Density and Acidic Solution Calorimetry Studies of the 0.333CaO-0.667[xSiO$_2$-(1-x)P$_2$O$_5$] Glassy System

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ABSTRACT

Glassy samples of the 0.333CaO-0.667[xSiO$_2$-(1-x)P$_2$O$_5$] system are prepared by the melt quenching technique. Accurate density and solution enthalpy measurements were performed by pycnometry at 296.15 K and acid solution calorimetry at 298.15 K, respectively. Excess molar volume and mixing enthalpy from the ideal behavior over the entire mole fraction range were calculated. These excess thermodynamic properties are negative over the whole composition range showing attractive and contraction behavior with the increase in the silica content. Excess properties were fitted to the Redlich-Kister type equation. Examination of the behavior of the excess properties indicates that deviations from ideality can be attributed mainly to the formation of mixed association complexes.

Indexing terms/Keywords

Glass; Solution calorimetry; Density; Glassy temperature; Mixing enthalpy.

Academic Discipline And Sub-Disciplines

Inorganic chemistry.

SUBJECT CLASSIFICATION

Calorimetry; Glass materials.

TYPE (METHOD/APPROACH)

Synthesis and experimental study.
INTRODUCTION

Oxide glasses are classically described as a network composed by building entities such as SiO₂, B₂O₃, P₂O₅, TeO₂ and modifiers such as alkaline oxides: Li₂O, Na₂O, K₂O, Ag₂O or alkaline earth oxides: CaO, MgO, SrO [1,2]. In such glasses, the oxygen from the metal oxide becomes part of the covalent glass network, creating new structural units. The cations of the modifier oxide are generally present in the neighborhood of the nonbridging oxygens (NBO) in the glass structure. The extent of the network modification obviously depends on the concentration of the modifier oxide present in the glass. It is known from NMR studies that the depolymerization of a glass network affects various physical properties such as density, molar volume, glass transition temperature,....

Calcium phosphosilicate glasses are characterized by an interesting structure on account of the presence of two glass-forming components. Literature data [3-5] reported that the structure of phosphosilicate glass is composed of tetrahedrals, combined at random with each other, forming a three-dimensional, disordered lattice in which every silicon atom is bound with four other silicon or phosphorus atoms by means of oxygen bonds (e.g. S-O-Si, Si-O-P); whereas each phosphorus atom has only three bridging bonds. In the four edges of the tetrahedron [PO₄], there is a non-bridging oxygen atom bound with the central phosphorus atom by a double bond (O=P). This oxygen atom does not form an oxygen bridge with another tetrahedron and therefore it does not participate in the formation of polymerized phosphate anions. Introduction of the modifying oxides of R₂O and RO-type (where R = K, Na, Mg, Ca,....) materials into the structure of the phosphosilicate glass results in the breaking of some part of the chemical bonds occurring in the oxygen bridges of the type: S-O-Si, Si-O-P and P-O-P [6] and leads to the formation of terminal oxygens of the type S-O’ and P-O’, and thereby depolymerizing the phosphosilicate network [5-9].

Thermodynamic characteristics of phosphosilicate glasses are rarely found in the literature. Information about glass transition and mixing enthalpy mainly concerns borophosphate[10, 11] or borosilicate glasses [12, 13]. In view of theoretical and practical importance of phosphosilicate glasses, the thermochemical study of calcium phosphosilicate is welcome to provide information about molecular interactions. Excess thermodynamic properties have also been used as a qualitative and quantitative guide to predict the extent of complex formation in these kinds of mixtures. These kinds of glasses have found widespread application in medicine as bone implants[14] or in agriculture as glassy ecological fertilizers [15].

The main reason for undertaking research on the effects of silicate on mixing enthalpy and excess molar volume of glasses from 0.333CaO-0.667xSiO₂-(1-x)P₂O₅ system was the lack of data concerning excess thermodynamic properties of calcium phosphosilicate glasses, an original glass family formed by a network as different as silicate and phosphorus. The results obtained from the DSC, picnometry and solution calorimetry are presented and discussed.

