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MOLAR VOLÜME OF SOME SODİUM SİLİCATE AND SODIUM BOROSILICATE GLASSES

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

*** Z. A. El-Hadi, Chemistry Department, üniversity College For Giriş, Ain-Shams Univer- sity, Heliopolis, Cairo, Egypt.**

**** H. Farouk, Physics Department, Faculty of Science, Al-Azhar üniversity, 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 volüme 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 volüme calculations aimed to throw some light on the structure of some sodiçum silicate and sodium boro-silicate glasses and possibly on the glass structure.

The experimcntal results obtained showed that the values of the molar volüme 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 volüme 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 netvvork 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 volüme, which is defined as the mean molecular weight of the glass com- position devided by its density, is used for the study of the glass structure. The subject of the glass density has been covered by many aut- hors such as Turner[1], Morey2 and Hugginsb Smallman[4] put forward tlıe hypotlıesis that ali the glass properties are functions of the density change. Some authors considered tlıat tlıe glass density is to some ex- tent additive and can thus be calculated on the basis of the glass composition[5]. Jen et al[6] suggested a model for describing the bridging to non- bridging oxygen ratio as a nınction of the glass composition: and the calculated values of the glass density, based on this model, were in ex- cellent agreement with the experımental values. Some measurements of density in the XPbO. (1-X)B_2O_3 system were reported by Shaw and Uhlmann[7], where X is the composition molar fraction, and the results obtained were in good agreement with those obtained by Klemn and Berger[8] for the same system. Recent studies on the density of some ca- bal, boro-silicate and silicate glasses wcre carried out°. Sanad et al[10] investigated the role of the halid ions on the density and the molar volüme 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 volüme than density as the formcr de- als with the spatial distribution of the ions forming that structure[10]; and the change in the molar volüme 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 volüme and the structure of some sodium silicate and sodium boro-silicate glasses and possibly on the glass structure.

EXPERIMENTAL

Raw materials melting and preparation of the glass samples:

The raw materials used, for ali the glass preparation, were of ehemi- cally püre grade. Silica was intıoduced 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.

Ali the melts were rnade in platinium-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 mol- ten glass was annealed at the appropriate temperature. Grinding and polishing werc 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 Archime- des method, according to the following formula:

$$p = \frac{\quad}{a-b} X\ 0.86 \qquad (1)$$ ..... whcre,

p is the density of the glass sample;

a is the mass of the glass sample in air;

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

0.86 is the density of xylene.

Molar volüme calculations:

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

$$\bar{V}m = \frac{M \text{ X mole fraction}}{P} \quad (2)$$ .... where;

M is the molar mass of the constituent oxides;

mole fraction means the mole fraction composition of the different cons- tituents; and

p 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 volüme 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 / cm^3 with the gradual increase of the soda content while the values of the molar volüme decrease from 25.29 to 23.93 cm^3 / 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 suitab- le factor of the various oxide percentages in the glass. If these calculations were to providc exact results, the conclusion could be drawn that the

Table 1. Chemical compositions and the values of density and molar volüme of a number of sodium silicate glasses.

Glass No.	Glass compositi-on (mole %)		Density	molar volüme
	SiO_2	Na_2O	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

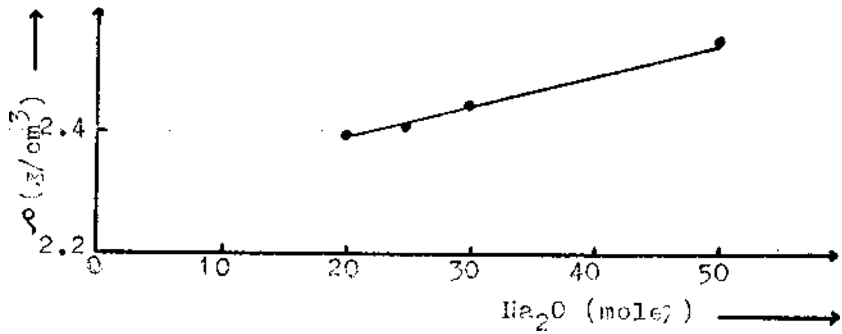

Fig. 1. represents the values of density (g/ cm^3) versus the soda content of a number of sodium silicate glasses.

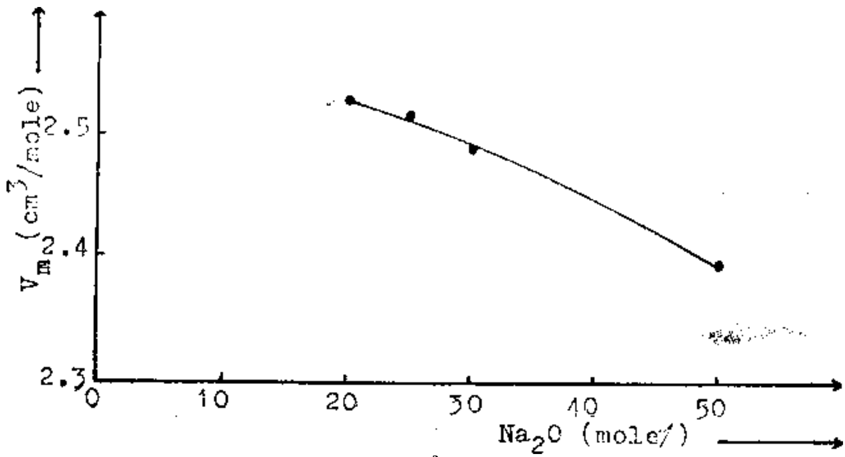

Fig. 2. represents the values of molar volüme (cm^3 / mole) versus the soda content of a number of sodium silicate glasses.

