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Pseudolattice Theory of Ionic Liquids

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1. Introduction

In this chapter we summarize the main features of the pseudolattice theory of ionic fluids, starting with the experimental evidence of the existence of this kind of structural arrangement in these systems. The so-called Bahe-Varela formalism of concentrated electrolyte solutions is reviewed, and its generalization to transport phenomena introduced. On the other hand, the pseudolattice approach to equilibrium and transport properties of pure room temperature molten salts (ILs) and their mixtures with molecular fluids is analyzed. Particularly, pseudolattice theory is seen to provide an adequate understanding of both volumetric and surface properties of ionic liquid mixtures, as well as of electrical and thermal transport in these systems.

Charged complex fluids play a leading role among the systems which comprise the whole category of complex fluids, a category that essentially covers the whole spectrum of liquid matter. The presence of charges –and consequently of central, long-ranged interaction potentials- tends to make objects soluble in water, and so structures and processes involving electrostatic interactions are ubiquitous in soft matter and play an important role in colloidal, polymeric, and biological systems (Boroudjerdi et al., 2005) The Coulomb interaction, the main contribution to the intermolecular potential, is responsible for most part of the properties of these systems, including homogeneization of molecular structures and the existence of concentration gradients and mesoscopic structures among others. Thus, the importance of this system in many theoretical and applied fields is beyond any doubt, and therefore, it is not surprising that very few topics in the field of physical chemistry have attracted so much attention as that of equilibrium and transport properties of ionic fluids. The paradigm of charged complex fluid is the ionic liquid, a category which comprises liquid metals, high-temperature and room-temperature molten salts, and ionic solutions.

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Among these, in this chapter we shall focus our attention essentially in the latter and in room-temperature molten salts (or simply referred to as ionic liquids, ILs).

Ionic solutions are neutral systems formed by a solute of positive and negative ions immersed in a neutral polar solvent. This category includes systems of very different complexity degree, ranging from electrolyte solutions with cations and anions of comparable size and charge, to highly asymmetric macromolecular ionic liquids in which macroions (polymers, micelles, proteins…) coexist with microscopic counterions. Undoubtedly, electrolyte solutions represent the model system for the whole category, and they were the first to concentrate research attention in the final part of the XIXth century and the beginning of XXth century. Due to the works of Kohlrausch, Lewis and other pioneers, it soon became clear that these systems have equilibrium and transport properties that greatly differ from those of conventional non-electrolyte systems.

Gouy and Chapman (GC) for inhomogeneous solutions (electric double layer) (Gouy, 1910; Chapman, 1913), and Debye and Hückel for homogeneous ones (Debye & Hückel, 1923), reported the theoretical framework for an adequate understanding of the behavior of ionic solutions. Particularly, the latter provided an essentially correct theoretical understanding of the thermodynamics of electrolyte solutions. Introducing the concept of the ionic atmosphere, they were able to show that the electrostatic potential created by an ion in the bulk solution is screened by the charges in its surroundings, the screening length being controlled by the ionic concentration of the solution. This screened potential is on the basis of the well-known universal law that the activity coefficients of electrolyte solutions obey at extremely low concentrations (Debye-Hückel limiting law), which states the proportionality of the logarithm of the average activity coefficient to the squared-root of concentration. This law for binary ionic solutions reads

$$ln\gamma_\pm = -\frac{k_D}{2}\frac{|q_+q_-|}{\varepsilon k_B T} \tag{1}$$

where k_D is Debye's parameter or Debye's screening constant, $q_{+(-)}$ is the cation (anion) charge, ε is the dielectric constant of the solvent (since Debye-Hückel mean-field theory is formulated in the framework of the primitive model of solutions, the solvent is assumed to provide only a uniform, structureless background), and $k_B T$ is the thermal energy. The Debye parameter is proportional to the square root of the ionic concentration

$$k_D^2 = \frac{1}{\varepsilon k_B T}\sum_{i=1}^{s} n_i q_i^2 \tag{2}$$

where n_i stands for the number density of ions of the i-th species, and the sum extends to all the species present in the bulk solution. This parameter controls the spatial range of the electrostatic interactions in the solution, since the electrostatic potential created by an ion immersed in a statistically distributed ensemble of ions is

$$\psi_i(r) = \frac{q_i}{4\pi\varepsilon}\frac{e^{-k_D r}}{r} \tag{3}$$

The inverse of the screening constant is called the Debye length, and it determines the range of the electrostatic interactions and, consequently, the size of the ionic atmosphere.

Debye-Hückel universal limiting law supposed a revolution in the understanding of the physics of ionic systems, and undoubtedly constitutes a major achievement of XXth century physics. It has been shown to be exact on statistical mechanical grounds by Kirkwood and Poirier (Kirkwood & Poirier, 1954) and the limit of validity of the Debye-Hückel model (in distinction to that of their mathematical approximations) has been set by Frank and Thompson (Frank & Thompson, 1959) at about 0.001 M (mole l[-1]) for aqueous solutions of 1:1 electrolytes at 25 °C, the concentration limit at which the thickness of the ionic cloud equals the average interionic distance. On the basis of this structural model of ionic solutions, the thermodynamic properties of extremely dilute ionic solutions have been successfully understood including surface properties (see, for example, the classic books of Harned and Owen (Harned & Owen, 1958) and of Robinson and Stokes (Robinson & Stokes, 1959) for a detailed overview of classical theory of electrolyte solutions). Nowadays, mean-field, Poisson Boltzmann (PB) equation-based theories which provide simple, elegant expression that can be applied in practical situations continue to be the most frequently used to describe ionic fluids, despite the huge amount of contributions to the field of ionic solutions reported during the last century, that include different extensions of the Debye-Hückel formalism, integral equation techniques, field theory studies and computer simulation results (for a review, see (Varela et al., 2003) and references therein). Indeed, the mean-field approach is very successful in describing qualitatively (and usually also quantitatively) experiments and simulation in Coulomb systems because every ion interacts with many other ions simultaneously. This is the reason why mean-field approximations, despite ignoring ion-ion correlations, continue to be the basis of the theoretical understanding of many phenomena like ionic and colloidal stability, electrolyte solutions thermodynamics and phase transitions in ionic fluids.

On the other hand, almost all our theoretical understanding of charge transport in ionic fluids is almost completely constrained to dilute ionic solutions, for which the so called Debye-Hückel-Onsager or Onsager-Fuoss theory was originally developed (for the series of results which constitute this theory see (Fuoss et al, 1965) and references therein). This framework is built on the structural basis of the Debye-Hückel model of ionic solutions, and therefore the basic structural feature continues to be the ionic atmosphere. According to the Debye-Hückel-Onsager theory, the perturbation of this structure by the external electric field provokes that the field actually experienced by an ion in the bulk differs from the external one due to the existence of an internal or relaxation field associated to the loss of spherical symmetry of the ionic cloud. Moreover, the ion-solvent interactions cause the solvent to be dragged during the motion of an ion together with its ionic cloud, so the motion does not take place in a medium at rest. This effect is known as electrophoretic effect, and together with the relaxation field, is responsible for the concentration-dependent decrease of the ionic mobilities with respect to their limiting values. Once again, both effects are proportional to the Debye parameter $k_D \sim c^{1/2}$ and therefore to the square-root of the ionic concentration, c, and this behavior is extrapolated to the ionic mobilities in solution. This leads to the so-called Onsager limiting law of ionic conductance

$$\Lambda = \Lambda^0 - S_\Lambda c^{1/2} \qquad (4)$$

where Λ^0 is the limiting conductance, and S_Λ is a concentration-independent coefficient peculiar to each electrolyte type. This universal law allowed an adequate understanding of the detailed conductivity measurements performed by Kolhrausch in the late nineties of the

XIXth century (Harned & Owen, 1958), and has been repeatedly verified for highly dilute ionic solutions.

