Infrared and chemical durability studies of some binary PbO and ZnO phosphate glasses and their corresponding sodium metaphosphate derivatives

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Abstract. Structural conclusions are obtained for glasses in the binary PbO and ZnO phosphate systems by IR spectroscopy. Alterations in bands, frequencies and intensities as a function of chemical composition are interpreted and these indicate various types of interlink between Pb^{2+} and Zn^{2+} cations and the host network, especially, when they are incorporated as NWF's. Moreover, the metaphosphate structure, theoretically possible to be achieved in the structure of glasses with equimolar compositions $50\text{M(II)O}\cdot 50\text{P}_2\text{O}_5$ (mol%) (where M is Zn or Pb), is not confirmed by their spectral patterns. However, this structure is confirmed to be achieved in the structure of glasses with $20\text{Na}_2\text{O}\cdot 30\text{PbO}\cdot 50\text{P}_2\text{O}_5$ and $40\text{Na}_2\text{O}\cdot 10\text{ZnO}\cdot 50\text{P}_2\text{O}_5$ (mol%). The dissolution rates of most of the studied glasses were measured as a function of pH and variation in chemical composition. The results are discussed in light of the conclusions obtained from the IR study, structural model of phosphate glasses (Van Wazer) and the previously suggested mechanisms for dissolution of phosphate glasses.

Keywords. Glass; phosphate; chemical durability; infrared.

1. Introduction

Among conventional oxide glasses, phosphate glasses are known to have comparatively low softening point but poor chemical durability. The durability of phosphate glasses containing zinc (Holliday 1977; Gray and Klein 1982) and lead (Ray *et al* 1973; Minami and Mackenzie 1977) has been studied in aqueous media. Of all the additions made to phosphate glasses to improve their durability, only PbO lowers the dissolution rate at the same time as it lowers the softening point (Tindyala and Ott 1978).

According to Kordes *et al* (1953) classification for the cations involved in binary phosphate glasses, Pb^{2+} is characterized as a normal cation, while Zn^{2+} is characterized as an anomalous cation. This classification has been made according to the evolution of properties versus the molar content of the cation in glasses. The normal cations lead to linear evolution of properties/composition curves (e.g. density, index of refraction, conductivity, viscosity, durability etc), whereas such curves are non-linear for the anomalous cations. In the case of Zn^{2+} , the nonlinearity was attributed to a gradual change of the coordination of Zn^{2+} , although the characterization was not found to be an easy matter (Palavit *et al* 1995).

On the other hand, Okura *et al* (1988) built a structural model to explain such nonlinearity, in the case of $\text{MgO}\cdot\text{P}_2\text{O}_5$ glasses, and attributed it to the coexistence of two structural models at $\text{Mg/P} = 1$ (four-membered rings of PO_4 -tetrahedra together with a dimer of PO_4 -tetrahedra) rather than coordination variation.

The present paper presents a new view to explain the difference in the way in which both Pb^{2+} and Zn^{2+} cations link themselves to the phosphate network and the reflection of such difference on the chemical durability values of the glasses in both systems.

2. Experimental

2.1 Preparation of glasses

Lead and zinc binary phosphate glasses were studied by preparing the glass compositions ranging from 40PbO (or ZnO) $\cdot 60\text{P}_2\text{O}_5$ to $57.5\text{PbO}\cdot 42.5\text{P}_2\text{O}_5$ and $60\text{ZnO}\cdot 40\text{P}_2\text{O}_5$ in 2.5 mol% stepwise increments. The materials used were reagent grade chemicals of $\text{NH}_4\text{H}_2\text{PO}_4$, Pb_3O_4 and ZnO . Na_2O used in the preparation of glasses in the $x\text{Na}_2\text{O}\cdot(50-x)\text{PbO}$ (or $\text{ZnO})\cdot 50\text{P}_2\text{O}_5$ ternary systems was added in the form of Na_2CO_3 .

Melting was carried out in 50 ml porcelain crucibles. The batches were first heated at 100°C and then at 500°C for several hours prior to melting, in order to

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remove H_2O , CO_2 and ammonia and to sinter, respectively. The products were melted at $750\text{--}1150^\circ\text{C}$ for 1 h after the last trace of batch was observed to disappear, and annealed at $250\text{--}400^\circ\text{C}$. The variation in the melting and annealing temperatures was in accordance with the glass composition variation. The glasses were stored in desiccator to prevent uptake of moisture.

