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The amount of ionic character - measure for oxide basicity

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As it is known, the optical basicity scale Λ, elaborated by Duffy and Ingram is in use from 1971 and was adopted with interest in our laboratory too. Very soon, were observed some disadvantages which, during a current use of the Λ scale in the domain of oxides, create a certain discomfort. May be mentioned: the artificially established and then corrected limit of basicity; the complicated theoretical calculation of basicity even using different ways, sometimes resulting different values; the lack of a memorable and suggestive measurement unit. For such reasons in our laboratory was elaborated in 1983 and studied a different basicity scale using as measuring magnitude the amount of the ionic character of the chemical bond proposed by Pauling and easily obtainable with his formula by means of the electronegativity. The natural basicity limit of this scale named pB (acronym of **p**onderea **b**azicității in Romanian) is O^{2-} and the pB values are expressed in percent The main ideas were included in 1984 in a text book and in 1985 was published the first paper in English. This communication, having a review character, contains many new and even original ideas too. The nature of the basicity of oxide and oxidic materials are discussed. The deduction of the formula for theoretical calculation is presented. The experimental method is described and, in addition, their use for evidencing the energetic effect of basicity and the structural nano-aggregates existing in nano-heterogeneous oxide glasses. Some results in interpreting the glass properties are shown as graphs, among them the correlation between basicity and the glass forming tendency; the magic basicity and the oxidic compound formation, the chemical reactivity and basicity, the interpretation of water pB and the glass resistance in water, the refractory resistance in molten glass. The accumulated results showed that pB basicity scale is friendly in applications, rich in scientific information and offer directly structural and practical orientation and data.

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1. Introduction

In the field of oxides the basicity is a leading property, influencing and correlating with all other chemical and physical properties of crystalline or glassy oxides and oxidic materials. This is why, in our laboratory dedicated to glasses, the optical basicity elaborated by Duffy and Ingram [1] was, from the beginning, intensively used. In some years the gathered experience evidenced the utility to improve the basicity measurement choosing a suggestive property a more convenient calculation formula and more expressive figures. This new basicity scale was suggested even by Lewis who mentioned (cited by Pauling [2]) that the electron equilibrium in a new chemical bond may have a certain ionic character. The amount of the ionic character may be easily calculated with the known formula given by Pauling, using the electronegativity [2]:

Amount of ionic character

$$1 - e^{-\frac{1}{4}(X_A - X_B)^2} \tag{1}$$

where X_A and X_B are the electronegativity values tabled by Pauling. For this application was used the name Amount of basicity, translated in Romanian as **p**onderea **b**azicitatii, with acronym pB. (It was preferred pB because suggest the similarity, in principle, with pH and pO^{2-} and also percent basicity). The amounts of ionic character and pB values are expressed in %. Very soon was observed that the original table of Pauling did not contain electronegativity values for some atoms having different oxidation state.

A tentative was made to correlate the results obtained with formula (1) with the ionization potentials in eV of the respective ions which are calculated or experimentally determined, and available in tables for all atoms with all possible oxidation state. The graph in figure 1 was obtained showing some interesting results [3, 4].

- The pB of O^{2-} was considered as 100 %, that is 2.0 on the left coordinate. The corresponding abscissa, of about -7 eV, is a kind of negative P_i, reflecting the endothermic effect at the attachment of the second electron to O^-, that is the maximum electron donating power of this anion and the minimal electron affinity. In this way the natural limit of the basicity become evident.

- The cloud of points representing the pB logarithms function of P_i evidenced an ordering after the coordination number CN of oxygen atoms around the cation. The respective straight lines converge in the point corresponding to oxygen anion, that is to log pB = 2. Such clear correlations are described by simple equation like, for example:

$$\log pB_{(CN=3)} = 1.94 - 0.00818 \cdot P_i \tag{2}$$

$$\log pB_{(CN=4)} = 1.9585 - 0.00567 \cdot P_i \tag{3}$$

Finally, with the help of my colleague Professor Dr. Engineer Dorel Radu, a general equation for pB function of P_i and CN resulted:

