

PROPERTIES OF SILICATE GLASSES AS A FUNCTION OF THE RATIO OF p -ELECTRONS TO THE NUMBER OF ATOMS

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Abstract. It has been shown¹ that if the ratio of the p -electrons in the outermost shell to the number of atoms (A) in an oxide or a system is greater than 2.6, the system can form a glass. Experiments conducted on some of binary, tertiary and quaternary silicate glasses have revealed that viscosity at strain point of the tertiary glasses and refractive index, density and thermal expansion coefficient in temperature range 0–100°C are an inverse function of this ratio nP/A . However, the viscosity values for binary glasses are directly proportional to the ratio nP/A .

Glassy state of an oxide or a system lacks the internal structure which is characteristic of crystalline forms, that is, the atoms have only a random arrangement and not the regular lattices which become manifest in perfectly formed crystals as geometric solids. Every oxide or a system when its melt is cooled down has not got the tendency to form a glass. There are certain prerequisites, which it fulfills if it is to exist in the glassy state. Zachariasen² holds responsible the geometrical rearrangement of the oxides while Stanworth³ says that the electronegativity is a predominant factor in glass formation. Dietzel⁴ pleads the utility of the field strength of the cations. Winter¹ says that the ratio, between the p -electrons and the number of atoms greater than 2.6, is necessary for glass formation.

The merit of Winter's theory, with a few exceptions,⁵ is that it attributes the cause of the vitreous state not to the presence of certain kinds of atoms but the chemical bonding between the atoms. The p -electron is a directed bond which owing to the extended form of its orbits, easily gives rise to covalent bond. Moreover, directed bonds imply the tendency to 'open' structures and high viscosities, both of these features promote glass formation. In a similar manner the relationship between field strength and viscosity and thermal expansion has been mentioned by some of the previous workers.⁶

The aim of the present investigation is to describe the properties of the binary, tertiary and quaternary systems of glasses as a function of this ratio nP/A . The present study will also allow empirically to predict the working behaviour and the properties of glasses by the knowledge of the ratio of p -electrons to the number of atoms, just from the chemical composition.

Experimental

Batch Ingredients. The quartz used had 99.98% SiO_2 whereas the other batch materials like soda ash, calcium carbonate, alumina were of analytical grade.

Preparation of Glass. The binary glasses were melted in platinum crucible at temperatures not

exceeding 1300°C. The tertiary and quaternary glasses needed temperatures above 1425°C. The melts were made free of bubbles and seeds and were poured on cast iron plates. After proper annealing, the samples were stored in desiccator for further experiments.

The glass compositions found by chemical analysis and those calculated from batch composition agreed within reasonable limits of experimental error. The results are given in Table 1.

Measurement of Refractive Index. The glass samples were ground in a gun-metal pestle mortar and the refractive index was obtained by the immersion method using standard liquids of known refractive indices.⁷ The results are shown in Table 2.

Determination of the Coefficients of Thermal Expansion and Strain Points. The coefficient of thermal expansion of tertiary and quaternary glass compositions was determined after DIN 52328,⁸ using the dilatometer of the firm Leitz. The results for binary compositions are interpolated from those given by Karkhanawala⁹ in Table 2. The strain points are found by the plots of $\Delta l/l$ against temperature and the results are also given in Table 2.

Density Determination. Density was measured on small specimens by the method of Archimedes for binary, tertiary and quaternary glasses. Toluol due to its low surface tension was used as the immersion liquid. Larger specimens were ground to the precise dimensions of rectangular prisms and densities were computed from their volumes and weights. Measurement were repeated for discrepancies of 0.5% or greater in the values obtained by both methods.

Results and Discussions

The present study extends over a wide range of chemical compositions. Among the glass compositions chosen are the binary, tertiary and quaternary systems of glasses containing varied amounts of mono, di- and trivalent cations. As can be seen from Table 1, the first three binary glass compositions contain increasing amounts of Na_2O , while no. 6 and 7 glasses have CaO increased in these.

TABLE 1. CHEMICAL COMPOSITION OF THE GLASSES STUDIED.

