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**Density, refractive index and volumetric properties of water-ionic liquid binary systems
with imidazolium-based cations and tetrafluoroborate, triflate and octylsulphate anions at
 $T=293$ to 343 K and $p=0.1$ MPa**

Guzmán Carissimi⁽¹⁾, Mercedes G. Montalbán⁽²⁾, F. Guillermo Díaz Baños⁽³⁾ and Gloria
Víllora^{(1)*}

⁽¹⁾*Department of Chemical Engineering, Faculty of Chemistry, Regional Campus of
International Excellence "Campus Mare Nostrum", University of Murcia, 30071
Murcia, Spain*

⁽²⁾*Department of Chemical Engineering, University of Alicante, Apartado 99, 03080,
Alicante, Spain*

⁽³⁾*Department of Physical Chemistry, Faculty of Chemistry, Regional Campus of
International Excellence "Campus Mare Nostrum", University of Murcia, 30071
Murcia, Spain*

* Corresponding author. E-mail address: gvillora@um.es

ABSTRACT

The density and refractive index of ionic liquids (ILs) + water binary mixtures were determined as a function of temperature (from 293.15 to 343.15 K) at atmospheric pressure over the whole composition range in which the mixtures were miscible. To carry out a systematic study, all the ILs selected are imidazolium-based ILs with a different number of carbons in the alkyl chain of the cation and also different anions (tetrafluoroborate, triflate and octylsulphate). Specifically, the studied ILs were 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄], 1-hexyl-3-methylimidazolium tetrafluoroborate [hmim][BF₄], 1-methyl-3-octylimidazolium tetrafluoroborate [omim][BF₄], 1-ethyl-3-methylimidazolium triflate [emim][TfO], 1-butyl-3-methylimidazolium triflate [bmim][TfO] and 1-butyl-3-methylimidazolium octylsulphate [bmim][OcSO₄]. The excess molar volumes and the deviation in the molar refraction of the binary mixtures were calculated for a better understanding of the interactions that take place between the components and successfully correlated by the Redlich-Kister empirical correlations. Bahe-Varela model, which has a more physical meaning, was also used to successfully correlate the excess molar volume

values. Volumetric properties, such as apparent molar volumes, partial molar volumes, isobaric thermal expansion coefficients, partial molar volumes at infinite dilution and excess partial molar volumes at infinite dilution were also calculated in order to obtain information about the influence of composition and temperature on the thermodynamic behavior of the selected ILs and water in the mixture. The results are discussed in order to understand the formation of hydrogen bonds between components of the mixture and the possible packing effects that take place in the mixing process. Density and refractive index experimental data were correlated by the Lorentz-Lorenz, Wiener, Dale-Gladstone and Eykman equations to determine the relationship between both parameters, and a good agreement between the experimental and calculated refractive index values was obtained.

Keywords: Imidazolium-based ionic liquids, Aqueous binary mixtures, density, refractive index, volumetric properties, structure-making properties.

1.- INTRODUCTION

In recent years, ionic liquids (ILs) have received much attention as an attractive and environmentally-friendly alternative to conventional organic solvents. This is mainly due to their many remarkable properties, such as their negligible volatility and wide liquid range (more than 400 K¹). For this reason, they are known as “green” solvents². One of their most distinctive features is probably their ability to tune their properties to structural modifications such as different combinations of anions and cations, which has earned them the name of “designer solvents” because it is possible to select the most suitable ionic liquid for every required application³.

In order to find new applications for ILs, knowledge of their physicochemical properties is crucial. Although many studies in the literature are related to ILs properties; an accurate and systematic physicochemical characterization of the different systems containing ILs is required. In this context, apart from experimental data of the properties of the pure ILs⁴⁻⁸, more studies including mixtures of ILs with other solvents are necessary, especially for industrial application⁹. Since

water is the “greenest” solvent and has high solubility in ILs, many chemical processes could use ionic liquid-water mixtures. For instance, an ionic liquid can act as solvent and water as coagulation agent in polymer processing¹⁰. Experimental determination of the physicochemical properties of pure ILs and their mixtures with water and organic solvents will also contribute to the enhancement of predictive modeling.

Among all the physicochemical properties of ILs, density is probably the most widely studied due to its importance and experimental accessibility. However, the refractive index has received less attention even though the experimental methods available for the determination of this property are generally fast and accurate and require only small quantities of sample. It is quite usual to find density values for some compounds, such as non-electrolytes, next to refractive index values as proof of the purity of the materials. Nevertheless, there are few studies that consider both properties together for ILs despite the close relationship demonstrated by empirical correlations such as the Lorentz-Lorenz, Newton and Dale-Gladstone equations⁴.

Many authors have determined the density of binary mixtures of ILs with water¹¹⁻³³, but few^{9, 34-42} have measured the density and refractive index of binary ionic liquid-water mixtures at the same time. Moreover, most such studies only provide experimental data of density and refractive index at one temperature value. In all studies, the water content of the ILs was found to strongly affect the physicochemical properties. Experimental data of density and refractive index for binary ionic liquid-water mixtures enable other properties to be calculated, such as the excess molar volume and the refractive index deviation. These properties reveal any deviation in the behavior of the mixture from to the ideal behavior, information that is relevant in order to understand the molecular interactions⁴³ between the ionic liquid and the water. The theory of the solution is still far from providing a complete explanation for the non-ideality of the solution in terms of the properties of the constituent molecules. Experimental data on macroscopic properties such as excess molar volumes and refractive index deviations often provide valuable information for understanding the nature of the molecular interactions that take place. Volumetric properties are very sensitive to solute-solvent interactions. The partial molar volumes depend on several

factors, including the relative size and the molecular structure of the molecules of the solute as well as on solute-solvent and solute-solute interactions. The relationship between the partial molar volumes and concentration provides useful information about solute-solute interactions, whereas partial molar volumes at infinite dilution are related to solute-solvent interactions. Some studies consider that the partial molar volume is a combination of volumetric contributions, which include the intrinsic solute volume and the contributions due to the interaction of the solute with the solvent. In binary aqueous mixtures, the properties of the water molecules in the hydration sphere depend on the nature of the solute molecules and their interactions with the water⁴⁴.

The main aim of this work was to experimentally determine the density and refractive index of binary mixtures of ILs and water in a wide range of temperatures. In addition, the relationship between both properties was studied under different experimental conditions for the same binary systems using empirical correlations. From the experimental data of density and the refractive index, the excess molar volumes, V_m^E , excess isobaric thermal expansion coefficients, α_p^E , and the deviation in molar refraction, ΔR , for the ionic liquid-water systems were also obtained in the range of temperature used. Furthermore, volumetric properties such as apparent molar volumes ($V_{\phi i}$), partial molar volumes (V_i), excess partial molar volumes, V_i^E , partial molar volume at infinite dilution (V_i^∞), excess partial molar volume at infinite dilution (V_i^E)[∞] were calculated for the components of the mixtures at the studied temperatures.

To carry out a systematic study, the ILs were selected according to their chemical structure; most of them have a common ion which permits to study the effect of their chemical structure on the evaluated properties. The following ILs were used: 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄], 1-hexyl-3-methylimidazolium tetrafluoroborate [hmim][BF₄], 1-methyl-3-octylimidazolium tetrafluoroborate [omim][BF₄], 1-ethyl-3-methylimidazolium triflate [emim][TfO], 1-butyl-3-methylimidazolium triflate [bmim][TfO] and 1-butyl-3-methylimidazolium octylsulphate [bmim][OcSO₄]. The density and refractive index of the binary ionic liquid-water systems were determined in a temperature range of 293.15 to 343.15K at atmospheric pressure. To the best of

our knowledge, this work provides a large quantity of new experimental data, because the refractive index of binary aqueous mixtures involving [omim][BF₄] and [bmim][OcSO₄] has not been measured before and the density of binary systems of [emim][BF₄]^{12,25}, [hmim][BF₄]^{12,32} and [omim][BF₄]⁴⁵ with water and the refractive index of mixtures containing [emim][BF₄]⁴⁶ and [hmim][BF₄]⁴⁶ and water has only been measured at 298 K. In addition, in some cases, such as the measurement of the density of [bmim][OcSO₄]-water binary systems¹⁸ and the measurement of the refractive index of [emim][TfO]-water binary systems⁴⁷, the influence of temperature on these physical properties is only studied in one citation. The rest of system-property (density or refractive index) combinations have been previously studied on the literature with a fraction molar range and temperature range similar to those used in this paper. Then, we will cite these works: density and/or refractive index of [bmim][BF₄]-water systems^{12,23,26,27,32-35,40-43,45,48}, density and/or refractive index of [emim][TfO]-water systems^{11,24,30,47} and density and/or refractive index of [bmim][TfO]-water systems^{9,11,29,31,43,47}. In this paper, a systematic study of the volumetric properties of aqueous binary mixtures of these ILs is addressed for the first time.

2.- EXPERIMENTAL

2.1. Materials

All the ILs used in this work were supplied by IoLiTec (Germany) except [bmim][TfO] and [bmim][OcSO₄], which were purchased from Solvent-Innovation (Germany) (Table 1). The purity of all the ILs was above 98%. The ILs were treated with phosphorus pentoxide for 24 hours at 35 °C in vacuum before use. Then, the remaining water content of a known mass of each ionic liquid was measured by a Metrohm 831 KF coulometric Karl Fischer. Hydranal-Coulomat AG provided from Fluka Analytical was used as the titration reagent. A Standard of HYDRANAL-water 1000 ppm (Honeywell/Fluka) was run before and after the measurements to check the equipment. The values of the water content were low in all cases ($w < 0.001$). The standard uncertainty, u , of the water content measurements of the ILs was $u(w) = 0.0001 \text{ kg/m}^3$. The ILs were manipulated under nitrogen atmosphere in a homemade dry box in order to avoid moisture

absorption and Schlenk tubes were used to keep the binary mixtures before to load them into the corresponding apparatus. The water used to achieve the binary mixtures ionic liquid-water was obtained from a Merck Millipore System Milli-Q with a resistivity value of 18.2 M Ω ·cm.

Table 1. Sample Table.

Compound	CAS number	Source	Molecular mass/ g·mol ⁻¹	Initial Mole Fraction Purity	Purification Method	Water Content/ wt (%)
[emim][BF ₄]	143314-16-3	IoLiTec	197.97	≥0.98	Vacuum drying	0.063
[bmim][BF ₄]	174501-65-6	IoLiTec	226.02	≥0.99	Vacuum drying	0.057
[hmim][BF ₄]	244193-50-8	IoLiTec	254.08	≥0.99	Vacuum drying	0.032
[omim][BF ₄]	244193-52-0	IoLiTec	282.13	≥0.99	Vacuum drying	0.034
[emim][TfO]	145022-44-2	IoLiTec	260.24	≥0.99	Vacuum drying	0.068
[bmim][TfO]	174899-66-2	Solvent-Innovation	288.29	≥0.99	Vacuum drying	0.063
[bmim][OcSO ₄]	445473-58-5	Solvent-Innovation	348.50	≥0.98	Vacuum drying	0.092

2.2. Apparatus and procedure

The binary mixtures studied were prepared in glass vials by weighing the mass of ionic liquid and the mass of water on a Sartorius BF121S balance with a precision of 10⁻⁷ kg, in order to obtain a mixture with a known composition over the whole composition range. Every mixture was prepared immediately prior to measuring the properties.

Density measurements were taken with an oscillating U-tube Anton Paar densitometer (DMA 4500M) at temperatures ranging from 293.15 to 343.15 K. The temperature was controlled by a Peltier system. Standard uncertainties are $u(T^p) = 0.03$ K, $u(\rho) = 0.05$ kg·m⁻³ and, given the purity of sample (≥0.98), the estimated expanded uncertainty, U , is $U(\rho)=2$ kg·m⁻³ (with 0.95 level of confidence and coverage factor $k=2$)⁴⁹. The densitometer was previously calibrated before the assays by measuring the density of Milli-Q water and the air present in the laboratory according to the instructions of the supplier and a reproducibility < 2 % and a repeatability < 0.1 % were found. The quantity of sample required was about 10⁻³ L to fill the U-tube and was introduced into the equipment with a syringe, carefully avoiding the appearance of bubbles in the tube. The measurements were done at least three times to ensure the repeatability of the results and the coefficient of variation for all measurements of the density (293.15 K to 343.15 K) was 0.078 %.

Refractive index measurements for the binary mixtures were determined using an Atago ABBE DR-A1 refractometer at 589 nm sodium wavelength and temperatures from 293.15 to 343.15 K. Standard uncertainties, u , are $u(T) = 0.5$ K, $u(n)=0.0002$ (nD) and, given the purity of sample (≥ 0.98), the estimated expanded uncertainty, U , is $U(n)=0.0016$ (nD) (with 0.95 level of confidence ($k=2$)). In this case, the equipment was calibrated with Milli-Q water before the experiments and diethyl ether was used to clean the prism surface of the refractometer. An external thermostatic bath was used to control the temperature in the cell. As in the case of the density measurements, these were carried out in triplicate at least and the repeatability coefficient of variation for all refractive index measurements (293.15 K to 343.15 K) was 0.0026 %.

Definitions of all values related to the expression of uncertainty in this paper are from the *Guide to the Expression of Uncertainty in Measurement*, ISO (International Organization for Standardization), October, 1993⁵⁰. These ISO recommendations were adopted with minor editorial changes as the *U.S. Guide to the Expression of Uncertainty in Measurement* and is commonly referred to by its abbreviation; the *GUM*. The recommendations have been summarized in *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results* (free download from <http://physics.nist.gov/cuu/>)⁵¹.

3.- RESULTS AND DISCUSSION

The properties of the pure ILs at the temperatures used in this study were previously published by the authors of this paper⁴ and other authors⁵². Tables S1 to S7 of the Supporting Information show the experimental values for density and refractive index for the (ionic liquid + water) binary mixtures at temperatures from 293.15 to 343.15K. The experimental method was validated in a previous work⁴ by a comparison of the experimental and literature values of the density of pure [bmim][BF₄] in different ranges of temperature. To check the reliability of experimental density and refractive index values obtained in this work for the binary mixtures, the data obtained for [bmim][BF₄]-water systems were compared with those from the literature (Figures 1 and 2),

finding a satisfactory agreement, with a relative deviation $< \pm 0.5\%$. Binary mixtures of [bmim][BF₄] and water were chosen because this is the most studied system in the literature.