As stated above, the central concepts in the Debye-Hückel theory of homogeneous electrolyte solutions, and in Gouy-Chapman theory of inhomogenous ionic solutions are the ionic atmosphere (Debye-Hückel, homogeneous case) or the electrical double layer (Gouy-Chapman, inhomogeneous case). These inhomogeneities in the distribution of charge in the bulk solution are associated to local electroneutrality and they provide the structural tools for the understanding of these systems in the dilute concentration regime. Moreover, it is now well-stated that the mean-field Poisson-Boltzmann formalism can be extended to regions where it should not be qualitatively valid (Varela et al. 2003; Kjellander & Mitchell, 1992; Kjellander & Mitchell, 1994; Attard, 1993; McBride et al, 1998; Varela et al. 1998; Varela et al. 1999,a,b). Indeed, an effective, formally exact mean-field theory can be defined where the screening length and charges are renormalized from their bare values (Varela et al., 2003). Using these extensions, the Poisson-Boltzmann formalism can be extended in order to treat solutions of very high ionic concentrations for which the interionic correlations must be considered.

However, it has long been known that the preservation of the continuous ionic atmosphere underlying the Poisson-Boltzmann formalism at concentrations beyond 0.01 M is doubtful since, as pointed out by Bockris (Bockris, 2000), at this concentration "*only one ion produces the 50% of the effect of the ionic atmosphere on the central io*n" and it is to be smeared out over a sphere of about 25 Å. In order to interpret the X-ray diffraction patterns of concentrated electrolyte solutions, Prins suggested long ago (Prins, 1935) the existence of medium range correlations in the positions of heavy ions in solution. Frank and Thompson (Frank & Thompson, 1959a,b) suggested that the structure of the ionic solution must vary with concentration: a continuous ionic cloud model is correct for very dilute solutions, but a disordered lattice model would be more satisfactory at intermediate and high concentrations and lead to a cube-root law in salt concentration for the logarithm of the activity coefficient. Robinson and Stokes (Robinson & Stokes, 1959) included experimental evidence of the existence of a lattice arrangement in concentrated NaCl solutions and a short description of a pseudolattice model in their classical book in electrolytes. Beck (Bahe, 1972a) reported X-ray data for concentrated solutions of LiBr (up to 12.3 M) and LiCl (up to 13.3 M). The curves of LiBr and LiCl showed distinct peaks at about $2\theta = 21^o$ and $2\theta = 19^o$ with unit cell lengths of face-centered-cubic structures at maximum concentrations of 8.14 and 7.94 Å respectively. Moreover, Hyman and Vaughn (Hyman and Vaughn, 1967) reported the dispersion curves for aqueous solutions of chloroplatinic acid, and they showed that the X-ray diffracting anions can be examined as an fcc lattice with a unit cell length of the corresponding fluorite cell, a fact this compound shares with all the other 1:2 and 2:1 electrolytes (Bahe, 1972a,b; Bahe & Parker, 1975). Desnoyers and Conway (Desnoyers & Conway, 1964) experimentally demonstrated the validity of the cube-root law both for 1:1 electrolyte solutions and for 1:2 electrolyte solutions, although in this latter case they suggested that corrections for finite size of the ions must be taken into account because the distance of closest approach is important for highly hydrated ions and multivalent ions. To end this list of experimental evidence of the existence of loose-lattice structure in ionic solutions, we must mention a series of papers which started in the beginnings of the 60's and still continues nowadays (see for example (Alves Marques et al., 2007) and references therein). In this series, Alves Marques and collaborators demonstrated the existence of "*well-*

defined positional correlations of the ions of the larger valence in concentrated aqueous solutions" by means of Raman spectroscopy, neutron scattering and X-ray scattering.

The result which constitutes the basis of the contemporary pseudolattice theory of ionic solutions is due to Lowell W. Bahe (Bahe, 1972a). In this paper the author reports a qualitatively and quantitatively correct interpretation of the thermodynamic properties of concentrated electrolyte solutions in terms of the existence of a statistical arrangement of the ions in the bulk –in agreement with X-ray data- induced by long-range Coulomb interactions and dielectric constant gradients. He provided an essentially correct deduction of the cube-root law which was known to fit activity coefficient data down to concentrations as low as 0.01 M and even lower, taking into account Coulomb forces and the interactions between the electric fields of the ions and the gradient of dielectric constant near the surface of ions in solution induced by their electric fields.

In 1997 Varela et al. (Varela et al., 1997) generalized Bahe's theory introducing short-range ion–ion interactions in the pseudolattice formalism modeling them by a hard-core potential with an attractive tail representing van der Waals interactions. The resulting theory is capable of describing the thermodynamic and transport properties of highly concentrated solutions in a satisfactory manner. Indeed, as we shall see later, the validity of this theoretical framework extends almost to the whole concentration range of electrolyte solutions and IL mixtures (excluding extremely diluted solutions, where the previously revisited Debye-Hückel limiting law applies).

After 1997, other pseudolattice approaches to equilibrium properties of electrolyte solutions deserve some comment. Moggia and Bianco (Moggia & Bianco, 2007; Moggia, 2008) provided expressions for the activity and osmotic coefficients following a pseudolattice approach. The authors assumed that the solute ions evolve from a disordered lattice model within a continuous solvent at extremely dilute solutions to a disordered lattice of local arrangements of both solute ions and solvent dipoles at higher concentrations, and they were able to satisfactorily explain the thermodynamic properties of these systems.

On the other hand, in what transport theory is concerned, very limited activity has been registered. Indeed, up to our knowledge, until this year 2010, the only reported results are those due to the group of D. Lemordant and coworkers in Tours (Chagnes et al., 2001; Chagnes et al., 2002; Chagnes et al., 2003), who showed that if the Debye constant corresponding to an ionic cloud model is replaced by the average distance between ions,

$$k_D \rightarrow R = \left(\frac{V}{N}\right)^{\frac{1}{3}} = M'' \left(\frac{2N_A c}{1000}\right)^{-\frac{1}{3}} \tag{5}$$

where M'' is a Madelung–like constant for the pseudolattice, N_A is Avogadro's number and c the molar concentration of the solution, then the Debye-Hückel-Onsager result in Eq. (4) leads to an expression for the electrical conductance

$$\Lambda = \Lambda^{0'} - S_\Lambda' c^{1/3} \tag{6}$$

Indeed, at concentrations higher than 0.2 M, the authors proved that the molar conductivity of aqueous (Chagnes et al, 2001) and non-aqueous (Chagnes et al., 2002) solutions of LiClO$_4$ follows a $c^{1/3}$ law, reflecting the underlying lattice-like arrangement of the ions of this strong binary electrolyte. Moreover, the experimental value found by these authors for the slope of the conductance vs. $c^{1/3}$ plot was in good agreement with the calculated one.

As it is perfectly known, room temperature molten salts or ionic liquids (ILs) are charged complex fluids formed exclusively by ions. They can be seen as an infinitely concentrated electrolyte solution, and one can think about these systems as the opposite limit to that of the applicability of the DH theory of ions solutions. It is well-known that a polar network exists in these systems, as can be seen for example in (Wei Jiang et al., 2007), so, from the theoretical perspective, one expects that a pseudolattice model is particularly well adapted to the peculiarities of ILs. Indeed, Turmine and coworkers (Bou Malham et al., 2007; Bouguerra et al. 2008) proved that the so called Bahe-Varela (BV) pseudolattice theory of electrolyte solutions is capable of accounting for the thermodynamic properties of binary and ternary mixtures of ILs up to the limit of pure IL.

The structure of this chapter is as follows. The next section is devoted to the presentation of the main features of the BV theory, and in section 3 we present some experimental results concerning equilibrium and transport properties of ionic solutions and ILs analyzed in this theoretical framework. Finally, in section 4 we summarize the main conclusions of the chapter.

