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ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF MIXING BINARY SYSTEMS BASED ON SILVER NITRATE AND ALKALI NITRATES USING IONIC MODEL

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ABSTRACT

This work was devoted to the formulation of thermodynamic properties of binary systems of molten salts by using an ionic model which requires three physical parameters for each salt : the crystal lattice energy, the latent heat of melting and the sum of the ionic radii. This formulation, whose adjustable parameters have been obtained by smoothing from the experimental mixing properties available in the literature, allowed us to calculate the molar enthalpies of mixing for twelve (12) binary systems of alkali nitrate and silver nitrate. The different results obtained show satisfactory general agreement between calculation and experiment with regression coefficients within the range 0.992 and 0.999 and relative uncertainties between experimental and calculated values of less than 6% throughout the compositional range for all systems studied. The present formulation more accurately determines the enthalpies of mixing of binary systems with a volume effect (without intermediate compounds) predominating over the chemical effect (formation of intermediate compounds) ; Furthermore, we were able to show that in binary systems of alkali nitrates based on lithium nitrate and sodium nitrate, the solutions are strictly regular and that the deviation from regularity increases as one goes down in the alkali metal family namely from lihium to caesium.

Contribution/Originality: This study first of all made it possible to establish a new expression for the molar enthalpy of mixing of molten salt binary systems as a function of temperature. In addition, an evolution of the regularity of solutions of binary systems of alkali nitrates was obtained.

1. INTRODUCTION

The thermodynamic properties of mixing are of considerable interest both on a theoretical level (structure-properties link, nature of interactions between particles, possible existence of species in solution, etc.) and on a practical level (estimate of phase diagrams, elaboration of materials,. . .). For example, a positive mixing enthalpy can be interpreted as a tendency to homoassociations or demixing, whereas a negative value of this one suggests a tendency to heteroassociation that can lead to the formation of intermediate compounds.

In practice, if the thermochemical data relating to binary systems are abundant, this is not always the case for multiconstituted systems, the simplest of which are ternary systems. Due to their practical interest, the establishment of models offering possibilities of estimating their mixing quantities from experimental information obtained on lower order systems, is sought. The modeling of mixing quantities constitutes an important field of research in thermodynamics, with challenge today being the feeding of the codes used for the calculation of phase diagrams and thermochemical properties. Several works devoted to molten salts have enabled the estimation of thermochemical properties with success [1-3].

In the specific case of alkali nitrates and silver nitrate which could be used as phase change materials (PCM) for the storage and transfer of solar energy, due to their thermal stability, their non-corrosive character and above all their low melting point [4, 5] the thermodynamic quantities of mixture of binary liquids $AgNO_3 - MNO_3$ (M = Li, Na, K, Rb, Cs) have been satisfactorily translated by the Regular Model in Modified Pair of Arms (RMMPA) [6]. This model has nevertheless shown limitations in estimating the mixing enthalpies of ternary liquids. This is probably due to the fact that this model considers each pure nitrate as constituent (neutral species). However, mixtures of molten salts are considered as an arrangement of cations and anions within which the strong Coulomb repulsions between charges of the same sign and attraction between charges of opposite signs must be taken into account during the formulation of the model. Hence the importance of considering mixtures of molten salts as systems with two ionic sublattices (anionic lattice and cationic lattice).

In the present work, the ionic model which takes into account two sublattices is used to estimate the thermodynamic quantities of twelve binary systems of alkali nitrates and silver nitrate.

2. PRESENTATION OF THE IONIC MODEL

2.1. Introduction of the Ionic Model

According to Temkin's hypothesis [1] a binary solution of molten salts of the AX-BY type (A and B being cations, X and Y being anions) consists in the liquid state of two quasi-lattices which interpenetrate . An anionic lattice and a cationic lattice, in each of which the different ions are randomly distributed between them.

The most rigorous calculation of the ionic interaction, presented by the conformal ionic solution (CIS) theory [7], led to a mixing enthalpy of the binary system that depends on the composition and a size parameter. This theory has been successfully applied to calculate the liquidus temperature as well as the miscibility gaps of phase equilibrium diagrams [8-12]. This CIS theory, although predicting satisfactorily the excess thermodynamic properties of molten salts according to the composition of the salt and the size of the constituent ions, did not give the expressions of the properties themselves. In order to obtain the expression of the excess quantities, an ionic interaction model was developed by Gal and Paligorić [13] and applied to common anion molten salt binary systems. This model requires only three physical parameters of each constituent : the energy of the crystal lattice, the latent heat of fusion and the sum of the ionic radii. The model assumes simple "hard core" interactions and ignores the effect of polarization resulting from the mixing of ions of different size and/or charge.

2.2. Expressions of Excess Quantities

According to Gal and Paligorić [13], in a binary mixture of molten salts containing monovalent ions and a common anion X^- of the AX-BX type, the pairwise interaction potentials between oppositely charged ions (A^+ and X^- ; B^+ and X^-) and cations (A^+ and A^+; B^+ and B^+; A^+ and B^+) nearest to each other are given by the expressions in Equations 1, 2 and 3:

$$\varepsilon_{AX} = -\frac{e^2}{(4\pi\varepsilon_0)d_{AX}} \text{ et } \varepsilon_{BX} = -\frac{e^2}{(4\pi\varepsilon_0)d_{BX}} \quad (1)$$

$$\varepsilon_{AA} = \frac{e^2}{(4\pi\varepsilon_0)kd_{AX}} \text{ et } \varepsilon_{BB} = \frac{e^2}{(4\pi\varepsilon_0)kd_{BX}} \quad (2)$$

$$\varepsilon_{AB} = \frac{e^2}{(4\pi\varepsilon_0)k(d_{AX} + d_{BX})/2} \quad (3)$$

With :

e : elementary charge ;

ε_0 : permittivity of vacuum ;

d_AX and d_BX: interionic distances (the sum of the radii of the cation and the anion) between A^+ and X^- and between B^+ and X^- respectively;

k: geometric factor which depends on the geometry of the quasi-lattice.

