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ABSTRACT

By considering the solution of the Mean Spherical Approximation (MSA) given by Lesser Blum, we addressed the problem of specificity in aqueous electrolyte solutions. The reference diameter of the cations is defined as the biggest possible diameter of the cation (obtained with the less associating anion). Then the specificity is taken into account by an association term similar to Bjerrum theory. The resulting activity coefficients can be used to describe pure electrolyte and electrolyte mixtures up to molar concentrations. Hydration appear to be relatively stable with small cations but it strongly depends on the anion for big cations. The validity of Zdanovskii-Stokes-Robinson mixing rule has also been tested and it appears to be valid with typically a 1% accuracy for molar concentrations.

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1. Introduction

From a long time, thermodynamic properties of electrolyte solutions are described considering the solvent as a continuum characterized only by its dielectric constant. For systems where the solvent does not appear explicitly, thermodynamic and structural quantities can be deduced from the McMillan Mayer's theory [1]. In particular thermodynamic properties such as the chemical potential of the ions or the osmotic coefficient can be calculated from the Helmholtz energy $\mathcal{F}$. Specifically, in order to describe solely the deviations from ideality, these quantities are calculated from the excess of Helmholtz energy (per volume unit) f_v^{exc}.

For weakly charged electrolytes, completely dissociated in aqueous solutions, Debye and Hückel have shown that the excess thermodynamic properties of the solution at very low concentrations can be described by considering only the electrostatic interactions at long distances between the components of the electrolyte. The ions are characterized only by their charges. Then the interaction potentials between charged species are given by

$$V_{ij}(r) = \frac{z_i z_j e^2}{4\pi\varepsilon_0 \varepsilon_r r}$$

where z_i is the valence of ion i and e is the elementary charge. The relative dielectric constant of the solvent ε_r in the denominator accounts for the screening of interactions due to the solvent molecules present between species i and j.

However for more concentrated electrolytes, interactions at shorter distances are becoming increasingly important. To prevent a possible overlap of ions, a distance of closest approach must be taken into account in the interaction between the ions at short distance. Regarding the interaction between ions of the same sign, Coulomb repulsion is sufficient to prevent the overlap of ions at low concentrations. By contrast for interactions between ions of opposite sign, a short-range repulsion is necessary to oppose the Coulomb attraction. Accordingly, the distances of closest approach introduced to improve the description of thermodynamic properties, are, especially at low concentrations, representative of the repulsive interactions between ions of opposite sign. In practice, these short range repulsions are described by considering all the ions i as hard spheres of diameter σ_i. Considering that these interactions are additive, the distance of lowest approach between an ion i of diameter σ_i and an ion j, different from i, of diameter σ_j is equal to $(\sigma_i + \sigma_j)/2$. This choice was made because it allows to obtain analytical expressions for the structure and the thermodynamics of mixture of charged hard spheres. For highly solvated monoatomic ions, the distance of less approach deduced from measured thermodynamic properties appears to be greater than the sum of the crystallographic radii. To explain this fact we consider that these ions are surrounded by an impenetrable layer of solvent. The relatively simple solution of the

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Mean Spherical Approximation given by Blum et al. [2–5] for the Primitive Model (for which ions are modeled as hard spheres) has been able to take proper account of these hard sphere effects in the ionic atmosphere even if the solution is concentrated. This solution is able to interpret activity coefficients of dissociated electrolytes [6–8] up to moderately concentrated solutions (typically up to 1 mol.L^{-1}). Even transport coefficients [9–12] can be obtained with the same approach when the MSA solution is coupled to Fuoss-Onsager approach and Brownian theory.

Nevertheless, Debye and Hückel used a linearized analytical theory to account for the electrostatic interactions. This approach must be corrected to properly account for the Coulomb interactions at short distances. The Bjerrum's approach allows a better description of these short range electrostatic interactions and thus completes the Debye Hückel (DH) theory in the treatment of these interactions. It adds the concept of ion pairs. Cations and anions can form a new species, the pair because of the magnitude of the electrostatic force. In fact for many real electrolytes, additional specific interactions must be considered to account for the observed properties. The most striking case is that of weak electrolytes, acids, or basic solutions in which chemical bonds occur between the components. For these systems, new species of long life are formed and their interactions with existing species must be considered. More generally, many ionic species seem to have a solvent averaged interaction potential comprising a short range attractive contribution of non-electrostatic origin. Thus extended version of the MSA has been proposed in order to consider this association effect. For example, Holovko et al. proposed an associated MSA scheme [13–16]. The Wertheim formalism [17] gives similar results for the treatment of association. Globally these associated models [13,18,19] are in agreement with the experiments for associated electrolytes but the ion sizes and sometimes the association constant have be fitted. Moreover, it is not possible to give a universal value of an ion size because it depends on the nature of the counterion.

Recently, molecular dynamics clarified our view of activity coefficients in electrolyte solutions. Indeed, the McMillan-Mayer theory [1] proposes a rigorous framework for these continuous solvent approaches. The average over the configurations can be done in a two stages procedure. In the first stage the force between the ions is averaged over the solvent configuration and a McMillan-Mayer potential between the ions can be calculated. Then in a second stage, the average over the ion configuration can be done. That as exactly what the MSA does from a primitive model for which the solvent averaged McMillan potential between the solute particles is the one of charged hard spheres. Molecular dynamics simulations [20–23] confirm that the potential between ions is globally Coulombic, but a short term part has to be added and it is not a hard sphere repulsion. Globally it is an oscillating potential [24] that represents the hydrophilic/phobic interactions between the solute particles. At short distances there is generally a minimum which represents the Contact Ion Pairs for which there is no solvent molecules between the two ions. Further minima can exist represented Solvent Separated Ion Pair or more complicated species. All these minima are separated by unlikely domain with activation energies. Generally, the magnitude of the oscillating short-range potential between the ions is more than $k_B T$ for the first minima so that it is rigorously impossible to consider an equivalent hard-sphere model [24] and at least the contact ion pair has to be taken into account rigorously if the structure of the solution is to be described. If only the free energy of the solution is required, then an effective diameter is possible, but there is a price to pay: non-additivity: the short-range potential strongly depends on the nature of the ions and specific attraction can occur between ions. For example it is often stated [25] that small ions are dehydrated when they interact with small ions whereas they stay hydrated when they interact with bigger ions. Hence the impossibility to derive universal hydrated diameter tables.

Considering this non-additivity, we propose in this article to use the concept of ion pairs in order to take proper account of ion specificity and non-additivity in electrolyte solutions. First we will write down an associated MSA theory in order to describe activity coefficients for electrolyte mixtures. Then we will deduce the hydrated ion diameters by considering the maximum size of the ions when no association is considered. Then, the mixing effect will be modeled by adding when necessary ion pairs in order to take into account the possible dehydration of ions at contact. The case of mixtures and the validity of mixtures rules are described in the last part.