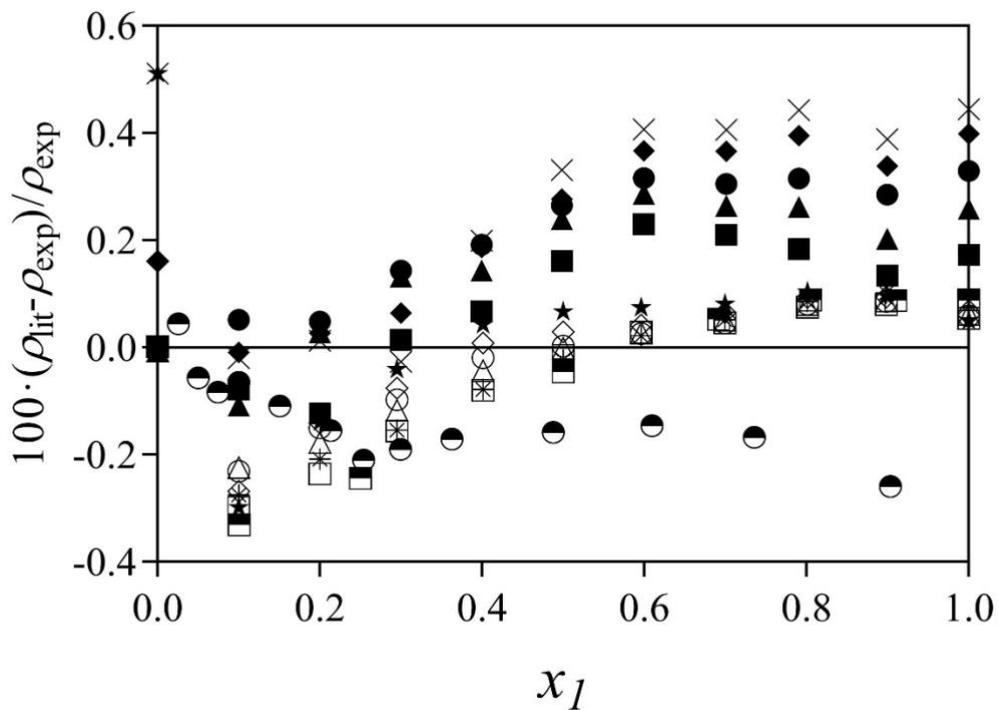


Figure 1. Plot of relative deviation of density data for [bmim][BF₄]-water binary system plotted against molar fraction of [bmim][BF₄] between our experimental data and those from literature.

Zhou *et al.*³³: ■ 303.15 K; ▲ 313.15 K; ● 323.15 K; ◆ 333.15K; × 343.15 K. Taib and Murugesan⁴¹: *293.15 K; □ 303.15 K; △ 313.15 K; ○ 323.15 K; ◇ 333.15K; * 343.15 K. Chaudhary *et al.*⁴⁰: ● 303.15K. Wang *et al.*⁴⁸: ■ 303.15K.

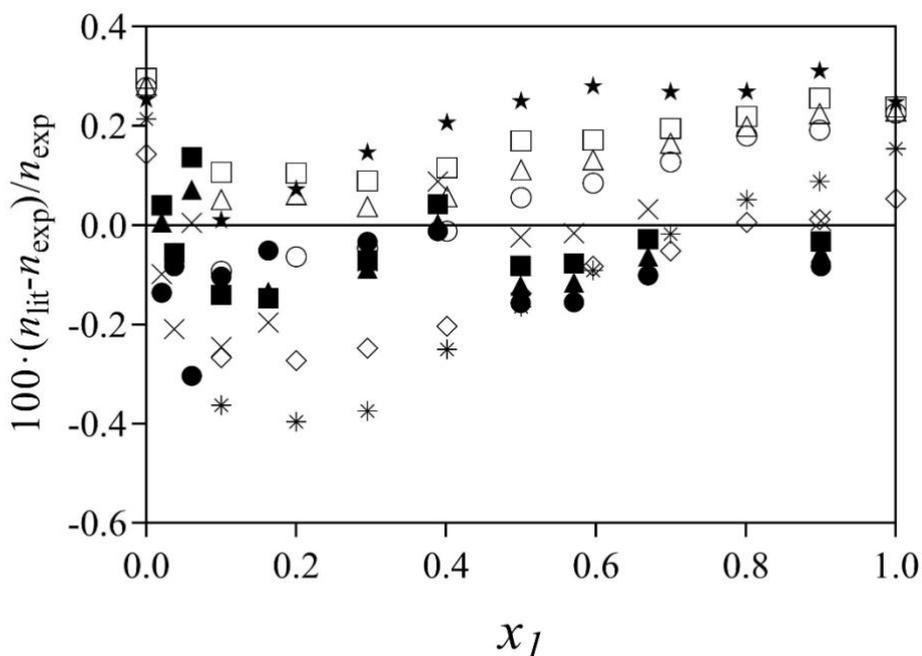


Figure 2. Plot of relative deviation of refractive index data for [bmim][BF₄]-water binary system plotted against molar fraction of [bmim][BF₄] between our experimental data and those from literature. Chaudhary *et al.*⁴⁰: ×293.15 K; ■ 303.15 K; ▲ 313.15 K; ● 323.15 K. Taib and Murugesan⁴¹: ★293.15 K; □ 303.15 K; △ 313.15 K; ○ 323.15 K; ◇ 333.15K; * 343.15 K.

The rest of literature comparisons can be found in Figures S1 and S2 of Supporting Information. In a previous work, Cabeza *et al.*⁵³ reported the existence of hydrophobically driven lyotropic rigid gel phase in aqueous mixtures of the IL 1-ethyl-3-methylimidazolium octylsulfate, [emim][OcSO₄], for IL mole fraction from 0.12 to 0.5. However, this phenomenon has not been observed for [bmim][OcSO₄] in this work and neither for other authors¹⁸.

The results on tables S1 to S7 show that density and refractive index increase as the ionic liquid mole fraction increases and the temperature decreases, for all the studied binary systems. Similar results were found in studies previously published in the literature^{9,11,12}.

Density and refractive index experimental values for the binary mixtures were correlated by linear regression with temperature according to eqs. 1 and 2.

$$\rho = \rho_0 T + \rho_1 \quad (1)$$

$$n = n_0 T + n_1 \quad (2)$$

Figures S3 to S9 of the Supporting Information show the fitted and experimental values of the densities and refractive index for the seven binary systems studied, as a function of temperature for different compositions. It can be observed that the density decreases with temperature and increases with the ionic liquid concentration in the systems. The values generated by least-square fits are listed in Tables S8 to S14 of Supporting Information. As can be observed, the linearity of the correlation of density decreases with increasing water concentration. Nevertheless, we can state that density of all the studied ionic liquid-water mixtures shows a good linear dependence with temperature and, as it is well-known, this dependence moves away from linearity in the case of pure water. The refractive indices of the mixtures always increased as the ionic liquid mole fraction increased and decreased with increasing temperature. A linear dependence of the refractive indices on temperature was observed for all the studied systems. When possible, the results were compared with those found in the literature and good agreement was observed in most cases considering the strong effect of impurities in these physical properties.

To study the influence of the alkyl chain length of the cation of the ionic liquid on the density and refractive index of the binary mixtures, the results obtained for two families of ILs ($[\text{C}_n\text{mim}][\text{BF}_4]$ and $[\text{C}_n\text{mim}][\text{TfO}]$) at 293.15 K were analyzed (Figures 3 and 4). It was found that an increase in the length of the alkyl chain of the cation was accompanied by a lower density value and a higher refractive index value.

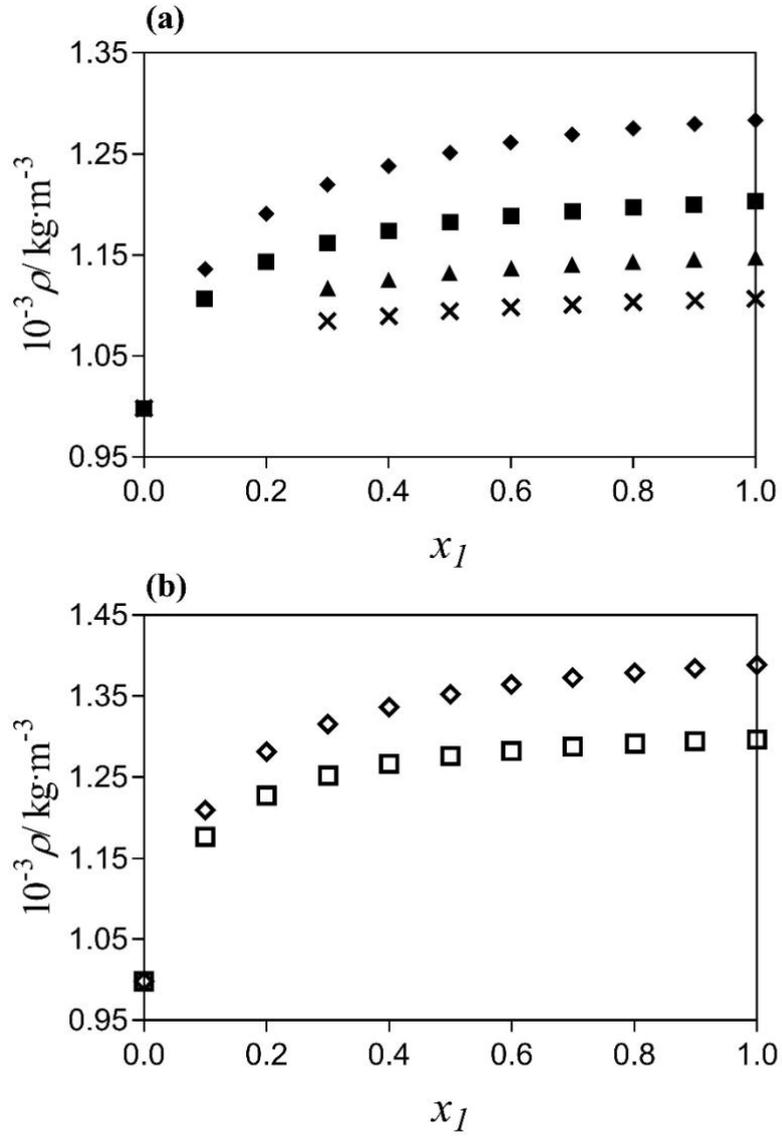


Figure 3. Effect of the alkyl chain length of the cation on the density of ionic liquid (1) -water binary mixtures at 293.15 K: (a) \blacklozenge [emim][BF₄], \blacksquare [bmim][BF₄], \blacktriangle [hmim][BF₄] and \times [omim][BF₄]; (b) \diamond [emim][TfO] and \square [bmim][TfO].

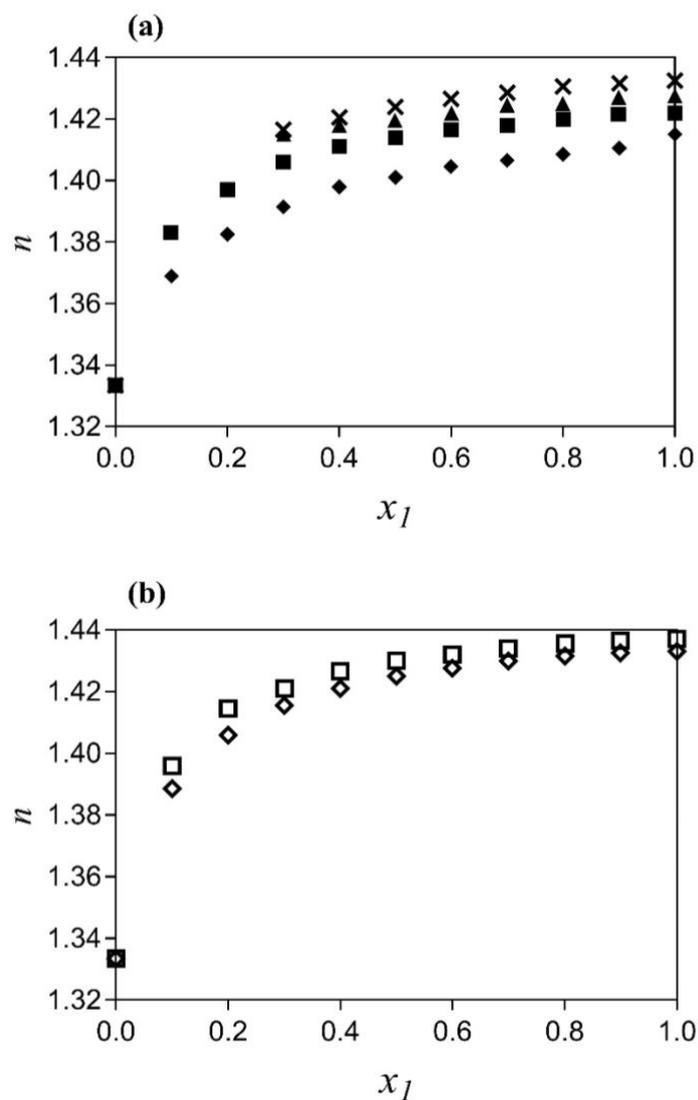


Figure 4. Effect of the alkyl chain length of the cation on the refractive index of ionic liquid (1)-water binary mixtures at 293.15 K: (a) \blacklozenge [emim][BF₄], \blacksquare [bmim][BF₄], \blacktriangle [hmim][BF₄] and \times [omim][BF₄]; (b) \diamond [emim][TfO] and \square [bmim][TfO].

The effect of the ionic liquid anion on both parameters was also studied. The results at 293.15 K revealed the following order [TfO] > [BF₄] > [OcSO₄] for density values of the binary mixtures (Figure 5). The order of the density values was explained by the authors in a previous work⁴ in which it was observed that the volume of the anion is the fundamental factor in determining the molecular volume (the higher the volume of the anion, the higher V_m), although other factors (geometry of the anion, distribution of charge, etc.) have some influence on the global volume. However, according to the results, their importance was less than that of the volume of the anion.