2.2 FTIR measurements

Dispersions of powdered glass with KBr (1.5%) led to transparent pellets by subjecting them to hydraulic press equal to 2000 kg/cm^2 under vacuum. Transmission spectra were recorded in the range $200\text{--}2000\text{ cm}^{-1}$ on a Jasco-300 E FTIR spectrophotometer.

2.3 Dissolution experiments

All samples were tested as powders. They were ground and passed through 45- and 60-mesh sieves. The grains were applied to a magnet to remove any contaminant of iron that may have been introduced during the crushing process. Thereafter, they were cleaned and washed with acetone, methanol and bidistilled water, respectively.

From density measurements it was possible to know the volume corresponding to 2 g of sample, and from the average diameter of grains (ca. 0.03 cm) was obtained their number and the whole surface of the sieved sample.

The effect of six buffer solutions, ranging from 4.3 to 9.0, was studied. To each of the samples was added 100 ml of the freshly-prepared buffer solution at 70°C for 1 h in a sealed polypropylene container. The pH values of the solutions were measured before insertion of the sample and after its removal and the change in the pH was less than 0.2.

After the soak time had elapsed, the grains were washed with acetone and dried in vacuum-tight oven at 120°C to eliminate the residual traces of superficial water. The dissolution rate was calculated from the amount of total weight consumed over the time frame of the experiment and expressed in moles of glass dissolved per cm^2 per min. Each data point on the present curves represent the average of three times experimental repetitions.

3. Results

3.1 IR measurements

For presenting our results and discussion, glasses will be referenced in this paper by their molar fraction ratios, x 's, of PbO (or ZnO), in the case of binary systems, and Na_2O , in the case of ternary systems. Binary glasses with x values equal to 0.400 and 0.425 were not measured because of the expected difficulties which may arise from their highly hygroscopic nature. Moreover, all the spectra are normalized between 30 and 60 T% at 2000 cm^{-1} .

3.1a $x\text{PbO} \cdot (1-x)\text{P}_2\text{O}_5$ system: The IR spectra of six members belonging to this system with x values extending from 0.450 to 0.575, are displayed in figure 1. Further attempts to produce glasses with higher x values failed; this is consistent with the previous finding of Furdanowicz and Klein (1983).

The compositional range that was studied can be subdivided into two regions according to the intensity in the modification performed on the phosphate network and mirrored by the obtained IR spectra. The first region extends from $x=0.450$ to 0.500 and is characterized by subtle changes in the studied domain ($200\text{--}2000\text{ cm}^{-1}$) corresponding to stretching modes of PO_4 groups ($\nu > 900\text{ cm}^{-1}$), P-O-P bridges ($600\text{--}1000\text{ cm}^{-1}$) and bending modes of PO_4 ($400\text{--}600\text{ cm}^{-1}$) (Rousselot *et al* 1992). These changes can be summarized as follows: (i) the well-defined peak at 1300 cm^{-1} ($x=0.450$) is converted to a shoulder in the spectra of the glasses with $x=0.475$ and 0.500, this is accompanied with a downshift in its frequency value from 1300 to 1295 cm^{-1} ; and (ii) the frequencies of the bands at 1185, 870 and 475 cm^{-1}

Figure 1. The IR spectra of the binary $x\text{PbO} \cdot (1-x)\text{P}_2\text{O}_5$ glasses in the range 45–57.5 mol% PbO . (The curves are displaced vertically to avoid confusion).

($x=0.450$) are upshifted to 1210, 885 and 485 cm^{-1} ($x=0.500$), respectively.

On the other hand, the second compositional region which extends from $x > 0.500$ to $x = 0.575$ exhibits drastic changes on the IR spectral profiles of the glass samples upon increasing the value of x . The changes can be summarized as follows: (i) the 1300 cm^{-1} band ($x=0.450$) continues its downshift till it eventually disappears at $x=0.575$; (ii) the most intensive 1265 cm^{-1} band is weakened and is observed as a shoulder located at 1250 cm^{-1} ($x=0.575$); and (iii) the appearance of three new bands at 1220, 1050 and 960 cm^{-1} (at $x=0.550$ and/or 0.575).

