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Density and viscosity of several pure and water-saturated ionic liquids

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Densities and viscosities were measured as a function of temperature for six ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium ethylsulfate and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide . The density and the viscosity were obtained using a vibrating tube densimeter from Anton Paar and a rheometer from Rheometrics Scientific at temperatures up to 393 K and 388 K with an accuracy of 10^{-3} g cm^{-3} and 1%, respectively. The effect of the presence of water on the measured values was also examined by studying both dried and water-saturated samples. A qualitative analysis of the evolution of density and viscosity with cation and anion chemical structures was performed.

Introduction

Room temperature ionic liquids (ILs) constitute a new class of substances that are considered as potential substitutes to many traditional organic solvents in reaction and separation systems.[1,2] The great interest of these organic salts, composed of bulky ions, is their negligible vapour pressure, low melting point and good thermal stability which make them liquid over a large temperature range (typically 300 K) including ambient temperature. Furthermore, they are non-flammable and easy to recycle. These properties make them very attractive especially in the emerging field of green chemistry.

Even if the number of articles on ILs is increasing exponentially, there is still a lack of data on their thermo-dynamic and thermophysical properties. The first reason for that is the wide variety of ILs. Indeed, in order to obtain these liquids with properties suitable for a particular industrial application (in terms of chemical reactivity and process engineering), new ILs are being continuously designed. The aim is to achieve exactly the desired chemical and physical properties by a judicious combination of an anion and a cation. Furthermore, although different ways of synthesizing this new class of liquid are better understood and controlled, it still remains difficult to obtain them with a high purity or at least with well defined admixtures. The identification of the impurities in the samples is of importance as their presence has a strong impact on the physico–chemical properties of ILs.[3] Thus the comparison of data sets obtained with samples of different origins is not always concluding and can lead to confusion. Finally, many physico–chemical data presented in the literature are collected mainly to characterise an IL after synthesis work and are thus often of limited reliability. In this context, our aim is to study closely two key thermophysical properties, density and viscosity, for several ILs with special

attention paid to the influence of the presence of a major impurity: water.

A considerable amount of data on the density of ILs are available in the literature (many in communications dedicated primarily to synthesis) as it is a typical property for characterising a substance. A recent review of density measurements of ILs has been published by Mantz and Trulove.[4] By far the most studied liquids are those containing imidazolium and, to a lesser extent, pyridinium-based cations. Usually the influence of the alkyl chain length in these cations on the density is studied as well as the effect of different anions (chloride Cl$^-$, tetrafluoroborate BF$_4^-$, hexafluorophosphate PF$_6^-$, bis(trifluoromethylsulfonyl)imide NTf$_2^-$). Several authors[5,6] have worked on other types of cation (ammonium, pyrrolidinium) but only at 298 K. The most frequently studied IL was 1-butyl-3-methylimidazolium hexafluorophosphate Bmim$^+$PF$_6^-$. The interest has, however, weakened over the last few years as it has been shown that this IL can degrade in the presence of water at temperatures above 323K[7] leading to formation of HF. ILs are generally denser[4,8,9] than either organic solvents and water, with typical values of densities ranging from 1 to 1.6 g cm^{-3}. The density generally decreases with increasing length of an alkyl chain in a cation or anion as was documented for imidazolium-based cations.[8,10,11] The density values are often reported at a single temperature, usually 293 K or 298 K. Knowledge of the temperature dependence of this property is, however, very useful and several recent studies[10,12–15] present data as a function of temperature. They have reported an approximately linear decrease of density with temperature, corresponding to typical values[14] for the thermal expansion coefficient near 5×10^{-4} K^{-1} which is about twice higher compared to water and three times lower compared to common organic solvents (such as methanol, acetone, benzene and n-hexane). Sun *et al.*[6] and Gu and Brennecke[14] examined also the variation of the density of ILs with pressure. They came to a conclusion of an isothermal compressibility comparable with water and lower than that for organic solvents.

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The knowledge of the viscosity of ILs is of prime importance from an engineering point of view as it plays a major role in stirring, mixing and pumping operations; in addition, it also affects other transport properties such as diffusion. Nevertheless, the viscosity is much less investigated than the density and only limited data are available in the literature. Most of the studies[10,15–18] concern imidazolium-based ILs, differing in the length and ramification of the alkyl chains. Okoturo et al.[18] have also studied pyrrolidinium cations. ILs are generally viscous liquids[8,9] with viscosities ranging typically from 10 to 500 mPa s at ambient temperature. This is comparable with the values obtained for oils, that is to say two or three orders of magnitude higher than viscosities of traditional organic solvents. This is obviously a real disadvantage for their industrial application and it explains the quest for new ILs exhibiting lower viscosity. The influence of temperature on viscosity is much more important than on density: a strong decrease is observed with increasing temperature[10,15,17,18] making ILs easier to apply at super-ambient conditions.

Both for densities and viscosities, a comparison of all the data presented in the literature allows one to make some general qualitative conclusions about trends, but a detailed analysis indicates that a quantitative description is much more difficult to make. Particularly, the effect of impurities present in the samples on the measured physico–chemical properties of ILs was put forward by Marsh et al.[8] An exhaustive study of this problem was published by Seddon et al.[3] with a focus on the influence of chloride and water. The presence of this latter component in an IL sample can indeed greatly modify both the values of thermophysical properties and the reactivity. Even so, very few authors have identified the water quantity in their samples before performing physicochemical measurements. This information is lacking and makes comparison of literature data difficult. Huddleston et al.[17] have studied at 298 K water-saturated and dried samples in order to report the effect of the presence of water on several properties of the ILs (melting point, thermal stability, viscosity, surface tension, density…). They have examined how sensitive the physicochemical properties studied are on the water content, an effect that sometimes shifts the results by an order of magnitude. In this context, the preparation of ILs of well-defined purity is absolutely necessary and the development of analytical techniques to quantify major impurities in samples appears to be crucial. Furthermore, care should be taken to avoid contamination of the samples during measurement. For example, Okoturo et al.[18] have conducted viscosity measurements in an atmosphere with oxygen and water controlled levels in order to minimise inaccuracies in the measured properties caused by the presence of air or moisture. Without this meticulous analytical work, no definitive conclusions on property–structure relationship in ILs will ever be found.