On the other hand, the trend observed in the experimental values of the refractive index showed that it decreases with decreasing molar mass: $[\text{OcSO}_4^-]$ ($209.280 \text{ g}\cdot\text{mol}^{-1}$) > $[\text{TfO}^-]$ ($149.062 \text{ g}\cdot\text{mol}^{-1}$) > $[\text{BF}_4^-]$ ($86.802 \text{ g}\cdot\text{mol}^{-1}$).

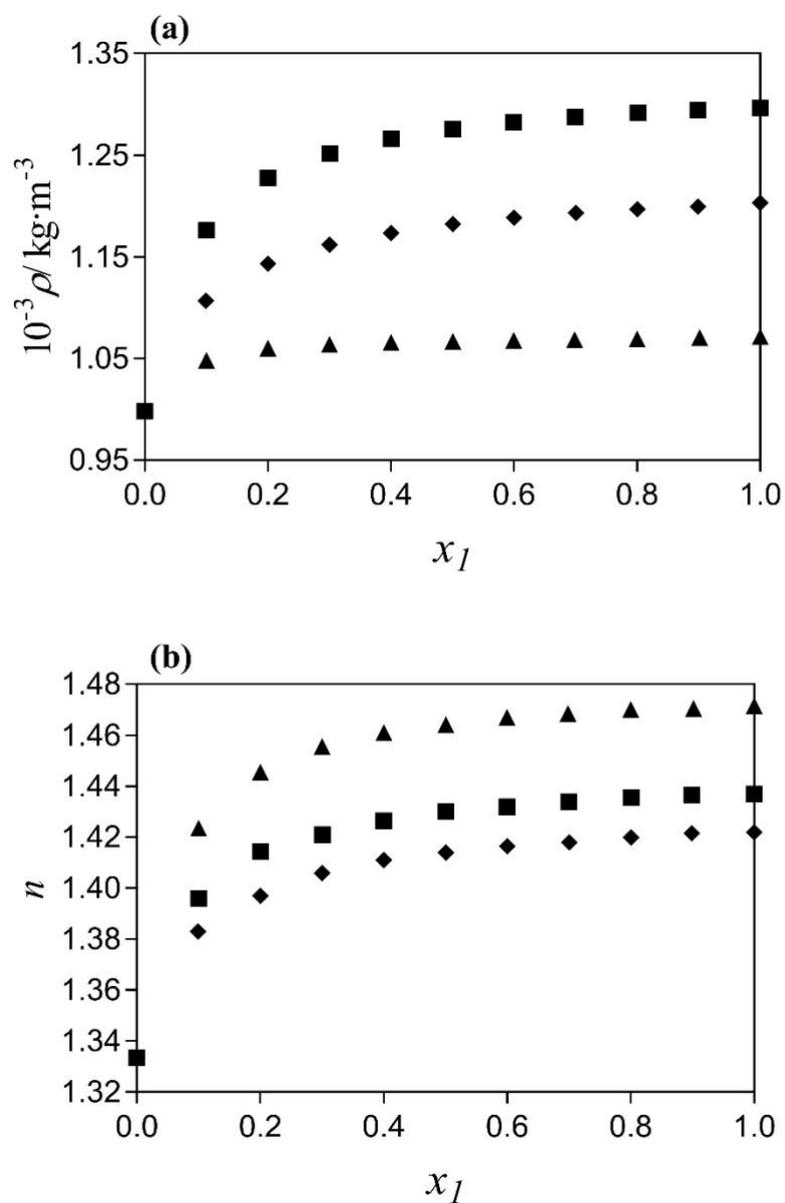


Figure 5. Effect of the anion on (a) density and (b) refractive index of ionic liquid (1)-water binary mixtures at 293.15 K: ◆ $[\text{bmim}][\text{BF}_4]$, ■ $[\text{bmim}][\text{TfO}]$ and ▲ $[\text{bmim}][\text{OcSO}_4]$.

3.1.-Calculation of the volumetric parameters

3.1.1. Excess Molar Volumes

From the experimental data of the density, provided in Tables S1 to S7 of Supporting Information, the values of the excess molar volume of the binary mixtures studied in this work were calculated for a temperature range from 293.15 to 343.15 K using eq. 3 to estimate the non-ideality of the systems (see Tables S15 to S21 and Figure S10 of the Supporting Information).

$$V_m^E = \frac{M_1x_1 + M_2x_2}{\rho} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2} \right) \quad (3)$$

In this equation, ρ is the density of the mixture; ρ_i and M_i are density and molecular weight of the pure compounds (i), respectively, with $i=1$ for ionic liquid and $i=2$ for water. The first half of the equation is considered as the real volume of the mixture, while the second half represents its ideal volume. The estimated combined standard uncertainty, u_{comb} , of V_m^E is $u_{comb}(V_m^E) < 1.73 \cdot 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$. Figure S10 of the Supporting Information shows the influence of temperature and molar composition on the excess molar volume for the (IL + water) binary mixtures. As can be seen in Figure S10 and Tables S15 to S21 of the Supporting Information, excess molar volumes are very small (less than 1% of the corresponding molar volume) for all the mixtures. Therefore, we can conclude that all presented mixtures are quasi-ideal as it has been reported before by many authors^{9,11,40,41}.

Excess molar volumes, V_m^E , at each mole fraction and temperature were fitted by a fourth degree Redlich-Kister polynomial eq. 4.

$$F(x) = x_1x_2 \sum_{i=0}^n A_i (2x_1 - 1)^i \quad (4)$$

where $F(x)$ represents the excess property.

The fitting parameters, A_i , for all the binary mixtures at each studied temperature were adjusted by least squares method (see Table 2).

Table 2. Fitting parameters, A_i , and Standard Deviations, σ , for the Excess Molar Volume, V_m^E , for the (ionic liquid + water) binary mixtures.

	T/K	A_0	A_1	A_2	A_3	σ / $10^6\text{m}^3\cdot\text{mol}^{-1}$
[emim][BF ₄]	293.15	0.6252	-0.6521	-0.9324	0.7671	0.01324
	303.15	0.7164	-0.7313	-0.6553	0.5115	0.01385
	313.15	0.8582	-0.9247	-0.5636	0.5280	0.01396
	323.15	1.0110	-1.0220	-0.4756	0.3104	0.01598
	333.15	1.0540	-1.0490	-0.4826	0.7067	0.01428
	343.15	1.0600	-1.1660	-0.2384	0.9656	0.01265
[bmim][BF ₄]	293.15	1.0600	-0.5071	0.1558	2.3770	0.00491
	303.15	1.4910	-0.5892	0.6545	2.7680	0.00945
	313.15	1.6570	-0.8095	0.9143	2.4500	0.00990
	323.15	1.8510	-1.0080	1.0650	2.2910	0.01044
	333.15	2.0160	-1.1260	1.1700	2.7960	0.01242
	343.15	2.1410	-1.0890	0.9287	3.1100	0.00841
[hmim][BF ₄]	293.15	1.8220	-1.7230	-0.4688	3.0110	0.01281
	303.15	2.1300	-2.1100	-0.4788	3.4800	0.01722
	313.15	2.3810	-2.3990	-0.3422	3.4750	0.01789
	323.15	2.6400	-2.6960	-0.2104	3.5080	0.01849
	333.15	2.8440	-2.9570	-0.1993	3.7340	0.01958
	343.15	2.9800	-3.1800	-0.2816	4.1090	0.02231
[omim][BF ₄]	293.15	2.5850	-1.5830	-2.0070	3.1380	0.03214
	303.15	2.9120	-1.8400	-1.5370	2.7220	0.03169
	313.15	3.2450	-2.1340	-1.3860	2.7680	0.03326
	323.15	3.5930	-2.5060	-0.8094	2.2170	0.03465
	333.15	4.0590	-3.4340	1.4830	-0.0057	0.03973
	343.15	4.9860	-4.5080	3.2600	-1.8770	0.06816
[emim][TfO]	293.15	0.4739	-0.7473	-1.4460	2.2870	0.02523
	303.15	0.6505	-1.2180	-1.2120	2.4260	0.02704
	313.15	0.8575	-1.0250	-0.7534	1.1960	0.02273
	323.15	1.1030	-1.3780	-0.3775	1.0900	0.01782
	333.15	1.3700	-1.7340	0.1540	0.7550	0.00849
	343.15	1.5600	-1.9500	0.9787	-0.0525	0.01445
[bmim][TfO]	293.15	-0.5364	0.1211	-1.1170	1.0060	0.01221
	303.15	-0.3721	0.0734	-0.4494	0.8382	0.01502
	313.15	-0.1817	-0.1414	-0.0181	0.4906	0.01352
	323.15	0.0463	-0.6260	0.3297	0.7792	0.01419
	333.15	0.2258	-0.6972	0.5223	0.1022	0.00627
	343.15	0.4536	-0.9374	0.7186	0.0368	0.00579
[bmim][OcSO ₄]	293.15	0.3561	2.3550	0.1310	-1.3580	0.01136
	303.15	0.5594	2.0260	0.4128	-1.6500	0.01167
	313.15	0.8200	1.9460	0.3835	-1.8180	0.01690
	323.15	1.0880	1.8000	0.6553	-1.8980	0.01801
	333.15	1.3310	1.7920	0.6379	-2.0560	0.01665
	343.15	1.6500	2.0360	0.1593	-2.3980	0.01422

Figure 6 shows the excess molar volumes (V_m^E) calculated from the experimental densities and by the fourth degree Redlich-Kister polynomial equation at 293.15 K. The V_m^E are grouped by

families with the same anion $[\text{BF}_4]$ and different cation (Figure 6a): [emim], [bmim], [hmim], [omim] and the same cation [bmim] and different anion (Figure 6b): $[\text{BF}_4]$, [TfO], $[\text{OcSO}_4]$.

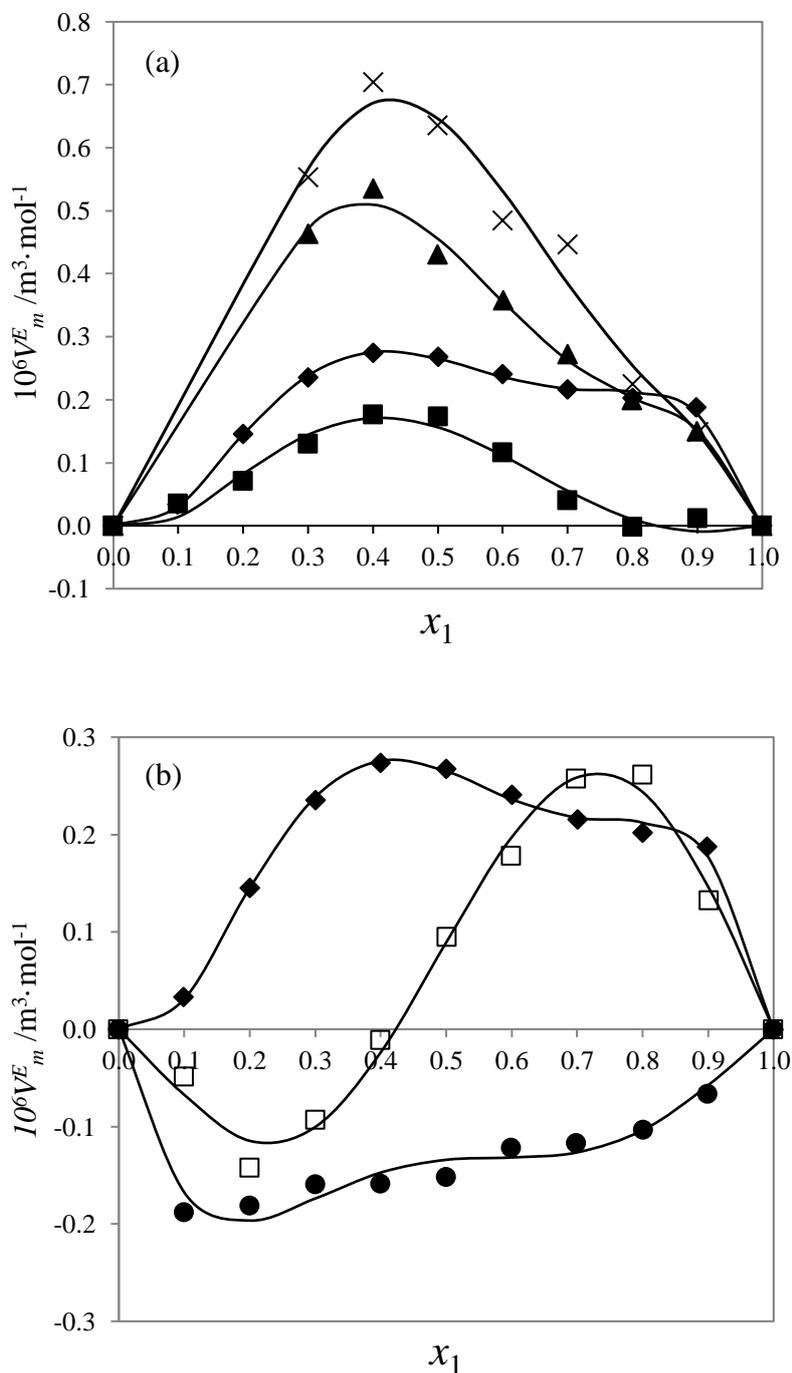


Figure 6. Influence of the alkyl chain length of the cation (a) (■ [emim][BF₄], ◆ [bmim][BF₄], ▲ [hmim][BF₄] and × [omim][BF₄]) and (b) the effect of the anion (◆ [bmim][BF₄], ● [bmim][TfO] and □ [bmim][OcSO₄]) on V_m^E of ionic liquid (1)-water (2) binary mixtures at 293.15 K. The estimated combined standard uncertainty, u_{comb} , of V_m^E is $u_{comb}(V_m^E) < 1.73 \cdot 10^{-8} \text{ m}^3 \cdot \text{mol}^{-1}$.

The solid lines represent the fitting functions by Redlich-Kister; the fitting parameters and standard deviation for V_m^E are collected in Table 2.

