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Physical Properties of Binary Mixtures of ILs with Water and Ethanol. A Review.

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1. Introduction

The interest on ionic liquids (ILs) began in the present century, because these compounds have many physico-chemical interesting properties to be one of the most promising new materials family for the development of the novel Green Chemical industry, where generated pollution would be negligible (Rogers & Seddon, 2002; Rogers et al., 2002). To develop the novel green processes in the chemical industry using ILs it is necessary to know and to understand the physical properties of the fluids to be used, both pure ILs as mixed with other solvents (Rogers & Seddon, 2005; Danek, 2006). This last is particularly important to develop one of the most promising uses of the ILs, as electrolytes for lithium batteries, dye-sensitized solar cells (DSSC) and electrochemical processes (as deposition or metal recovery) (Ohno, 2005; Brennecke et al., 2007). Electrolytes are materials with free ions, which can move transporting electrical charge. They can be solid, liquid or even gaseous, but the most interesting for the chemical industries are liquid or gel. The use of a pure liquid as electrolyte is not very common, because the optimum efficiency in the charge transport process is given by a mixture of different substances, as it is well known for molten salt electrolytes (Danek, 2006). Furthermore, pure ILs have the problem of being very viscous at room temperature, and hence its electrical conductivity is relatively low. If we heat the IL those problems are minimized, because viscosity reduces and electrical conductivity increases, both exponentially. Usually pure ILs have a boiling temperature high enough to allow warming, although decomposition temperature is usually much lower (not higher than 400 K) (Rogers & Seddon, 2002). A much cheaper alternative to decrease viscosity and to increase electrical conductivity of the ionic liquid is to make a solution using a solvent. Thus, while viscosity decreases exponentially with the solvent molar fraction, electrical conductivity increases more than 10 times for a given IL + solvent concentration (Seddon et al., 2000). This last behaviour have been observed in aqueous solutions of metal salts, as aluminium halogen ones (Vila et al., 2005) and indicates that the increase of mobility of the IL ions is higher than the decrease of ion concentration when solvent is added, up to an optimum content.

In spite of its interest, the measurement of the physical properties of IL mixtures begins in the present decade, and before 2005 the amount of papers published about it was scarce (Marsh et al., 2004). From that year the publication rhythm increased a lot, as can be

observed in the references included in this chapter, which majority were published in the last five years. Furthermore its evident applied interest, from the theoretical point of view the study of the physical properties of IL mixtures has contributed to the development of the first theoretical models to explain the ionic structure of the IL ions and the electrical transport mechanisms (Malhan et al., 2007; Varela et al., 2009; Woodward & Harris, 2010). The most promising one is the Bahe-Varela theory, which supposes a pseudo-lattice in the IL formed by the anions and cations, which do not allow the free movement of the ions, but they will hop from one pseudo-lattice position to another free contiguous if they have enough energy (Bahe, 1972; Varela et al., 1997). The presence of some solvent molecules will not break the ionic structure, because the solvent molecules will place in the free space among ions. When the solvent quantity is increased their molecules cannot accommodate and destroy the pseudo-lattice, resulting in a structural phase transition (Varela et al., 2009). See the chapter entitled *Pseudolattice theory of ionic liquids* by L.M. Varela et al., in this same book

In this work we perform a review of the many experimental measurements published in literature about IL + solvent mixtures for different physical magnitudes. Among all measured systems published in the literature (more than 200) we have chosen those reporting data for mixtures of any IL with water or ethanol as solvents. These are those solvents we work in our own laboratory and also they are the most used by researchers, mainly because they are the most promising for applications. The range of physical properties analysed includes density (which gives information about volumetric properties), refractive index (which gives information about ionic interactions), viscosity (the most common transport property studied), electrical conductivity (the key magnitude for electrolyte applications) and surface tension (to know the surface interactions and its composition). We will include in the study all data published using as mean reference the IL thermo webpage, updated in May of 2010, where all experimental physicochemical data is saved for the pure compounds and for binary and ternary mixtures (<http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix>).

This work is organized in chapters, each of them dedicated to the different physical magnitudes revised here. The data published for the different IL families at 298.15 K will be plotted in graphs and commented the IL and/or solvent influence in the magnitude value. If there are published different measured values for the same mixture and magnitude we will discuss them. Also, a study about the temperature influence in each magnitude for a single mixture will be also given. Finally we will relate the measured values for density and refractive index, in one hand, and for viscosity and electrical conductivity in the other.

2. Chemical compounds

The mixtures of IL + water or + ethanol presented include majority of commercial ILs miscible with water or ethanol in a broad range of concentrations. There are some ILs miscible in both solvents, other do not mix with one of them, and many of them are not miscible with any of the two solvents (obviously this last will not be considered in this work). In any case, the IL mixtures measured up to now are a small part of all the millions of ILs that can be synthesized. The ILs cation presented include: 1-alkyl-3-methyl imidazolium, with the alkyl chain being methyl (dMIM), ethyl (EMIM), butyl (BMIM), octyl (OMIM); also the similar cation 1-alkyl-2,3-dimethyl imidazolium, with the alkyl chain being propyl (PdMIM) or butyl (BdMIM). Some pyridinium based cations are reported, the 1-alkyl-pyridinium with the alkyl chain being ethyl (EPy) or butyl (BPy); and the 1-butyl-4-methyl pyridinium (BMPy). Ammonium and phosphonium based ILs are not miscible in water or ethanol (Galan et al., 2003; Huddleston et

al., 2001). The anions reported here include halogens as chlorine (Cl), bromine (Br) and perchlorate (pCl); alkyl sulphates, as methyl sulphate (MS) and ethyl sulphate (ES). Also we report data for ILs with anion dicyanamide (dCy), tricyanamide (tCy) and tricyanomethane (tCyM); trifluoromethanesulfonate (OTf), bis(trifluoromethylsulfonyl)imide (NTf₂), nitrate (NO₃), hexafluoro phosphate (PF₆), and the most popular, the tetrafluoro borate (BF₄). Obviously, not all possible combinations of anions and cations have been reported, but here we present mixtures of more than 25 different ILs with water and/or ethanol. All details about compounds and experimental techniques are in the corresponding reference.

3. Density

Density, ρ , is defined as the mass per unit volume at constant temperature and pressure, so the unit for density is kg/m³. Density for ILs decreases with temperature in their liquid range and increases with pressure, both linearly (Gardas et al., 2007; Rilo et al., 2010c). The reciprocal value of density is the specific volume, which is usually referred as the molar volume, V_m , calculated from density and the molar mass value, M ,

$$V_m = \frac{M}{\rho} \quad (1)$$

When studying binary mixtures, the ideal behaviour is defined using the molar volume instead density, and so the excess molar volume, V_m^E , is defined as:

$$V_m^E = V_m - V_m^{id} = V_m - (x_1 V_{m1} + x_2 V_{m2}) \quad (2)$$

where x_i and V_{mi} are the molar fraction and the molar volume of the pure compound i , respectively. In the case of IL mixtures with water and ethanol the excess molar volume is very small (lower than a 1% of the V_m value in all range of concentrations), and so mixtures are quasy ideal (Rilo et al., 2009).