2. Theory and calculation procedure

The electrolyte is modelled by the primitive model for which the various solute species (free cations, free anions, and ions pairs) are modelled by charged hard spheres. The thermodynamical properties of such a model are calculated by the MSA. Within that approximation, the McMillan-Mayer [1] excess free energy of the solution is decomposed into two terms as:

$$\beta f_V^{ex} = \beta f^{el} + \beta f^{HS} \tag{1}$$

where f^{el} is the electrostatic contribution and f^{HS} is the hard sphere contribution that takes into account short range repulsions. $\beta = 1/k_B T$ with k_B the Boltzmann's constant and T the temperature. Debye-Hückel's limiting-law is only applicable at low concentrations (below 10^{-2} M). The MSA is able to describe concentrated solutions because the electrostatic contribution f^{el} is not the one of DH theory, the size of the ions being taken into account in the ionic atmosphere. Moreover the hard sphere contribution f^{HS} which represents the free energy of an equivalent hard sphere mixture, *i.e.* the free energy of the system at infinite temperature (entropic effects,) is considered. The MSA recovers at low concentrations the variations given by the DH theory. Thus it can be understood as an extension of the DH theory when the size of the electrolyte is properly taken into account.

2.1. MSA calculation procedure

Here we consider the case where there is no association. Only free ions are present. The mean activity coefficient of the electrolyte solution in a binary system is calculated as:

$$\gamma_{\pm} = \left(\gamma_+^{\nu_+} \ \gamma_-^{\nu_-} \right)^{\frac{1}{\nu_+ + \nu_-}} \tag{2}$$

where ν_+ and ν_- are, respectively, the stoichiometric coefficient of the cation and the anion. The excess free energy derived from the MSA theory is then the sum of two terms. The first one is the electrostatic term and the second one is the hard sphere contribution:

$$\beta f_V^{ex} = \left(\beta \frac{F^{elec}}{V} + \beta \frac{F^{HS}}{V} \right) \tag{3}$$

The chemical potential reads

$$\mu_i = \frac{\partial F}{\partial N_i} = \frac{\partial f_V^{ex}}{\partial \rho_i} \tag{4}$$

where ρ_i the molar concentration of the i species:

$$\rho_i = \frac{N_i}{V}$$

with V the volume and N_i the number of particles i.

The mathematical expression of the excess free energy of the hard sphere [26] term is defined as:

$$\beta f_V^{HS} = \left[\left(\frac{\xi_2^3}{\xi_0 \, \xi_3^2} - 1 \right) \ln \Delta + \frac{3 \, \xi_1 \, \xi_2}{\xi_0 \, \Delta} + \frac{\xi_2^3}{\xi_3 \, \xi_0 \, \Delta^2} \right] \sum_i \rho_i \tag{5}$$

with

$$\xi_i = \frac{\pi}{6} \sum_j \rho_j \sigma_j^i \qquad i = 0, 1, 2, 3 \tag{6}$$

where σ_i is the diameter of an ion of type i,

$$\Delta = 1 - \xi_3 \tag{7}$$

The expression of the hard sphere activity coefficient can be calculated from Eqs. (3), (4) and (5) and it is given by [27]:

$$\ln \gamma_{\pm}^{HS} = \left(\frac{\xi_2^3}{\xi_0 \, \xi_3^2} - 1 \right) \ln \Delta + \frac{\xi_3}{\Delta} + \frac{\xi_2^3 \, (1 + 2\xi_3 - \xi_3^2)}{\xi_0 \, \xi_3 \Delta^2} + \frac{3\xi_1 \, \xi_2(2 - \xi_3)}{\xi_0 \Delta^2} \tag{8}$$

The hard sphere contribution to the osmotic pressure is given by:

$$\Phi^{HS} = \frac{\xi_3}{1 - \xi_3} + \frac{3\xi_1 \, \xi_2}{\xi_0(1 - \xi_3)^2} + \frac{\xi_2^3(3 - \xi_3)}{\xi_0(1 - \xi_3)^3} \tag{9}$$

The mathematical expression of the electrostatic excess free energy i [5] is:

$$\beta \frac{F^{elec}}{V} = \beta E^{elec} + \frac{\Gamma^3}{3\pi} \tag{10}$$

$$\beta E^{elec} = -L_B \left(\Gamma \sum_i \rho_i \frac{z_i^2}{1 + \Gamma\sigma_i} + \frac{\pi \Omega P_n^2}{2\Delta} \right) \tag{11}$$

$$\Gamma^2 = \pi \, L_B \sum_i \rho_i \left(\frac{z_i - \frac{\pi}{2\Delta} \, P_n \sigma_i^2}{1 + \Gamma\sigma_i} \right)^2 \tag{12}$$

$$P_n = \frac{1}{\Omega} \sum_i \frac{\rho_i \sigma_i z_i}{(1 + \Gamma\sigma_i)} \tag{13}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_i \frac{\rho_i \sigma_i^3}{(1 + \Gamma\sigma_i)} \tag{14}$$

The electrostatic activity coefficient can be obtained from Eqs. (3), (4) and (10), as the hard sphere contribution, and it is given by:

$$\ln y_{\pm}^{elec} = \frac{\beta E^{elec}}{\xi^0} - \pi L_B \frac{P_n^2}{2\xi_0 \Delta^2} \tag{15}$$

The electrostatic contribution to the osmotic pressure is given by

$$\Phi^{elec} = -\frac{\Gamma^3}{3\pi \xi_0} - \pi L_B \frac{P_n^2}{2\xi_0 \Delta^2} \tag{16}$$

with the Bjerrum length:

$$L_B = \frac{e^2}{4\pi \varepsilon_r \varepsilon_0 k_B T} \tag{17}$$

where e is the elementary charge, T the absolute temperature, k_B the Boltzmann constant, ε_0 the vacuum permittivity and ε_r the water permittivity.

The mean activity coefficient of the system can be expressed as the sum of the electrostatic and hard sphere terms as:

$$\ln y_{\pm} = \ln y_{\pm}^{elec} + \ln y_{\pm}^{HS} \tag{18}$$

These equations are valid for a dissociated electrolyte.

