Corelations between compositions–properties–basicity in vitreous oxides systems

D.Radu
Cathedra SIMO, University "Polytechnic" Bucharest, P.O. Box 12-134, Bucharest, Romania

C.Mazilu, M.Eftimie
National Glass Institute, Th.Pallady, No 47, 74854, Bucharest, Romania

It is known that in the majority of cases, the glass properties are calculated in relation with the oxidic composition, the shape of dependence functions differing from author to author and provinding different precisions of calculus. Considering the oxidic glasses as chemical systems, the importance of their acido-basic characteris emphasised. In this way it is possible to colligate the different properties, especially those concerning the composition (the viscousness, dilatation coefficient, the refraction index, etc.), with fundamental of the vitreous systems, the basicity. On this basis in the paper a model on how to calculate the basicity percentage (pB) is presented, taking into account the different coordinations which apear within the glasses for the present ions. The obtained basicity for different typs and compositions of glasses has been corelated with their viscousness at different temperatures.

1.Introduction

The vitreous systems represent solids which from the point of view of the arranging degree are placed between the ideal crystals (perfectly arranged) and the amorphe systems(perfectly disordered). Goldschmidt (1927), Zachariasen (1932), Dietzel (1942), Huggins and Sun (1947), Muller (1967), Goodman (1976) and othershave proposed a series of theories which correlated the oxides capacity to form vitreous systems with a series of atomic characteristics such as: ionic rays, coordination number, ionisation potential, oxidizing cipher, etc. A synthesis of these theories is presented in [1,2]. Inspite of the registered successes through this way of approaching the structure and characteristics of the simple vitreous systems, a major deadlock could not be surpassed: the impossibility of extending the quantitative analysis to complex glasses. In this work, the use of the basicity degree as a structural inglobing parameter is proposed to which a series of properties of the vitreous systems are correlated.

2. The theoetical basis

The description of the acid-basic characteristic of glasses has known different theoretical and experimental approaches. Yet, only recently, relations that permit the quantitative evaluation of this characteristic have been reported in the specialty literature.

2.1.The evolution of the acid-basis theories

Along the time numerous acid-basis theories have been developed, which have more or less limited application domains. Latest researches in the domain of glass have led to new and interesting ideas concerning the acid-basis concept for glasses. A synthesis of these theories (Paul and Douglas, Lux and Flood, Weyl and Marboe, Lewis, etc.) is presented in [3,4]. The majority of the elaborated theories concerning the acid-basis character of glasses, have in commune the qualitative aspects of this characteristic. At the same time a series of experimental methods to determinate this property has been developed. Far less are the essays of theoretical calculus.

In this way, Duffy and Ingram [5], have established that the optical basicity of a glass can be calculated from the parameters attributed to the constitutive oxides and from stereochemistry. Such calculus, when applied to a series of compositions in a system, indicate the tendency of the basicity and usually approaches that what is experimentally obtained using probing ions, such as Pb^{2+}. They have also proposed a relation for the optical theoretical calculus Λ., with the form:

$$\Lambda = X_{AO_{a/2}} \cdot \Lambda(AO_{a/2}) + X_{BO_{b/2}} \cdot \Lambda(BO_{b/2}) + \ldots \quad (1)$$

$X_{AO_{a/2}}, X_{BO_{b/2}}$ - molar fractions of the constitutive oxides ;

$\Lambda(AO_{a/2}),\ \Lambda(BO_{b/2})$ - optical basicity of individual oxides.

2.2. Establishin the basicity degree of the glass

In another approach, Balta and his co-workers [6] have proposed the notion of basicity degree pB, taking into account the ionic character of the chemical bonds. Considering that O^{2-} has in principle the greatest power to donate electrons, also proved by the extremely low ionization potential (between -6.5 and 7.35eV) it has been attributed with the maximal value, respectively pB=100%. This species of oxygen, the existence of which is highly unprobable, constitutes an end of the oxide basicity, thus becoming evident its natural character. In this conditions the calculus of the basicity degree, in %, for an oxide can be done with the relation Balta and Radu :

$$\lg pB = 1{,}9(NC)^{0{,}02} - 0{,}023P_i/NC \quad (2)$$

in which NC is the coordination number of the cation in relation with the oxygen,
P_i - the ionization potential of the cation in the given valence state.