3.1 Discussion of results

In the following four figures we will plot density data of all mixtures IL + water at 298.15 K reported in literature versus the molar fraction of the corresponding IL, x_{IL} . If more than one author have published the same system, we include only one of them (except discrepancies between both sets of data were important). The source of each set of data is included in the corresponding figure. Thus, in Figure 1 we plot density vs. IL molar fraction for aqueous mixtures of five imidazolium (Rilo et al., 2009; Malhan et al., 2007; Ge et al., 2009) and the only two pyridinium based ILs (Ortega et al., 2008; Mokhatarani et al., 2009b), all of them with BF₄ as common anion. Other authors also measured some of those systems, but results are very similar (Zhou et al., 2006; Zhang et al., 2006; Wu et al., 2009). The behaviour is very similar for all of the systems with BF₄ anion, and the absolute value decreases with the cation size. In Figure 2 we plot BMIM, HMIM and OMIM-Cl aqueous systems (Gomez et al., 2006a; Yang et al., 2010), being the BMIM-Cl only partially miscible (for $x_{IL} < 0.5$). These systems have been also measured by other authors with very similar results (Gaillon et al., 2004; Zafarani et al., 2005; Gardas et al., 2008; Dong et al., 2009; Calvar et al., 2007). As observed density increases from the pure IL value when water is added for HMIM-Cl and OMIM-Cl, and then it decreases for more water content. This is a curious fact that we have

not found in any other aqueous system with IL. In Figure 3 we plot data for ILs with alkyl sulfate anion (Rodríguez et al., 2006; García-Miaja et al., 2009; Domanska et al., 2006). Again the lowest size of the cation and anion means higher ρ values, but curves are essentially the same than for the aqueous systems presented in Figure 1. Other published results for these same systems exist in literature (Calvar et al., 2007; Vicent et al., 2006; Yang et al., 2005). Finally, in Figure 4 we include data for ILs with anions containing cyanamide (Cy) (Stoppa et al., 2009; Carbalho et al., 2010) and trifluoromethanesulfonate (OTf) (Rodríguez et al., 2006; García-Miaja et al., 2009). Density of the ILs with OTf anion has a very high density value taking into account its size, while the ILs with Cy anion present a very small ρ value. The ILs with hexafluoro phosphate as anion is not miscible in water except for very diluted mixtures, and so data are not plotted (Ali et al., 2007; Fu et al., 2006; Jacquemin et al., 2006).

Fig. 1. Density vs. IL molar fraction for seven aqueous systems with BF_4 as anion.

Fig. 2. Density vs. IL molar fraction for three aqueous systems with halogen anion.

Fig. 3. Density vs. IL molar fraction for three aqueous systems with alkyl sulfate anion.

Fig. 4. Density vs. IL molar fraction for four aqueous systems with organic anion.

In Figures 5 to 9 we present the density data for the published IL + ethanol systems also at 298.15 K. Thus in Figure 5 we present systems with ILs containing the BF₄ anion, four alkyl imidazoliums (Rilo et al., 2009) and one pyridinium (Ortega et al., 2008). Curves are similar that those with water, but the density value decreasing is more progressive than corresponding systems with water. In Figure 6 we plot data for three alkyl imidazoliums with PF₆ as anion (Pereiro et al., 2007) with a same behaviour with x_{IL} than those of Figure 5. In Figure 7 we present data for three alkyl imidazolium (Arce et al., 2006b; Pereiro et al., 2007; Garcia-Miaja et al., 2008) and one pyridinium (Gonzalez et al., 2009) alkyl sulfates. Again the decrease of density is similar in shape than in the systems presented before. In Figure 8 we plot four alkyl imidazolium with Cl (Gomez et al., 2006; Gonzalez et al., 2006; Calvar et al., 2006) or pCl anion (Mokhtarani et al., 2008). Now the halogenated ILs decrease continuously with ethanol content, in contrast with the same aqueous systems plotted in

Fig. 5. Density vs. IL molar fraction for five systems with ethanol and BF₄ anion.

Fig. 6. Density vs. IL molar fraction for three systems with ethanol and PF₆ anion.

Fig. 7. Density vs. IL molar fraction for four systems with ethanol and alkyl sulfate anion.

Fig. 8. Density vs. IL molar fraction for four systems with ethanol and chlorate anion.

Fig. 9. Density vs. IL molar fraction for four systems with ethanol and organic anion.

Fig. 10. Density vs. temperature for an aqueous mixture with $x_{IL} = 0.59$ (solid dots) and with ethanol with $x_{IL} = 0.49$. The curves are the best fit of a straight line.

Figure 2. Also note that pCl anion increases considerably the density value, which seems to be opposite to the effect of increasing cation length, which decreases density value. Finally, in Figure 9 we show data for six systems with alkyl imidazolium based ILs, being cations NTf₂ (Gonzalez et al., 2006; Mokhtarani et al., 2009), OTf (Vercher et al., 2007; Garcia-Miaja et al., 2009), NO₂ (Mokhtarani et al., 2009) and tCy (Domanska et al., 2009). For these compounds a bigger size of the anion implies a bigger density value.

3.2 Temperature influence

The temperature dependence of a mixture about equimolar have been also taken from literature. As observed in Figure 10 (above) density decreases linearly with temperature for a aqueous mixture of EMIM-ES (Rodriguez et al., 2006) with $x_{IL} = 0.59$, and also for a mixture of HMIM-BF₄ with ethanol (Garcia-Miaja et al., 2008) having $x_{IL} = 0.49$. We guess that this linear behaviour of density with temperature is a common trend for all mixtures with water and ethanol. In fact, pure ILs also present the same linear trend with temperature (Lu et al., 2005; Zafarani et al., 2005).

4. Refractive index

The refractive index, n_D , of a compound is defined as the ratio of the speed of light in a vacuum to that in a medium. This phenomenon is described by the well known Snell's law, which expresses the relationship between the refractive index, the incident and the transmitted angles of the light. In general refractive indices of compounds increase with increasing atomic number of the constituent atoms (Roger & Seddon, 2005) and furthermore, the refractive index of a compound is a physical property that can potentially be used, like a melting point, to establish its identity very easily. In the case of mixtures with solvents, the refractive index values can be related with density of the same mixture using some phenomenological models that work fairly well, as we will observe later.

The refractive indices of liquids are generally measured using commercially available refractometers, which provide simple and rapid measurements. For pure ILs n_D decreases with the increase of temperature smoothly, following a second order polynom, similarly to the behaviour of density.

4.1 Discussion of results

In this section we will present refractive index measurements published up to now for ILs with water and ethanol, thus in Figures 11 to 13 we plot data for aqueous mixtures while in Figures 14 to 16 the IL + ethanol systems. Figure 11 present data for three systems with alkyl sulfate anion (Gomez et al., 2006b; Gomez et al., 2008; Gonzalez et al., 2008) while in Figure 12 we include two systems with BF₄ as anion (Malhan & Turmine, 2008) comparing the data for BMIM and BdMIM as cations. In Figure 13 we show n_D data of three systems with alkyl-MIM-Cl (Calvar et al., 2006, Gomez et al., 2006c; Gonzalez et al., 2006). A longer alkyl chain means a lower refractive index value, just as happens for density. All data presents a rounded decreasing of n_D with x_{IL} , similar to that presented by density, and this will be the norm for all systems.

