Published in final edited form as:

Fluid Phase Equilib. 2016 January 15; 407: 188–196. doi:10.1016/j.fluid.2015.05.023.

Densities, Viscosities and Derived Thermophysical Properties of Water-Saturated Imidazolium-Based Ionic Liquids

Mónia A. R. Martins¹, Catarina M. S. S. Neves¹, Kiki A. Kurnia¹, Pedro J. Carvalho¹, Marisa A. A. Rocha^{2,3}, Luís M. N. B. F. Santos², Simão P. Pinho^{4,5}, and Mara G. Freire^{1,*}

¹CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal ²Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal ³Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands ⁴Associate Laboratory LSRE/LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança, Portugal ⁵UNIFACS-Universidade de Salvador, Rua Dr. José Peroba 251, CEP 41770-235, Salvador, Brazil

Abstract

In order to evaluate the impact of the alkyl side chain length and symmetry of the cation on the thermophysical properties of water-saturated ionic liquids (ILs), densities and viscosities as a function of temperature were measured at atmospheric pressure and in the (298.15 to 363.15) K temperature range, for systems containing two series of bis(trifluoromethylsulfonyl)imide-based compounds: the symmetric $[C_nC_n\text{im}][\text{NTf}_2]$ (with $n = 1-8$ and 10) and asymmetric $[C_nC_1\text{im}][\text{NTf}_2]$ (with $n = 2-5, 7, 9$ and 11) ILs. For water-saturated ILs, the density decreases with the increase of the alkyl side chain length while the viscosity increases with the size of the aliphatic tails. The saturation water solubility in each IL was further estimated with a reasonable agreement based on the densities of water-saturated ILs, further confirming that for the ILs investigated the volumetric mixing properties of ILs and water follow a near ideal behaviour. The water-saturated symmetric ILs generally present lower densities and viscosities than their asymmetric counterparts. From the experimental data, the isobaric thermal expansion coefficient and energy barrier were also estimated. A close correlation between the difference in the energy barrier values between the water-saturated and pure ILs and the water content in each IL was found, supporting that the decrease in the viscosity of ILs in presence of water is directly related with the decrease of the energy barrier.

Keywords

Ionic Liquids; Water; Imidazolium; Bis(trifluoromethylsulfonyl)imide; Density; Viscosity

*Corresponding author: Phone: +351 234370200; Fax: +351 234370084; maragfreire@ua.pt.

1 Introduction

Over the last years, ionic liquids (ILs) have been the subject of intensive investigations as a new class of neoteric solvents. ILs consist of large organic cations, with various alkyl substituents and/or functionalized groups, and inorganic or organic anions. The bulky and asymmetric characteristics of their ions are the major reasons behind the ILs' low melting temperatures [1]. Due to their ionic nature, most ILs are known to present interesting properties, such as a negligible vapor pressure [2], non-flammability [3], high thermal stability [4], and high conductivity [5]. Nevertheless, one of the most important features associated to ILs is the possibility to tune their properties for a given task by adjusting the chemical structure of the constituting ions. Actually, the tuning of ILs is even broader, and in addition to the different combinations of their cations and anions in pure compounds, a relevant attention has been given recently to ionic liquids mixtures [6–8].

Due to their unique solvent properties, ILs have been widely investigated in a large range of processes in the chemical industry [9], including separations processes, reactions and biomass processing [1]. It is well-known that the ILs phase equilibrium and their thermophysical properties are significantly influenced by the presence of water [10, 11]. Thus, in the last years, a significant number of works has been addressing the thermophysical and thermodynamic properties of water-saturated ILs, in particular for densities and viscosities [10–17]. Rodríguez and Brennecke [17] studied the density and viscosity of aqueous solutions of imidazolium-based ILs with the anions ethylsulfate, trifluoroacetate and trifluoromethanesulfonate. Both properties were found to decrease with an increase in either temperature or in mole fraction of water. The same behavior was observed by Ge et al. [13] and by Carvalho et al. [12] with additional imidazolium-based ILs, and by Neves et al [11] with phosphonium-based compounds. In all situations it was found that the water content has a strong effect on the viscosity of the ILs, while the effect is less significant on their densities [10–17].

Viscosity is one of the most important physical properties when considering the scale-up of IL-based applications. Generally, while higher viscosities may be advantageous for lubrication [1, 9], a low viscosity is desired for solvent applications in order to increase the mass transfer rates and to minimize pumping costs. The viscosities of ILs are widely dependent on the type of cation and anion and are relatively high when compared to those of common molecular solvents. Density has also been widely studied with ILs [18]. Usually, density is found to largely depend on the IL anion and cation [10, 11, 15]. Like with molecular solvents, the densities are closely related to the molar mass of the fluid and ILs containing heavier atoms are usually more dense [1, 19].

Despite the importance on the knowledge of the ILs' physicochemical properties, few works have systematically studied the relationships between the structures of ILs and their fundamental properties [20–23]. On the other hand, systematic studies on the effect of water through the ILs' densities and viscosities are still scarce [12, 13, 17, 24–28]. On the basis of the described scenario, the densities and viscosities of binary mixtures of water and ILs, namely for ILs saturated with water at 298.15 K, and composed of the common anion bis(trifluoromethylsulfonyl)imide, $[\text{NTf}_2]^-$, were measured at atmospheric pressure and in

the (298.15 to 363.15) K temperature range. The selected ILs comprise two types of cations: (i) a symmetric series of 1,3-dialkylimidazolium cations; and (ii) an asymmetric series of 1-alkyl-3-methylimidazolium-based ILs. The isobaric thermal expansion coefficient and the energy barrier of the water-saturated ILs investigated were also derived from the experimental density and viscosity data, respectively.

