Study of the Relationship between Specific Volume and Composition for Me_2O–SiO_2 and MeF–BeF_2 Glasses with a Random Graph Model

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Abstract: Graph theory is applied to study the relationship between specific volume and chemical composition of several alkali silicate and alkali fluoroberyllate glasses. A new topological index is introduced which is a measure of the rigidity of covalently bonded structures. Changes in rigidity arise from variations in composition and can be related to changes in specific volume. As glasses are polymers without regular patterns, probabilistic techniques are employed to study random graphs in order to calculate graph invariants and topological indices for these structures. Taking into account the high values obtained for the correlation coefficients, the results achieved are good.

Introduction

Many of the physical and chemical properties of substances are intimately related to the topological properties of their structures such as connectedness and adjacency, branching, bridging, linearity, cyclicity, etc. In order to study correlations between physicochemical and structural properties convenient quantitative measures of such topological properties are needed. Graph theory presents appropriate mathematical models. In fact, every chemical structure has an associated graph in which the vertices represent specific atoms within that structure and the edges represent the chemical bonds. On the other hand, mathematical functions that associate one real number to each graph are defined by means of special formulae that manipulate local graph invariants. These functions, called topological indices, are defined in such a way that they supply the appropriate quantitative description of the required topological properties. In this way, graph theory successfully supported studies of correlations between properties and structure, especially in organic chemistry for simple molecules and also, although to a lesser extent, for polymers with regularly repeating patterns.[1-3]

Here these techniques are applied in inorganic chemistry to study polymers with disordered structures. To do so, we must deal with random graphs. In fact, the processes of formation and rupture of such disordered structures can be represented in our model by means of certain random graph generation processes. Although various authors have studied random graphs previously,[4,5] a new and particular treatment is presented in this paper.

The purpose of this work is to show an example of the application of random graphs in chemistry, particularly to the correlation between the specific volume and the degree of rigidity of the chemical structure for some inorganic glasses.

Graph Model

The smallest building unit in silicate glass structures is generally accepted to be the $[SiO_4]$ tetrahedron. These tetrahedra are interconnected in a disordered spatial network. We can associate with this structure a graph in which the vertices represent Si atoms and the edges the Si–O–Si bridges. In the case of SiO_2 glass, each group $[SiO_4]$ is (if the surface is neglected) linked to four other tetrahedra through its vertices.[6] Thus, the graph associated with SiO_2 glass is one in which every vertex is adjacent to another four vertices. Such a graph is called[7] a regular graph of degree 4 and in this paper it will be denoted by G_0.

On introducing alkali oxides some of the Si–O–Si linkages are broken: the O atom coming from the alkali oxide is incorporated into the network as a nonbridging oxygen, while the alkali ions are situated in the voids in the network formed by the $[SiO_4]$ tetrahedra, near the single-bonded oxygen ions. In our graph model, this network rupture is represented by an edge deletion from the original graph G_0.

As alkali oxides are added to silica glass the structure becomes increasingly broken up. The network loses its rigidity becoming looser and more easily distendable. In addition, the alkali ions that are located in the voids induce a network expansion to a degree that depends on the size and charge of those ions.[6] Thus, the network expansion is related to the loss of the structural rigidity.

This network expansion is a physical property that can be measured through the change in specific volume. On the other hand, the network rigidity is a structural property, and so a particular topological index is necessary to give a quantitative description of it. The following θ index is introduced for that purpose:

$$\theta(G) = X(G)A(G) \tag{1}$$

where $X(G)$ is the Randič index[8] of the graph G and $A(G)$ is the number of edges in G. Then the relative loss of rigidity when G is compared with G_0 is

$$\delta = (\theta(G_0) - \theta(G))/\theta(G_0) \tag{2}$$

Everything discussed above can also be applied to the alkali fluoroberyllate glasses.[9] In fact, the structure of these glasses is similar to that of the silicate glasses. In this case, the basic structural units are the $[BeF_4]$ tetrahedra that are joined together at their corners through the Be–F–Be ionic linkages. On introducing alkali fluoride a similar process of linkage breakdown takes place.