2. Theoretical section

Let us consider an aqueous binary electrolyte solution of type $z_+ : z_-$, charge density ρ, and mass density ρ_m. We shall adopt a primitive model description of the bulk solution, assuming a continuous model for the solvent and that the only relevant property with which it contributes to the problem is its dielectric constant, ε. Moreover, the ions are assumed to be incompressible spheres with charge located at the center. The volume force vector acting on a region of space in a dielectric is given by (Panofsky & Phillips, 1977)

$$\vec{F} = \rho\vec{E} - \frac{1}{2}E^2\vec{\nabla}\varepsilon + \frac{1}{2}\vec{\nabla}\left(E^2\frac{d\varepsilon}{d\rho_m}\rho_m\right) \tag{7}$$

The first term on the right hand side of the above equation is the standard Coulomb term and the second one stands for the coupling of the electric field in the bulk solution with the gradient of dielectric field in the region. On the other hand, the third term is the electrostriction term which can be ignored –as we shall do in the rest of the chapter- for incompressible fluids. Considering the region of the ionic solution between an anion and a cation whose centers are separated by a distance R*, we can obtain the force acting on the anion integrating Eq. (7) in the relevant volume. For what the first term on the right hand side of that equation is concerned,, the integration region corresponds to that where the charge generating the field (the cation in our case) is placed, and the integration region for the second term on the right is that containing a gradient in the dielectric constant. In this region, of approximately 3 Å deep as shown by Padova (Padova, 1963), and known as the dielectric sea, the transition between the dielectric constant of bulk water to that of the ions takes place. The integral of the first term immediately leads to the conventional Coulomb force between the ions,

$$\int_V \rho E\, dV = \frac{q_+ q_-}{4\pi\varepsilon}\frac{1}{R^{*2}}. \tag{8}$$

On the other hand, as shown by Bahe in the Appendix to the first of his 1972 papers, to a first approximation the integral in the volume of the dielectric sea of the second term in the right hand side of Eq. (7) leads to the following form for the field-dielectric-gradient force between the two ions along the line of centers:

$$-\int_V E^2 \vec{\nabla}\varepsilon \, dV = \frac{3q_+^2}{32\pi^2\varepsilon_0^2} \left|\frac{d\varepsilon}{dR^*}\right| V_{sea} \frac{1}{R^{*4}}. \tag{9}$$

The total force acting on the anion in an incompressible fluid is obtained from the addition of Eqs. (8) and (9), and the Helmholtz free energy of interaction of the two ions can be straightforwardly proved to be

$$F(T,V) = \frac{q_+ q_-}{4\pi\varepsilon R^*} + \frac{q_+^2}{32\pi^2\varepsilon_0^2} \left|\frac{d\varepsilon}{dR^*}\right| V_{sea} \frac{1}{R^{*3}}. \tag{10}$$

As pointed out by Bahe (Bahe, 1972a), this Helmholtz free energy is essentially identical to the Gibbs free energy for ionic solutions.

Taking now into account the previously mentioned experimental facts about the existence of loose lattice structures in electrolyte solutions, the electrical contribution to the free energy of the ions can be calculated from Eq. (10) just by inserting a Madelung constant, A'', in the Coulomb term and a Madelung-like constant, B'', in the second term on the right hand side to give

$$\frac{G_{el}}{N} = A'' \frac{q_+ q_-}{4\pi\varepsilon R^*} + B'' \frac{q_+^2}{32\pi^2\varepsilon_0^2} \left|\frac{d\varepsilon}{dR^*}\right| V_{sea} \frac{1}{R^{*3}} \tag{11}$$

One must recall that R^* represents the minimum distance between cations and anions in the loose lattice fcc structure, so for a binary electrolyte solution it can be replaced by

$$R^* = \left(\frac{V}{N}\right)^{\frac{1}{3}} = \left(\frac{2N_A c}{1000}\right)^{-\frac{1}{3}}, \tag{12}$$

Thus, it is straightforward to obtain the expression for the rational activity coefficient of the electrolyte solution

$$ln f_{\pm} = \frac{G_{el}}{2RT} = -Ac^{1/3} + Bc \quad 2RT ln f_{\pm} = G_{el} = -Ac^{1/3} + Bc, \tag{13}$$

being R the gas constant, and the constants A and B given by

$$A = A'' \frac{q_+ q_-}{8\pi\varepsilon RT} \left(\frac{2N_A}{1000}\right)^{\frac{1}{3}}$$
$$B = B'' \frac{q_+^2}{64\pi RT\varepsilon_0^2} \left|\frac{d\varepsilon}{dR}\right| V_{sea} \frac{2N_A}{1000} \tag{14}$$

As noted by Bahe, A=0.28894 at 298,15 K in H_2O, and B could be estimated but is normally used as a fitting parameter. Simple as it is, Eq. (13) contains the whole thermodynamic

properties of the solutions[2], and it somehow culminated five decades of efforts devoted to get a clear understanding of the microscopic origin of the cube-root law for thermodynamic properties of electrolyte solutions. This result allowed Bahe to give an adequate interpretation to the huge number of observations of activity coefficients of electrolyte solutions reported during precedent decades, and also of other magnitudes of aqueous solutions of 1:1 electrolytes such as the relative partial molar enthalpies and heats of dilution (Bahe, 1972b). 1:2 and 2:1 electrolytes were also considered by Bahe in collaboration with D. Parker (Bahe & Parker, 1975), who proved that the activity coefficients of these asymmetric electrolytes can be accurately fitted by Eq. (13) considering now that the ions form a loose fluorite-like structure.

Successful as it proved to be, the original formalism of Bahe could not give account of the thermodynamic properties of highly concentrated electrolyte solutions. Indeed, the theory is not able to fit the experimental data of 1:1 electrolytes beyond 4 M, and of 1:2 electrolytes beyond 3 M. For more concentrated solutions, deviations of the activity coefficients experimental results from the prediction of Eq. (13) are registered due to the influence of short-ranged, non-coulombic interactions, essentially hard sphere repulsions and van der Waals attraction forces. As the concentration of the electrolyte solution increases, the average distance between ions decreases, so the short-range interactions between them become progressively more important with respect to their Coulomb counterparts. In 1997, Varela et al. (Varela et al., 1997) introduced short-range ion–ion interactions in the pseudolattice formalism modeling them by a hard-core potential with an attractive tail. Indeed, the authors considered an interaction potential $U^{SR}(r_{ij})$ modeling short-range ion–ion forces in solutions by a hard-core potential and an attractive tail representing van der Waals interactions. Assuming a restricted primitive model (RPM) description, all the ions were treated in this article as having the same hard-core radius, $r_m = (r_+ + r_-)/2$, where r_+ and r_- are the radii of cations and anions, respectively. The energy of interaction between ions i and j separated by a distance r_{ij} is

$$U^{SR}(r_{ij}) = \begin{cases} -\dfrac{\Lambda}{r_{ij}^6} & r_{ij} > r_m \\ \infty & r_{ij} \leq r_m \end{cases} \tag{15}$$

The attractive tail of the potential defined in the above result includes attractive dispersive London forces together with permanent dipole–permanent dipole (Keesom) and permanent dipole-induced dipole (Debye) forces, if any of the ions in the bulk has a permanent dipole. Thus, the constant Λ in Eq. (15) is formed by the contribution of three terms, $\Lambda = \Lambda_{Keesom} + \Lambda_{Debye} + \Lambda_{London}$. London dispersion interaction takes place between dipoles instantaneously induced in the ions, arising from fluctuations in the electronic charge cloud of an ion caused by the electric field created by another one in its neighbourhood. Recalling the quantum mechanical theory of dispersion forces, the dispersive interaction energy between two dipoles is given by (Cohen-Tannoudji et al., 2006)

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[2] However, it is interesting to note that the activity coefficient (equivalently, the Gibbs free energy) is not expressed in terms of its natural variables T,P,N, but it instead contains the volume as a variable, so this result cannot be considered to be a proper expression of a thermodynamic potential.

$$U^{disp}(r_{ij}) = -\frac{3\alpha_i\alpha_j I_i I_j}{4\pi\varepsilon(I_i+I_j)}\frac{1}{r_{ij}^6},$$ (16)

so the constant Λ in Eq. (15) can be straightforwardly deduced from the above result. Recalling that in the pseudolattice formalism, $r_{ij} = a_{ij}R$, then $U^{disp}(r_{ij}) \sim c^2$. The same applies to Keesom and Debye forces in the case of ions with permanent dipoles, since both them show the same dependence on the interionic distance as that of the London interaction (Israelachvili, 1992).

In their original 1997 paper, Varela et al. proved that the contributions of both hard sphere repulsive part of the interionic potential, and that of the van der Waals forces to the activity coefficient are given by

$$lnf_{\pm}^{att} = -\frac{\Lambda D'' \nu N_A^3}{2.10^6 RT a_A^6}c^2$$ (17)
$$lnf_{\pm}^{HS} = 2.2063 \times 10^{-3} r_m^3 c + 2.6269 \times 10^{-6} r_m^6 c^2,$$

where $D'' = \sum_{ij} a_{ij}^{-6}$ is a Madelung-like constant. Consequently, combining the above expression with that in Eq. (13) we get

$$lnf_{\pm} = \frac{G_{el}}{2RT} = -Ac^{1/3} + Bc + Dc^2$$ (18)

The above result states that at high concentrations the rational activity coefficient exhibits quadratic concentration dependence rather than the linear one predicted by Bahe's purely electrostatic pseudolattice treatment. As can be seen in Table I, this dependence can be proved to be valid for several electrolytes (Varela et al., 1997), where $lnf_{\pm} + Ac^{1/3} - Bc$ is fitted to Dc^x. As can be seen in the table, Varela et al. obtained that, for several 1:1 and 1:2 electrolytes, the calculated exponent is $x=2$, within the limits of experimental uncertainty for all the analyzed data.