In Figure 14 we include the only two systems formed by ethanol and a IL with BF₄ anion, being the cation OMIM (Arce et al., 2006a) and BMIM (Iglesias-Otero et al., 2008), and also we show data for the three published systems with Cl anion and alkyl imidazolium cation (Calvar et al., 2006, Gomez et al., 2006c; Gonzalez et al., 2006). The dependence of n_D with x_{IL}

is similar to that presented by ρ for the corresponding systems with ethanol, and it is more rounded than that presented by the aqueous systems. In Figure 15 we plot the data for IL systems having NTf_2 anion (Andreatta et al., 2009; Andreatta et al., 2010), while in Figure 16 systems with alkyl imidazolium with other kind of anions as OTf (Vercher & Rodriguez, 2010), PF_6 and MS (Pereiro et al., 2007). The behaviour is very similar for all systems.

4.2 Temperature influence

There are very scarce published data about dependence of n_D with temperature for mixtures with water and ethanol. We have not found any measurement for any aqueous system, and in Figure 17 we plot the data for a equimolar mixture of OMIM- BF_4 + ethanol (Mokhtarani et al., 2008). The curve is the best fit of a straight line.

Fig. 11. Refractive index vs. IL molar fraction for three aqueous systems with alkyl sulfate anion.

Fig. 12. Refractive index vs. IL molar fraction for two aqueous systems with tetrafluoroborate anion.

Fig. 13. Refractive index vs. IL molar fraction for three aqueous systems with halogen anion.

Fig. 14. Refractive index vs. IL molar fraction for systems with ethanol, three with halogen anion and two with tetrafluoro borate anion.

Fig. 15. Refractive index vs. IL molar fraction for two systems with ethanol and bis(trifluoromethylsulfonyl)imide anion.

Fig. 16. Refractive index vs. IL molar fraction for three systems with ethanol and different anions.

4.3 Relationship with density

The refractive index n_D of any mixture can be correlated with the corresponding density of the same system using different expressions, as it happens with mixtures of non electrolyte organic compounds (Rilo et al., 2003). Among the different empirical expressions to do that, which gives the best results is that given by Newton, which reads

$$n_D = \left[1 + \phi_1 \left(n_{D1}^2 - 1 \right) + \phi_2 \left(n_{D2}^2 - 1 \right) \right]^{1/2}.$$

(3)

where n_{Di} is the refractive index of the pure compound. The parameter ϕ_i represents the volume fraction of component i^{th} in the mixture, and can be defined as

$$\phi_i = \frac{x_i M_i}{x_1 M_1 + x_2 M_2} \frac{\rho}{\rho_i},$$

(4)

where x_i , M_i and ρ_i are, respectively, the mole fraction, the molecular mass and the density of compound i , and ρ is the density of the corresponding mixture. Let observe that there is not any fitting parameter, and n_D for each mixture only depends on its density. In Figure 18 the continuous line represents Newton’s model given in equation (3) applied to data of BMIM-BF₄ + water, being the fit obtained very good. This is the first time that some of the data plotted in Figure 18, and the relationship between ρ and n_D in any IL system, is published. There exist in the literature many more empirical equations to estimate the refractive index of a binary mixture from their corresponding density (Rilo et al., 2003) but results are not so good as with Newton’s model, at least for the systems investigated.

Fig. 17. Refractive index vs. temperature for a mixture with ethanol $x_{IL} = 0.51$. The curve is the best fit of a straight line.

Fig. 18. Refractive index vs. IL molar fraction for the BMIM-BF₄ + ethanol system. The curve is the prediction from Newton’s model.

5. Viscosity

Viscosity, η , characterizes the inner friction of liquids. Its value is necessary for all process where liquid flow exists, so its knowledge in chemical engineering is of great interest. The viscosity of ILs ranges from 0.1 to 20 Pa s, which results too high for many applications (Rogers et al., 2002). The mixture with a solvent such water or ethanol decreases its value exponentially for all ILs studied and for both solvents, but there are differences among the systems studied. Also, temperature reduces exponentially its value following in ILs a Vogel-Tamman-Fulcher (VTF) behaviour (Seddon et al., 2002).

$$\eta(T) = A \cdot \exp\left(\frac{B}{T - T_g}\right) \quad (5)$$

where T_g is roughly the glass transition temperature, at which the relaxation time of the melt equals infinity, i.e., the pseudo-lattice structure characteristic of the liquid and under-cooled liquid gets frozen in a crystal structure similar to the ordinary inorganic salts. The parameter B in Equation (5) is related with the activation energy needed by a particle in the pseudolattice to jump to the neighbour free site. In the case of ILs, where the organic cation size is usually much bigger than the inorganic anion size, it could be expected that the viscosity value would be given by the motion of the bigger, thus the more sluggish ion. In fact, as we will observe, it does not work like that exactly.

The experimental techniques to measure viscosity are falling ball, capillary tube or the two cylinder Stabinger method. We think this last is the ideal to measure IL mixtures, where the viscosity value changes some orders of magnitude with the concentration of solvent, because there is not necessary vary the measurement cell with the viscosity value, as it happens in the two first techniques.

5.1 Discussion of results

In Figures 19 to 23 we present viscosity for all mixtures of IL + water published, while in figures 24 to 27 all systems IL + ethanol. As observed, all ILs analyzed for both solvents decrease exponentially with the molar fraction of the IL, but that behaviour is not complete because for mixtures rich in the solvent the exponential behaviour disappears (linear relationship in the semi-logarithm representation shown), and the fall of η to the value of the pure solvent is increased. The excess viscosity ($\Delta\eta = \eta - \eta_{id}$) is negative for all mixtures if we define the ideal viscosity as usual

$$\eta_{id} = x_S \eta_S + x_{IL} \eta_{IL} \quad (6)$$

where the suffix S means solvent. If we define η_{id} as,

$$\eta_{id} = \eta_S^{x_S} \cdot \eta_{IL}^{x_{IL}} \quad (7)$$

the excess is positive and it represents only a maximum about a 20% of the measured η .

We have found 17 different systems of any IL with water. In Figure 19 we present η data for BMIM-Cl and EMIM-Br (Liu et al., 2008), which concentration as molarity, m(mol/L). As observed the viscosity is bigger for the smallest ion (Cl), probably due to the fact that its electrical charge surface density is higher and so electrostatic interactions with the cation are also higher. In Fig. 20 we plot three systems with common Cl anion and cation of the same

alkyl-MIM family with the alkyl chain increasing (Gomez et al., 2006c). Except for OMIM-Cl at high solvent concentration (which could be wrong data), it seems that the three systems present a similar viscosity value. In Figure 21 we present six different systems with common BF_4 anion and different cations: three alkyl-MIM (Rilo et al., 2010a), two alkyl-dMIM (Malhan& Turmine, 2008; Ge et al., 2009) and one alkyl pyridinium (Mokhtarani et al., 2009b). As expected the viscosity value increases with the size of the cation, being much higher for the dimethyl cation IL mixtures. We plot in Fig. 22 the only three aqueous mixtures of IL with a alkyl-sulphate anion (Gomez et al., 2006b; Gonzalez et al., 2008). As expected the length of the cation alkyl chain marks the value of viscosity. Finally, in Figure 23 we include the last three aqueous systems found, here all anions are organic ones (Rodriguez et al., 2006; Carvalho et al., 2010). In spite of the very different anions, viscosity is very similar for all of systems.

