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IMPLICATIONS OF THE ACID-BASE CHARACTER FOR SOME FIXED VISCOSITY POINTS, FOR OXIDE VITREOUS SYSTEMS

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Considering the oxide glasses as chemical systems, the acid-basic character of the glasses has known in time, different theoretical approaches. One of the theories proposed the basicity percentage (pB) notion as a measure of the acid-base character for oxide glasses. This work shows that, by its defining mode, the basicity percentage is a complex parameter which considers a series of structural characteristics such as bond's ionicity percentage, coordination number, pB correlating in fact with all the other structural characteristics at an atomic level (the electrostatic field's strength, the electronegativity, the oxygen's electronic ability to polarize, the oxidation number, bonding energies, etc.).
Taking into account that the basicity percentage is an indicator which "senses" the modification of the structural characteristics of oxide glasses, it is to be expected that the properties which present interest (temperatures corresponding to the structural transformation, the thermal expansion coefficient, the refraction index, etc.) to have an important correlation with the basicity percentage. In the present work, a series of correlations between the values of some fixed viscosity points of practical interest and the basicity percentage for the studied glasses have been presented. These correlations are seen for some simpler glasses as well as for some complex oxide compositions of industrial type.

INTRODUCTION

The vitreous systems are solids that from the point of view of the degree of order are placed between the ideal crystals (perfectly ordered) and the amorphous systems (perfectly disordered).

Goldschmidt (1927), Zachariasen (1932), Dietzel (1942), Huggins and Sun (1947), Muller (1967), Goodman (1976) have proposed a series of theories which correlated the oxides capacity of forming vitreous systems with a series of atomic characteristics such as: ionic radii, coordination number, ionization potential, oxidation state, electronegativity, etc. A synthesis of these theories is presented. [1,2] At the same time, especially for the simple vitreous systems, a series of properties were correlated qualitatively and, sometimes, quantitatively with different structural characteristics at atomic level. Since now, with all recorded success this kind of approach for the simple vitreous systems' structure and characteristics, a major impediment could not be surpassed: the impossibility of using the quantitative analysis on complex glasses. This was the case for one fundamental property of the oxide glasses: their acid-base character.

1. The evolution of the acid-basis theories

In time numerous acid-base theories have been developed, having more or less limited application domains. Latest researches in the field of glass have led to new and interesting ideas concerning the acid-base 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 most of the elaborated theories concerning the acid-base character of glasses have in common the qualitative aspects of this characteristic. At the same time, a series of experimental methods to determine this property have 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 of glass. Such calculus, when applied to a series of compositions in a system,

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indicates the tendency of the basicity and usually approaches what is experimentally obtained.

2. Establishing the glass basicity (pB)

In order to evaluate the basicity of the oxide vitreous systems, Balta and co-workers [2, 6] have proposed the notion of basicity percentage (pB), taking into account the ionic degree of the chemical bonds. Considering that O^{2-} has, in principle, the highest electron donor power, also proven by the extremely low ionization potential (–6.5eV), it was assigned with the maximal value, pB=100%, respectively.

This oxygen species constitutes an end of the oxide basicity scale, thus showing its natural character. In these conditions, the calculation of the basicity (pB), in %, for an oxide can be done with the Balta and Radu relation: [2]

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

where: NC is the coordination number of the cation related to the oxygen;
P_i the ionization potential of the cation in the given valence state.

In the case of oxide glasses, the basicity (pB) is calculated with the relation:

$$pB = \sum_{i=1}^{n} c_i \cdot pB_i \quad (2)$$

where: c_i is the gravimetric fraction of oxide i;
pB_i the basicity of oxide i.

As the basicity percentage is a "sensitive" indicator of the characteristics and structural changes of the oxide glasses [6-8] it would be most probable that their properties, in a great proportion, present an important correlation with this parameter. In this direction, correlations have been reported in literature [2, 6-9] between pB and:

The vitreous transition temperature for binary and ternary silicate systems;

The refraction index for binary and industrial silicate glasses;

The biocompatibility of vitreous bio-materials;

The chemical stability of glasses, including the reinforcement fibers;

The interaction between glass melting – refracting bricks;

The reactivity of the raw materials batch, etc.

In present work, there are presented new results, for different types of industrial glasses, concerning the correlation of certain fixed points of viscosity with the pB.

THE THEORETICAL BASIS

As it can be seen from relations (1) and (2), the basicity percentage, besides the fact that it represents a natural scale for the oxide systems, also has the advantage that it is defined in comparison with a series of characteristics that mirror the structural characteristics of the vitreous system: coordination number, oxidation number, ionization potential. Besides these dependencies, a series of correlations were shown between the basicity percentage and other structural characteristics such as: the intensity of the electrostatic field, Z/a^2, electronic polarization capability of the oxygen ion, $\alpha_{O^{2-}}$, Sanderson's electronegativity, x(S), and Gordy's electronegativity, x(G). [10] Additionally, although they have different starting bases, between the optical basicity and the basicity percentage a strong interdependency was discovered [8] for the most often found oxides in the glass composition.