For one mole of pure molten salt AX and BX, the interaction energies as a function of the potentials of the nearest ion pairs are given by the following expressions:

$$E_A = NZ\varepsilon_{AX} + \tfrac{1}{2}NZ'\varepsilon_{AA} \quad (4)$$

$$E_B = NZ\varepsilon_{BX} + \tfrac{1}{2}NZ'\varepsilon_{BB} \quad (5)$$

With N Avogadro's number, Z and Z' are respectively the nearest numbers of anions and cations around a cation.

For one mole of mixture xAX + (1 - x)BX (x being the mole fraction of AX), assuming a random distribution of cations, the corresponding Ex energy has the expression :

$$E_x = NZ[x\varepsilon_{AX} + (1-x)\varepsilon_{BX}] + NZ'\left[\tfrac{1}{2}x^2\varepsilon_{AA} + \tfrac{1}{2}(1-x)^2\varepsilon_{BB} + x(1-x)\varepsilon_{AB}\right] \quad (6)$$

The energy of the mixture is defined by the following expression :

$$\Delta E_m = E_x - xE_A - (1-x)E_B = x(1-x)\frac{NZ'}{2}(2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}) \quad (7)$$

In order to take into account the long-range interactions in the mixing energy, Gal and Paligorić [13] introduce a dimensionless parameter (a). Taking this parameter into account, and from Equations 2 and 3, Equation 7 becomes :

$$\Delta E_m = -\frac{1}{2}x(1-x)\left(\frac{Z'}{ak}\right)\frac{Ne^2}{4\pi\varepsilon_0}\left(\frac{1}{d_{AX}} + \frac{1}{d_{BX}}\right)\left(\frac{d_{AX} - d_{BX}}{d_{AX} + d_{BX}}\right)^2 \quad (8)$$

The factor $\frac{Z'}{ak}$ in Equation 8, which takes into account the geometric configuration beyond the nearest ions, behaves similarly to the Madelung constant in a solid crystal. Gal and Paligorić [13] therefore consider this factor as the Madelung constant (M), of the quasi-lattice of the mixture :

$$M = \frac{Z'}{ak} \quad (9)$$

They also define the Coulomb energies of the quasi-lattices of the pure salts AX and BX at their melting point, respectivelyU_A^1 and U_B^1, by :

$$U_A^1 = -\frac{Ne^2M}{(4\pi\varepsilon_0)d_{AX}} \quad (10)$$

$$U_B^1 = -\frac{Ne^2M}{(4\pi\varepsilon_0)d_{BX}} \quad (11)$$

These energies U^1, can be obtained with a good approximation from the standard energy of the crystal lattice (U) and the melting enthalpy of pure salt (ΔH_m) according to the expression :

$$U^1 \simeq 0{,}95(U - \Delta H_m) \qquad (12)$$

Finally, mixing energy expression obtained by Gal and Paligorić [13] for a binary system of molten salts with monovalent ions AX – BX type is :

$$\Delta E_m = x(1 - x)\lambda \qquad (13)$$

With λ, the binary interaction parameter which depends on lattice energies and interionic distances, given by :

$$\lambda = -\frac{1}{2}\left(U_A^1 + U_B^1\right)\left(\frac{d_{AX} - d_{BX}}{d_{AX} + d_{BX}}\right)^2 \qquad (14)$$

If the volume change upon mixing is neglected, one can write A&, = AHE, where

AHE is the excess enthalpy of mixing Gal and Paligorić [13] first assume that $\Delta E_m = \Delta H^E$ (ΔH^E: excess enthalpy of mixing). Then, as in the case of regular solution theory [14], they define an ideal binary mixture with $\Delta H_m^{id} = 0$ ($\Delta H_m^{id} = 0$: ideal enthalpy of mixing). Finally, according to these authors, the random distribution of ions in the lattice implies zero excess entropy ($\Delta S^E = 0$).

Thus, the expression for the excess Gibbs free enthalpy of mixing obtained by Gal and Paligorić [13] is :

$$\Delta G^E = \Delta H^E = x(1 - x)\lambda \qquad (15)$$

3. RESULTS AND DISCUSSIONS

3.1. Applicability of the Model

The expression of the excess enthalpy obtained by Gal and Paligorić [13] and presented in relation (15) was made on the basis of several assumptions, the main one being to consider the theory of regular solutions. However, considering the theory of regular solutions [15] when studying binary systems of molten salts of alkali nitrates and silver nitrate assuming that for some systems the excess enthalpy had a linear variation with temperature. This observation is confirmed by some authors [16, 17] who during their various studies obtained for the same binary systems of alkali nitrates, experimental values of mixing enthalpy which vary with temperature.

From the expression of the excess enthalpy of relation (15), taking into account the observation of Vallet [15] and considering the theory of regular solutions which states that the excess enthalpy is equal to the enthalpy of mixing, expression of the latter retained in this work, for the ionic model, is as follows :

$$\Delta H_m = (\lambda + \beta T)x(1 - x) \qquad (16)$$

Where λ is the interaction parameter defined by Gal and Paligorić [13] and β an adjustable parameter obtained by smoothing experimental data.

3.2. Application of the Ionic Model

In this work, expression of the enthalpy of mixing obtained at relation (16), within the framework of the ionic model, is used to estimate the enthalpies of mixing of twelve binary systems of alkali nitrates and silver nitrate.