Fig. 19. Viscosity vs. molarity for two aqueous systems with halogen anion.

Fig. 20. Viscosity vs. IL molar fraction for three aqueous systems with halogen anion.

Fig. 21. Viscosity vs. IL molar fraction for six aqueous systems with tetrafluoroborate anion.

Fig. 22. Viscosity vs. IL molar fraction for three aqueous systems with alkyl sulfate anion.

Fig. 23. Viscosity vs. IL molar fraction for three aqueous systems with organic anion.

Fig. 24. Viscosity vs. IL molar fraction for two systems with ethanol and chlorate anion.

In figures 24 to 27 we plot the 14 systems IL + ethanol at 298.15 published. Thus, in Figure 24 (above) we plot the two published mixtures with a halogen anion (Mokhtarani et al., 2008; Gonzalez et al., 2006). In Figure 25 the systems with alkyl-MIM-BF₄ (Rilo et al., 2010b; Mokhtarani et al., 2008), where the dotted lines represent the ideal behaviour given in Eq. (7). In figure 26 we show the η data for systems with alkyl sulphate as anion (Gonzalez et al., 2009; Gomez et al., 2008). Finally in 27 we plot the published η data in systems with IL + ethanol with an organic anion (Andreatta et al., 2009; Domanska & Laskowska, 2009) or nitrate one (Mokhtarani et al., 2009a). All systems present an exponential dependence of η with x_{IL} for rich mixtures, being the curves very similar to the aqueous systems, except that the linearity between $\log \eta$ and x_{IL} is lost for lower IL content, i.e. the exponential behaviour extends a smaller range of concentrations. Other experimental data for some of the systems presented have been also published, with similar results (Andreatta et al., 2009; Andreatta et al., 2010).

5.2 Temperature influence

The temperature dependence of viscosity for mixtures with water or ethanol also follows an exponential dependence, as observed for two selected equimolar IL mixtures with water (Ge et al., 2008) and ethanol (Rilo et al., 2010b), plotted in Figure 28. We have chosen two mixtures with the same cation and very different anions among those scarce data published.

Fig. 25. Viscosity vs. IL molar fraction for four systems with ethanol and tetrafluoro borate anion. Lines represent the ideal behavior from Eq. (7).

Fig. 26. Viscosity vs. IL molar fraction for two systems with ethanol and alkyl sulfate as anion.

Fig. 27. Viscosity vs. IL molar fraction for four systems with ethanol and organic or nitrate anions.

Fig. 28. Viscosity vs. temperature for two mixtures with $x_{IL} = 0.50$. The lines are the best fit of an exponential curve.

6. Electrical conductivity

Electrical conductivity, κ , of IL mixtures is of considerable interest both from practical as well as theoretical points of view. By means of conductivity data, conclusions on the structure and transport theories of ILs may be tested. Furthermore, the current and energy efficiencies of electrolytic processes are closely related to the electrical conductivity of the electrolyte. It has been observed that the electrical conductivity of the ILs increases more than 10 times when mixed with water, and about 5 times if mixed with ethanol. Electrical conductivity of pure ILs increases exponentially with temperature following a VTF type equation, as that given in Equation (5) (Vila et al., 2006b; Vila et al., 2007). The obtained value of the activation energy for κ does not agree with that taken from viscosity data because both have a different physical origin. Also T_g obtained with both magnitudes does not exactly match.

6.1 Discussion of results

We have found in literature only nine systems IL + water measured, and only four systems with ethanol as solvent. As in previous curves, all the data presented was measured at 298.15 K. In Figure 29 we plot the κ data published for mixtures of ILs with a halogen anion (Liu et al., 2008) with the concentration given in molarity (mol/L) as it was in the original paper. As observed the electrical conductivity decreases with the size of the cation but increases with the size of the anion (with a common cation). This last behaviour was found before in concentrated solutions of halogenated aluminium salts (Vila et al., 2005), and it is explained taking into account the fact that the electrostatic interactions are lower for bigger anions, and so its mobility is increased. In contrast, the increase of the alkyl chain length of the cation will decrease its mobility (now electrical charge is not located in the alkyl chain). In Figure 30 we include data for the only three aqueous miscible systems of the family alkyl-MIM-BF₄ (Vila et al., 2006; Rilo et al., 2010a; Stoppa et al., 2009). As in the previous case, the increase of the alkyl chain length decreases the electrical conductivity value. Data of the two sources agree fairly well among them for BMIM and HMIM, but for EMIM-BF₄ there are some differences in the published κ values, probably due to the presence of different impurity grades in both EMIM samples. In figure 31 we plot the three remain aqueous systems found in literature (Vila et al., 2006; Lin et al., 2009; Stoppa et al., 2009). Again the value of the electrical conductivity increases with the anion size. The values for the two system with EMIM-ES published do not agree between the two references, probably due again to the sample impurities.

The data published about electrical conductivity of systems with ethanol is really scarce, and we have only found a very recent paper from us reporting κ for three alkyl-MIM-BF₄ systems (Rilo et al., 2010b), which data are shown in Figure 32. If we compare with data for the same ILs but with water, shown in Figure 30, we observe that with ethanol the maximum value of κ is roughly half of that with water, it appears at higher molar fraction of the IL, and also the peak is more rounded. Let us note that while HMIM-BF₄ is only partially

Fig. 29. Electrical conductivity vs. molarity for three aqueous systems with halogen anions.

Fig. 30. Electrical conductivity vs. IL molar fraction for three aqueous systems with tetrafluoro borate anions.

Fig. 31. Electrical conductivity vs. IL molar fraction for three aqueous systems with different anions.

Fig. 32. Electrical conductivity vs. IL molar fraction for four systems with ethanol and tetrafluoro borate anion.

miscible with water and all the other members with shorter alkyl chain are completely miscible, for ethanol it happens opposite. EMIM is partially miscible and all the other members with longer alkyl chain are totally miscible with ethanol.

6.2 Temperature influence

As it is expected, electrical conductivity of the mixtures increases with temperature, because mobility of ions also increases. In contrast with viscosity, that increase is not exponential, but it follows a second order polynomial relationship, at least for the temperature range measured. This behaviour can be observed in Figure 33 where we plot two mixtures with $x_{IL} = 0.6$ for two different IL systems (Lin et al., 2009).

Fig. 33. Electrical conductivity vs. temperature for two mixtures with $x_{IL} = 0.60$. The lines are the best fit of a second order polynomial curve.