The difference in behavior of each system was considered according to the ionic liquid structure in order to understand the molecular organization of the ionic liquid + water mixtures, bearing in mind the special “iceberg” structure of the water molecules and the important modifications that this structure suffers as a function of composition and temperature in the presence of polar compounds such as ILs. Generally, on dissolution into H₂O at infinite dilution, IL molecules break away from their pure environment and settle in the H₂O environment, presumably as ions. As the concentration of IL increases, IL ions and the counter anions begin to interact with each other, either directly or in an H₂O mediated manner. At higher concentration of the IL, some organization among the ions takes place and, eventually, at about $x_{IL} > 0.5$ to 0.6, IL molecules cluster together with a very similar local arrangement as in the pure IL state. Therefore, depending on the degree of dissociation, the subsequent interaction with liquid H₂O, direct hydration or “iceberg” formation around IL ions, would be more or less strong⁵⁴.

According to the results shown in Tables S15 to S21 and Figure S10 of Supporting Information, we have found that excess molar volumes are generally positive in most of the binary mixtures studied, and for all compositions and temperatures involving [emim][BF₄]-water and [bmim][BF₄]-water systems. This means that expansion occurs during the dissolution process, which could be due to the breaking of hydrogen bonds between the water molecules³⁷ and/or to the weak interaction of ILs with water, insufficient to cause volume reduction. The V^E increases with increasing ionic liquid mole fraction up to $x_l = 0.4$, behavior which is reversed for both ionic liquid systems at higher mole fractions of ionic liquid. The results obtained for the [emim][BF₄]-water binary system agree with those previously published in the literature⁵⁵. In the case of [hmim][BF₄] + water and [omim][BF₄] + water, the behavior was similar in the composition range in which the mixtures are miscible and the maximum was reached at approximately the same composition values. Significant negative values were found for [emim][TfO] + water (only for low ionic liquid mole fractions at 293.15 K), [bmim][TfO] + water (at temperatures lower than

323.15 K) and [bmim][OcSO₄] + water (only for low ionic liquid mole fractions and temperatures lower than 313.15 K). In the cases of [emim][TfO] + water and [bmim][OcSO₄] + water, a small negative minimum was observed for low compositions at 293.15 K, because of packing effects during the mixing process which are the result of the stronger interaction between these ILs and water and their higher hygroscopic character, particularly for [emim][TfO]. Similar results for [emim][TfO]-water^{24,30} and [bmim][TfO]-water²⁹ systems were found by other authors. All the studied systems present asymmetrical curves due to the fact that both components (ionic liquid and water) present very different molar volumes. Figure S10 of the Supporting Information shows that the excess molar volume generally increases with temperature at a fixed composition of the mixture, possibly due to the breaking of specific interactions in the IL-water mixture (usually H-bonds) when temperature increases, although, generally, the V_m^E values in ionic liquid-rich region change less with temperature, suggesting the prevalence of ion-ion interactions which are not temperature sensitive. In addition, it was seen that non-specific interactions only slightly depend on temperature so their influence on excess molar volume is normally negligible^{36,56}. Figure 6 shows that for binary systems containing BF₄-based ILs, the maximum value reached of the excess molar volume increases with the length of the alkyl chain of the cation, which means that interactions and better packing are particularly pronounced in the [emim][BF₄]-water solutions. Furthermore, hydrogen bonding between solvent molecules also need to be taken into account, since hydrogen bonds between water molecules are very strong, although the orientation of water molecules and interactions with ions are hindered when the alkyl chain length of the cation increases. This may be attributed to the bigger steric effect produced by longer alkyl chains. Furthermore, it has been observed for ILs with the same cation that values of the excess molar volume decrease in the order [bmim][BF₄] > [bmim][OcSO₄] > [bmim][TfO], which means that interactions and packing are greater in the [TfO]-water solutions. There are large discrepancies in the literature concerning the excess molar volume of the [bmim][BF₄]-water binary system^{27,33,40-42,48,57-59}. These discrepancies could be due to many factors, but the most important is the experimental uncertainties of the density value which compete with the small value of the magnitude. However, our results reflect those reported in two recent papers^{58,59}.

3.1.2. Apparent Molar Volumes and Partial Molar Volumes

Apparent molar volumes ($V_{\phi i}$) were calculated for water and for the ionic liquid in the solution from the experimental density using the following expressions:

$$V_{\phi 1} = \frac{(\rho_2 - \rho)}{m_1 \rho \rho_2} + \frac{M_1}{\rho} \quad (5)$$

$$V_{\phi 2} = \frac{(\rho_1 - \rho)}{m_2 \rho \rho_1} + \frac{M_2}{\rho} \quad (6)$$

where m_1 and m_2 are the molalities related to the ionic liquid and the water, respectively. The molalities of the mixtures studied are given in Table S22 of the Supporting Information.

The partial molar volumes of the components, V_1 and V_2 , were also calculated, from the eqs. 7 and 8, using the parameters A_i obtained from eq. 4.

$$V_1 = V_1^o + (1 - x_1)^2 \sum_{i=0}^{i=n} A_i (1 - 2x_1)^i - 2x_1 (1 - x_1)^2 \sum_{i=0}^{i=n} A_i (i) (1 - 2x_1)^{i-1} \quad (7)$$

$$V_2 = V_2^o + x_1^2 \sum_{i=0}^{i=n} A_i (1 - 2x_1)^i + 2x_1^2 (1 - x_1) \sum_{i=0}^{i=n} A_i (i) (1 - 2x_1)^{i-1} \quad (8)$$

with

$$V_1^o = \frac{M_1}{\rho_1} \quad (9)$$

$$V_2^o = \frac{M_2}{\rho_2} \quad (10)$$

The apparent molar volumes, $V_{\phi i}$, and partial molar volumes, V_i , are reported in Tables S15 to S21 of Supporting Information and represented in Figure 7 and Figure S11 of Supporting Information. It can be seen that the change of $V_{\phi 1}$ and V_1 with temperature is more pronounced than the variation with the ionic liquid mole fractions. Both parameters increase with the length of the alkyl chain of the cation, and the order for the mixtures with the same anion is [bmim][OcSO₄] > [bmim][TfO] > [bmim][BF₄]. $V_{\phi 1}$ and V_1 data are nearly constant with molar fraction for all IL mixtures studied. Any variation of the apparent molar volume of the ILs, $V_{\phi 1}$,

with composition at constant temperature is slight as a consequence of the stronger self-association of the water molecules. The apparent molar volumes of water, $V_{\phi 2}$, decrease with IL mole fraction being this reduction higher when the alkyl chain of the cation is shorter.

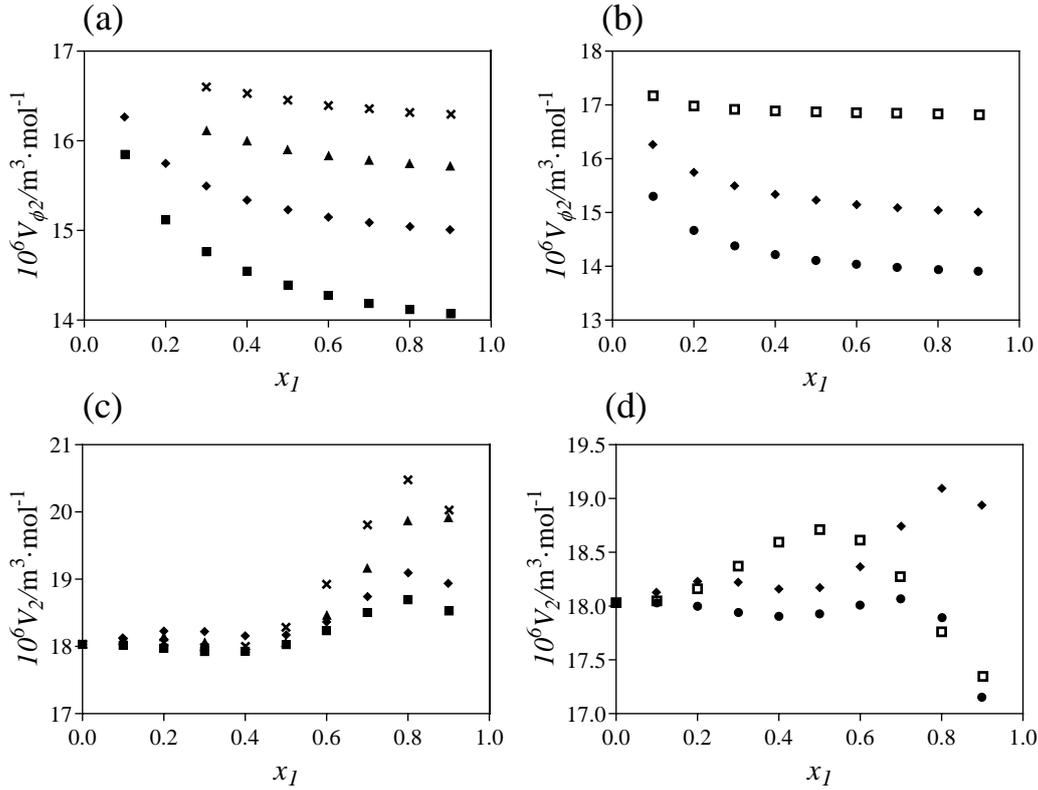


Figure 7. Apparent (a, b) and partial (c, d) molar volumes of binary mixtures as a function of the ionic liquid mole fraction (x_1) at $T = 293.15$ K (■ [emim][BF₄], ◆ [bmim][BF₄], ▲ [hmim][BF₄], × [omim][BF₄], ● [bmim][TfO] and □ [bmim][OcSO₄]).

Useful information about ionic liquid–water interactions can be obtained from knowing the partial molar properties at infinite dilution, when solute–solute interactions can be neglected. The partial molar volumes of the components at infinite dilution, V_1^∞ and V_2^∞ , were calculated as a function of R-K parameters, by transformation of V_1 and V_2 when $\lim_{x_1 \rightarrow 0} V_1$ and $\lim_{x_2 \rightarrow 0} V_2$ from the eqs. 7 and

8.

$$V_1^\infty = V_1^0 + \sum_{i=0}^{i=n} A_i(x_1 \rightarrow 0) \quad (11)$$

$$V_2^\infty = V_2^o + \sum_{i=0}^{i=n} A_i(x_2 \rightarrow 0) \quad (12)$$

Thus, rearrangement of the eqs. 7 and 8 gives the partial excess molar volumes at infinite dilution of ionic liquid and water, $(V_1^E)^\infty$ and $(V_2^E)^\infty$, respectively⁵⁹:

$$(V_1^E)^\infty = \sum_{i=0}^{i=n} A_i \quad (13)$$

$$(V_2^E)^\infty = \sum_{i=0}^{i=n} A_i(-1)^i \quad (14)$$

The values of the partial molar volume at infinite dilution (V_i^∞) and excess partial molar volume at infinite dilution ($(V_i^E)^\infty$) for the components of the mixtures at the studied temperatures are given in Table S22 of the Supporting Information. The partial molar volumes at infinite dilution, V_i^∞ , increase with temperature and as the length of the alkyl chain of the cation increases. Most of values of $(V_I^E)^\infty$ are positive at all temperatures, due to the volume expansion that occurs when ionic liquid is added in an infinite volume of water, indicating that the dissociation effect is greater than any association effect. Only $(V_I^E)^\infty$ of [emim][BF₄] + water and [bmim][TfO] + water show negative values at low temperature, perhaps because not all hydrogen bonds are broken with a small amount of ionic liquid and become positive at higher temperatures. On the other hand, most $(V_2^E)^\infty$ values are also positive as a consequence of the weaker interactions between the components of the mixtures.

For comparison purposes, the partial molar volumes of the IL at infinite dilution, V_I^∞ , have been also calculated with the Bahe-Varela model^{27,60} and the results are shown on Table S23 of the Supporting Information. This theoretical model has also been chosen because of their physical meaning, in contrast with Redlich-Kister model, which is an empirical correlation. Eq. 15 was used to determine the V_I^∞ values by Bahe-Varela⁶⁰ as:

$$V_1 = V_1^\infty + \alpha C^{1/3} + \beta C + \gamma C^2 \quad (15)$$

where C is the IL concentration in mol per dm³ and the parameters α , β and γ are expressed by the following equations²⁷:

$$\alpha = 4.6RT \left(-a \left(\left(\frac{\partial \ln a}{\partial P} \right)_T + \frac{\chi}{3} \right) \right) \quad (16)$$

where R is the perfect gas constant, P the pressure, T the absolute temperature, χ the isothermal compressibility of the solution and a may be calculable for a salt by:

$$a = \frac{A'' z_+ z_- N}{2.3026 \nu RT \varepsilon} a_{A''} \left(\frac{N}{1000} \right)^{1/3} \quad (17)$$

where A'' is the Madelung-like constant, z_+ and z_- are, respectively, cation and anion charges ($\nu = \nu_+ + \nu_-$), N is Avogadro's number, ε the dielectric constant and $a_{A''}$ is a factor for converting a given structure into the distance separating the ions.

$$\beta = \left(\left(\frac{\partial b}{\partial P} \right)_T + b\chi \right) \quad (18)$$

The literal expression of the parameter b involves variables specific to the system, for example, the volume of the region around each ion in which the dielectric constant varies from ε to ε_0 .

$$\gamma = \left(\left(\frac{\partial c}{\partial P} \right)_T + 2c\chi \right) \quad (19)$$

The parameter c depends on the characteristics of the mixture components. The values of the coefficients b and c may be obtained experimentally and thus serve as adjustable parameters.

Fitting parameters of the Bahe-Varela model are shown on Table S24. Values of β and γ have been determined from fitting to experimental data, while α values can be obtained theoretically and are temperature-dependent. As can be seen, the V_I^∞ obtained by Bahe-Varela model increases linearly with temperature due to the thermal expansion, which means lower concentration for a given mixture as temperature increases. The values of β can be positive or negative depending of the nature of the salt. Our results showed that for the same cation, β increases as the molecular weight decreases and for the same anion, β increases as the molecular weight of the cation increases. As Malham *et al.*²⁷ state, presumably, these rules reflect different interactions between ions and their dielectric environment according to their size. The values of γ are negative and small except for [bmim][OcSO₄], then the group $\left[\alpha C^{1/3} + \gamma C^2 \right]$, which describes the contribution of the interactions between the charges within the face-centered-cubic structure and the contribution of short-range ion-ion interactions, is always positive and small. The root mean

square deviation (RMSD) between V_1^∞ values obtained by both methods, Redlich-Kister and Bahe-Varela, have ranged from 0.46 to 9.92%.