2.2. Paired systems and association constant

In order to fit the experimental data, we have chosen to introduce a new parameter: the ion pair which is characterized by an association constant. The associative contribution to the excess free energy is inserted in the same spirit as in a previous article [28]. This contribution was added previously to take into account the attractive interactions at short distances found into the solvent averaged potentials deduced from simulations dealing explicitly the solvent. In the same way, specific attractive interactions at short distance required to describe real electrolytes have been taken into account in this study. Accordingly a system containing two ionic species (anions and cations) is described as a system in which the cations and anions can form pairs. These pairs are described as sphere of charge equal to the sum of those of its constituents. The ionic diameter of the associated pair has been calculated as the co-volume of the hard sphere [29] (Eq. (19)). The value of the association constant has been fitted by the least-square method with the Pauling's diameter for the anions and the biggest hydrated diameter for each cations. The results have been summarized in Table 4. The MAL reads

$$K_{asso} = \frac{P_{pair}^{n-m+}}{A^{n-} C^{m+}} \tag{19}$$

where the activity of the species are present in the right-hand side of the equation. The diameter of the pair is defined by [29]

$$\sigma_{pair} = \sqrt[3]{\sigma_{A^{n-}}^3 + \sigma_{C^{m+}}^3} \tag{20}$$

When the association is due only to electrostatic interactions, the value of the association constant can be calculated using an integral such as that of Bjerrum [29] (Eq. (21)):

$$K_0 = 4\pi \int_{\sigma_{contact}}^{\sigma_{sup}} \exp\left(-\frac{z_+ z_- e^2 \beta}{4\pi \varepsilon_0 \varepsilon_r r} \right) r^2 dr \tag{21}$$

where β is $\frac{1}{k_B T}$. Originally, this association constant was obtained from an integral whose lower bound $\sigma_{contact}$ was the distance of closest approach between a given pair of ions. The upper limit σ_{sup} was the distance beyond which the ions are not associated because the attractive interactions are no longer large enough. This upper bound was set by Bjerrum to the value $L_B/2$. It must be noted that this value of the upper bound is arbitrary and that other choices have been made. An alternative expression to that of Bjerrum, was defined also by Ebeling in which an upper limit was not necessary. When the electrostatic interactions at short distance are very important, both expressions lead to numerically similar values. This is because those integrals are much more sensitive to the choice made for the lower limit, than to the choice made for the upper limit of integration. In view of the similarity of the numerical values obtained using these alternative choices when the electrostatic interactions at short distance are very important, we have not tried other types of expressions in this study. In this study we have considered arbitrarily that the upper limit of integration, for a given pair anion-cation was given by: $\sigma_{sup} = (\sigma_+ + \sigma_-)/2$, were σ_- is the crystallographic

diameter and σ_+ the diameter of the cation fitted previously. Now considering that the association constant K_0, calculated using this expression, is equal to the fitted one K_{asso}, we have deduced the lower limit of integration $\sigma_{contact}$.

Then the Bjerrum size has been calculated from the anionic diameter and cationic diameter and the association constant, summarized in Tables 1, 3 and 4. The Bjerrum size's results have been summarized in Table 5.

In order to determine the mean activity coefficient for the three components model 3CM (free ions + pair), we match this 3CM into an equivalent two components model 2CM (cations and anions without distinguishing if they are free or associated). We start from the Gibbs energy of 2CM which is defined as:

$$dG = \mu_+ dn_+ + \mu_- dn_- = \mu dn \tag{22}$$

where the chemical potential of the salt is $\mu = \mu_+ \nu_+ + \mu_- \nu_-$. The Gibbs energy of the 3CM reads

$$dG = \mu_+^f dn_+^f + \mu_-^f dd_-^f + \mu_p dn_p \tag{23}$$

The two models (3CM and 2CM) match at chemical equilibrium where

$$\mu_p = \mu_+^f \nu_+ + \mu_-^f \nu_- \tag{24}$$

where the subscript f means free and the subscript p means associated. By identifying the differentials of two Gibbs energy, we obtain

$$\mu = \mu_+^f \nu_+ + \mu_-^f \nu_- \tag{25}$$

The means activity coefficient for three components is therefore described by:

$$\gamma_\pm^f = \left(\gamma_+^{f\ \nu_+} \gamma_-^{f\ \nu_-} \right)^{\frac{1}{\nu_+ + \nu_-}} \tag{26}$$

Thus, the global formula is the same as the one for dissociated electrolyes, but the activity coefficients are the one of free ions.

2.3. McMillan-Mayer to Lewis-Randall conversion

The calculated activity coefficient of the electrolyte has been converted from the McMillan-Mayer reference to the Lewis-Randall reference thanks to Eq. (27).

$$\ln \gamma_\pm^{LR} = \ln \gamma_\pm^{MM} - \phi^{MM} \bar{v}_\pm \sum_j \rho_j \tag{27}$$

where $\ln \gamma_\pm^{MM} = \ln y_\pm$; ϕ^{MM} is the osmotic coefficient in the McMillan-Mayer reference, $\bar{v}_\pm$ is the mean partial molar volume, and ρ_j the concentration of the j in particles·m^{-3}.

$$\phi^{MM} = 1 + \frac{\sum_i \rho_i \ln \gamma_i^{MM} - f_V^{ex}}{\sum_i \rho_i} \tag{28}$$

Table 1
The different anion's diameters which are equal to the Pauling's diameter expressed in Å.

anions	CH$_3$COO$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	NO$_3^-$	ClO$_4^-$	SCN$^-$
$\sigma_{-Pauling}$	3.18	2.72	3.62	3.9	4.32	3.78	4.72	4.26

These equations have been successfully used in the calculation of mean activity coefficient of pure electrolyte solution [7,12,30,31].

The experimental data have been taken from references [32–34]. Nevertheless, the activity coefficients are commonly measured in the molality scale (mol·kg^{-1} of solvent) whereas the MSA formulae is typically in the molarity scale (particles·m^{-3} of solvent). Therefore, a conversion is needed. We conversed the experimental activity coefficient from the molality scale to the molarity scale (Eq. (29)). This latter equation is valid because at infinite dilution 1 mol·L^{-1} is equal to 1 mol·kg^{-1}.

$$\gamma_\pm^C = \frac{m_\pm \gamma_\pm^m}{C_\pm} \tag{29}$$

where the superscript C and m correspond, respectively, to molarity and molality scale. Conversion has been performed in the following way:

$$\ln \gamma^{LR}(m) = \ln \gamma^{LR}(c) + \ln \frac{c}{d_w m} \tag{30}$$

d_w is the density of water, the density of pure water has been taken approximately equal to 1 kg· L^{-1} at 25°C. The ratio $\frac{c}{m}$ is the density of the solution and it is defined by:

$$\frac{c}{m} \approx \frac{1}{\sum_i m_i \bar{\nu}_i + d_w^{-1}} = \frac{d_w}{1 + d_w \sum_i m_i \bar{\nu}_i} \tag{31}$$

In this formula, the partial molar volume of the ion is assumed to be constant and the tabulated values of Marcus reference tables [35] have been chosen.

