Organic electrolyte solutions: Modeling of deviations from ideality within the binding mean spherical approximation

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Abstract

Deviations from ideality in organic electrolyte solutions are described within the Binding Mean Spherical Approximation (BiMSA) theory, in which ions are regarded as charged hard spheres and unlike ions may associate to form an ion pair. Association is modeled within the Wertheim theory (as done in SAFT-type models). The model includes a mass action law with a thermodynamic association constant. The literature about the thermodynamic properties of this type of solution is reviewed. Besides, it is attempted to gain some insight into the solvation of ions by computing their Stokes hydrodynamic diameters from conductivity experiments, and by employing an original analysis introduced by Fawcett. The BiMSA model is used to represent the osmotic coefficient of 1-1 electrolytes in pure methanol, ethanol, 2-propanol, acetone and acetonitrile. The optimized cation sizes in the solvents are compared with their hydrodynamic diameters. The regressed association constants are compared with literature values derived from conductivity and vapor pressure experiments.

Keywords: Electrolytes, Organic solutions, Thermodynamics, Binding Mean Spherical Approximation (BiMSA), MSA.

1. Introduction

Mixed solvent (aqueous-organic) electrolytes have been used for some time now in many industrial processes, for example in order to optimize crystallization [1] and other separation processes in the chemical and pharmaceutical industries, such as water-alcohol distillation [2]. In probably more recent times, solutions of salts in *pure* organic solvents have been used increasingly in industrial processes and devices as, e.g., in the fabrication of lithium-ion batteries involving different types of carbonates as the solvent [3], of wet double-layer capacitors and supercapacitors, and in electrodeposition, electroplating, etc. [4].

Experimental data about deviations from ideality in binary organic electrolyte solutions are by far not as plentiful as in the case of aqueous electrolytes. This is likely partly due to the fact that this type of solution is not found in nature. Moreover careful experiments require the use of absolutely dry salts and solvents, which may not be easy to achieve. Furthermore the solubility of common salts is generally limited in organic solvents. They are not as good solvents as water for salts.

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Seminal works about such systems were apparently published at the beginning of the 20th century. They dealt with vapor-liquid equilibria (VLE) of alcoholic salt solutions. Seemingly one of these first experimental studies was reported in 1914 by Tower and Germann [5] about VLE of methanol and ethanol salt solutions at 15°C. Then Hayward and Perman investigated in 1931 the vapor pressures of alcoholic solutions of calcium chloride at various temperatures from 20 to 60°C [6]. This work was pursued in 1981 by Mar and Carling [7]. After these first publications the study of deviations from ideality in (anhydrous) alcohols, and then other pure organic solvents, has been developed for a number of salts (see section 2).

Efforts have also been dedicated to the modeling of the deviations from ideality for these non-aqueous ionic solutions [8, 9, 10, 11]. These models were mostly proposed at the McMillan-Mayer (MM) level of description [12] which is the generalization of the concept introduced van't Hoff according to which a dilute solution may be viewed as an ideal gas of solute. The MM theory offers a rigorous framework that allows one to consider concentrated solutions and non-idealities. At the MM level of description the chemical potential of the solvent is kept constant by exerting a pressure on the solution (amounting to the osmotic pressure as in van't Hoff theory) [13, 14, 15], and the solute particles interact through solvent-averaged interactions [12, 16]. Other modeling attempts have been proposed in which the solvent was explicitly taken into account, within the SAFT framework, in the case of alcohols as the solvent [17, 18]. These models involved the use of 7 SAFT parameters to describe the properties of the alcohol alone, and 2 specific parameters for every cation and anion.

Because the dielectric constant of organic solvents is generally lower than that of water, cation-anion attraction and therefore ion pairing are expected to be enhanced as compared to aqueous solutions for a given salt. The most appealing and successful model applied to non-aqueous ionic solutions has certainly been the so-called chemical model (CM) promoted by Barthel and collaborators [19, 20, 21, 22, 23, 24] in which a part of the ions is supposed to form ion pairs and this process is assumed to obey a mass action law (MAL). The activity coefficient of the free ions is calculated within the framework of the Debye-Hückel (DH) theory. The latter feature limits the applicability of the CM to dilute solutions, typically below 0.1M. It has been applied to a number of salts, such as alkali halides and perchlorates, in various solvents (alcohols, acetone, acetonitrile,...). Apart from the CM, the Pitzer model has been utilized to represent osmotic and activity coefficients up to high concentrations [22, 24, 25]. Another class of model that has been used in the literature is the mean spherical approximation (MSA) [10], and the associative MSA (AMSA) [11, 26]. The MSA has similarities with the DH theory, but it accounts for excluded volume effects in a better way than the DH theory does [27]. Consequently models based on the MSA should be applicable to solutions more concentrated than within the DH framework. The MSA and the AMSA have been utilized to describe the properties of organic ionic solutions in which ion pairing was expected on the basis of conductivity experiments [10, 11, 26]. In the case of the MSA [10, 11, 26] association was introduced in the same way as in the CM by introducing a MAL for ion pairs and deviations from ideality were estimated within the MSA (in lieu of the DH theory in the CM). In the AMSA [11, 26] cation-anion pairing is accounted for

explicitly in the model by means of the Wertheim theory [28, 29] for association (which is also employed in SAFT models), which introduces extra terms in the expressions of the activity and osmotic coefficients. The MSA combined with a MAL for the formation of ion pairs (MSA-MAL model) has been employed for a representation of the mean salt activity coefficients at 25°C of sodium halides and perchlorate and of tetrabutylammonium bromide, iodide and perchlorate in methanol up to concentrations ranging from 0.14M to 1.1M [10], and of lithium perchlorate in acetonitrile up to 0.9M [26]. The AMSA was utilized to represent the osmotic coefficient for solutions of a few tetraalkylammonium bromides in acetone and ethanol, of bispiperidinium bromide in ethanol, and of $LiClO_4$ in acetone, acetonitrile and 2-propanol, up to typical concentrations of 0.5M-0.9M [11, 26]. A modified version of the AMSA was also proposed in order to include the effect of trimers and tetramers that are present in organic solvents of very low dielectric constant [11].

In this work, we use a model called the binding mean spherical approximation (BiMSA) [30, 31] which is equivalent to AMSA in the case of the formation of pairs. In this model it is considered that two unlike free ions may stick to each other to form an ion pair. In the past we have used the BiMSA to describe deviations from ideality in aqueous ionic solutions that exhibit ionic association [32, 33, 34].

The first aim of the present work was to examine whether it is possible to apply also this model to the case of organic electrolyte solutions, in a systematic way and for a greater number of systems (as we have been done before in the case of aqueous solutions [35, 32]). This meant in particular: Can the thermodynamic description be done up to the maximum concentrations to which data are available ? If so is it possible to find consistent values for cation sizes in a given organic solvent ? Finally, how do the regressed association constants compare with literature values determined from conductivity experiments ?

The remainder of this article is organized as follows. In the next section the available literature in which experimental data may be found is reviewed. Then a theoretical section presents the BiMSA model and the main features of an analysis proposed by Fawcett for the solvation of ions in a solvent [36]. The fourth section is dedicated to the presentation of the results and to their discussion. Finally the last section contains a summary of this work and some concluding remarks and prospects.

2. Experimental thermodynamic data in the literature

The thermodynamic properties of organic electrolyte solutions have been investigated by measuring vapor pressures (or vapor pressure lowering in practice) above solutions. Organic solvents capable of dissolving ions in substantial amounts may be classified into two main categories: protic, and dipolar aprotic solvents [19]. The first category includes water and alcohols, and the second acetone and acetonitrile, inter alia.

Protic solvents may solvate cations through two types of interaction: the first one is between the cation and the solvent dipole, and the second one is between the cation and the lone electrons on the oxygen atom of the solvent molecule. Anions may be solvated through hydrogen bonding [37, 38]. At the same time, in water, the residence time of water molecules in the vicinity of anions has been shown to be several orders of magnitude shorter than close to cations [37]. Thus, in protic solvents in general, the solvation of anions

is likely to be much weaker than that of cations. Dipolar aprotic solvents may stabilize cations through ion-dipole attraction. The solvation of anions in this type of solvent is not as clear.

Vapor pressure measurements have been carried out at 25°C above solutions of alkali halides and perchlorates in methanol [20, 22, 39, 40, 41, 42, 43, 44, 45], in ethanol [21, 22, 24, 46], and in 2-propanol [21, 22, 47]. Other measurements were carried out at the same temperature on the 2-1 salts calcium chloride and nitrate in methanol and ethanol [48, 49], on tetraalkylammonium salts in methanol [50], and on some more unusual salts such as tetramethylguanidinium chloride and perchlorate in ethanol [51]. Let us note here that the interest of $CaCl_2$-methanol and ethanol systems for adsorption refrigeration and thermal energy storage has been highlighted lately[52, 53].

Besides alcohols, various (dipolar) aprotic solvents have been employed in thermodynamic vapor pressure experiments. These systems included solutions of LiBr and $LiClO_4$ in acetone [23, 54], of LiBr, $LiClO_4$ and NaI in acetonitrile [21, 54, 55] and of $LiClO_4$ in dimethoxyethane (DME) and dimethylcarbonate (DMC) [54]. $LiClO_4$ is an interesting salt because it is quite soluble in organic solvents [54]. The solvents used in the experiments provided a wide range of dielectric constants (see Table 1) going from 32.6 for methanol to as low as 3.1 for DMC. Let us recall that ion-pairing is expected to increase when the solvent permittivity is decreased.

No thermodynamic data could be found in the literature or within the ELDATA databank [56] about salts in other common solvents like dioxane or propylene carbonate.

3. Modeling

3.1. The BiMSA model

We first present briefly the main features of the basic MSA model for strong electrolytes [27, 57]. The theory is developed at the MM level of solutions [12]. In this model an electrolyte solution is modeled as charged hard spheres (the ions) placed in a dielectric continuum (the solvent). The ions may have different diameters. As compared to the Debye-Hückel (DH) theory, the MSA accounts in a consistent way for the effect of the minimum distances of approach (excluded volume) between the ions in the cloud around an ion (not only with respect to a central ion as the DH theory does) [27]. Consequently, it better describes the distribution of ions about a given ion in concentrated solutions. For these reasons, although this has been questioned sometimes in the literature [58], it seems preferable to use the MSA for a description of electrolyte solutions at high concentrations. Similarly to the DH model, the MSA is a linearized theory which provides analytic expressions. At the MM level, the diameter of an ion is expected to reflect its degree of solvation. Then it should be appreciably larger than its crystallographic diameter if the ion is strongly solvated. On the other hand, it should be of the same magnitude if the ion is weakly solvated, which is the case of monovalent anions in water [37, 38].