6.3 Relationship with viscosity. Walden's rule.

As it happens for molten salts (Daneš, 2006) the original Walden's rule that relates viscosity with the specific conductivity ($\Lambda = \kappa/m$, where m is molarity in mol/L) does not work for IL mixtures. That rule affirms that

$$\Lambda \eta = K \quad (8)$$

where K is constant. This relationship does not happen for the IL + solvent, as published recently (Rilo et al., 2010a; Rilo et al., 2010b) and shown in Figure 34 for systems with

ethanol. Thus, in systems with an IL we must use the so called fractional Walden's rule, where viscosity is elevated to a given power γ (which value is between 0 and 1). So the modified Walden's rule will be

$$\Lambda \eta^\gamma = K \quad (9)$$

which is most adequate when sizes of cation and anion are very different, and so the ionic motion is not coupled (Gaune-Escard & Seddon, 2010).

Fig. 34. Application of Walden's rule to four systems with ethanol and alkyl-MIM-BF₄.

7. Surface tension

This is one of the most important technological parameters in ionic liquid chemistry, as the majority of reactions take place at the interface of electrolytes. The surface tension, σ , is related with the inter-ionic forces that take place in the surface of a liquid. Its unity is N/m, being the σ value the same than the surface energy or energy of the unit area, which unities are J/m². The surface tension of pure ILs decreases linearly with temperature (Lin et al., 2009). When mixing two components the surface tension value depend on the surface composition, not in the bulk composition as all other magnitudes presented here do, so it will give information about the surfactant character of each IL with the different solvents. As we will observe, σ is the analyzed magnitude that changes more with the nature of the solvent. The best experimental technique to measure the surface tension is the falling drop volume, because others as suspended ring or plate techniques have a much bigger uncertainty.

7.1 Discussion of results

We have only found five papers presenting experimental measurements of the surface tension of aqueous mixtures of ILs, four of them for systems with alkyl-MIM (Yang et al., 2007; Liu et al., 2006; Liu et al., 2008; Rilo et al., 2009), one for EMIM-ES (Torrecilla et al., 2008) and another one for halogenated alkyl-MIM (Liu et al., 2008). One of the references cited is the only found that includes data for mixtures with ethanol (Rilo et al., 2009). Thus, in Figure 35 we show data for aqueous mixtures of alkyl-MIM-BF₄, where we observe a sharp drop of σ from pure water value for very small IL concentrations. From that sharp drop surface tension is nearly constant equal to that of the pure IL, independently of the solvent concentration. The other authors that measure the same samples do not study the range of very diluted samples, and so they do not report the sharp drop, being the data in

the concentration range they present very similar to ours. In Figure 36 we plot the EMIM-Br, BMIM-Br and EMIM-Cl aqueous systems with the concentration expressed in molarity, $m(\text{mol/L})$ (Liu et al., 2008). For these systems it is not observed the sharp drop. Another interesting fact is that the halogen anion has more influence in the σ value than the alkyl chain length and in an opposite form, bigger anion means higher σ value, but longer alkyl chain means lower σ value. We do not plot data for EMIM-ES because it is very noisy and do not covers the very diluted region, where the sharp drop of σ takes place.

As mentioned, only one very recent paper publish data for surface tension in any system IL + ethanol. In Figure 37 we plot those data for four systems with alkyl-MIM- BF_4 (with EMIM- BF_4 being only partially miscible with ethanol). We observe a complete different behavior than the corresponding aqueous systems shown in Figure 35. Now σ varies linearly with x_{IL} for the four systems, being the σ value of the equimolar mixture the same for the four systems, decreasing linearly with x_{IL} to the pure ethanol value, following the three miscible ILs the same straight line.

7.2 Temperature influence

If data of surface tension is scarce, data about the temperature dependence of surface tension is even scarcer. In fact we have only found one paper where σ vs. T appears (Yang et al., 2007). Those data are plotted in Figure 38 for the aqueous system with EMIM- BF_4 , which roughly follows a quadratic polynomial equation with temperature (line in the figure).

Fig. 35. Surface tension vs. IL molar fraction for three aqueous systems with 1-alkyl-3-methyl-imidazolium tetrafluoro borate.

Fig. 36. Surface tension vs. IL molar fraction for three aqueous systems with 1-alkyl-3-methyl-imidazolium halogenated.

Fig. 37. Surface tension vs. IL molar fraction for four systems with ethanol and 1-alkyl-3-methyl-imidazolium tetrafluoro borate.

Fig. 38. Surface tension vs. temperature for a mixtures with $x_{IL} = 0.875$. The line is the best fit of a second order polynomial curve.

8. Conclusion

We present in this work all published data on density, refractive index, viscosity, electrical conductivity and surface tension for all systems IL + water and + ethanol covering a broad range of concentrations. For density, refractive index and viscosity the data for mixtures with water or ethanol are very similar, and also their behaviour with concentration is not really dependent of the IL mixed with any solvent (except for its value). Density and refractive index can be deduced one from another using Newton's model, which demonstrates the close relationship between both magnitudes. For electrical conductivity and surface tension, the solvent nature determines the data behaviour obtained. Thus, the electrical conductivity value of the pure IL for aqueous systems increases up to 10 times, while that increase is halved for ethanol systems. In the case of surface tension the behaviour is completely different depending on the solvent and IL studied. For alkyl-methyl-imidazolium tetrafluoroborate the IL acts like a surfactant in water, and the surface tension value decreases sharply from that of water to that of the pure IL for small concentrations of this last, effect that does not appear for halogenated imidazolium ILs. If we change the water for ethanol, that surfactant like effect disappear, and the surface tension value of the only four ILs measured decreases linearly with the ethanol content down to a common value at about equimolar mixture, and then all data has the same value,

decreasing linearly again down to the pure ethanol value. As observed, the behaviour of water and ethanol in the surface of IL is completely different.

