

# Description of electrolytes at high temperatures within the binding mean spherical approximation (BiMSA)

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## ABSTRACT

In this work, the binding mean spherical approximation (BiMSA) theory is used to describe osmotic and activities coefficients for electrolytes solutions up to high temperatures. Four salts are analyzed: NaCl, LiCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>, in the temperature range of 25°C to 300°C and molalities from 0.05 to 6 molal. A good representation of experimental data is obtained for all salts and temperatures considered by introducing temperature-dependent cation size and permittivity in a suitable way. The proportion of ion pairs (that are formed at sufficiently high temperature in these solutions) for each salt is predicted from the theory, showing a pronounced increase for temperatures above 100°C. A good agreement is found between the values of optimized and experimental association constants given in the literature.

## KEYWORDS

BiMSA theory; electrolytes solutions; high temperatures; ion pair.

## 1. Introduction

Electrolyte solutions play a significant role in the biological mechanisms observed in living bodies, and in a wide range of industrial processes, including the construction of thermal batteries, production of chemical fertilizers, the refinement of metals, etc [1–7]. The properties of these systems are influenced by temperature, which affects the degree of ionization and the activity coefficients of the species present.

In the past years some studies implement some theoretical models in order to describe different thermodynamic properties at temperatures above 25°C [8–11]. Almost all of these implementations are based on the Pitzer thermodynamic model [8], which originally was implemented for general electrolytes solution for temperatures not too different from 25°C.

More recently, there has been a growing interest in the study of electrolyte solutions at high temperatures [12–14]. The behavior of such systems is not well understood, especially from the perspective of statistical mechanical models. High temperature electrolytes are of particular interest as they can exhibit complex behavior, such as the development of ion clusters and the formation of solid-like structures [13–15]. The

purpose of this research is to provide an analysis of the thermodynamic properties of aqueous electrolytes at high temperature within the framework of a statistical mechanical model (the BiMSA).

In geochemistry, the semi-empirical Pitzer's model has been extensively employed to describe various thermodynamics properties with high accuracy [16, 17]. However, this model involves many parameters that need be adjusted using available experimental data. These parameters have no simple physical meaning, in contrast with models like the mean spherical approximation (MSA) which is expressed in terms of ion sizes and solution permittivity, or the binding MSA (BiMSA) that is used in this work, which moreover accounts for ion pairing.

In previous works, the MSA and BiMSA theories has been used to model several types of electrolyte solutions [18–30]. In ref. 20, the theory was applied to an extended set of associating aqueous electrolyte solutions, including perchlorates, nitrates, hydroxides, and sulfates. In reference 28 lanthanide salt solutions and ternary mixtures were described within the same formalism. In ref. 29, polyelectrolyte chains and rings were discussed within the BiMSA. In ref. 30, electrolyte solutions exhibiting ion-pairing in pure organic solvents were considered. As can be seen, the formalism has been applied to a broad class of electrolytes solutions.

The cation diameter and the permittivity of solution are assumed to be simple concentration-dependent functions. Good results were obtained for the description of osmotic and activity coefficients of a number of binary and ternary aqueous solutions. The behavior of these parameters was physically discussed.

A few publications have considered electrolyte solutions at high temperatures within the MSA [31–33]. In these works, cation size and permittivity variation were also proposed as a function of temperature. The values of the parameters related to these quantities were found through minimization processes between the experimental data and the theoretical expressions. In Ref. 32 several adjustments were made to fixed temperatures while in Refs. 31 and 33 a global adjustment was done on the entire set of data at different temperatures simultaneously. However, ion-pair formation was not addressed in any of these investigations, a phenomenon that is expected to may play an important role in ionic solutions at high temperatures.

In this work, a statistical mechanical theory including association, BiMSA, was used to analyze the behavior in a broader range of temperatures, including at the same time effects arising from the variation of solvation and solution permittivity with temperature and concentration. Four chloride salts were considered: NaCl, LiCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>, using the BiMSA model in the temperature range of 25°C to 300°C, and for concentrations up to 6 molal. Experimental data for osmotic and activity coefficients up to high temperatures were retrieved from the literature. They were utilized to fit the free parameters of the model. Simple mathematical expressions were proposed for the variation of cation size and permittivity with temperature and concentration. To include ion-pair formation in the solutions, a temperature dependent association constant was introduced. The model parameters associated with these functions were adjusted to fit our model to the experimental data, using the entire data set at different temperatures for each binary salt solution.

This paper is organized as follows. In section II the main theoretical ingredients of the BiMSA are provided, including the proposed expressions for the variation of cation size, permittivity and pairing association constant as functions of temperature and concentration. Then, new fits for the solution densities for each salt considered in this work are given. In section III the main results are presented and discussed. Finally, in section IV, some conclusions about this study are presented.

## 2. Theory

In this work, ions are modeled as charged hard spheres interacting through a Coulomb potential, with diameters  $\sigma_+$  for cations and  $\sigma_-$  for anions. The two can form ion pairs, which are neutral in the present case. The solvent is represented as a continuum, and the permittivity of solution is  $\epsilon$ . Furthermore, the effect of solvation and the variation of the permittivity with respect to concentration and temperature are taken into account. Within the framework of this theory [25–27], the excess BiMSA Helmholtz free energy,  $A$ , per volume unit is given by

$$\beta\Delta A^{BiMSA} = \beta\Delta E^{BiMSA} + \frac{\Gamma^3}{3\pi} + \sum_{i=+,-} \rho_i \ln \alpha_i + \rho_p - 2\lambda \frac{\rho_p}{\sigma_p} z'_+ z'_-, \quad (1)$$

where  $\beta\Delta E^{BiMSA}$  is the electrostatic excess internal energy per volume unit expressed by

$$\beta\Delta E^{BiMSA} = -\lambda \sum_{i=+,-} \rho_i z_i \frac{\Gamma z_i + \eta \sigma_i}{1 + \Gamma \sigma_i} + \lambda \frac{\rho_p}{\sigma_p} \left( \frac{z_+ z'_-}{1 + \Gamma \sigma_+} + \frac{z_- z'_+}{1 + \Gamma \sigma_-} \right), \quad (2)$$

with  $z'_i \equiv (z_i - \eta \sigma_i^2)/(1 + \Gamma \sigma_i)$ ,  $\lambda \equiv \beta e^2/(4\pi\epsilon_0\epsilon)$  and  $\sigma_p \equiv \sigma_+ + \sigma_-$ . The equations below for the MSA parameters  $\Gamma$  and  $\eta$  constitute two coupled equations that can be solved by numerical iterations. Analytically they are given by

$$\frac{\Gamma^2}{\pi\lambda} = \sum_{k=+,-} \rho_k z_k^2 + \frac{2\rho_p}{\sigma_p} \left( \frac{\sigma_+}{1 + \Gamma \sigma_+} + \frac{\sigma_-}{1 + \Gamma \sigma_-} \right) z'_+ z'_-, \quad (3)$$