The BiMSA theory [30, 31] accounts for the association of spherical ions within the framework of the Wertheim theory in which the spheres possess binding sites at their surface [59]. The sites on unlike ions

interact through highly directional attractive forces (as in SAFT models). After averaging on the orientations of the spheres, the potential $u_{ij}^{attr}(r)$ between two particles i and j is given by [30],

$$\exp[-\beta u_{ij}^{attr}(r)] = \mathcal{B}_{ij}\,\delta(r - \sigma_{ij}) \tag{1}$$

in which δ is the Dirac distribution, σ_{ij} is the minimum approach distance between i and j, and $\mathcal{B}_{ij}$ is the strength of this 'sticky' interaction.

In the BiMSA model a pair is defined as two unlike ions being in contact. The association scheme is sketched in Figure 1. In this respect it should be also noted that the effect of electrostatic forces on cation-
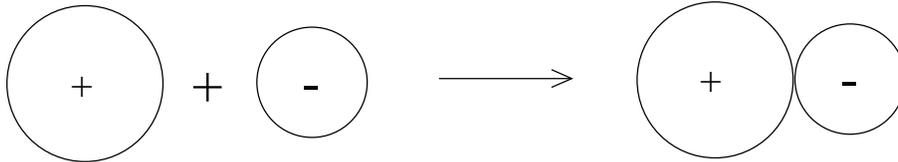
Figure 1: Association of two ions forming a pair.

anion association is consistently taken into account in the model. This effect appears in the expression of the cation-anion contact probability which is composed of a HS and an electrostatic contribution (see Eq. 69 of Ref. [31] in which the exponential approximation is used). Interestingly, this feature thus accounts for the influence of electrostatic screening on ion-pairing. It brings a contribution in the Helmholtz energy of the system and in the deviations from ideality of the solution.

Application of this model has been presented in previous work for associated aqueous ionic solutions [32, 34].

The valences, diameters and total number densities of the ions are $z_+, z_-, \sigma_+, \sigma_-, \rho_+, \rho_-$, respectively. We denote by α_+ and α_- the unbound ion fractions.

We will recall here the main formulas useful for this work.

The model includes a mass action law (MAL) at the MM level as [31, 34],

$$K_0 \equiv \frac{\rho_P}{(\rho_+\alpha_+)(\rho_-\alpha_-)} = K\,g_c^{HS}\,\exp\left[-2\lambda\frac{z'_+z'_-}{\sigma_P} + 2\lambda_0\frac{z_+z_-}{\sigma_{P,0}}\right] \tag{2}$$

in which K is the thermodynamic association constant (related to the parameter $\mathcal{B}$ in Eq. 1), ρ_P is the pair number density, g_c^{HS} is the contact radial distribution function for the fluid of neutral hard spheres (HS) and,

$$z'_i \equiv (z_i - \eta\sigma_i^2)/(1 + \Gamma\sigma_i) \tag{3}$$

$$\lambda \equiv \beta e^2/(4\pi\varepsilon_0\varepsilon)$$

$$\sigma_P \equiv \sigma_+ + \sigma_-$$

where λ is the Bjerrum distance, λ_0 and $\sigma_{P,0}$ are the value of λ and σ_P at infinite dilution, η and Γ are classical MSA parameters defined below, ε_0 is the permittivity of a vacuum, and ε is the relative permittivity of solution.

Note that Eq. 2 differs slightly from the expression originally taken in ref. [32]. It better takes into account the infinite dilution reference state [34].

For a given K, the pair number density is deduced from Eq. 2,

$$\rho_P = \frac{2K_0\rho_+\rho_-}{1 + K_0\rho_t + [1 + 2K_0\rho_t + K_0^2(\rho_+ - \rho_-)^2]^{1/2}} \tag{4}$$

with $\rho_t \equiv \rho_+ + \rho_-$ the total number density of ions, including free ions as well as those present in ion pairs.

The MSA parameters Γ (the MSA screening parameter, analog of the DH screening parameter κ) and η satisfy the following relations,

$$\frac{\Gamma^2}{\pi\lambda} = \sum_{k=+,-} \rho_k z_k'^2 + \frac{2\rho_P}{\sigma_P}\left(\frac{\sigma_+}{1 + \Gamma\sigma_+} + \frac{\sigma_-}{1 + \Gamma\sigma_-}\right)z_+'z_-' \tag{5}$$

$$\eta = \frac{\pi}{2\Delta\Omega}\left[\sum_{k=+,-}\frac{\rho_k\sigma_k z_k}{1 + \Gamma\sigma_k} + \frac{\rho_P}{\sigma_P}\frac{z_+\sigma_-^2 + z_-\sigma_+^2}{(1 + \Gamma\sigma_+)(1 + \Gamma\sigma_-)}\right] \tag{6}$$

with

$$\Omega = 1 + \frac{\pi}{2\Delta}\left[\sum_{k=+,-}\frac{\rho_k\sigma_k^3}{1 + \Gamma\sigma_k} + \frac{2\rho_P}{\sigma_P}\frac{\sigma_+^2\sigma_-^2}{(1 + \Gamma\sigma_+)(1 + \Gamma\sigma_-)}\right] \tag{7}$$

and

$$\Delta = 1 - \frac{\pi}{6}\sum_k \rho_k\sigma_k^3 \tag{8}$$

is the fraction of space not occupied by the solute. Eqs. 5 and 6 constitute two coupled equations that can be easily solved numerically by iterations, using Eqs. 2 and 4 for a given value of K and starting with the initial values $\Gamma_0 = \kappa/2$ and $\rho_P = 0$ in Eqs 6 and 7. These values for Γ and η are then inserted into Eq. 5 and the same procedure is repeated until convergence.

The excess electrostatic MSA internal energy per volume unit is,

$$\beta\Delta U^{MSA} = \beta\Delta U_0^{MSA} + \lambda\frac{\rho_P}{\sigma_P}\left(\frac{z_+z_-'}{1 + \Gamma\sigma_+} + \frac{z_-z_+'}{1 + \Gamma\sigma_-}\right) \tag{9}$$

with

$$\beta\Delta U_0^{MSA} = -\lambda\sum_{i=+,-}\rho_i z_i\frac{\Gamma z_i + \eta\sigma_i}{1 + \Gamma\sigma_i}$$

the excess internal energy in the absence of association. The excess MSA Helmholtz energy A per volume unit is,

$$\beta\Delta A^{MSA} = \beta\Delta U^{MSA} + \frac{\Gamma^3}{3\pi} + \beta\Delta A^{MAL} - 2\lambda\frac{\rho_P}{\sigma_P}z_+'z_-' \tag{10}$$

In this equation the MAL contribution is given by

$$\beta\Delta A^{MAL} = \sum_{k=+,-}\rho_k\ln\alpha_k + \rho_P \tag{11}$$

The excess osmotic coefficient is expressed as,

$$\Delta\phi^{MSA} = \Delta\phi_0^{MSA} + \Delta\phi_{\sigma_+} + \Delta\phi_\varepsilon \tag{12}$$

where the last two terms account for the possible variation of the cation diameter and of the solution permittivity with salt concentration. One has,

$$\Delta\phi_0^{MSA} = \Delta\phi_0^{el} + \Delta\phi_0^{MAL} \tag{13}$$

$$\Delta\phi_0^{el} = -\frac{\Gamma^3}{3\pi\rho_t} - \frac{\lambda}{\rho_t}\frac{2}{\pi}\eta^2 \tag{14}$$

$$\Delta\phi_0^{MAL} = -\frac{\rho_P}{\rho_t}\left(1 + \rho_t\frac{\partial\ln g_c^{HS}}{\partial\rho_t}\right) \tag{15}$$

and

$$\Delta\phi_{\sigma_+} = \frac{1}{\rho_t}\left[\frac{\partial\beta\Delta A^{MSA}}{\partial\sigma_+}\right]_\Gamma \times \mathrm{D}(\sigma_+) \tag{16}$$

$$\Delta\phi_\varepsilon = \frac{\beta\Delta U^{MSA}}{\rho_t}\varepsilon\mathrm{D}(\varepsilon^{-1}) \tag{17}$$

with

$$\mathrm{D} \equiv C_S\frac{\partial}{\partial C_S} \tag{18}$$

in which C_S is the salt concentration. One has,

$$\left[\frac{\partial\beta\Delta A^{MSA}}{\partial\sigma_+}\right]_\Gamma = \left[\frac{\partial\beta\Delta U^{MSA}}{\partial\sigma_+}\right]_{\Gamma,\rho_P} - \rho_P\left[\frac{\partial\ln g_c^{HS}}{\partial\sigma_+} + 2\frac{\lambda z_+' z_-'}{\sigma_P^2}\right] \tag{19}$$

with

$$\left[\frac{\partial\beta\Delta U^{MSA}}{\partial\sigma_+}\right]_{\Gamma,\rho_P} = \lambda\rho_+\frac{z_+'\left[\Gamma^2(z_+ + \eta\sigma_+^2) - 2\eta\right]}{1 + \Gamma\sigma_+} - \lambda\frac{2\rho_P}{\sigma_P}\frac{\Gamma\left(z_+ + \eta\sigma_+^2\right) + 2\eta\sigma_+}{(1 + \Gamma\sigma_+)^2}z_-' \tag{20}$$

The expression of g_c^{HS} and of its derivatives may be found in refs. [32, 34].

The total osmotic coefficient at MM level is,

$$\phi = 1 + \Delta\phi^{MSA} + \Delta\phi^{HS} \tag{21}$$

in which $\Delta\phi^{HS}$ is the hard sphere contribution that can be calculated from the Carnahan-Starling expression, as described elsewhere [60].

For comparison with experimental data it is needed to convert the value obtained for ϕ at the MM level to the experimental level (the Lewis-Randall (LR) level). This may be done by using the so-called MM-to-LR conversion formula as explained elsewhere [14, 15, 60], that requires only the availability of solution density data.

The excess MSA mean activity coefficient can be obtained simply from the formula

$$\Delta\ln\gamma_\pm^{MSA} = \frac{\beta\Delta A^{MSA}}{\rho_t} + \Delta\phi^{MSA} \tag{22}$$

The BiMSA contributions to the osmotic and activity coefficients, Eqs. 12 and 22, naturally satisfy the Gibbs-Duhem relation.