In the case of the oxidic glasses, the basicity degree pB is calculated with the relation:

$$pB = \sum_{i=1}^{n} f_i \cdot pB^i \quad (3)$$

in which f_i is the gravimetric force of the i oxide and pB_i the degree of basicity of the i oxide.

Balta [7] also proposes a quantitative method of determination the basicity of the oxide glasses using the absorption by transferring the charge of the 3d ions. The experimental measure utilized as a measure of the basicity is the minimal energy, expressed as wave number, to which takes place the absorption by transferring the charge of the $Cu^{2+}O_6$ complex. In this way, a dependence of pB with the wave number, ν (cm-1), was obtained in the form:

$$pB = 151 - 0.00259 \cdot \nu \quad (4)$$

This way the experimental determination of pB becomes possible by measuring ν of the maximal absorption and by calculating pB with the 4th relation.With rare exceptions, the differences between the pB values calculated with the 4th relation and the theoretical ones, calculated with the 2nd relation, do not exceed +0.5%.

2.3.Correlations between pB and the optical basicity,the electronic polarizability,electronegativity.

Although they have different starting basis, between the optical basicity, the coefficients of Duffy and Ingram and the basicity degree pB, exists a close correlation. In the 1st table a series of oxides usual in glasses, the values for the basicity degree calculated conforming to the 2nd relation and the optical basicity of the glasses Λ. are presented .

Element	NC	Oxide	pB(%)	Λ	$\alpha_{O^{2-}}$	$1/\Lambda$	$1/\alpha_{O^{2-}}$	x(S)	x(G)
Li	4	Li2O	83.6	1.00	-	1.00	-	0.70	0.95
Na	6	Na2O	89.0	1.15	-	0.87	-	0.65	0.90
K	9	K2O	94.2	1.40	-	0.71	-	0.60	0.80
Cs	12	Cs2O	97.5	1.70	-	0.59	-	0.54	0.75
Mg	4	MgO	73.3	0.78	1.71	1.28	0.585	1.09	1.20
Ca	6	CaO	80.8	1.00	2.49	1.00	0.4	1.05	1.00
Sr	8	SrO	88.9	1.10	3.07	0.90	0.326	1.01	1.00
Ba	8	BaO	89.5	1.15	3.70	0.87	0.27	0.90	0.90
B	3	B2O3	44.8	0.42	1.39	2.38	0.72	2.64	2.00
Al	4	Al2O3	61.6	0.60	1.46	1.66	0.685	1.60	1.50
Si	4	SiO2	49.4	0.48	1.41	2.08	0.71	2.22	1.80
P	4	P2O5	38.0	0.40	1.33	2.50	0.752	2.96	2.10

We can observe that although Mg, Ca, Na, Li, Al present different NC and corresponding to these, different pB values, for each of them there have been selected the NC values that best correspond to the correlation of Λ with pB. With this data, utilizing the method of mathematical regression the following relation is obtained:

$$1/\Lambda = 3.7282 - 0.0326pB \quad \text{with the correlation coefficient } r = 0.995 \qquad (5)$$

Also in the 1st table the electronic polarizability as well as the electronegativities after Sanderson and Gordy. These are the structural parameters which influences essentially the basicity of the glass.With these parameters too the basicity degree correlates closely resulting the relations: $1/\alpha_{O^{2-}} = 1.156 - 0.009 \cdot pB$ with the correlation coefficient r=0.95 (6)

$$x(S) = 4.2538 - 0.0394 \cdot pB \quad \text{with the correlation coefficient } r = 0.974 \qquad (7)$$

$$x(G) = 2.9636 - 0.0232 \cdot pB \quad \text{with the correlation coefficient } r = 0.9926 \qquad (8)$$

3. Results and discussions

3.1. The relationship between viscosity and the basicity degree

The viscosity of the silicates is depending on the polymerization degree of the glasses and melting. The dependence of the temperature on the viscosity of the silicate melting's can be represented in the undercooled liquids domain (between T_{liq}.- T_g) by the relation Vogel-Fulcher-Tammann : $\lg \eta = A + B/(T-T_0)$ (9) where A, B and T_0 – constants Yan, Wood and Mills[8] have utilized the optical basicity in the developing of a model to estimate the viscosity of glasses, at temperatures between T_{liq}. and T_g. This way, for the silicate glasses, the relation between the optical basicity and the A, B, T_0 associated to the (9)th equation, were obtained by the analysis of the multiple regression from the viscosity-temperature data presented by Lakatos in [9] .