$$\eta = \frac{\pi}{2\Delta\Omega} \left[ \sum_{k=+,-} \frac{\rho_k \sigma_k z_k}{1 + \Gamma \sigma_k} + \frac{\rho_p}{\sigma_p} \frac{z_+ \sigma_-^2 + z_- \sigma_+^2}{(1 + \Gamma \sigma_+)(1 + \Gamma \sigma_-)} \right], \quad (4)$$

with

$$\Omega = 1 + \frac{\pi}{2\Delta} \left[ \sum_{k=+,-} \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_+} + \frac{2\rho_p}{\sigma_p} \frac{\sigma_+^2 \sigma_-^2}{(1 + \Gamma \sigma_+)(1 + \Gamma \sigma_-)} \right], \quad (5)$$

where  $\Delta = 1 - X_3$  and  $X_n = \frac{\pi}{6} \sum_k \rho_k \sigma_k^n$ . The analytical expressions for the osmotic and activity coefficients can be calculated using the following thermodynamics relations

$$\Delta\phi^{BiMSA} = \rho_t \frac{\partial}{\partial \rho_t} \left[ \frac{\beta\Delta A^{BiMSA}}{\rho_t} \right]_{\Gamma}, \quad (6)$$

$$\Delta\gamma_{\pm}^{BiMSA} = \frac{\partial}{\partial \rho_t} [\beta\Delta A^{BiMSA}]_{\Gamma}, \quad (7)$$

where  $\rho_t \equiv \rho_+ + \rho_-$  is the total number density. The activity coefficient at the McMillan-Mayer (MM) level can be split as

$$\Delta \ln \gamma^{MM} = \Delta \ln \gamma^{HS} + \Delta \ln \gamma^{BiMSA}, \quad (8)$$

where the superscript  $HS$  denotes a hard sphere contribution calculated using the Helmholtz free energy for hard spheres [34, 35]

$$\frac{\pi}{6} \beta \Delta A^{HS} = \left( \frac{X_2^3}{X_3^2} - X_0 \right) \ln(1 - X_3) + \frac{3X_1 X_2}{1 - X_3} + \frac{X_2^3}{X_3(1 - X_3)^2}. \quad (9)$$

Then,

$$\Delta \ln \gamma^{HS} = \Delta \ln \gamma_0^{HS} + \Delta \ln \gamma_{\sigma_+}^{HS}, \quad (10)$$

here  $\Delta \ln \gamma_0^{HS}$  is the hard sphere contribution, obtained for constant diameters and  $\Delta \ln \gamma_{\sigma_+}^{HS}$  take into account the variation of the cation size. Moreover, the BiMSA contribution to the activity coefficient is given by

$$\Delta \ln \gamma^{BiMSA} = \Delta \ln \gamma_0^{BiMSA} + \Delta \ln \gamma_{\sigma_+, \epsilon}^{BiMSA}, \quad (11)$$

where  $\Delta \ln \gamma_0^{BiMSA}$  is the BiMSA contribution keeping the cation size and permittivity fixed, and in  $\Delta \ln \gamma_{\sigma_+, \epsilon}^{BiMSA}$  these variations are included. Similarly, the osmotic coefficient may be expressed as

$$\phi^{MM} = 1 + \Delta \phi^{HS} + \Delta \phi^{BiMSA}, \quad (12)$$

with

$$\Delta \phi^{HS} = \Delta \phi_0^{HS} + \Delta \phi_{\sigma_+}^{HS}, \quad (13)$$

and

$$\Delta \phi^{BiMSA} = \Delta \phi_0^{BiMSA} + \Delta \phi_{\sigma_+, \epsilon}^{BiMSA}. \quad (14)$$

To account for association, a mass action law (MAL) is included in the model. This can be expressed by considering an apparent association constant defined by

$$K_0 \equiv \frac{\rho_p}{(\rho_+ \alpha_+)(\rho_- \alpha_-)} = K g_{+-}^{HS} \exp \left[ -2\lambda (z_+ z'_- - z_+ z_- \epsilon / \epsilon_w) / \sigma_p \right], \quad (15)$$

where  $\rho_+$  and  $\rho_-$  are the number densities of cations and anions, respectively, and  $\alpha_+$  and  $\alpha_-$  are their free ion fractions.  $K$  is the thermodynamic equilibrium constant and  $g_{+-}^{HS}$  is the contact value of the pair distribution function [34, 36]. The  $\rho_p$  is the number density of ion pairs, which in this case can be expressed in a closed analytical form as [27]

$$\rho_p = \frac{2K_0 \rho_+ \rho_-}{1 + K_0 \rho_t [1 + 2K_0 \rho_t + K_0^2 (\rho_+ - \rho_-)^2]^{1/2}}. \quad (16)$$

From these expressions one can define the ratio of formed ion pairs as

$$X_P \equiv \frac{\rho_p}{\rho_+}. \quad (17)$$

For more details on the development of this model as well as the complete expressions of the activity and osmotic coefficients, the reader can consult the previous works where this model is explained in detail [27, 37]

The effect of the change in cation hydration is introduced as a variation of the cation size as a function of concentration and temperature. A linear behavior respect to concentration is proposed

$$\sigma_+(T, C) = \sigma^{(0)}(T) + \sigma^{(1)}(T) C, \quad (18)$$

where  $\sigma^{(0)}(T)$  is the size of the cation at infinite dilution at a given temperature  $T$ , and  $\sigma^{(1)}(T)$  is a parameter that takes into account the variation of the cation size with concentration. As in previous work [26, 27], the anion size will be considered as a constant, because it is assumed that the chloride ion is known to be weakly hydrated [38]. Following previous work, the effect of varying solution permittivity can be described as

$$\epsilon = \frac{\epsilon_w(T)}{1 + \alpha(T)C}, \quad (19)$$

where  $\epsilon_w(T)$  is the permittivity of water, taken from [39] for temperatures in the range from 0 to 367°C and  $\alpha(T)$  is a parameter accounting for the permittivity variation with respect to concentration. In order to compare the results from the model with experimental data, and consider temperature as a variable, quadratic functions are proposed for the behavior of the parameters  $\sigma^{(0)}(T)$ ,  $\sigma^{(1)}(T)$ ,  $\alpha(T)$  in the following way:

$$\sigma^{(0)}(T) = \sigma_0^{(0)} + \sigma_1^{(0)}(T - T_0) + \sigma_2^{(0)}(T - T_0)^2, \quad (20)$$

$$\sigma^{(1)}(T) = \sigma_0^{(1)} + \sigma_1^{(1)}(T - T_0) + \sigma_2^{(1)}(T - T_0)^2, \quad (21)$$

and

$$\alpha(T) = \alpha_0 + \alpha_1(T - T_0) + \alpha_2(T - T_0)^2, \quad (22)$$

where  $T$  is the absolute temperature, and  $T_0 = 298.15K$  corresponding to 25°C at which the MSA model was parameterized in previous work [26, 27] and therefore serves as a reference.

Moreover, the thermodynamic association constant, which is a function of temperature only for a given salt, was assumed to have an exponential dependence of Arrhenius type, as

$$K(T) = A_0 \exp(A_1/T). \quad (23)$$

Parameters related to these functions can be obtained by fitting experimental data for osmotic or activity coefficients at different concentrations and temperatures.