3. Results and discussion

3.1. Derivation of ionic diameters without association constant

It has long been recognized that the MSA theory is powerful and able to evaluate the activity coefficients of simple aqueous electrolyte solutions [7,31]. Then, as a first step, we used the MSA theory with no association to evaluate the average activity coefficient of binary electrolyte solutions. This theory requires only the ionic diameter of each ions composing this electrolyte. Different procedures can be used to determine the ionic diameter. We have chosen, classically, to set that the anionic diameter equals the Pauling's diameter [35] (Table 1) whereas the cationic diameter has been fitted thanks to the least-square method. The results have been

Table 2
Cationic's diameters without association constant expressed in Å. The red value represents the highest cationic diameter. This diameter has been chosen as reference diameter.

	CH$_3$COO$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	NO$_3^-$	ClO$_4^-$	SCN$^-$
H$^+$			4.61	4.81	5.04	4.00	3.95	
Li$^+$	4.35		4.36	4.38	4.81	4.12	4.37	
Na$^+$	4.89	2.89	3.27	3.49	3.61	1.81	2.13	
K$^+$	5.17	3.89	2.80	2.77	2.84	2.05	0.93	
Rb$^+$	5.42	4.49	2.55	2.27	1.92	0.15	−0.78	
Cs$^+$	5.42	4.82	1.99	1.7	1.33	0.096	−1.08	
NH$_4^+$			2.92	2.11	2.41	1.27	0.14	2.28
Mg^{2+}	3.87		5.74	6.12	6.3	5.57	6.04	
Ca^{2+}			5.39	5.67	5.88	4.1	5.53	
Sr^{2+}			5.18	5.37	5.68	3.43	5.08	
Ba^{2+}	4.85		4.76	5.05	5.59	2.29	4.53	

Table 3
Pauling's and hydrated's diameter for the cations expressed in Å.

Cation	H$^+$	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	NH$_4^+$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\sigma_{+Pauling}$		1.2	1.9	2.66	2.96	3.38	2.96	1.3	1.98	2.26	2.7
$\sigma_{+Hydrated}$	5.04	4.81	4.89	5.17	5.42	5.42	2.92	6.3	5.88	5.68	5.59

summarized in Table 2 where the red values represent the biggest diameter for each cationic series.

Table 1 summarized the different anion's diameters used in this paper. Each anionic diameter corresponds to the Pauling's diameter extracted from reference [35]. We have chosen to order the different anions following the Hofmeister series. Nitrate is to be placed between the bromide and the iodide in order to respect the Hofmeister series.

Table 2 summarized the different cationic diameters fitted without association constant expressed in Å. The root mean square deviation for each cation without association has been reported in the supporting information. The red value corresponds to the biggest cationic diameter used and later it will be used in order to calculate the mean activity coefficient with the association constant.

For the acetate and the fluoride, the diameter increases along the alkaline and alkaline earth series. This means that the cation is bigger along the alkaline and alkaline earth series. This effect actually corresponds to the one of bare ions given by then Pauling diameters. For the halide series, from chloride to iodide, the diameter decreases along the alkaline and alkaline earth series. This is a reverse effect compared to the bare diameters: The smaller the ion in a crystal (Pauling diameter), the bigger it is in water because of hydration. Indeed, small ions like lithium are heavily linked to the solvent and big anions (as halides) cannot replace water molecules [29]. For nitrate and perchlorate, the cation diameter similarly decreases along the alkaline earth series (excepted for the hydrogen).

Rubidium and caesium have a negative diameter with respect to perchlorate, which is physically impossible. It is possible that a strong association occurs and that rubidium and caesium are strongly associated to the perchlorate tetrahedron. This effect strengthens our choice to introduce the association constant in order to reduce artificially the diameter. For the nitrate, the diameter decreases along the alkaline series excepted for the hydrogen, like the perchlorate, and the potassium. The rubidium and the caesium present a diameter close to 0 which is physically impossible for nitrate. It is possible, like for the perchlorate, that the nitrate approaches the rubidium and the caesium by its thickness. Indeed the nitrate is a flat anion therefore its diameter is not properly defined.

Lithium diameter changes little along the anion series. It means that the lithium does not in fact dehydrate in the presence of the different anions. The first shell of four water molecules around it is very rigid and hydration appears to be stable. On the other hand,

rubidium and caesium present a wide range of diameters. It means that this two alkaline cations strongly modify their hydration as a function of the anion. They are indeed the biggest alkali: the water molecules around them are not firmly sticked in the first sphere so that hydration strongly depends on the cation environment. Acetate and iodide anions are mainly dissociated with the different cations. The ammonium seems to be different from the other cations but it is a molecular ion contrary to the alkaline and alkaline earth ions and it misses data with acetate or fluoride anions.

Considering this study, the recommended hydrated diameters are given in Table 3. It should be noted that they are not universal. They represent the highest possible cation diameter, which is the one when it interacts with the less associating anions. It is always equal or bigger than Pauling diameter. Typically it represents one water molecule whose diameter is around 3 Å, but there are exceptions since NH$_4$ is not hydrated and magnesium cation has the biggest solvation shell (5 Å).

3.2. Procedure for the derivation of consistent ionic diameters and association constants

If there is no specific effects, in different binary electrolytes having a common ion, the latter must have the same size so that the distance of closest approach between cations and anions is given by half the sum of their diameters ($\sigma_{+-} = (\sigma_+ + \sigma_-)/2$). We note that the use of a larger diameter for a given ion, in order to evaluate the average activity coefficient leads to an upward deviation of the theoretical curve. On the contrary, the fact of taking into account an additional short range attractive interaction leads to a downward deviation of the calculated curve. Accordingly, in a series of binary electrolyte solutions having a common cation, the solution in which the cation is the largest can be regarded as the one where short attractions are the smallest. That is the reason why we assumed that in this solution attraction can be considered to be zero: the biggest cationic diameter has to be chosen. Therefore, this latter has been chosen as the reference for each cation (Table 3).

If this reference cation diameter is chosen, specific effects are represented by a decrease of the diameter when further anions are considered. A possible method would be the treatment of non-additive hard spheres. Unfortunately, the solution of the primitive model with non-additive hard spheres does not exist. So the specificity has been taken into account by an attraction at short distance

Table 4
Association constant (K_{asso}).

	CH$_3$COO$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	NO$_3^-$	ClO$_4^-$	SCN$^-$
H$^+$			0.24	0.12	0	0.58	0.6	
Li$^+$	0.24		0.24	0.225	0	0.36	0.22	
Na$^+$	0	1.11	0.86	0.76	0.696	1.76	1.58	
K$^+$	0	0.77	1.40	1.42	1.37	3.48	2.67	
Rb$^+$	0	0.59	1.82	2.00	2.22	4.06	3.39	
Cs$^+$	0	0.37	2.19	2.4	2.7	4.12	3.7	
NH$_4^+$			0	0.36	0.22	0.79	1.64	0.28
Mg^{2+}	3.43		0.87	0.25	0	1.12	0.32	
Ca^{2+}			0.78	0.32	0	3.19	0.46	
Sr^{2+}			0.83	0.48	0	4.42	0.85	
Ba^{2+}	1.35		1.43	0.87	0	6.58	1.61	

Table 5
Cation diameters fitted from the association constant thanks to the Bjerrum formula (Eq. (21)).