Scope and objectives of the study

Our aim was to obtain original and highly accurate data on density (ρ) and viscosity (η) as a function of temperature for several ILs and to examine the effect of water content on the results. Six ILs were chosen for this study: 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim$^+$PF$_6^-$), 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim$^+$BF$_4^-$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Bmim$^+$NTf$_2^-$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Emim$^+$NTf$_2^-$), 1-ethyl-3-methylimidazolium ethylsulfate (Emim$^+$EtSO$_4^-$) and butyltrimethylammonium bis(trifluoromethylsulfonyl)imide (N$_{4111}^+$NTf$_2^-$).

The first two ILs are commercially available and widely investigated. They were chosen in order to compare our results with numerous data in the literature that present, however, an important dispersion. The NTf$_2^-$-containing ILs are hydrophobic and chemically stable. They exhibit a wide liquid range even if a recent study of Fox et al.[19] indicates that decomposition temperatures were overestimated in previous thermal studies. However, the relatively high cost of the NTf$_2^-$-containing ILs is a limiting factor for their industrial use. The presence of fluorine in anions that can decompose is, similarly as for PF$_6^-$ and BF$_4^-$, a real disadvantage for components referred to as green. The hydrophilic ILs containing the EtSO$_4^-$ anion belong to a new generation of fluorine-free ILs valued from an environmental point of view. The imidazolium-based cations were here considered because they are among the most promising ions for applications despite their cost and their somewhat poor chemical stability in the presence of impurities. Finally, one IL with an alkylammonium cation was included as a representative of another class of salt for which very few data are available in the literature. Its higher viscosity compared to ILs with imidazolium ions is, however, a limitation. This selection should allow one to study on one hand the effect of the cation structure for the NTf$_2^-$-based ILs and, on the other hand, the effect of the anion structure for the imidazolium-based ILs.

Finally, given the importance impurities can have on the physico–chemical properties, the influence of water on the density and the viscosity was also systematically investigated. The experiments were thus performed first with samples carefully dried and then for the four hydrophobic ILs (Emim$^+$NTf$_2^-$, Bmim$^+$NTf$_2^-$, Bmim$^+$PF$_6^-$, N$_{4111}^+$ NTf$_2^-$) also with samples saturated with water.

Experimental

Samples

The Bmim$^+$BF$_4^-$ sample was purchased from Sigma Aldrich with a minimum stated mole fraction purity of 0.97 and Bmim$^+$PF$_6^-$ was obtained from Acros Organics with a minimum stated mole fraction purity of 0.999. As they were synthesized from Bmim$^+$Cl$^-$, chloride can remain in the samples. The quantity of this anion, measured following the Mohr method, was of 0.01% in mass. The samples of the four other ILs (minimum stated purity of 0.99 in mole fraction) were supplied by the group of P. Wasserscheid (University of Erlangen-Nürnberg, Germany). The Bmim$^+$NTf$_2^-$ and Emim$^+$NTf$_2^-$ were synthesized via ion exchange from Bmim$^+$Cl$^-$ and Emim$^+$Br$^-$ respectively and have contents of chloride and bromide respectively lower than 50 ppm. The last two samples (N$_{4111}^+$ NTf$_2^-$ and Emim$^+$EtSO$_4^-$) do not contain any chloride or bromide ions.

In the following sections, an IL sample treated for 15 h at 323 K under vacuum will be referred to as 'dried sample'. It was then conditioned under a nitrogen atmosphere. This inert gas was chosen because of its very low solubility in the ILs investigated.[20] To avoid any contact of the sample with atmosphere, a schlenk and a syringe equipped with a luer lock valve were used to measure the water quantity and to load the samples into the instruments. A coulometric Karl–Fisher titration (Mettler Toledo DL31) on water was performed before and after each series of measurements and it was found that there was no variation of the water quantity in the samples. The water-saturated samples were obtained by adding water to the conditioned ILs until the second (aqueous) phase appeared and the water composition in the IL, measured by coulometric Karl–Fisher titration, was constant (typically after 5 days of a gently stirring).

The water contents of the dried and saturated samples are presented in Table 1. Given the high molar masses of the ILs, the water quantity expressed in mole fraction is at least one order of magnitude higher than the corresponding mass fraction. The water quantities in the dried samples are of the order 10^{-4} and 10^{-3} in mass and mole fraction, respectively. The water-saturated samples contain typically between 10^{-2} and 3×10^{-2} of water in mass fraction which corresponds to mole fractions up to 3×10^{-1}.

Measurements

Densities were measured using a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode. The temperature was maintained constant to 0.01 K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring temperature a 100 Ω platinum resistance thermometer (precision 0.02 K, accuracy 0.04 K) was used. Its calibration was performed against a 100 Ω platinum resistance Hart Scientific model 1502A. The measured period of vibration (τ) of a U tube is related to the density (ρ) according to: $\rho = A\tau^2 + B$ where A and B are parameters that are a function of temperature. They were determined in the range between 293 and 393 K using air, tridistilled water and aqueous solutions of NaCl (molalities of 1 M and 3 M). These latter two fluids were chosen in order to cover a range of densities corresponding to the density of ILs studied. Measurements were performed with a step of 10 K and at least three independent values were obtained at each temperature. The precision of the density measurement is of the order 10^{-4} g cm^{-3}, the results are expected to be accurate to 10^{-3} g cm^{-3}.

