Research Article

Application of the Van Laar model to oxide glasses of the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system

A. Kouyate[1]*, M. A. Tigori[1], O. Kambire[2], K. L. Koroma[3], A. P. Ahoussou[3], M. P. Niamien[3], B. K. Dongui[1] and A. Trokourey[3]

[1]UFR Environnement, Université Jean Lorougnon Guédé, BP 150 Daloa, Côte d'Ivoire
[2]UFR Sciences et Technologies, Université de Man, BP 20 Man, Côte d'Ivoire
[3]Laboratoire de Constitution et de Réaction de la Matière, Université Félix Houphouët Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire

Abstract

This study focuses on the application of Van Laar's model to oxide glasses and more particularly on the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system. Dissolution calorimetry allowed to measure the enthalpies of mixing. The interaction parameters values allowed to estimate the enthalpy of mixing at any concentration in the system. Van Laar's model significantly improves the results.

Keywords: Oxide glass, Dissolution calorimetry, Van Laar model, Enthalpy of mixing

***Correspondence**
Author: A. Kouyate
Email: amadoukyte@yahoo.fr

Introduction

Borosilicate [1-3] and borophosphate [4-6] based systems benefit from an important revival of interest in many fields thanks to the development of new tools for elaboration, observation and analysis. This is the case of oxide glasses which are used for nuclear waste containment [7-10]. These oxide glasses are also used in the biomaterials industry [11-13] and are particularly useful for repairing bone and / or cartilage defects, deficiencies associated with pathologies and injuries in the following cases: formation of bone tissue in a fracture, repair of bone defects such as those due to the removal of a tumor or a cyst, treatment of dental or skeletal anomalies.

Borosilicate glass has been chosen as the basic matrix for its thermal stability, chemical durability and resistance to self-irradiation [14]. It is therefore important to know the different physicochemical properties that characterize them, both in the solid and liquid state.

In general, the experimental approach is essential to quantify thermodynamic quantities in binary or polyconstituted systems. However, due to the multiplicity of constituents and the experimental difficulties related to the nature of the constituents and the calorimetric methods, other complementary approaches are often envisaged. This is the case of the analysis, with the help of models, of all the available data, with the aim of optimizing and calculating the thermodynamic quantities of these systems.

It is within this framework that this study was conducted. The general objective of this work is to apply Van Laar's thermodynamic model to glasses of the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system in order to reproduce the experimental results; this with a view to estimating the enthalpies of mixing.

Materials and Methods

Elaboration of glasses

Glass manufacturing techniques [15-18] may vary depending on the initial composition, the type of glass, the expected structure and the resulting application. For oxide glasses, most of them consist in bringing a heterogeneous mixture of vitrifiable oxides (which can form a glass) to a melting temperature between (about 1200 and 1400°C) in a crucible. The resulting molten liquid, called molten glass or melt, is properly cooled so that a vitreous liquid is formed. This is why glasses are considered as frozen liquids [17].

Measurements of the enthalpies of mixing the glasses

In this study, the aim was to model the enthalpy of mixing of the system under study. The available thermodynamic data were used for this system for achieving our objective. To our knowledge, the work of Ahoussou *et al.* [3] is the only source of experimental thermodynamic data available for this system. These authors performed enthalpy of mixing measurements by dissolution calorimetry at 298 K where different compositions of alkali borosilicate glasses

of the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system, 50 ml of the mixture HF (6M) + HNO_3 (4M) were used as solvent. In order to facilitate dissolution, various sample masses of about 3 mg were dissolved. Seven different compositions were studied. The corresponding experimental values of enthalpies of mixing are given in **Table 1**.

Table 1 Experimental data of enthalpy of mixing at 298 K for alkali borosilicate glasses

x	**Experimental data of mixing enthalpy [3] ΔHm (kJ.mol^{-1})**
0	0.00 ± 0.33
0.15	-2.00 ± 0.27
0.25	-2.70 ± 0.27
0.50	-3.28 ± 0.33
0.75	-2.19 ± 0.27
0.9	-0.87 ± 0,39
1	0.00 ± 0.33

Sub-regular solutions model approach

It should be noted that data processing according to the sub-regular solution model was developed by Ahoussou [19]. This work has led to the expression of the enthalpy of mixing below Equation 1:

$$\Delta H_m = x(1-x)(ax+b) \qquad (1)$$

with $a = (\overline{\Delta H}^{\infty}_{21} - \overline{\Delta H}^{\infty}_{12})$ and is equivalent to $a = \overline{\Delta H}^{\infty}_{21} - b$ where $b = \overline{\Delta H}^{\infty}_{12}$, x the molar fraction of component i (B_2O_3).