Generally, the established correlations have the form:

$$y = a - b \cdot pB\ ; \quad (3)$$

in which y is the considered structural parameter and a and b – coefficients.

In Table 1 the values of these coefficients are given taking into account the nature of the y parameter.

Table 1

The values of the statistic coefficients from relation (3)

Nr.	Nature of y parameter	a	b	Correlation coefficient, R
1	Z/a^2	3.1452	0.0330	0.980
2	$1/\alpha_{O^{2-}}$	1.1560	0.0090	0.950
3		4.2538	0.0394	0.974
4	x(S)	2.9636	0.0232	0.993
5	x(G)	3.7282	0.0326	0.995
	$1/\Lambda$			

There is also to be taken into account that a high value of the correlation coefficient is recorded in the case when the analysis extends to a greater number of oxides. In this way, by processing the primary data obtained for a number of 32 oxides, [11] the function that correlates the ability of polarization of oxygen ion with the pB is plotted in Fig. 1.

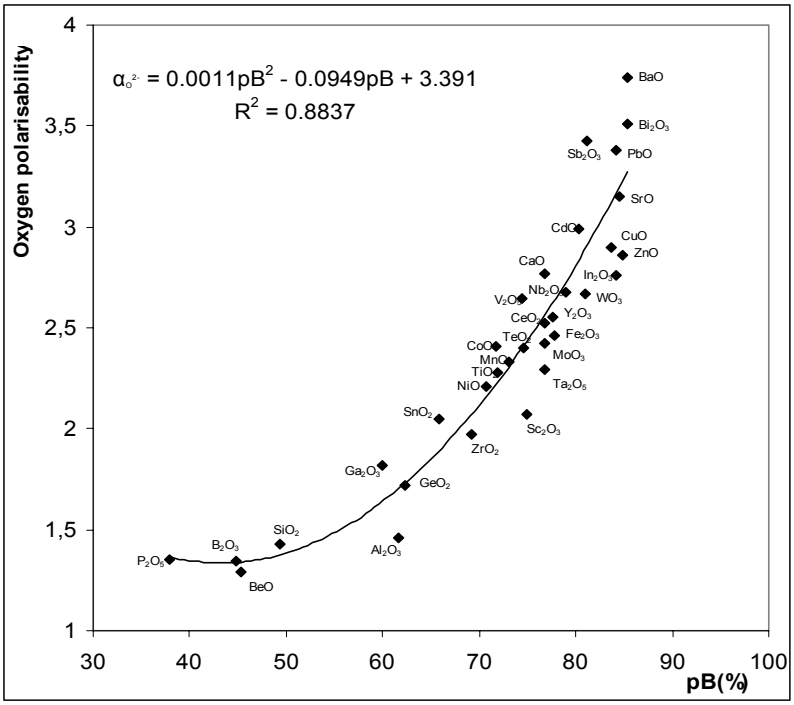

Fig. 1 – The dependence between the electronic ability to polarize of oxygen and the basicity percentage, for crystalline oxides.

More over, for the considered oxides, the dependencies of the form (3) were obtained between the bonding energy (O1s) E_b,[11] the bonding energy of the cation from the oxide, E_c,[11] and pB. These results are presented in Figs. 2 and 3, respectively.

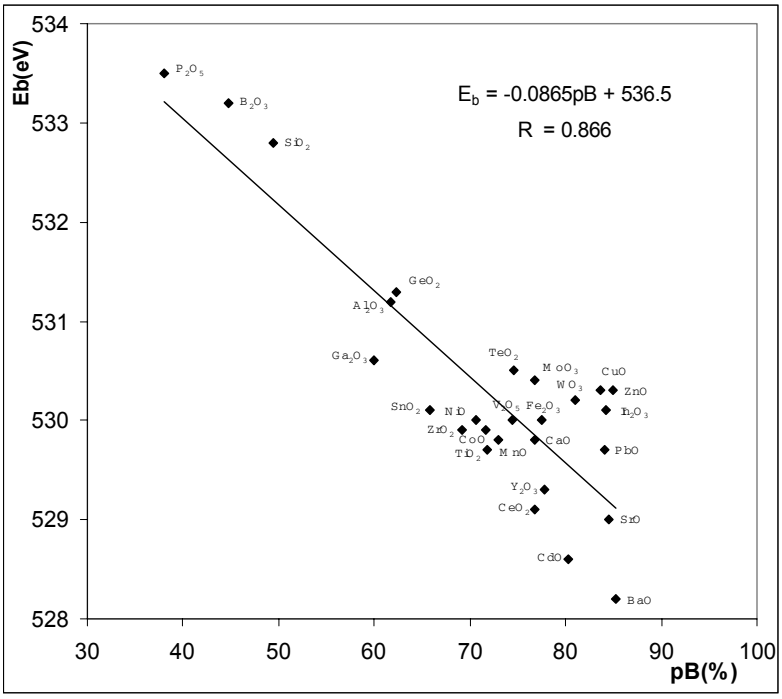

Fig. 2 – The dependence between the bonding energy (O1s) E_b and the basicity percentage, for crystalline oxides.