	CH$_3$COO$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	NO$_3^-$	ClO$_4^-$	SCN$^-$
H$^+$			4.38	4.72	5.04	3.44	3.44	
Li$^+$	4.14		4.15	4.20	4.81	3.82	4.23	
Na$^+$	4.89	1.95	2.51	2.79	2.98	0.34	0.60	
K$^+$	5.17	3.04	1.38	1.31	1.43	−1.37	−1.33	
Rb$^+$	5.42	3.78	0.65	0.22	−0.30	−1.27	−1.97	
Cs$^+$	5.42	4.39	−0.01	−0.44	−1.04	−1.58	−2.18	
NH$_4^+$			2.92	1.93	1.94	0.88	−1.05	2.14
Mg^{2+}	4.56		5.79	6.15	6.3	5.64	6.09	
Ca^{2+}			5.44	5.69	5.88	4.21	5.59	
Sr^{2+}			5.23	5.40	5.68	3.53	5.16	
Ba^{2+}	4.93		4.83	5.10	5.59	2.72	4.63	

represented by the formation of pairs. The new hypothetical activity coefficient curve with the biggest diameter parameter doesn't pass through the experimental data, except for the salt with this biggest cation because the specific effects are neglected and they will be treated now by a chemical model.

Table 3 summarized the cationic Pauling's size and the biggest cation hydrated's size. The alkaline series presents a difference, between the hydrated and Pauling's diameter, close to 2–3 Å which corresponds to the size of one water molecule. The alkaline earth series presents a difference, between hydrated and Pauling's diameter, between 3 and 5 Å which corresponds to the size of 1.5 water molecules which implies that the half particles are hydrated by 1 water molecule and the second half are hydrated by 2 water molecules. The ammonium diameter is equal to the Pauling's diameter in solution, as already noticed. It means that the ammonium is non-hydrated in solution. The hydrated alkaline diameters increase along the series like the Pauling's diameters whereas the hydrated alkaline earth diameters decrease along the series unlike the Pauling's diameters. Similar hydrogen diameter has been obtained by Simonin et al. [36] by another procedure.

Table 4 represents the different association constants for the whole electrolyte studied in this paper. The root mean square deviation for each cation with association has been reported in the supporting information. For the chloride and bromide, the association constant increases along the alkaline and alkaline earth series. Whereas the association constant decreases along the alkaline series for the fluoride. The association constant for the nitrate and perchlorate increases along the alkaline and alkaline earth series except for the hydrogen. The iodide is not associated for the whole alkaline earth and for the hydrogen and the lithium while the acetate is not associated with the rest of the alkaline series. The smaller the Pauling's diameter, the more associated the alkali acetate is. The ammonium presents a specific association which is not classified like the other cations.

For the beginning of the alkaline series, from the hydrogen to the sodium, and the alkaline earth series, the association constant decreases along the halide series. For the rubidium and the caesium, the association constant increases along the halide series. The potassium presents a middle behaviour. The association constant for the nitrate is higher than the perchlorate for the whole cations except the hydrogen and the ammonium. The small cations, in point of view of the Pauling's diameter (the hydrogen and the lithium), have an association constant fairly constant with the whole anions. It is quite difficult to dehydrate this cations which implies that the hydrogen and the lithium present one shape: hydrated. The big cations, in point of view of the Pauling's diameter (the potassium, the rubidium and the caesium), have an association constant which varies a lot. It means these cations can be dehydrated easily as a function of the counter ions present in the solution which implies these cations don't present a specific shape. The sodium presents a middle behaviour which implies that the sodium presents, mainly, two shapes: one hydrated and one non-hydrated. This specific behaviour of sodium has been obtained from molecular dynamics by Molina et al. [29].

In his paper, Collins [37] has resumed an appendix written by Morris [38] in which he presented the standard heat of solution of a crystalline alkali halide as a function of the difference between the absolute heats of hydration of the corresponding gaseous anion and cation. In general, the potassium, the rubidium and the caesium chloride, bromide and iodide present a positive value of the Gibbs energy which corresponds to an association constant value upper than 1. Whereas the lithium and sodium halide and the potassium, rubidium and caesium fluoride present a negative value of Gibbs energy which correspond to an association constant value lower than 1. These blocks agree with the blocks of kosmotropes and chaotropes described in the paper written by Collins [37] and resumed by Kunz [39].

3.3. An attempt to interpret fitted constants with the theoretical expression of the type of Bjerrum (purely electrostatic):

To assess if the previously fitted association constants are only due to the effect of electrostatic interactions at short distances, we now present the result of the evaluation of these constants with the theoretical expression of the type introduced by Bjerrum. We recall that by considering that the calculated association constant is equal to the adjusted one, we deduced the lower limit of integration $\sigma_{contact}$. Given the fact that only the electrostatic interactions were taken into account for this calculation, the value of $\sigma_{contact}$ deduced is not necessarily relevant physically. If this quantity is between the distance of lowest approach deduced from the crystallographic radii of both ions on the one hand and the adjusted distance σ_{pm}, then the specific interactions between these ions are not necessary to account for the adjusted constants.

Table 5 summarized the different cationic diameters calculated thanks to the Bjerrum formula (Eq. (21)). When the electrolyte is dissociated, the Bjerrum cationic is equal to the MSA cationic (the red value in Table 2). For the alkali acetate and fluoride the cationic diameter increases along the series like the cationic diameter calculated by the MSA formula. For the alkali and alkali earth chloride, bromide and iodide, the cationic diameter decreases along the series like the cationic diameter calculated by the MSA formula. For the alkali and alkali earth nitrate and perchlorate, the cationic diameter decreases along the series except for the hydrogen and the lithium.

For the hydrogen, the lithium and the alkali earth, the cationic diameter changes little with the different anions and is always higher than the Pauling's diameter. For sodium, potassium, rubidium and caesium, the cationic diameter changes widely. The more the atomic number increases, the more the negative cationic diameters are calculated. These values are physically meaningless. The ammonium diameter is always smaller than the Pauling's diameter except for the chloride. Every time the negative diameter corresponds to the diameter smaller than the Pauling's diameter calculated with the MSA formula.