Let us consider a specimen of glass of composition $x\mathrm{Me}_a\mathrm{Y}\cdot(1-x)\mathrm{ZY}_2$, where Me = alkali and ZY_2 = BeF_2 or SiO_2, and let $V(x)$ be the volume of this glass per mole of former cation Z. The relative difference between $V(x)$ and the molar volume of the ZY_2 glass, $[V(x) - V(0)]/V(0)$, is a measure of the relative expansion of the structure due to the introduction of $x/(1-x)$ moles of $\mathrm{Me}_a\mathrm{Y}$ per mole of ZY_2.

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If there are N atoms of Z in this specimen, its associated graph, G, is a spanning graph[7] of G_0, with N vertices. Obviously, $A(G_0) = 2N$. Given that one edge is deleted for each Me_aY group introduced, we can assume that G is obtained from G_0 by deleting $Nx/(1 - x)$ edges. Thus,

$$A(G) = [2 - x/(1 - x)]N \tag{3}$$

To calculate $X(G)$ we should know which edges are deleted. However, in our case we cannot know this because the process is assumed to be random. For this reason, in order to estimate $\theta(G)$, the expected value of X after the process of edge deletion, $E(X)$, must be employed instead of $X(G)$

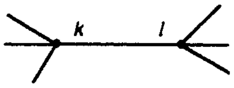
$$X(G) = \sum_{\substack{i,j=1\\ i\leq j}}^{i,j=4} (ij)^{-0.5}A_{ij}^{(G)}$$

where $A_{ij}^{(G)}$ is the number of edges in G joining vertices of degree i and j, and then

$$E(X) = \sum_{\substack{i,j=1\\ i\leq j}}^{i,j=4} (ij)^{-0.5}E(A_{ij}) \tag{4}$$

To calculate $E(A_{ij})$ it is necessary to take into account the way in which the edges are deleted. Several theories[10-18] have referred to the degree of order of the network and to the randomness in which the network rupture takes place when introducing modifiers. Here, a completely random process of edges deletion in which each edge in G_0 has the same probability of being deleted is considered.

Let us consider two adjacent vertices k and l and the joining edge (kl).



The edges of G_0 can be classified with regard to the edge (kl) into four classes: (1) the edge (kl), (2) the other three edges incident with the vertex k, (3) the other three edges incident with the vertex l, and (4) the remaining $2N - 7$ edges. Suppose that after deleting D edges the edge (kl) remains undeleted, and the degrees of vertices k and l become i and j, respectively. In that case the deleted edges must be the following: $(4 - i)$ from class 2, $(4 - j)$ from class 3, and the other $(D - 8 + i + j)$ from class 4. The probability of that event is

$$P_{ij} = \binom{3}{i-1}\binom{3}{j-1}\binom{2N-7}{D-8+i+j}\bigg/\binom{2N}{D}$$

Since the glass specimens studied are formed by a vary large number of atoms the limiting value when $N \to +\infty$ can be used.[19]

$$P_{ij} = \binom{3}{j-1}\binom{3}{i-1}\frac{(2N/D - 1)^{i+j-1}}{(2N/D)^7} \tag{5}$$

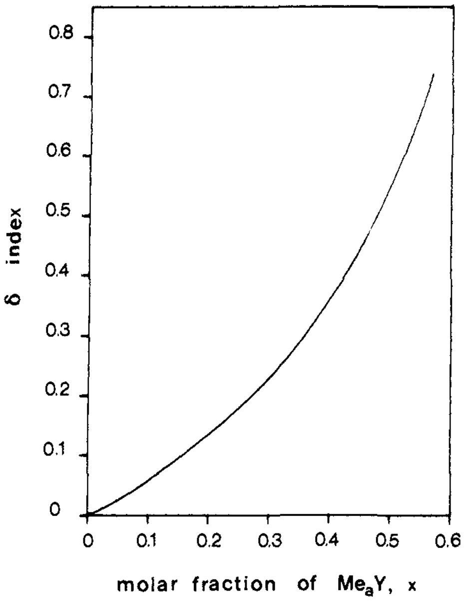


Figure 1. Relation between δ index and molar fraction of Me_aY given by eq 7.