3.1b $x\text{ZnO} \cdot (1-x)\text{P}_2\text{O}_5$ system: The IR spectra of seven members belonging to this system, with x values extending from 0.450 to 0.600, are shown in figure 2. The experimental results shown in this figure can be summarized as follows: (i) the bands at 1275, 1150 and 1090 cm^{-1} show roughly similar intensity behaviours. They decrease

and increase with the initial and second rise in x values, respectively, while they decrease with subsequent rises, (ii) the frequencies of the bands at 1340, 1275 and 915 cm^{-1} ($x=0.450$) are downshifted to 1315, 1265 and 900 cm^{-1} at $x=0.550$ while they are upshifted to the values of 1335, 1275 and 925 cm^{-1} at $x=0.600$ and (iii) the intensity of the band at 760 cm^{-1} decreases with the increase in x value till it, eventually disappears at $x=0.600$. On contrary, the intensity of the band at 725 cm^{-1} increases by the same measure.

3.1c $x\text{Na}_2\text{O} \cdot (0.50-x)\text{PbO} \cdot 0.50\text{P}_2\text{O}_5$ system: Figure 3 shows the effect of replacing parts of PbO by Na_2O on the IR spectrum of 0.50 PbO-0.50 P_2O_5 (mol%) glass (i.e. the stoichiometric composition of lead metaphosphate). The observed changes can be summarized as follows: (i) the bands at 1265 and 485 cm^{-1} are intensified along the rise in x value. The intensification is more pronounced with the initial rise in x value, (ii) the disappearance of the shoulder at 1295 cm^{-1} ($x=0$) in the spectrum of the glass with $x=0.20$, (iii) the appearance of a new band at 1045 cm^{-1} in the spectra of the Na_2O containing glasses and (iv) the well-defined band at 1075 cm^{-1} at

Figure 2. The IR spectra of the binary $x\text{ZnO} \cdot (1-x)\text{P}_2\text{O}_5$ glasses in the range 45–60 mol% ZnO. (The curves are displaced vertically to avoid confusion).

Figure 3. The IR spectra of different compositionally suggested metaphosphates in the system $x\text{Na}_2\text{O} \cdot (0.50-x)\text{PbO} \cdot 0.50\text{P}_2\text{O}_5$. (The curves are displaced vertically to avoid confusion).

$x=0$ is upshifted to 1100 cm^{-1} in the rest of the glasses spectra and is identified as a shoulder.

3.1d $x\text{Na}_2\text{O} \cdot (0.50 - x)\text{ZnO} \cdot 0.50\text{P}_2\text{O}_5$ system: The IR spectra of the glasses belonging to this system are shown in figure 4. The experimental observations are similar to those described for the PbO -ternary system except that the present system shows some differences which are summarized as follows: (i) the influence of the initial increase in x values on the spectral profile of Na_2O -free glass spectrum is less pronounced, (ii) the disappearance of the band at 1330 cm^{-1} , which is of the same origin as that observed at 1295 cm^{-1} in figure 3 (i.e. due to $\nu(\text{P}=\text{O})$), is seen to occur at $x=40\text{ mol}\%$ rather than $20\text{ mol}\%$ as in the case of PbO -ternary glasses and (iii) the band which appears at 1045 cm^{-1} in the Na_2O -containing glasses of the PbO -ternary system does not appear in the present system.

3.2 Chemical durability

3.2a Binary lead phosphate glasses: Leach rates based on total weight loss expressed in $(\text{mol glass} \cdot \text{cm}^{-2} \cdot \text{min}^{-1})$,

Figure 4. The IR spectra of different compositionally suggested metaphosphates in the system $x\text{Na}_2\text{O} \cdot (0.50 - x)\text{ZnO} \cdot 0.50\text{P}_2\text{O}_5$. (The curves are displaced vertically to avoid confusion).

are plotted as a function of glass composition variation at different pH values in figure 5. Strong compositional dependences are observed at all pH's except pH 7, where the rates seem to be unaffected by the variation in glass composition. More specifically, the rates show increasing tendencies by a factor of nearly 10, along the rise in P_2O_5 content from 42.5 to 50 mol%. However, marked decreases in the rates are observed to take place in the solutions with $\text{pH} < 7$ upon increasing the P_2O_5 content up to 52.5 mol%, followed by a steady increase with further increments in P_2O_5 content. Because the data obtained for glasses with 57.5 and 60 mol% P_2O_5 contents are not reliable they are plotted only as examples at certain pH's.