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As in previous work [34, 60, 35] it will be assumed that the anion size may be kept constant and that the diameter of the cation and the inverse of solution relative permittivity vary as linear functions of the concentration,

$$\sigma_+ = \sigma_+^{(0)} + \sigma_S^{(1)} C_S \tag{23}$$

$$\varepsilon^{-1} = \varepsilon_{org}^{-1} (1 + \alpha C_S) \tag{24}$$

with $\sigma_+^{(0)}$ the cation diameter at infinite dilution (the 'intrinsic' diameter of cation), C_S the molar concentration of the salt and ε_{org} the relative permittivity of pure solvent. Eqs 23 and 24 introduce two adjustable parameters $\sigma_S^{(1)}$ and α that are characteristic of the electrolyte while $\sigma_+^{(0)}$ is characteristic of the cation considered.

Let us underline that experimental data for the relative solution permittivity, ε_{exp} (if available), are not used in our MSA model because one needs to describe electrostatic interactions between ions at short separations in concentrated solutions [35, 61]. In contrast, experimental data correspond to large (macroscopic) interionic distances. Consequently it should be expected that $\varepsilon > \varepsilon_{exp}$ for any salt concentration. However, it makes sense to use experimental values when sufficiently dilute solutions are considered, probably typically below 1M [62].

From Eqs. 18, 23 and 24 we get,

$$D(\sigma_+) = \sigma_+ - \sigma_+^{(0)} \tag{25}$$

$$\varepsilon D(\varepsilon^{-1}) = 1 - \varepsilon/\varepsilon_{org} \tag{26}$$

3.2. Analysis of ion solvation in organic solvents within the ion-dipole MSA

It has been shown that anions in water are solvated through hydrogen bonding [37, 38]. Alcohols may be expected to solvate anions in the same way because they also offer the possibility of H-bonding [10]. This is not the case of aprotic solvents.

Fawcett proposed a method to analyze the solvation of simple cations and anions [36] in a solvent in the framework of the ion-dipole MSA [63, 64]. In the latter a solvent molecule is represented as a hard sphere with an embedded point dipole at its center. Then, within the ion-dipole MSA model applied to the present study, the molar solvation Gibbs energy of an ion, ΔG, should satisfy the original Born equation in the form,

$$\Delta G = \frac{\mathcal{N} z^2 e^2 f_{dd}}{4\pi \varepsilon_0 \sigma_B} \left(1 - \frac{1}{\varepsilon_{org}}\right) \tag{27}$$

with $\mathcal{N}$ the Avogadro number and z the ion valency. Moreover, f_{dd} is a parameter accounting for the effect of dipole-dipole interactions in the solvation process and σ_B is the Born diameter. In the case of cations, one has [36] $f_{dd} = 1$ and,

$$\sigma_B = \sigma_{cr} + \Delta_{org} \tag{28}$$

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Table 1: A few properties of pure solvents at 25°C

Solvent	d_{org} /(kg m^{-3})	η_{org} /(10^{-3} kg m^{-1} s^{-1})	ε_{org}	m_{org} /Debye[a]
Methanol	786.36	0.542	32.63	1.70[b]
Ethanol	784.95	1.087	24.35	1.69[b]
2-propanol	780.97	2.08	19.40	1.66[c]
Acetone	784.35	0.303	20.56	2.88[b]
Acetonitrile	776.75	0.341	35.95	3.91[c]

[a]1 Debye= 3.3356×10^{-30} C m; ; [b]Ref. [66]; [c]Ref. [67].

in which σ_{cr} is the crystallographic diameter of the ion and Δ_{org} is a distance characteristic of the solvent only. The presence Δ_{org} in this relation reflects the fact that the solvent is not a dielectric continuum as in Born theory (in which $\Delta_{org} \equiv 0$) but it has a granular structure.

In the case of anions, one expects to have $f_{dd} < 1$ and $\Delta_{org} = 0$ ($\sigma_B = \sigma_{cr}$).

By virtue of Eq. 28, Eq. 27 may be rewritten as,

$$-\frac{\mathcal{N}z^2 e^2 (\varepsilon_{org} - 1)}{4\pi\varepsilon_0 \varepsilon_{org} \Delta G} = \frac{1}{f_{dd}}\sigma_{cr} + \frac{\Delta_{org}}{f_{dd}} \tag{29}$$

which indicates that a plot of the l.h.s. of this equation as a function of σ_{cr} for various (simple) ions should give a straight line and values for f_{dd} and Δ_{org} by linear regression.

This has been done by Fawcett for monovalent cations and anions in water [36], which confirmed the expectation that $f_{dd} = 1$ for cations and $f_{dd} < 1$ for anions. Furthermore he found an optimum value $\Delta_{org}=$ 0.49 Å for cations and he indeed obtained $\Delta_{org} \sim 0$ for anions.

In the present work, the same method of analysis has been applied to the solvation of anions in some organic solvents in order to gain some insight into the solvation of these ions.

4. Preliminary results

In this section we present results needed in the description of the thermodynamic properties of organic electrolyte solutions within the BiMSA model.

4.1. Data for pure solvents and electrolyte solutions densities

The following data will be useful below. The densities (d_{org}), dynamic viscosities (η_{org}), dielectric constants (ε_{org}) and dipole moments of molecules in the gas phase (m_{org}) of the pure solvents at 25°C are collected in Table 1. They were all taken from ref. [65].

The densities of the ionic solutions are needed in order to perform the MM-to-Lewis-Randall conversion [14, 15, 60]. Experimental data were regressed according to the following formula,

$$d = d_{org} + d_1 C_S - d_2 C_S^{3/2} \tag{30}$$

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as has been done in the case of aqueous solutions [68]. Let us note that the parameter d_1 is given by [68],

$$d_1 = M_S - d_{org} \, V_S^0 \tag{31}$$

in which M_S is the molar mass of the salt and V_S^0 is its partial molar volume at infinite dilution.

The values of the parameters d_1 and d_2 are given in Table 2. No density data could be found in the case of solutions of LiCl in 2-propanol. For this solution the values of d_1 and d_2 in Table 2 were estimated empirically from the values for solutions of LiCl in methanol and ethanol. Only one density value was retrieved in the case of NaI in 2-propanol at saturation [69]. In this case the value of d_1 was estimated from those for NaI in methanol and ethanol, and that of d_2 was deduced from the density at saturation.

It may be noticed in Table 2 that most lithium halides exhibit d_1 values that are larger than the molar mass of the salt, M_S. By virtue of Eq. 30, this entails that the partial molar volumes of these salts in these solvents, V_S^0, are negative. We also note that this is not so for these same salts in water, for which d_1 is much smaller than M_S and thus V_S^0 is positive ($d_1 \sim 23.6$ g mol^{-1} and $M_S \sim 42.4$ g mol^{-1} for LiCl, and $d_1 \sim 60.5$ g mol^{-1} and $M_S \sim 86.8$ g mol^{-1} for LiBr). These two remarks indicate that lithium halides salts are strongly solvated in the organic solvents considered here.

Table 2: Solution densities: Values of parameters to be used in Eq. 30 (with C_S in mol dm^{-3}).

Solvent	Salt	Max. m_S^a /(mol kg^{-1})	$10^3 \times M_S$ /(kg mol^{-1})	$10^3 \times d_1$ /(kg mol^{-1})	$10^3 \times d_2$ /(kg dm$^{3/2}$ mol$^{-3/2}$)	AARD^b	Refs.^{c}
Methanol	LiCl	1.1	42.39	46.828	7.5891	0.08 %	[70]
	LiBr	3.5	86.84	84.316	4.6847	0.03 %	[71] ([72])
	LiClO$_4$	4	106.39	95.592	10.669	0.2 %	[44] ([22])
	NaCl	0.17	58.44	73.949	39.044	0.007 %	[70, 73] ([72])
	NaBr	0.86	102.89	99.336	5.4909	0.1 %	[72]
	NaI	5.65^d	149.89	151.25	12.673	0.01 %	[70, 74]
	NaClO$_4$	1.05	122.44	105.18	5.9898	0.07 %	[73] ([20])
	KBr	0.13	119.00	92.287	7.6461	0.004 %	[72]
	KI	0.68	166.00	147.34	6.9240	0.003 %	[72] ([70])
Ethanol	LiCl	3.4	42.39	47.066	7.2109	0.03 %	[70]
	LiBr	1.2	86.84	88.439	9.4567	0.01 %	[71]
	LiClO$_4$	1.5	106.39	93.835	9.7951	0.002 %	[22]
	NaI	2.11^d	149.89	137.44	9.2649	0.002 %	[75, 69]
2-Propanol	LiCl^e		42.39	47.4	6.8		
	LiBr	1.3	86.84	88.238	9.6990	0.007 %	[71]
	LiClO$_4$	1.5	106.39	91.990	8.5178	0.007 %	[54]
	NaI	1.76^d	149.89	123.4	0.2612		[69]
Acetone	LiBr	0.83	86.84	92.092	4.7203	0.01 %	[23]
	LiClO$_4$	2.6	106.39	109.45	21.465	0.02 %	[54]
Acetonitrile	LiBr	0.83	86.84	91.520	9.4629	0.01 %	[55] ([71])
	LiClO$_4$	1.2	106.39	94.159	8.7667	0.004 %	[54]
	NaI	0.9	149.89	146.05	11.339	0.02 %	[76]

^{a}Molality of salt; ^{b}Average absolute relative deviation (accuracy of fit); ^{c}References in parentheses indicate other (unused) data; ^{d}Saturated solution [69]; ^{e}Estimated d_1 and d_2 values (see text).

4.2. Stokes hydrodynamic diameters of ions from conductivity experiments

In this section we calculate the Stokes hydrodynamic diameters of the ions in the organic solvents considered in this work. They will be useful in the treatment below.

The hydrodynamic diameter of an ion is the diameter of a rigid sphere that would have the same diffusion coefficient (or equivalently the same ionic mobility) as the ion. The diameters were derived from Stokes' law [77] for no-slip condition of the fluid at the surface of the sphere,

$$\sigma_{hyd} = 2\frac{|z|\mathcal{N}e^2}{6\pi\eta_{org}\lambda_0} = \frac{16.404\,|z|}{\eta_{org}\,\lambda_0} \tag{32}$$

in which λ_0 is the limiting equivalent conductance of the ion (expressed in cm^2 Ω^{-1} mol^{-1}), and the solvent viscosity η_{org} (expressed in SI units) was taken from Table 1.

The λ_0 values and the Stokes diameters obtained from Eq. 32 for the cations and anions considered in this work are gathered in Table 3. Unfortunately no conductivity data could be found in the case of 2-propanol. Values for ions in water are recalled in this table.

The numerical values of Table 3 may be commented as follows.

The hydrodynamic diameters (HD's) of Li$^+$ and Na$^+$ in water are appreciably larger than their crystallographic diameters (CD's) because of the effect of their hydration shell. On the other hand the HD's of K$^+$ and of anions in water are smaller than the corresponding CD's. This outcome is likely due to the fact that Stokes law is not accurate for spherical ions whose of size comparable to that of the solvent, as is the case for these weakly hydrated ions. This suggests also that Stokes law underestimates the effective size of an ion in water.