EXPERIMENTAL

Calcium phosphosilicate glasses were prepared by the melt quenching technique from high-purity reagent grade SiO₂, CaCO₃ and (NH₄)₂HPO₄. The raw materials were mixed up in the desired proportions and thoroughly ground in an agate mortar. The mixtures were fired in air in a platinum crucible into a programmed kiln, in the following manner :

(a) reaching 500°C at the end of 80 min and keeping steady at this temperature for 30 min to allow the evaporation of water from the powders to be as complete as possible;
(b) reaching 1000°C in 85 min and keeping steady at this temperature for 30 min to allow all the gases removal (CO₂, NH₃, H₂O);
(c) reaching 1500°C in 85 min and keeping steady at this temperature for 90 min to allow a complete homogenization of the melt.

The melt was quenched by dipping the bottom of the crucible into cold water. The samples were then kept in vacuum desiccators to avoid possible moisture sorption before testing.

X-Ray Diffraction measurements at room temperature confirmed the amorphous state of the samples.

A Setaram DSC 111 system operating in heat flux DSC mode, under argon atmosphere and a heating rate of 5°C per minute was used for glass transition effect measurements. The samples (about 50 mg) were heated in platinum up to 700°C. The glass transition temperature (Tg) was registered in a half of the endothermal inflection on DSC curve. The estimated error on the temperature measurements is ± 3°C for the glass transition.

Densities of glass samples were measured at 296.15 K by using a pycnometer with diethylptalate (d = 1.118) as the immersion fluid. The pycnometer consists in glass flask with a close-fitting ground glass stopper surmounted by a capillary indexed tube. This tube releases a part of the liquid after closing the top-filled pycnometer and allows to measure with a very high accuracy, masses of constant volumes of working liquid or liquid and solid. Care was taken to make sure that all of the cast samples were bubble free and that the glass samples were fully wetted when immersed in the diethylptalate. All the weight measurements have been made using a digital balance Sartorius, having an accuracy of ± 0.1 mg. The reported values of density are averages of the four to five independent measurements. Experimental accuracy in the density measurement is ± 0.03 g.cm⁻³.

As the reaction between the glassy oxides cannot be carried out directly into the calorimeter at ambient temperature due to kinetic limitations, the well-known dissolution method is applied. This indirect method based on a Hess thermodynamic cycle consists in the successive dissolutions in the same solvent and at the same temperature of all the compounds involved in the reaction of formation [16]. HF calorimetric experiments were performed with a swinging calorimeter. The
calorimeter and standard procedures have been described previously [10] and so only a brief description will be given here. The whole measurement cell, made of PolyTetraFluoroEthylene (PTFE) resin allows dissolutions in all mineral acidic or basic aqueous solutions. The stirring rate was 3 rpm. The calorimeter is in a thermally regulated room at ±1 K and the dissolutions are carried out at 298.15 ± 0.01 K. Before dissolution, the solute and the solvent are whole isolated each together in two distinct compartments separated by a platinum cap and a n-decane liquid joint. The acidic vapor cannot react with the solute during the thermal stabilization time of the calorimeter. After thermal equilibrium during about 4h, the solute is put in touch with the solvent which consists in a 25 mL HF (6M) and 25 mL HNO₃ (4M) mixture by rotating the calorimeter. The dissolution starts with the first rotation. The rotation of the calorimeter is stopped as soon as the flow of energy produced by the reaction is cancelled. The data acquisition is stopped about an hour after the end of the dissolution so the final thermal and mechanical state of the calorimeter is identical to the initial state. The calorimeter was calibrated by using the heat effect of the well-known enthalpy of dissolution of tris-hydroxy-methylaminomethane in hydrochloric solution [17].

RESULTS

Seven glasses of various compositions in the 0.333CaO-0.667[xSiO₂-(1-x)P₂O₅] system with x varying between 0 and 1 were studied. The amorphous state of the samples was confirmed by XRD patterns which exhibited no diffraction peaks. The DSC thermograms confirm the assertion by showing the characteristic inflexion point at the glassy transition. The T_g data are gathered in Table 1 and shown as a function of the SiO₂ content in Fig.1. The uncertainty of T_g measurements is ±3°C. The line is only drawn as a guide to the eye. It has been found that T_g increased from 232°C to 579°C with the increase in the SiO₂ mole fraction from nought to one.

