

MOLAR VOLUME OF SOME SODIUM SILICATE AND SODIUM BOROSILICATE GLASSES

Z. A. EL-HADI*, H. FAROUK**, F A KHALIFA and F. A. MOUSTAFFA

* Z. A. El-Hadi, Chemistry Department, University College For Girls, Ain-Shams University, Heliopolis, Cairo, Egypt.

** H. Farouk, Physics Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

Glass Research Laboratory, National Research Centre, Dokki, Cairo Egypt.

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ABSTRACT

In spite of density is considered as one of the most important and characteristic properties which can be used only for confirming the structure of different types of glass, it is more liked to explain the glass structure in terms of the molar volume than density as the former deals with the spatial distribution of the ions forming that structure.

Such investigations of the density measurements and the molar volume calculations aimed to throw some light on the structure of some sodium silicate and sodium boro-silicate glasses and possibly on the glass structure.

The experimental results obtained showed that the values of the molar volume decreased with the gradual increase of the soda content in sodium silicate glasses which may be due to formation of the more non bridging oxygens. Also, for sodium boro-silicate glasses the values of the molar volume were found to decrease with increasing of the soda content and this can be explained according to the type of the introduced cations and their arrangements in the glassy network structure.

INTRODUCTION

Density, which is one of the most important and characteristic properties of the glass, was early used for the study of the glass constitution and also for the quality control in the glass industry; while the molar volume, which is defined as the mean molecular weight of the glass composition divided by its density, is used for the study of the glass structure. The subject of the glass density has been covered by many authors such as Turner¹, Morey² and Huggins³. Smallman⁴ put forward

the hypothesis that all the glass properties are functions of the density change. Some authors considered that the glass density is to some extent additive and can thus be calculated on the basis of the glass composition⁵. Jen et al⁶ suggested a model for describing the bridging to non-bridging oxygen ratio as a function of the glass composition; and the calculated values of the glass density, based on this model, were in excellent agreement with the experimental values. Some measurements of density in the $X\text{PbO} \cdot (1-X)\text{B}_2\text{O}_3$ system were reported by Shaw and Uhlmann⁷, where X is the composition molar fraction, and the results obtained were in good agreement with those obtained by Klemm and Berger⁸ for the same system. Recent studies on the density of some cal- borosilicate and silicate glasses were carried out⁹. Sanad et al¹⁰ investigated the role of the halid ions on the density and the molar volume of some sodium silicate glasses containing vanadium and their results were explained on the basis of polarization, field strength and ionic radii of the different corporated cations. It is more likely to explain the glass structure in terms of molar volume than density as the former deals with the spatial distribution of the ions forming that structure¹⁰; and the change in the molar volume with the molar composition of an oxide is suggested to explain the preceding structural changes through a formation or modification process in the glass network. The purpose of the present work is to throw some light on the change in both the molar volume and the structure of some sodium silicate and sodium borosilicate glasses and possibly on the glass structure.

EXPERIMENTAL

Raw materials melting and preparation of the glass samples:

The raw materials used, for all the glass preparation, were of chemically pure grade. Silica was introduced in the form of finely pulverised Dutch sand of the highest grade available. Sodium oxide was introduced as sodium carbonate while boric oxide was introduced in the form of boric acid.

All the melts were made in platinum-2 % rhodium crucibles in a gas furnace. The temperature of melting ranged from 1400 to 1600 °C and the duration of melting was four hours. After complete melting, the molten glass was annealed at the appropriate temperature. Grinding and polishing were carried out in the usual way but with minimum amount of water, and in the final stages of polishing paraffin oil was used.

Density measurements:

The density of each glass sample was determined, using Archimedes method, according to the following formula:

$$\rho = \frac{a}{a-b} \times 0.86 \quad (1) \dots \text{where,}$$

ρ is the density of the glass sample;

a is the mass of the glass sample in air;

b is the mass of the glass sample in xylene; and

0.86 is the density of xylene.

Molar volume calculations:

The following formula was used for calculating the molar volume of the glass samples investigated in the present work:

$$V_m = \frac{M \times \text{mole fraction}}{\rho} \quad (2) \dots \text{where;}$$

M is the molar mass of the constituent oxides;

mole fraction means the mole fraction composition of the different constituents; and

ρ is the density of each glass sample.