$$\log pB = 1.9 \cdot (CN)^{0.02} - 0.023 \cdot \frac{P_i}{CN} \tag{4}$$

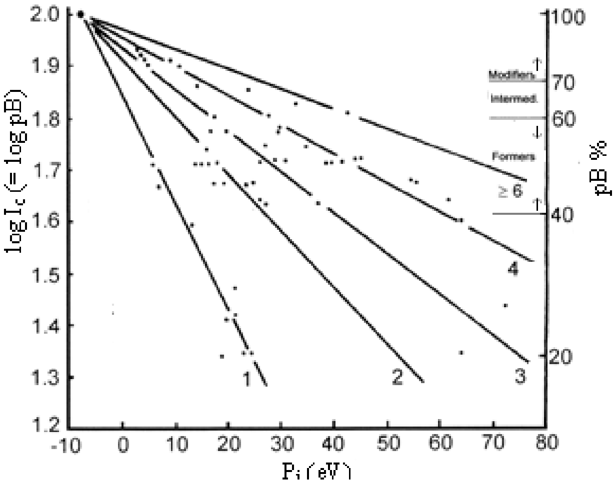

Fig.1. The correlation between the logarithms of the amount of the ionic character Ic, or of pB calculated with (1) and the ionization potential P_i

The formula (4) characterizes the electron donating power of an oxide after the re-equilibration of the donating ability of oxygen and the acceptor ability of cation due to the formed chemical bond and the new position of the electronic cloud between the bonded atoms. This alteration of the electronic structure of the respective atoms influences all the properties of the oxide.

For complex oxidic compositions was used a simple additive formula inspired from glass science and technology [3]:

$$pB = \sum_i pB_i \cdot c_i \tag{5}$$

where pB_i are basicity of the component oxides and c_i the respective weight fractions.

- The main result is the fact that two of the important properties of oxides: the amount of the ionic character of the chemical bonds and the amount of basicity are intrinsic values and can be expressed by a single figure. The percents allow the instant appreciation of the magnitude and easy comparison with other similar values.

2. The experimental method for basicity determination

The experimental method is based on the known principle of probe ions. Copper was chosen after a hard experimental work on transition elements of the first row [5, 6], introduced in glasses with basicity ranging between about 40 % and about 70 % in a concentration of 0.1 element %. The influence of pB on copper ion in octahedral coordination was explained [7 - 10] by the influence of the four ligands placed in plane, at the corners of a square, which are more strongly attracted by the copper ion when the electron donating power (pB) of ligands is higher. The octahedron is deformed (the Jahn-Teller effect), the *p* orbital of oxygen ligands become closer to the *d* orbital of copper and the electron transition needs less energy.

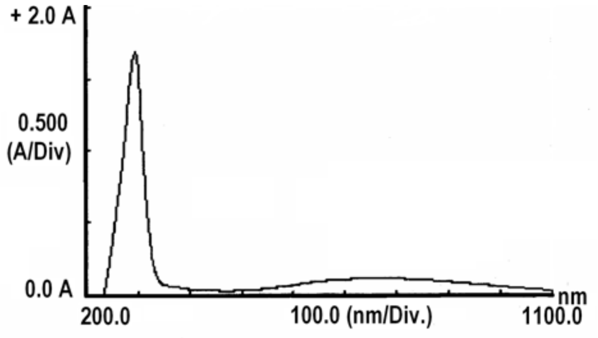

Fig. 2. The recorded spectrum of Cu^{2+} probe ion in an oxide glass.

Between the arguments supporting this choice may be numbered: the stable CN = 6 in the entire pB range; the moderate variation of Cu^{2+}/Cu^{+} in the absence of the redox agents; the practically linear character of the shift of energy peak of charge transfer absorption in the usual range of pB variation; the good diffusivity of Cu^{2+} and his apparent tendency to occupy the modifier sites in glass.

Such a spectrum for Cu^{2+} as a probe ion, recorded in comparison with a glass having the same composition but without copper, is shown in the Fig. 2. The basicity of a glass is determined by means of the Cu^{2+} charge transfer absorption maximum, in UV, using the respective wavelength ν, expressed in cm^{-1}.