The physical parameters of the pure salts used to calculate the binary interaction parameters λ are given in Table 1.

The β parameters were obtained by smoothing the experimental data compiled and presented by Meschel and Kleppa [16]. The values of the parameters λ and β obtained, in the present work, for the twelve binary systems studied are presented in Table 2.

Table 1. Physical parameters of pure salts.

Pure salts	T_m (K) [17]	ΔHm (J.mol⁻¹) [17]	U (J.mol⁻¹) [18]	U^1 (J.mol⁻¹) (present work)	d_{AX} (nm) [19]
$AgNO_3$	483	12063	832000	778940.15	0.284
$LiNO_3$	527	24916	671000	613779.80	0.257
$NaNO_3$	583	15449	763000	710173.45	0.289
KNO_3	610	10086	694000	649718.30	0.322
$RbNO_3$	589	4619	671000	633061.95	0.334
$CsNO_3$	678	13430	650000	604741.50	0.355

Note: T_m: melting temperature.

Table 2. Parameters of the ionic model obtained in the present work.

Binary systems	$\lambda\ (J.mol^{-1})$	$\beta\ (J.mol^{-1}.K^{-1})$
$AgNO_3 - LiNO_3$	-1734.47	7.19
$AgNO_3 - NaNO_3$	-56.69	4.03
$AgNO_3 - KNO_3$	-2808.80	1.68
$AgNO_3 - RbNO_3$	-4621.35	-0.12
$AgNO_3 - CsNO_3$	-8541.24	0.20
$LiNO_3 - NaNO_3$	-2273.83	0.59
$LiNO_3 - KNO_3$	-7961.85	0.40
$LiNO_3 - RbNO_3$	-10582.49	-1.19
$LiNO_3 - CsNO_3$	-15622.57	-0.98
$NaNO_3 - KNO_3$	-1983.44	0.33
$NaNO_3 - RbNO_3$	-3504.06	-0.23
$NaNO_3 - CsNO_3$	-6905.32	2.15

In order to analyze the effect of the substitution of atoms in binary systems, we will consider the matrix $AgNO_3$, $LiNO_3$ et $NaNO_3$.

3.2.1. Binary Systems $AgNO_3 - MNO_3$ (M = Li, Na, K, Rb and Cs)

The mixing enthalpies calculated from the present ionic model and compared to the experimental data are presented in Figures 1 to 5.

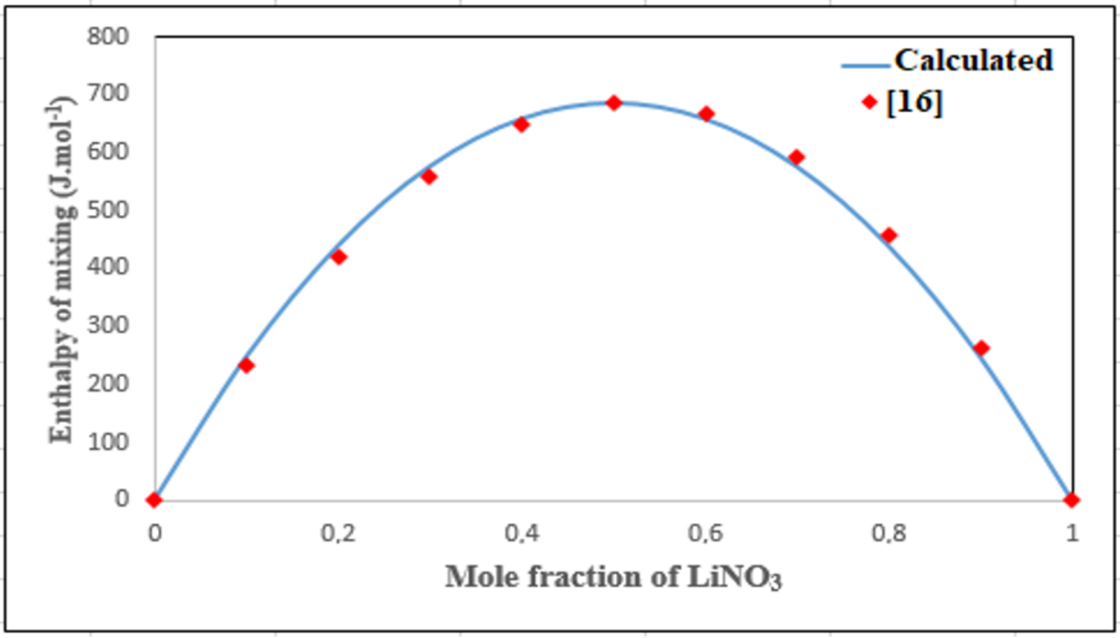

Figure 1. Molar enthalpy of mixing of the $AgNO_3 - LiNO_3$ binary system calculated and compared to experimental data [16].