2 Experimental Section

2.1 Materials

The densities and viscosities of water-saturated ILs were measured for the following bis(trifluoromethylsulfonyl)imide-based compounds: 1,3-dialkylimidazolium, $[C_nC_n\text{im}][\text{NTf}_2]$ (with $n = 1-8$ and 10); and 1-alkyl-3-methylimidazolium, $[C_nC_1\text{im}][\text{NTf}_2]$ (with $n = 2-5, 7, 9$ and 11). The ILs investigated in this work are displayed in Table 1 and their chemical structure are depicted in Figure 1. In general, two series of fluids were investigated: (i) ILs with symmetric alkyl side chains at the imidazolium cation; and (ii) a group of ILs with alkyl side chains of different length at the cation and where one aliphatic moiety is always a methyl group. All ILs were purchased from Iolitec with mass fraction purities higher than 99%. To reduce the impurities, all ILs were dried and purified under vacuum (1 Pa) and at moderate temperature (353 K) for a minimum period of 48 h before the experimental measurements. The purity of each IL was further confirmed by us by ^1H , ^{13}C , and ^{19}F NMR. Ultra-pure water, double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus was used. It presented a resistivity of 18.2 M Ω -cm, a TOC (Total Organic Content) smaller than 5 $\mu\text{g}\cdot\text{dm}^{-3}$ and was free of particles $> 0.22 \mu\text{m}$.

2.2 Apparatus and Procedure

Densities and viscosities measurements of water-saturated ILs (of the IL-rich phase) were carried out at atmospheric pressure and in the (298.15 and 363.15) K temperature range using an automated SVM3000 Anton Paar rotational Stabinger viscometer-densimeter. The uncertainty of temperature is ± 0.02 K, the relative uncertainty in the dynamic viscosity is $\pm 0.35\%$, and the absolute uncertainty in density is $\pm 5\cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$. Saturated solutions were prepared, at 298.15 K, by mixing ILs and water in excess amounts and allowing the mixture to reach the equilibrium by the complete separation of the two phases, and for at least 48h [10, 29]. Additional details related with the equipment can be found elsewhere [12]. The ILs water content, *i.e.*, the saturation values of water in each IL at 298.15 K, used in the density and viscosity measurements, are presented in Table 2.

3 Results and Discussion

Although the density and viscosity values determined in this work majorly correspond to novel ILs saturated with water at 298.15 K, it should be remarked that Jacquemin et al. [27] already reported the density and viscosity of the water-saturated $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ at several temperatures. The maximum relative deviations between the experimental values measured in this work and those reported in the literature [27] are 0.2% and 9.0% for the water-saturated $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$, and 0.4% and 14.9% for the water-

saturated $[\text{C}_4\text{C}_{1\text{im}}][\text{NTf}_2]$, for density and viscosity, respectively. Moreover, the equipment used by us was already validated and proven to be adequate for the measurements of densities and viscosities of IL-rich phases [10, 11, 16].

3.1 Density of Water-Saturated Ionic Liquids

The new experimental density data for the water-saturated ILs are presented in the Supporting Information. Figure 2 depicts the density results obtained in this work alongside with the relative deviations between the pure ILs, reported previously by us [15], and the water-saturated ones. As previously observed with the pure fluids [15], also in both series of the water-saturated ILs, the density decreases with the increase on temperature.

In general, and for both symmetric and asymmetric series of ILs, the density decreases with the increase of the alkyl chain length, which is a direct effect of the increasing fraction of methylene groups ($-\text{CH}_2$). In addition, the presence of water leads to a decrease on the density of ILs ranging between (0.19 to 1.6)% - values that depend on the IL hydrophobicity and associated water content. This decrease on density is more pronounced in ILs with shorter alkyl chains, and it is related with the higher water solubility in these ILs when compared to those with longer alkyl chains – *cf.* Table 2. For instance, at 298.15 K, the density relative deviations of the pure ILs in respect to the water-saturated samples are 1.4% and 0.23% for $[\text{C}_1\text{C}_{1\text{im}}][\text{NTf}_2]$ and $[\text{C}_{10}\text{C}_{10\text{im}}][\text{NTf}_2]$, respectively, and 0.75% and 0.29% for $[\text{C}_3\text{C}_{1\text{im}}][\text{NTf}_2]$ and $[\text{C}_{11}\text{C}_{1\text{im}}][\text{NTf}_2]$, respectively.

When addressing the results obtained for the structural pairs of isomers some discussions and conclusions can be drawn. For all the isomeric pairs, the asymmetric series present slightly higher values of densities than the corresponding symmetric ones. The more pronounced differences in densities were observed for the pairs $[\text{C}_3\text{C}_{3\text{im}}][\text{NTf}_2]/[\text{C}_5\text{C}_{1\text{im}}][\text{NTf}_2]$ and $[\text{C}_6\text{C}_{6\text{im}}][\text{NTf}_2]/[\text{C}_{11}\text{C}_{1\text{im}}][\text{NTf}_2]$. A similar behaviour on densities was already reported for the pure ILs [15]. In general, and due to the slightly differences between the isomeric pairs (which most of the times fall within the densities uncertainty), it can be postulated that the cation isomerism, at least derived from symmetric/asymmetric series of imidazolium-based ILs, does significantly lead to different densities – whereas the contribution of the $-\text{CH}_2$ groups towards the IL molar volume seems to be independent on its localization at one of the aliphatic tails [32, 33].

Figure 3 depicts the dependency of the ILs density at a fixed temperature along with the cation's alkyl side chain length. In both series of ILs, larger differences in densities amongst the pure and water-saturated ILs are observed in compounds with shorter alkyl side chains. This is a major result of a higher water content in ILs with alkyl side chains of smaller size as highlighted before. Overall, the densities of the water-saturated and pure ILs, in both series, become almost equal for $N=8$ (where N represents the total number of carbon atoms in the two aliphatic tails).