Table I. Glass Systems Studied

glass system	range of compositions studied (molar fraction of Me_aY)	no. of glasses studied	ref
Li_2O-SiO_2, 25 °C	0.26–0.40	9	20
Na_2O-SiO_2, 25 °C	0.13–0.46	9	20
K_2O-SiO_2, 25 °C	0.11–0.30	9	20
Li_2O-SiO_2, 1300 °C	0.22–0.46	6	21
Na_2O-SiO_2, 1300 °C	0.19–0.50	5	21
K_2O-SiO_2, 1300 °C	0.16–0.33	7	21
$LiF-BeF_2$, 20 °C	0.36–0.57	10	9
$NaF-BeF_2$, 20 °C	0.27–0.58	14	9
$KF-BeF_2$, 20 °C	0.17–0.52	18	9
$RbF-BeF_2$, 20 °C	0.07–0.34	11	9

Then the probability of any edge (kl) of G_0 to become an edge joining vertices of degree i and j is

$$P\{(kl)\} = \alpha_{ij}P_{ij}$$

where

$$\alpha_{ij} = \begin{cases} 2 \text{ if } i \neq j \\ 1 \text{ if } i = j \end{cases}$$

and the expected value of $A_{ij}^{(G)}$ is

$$E(A_{ij}) = \sum_{\substack{(kl)\\ \text{edges of } G_0}} P\{(kl)\} = 2N\alpha_{ij}P_{ij} \tag{6}$$

For a glass of composition $x\mathrm{Me}_a\mathrm{Y}\cdot(1 - x)\mathrm{ZY}_2$

$$2N/D = 2(1 - x)/x$$

Then from eq 1–6

$$\delta = 1 - (2 - 3x)^2[x^3 + 3(2 - 3x)x^2/\sqrt{2} + \sqrt{3}(2 - 3x)^2x + 0.5(2 - 3x)^3]^2/[64(1 - x)^8] \tag{7}$$

A plot of δ as a function of χ is shown in Figure 1.

Results and Discussion

The relationship between the specific volume of the glass per mole of network former and the structural rigidity index has been

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Table II. Results of the Correlations of the Relative Increase of Network Volume per Mole of Former Cation with the δ Index[a]

glass system	parameters in eq 8 K	β	S	R	parameter K' in eq 9
Li_2O–SiO_2, 25 °C	0.752	1.113	0.0053	0.9987	0.70
Na_2O–SiO_2, 25 °C	1.380	1.066	0.0074	0.9987	1.35
K_2O–SiO_2, 25 °C	2.260	1.034	0.0024	0.9999	2.27
Li_2O–SiO_2, 1300 °C	1.147	1.050	0.0029	0.9999	1.13
Na_2O–SiO_2, 1300 °C	1.851	0.975	0.0038	0.9999	1.99
K_2O–SiO_2, 1300 °C	3.057	1.005	0.0042	0.99996	3.22
LiF–BeF_2, 20 °C	0.730	1.044	0.0026	0.9999	0.73
NaF–BeF_2, 20 °C	1.027	1.059	0.0057	0.9996	1.02
KF–BeF_2, 20 °C	1.525	1.014	0.0066	0.9996	1.55
RbF–BeF_2, 20 °C	2.047	1.059	0.0090	0.9995	1.97

[a] S = standard deviation; R = correlation coefficient.

studied for several glass systems: LiF–BeF_2, NaF–BeF_2, KF–BeF_2, RbF–BeF_2 at 20 °C; Li_2O–SiO_2, Na_2O–SiO_2, K_2O–SiO_2 at 25 °C and at 1300 °C. The correlation of the relative increase of network volume per mole of former cation with the δ index for each system was calculated by the least-squares method. The number of glasses studied and the range of compositions covered for each system are shown in Table I. The values of $[V(x) - V(0)]/V(0)$ were calculated from the experimental data taken from the references listed in Table I, and the values of δ were calculated by using eq 7. In all cases the general form of a Walker-type equation[22] was obtained:

$$[V(x) - V(0)]/V(0) = K\delta^{\beta} \qquad (8)$$

The results of these correlations are summarized in Table II.