RESULTS AND DISCUSSION

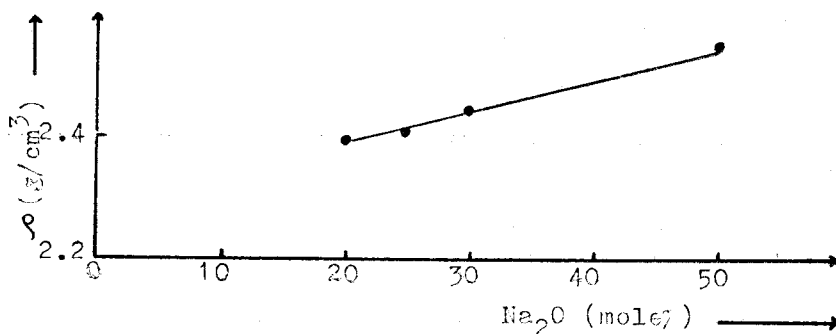
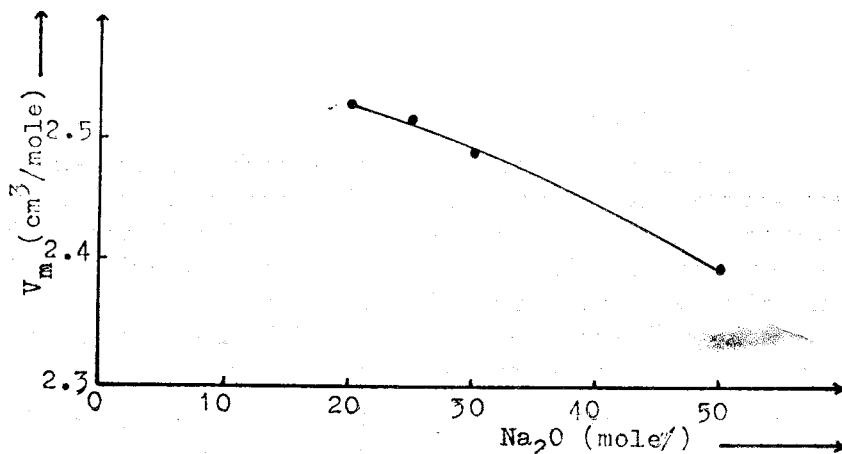
a. Sodium silicate glasses:

The chemical compositions and the values of the density measurements and the molar volume calculations for the sodium silicate glasses studied are given in Table (1) and are shown in Figs. (1 & 2), from which it can be seen that the values of the density increase from 2.3881 to 2.5485 g/cm³ with the gradual increase of the soda content while the values of the molar volume decrease from 25.29 to 23.93 cm³/mole. The experimental results obtained can be discussed as follows:

Concerning the glass density, Winkelman et al^{5a} proved that the additive calculation of this is possible by the multiplication of a suitable factor of the various oxide percentages in the glass. If these calculations were to provide exact results, the conclusion could be drawn that the

Table I. Chemical compositions and the values of density and molar volume of a number of sodium silicate glasses.

Glass No.	Glass composition (mole %)		Density molar volume	
	SiO ₂	Na ₂ O	g/cm ³	cm ³ /mole
1	80	20	2.3881	25.29
2	75	25	2.4052	25.25
3	70	30	2.4396	24.89
4	50	50	2.5485	23.93

Fig. 1. represents the values of density (g/cm³) versus the soda content of a number of sodium silicate glasses.Fig. 2. represents the values of molar volume (cm³/mole) versus the soda content of a number of sodium silicate glasses.

glass is virtually a mixture of the constituent oxides. The density is in close connection with the volume, and is expressed in 10^{-24} cm³ units. For simple oxide glasses, the value of the volume is always higher than that for the crystalline modification of the corresponding oxide¹¹. The density of the glass is an expression of the volume effect of the constituent ions, that is it depends on their nature, number and on the way by which they can enter the glass structure⁶. It is well known that the nature of silica-glass is composed of rings of SiO₄ groups linked together to form three-dimensional network¹² in which the alkali ions occupy the interstices. Also, it was stated that¹³ the introduction of soda in soda-silica glasses results in the formation of "single-bonded" or "non-bridging" oxygen atom; and the sodium ions are linked to the surrounding oxygens by bonds which are much more ionic and also much weaker than the silicon oxygen bonds. Thus, the structure of the alkali silicate glasses is weaker than that of vitreous silica¹³. As the alkali oxide content is increased, more and more non-bridging oxygens are formed until eventually the material consists of isolated SiO₄ tetrahedra linked together by ionic R-O bonds, where R is the sodium ion present. Therefore, the increase of the soda content in the glasses studied is responsible for increasing the number of the non-bridging oxygens and this may cause a decrease in the volume of the glass network structure, and this may be the reason for the increase in the values of density, i.e., the decrease in the values of the molar volume.

b. Sodium boro-silicate glasses:

The chemical compositions, the values of the density and the calculated values of the molar volume of the glasses studied are given in Table (2) and are shown in Figs. (3-8), from which it can be seen that the values of the density increase with the gradual increase of the soda content while the values of the molar volume decrease. The experimental results obtained can be discussed as follows:

In the alkali borate glasses, the boron atoms are always part of the glass network and can be surrounded by either three or four oxygen atoms. Thus, no modifiers are required for the boron oxide to act as network former in the boro-silicate glasses but one is required for the boron atom to be four-fold coordinated by the oxygen to the extent of one excess oxygen atom. Accordingly, the effect of increasing the soda content, i.e., decreasing the boric oxide content can be understood by recalling the change in the boron coordination. Therefore, the increase in the values of the density, i.e., the decrease in the values of the molar volume for

the glasses studied can be seen to be nearly additive⁹; also the positive curvature for all the curves of density may be explained due to the assumption of Show and Uhlmann⁷.

All the above conclusions are in complete agreement with the experimental results obtained.

Table 2. Chemical compositions and the values of density and molar volume of a number of sodium boro-silicate glasses.

Glass No.	Glass composition (mole %)			Density molar volume	
	SiO ₂	Na ₂ O	B ₂ O ₃	g/cm ³	cm ³ /mole
4	50	50	—	2.5485	23.93
5	50	40	10	2.5444	24.24
6	50	30	20	2.5397	24.56
7	50	20	30	2.5120	25.11
8	50	10	40	2.2147	28.80
9	66.66	33.33	—	2.5183	24.08
10	66.66	26.66	06.66	2.5078	24.37
11	66.66	20.00	13.33	2.5033	24.60
12	6.666	13.33	20.00	2.4409	25.42
13	66.66	06.66	26.66	2.1772	28.71
2	75	25	—	2.4052	25.25
14	75	20	05	2.4502	24.83
15	75	15	10	2.4385	25.09
16	75	10	15	2.3702	25.96
17	75	05	20	2.2050	28.07

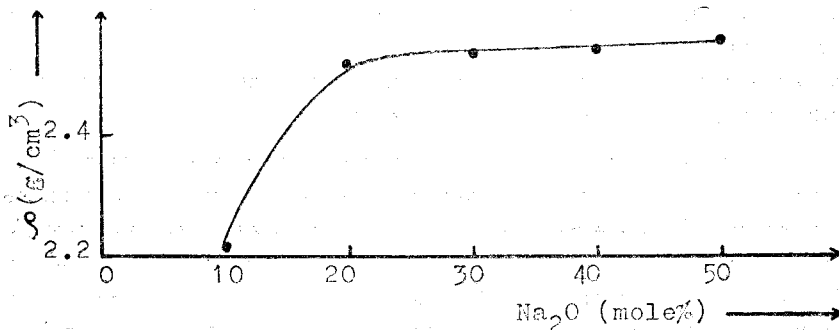


Fig. 3. represents the values of density (g/cm³) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (4-8).

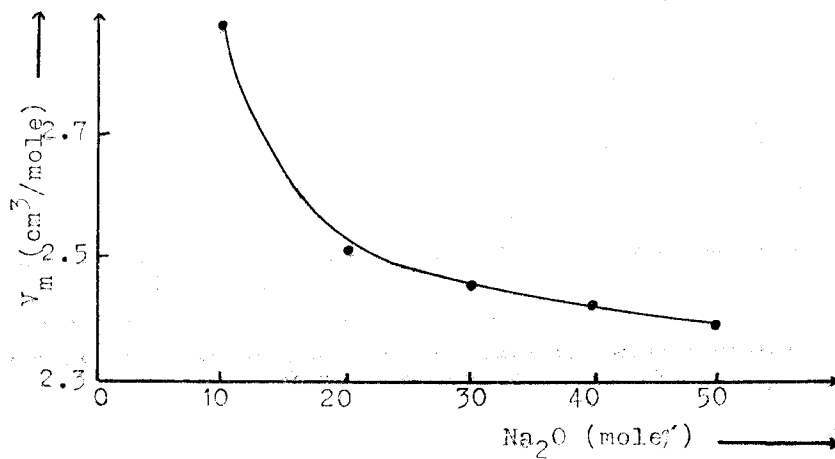


Fig. 4. represents the values of molar volume (cm^3/mole) versus the soda content of a number of sodium borosilicate glasses, Glasses No. (4-8).