The relationship between the UV peak position and the glass basicity, resulted from the graph in Fig. 3, constructed by means of a number of synthesized glasses [11], is:

$$pB = 151 - 0.00259 \cdot \nu \tag{6}$$

Making explicit ν and transforming in nm it results:

$$\nu = 25900 / (151 - pB) \tag{7}$$

Or in eV:

$$\nu = 7.2259 - 0.0478 \cdot pB \qquad (8)$$

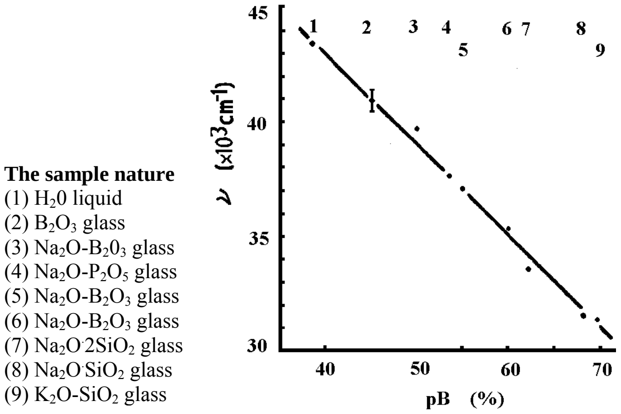

Fig. 3. The pB influence on the recorded peak position in UV, corresponding to the charge transfer of Cu^{2+} in different glasses.

3. The energetic effect of pB

The formulas (7) and (8) suggest that pB may be indicated by the energy necessary for Cu^{2+}charge transfer too. The formula (8) allows the evaluation of this energy. Considering, for example, that the indicator ion is in an environment with pB=0 % then, from formula (8) results that for this process the incident photons must correspond to an energy of 7.2259 eV, in far UV If pB is, say, 100 % then formula (8) shows that only the energy of 2.4459 eV is needed from the incident photons for Cu^{2+}charge transfer, the rest of 7.2259 – 2.4459 eV is furnished by the pB of the environment, the peak being at about 508 nm. Appears the idea that an important quantity of energy is furnished by the environmental oxide pB. This energy of the oxidic medium was named basicity potential Bp and may be calculated, in eV, with formula (9), where pB, measured by means of Cu^{2+} charge transfer peak is, as usual, in %:

$$B_P = pB \cdot 0.0478 \qquad (9)$$

This influence of pB, on the foreign ions, has different results function of the electronic structure of ions. During the experiments for indicator ion selection in our laboratory were tested many ions [5, 6] especially for a higher response to pB increase. The pB influence was observed, with different intensities, on charge transfer transition of 3d ion. It is also well known the pB influence on the $^1S_0$ – $^3P_1$ transition of Tl^+, $Pb^{2+}$and Bi^{3+} [1]. The electron donating power of oxygen atoms has a measurable influence even on the core-level electrons, as showed Miura and Nanba using a XPS technique to record sharp O1s peaks for a series of oxide glasses [12].

The amount of the ionic character and basicity indicated by pB, together with the basicity potential B_P showing the energetic basicity contribution, completes the complex image of the basicity phenomenon enlarging the interpretation possibilities of glass properties and making more obvious the fact that all aspects of the oxides behaviour are influenced by basicity.

4. New interpretations concerning the glass forming ability of oxides and pB

Considering the accumulated knowledge concerning the glass forming ability of oxides, in Fig. 1, on the right ordinate, are indicated the limits for glass formers, between 40 % pB and 60 % pB; the modifiers with pB over 70 % and the intermediates with pB between 60 and 70 %. These limits are not very rigid and complete, remaining, for example, the oxides with pB values under 40 %, with unclear glass forming tendency.

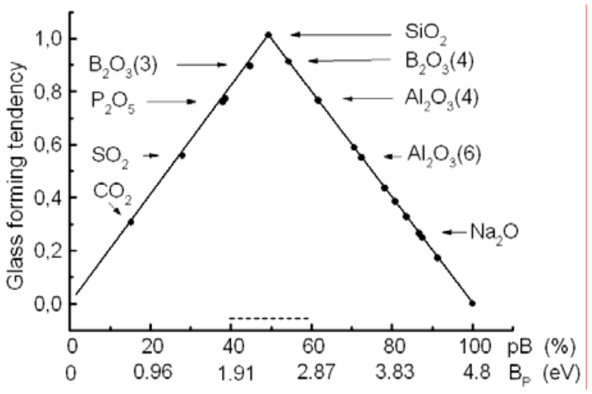

Fig. 4. A suggestive graph allowing the discussion of the pB influence on glass forming ability of oxides.

To visualise easier the glass forming ability dependence in the entire field of pB variation the graph in Fig. 4 was imagined [10], although the values on the ordinate are only approximate with figures between 0.0 and 1.0. It can be observed that the glass forming ability is preponderantly manifested in the middle of the scale, around SiO_2. In the high basicity half of the scale the delimitations mentioned above are quite corectly reproduced.