To perform this procedure, it is necessary to convert the theoretical quantities (at the McMillan-Mayer level) to the level of the experimental quantities (at the Lewis-Randall level). This conversion was done using the following expressions [26, 40]

$$\phi^{(LR)} = \phi^{MM}(1 - C_t V_{\pm}), \quad (24)$$

$$\ln y_i^{(LR)} = \ln y_i^{(MM)} - C_t V_i \phi^{(MM)}, \quad (25)$$

and

$$y_i^{(LR)} = \gamma_i^{LR} V d_w, \quad (26)$$

where  $C_t$  is the total solute concentration ( $C_t = \nu C$ , with  $\nu$  the stoichiometric number of the salt),  $V_{\pm}$  is the mean solute partial molal volume,  $V$  is the specific volume,  $V_i$  is the partial molal volume of species  $i$ ,  $\gamma_i^{LR}$  is the LR activity coefficient of  $i$ , and  $d_w(T)$  is the density of pure water at temperature  $T$ . From previous expressions it follows that a knowledge of the solution density as a function of  $T$  and  $C$  is required in order to carry out the conversion. The concentration is calculated using the simple conversion for a given molality  $m$

$$C = \frac{m d(m, T)}{1 + mM}, \quad (27)$$

where  $d(m, T)$  is the solution density and  $M$  is the molar mass of the salt. To homogenize the expression of density for all the salts used throughout this research, an expression inspired by the results of Novotny [41] is proposed. So, solutions densities are parameterized through the following equation

$$d(m, T) = d_w(T) + d_1(T) m + d_2(T) m^{3/2}, \quad (28)$$

where  $d_w(T)$  is the density of pure water [42], and  $d_1(T)$  and  $d_2(T)$  are quantities depending on temperature according to

$$d_i(T) = \sum_j d_{i,j} (T - T_0)^j \quad (29)$$

with  $j = 0, 1, 2, 3, 4$ , and  $d_{i,j}$  are parameters whose values are obtained by adjusting data reported in the literature [43–45] at saturation pressure. These values are collected in Table 1.

### 3. Procedures and Results

Four chloride salts were studied: Sodium chloride (NaCl) in a range of temperature from 25°C to 300°C and molalities from 0.05 to 5 molal [46, 47]; lithium chloride (LiCl) from 25°C to 250°C and from 0.4 to 6.0 molal [48–51]; magnesium chloride (MgCl<sub>2</sub>) from 25°C to 250°C and from 0.1 to 5.0 molal [52], and calcium chloride

**Table 1.** Parameter values used in eq. 29 at saturation pressures for the salts considered in this work.

Parameter <sup>a</sup>	NaCl	LiCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>
$d_{1,0} \times 10^2$	4.42264	2.58432	8.51592	10.1291
$d_{1,1} \times 10^4$	-4.40552	-0.88616	-1.12753	-1.46619
$d_{1,2} \times 10^6$	5.99165	3.16675	3.9993	3.87038
$d_{1,3} \times 10^8$	-2.20673	-1.30471	-1.52684	-1.54946
$d_{1,4} \times 10^{11}$	3.03429	2.19338	2.57219	2.67898
$d_{2,0} \times 10^3$	-7.31016	-2.4407	-11.1619	-14.7012
$d_{2,1} \times 10^4$	1.59541	0.33411	0.377005	0.31633
$d_{2,2} \times 10^6$	-2.18626	-1.05275	-1.32442	-1.17937
$d_{2,3} \times 10^9$	8.76135	4.53665	5.19612	4.95342
$d_{2,4} \times 10^{11}$	-1.22716	-0.761681	-0.84999	-0.85406

<sup>a</sup>  $d_{1,j}$  in  $\text{m}^{-1} \text{ }^\circ\text{C}^{-j}$  and  $d_{2,j}$  in  $\text{m}^{-3/2} \text{ }^\circ\text{C}^{-j}$ .

(CaCl<sub>2</sub>) from 25°C to 250°C and from 0.1 to 6.0 molal [53, 54]. The reason for this choice was the availability of experimental data reported for the osmotic and activity coefficients and the densities of these salts. The Pauling diameter was taken for Cl<sup>-</sup>,  $\sigma_- = 3.62 \text{ \AA}$ , which value was assumed to be a constant with  $T$  and  $C$ . Moreover, the pressure for all solutions was taken equal to the saturation pressure of water for every temperature. Experimental data for the osmotic coefficient for NaCl solution as a function of temperature for a fixed concentration [47] (see figure 3a of this reference) indicate that, for temperatures in the range of 273 K to 373 K, there are two values of the temperature for a given concentration at which the same value for the osmotic coefficient is observed. This behavior is not seen at higher temperatures where the osmotic coefficient has a monotonous behavior as a function of  $T$ . This induces the crossing observed in the curves for NaCl at lower temperatures. Among the four salts considered in this work, the previous behavior is more pronounced in the case of NaCl, less for LiCl, and practically inexistent for MgCl<sub>2</sub> and CaCl<sub>2</sub>.

To compare our theoretical framework with the experimental data, a global fit was performed for each salt using the values of the osmotic and activity coefficients over a range of concentrations and temperatures. The procedure was performed using the Levenberg-Marquardt (least squares) algorithm programmed in a FORTRAN routine. Parameters associated with eqs. 20 - 23 were adjusted except for  $\sigma_0^{(0)}$  (the size of cation at infinite dilution), which was taken as the optimum value obtained in prior work [26] in fits for various solutions containing the same cation (without association at 25°C). Thus, 10 free parameters were used.

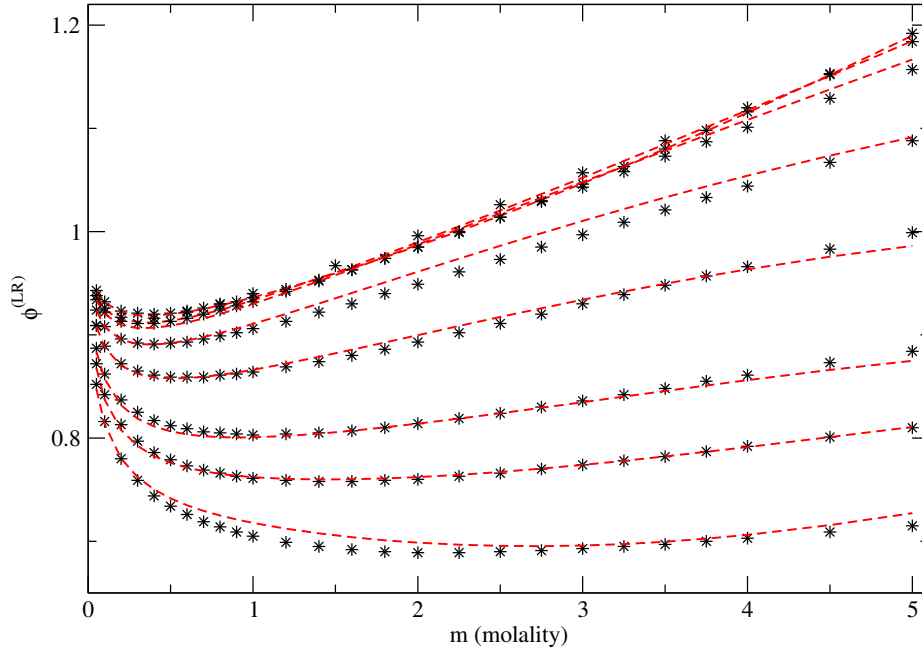
The values obtained for these parameters, as well as the average relative deviation (AARD) of each adjustment, are shown in Table 2. Good fits were obtained for all salts even at high temperatures. A comparison between the results from the model and experimental data for the osmotic coefficient is shown in Figs. 1 to 4, where it can be seen that the experimental data are well represented by the model. Also a plot for the activity coefficients for the same salts and temperatures is displayed in Fig. 5. As can be seen a good fit is also obtained for this thermodynamic quantity.