Figure 6 shows the behaviour exhibited by individual glasses when exposed to solutions over the pH range 3.4–9. The obtained results show roughly the same pH dependences for all the studied glasses except those with the lowest P_2O_5 content. Marked decrease in the chemical durability of the glasses is observed to take place as the pH value increases in the acidic regime, while the chemical durability decreases suddenly as the neutrality point is achieved, further decrease in chemical durability is observed as the pH value is raised to 9.0.

3.2b Binary zinc phosphate glasses: Figure 7 shows the effect of variation in the composition of glass on dissolution rates of the glasses included in this system. The leaching behaviour of these glasses follows the same general trends observed for the lead phosphate glasses. This is accompanied by two main differences: (i) the dissolution rates of ZnO -glasses is higher than their corresponding PbO -glasses by a factor of ~ 100 times; and (ii) the minimum which appears in the ultraphosphate compositional range is located at 55 mol% in case of ZnO -glasses rather than at 52.5 mol% in case of PbO -glasses.

Figure 8 shows the change in the dissolution rates of part of these glasses as a function of pH. In contrast to the results obtained for binary lead phosphate glasses, the rates decrease as the pH values of the attacking solutions were increased in the acidic regime, and the rates increase suddenly as the neutral point is achieved. This is followed by a decrease in the rates of the studied glasses as the pH value exceeds 7.0.

3.2c Ternary $x\text{Na}_2\text{O} \cdot (0.50 - x)\text{PbO} \cdot 0.50\text{P}_2\text{O}_5$ system: The effect of variation in the glass composition on the dissolution rates of the glasses included in this system at three different pH values (pH 3.4, 7 and 9) are depicted in figure 9. The values were selected to explore the effect in the three conventional solutions media (acidic, neutral and basic). Although the dissolution rates of the studied glasses exhibit the same compositional

dependence for all the values of pH's that were studied, the behaviours varied according to the compositional range they are working in. The most characteristic features are: (i) sharp increase in the dissolution-rate accompanied

with the initial increase in x value (10 mol% Na_2O), and (ii) before the rate continues its steady increase it has been found to be retarded (or slightly decreased) as x approaches the value of 20 mol%.

Figure 5. Rates of dissolution of binary $x\text{PbO} \cdot (100-x)\text{P}_2\text{O}_5$ glasses in different buffer solutions as a function of P_2O_5 content (at 70°C).

Figure 6. Rates of dissolution as a function of pH values at 70°C for binary lead phosphate glasses of the following P_2O_5 contents (mol%): (a) 55; (b) 52.5; (c) 50; (d) 47.5; (e) 45; (f) 42.5.

4. Discussion

4.1 Infrared

4.1a $x\text{PbO} \cdot (1-x)\text{P}_2\text{O}_5$ system: It is conventional to all glass researchers that both PbO and ZnO have the ability to reside in glassy structures either in network-forming or modifying positions. Their incorporations as NWF's is expected to reduce the number of PO_4^- groups, while their incorporations as NWM's is believed to increase this number. Consequently, the IR bands correlated to such groups should decrease in the former case and increase in the latter. However, the apparent constancy in the intensity and frequency values of the band at 1075 cm^{-1} [$\nu_1(\text{PO}_4^-)$] in the first compositional range ($0.450 \leq x \leq 0.500$; figure 1) indicates that this group is not involved in the interaction between P_2O_5 and PbO, on the other hand the changes in the 1300 cm^{-1} band indicate that the $\text{P}=\text{O}$ (phosphoryl) groups are involved. This may suggest the incorporation of PbO as

NWF in the way described by Selvaraj and Rao (1988), where the π -bonds of the phosphoryl groups are delocalized to interlink the Pb^{2+} ions (as seen below) forming the so-called iso-silicate structure.