Under approximately 40 % of pB, the glass forming ability of oxides and of their compounds is not always clear. B_2O_3 and P_2O_5 are volatile; SO_2 and CO_2 are gases, all posing difficult technological problems in obtaining glass. It results accordingly that when the basicity diminishes under 40 % the glass forming ability diminishes too.

The facts that pB represents also the amount of the ionic character of the bond and now is available the basicity potential Bp in eV too, increase the possibility of finding a reasonable interpretation. One begins with the idea that, according to the formula (3), the cation acceptor ability “consumes” a part of the electron donating power of the oxygen. Therefore, the oxide can interact with other atoms or oxides by means of the remained pB. In this way the low basic oxides, unlike the high basic ones, consume their resources – electron donating power or basicity potential – toward the interior, forming closed small molecules, the remained basicity potential for external interaction being too small for complex network structure formation.

Only the oxides having the amount of the ionic character between 40 and 60 %, respectively basicity potentials between approximately 2 and 3 eV, have the possibility of constructing complex and extended networks and consequently to form glass structures..

Such interpretations are accessible both from pB in %, expressing the rates of coulomb and covalent interactions, and from basicity potentials in eV suggesting the interactions at the electronic levels. This apparently oversimplified presentation reflects indeed the reality and is quite easily understandable.

As a consequence, the domain of the true glass former oxides is comprised only between approximately 40 % pB and about 60 % pB, these figures representing also the amount of the ionic character of bonds and corresponding to the interval 2 – 3 eV of basicity potential. It seems that in the less basic region one have to delimit, like in the high basicity domain, some acid intermediary oxides, under 40 % pB, and also some acid modifiers oxides, down to near 0 % pB, the hypothetical 100 % acid.

5. The chemical reactivity and basicity

In some published works [13, 14] it was shown that the reaction between oxides might be written in terms of the reactant oxides basicity:

$$O_{(pBi)} + O_{(pBj)} = 2O_{(pBd)} \tag{10}$$

The $O_{(pBi)}$ and $O_{(pBj)}$ are oxides with different pB values, in different oxidic compounds and $O_{(pBd)}$ is the resulted oxidic compound, having theoretically a mean basicity, but actually representing the mean basicity of the resulted nano aggregates distribution. The equation (10) clearly evidences that the chemical interactions are dependent on the basicity difference between the oxide reactants. The equilibrium constant of such a reaction may be written, in principle, as:

$$\log K = C \cdot \Delta pB \tag{11}$$

The value of C depends on the oxidic system examined. For the system Na_2O-SiO_2, for example, the coefficient C was approximated to 0.2, giving K values quite close to the calculated, for high temperatures, in the classical way ones.

5.1 The compound formation between oxides

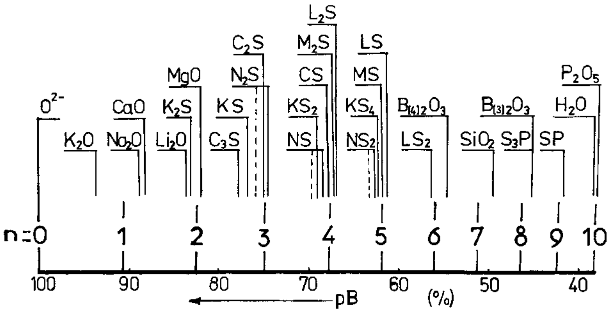

Fig. 5. The magic basicities.

The above observation may be correlated with the pB influence on the compound formation between oxides. If comparing the pB values of the oxides and simple binary compounds an interesting grouping may be evidenced [10, 15]. It seems that in the binary compound formation some particular pB values “are preferred”. To emphasize the quite strange aspect of this observation these special values were named magic ones pB_μ. They respect the rule:

$$pB_\mu = 100 \cdot 0.908^n \tag{12}$$

n having values between 0 and 10 for usual oxides. The greater is the basicity difference between two oxides the greater is the number of formed compounds. A certain spreading of the pB values around the magic ones is partly due to the not exactly known CN values. Examples in this sense are the basicities of sodium silicates. When calculated with classical $CN_{Na} = 6$ the respective positions (indicated by dotted lines) are farther from the magic basicities as in the case of using the X-ray determined CN values for the crystalline compounds. When the basicity difference is less than 10 %, the probability of compound formation is lower. The rise in ΔpB determines the increase of the compound number, suggesting that for the formation of a stable chemical compound a basicity difference of about 10 % is necessary between the reactant oxides. A fractional **n** value indicates lower stability of the respective compound, reflecting in another way the fundamental role of reactant oxide basicity difference.