One feature of this model is that it allows one to physically interpret the behavior of  $\sigma_+(T, C)$ ,  $\epsilon(T, C)$  and  $K(T)$  in the theory. In Fig. 6 the cation size and permittivity are plotted as a function of temperature and concentration for NaCl solution. The same behavior was found for the other salts: At a fixed concentration, the cation size

**Table 2.** Values obtained for the parameters in eqs. 20-23 for the salts considered in this work.

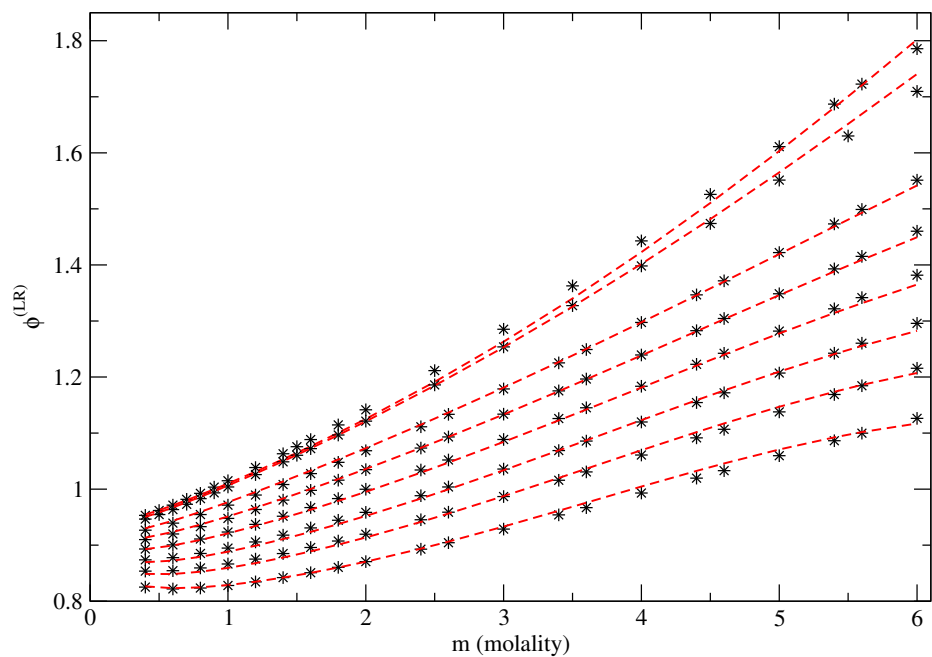
Salt	$\sigma_0^{(0)}$ Å	$\sigma_1^{(0)} \times 10^3$ Å K <sup>-1</sup>	$\sigma_2^{(0)} \times 10^6$ Å K <sup>-2</sup>	$\sigma_0^{(1)} \times 10^2$ Å mol <sup>-1</sup> L	$\sigma_1^{(1)} \times 10^4$ Å mol <sup>-1</sup> K <sup>-1</sup>	$\sigma_2^{(1)} \times 10^6$ Å mol <sup>-1</sup> K <sup>-2</sup>	
NaCl	3.87	2.22	13.34	-5.062	-6.868	-1.156	
LiCl	5.43	1.4	8.59	-8.08	-2.71	-0.157	
MgCl <sub>2</sub>	6.0	2.95	17.5	-14.15	1.95	-1.115	
CaCl <sub>2</sub>	6.1	2.01	5.47	-16.25	-5.96	0.810	
	$\alpha_0 \times 10^2$ mol <sup>-1</sup> L	$\alpha_1 \times 10^4$ mol <sup>-1</sup> L K <sup>-1</sup>	$\alpha_2 \times 10^6$ mol <sup>-1</sup> L K <sup>-2</sup>	$A_0$ mol <sup>-1</sup> L	$A_1$ K	AARD % <sup>a</sup>	
						$\phi$	$\gamma$
NaCl	6.824	-5.413	2.344	42766.6	-5203.19	0.45	1.21
LiCl	16.47	-6.55	2.14	1597.74	-3331.59	0.46	1.05
MgCl <sub>2</sub>	1.05	1.06	1.35	39996.1	-3823.36	1.24	2.91
CaCl <sub>2</sub>	5.01	1.09	1.45	99998.7	-4348.42	1.16	2.11

<sup>a</sup>AARD% for a quantity X (=  $\phi$  or  $\gamma$ ) is the average absolute relative deviation for the calculated value of X against the experimental:  $\text{AARD} (\%) = (100/N) \sum_{i=1}^N |X_i^{\text{cal}}(T, C) - X_i^{\text{exp}}(T, C)| / X_i^{\text{exp}}(T, C)$ , with  $N$  the number of  $(T, C)$  points.

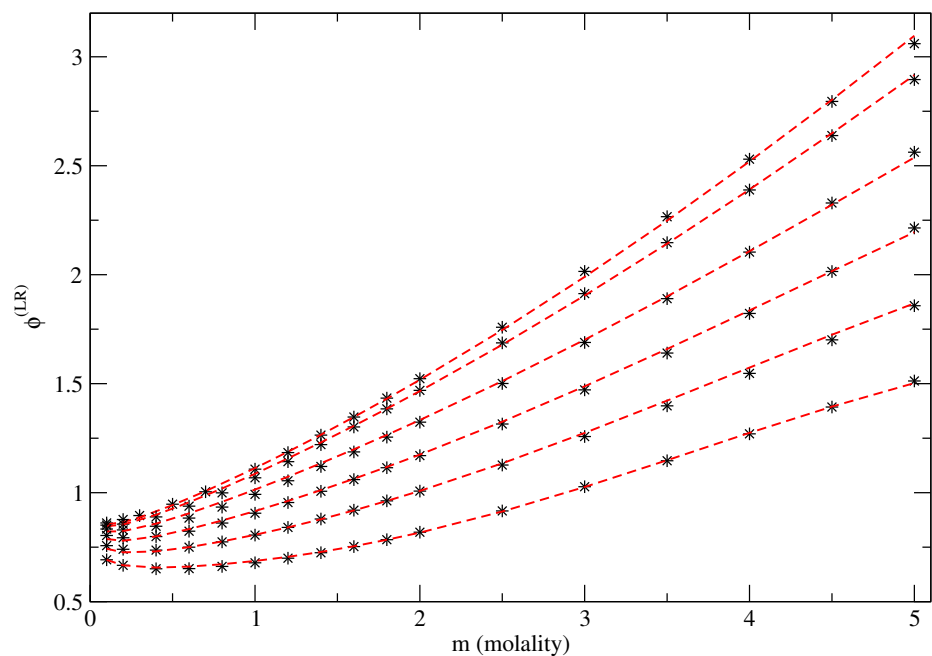


**Figure 1.** Osmotic coefficients for NaCl solutions, from top to bottom, 25°C, 75°C, 100°C, 150°C, 200°C, 250°C, 275°C and 300°C. Experimental data (black stars) and theoretical results (red dashed lines).