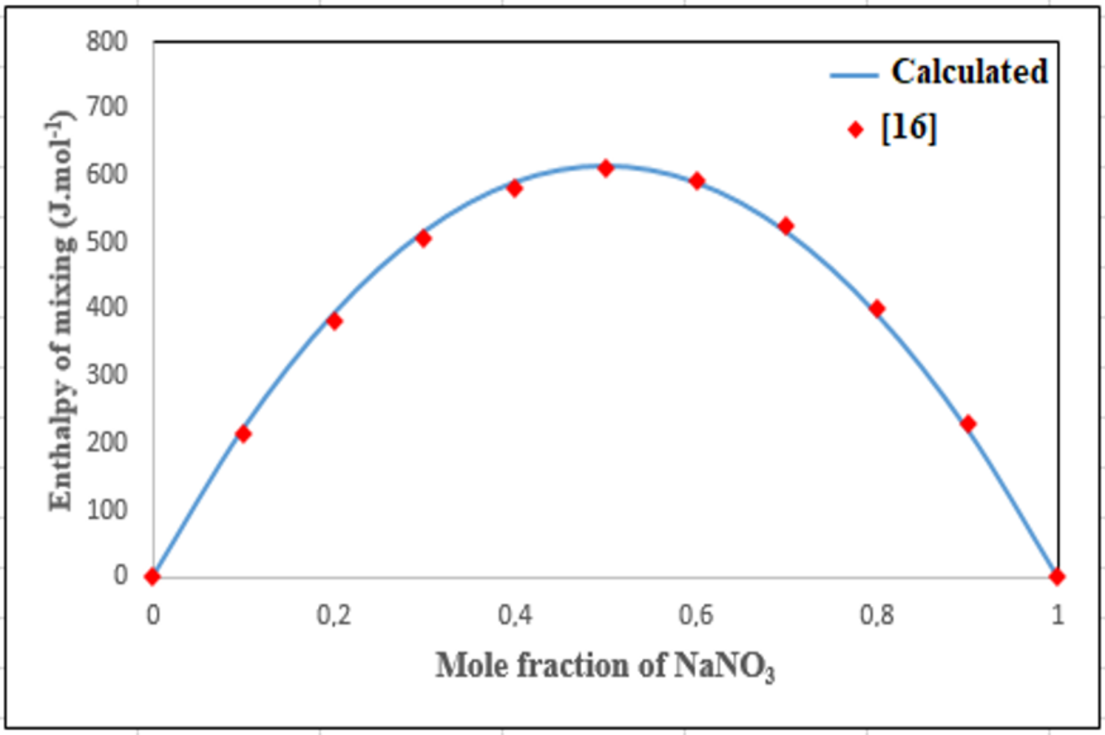

Figure 2. Molar enthalpy of mixing of the $AgNO_3 - NaNO_3$ binary system calculated and compared to experimental data [16].

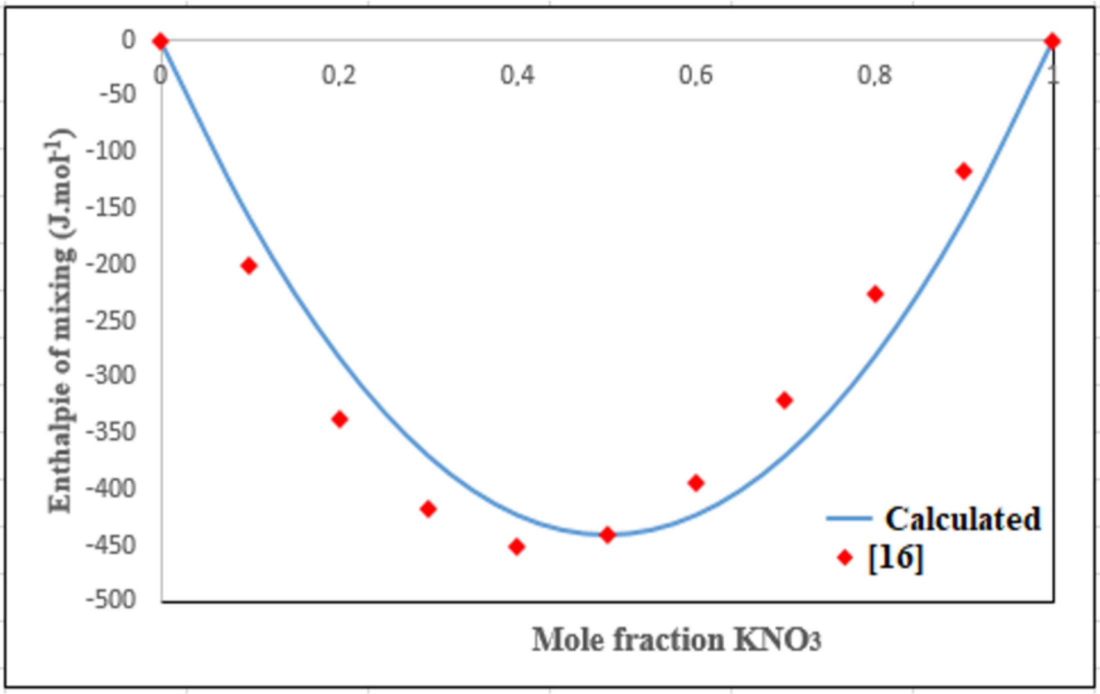

Figure 3. Molar enthalpy of mixing of the $AgNO_3 - KNO_3$ binary system calculated and compared to experimental data [16].