Except for the Li_2O–SiO_2 system at 25 °C, the correlation coefficient exceeded 0.9995. These results are better than the correlations obtained on the basis of the number of edges only instead of the θ index.

All values of β are very close to 1. That means that for a given glass system at a given temperature the relative increase of network volume per mole of former cation is practically proportional to the δ index. In spite of the fact that the hypothesis of a single value of β for all the cases cannot be accepted statistically, eq 9,

$$[V(x) - V(0)]/V(0) = K'\delta^{1.038} \qquad (9)$$

where K' takes for each system the values listed in Table II, predicts the volume $V(x)$ of these glasses with an error less than 1.3% over the whole range of concentrations studied. If we compare glasses of the same group we observe that the constant K' increases with the size of the modifier ions. This fact was expected from our previous statement about the location of these ions in the voids of the network.

It can also be observed that for the alkali silicate glasses, which have been studied at two different temperatures, the constant K increases with temperature. Obviously, for the same degree of structural rigidity, the network expansion increases with the degree of thermal oscillation.

Conclusions

In this paper we have illustrated the way in which graph theory can help us to study relationships between properties and structure for polymeric disordered structures. The results obtained for some inorganic glasses show a very simple relationship between the δ index (defined as a measure of the structural rigidity and directly related to the chemical composition) and the degree of expansion of the network due to the introduction of modifier ions.

Registry No. SiO_2, 7631-86-9; BeF_2, 7787-49-7.

Theoretical Analysis of Acetyltriazene and the Mechanistic Implications of Its Reaction with Acid

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Abstract: Theoretical calculations have been carried out on the protonation of 3-acetyltriazene in order to provide insight into the mechanism of the acid-catalyzed decomposition of acyltriazenes. We have previously reported the results of calculations on a series of alkyltriazenes. Ab initio RHF calculations were carried out at the 3-21G level to determine the optimized SCF energies and geometries of the neutral molecule and some site-specific protonated species. This allowed an estimate of the proton affinity at each site. Experimental studies on alkyltriazenes indicated that initial protonation at the N_3 site was critical in the acid catalysis mechanism, even though the calculated proton affinities indicated that N_1 was a more basic site. In the case of the acyltriazenes, the calculations showed that the proton affinity at N_3 was much lower than that at N_1 or at the carbonyl oxygens. The geometrical changes produced by protonations at the various sites indicated that the N_2–N_3 bond shows a propensity for cleavage upon protonation at either N_3 or at the carbonyl oxygen. These results suggest that acid-catalyzed decomposition of acetyltriazene would involve the breakage of the N_2–N_3 bond, rather than the hydrolysis of the acyl group. Subsequent experimental data supported this conclusion. A linear scaling method was applied to the geometric and energetic results from the semiempirical AM1 code to predict the results of the 3-21G calculations with a surprising degree of success. A predictor function to allow AM1 geometries and proton affinities to provide a good estimate of 3-21G results is given, and the limitations are discussed.

I. Introduction

We initiated a theoretical study of various triazenes as a means of elucidating some of the mechanistic details of their aqueous decomposition reactions. Extensive laboratory studies have been carried out to improve the syntheses and document the decomposition kinetics of many representative members of the triazene family. The importance of these compounds stems from their ability to decompose into reactive diazonium ions. The alkyltriazenes undergo a specific acid-catalyzed decomposition to alkyldiazonium ions and the corresponding amines (eq 1).

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