Table 6 summarized the ration of the cation diameter calculated from the association constant thanks to the Bjerrum formula (Eq. (21)) divided by the MSA diameter where no association is included (non-hydrated diameter). The idea is that if it is close to one it is mainly an electrostatic effect whereas if it is very different, specific effects are from another nature. For the hydrogen, lithium and alkali earth electrolyte, the association is mainly an electrostatic association. Indeed, the cationic diameter calculated by the Bjerrum formula (Eq. (21)) is very close to the cationic diameter calculated by the MSA formulas. The association for the sodium, potassium, rubidium and caesium is due to more than the electrostatic interaction except for the acetate electrolyte. For the

Table 6
Ratio of the cation diameter calculated from the association constant thanks to the Bjerrum formula (Eq. (21)) divided by the MSA diameter where no association is included (non-hydrated diameter).

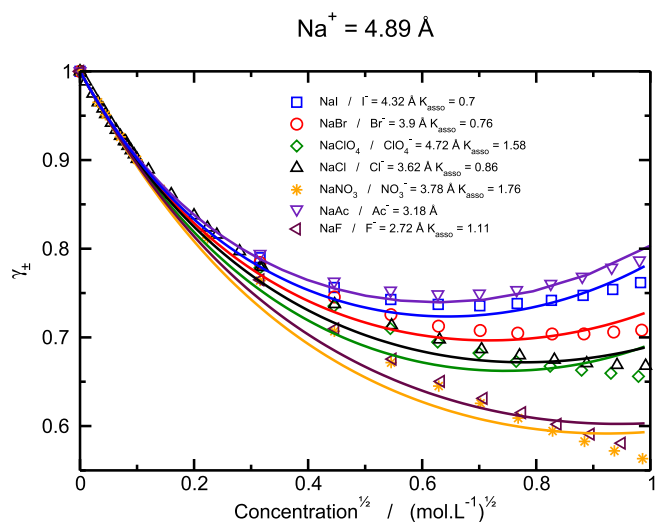|	CH_3COO^-	F^-	Cl^-	Br^-	I^-	NO_3^-	ClO_4^-	SCN^-
H^+			0.95	0.98	1.00	0.86	0.87	
Li^+	0.95		0.95	0.96	1.00	0.93	0.97	
Na^+	1.00	0.67	0.77	0.80	0.83	0.19	0.28	
K^+	1.00	0.78	0.49	0.47	0.5	−0.69	−1.43	
Rb^+	1.00	0.84	0.25	0.10	−0.16	−8.47	2.53	
Cs^+	1.00	0.91	−0.005	−0.26	−0.78	−16.46	2.02	
NH_4^+			1.00	0.91	0.80	0.69	−7.5	0.94
Mg^{2+}	1.18		1.01	1.00	1.00	1.01	1.01	
Ca^{2+}			1.01	1.00	1.00	1.03	1.01	
Sr^{2+}			1.01	1.01	1.00	1.03	1.02	
Ba^{2+}	1.02		1.01	1.01	1.00	1.19	1.02	

Fig. 1. The mean activity coefficient of sodium salt as a function of square root of the total salt molar concentration.

fluoride, the more the atomic number increases, the more association is mainly electrostatic. The different negative ratios for the potassium, rubidium and caesium correspond to the cationic diameter smaller than the Pauling's diameter. For the rubidium and caesium perchlorate the ratio is positive but both cationic diameter, MSA and Bjerrum, are negative. The association for the nitrate and the perchlorate, more than the other anions, seems to be different than a solely electrostatic interaction. Probably it is due to the fact that this two anions are poly atomic anions.

Generally, the ratio of both cationic diameter is close to 1 which implies to introduce that the association constant is equal to

reduce the ionic diameter. In order to calculate the mixture activity coefficient, it is in our interest to choose and take the higher cationic diameter for each cation.

Fig. 1 represents the mean activity coefficient, for the different anions, as a function of the square root of the total salt molar concentration. The experimental values have been taken from references [32,34]. The blue square is the sodium iodide, the red circle is the sodium bromide, the green diamond is the sodium perchlorate, the black triangle up is the sodium chloride, the orange star is sodium nitrate, the violet down triangle is sodium acetate and the brown left triangle is sodium fluoride. As described previously, for each sodium salt, the cationic diameter has been fitted in order to reproduce the experimental data by fixing the anionic diameter equal to the Pauling's size (cf. Table 1). Table 2 summarized the different cationic diameter for each alkali and alkali earth salt. Then, the biggest diameter has been chosen as the reference. Finally the association constant has been fitted in order to reproduce at the best the experimental data. The association constants have been summarized in Table 4. The better fit is for the non-associating pair. The association returns a sense more natural but the fit is less accurate.

From $0\,mol \cdot L^{-1}$ to $10^{-2}\,mol \cdot L^{-1}$, the whole curves are superimposed. It is due to the limiting law described by Debye and Hükel [40]. The chloride and perchloride sodium present an activity coefficient very close like the fluoride and nitrate. The difference of the mean association constant is due to the difference of the diameter of each anions. The sodium chloride, bromide and iodide are likewise associated. The more association is important, the more the difference between the experimental data and the AMSA calculated curve is important.

The same graphic has been plotted for the whole alkali and alkali earth salts (cf. supplementary information) and the results have been summarized in the Table 3.

In order to understand the influence of the anions on the association, the mean activity coefficient of the bromide and acetate
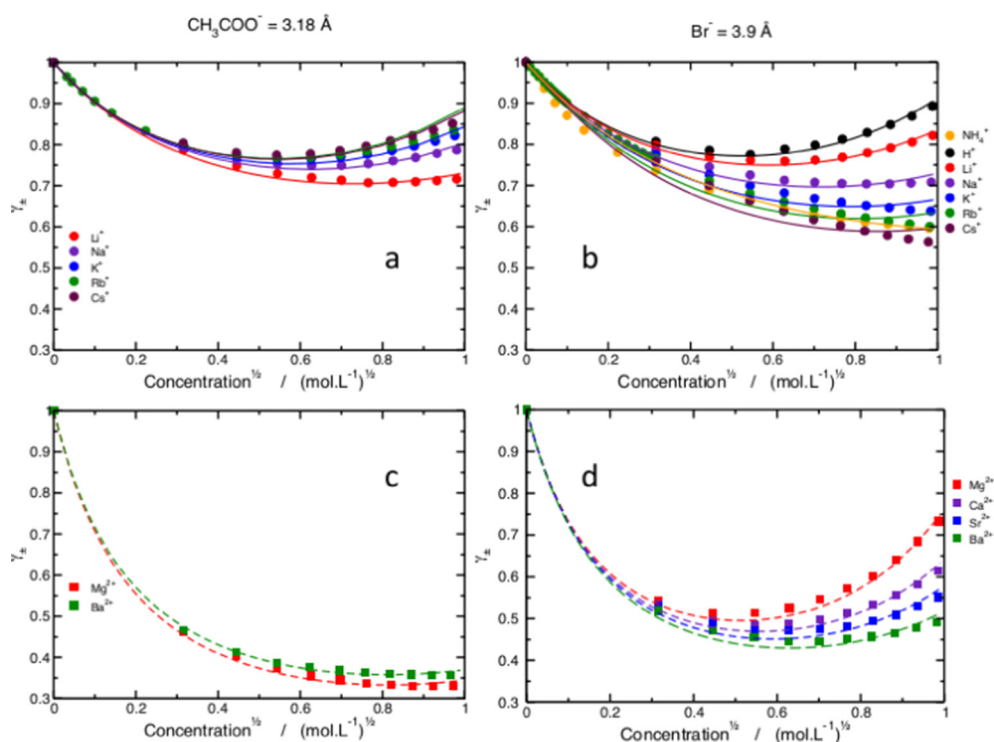