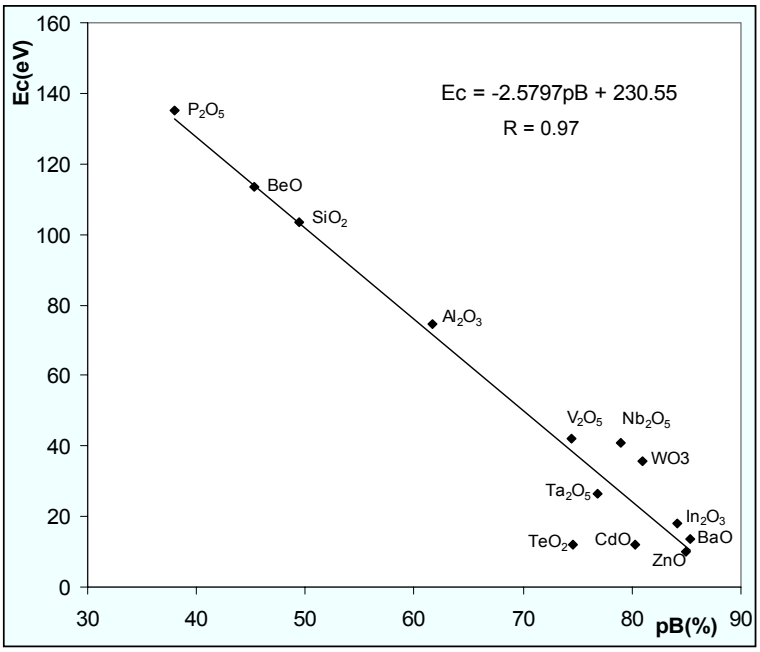

Fig. 3 – The dependence between the bonding energy of the cation in oxides E_B^c and the basicity percentage, for crystalline oxides.

The high values of the correlation coefficients associated to the Figs.1-3 seem to bring sufficient arguments to consider the pB a complex structural parameter which includes implicitely, as well as explicitely the majority of the structural characteristics of the atoms present within the crystalline oxides. From this point of view it is expected that a series of properties, such as thermal expansion coefficient and viscosity, to be correlated with the pB. This is because that effective values of some « fixed viscosity points » are influenced by the nature and the weight of oxides in the chemical composition, as well as by a series of structural particularities (the type and the way of interconnection of the coordination polyhedra, the energy of the cation-oxygen bonds, etc.), and the majority of the structural parameters are closely correlated with pB.

The dependence of the temperature on the viscosity of the silicate melts can be represented in the under cooled liquids domain (between $T_{liq.}$- T_g) by the Vogel-Fulcher-Tammann relation: [1,2]

$$\lg \eta = A + B/(T-T_0) \tag{4}$$

where A, B and T_0 – constants that depend on the oxide composition of glasses.

Yan, Wood and Mills [12] have used the optical basicity to develope a model to estimate the viscosity of glasses, at temperatures between $T_{liq.}$ and $T_{g.}$. This way, for the silicate glasses, the relations [12] between the optical basicity and coefficients A, B, T_0 associated to the equation (4), were obtained by the analysis of the multiple regression from the viscosity-oxide composition data presented by Lakatos in. [13]

Taking into account the relation between the optical basicity and the basicity percentage, the A,B and T_0 coefficients can be written in relation with pB :

$$A = \frac{474.78 - pB}{571.8 - 5 \cdot pB} \tag{5}$$

$$B = \frac{82.6 - pB}{0.011 - 0.98 \cdot 10^{-4} \cdot pB} \tag{6}$$

$$T_o = \frac{99.45 - pB}{0.15 - 0.0013 \cdot pB} \quad (7)$$

It can be seen that in such an approach, the viscosity of the glasses is put in dependency with the temperature, the chemical composition and a series of structural characteristics, correlated with the pB parameter which can be easily calculated.

RESULTS AND DISCUSSION

For the oxide vitreous systems (in particular), the viscosity represents one of the most important properties, for the melted glass, when lgη = 1- 4, as well as for the solid state glass, when lgη = 15- 16. This is motivated by the fact that viscosity is a property highly influenced by the structure of the glass. On the other hand, this property has an important role in different technological stages that are passed through until obtaining a finite product from the mix of raw materials (melting, homogenization, annealing).