From the linear dependency of the density with temperature, at 0.1 MPa, the isobaric thermal expansion coefficient, α_p (which considers the volumetric changes with temperature), can be calculated according to Equation 2, that is further derived from Equation 1 used to correlate the density as a function of temperature,

$$\ln \rho = A_0 + A_1 T \quad (1)$$

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = - \left(\frac{\partial \ln \rho}{\partial T} \right)_p = -A_1 \quad (2)$$

where A_0 , and A_1 are fitting parameters, ρ is the density in $\text{kg}\cdot\text{m}^{-3}$ and T is the absolute temperature in K.

Despite the current debate surrounding the application of a linear correlation or a second order polynomial equation to describe the density data of ILs [16], it was found that the use of a linear equation satisfactorily describes the experimental data within the temperature studied in this work. The fitting parameters of Equation 1 are given in the Supporting Information.

Table 3 lists the thermal expansion coefficients calculated at 323.15 K and 0.1 MPa, using Equation 2, for all the studied water-saturated ILs, together with the values previously reported for the corresponding pure ILs [15]. This temperature was chosen to allow a direct comparison of all ILs at their liquid state. Even though similar thermal expansion coefficients for both symmetric and asymmetric ILs are observed, the presence of water leads to a slightly increase on α_p . The α_p for water-saturated ILs varies between $(6.82$ and $7.00) \times 10^{-4} \text{ K}^{-1}$, *i.e.*, between $[\text{C}_7\text{C}_1\text{im}][\text{NTf}_2]$ and $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$, respectively.

The representation of the thermal expansion coefficient for the water-saturated ILs along with the pure ILs [15], at 323.15 K and 0.1 MPa, as a function of the cation structure and alkyl side chain length is depicted in Figure 4. Although a straight dependence of α_p with the alkyl chain length is not observed, there are pronounced effects on general trends according to the alkyl chain length increase that agree well those observed with pure ILs [15].

Methods to estimate the mutual solubilities of ILs and water are of utmost importance due to the innumerable possible combinations of cations and anions to form ILs and, consequently, the extended number of experimental measurements necessary. For the prediction of the solubility of ILs in the water-rich phase, several methods have been proposed [30, 34]. However, and as a consequence of the dominant hydrogen-bonding interactions, the solubility of water in the IL-rich phase is more difficult to predict. In this sense, a faster, easier, and reliable method supported on the densities of pure and water-saturated ILs can be used [11]. Thus, and assuming that the excess molar volumes are negligible in the narrow mole fraction solubility range, the ILs water solubility can be estimated using the following equations,

$$V_{m,mixture} = V_{m,IL} \times (1 - x_w) + V_{m,w} \times x_w \quad (3)$$

$$V_{m,mixture} = \frac{(1 - x_w) \times M_{IL} + x_w \times M_w}{\rho_{mixture}} \quad (4)$$

where M is the molecular weight in $\text{kg}\cdot\text{mol}^{-1}$ and V_m is the molar volume in $\text{m}^3\cdot\text{mol}^{-1}$. The subscripts IL , w , and $mixture$ are IL, water and water-saturated ILs, respectively.

The results obtained at 298.15 K are reported in Table 2. Albeit with some deviations, this approximation can be used to estimate water saturation values when no experimental data are available while foreseeing an initial screening on ILs to be applied in a particular application. These close values are also an indication that the volumetric mixing properties of the two IL series and water follow a near ideal behaviour.

3.2 Viscosity of Water-Saturated Ionic Liquids

The viscosity data for water-saturated ILs were determined from (298.15 to 363.15) K and the detailed values are given in the Supporting Information. Figure 5 shows the viscosity results obtained in this work alongside with the deviations between the pure ILs, previously reported [15, 35], and the water-saturated ILs. The viscosity of water-saturated ILs increases with the increase on the size of the alkyl side chain, following the general trend already shown for pure ILs [15].

It is striking to see the impact of water content in the viscosity of ILs, which significantly decreases (from 16% to 51%). Figure 5 also reveals the higher viscosity of water-saturated asymmetric ILs compared to the symmetric isomeric pairs, a pattern already reported for pure ILs [15]. The isomeric pair $[\text{C}_5\text{C}_1\text{im}][\text{NTf}_2]/[\text{C}_3\text{C}_3\text{im}][\text{NTf}_2]$ presents the smallest differences for their viscosities at the same temperature, whereas the other pairs exhibit more noticeable differences. These differences decrease with increasing temperature and increase with the length of the alkyl chain for both series of ILs. Moreover, the difference in viscosity between pure and water-saturated ILs is higher in the asymmetric series.

In recent works we have shown, not only for viscosity but also for other properties, such as vapour pressures, heat capacity and surface tension [15, 36–38], that both the asymmetric $[\text{C}_n\text{C}_1\text{im}][\text{NTf}_2]$ and symmetric $[\text{C}_n\text{C}_n\text{im}][\text{NTf}_2]$ series of ILs present a trend shift in these properties along the alkyl side chain length increase [15, 36, 38]. Similarly to the case of the pure ILs viscosity [15], this trend shift for the water-saturated ILs occurs around $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ for the asymmetric ILs and $[\text{C}_6\text{C}_6\text{im}][\text{NTf}_2]$ for the symmetric ones, as depicted in Figure 6. This trend shift is related with the structural organization of the liquid above a critical alkyl size (CAS) and, similar to the pure ILs viscosity, it is particularly emphasized in the cations with higher symmetry. Some molecular dynamics studies for the asymmetric series aiming at understanding the structural shifts observed have been already performed [39], while demonstrating the progressive increase and segregation of the nonpolar parts (tails) of the cations as the alkyl side chains become larger. The pure ILs with shorter alkyl chain lengths also display a clearly discernible odd-even effect on the viscosities [15], that albeit the presence of water seems to smooth, is also observed in the water-saturated ILs.