Table 1: Density (ρ), molar volume (V_m), excess molar volume (V^E) at 296.15 K, glass transition temperature (T_g), molar solution enthalpy at infinite dilution (Δ_diss H^∞) and mixing molar enthalpy (ΔH_m) at 298.15 K of 0.333CaO-0.667[xSiO₂-(1-x)P₂O₅] glasses.

<table>
<thead>
<tr>
<th>x</th>
<th>ρ (g.cm⁻³)</th>
<th>V_m (cm³.mol⁻¹)</th>
<th>OPD</th>
<th>V^E (cm³.mol⁻¹)</th>
<th>T_g (°C)</th>
<th>Δ_diss H^∞ (kJ.mol⁻¹)</th>
<th>ΔH_m (kJ.mol⁻¹)</th>
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<tbody>
<tr>
<td>0.0</td>
<td>2.544</td>
<td>44.54</td>
<td>1.317</td>
<td>0.00</td>
<td>232</td>
<td>-40.3</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
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<td>41.92</td>
<td>1.323</td>
<td>-0.39</td>
<td>312</td>
<td>-36.6</td>
<td>-12.9</td>
</tr>
<tr>
<td>0.3</td>
<td>2.626</td>
<td>36.92</td>
<td>1.329</td>
<td>-0.92</td>
<td>325</td>
<td>-37.0</td>
<td>-30.8</td>
</tr>
<tr>
<td>0.5</td>
<td>2.666</td>
<td>32.27</td>
<td>1.322</td>
<td>-1.10</td>
<td>561</td>
<td>-54.3</td>
<td>-31.8</td>
</tr>
<tr>
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<td>2.664</td>
<td>28.18</td>
<td>1.287</td>
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<td>565</td>
<td>-84.7</td>
<td>-19.7</td>
</tr>
<tr>
<td>0.9</td>
<td>2.653</td>
<td>24.20</td>
<td>1.234</td>
<td>-0.24</td>
<td>579</td>
<td>-112.6</td>
<td>-10.1</td>
</tr>
<tr>
<td>1.0</td>
<td>2.646</td>
<td>22.20</td>
<td>1.201</td>
<td>0.00</td>
<td>579</td>
<td>-131.8</td>
<td>0.0</td>
</tr>
<tr>
<td>±0.03</td>
<td>±0.5</td>
<td>±0.5</td>
<td>±0.5</td>
<td>±3</td>
<td>±1.5</td>
<td>±4.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Glass transition temperature (T_g) as a function of the SiO₂ mole fraction, x, for the 0.333CaO-0.667[xSiO₂-(1-x)P₂O₅] glasses. The line is drawn as a guide for the eye.
The effect of changes in the chemical composition of the analyzed glasses on the density \(\rho\) is also shown in Table 1. It has been found that the increase in the amount of \(\text{SiO}_2\) in the glass structure of the examined glasses correlated with the increase of their density up to about \(x = 1/2\) concentration and then slightly decreased after. Molar volume values \(V_m\) at 296.15 K are reported in Table 1, too. The excess molar volume \(V^E\) were computed from experimental density data using the relationship

\[
V^E = \left[ \frac{x_1 M_1 + x_2 M_2}{\rho} \right] - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}
\]

(1)

where \(x_1\), \(x_2\), \(M_1\), \(M_2\), \(\rho_1\) and \(\rho_2\), are the mole fractions, molecular weights and experimental density data of the end members of the glassy solution, respectively. The results are also listed in Table 1 and reported in Fig.2. Maximum error on \(V^E\) is estimated to be less than 0.5 cm\(^3\).mol\(^{-1}\).