The HD's of cations in the organic solvents are all clearly larger than their CD's, and also larger than their HD's in water. This seems to indicate that the solvation shells of cations in the solvents are thicker than their hydration shells. Contrary to what occurs in water, the HD's of Br$^-$ and I$^-$ in the aprotic solvents acetone and acetonitrile are a bit greater than the CD's. It is striking that the HD's of ClO$_4^-$ in these solvents, 4.57 and 4.65 Å respectively, are just a bit larger than its thermochemical diameter of 4.52 Å. This is in contrast with the case of water for which the HD of the ClO$_4^-$ anion (2.74 Å) is much smaller that its thermochemical diameter.

In the next section, some information about the solvation of anions in the solvents is obtained within the ion-dipole MSA framework.

4.3. Solvation of anions in organic solvents.

The analysis proposed by Fawcett and described in section 3.2 was applied to the solvation of halide anions (except the fluoride ion) in a few organic solvents, namely methanol, acetone and acetonitrile. Values for the standard Gibbs energies of transfer of single ions from water to a few solvents (methanol, acetone and acetonitrile) were obtained from the work of Conway [88]. The values of the single ion Gibbs energies of hydration were taken from the same paper by Fawcett [36]. Combination of these latter two quantities provided the single ion Gibbs energies of solvation in the organic solvents. The Shannon and Prewitt values

Table 3: Limiting equivalent conductances (λ_0), hydrodynamic Stokes diameters (σ_{hyd}) and crystallographic diameters of ions.

Solvent	Ion	λ_0 /(cm^2 Ω^{-1} mol^{-1})	σ_{hyd} /Å	$\sigma_{cr}{}^a$ /Å	Refs.[b]
Water	Li$^+$	38.68	4.76	1.80	[77]
	Na$^+$	50.10	3.68	2.32	[77]
	K$^+$	73.50	2.51	3.04	[77]
	Cl$^-$	76.35	2.41	3.34	[77]
	Br$^-$	78.14	2.36	3.64	[77]
	I$^-$	76.84	2.40	4.12	[77]
	ClO$_4^-$	67.36	2.74	4.52^c	[77]
Methanol	Li$^+$	39.82	7.56	1.80	[78]
	Na$^+$	45.05, 45.22	6.65	2.32	[79, 78]
	K$^+$	52.40	5.74	3.04	[78]
Ethanol	Li$^+$	17.05	8.87	1.80	[80]
	Na$^+$	20.31	7.46	2.32	[80]
Acetone	Li$^+$	72.52	7.46	1.80	[81]
	Br$^-$	118.94	4.55	3.64	[82]
	ClO$_4^-$	118.35	4.57	4.52	[82]
Acetonitrile	Li$^+$	70.8	6.77	1.80	[83, 84]
	Na$^+$	77.3	6.20	2.32	[84]
	Br$^-$	100.7	4.76	3.64	[83, 84]
	I$^-$	102.2	4.69	4.12	[83, 84]
	ClO$_4^-$	103.38	4.65	4.52	[85]

[a]From ref. [86] for a coordination number of 6; [b]References for conductance values; [c]Thermochemical value from ref. [87, 86].

Table 4: Values of parameters f_{dd} and Δ_{org} introduced in Eq. 27, obtained from linear fits using Eq. 29 in the case of the halide anions, Cl^-, Br^- and I^-.

Solvent	f_{dd}	Δ_{org} (/Å)
Water	0.74^a	0^a
Methanol	0.726 ± 0.011	0.013 ± 0.055
Acetone	0.975 ± 0.036	1.55 ± 0.19
Acetonitrile	0.960 ± 0.006	1.61 ± 0.03

^{a}Results found by Fawcett [36].

[86] were adopted in Eq. 29 for the crystallographic ionic diameters as was done by Fawcett [36], that is $\sigma_{Cl^-} = 3.34$ Å, $\sigma_{Br^-} = 3.64$ Å and $\sigma_{I^-} = 4.12$ Å.

The results are presented in Table 4 and in Figure 2 in which the function $\psi \equiv -\mathcal{N}z^2 e^2(\varepsilon_{org} - 1)/(4\pi\varepsilon_0 \varepsilon_{org} \Delta G)$ (see Eq. 29) is plotted against σ_{cr}.
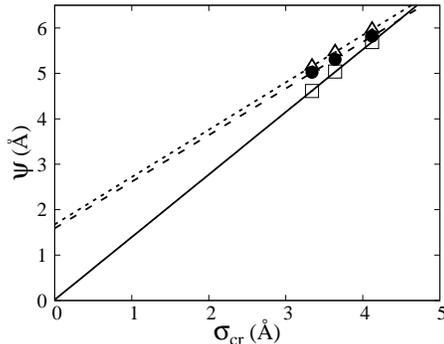
Figure 2: Plot of the l.h.s. of Eq. 29 (denoted by the symbol ψ) as a function of the crystallographic radius of the halide anions, Cl^-, Br^- and I^-. Symbols: Ions in ($\boxdot$) methanol, ($\bullet$) acetone, ($\triangle$) acetonitrile. Straight lines show the results of two-parameter linear fits (see Table 4).

The results of Table 4 are striking. Two clearly distinct cases are observed: either f_{dd} is significantly smaller than 1 and Δ_{org} is close to zero (case of water and methanol), or $f_{dd} \sim 1$ and Δ_{org} has a finite value (case of the aprotic solvents).

These results suggest that the solvation of simple anions in methanol is similar to that in water, with anions solvated through H-bonding, which is reflected in f_{dd} being smaller than 1 and Δ_{org} being very small, as was the case for water in ref. [36]. According to the analysis of ref. [36] the fact that $f_{dd} < 1$ indicates that dipole-dipole repulsive interactions significantly reduce the ion-dipole attractive energy, and $\Delta_{org} \sim 0$ points to a much less disruptive effect of anions on water structure than cations.

The results obtained for the solvents acetone and acetonitrile are in sharp contrast with those for methanol, as could be expected because these solvents are aprotic. Here one gets $f_{dd} \simeq 1$ and Δ_{org} has appreciable values of the order of 1.6 Å. This situation is similar to that of cations in water for which it

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Table 5: Values of infinite dilution cation diameters in water in MSA model [35] vs. Stokes diameters at 25°C

Ion	σ_{hyd} (/Å)	$\sigma_+^{(0)}$ (/Å)
Li$^+$	4.76	5.43
Na$^+$	3.68	3.87
Mg^{2+}	6.95	6.71
Ca^{2+}	6.19	7.03
Sr^{2+}	6.20	6.69
Ba^{2+}	5.79	6.01

was pointed out that $f_{dd} \sim 1$ suggests that dipole-dipole interactions (between water molecules) are not important in determining the solvation of cations. The result $\Delta_{org} > 0$ suggests that the solvation of anions in acetone and acetonitrile might be mediated by ion-dipole interactions, and that it is stronger than in water. This view may be supported by the fact that these two organic molecules bear strong dipole moments of 2.88 D and 3.91 D, respectively (see Table 1). As a consequence the effective diameter of anions in these two solvents, within the BiMSA theory at the MM level, should certainly be taken larger than their crystallographic value.

5. Results from BiMSA model and discussion

We now have to choose values for the anion diameters for input into the BiMSA model.

It has been seen in the preceding section that their solvation in the protic solvents (methanol, ethanol and 2-propanol) seems similar to that in water (through H-bonding). Therefore, as in previous work [32, 34, 35], the Pauling diameters were taken for the anions in these solvents, namely for Cl$^-$ (3.62 Å), Br$^-$ (3.90 Å) and I$^-$ (4.32 Å). Moreover a value of 4.53 Å (optimized in ref. [35]) was used for the perchlorate anion. This value is besides in excellent accord with the thermochemical value of 4.52 Å [86, 87].

The preceding section also has suggested that in the aprotic solvents acetone and acetonitrile anion solvation is similar to the solvation of *cations* in water. Besides, the results of Table 5 show some correlation between the cation diameter at infinite dilution, $\sigma_+^{(0)}$, and the hydrodynamic diameter. On this basis it was chosen to use the HD of anions in these solvents for their effective diameter in the BiMSA model.

Then the osmotic coefficient data were fitted within the BiMSA model by using Eq. 21 (which expresses ϕ at the MM level) and the MM-to-LR conversion [14, 15, 60] in which the parametrization of the solution densities of Table 2 was utilized. No variation of the anion diameter with concentration was assumed because it was considered that the desolvation of the more solvated cation had the strongest effect on the thermodynamics of the solution. This description thus involves the use of 4 parameters, viz. $\sigma_+^{(0)}$ and $\sigma_S^{(1)}$ (Eq. 23), α (Eq. 24) and the association constant K. These parameters were regressed by using a least-squares algorithm of the Marquardt type in a FORTRAN program.

Let us underline that data for salts in dimethoxyethane (DME) and dimethylcarbonate (DMC) [54]

were not treated in this work because these solvents give rise to aggregates that go beyond ion-pair, with the formation of triple ions and "quadrupoles" [89, 90, 91]. As mentioned in the Introduction section, the influence of this type of association has been modeled within the AMSA [11].

The results of the adjustments are presented in Table 6.

Let us underline that $\sigma_+^{(0)}$, the cation diameter at infinite dilution, should have a common value for all salts containing the same cation, in a given solvent. Actually this is a stringent requirement when adjustments are made up to high concentrations because in this case the sizes of the ions (and of the cation in particular) have a strong influence on the calculated deviations from ideality (ϕ in the present case).

Moreover, besides a low value of the deviation (AARD in Table 6), a good fit should be characterized by values of $\sigma_S^{(1)}$ and α that are respectively negative and positive, and do not have unrealistic values. These latter two conditions express the fact that the cation diameter and the relative permittivity are expected to decrease with concentration if the model indeed has some physical meaning.

It is observed in Table 6 that these two conditions, $\sigma_S^{(1)} < 0$ and $\alpha > 0$, are fulfilled, which is a satisfactory outcome, and that the fits are generally of good accuracy. Overall, most values for $\sigma_S^{(1)}$ are of the same order of magnitude (of the order of -0.2 or -0.3). However, no clear trend emerges in the $\sigma_S^{(1)}$ and α values as a function of the nature of the salt or of another parameter characteristic of the system. Nonetheless, it is noticed that the higher $\sigma_S^{(1)}$ values are found in the case of lithium salts in ethanol in which the Li$^+$ cation has the greater $\sigma_+^{(0)}$ value. Indeed this feature may be expected on the ground that the solvation shell of the biggest cation should shrink more rapidly when the salt concentration is increased, because then the amount of free solvent should drop more quickly.

