

Influence of chloride, water, and organic solvents on the physical properties of ionic liquids*

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Abstract: We report here the first systematic study of the effect of impurities and additives (e.g., water, chloride, and cosolvents) on the physical properties of room-temperature ionic liquids. Remarkably, it was discovered that the viscosity of mixtures was dependent mainly on the mole fraction of added molecular solvents and only to a lesser extent upon their identity, allowing viscosity changes during the course of a reaction to be entirely predictable. While the addition of such molecular solvents decreases the viscosity and density, chloride impurities, arising from the preparation of the ionic liquids, increase viscosity dramatically. The commonly used methods of preparation were validated with respect to chloride impurity.

INTRODUCTION

The recognition of room-temperature ionic liquids as neoteric [1] green solvents has prompted a fast-growing literature. It has been shown that ionic liquids can be used as substitutes for commonly used, highly volatile and/or toxic solvents, such as those banned by the Montreal Protocol of 1989 [2]. Reactions in ionic liquids and their physical properties have been reviewed recently [3–6]. As part of our ongoing program to characterize ionic liquids, we determined the level of impurities present in ionic liquids and show how these affect their physical properties. We also investigated the effects of organic cosolvents on the physical properties. This study provides both a useful set of data for chemical engineering purposes and an insight into the interionic interactions in these novel solvents.

WHAT ARE IONIC LIQUIDS?

Room-temperature ionic liquids are salts with melting points of below *ca.* 100 °C, and sometimes as low as –96 °C, so that they can be used as solvents under conventional organic liquid-phase reaction conditions. They possess a wide liquidus range, in some cases in excess of 400 °C. Many organic salts have low melting points, but the most investigated consist of the organic 1-alkyl-3-methylimidazolium (abbreviated [C_{*n*}mim]⁺, where *n* = number of carbon atoms in a linear alkyl chain), *N*-alkylpyridinium (accordingly abbreviated [C_{*n*}py]⁺), tetraalkylammonium or tetraalkylphosphonium cations. These cations are combined with either organic or inorganic anions, such as hexafluorophosphate, tetrafluoroborate, trifluoromethylsulfonate, trifluoroethanoate, ethanoate, nitrate, halide, etc., as shown in Fig. 1. Although the haloaluminate-based ionic liquids have been studied since the 1950s [7,8], these are not part of our studies since they are not water-stable and need to be handled under an inert atmosphere.

This list of building blocks appears somewhat complicated at first sight, but we can compare it with a box of Lego[®] bricks of different colors and sizes, from which we choose an alkyl chain length,

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a cation and an anion to construct a structure with particular properties. It is clear that with only three different alkyl types, three anions and three cations, we can make 27 ionic liquids, with different properties! In order to limit the number of ionic liquids to be studied, we confined ourselves for this study to the $[C_n\text{mim}]^+$ -based ionic liquids. The most commonly used methods of preparation are now discussed.

PREPARATION OF IONIC LIQUIDS

The imidazolium-based ionic liquids used in this study are derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide, in general the chloride. This precursor is prepared by alkylation of 1-methylimidazole, as depicted in Fig. 2. The alkylation is carried out in an autoclave, at

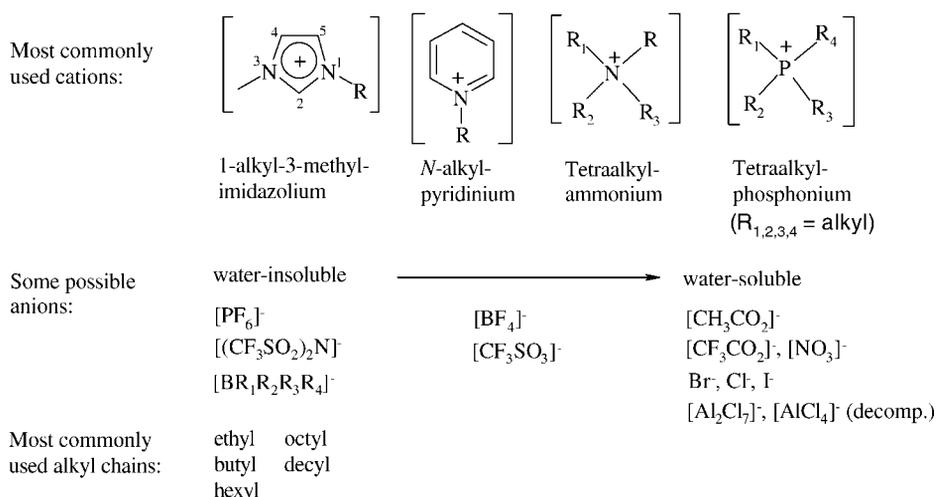


Fig. 1 The building blocks of ionic liquids.