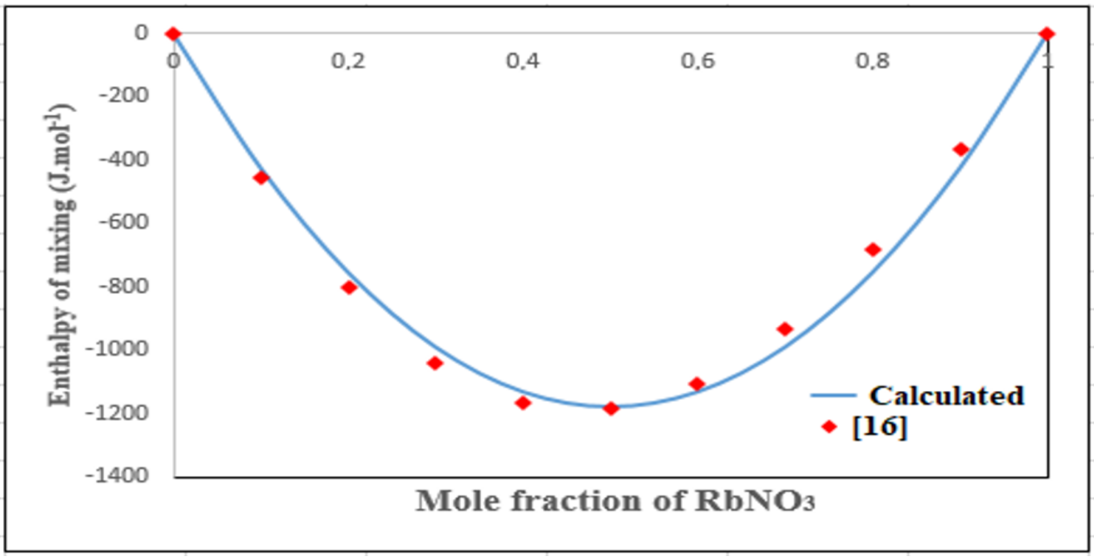

Figure 4. Molar enthalpy of mixing of the $AgNO_3 - RbNO_3$ binary system calculated and compared to experimental data [16].

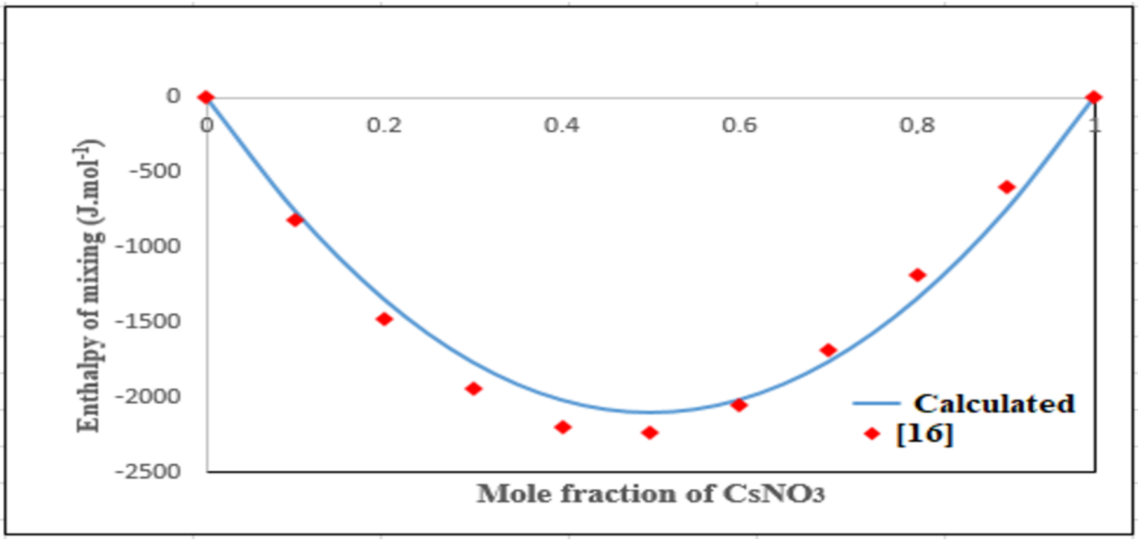

Figure 5. Molar enthalpy of mixing of the $AgNO_3 - CsNO_3$ binary system calculated and compared to experimental data [16].

The agreement between calculation and experiment is very satisfactory in the binary systems $AgNO_3 - LiNO_3$ and $AgNO_3 - NaNO_3$ where regression coefficients are greater than or equal to 0.998 and relative uncertainties between experimental and calculed values are less than 6 % in the entire composition range.

In $AgNO_3 - KNO_3$, $AgNO_3 - RbNO_3$ et $AgNO_3 - CsNO_3$ systems agreement between the calculation and experiment, although satisfactory, is less so than in the two binary systems mentioned above with regression coefficients 0.971, 0.994 and 0.989 respectively.

In a previous work [6], it have been shown that in $AgNO_3$–$LiNO_3$ and $AgNO_3$–$NaNO_3$ binary systems the volume effect prevails over the chemical effect while in $AgNO_3$–$RbNO_3$ and $AgNO_3$–$CsNO_3$ systems the chemical effect predominated. In the $AgNO_3 - KNO_3$ system there was rather a competition between the two effects. It is therefore deduced that, in the matrix $AgNO_3$, the present ionic model determines with more precision the enthalpies of mixing of binary systems with a larger volume effect than the chemical effect.

3.2.2. Binary systems $LiNO_3 - MNO_3$ (M = Na, K, Rb and Cs)

The experimental and calculated data in the present work are compared and presented in Figures 6 to 9.