Samples only from 4 to 12 mg were dissolved in the PTFE-cell of the calorimeter in 50 mL of solvent. Table 2 gathers the results of the solution calorimetric measurements at 298.15 K. Table 1 showed the values of solution enthalpy at infinite dilution \(\Delta_{\text{diss}}H^\infty\) at 298.15 K. They were deduced by linear extrapolation to zero concentration of the solution enthalpy. The accuracy of determination was \(\pm 3\) kJ.mol\(^{-1}\).

Table 2 : Experimental solution enthalpies \(\Delta_{\text{diss}}H\) of 0.333CaO-0.667[xSiO\(_2\)-(1-x)\(\text{P}_2\text{O}_5\)] glasses in a 25 mL HF (6M) and 25 mL HNO\(_3\) (4M) mixture at 298.15 K.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(m) (mg)</th>
<th>(C) (mol/L)</th>
<th>(\Delta_{\text{diss}}H) (kJ.mol(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>0.00110809</td>
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</tr>
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</tr>
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<td>0.00164801</td>
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</tr>
<tr>
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<td>5.15</td>
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<td>-36.27</td>
</tr>
<tr>
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<td>0.00122905</td>
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</tr>
<tr>
<td>0.1</td>
<td>9.54</td>
<td>0.0017685</td>
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<tr>
<td>0.1</td>
<td>9.27</td>
<td>0.00171845</td>
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</tr>
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<td>0.1</td>
<td>9.12</td>
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<tr>
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<td>6.82</td>
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</tr>
<tr>
<td>0.3</td>
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<td>0.3</td>
<td>9.68</td>
<td>0.00199657</td>
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<tr>
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<td>10.46</td>
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<tr>
<td>0.5</td>
<td>9.33</td>
<td>0.00216863</td>
<td>-54.69</td>
</tr>
</tbody>
</table>
Classically, the mixing enthalpy determined by the dissolution method is obtained with the algebraic sum of the dissolution enthalpies: Let be a mixture of the A and B compounds in the same physical state:

\[ xA + (1-x)B \rightarrow A_xB_{1-x} \quad \Delta H_m \]

Let be the dissolution reactions extrapolated at infinite dilution at the same temperature and in the same solvent S, the \( \Delta_{\text{diss}}H_i^\infty \) being the enthalpies at infinite dilution previously calculated.

\[ A + S \rightarrow ((A,S,\infty)) \quad \Delta_{\text{diss}}H_A^\infty \]
\[ B + S \rightarrow ((B,S,\infty)) \quad \Delta_{\text{diss}}H_B^\infty \]
\[ A_{x}B_{1-x} + S \rightarrow ((A_xB_{1-x},S,\infty)) \quad \Delta_{\text{diss}}H_{AxB_{1-x}}^\infty \]

The mixing enthalpy is obviously calculated by:

\[ \Delta \text{H} = x \Delta_{\text{diss}}H_A^\infty + (1-x) \Delta_{\text{diss}}H_B^\infty - \Delta_{\text{diss}}H_{AxB_{1-x}}^\infty \]  

(2)

because the interaction between the solutes at infinite dilution in the solvent S is null or:

\[ ((A_xS,\infty)) + ((A_xS,\infty)) \rightarrow ((A_xB_{1-x},S,\infty)) \quad \Delta \text{H}=0 \]

The so calculated mixing enthalpies are listed in Table 1 and reported on Fig.3. The uncertainties in the mixing enthalpies are extracted from the errors in the enthalpies of solution.

The data are connected by a Redlich-Kister polynomial, frequently used in describing excess thermodynamic properties:

\[ x^E = x(1-x)[C_0+C_1(1-2x)+C_2(1-2x)^2+C_3(1-2x)^3...] \]  

(3)

where \( x^E \) is \( V^E \) or \( \Delta H_m \) and \( \sigma \) some polynomial coefficients.

Table 3 shows the appropriate values of the coefficients \( C_i \) for \( V^E \) and \( \Delta H_m \), calculated by least squares analysis with \( \sigma \), the standard error of estimate associated with the use of the Redlich-Kister representation. The symbols in Figs. 2 and
3 present the experimental $V^E$ and $\Delta H_m$ values, while the solid lines refer to the values calculated from the modified Redlich–Kister equation using the $C_i$ parameters given in Table 3.