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10. References

- Ali, M.; Sarkar, A.; Tariq, M.; Ali, A. & Pandey, S. (2007). Dilute aqueous 1-butyl-3-methylimidazolium hexafluorophosphate properties and solvatochromic probe behavior. *Green Chem.* 9, 11 (2007) 1252-1258.
- Andreatta, A.E.; Arce, A.; Rodil, E. & Soto, A. (2009). Physical Properties of Binary and Ternary Mixtures of Ethyl Acetate, Ethanol, and 1-Octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide at 298.15 K. *J.Chem.Eng.Data* 54, 3 (March 2009) 1022-1028.
- Andreatta, A.E.; Arce, A.; Rodil, E. & Soto, A. (2010). Physico-chemical Properties of Binary and Ternary Mixtures of Ethyl Acetate + Ethanol + 1-Butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide at 298.15 K and Atmospheric Pressure. *J.Sol.Chem.* 39, 3 (March 2010) 371-383.
- Arce, A.; Rodríguez, H. & Soto, A. (2006a). Effect of anion fluorination in 1-ethyl-3-methylimidazolium as solvent for the liquid extraction of ethanol from ethyl tert-butyl ether. *Fluid Phase Equilib.* 242, 2 (May 2006) 164-168.
- Arce, A.; Rodil, E. & Soto, A. (2006b). Volumetric and Viscosity Study for the Mixtures of 2-Ethoxy-2-ethylpropane, Ethanol, and 1-Ethyl-3-methylimidazolium Ethyl Sulfate Ionic Liquid. *J.Chem.Eng.Data* 51, 4 (July 2006) 1453-1457.
- Bahe, L.W. (1972) Structure in concentrated solutions of electrolytes. Field-dielectric-gradient forces and energies. *J. Phys. Chem.* 76, 7 (July 1972) 1062-1071.
- Brennecke, J.F.; Rogers, R.D. & Seddon, K.N. Ed. (2007). *Ionic Liquids IV: not just solvents anymore*, American Chemical Society, ISBN:978-0-8412-7445-7, Washington.
- Calvar, N.; González, B.; Gómez, E. & Domínguez, A. (2006). Vapor-Liquid Equilibria for the Ternary System Ethanol + water + 1-Butyl-3-methylimidazolium Chloride and the Corresponding Binary Systems at 101.3 kPa. *J.Chem.Eng.Data*, 51, 6 (Nov. 2006) 2178-2181.
- Calvar, N.; Gómez, E.; González, B. & Domínguez, A. (2007). Experimental Determination, Correlation, and Prediction of Physical Properties of the Ternary Mixtures Ethanol + Water with 1-Octyl-3-methylimidazolium Chloride and 1-Ethyl-3-methylimidazolium Ethylsulfate. *J.Chem.Eng.Data*, 52, 6 (Nov. 2007) 2529-2535.
- Carvalho, P.J.; Regueira, T.; Santos, L.M.N.B.F.; Fernandez, J. & Coutinho, J.A.P. (2010). Dicyanamide and 1-Butyl-3-methylimidazolium Tricyanomethane at Atmospheric Pressure. *J.Chem.Eng.Data*, 55, 2 (Feb. 2010) 645-652.
- Danek, V. (2006). *Physico-Chemical Analysis of Molten Electrolytes*, Elsevier, ISBN-10:0-444-52116-X, Netherlands.
- Domńska, U.; Pobudkowska, A. & Wisniewska, A. (2006). Solubility and Excess Molar Properties of 1,3-dimethylimidazolium Methylsulfate, or 1-Butyl-3-

- Methylimidazolium Methylsulfate, or 1-Butyl-3-Methylimidazolium Octylsulfate Ionic Liquids with *n*-Alkanes and Alcohols: Analysis in Terms of the PFP and FBT Models1. *J.Sol.Chem*, 35, 3 (March 2006) 311-334.
- Domńska, U. & Laskowska, M. (2009). Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of {1-Butyl-3-methylimidazolium Thiocyanate + 1-Alcohols}. *J.Chem.Eng.Data*, 54, 7 (July 2009) 2113-2119.
- Dong, L.; Zheng D.X.; Wei, Z. & Wu, X.H. (2009). Synthesis of 1,3-Dimethylimidazolium Chloride and Volumetric Property Investigations of Its Aqueous Solution. *Int.J.Thermophys.* 30, 5 (2009) 1480-1490.
- Fu, D.; Sun, X.; Pu, J. & Zhao, S. (2006). Effect of Water Content on the Solubility of CO₂ in the Ionic Liquid [bmim][PF₆]. *J.Chem.Eng.Data*, 51, 2 (March 2006) 371-375.
- Gaillon, L.; Sirieix-Plenet, J. & Letellier, P. (2004). Volumetric Study of Binary Solvent Mixtures Constituted by Amphiphilic Ionic Liquids at Room Temperature (1-Alkyl-3-Methylimidazolium Bromide) and Water. *J.Sol.Chem*, 33, 11 (Nov. 2004) 1333-1347.
- Galán, J.J.; Del Castillo, J.L.; González-Pérez, A.; Czapkiewicz, J. & Rodríguez, J.R. (2003). Density and Sound Velocity Studies of Aqueous Solutions of Tetradecyltrimethylammonium Nitrate at Different Temperatures. *J.Sol.Chem*, 32, 10 (Oct. 2003) 919-927.
- García-Miaja, G.; Troncoso, J. & Romaní, L. (2008). Excess properties for binary systems ionic liquid + ethanol: Experimental results and theoretical description using the ERAS model. *Fluid Phase Equilib.* 274, 1-2 (Dec. 2008) 59-67.
- García-Miaja, G.; Troncoso, J. & Romaní, L. (2009). Excess enthalpy, density, and heat capacity for binary systems of alkylimidazolium-based ionic liquids + water. *J.Chem.Thermodynamics* 41, 2 (March 2009) 161-166.
- Gardas, R. L.; Dagade, D.H.; Terdale, S.S.; Coutinho, J.A.P. & Patil, K.J. (2008). Acoustic and volumetric properties of aqueous solutions of imidazolium based ionic liquids at 298.15 K. *J.Chem.Thermodynamics* 40, 4 (April 2008) 695-701.
- Gardas, R.L.; Freire, M.G.; Carvalho, P.J.; Marrucho, I.M.; Fonseca, I.M.A.; Ferreira, A.G.M. & Coutinho, J.A.P. (2007). High-Pressure Densities and Derived Thermodynamic Properties of Imidazolium-Based Ionic Liquids. *J.Chem.Eng.Data*, 52, 1 (January 2007) 80-88.
- Gaune-Escard, M. & Seddon, K.N. Ed. (2010). Molten salts and ionic liquids, never the twain?, J. Wiley & Sons, ISBN: 978-0-471-77392-4, USA.
- Ge, M.-L.; Zhao, R.-S.; Yi, Y.-F.; Zhang, Q. & Wang, L.-S. (2008). Densities and Viscosities of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate + H₂O Binary Mixtures at T) (303.15 to 343.15) K. *J.Chem.Eng.Data*, 53, 10 (Oct. 2008) 2408-2411.
- Ge, M.-L.; Ren, X.-G.; Song, Y.-J. & Wang, L.-S. (2009). Densities and Viscosities of 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate + H₂O at T) (298.15 to 343.15) K. *J.Chem.Eng.Data*, 54, 4 (April 2009) 1400-1402.
- Gómez, E.; González, B.; Domínguez, A.; Tojo, E. & Tojo, J. (2006a). Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J.Chem.Eng.Data*, 51, 2 (March 2006) 696-701.
- Gómez, E.; González, B.; Calvar, N.; Tojo, E. & Domínguez, A. (2006b). Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Its Binary Mixtures with