$A = 0.2 + 2.35 \cdot \Lambda$ (10); $B = 10169 - 10530 \cdot \Lambda$ (11); $T_o = 758.1 - 368.9 \cdot \Lambda$ (12)

Taking into account the (5)th relation between the optical basicity and the basicity degree, the relations (10-12)th become:

$$A = \frac{474.78 - pB}{571.8 - 5 \cdot pB} \quad (13); \quad B = \frac{82.6 - pB}{0.011 - 0.98 \cdot 10^{-4} \cdot pB} \quad (14); \quad T_o = \frac{99.45 - pB}{0.15 - 0.0013 \cdot pB} \quad (15);$$

The values calculated for lg η with the (9)th and (13-15)th equations, have been compared with the values determined experimentally resulting a good concordance.

3.2. Correlations pB - viscosity

On the basis of three different sets of silicate glass compositions, Lakatos[9], the correlation of the glass basicity degree (calculated with the aid of the 3rd relation) with the temperatures experimentally determined for which lg η is 2, 4 and 6 was attempted. The first determined set is formed out of 11 silico-calcosodic glasses which is framed between the oxidic values (%gravimetric): SiO_2: 70÷76, Al_2O_3: 1,2÷1.3, Na_2O: 12÷15, CaO: 6÷12.

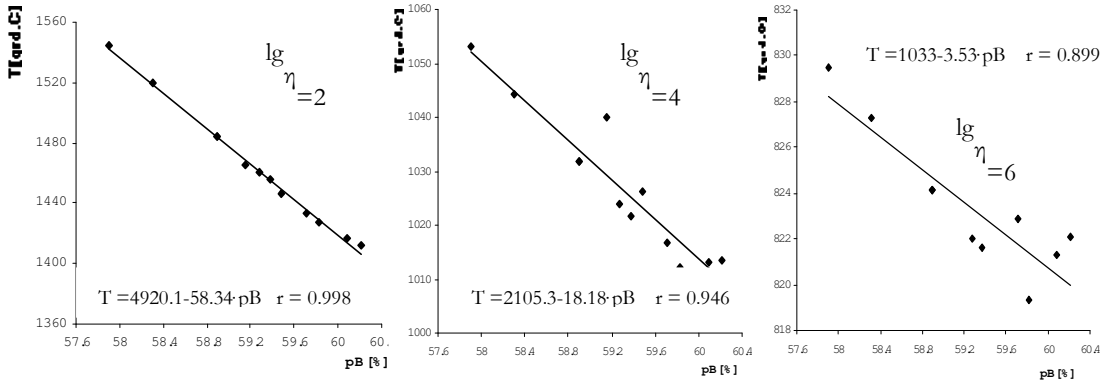

Fig. 1-3 Correlation's pB -T(°C) at lg η =2, 4 and 6 for the first set of compositions.

For lg η=6 two compositions which did not frame in the tendency followed by the others were eliminated.The second set of compositions(9 glasses), investigate the effect of the additions separated by Li_2O, BaO, ZnO, PbO, K_2O and frames between the oxide limits: SiO_2: 65÷73, Al_2O_3: 1.1÷1.25, Na_2O: 12÷14, CaO: 7÷12.

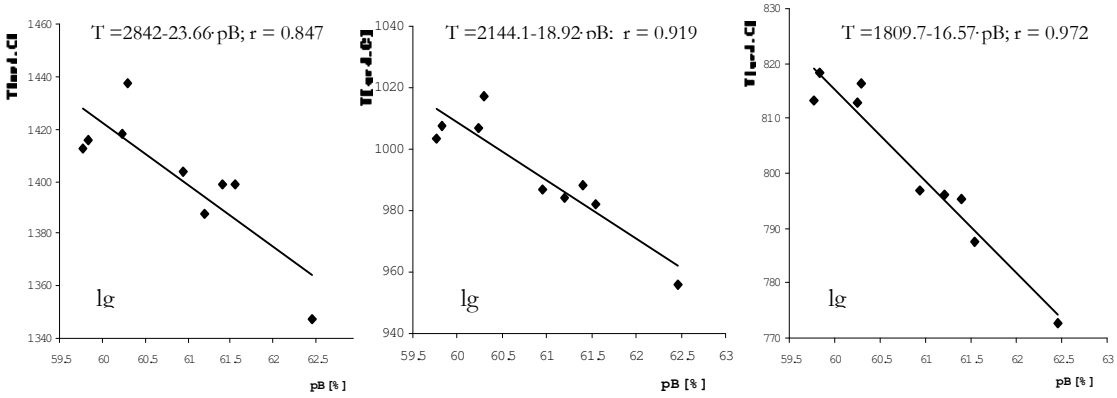

Fig. 4-6 Correlation's pB -T(°C) at lg η = 2, 4 and 6 for the second set of compositions.