Table 1 Molar masses (M_{IL}) and water content in mass fractions (w_w) and mole fractions (x_w) of the dried and water saturated ILs

	M_{IL}/g mol^{-1}	$w_w \times 10^3$ Dried	$w_w \times 10^3$ Saturated	$x_w \times 10^3$ Dried	$x_w \times 10^3$ Saturated
Bmim$^+$PF$_6^-$	284.18	0.19	26.8	3.00	303
Bmim$^+$NTf$_2^-$	419.37	0.05	19.9	1.20	321
Bmim$^+$BF$_4^-$	226.03	0.70	Miscible	8.60	Miscible
N$_{4111}^+$NTf$_2^-$	396.38	0.07	14.3	1.50	242
Emim$^+$NTf$_2^-$	391.31	0.05	19.8	1.10	305
Emim$^+$EtSO$_4^-$	236.29	0.10	Miscible	1.30	Miscible

The rheometer used (Rheometrics Scientific, SR200) allows measurements from 293 to 393 K at atmospheric pressure and in a wide viscosity range (from 1 to 3000 mPa s) depending on the geometry of the vessel used. A couette geometry (concentric cylinders) was chosen for this study. Temperature was maintained constant to 0.01 K by means of a recirculating bath similar to that used for the densimeter and was measured with the same accuracy. To avoid any water contamination of the sample during the measurement, the rheometer was placed inside a glove-box in an isolating atmosphere of purified and dried air. The rheometer was calibrated with an oil of known viscosity (viscosity standard oil from Brookfield, 95 mPa s at 298 K). Measurements were performed with a step of 10 K and at least three independant values were obtained at each temperature. A statistical analysis of our results indicates a precision in the viscosities of 0.2% and an expected overall uncertainty lower than 1%.

Results and discussion

Densities

The densities of the six dried samples were first obtained as a function of temperature from 293 K to 393 K. The four hydrophobic ILs were then saturated with water, as described above, and their density was remeasured from 293 K to 343 K. We have decided not to measure the density of these samples at higher temperatures to avoid changes in the composition of the sample due to the vaporization of water. Below 343 K, the vapor pressure of water is sufficiently low (less than 0.031 MPa) to consider this change in composition as negligible. For the six ILs studied, the experimental densities of the dried and saturated samples are presented in Table 2.

For the dried ILs, the values vary typically from 1.20 to 1.53 g cm^{-3} at 293 K and from 1.13 to 1.43 g cm^{-3} at 393 K. As expected, the densities are related to the molar masses of the ions and ILs containing heavy atoms are in general denser as is observed for those composed of NTf$_2^-$ when compared to those with PF$_6^-$. Similarly, the IL containing the latter is denser compared to that containing BF$_4^-$. This is not however valid for strongly asymmetric cations; the density decreases with increasing length of the alkyl chain on the imidazolium cation. Such trends are well documented in the literature.[8,10,15,21,22]

The densities of the water-saturated ILs are somewhat lower when compared with the dried samples; the observed difference, of 1 to 2%, is almost negligible from the practical point of view. This minor change in density with water content appears to be largely independent of temperature.

In the temperature range studied, the density decreases linearly with temperature for both dried and water-saturated ILs. Fig. 1 illustrates this for the dried samples. A linear equation was used to express the correlation with temperature:

$$\rho \text{ (g cm}^{-3}) = a + b(T/K - 273.15) \quad (1)$$

The characteristic parameters a and b for temperature in K are given in Table 3.

It is also of interest to express the volumetric behaviour of ILs in terms of molar volume $V_m = M/\rho$ reflecting the size of

Table 2 Experimental densities (ρ) of dried and water saturated ILs as a function of temperature at atmospheric pressure

Bmim$^+$PF$_6^-$				Bmim$^+$NTf$_2^-$				Bmim$^+$BF$_4^-$	
Dried		Saturated		Dried		Saturated		Dried	
T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}
292.87	1.3705	292.88	1.3539	292.88	1.4431	292.9	1.4279	292.89	1.2048
302.73	1.3620	302.63	1.3451	302.80	1.4334	302.81	1.4178	302.77	1.1975
312.69	1.3535	312.53	1.3358	312.79	1.4239	312.79	1.4071	312.71	1.1900
322.69	1.3451	322.49	1.3278	322.81	1.4144	322.77	1.3980	322.72	1.1830
332.65	1.3370	332.44	1.3194	332.54	1.4048	332.50	1.3881	332.71	1.1760
342.58	1.3287	342.32	1.3114	342.72	1.3949	342.67	1.3791	342.67	1.1694
352.31	1.3209			352.31	1.3866			352.31	1.1611
373.34	1.3043			373.34	1.3668			373.33	1.1465
391.27	1.2902			391.28	1.3510			391.28	1.1345
N$_{4111}^+$NTf$_2^-$				Emim$^+$NTf$_2^-$				Emim$^+$EtSO$_4^-$	
Dried		Saturated		Dried		Saturated		Dried	
T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}	T/K	ρ/g cm^{-3}
292.97	1.3966	292.86	1.3892	292.79	1.5235	292.87	1.5042	292.8	1.2430
302.84	1.3878	302.62	1.3800	302.68	1.5134	302.64	1.4936	302.71	1.2369
312.82	1.3788	312.50	1.3701	312.64	1.5034	312.54	1.4827	312.66	1.23050
322.81	1.3701	322.47	1.3616	322.62	1.4932	322.47	1.4728	322.65	1.2241
332.75	1.3613	332.43	1.3527	332.58	1.4834	332.21	1.4627	332.61	1.2176
342.67	1.3528	342.32	1.3441	342.49	1.4738	342.33	1.4529	342.51	1.2111
352.31	1.3422			352.32	1.4638			352.30	1.2075
373.33	1.3249			373.33	1.4429			373.33	1.1946
391.27	1.3104			391.29	1.4263			391.27	1.1838

the ions. The molar volumes of the dried and water-saturated samples, obtained from the densities calculated *via* eqn (1), are presented at 293 K and 343 K in Table 4.