Moreover, the apparent constancy in the intensity and frequency values of the 1265 cm^{-1} band [$\nu_{as}(\text{PO}_2)$], as x goes from 0.450 to 0.500, provides an additional support to such conclusion.

Figure 7. Rates of dissolution of binary $x\text{ZnO} \cdot (100-x)\text{P}_2\text{O}_5$ glasses in different buffer solutions as a function of P_2O_5 -content (at 70°C).

Figure 8. Rates of dissolution as a function of pH values at 70°C for binary zinc phosphate glasses of the following P_2O_5 -contents (mol%) (a) 55; (b) 52.5; (c) 50; (d) 47.5; (e) 45; (f) 40.

The formation of the above structure would result in increasing the network order of polymerization (according to Grimmer and Wolf (1991) notation). This may explain the upshift of the ν_{as} (P-O-P) band from 870 ($x=0.450$) to 885 cm^{-1} ($x=0.500$), in an opposite manner to that suggested by Gray and Klein (1989). These authors suggested that this band should shift downward upon crossing the ultraphosphate range towards the metaphosphate composition, since the symmetry of PO_4 increases in this direction.

As x exceeds the value of 0.500 (figure 1), the number and intensities of the IR bands change significantly, suggesting, extensive chemical reaction between PbO and P_2O_5 . More specifically, the weakening of the bands at 1265 cm^{-1} [$\nu_{as}(\text{PO}_2)$] and 780 cm^{-1} [$\nu_{as}(\text{P-O-P})$] reflects the occurrence of continuous structural breakdown, and the 15 cm^{-1} shift of the former band is consistent with the results reported (Kang Sun and Risen 1986; Bruni *et al* 1994) about vibrational, IR and Raman spectra of phosphate glasses containing chains of variable lengths, with unique difference that occurs here as x goes from 0.550 to 0.575.

The replacement of the 1265 cm^{-1} strong band by new band at 1217–1220 cm^{-1} , reveals (Rousselot *et al* 1992) that there are, approximately, no more PO_2 groups but only PO_3 ones which give rise to the latter new line at $x=0.550$ and 0.575. Furthermore, the presence of new small band at 960 cm^{-1} may be assigned to $\nu_s\text{PO}_3$ mode of $\text{P}_2\text{O}_7^{4-}$ (Sammet and Brückner 1987). On the other hand, the 1300 cm^{-1} shoulder, which survives up to $x=0.550$, disappears at $x=0.575$ reflecting complete delocalization for the π -bonds of the phosphoryl groups in the structure of this glass.

Finally, the metaphosphate structure suggested by the stoichiometric composition of the glass with $x=0.500$ is not confirmed. This may be attributed to the presence of 1295 cm^{-1} band [$\nu(\text{P=O})$] in the spectral pattern of this glass. In other words, the band should disappear if the metaphosphate structure was achieved (Brow *et al* 1994).

4.1b $x\text{ZnO} \cdot (1-x)\text{P}_2\text{O}_5$ system: The structural changes which occur in these glasses, as the composition is altered can be deduced from the IR spectra shown in figure 2. The changes in the spectral profile accompanied with the rise in x value from 0.450 to 0.475, suggest that Zn^{2+} ions are incorporated mainly as NWF's in this compositional region. This may be manifested by decrease in the intensities of the bands at 1275 [$\nu_{as}(\text{PO}_2)$], 1150 [$\nu(\text{PO}_3)$] and 1090 cm^{-1} [$\nu_s(\text{PO}^-)$] together with the downshift of the latter band to 1070 cm^{-1} . However, the decrease in the intensity $\nu_s(\text{PO}^-)$ band suggests that Zn^{2+} ions interlink themselves to the network through these groups rather than the π -bonds of the phosphoryl groups. The incapability of the Zn ions to make use of π -bonds can be understood on the basis of zinc being regarded as a nontransition element, since it cannot form a compound in which the d -shell is other than full. Thus the possibility of $d\pi$ -bonding is very much lowered (Cotton and Wilkinson 1972). Accordingly the following interaction may be suggested:

Figure 9. Rates of dissolution of ternary $x\text{Na}_2\text{O} \cdot (50-x)\text{PbO} \cdot 50\text{P}_2\text{O}_5$ glasses in acidic, neutral and alkaline buffer solutions as a function of PbO-content.