Speci- fica- tion	Molar composition	Weight (%) composition			
		Na ₂ O	CaO	Al ₂ O ₃	SiO ₂
1	Na ₂ O: 3SiO ₂	25.61	—	—	74.38
2	Na ₂ O.2.5SiO ₂	29.24	—	—	70.75
3	Na ₂ O.1.5SiO ₂	40.78	—	—	59.21
4	Na ₂ O.0.1Al ₂ O ₃ CaO.4.9SiO ₂	14.68	13.26	2.41	69.63
5	Na ₂ O.0.2Al ₂ O ₃ CaO.5.8SiO ₂	14.55	13.14	4.69	676.0
6	Na ₂ O ₃ .0.75CaO.5.25SiO ₂	14.79	10.02	—	75.17
7	Na ₂ O.CaO.5SiO ₂	14.83	13.39	—	71.77

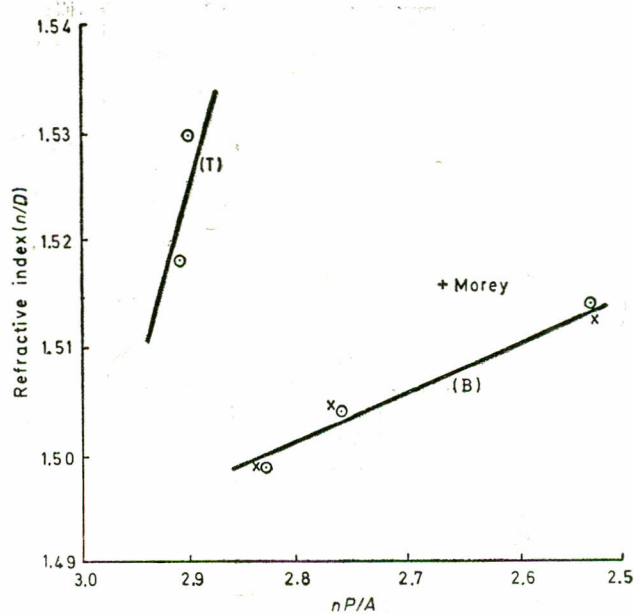
TABLE 2. nP/A AND THE PROPERTIES OF GLASS.

Specifica- tion	nP/A	Refractive index (n_D)	Strain point	Thermal expansion ($\times 10^{-7}$) (0–100°C)	Density (g/cm ³)
1	2.83	1.499	430	109.2	2.4260
2	2.76	1.504	415	121.1	2.4589
3	2.53	1.514	406	151.6	2.5210
4	2.89	1.530	528	77.5	2.5312
5	2.88	1.523	532	77.3	2.5382
6	2.93	1.518	525	75.4	2.4845
7	2.90	1.530	540	77.6	2.5223

The results of the refractive index measurements are shown in Table 2 and plotted against the Winter's ratio nP/A (Fig.1). The results reported by MOREY¹⁰ for binary glasses are also shown in Fig.1 for comparison and are found to be in close agreement with those found in the present study. With increasing Winter's ratio, except for glasses containing Al₂O₃ the refractive index decreases. For binary and tertiary glasses although the trend is the same yet the slope of the tertiary glass compositions curve (T) is very sharp. The successive additions of network modifiers, decreasing nP/A , increase the refractive index because the interstices are filled in and complex structural groups having sufficient amounts of easily polarisable non-bridged O⁻² ions are formed. According to the findings, of Rindones,⁹ the Al³⁺ ions in presence of alkali ions form AlO₄ tetrahedra and enter the three dimensional silica network. Therefore, the velocity of light in glasses with progressive additions of Al₂O₃ nos. 6 and 7 remains the same or improves a bit and the refractive indices register a similar change.

The thermal expansion coefficients in the temperature range 0–100°C are given in Table 2 and for binary glasses are plotted against the Winter's ratio nP/A . Binary and tertiary glass compositions register an increase in thermal expansion coefficient with decreasing Winter's ratio nP/A . Further the increase in the thermal expansion coefficient with decreasing nP/A , is conspicuous in case of binary glass compositions. The expansion remains almost constant for quaternary glasses containing Al₂O₃.

SiO₂ glass due to its strong internal directional bonds and the bridged oxygen ions links has the lowest thermal expansion coefficient. The addition of network modifiers, decreasing nP/A , subsequently decreases the bridged oxygen ions and as a result thereof the ionic character of the silica network is

Fig. 1. Desendence of refractine index on $\eta p/A$.

enhanced. The defects produced in the form of nonbridged oxygen ions and ionic bonds in the three dimensional silica network increase the thermal expansion coefficients of the binary, ternary and quaternary glasses in general.

