 2. Thus one may take in consideration the values of  $V_\phi$  and  $V_{Sp}$  for the corresponding region when dealing with equation (20). Figure 6 shows the free volume of  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$  and  $\text{Cs}_2\text{O-SiO}_2$  glasses as a function of the alkali oxide content. Values of  $V_f$  obtained from equation (19) agree well with those obtained from equation (20).

The model can also be tested for mixed alkali glasses. In the region of  $0 \text{ mol}\% < R_2O \leq 33.3 \text{ mol}\%$  the content of each type of alkali oxides would be incorporated in the silicate network converting  $Q_4$  units into  $Q_3$  units. For example, in  $\text{Li}_2\text{O-Na}_2\text{O-SiO}_2$  glasses there are  $Q_4$ ,  $Q_{3(\text{Li})}$  and  $Q_{3(\text{Na})}$  units.  $Q_{3(\text{Li})}$  units are those resulting from introducing  $\text{Li}_2\text{O}$  into the silicate matrix while  $Q_{3(\text{Na})}$  are due to  $\text{Na}_2\text{O}$ . The concentration of each of these units would depend on the total alkali content as well as the concentration of each alkali oxide. It is assumed here that alkali oxides incorporate homogeneously in the glass matrix, i.e. there is no preferential association of any alkali type with certain silicate sites. In these glasses there are four types of sites. These are bridging oxygen, nonbridging oxygen, Li and Na sites. To calculate the free volume in such glasses we have to get the concentration of each



**Figure 7.** Free volume of  $x\text{Li}_2\text{O}\cdot(0.25-x)\text{Na}_2\text{O}\cdot 0.75\text{SiO}_2$  glasses as a function of  $\text{Li}_2\text{O}$  content. The O-symbol represents data based on densities given in [27]. The ●-symbol represents data obtained from equation (29) and the data given in tables 1 and 2. Data obtained from equations (27) and (28) represent, respectively, the free volume of the portion of silicate matrix that contains  $\text{Li}^+$  ions ( $V_{f(\text{Li})}$ , □) and that of the portion of silicate matrix containing  $\text{Na}^+$  ions ( $V_{f(\text{Na})}$ , ◇).

type of site. Generally, in a glass containing two alkali oxides,  $(\text{R}_2\text{O})_a$  and  $(\text{R}_2\text{O})_b$  with  $0 \text{ mol}\% < \text{R}_2\text{O} \leq 33.3 \text{ mol}\%$ , the distribution of structural units follows the relation [13]



where  $x_a$  and  $x_b$  are the mole fractions of alkali oxides.

A  $Q_4$  unit has two bridging oxygen ions whereas each  $Q_3$  unit has 1.5 bridging oxygen ions and a half NBO. The number of units per mole of glass is then

$$N_\phi = \{2[1 - 3(x_a + x_b)] + 2 \times 1.5x_a + 2 \times 1.5x_b\}N_A, \quad (25)$$

$$N_O = 2(x_a + x_b)N_A, \quad (26)$$

$$N_{\text{Li}} = 2x_aN_A \quad (27)$$

and

$$N_{\text{Na}} = 2x_bN_A. \quad (28)$$

Then, the free volume can be taken as the resultant space related to these sites. Considering the volume of space associated with each type of site, free volume in these glasses can be expressed as

$$V_f = N_\phi \times (15.39 \times 10^{-24}) + N_O \times (6.5 \times 10^{-24}) + N_{\text{Li}} \times (4.05 \times 10^{-24}) + N_{\text{Na}} \times (8.56 \times 10^{-24}). \quad (29)$$

In figure 7 is presented the free volume of  $x\text{Li}_2\text{O}\cdot(0.25-x)\text{Na}_2\text{O}\cdot 0.75\text{SiO}_2$  glasses. The experimental  $V_f$  values (O) are obtained from density data given in [27]. The calculated  $V_f$  values are obtained from equation (29). The calculated values agree well with those obtained from experimental data. This result reveals that in mixed alkali silicate glasses all sites do maintain the associated space as is the case in the corresponding binary glass.

In figure 7 is also shown the change in the free volume of the sites of  $\text{Li}^+$  and  $\text{Na}^+$ ,  $V_{f(\text{Li})}$  and  $V_{f(\text{Na})}$ , respectively. Although the total free volume decreases slightly with composition, there is a marked change in  $V_{f(\text{Li})}$  and  $V_{f(\text{Na})}$ . A linear increase in  $V_{f(\text{Li})}$  and a linear decrease in  $V_{f(\text{Na})}$  are observed when increasing  $\text{Li}_2\text{O}$  content. The lines intersect each other at nearly equal

concentrations of alkali oxides. The increase in  $V_{f(Li)}$  would cause an increase in the mobility of  $Li^+$  ions, whereas an opposite effect would arise for  $Na^+$  ions. These effects might well be connected with the phenomenon known as ‘the mixed alkali effect’. This explains the opposite changes in the mobility of different alkali ions in mixed alkali glasses [28, 29].

## 5. Conclusion

The presented model seems to be useful in calculating the volume of spaces associated with various ions in silicate glasses. The obtained volumes with the given relations predict free volumes that agree with experimental values for binary and mixed alkali silicate glasses. The model can be used to follow the change in the free volume due to each alkali oxide in mixed alkali silicate glasses. The results show that, in such glasses, the free volume related to a certain type of alkali oxide increases with increasing content.

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