Fig. 2. The mean activity coefficient of alkali acetate (a), bromide (b), alkali earth acetate (c) and bromide (d) as a function of the square root of the total molar concentration.
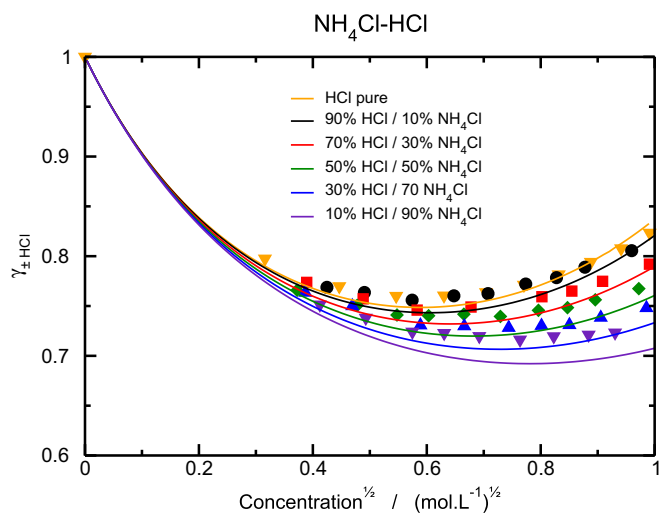
Fig. 3. The mean activity coefficient of the hydrochloric acid in the mixture of HCl-NH$_4$Cl as a function of the square root of the total chloride molar concentration.

salts for the whole cations (alkali and alkali earth) have been plotted, Fig. 2 a) and c) for the acetate and b) and d) for the bromide.

Thus, Fig. 2 represents the mean activity coefficient of the different acetate and bromide salts as a function of the square root of the total molar salt concentration. The experimental data have been extracted from the references [32–34]. The alkali acetate and bromide salts have been plotted, respectively, in the quarter a) and b). The alkali have been represented by different colored circles: the orange ammonium (for the bromide), the black hydrogen, the red lithium, the violet sodium, the blue potassium, the green rubidium and the maroon caesium. The alkali earth acetate and bromide salts have been plotted, respectively, in the quarter c) and d). The alkali earth have been represented by different colored squares: the red magnesium, the violet calcium, the blue strontium and the green barium.

Two blocks can be highlighted: the first is the alkali blocks and the second is the alkali earth. In function of the anion, the block is more or less extended. The whole mean activity coefficient of the different alkali acetate is concentrated around 0.8 ± 0.1 whereas the alkali bromide is extended from around 0.55 to 0.9. For the bromide the order of the mean activity coefficient corresponds to the atomic number whereas for the acetate salts is the reverse. As the alkali acetate and bromide salts, the alkali earth acetate is concentrated around 0.35 whereas the alkali earth bromide is extended

from 0.5 to 0.75. As the alkali bromide, the order of the activity coefficient of the different alkali earth corresponds to the atomic number whereas for the alkali earth acetate is the reverse, like the alkali acetate. The calcium and strontium acetate activity coefficient should be present between the magnesium and barium acetate activity coefficient. The alkali earth bromide block and alkali bromide block are interpenetrated whereas the alkali earth acetate block and alkali acetate block are perfectly separated. Up to 10^{-2} mol·L^{-1} the whole alkali salts present the same linear coefficient representative of the salt 1:1 (1 cation for 1 anion) which corresponds to the limiting law. The whole alkali earth salts present, as the alkaline salts, their specific linear coefficient representative of the salts 1:2.

The alkali acetate salts are not associated except for the lithium acetate and hydrogen acetate (acetic acid), indeed it is a weak acid therefore it is associated. The difference between the different alkali acetate salts non-associated is only due to their diameter. The ammonium cation is different because it is a poly-atomic cation which explains why the curve is little different than the other monovalent cation.

3.4. Mixture

Fig. 3 represents the mean activity coefficient of the hydrochloric acid in the mixture HCl-NH$_4$Cl as a function of the square root of the total chloride molar concentration. The experimental data have been extracted from [41]. The orange triangles left represent the experimental data of a pure hydrochloric acid. The black circles represent the mix of 90% of hydrochloric acid and 10% of ammonium chloride. The red squares represent the mix of 70% of hydrochloric acid and 30% of ammonium chloride. The green diamonds represent the mix of 50% of hydrochloric acid and 50% of ammonium chloride. The blue triangles up represent the mix of 30% of hydrochloric acid and 70% of ammonium chloride. The violet triangles down represent the mix of 10% of hydrochloric acid and 90% of ammonium chloride. The cyan triangles right represent the experimental data of a pure hydrochloric acid. The cationic diameters and the association constants of the different salts have been summarized in Tables 3 and 4 respectively.

This mixture salt has been chosen because the ammonium chloride, in this paper, is not associated whereas the hydrochloric acid is little associated. The whole calculated curves respect the order of the percentage rate of hydrochloric acid and ammonium chloride. The curve for the pure component presents the best fit compared to the other different mixture's curves. The mean hydrochloric acid activity coefficient of the different mixture's curves appears to be underestimated. This difference can come from a problem of offset in the experimental data because the measure for the rate of 90% of HCl and 10% of NH$_4$Cl is equal to the pure hydrochloric acid, which
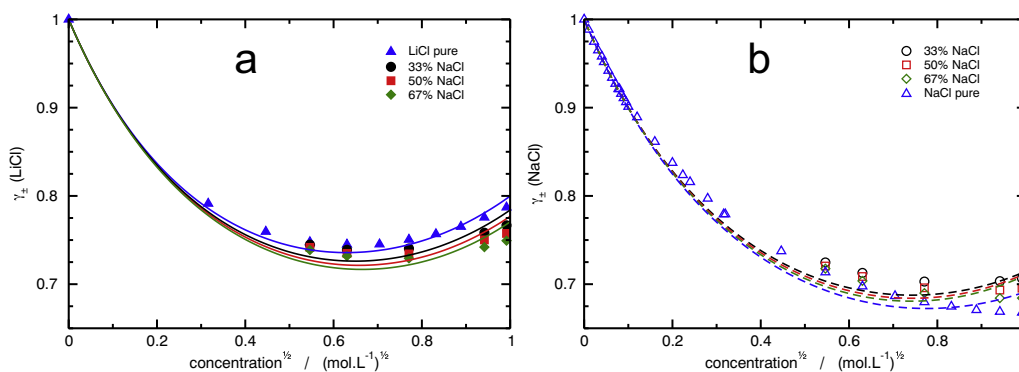