Due to the bridging action $\equiv\text{Si}-\text{O}-\text{Ca}-\text{O}-\text{Si}\equiv$, of the divalent calcium ions at low temperatures, the nonbridged oxygen ions are consumed and the expansion decreases to some extent. Therefore, the addition of Ca⁺⁺ ions increases the thermal expansion coefficient slowly and steadily but not to the extent as in binary alkali glasses.

Quaternary glass compositions even if Al₂O₃ is increased from 2.4 to 4.7% register almost a negligible thermal expansion increase because of the appearance of Al₃₊ ions as AlO₄ groups and entering the silica network. This behaviour of Al₂O₃ in the presence of alkali oxides is contrary to the other network modifiers. Such an abnormal behaviour has already been reported by previous workers.¹¹

The flow parameters gradually grow as the electrostatic bonding of the nonbridged O⁻² ions of the damaged silica network by the divalent calcium ions slowly proceeds as the temperature approaches the strain point ($\eta 10^{13}$ poise). This phenomenon results in closed packing of the silicate structure, and hence an increase in the viscosity values (Fig. 2). The strain point for the glass Na₂O.0.5CaO.5.5iO₂ ($nP/A=2.91$), reported in Fig. plot T, is taken from a previous work.¹² The binary alkali silicates lack this electrostatic bonding capacity due to their monovalent charge and hence the viscosity decreases with decreasing winter's ratio nP/A or increasing alkali contents. The strain points (10^{13} poise) for glasses containing Al₂O₃ are also given in Table 2. The addition of Al³⁺ ions also consumes the nonbridged O⁻² ions and give rise to AlO₄ groups which become a part and parcel of three dimensional SiO₂ network and strain points register an increase.

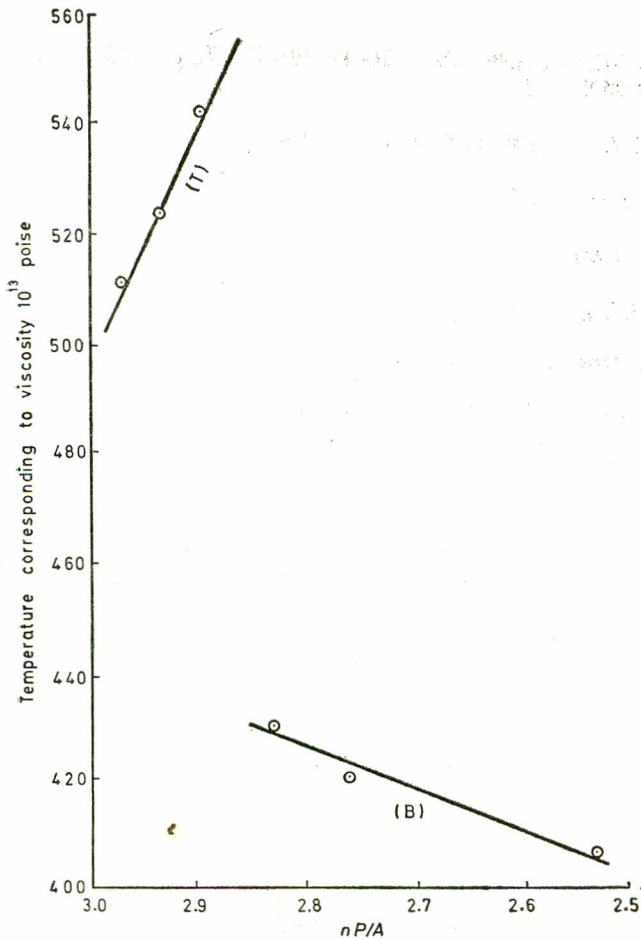


Fig. 3. Strain points ($\eta=10^{13}$ poise) for binary and tertiary glasses.

The values of the experimentally determined density for binary, tertiary and quaternary glasses are given in Table 2. As is evident from the results the density of all types of glasses increases when the

amount of network modifiers increases (nP/A decreases at the expense of silica. The density values for binary and ternary glass $\text{Na}_2\text{O}\cdot\text{O.75Ca}\cdot\text{0.5.25SiO}_2$ are also mentioned in previous studies¹² and are very closer to the present findings. The increase in density is explained on the basis that when oxides of the ions network modifiers are introduced, the cations go into the interstices (near the nonbridged O^{2-} to balance the charge) while O^{2-} ions add to the packing of the glass structure. The greater the addition of the cations, the greater the filling of the cavities.

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