In Figure 8 the experimental values of partial molar volume (represented by points), the best fitting obtained with Bahe–Varela model (eq. 15) to the data points (represented by continuous line) and the best fitting obtained by Redlich Kister equation (represented by discontinuous line) are represented. In all cases, the best fitting to the experimental data was obtained with Bahe–Varela model, except for [bmim][BF₄] at high temperature. In spite of the simplicity of the Bahe–Varela equation, with only three fitting parameters, the fitting quality of the Bahe-Varela model is quite good for all analyzed systems, which tends to confirm its validity.

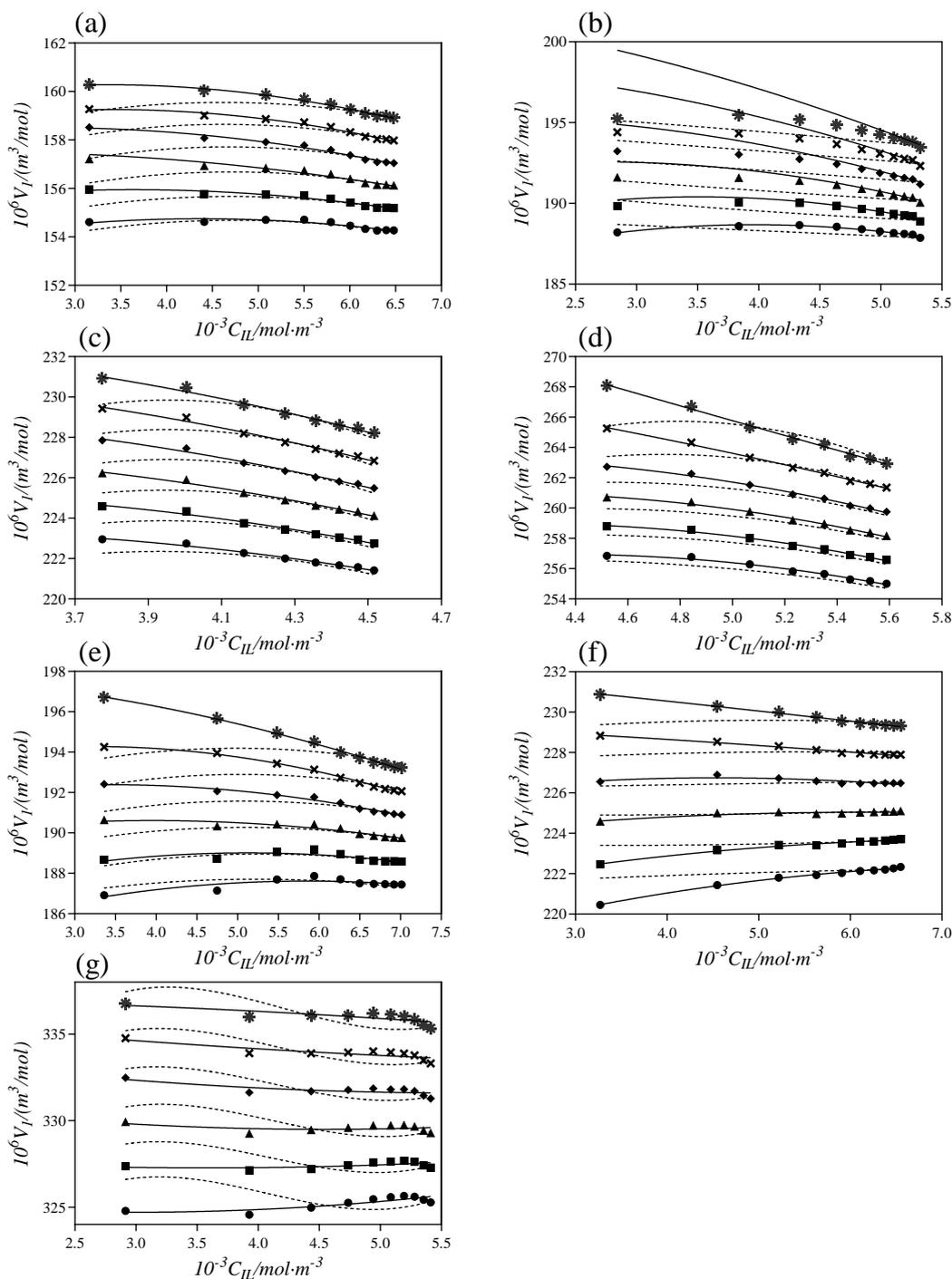


Figure 8. Partial molar volume of the IL vs. concentration of IL for aqueous systems of (a) [emim][BF₄], (b) [bmim][BF₄], (c) [hmim][BF₄], (d) [omim][BF₄]; (e) [emim][TfO], (f) [bmim][TfO], (g) [bmim][OcSO₄]. Experimental V_1 : ● 293.15 K; ■ 303.15 K; ▲ 313.15 K; ◆ 323.15 K; × 333.15 K, * 343.15 K. V_1 obtained with Bahe-Varela are represented by continuous line and V_1 obtained with Redlich – Kister are represented by discontinuous line.

In Figure 9, the approach of Desnoyers and Perron⁶¹ shows the variation of V^E/x_1x_2 with the ionic liquid mole ratio, x_1 . Using this plot, the same influence of temperature on volumetric properties can be observed. The trend is far from linearity due to the difference in size and polarity of the components in the mixture. The temperature effect is greater for low mole fractions of the ionic liquid, V^E/x_1x_2 values being lower at lower temperatures due to a packing effect between components.

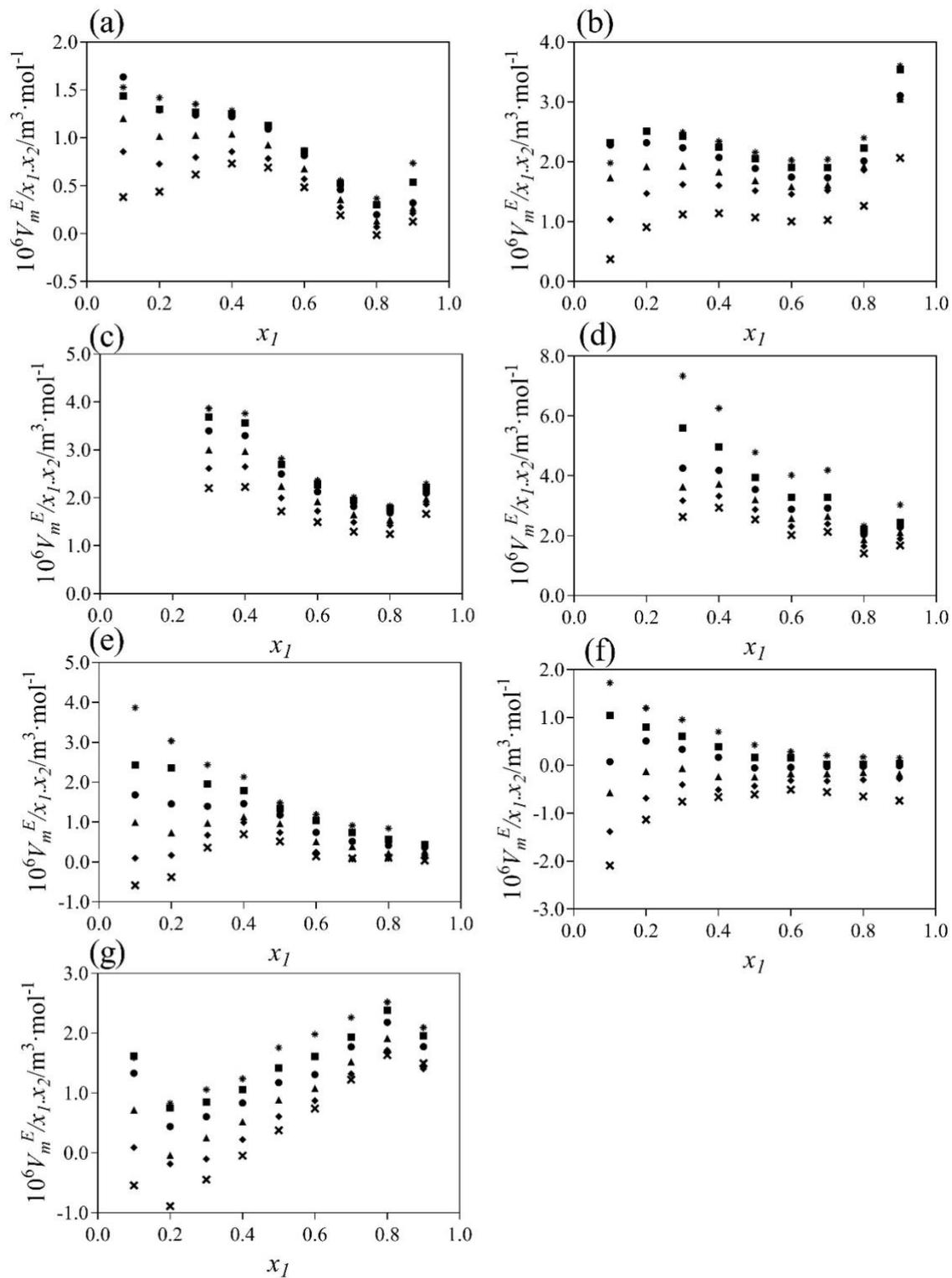


Figure 9. Variation of V^E/x_1x_2 with ionic liquid mole fraction (x_1): (a) [emim][BF₄], (b) [bmim][BF₄], (c) [hmim][BF₄], (d) [omim][BF₄], (e) [emim][TfO], (f) [bmim][TfO] and (g)

[bmim][OcSO₄] at × 293.15 K, ◆ 303.15 K, ▲ 313.15 K, ● 323.15 K, ■ 333.15 K and ✕ 343.15 K.

3.1.3. Thermal expansion coefficients

The self-association and interactions in the solutions can also be discussed from the corresponding isobaric thermal expansion coefficients, calculated on the basis of the volumetric data. The thermal expansion coefficients, α_{ip} and α_p , for the pure components and mixtures, respectively, are defined by eqs. 20 and 21:

$$\alpha_{ip} = \frac{1}{V_i^o} \left(\frac{\partial V_i^o}{\partial T} \right)_p \quad (20)$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (21)$$

The excess thermal expansion, α_p^E , was calculated with eq. 22:

$$\alpha_p^E = \alpha_p - \sum_{i=1}^{i=2} \phi_i \alpha_{ip} \quad (22)$$

where ϕ_i is the volume fraction of component i , defined by eq. 23:

$$\phi_i = x_i V_i^o / \sum_{i=1}^{i=2} x_i V_i^o \quad (23)$$

The values of these coefficients, α_p and α_p^E , are given in Table S25 of Supporting Information for different temperatures and ionic liquid volume fractions. The estimated combined standard uncertainties, u_{comb} , of α_p and α_p^E are $<4.2 \cdot 10^{-4} \text{ K}^{-1}$ and $6 \cdot 10^{-4} \text{ K}^{-1}$, respectively. In Figure 10, α_p^E values are represented at 293.15 K. It can be seen that positive deviation of the excess thermal expansion coefficient occurs for all systems over the whole composition and over the all temperature ranges. α_p^E presents a maximum and slightly decrease with the temperature. In the water-rich region, water molecules are reoriented to form hydrophobic hydrogen bonds around the ionic liquid molecules and the effect of the self-interaction dominates, making α_p^E positive. In the mid and water-poor regions, the effect of hydrogen bonding between dissimilar molecules of water and the ionic liquid plays a primary role⁶²⁻⁶⁴. The addition of ionic liquid to the water

acts as a structure-making reagent⁶⁵. This effect is more pronounced as the alkyl chain length increases.

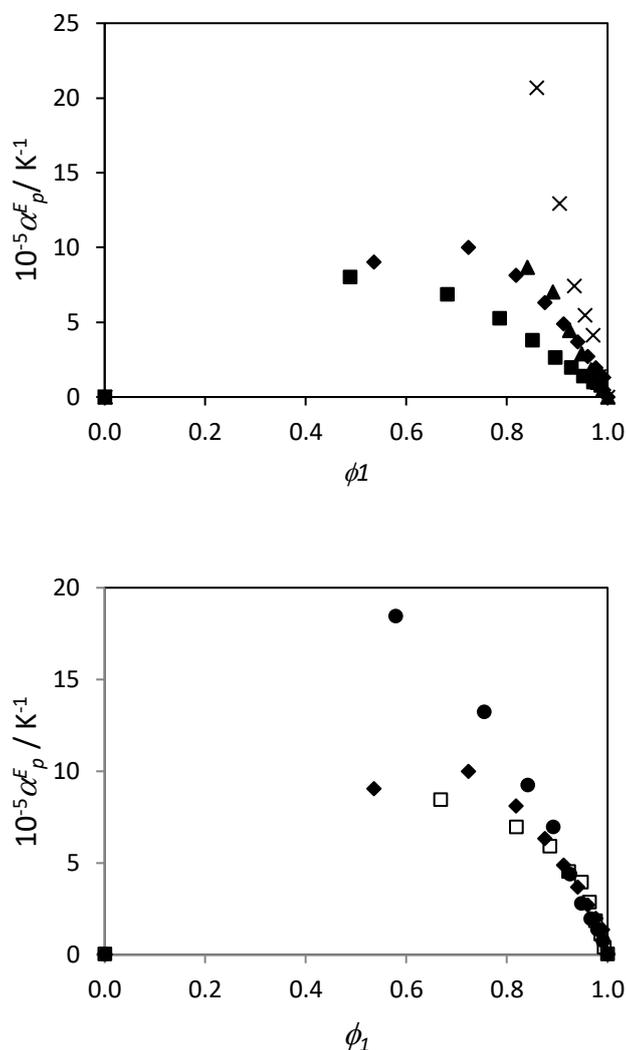


Figure 10. Variation of excess thermal expansion coefficients, α_p^E , with volume fraction of ionic liquid (1) at $T = 298.15$ K (\blacksquare [emim][BF₄], \blacklozenge [bmim][BF₄], \blacktriangle [hmim][BF₄], \times [omim][BF₄]), \bullet [bmim][TfO] and \square [bmim][OcSO₄]). The estimated combined standard uncertainty, u_{comb} , of α_p^E is $6 \cdot 10^{-4} \text{ K}^{-1}$.