For both sets can be observed the diminution of the temperature corresponding to a certain viscosity with the increase of the basicity degree of the glass as soon as the alkali content rised. At the same time the increase of the content in alkalis determines a more accentuated depolimerization of the silicate structure which determines a diminution of the viscosity of the glass or, at a constant viscosity, a diminution of the corresponding temperature.

3.3. Correlations pB - Tg, pB - Mg.

The bioactive glasses are defined as glasses that form chemical bonds with the bone cells and are used as vitreous coverings of the metallic prosthesis. For a series of 15 compositions of bioactive glasses, presented in[10], which are framed between the limits Na_2O: 0÷20, K_2O: 0÷15, CaO: 10÷20, MgO: 0÷5, B_2O_3: 0÷3, P_2O_5: 0÷6, SiO_2: 39÷70, the basicity degree has been calculated and has been correlated with Tg and Mg.

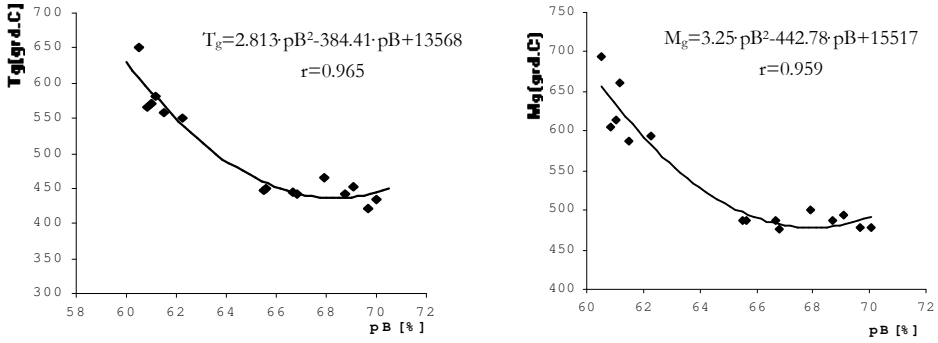

Fig. 17-18 The Correlation pB - Tg and pB - Mg.

A linear correlation of pB with Tg and Mg can be observed until approximately 65% pB, over this value, due to the content rich in alkalis, respectively to the depolimerization of the structure, the dependence pB on Tg and Mg is less evident as expected.

4. Conclusions

The basicity degree represents a synthetic indicator to which a series of properties of the glasses can be correlated.By its way of defining as well as by the very good correlation's in rapport with the electronic polarizability and elecronegativity, the basicity degree pB appears as a natural dimension of appreciating the glass basicity, sensible to diverse structural modifications. For diverse types of glasses a close correlation between the viscosity or/and the temperature at which the viscosity has certain values and the basicity degree is evidentiated.

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[1] H.Scholze, in *Le verre* (Ed. Dunod, Paris, 1990).

[2] P.Balta, E.Balta, in *Introduction to the Physical Chemistry of the Vitreous State* (Abacus Press, Kent, 1976).

[3] V.G.Konakov, A.B. Sholchmatkin, M.Shultz, Fiz.Khim.Stekla **20**, p. 443-448 (1994).

[4] S.Matsumoto,Y.Miura, T.Nauba in *17 Inter. Congress on Glass,* 1995, p. 72-77.

[5] A.I.Duffy, M.D.Ingram, J.Non-Cryst.Solids **21**, p. 373-411 (1976).

[6] P.Balta, C.Spurcaciu, D.Radu, O.Dumitrescu, J.Non-Cryst.Solids **71**, p. 69-75 (1985).

[7] P.Balta in *15 International Congress on Glass,* 1989, p. 211-214

[8] F.Y.Yan,F.J.Wood, K.C.Wills in *17 Intern. Congress on Glass,* 1995, p. 177-182.

[9] T.Lakatos, L.G.Johansson, B.Simmingskold, Glass Technol. **13**, p. 88-95 (1972).

[10] K.H.Karlsson, M.Ronulof, Glastech.Ber.Glass Sci.Technol. **71**, p. 141-145 (1998).