Electrolyte	x
$HClO_4$	2.05 ± 0.03
HNO_3	1.93 ± 0.05
LiBr	1.93 ± 0.05
$LiNO_3$	1.90 ± 0.10
NaOH	2.00 ± 0.20
KCl	1.80 ± 0.20
NaBr	2.04 ± 0.04
$MgCl_2$	2.01 ± 0.02
$MnCl_2$	2.04 ± 0.04

Table 1. Results of fitting $lnf_{\pm} + Ac^{1/3} - Bc$ to Dc^x for several 1:1 and 1:2 electrolytes (Varela et al., 1997).

Considering short range forces, Varela et al. were able to fit reported activity coefficient for symmetric 1:1 and asymmetric 1:2 and 2:1 electrolytes up to concentrations of 14 M (LiBr,

HNO_3, $HClO_4$) and 6 M respectively. Moreover, they were able to give quantitative account of the relative partial molar enthalpies of these strong electrolyte solutions in terms of expressions quadratic in the molar concentration.

Fig. 1 shows previously reported data of the molar dependence of the relative partial molar enthalpy of KF (Lobo, 1990), together with the predictions of the above equation and those of Bahe original formalism. As one can see, the relative partial molar enthalpies of concentrated KF solutions are completely impossible to be reproduced by a linear equation such as that predicted in Bahe original formalism. However, the quadratic term associated to short-range interactions in the bulk solution allows the theoretical prediction of the experimental results up to high concentrations. In this way, the role of short-range interactions in highly concentrated electrolyte solutions is completely clarified.
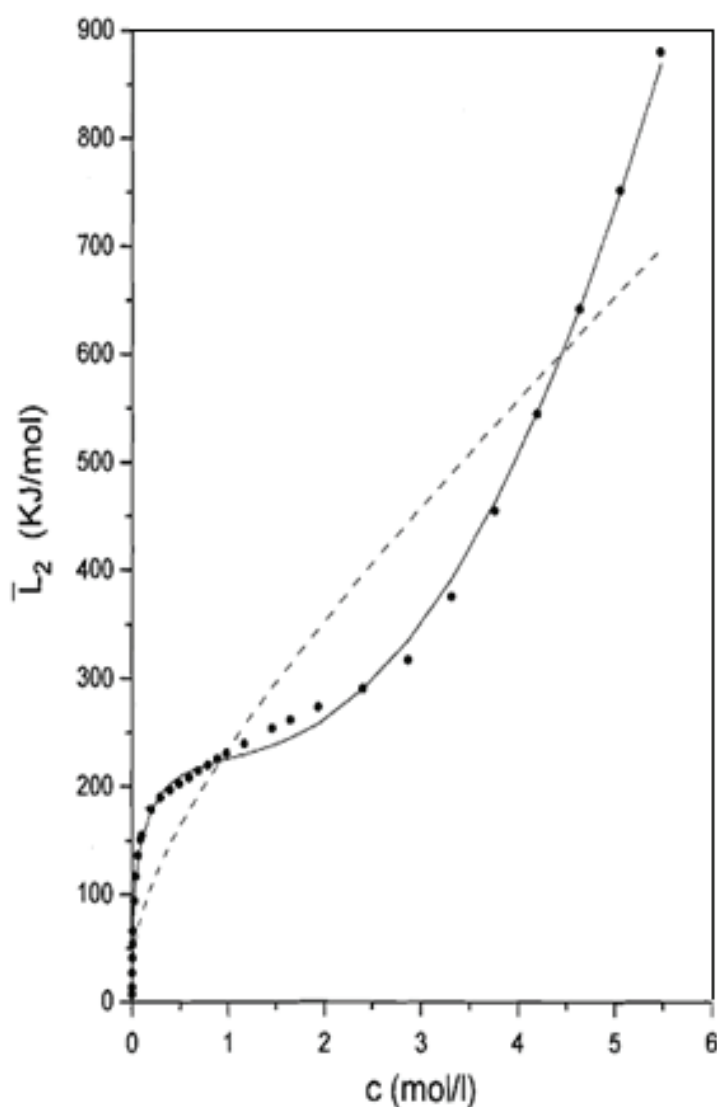
Fig. 1. Relative partial molar enthalpy of an aqueous solution of KF. (---) Bahe predictions (—) BV predictions. Data taken from (Lobo, 1990).

In what the transport properties of concentrated aqueous solution is concerned, they are expected to be determined by the structural features of the system. The predictions of the

Debye-Hückel-Onsager theory mentioned in the Introduction to this chapter are expected to break down as soon as the totally random structure found in highly dilute solutions gives way to the statistical lattice. Indeed, as can be seen in Fig. 2, the electrical conductance of electrolyte solutions is fitted by a relation linear in $c^{1/3}$ over a large range of concentrations, while the validity of the predictions of the Debye-Hückel-Onsager theory based on the existence of inhomogeneous charge clouds in the bulk is restricted to extremely dilute systems. As we have seen in the Introduction, Lemordant and coworkers introduced a purely heuristic derivation of a pseudolattice expression for the electrical conductance of electrolyte solutions linear in the cube root of the molar concentration. Up to our knowledge, a detailed derivation of this relation has not been reported yet in literature, and a tentative demonstration is included in the following.
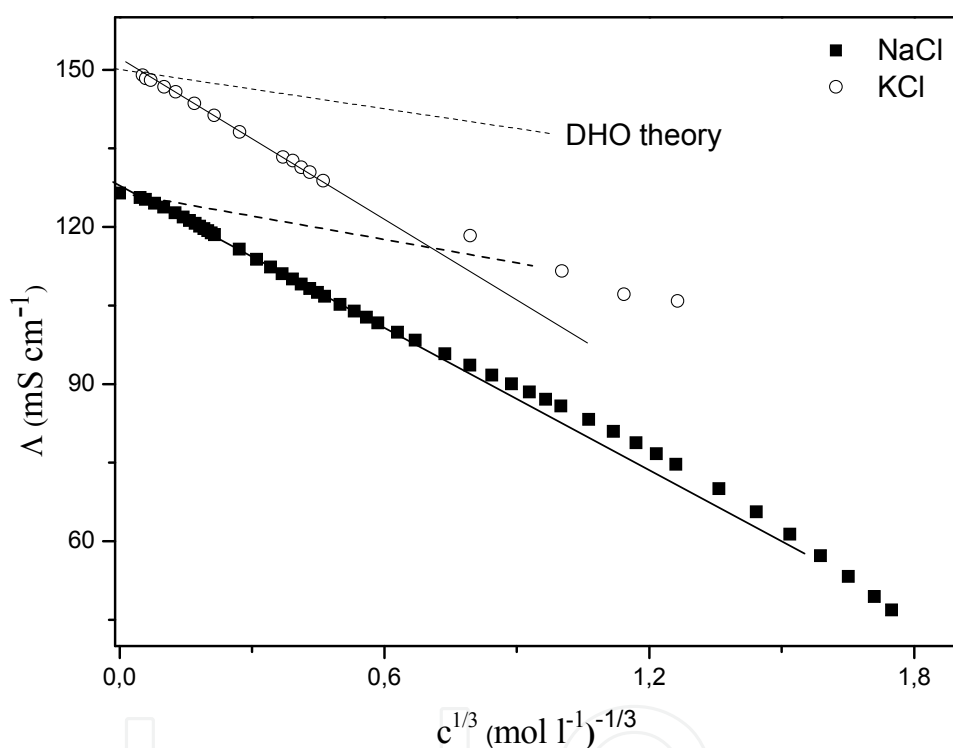

Fig. 2. Electrical conductance of 1:1 electrolyte solutions at 298.15 K (data taken from Lobo, 1990). The solid lines and the dashed lines represent, respectively, the predictions of a cube-root linear law (pseudolattice theory) and a square-root linear law in concentration (Debye-Hückel-Onsager theory).