Taking this into account, a series of viscosity "fixed points" were defined, such as: the vitreous transition temperature T_g, when lgη = 13.3, the processing interval, "the glass length" ΔT respectively, for which lgη ranges between 4 and 7.6, "the melting temperature", T_f, when lgη ≈ 2, etc. [1, 2]

1. The correlation between the vitreous transition temperature (T_g) and basicity (pB)

For a series of binary and ternary silicate glasses, the experimental data have shown a decrease of the T_g values with the increase of the pB. [8, 9] By processing some primary literature data, the verification of this type of dependency is also thought for glasses with complex oxide compositions.

Some inorganic glasses are also used as materials for waveguides in hi-tech domains such as: optical communication systems, optical integrated circuits, etc.

A series of compositions of oxide silicate glasses used as waveguide and lain down through the serigraphy process, are presented in.[14] They are framed in the base system SiO_2 –B_2O_3 – PbO(ZrO_2)- Na_2O- K_2O to which small quantities of Al_2O_3, BaO, La_2O_3, Bi_2O_3 can be added.

Knowing the oxide composition for a number of 16 glasses,[14] the basicity percentage was calculated with relations (1) and (2). In Fig. 4 the correlation between the measured values for T_g and pB is shown.

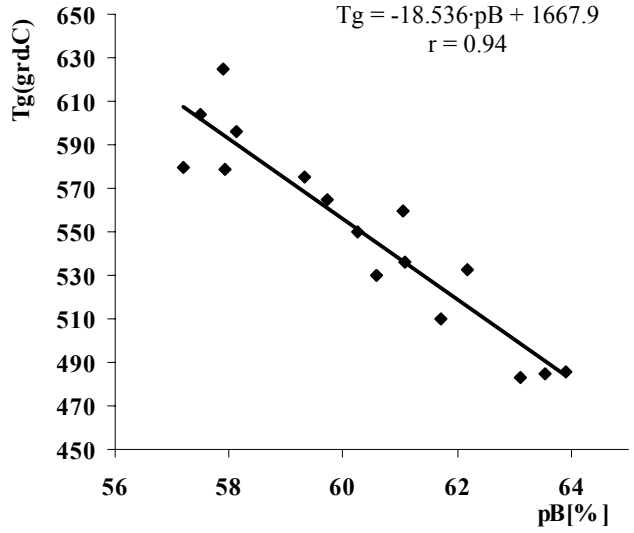

Fig. 4 – The correlation between T_g – pB.

A linear decrease of the vitreous transition temperature with an increase of basicity (pB) can be observed, with an increase of alkaline oxides quantity, respectively. The explanation consists in the decrease of the viscosity of glasses at the same temperature for the presented compositions, with the introduction of new quantities of network-modifying oxides. At the same time, it is known that alkaline oxides have higher basicities (pB) than the glass forming oxides that they replace in the structure of

the glass. As a consequence, a diminishing of the degree of polymerization of the vitreous structure is recorded, which leads in the end, to smaller values for the vitreous transition temperature.

An interdependency of the same nature was found for another category of glasses of great practical interest: bio-glasses. The bioactive glasses are defined as glasses that form chemical bonds with the bone cells and are used in prosthetics, in modern reparatory medicine.

For a series of 15 compositions of bioactive glasses, presented in [15], their basicity (pB) have been calculated and correlated with their Tg. The results are presented in Fig. 5.

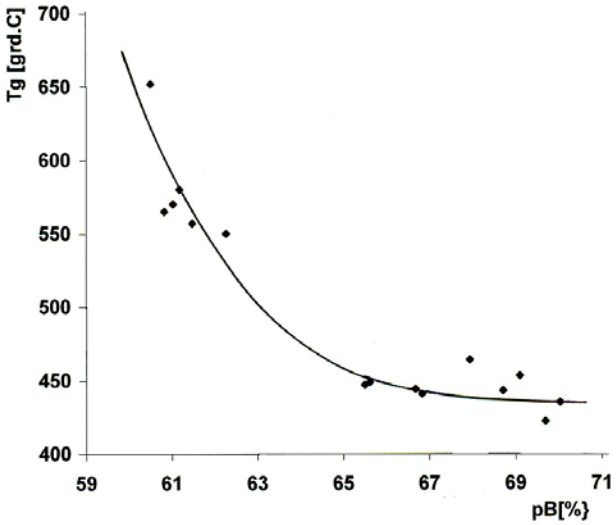

Fig. 5 – The T_g - pB correlation, for a series of bioactive glasses.

A linear correlation of pB with Tg can be observed until approximately 65% pB, due to depolimerization of the vitreous structure, with the increasing of the alkalis percentage and basicity percentage. In basic medium (>65% pB) it is expected that the basicity (pB) is less influenced by the decreasing of Tg, as a consequence of the fact that the depolimerization is less obvious like in the first step.