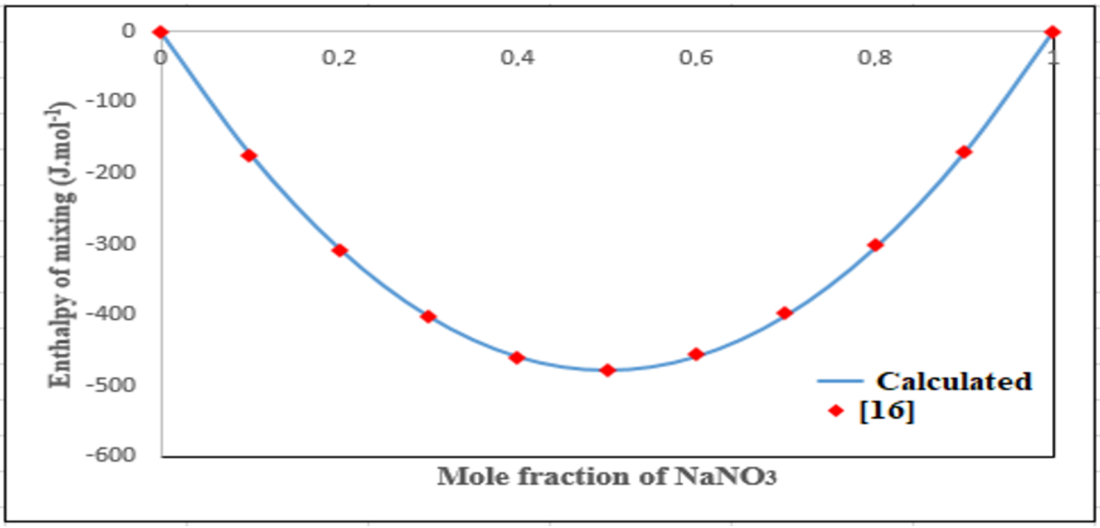

Figure 6. Molar enthalpy of mixing of the $LiNO_3 - NaNO_3$ binary system calculated and compared to experimental data [16].

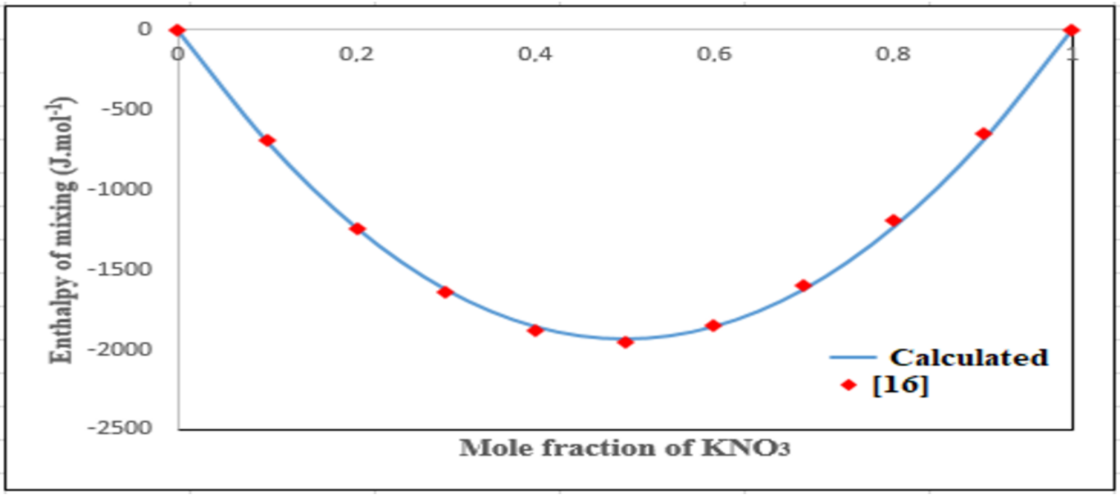

Figure 7. Molar enthalpy of mixing of the $LiNO_3 - KNO_3$ binary system calculated and compared to experimental data [16].

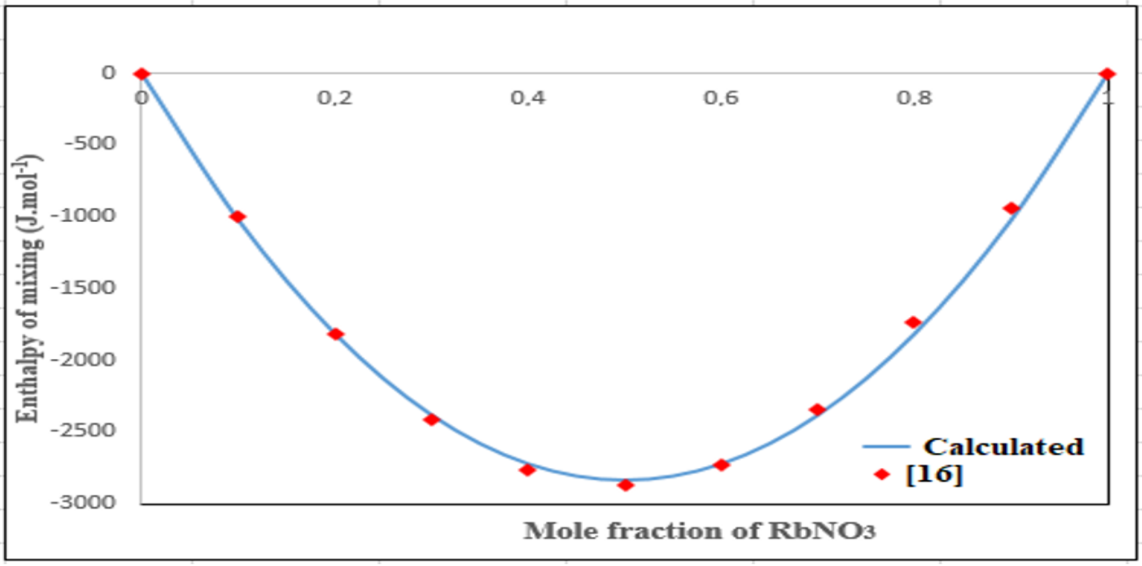

Figure 8. Molar enthalpy of mixing of the $LiNO_3 - RbNO_3$ binary system calculated and compared to experimental data [16].