glass is vertually a mixture of the constituent oxides. The density is in close connection with the volüme, and is expressed in 10”^{24} cm? units. For simple oxide glasses, the value of the volüme is always higher than that for the crystalline modification of the corresponding oxide[11]. The density of the glass is an expression of the volüme effect of the constituent ions, that is it depends on their nature, number and on the way by which they can cnter the glass structure[6]. It is well known that the na- tuıe of silica-glass is composed of rings of SİO4 gıoups linked together to form three-dimensional network[12] in which the alkali ions occupy the interstices. Also, it was stated that[13] 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 silica[13]. As the alkali oxide content is increased, more and more non-bridging oxygens are formed until eventially the rnaterial consists of isolated SİO4 tetrahedra linked together by ionic R-0 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 volüme 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 volüme.

b. Sodium boro-silicate glasses:

The Chemical compositions, the values of the density and the cal- culated values of the molar volüme 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 volüme decrease. Tlıe experinıental results obtained can be discussM as follows:

In the alkali borate glasses, the horon 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 horon oxide to act as network former in the boro-silicate glasses but one is required for the horon atom to be four-fold coordinated by the oxygen to the extent of one excess oxygen atom. Accordingly, the effect of increasmg the soda content, i.e., decreasing the boric oxide content can be understood by recalling the change in the horon coordination. Therefore, the increase in the values of the density, i.e., the decrease in the values of the molar volüme for the glasses studied can be seen to be nearly additive[9]; also the positive curvature for ali the curves of density may be explained due to the as- sumption of Show and Uhlmann[7].

Ali the above conclusions are in complete agreement with the ex- perimental results obtained.

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

Glass No.	Glass composition (mole %)			Density molar volüme	
	$S\dot{I}O_2$	Na_2O	B_2O_3	g/ ™5	cm^3 /mole
4	50	50	—.	2.5485	23.93
S	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
1 16	75	10	15	2.3702	25.96
1 17	75	05	20	2.2050	28.07

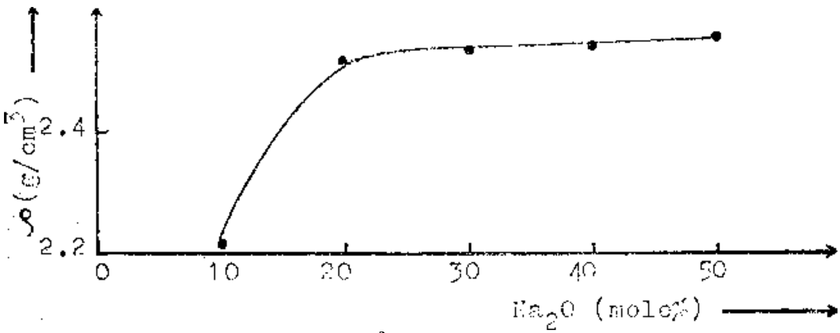

Fig. 3. represents the values of density (g/ cm³) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (4-8).

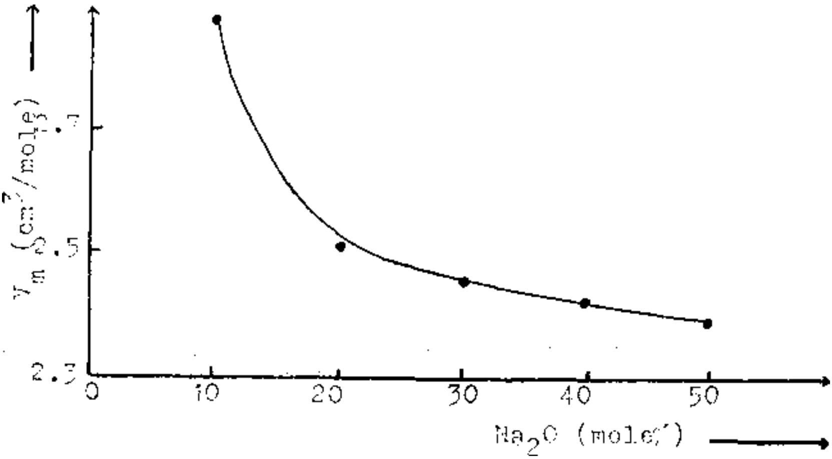

Fig. 4. represents the values of molar volüme (cm^3 / mole) versus the soda content of a number of sodium borosilicate glasscs, Glasses No. (4-8).