These results also show that for silicate glasses, an increase of basicity determines the decrease of the vitreous transition temperature. Some experimental data for glasses of certain composition show an inverse dependency. Thus, for glasses within the binary system $SiO_2 – P_2O_5$ [16], for a percentage of SiO_2 between 56 and 100% is presented in Fig. 6 the variation of T_g with pB.

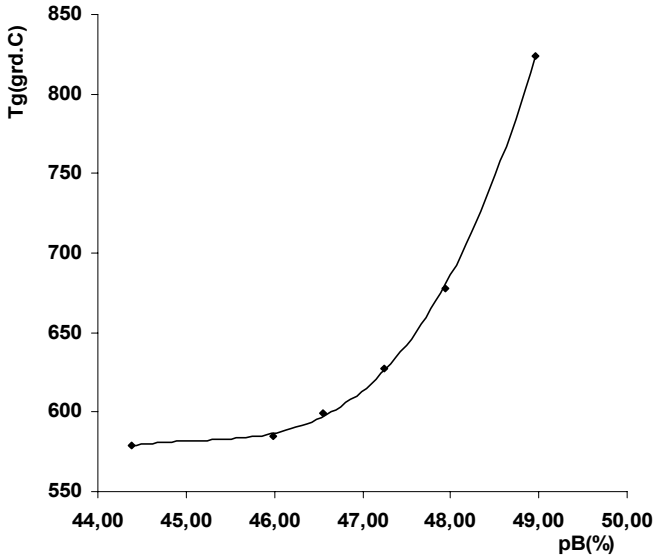

Fig. 6 – The correlation T_g - pB for glasses from the binary system $SiO_2 – P_2O_5$.

It is shown that an increase of the pB determines an increase for T_g. This result is explained by the fact that the basicity percentage for SiO_2 is higher than that of P_2O_5. By increasing the SiO_2 percentage pB increases, but simultaneously the refractoryness of the system increases, too (the melting temperature of SiO_2 is several time higher than that of P_2O_5). The consequence is an increase of Tg.

2. The correlation between the temperature corresponding to some fixed viscosity values and basicity (pB)

Being a transport property, and therefore depending on the characteristics of the ions present in the glass, viscosity can be correlated with basicity (pB). To verify this hypothesis, a first analysis was done on a number of 20 glasses using their oxide compositions given in literature. [13] For these glasses, the values of the temperatures at which lgη = 2, 4 and 6 were determined experimentally. The first investigated set was formed of glasses 1-11 having the compositions within the oxide system SiO_2 - Al_2O_3 - CaO - Na_2O, considered as referential.

The second considered set represents glasses with complex chemical composition, resulted by adding to the basic system different oxides (Li_2O, K_2O, BaO, ZnO, PbO); they are numbered 12-20 in Tab. 2.

Table 2
The oxide composition of glasses and the temperature of the melts at 3 viscosity values

		%weight												
		SiO_2	Al_2O_3	Na_2O	CaO	Li_2O	BaO	ZnO	PbO	K_2O	MgO	T(°C)		
No. Gl	**pBox / pBgl.**	**49.42**	**72.49**	**89.05**	**86.38**	**88.85**	**87.61**	**79.52**	**84.11**	**91.44**	**78.17**	**lgη=2**	**lgη=4**	**lgη=6**
1	59.71	72.69	1.23	13.87	12.21	0	0	0	0	0	0	1433.9	1016.8	822.9
2	59.49	73.23	1.24	13.22	12.30	0	0	0	0	0	0	1446.7	1026.2	830.2
3	59.16	74.07	1.26	12.23	12.44	0	0	0	0	0	0	1465.5	1040.1	841.1
4	58.89	74.95	1.27	14.69	9.09	0	0	0	0	0	0	1484.2	1031.9	824.1
5	57.90	77.66	1.32	15.22	5.80	0	0	0	0	0	0	1544.1	1053.0	829.5
6	59.28	73.91	1.25	14.49	10.35	0	0	0	0	0	0	1461.0	1023.8	822.0
7	58.31	76.55	1.30	15.00	7.15	0	0	0	0	0	0	1519.7	1044.4	827.3
8	59.83	72.41	1.23	14.19	12.17	0	0	0	0	0	0	1427.5	1012.1	819.3
9	59.38	73.66	1.25	14.44	10.66	0	0	0	0	0	0	1455.3	1021.8	821.6
10	60.09	71.37	1.21	13.99	11.99	0	0	0	0	0	1.44	1417.0	1013.2	821.3
11	60.22	70.86	1.20	13.89	11.91	0	0	0	0	0	2.14	1411.7	1013.5	822.1
12	61.86	66.89	0.57	2.86	6.91	0.64	2.90	3.83	4.97	10.43	0	1484.0	1048.2	833.7
13	62.33	65.87	0.56	2.47	6.81	0	2.86	3.77	4.89	12.77	0	1502.8	1072.6	860.9
14	61.97	66.71	0.57	1.74	6.90	0.77	2.89	3.82	4.96	11.65	0	1491.4	1064.2	838.8
15	61.43	67.76	0.57	4.21	7.00	0.93	2.94	3.88	5.03	7.67	0	1467.8	1027.4	811.5
16	61.84	66.90	0.57	3.77	6.91	0.42	2.90	3.83	4.97	9.73	0	1483.2	1047.6	834.0
17	62.17	66.19	0.56	3.41	6.84	0	2.87	3.79	4.92	11.42	0	1495.4	1064.1	852.2
18	61.71	67.12	0.57	6.16	6.94	0	2.91	3.85	4.99	7.48	0	1474.4	1040.0	828.8
19	61.56	67.48	0.57	4.60	6.97	0.64	2.93	3.87	5.01	7.93	0	1472.3	1033.6	819.0
20	61.83	66.89	0.57	4.22	6.91	0.31	2.90	3.83	4.97	9.40	0	1481.3	1046.7	833.8