The viscosity describes the internal resistance of a fluid to a shear stress, and as it is well-known, most ILs display higher viscosities than common molecular solvents. The ILs high viscosities are a direct consequence of their high molecular weights as well as their multiple intermolecular interactions (H-bonding, dispersive and electrostatic interactions). The energy barrier (E) is the energy value that must be overcome in order for the ions to move past each other in the fluid [40]. The larger is E , the harder it is for the ions to move past each other, which is inherently related with the interactions occurring in the fluid. The energy barrier can thus be correlated with structural information on the IL, and can be determined based on the viscosity dependence with temperature using the following equation [15],

$$E = R \frac{\partial (\ln [\eta(T)])}{\partial (1/T)} \quad (5)$$

where η is viscosity in mPa·s, and R is the gas constant ($R = 8.3144621 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) [41].

In order to calculate the energy barrier of the water-saturated ILs studied in this work, the experimental viscosity data were initially correlated through the Vogel–Tammann–Fulcher (VTF) model [16], expressed by equation 6,

$$\eta(T) = A_\eta \exp \left[\frac{B_\eta}{T - C_\eta} \right] \quad (6)$$

where A_η , B_η and C_η are adjustable parameters estimated from experimental data.

The fitting parameters resulting from the application of the VFT model are presented in Table 4. The maximum absolute relative deviation between the correlated and experimental values is 2.08%, with an average absolute relative deviation of 0.17%. Thus, the application of the Vogel–Tammann–Fulcher correlation to the viscosity data [16] provides a good description of the viscosity dependence of water-saturated ILs as well.

The calculated energy barrier for the water-saturated ILs, at 323.15 K, together with the data for the pure ILs (reported in a previous work [15, 35]), are listed in Table 4 and depicted in Figure 7.

As can be seen in Figure 7, and in both series of ILs, the energy barrier increases monotonically with the cation alkyl side chain length increase since the van der Waals interactions start to overwhelm the cation-anion electrostatic interactions. $[\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$ has an outlier behavior for the viscosity and energy barrier according to the increase on the alkyl side chains size due to its high charge density afforded by two small methyl groups, and as already proved for the same properties regarding the pure IL [15]. For ILs with the same number of carbon atoms at the aliphatic moieties, *i.e.*, structural isomers, the symmetric series of water-saturated ILs display lower energy barrier values, following the same trend observed in pure ILs [15]. Figure 7 also reveals that the presence of water reduces the energy barrier of the respective ILs.

In general, the difference in the energy barrier between water-saturated and pure ILs values, correlates well with the total number of carbons in the alkyl side chains, N , either for the symmetric or asymmetric series of ILs – Figure 8a. Moreover, the difference of the energy barriers at 323.15 K slightly correlates with the mole fraction of water in each IL (including both series of compounds) - Figure 8b. The observed correlation is a clear indication that the presence of water is a major factor contribution for the decreasing of the energy barrier in all the ILs investigated, as well as a strong indication that the water molecules are solvated and mainly interacting with the polar regions of the IL (IL anion and imidazolium high-charge region). In fact, the lower is the energy barrier, the less difficult is for the ions to move past each other, which seems to be favored in the presence of water due to the weakening of IL-IL interactions. The decrease of viscosity in ILs in presence of water is thus a result of a decrease on the energy barrier, which is further connected to the water content in each IL.

4 Conclusions

The impact of the IL cation symmetry and alkyl side chain length, as well as the water effect, on the density and viscosity of ILs was evaluated for systems containing two series of ILs, namely 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_nC_1im][NTf_2]$) and 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_nC_nim][NTf_2]$). For both pure and water-saturated ILs, the density and viscosity values decrease with increasing temperature. The density decreases with the increase of the alkyl side chain length while the viscosity increases with the size of the aliphatic tails – trend observed either for the pure or water-saturated ILs. Although the density is only slightly affected by the presence of water, the water solubility in each IL was estimated in a reasonable agreement with the experimental solubility data being an indication that the volumetric mixing properties of ILs and water follow a near ideal behaviour. Furthermore, the water-saturated symmetric series of ILs generally present lower densities and viscosities than their asymmetric counterparts. The water effect on the viscosity trends shows that for pure and water-saturated ILs there is a trend shift along the alkyl side chain length. Moreover, the presence of water also affects the derived properties, leading to an increase of 2% in the thermal expansion coefficients, while the energy barrier is reduced. The latter property reveals that the symmetric series of ILs require less energy to move freely in the bulk than the asymmetric counterparts. The differences in the energy barrier values between the water-saturated and pure ILs closely correlate with the water content, meaning that the decrease on viscosity is a direct consequence of the presence of water which favour the ions to move past each other.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This work was developed in the scope of the projects CICECO-Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013) and LSRE/LCM-Laboratory of Separation and Reaction Engineering (Ref. FCT UID/EQU/50020/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. The authors also thank FCT for the doctoral and post-doctoral grants SFRH/BD/87084/2012, SFRH/BD/70641/2010, SFRH/BPD/88101/2012, SFRH/BPD/82264/2011 for M.A.R.M.,

C.M.S.S.N., K.A.K., and P.J.C respectively. M.G.F. acknowledges the European Research Council (ERC) for the grant ERC-2013-StG-337753 and S.P.P. thanks a grant from FAPESB.