The regressed values for K were compared with data found in the literature, K_{lit}. When the latter was expressed on the molal scale ($K_{lit}^{(m)}$) it was converted to the molar scale by using the formula, $K_{lit} = K_{lit}^{(m)}/d_{org}$, which may be obtained easily by expressing K_{lit} and $K_{lit}^{(m)}$ as a function of the concentrations of the involved species, on molar and molal bases respectively, and using the relation $C_i = m_i d_{org}$ at infinite dilution.

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Table 6: Results for the representation of osmotic coefficients of solutions within the BiMSA.

Solvent	Salt	Max. m_S[a] /(mol kg⁻¹)	$\sigma_+^{(0)}$ /(Å)	$\sigma_S^{(1)}$ /(Å mol⁻¹ dm³)	α /(mol⁻¹ dm³)	K /(mol⁻¹ dm³)	K_{lit}[b] /(mol⁻¹ dm³)	AARD[c]	Ref.[d]
Methanol	LiCl	8.9	7.143	-0.2072	0.1055	0.8566	21.0 [92]	1.4 %	[43, 41, 39]
	LiBr	12.2	7.143	-0.2014	0.1254	0.4897	19.0 [92]	0.9 %	[45, 39]
	LiClO$_4$	5.1	7.143	-0.2316	0.1584	0		1.5 %	[22, 44]
	NaCl	0.25	6.665	-0.06705	0.04460	0	22.9 [92]	0.5 %	[20, 40]
	NaBr	1.66[e]	6.665	-0.2791	0.03845	0.8043	68.0 [92]	0.8 %	[20, 40]
	NaI	4.5	6.665	-0.2017	0.07826	0.3714	19.3 [92]	0.6 %	[20, 41, 93]
	NaClO$_4$	1.3	6.665	-0.1735	0.1423	2.191	23.8 [92]	0.4 %	[20]
	KBr	0.13	5.847	-0.1023	0.08239	0	17.3 [92]	0.2 %	[20]
	KI	0.73	5.847	-0.3502	0.06702	0	17.5 [92]	0.4 %	[20]
Ethanol	LiCl	1.9	8.898	-0.4508	0.1885	24.94	71.7 [94]	0.6 %	[46]
	LiBr	3.4	8.898	-0.4074	0.2756	3.588		0.7 %	[24]
	LiClO$_4$	1.5	8.898	-0.5159	0.2270	12.07	43.1 [94]	0.4 %	[22]
	NaI	1.9	7.642	-0.2480	0.1064	13.76	62.2 [94]	0.9 %	[25]
2-Propanol	LiCl	1.5	7.190	-0.2559	0.04511	1640.		1 %	[47]
	LiBr	1.5	7.190	-0.05094	0.07117	471.2		0.9 %	[47]
	LiClO$_4$	1.5	7.190	-0.1701	0.08684	647.7	1550[f] [22]	0.9 %	[22]
	NaI	1.5	7.027	-0.2837	0.03516	546.2	704, 2817[f] [21]	2 %	[21]
Acetone	LiBr	0.83	6.115	-0.8320	0.0464	5849	2000, 4570 [95], 3400 [96]	0.7 %	[23]
	LiClO$_4$	5.85	6.115	-0.06361	0.07620	55.60	132 [81] - 1550[97]	0.9 %	[54]
Acetonitrile	LiBr	0.83	7.399	-0.2324	0.3753	155.4	163 [98], 175 ± 25 [83]	1.1 %	[55]
	LiClO$_4$	1.2	7.399	-0.4538	0.2206	14.70	22 [54]	0.1 %	[54]
	NaI	1.5	6.620	-0.2833	0.1635	7.203	12.9[f] [21], 27.6 [98]	0.3 %	[21]

[a]Maximum molality to which data are available; [b]Literature K values generally derived from conductivity experiments except otherwise noted (see note f); [c]Average absolute relative deviation; [d]References for ϕ data; [e]Saturated solution [40]; [f]Value derived from fit of vapor pressure measurements.

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We now examine the results in more detail for each solvent. In each case the diameter at infinite dilution (DID) for a given cation, $\sigma_+^{(0)}$, is determined in a first step.

5.1. Solutions in methanol

Four-parameter fits of ϕ for solutions of LiCl and LiBr up to the highest concentrations of 8.9 mol kg^{-1} and 12.2 mol kg^{-1}, respectively, yielded values of 7.152 Å and 7.134 Å, respectively, for the DID. This agreement is a very satisfactory (and somewhat surprising) result. It must be noticed that these DID values are very constrained because the two maximum concentrations are quite high. As a consequence there is very little flexibility in the choice of the DID for this cation. The mean value of these two results for $\sigma_+^{(0)}$, 7.143 Å, was adopted for the DID of the Li$^+$ cation.

The results of the adjustments of ϕ are shown in Figures 3 and 4 for LiCl and LiBr, respectively. It is unfortunate that few data are available at high concentration for these two salts. Moreover there are no experimental data in the case of LiBr in the region where the osmotic coefficient tops out.
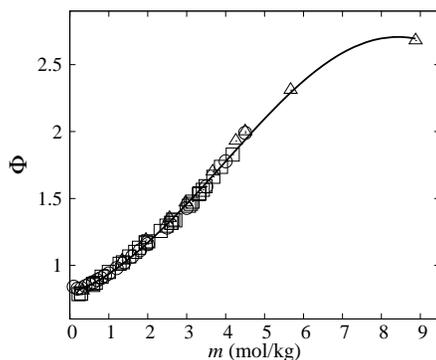
Figure 3: Osmotic coefficient for solutions of LiCl in methanol. Symbols: (□) data from ref. [43], (⊙) data from ref. [41], (△) data from ref. [39]. Solid line: result from BiMSA model.
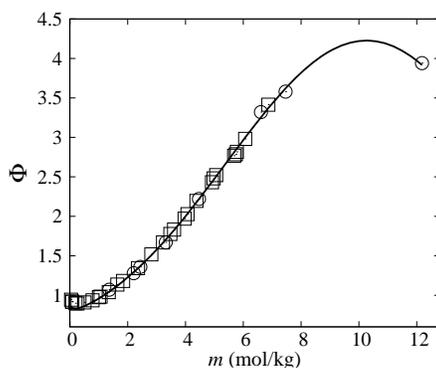
Figure 4: Osmotic coefficient for solutions of LiBr in methanol. Symbols: (□) data from ref. [45], (⊙) data from ref. [39]. Solid line: result from BiMSA model.

The results for the mean salt activity coefficient, $\gamma_{\pm}$, computed using Eq. 22 and Eq. 30 of Ref. [60] for the HS part, are displayed in Figure 5 in the case of LiCl and LiBr. Let us note that no experimental values (e.g., obtained using an electrochemical method) are available for the activity coefficients of these salts.
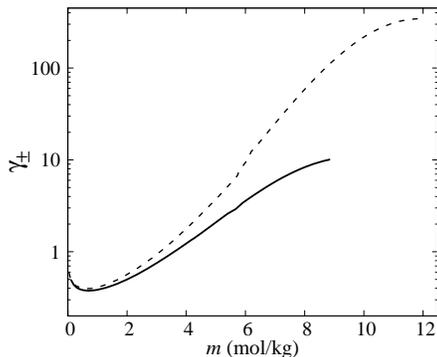
Figure 5: Mean salt activity coefficient computed using the BiMSA model for solutions of LiCl (solid line) and LiBr (dashed line) in methanol.

The DID of Na^+ was obtained from a fit of data for NaI that are available up to 4.5 mol kg^{-1}.

The DID of K^+ was optimized by performing simultaneous fits of the data for KBr and KI. It is noticed that the DID value for this cation (5.847 Å) is just a little larger than its hydrodynamic diameter (HD) in methanol (5.74 Å), which is in keeping with the correlation observed for cations in water (see Table 5).

5.2. Solutions in ethanol

The DID of Li^+ was taken from the fit of ϕ in the case of LiBr, $\sigma_+^{(0)} = 8.898$ Å, because, of the three lithium salts, ϕ for LiBr was experimentally measured to the highest concentration. Again we notice that this value is close to the HD of Li^+ in ethanol, 8.87 Å (see Table 5), which is worth of note.

The results of the fits of ϕ for the three lithium salts are displayed in Figure 6.
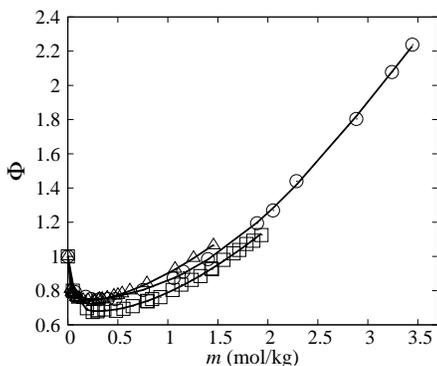
Figure 6: Osmotic coefficient for solutions of lithium salts in ethanol. Symbols: (⊡) LiCl, (⊙) LiBr, (△) LiClO$_4$. Solid lines: results from BiMSA model.

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The results for the mean salt activity coefficient, $\gamma_\pm$, are displayed in Figure 7 in the case of LiCl, LiBr and LiClO$_4$. Again no experimental values are available for the activity coefficients of these salts.
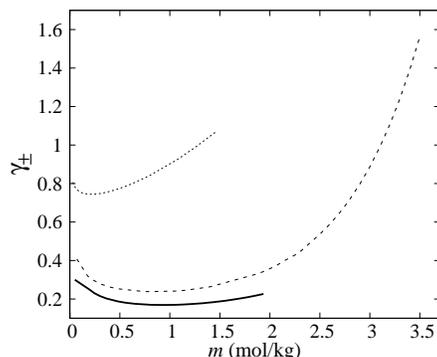
Figure 7: Mean salt activity coefficient computed using the BiMSA model for solutions of LiCl (solid line), LiBr (dashed line) and LiClO$_4$ (dotted line) in ethanol.

The DID for Na$^+$ resulted from the adjustment of ϕ for the NaI salt. Nevertheless it must be mentioned that the uncertainty on the values of the parameters (in particular on the DID) was not negligible because the maximum concentration ($\sim$ 1.9 mol kg^{-1}) was not sufficiently high and because data for only one salt was available.

5.3. Solutions in 2-propanol

Here the osmotic coefficients of the three lithium salts are available up to the same moderate concentration of 1.5 mol kg^{-1}. The DID of Li$^+$ was derived from the fits of ϕ in the case of LiBr and LiClO$_4$ which gave $\sigma_+^{(0)}=$ 7.07 Å and 7.31 Å, respectively (mean value= 7.19 Å).