In Tab. 2 there are also given the pB values of the component oxides ($pB_{ox.}$) calculated with relation (1), as well as the pB value of the glass ($pB_{st.}$), established with relation (2). The coordination number for the cations was considered as the most probable for these type of glasses. For the glasses 1-11, in Fig.7-9 are presented the correlations temperature - pB for lgη=2 case (a); lgη= 4 case (b); lgη=6 case (c). It can be seen that, for a constant value of viscosity, the temperature of the glass decreases with the increase of the basicity. This result is understood because, for the first 11 analyzed glasses, an increase of the percentage of (Na_2O+CaO) is realized in the detriment of SiO_2 percentage, which leads to a more and more depolimerization degree of the structure. This favors the flowing process of glass at lower temperatures of treatment (for η = constant).

The correlation coefficient r drops from the value 0.998 (case a), to under 0.9 (case c). This observation confirms that pB has a more important

influence in the case of molten glass (case a), than in the case of more viscous glasses corresponding to lower temperatures. At higher viscosities (cases b and c), apart from the influence of basicity, it is expected to be sensed the action of the glass, which becomes more and more rigid. Moreover, the variation with ± 1% of the value for pB, implies the modification with approximately ±60°C of the temperature of the glasses for lgη=2 and with aprox. 20°C and 4°C, in cases b and c respectively.

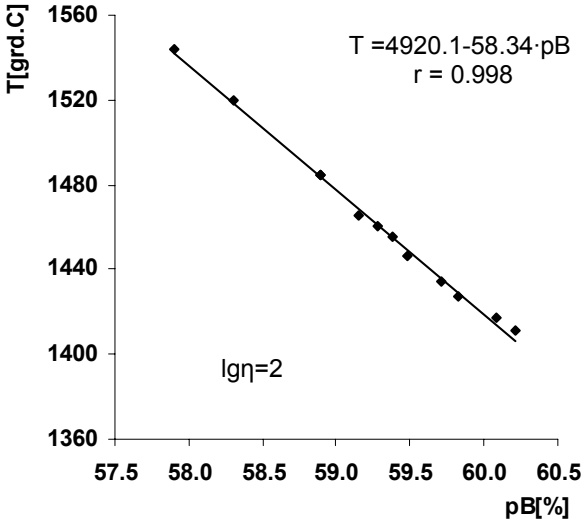

Fig. 7 – Correlation T(°C) - pB la lg η = 2 for the 1-11 compositions.

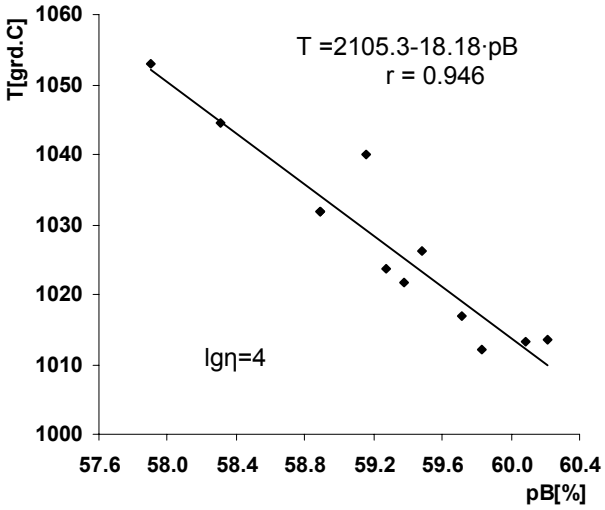

Fig. 8 – Correlation T(°C) - pB at lg η = 4 for the 1-11 compositions.