Let us assume that point ions move in a concentrated electrolyte solution under the influence of an external electric field weak enough so as to preserve the underlying pseudolattice structure throughout the ionic motion. However, the external electric field perturbs the pseudolattice cell structure in the way that is shown in Scheme 1.

As with the perturbed ionic cloud, the perturbed pseudolattice cell reduces the mobility of the ions with respect to the infinitely dilute system, so $\mu_j = \mu_j^0 - \left| \delta\mu_j \right|$. The ions wander under the action of the electric field from one position to another of the pseudolattice in a

(a)   (b)
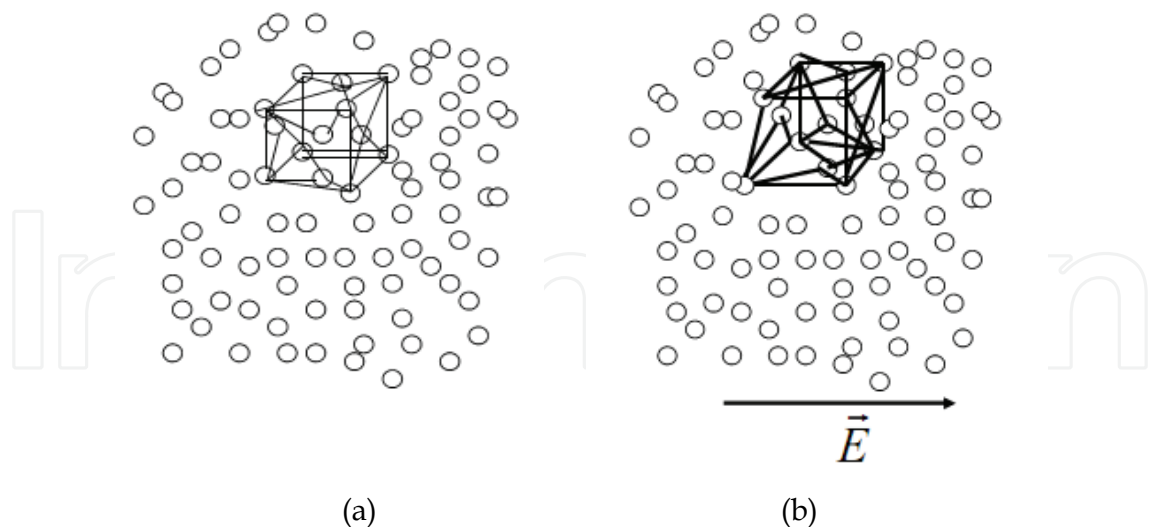
Scheme 1. Action of the electric field on the structure of a bulk electrolyte solution. (a) Unperturbed situation, b) perturbed situation.

kind of "erratic hopping" due to the collisions with the solvent molecules. As shown in Scheme 2, the average of the squared displacement is approximately equal to the lattice distance between ions (cell size), so the relaxation time associated to this diffusion mechanism is

$$\tau = \frac{\langle x^2 \rangle}{2D} = \frac{R^{*2}}{2D} \tag{19}$$

(a)   (b)
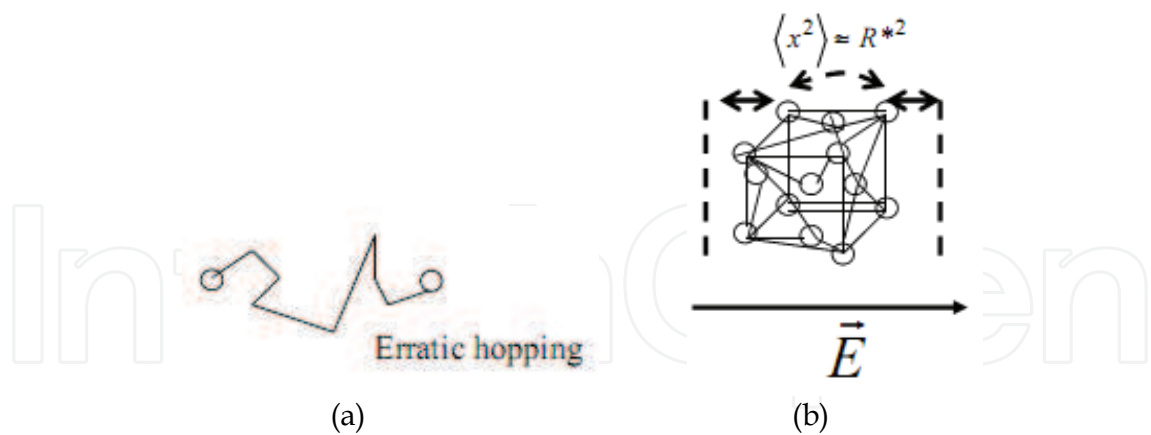
Scheme 2. Average of the squared displacement of an ion under the action of an external electric field. The lateral arrows in (b) represent the limits of the distorted cell.

The amount by which the pseudolattice cell is distorted during the motion of the ion under the effect of the external electric field is equal to the distance travelled by the ion during its relaxation time

$$d \approx v^0 \tau = v^0 \frac{R^{*2}}{2D} . \tag{20}$$

Inside the distorted pseudolattice cell, a force exists associated to the internal electric field associated to the breaking of the symmetry of the equilibrium structure. In the case of the distorted ionic cloud, this field is called the relaxation field and is one of the components responsible for the reduction of the mobility of the ions with respect to the ideal, non-interacting situation (Harned & Owen, 1958; Robinson & Stokes, 1959). This relaxation force can be proved to be

$$
\vec{F}_R = -\frac{q^2}{4\pi\varepsilon R^{*2}}\left(\frac{\vec{d}}{R^*}\right) \approx -\frac{q^2}{4\pi\varepsilon R^*}\left(\frac{\vec{v}^0}{2D}\right)
$$
$$
= -\frac{q^2}{4\pi\varepsilon R^*}\left(\frac{\vec{v}^0}{2\mu^0 k_B T}\right) = -\frac{q^3}{8\pi\varepsilon k_B T}\frac{1}{R^*}\vec{F}_{ext}
$$

(21)

The dependence in $1/R^*$ of the above force clearly suggests that the dependence of the associated mobility reduction will show a $c^{1/3}$ dependence, in line with the experimental results and the previously reported theoretical results of Lemordant and coworkers previously cited.

The other physical phenomenon responsible for the reduction of the ionic mobility in the bulk electrolyte solution is the electrophoretic effect, which arises from the motion of an ion in a medium (solvent) not at rest. This electrophoretic correction to the mobility of the ions in the bulk concentrated electrolyte solutions can be calculated by the following arguments. In the steady state of the ionic transport the electrophoretic velocity is the result of the equilibrium between the electric force driving the ionic cloud and the viscous force

$$
q\vec{E} = 6\pi\eta R^* \vec{v},
$$

(22)

where we have used the conventional Stokes-Einstein relation for the viscous force acting on a spherical particle of radius R^* in a fluid of viscosity η. Obviously, this implies that we are ignoring the effects of the distortion of the ionic clouds, which is a good approximation for low electric fields). Taking now into account that the radius of our moving entity is approximately that of the distorted pseudolattice cell, R^*, in the above equation acquires the meaning of the distance between ions in the statistical arrangement in the bulk, so

$$
v = \frac{qE}{6\pi\eta R^*} \approx c^{1/3}
$$

(23)

As follows from Eqs. (21) and (23), both the electrophoretic correction and the relaxation field correction to the mobility are directly dependent functions of $c^{1/3}$. Consequently, the mobility of the ions submitted to the relaxation force and the electrophoretic correction is reduced by

$$
\vec{v} = \mu^0\vec{F}_{eff} = \mu^0\left[1 - g(q,T)c^{1/3}\right]\vec{F}_{ext}
$$
$$
\mu_{eff} = \mu^0\left[1 - g(q,T)c^{1/3}\right]
$$

(24)

where $\vec{F}_{eff}$ is the total force acting on the central ion due to the external electric field, the internal relaxation field and the electrophoretic effect. Therefore, it is straightforward to see

that the ionic conductance follows a linear law in the cube root of the concentration in accordance with the experimental observations.