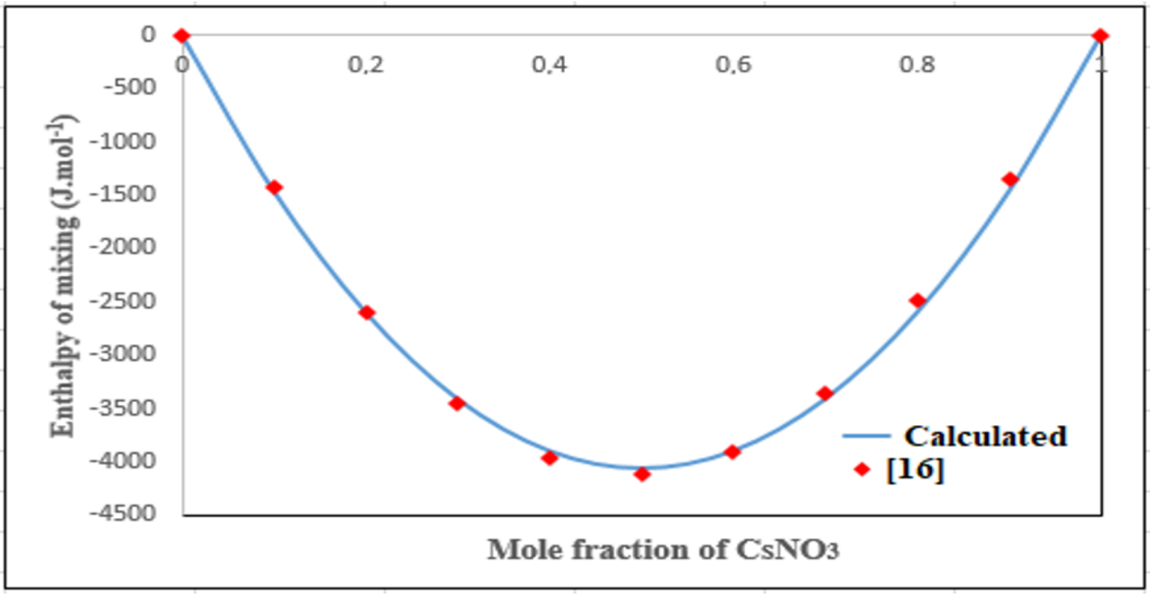

Figure 9. Molar enthalpy of mixing of the $LiNO_3 - CsNO_3$ binary system calculated and compared to experimental data [16].

The mixing enthalpies calculated from ionic model in $LiNO_3$ matrix are perfect agreement with experimental data with regression coefficients 0.999 and uncertainties lower than 2.5%.

This satisfactory agreement between calculation and experiment allows us to deduce that binary systems based on lithium nitrate are strictly regular solutions. These results are in agreement with those of Guion and Brenet [18] who electrochemically had come to the same conclusion.

Moreover, when we go down in the group of alkali metals (from Na to Cs), the uncertainty between experimental and calculated values increases (from 0.73% to 2.32%). We deduce that the deviation from the regularity of the solutions increases when the difference in radius between the two cations increases.

3.2.3. Binary Systems $NaNO_3 - MNO_3$ (M = Li, K, Rb and Cs)

The mixing enthalpies of these binary systems obtained in the present work and compared to the experimental data are presented in Figure 6 and Figures 10 to 12.

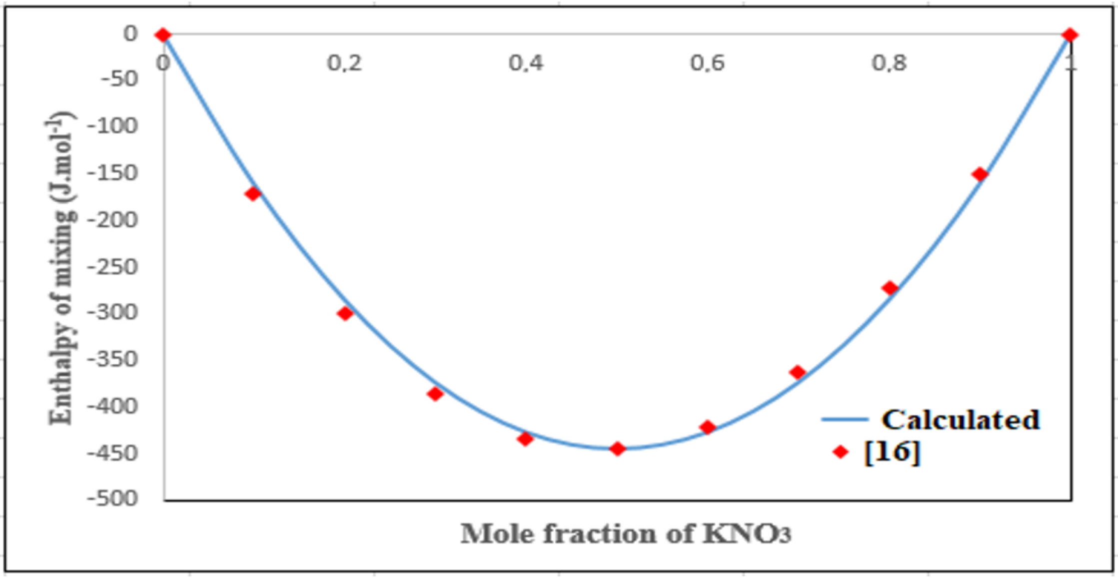

Figure 10. Molar enthalpy of mixing of the $NaNO_3 - KNO_3$ binary system calculated and compared to experimental data [16].