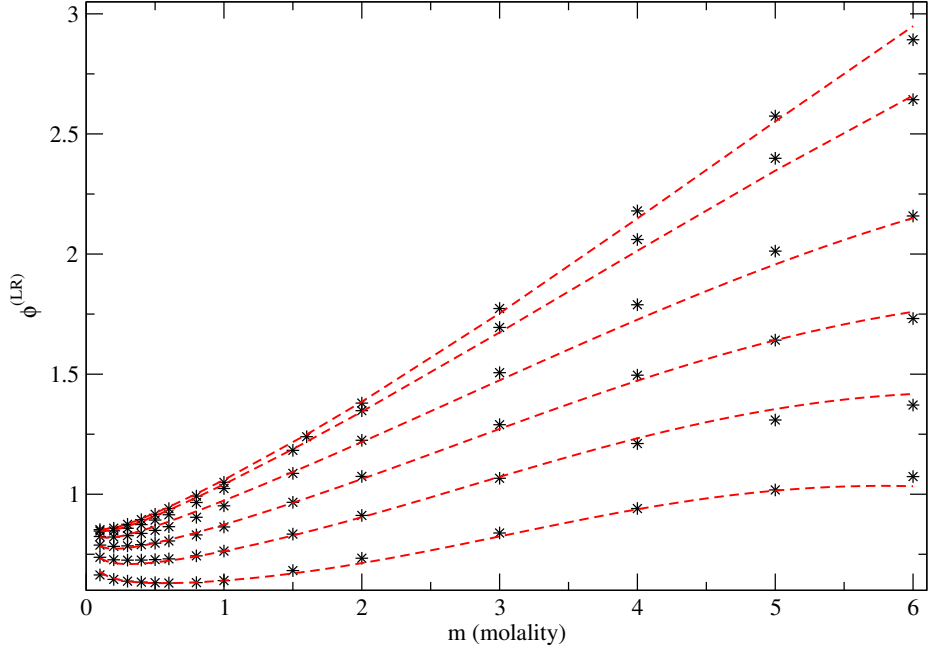




**Figure 2.** Osmotic coefficients for LiCl solutions, from top to bottom: 25°C, 50°C, 110°C, 140°C, 170°C, 200°C, 225°C and 250°C. Experimental data (black stars) and theoretical results (red dashed lines).



**Figure 3.** Osmotic coefficients for MgCl<sub>2</sub> solutions, from top to bottom: 25°C, 50°C, 100°C, 150°C, 200°C and 250°C. Experimental data (black stars) and theoretical results (red dashed lines).



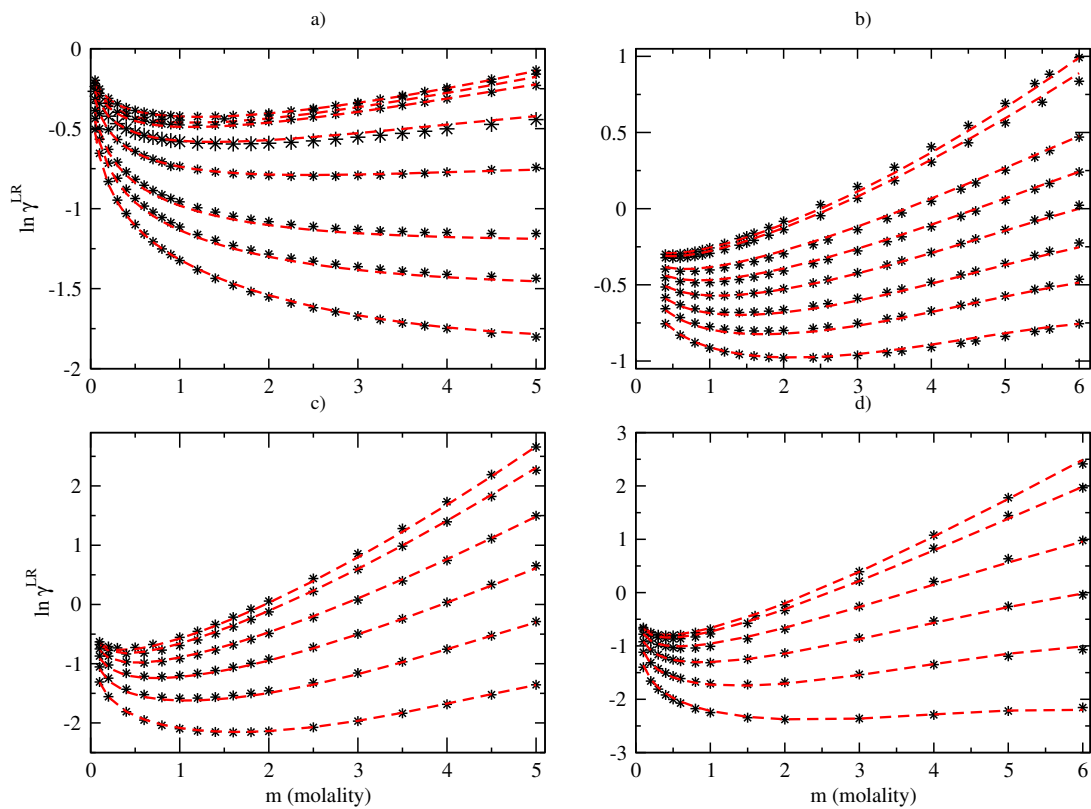
**Figure 4.** Osmotic coefficients for  $\text{CaCl}_2$  solutions, from top to bottom:  $25^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $100^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $200^\circ\text{C}$  and  $250^\circ\text{C}$ . Experimental data (black stars) and theoretical results (red dashed lines).

is found to increase with temperature while the permittivity decreases. On the other hand, at a fixed temperature, both quantities decrease.