- Ethanol and Water at Several Temperatures. *J.Chem.Eng.Data*, 51, 6 (Nov. 2006) 2096-2102.
- Gómez, E.; Calvar, N.; Domínguez, I. & Domínguez A. (2006c). Physical properties of the ternary mixture ethanol water 1-hexyl-3-methylimidazolium chloride at 298.15 K. *Phys.Chem.Liq.* 44, 4 (2006) 409-417.
- Gómez, E.; González, B.; Calvar, N. & Domínguez, A. (2008). Excess molar properties of ternary system (ethanol + water + 1,3-dimethylimidazolium methylsulphate) and its binary mixtures at several temperatures. *J.Chem.Thermodynamics* 40, 8 (August 2008) 1208-1216.
- González, E.J.; Alonso, L. & Domínguez, A. (2006). Physical Properties of Binary Mixtures of the Ionic Liquid 1-Methyl-3-octylimidazolium Chloride with Methanol, Ethanol, and 1-Propanol at $T = (298.15, 313.15, \text{ and } 328.15) \text{ K}$ and at $P = 0.1 \text{ MPa}$. *J.Chem.Eng.Data*, 51, 4 (July 2006) 1446-1452.
- González, B.; Calvar, N.; Gómez, E. & Domínguez, A. (2008). Physical properties of the ternary system (ethanol + water + 1-butyl-3-methylimidazolium methylsulphate) and its binary mixtures at several temperatures. *J.Chem.Thermodynamics* 40, 8 (August 2008) 1274-1281.
- González, B.; Calvar, N.; Gómez, E.; Domínguez, I. & Domínguez, A. (2009). Synthesis and Physical Properties of 1-Ethylpyridinium Ethylsulfate and its Binary Mixtures with Ethanol and 1-Propanol at Several Temperatures. *J.Chem.Eng.Data*, 54, 4 (April 2009) 1353-1358.
- Huddleston, J.G.; Visser, A.E.; Reichert, W.M.; Willauer, H.D.; Broker, G.A. & Rogers, R.D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* 3 (2001) 156-164.
- Iglesias-Otero, M.A.; Troncoso, J.; Carballo, E. & Romani, L. (2008). Density and refractive index in mixtures of ionic liquids and organic solvents: Correlations and predictions. *J.Chem.Thermodynamics* 40, 6 (June 2008) 949-956.
- Jacquemin, J.; Husson, P.; Padua, A.A.H. & Majer, V. (2006). Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem.* 8, 2 (2006) 172-180.
- Lin, P.-Y.; Soriano, A. N.; Caparanga A.R. & Li, M. -H. (2009). Electrolytic conductivity and molar heat capacity of the solvent system: 1-ethyl-3- methylimidazolium ethylsulfate + water and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate + water. *Thermochim. Acta* 496, 1 (December 2009) 105-109.
- Liu, W.; Zhao, T.; Zhang, Y.; Wang, H. & Yu, M. (2006). The Physical Properties of Aqueous Solutions of the Ionic Liquid [BMIM][BF₄]. *J.Sol.Chem*, 35, 10 (Oct. 2006) 1337-1346.
- Liu, W.; Cheng, L.; Zhang, Y.; Wang, H. & Yu, M. (2008). The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation. *Journal of Molecular Liquids*, 140, 1 (January 2008) 68-72.
- Lu, X.-M.; Xu, W.-G.; Gui, J.-S.; Li, H.-W. & Yang, J.Z. (2005). Volumetric properties of room temperature ionic liquid 1. The system of {1-methyl-3-ethylimidazolium ethyl sulfate + water} at temperature in the range (278.15 to 333.15) K. *J.Chem.Thermodynamics* 37, 1 (January 2005) 13-19.
- Malham, I.B.; Letellier, P.; Mayaffre, A. & Turmine, M. (2007). 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.Thermodynamics* 39, 8 (July 2007) 1132-1143.
- Malham, I.B. & Turmine, M. (2008). Viscosities and refractive indices of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate with water at 298 K. *J.Chem.Thermodynamics* 40, 4 (April 2008) 718-723.
- Marsh, K.N.; Boxall, J.A. & Lichtenthaler, R. (2004). Room temperature ionic liquids and their mixtures-a review. *Fluid Phase Equilib.* 219, 1 (May 2004) 93-98.
- Mokhtarani, B.; Mojtahedi, M.M.; Mortaheb, H.R.; Mafi, M.; Yazdani, F. & Sadeghian, F. (2008). Densities, Refractive Indices, and Viscosities of the Ionic Liquids 1-Methyl-3-octylimidazolium Tetrafluoroborate and 1-Methyl-3-butylimidazolium Perchlorate and Their Binary Mixtures with Ethanol at Several Temperatures. *J.Chem.Eng.Data*, 53, 3 (March. 2008) 677-682.
- Mokhtarani, B.; Sharifi, A.; Mortaheb, H.R.; Mirzaei, M.; Mafi, M. & Sadeghian, F. (2009a). Density and viscosity of 1-butyl-3-methylimidazolium nitrate with ethanol, 1-propanol, or 1-butanol at several temperatures. *J.Chem.Thermodynamics* 41, 12 (Dec. 2009) 1432-1438.
- Mokhtarani, B.; Sharifi, A.; Mortaheb, H.R.; Mirzaei, M.; Mafi, M. & Sadeghian, F. (2009b). Density and viscosity of pyridinium-based ionic liquids and their binary mixtures with water at several temperatures. *J.Chem.Thermodynamics* 41, 3 (March 2009) 323-329.
- Ohno, H. Ed. (2005). *Electrochemical aspects of ionic liquids*, Wiley, ISBN: 0-471-64851-5, New Jersey.
- Ortega, J.; Vreekamp, R.; Penco, E. & Marrero, E. (2008). Mixing thermodynamic properties of 1-butyl-4-ethylpyridinium tetrafluoroborate [b4mpy][BF₄] with water and with an alkan-1ol (methanol to pentanol). *J.Chem.Thermodynamics* 40, 7 (July 2008) 1087-1094.
- Pereiro, A.B. & Rodríguez, A. (2007). Study on the phase behaviour and thermodynamic properties of ionic liquids containing imidazolium cation with ethanol at several temperatures. *J.Chem.Thermodynamics* 39, 6 (June 2007) 978-989.
- Rilo, E.; Freire, S.; Segade, L.; Cabeza, O.; Franjo, C. & Jiménez, E. (2003). Surface tensions, densities and refractive indexes of mixtures of dibutyl ether and 1-alkanol at T=298.15 K. *J.Chem.Thermodynamics* 35, 5 (May 2003) 839-850.
- Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L.M. & Cabeza, O. (2009). Density and surface tension in binary mixtures of C_nMIM-BF₄ ionic liquids with water and ethanol. *Fluid Phase Equilib.* 285, 1-2 (Nov. 2009) 83-89.
- Rilo, E.; Vila, J.; Pico, J.; García-Garabal, S.; Segade, L.; Varela, L.M. & Cabeza, O. (2010a). Electrical Conductivity and Viscosity of Aqueous Binary Mixtures of 1-Alkyl-3-methyl Imidazolium Tetrafluoroborate at Four Temperatures. *J.Chem.Eng.Data*, 55, 2 (February 2010) 639-644.
- Rilo, E.; Vila, J.; García, M.; Varela, L.M. & Cabeza, O. (2010b). Viscosity and electrical conductivity of binary mixtures of C_nMIM-BF₄ with ethanol at 288 K, 298 K, 308 K and 318 K. Accepted for publication in *J.Chem.Eng.Data*.
- Rilo, E.; Ferreira, A.G.M.; Fonseca, I.M.A. & Cabeza, O. (2010c). Densities and derived thermodynamic properties of ternary mixtures 1-butyl-3-methyl-imidazolium