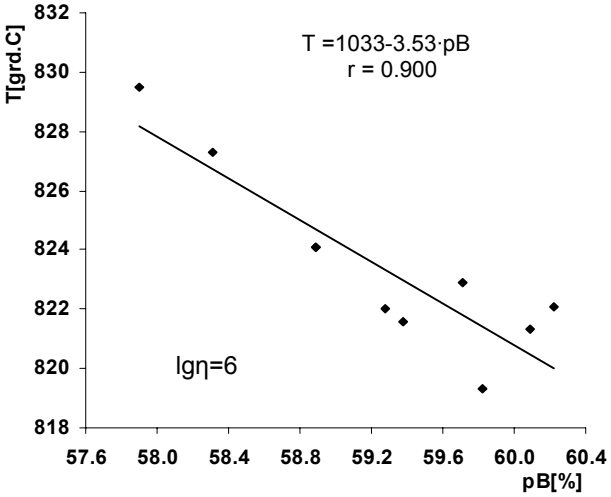

Fig. 9 – Correlation T(°C) - pB at lg η = 6 for the 1-11compositions.

In Figs.10-12 is presented the variation of the temperature of the glasses 12-20 with pB, for the same constant value of viscosity. In this case, somewhat surprisingly, the increase of the values for pB determines the increasing of temperature values for η=const; the modification of the basic oxide composition (glasses 1-11) by introducing some new oxides implies contrary effects over the viscosity. In this way, the decrease of $\%Na_2O$ and increase of K_2O determines an increase of the viscosity of glasses. In exchange, the decrease of %CaO and increase of ZnO, BaO and PbO implies the decrease of the viscosity (at T=const.), the decrease of the temperature (at η=const.), respectively. Practically, in case c), for lgη=6, the effect of the increase of the glasses' temperature is quite strongly correlated with the presence, in an always increasing manner, of K_2O, as it can be

seen in Fig.13. As K_2O has the highest basicity value compared with any other oxide component, then the glass pB increases with the increase of the temperature (for η=const.).

It must be also remarked that, for this set of glasses, the effect of the basicity is not so different for different values of viscosity.

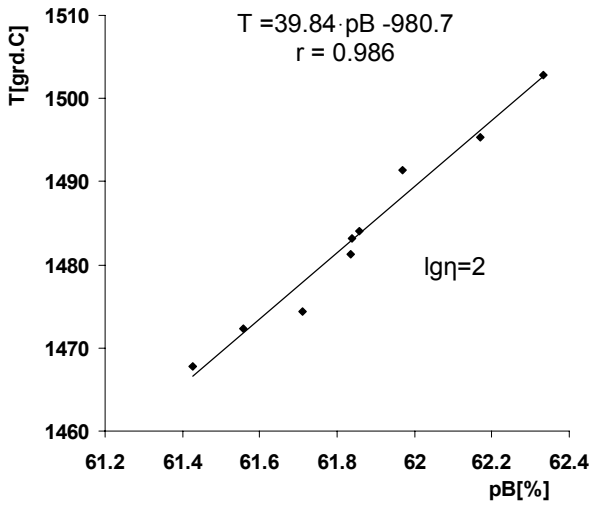

Fig. 10 – Correlation T(°C) - pB at lg η = 2 for the 12-20 composition.

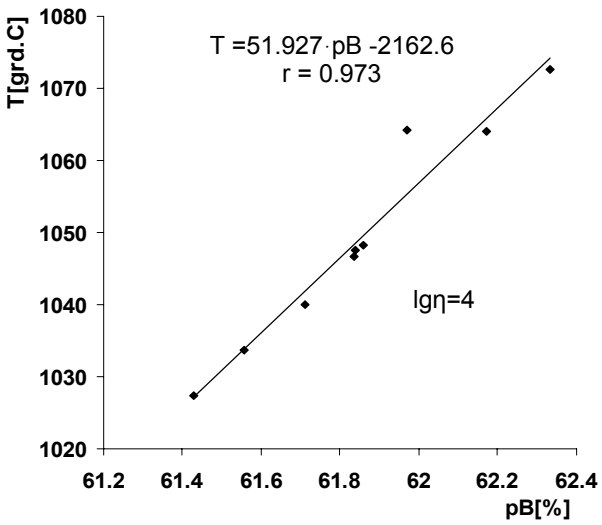

Fig. 11 – Correlation T(°C) - pB at lg η = 4 for the 12-20 compositions.