This statement is another aspect of the rule discovered by Dietzel [16] by means of the electrostatic field strength. It seems that both correlations have the same structural-chemical basis, probable related to the cations need of shielding discussed by Weyl [17].

5.2 Chemical interactions with water

Frequently, one of the reactants in reaction (10) is water or an aqueous solution. In water basicity calculation it is necessary to take into consideration that the coordination number of hydrogen may be 1 only in pure water. In usual, impure water and in aqueous solutions hydrogen bonds are present in different proportion [18, 19] and consequently in many molecules the hydrogen coordination number CN is 2. The calculated basicity values using the equation (4) are $pB_{(H1)}$ = 38.7 % and respectively $pB_{(H2)}$ = 58.9 % for associated water with $CN_{(H)} = 2$. It is evident that the calculated ΔpB values and consequently the intensity of interactions are strongly influenced by the presence of hydrogen bonds.

Information concerning the basicity and the structure of aqueous solutions may be obtained by using the experimental methods described in section 2. [11]. Cu^{2+} probe ion is introduced as a water soluble salt. The experimentally obtained pB values for aqueous solutions of Na_2O suggest that the solvent is a mixture of the above mentioned two kinds of water. The solution is a ternary oxidic system and pB is a weighted sum of the pB values of the three component oxides. The accumulated data, presented in the figure 6 [14], reveal an interesting phenomenon: the presence of sodium oxide determines a rapid hydrogen CN modification. The maximum concentration of associated water is observed at a sodium oxide concentration of about 5 % and attains about 42 % of the total water content. After that the concentration of water with dicoordinated hydrogen decreases. This phenomenon reminds the boron CN changes in alkali-borate glasses.

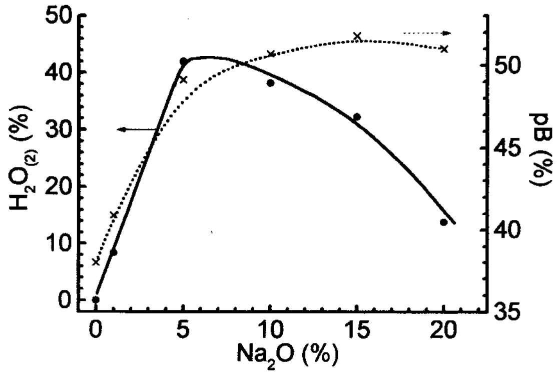

Fig. 6. The $H_2O_{(2)}$ quantity in an aqueous solution of Na_2O. On the right hand ordinate the solution basicity is represented.

Related to water reactivity the presence of two kinds of water complicate the chemical interactions. Indeed, the more basic water, having a greater amount of ionic character has a higher reactivity than the acid and more covalent one. After a certain inpurification of water, determining the more basic water apparition, this water species seems to have the main role in chemical interactions. May be this is one of the explanations of the observation of Scholze, in Ref. [20], concerning the influence of different inorganic salts, present in solutions, on the glass corrosion rate. The impurities contained in usual water, including the extracted ions from glass in the first stage of the chemical contact, determine the hydrogen bonds apparition and in this way the presence of more basic and more reactive $H_2O_{(2)}$.

From such points of view the pure H_2O, as an acid oxide, deserves more attention. In a very acid medium of pure water (pB = 38.7 %), SiO_2, having pB = 49.4 %, behaves as a basic partner adopting the coordination number 6, according to the known quite general rule.

It is possible that this new vision on water may bring some new ideas and explanation of so many complex phenomena encountered in water interactions with glasses.