References

- [1]. Kirchner, B. Ionic Liquids. Top Curr Chem. Springer; Heidelberg, Germany: 2010.
- [2]. Holbrey, JD.; Rogers, RD.; Mantz, RA.; Trulove, PC.; Cocalia, VA.; Visser, AE.; Anderson, JL.; Anthony, JL.; Brennecke, JF.; Maginn, EJ.; Welton, T., et al. Physicochemical Properties. Ionic Liquids in Synthesis. Wiley-VCH Verlag GmbH & Co. KGaA; 2008. p. 57-174.
- [3]. Smiglak M, Reichert WM, Holbrey JD, Wilkes JS, Sun L, Thrasher JS, Kirichenko K, Singh S, Katritzky AR, Rogers RD. Chem Commun (Camb). 2006;2554–2556. [PubMed: 16779475]
- [4]. Pucheault M, Vaultier M. Top Curr Chem. 2010; 290:83–126. [PubMed: 21107795]
- [5]. Bonhôte P, Dias A-P, Papageorgiou N, Kalyanasundaram K, Grätzel M. Inorg Chem. 1996; 35:1168–1178. [PubMed: 11666305]
- [6]. Chatel G, Pereira JFB, Debbeti V, Wang H, Rogers RD. Green Chem. 2014; 16:2051–2083.
- [7]. Bidikoudi M, Zubeir LF, Falaras P, Mater J. Chem A. 2014; 2:15326–15336.
- [8]. Clough MT, Crick CR, Grasvik J, Hunt PA, Niedermeyer H, Welton T, Whitaker OP. Chem Sci. 2015; 6:1101–1114.
- [9]. Plechkova NV, Seddon KR. Chem Soc Rev. 2008; 37:123–150. [PubMed: 18197338]
- [10]. Neves CMSS, Batista MLS, Claudio AFM, Santos LMNBF, Marrucho IM, Freire MG, Coutinho JAP. J Chem Eng Data. 2010; 55:5065–5073.
- [11]. Neves CMSS, Carvalho PJ, Freire MG, Coutinho JAP. J Chem Thermodyn. 2011; 43:948–957.
- [12]. Carvalho PJ, Regueira T, Santos LMNBF, Fernandez J, Coutinho JAP. J Chem Eng Data. 2009; 55:645–652.
- [13]. Ge M-L, Ren X-G, Song Y-J, Wang L-S. J Chem Eng Data. 2009; 54:1400–1402.
- [14]. Gardas RL, Coutinho JAP. Fluid Phase Equilib. 2008; 266:195–201.
- [15]. Rocha MAA, Neves CMSS, Freire MG, Russina O, Triolo A, Coutinho JAP, Santos LMNBF. J Phys Chem B. 2013; 117:10889–10897. [PubMed: 23915346]
- [16]. Neves CMSS, Kurnia KA, Coutinho JAP, Marrucho IM, Lopes JNC, Freire MG, Rebelo LPN. J Phys Chem B. 2013; 177:10271–10283. [PubMed: 23941052]
- [17]. Rodríguez H, Brennecke JF. J Chem Eng Data. 2006; 51:2145–2155.
- [18]. Aparicio S, Atilhan M, Karadas F. Ind Eng Chem Res. 2010; 49:9580–9595.
- [19]. Xue H, Verma R, Shreeve JnM. J Fluorine Chem. 2006; 127:159–176.
- [20]. Bhattacharjee A, Carvalho PJ, Coutinho JAP. Fluid Phase Equilib. 2014; 375:80–88.
- [21]. Carvalho PJ, Ventura SPM, Batista MLS, Schröder B, Gonçalves F, Esperança J, Mutelet F, Coutinho JAP. J Chem Phys. 2014; 140:064505. [PubMed: 24527930]
- [22]. Batista MLS, Neves CMSS, Carvalho PJ, Gani R, Coutinho JAP. J Phys Chem B. 2011; 115:12879–12888. [PubMed: 21954861]
- [23]. Bhattacharjee A, Luís A, Lopes-da-Silva JA, Freire MG, Carvalho PJ, Coutinho JAP. Fluid Phase Equilib. 2014; 381:36–45. [PubMed: 25516634]
- [24]. Gardas RL, Dagade DH, Coutinho JAP, Patil KJ. J Phys Chem B. 2008; 112:3380–3389. [PubMed: 18302364]
- [25]. Gómez-Díaz D, Navaza JM, Sanjurjo B. J Chem Eng Data. 2007; 52:889–891.
- [26]. Gong, Y-h; Shen, C.; Lu, Y-z; Meng, H.; Li, C-x. J Chem Eng Data. 2011; 57:33–39.
- [27]. Jacquemin J, Husson P, Padua AAH, Majer V. Green Chem. 2006; 8:172–180.
- [28]. Oliveira FS, Freire MG, Carvalho PJ, Coutinho JAP, Lopes JNC, Rebelo LPN, Marrucho IM. J Chem Eng Data. 2010; 55:4514–4520.
- [29]. Freire MG, Carvalho PJ, Gardas RL, Marrucho IM, Santos LMNBF, Coutinho JAP. J Phys Chem B. 2008; 112:1604–1610. [PubMed: 18201080]
- [30]. Martins MAR, Neves CMSS, Kurnia KA, Luís A, Santos LMNBF, Freire MG, Pinho SP, Coutinho JAP. Fluid Phase Equilib. 2014; 375:161–167.