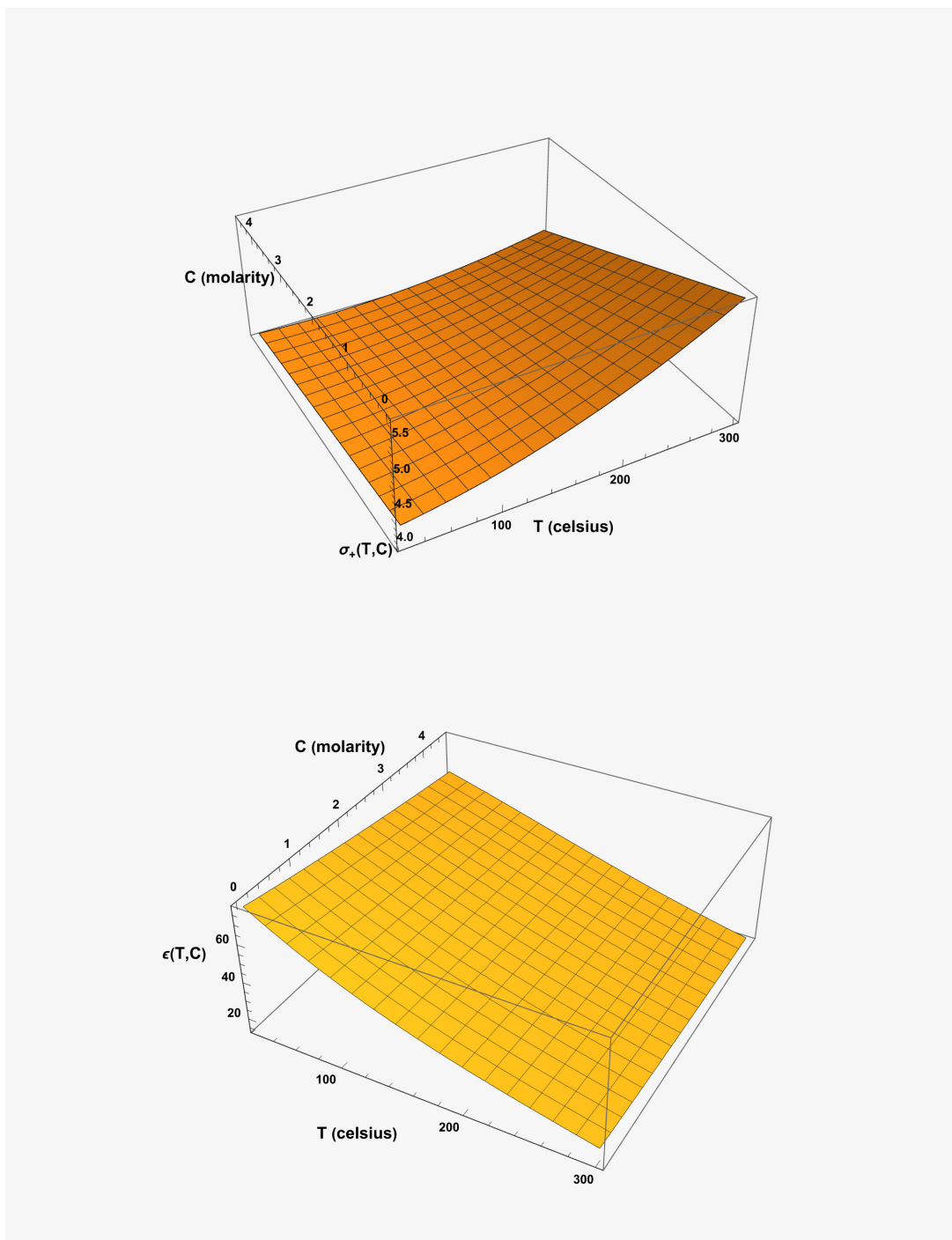
The variation of the cation size can be discussed on the basis of decrease of the permittivity of water with the temperature. Then it might be expected that ion-water forces be strengthened when  $T$  is increased, and so would the hydration degree of the cation. Therefore,  $\sigma_+$  should be increasing with temperature at infinite dilution, which is indeed observed through the increase with  $T$  of  $\sigma_+$  for  $C = 0$  ( $= \sigma^{(0)}$ ). This behavior is observed for all the salts considered in this work. On the other hand,  $\sigma_+$  is a decreasing function of concentration since  $\sigma^{(1)}(T)$  is always negative in the considered temperature range. Besides,  $\sigma^{(1)}(T)$  is a monotonic function of temperature except for  $\text{MgCl}_2$ . Considering the permittivity variation,  $\alpha(T)$  is always positive in the studied range and not a monotonic function of temperature saving the case of  $\text{MgCl}_2$ .

As in previous studies [26, 27], it is also observed that  $\sigma_+$  drops with the salt concentration. This effect is simply interpreted by the reduced number of water molecules per cation in more concentrated solutions.

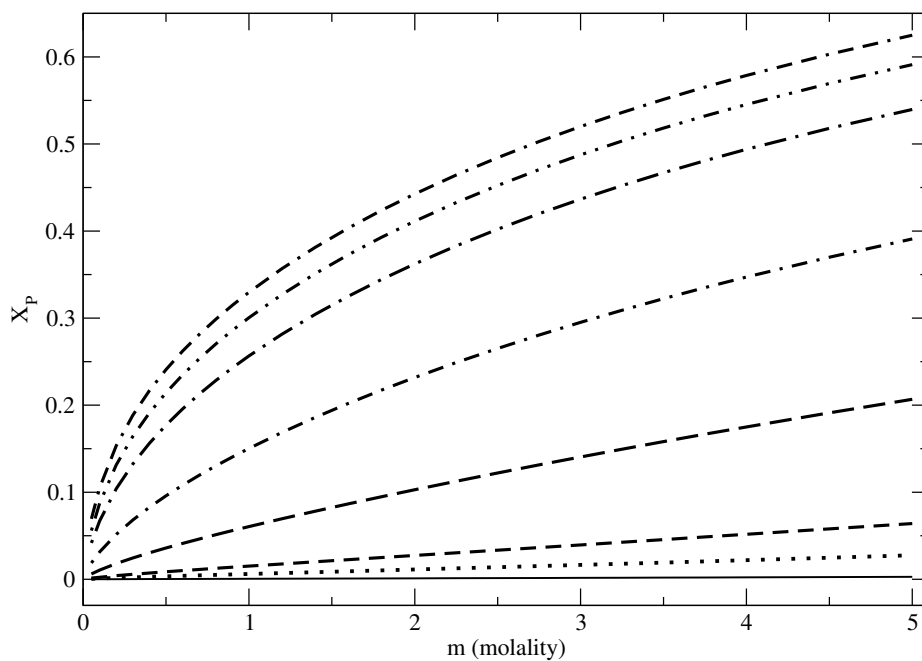
As already mentioned, the model includes the formation of cation-anion pairs. It is noted that this phenomenon is expected to occur in aqueous solutions at higher temperatures. In that case the permittivity of water decreases, which enhances also the attractive interactions between unlike ions. The amount of pairs can be analyzed using the quantity  $X_P$  (eq. 17). Plots of this quantity are presented in Figs. 7 to 10 for the salts considered in this work at different temperatures. As expected from first principles (lowering of water dielectric constant and mass action law),  $X_P$  must be an increasing function of  $T$  and  $C$ . For  $\text{MgCl}_2$  and  $\text{CaCl}_2$  salts the fraction of pairs is almost 1 at high temperatures and concentrations. It is possible that other types of complexes can form under these conditions, however, only pair formation is considered in this work.