Table 3: Coefficients $C_i$ for least-squares representation by Eq[3] and standard deviations $\sigma$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^E$ (cm$^3$.mol$^{-1}$)</td>
<td>-4.260</td>
<td>1.161</td>
<td>1.516</td>
<td>-0.186</td>
<td>0.002</td>
</tr>
<tr>
<td>$\Delta H_m$ (kJ.mol$^{-1}$)</td>
<td>-123.165</td>
<td>81.614</td>
<td>2.262</td>
<td>-97.139</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Fig. 2. Excess molar volume $(V^E)$ for the 0.333CaO-0.667[xSiO$_2$-(1-x)P$_2$O$_5$] glasses as a function of the SiO$_2$ mole fraction at 296.15 K. The solid curve is the representation of the Redlich-Kister equation (Eq.(3)) which fits the data by the square root method. The error bars are also indicated.
Fig. 3. Excess molar enthalpy ($\Delta H_m$) for the 0.333CaO-0.667[xSiO$_2$-(1-x)P$_2$O$_5$] glasses as a function of the SiO$_2$ mole fraction, (x) at 298.15 K. The solid curve is the representation of the Redlich-Kister equation (Eq.(3)) which fits the data by the square root method. The error bars are also indicated.

DISCUSSION

As shown in Fig. 1, the glass transition temperature increases considerably from 232°C to 565°C versus the SiO$_2$ content from x = 0 to x = 0.6 and moderately from x = 0.6 to x = 1. The variations in the Tg of an oxide glass is in general attributed to the changes in bond strength, degree of cross-link density and closeness of packing. The cross-link density has in general a greater effect on Tg than the bond strength in oxides glasses. Moreover, Tg can also be correlated to the tightness of packing in the network, which is also related to the oxygen packing density. As a consequence, oxygen packing density (OPD) was calculated to measure the compactness of the glass network. The oxygen density is calculated by dividing the mass of oxygen atoms in one mole of glass by the experimental density ($\rho$):

$$\text{OPD} = \frac{m_O}{\rho} = \frac{M_O \times (2x_{SiO_2} + 5x_{P_2O_5} + x_{CaO})}{\rho}$$

The OPD data calculated from the glass density measurements are also given in Table 1. The oxygen density (OPD) increased with silica subs.

As we may notice from Fig. 2, the values of $V^E$ for the present investigated glass system are very small and close to zero. However, these values are negative over the entire composition range and with the observed minimum in the 0.4<x<0.5 range. Similarly, the mixing enthalpy values at 298.15 K shows relatively strong exothermic mixing enthalpy referred to the two glass former end members. Literature reported that the negative values of $V^E$ can be explained by considering the chemical or specific interactions which have resulted from differences in molecular volumes and free volumes, possible association by hydrogen bonds and/or dipole–dipole interactions leading to weak complex formation [18]. In addition, it means that the negative signs of $V^E$ and $\Delta H_m$ indicate a net packing effect contributed to by structural modifications arising from partial substitution of SiO$_2$ by P$_2$O$_5$ in this glass system which leads to the formation of a continuous framework connected with [SiO$_4$] and [PO$_4$] tetrahedra. As can be seen from Fig. 3, the minimum of mixing enthalpy is observed at about x = 1/3 concentration. Hence, the negative $\Delta H_m$ values of the investigated system assume that heteroassociates form cross complexes between silica and phosphorus anions like the [Si$_2$P$_6$O$_{27}$]$^-$ complex anion.
CONCLUSION

The present work contains original experimental data on the density and solution enthalpy of a calcium phosphosilicate glass system at ambient temperature. Mixing enthalpies were calculated using Hess cycle involving the solution enthalpy of oxides and their compositions in acidic mixture. Excess molar volumes were also evaluated. These excess properties are successfully described by means of the Redlich-Kister model. These new results are thus useful to understand how such different anionic units mix in the amorphous state.

REFERENCES


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