The partial enthalpies at infinite dilution at 298 K for alkali borosilicate glasses in regular solution are shown in the **Table 2**.

Table 2 Enthalpies of dissolution at infinite dilution at 298 K for alkali borosilicate glasses of sub-regular solution

System	$\overline{\Delta H}^{\infty}_{0.8B_2O_3-0.2Na_2O}$ ($\overline{\Delta H}^{\infty}_{12}$) **(kJ.mol^{-1})**	$\overline{\Delta H}^{\infty}_{0.8SiO_2-0.2Na_2O}$ ($\overline{\Delta H}^{\infty}_{21}$) **(kJ.mol^{-1})**
$0.8[B_2O_3-(1-x)SiO_2]-0.2Na_2O$	-16.4	-10.0

In the case of the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system, the experimental results at 298 K lead to Equation 2:

$$\Delta H_m = x(1-x)(6.4x-16.4) \text{ (kJ.mol}^{-1}\text{)} \qquad (2)$$

Approach using the Van Laar model

In this formalism, the number of close neighbors or coordination is a function of the nature of the central atom. The number of each type of pair depends not only on the molar fractions (as is the case in the regular solution model), but also on the volume molar fractions. This model is an example of interaction models. The expression of the resulting enthalpy of mixing is of the form:

$$\Delta H_m = \frac{\sum_{i=1}^{i=m}\sum_{j\neq i}^{j=m} \overline{\Delta H}^{\infty}_{i(j)} x_i x_j V_j}{\sum_{i=1}^{i=m} x_i V_j} \qquad (3)$$

Where V_i and x_i are respectively the molar volume and molar fraction of component *i*. $\overline{\Delta H}^{\infty}_{i(j)}$ represents the enthalpies of dissolution at infinite dilution of *i* in *j*. The entropy of mixing in this formalism is ideal [19].

Results and Discussion

The results obtained are shown in **Figure 1**. The values of enthalpies of mixing are slightly negative. These values are characteristic of an attractive behavior within the solid and responsible for a short distance order as in the case of a system of the same type such as $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2K_2O$ [1]. The values of enthalpies of mixing being negative, the reaction is exothermic, reflecting a release of heat within the system. These low mixing enthalpy values are the cause of a large dispersion of the results.

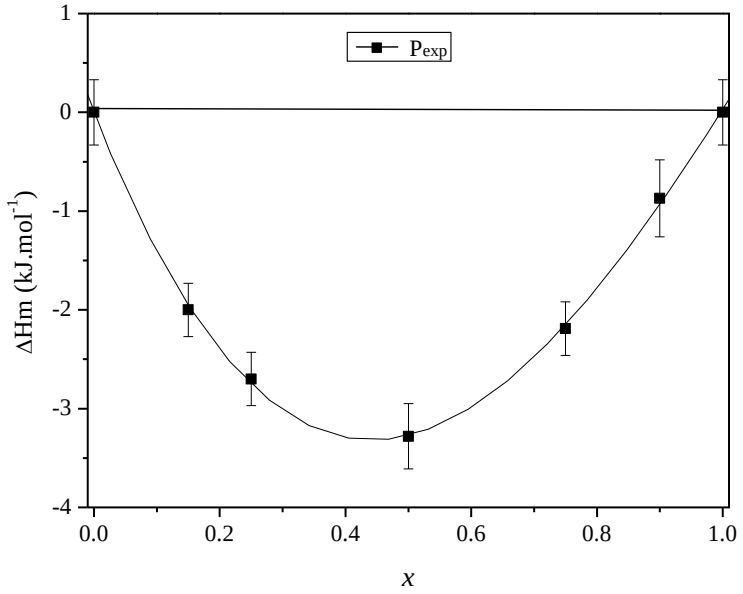

Figure 1 Variation of enthalpy of mixing as a function of the B_2O_3 content of the system $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$

This information is necessary for modeling the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system. However, a first modeling approach exists in the literature [4].

Figure 2 shows the experimental points and the curve showing the evolution of the estimated values according to the sub-regular solution model. It appears that the sub-regular model sufficiently accounts for all the thermodynamic experimental data. Indeed, a good representation of the experimental points is to be pointed out, with a standard deviation lower than 3 %, with the exception of the two compositions (x = 0.25 and 0.9) with standard deviations of 23.8 % and 9.4 %, respectively.