- [31]. Kurnia KA, Neves CMSS, Freire MG, Santos LMNBF, Coutinho JAP. J Mol Liq. 2015 Submitted for Publication.
- [32]. Esperança JMSS, Guedes HJR, Blesic M, Rebelo LPN. J Chem Eng Data. 2005; 51:237–242.
- [33]. Blesic M, Swadzba-Kwasny M, Belhocine T, Gunaratne HQN, Lopes JNC, Gomes MFC, Padua AAH, Seddon KR, Rebelo LPN. PCCP. 2009; 11:8939–8948. [PubMed: 20449040]
- [34]. Martins MAR, Neves CMSS, Kurnia KA, Santos LMNBF, Freire MG, Pinho SP, Coutinho JAP. Fluid Phase Equilib. 2014; 381:28–35.
- [35]. Tariq M, Carvalho PJ, Coutinho JAP, Marrucho IM, Lopes JNC, Rebelo LPN. Fluid Phase Equilib. 2011; 301:22–32.
- [36]. Rocha MAA, Lima CFRAC, Gomes LgR, Schröder B, Coutinho JoAP, Marrucho IM, Esperança JMSS, Rebelo LsPN, Shimizu K, Lopes JNC, Santos LMNBF. J Phys Chem B. 2011; 115:10919–10926. [PubMed: 21815684]
- [37]. Rocha MAA, Coutinho JAP, Santos LMNBF. J Phys Chem B. 2012; 116:10922–10927. [PubMed: 22873766]
- [38]. Almeida HFD, Freire MG, Fernandes AM, Lopes-da-Silva JA, Morgado P, Shimizu K, Filipe EJM, Canongia Lopes JN, Santos LMNBF, Coutinho JAP. Langmuir. 2014; 30:6408–6418. [PubMed: 24834955]
- [39]. Shimizu K, Bernardes CES, Canongia Lopes JN. J Phys Chem B. 2013; 118:567–576. [PubMed: 24358956]
- [40]. Okoturo OO, VanderNoot TJ. J Electroanal Chem. 2004; 568:167–181.
- [41]. Mohr PJ, Taylor BN, Newell DB. Rev Mod Phys. 2012; 84:1527–1605.

Figure 1.
Schematic representation of the chemical structure of the studied imidazolium-based ILs.

Figure 2.

Density of the symmetric and asymmetric water-saturated ILs as function of temperature, (a, b), respectively; and density relative deviations between the pure [15] and the symmetric and asymmetric water-saturated ILs, (c, d), respectively: (●), [C₁C₁im][NTf₂]; (●), [C₂C₂im][NTf₂]; (▲), [C₃C₃im][NTf₂]; (■), [C₄C₄im][NTf₂]; (◆), [C₅C₅im][NTf₂]; (▼), [C₆C₆im][NTf₂]; (●), [C₇C₇im][NTf₂]; (●), [C₈C₈im][NTf₂]; (▶), [C₁₀C₁₀im][NTf₂]; (*), [C₂C₁im][NTf₂]; (○), [C₃C₁im][NTf₂]; (×), [C₄C₁im][NTf₂]; (△), [C₅C₁im][NTf₂]; (□), [C₇C₁im][NTf₂]; (◇), [C₉C₁im][NTf₂]; and (▽), [C₁₁C₁im][NTf₂].

Figure 3.

Density of the studied pure [15] (empty symbols) and water-saturated (full symbols) [NTf₂]-based ILs as a function of the cation structure (alkyl side chain length increase) at 298.15 K. Colorful symbols correspond to isomers, and black symbols correspond to ILs with no corresponding isomers.

Figure 4.

Thermal expansion coefficient of pure [15] and water-saturated ILs at 323.15 K and 0.1 MPa as a function of the cation structure (alkyl side chain length increase). The full and empty symbols represent water-saturated and pure ILs, respectively. Colorful symbols correspond to isomers, and black symbols correspond to ILs with no corresponding isomers.

Figure 5.

Viscosity of the of the symmetric and asymmetric water-saturated ILs as function of temperature, (a, b), respectively, and viscosity relative deviations between the pure [15, 35] and the symmetric and asymmetric water-saturated ILs (c, d), respectively: ($\blacklozenge$), [C₁C₁im][NTf₂]; ($\ast$), [C₂C₁im][NTf₂]; ($\circ$), [C₃C₁im][NTf₂]; ($\bullet$), [C₂C₂im][NTf₂]; ($\times$), [C₄C₁im][NTf₂]; ($\triangle$), [C₅C₁im][NTf₂]; ($\blacktriangle$), [C₃C₃im][NTf₂]; ($\square$), [C₇C₁im][NTf₂]; ($\blacksquare$), [C₄C₄im][NTf₂]; ($\diamond$), [C₉C₁im][NTf₂]; ($\blacklozenge$), [C₅C₅im][NTf₂]; ($\blacktriangledown$), [C₁₁C₁im][NTf₂]; ($\blacktriangledown$), [C₆C₆im][NTf₂]; ($\bullet$), [C₇C₇im][NTf₂]; ($\blacklozenge$), [C₈C₈im][NTf₂]; and ($\blacktriangleright$), [C₁₀C₁₀im][NTf₂].

Figure 6.

Viscosity dependence of the pure [15, 35] and water-saturated [NTf₂]-based ILs studied, at 298.15 K, as a function of the cation structure (alkyl side chain length increase). The matching empty and colorful symbols represent, respectively, the pure and water-saturated ILs. Colorful symbols correspond to isomers, and black symbols correspond to ILs with no corresponding isomers.

Figure 7.

Energy barrier of pure [15, 35] and water-saturated ILs at 323.15 K and 0.1 MPa, as a function of the cation structure (alkyl side chain length increase). The matching empty and colorful symbols represent, respectively, the pure and water-saturated ILs. Colorful symbols correspond to isomers, and black symbols correspond to ILs with no corresponding isomers.

Figure 8.

