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Enthalpy of mixing in $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ glasses at 298 K

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Abstract

$0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ (with $0 \le x \le 1$) glasses have been characterized by solution calorimetry at 298 K in acid solvent. The experimental data showed a strong negative departure of the enthalpy of mixing from the ideality described by the equation (in kJ/mol): $\Delta H = x(1-x)(-660.2+570x)$. The results were interpreted on the basis of the structural data. Enthalpies of mixing were consistent with sub-regular solution behaviour.

Keywords: Sodium borophosphate; Solution calorimetry; Enthalpy of mixing

1. Introduction

A large family of glasses based on the combination of both B_2O_3 and P_2O_5 with various network modifiers has been developed for widespread applications, including hermetic sealing materials [1,2] and fast ion conductors in solid state batteries [3]. Previous investigations in borophosphate glasses have focused on some specific physical properties [3–7] (chemical durability, refractive index (n), glass transition temperature (T_g), thermal expansion coefficient (α), thermo-optic coefficient (dn/dT), density) and on the glass structure [1,8–11]. In contrast, there is little published work regarding the thermochemistry of borophosphate glasses. Only one high-temperature direct reaction calorimetric measurements [12] was performed for the composition series $(NaPO_3)_2–B_2O_3$ and $Na_4P_2O_7–(NaBO_2)_2$. Recent developments in ambient-temperature solution calorimetry in our laboratory enable us to measure the thermodynamic properties of such glass systems over a wide range of composition and temperature to obtain a better understanding of the structure and the physical properties of the glass.

In this paper, the results of a calorimetric study of $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ are presented. The data on the enthalpy of mixing were measured over the whole composition range with progressive substitution of P_2O_5 by B_2O_3. The data are discussed in structural terms.

2. Experimental

Sodium borophosphate glasses of composition (mol%) $0.2Na_2O–0.8[xB_2O_3–(1-x)P_2O_5]$, $0 \le x \le 1$, were prepared under atmospheric conditions using analytical grade $(NH_4)_2HPO_4$ (Prolabo R.P.), Na_2CO_3 (Merck) and B_2O_3 (Merck). The raw materials were weighed and the mixture was heated in a platinum crucible first at 800 °C for 1 h to remove the volatile products and then melted at 1000–1050 °C, depending on composition, for about 30 min with frequent stirring to ensure a good homogeneity. The melt was rapidly quenched by dipping the bottom of the crucible into water. The samples were stored in vacuum desiccators just prior to calorimetric dissolution in order to prevent reaction with oxygen or moisture.

Powder X-ray diffraction (XRD) patterns were collected at room temperature on all samples in order to detect any crystallization of the quenched samples. A Diffractometer D5000 Siemens apparatus with Cu Kα radiation ($\lambda = 1.5418$ Å) was used. The data were obtained in a stepwise mode with 2θ ranging from 5 to 55°.

Glass transition temperature (T_g) were evaluated by using DSC under argon flux. DSC tests were performed in a SETARAM DSC 111 differential scanning calorimeter

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calibrated with zinc standards [13]. The heating rate was 15 K min^{-1}. The weight samples were about 20 mg. The mean values of T_g were determined from four measurements; the reproducibility is ±2 °C.

The enthalpy of mixing of glasses cannot be measured directly in the entire concentration range due to kinetic limitations. All calorimetric measurements were performed in a laboratory design solution calorimeter at 298 K. This calorimeter was built several years ago in the “Centre de Thermodynamique et Microcalorimétrie du CNRS – Marseille”. Details of the calorimetric apparatus and measurement procedures have been extensively described elsewhere in the literature [14]. The thermopiles constituted by hundreds of chromel–alumel thermocouples are inserted in an isothermal aluminium block. The great stability of the apparatus allows very long experiment around ambient-temperature (293–350 K). The values of heat effects 0.1, 1 and 10 J were measured with 1.06, 0.40 and 0.05% accuracy, respectively. The stirring procedures were standardized and corrections were made for the small heat effects associated with stirring. All measuring cells are in PolyTetraFluoroEthylene (PTFE). According to the recommended procedure, the solvent was added directly into the calorimeter cell. Samples of about 5–20 mg were placed in the container ca. 5 cm^3. The container was closed and stored in the calorimeter cell at the calorimeter temperature (298 K) for 4 h to reach thermal equilibrium. During the dissolution, the sample was broken in the calorimeter cell which contained in a mixture of 25 ml of HF (6 M) and 25 ml of HNO_3 (4 M) solvent. The dissolution took 3 h and the heat effect was measured. Experimental conditions were identical for all samples. The calorimeter was calibrated by using the heats effects of the well known enthalpy of the protonation of THAM 0.37 M in HCl 0.12 M [14].