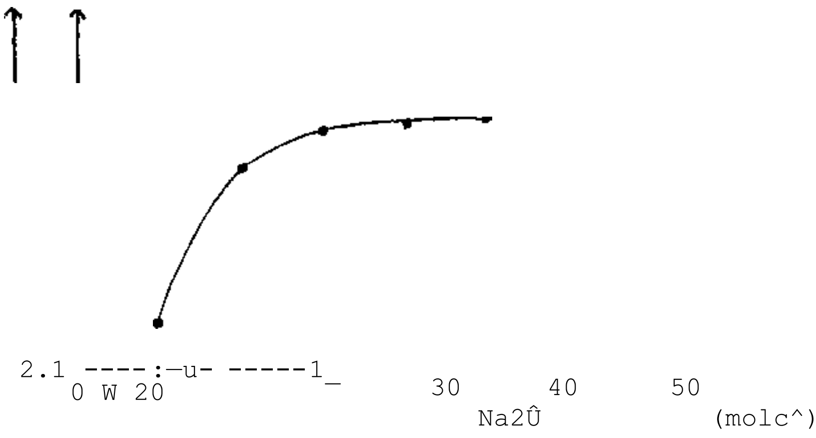

Fig. 5. represents the values of density (g / cm^3) versus the soda content of a number pf sodium boro-silicate glasses, Glasses No. (9-13).

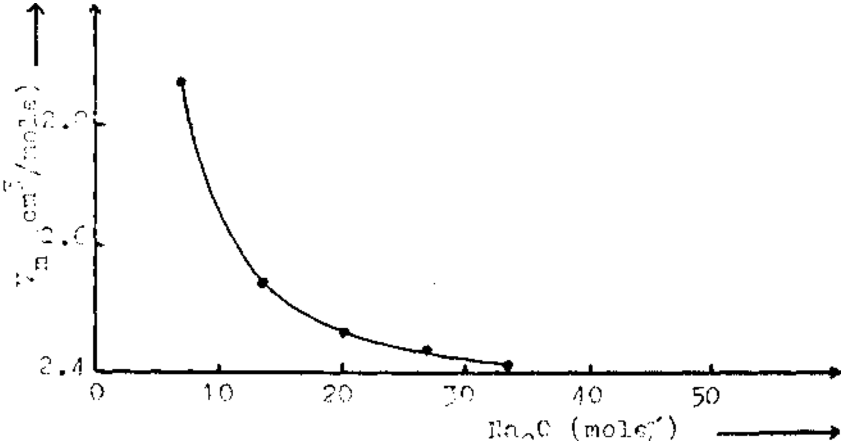

Fig. 6. represents the values of molar volume (cm³ / mole) versus the soda content of a number of sodium borosilicate glasses, Glasses No. (9-13).

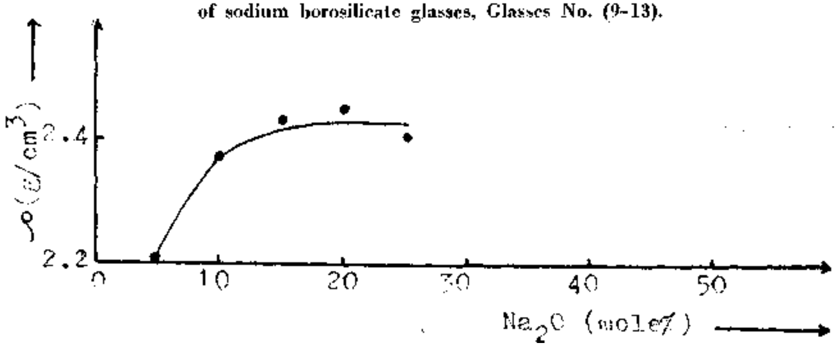

Fig. 7. represents the values of density (g/ cm³) versus the soda content of a number of sodium boro-silicate glasses, Glasses No. (2-17).

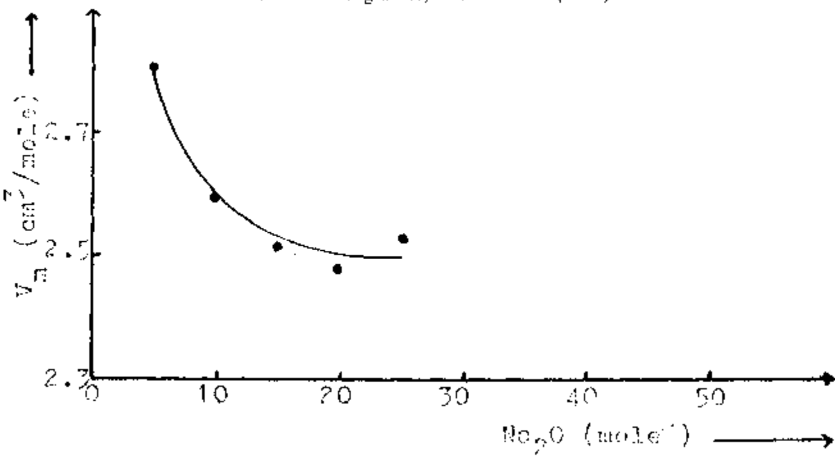

Fig. 8. represents the values of molar volüme (cm³ / mole) vcrsus the soda content of a number of sodium boro-silicate glasses, Glasscs No. (2-17).

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