Deviation (E_{Dev}) between the water-saturated and the pure ILs energy barriers at 323.15 K, as a function of: (a) the total number of carbons in the alkyl chain length, N ; and (b) the experimental mole fraction water solubility, x_w (at 298.15 K).

Table 1Investigated ionic liquids: chemical name, abbreviation, source, molecular weight (M_w) and purity.

Chemical Name	Abbreviation	Source	M_w / (g·mol ⁻¹)	Purity / (wt %)
1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₂ C ₁ im][NTf ₂]	Iolitec	391.31	> 99
1-methyl-3-propylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₃ C ₁ im][NTf ₂]	Iolitec	405.34	> 99
1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₄ C ₁ im][NTf ₂]	Iolitec	419.37	> 99
1-methyl-3-pentylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₅ C ₁ im][NTf ₂]	Iolitec	433.39	> 99
1-heptyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₇ C ₁ im][NTf ₂]	Iolitec	461.45	> 99
1-methyl-3-nonylmethylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₉ C ₁ im][NTf ₂]	Iolitec	489.50	> 99
1-methyl-3-undecylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₁₁ C ₁ im][NTf ₂]	Iolitec	517.55	> 99
1,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₁ C ₁ im][NTf ₂]	Iolitec	377.29	> 99
1,3-diethylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₂ C ₂ im][NTf ₂]	Iolitec	405.34	> 99
1,3-dipropylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₃ C ₃ im][NTf ₂]	Iolitec	433.39	> 99
1,3-dibutylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₄ C ₄ im][NTf ₂]	Iolitec	461.45	> 99
1,3-dipentylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₅ C ₅ im][NTf ₂]	Iolitec	489.50	> 99
1,3-dihexylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₆ C ₆ im][NTf ₂]	Iolitec	517.55	> 99
1,3-diheptylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₇ C ₇ im][NTf ₂]	Iolitec	545.60	> 99
1,3-dioctylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₈ C ₈ im][NTf ₂]	Iolitec	573.66	> 99
1,3-didecylimidazolium bis((trifluoromethyl)sulfonyl)imide	[C ₁₀ C ₁₀ im][NTf ₂]	Iolitec	629.76	> 99

Table 2

Experimental and estimated mole fraction solubility of water (x_w) in the investigated ILs, at 298.15 K and 0.10 MPa.

Ionic Liquid	x_w		x_{Dev}^b
	Estimated	Experimental ^a [29–31]	
[C ₂ C ₁ im][NTf ₂]	0.345 (0.002)	0.298 (0.009)	0.0467
[C ₃ C ₁ im][NTf ₂]	0.264 (0.002)	0.272 (0.007)	-0.0079
[C ₄ C ₁ im][NTf ₂]	0.142 (0.002)	0.257 (0.006)	-0.1149
[C ₅ C ₁ im][NTf ₂]	0.225 (0.002)	0.221 (0.005)	0.0042
[C ₇ C ₁ im][NTf ₂]	0.298 (0.002)	0.197 (0.004)	0.1010
[C ₉ C ₁ im][NTf ₂]	0.248 (0.002)	0.174 (0.001)	0.0748
[C ₁₁ C ₁ im][NTf ₂]	0.244 (0.002)	0.157 (0.001)	0.0871
[C ₁ C ₁ im][NTf ₂]	0.354 (0.002)	0.355 (0.004)	-0.0011
[C ₂ C ₂ im][NTf ₂]	0.282 (0.002)	0.277 (0.001)	0.0043
[C ₃ C ₃ im][NTf ₂]	0.251 (0.002)	0.223 (0.001)	0.0277
[C ₄ C ₄ im][NTf ₂]	0.235 (0.002)	0.184 (0.003)	0.0508
[C ₅ C ₅ im][NTf ₂]	0.147 (0.002)	0.158 (0.001)	-0.0109
[C ₆ C ₆ im][NTf ₂]	0.183 (0.002)	0.149 (0.001)	0.0337
[C ₇ C ₇ im][NTf ₂]	0.208 (0.002)	0.137 (0.001)	0.0711
[C ₈ C ₈ im][NTf ₂]	0.297 (0.002)	0.125 (0.001)	0.1728
[C ₁₀ C ₁₀ im][NTf ₂]	0.349 (0.002)	- ^c	-

^aStandard deviation between brackets. Uncertainties are $u(T) = 0.01$ K and $u(p) = 0.05$.

^b $x_{Dev} = x_w(\text{Estimated}) - x_w(\text{Experimental})$.

^cNot experimentally determined at 298.15 K due to the higher melting temperature of this ionic liquid. However, the water solubility in [C₁₀C₁₀im][NTf₂] at 308.15 K is 0.1337 (in mole fraction) [31].

Table 3

Thermal expansion coefficients, α_p , of pure [15] and water-saturated ILs, estimated using Equation 2 at 323.15 K and 0.1 MPa.^a