In the case of samples saturated with water the molar mass of the ILs (M_{IL}^{sat}) was corrected because of the presence of water as:

$$M_{IL}^{sat} = M_{IL}(1 - x_w) + M_w x_w \qquad (2)$$

where M_w is the molar mass of water. The values vary between 190 and 300 cm^3 mol^{-1} for the dried samples and are 20 to 30% lower in the case of water-saturated samples, depending on the water content. When comparing the molar volumes of the different dried ILs studied it is obvious that the molar mass governs the molar volume. Indeed, Bmim$^+$NTf$_2^-$ having the highest molar mass (M_{IL} = 419.4 g mol^{-1}) exhibits the highest molar volume among the investigated ILs.

Both in the cases of the dried and water-saturated ILs, a logical increase of V_m with increasing temperature was observed. The evolution of the volumetric properties with temperature can be expressed by calculating the coefficient of thermal expansion, α_p, defined as

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (3)$$
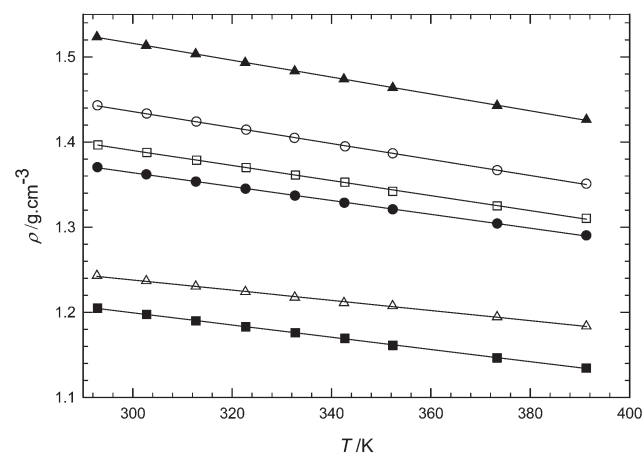

Fig. 1 Experimental densities of the dried ILs as a function of temperature: (●), Bmim$^+$PF$_6^-$; (○), Bmim$^+$NTf$_2^-$; (■), Bmim$^+$BF$_4^-$; (□), N$_{4111}^+$NTf$_2^-$; (▲), Emim$^+$NTf$_2^-$; (△), Emim$^+$EtSO$_4^-$. The lines correspond to the fit of the data by eqn (1).

Table 3 Correlation parameters a and b and standard deviation σ for the density of dried and water-saturated ILs as a function of temperature determined from measurements between 293 K and 393 K for the dried samples and between 293 K and 343 K for the water-saturated samples

		a/g cm^{-3}	b/10^{-4} g cm^{-3} K^{-1}	σ/10^{-4} g cm^{-3}
Bmim$^+$PF$_6^-$	Dried	1.3859	−8.15	5
	Saturated	1.3703	−8.60	4
Bmim$^+$NTf$_2^-$	Dried	1.4610	−9.38	6
	Saturated	1.4469	−9.80	5
Bmim$^+$BF$_4^-$	Dried	1.2186	−7.17	5
N$_{4111}^+$NTf$_2^-$	Dried	1.4139	−8.85	8
	Saturated	1.4067	−9.10	4
Emim$^+$NTf$_2^-$	Dried	1.5425	−9.90	4
	Saturated	1.5242	−10.40	4
Emim$^+$EtSO$_4^-$	Dried	1.2541	−5.98	8

^{a} $\sigma = \left(\dfrac{\sum(\rho_i^{exp} - \rho_i^{cal})^2}{n - v}\right)^{0.5}$ where n is the number of experimental points, v the number of adjustable parameters.

Table 4 Calculated molar volumes (V_m/cm^3 mol^{-1}) and the coefficients of the thermal expansion (α_p/cm^3 mol^{-1}) of dried and water-saturated ILs at 293.15 K and 343.15 K

| | Bmim$^+$PF$_6^-$ | | | | Bmim$^+$NTf$_2^-$ | | | | Bmim$^+$BF$_4^-$ | |
| | V_m/cm^3 mol^{-1} | | α_p/10^{-4} K^{-1} | | V_m/cm^3 mol^{-1} | | α_p/10^{-4} K^{-1} | | V_m/cm^3 mol^{-1} | α_p/10^{-4} K^{-1} |
T/K	Dried	Saturated	Dried	Saturated	Dried	Saturated	Dried	Saturated	Dried	Dried
293.15	207	150	5.95	6.35	291	204	6.51	6.90	188	5.95
343.15	214	155	6.13	6.55	301	211	6.72	7.15	193	6.13

| | N$_{4111}^+$NTf$_2^-$ | | | | Emim$^+$NTf$_2^-$ | | | | Emim$^+$EtSO$_4^-$ | |
| | V_m/cm^3 mol^{-1} | | α_p/10^{-4} K^{-1} | | V_m/cm^3 mol^{-1} | | α_p/10^{-4} K^{-1} | | V_m/cm^3 mol^{-1} | α_p/10^{-4} K^{-1} |
T/K	Dried	Saturated	Dried	Saturated	Dried	Saturated	Dried	Saturated	Dried	Dried
293.15	284	220	6.34	6.56	257	185	6.50	6.91	190	4.82
343.15	293	227	6.55	6.78	266	191	6.72	7.16	195	4.94