3.2.- Molar Refraction Deviation

The refractive index n is a good tool for studying the molecular interactions that occur between the component molecules of a liquid mixture. In the same way as for density, the deviation in

molar refraction was calculated from refractive index experimental data for the binary mixtures studied in the whole range of temperature from 293.15 to 343.15 K, in order to determine the non-ideality of the studied systems. The results are shown in Tables S26 to S32 of the Supporting Information.

The following is the most commonly used equation to determine the experimental values of the refractive index deviation:

$$\Delta n = n - n^{id} \quad (24)$$

where n is the real refractive index of the binary mixture and n^{id} represents the ideal refractive index of the mixture calculated with the following equation as in Reis *et al.*⁶⁶:

$$n^{id} = (\phi_1 \cdot n_1^2 + \phi_2 \cdot n_2^2)^{1/2} \quad (25)$$

Where ϕ_1 and ϕ_2 are the volume fraction of the IL and water, respectively, which are calculated with eq. 23 and n_1 and n_2 are the refractive indices of the pure IL and water, respectively.

However, analysis of the refractive index deviation is not such a straightforward test as it is for other thermodynamic properties, such as the volume, heat capacity or viscosity, because the ideal refractive index of the mixture is not so easily calculated. In eq. 23, the ideal refractive index of the mixture is defined through thermodynamic relationships with these other properties but, and this is only an approximation, the results could be inaccurate.

For this reason, the deviation in refractive index was calculated in terms of the deviation in molar refraction, ΔR , following the procedure described by Chaudhary *et al.*⁴⁰:

$$\Delta R = R_m - \sum R_i \phi_i \quad (26)$$

where R_i and R_m are the molar refraction of the pure components and the mixture, respectively, and ϕ_i is the volume fraction of the component i , which is calculated with eq. 19. According to Piñeiro *et al.*⁶⁷, the molar refraction R_i of a compound is related to the mean polarizability and represents the ease with which the molecule's electrons can be displaced by an electric field. In addition, the molar refraction is proportional to the dispersion forces by means of the resonance frequencies or, within a quantum mechanical frame, the transitions between different energy levels in the molecule.

From the Lorentz-Lorenz equation, R_m and R_i are calculated with eqs. 27 and 28:

$$R_m = \frac{n_{Dm}^2 - 1}{n_{Dm}^2 + 2} V_m \quad (27)$$

$$R_i = \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} V_i \quad (28)$$

Figure S12 in the Supporting Information shows the influence of temperature and molar composition on the deviation in molar refraction for the ionic liquid + water binary mixtures. The estimated combined standard uncertainty, u_{comb} , of ΔR is $<0.024 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. As in the case of excess molar volumes, the deviation in molar refractions, ΔR , at each mole fraction and temperature were fitted by a fifth degree Redlich-Kister polynomial equation (eq. 4). Fitting parameters, A_i , for all the binary mixtures at each studied temperature are shown in Table 4 adjusted by least squares method.

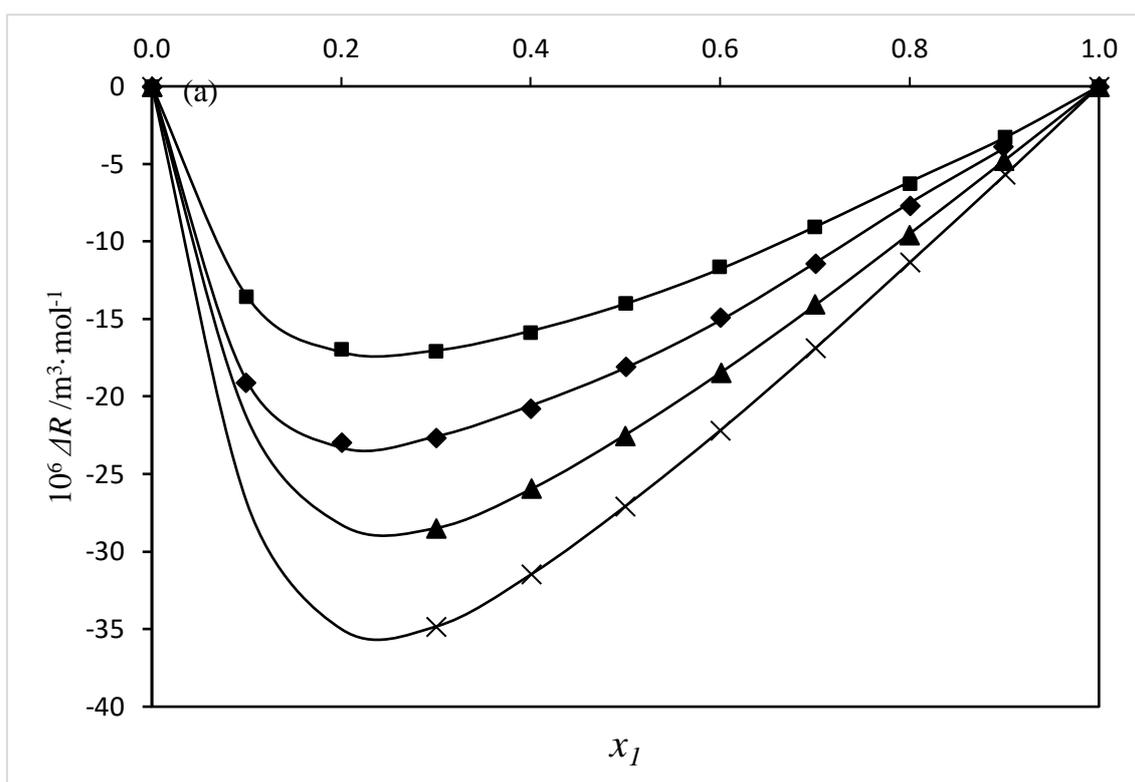
Table 4. Fitting parameters, A_i , and Standard Deviations, σ , for the Deviation in Molar Refraction, ΔR , for the (ionic liquid + water) binary mixtures.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
[emim][BF ₄]	293.15	-56.09	39.63	-31.04	48.64	-42.91	0.09
	303.15	-55.25	39.91	-29.93	49.86	-42.1	0.09
	313.15	-55.18	39.91	-30.16	51.02	-41.75	0.1
	323.15	-55.4	39.93	-31.2	50.37	-41.42	0.09
	333.15	-55.18	40.13	-31.53	50.49	-40.69	0.1
	343.15	-55.22	40.23	-30.31	50.02	-42.52	0.1
[bmim][BF ₄]	293.15	-72.61	54.08	-40.44	77.91	-70.94	0.16
	303.15	-72.58	54.54	-40.8	78.03	-71.37	0.17
	313.15	-72.83	54.14	-40.2	79.35	-72.76	0.18

	323.15	-73.03	54.21	-38.25	78.98	-76.56	0.17
	333.15	-73.08	54.21	-40.43	79.29	-74.5	0.16
	343.15	-73.06	53.32	-42.32	79.37	-72.91	0.16
[hmim][BF ₄]	293.15	-89.88	75.63	-67.9	61.29	-28.84	0.04
	303.15	-90.24	76.12	-66.89	58.33	-26.62	0.02
	313.15	-90.16	77.95	-70.63	55.65	-21.48	0.02
	323.15	-90.2	76.89	-69.5	62.33	-29.57	0.01
	333.15	-90.12	76.03	-71.21	66	-31.64	0.01
	343.15	-89.8	76.36	-69.9	61.18	-27.22	0.01
[omim][BF ₄]	293.15	-108.3	93.51	-86.56	82.1	-41.9	0.01
	303.15	-108.4	94.04	-88.65	80.9	-38.49	0.03
	313.15	-108.6	94.38	-87.17	80.39	-41.63	0.01
	323.15	-108.5	94.96	-89.43	75.48	-32.64	0.03
	333.15	-108.4	93.61	-88.16	81.15	-39.13	0.01
	343.15	-107.8	94.27	-89.08	73.13	-28.65	0.02
[emim][TfO]	293.15	-74.17	55.69	-40.73	78.58	-73.92	0.16
	303.15	-74.66	55.82	-39.93	78.2	-76.51	0.18
	313.15	-74.64	56.06	-40.96	78.55	-74.12	0.18
	323.15	-74.44	56.11	-40.61	78.61	-74.95	0.18
	333.15	-74.61	55.34	-40.48	79.91	-75.09	0.17
	343.15	-74.12	55.21	-41.46	79.33	-73.17	0.16
[bmim][TfO]	293.15	-93.11	70.3	-50.81	112.7	-111.9	0.28
	303.15	-93.09	70.47	-51.69	113.8	-110.6	0.27
	313.15	-93.04	70.54	-51.53	114.5	-111.3	0.28
	323.15	-92.84	69.86	-50.8	116.6	-111.2	0.28
	333.15	-92.95	70.08	-50.53	115.9	-112.3	0.27
	343.15	-93.15	70.01	-52.54	116.2	-110.4	0.27
[bmim][OcSO ₄]	293.15	-157.2	119.7	-83.39	246.4	-264	0.68
	303.15	-157.1	119.7	-84.48	248.3	-261.5	0.69
	313.15	-157.2	119.3	-84.19	250	-263.1	0.67
	323.15	-157.3	119.3	-85.53	250.1	-261.8	0.69
	333.15	-157.8	118.8	-83.14	251.1	-266.8	0.68
	343.15	-157.7	119.9	-84.68	248.9	-264.6	0.7

Similar trends were found for the dependence of deviation in molar refraction, ΔR , on the composition of all the binary mixtures studied as can be seen in Tables S26 to S32 and Figure S12 in the Supporting Information. The ΔR values were negative over the whole composition range at all the temperatures, indicating the presence of dispersion forces in the aqueous mixtures of ionic liquid reaching a minimum value for a mole fraction of ionic liquid of around 0.2-0.3 for the seven studied systems. A correlation between the sign of ΔR and V^E was observed in most of

our mixtures as well as for a number of solvent systems⁶⁸. When V^E is positive, ΔR is negative and vice versa, which means that a greater free volume is available in the aqueous mixtures of ionic liquid than in the ideal solution. Our results clearly show that the dependence of ΔR on temperature is less important than in the case of excess molar volumes. In addition, as can be observed in Figure 11, lower minimum values of ΔR were obtained with ILs with longer alkyl chains. These results agree with the excess molar volume results obtained, since the lower values of ΔR may be due to a low packing efficiency for greater steric effects. Comparing ILs with the same alkyl chain ([bmim]) and different anions, the following order can establish for the values of the deviation in molar refraction of the ionic liquid in the mixture: $[\text{BF}_4] > [\text{TfO}] > [\text{OcSO}_4]$. The explanation could be that bulkier anions lead to a higher steric hindrance.



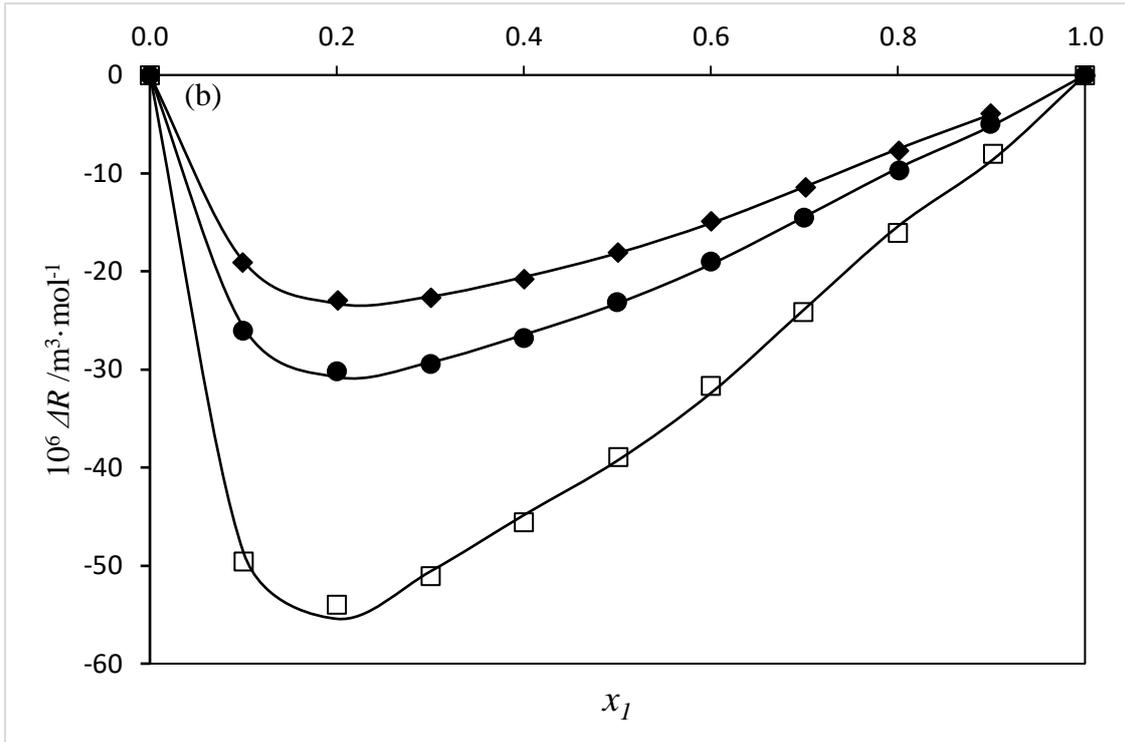


Figure 11. Influence of the alkyl chain length of the cation (a) (■ [emim][BF₄], ◆ [bmim][BF₄], ▲ [hmim][BF₄] and × [omim][BF₄]) and (b) the effect of the anion (◆ [bmim][BF₄], ● [bmim][TfO] and □ [bmim][OcSO₄]) on ΔR of ionic liquid (1)-water (2) binary mixtures at 293.15 K. The estimated combined standard uncertainty, u_{comb} , of ΔR is $<0.024 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. The solid lines represent the fitting functions by Redlich-Kister; the fitting parameters and standard deviation for ΔR are collected in Table 4.