3. Pseudolattice theory models of room temperature molten salts

After the work of Varela et al. in 1997, very limited activity was registered in the field of pseudolattice theory of concentrated electrolyte solutions, besides the previously cited works of Moggia and Moggia & Bianco reported in this decade. However, in 2006 the group of Prof. Turmine in Paris described the acid–base properties of aqueous solutions of ILs up to the highest concentrations (pure IL) using Bahe's approach completed by Varela et al. concerning structured electrolyte solutions with large short-range interactions (Bou Malham et al., 2007). As we have previously mentioned, this group successfully applied the Bahe-Varela formalism to the understanding of volumetric properties (apparent molar volumes and partial molar volumes) of several aqueous and non-aqueous mixtures of ILs. Consequently, the pseudolattice theory was for the first time proved to be valid for mixtures of conventional molecular solvent and room-temperature molten salts, for which it can be applied throughout the whole concentration range, without the limitations of precipitation phenomena. In this fashion, the pseudolattice proved to be a unifying structural framework for the understanding of IL-solvent mixtures, and consequently of pure ILs themselves.

Recently, some of us have completed the pseudolattice Bahe-Varela theory analyzing the implications of the existence of a statistical lattice arrangement of ions in the bulk ionic fluid on the surface and transport phenomena of ionic solutions and IL-solvent mixtures (Varela et al, 2009; Varela et al. 2010). In what the surface properties are concerned, up to our knowledge, until 2009 the only reported theory of the surface tension of electrolyte solutions was the so called Onsager-Samaras theory (Onsager and Samaras, 1934), based on the continuous model underlying Debye-Hückel theory of ionic solutions and valid for infinitely diluted solutions. In 2009 some of us reported a pseudolattice theory of the surface tension of electrolyte solutions and IL-solvent mixtures. Despite in the original version of the pseudolattice theory a hard-core potential was used to model the short-range interionic repulsions (Varela et al. 1997), the importance of these interactions in the pure IL regime and in extremely concentrated solutions lead the authors to assume that the short-range non-Coulomb interactions are well described by a Lennard-Jones (LJ) potential with a r^{-12} attractive tail

$$u_{ij}^{LJ}(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{\Lambda}{r_{ij}^6}.$$ (25)

On the basis of this potential, and using similar arguments to those which lead to Eq. (10) it is rather easy to prove that the free energy of the system is

$$F = A'' \frac{q_+ q_-}{4\pi\varepsilon} \frac{1}{R*} + B'' \frac{q_+^2}{(4\pi\varepsilon_0)^2} \left| \frac{d\varepsilon}{dR*} \right| V_{sea} \frac{1}{R*^3} - D'' \frac{\Lambda}{R*^6} + E'' \frac{A}{R*^{12}}$$ (26)

Given their structural characteristics, the surface tension of the pseudolattice ionic systems can be calculated as that of solids. As shown by Shuttleworth (Shuttleworth, 1950) the surface tension of a crystal face is related to the surface free energy by the relation

$\gamma=F+S(dF/dS)$, where S stands for the area of the surface. This surface area can be related to the pseudolattice cell size since it scales as $S\sim R^{*2}$, so

$$\gamma = A''\frac{q_+q_-}{8\pi\varepsilon}\frac{1}{R*} - B''\frac{q_+^2}{2\left(4\pi\varepsilon_0\right)^2}\left|\frac{d\varepsilon}{dR*}\right|V_{sea}\frac{1}{R*^3} + 2D''\frac{\Lambda}{a_A^6}\frac{1}{R*^6} - 5E''\frac{1}{R*^{12}} \qquad (27)$$

Considering that in pure ILs ion-solvent interactions are absent, and that the short-range repulsive term is expected to be dominant due to the great number of ionic contacts, the main contribution to the surface tension of pure ILs is expected to scale like $R^{*-12}\sim\rho^4$, where ρ is the IL density

$$P = CF_W = \frac{F_W\gamma^{1/4}}{\rho - \rho_v} \cong \frac{F_W\gamma^{1/4}}{\rho} \qquad (28)$$

F_W being the formula weight, C a constant characteristic of the liquid, and ρ_v the density of air. The above equation agrees with the predictions for the parachor of liquids, which establishes the proportionality between the surface tension and the density of the liquid, $\gamma \propto \rho^4$, a result recently verified for ILs by Deetlefs et al. (Deetlefs, 2006). Eq. (28) stands exclusively on the basis of a pseudolattice model for the bulk liquid, in contrast with what happens in the hole and interstice models, where surface tension is treated as a purely experimental input necessary for the determination of the hole or interstice average radius respectively.

Moreover, in the same paper (Varela et al., 2009) the reduced surface pressure of IL-water mixtures was calculated assuming a pseudolattice structure in the bulk, and a localized adsorption scheme on the surface of the liquid employing the Langmuir isotherm. Thus, cations are assumed to migrate through the mixture and to be adsorbed on localized adsorption sites on the surface of the mixture. The interactions of cations with other molecules present in the system are treated in the Bragg-Williams approximation. Under these assumptions the calculated reduced surface pressure of the system was

$$\pi^* = \frac{\gamma - \gamma_B}{\gamma_A - \gamma_B} = \frac{x_A\exp\left(e^{-\frac{\beta z\omega_{AA}}{2}}\right)e^{-\frac{\beta z\omega(1-x_A)^2}{2}}}{1 + x_A\exp\left(e^{-\frac{\beta z\omega_{AA}}{2}}\right)e^{-\frac{\beta z\omega(1-x_A)^2}{2}}} \qquad (29)$$

where z stands here for the number of neighbors in the pseudolattice, ω_{AA} (ω_{BB}) represents the interaction between molecules of the A (B) species in the pseudolattice and $\omega = \omega_{AA} + \omega_{BB} - 2\omega_{AB}$ and x_A the molar fraction of the cation species. The predictions of Eq. (29) for IL-water mixtures are shown in Fig. 3 for EMIM-BF$_4$ and BMIM-BF$_4$.

On the other hand, transport theory has been the last update (up to now) of the pseudolattice theory of concentrated electrolyte solutions and IL mixtures (Varela et al., 2010). In this latter reference a statistical mechanical pseudolattice model of charge transport in ionic fluid-solvent mixtures was introduced, and the predictions were compared with data of the electric conductivity of aqueous electrolyte solutions, IL-water and IL-ethanol
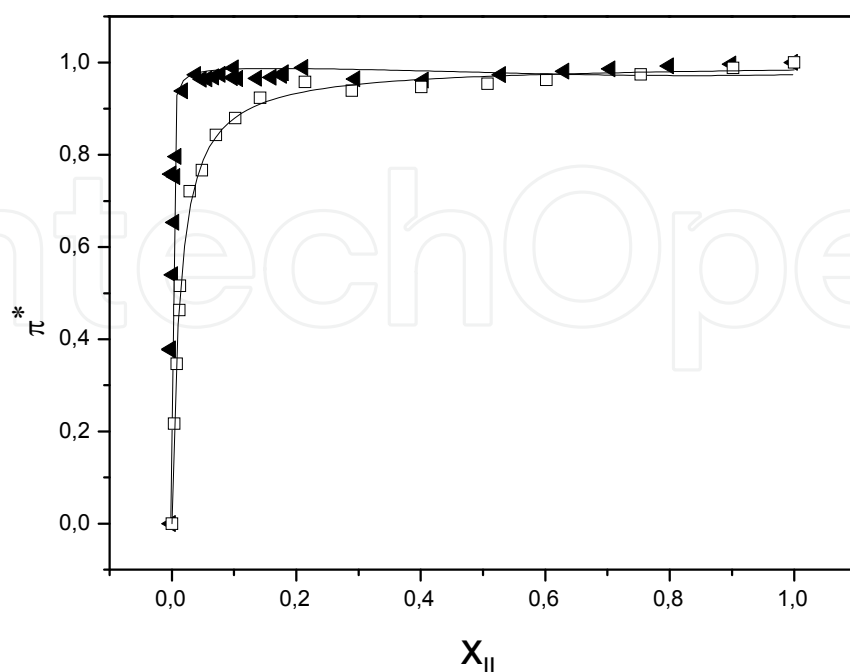
Fig. 3. Reduced surface pressure of aqueous mixtures of EMIM-BF₄ (□) BMIM-BF₄ mixtures
(◄). The solid lines correspond to the predictions of Eq. (29) and the fitting parameters can
be found in (Varela et al., 2009). Data taken from (Rilo et al., 2009**).**

mixtures. The ions were assumed to move randomly between the cells in a statistical lattice
representing the cooperatively rearranging regions in the liquid, defined by Adam and
Gibbs as "*the smallest region that can undergo a transition to a new configuration without a
requisite simultaneous configurational change on and outside its boundary*" (Adams & Gibbs,
1965). Classical hopping over energy barriers is between adjacent cells are the main
mechanism by which the charge transport takes place. On average, only two different types
of ionic environments of an ion were supposed to occur: i) β-cells with no ions in nearest
neighbour cells, on which an ion experiences an energy barrier ε_β , and ii) α-cells associated
to ions in its neighbourhood, with a well depth ε_α The first ones are mainly associated to
solvent molecules in the lattice or even to low density regions in the bulk (hole-like regions),
and the latter to other ions.