Generally, the kinetic nature of the glass transition means that the calorimetric measurements will be influenced by the glass thermal history [15,16]. The glass transition temperature for the studied glass system is estimated, on the basis of DSC measurements to be greater than 298 K. The thermal history of the samples did not affect significantly the calorimetric results at 298 K [17]. Details of the effect of difference of the thermal history are obscured by the fact that experimental uncertainties (2–2.5 kJ/mol) are of the same order of magnitude as the variations in enthalpy of mixing caused by thermal history change. Therefore, it is not necessary to apply a correction to the values of enthalpy of mixing on glasses obtained by means of the Hess’s cycle, in order to get the enthalpy of mixing relative to the hypothetical liquid sate.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns, registered at room temperature, for the $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ glasses. They revealed typical characteristic pattern for amorphous materials broaden diffraction lines and confirmed the vitreous nature of the glasses.

The glass transition temperature data are listed in Table 1 and plotted in Fig. 2. For each sample, a single value of the glass transition is observed, which is intermediate between the T_g associated with $0.8B_2O_3–0.2Na_2O$ and $0.8P_2O_5–0.2Na_2O$. This feature suggests that $0.8B_2O_3–0.2Na_2O$ and $0.8P_2O_5–0.2Na_2O$ are miscible in the whole range of composition. The glass transition temperature increases abruptly for a small addition of B_2O_3 and reaches a maximum near the composition $x = 0.50$. As more boron is added, T_g decreases. This behaviour corresponds to some changes in the nature of bonding in the structural network. As shown by Ray [18], the glass transition temperature is a

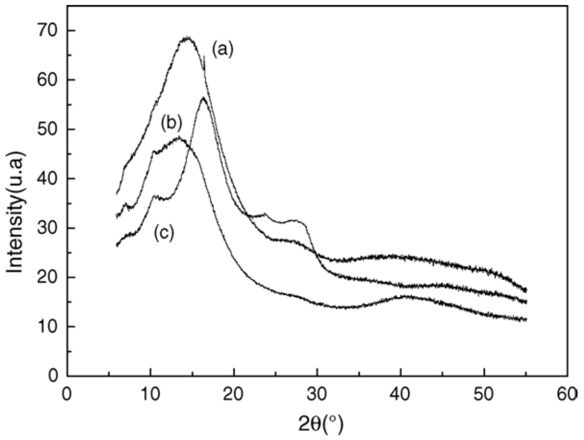

Fig. 1. X-ray diffraction patterns of $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ glasses: (a) $x = 0.15$, (b) $x = 0.5$ and (c) $x = 0.9$.

Table 1
Glass transition temperature (T_g), enthalpy of solution at infinite dilution ($\Delta_{sol}H$) and enthalpy of mixing (ΔH) in $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ glasses at 298 K

x	T_g (°C)	$\Delta_{sol}H^\infty$ (kJ/mol)	ΔH (kJ/mol)
0	197.8 ± 2.0	−75.6 ± 1.5	0 ± 2.1
0.15	286.7 ± 2.0	−12.5 ± 1.2	−73.5 ± 2.0
0.25	397.6 ± 2.0	4.3 ± 1.0	−97.3 ± 2.2
0.50	534.7 ± 2.0	−17.2 ± 1.1	−93.5 ± 1.7
0.75	463.7 ± 2.0	−84.7 ± 1.1	−43.7 ± 2.4
0.90	429.6 ± 2.0	−124.4 ± 1.3	−14.5 ± 2.0
1	487.3 ± 2.0	−143.2 ± 1.2	0 ± 2.2