5.3 Glass interaction with water and aqueous solutions

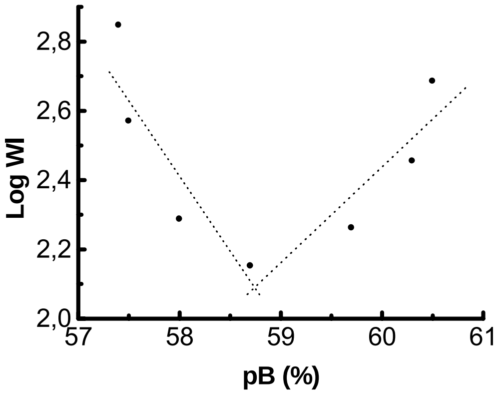

Fig. 7. The weight loss in boiling water of glasses with compositions: 18%Na_2O + xMgO + (82-x)SiO_2 [21]

In order to begin with the oxide reaction with water, in the Fig. 7 data are presented, resulted from a reprocessing of an old diagram of Enas (1928), reproduced by Rawson in Ref. [21]. In that time the basicity theories were unknown. The glasses used had the compositions 18 weight % Na_2O + x%MgO + (82-x)%SiO_2.

The pB value showed by the crossing point of the two straight lines is practically the same as for $H_2O_{(2)}$, namely 58.9, and consequently, in this point, ΔpB ≈ 0. Inflexions in the same basicity region may be observed in many graphs concerning the reactivity with water of very different glass compositions.

5.4 The interaction with water of cements containing glassy high furnace slag

In Fig. 8 data are presented obtained with more complex materials formed from glassy synthetic slag of the type of metallurgical high furnace slag mixed with constant quantities of Portland cement having the role of activator [22]. The figures on the ordinate show the hydraulic activity of the binding materials obtained in this way. The graph may be compared with the right side of the Fig. 7. One may expect that the descending trend will continue up to the basicity value of $H_2O_{(2)}$.

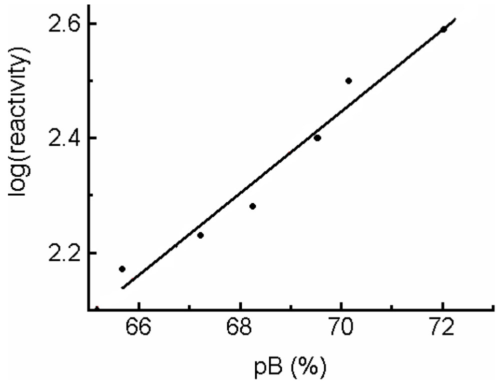

Fig. 8. The reactivity versus pB of some cements containing glasses of the type of metallurgical high furnace slag.

These results suggest that the driving force ΔpB act on all oxidic materials and may conduct to useful findings and interpretations not only in the field of glasses.

5.5 The chemical interaction of molten glass with refractory materials

The graph in Fig. 9 is obtained by reprocessing the results obtained in a PhD Thesis [23]. Due to the compositions covering a large domain of basicity values the experimental points corresponding to the weight losses in E glass melt at 1400 °C define, the already well known, two straight lines crossing at a minimum corrosion intensity. This minimum corresponds, in this case, with the basicity of E glass, marked with a tick on the abscissa, indicating also a minimum value of ΔpB between glass melt and refractory material.

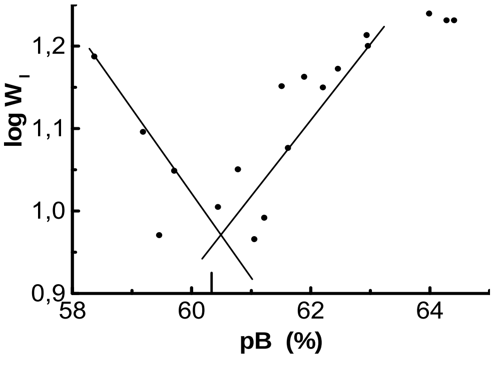

Fig. 9.The weight loss of synthetic refractory compositions from the system MgO-CaO-Al_2O_3-ZrO_2-SiO_2 in molten E glass at 1400°C, function of pB.

The industrial casting refractory, having a restrained variety of compositions the obtained graphs are simpler. The figure 10 show the behaviour of some refractory in molten container glass, evidencing also the strong influence of temperature [24]. It can be clearly observed the decreasing tendency of the corrosion intensity towards the zero ΔpB value. As a practical consequence, ΔpB may be used as a criterion for refractory selection for melting a given glass, providing that other refractory properties, like porosity and crystalline structure, be the same.