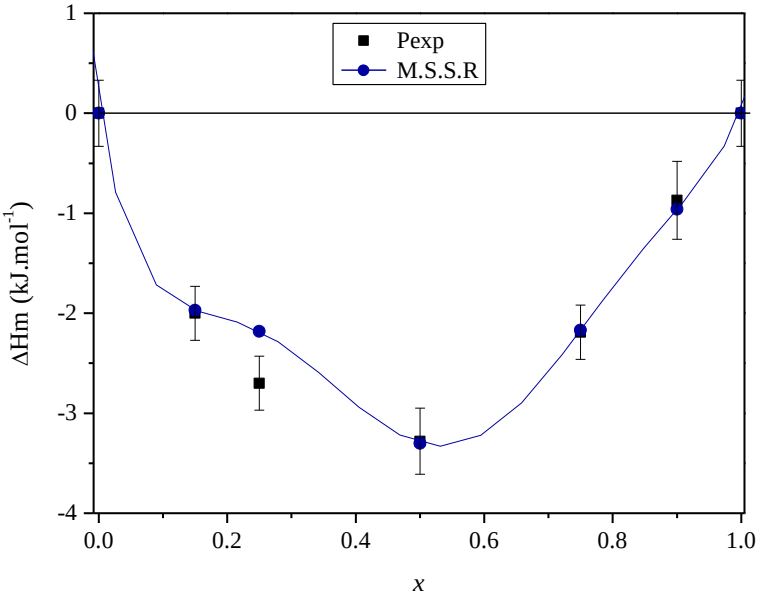

Figure 2 Experimental values and curve of enthalpy of mixing according to the sub-regular solution model applied to the $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ system

These data can be used to optimize the system under study, so it seems necessary to improve their reliability. To achieve this, a new estimation is proposed, in order to refine this model through a new approach. This approach is based on the Van Laar model. Van Laar's model allows to determine new values of parameters of binary interactions and to use them to improve the calculations of thermodynamic properties, especially the quantities of mixtures in binary systems.

Data processing was carried out on the basis of Van Laar's equation (Equation 3) with the "Curveexpert" software. **Table 3** gathers the values of the different adjustable parameters (partial enthalpies at infinite dilution and partial molar volumes) from the Van Laar model.

Figure 3 shows a good consistency of the enthalpies of mixing calculated according to Van Laar model with the experimental data. Therefore, this approach is in agreement with the values in the literature [4].

In **Table 4**, the Van Laar model estimates are compared with experimental mixing enthalpy data.

Van Laar's model gives a good representation of the experimental points, with a deviation of less than 3 per cent (**Figure 4**).

Table 3 Adjustable parameters according to the Van Laar model

Enthalpy with infinite dilution of B_2O_3 ($\overline{\Delta H}_{12}^{\infty}$) (kJ.mol^{-1})	Enthalpy with infinite dilution of SiO_2 ($\overline{\Delta H}_{21}^{\infty}$) (kJ.mol^{-1})	Molar volume of B_2O_3 (V_1) (cm^3.mol^{-1})	Molar volume of SiO_2 (V_2) (cm^3.mol^{-1})
-3.67	-8.16	0.6	0.36

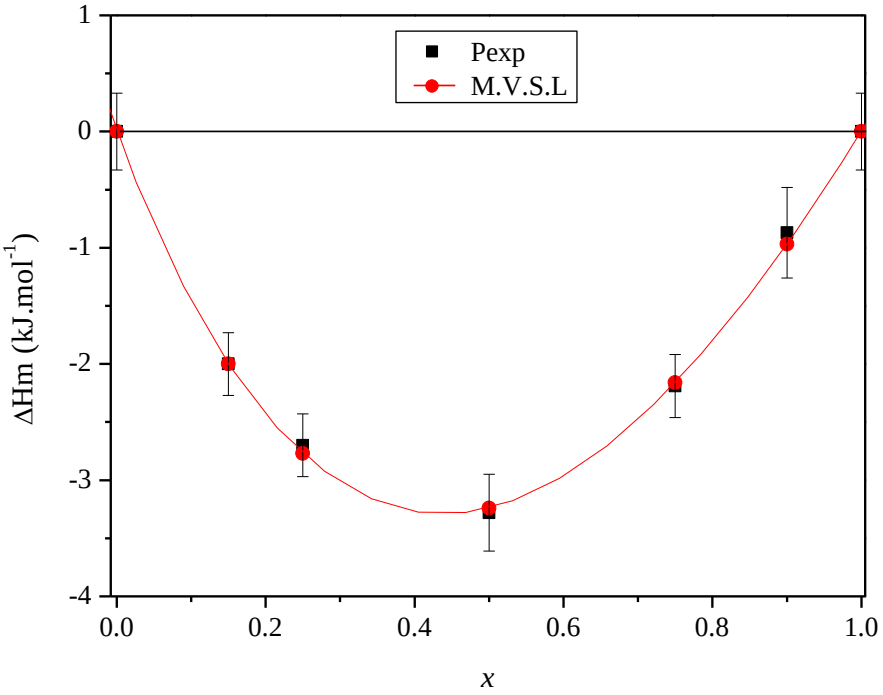

Figure 3 Comparative study of values of enthalpy of mixing according to the Van Laar model and experimental points