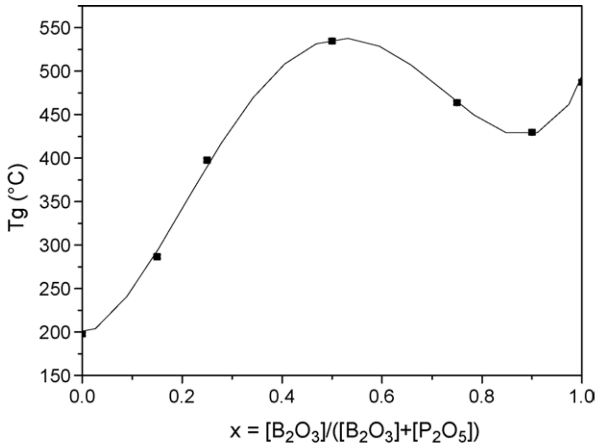

Fig. 2. Glass transition temperature (T_g) for $0.8[xB_2O_3–(1-x)P_2O_5]–0.2Na_2O$ glasses as function of x content.

Table 2
Summary of experimental enthalpies of solution ($\Delta_{\mathrm{sol}}H$) for $0.8[x\mathrm{B_2O_3}–(1-x)\mathrm{P_2O_5}]–0.2\mathrm{Na_2O}$ in HF (6 M) + $\mathrm{HNO_3}$ (4 M) solvent at 298 K

x	Mass (mg)	$\Delta_{\mathrm{sol}}H$ (kJ/mol)
0	5.82	−75.88
	8.99	−76.46
	10.27	−76.78
	9.53	−74.89
	19.14	−76.32
	10.17	−74.53
0.15	5.49	−12.82
	9.99	−13.47
	8.69	−11.99
	10.98	−11.83
	7.05	−11.98
	11.55	−13.11
0.25	5.14	5.82
	9.30	5.21
	10.12	4.41
	9.26	3.46
	5.30	4.23
	6.43	3.53
0.50	5.21	−17.50
	7.06	−17.91
	5.25	−17.28
	8.09	−16.76
	7.56	−16.69
	10.71	−18.80
	5.06	−18.06
0.75	5.60	−85.62
	5.96	−86.05
	10.24	−83.03
	10.78	−84.46
	12.17	−84.84
	5.64	−85.99
0.90	5.63	−124.63
	6.37	−125.15
	5.19	−124.01
	7.68	−122.27
	10.89	−123.83
1	5.62	−142.98
	8.33	−144.79
	8.94	−143.98
	11.32	−143.32
	10.35	−142.04
	5.35	−143.12

structural sensitive parameter depending on the changes in bond strength, in the degree of cross-link density and in the closeness of packing.

For each composition, the enthalpy of solution has been measured six times. The obtained experimental data of enthalpy of solution are listed in Table 2. A constrained least-squares method was applied to fit the data, taking into account a linear variation of the slopes with the composition of the composite. This correction is often neglected in common calorimetric work, but the concentration effect, although small, must be taken into account when high precision is required. Following this procedure, we obtained the enthalpies of solution at infinite dilution for each composition of the glass system. The results are summarized in Table 1 and plotted in Fig. 3. The data showed a positive deviation from ideality, implying negative enthalpies of mixing. The enthalpies of mixing are deduced from the difference between the ideal enthalpy of solution (a linear combination of the end-members $0.8\mathrm{B_2O_3}–0.2\mathrm{Na_2O}$ (A) and $0.8\mathrm{P_2O_5}–0.2\mathrm{Na_2O}$ (B) enthalpies) and the observed enthalpy of solution of glasses at infinite dilution, using the expression:

$$\Delta H = x\Delta_{\mathrm{sol}}H^{\infty}_{\langle \mathrm{A}\rangle} + (1-x)\Delta_{\mathrm{sol}}H^{\infty}_{\langle \mathrm{B}\rangle} - \Delta_{\mathrm{sol}}H^{\infty}_{\langle x\mathrm{A}(1-x)\mathrm{B}\rangle} \qquad (1)$$

where $\Delta_{\mathrm{sol}}H^{\infty}_{\langle \mathrm{Y}\rangle}$ represents the molar solution enthalpy of the substance Y at infinite dilution.