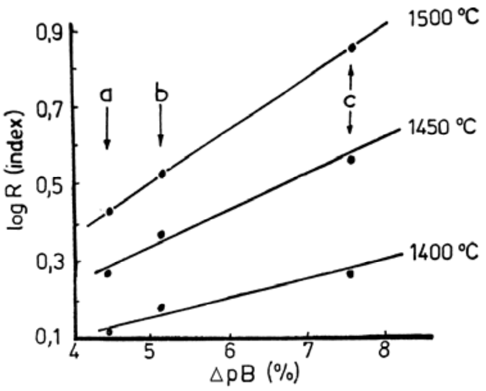

Fig. 10 Refractory corrosion in molten container glass: (a) Al_2O_3 with 41 % ZrO_2; (b) Al_2O_3 with 32 % ZrO_2; (c) Al_2O_3 100 %.

5.6 The glass interactions with body fluids and pB

The bioactivity seems to be related to the ability of some glasses or glass ceramics to develop an interface of hydroxyl apatite between organic and inorganic mater and also to integrate into living tissue. Being in essence chemical interactions a correlation with basicity may be expected. To check the correlation between bioactivity and basicity of glasses were used the data collected by Rawlings [25] from seven sources.

In Fig. 11 the basicity is represented on the ordinate the glasses being listed on the abscissa using the codification from [25]. It may be observed that all bioactive glasses are in the upper part of the diagram above a basicity value of about 62 %, evidencing a simple criterion for bioactivity of a glass [26]:

$$pB \geq 62\% \qquad (13)$$

This rule may be understand by taking into consideration the depolymerization of the structure of glass and the decreasing of covalent character of bonds when pB increases. In this way glass becomes more reactive, more soluble in the complex body fluids. It may be remarked also that the basicity limit of bioactivity is above the value corresponding to the basicity of $H_2O_{(2)}$.

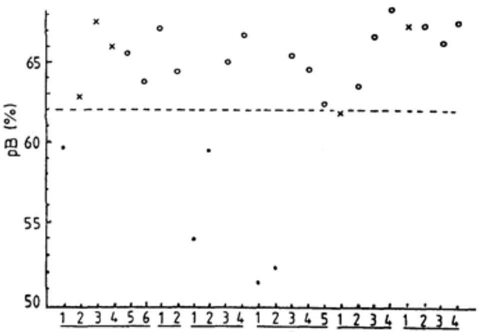

*Fig. 11. pB values of glasses: **o** bio-active; • not bio-active; **x** doubtful.*

6. The method for glass nano heterogeneity Studying

The spectrum in the Fig. 2 shows, as usual in glass, maximums with a higher breadth, as in crystals. The explanation is the disordered glass structure, in which Cu^{2+}, in our case, is dispersed absorbing the photon energy as determined by the environment. According to the formula (7) the position in nm indicates the pB value of the respective site.

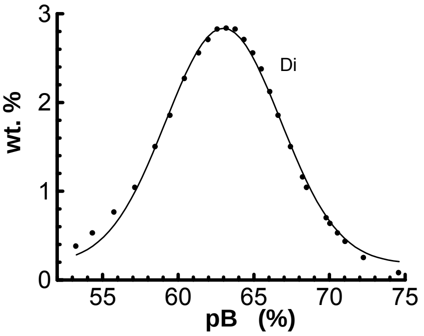

Fig. 12. The distribution of the pB values of the nano-aggregates in a sodium silicate glass, near disilicate.

By means of formula (5) the composition of nano-aggregate in this site can be easily determined in a binary glass. In this quite simple way the nanometers on the abscissa corresponding to the peak of the charge transfer of Cu^{2+} can be replaced with the corresponding pB values, like in Fig. 12, where the recorded maximum, in a sodium silicate glass was conveniently amplified.

To replace the pB values with the corresponding SiO_2 in mol % compositions the equation (14) can be used, deduced by means of the known chemical compounds in the respective binary silicate system. For example equation (14) is specific for the Na_2O-SiO_2 system.

$$SiO_2\ (\%\ mol) = 266.89 - 0.6843 \cdot \nu\ (nm) \qquad (14)$$

So, the Fig. 13 illustrates the distribution of nano-aggregates compositions, in SiO_2 mol percents, in two sodium silicate glasses. The Figs. 14 and 15 complete the information concerning the alkali silicate glasses showing also the displacement of peaks and distributions function of the alkaline ion present in the binary glass.