3.3.- Refractive index and density predictions

The refractive index of a binary mixture can be predicted from its density and the density and refractive index of the pure compounds^{2,46}. We have used four expressions to determine the calculated refractive index of the binary mixtures: Lorentz-Lorenz (eq. 29), Wiener (eq. 30), Dale-Gladstone (eq. 31) and Eykman (eq. 32).

$$\frac{n_{Dm,calc}^2-1}{n_{Dm,calc}^2+2} = \phi_1 \left(\frac{n_{D1}^2-1}{n_{D1}^2+2} \right) + \phi_2 \left(\frac{n_{D2}^2-1}{n_{D2}^2+2} \right) \quad (29)$$

$$\frac{n_{Dm,calc}^2 - n_{D1}^2}{n_{Dm,calc}^2 + 2n_{D2}^2} = \phi_2 \left(\frac{n_{D2}^2 - n_{D1}^2}{n_{D2}^2 + 2n_{D1}^2} \right) \quad (30)$$

$$n_{Dm,calc} - 1 = \phi_1(n_{D1} - 1) + \phi_2(n_{D2} - 1) \quad (31)$$

$$\frac{n_{Dm,calc}^{-1} - 1}{n_{Dm,calc} + 0.4} = \phi_1 \left(\frac{n_{D1}^{-1} - 1}{n_{D1} + 0.4} \right) + \phi_2 \left(\frac{n_{D2}^{-1} - 1}{n_{D2} + 0.4} \right) \quad (32)$$

where $n_{Dm,calc}$ is the calculated refractive index of the binary mixtures and n_{Di} and ϕ_i are the refractive index and the volumetric fraction of component i , respectively [1]. The standard deviations of the calculated refractive index values with respect to the experimental values are depicted in Table 5.

Table 5. Global Standard Deviations (SD) between experimental refractive index and the values calculated by Lorentz-Lorenz (L-L), Wiener (W), Dale-Gladstone (D-G) and Eykman (E) correlations for the studied (ionic liquid +water) binary mixtures in the whole range of temperature (from 293.15 K to 343.15 K).

	L-L	W	D-G	E
[emim][BF ₄] + water	0.0019	0.0364	0.0022	0.0016
[bmim][BF ₄] + water	0.0009	0.0382	0.0008	0.0013
[hmim][BF ₄] + water	0.0012	0.0391	0.0011	0.0014
[omim][BF ₄] + water	0.0011	0.0411	0.0011	0.0010
[emim][TfO] + water	0.0020	0.0422	0.0017	0.0025
[bmim][TfO] + water	0.0025	0.0421	0.0022	0.0031
[bmim][OcSO ₄] + water	0.0015	0.0529	0.0012	0.0022
SD (Average value)	0.0016	0.0417	0.0015	0.0019

The experimental values of the refractive index of the (ionic liquid + water) binary mixtures obtained in this work were in very good agreement with the values calculated using the Lorentz-Lorenz, Wiener, Dale-Gladstone and Eykman equations. While Lorentz-Lorenz and Dale-Gladstone predictions has similar standard deviations, Dale-Gladstone is the simplest and so easiest to apply.

4.-CONCLUSIONS

The volumetric properties of binary liquid mixtures of seven ILs with water in the whole composition range were determined at various temperatures at atmospheric pressure. Based on the experimental density measurements, the excess molar volumes, V_m^E , apparent molar volumes, $V_{\phi i}$, partial molar volumes, V_i , excess partial molar volumes, V_i^E , partial molar volume at infinite dilution, V_i^∞ , excess partial molar volume at infinite dilution, $(V_i^E)^\infty$, the coefficient of thermal expansion, α_p , and the excess of thermal expansion coefficient, α_p^E , were calculated. Excess molar volumes, V_m^E , are positive over the whole concentration range for all systems with an ionic liquid containing the $[\text{BF}_4]$ anion and the magnitude of any dispersion forces was more prominent at higher temperatures and with increased the alkyl length of the cation. In these systems, the breaking of ion-pair interactions of the ionic liquid and the hydrogen bond network of water are dominating. However, significant negative values for excess molar volumes were found in the $[\text{emim}][\text{TfO}]$ -water, $[\text{bmim}][\text{TfO}]$ -water and $[\text{bmim}][\text{OcSO}_4]$ -water mixtures at low ionic liquid mole fractions and low temperatures as a consequence of packing effects upon mixing due to the differences in size, shape and polarity of the molecules or as result of the stronger interaction between these ILs and water. The partial molar volumes at infinite dilution, V_i^∞ , increased with temperature and as the length of the alkyl chain of the cation increased. Most of values of $(V_i^E)^\infty$ are positive at all temperature due to a volume expansion when ionic liquid is added to an infinite volume of water. Positive deviation of the excess thermal expansion coefficient, α_p^E , also occurs for all systems over the whole composition and temperature range.

From refractive index experimental data, the deviation in molar refraction, ΔR , was calculated for the binary mixtures studied in the whole range of temperature from 293.15 to 343.15 K in order to determine the non-ideality of the studied systems. Deviation in molar refraction showed negative values over the whole composition range at all the studied temperatures, indicating the presence of dispersion forces in the aqueous mixtures of ionic liquid, reaching a minimum value for a mole fraction of ionic liquid of around 0.2-0.3 for the seven systems.

Excess molar volumes and deviation in molar refraction at each mole fraction and temperature were fitted by fourth and fifth degree Redlich-Kister polynomial equations, respectively. Volumetric data have been also analysed by Bahe-Varela model, with more physical meaning.

The density and refractive index measurements were correlated using the empirical equations of Lorentz-Lorenz, Wiener, Dale-Gladstone and Eykman. These equations gave very good results, particularly the Dale-Gladstone equation, and may be useful for predicting density from refractive index values with the advantage that the measurements of refractive index are easier to obtain than density.

Finally, the addition of water to the ILs and a change in temperature can be used to tune properties for a specific industrial application.

Supporting Information Available:

Experimental values of Density, ρ , and Refractive Index, n , of the IL+water binary mixtures and their fitting parameters with Temperature, T . Excess Molar Volumes, V_m^E , Apparent Molar Volumes ($V_{\phi i}$), Partial Molar Volumes (V_i) and Excess Partial Molar Volumes, V_i^E , of the binary mixtures. Fitting parameters (V_i^∞ , β and γ) and standard deviation, s , of Bahe-Varela equation. Thermal Expansion Coefficients, α_p , and Excess Thermal Expansion Coefficients, α_p^E , as a function of Ionic Liquid Volume Fraction, ϕ_i , for the investigated mixtures. Experimental deviations in molar refraction, ΔR , of the binary mixtures.

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References:

- (1) Cserjési, P.; Bélafi-Bakó, K.; Nemestóthy, N.; Gubicza, L. Recent trends on application

of ionic liquids in organic synthesis. *Hungarian Journal of Industrial Chemistry*. **2008**, *36*(1-2), 27-34.

- (2) Kurnia, K.A.; Taib, M.M.; Abdul Mutalib, M.I.; Murugesan, T. Densities, Refractive Indices and Excess Molar Volumes for Binary Mixtures of Protic Ionic Liquids with Methanol at $T = 293.15$ to 313.15 K. *J. Mol. Liq.* **2011**, *159*, 211–219. doi:10.1016/j.molliq.2011.01.005.
- (3) Iglesias-Otero, M.A.; Troncoso, J.; Carballo, E.; Romani, L. Density and Refractive Index in Mixtures of Ionic Liquids and Organic Solvents: Correlations and Predictions. *J. Chem. Thermodyn.* **2008**, *40*, 949–956. doi:10.1016/j.jct.2008.01.023.
- (4) Montalbán, M.G.; Bolívar, C.L.; Díaz Baños, F.G.; Vllora, G. Effect of Temperature, Anion, and Alkyl Chain Length on the Density and Refractive Index of 1-Alkyl-3-methylimidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2015**, *60*, 1986–1996. doi:10.1021/je501091q.
- (5) Muhammad, A.; Abdul Mutalib, M.I.; Wilfred, C.D.; Murugesan, T.; Shafeeq, A. Thermophysical Properties of 1-Hexyl-3-methyl Imidazolium Based Ionic Liquids with Tetrafluoroborate, Hexafluorophosphate and Bis(trifluoromethylsulfonyl)imide Anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438. doi:10.1016/j.jct.2008.04.016.
- (6) Tariq, M.; Forte, P.A.S.; Gomes, M.F.C.; Lopes, J.N.C.; Rebelo, L.P.N. Densities and Refractive Indices of Imidazolium- and Phosphonium-based Ionic Liquids: Effect of Temperature, Alkyl Chain Length, and Anion. *J. Chem. Thermodyn.* **2009**, *41* 790–798. doi:10.1016/j.jct.2009.01.012.
- (7) Soriano, A.N.; Doma, B.T.; Li, M.-H. Density and Refractive Index Measurements of 1-Ethyl-3-methylimidazolium-based Ionic Liquids, *J. Taiwan Inst. Chem. Eng.* **2010**, *41*, 115–121. doi:10.1016/j.jtice.2009.07.002.
- (8) Hasse, B.; Lehmann, J.; Assenbaum, D.; Wasserscheid, P.; Leipertz, A.; Fröba, A.P. Viscosity, Interfacial Tension, Density, and Refractive Index of Ionic Liquids [EMIM][MeSO₃], [EMIM][MeOHPO₂], [EMIM][OcSO₄], and [BBIM][NTf₂] in Dependence on Temperature at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54*, 2576–2583. doi:10.1021/je900134z.
- (9) González, E.J.; Domínguez, Á.; Macedo, E.A. Physical and Excess Properties of Eight Binary Mixtures Containing Water and Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2165–2176. doi:10.1021/je201334p.

- (10) Ariño, R.; Brodin, M.; Boldizar, A.; Westman, G. Thermal and Viscoelastic Properties of Cellulosic Gels with Different Ionic Liquids and Coagulation Agents. *BioResources* **2013**, *8*, 2209–2221.
- (11) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess Enthalpy, Density, and Heat Capacity for Binary systems of Alkylimidazolium-based Ionic Liquids + Water. *J. Chem. Thermodyn.* **2009**, *41*, 161–166. doi:10.1016/j.jct.2008.10.002.
- (12) Rilo, E.; Pico, J.; García-Garabal, S.; Varela, L.M.; Cabeza, O. Density and Surface Tension in Binary Mixtures of CnMIM-BF₄ Ionic Liquids with Water and Ethanol. *Fluid Phase Equilib.* **2009**, *285*, 83-89. doi:10.1016/j.fluid.2009.07.010.
- (13) Mokhtarani, B.; Sharifi, A.; Mortaheb, H.R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and Viscosity of Pyridinium-based Ionic Liquids and their Binary Mixtures with Water at Several Temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 323–329. doi:10.1016/j.jct.2008.09.001.
- (14) Domańska, U.; Królikowska, M. Density and Viscosity of Binary Mixtures of Thiocyanate Ionic Liquids + Water as a Function of Temperature. *J. Solution Chem.* **2012**, *41*, 1422–1445. doi:10.1007/s10953-012-9875-7.
- (15) Cao, Q.; Lu, X.; Wu, X.; Guo, Y.; Xu, L.; Fang, W. Density, Viscosity, and Conductivity of Binary Mixtures of the Ionic Liquid N-(2-Hydroxyethyl)piperazinium Propionate with Water, Methanol, or Ethanol. *J. Chem. Eng. Data* **2015**, *60*, 455–463. doi:10.1021/je500380x.
- (16) Shekaari, H.; Mansoori, Y.; Sadeghi, R. Density, Speed of Sound, and Electrical Conductance of Ionic Liquid 1-Hexyl-3-methyl-imidazolium Bromide in Water at Different Temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 852–859. doi:10.1016/j.jct.2008.01.003.
- (17) Królikowska, M.; Lipiński, P.; Maik, D. Density, Viscosity and Phase Equilibria Study of {Ethylsulfate-based ionic liquid + Water} Binary Systems as a Function of Temperature and Composition. *Thermochim. Acta* **2014**, *582*, 1–9. doi:10.1016/j.tca.2014.02.019.
- (18) Orchillés, A.V.; González-Alfaro, V.; Miguel, P.J.; Vercher, E.; Martínez-Andreu, A. 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. Thermodyn.* **2006**, *38*, 1124–1129. doi:10.1016/j.jct.2005.11.008.
- (19) Chen, L.; Chen, J.; Song, Z.; Cui, G.; Xu, Y.; Wang, X.; Liu, J. Densities, Viscosities, and

- Excess Properties of Binary Mixtures of Two Imidazolid Anion Functionalized Ionic Liquids with Water at T=(293.15 to 313.15)K. *J. Chem. Thermodyn.* **2015**, *91*, 292–300. doi:10.1016/j.jct.2015.08.010.
- (20) Zawadzki, M.; Królikowska, M.; Antonowicz, J.; Lipiński, P.; Karpińska, M. Physicochemical and Thermodynamic Properties of the {1-Alkyl-1-methylmorpholinium Bromide, [C₁C_n=3,4,5MOR]Br, or 1-Methyl-1-pentylpiperidinium Bromide, [C₁C₅PIP]Br+Water} Binary Systems. *J. Chem. Thermodyn.* **2016**, *98*, 324–337. doi:10.1016/j.jct.2016.03.030.
- (21) Królikowska, M.; Zawadzki, M.; Domańska, U.; Ramjugernath, D.; Naidoo, P. The Influence of Temperature and Composition on the Density, Viscosity and Excess Properties of Aqueous Mixtures of Carboxylic-based Ionic Liquids. *J. Chem. Thermodyn.* **2017**, *109*, 71–81. doi:10.1016/j.jct.2016.10.034.
- (22) Królikowska, M.; Zawadzki, M.; Królikowski, M. Physicochemical and Thermodynamic Study on Aqueous Solutions of Dicyanamide – based Ionic Liquids. *J. Chem. Thermodyn.* **2014**, *70*, 127–137. doi:10.1016/j.jct.2013.10.034.
- (23) Bou Malham, I.; Turmine, M. Viscosities and Refractive Indices of Binary Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate with Water at 298K. *J. Chem. Thermodyn.* **2008**, *40*, 718–723. doi:10.1016/j.jct.2007.10.002.
- (24) Rodríguez, H.; Brennecke, J. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water+ Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155. doi:10.1021/je0602824.
- (25) Vila, J.; Ginés, P.; Rilo, E.; Cabeza, O.; Varela, L.M. Great Increase of the Electrical Conductivity of Ionic Liquids in Aqueous Solutions. *Fluid Phase Equilib.* **2006**, *247*, 32–39. doi:10.1016/j.fluid.2006.05.028.
- (26) Shekaari, H.; Zafarani-Moattar, M.T.; Kazempour, A.; Ghasedi-Khajeh, Z. Volumetric Properties of Aqueous Ionic-Liquid Solutions at Different Temperatures. *J. Chem. Eng. Data* **2015**, *60*, 1750–1755. doi:10.1021/je501161t.
- (27) Bou Malham, I.; Letellier, P.; Mayaffre, A.; Turmine, M. 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.* **2007**, *39*, 1132–1143. doi:10.1016/j.jct.2007.01.007.