In the presence of an external electric field the weighted average excess probability of
jumping in the direction of the field can be written as (Varela et al., 2010)

$$\bar{v}_p = \sum_{i=\alpha,\beta} \phi_i \bar{v}_{pi} = \frac{1}{3} \frac{(k_B T)^3}{h^3} \left(\phi_\alpha \frac{e^{-\varepsilon_\alpha / k_B T}}{v_{s\alpha}^2} + \phi_\beta \frac{e^{-\varepsilon_\beta / k_B T}}{v_{s\beta}^2} \right) \frac{aqE}{k_B T} ,$$

$$= \frac{qa}{k_B T} \left(\phi_\alpha \bar{v}_\alpha + \phi_\beta \bar{v}_\beta \right) E$$

(30)

where $k_B T$ is the thermal energy, h is Planck's constant and v_{si} is the vibration frequency of
an ion in the two directions of the saddle point perpendicular to the direction of flow in a
cell of the i type ($i=\alpha,\beta$). On the other hand, ε_i represents the energy barrier height of cells

of the i-th type and $\bar{v}_i$ is the probability per unit time of an ion jumping a barrier of the i-th type. The electric polarization associated to each ion jump is qa (with a the lattice constant and q the ionic charge), so, if we represent by n_α the number density of mobile ions in the pseudolattice, and considering that for low excess volumes of ILs it can be assumed that $n_\alpha \approx \phi_\alpha / V_\alpha$, where V_α is the ionic volume, then the current density is given by $j_\alpha = n_\alpha q a \bar{v}_p$. So, the electrical conductivity of the pseudolattice mixture reads

$$\kappa = \frac{q^2 a^2}{V_\alpha k_B T}\left[\phi_\alpha^2 \bar{v}_\alpha + (1-\phi_\alpha)\phi_\alpha \bar{v}_\beta \right].$$ (31)

One can easily notice that the coefficients $\bar{v}_i$ in the right hand side of the above result comprise all the relevant features of ion-ion and ion-solvent interactions, so they are expected to be functions of the concentration (Varela et al., 2010). For non-correlated ion transport, conductivity maxima are predicted in terms of the probability of jumping between different types of cells, and the behaviour of the conductivity normalized to its maximum value with the scaled ionic concentration is seen to approximately fit to a universal corresponding states law given by

$$\frac{\kappa}{\kappa_{max}} = 2\xi_\alpha \left(1 - \frac{\xi_\alpha}{2} \right)$$ (32)

$\xi_\alpha = \phi_\alpha / \phi_{max}$ being the scaled ionic concentration. κ_{max} and ϕ_{max} are the maximum electrical conductivity of the mixture and the volume fraction at which it is reached, respectively. As can be seen in (Varela et al., 2010), the above equation accurately predicts the electrical conductivity of electrolyte solutions and IL mixtures throughout the whole range of concentration. Deviations from this law registered at high volume fractions are attributable to ion-ion and ion-solvent interactions, and they were analyzed in the same paper in the Bragg-Williams (BW) mean-field approximation.

Finally, we must mention that the thermal conductivity of pure ILs is known to exhibit a very weak dependence on temperature (van Valkenburg et al., 2005). These constancy clearly suggests that the mechanism that phonon scattering at the grain boundaries of the nanostructured IL prevails over phonon interactions. The pseudolattice theory –with its microscopic picture of an IL as a disordered ensemble of nanostructured lattice rearranging regions- is expected to provide the structural framework which, combined with a mechanism of phonon hopping through the boundaries of these regions (Bragisnky et al., 2002), gives a satisfactory explanation of this magnitude.

4. Conclusions

In the present chapter we have reviewed the origins and historical evolution of the pseudolattice theory of ionic solutions, from the seminal work of Gosh in the second decade of the XXth century, to the contemporary Bahe-Varela theory, which includes interionic Coulomb interactions, the coupling of the electric field in the bulk solution with the gradient of dielectric field in the region, and short-range ion-ion interactions in a statistical lattice environment. The main features of the equilibrium formalism were revisited, and a heuristic derivation of a pseudolattice equation of the electric conductance introduced. Moreover, the

main applications of the theory to concentrated electrolyte solutions and IL-solvent mixtures (predictions of volumetric properties, surface properties and charge transport) were reviewed. From all the exposed material, pseudolattice theory emerges as the unifying theoretical framework which accounts for the properties of ionic fluids irrespective of their ionic concentrations. In future works, the extension of the transport theory to give account for the deviations of the electrical conductivity from the ideal behavior represented by Eq. (32) is to be done, together with the systematic application of the theory to new experimental data of IL mixtures. Finally, it is worth mentioning that a pseudolattice theoretical framework for the thermal conductivity of ILs is under current investigation.

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6. References

Adam, G. & Gibbs, J. H. (1965) On the temperature dependence of cooperative relaxation properties of glass-forming liquids. *J. Chem. Phys*. 43, 1, 139-146, ISSN 0021-9606

Alves Marques, M.; de Barros Marques, M. I.; Cabaço, M. I.; Gaspar, A. M.; Marques, M. P. M.; Amado, A. M. & Amorim da Costa A. M. (2007) Evidence of a local order in concentrated aqueous solutions of salts constituted by ions of different valences: X-ray diffraction and Raman spectroscopy experiments. *J. Mol. Liquids* 134, 1-3, 142–150, ISSN 0167-7322

Attard, P. (1993) Asymptotic analysis of primitive model electrolytes and the electrical double layer. *Phys. Rev. E* 48, 5, 3604-3621, ISSN 1063-651X

Bahe, L. W., (1972a) Structure in concentrated electrolyte solutions. Field-dielectric-gradient forces and energies. *J. Phys. Chem*., 76, 7, 1062-1071, ISSN 0022-3654

Bahe, L. W., (1972b) Relative partial molar enthalpies and heats of dilution of electrolytes in water. *J. Phys. Chem*., 76, 11, 1608-1611, ISSN 0022-3654

Bahe, L. W. & Parker, D. (1975) Activity coefficients of 2:1 electrolytes in structured electrolyte solutions. *J. Am. Chem. Soc.*, 92, 20, 5664-5670, ISSN 0002-7863

Bockris, J. O'M. & Reddy, A. K. N (2000) *Modern Electrochemistry. Vol. 1 Ionics. 2nd edition.* Plenum Press, ISBN 9783527323906, New York

Boroudjerdi, H.; Kim, Y.-W.; Naji A.; Netz, R. R.; Schlagberger, X. & Serr, A. (2005) Statics and dynamics of strongly charged soft matter. *Phys. Rep.* 416, 3-4, 129–199 ISSN 0370-1573

Bou Malham, I.; Letellier, P. & Turmine, M. (2007a) Application of the Bahe's pseudolattice-theory to water−1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$) mixtures at 298.15 K: Part I. Autoprotolysis constants. *Talanta*, 72,1, 155–164, ISSN: 0039-9140

Bou Malham, I.; Letellier, P.; Mayaffre, A. & Turmine, M. (2007b) Part I: Thermodynamic analysis of volumetric properties of concentrated aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate,   1-butyl-2,3-dimethylimidazolium

tetrafluoroborate, and ethylammonium nitrate based on pseudo-lattice theory. *J. Chem. Thermodyn.*, 39, 8, 1132-1143, ISSN 0021-9614

Bouguerra, S.; Bou Malham, I.; Letellier, P.; Mayaffre, A. & Turmine, M. (2008) Part 2: Limiting apparent molar volume of organic and inorganic 1:1 electrolytes in (water + ethylammonium nitrate) mixtures at 298 K – Thermodynamic approach using Bahe–Varela pseudo-lattice theory. *J. Chem. Thermodyn.*, 40, 2, 146-154, ISSN 0021-9614

Braginsky, L; Lukzen, N.; Shklover, V. & Hofmann, H. (2002) High-temperature phonon thermal conductivity of nanostructures. *Phys. Rev. B* 66, 13, 134203, 1-7, ISSN 1098-0121

Chagnes, A.; Carre, B.; Willmann, P. & Lemordant, D. (2001) Ion transport theory of nonaqueous electrolytes. LiClO$_4$ in γ-butyrolactone: the quasi lattice approach *Electrochimica Acta* 46, 12, 1783–1791, ISSN 0013-4686.