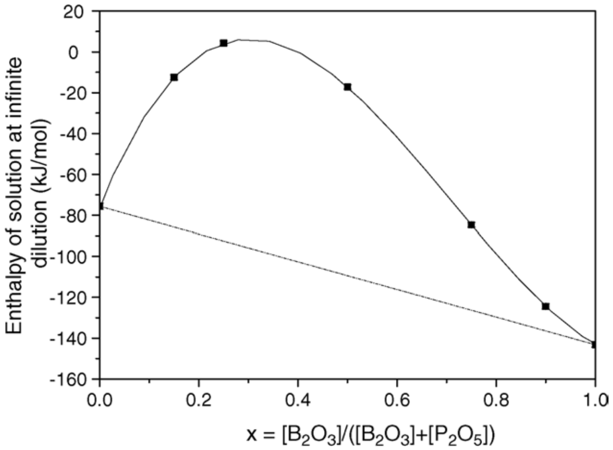

Fig. 3. Enthalpy of solution at infinite dilution ($\Delta_{\mathrm{sol}}H^{\infty}$) at 298 K vs. composition x. The solid curve represents the fit to the experimental data; the dashed line represents ideal mixing.

The obtained data of enthalpies of mixing corresponding to the glass state of this system, are given in Table 1. The uncertainties in the enthalpies of mixing are extracted from the errors in the enthalpies of solution.

The effect of $\mathrm{B_2O_3}$ on the enthalpy of mixing of these glasses is shown in Fig. 4. The enthalpies of mixing are clearly dependent on chemical composition and are significantly more

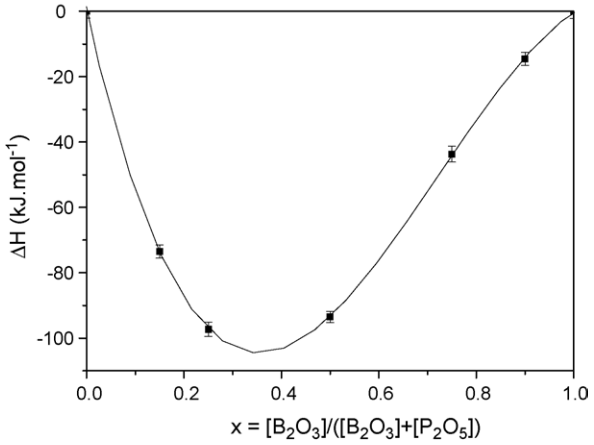

Fig. 4. Enthalpy of mixing for $0.8[x\mathrm{B_2O_3}–(1-x)\mathrm{P_2O_5}]–0.2\mathrm{Na_2O}$ glasses as a function of x content at 298 K. Points, experimental data; solid lines, interpolation using Eq. (2) and the straight lines represent mechanical mixing lines. The errors bars are also indicated.

exothermic. The enthalpy of mixing decreases with increasing B_2O_3 content and reaches a minimum value near $x = 1/3$, before starting to increase as more boron is added. These measurements slow that the enthalpies of mixing can be expressed as (in kJ/mol):