The values of α_p for the dried and saturated samples calculated at 293 K and 343 K from the fitted densities are presented in Table 4. Since the densities decrease linearly with temperature it is obvious that α_p values are positive increasing with temperature. The values obtained vary between 5×10^{-4} and 7×10^{-4} K^{-1} in the case of dried samples, and are up to 7% higher for the water-saturated samples. Values for α_p of the same order of magnitude ($5–6 \times 10^{-4}$ K^{-1}) were reported by Gu and Brennecke[14] for several ILs containing BF$_4^-$ and PF$_6^-$ anions and imidazolium and pyridinium-based cations. The trends observed for the densities can be also noticed in the thermal expansion coefficients. The imidazolium-based ILs exhibit a higher thermal expansion than the ammonium-based IL. The results also suggest that the presence of the NTf$_2^-$ anion strongly increases the thermal expansion coefficient compared to the other anions. The presence of the EtSO$_4^-$ anion seems to yield a smaller thermal expansion coefficient, the difference between α_p for Emim$^+$ NTf$_2^-$ and Emim$^+$EtSO$_4^-$ being about 30%.

Viscosities

A second series of measurements, analogous to those for densities, allowed us to obtain dynamic viscosities of dried and water-saturated samples. For the ILs studied we have first observed that the viscosity remains constant with increasing shear rates (from 0 to 200 s^{-1}). This linear relationship between the shear stress and the shear rate corresponds to a Newtonian behaviour. This seems to be consistent with the findings of Huddleston et al.[17] and Seddon et al.[10] They reported a Newtonian behaviour for ILs of alkylimidazolium BF$_4^-$ family (with the alkyl chain length between 4 and 8 carbon atoms) while the ILs with longer alkyl chains (number of carbon atoms typically 12) are thixotropic fluids whose viscosity decreases when increasing the shear rate.

In Table 5 are presented the experimental viscosities of the dried samples from 293 K to 388 K and those of the water-saturated samples from 293 K to 343 K. The viscosity was not measured at higher temperatures on these samples since the results would be affected by vaporization of water. The trends in the evolution of viscosity with the structure of the cations and the anions are in many aspects inverse to those observed for density. The NTf$_2^-$ anion lowers the viscosity compared to the other investigated anions. Particularly the contribution of the PF$_6^-$ anion to the viscosity increase is exceptionally strong. On the basis of a similar analysis to that for density, it can be concluded that the EtSO$_4^-$ anion increases viscosity compared to the BF$_4^-$ anion. These differences in viscosities are one of the reasons behind the recent development of many NTf$_2^-$-based ILs which are relatively less viscous compared to ILs containing other anions.

The alkylammonium-based IL exhibits a higher viscosity than the imidazolium-based ILs with the same anion; furthermore, the viscosity of the latter ILs increases with the length of the alkyl chain on the imidazolium ring. This is a somewhat surprising result, since one would expect at first view that, as the side-chain length increases, the overall contribution of the strong, associating, electrostatic (and hydrogen-bond) terms to the interactions diminishes, while the contribution of weaker, non-associating, dispersion forces increases. As a consequence, it could be anticipated that the viscosity would decrease as the size of the non-polar part of the cations becomes larger. Evidently, this is not the case and this observation has been discussed in the literature by several authors.[11,16] The justification put forward by Bonhôte et al.[16] is that it is the increase in the van der Waals interactions due to the presence of a long alkyl chain that leads to higher viscosities. However, this argument seems to come from a simple correlation of what is observed, not having a strong molecular basis. The study of Tokuda et al.[11] is more profound, since it relates the behaviour of the transport properties, viscosity and diffusion, to a ratio of ionic conductivities that can be interpreted as a measure of ionic dissociation or "ionicity". These authors observe that the "ionic dissociation" is directly related to the diffusion coefficient, and inversely related to the viscosity, and they attribute this to a preponderance of the effect of the Van der Waals interactions over electrostatic terms. Computer simulations performed in our group[23] would lead to a different interpretation of the reasons behind this dependence on the alkyl chain length. Simulations have shown that imidazolium ILs with side chains above butyl (and up to C$_{12}$) exist in the pure liquid phases as microstructured fluids, in which non-polar domains are formed by the alkyl chains and, at the same time, the charged parts form ionic domains which tend to be continuous (channels). Such microstructuring has been

Table 5 Experimental viscosities (η) of dried and water saturated ILs as a function of temperature at atmospheric pressure

Bmim⁺PF₆⁻				Bmim⁺NTf₂⁻				Bmim⁺BF₄⁻	
Dried		Saturated		Dried		Saturated		Dried	
T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s
293.59	375.9	296.73	84.8	293.40	59.8	293.33	32.0	293.67	109.2
302.61	209.1	302.97	60.9	302.93	40.6	302.84	22.4	303.22	75.4
312.21	135.0	312.34	41.5	312.45	28.7	312.41	17.0	312.74	50.0
321.95	91.6	322.03	30.8	321.88	21.5	322.00	13.3	322.00	35.1
331.45	60.3	331.49	23.8	331.12	16.2	331.26	10.9	331.56	24.9
340.94	43.1	340.92	17.7	340.66	12.4	340.73	8.7	341.04	19.1
350.29	32.0			350.47	9.6			350.47	14.8
360.16	24.2			359.66	7.5			359.81	11.8
369.55	16.8			368.87	6.2			369.15	9.4
378.90	14.0			377.93	5.1			378.38	7.4
388.19	12.8			387.51	4.2			388.04	5.8