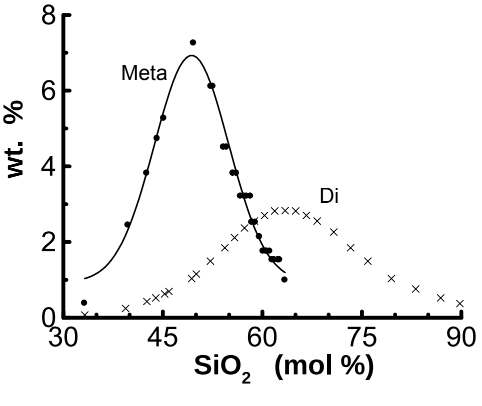

Fig.13. The distributions of nano-aggregates compositions in sodium meta and di silicate glasses.

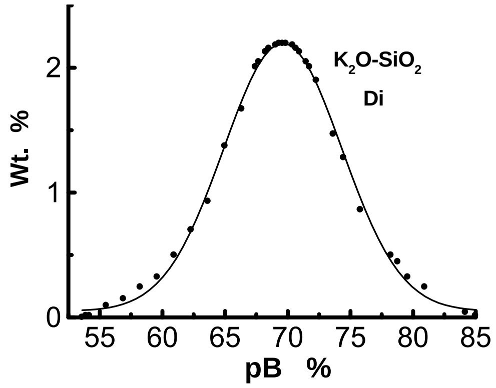

Fig. 14. Nano-aggregates basicity distribution in a potassium silicate glass with a composition in the near of disilicate.

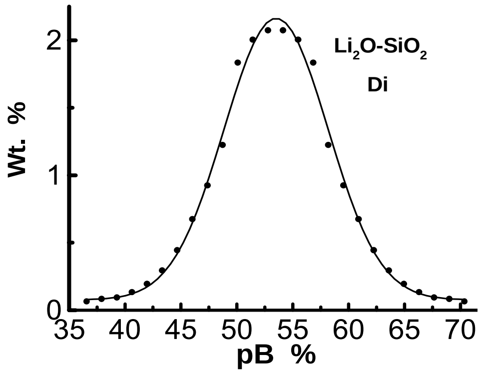

Fig. 15 Nano-aggregates basicity distribution in a lithium silicate glass with the composition of disilicate

In the case of ternary or multi component glasses the nano-aggregates compositions calculations, based on the formula (5) needs in addition basicity correlations with other one or more glass properties. Such correlations can be found in two recent books [27, 28]. With the glass property obtained in this way, and the usual correlation of that property with glass composition, equation systems with three (or more) unknown may be written and then solved.

The spectral basicity distribution SBD, using the data obtained by means of experimental basicity determination method, offers the first and the unique experimental method allowing the nano-aggregates evidencing in glass, approximating also their compositions, structures and properties. The new experimental method may be useful to follow the influences of technological peculiarities on glass structure and properties even in industry.

7. Conclusions

Among many interesting ideas mentioned in this communication some deserve to be reminded.

- The choice of the amount of ionic character for measuring the basicity has the advantage of using directly, as suggested by Lewis, the electron equilibrium in chemical bonds which practically determine all the interrelations and properties of atoms and chemical compounds. The established simple formula for pB calculation use the easy accessible P_i and quite known CN in oxides and for complex compositions an additive formula of the type currently used in glass science and technology.

- The use of Cu^{2+} as probe ion for the experimental pB determination valorise one of the processes taking place at the electronic levels of the ion. This method facilitates the observation of a kind of energetic effect of basicity named basicity potential Bp (in eV). The same method allowed the elaboration of the spectral basicity distribution SBD which seems to be the unique experimental method for evidencing the nano-aggregates present in oxide glasses, their compositions and properties confirming the nano-heterogeneous structure of oxide glasses.

- The glass forming tendency of the oxide and oxidic compound can be better understand by means of accumulated pB data. Were discovered the so called magic basicity which seems to control the oxidic compound formation.

- The chemical interactions are dependent on the pB difference. From this point of view seems to be of interest the CN of H in water: only in pure water CN of water is 1 and pB 38.7 %. In the presence of some impurities appears the hydrogen bonds and CN of H become 2 and pB 58.9 %. This fact has important consequences in reactions of oxides with water.

- Data concerning the chemical reaction of refractory materials with molten glass are presented and glass with body fluids interactions.

- The accumulated in 28 years results showed that pB basicity scale is friendly in applications, rich in scientific information and offer directly structural and practical orientation and data of

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