Fig. 4. The mean activity coefficient for the lithium chloride (a) and the sodium chloride (b) in the mixture NaCl-LiCl as a function of the square root of the total molar chloride concentration. The filled symbol represent the lithium chloride mean activity, plot a, and the empty symbols represent the sodium chloride mean activity, plot b.
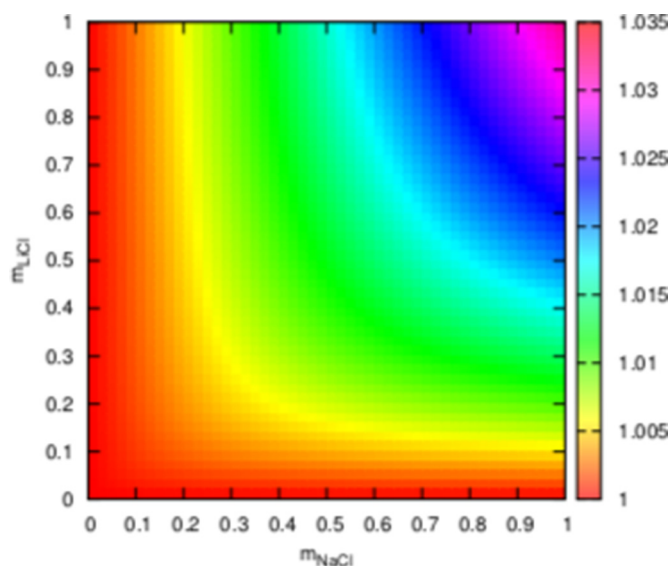
Fig. 5. The molality lithium chloride concentration as a function of the molality sodium chloride concentration. Each points correspond to the value of the ZSR relation in the mixture of NaCl-LiCl.

is practically impossible. The more hydrochloric acid-ammonium chloride mixture is composed by the hydrochloric acid, the better the fit is. The difference between the experimental data and the calculated curve is quite small. The limiting law is respected from 0 to 10^{-2} mol·L^{-1}.

Fig. 4 represents the mean activity coefficient for the lithium chloride (a) and the sodium chloride (b) in the mixture of NaCl-LiCl as a function of the square root of the total molar chloride concentration. The experimental data have been extracted from [42]. The filled symbols represent the lithium chloride mean activity coefficient, Fig. 4-(a), and the empty symbols represent the sodium chloride mean activity coefficient, Fig. 4-(b). The blue triangles up represent the solution containing only the lithium chloride or only sodium chloride. The green diamonds are the mixture of 67% of sodium chloride and 33% lithium chloride. The red squares are the mixture of 50% of sodium chloride and 50% lithium chloride. The black circles are the mixture of 33% of sodium chloride and 37% lithium chloride. The filled blue triangles represent the pure lithium chloride whereas the empty blue triangle represents the pure sodium chloride. The blue, black, red and green curves represent the mean activity coefficient of the lithium chloride. The dashed blue, black, red and green curves represent the mean activity coefficient of the sodium chloride.

This mixture of lithium chloride and sodium chloride has been chosen because it presents two associations (Table 4) with one counter ions which simplify the calculation. The cationic and anionic diameters have been summarized in Tables 3 and 1 respectively.

The order of the different calculated curves for the two plots respects the order of the experimental data. The limiting law is always respected, both for the lithium and sodium chloride, then the curves slightly underestimate the mean activity coefficient before slightly overestimating it at the end of the plot. Whatever the sodium chloride rate, the mean activity coefficient calculated for the lithium chloride is better than the sodium chloride mean activity coefficient.

Therefore the AMSA model and the fitting procedure presented here allows the calculation and the prediction of mean activity coefficient for a ternary system, a mixture of two salts in aqueous phase.

3.5. Zdanovskii-Stokes-Robinson (ZSR)

The ZSR relation is an empirical relation for a mixture at water activity constant, discovered independently by Zdanovskii [43] and Stokes and Robinson [44], which is expressed as

$$\sum_i \frac{m_i}{m_i^0} = 1 \tag{32}$$

where m_i is the molality concentration of the i species in the ternary system and m_i^0 is the molal concentration of the i species alone in the water (pure solution) at the same water activity. The water activity has been calculated by Eq. (33)

$$\ln a_w = -\phi M_{water} \sum_i m_i \tag{33}$$

where a_w is the water activity, ϕ is the osmotic coefficient, M_{water} is the molecular weight of the water ($18 \cdot 10^{-3}$ kg·mol^{-1}), m_i is the molality concentration of the i species.

Fig. 5 represents the molality concentration of the lithium chloride as a function of the molality concentration of the sodium chloride. Each point corresponds to the value of the ZSR relation in the mixture of NaCl-LiCl. The value of each point is equal to or larger than 1. The ZSR relation is rigorously valid when it is equal to 1 which implies it is valid only for a dilute solution. Fig. 5 is not symmetric. This dissymmetry is due to the difference between the two association constants of the lithium and sodium chloride. The greater the association constant, the more associating pairs appear, and the faster the ZSR relation is invalidated. Considering the manipulation uncertainty, the ZSR relation could be considered as true for the mixture of lithium and sodium chloride with an uncertainty of 1%. This work is in agreement with the work by Rowland and May [45] who have identified a wide range of ternary system, a mixture of two salts in aqueous phase, where the ZSR relation is not verified.

4. Conclusion

We proposed a new method to address the problem of specificity and the Hofmeister series of cations in aqueous electrolyte solutions with the help of the MSA calculated by Lesser Blum. First we considered the hydrated diameter as the biggest possible cation diameter in front of the various anions. Then the specific effects between the species are treated thanks to an associated MSA model. The result is in agreement with the experiments up to molar concentrations, as usual when MSA is used. What is more interesting is the fact that mixtures can be treated because specific effects are properly taken into account. Globally, hydration of small ions appears to be stable and the one of big ions fluctuate. Electrostatics is the main force for association. The validity of Zdanovskii-Stokes-Robinson mixing rule has also been tested and it appears to be valid with typically a 1% accuracy for molar concentrations.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2018.01.125.

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