N₄₁₁₁⁺NTf₂⁻				Emim⁺NTf₂⁻				Emim⁺EtSO₄⁻	
Dried		Saturated		Dried		Saturated		Dried	
T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s	T/K	η/mPa s
293.79	140.7	293.77	72.6	293.39	40.1	296.06	21.9	296.80	107.7
303.31	85.5	303.00	43.4	303.48	28.7	303.47	16.8	303.52	78.5
312.91	56.5	312.24	29.8	313.03	21.1	312.85	13.4	313.05	52.2
322.54	40.0	321.68	21.7	322.59	16.2	322.06	10.8	322.51	36.3
331.91	29.1	331.29	15.6	332.12	12.7	331.51	8.7	331.97	26.6
341.39	21.0	341.25	13.3	341.45	10.3	341.32	7.2	341.41	20.3
350.72	16.0			350.79	8.5			350.81	15.8
359.86	12.9			360.16	7.2			360.20	12.6
368.90	10.7			369.23	6.2			369.06	10.6
378.15	8.4			378.90	5.0			378.90	8.6
388.51	6.6			388.19	4.1			388.19	7.2

suggested by Dupont *et al.*[24,25] to explain the properties of ILs containing dissolved water. The dual nature of the interactions (nonpolar-dispersive and ionic domains) has also been reported connected to the use of ILs as stationary phases for gas chromatography.[26]

This segregation into domains is not observed for Emim⁺-based ILs,[23] since the non-polar part is too small, and in structural terms these just show charge ordering like "simple molten salts".[27] The formation of the microstructures is likely to be responsible for the increase in viscosity and for the decrease in ion mobility (meaning a decrease in conductivity and in diffusion). Therefore, it is not a strong interaction between the non-polar parts that is giving rise to a more viscous fluid. In ILs with longer side-chains, the non-polar parts are being driven into domains, excluded by the strong electrostatic attraction between the anions and charged parts of the cations.

The presence of water strongly decreases the viscosity of the sample (see Table 5). This phenomenon is particularly dramatic in the case of the more viscous IL, Bmim⁺PF₆⁻ for which the viscosity at 293 K is four times lower in the saturated sample compared to the viscosity in the dried one. For the other ILs investigated the viscosity drops roughly twice.

As illustrated in Fig. 2, in the temperature range studied, the viscosity drastically decreases with increasing temperature. It is again most striking for dried Bmim⁺PF₆⁻, 30 times more viscous at 293 K than at 388 K. At room temperature we can observe great differences in the data measured for the investigated ILs (from 40 to 376 mPa s at 293 K for the dried samples and from 22 to 85 mPa s at the same temperature for

the water-saturated samples) whereas at higher temperature all the ILs tend to have closer viscosities (from 4 to 13 mPa s at 388 K for the dried samples). Thus it is obvious that as the viscosity decreases with temperature the effect of water is much less important, as documented in Table 5.

The most commonly used equation to correlate the variation of viscosity with temperature is the Arrhenius-like law:

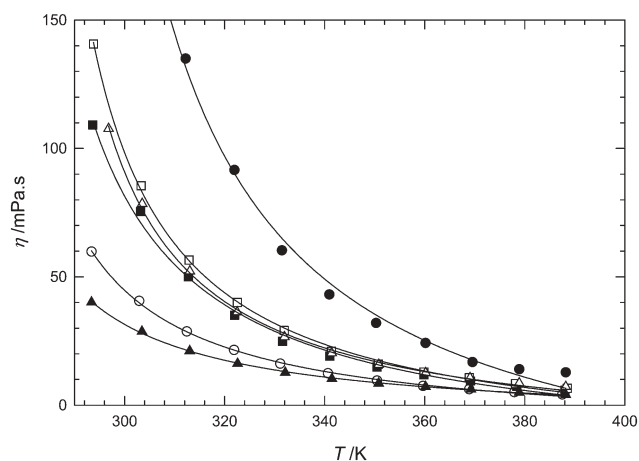$$\eta = \eta_{\infty}\exp(-E_a/RT) \qquad (4)$$

Fig. 2 Experimental viscosities of the dried ILs as a function of temperature: (●), Bmim⁺PF₆⁻; (○), Bmim⁺NTf₂⁻; (■), Bmim⁺BF₄⁻; (□), N₄₁₁₁⁺NTf₂⁻; (▲), Emim⁺NTf₂⁻; (△), Emim⁺EtSO₄⁻. The lines correspond to the fit of the data by eqn (5).

Table 6 Correlation parameters of the Arrhenius equation (η_∞, E_a), and of the VFT equation (k, A and T_0) with the deviations of the fit σ_r for the viscosity of dried and water saturated ILs as a function of temperature determined from measurements between 293 K and 388 K

		Arrhenius eqn (4)			VFT eqn (5)			
		$\eta_\infty/10^{-4}$ mPa s	$-E_a$/kJ mol^{-1}	σ_r	k/K	$A/10^{-3}$ mPa s K$^{-1/2}$	T_0/K	σ_r
Bmim$^+$PF$_6^-$	Dried	2.72	34.1	0.08	1320	2.43	148	0.04
	Saturated	6.24	29.0	0.04	512	27.6	198	0.02
Bmim$^+$NTf$_2^-$	Dried	10.59	26.6	0.02	2240	0.21	62.7	0.01
	Saturated	31.20	22.4	0.03	579	15.1	173	0.01
Bmim$^+$BF$_4^-$	Dried	6.62	29.2	0.04	1970	0.41	89.6	0.02
N$_{4111}^+$NTf$_2^-$	Dried	5.70	30.1	0.06	1340	1.75	135	0.02
	Saturated	3.10	30.0	0.07	290	56.1	227	0.02
Emim$^+$NTf$_2^-$	Dried	43.39	22.2	0.03	1620	1.11	81.8	0.02
	Saturated	54.62	20.3	0.02	591	13.7	165	0.02
Emim$^+$EtSO$_4^-$	Dried	10.81	28.1	0.06	945	5.68	162	0.01

^{a} $\sigma_r = \left(\dfrac{\sum [(\eta_i^{exp} - \eta_i^{cal})/\eta_i^{cal}]^2}{n-v} \right)^{0.5}$ where n is the number of experimental points, v the number of adjustable parameters.