- tetrafluoroborate + ethanol + water at seven pressures and two temperatures. *Fluid Phase Equilib.* 296, 1 (September 2010) 53-59.
- Rodríguez, H.; Brennecke, J.F. (2006). Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J.Chem.Eng.Data*, 51, 6 (Nov. 2006) 2145-2155.
- Rogers, R.D. & Seddon, K.N. Ed. (2002). *Ionic Liquids. Industrial applications to green chemistry*, ACS Symp. Series 818. ISBN: 0-8412-3789-1, USA.
- Rogers, R.D. & Seddon, K.N. Ed. (2005). *Ionic Liquids IIIA: Fundamentals, Progress, Challenges and Opportunities*, American Chemical Society, ISBN: 0-8412-3893-6, USA.
- Rogers, R.D.; Seddon, K.N. & Volkov, S. Ed. (2002). *Green Industrial Applications of Ionic liquids*, Nato Science Series, ISBN: 1-4020-1136-9, Netherlands.
- Seddon, K.R.; Stark, A. & Torres, M.J. (2000). Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.*, 72, 12 (December 2000) 2275-2287.
- Stoppa, A.; Hunger, J. & Buchner, R. (2009). Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J.Chem.Eng.Data*, 54, 2 (February 2009) 472-479.
- Torrecilla, J.S.; Rafione, T.; García, J. & Rodríguez, F. (2008). Effect of Relative Humidity of Air on Density, Apparent Molar Volume, Viscosity, Surface Tension, and Water Content of 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquid. *J.Chem.Eng.Data*, 53, 4 (April 2008) 923-928.
- Varela, L.M.; Garcia, M.; Sarmiento, F.; Attwood, D. & Mosquera, V. (1997). Pseudolattice theory of strong electrolyte solutions. *J. Chem. Phys.* 107, 16 (October 1997) 6415-6419.
- Varela, L.M.; Carrete, J.; Turmine, M.; Rilo, E. & Cabeza, O. (2009). Pseudolattice theory of the surface tension in ionic liquid-water mixture. *J. Phys. Chem. B* 113, 37 (September 2009) 12500-12505.
- Vercher, E.; Vicent Orchillés, A.; Miguel, P.J. & Martínez-Andreu, A. (2007). Volumetric and Ultrasonic Studies of 1-Ethyl-3-ethylimidazolium Trifluoromethanesulfonate Ionic Liquid with Methanol, Ethanol, 1-Propanol, and Water at Several Temperatures. *J.Chem.Eng.Data*, 52, 4 (July 2007) 1468-1482.
- Vercher, E.; Llopis, F.J.; González-Alfaro, V. & Martínez-Andreu, A. (2010). Refractive Indices and Deviations in Refractive Indices for Binary Mixtures of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate with Methanol, Ethanol, 1-Propanol, and 2-Propanol at Several Temperatures. *J.Chem.Eng.Data*, 55, 3 (March 2010) 1430-1433.
- Vicent-Orchillés, A.; González-Alfaro, V.; Miguel, P.J.; Vercher, E. & Martínez-Andreu, A. (2006). Volumetric properties of binary mixtures of ionic liquid 1-butyl-3-methylimidazolium octylsulfate with water or propanol in the temperature range of 278.15 K to 328.15 K. *J.Chem. Thermodynamics* 38, 9 (Sept. 2006) 1124-1129.
- Vila, J.; Rilo, E.; Segade, L.; Varela, L.M. & Cabeza, O. (2005). Electrical conductivity of aqueous solutions of aluminum salts. *Phys. Rev. E* 71, 3 (March 2005) 031201 1-8.
- Vila, J.; Ginés, P.; Rilo, E.; Cabeza, O. & Varela, L.M. (2006a). Great increase of the electrical conductivity of ionic liquids in aqueous solutions. *Fluid Phase Equilib.* 247, 1-2 (September 2006) 32-39.
- Vila, J.; Ginés, P.; Pico, J.M.; Franjo, C.; Jiménez, E.; Varela, L.M. & Cabeza, O. (2006b). Temperature dependence of the electrical conductivity in EMIM-based ionic

- liquids. Evidence of Vogel-Tamman-Fulcher behavior. *Fluid Phase Equilib.* 242, 2 (April 2006) 141-146
- Vila, J.; Varela, L.M. & Cabeza, O. (2007). Cation and anion sizes influence in the temperature dependence of the electrical conductivity in nine imidazolium based ionic liquids. *Electrochimica Acta* 52, 26 (June 2007) 7413-7417.
- Woodward, C.E. & Harris, K.R. (2010). A lattice-hole theory for conductivity in ionic liquid mixtures: application to ionic liquid + water mixtures. *Phys. Chem. Chem. Phys.* 12, 5 (February 2010) 1172-1176.
- Wu, B.; Zhang, Y.M. & Wang, H.P. (2009). Volumetric Properties and Conductivities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + Sucrose + Water Mixtures. *J.Chem.Eng.Data*, 54, 5 (May 2009) 1430-1434.
- Yang, J.-Z.; Lu, X.-M.; Gui, J.-S.; Xu, W.-G. & Li, H.-W. (2005). Volumetric properties of room temperature ionic liquid 2.The concentrated aqueous solutions of {1-methyl-3-ethylimidazolium ethyl sulfate + water} in a temperature range of 278.2 K to 338.2 K. *J.Chem.Thermodynamics* 37,11 (Nov. 2005) 1250-1255.
- Yang J.-Z.; Li, J.; Tong, J. & Hong, M. (2007). Study on the Density and Surface Tension of Ionic Liquid EMIBF₄ in Terms of Standard Addition Method. *Acta Chimica Sinica* 65, 8 (April 2007) 655-659.
- Yang, Q.; Zhang, H.; Su, B.; Yang, Y.; Ren, Q. & Xing, H. (2010). Volumetric Properties of Binary Mixtures of 1-Butyl-3-methylimidazolium Chloride + Water or Hydrophilic Solvents at Different Temperatures. *J. Chem. Ing. Data* 55, 4 (April 2010) 1750-1754.
- Yu, Y.-H.; Soriano, A.N. & Li, M.-H. (2009). Heat capacities and electrical conductivities of 1-ethyl-3-methylimidazolium-based ionic liquids. *J.Chem.Thermodynamics* 41, 1 (January 2009) 103-108.
- Zafarani-Moattar, M.T. & Shekaari, H. (2005). Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at T = (298.15 to 318.15) K. *J.Chem.Thermodynamics* 37, 10 (Oct. 2005) 1029-1035.
- Zafarani-Moattar, M.T.; Majdan-Cegincara, R. (2007). Viscosity, Density, Speed of Sound, and Refractive Index of Binary Mixtures of Organic Solvent + Ionic Liquid, 1-Butyl-3-methylimidazolium Hexafluorophosphate at 298.15 K. *J.Chem.Eng.Data*, 51, 6 (November 2007) 2359-2364.
- Zhang, Q.-G.; Xue, F.; Tong, J.; Guan, W. & Wang, B. (2006). Studies on Volumetric Properties of Concentrated Aqueous Solutions of the Ionic Liquid BMIBF₄. *J.Sol.Chem*, 35, 3 (March 2006) 297-309.
- Zhou, Q.; Wang, L.-S. & Chen, H.-P. (2006). Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H₂O Binary Mixtures from (303.15 to 353.15) K. *J.Chem.Eng.Data*, 51, 3 (May 2006) 905-908.

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Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

How to reference

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