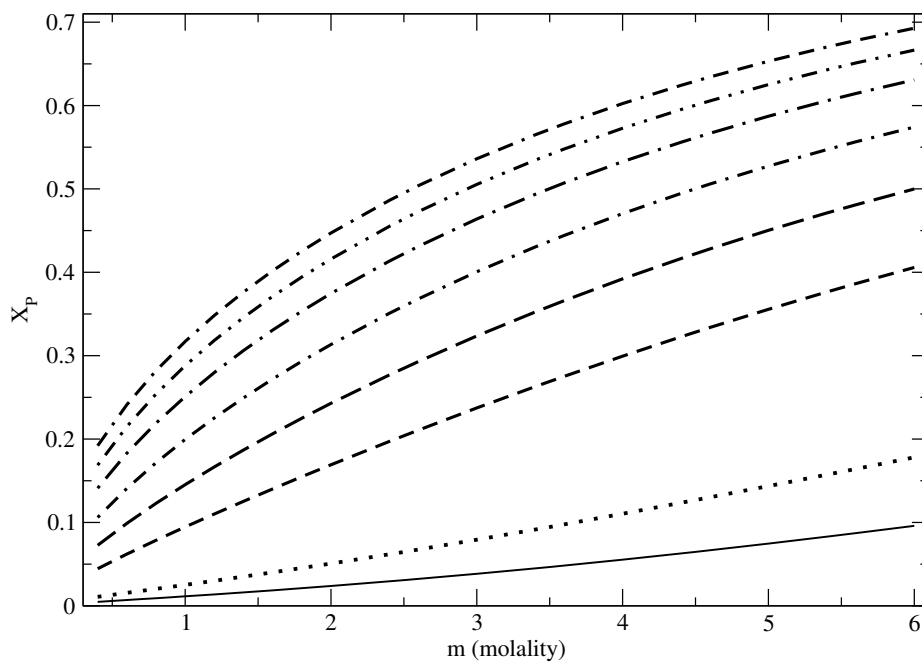
**Figure 5.** Natural logarithm of the activity coefficient for all salts analyzed in this work. a) Sodium Chloride, b) Lithium Chloride, c) Magnesium Chloride and d) Calcium Chloride. From top (lower temperature) to bottom (higher temperature). Experimental data (black stars) and theoretical results (red dashed lines).



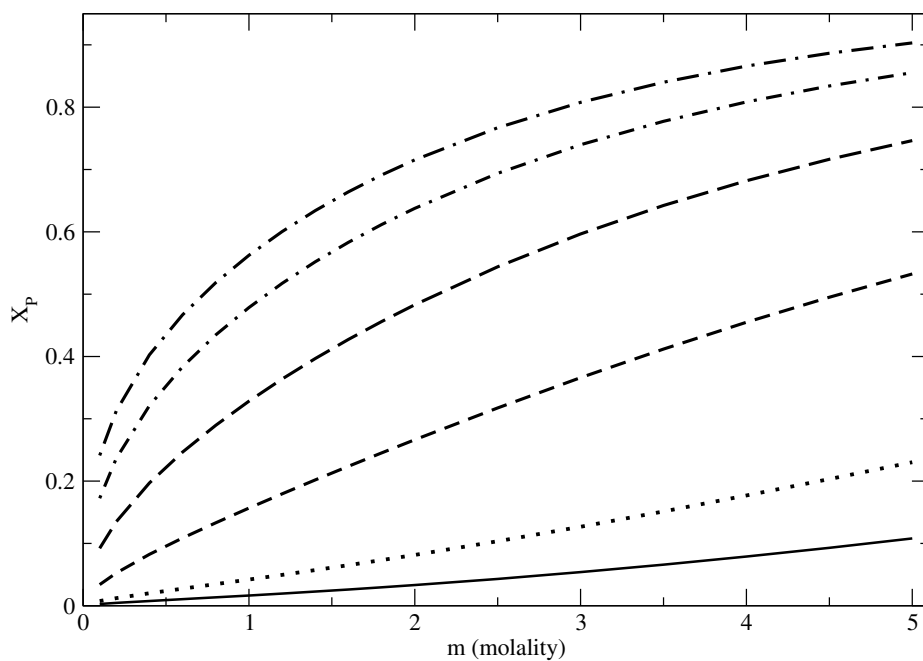
**Figure 6.** Behavior of a) cation size and b) permittivity for NaCl solutions, as a function of temperature and concentration, for all the range considered in this work.



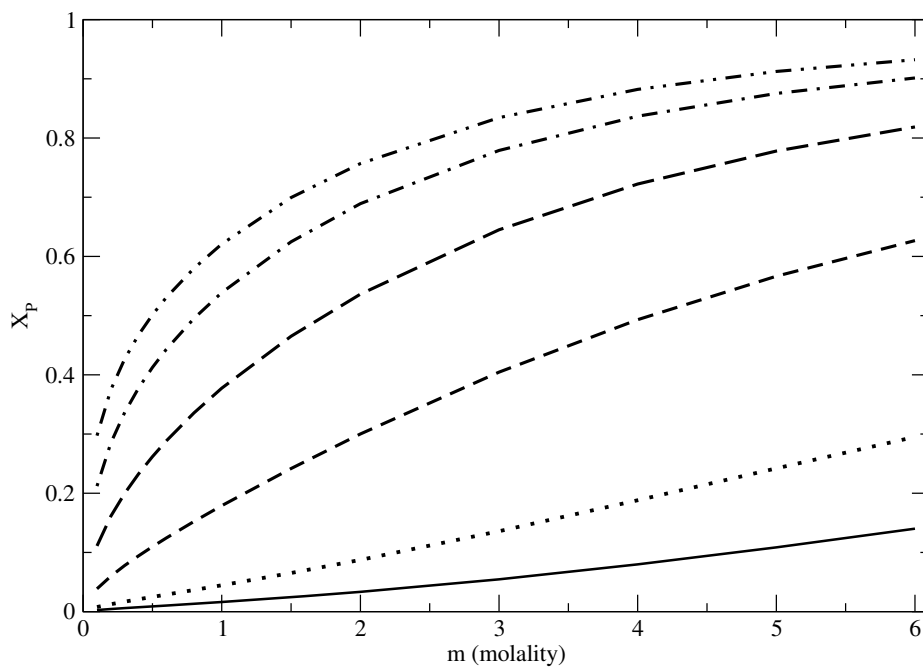
**Figure 7.** Proportion of pairs for NaCl solutions. From top to bottom: 300°C, 275°C, 250°C, 200°C, 150°C, 100°C, 75°C and 25°C.