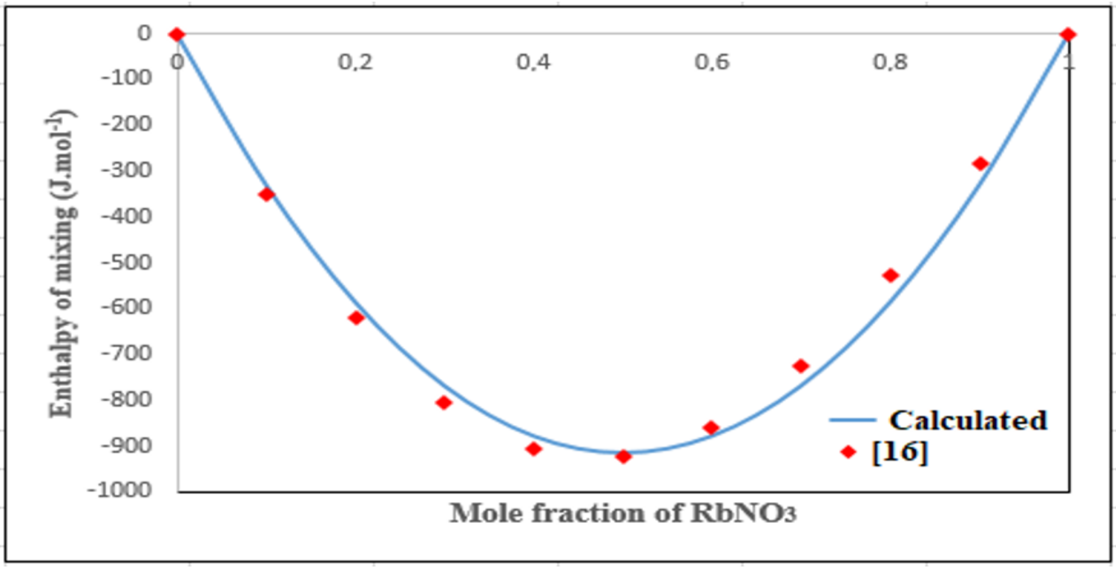

Figure 11. Molar enthalpy of mixing of the $NaNO_3 - RbNO_3$ binary system calculated and compared to experimental data [16].

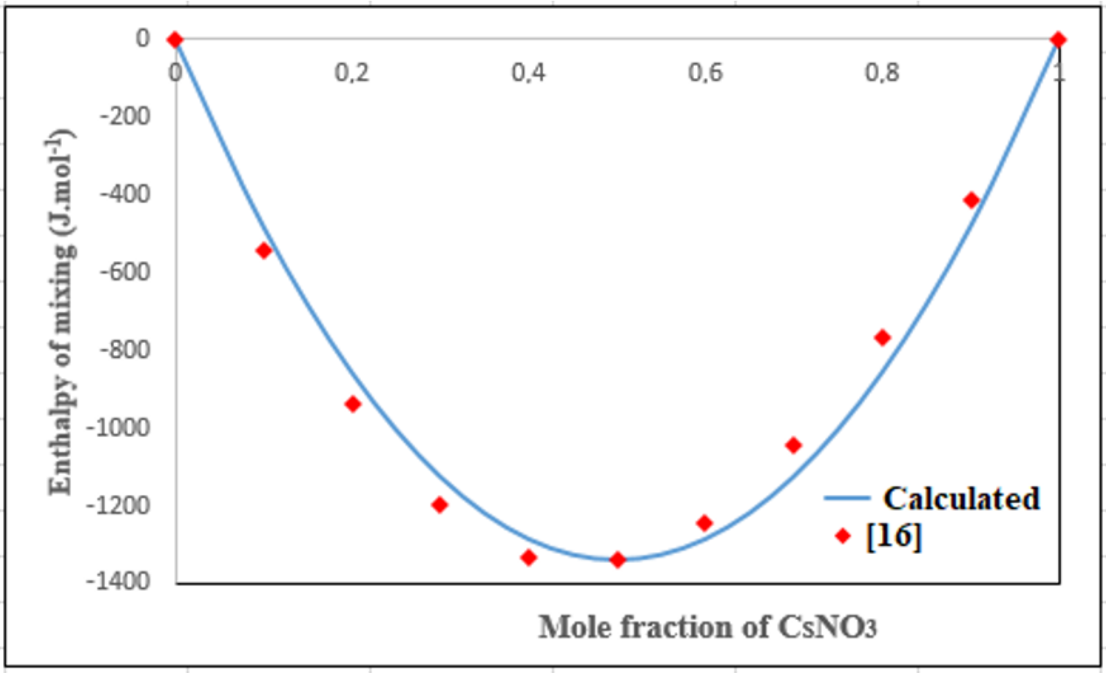

Figure 12. Molar enthalpy of mixing of the $NaNO_3 - CsNO_3$ binary system calculated and compared to experimental data [16].

These figures show good agreement between calculation and experiment with regression coefficients greater than 0.992 and uncertainties less than 8%. In view of this satisfactory agreement, we can therefore say that these binary systems based on $NaNO_3$ are strictly regular solutions. Moreover, just as in systems based on lithium nitrate, the deviation from regularity increases when the difference in radius between cations increases. Indeed, from Li to Cs the regression coefficients decrease from 0.999 to 0.992.

4. CONCLUSION

The ionic model developed in the present work was used to calculate the mixing enthalpies of twelve binary systems based on silver nitrate and alkali nitrates. A satisfactory general agreement was obtained between calculation and experiment.

This work has shown that:

1. For binary systems based on $AgNO_3$, the ionic model best described binary systems with a predominant volume effect over the chemical effect;
2. For the binary systems of $LiNO_3$ and $NaNO_3$ matrices, the solutions are strictly regular and the deviation from regularity increases when we go down in the family of alkali metals.

The binary parameters obtained in this work will be used to estimate the thermodynamic properties of mixing of higher order systems based on silver nitrate and alkali nitrates. These data will be essential in the optimization procedures for the complete thermodynamic description of the silver nitrate and alkali nitrate systems.

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