This reaction suggests an increase in the number of the P=O groups, and consequently the water content of the glass should increase. This can be concluded from the intensification of the band $\sim 1650\text{ cm}^{-1}$, attributed to the bending vibrations of H_2O molecules.

According to Bruni *et al* (1994), the intensity of the $\nu_{\text{as}}(\text{PO}_3)$ mode should decrease as we go apart from the metaphosphate composition, i.e. either in the direction of polyphosphates or ultraphosphates. Thus, the unexpected decrease in the intensity of this band (1275 cm^{-1}) as we go from $x=0.450$ to 0.475 is indicative of the action of ZnO as NWF.

On the contrary, the significant increase in the band intensity at 1276 and 1070 cm^{-1} ($x=0.475$) together with the upshift of the latter band as x goes from 0.475 to 0.500 is indicative of the action of ZnO as NWM. The depolymerization of the network results in the generation of increasing number of NBO's. The increase in such number per phosphate tetrahedra, increases the capability of phosphorous ions to compensate their high positive charges by performing closer coordination to their next nearest neighbour NBO's. This may be the cause of the observed 30 cm^{-1} shift of the $\nu(\text{PO}^-)$ band as x goes from 0.475 to 0.525 .

Moreover, the increase in the band intensity at 745 cm^{-1} due to $(\text{P}-\text{O}-\text{P})_{\text{cycl}}$ is at the expense of that at 770 cm^{-1} due to $\nu_s(\text{P}-\text{O}-\text{P})$ which marks the formation of increasing amounts of structures. The formation of such ring structures results in the polymerization of PO^{6-} groups, which increase the probability of localized double bond formation. This may account for the upshift of the P=O ($1315\text{--}1335\text{ cm}^{-1}$).

Finally, the metaphosphate structure which has not been confirmed in the case of PbO is neither confirmed in the present case due to the presence of the band at 1330 cm^{-1} [$\nu(\text{P}=\text{O})$] in the spectral pattern of the $x=0.500$ glass.

4.1c $x\text{Na}_2\text{O} \cdot (0.50 - x)\text{PbO} \cdot 0.50\text{P}_2\text{O}_5$ system: The replacement of PbO by Na_2O is expected to increase the order of depolymerization of the network by creating increasing number of NBOs. Such creation can be manifested by the sharp increase in the intensities of the bands at 1265 cm^{-1} [$\nu_{\text{as}}(\text{PO}_2)$] and 480 cm^{-1} [$\delta_{\text{as}}(\text{PO}_2)$], the upshift of the 1075 cm^{-1} band to 1100 cm^{-1} [$\nu_s(\text{PO}^-)$], and the appearance of the new band at 1045 cm^{-1} [$\nu_s(\text{PO}_3^{2-})$] (see figure 3). The formation of the NBOs is assumed to occur according to the following two reactions:

or

The second reaction is believed to be more favoured since the oxygens in the $(\text{P}-\text{O}-\text{Pb})$ units are more

polarizable than those in the $(\text{P}-\text{O}-\text{P})$ units, and hence their bonds are more susceptible to be broken.

The disappearance of the 1295 cm^{-1} band [$\nu(\text{P}=\text{O})$] in the spectrum of the glass with $x=0.20$ suggests the conversion of the three-dimensional network to one-dimensional network. In other words, the metaphosphate structure, which has not been confirmed by the structure of the $50\text{PbO} \cdot 50\text{P}_2\text{O}_5$ (mol%) glass, is established (i.e. Q^2 -moieties dominate). Moreover, the two bands which appear at 1045 and 1000 cm^{-1} reflect the formation of pyrophosphate and orthophosphate units (Tatsumisago *et al* 1988), respectively. The decrease in the intensities of these two bands, as x exceeds 0.15 , seems to be parallel to the increase in the intensity of the shoulder at 700 cm^{-1} . This reveals that the increase in the amount of cyclic structures is mainly performed at the expense of the low-molecular-weight molecules (e.g. pyro- and orthophosphates).