As in the case of ethanol, the DID for Na$^+$ resulted from the adjustment of ϕ for the NaI salt only. It is seen that the fit of ϕ in this case gives the lowest accuracy of all fits, exhibiting an AARD of 2%, but this result also seems to be due to a lack of accuracy in the experimental data which do not vary regularly with concentration for $m_S < 0.6$ mol kg^{-1} as seen in Figure 8.

5.4. Solutions in acetone

The DID of Li$^+$ ion was imposed by the fit of ϕ for LiClO$_4$ for which data exist up to 5.85 mol kg^{-1} while those for LiBr were measured up to 0.83 mol kg^{-1}.

5.5. Solutions in acetonitrile

The DID of Li$^+$ ion resulted from the fit of osmotic data for LiClO$_4$ which exhibits a low AARD of 0.1%. Moreover the DID value (7.399 Å) is only less than 10% larger than the HD value of 6.77 Å.

With this result for the DID the data for LiBr were fitted for $m_S > 0.1$ mol kg^{-1} because they exhibit a large scatter at low concentration. In this fit it was noted that taking the Pauling diameter for the Br$^-$ anion (3.90 Å) led to a regressed value for $\sigma_S^{(1)}$ that was positive, which is not satisfactory (as mentioned

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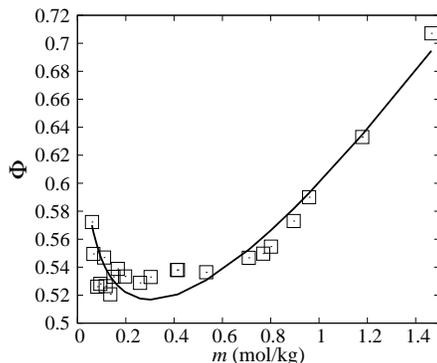
Figure 8: Osmotic coefficient for solutions of NaI in 2-propanol. Symbols: (□) Experimental data. Solid line: result from BiMSA model.

above $\sigma_S^{(1)}$ should be negative so that σ_+ decreases with concentration). On the other hand taking the hydrodynamic diameter for the Br^- anion in acetonitrile (4.76 Å) gave a negative value for $\sigma_S^{(1)}$.

Here too NaI was the only salt studied containing the Na^+ cation. However, the same remarks as in the case of NaI in ethanol may be made here about the uncertainty on the values of the parameters.

5.6. Regressed values of association constants

The adjusted values obtained for K (Table 6) are small for salts in methanol (in the range of 0 to $\sim$ 2.2). They are larger in ethanol (K between $\sim$ 3.5 and 25) and still larger in 2-propanol (from $\sim$ 470 to 640). The higher K value is obtained in the case of LiBr in acetone ($K \sim 5850$).

The regressed K values are all lower than those found in the literature (K_{lit}) except in the case of LiBr in acetone. They are much lower in the case of methanol, a few times smaller in the case of ethanol, and of more comparable magnitude in the case of 2-propanol, acetone and acetonitrile. They may even be vanishingly smaller ($K = 0$) as in the case of NaCl, KBr and KI in methanol. A similar trend has already been mentioned elsewhere [99].

Most literature values for K collected in Table 6 were obtained from conductivity experiments. We now briefly discuss the discrepancy observed between the present regressed K values and those estimated in conductivity.

Basically it must be underlined that conductivity measurements are usually carried out at low or very low salt concentrations, typically in the range of 10^{-4} to 10^{-1} M. This feature may entail non-negligible uncertainties on the K_{lit} values, in particular if they are not very high [99] (as it would be also the case with a thermodynamic model). Moreover different equations may be used to assess the parameters involved in conductivity experiments. These equations may differ in the ingredients employed to describe the effect of deviations from ideality. It must be noted that the latter are more complicated to calculate than those involved in a thermodynamic model at equilibrium because they require not only some static features regarding the ions (such as their sizes and charges) but also some dynamic characteristics of the ions (their

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diffusion coefficients) and also of the solvent (its viscosity).

For these reasons it has been pointed out that the estimation of K values smaller than ~ 12 M^{-1} from conductivity experiments depends on the equation used for their determination and are at the lower end of reliable determination, even when very accurate measurements are available [20]. The K_{lit} values shown in Table 6 are all greater than this limit of 12 M^{-1} but many are not that far from this value (the smallest one is 17.3 M^{-1}). Therefore the uncertainty on these K_{lit} data might be appreciable in the case of solutions in methanol for which they are mostly in the range of 17 to 24 M^{-1}. However it is unlikely that these values could be reconciled with the regressed K values displayed in Table 6, which are much smaller, of the order of unity.

Another, maybe more relevant, remark is that different types of ion-pairing may dominate in solution depending on the concentration at which the experiment is carried out [99]. So it has been observed experimentally using dielectric relaxation spectroscopy that association of LiClO$_4$ in acetonitrile seems to shift from preferential solvent-separated pairs at low concentration to contact ion pairs (CIP's) in concentrated solutions [100]. Therefore different types of association prevailing at low vs. high concentration are likely to lead to different association constants. This might be the case in this work. However, to be confirmed, this point would require a careful experimental study of the systems approached in this work, by using suitable techniques as in ref. [100].

It is also worth mentioning that a description of conductivity experiments in concentrated solutions leads to association constants values that are significantly smaller than with a 'classic' model used for dilute solutions [99].

5.7. MSA cation diameter vs. hydrodynamic diameter

The values of the infinite dilution cation diameters in the case of aqueous solutions (Table 5) together with those in organic solutions (Table 3) are presented in Figure 9. In this figure the MSA diameters $\sigma_+^{(0)}$ are plotted against the Stokes diameters σ_{hyd}. This plot suggests a correlation between the regressed MSA diameter, $\sigma_+^{(0)}$, and the HD, σ_{hyd}. A fit of the points of Figure gives, $\sigma_+^{(0)} = (1.008 \pm 0.026) \times \sigma_{hyd}$.

This result means that the Stokes diameter may provide a good estimate of the MSA diameter for use in the MSA or BiMSA model. This is what has been done in this work in the case of Na$^+$ in ethanol and acetonitrile.

6. Conclusion

A great deal of work has been accomplished in the literature about deviations from ideality in organic electrolyte solutions, mainly by Barthel and collaborators who have greatly contributed to both the experimental and modeling sides. Available experimental data showed that most salts are associated. Models need to account for ion-pairing.

In the present study, the BiMSA model has been applied to describe the osmotic coefficients for solutions of 1-1 salts in organic solvents. By and large, descriptions have been obtained with good accuracy up to the
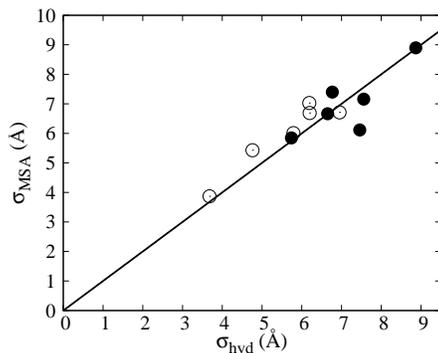
Figure 9: Optimum MSA cation diameters $\sigma_+^{(0)}$ obtained in ref. [35] for aqueous solutions ($\odot$), and in this work for organic solutions ($\bullet$), against the Stokes diameters, σ_{hyd}. The straight line represents the case $\sigma_+^{(0)} = \sigma_{hyd}$.

maximum concentrations to which data are available. The model is developed in terms of parameters that have a physical meaning, such as ion sizes, solution permittivity and association constants.

On the experimental side it would be interesting to acquire more data about the thermodynamic properties of organic electrolyte solutions. For instance the case of salts in solvents of high dielectric constant does not seem to have received much attention. A few solvents may have dielectric constants greater than that of water. Such solvents include formamide, n-methylformamide or n-methylacetamide, for which ε_{org} ranges from ~ 109 to ~ 187 [65].

Moreover, it would be interesting to extend the use of spectroscopic and relaxation techniques, as was done in refs. [65, 100], to a greater number of salts and solvents. This may provide more insight into the nature of ion-pairs that are formed in these solutions, possibly as a function of salt concentration. Depending on the type of association (solvent-separated ion pairs, contact ions pairs, triple ions, etc.) it could be attempted to build a suitable model to describe the structure and the thermodynamic properties of the electrolyte up to high concentrations. Certainly the MSA is a convenient framework to elaborate such models, as exemplified by a few past studies based on the AMSA or BiMSA theories [11, 101, 102].

Lastly, the nature of the solvation of anions in organic solvents does not seem to be quite clear presently. This phenomenon may also deserve further experimental examination in the future.

References

[1] Y. Peng, Z. Zhu, R. D. Braatz, A. S. Myerson, Gypsum crystallization during phosphoric acid production: Modeling and experiments using the mixed-solvent-electrolyte thermodynamic model, Ind. Eng. Chem. Res. 54 (2015) 7914–7924. `doi:10.1021/acs.iecr.5b01763`.

[2] D. Meranda, W. F. Furter, Vapor-liquid equilibrium in alcohol-water systems containing dissolved halide salts and salt mixtures, AIChE J. 18 (1972) 111–116. `doi:10.1002/aic.690180120`.

23

[3] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, Chem. Rev. 104 (2004) 4303–4418. doi:10.1021/cr030203g.

[4] H. Gores, J. Barthel, Nonaqueous electrolyte solutions: New materials for devices and processes based on recent applied research, Pure Applied Chem. 67 (1995) 919–930.

[5] O. F. Tower, A. F. O. Germann, Vapor pressures of certain alcoholic solutions., J. Am. Chem. Soc. 36 (12) (1914) 2449–2456. doi:10.1021/ja02189a003.

[6] A. M. Hayward, E. P. Perman, Vapour pressure and heat of dilution.- Part VII. Vapour pressures of aqueous solutions of sodium hydroxide and of alcoholic solutions of calcium chloride, Trans. Faraday Soc. 27 (1931) 59–69. doi:10.1039/TF9312700059.

[7] R. Mar, R. Carling, The calcium chloride-ethanol system, Thermochim. Acta 45 (1981) 213–217.

[8] J. Barthel, R. Neueder, W. Kunz, Osmotic coefficients of non-aqueous electrolyte solutions at thermodynamic and McMillan-Mayer level, Pure Applied Chem. 65 (1993) 889–894.

[9] J. Barthel, H. Krienke, R. Neueder, M. Holovko, The role of ion-aggregate formation in the calculation of physical properties of electrolyte solutions, Fluid Phase Equilib. 194 (2002) 107–122.

[10] W. R. Fawcett, A. C. Tikanen, Application of the mean spherical approximation to the estimation of electrolyte activity coefficients in methanol solutions, J. Mol. Liq. 73 (1997) 373–384.