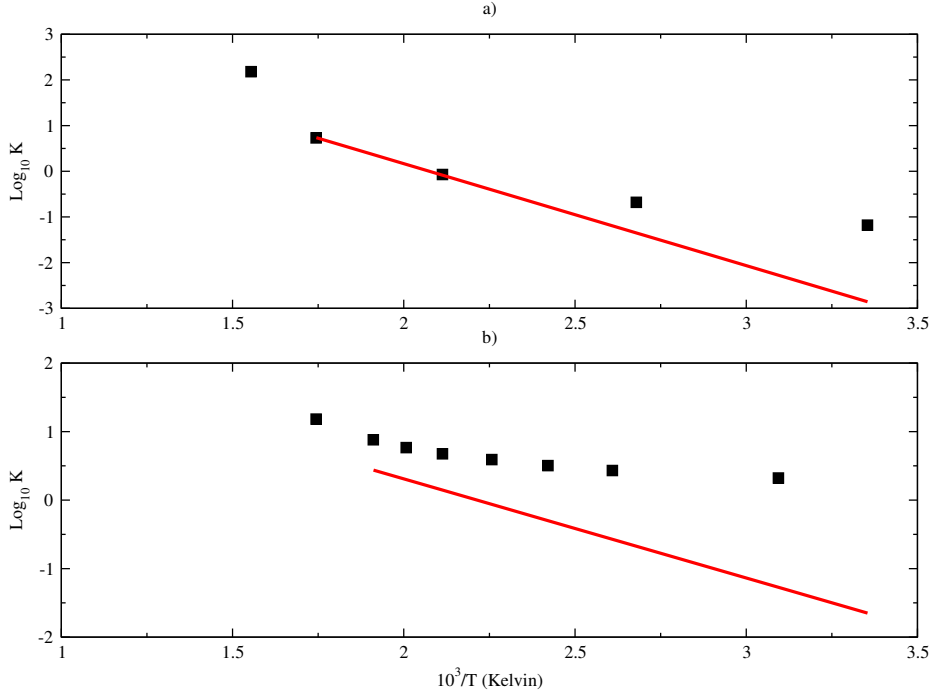
**Figure 8.** Proportion of pairs for LiCl solutions. From top to bottom: 250°C, 225°C, 200°C, 170°C, 140°C, 110°C, 50°C and 25°C.



**Figure 9.** Proportion of pairs for  $\text{MgCl}_2$  solutions. From top to bottom: 250°C, 200°C, 150°C, 100°C, 50°C and 25°C.



**Figure 10.** Proportion of pairs for  $\text{CaCl}_2$  solutions. From top to bottom: 250°C, 200°C, 150°C, 100°C, 50°C and 25°C.

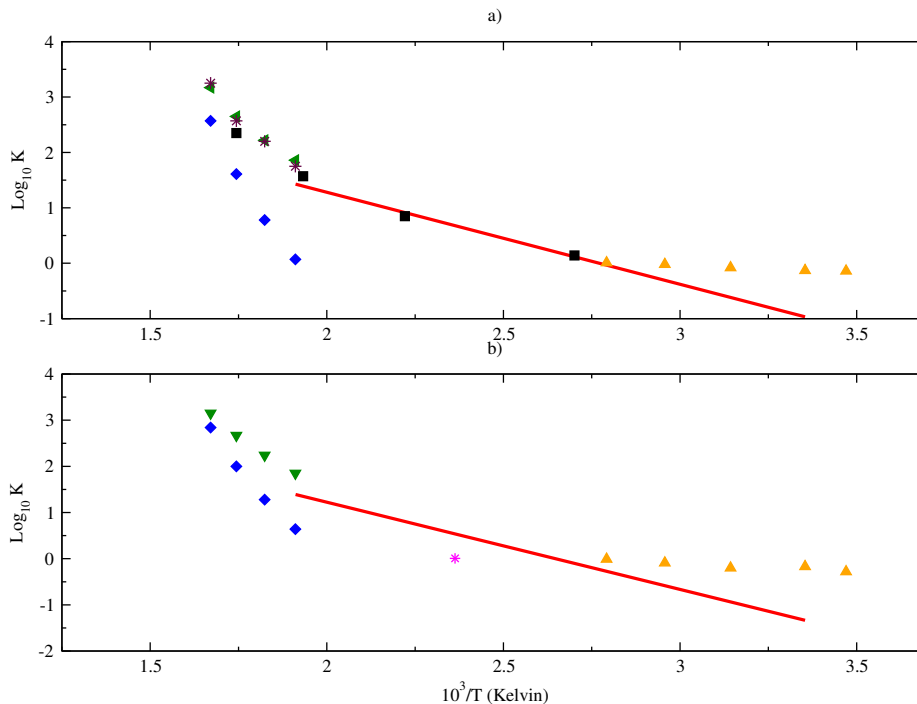


**Figure 11.** Association constants values for a) NaCl solutions; this work (red line), from Ref. 61 (black squares) and b) LiCl solutions; this work (red line), from Ref. 62 (black squares).

The values for the association constants obtained here were compared with those reported in the literature and obtained using various techniques. For  $\text{MgCl}_2$  and  $\text{CaCl}_2$ , the latter included potentiometry [55], conductivity [56], calorimetry [57], solubility [58, 59], and modeling [60]. For NaCl and LiCl, the methods were conductivity [61], and modeling [62]. These  $K$  values are plotted in Figs. 11 and 12. For the four salts at the lowest temperatures, the present model gives  $K$  values that are lower than previously reported in the literature [55, 61, 62], especially for LiCl and NaCl. In contrast, the values obtained for  $K$  at the highest temperatures considered in this work are similar to those of previous studies [55–62]. The discrepancy between theoretical and experimental results observed at low temperatures can be understood considering that the values of the association constants for NaCl and LiCl solutions were measured in experiments with dilute solutions. It has been reported that a description of conductivity experiments in concentrated solutions (that is our case) leads to association constants values that are significantly smaller than with a ‘classic’ model used for dilute solutions [30]. A potentiometric technique was used to determine  $K$  values for  $\text{MgCl}_2$  and  $\text{CaCl}_2$  [55] followed by an ideal treatment of data, without considering deviations from ideality for the various species (free ions and ion pairs). Also, the technique employed a cell with liquid junction, which is likely to have resulted in errors on the values of  $K$ .

#### 4. Conclusion

This study provides an analysis of the thermodynamic properties of high temperature electrolyte solutions in the framework of a statistical mechanical model, the binding mean spherical approximation (BiMSA), which considers the formation of ion pairs.



**Figure 12.** Association constants values for a) MgCl<sub>2</sub> solutions; this work (red line), from Ref. 60 (black squares), Ref. 55 (orange triangles up), Ref. 59 (stars), Ref. 56 (blue diamonds) and Ref. 57 (green triangles down). b) CaCl<sub>2</sub> solutions; this work (red line), from Ref. 55 (yellow triangles up), Ref. 58 (stars), Ref. 57 (green triangles down) and Ref. 56 (blue diamonds).

Good descriptions of the experimental osmotic and activity coefficients were obtained for the salts and temperature ranges considered in this work. The model involves parameters that account for the variation of the cation diameter and solution permittivity with temperature and salt concentration.

It is found that the cation size would increase with temperature. As expected from principles about ion hydration, and as observed in earlier work, it is a decreasing function of concentration. The degree of ion pairing for each salt exhibits a steeper rise for temperatures above 100°C. The regressed values for the association constants are in good agreement with the experimental ones reported in the literature. The results of this study will contribute to our understanding of the thermodynamic properties of these systems and have important implications for the development of more effective and efficient processes for the treatment of high temperature electrolyte solutions.

This work represents an alternative formalism to the Pitzer's treatment for a description of the thermodynamic properties of electrolyte solutions at high temperatures. In particular, in the present study, ion-pairing is accounted for in an explicit and consistent way. An extended version of this theoretical framework, capable of modeling the properties of charged chain molecules like oxalate, malonate and succinate, will be presented in a future communication.

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