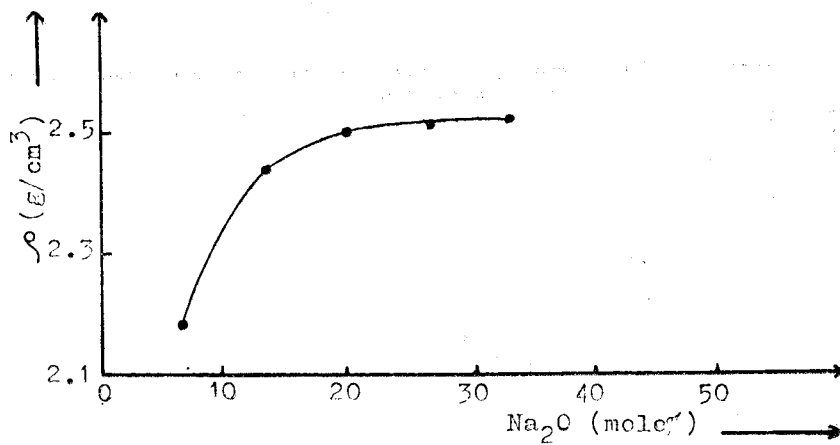


Fig. 5. represents the values of density (g/cm^3) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (9-13).

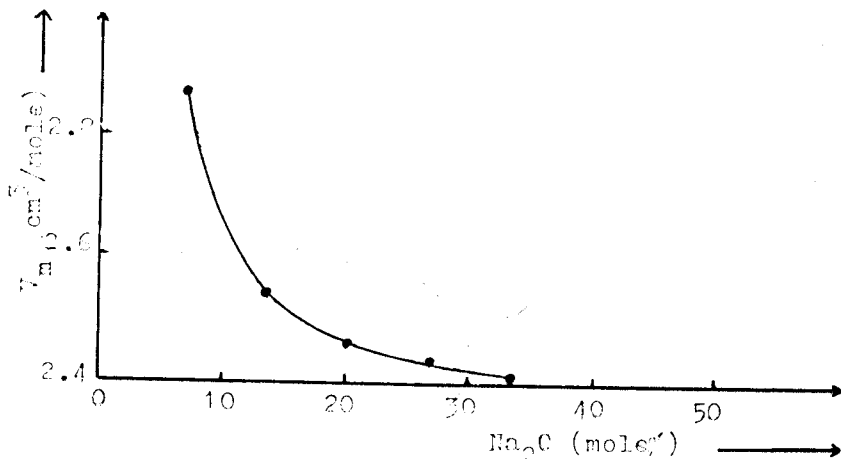


Fig. 6. represents the values of molar volume (cm^3/mole) versus the soda content of a number of sodium borosilicate glasses, Glasses No. (9-13).

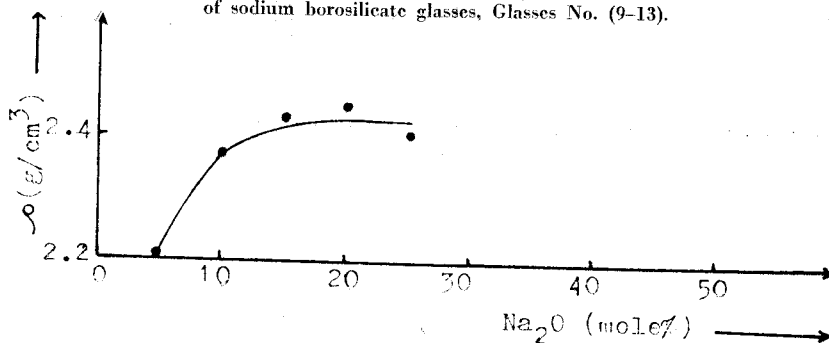


Fig. 7. represents the values of density (g/cm^3) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (2-17).

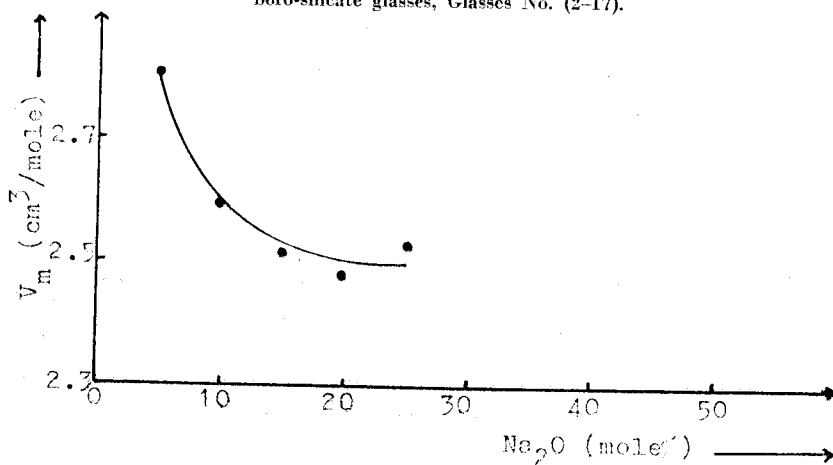


Fig. 8. represents the values of molar volume (cm^3/mole) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (2-17).

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