[11] J. Barthel, H. Krienke, M. Holovko, V. Kapko, I. Protsykevich, The application of the associative mean spherical approximation in the theory of nonaqueous electrolyte solutions, Condens. Matter Phys. 3 (2000) 657–674.

[12] W. G. McMillan, J. E. Mayer, The statistical thermodynamics of multicomponent systems, J. Chem. Phys. 13 (1945) 276–305.

[13] H. Friedman, Lewis-Randall to McMillan-Mayer conversion for the thermodynamic excess functions of solutions. Part I. Partial free energy coefficients, J. Solution Chem. 1 (5) (1972) 387–412.

[14] B. Pailthorpe, D. Mitchell, B. Ninham, Ion–solvent interactions and the activity coefficients of real electrolyte solutions, J. Chem. Soc. Faraday Trans. 2 80 (1984) 115–139.

[15] J.-P. Simonin, Study of experimental-to-McMillan–Mayer conversion of thermodynamic excess functions, J. Chem. Soc. Faraday Trans. 92 (1996) 3519–3523.

[16] D. Stigter, Interactions in aqueous solutions. II. Osmotic pressure and osmotic coefficient of sucrose and glucose solutions, J. Phys. Chem. 64 (1960) 118–124.

[17] B. Behzadi, B. Patel, A. Galindo, C. Ghotbi, Modeling electrolyte solutions with the saft-vr equation using yukawa potentials and the mean-spherical approximation, Fluid Phase Equilib. 236 (2005) 241 – 255. doi:https://doi.org/10.1016/j.fluid.2005.07.019.

[18] C. Held, A. Prinz, V. Wallmeyer, G. Sadowski, Measuring and modeling alcohol/salt systems, Chemical engineering science 68 (2012) 328–339.

[19] J. Barthel, H. Krienke, W. Kunz, Physical chemistry of electrolyte solutions: modern aspects, Vol. 5 of Topics in physical chemistry, Springer Science & Business Media, Steinkopff, Darmstadt, 1998.

[20] J. Barthel, R. Neueder, G. Lauermann, Vapor pressures of non-aqueous electrolyte solutions. Part 1. Alkali metal salts in methanol, J. Solution Chem. 14 (1985) 621–633.

[21] J. Barthel, G. Lauermann, Vapor pressure measurements on non-aqueous electrolyte solutions. Part 3: Solutions of sodium lodide in ethanol, 2-propanol, and acetonitrile, J. Solution Chem. 15 (1986) 869–877.

[22] J. Barthel, R. Neueder, H. Poepke, H. Wittmann, Osmotic and activity coefficients of nonaqueous electrolyte solutions. 1. lithium perchlorate in the protic solvents methanol, ethanol, and 2-propanol, J. Solution Chem. 27 (1998) 1055–1066.

[23] J. Barthel, R. Neueder, H. Poepke, H. Wittmann, Osmotic coefficients and activity coefficients of nonaqueous electrolyte solutions. Part 4. Lithium bromide, tetrabutylammonium bromide, and tetra-butylammonium perchlorate in acetone, J. Solution Chem. 28 (1999) 1277–1287.

[24] K. Nasirzadeh, R. Neueder, W. Kunz, Vapor pressures, osmotic and activity coefficients of electrolytes in protic solvents at different temperatures. 2. Lithium bromide in ethanol, J. Solution Chem. 33 (2004) 1429–1446.

[25] J. Barthel, G. Lauermann, Vapor pressure measurements on non-aqueous electrolyte solutions. Part 3: Solutions of sodium lodide in ethanol, 2-propanol, and acetonitrile, J. Solution Chem. 15 (1986) 869–877. doi:10.1007/BF00646093.

[26] H. Krienke, J. Barthel, M. Holovko, I. Protsykevich, Y. Kalyushnyi, Osmotic and activity coefficients of strongly associated electrolytes over large concentration ranges from chemical model calculations, J. Mol. Liq. 87 (2000) 191–216.

[27] L. Blum, Simple electrolytes in the mean spherical approximation, in: H. Eyring, D. Henderson (Eds.), Theoretical Chemistry, Advances and Perspectives, Vol. 5, Academic Press: New York, 1980, pp. 1–66.

[28] M. Wertheim, Fluids with highly directional attractive forces. I. Statistical thermodynamics, J. Stat. Phys. 35 (1984) 19–34.

[29] M. Wertheim, Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations, J. Stat. Phys. 35 (1984) 35–47.

[30] L. Blum, O. Bernard, The general solution of the binding mean spherical approximation for pairing ions, J. Stat. Phys. 79 (1995) 569–583.

[31] O. Bernard, L. Blum, Binding mean spherical approximation for pairing ions: an exponential approximation and thermodynamics, J. Chem. Phys. 104 (1996) 4746–4754.

[32] J.-P. Simonin, O. Bernard, L. Blum, Real ionic solutions in the mean spherical approximation. 3. Osmotic and activity coefficients for associating electrolytes in the primitive model, J. Phys. Chem. B 102 (1998) 4411–4417.

[33] J.-P. Simonin, O. Bernard, L. Blum, Ionic solutions in the binding mean spherical approximation: thermodynamic properties of mixtures of associating electrolytes, J. Phys. Chem. B 103 (1999) 699–704.

[34] A. Ruas, P. Moisy, J.-P. Simonin, O. Bernard, J.-F. Dufrêche, P. Turq, Lanthanide salts solutions: Representation of osmotic coefficients within the binding mean spherical approximation, J. Phys. Chem. B 109 (2005) 5243–5248.

[35] J.-P. Simonin, Real ionic solutions in the mean spherical approximation. 2. Pure strong electrolytes up to very high concentrations, and mixtures, in the primitive model, J. Phys. Chem. B 101 (1997) 4313–4320.

[36] W. R. Fawcett, Thermodynamic parameters for the solvation of monatomic ions in water, J. Phys. Chem. B 103 (1999) 11181–11185.

[37] S. Cummings, J. Enderby, G. W. Neilson, J. Newsome, R. Howe, W. Howells, A. Soper, Chloride ions in aqueous solutions, Nature 287 (1980) 714–716.

[38] G. Neilson, J. Enderby, The structure around nitrate ions in concentrated aqueous solutions, J. Phys. C 15 (1982) 2347–2352.

[39] P. Skabichevskii, Osmotic coefficients of lithium chloride and bromide solutions in methanol, Russ. J. Phys. Chem. 43 (1969) 1432–1433.

[40] Y. G. Vlaslov, P. Antonow, Activity of methanol and activity coefficients of salts in sodium choride–methanol and sodium bromide–methanol solutions at 25°c, Russ. J. Phys. Chem. 47 (1973) 1278–1279.

[41] O. Bonner, The colligative properties of certain electrolytes and non-electrolytes in methanol, J. Solution Chem. 16 (1987) 307–314.

[42] P. Tomasula, G. J. Czerwienski, D. Tassios, Vapor pressures and osmotic coefficients: electrolyte solutions of methanol, Fluid Phase Equilib. 38 (1987) 129–153.

[43] M. T. Zafarani-Moattar, K. Nasirzade, Osmotic coefficient of methanol + LiCl, + LiBr, and + LiCH$_3$COO at 25° C, J. Chem. Eng. Data 43 (1998) 215–219. `doi:10.1021/je970193e`.

[44] K. Nasirzadeh, R. Neueder, Measurement and correlation of osmotic coefficients and evaluation of vapor pressure for electrolyte solutions of LiClO$_4$ and LiNO$_3$ in methanol at 25° C, J. Mol. Liq. 113 (2004) 13–20.

[45] K. Nasirzadeh, N. Papaiconomou, R. Neueder, W. Kunz, Vapor pressures, osmotic and activity coefficients of electrolytes in protic solvents at different temperatures. 1. Lithium bromide in methanol, J. Solution Chem. 33 (2004) 227–245.

[46] M. T. Zafarani-Moattar, J. Jahanbin-Sardroodi, Isopiestic determination of osmotic coefficients and evaluation of vapor pressures for electrolyte solutions of some lithium salts in ethanol, Fluid Phase Equilib. 166 (1999) 207–223.

[47] M. T. Zafarani-Moattar, M. Aria, Isopiestic determination of osmotic and activity coefficients for solutions of LiCl, LiBr, and LiNO$_3$ in 2-propanol at 25° C, J. Solution Chem. 30 (2001) 351–363.

[48] M. T. Zafarani-Moattar, J. Jahanbin-Sardroodi, Measurement and correlation of osmotic coefficients and evaluation of vapor pressures for solutions of CaCl$_2$ and Ca(NO$_3$)$_2$ in ethanol at 298 K, Fluid Phase Equilib. 172 (2000) 221–235.

[49] M. Zafarani-Moattar, J. J. Sardroodi, K. Nasirzadeh, Isopiestic determination of osmotic coefficients and evaluation of vapor pressures for solutions of calcium chloride and calcium nitrate in methanol at 298.15 K, Fluid Phase Equilib. 200 (2002) 173–185.

[50] J. Barthel, G. Lauermann, R. Neueder, Vapor pressure measurements on non-aqueous electrolyte solutions. Part 2. Tetraalkylammonium salts in methanol. activity coefficients of various 1-1 electrolytes at high concentrations, J. Solution Chem. 15 (10) (1986) 851–867. `doi:10.1007/BF00646092`.

[51] O. Bonner, Š. Paljk, C. Klofutar, Association studies of tetramethylguanidinium perchlorate and tetramethylguanidinium chloride in ethanol solutions at 25° C, J. Solution Chem. 20 (1991) 539–550.

[52] K. E. N'Tsoukpoe, H. U. Rammelberg, A. F. Lele, K. Korhammer, B. A. Watts, T. Schmidt, W. K. Ruck, A review on the use of calcium chloride in applied thermal engineering, Appl. Therm. Eng. 75 (2015) 513–531.

[53] K. Korhammer, C. Apel, T. Osterland, W. K. Ruck, Reaction of calcium chloride and magnesium chloride and their mixed salts with ethanol for thermal energy storage, Energy Procedia 91 (2016) 161–171.

[54] J. Barthel, R. Neueder, H. Poepke, H. Wittmann, Osmotic coefficients and activity coefficients of non-aqueous electrolyte solutions. Part 2. Lithium perchlorate in the aprotic solvents acetone, acetonitrile, dimethoxyethane, and dimethylcarbonate, J. Solution Chem. 28 (1999) 489–503.

[55] W. Kunz, J. Barthel, L. Klein, T. Cartailler, P. Turq, B. Reindl, Lithium bromide in acetonitrile: thermodynamics, theory, and simulation, J. Solution Chem. 20 (1991) 875–891.