Viscosity at infinite temperature (η_∞) and the activation energy (E_a) are characteristic parameters generally adjusted from experimental data. According to Seddon *et al.*,[10] the Arrhenius law can generally be applied when the cation presents only a limited symmetry. If it is not the case, and especially in the presence of small and symmetrical cations with low molar mass, the Vogel–Fulcher–Tamman (VFT) equation, an empirical extension of eqn (4), is recommended:[9,10,18]

$$\eta = AT^{0.5}\exp(k/T - T_0)) \qquad (5)$$

where A, k and T_0 are adjustable parameters. Table 6 lists the parameters for both equations with the standard relative deviation of the fits (σ_r) which indicates clear improvement of the data fit when using the VFT equation both for dried and saturated samples independently of the ion structure. However, as can be seen both in Table 6 and in Fig. 2, the data fit by the VFT equation is not quite satisfactory for the dried Bmim$^+$PF$_6^-$.

Comparison with the literature data

As stated above the observed trends in the evolution of density and viscosity are generally consistent with information available in the literature. For a more detailed comparison, we have focused on two ILs: Bmim$^+$PF$_6^-$ and Bmim$^+$NTf$_2^-$. The first was selected as it is the most intensively studied IL in the past, and for which multiple data sources are available. The second was examined as an IL frequently considered for various practical applications and popular in theoretical studies. The relative deviations of the densities and viscosities reported by different authors from the fits of our experimental values (eqns (1) and (5)) for the dried samples are presented in Fig. 3 to 6. The deviations are also plotted for our water-saturated samples. All the authors claim to have dried their samples before the measurements; the quantity of water is not, however, always specified. As expected the literature data are generaly closer to our data for the dried samples than to those for the wet ILs. Yet it is apparent that in certain cases the differences between the literature data can be attributed to the presence of water.

In the case of Bmim$^+$PF$_6^-$, both for densities and viscosities, the data presented by Seddon *et al.*[10] on samples containing 76 ppm (w/w) of water, agree reasonably well with our results for the dried sample: they are 0.2 to 0.3% higher for densities and about 10% lower for viscosities. Except for the higher values of Suarez *et al.*[21] and Blanchard *et al.*,[30] all the densities for Bmim$^+$PF$_6^-$ are within ± 0.5% from our data set for the dried samples. Gu and Brennecke[14] have obtained lower densities, which is consistent with the larger amount of water (1500 ppm) they reported for their samples. Furthermore, they estimate the uncertainty of their data to be 0.008 g cm^{-3}, so our results are within this error margin. The densities of Bmim$^+$NTf$_2^-$ that are in better agreement with our results are those presented by Fredlake *et al.*[12] and by Krummen *et al.*[28] (± 0.1% from our data set for the dried sample). The densities reported by Dzyuba and Bartsch[15] for both ILs are lower than our data and the difference is increasing with temperature. The quantity of water in the samples is not specified in their paper. In the case of Bmim$^+$NTf$_2^-$ data of the same authors at 323 K are closer to our values for the water-saturated samples than to
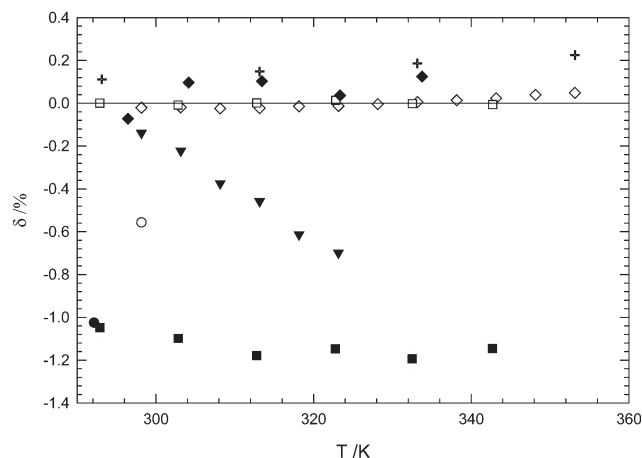