Table 4 Comparison of estimated values with experimental data of enthalpy of mixing for the system $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$

x	Experimental data [3] ΔH_m (kJ.mol^{-1})	Van Laar's model ΔH_m (kJ.mol^{-1})	Sub-regular solution model [19] ΔH_m (kJ.mol^{-1})
0	0.00 ± 0.33	0.00	0.00
0.15	2.00 ± 0.27	-2.00	-1.97
0.25	-2.70 ± 0.27	-2.77	-2.18
0.50	-3.28 ± 0.33	-3.24	-3.30
0.75	-2.19 ± 0.27	-2.16	-2.17
0.9	-0.87 ±0.39	-0.97	-0.96
1	0.00 ± 0.33	0.00	0.00

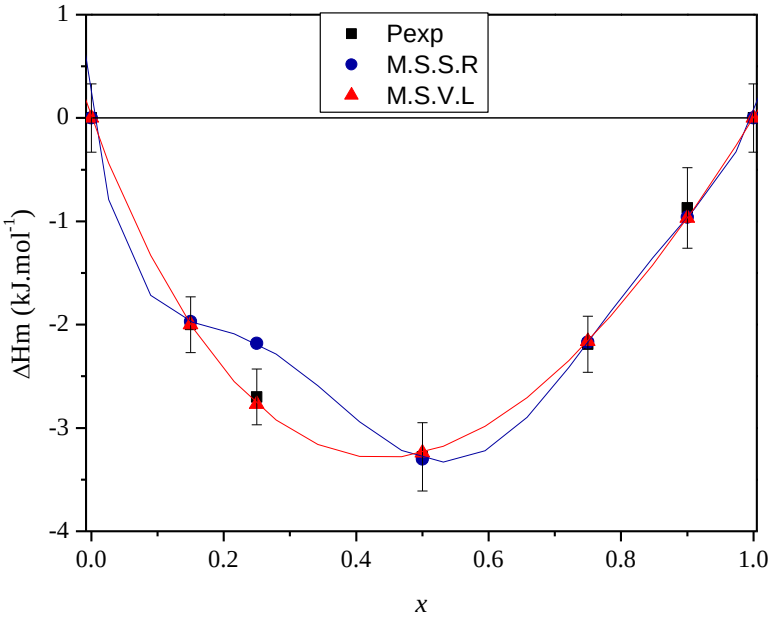

Figure 4 Comparative study of values of enthalpy of mixing according to the Van Laar and sub-regular solution models

Discussion

A comparative study of the estimates resulting from the Van Laar model with those resulting from the sub-regular solutions model was carried out. Fig. 4 shows that the difference in enthalpy of mixing between these two models does not exceed 3 %. Given the respective uncertainties of the two methods, the agreement is very satisfactory. However, it appears that the Van Laar model permits a much more satisfactory representation of the experimental data than the sub-regular solution model. In particular, it is noted that the experimental points are much better reproduced by the Van Laar model (with a determination coefficient R^2 of 0.9984) than by the sub-regular solutions model (with a determination coefficient R^2 of 0.9735). However, from a statistical point of view, the examination of the coefficients of determination as well as the margins of error shows that the two models lead to a quasi-similar representation. The differences remain very modest. It can therefore be considered that these differences are not significant and are representative of an order of magnitude of the experimental errors.

Conclusion

This work allowed to establish a thermodynamic description of the system $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ where $0 \leq x \leq 1$ based on the Van Laar model. The estimated interaction parameters allow to account for the evolution of the enthalpy of mixing with the composition.

The comparative study with the sub-regular solutions model shows that this approach is more representative of the experimental points although both models are acceptable.

References

[1] Ahoussou, A. P. Rogez, J. and Kone, A. 2006. Enthalpy of mixing in $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2K_2O$ melts at 973K. Thermochimica Acta, 447: 109-111.

[2] Ahoussou, A. P. Rogez, J. and Kone, A. 2007. Solution calorimetric study of mixing enthalpy in $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2K_2O$ glasses at 298 K. Materials Research Bulletin, 42: 1577-1581.