[56] I. Wichterle, J. Linek, Z. Wagner, H. V. Kehiaian, Vapor-liquid equilibrium in mixtures and solutions bibliographic database. EVLM'2003, 5th Edition, Electronic Data (ELDATA), Paris, France, 2003, electronic edition, 1888-2003.

[57] L. Blum, J. Høye, Mean spherical model for asymmetric electrolytes. 2. Thermodynamic properties and the pair correlation function, J. Phys. Chem. 81 (1977) 1311–1316.

[58] B. Maribo-Mogensen, G. M. Kontogeorgis, K. Thomsen, Comparison of the debye–huückel and the mean spherical approximation theories for electrolyte solutions, Ind. Eng. Chem. Res. 51 (2012) 5353–5363.

[59] M. Wertheim, Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and dispheres, J. Chem. Phys. 85 (5) (1986) 2929–2936.

[60] J.-P. Simonin, L. Blum, P. Turq, Real ionic solutions in the mean spherical approximation. 1. Simple salts in the primitive model, J. Phys. Chem. 100 (1996) 7704–7709.

[61] J.-P. Simonin, O. Bernard, L. Blum, Description of the thermodynamic properties of aqueous ionic solutions within the mean spherical approximation, Oil Gas Sci. Technol. 63 (2008) 321–327.

[62] W. R. Fawcett, A. C. Tikanen, Role of solvent permittivity in estimation of electrolyte activity coefficients on the basis of the mean spherical approximation, J. Phys. Chem. 100 (1996) 4251–4255.

[63] L. Blum, F. Vericat, W. R. Fawcett, On the mean spherical approximation for hard ions and dipoles, J. Chem. Phys. 96 (1992) 3039–3044.

[64] L. Blum, F. Vericat, W. R. Fawcett, Erratum: On the mean spherical approximation for hard ions and dipoles [J. Chem. Phys. 96, 3039 (1992)], J. Chem. Phys. 101 (1994) 10197–10197. doi:10.1063/1.468516.

[65] J. Barthel, H.-J. Gores, G. Schmeer, R. Wachter, Non-aqueous electrolyte solutions in chemistry and modern technology, in: Physical and Inorganic Chemistry, Vol. 111 of Topics in current chemistry, Springer Berlin Heidelberg, Berlin, Heidelberg, 1983, pp. 33–144. doi:10.1007/3-540-12065-3_2.

[66] R. D. Nelson Jr, D. R. Lide Jr, A. A. Maryott, Selected values of electric dipole moments for molecules in the gas phase, Tech. rep., National Standard Reference Data System, NBS (1967).

[67] C. Gray, K. Gubbins, Theory of molecular fluids, Vol. 1, Clarendon Press, Oxford, 1984.

[68] O. Söhnel, P. Novotnỳ, Densities of aqueous solutions of inorganic substances, Vol. 22, Elsevier Publishing Company, Amsterdam, 1985.

[69] R. Larson, H. Hunt, Molecular forces and solvent power, J. Phys. Chem. 43 (1939) 417–423.

[70] W. C. Vosburgh, L. Connell, J. Butler, The electrostriction produced by salts in some aliphatic alcohols, J. Chem. Soc. (1933) 933–942.

[71] M. T. Zafarani-Moattar, H. Shekaari, Density and speed of sound of lithium bromide with organic solvents: Measurement and correlation, J. Chem. Thermodyn. 39 (2007) 1649–1660.

[72] A. J. Pasztor, C. M. Criss, Apparent molal volumes and heat capacities of some 1:1 electrolytes in anhydrous methanol at 25° C, J. Solution Chem. 7 (1978) 27–44.

[73] L. Werblan, A. Rotowska, S. Minc, Viscosity of water-methanol solutions of $LiClO_4$, $NaClO_4$ and NaCl, Electrochim. Acta 16 (1971) 41–59.

[74] R. R. Pawar, C. S. Aher, J. D. Pagar, S. L. Nikam, M. Hasan, Solubility, density and solution thermodynamics of NaI in different pure solvents and binary mixtures, J. Chem. Eng. Data 57 (2012) 3563–3572.

[75] W. Cox, J. Wolfenden, The viscosity of strong electrolytes measured by a differential method, Proc. Roy. Soc. A 145 (1934) 475–488.

[76] R. Tomkins, E. Andalaft, G. Janz, Conductance, density, and viscosity of nai in anhydrous acetonitrile at 25° c, Trans. Faraday Soc. 65 (1969) 1906–1911.

[77] R. Robinson, R. Stokes, Electrolyte Solutions, Butterworths, London, 1968.

[78] R. Jervis, D. Muir, J. Butler, A. Gordon, The conductance at 25° of lithium chloride, sodium and potassium bromides and potassium iodide in methanol, and of lithium chloride, sodium bromide and potassium iodide in water, J. Am. Chem. Soc. 75 (1953) 2855–2858.

[79] J. Barthel, M. Krell, L. Iberl, F. Feuerlein, Conductance of 1-1 electrolytes in methanol solutions from -45 to +23° C, J. Electroanal. Chem. Interf. Electrochem. 214 (1986) 485–505.

[80] J. Graham, G. Kell, A. Gordon, Equivalent and ionic conductances for lithium, sodium and potassium chlorides in anhydrous ethanol at 25°, J. Am. Chem. Soc. 79 (1957) 2352–2355.

[81] N. Schmelzer, J. Einfeldt, M. Grigo, Measurements of the electrolyte conductivity of alkali-metal perchlorates and $LiNO_3$ in acetone at 25° C, J. Chem. Soc. Faraday Trans. 1 84 (1988) 931–939.

29

[82] D. F. Evans, J. Thomas, J. A. Nadas, S. M. A. Matesich, Conductance of electrolytes in acetone and in 1-propanol-acetone mixtures at 25°, J. Phys. Chem. 75 (1971) 1714–1722.

[83] H. P. Hopkins, D. Jahagirdar, A. B. Norman, Conductance studies on lithium salt-acetonitrile solutions at 25° C, J. Solution Chem. 8 (1979) 147–155.

[84] H. P. Hopkins Jr, A. B. Norman, Conductance and infrared studies on acetonitrile solutions containing crown ethers and alkali metal salts, J. Phys. Chem. 84 (1980) 309–314.

[85] J. Coetzee, G. Cunningham, Evaluation of single ion conductivities in acetonitrile, nitromethane, and nitrobenzene using tetraisoamylammonium tetraisoamylboride as reference electrolyte, J. Am. Chem. Soc. 87 (1965) 2529–2534.

[86] J. E. Huheey, E. A. Keiter, R. L. Keiter, O. K. Medhi, Inorganic chemistry: principles of structure and reactivity, Pearson Education India, 2006.

[87] H. Jenkins, K. Thakur, Reappraisal of thermochemical radii for complex ions, J. Chem. Educ. 56 (9) (1979) 576.

[88] B. Conway, The evaluation and use of properties of individual ions in slution, J. Solution Chem. 7 (1978) 721–770.

[89] Z. Chen, M. Hojo, Relationship between triple ion formation constants and the salt concentration of the minimum in the conductometric curves in low-permittivity solvents, J. Phys. Chem. B 101 (1997) 10896–10902.

[90] P. K. Muhuri, B. Das, D. K. Hazra, Ionic association of some lithium salts in 1,2-dimethoxyethane. A Raman spectroscopic and conductivity study, J. Phys. Chem. B 101 (1997) 3329–3332.

[91] M. Delsignore, H. Farber, S. Petrucci, Ionic conductivity and microwave dielectric relaxation of lithium hexafluoroarsenate ($LiAsF_6$) and lithium perchlorate ($LiClO_4$) in dimethyl carbonate, J. Phys. Chem. 89 (1985) 4968–4973.

[92] J. Barthel, R. Neueder, Conductivities, transference numbers, limiting ionic conductivities (of methanol solutions), in: Electrolyte Data Collection, Vol. XII, part 1 of DECHEMA Chemistry Data Series, DECHEMA, Frankfurt am Main, 1992.

[93] E. Bixon, R. Guerry, D. Tassios, Salt effect on the vapor pressure of pure solvents: Methanol with seven salts at 24.9 °C, J. Chem. Eng. Data 24 (1979) 9–11. `doi:10.1021/je60080a005`.

[94] J. Barthel, R. Neueder, Conductivities, transference numbers, limiting ionic conductivities of ethanol solutions, in: Electrolyte Data Collection, Vol. XII, part 1a of DECHEMA Chemistry Data Series, DECHEMA, Frankfurt am Main, 1993.

[95] L. G. Savedoff, Conductance of electrolytes in anhydrous acetone, J. Am. Chem. Soc. 88 (1966) 664–667.

[96] C. W. Jones, C. M. Cunningham, Electrolytic Conductance of Lithium Bromide in Acetone and Acetone-Bromosuccinic Acid Solutions, Vol. 155 of Adv. Chem., American Chemical Society, 1976, Ch. 14, pp. 244–262. `doi:10.1021/ba-1976-0155.ch014`.

[97] M. S. K. Niazi, Conductance of electrolytes in dipolar aprotic solvent mixtures. II. Conductance of lithium perchlorate in mixtures of ethyl methyl ketone and acetone with n,n-dimethylformamide at 25°C, Bull. Chem. Soc. Jpn. 61 (1988) 2165–2170. `doi:10.1246/bcsj.61.2165`.

[98] P. G. Glugla, J. H. Byon, C. A. Eckert, Pressure effects on conductivity and ionic association of some monovalent salts in aprotic dipolar solvents, J. Chem. Eng. Data 26 (1981) 80–84.

[99] J. Barthel, H. Graml, R. Neueder, P. Turq, O. Bernard, Electrolyte conductivity from infinite dilution to saturation, Curr. Top. Solution Chem. 1 (1994) 223–239.

[100] J. Barthel, R. Buchner, P.-N. Eberspächer, M. Münsterer, J. Stauber, B. Wurm, Dielectric relaxation spectroscopy of electrolyte solutions. recent developments and prospects, J. Mol. Liq. 78 (1) (1998) 83 – 109. `doi:http://dx.doi.org/10.1016/S0167-7322(98)00085-3`.

[101] T. Vilariño, O. Bernard, J.-P. Simonin, Ionic solutions in the binding mean spherical approximation. Thermodynamics of associating electrolytes up to very high concentrations, J. Phys. Chem. B 108 (2004) 5763–5770.

[102] S. Hlushak, J. P. Simonin, S. De Sio, O. Bernard, A. Ruas, P. Pochon, S. Jan, P. Moisy, Speciation in aqueous solutions of nitric acid, Dalton Trans. (2013) 2853–2860 `doi:10.1039/C2DT32256K`.