- (28) Wang, J.; Li, C.; Shen, C.; Wang, Z. Towards Understanding the Effect of Electrostatic Interactions on the Density of Ionic Liquids. *Fluid Phase Equilib.* **2009**, *279*, 87–91. doi:10.1016/j.fluid.2009.02.011.
- (29) Vercher, E.; Miguel, P.J.; Llopis, F.J.; Orchillés, A.V.; Martínez-Andreu, A. Volumetric and Acoustic Properties of Aqueous Solutions of Tri fluoromethanesulfonate-Based Ionic Liquids at Several Temperatures. *J. Chem. Eng. Data* **2012**, *57*, 1953–1963. doi:10.1021/je300134c.
- (30) Vercher, E.; Orchillés, A. V.; Miguel, P.J.; Martínez-Andreu, A. Volumetric and Ultrasonic Studies of 1-Ethyl-3-methyl- imidazolium Trifluoromethanesulfonate Ionic Liquid with Methanol, Ethanol, 1-Propanol, and Water at Several Temperatures. *J. Chem. Eng. Data* **2007**, *52*, 1468–1482. doi: 10.1021/je7001804.
- (31) Ge, M.; Zhao, R.; Yi, Y.; Zhang, Q.; Wang, L. Densities and Viscosities of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate + H₂O Binary Mixtures at T=(303.15 to 343.15) K. *J. Chem. Eng. Data* **2008**, *53*, 2408–2411. doi:10.1021/je8003832.
- (32) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, *54*, 472–479. doi: 10.1021/je800468h.
- (33) Zhou, Q.; Wang, L.-S.; Chen, H.-P. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H₂O Binary Mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905-908. doi:10.1021/je050387r.
- (34) Liu, W.; Zhao, T.; Zhang, Y.; Wang, H.; Yu, M. The Physical Properties of Aqueous Solutions of the Ionic Liquid [BMIM][BF₄]. *J. Solution Chem.* **2006**, *35*, 1337–1346. doi:10.1007/s10953-006-9064-7.
- (35) Liu, W.; Cheng, L.; Zhang, Y.; Wang, H.; Yu, M. The Physical Properties of Aqueous Solution of Room-temperature Ionic Liquids Based on Imidazolium: Database and Evaluation. *J. Mol. Liq.* **2008**, *140*, 68–72. doi:10.1016/j.molliq.2008.01.008.
- (36) Anouti, M.; Caillon-Caravanier, M.; Dridi, Y.; Jacquemin, J.; Hardacre, C.; Lemordant, D. Liquid Densities, Heat Capacities, Refractive Index and Excess Quantities for {Protic Ionic Liquids + Water} Binary System. *J. Chem. Thermodyn.* **2009**, *41*, 799–808. doi:10.1016/j.jct.2009.01.011.
- (37) Antón, V.; Artigas, H.; Muñoz-Embid, J.; Artal, M.; Lafuente, C. Thermophysical Properties of Two Binary Aqueous Mixtures Containing a Pyridinium-based Ionic Liquid.

- J. Chem. Thermodyn.* **2016**, *99*, 116–123. doi:10.1016/j.jct.2016.04.003.
- (38) Rocha Pinto, R.; Santos, D.; Mattedi, S.; Aznar, M. Density, Refractive Index, Apparent Volumes and Excess Molar Volumes of Four Protic Ionic Liquids + Water at T=298.15 and 323.15 K. *Brazilian J. Chem. Eng.* **2015**, *32*, 671–682. doi:10.1590/0104-6632.20150323s00003444.
- (39) Umapathi, R.; Attri, P.; Venkatesu, P. Thermophysical Properties of Aqueous Solution of Ammonium-Based Ionic Liquids. *J. Phys. Chem. B.* **2014**, *118*, 5971–5982. doi:10.1021/jp502400z.
- (40) Chaudhary, G.R.; Bansal, S.; Mehta, S.K.; Ahluwalia, A.S. Thermophysical and Spectroscopic Studies of Pure 1-Butyl-3- methylimidazolium Tetrafluoroborate and its Aqueous Mixtures. *J. Solution Chem.* **2014**, *43*, 340–359. doi:10.1007/s10953-014-0137-8.
- (41) Taib, M.M.; Murugesan, T. Density, Refractive Index, and Excess Properties of 1-Butyl-3- methylimidazolium Tetrafluoroborate with Water and Monoethanolamine. *J. Chem. Eng. Data* **2012**, *57*, 120–126. doi:10.1021/je2007204.
- (42) Navarro, P.; Larriba, M.; García, S.; García, J.; Rodríguez, F. Physical Properties of Binary and Ternary Mixtures of 2-Propanol, Water, and 1-Butyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid. *J. Chem. Eng. Data* **2012**, *57*, 1165–1173. doi:10.1021/je201010s.
- (43) Lal, B.; Sahin, M.; Ayranci, E. Volumetric Studies to Examine the Interactions of Imidazolium Based Ionic Liquids with Water by means of Density and Speed of Sound Measurements. *J. Chem. Thermodyn.* **2012**, *54*, 142–147. doi:10.1016/j.jct.2012.03.025.
- (44) Frenkel, M.; Hong, X.; Dong, Q.; Yan, X.; Chirico, R.D. *Thermodynamic Properties of Organic Compound and their Mixtures, Subvolume G, Densities of Alcohols. Group IV: Physical Chemistry. Volume 8.* Hall, K.R and Marsh, K.N. Eds., Springer, Berlin-Verlag, **1998**. doi:10.1007/b75928.
- (45) Singh, T; Kumar, A. Thermodynamics of dilute aqueous solutions of imidazolium based ionic liquids. *J. Chem. Thermodyn.* **2011**, *43*, 958-965. doi: 10.1016/j.jct.2011.01.013.
- (46) Rilo, E.; Domínguez-Pérez, M.; Vila, J.; Segade, L.; García, M.; Varela, L.M.; Cabeza, O. Easy Prediction of the Refractive Index for Binary Mixtures of Ionic Liquids with Water or Ethanol. *J. Chem. Thermodyn.* **2012**, *47*, 219–222. doi:10.1016/J.JCT.2011.10.016.

- (47) Vercher, E.; Llopis, F.J.; González-Alfaro, V.; Miguel, P.J.; Martínez-Andreu, A. Refractive Indices and Deviations in Refractive Indices of Trifluoromethanesulfonate-Based Ionic Liquids in Water. *J. Chem. Eng. Data* **2011**, *56*, 4499-4504. doi:10.1021/je200479e.
- (48) Wang, S.; Jacquemin, J.; Husson, P.; Hardacre, C.; Costa Gomes, M.F. Liquid-liquid Miscibility and Volumetric Properties of Aqueous Solutions of Ionic Liquids as a Function of Temperature. *J. Chem. Thermodyn.* **2009**, *41*, 1206–1214. doi:10.1016/j.jct.2009.05.009.
- (49) Chirico, R. D.; Frenkel, M.; Diky, V. V.; Marsh, K. N.; Wilhoit, R. C. ThermoML-an XML-based approach for storage and exchange of experimental and critically evaluated thermophysical and thermochemical property data. 2. Uncertainties. *J. Chem. Eng. Data* **2003**, *48*, 1344–1359. doi:10.1021/je034088i.
- (50) *Guide to the Expression of Uncertainty in Measurement* (International Organization for Standardization, Geneva, Switzerland, **1993**). This *Guide* was prepared by ISO Technical Advisory Group 4 (TAG 4), Working Group 3 (WG 3). ISO/TAG 4 has as its sponsors the BIPM, IEC, IFCC (International Federation of Clinical Chemistry), ISO, IUPAC (International Union of Pure and Applied Chemistry), IUPAP (International Union of Pure and Applied Physics), and OIML. Although the individual members of WG 3 were nominated by the BIPM, IEC, ISO, or OIML, the *Guide* is published by ISO in the name of all seven organizations.
- (51) <http://physics.nist.gov/cuu/>. Check out November **2018**.
- (52) Ionic Liquids Database–ILThermo (v2.0), updated on May 10, **2018**; <http://ilthermo.boulder.nist.gov/>.
- (53) Cabeza, O.; Vila, J.; Rilo, E.; Domínguez-Pérez, M.; Otero-Cernadas, L.; López-Lago, E.; Méndez-Morales, T.; Varela, L.M. Physical properties of aqueous mixtures of the ionic 1-ethyl-3-methylimidazolium octyl sulfate: A new ionic rigid gel. *J. Chem. Thermodyn.* **2014**, *75*, 52-57. doi:10.1016/j.jct.2014.04.016.
- (54) Katayanagi, H.; Nishikawa, K.; Shimozaki, H.; Miki, K.; Westh, P.; Koga, Y. Mixing Schemes in Ionic Liquid-H₂O Systems: A Thermodynamic Study. *J. Phys. Chem. B* **2004**, *108*, 19451-19457. doi:10.1021/jp0477607.
- (55) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of Physical Properties for the Binary System of 1-Ethyl-3-methylimidazolium Tetrafluoroborate + H₂O. *J. Chem. Eng. Data* **2004**, *49*, 760-764. doi:10.1021/je030191w.

- (56) Anouti, M.; Vigeant, A.; Jacquemin, J.; Brigouleix, C.; Lemordant, D. Volumetric Properties, Viscosity and Refractive Index of the Protic Ionic Liquid, Pyrrolidinium Octanoate, in Molecular Solvents. *J. Chem. Thermodyn.* **2010**, *42*, 834–845. doi:10.1016/j.jct.2010.01.013.
- (57) Rebelo, L.P.N.; Najdanovic-Visak, V.; Visak, Z.P.; Nunes da Ponte, M.; Szydłowski, J.; Cerdeiriña, C.A.; Troncoso, J.; Romaní, L.; Esperanza, J.M.S.S.; Guedes, H.J.R.; de Sousa, H.C. A Detailed Thermodynamic Analysis of [C₄mim][BF₄] + Water as a case Study to Model Ionic Liquid Aqueous Solutions. *Green Chem.* **2004**, *6*, 369–381. doi:10.1039/b400374h.
- (58) Gao, J.; Wagner, N.J. Non-ideal Viscosity and Excess Molar Volume of Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate ([C₄mim][BF₄]) with Water. *J. Mol. Liq.* **2016**, *223*, 678–686. doi:10.1016/j.molliq.2016.08.084.
- (59) Yin, Y.; Zhu, C.; Ma, Y. Volumetric and Viscometric Properties of Binary and Ternary Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate, Monoethanolamine and Water. *J. Chem. Thermodyn.* **2016**, *102*, 413–428. doi:10.1016/j.jct.2016.07.041.
- (60) Rilo, E.; Domínguez-Pérez, M.; Varela, L.M.; Cabeza, O. Experimental Evidence of the Validity of Bahe–Varela Theory to Describe the Volumetric Properties of Ionic Liquids. *J. Chem. Thermodyn.* **2012**, *54*, 68–75. doi:10.1016/j.jct.2012.03.012.
- (61) Desnoyers, J.E.; Perron, G. Treatment of Excess Thermodynamic Quantities for Liquid Mixtures. *J. Solution Chem.* **1997**, *26*, 749–755. doi:10.1007/BF02767781.
- (62) Tamura, K.; Nakamura, M.; Murakami, S. Excess Volumes of Water + Acetonitrile and Water + Dimethylsulfoxide at 30°C and the Effect of the Excess Thermal Expansivity Coefficients on Derived Thermodynamic Properties, *J. Solution Chem.* **1997**, *26*, 1199–1207. doi:10.1023/A:1022985208144.
- (63) Dožić, S.; Zec, N.; Tot, A.; Papović, S.; Pavlović, K.; Gadžurić, S.; Vraneš, M. Does the Variation of the Alkyl Chain Length on N1 and N3 of Imidazole Ring Affect Physicochemical Features of Ionic Liquids in the Same Way? *J. Chem. Thermodyn.* **2016**, *93*, 52–59. doi:10.1016/J.JCT.2015.09.025.
- (64) Treszczanowicz, A.J.; Treszczanowicz, T. Prediction of the Excess Volume and Isobaric Thermal Expansion for 1-Alkanol + n-Alkane Systems in terms of an Association Model with a Flory Contribution Term. *Fluid Phase Equilib.* **1997**, *135*, 179–192. doi:10.1016/S0378-3812(97)00085-X.

- (65) Zhao, H. Are Ionic Liquids Kosmotropic or Chaotropic? An Evaluation of Available Thermodynamic Parameters for Quantifying the Ion Kosmotropicity of Ionic Liquids. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 877–891. doi:10.1002/jctb.1449.
- (66) Reis, J.C.R.; Lampreia, I.M.S.; Santos, A.F.S.; Moita, M.L.C.J; Douhéret, G. Refractive Index of Liquid Mixtures: Theory and Experiment. *Chem. Phys. Chem.* **2010**, *11*, 3722–3733. doi: 10.1002/cphc.201000566.
- (67) Piñeiro, Á.; Brocos, P.; Amigo, A; Pintos, M.; Bravo, R. Surface tensions and refractive indices of (tetrahydrofuran + *n*-alkanes) at $T = 298.15$ K. *J. Chem. Thermodyn.* **1999**, *31*, 931-942. doi:10.1006/jcht.1999.0517.
- (68) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A. Refractive Indices, Molar Volumes and Molar Refractions of Binary Liquid Mixtures: Concepts and Correlations. *Phys. Chem. Chem. Phys.* **2003**, *5*, 550–557. doi:10.1039/b208765k.

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