Ionic Liquid	$10^4 \cdot (\alpha_{p, \text{water-saturated}} \pm \sigma)^b / \text{K}^{-1}$	$10^4 \cdot (\alpha_{p, \text{pure}} \pm \sigma)^b / \text{K}^{-1}$	%AD ^c
[C ₂ C ₁ im][NTf ₂]	6.959 ± 0.012	6.69 ± 0.09	4.01
[C ₃ C ₁ im][NTf ₂]	7.003 ± 0.007	6.71 ± 0.09	4.37
[C ₄ C ₁ im][NTf ₂]	6.893 ± 0.004	6.67 ± 0.12	3.35
[C ₅ C ₁ im][NTf ₂]	6.981 ± 0.005	6.67 ± 0.09	4.66
[C ₇ C ₁ im][NTf ₂]	6.819 ± 0.006	6.72 ± 0.16	1.48
[C ₉ C ₁ im][NTf ₂]	6.840 ± 0.004	6.72 ± 0.13	1.79
[C ₁₁ C ₁ im][NTf ₂]	6.889 ± 0.004	6.78 ± 0.11	1.61
[C ₁ C ₁ im][NTf ₂]	6.925 ± 0.003	6.63 ± 0.11	4.44
[C ₂ C ₂ im][NTf ₂]	6.966 ± 0.003	6.75 ± 0.07	3.19
[C ₃ C ₃ im][NTf ₂]	6.939 ± 0.008	6.75 ± 0.09	2.80
[C ₄ C ₄ im][NTf ₂]	6.855 ± 0.004	6.71 ± 0.09	2.16
[C ₅ C ₅ im][NTf ₂]	6.870 ± 0.007	6.75 ± 0.08	1.77
[C ₆ C ₆ im][NTf ₂]	6.893 ± 0.005	6.80 ± 0.14	1.36
[C ₇ C ₇ im][NTf ₂]	6.878 ± 0.004	6.77 ± 0.14	1.59
[C ₈ C ₈ im][NTf ₂]	6.898 ± 0.004	6.84 ± 0.15	0.85
[C ₁₀ C ₁₀ im][NTf ₂]	6.947 ± 0.004	6.87 ± 0.14	1.12

^aStandard uncertainties, u , are $u(T) = 0.02$ K, and $u(p) = 0.05$.

^bExpanded uncertainty with approximately 95% level of confidence.

^cPercentage average relative deviation on α_p between the water-saturated and pure ILs.

Table 4

Fitting coefficients of the VTF equation and derived energy barrier, E , of pure [15, 35] and water-saturated ILs at 323.15 K and 0.1 MPa.^a

Ionic Liquid	$(A_{\eta} \pm \sigma)^b$ / mPa·s	$(B_{\eta} \pm \sigma)^b$ / K	$(C_{\eta} \pm \sigma)^b$ / K	$(E_{\text{water-saturated}} \pm \sigma)^b$ / kJ·mol ⁻¹	$(E_{\text{pure}} \pm \sigma)^b$ / kJ·mol ⁻¹	%AD ^c
[C ₂ C ₁ im][NTf ₂]	0.203 ± 0.007	645.7 ± 11.5	155.8 ± 1.4	20.03 ± 0.76	22.35 ± 0.24	2.32
[C ₃ C ₁ im][NTf ₂]	0.181 ± 0.006	671.4 ± 10.2	163.6 ± 1.2	22.90 ± 0.77	25.48 ± 0.15	2.58
[C ₄ C ₁ im][NTf ₂]	0.184 ± 0.004	678.0 ± 5.8	166.2 ± 0.7	23.89 ± 0.46	26.41 ± 0.31	2.52
[C ₅ C ₁ im][NTf ₂]	0.158 ± 0.002	734.0 ± 3.1	164.8 ± 0.3	25.40 ± 0.24	27.87 ± 0.16	2.47
[C ₇ C ₁ im][NTf ₂]	0.164 ± 0.005	742.2 ± 9.1	169.6 ± 0.9	27.34 ± 0.75	29.83 ± 0.09	2.49
[C ₉ C ₁ im][NTf ₂]	0.116 ± 0.028	880.0 ± 74.1	161.5 ± 6.5	29.23 ± 5.30	31.50 ± 0.54	2.27
[C ₁₁ C ₁ im][NTf ₂]	0.115 ± 0.012	906.8 ± 31.3	163.5 ± 2.6	30.89 ± 2.31	32.99 ± 0.74	2.10
[C ₁ C ₁ im][NTf ₂]	0.227 ± 0.007	600.0 ± 9.3	162.0 ± 1.2	20.06 ± 0.68	23.15 ± 0.37	3.09
[C ₂ C ₂ im][NTf ₂]	0.165 ± 0.005	717.1 ± 10.3	147.6 ± 1.2	20.20 ± 0.59	22.33 ± 0.47	2.13
[C ₃ C ₃ im][NTf ₂]	0.178 ± 0.003	681.8 ± 5.1	169.5 ± 0.6	25.07 ± 0.43	27.43 ± 0.16	2.36
[C ₄ C ₄ im][NTf ₂]	0.144 ± 0.004	768.6 ± 9.3	166.1 ± 0.9	27.07 ± 0.72	28.92 ± 0.25	1.85
[C ₅ C ₅ im][NTf ₂]	0.117 ± 0.002	846.5 ± 6.3	164.8 ± 0.6	29.31 ± 0.48	31.21 ± 0.44	1.90
[C ₆ C ₆ im][NTf ₂]	0.105 ± 0.001	899.6 ± 2.0	163.6 ± 0.2	30.66 ± 0.15	32.34 ± 0.54	1.68
[C ₇ C ₇ im][NTf ₂]	0.093 ± 0.004	953.7 ± 13.3	161.7 ± 1.1	31.75 ± 0.95	33.30 ± 1.30	1.55
[C ₈ C ₈ im][NTf ₂]	0.095 ± 0.003	962.7 ± 10.4	163.4 ± 0.8	32.74 ± 0.76	34.47 ± 0.92	1.73
[C ₁₀ C ₁₀ im][NTf ₂]	0.083 ± 0.004	1034.3 ± 15.5	162.3 ± 1.1	34.70 ± 1.11	35.70 ± 2.70	1.00

^aUncertainties are $u(T) = 0.02$ K, and $u_p(p) = 0.05$.

^bExpanded uncertainty with an approximately 95% level of confidence. The energy barrier values for the pure ionic liquids are from reference [15].

^cPercentage average absolute deviation on E between the pure and the water-saturated ILs.