Fig. 3 Relative deviations ($100(\rho_{lit} - \rho_{fit})/\rho_{fit}$) of the literature densities for Bmim$^+$NTf$_2^-$ from our fitted data for the dried sample: (●), Bonhote *et al.*;[16] (○), Huddleston *et al.*;[17] (◇), Krummen *et al.*;[28] (▼), Dzyuba *et al.*;[15] (◆), Fredlake *et al.*;[12] (+), Tokuda *et al.*;[11] (■), this work—water saturated IL; (□), this work—dried IL.
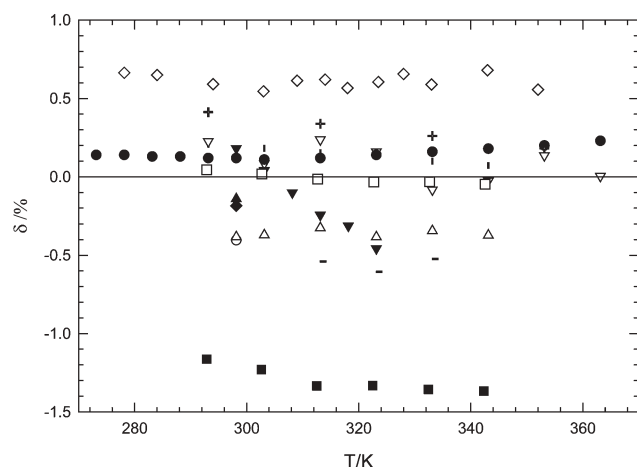
Fig. 4 Relative deviations ($100(\rho_{lit} - \rho_{fit})/\rho_{fit}$) of the literature densities for $Bmim^+PF_6^-$ from our fitted data for the dried sample: ($\diamond$), Suarez et al.;[21] ($\bigcirc$), Huddleston et al.;[17] ($\blacktriangle$), Hyun et al.;[29] ($\triangle$), Gu et al.;[14] (–), Blanchard et al.;[30] (|), Seddon et al.;[31] ($\triangledown$), Seddon et al.;[10] ($\blacktriangledown$), Dzyuba et al.;[15] ($\bullet$), Harris et al.;[32] (+), Tokuda et al.;[11] ($\blacksquare$), this work—water saturated IL; ($\square$), this work—dried IL.
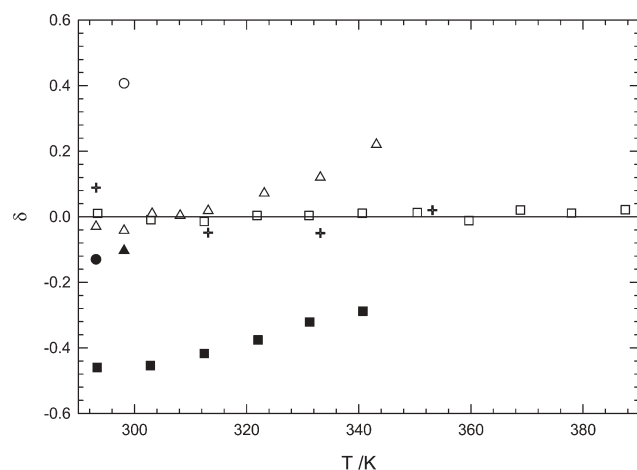
Fig. 5 Relative deviations (($\eta_{lit} - \eta_{fit})/\eta_{fit}$) of the literature viscosities for $Bmim^+NTf_2^-$ from our data fitted with VFT equation for the dried sample: ($\bullet$), Bonhote et al.;[16] ($\bigcirc$), Huddleston et al.;[17] ($\blacktriangle$), Hyun et al.;[29] ($\triangle$), Okoturo et al.;[18] (+), Tokuda et al.;[11] ($\blacksquare$), this work—water saturated IL; ($\square$), this work—dried IL.

those for the dried ones. This could be due to an increase of the water quantity in their samples, kept in contact with atmosphere during measurements.

Concerning the viscosities, for both ILs important differences between individual authors are observed, especially for $Bmim^+PF_6^-$ at low temperatures. Considering the strong dependence of viscosity on temperature, the discrepancies could be also attributed (beside the presence of water) to problems of temperature control and its determination. For example, Okoturo et al.[18] reported a viscosity of 201 mPa s for $Bmim^+ NTf_2^-$ at 293 K compared to 378 mPa s for our dried sample, which corresponds to a difference of 47%. At higher temperatures, these differences are generally reduced to 20% or so. At low temperatures, Okoturo et al.[18] obtains for $Bmim^+PF_6^-$ the data which are between the values for our
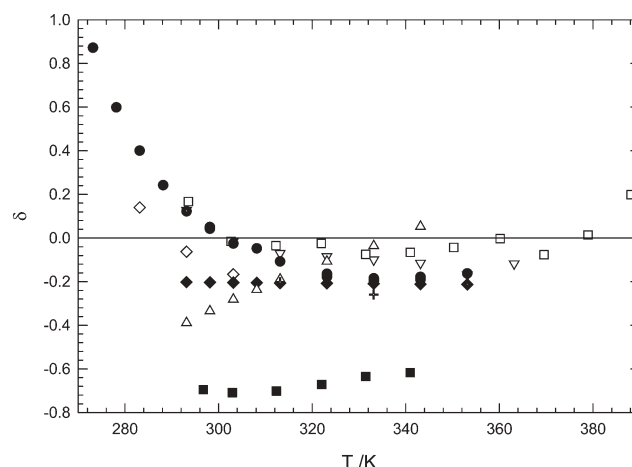

Fig. 6 Relative deviations (($\eta_{lit} - \eta_{fit})/\eta_{fit}$) of the literature viscosities for $Bmim^+PF_6^-$ from our data fitted with VFT equation for the dried sample: ($\triangledown$), Seddon et al.;[10] ($\diamond$), Branco et al.;[33] ($\blacklozenge$), Fadeev et al.;[34] ($\triangle$), Okoturo et al.;[18] ($\bullet$), Harris et al.;[32] (+), Tokuda et al.;[11] ($\blacksquare$), this work—water saturated IL; ($\square$), this work—dried IL.

dried and water-saturated samples, while at higher temperatures their viscosities cross our data and eventually become higher. Finally, the lower densities and higher viscosities reported by Huddleston et al.[17] suggest the presence of a higher quantity of chloride in their samples.

Due to this comparison with a wide variety of data sources for $Bmim^+PF_6^-$ and for $Bmim^+NTf_2^-$ it can be supposed that our results for all of the investigated salts are free of important systematic errors and our uncertainty estimates are realistic. At the same time we have quantified the effect of water on the density and viscosity results.

Conclusion

This paper presents a collection of experimental densities and viscosities for a selection of six hydrophobic and hydrophilic ILs. The aim was to provide practical information on the evolution of these two properties with temperature and with the water presence in the samples, the relationship property–ion structure was also examined qualitatively. In the temperature range investigated, the densities are little affected by the temperature while viscosities decrease dramatically when increasing temperature. While the evolution of the volumetric properties of ILs with the presence of water is almost negligible (1–2%), it strongly decreases the viscosity of the samples. It was also found that some analogies can be drawn in the changes of density, thermal expansivity and viscosity with the structure of cations and anions. Finally, this study highlighted the disparity in the experimental data presented in the literature, that is mainly due to the differences in the sample purities.

Acknowledgements

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