4.1d $x\text{Na}_2\text{O} \cdot (0.50 - x)\text{ZnO} \cdot 0.50\text{P}_2\text{O}_5$ system: Because of the similarity between the changes in the IR spectra of the PbO-ternary system (figure 3) and the present system (figure 4), the same discussion carried out previously can be reported here. However, the differences are presented as follows: (i) the metaphosphate structure (built up as infinite PO_4 -tetrahedral chains) is established at $x=0.40$ rather than at 0.20 in the previous system, (ii) the comparison between the area of $\nu_{\text{as}}(\text{PO}_2)$ band in both the systems suggest shorter metaphosphate chains in the present system. This can be attributed to the higher field strength of Zn^{2+} cations as compared to Pb^{2+} cations (Bartholomew 1972), and (iii) the pyrophosphate groups are not observed to exist in the present case.

4.2 Chemical durability

4.2a The effect of composition: Chemical durability results can be discussed on the basis of the polymeric structural model of phosphate glasses suggested by Van Wazer (1951). Accordingly, the basic unit is the tetrahedral PO_4 group which can be bonded to a maximum of three neighbouring groups through bridging oxygens. The addition of modifier oxides disrupts the bridging $(\text{P}-\text{O}-\text{P})$ bonds and lowers the number of bridging PO_4 tetrahedra.

In polyphosphate region ($\text{P}_2\text{O}_5 < 50\text{ mol}\%$), glasses are considered to be composed of unbranched polymer of variable chain lengths. The average length of the chains increases with increasing P_2O_5 content of the glasses. However, since the mechanism of hydrolysis comprises the rapid suspension of intact polymers in aqueous solutions, the shorter the chains the easier their dissolution (i.e. glass compositions with higher P_2O_5 contents, with longer chains, will have improved chemical durabilities (Gray and Klein 1983; Bae and Weinberg 1994)).

In contrast to the above point of view, Dickenson (1994) suggested, on the basis of the stability constant criterion, that glass compositions with lower P_2O_5 contents (i.e. shorter chains) will have improved chemical durabilities. This is built on the fact that the stability constants increase in the direction meta- < tetra- < tri- < pyro- < orthophosphates. However, the present results in both cases of PbO-binary glasses (figure 5) and ZnO-binary glasses (figure 7), in the region $P_2O_5 \leq 50$ mol%, are consistent with Dickenson's point of view. Fortunately, similar behaviour has been obtained previously (Furdanowicz and Klein 1983) upon subjecting binary lead phosphate glasses to the action of water at ambient temperature. The results were explained on the basis that PbO has a dramatic effect on the rate of dissolution of phosphate glasses as it apparently behaves as network-former with respect to the dissolution of the glass in solutions, cross-linking the relatively inert polyphosphate polymers into a very durable network.

As P_2O_5 contents exceed 50 mol%, branching tetrahedra are introduced, serving as steric hindrance to the diffusion of the attacking species into the glass and, consequently, lower the rates of dissolution (figures 5 and 7). However, as the fraction of branching PO_4 tetrahedra increases, good deal of strain is introduced into the network which encourages the hydrolytic cision of these branching units, leading to an increase in the rates of dissolution.

The minimum corresponding to the lowest dissolution rates in the ultraphosphate region was predicted (Bae and Weinberg 1994) to be, at approximately, 60 mol% P_2O_5 . The ability of both Pb^{2+} and Zn^{2+} cations to act as NWFs increases the real value of Q^3/Q^2 over the theoretical one calculated from the following equation.

$$Q^3/Q^2 = \frac{1-2x}{x},$$

where x is the mole fraction of the modifying oxide in the ultraphosphate region of a binary glass.

This may be the reason which stands behind the appearance of such minimum at 52.5 and 55 mol% P_2O_5 in the cases of binary PbO glasses and ZnO glasses (figures 5 and 7), respectively.

4.2b The effect of pH: The dissolution of most phosphate glasses is governed by the 'hydration mechanism', which includes the protonation of the phosphate chains, in acidic solution, and disruption of the cross-links between them via the following chemical reaction:

Once phosphate cross-links are broken by the above reaction the entire chains rapidly dissolve, leading to

what is called 'uniform dissolution'. It is obvious that the rate of such dissolution is accelerated with the rise in (H^+) .