$$\Delta H = x(1-x)(-660.2 + 570x) \tag{2}$$

for which $R^2 = 0.96$, where

$$x = \frac{[B_2O_3]}{[B_2O_3] + [P_2O_5]}.$$

Negative enthalpies of mixing were obtained in all the composition range. A proof of miscibility of $0.8B_2O_3$–$0.2Na_2O$ and $0.8P_2O_5$–$0.2Na_2O$ is given here. The negative values of enthalpies of mixing can be attributed to the specific interaction between the two networks former B_2O_3 and P_2O_5. Structural investigations of borophosphate glasses [1,7–10] showed tetrahedral boron sites, B(4) in the phosphate-rich domain and trigonal boron sites, B(3), in the borate-rich. B(4) dominates in high phosphate compositions and hence forms B–O–P bridges that cross-link the phosphate chains. This polymerises the glass network and increases the packing density of atoms, creating a more compact borophosphate network and leading to an increase in density. This increase in density is confirmed by the results reported in a study of calcium borophosphate glasses [19]. At high boron composition, B(3) becomes the preferred coordination and the glass network is dominated by a borate network. The covalent cross-link density decreases due to the depolymerisation of the glass structure as the number of B–O–P bridges decreases. The result suggested that increasing B_2O_3 content efficiently stabilizes the glasses in respect to devitrification, in both a kinetic and a thermodynamic sense. This effect is particularly evident in the phosphate-rich region, which corresponds to a sharp energetic stabilization with increasing B_2O_3 content. Enthalpies of mixing at 298 K for sodium borophosphate glasses might provide direct evidence for the existence of miscibility gaps. In binary liquid solutions, a zero enthalpy of mixing is often taken as an indication of Raoultian (ideal) behaviour. Deviations from such a behaviour as positive enthalpies of mixing, which drive the solution towards immiscibility [20–23] or negative enthalpies of mixing, for homogeneous single phase [24,25]. The enthalpies of mixing for $0.8[xB_2O_3$–$(1-x)P_2O_5]$–$0.2Na_2O$ glasses are asymmetric and significantly negative (Fig. 4), indicating an absence of immiscibility. Maximum stabilization occurs at $x = 1/3$ for fully polymerised glasses. This may be related to the energetics of the reaction B–O–B + P–O–P = 2B–O–P [26,27], which suggests that the B–O–P linkage is stable relative to a mixture of B–O–B and P–O–P linkages for the studied sodium borophosphate glasses. The strongly negative enthalpies of mixing support a large thermodynamically favoured glass forming region in which all ions are in relatively low energy coordination environments. There is no thermodynamic evidence for phase separation. The present study can be compared to the published data. The data of the enthalpy of mixing on borophosphate glass system available in the literature are given at different temperatures. For a strict comparison, all the data should be corrected by a ΔC_p factor following the relation:

$$\Delta H(T) = \Delta H(T_0) + \int_{T_0}^{T} \Delta C_p \, dT \tag{3}$$

where ΔC_p is the difference between the heat capacities of the compound and of the reactants. To our knowledge, the thermodynamic measurements (heat capacity, enthalpy of mixing, ...) of sodium borophosphate glasses have not been investigated a lot. The published data in the literature concerned the sodium borophosphate glasses performed on a Tian–Calvet calorimeter at 1272 and 1248 K, respectively [12]. Only a qualitative comparison can be made as it is not straightforward to compare these two kinds of data that differ in both the temperature of investigation and the glass content. The literature data show a similar trend but the enthalpies of mixing become less exothermic with increasing B_2O_3 content than in the present study.

Taking into account the pronounced asymmetry of the calorimetric data (Fig. 4), the formalism of the regular solution model [28] and the quasichemical model [29] are clearly inappropriate in the present case. The expression of the enthalpy of mixing is equivalent to these of sub-regular model [30]:

$$\Delta H = x(1-x)(\Delta \overline{H}_A^{\infty} + (\Delta \overline{H}_B^{\infty} - \Delta \overline{H}_A^{\infty})x) \tag{4}$$

where $\Delta \overline{H}_A^{\infty}$ and $\Delta \overline{H}_B^{\infty}$ are the limiting partial enthalpies at infinite dilution of $0.8B_2O_3$–$0.2Na_2O$ (A) and $0.8P_2O_5$–$0.2Na_2O$ (B), respectively. The sub-regular solution model (Eq. (4)) was used to fit experimental data rather than introduce empirical equation (Eq. (2)) equivalent to it. The corresponding values of the limiting partial enthalpies of mixing at infinite dilute are −660.2 and −90.2 kJ/mol, respectively.

4. Conclusion

The solution calorimetric determinations allow us to obtain reliable enthalpies data on sodium borophosphate glasses at 298 K. The enthalpies of $0.8[xB_2O_3$–$(1-x)P_2O_5]$–$0.2Na_2O$ show significant exothermic values reflecting a strong chemical interaction between the components. Asymmetric strong negative enthalpies of mixing are consistent with sub-regular solution behaviour.

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