Chagnes, A.; Carre, B.; Willmann, P. & Lemordant, D. (2002) Modeling viscosity and conductivity of lithium salts in γ-butyrolactone, *J. Power Sources* 109, 1, 203-213, ISSN 0378-7753

Chagnes, A.; Nicolis, S.; Carre, B.; Willmann, P. & Lemordant, D. (2003) Ion -dipole interactions in concentrated organic Electrolytes. *Chem. Phys. Chem.* 4, 6, 559 -566 ISSN 1439-4235

Chapman, D.L.(1913) A contribution to the theory of electrocapillarity. *Phil. Mag.* 25, 475-481

Cohen-Tannoudji, C., Diu, B. & Laloe, F. (2006) *Quantum Mechanics.* Wiley-Interscience, ISBN 0471569526, New York.

Debye, P.; Hückel, E. (1923) On the Theory of Electrolytes. I. Freezing Point Depression and Related Phenomena. *Phys. Z.* 24 , 185-206

Deetlefs, M.; Seddon, K. R. & Sharab, M. (2006) Predicting physical properties of ionic liquids. *Phys. Chem. Chem. Phys.*, 8, 642–649, ISSN 1463-9076

Desnoyers, J. E. & Conway, B. E., (1964) Activity Coefficients of Electrolytes at Intermediate Concentrations and the "Cube-Root" Law. *J. Phys. Chem.* 68, 8, 2305-11, ISSN 0022-3654

Frank H. S. & Thompson, P. T. (1959a) Fluctuations and the Limit of Validity of the Debye-Hückel Theory *J. Chem. Phys.* 31, 4, 1086-1095, ISSN 0021-9606

Frank H. S. & Thompson P. T. (1959b) *The Structure of Electrolyte Solutions.* W. J. Hamer, Ed., John Wiley and Sons, Inc., New York.

Fuoss, R. M.; Onsager, L. & Skinner, J. F. (1965) The conductance of symmetrical electrolytes V. The conductance equation. *J. Phys. Chem.*, 69, 8, 2581-2594, ISSN 0022-3654

Ghosh, G. C. (1918) The abnormality of strong electrolytes. Part I. Electrical conductivity of aqueous salt solutions., *J. Chem. Soc.* 113, 449-458

Gouy, G. (1910) Sur la constitution de la charge électrique à la surface d'un électrolyte, *J. Phys.* 9, 1, 457-468

Harned, H.S. & B.B. Owen (1958), *The Physical Chemistry of Electrolyte Solutions*, 3rd edition, Reinhold, New York.

Hyman, A. & Vaughn, V. (1967) *Small-Angle Scattering*, Proceedings of the Conference Held at Syracuse University, June, 1966, Gordon and Breach, ISBN , New York.

Israelachvili, J. (1992) *Intermolecular and Surface Forces*, 2nd Ed., Academic Press, ISBN 0123751810, London

Jiang, W.; Wang, T. & Voth, G. A. (2007) Molecular Dynamics Simulation of Nanostructural Organization in Ionic Liquid/Water Mixtures *J. Phys. Chem. B* 111, 18, 4812-4818, ISSN 1089-5647

Kirkwood, J. G. & Poirier, J. C. (1954) The Statistical Mechanical Basis of the Debye–Hückel Theory of Strong Electrolytes. *J. Phys. Chem.* 58, 8, 591-596, ISSN 0022-3654

Kjellander, R. & Mitchell, D.J. (1992) An exact but linear and Poisson—Boltzmann-like theory for electrolytes and colloid dispersions in the primitive model. *Chem. Phys. Lett.* 200, 1-2, 76-82, ISSN 0009-2614

Kjellander, R. & Mitchell, D.J. (1994) Dressed-ion theory for electrolyte solutions: A Debye–Hückel-like reformulation of the exact theory for the primitive model. *J. Chem. Phys.* 101, 1, 603-626, ISSN 0021-9606

Lobo, V.M.M. (1990) *Handbook of electrolyte solutions,* Elsevier, ISBN 0444988475, Amsterdam

McBride, A.; Kohonen, M. & Attard, P. (1998) The screening length of charge-asymmetric electrolytes: A hypernetted chain calculation. *J. Chem. Phys.* 109, 6, 2423-2428, ISSN 0021-9606

Moggia, E. & Bianco, B. (2007) Mean activity coefficients of electrolyte solutions. *J. Phys. Chem. B* 111, 12, 3183-3191, ISSN 1089-5647

Moggia, E. (2008) Osmotic coefficients of electrolyte solutions. *J. Phys. Chem. B*, *112*, 4, 1212–1217, ISSN 1089-5647

Onsager, L. & Samaras, N.N.T. (1934) The surface tension of Debye-Hückel electrolytes. *J. Chem. Phys.* 2, 8, 528-536, ISSN 0021-9606

Padova, J. (1963) Ion—Solvent Interaction. II. Partial Molar Volume and Electrostriction: a Thermodynamic Approach. *J. Chem. Phys.* 39, 6, 1552-1557, ISSN 0021-9606

Panofsky, W. and *Phillips,* M. (1977). *Classical electricity and magnetism.* Addison-Wesley, Reading, Massachusetts.

Prins, J. A. & Fonteyne, R. (1935) Molecular Arrangement and X-Ray Diffraction in Ionic Solutions, *J. Chem. Phys.* 3, 2, 72-80, ISSN 0021-9606

Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L.M. & Cabeza, O. (2009) *Fluid Phase Equilibria,* 285, 1-2, 83-89, ISSN 0378-3812

Robinson, R.A. & Stokes R.H. (1959), *Electrolyte Solutions*, Butterworths, London.

van Valkenburg, M. E. Vaughn, R. L.; Williams, M. & Wilkes, J. S. (2005) Thermochemistry of ionic liquids heat-transfer fluids. *Thermochimica Acta* 425, 1-2, 181–188, ISSN 0040-6031

Varela, L.M.; García, M.; Sarmiento, F.; Attwood, D. & Mosquera, V. (1997) Pseudolattice theory of strong electrolyte solutions. *J. Chem. Phys.* 107, 16, 6415- 6419, ISSN 0021-9606

Varela, L.M.; Pérez-Rodríguez, M.; García, M.; Sarmiento, F. & Mosquera, V. (1998) Static structure of electrolyte systems and the linear response function on the basis of a dressed-ion theory. *J. Chem. Phys.* 109, 5, 1930- 1938, ISSN 0021-9606

Varela, L.M.; Ruso, J.M.; García, M. & Mosquera, V. & Sarmiento, F. (1999a) Relaxation of the ionic cloud on the basis of a dressed-ion theory *J. Chem. Phys.* 110, 9, 4483-4492, ISSN 0021-9606

Varela, L.M.; Pérez-Rodríguez, M.; García, M.; Sarmiento, F. & Mosquera, V. (1999b) Conductance of symmetric electrolyte solutions: Formulation of the dressed-ion transport theory (DITT). *J. Chem. Phys.* 111, 24, 10986-10997, ISSN 0021-9606

Varela, L. M.; García, M. & Mosquera, V. (2003) Exact mean field theory of ionic solutions: Non-Debye screening *Phys. Rep.* 382, 1-2, 1–111, ISSN: 0370-1573.

Varela, L.M.; Carrete, J.; Turmine, M.; Rilo, E. & Cabeza, O. (2009) Pseudolattice Theory of the Surface Tension of Ionic Liquid−Water Mixtures. *J. Phys. Chem. B*, 113, 37, 12500–12505, ISSN 1089-5647

Varela, L.M.; Carrete, J.; García, M.; Gallego, L. J.; Turmine, M.; Rilo, E. & Cabeza, O. (2010) *Fluid Phase Equilibria*, 298, 2, 280-286, ISSN 0378-3812

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