Although this acceleration is confirmed by the results obtained in the case of ZnO-binary glasses (figure 8), in the acidic regime, it is not confirmed by those obtained in the case of PbO-binary glasses (figure 6). This does not conclusively suggest that the hydration mechanism is invoked. Repeatedly, such unusual behaviour may be attributed to the partial action of PbO as network-former. In this case, the P-O-Pb bond has some covalent characteristics. Thus, the ion exchange process, between H_3O^+ and the Pb^{2+} cations located between phosphate chains, is thermodynamically less favourable (Peng and Day 1991). This may indicate that the above hydration reaction is not the rate determining step governing the dissolution of the phosphate network.

On the other side, the increase in rates of the ZnO-binary glasses (figure 8) upon achieving the neutrality point represents another unusual behaviour. This may be attributed to the increase in the water content in the structure of the glasses as a consequence of the increase in the P=O groups upon the incorporation of the ZnO as NWF and the formation of cyclic structures as has been concluded from the IR study.

Although Zn^{2+} possesses higher field strength than Pb^{2+} and is assumed to express greater blocking effect to the glass structure, the obtained results reveal opposite trend. More specifically, the dissolution rates of the ZnO-binary glasses are higher than their corresponding PbO ones by ~100 times. This may be referred to the following two reasons.

First, the hydration mechanism is most likely controlled by two factors: (i) the bond strength of the cross-link between modifier cation and phosphate chain, and (ii) the affinity of the cation to water. According to the first factor, the hydration in the case of Pb^{2+} is expected to be easier than in the case of Zn^{2+} because of its lower field strength which leads to a weaker bond strength. However, in hydration reaction, ion-dipole (Pb^{2+} - or Zn^{2+} - H_2O) interaction plays an important role in determining how soluble an ionic compound will be in solution. Zn^{2+} cation has a greater electrostatic interaction with water than Pb^{2+} since it is smaller in size and its charge is more concentrated. Thus, Zn^{2+} cation possesses higher in-dipole interaction. The obtained results suggest more importance for second factor than the former one.

Secondly, the ability of Pb^{2+} cations to link themselves through the π -bonds of the phosphoryl groups, thus building a network which mimics that of silicate glasses, together with the incapability of Zn^{2+} cations to make such compact structure as has been seen from the discussion of the IR results.

The dramatic increase in the dissolution rate of the

equimolar $\text{PbO-P}_2\text{O}_5$ glass accompanied with the initial 10 mol%, replacement of Na_2O for PbO (figure 9) may be attributed to the relieving of the previously suggested silicate like structure. This suggests the preference of the second reason over the first one.

On the other hand, the above behaviour is followed by a slight decrease in the dissolution rates accompanied by the second replacement of Na_2O for PbO , exhibiting a minimum at $x=0.20$. This composition ($20\text{Na}_2\text{O-30PbO-50P}_2\text{O}_5$) resembles that suggested from the IR study to achieve the ideal metaphosphate structure. This structure has supposedly improved chemical durability. Although further replacements of Na^+ (low field) for Pb^{2+} (high field strength) would result in increasing the lengths of the metaphosphate chains (Bartholomew 1972) no further decrease (or retardation) to the increase in rates are observed. This may indicate that such elongation in chain lengths cannot withstand the effect of replacing monovalent cations (Na^+) for divalent cations (Pb^{2+}) anymore.

5. Conclusion

The results show that the dissolution rates of the binary zinc phosphate glasses are higher than their corresponding lead glasses by about 100 times. Such difference in the dissolution rates of the glasses in both systems was destroyed by replacing 10 mol% Na_2O for PbO in the $50\text{PbO-50P}_2\text{O}_5$ (mol%) glass composition. The results could not be correlated to the difference in the field strengths of the Pb^{2+} and Zn^{2+} ions. They were rather correlated, according to the IR results, to the difference in which both cations interlink themselves to the phosphate network when they are incorporated as NWFs. Moreover, Pb^{2+} cations exhibit the ability to form compact iso-silicate structure, while Zn^{2+} cations do not.

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