[3] Ahoussou, A. P. Rogez, Yapi, A. Mikalean, V. and Kone, A. 2009. Contribution to thermochemical studies of in $0.8[xB_2O_3\text{-}(1\text{-}x)SiO_2]\text{-}0.2Na_2O$ glasses. Chinese Chemical Letters, 20: 245-249.

[4] Ahoussou, A. P. Rogez, J. and Kone, A. 2006. Enthalpy of mixing in $0.8[xB_2O_3\text{-}(1\text{-}x)P_2O_5]\text{-}0.2Na_2O$ glasses at 298 K. Thermochimica Acta, 441: 96-100.

[5] Ahoussou, A. P. Rogez, J. and Kone, A. 2007. Thermodynamical miscibility in $0.8[xB_2O_3\text{-}(1\text{-}x)P_2O_5]\text{-}0.2K_2O$. Journal of Non-crystalline Solids, 353: 271-275.

[6] Ahoussou, A. P. Kouyate, A. Diabate, D. Rogez, J. and Kone, A. 2007. Synthesis and glass transition temperature measurements in mixed former glasses. Phys. Chem. News, 38: 74-77.

[7] Cauranta, D. Majerusa, O. Loiseaua, P. Bardeza, I. Baffiera, N. Dussossoy. J. L. 2006. Crystallization of neodymium-rich phases in silicate glasses developed for nuclear waste immobilization. Journal of Nuclear Materials, 354: 143-162.
[8] de Bonfils, J. Peuget, S. Panczer, G. de Ligny, D. Henry, S. Noël, P.-Y. Chenet, A. Champagnon, B. 2010. Effect of chemical composition on borosilicate glass behavior under irradiation. J. Non-Crypt. Solids, 356: 388-393.
[9] Angeli, F. charpentier, T. Molières, E. Soleilhavoup, A. Jollivet, P. Gin, S. 2013. Influence of lanthanum on borosilicate glass structure: A multinuclear MAS and MQMAS NMR investigation. Journal of Non-Crystalline Solids, 376: 189-198.
[10] Galoisy, L. Pélegrin, E. Arrio, M. –A. Ildefonse, P. Calas, G. Ghaleb, D. Fillet, C. Pacaud, F. 1999. Evidence for 6-Coordinated Zirconium in Inactive Nuclear Waste Glasses. J. Am. Ceram. Soc, 82: 2219-2224.
[11] Katz, J. M. Nataraj, C. Jaw, R. Deigl, E. and Bursac, P. 2009. Demineralised bone matrix as an osteoinductive biomaterial and in vitro predictors of its biological potential. J Biomed Mater. Res B Appl Biomater, 89: 127-134.
[12] Kouyaté, A. Ahoussou, A. P. Rogez, J. and Benigni, P. 2013. Application of Solution Calorimetry to the Prediction of $20.15[(2.038+x)SiO_2$-$(1.457-x)Na_2O]$-$2.6P_2O_5$-$26.95CaO$ Glass Bioactivity. Advances in Chemical Engineering and Science, 3: 123-129.
[13] Wers, E. Oudadesse, H. Lefeuvre, B. Bureau, B. Merdrignac-Conanec, O. 2014. Thermal investigations of Ti and Ag-doped bioactive glasses. Thermochimica Acta, 580: 79-84.
[14] Linard, Y. Advocat, T. Jégou, C. Richet, P. 2001. Thermochemistry of nuclear waste glasse: application to weathering studies. Journal of Non-Crystalline Solids, 289: 135-143.
[15] Zarzycki, J. 1982. Glass structure. Journal of Non-Crystalline Solids, 52: 31-43.
[16] Barton, J. and Guillemet, C. Glass Science and technology. EDP Sciences 2005
[17] Goutaland, F. Colombier, J.-P. Sow, M. C. Ollier, N. and Vocanson, F. 2013. Laser-induced periodic alignment of Ag nanoparticles in soda-lime glass. Optics Express, 21: 31789-31799.
[18] Broyer, M. Vigue, J. and Lehmann, J. C. 1975. Direct evidence of the natural predissociation of the 12 B state through systematic measurements of lifetimes. The Journal of Chemical Physics, 63: 5428-5431.
[19] Ahoussou, A. P. Rogez, J. and Koné, A.. 2006. Etude par calorimetrie de dissolution d'électrolytes vitreux du système $0.67[xB_2O_3$-$(1-x)P_2O_5]$-$0.33K_2O$, J. Soc. Ouest-Afr. Chim, 022: 53- 58.

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