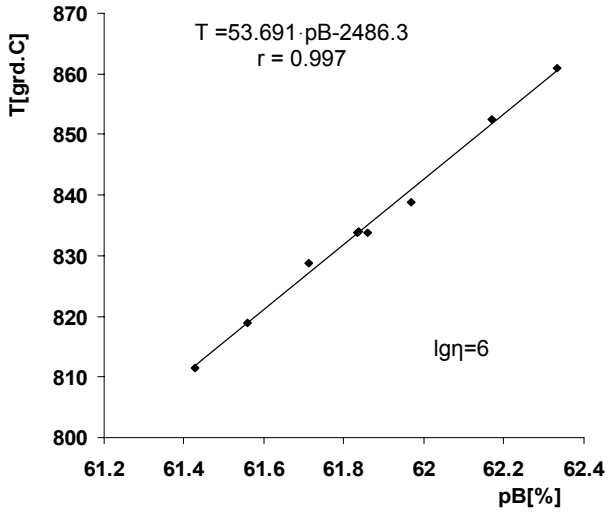

Fig. 12 – Correlation T(°C) - pB at lg η = 6 for the 12-20 compositions.

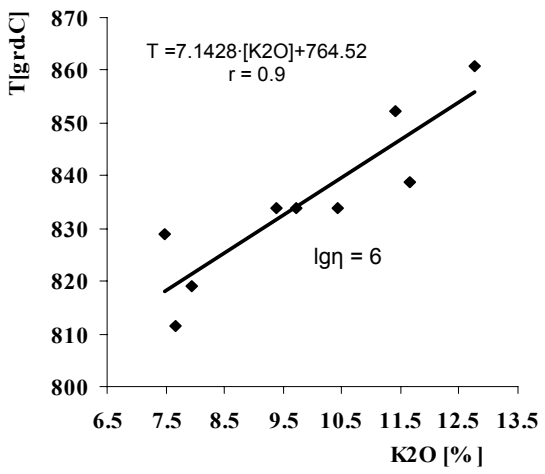

Fig. 13 – Correlation T(°C) – %(grav.)K_2O at lg η =6.

As it is shown in the plottings presented in Figs. 7-9, and 10-12, respectively, the two glass groups present a dependency between the temperature corresponding to some fixed viscosity points and their basicity percentage (pB). These results also lead to the conclusion that it can not be always said that there is a direct or inverse proportionality between temperature (for η = ct.) and pB. The interdependency type is established for each case in particular taking into account the particularities of the each studied oxide system. Of practical interest is also the establishing of the glass "length", which is a measure of its processing ability. "Long" glasses have greater values for ΔT than the "short" glasses, harder to process, where:

$$\Delta T = T_{(\lg\eta=4)} - T_{(\lg\eta=7.6)} \; ; \qquad (8)$$

In the vitreous system SiO_2 - Na_2O, for 8 compositions between SiO_2 and $Na_2O{\cdot}SiO_2$ the ΔT intervals and the corresponding pB values were calculated. In Fig.14 is presented the interdependence of these 2 quantities that can be described by the regression equation:

$$\ln\Delta T = 10.35 - 0.078 \cdot pB; \qquad r = 0.93 \qquad (9)$$

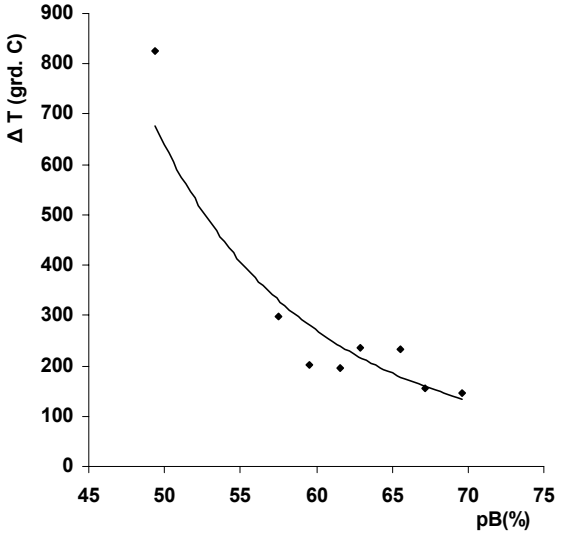

Fig. 14 – Correlation ΔT – pB, for glasses of the SiO_2 - Na_2O oxide system.

The result as shown in Fig. 14 is that the basicity percentage strongly influences the length of the glass processing interval. The increase of pB determines an increase of the tendency of glass crystallization, a decrease of their stability and, as a consequence, the glass is characterized by smaller ΔT values (the glass becomes "shorter").

CONCLUSIONS

The basicity percentage represents a complex structural parameter for the oxide glasses. It strongly correlates with, practically, any other structural characteristic at atomic level (the strength of the electrostatic field, the electronegativity, the electronic polarizability of the oxygen, the coordination number, the oxidation number, the bonding energies, etc.). Because of this, pB can be considered a "globalizing structural indicator" for oxide glasses.

In the present work, the concept through which the properties of the glasses are determined by their structural particularities has been tested. The applications have shown strong inter-correlations between the values of some fixed viscosity points of practical interest, and the basicity percentage for the studied glasses. These correlations are seen for some simpler glasses as well as for some complex oxide compositions of industrial type.

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