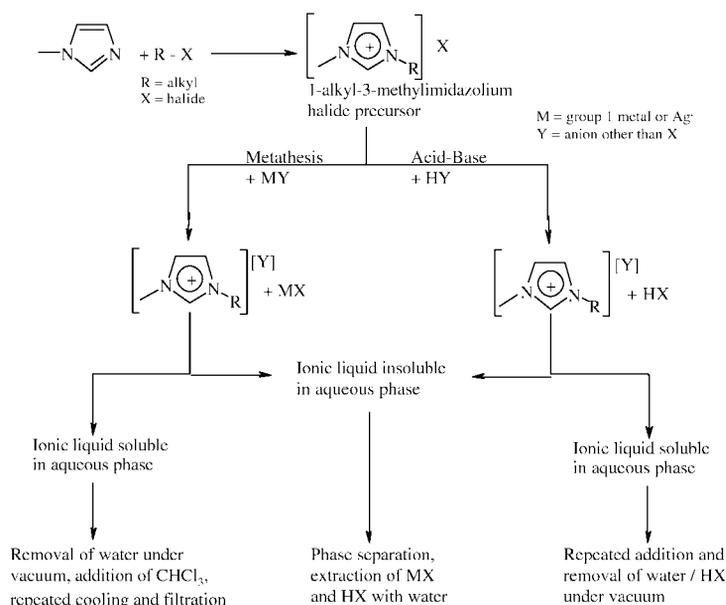


Fig. 2 Preparation and work-up procedures used in this study.

6 atm of dinitrogen and 90 °C without addition of solvent, if the chloroalkane is gaseous at room temperature (e.g., chloroethane). Higher homologues can be prepared under atmospheric pressure.

This precursor is then either used in a metathetic reaction, where the 1-alkyl-3-methylimidazolium halide is reacted with a Group 1 metal salt, in particular a sodium salt, or a silver salt of the desired anion, or in an acid-base neutralization reaction. This reaction is stoichiometric and, therefore, equimolar amounts of waste MX or HX are produced. This could be circumvented by the direct alkylation of 1-methylimidazole with, for example, alkyl trifluoromethanesulfonate or alkyl bis(trifluoromethanesulfonyl) amide [9]. We carry out the metathetic and acid-base method in water at room temperature, although some authors use organic solvents [3]. Depending on the anion chosen, the resulting ionic liquid forms either a biphasic system with water, or a homogeneous solution. If the resulting ionic liquid forms a biphasic system with water (i.e., if the anion is $[\text{PF}_6]^-$ or $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, see Fig. 1), an aqueous extraction follows to remove the halide (i.e., the Group 1 metal halide or the acid), resulting in halide-free ionic liquids. For water-miscible ionic liquids, the work-up of the metathetic reaction involves the removal of water under reduced pressure, addition of trichloromethane, and repeated cooling to 5 °C to precipitate the Group 1 metal halide [10], followed by several filtration steps. The work-up of the water-miscible ionic liquids prepared by the acid-base method includes repetitive addition of water and removal of water/acid under reduced pressure. In both cases, this is very cumbersome and the effectiveness of the removal of halide is only mediocre (*vide infra*). Halide-free ionic liquids can be obtained in the metathetic reaction, if the silver salt is used instead of the Group 1 metal salt, and residual silver ions can be removed electrochemically [11]. However, this involves yet another clean-up stage, and silver salts are produced as by-products. A procedure involving lead(II) salts [12] has recently been shown not to be viable [13].

PURITY OF IONIC LIQUIDS

Halides are known to coordinate to the transition-metal centers of catalysts, and thus influence (usually negatively) the rate of reaction. Thus, in ionic liquids, chloride impurities have been reported to have a detrimental effect on transition-metal catalyzed reactions, such as hydrogenations [14,15], whereas in Heck-type reactions, bromide has a stabilising effect on palladium [16]. Water present in ionic liquids may also co-ordinate to the transition metal catalyst, thus affecting the rate of reaction. The purity of ionic liquids used by chemists appears to be a somewhat neglected issue, especially with regards to trace level contamination. This can be illustrated by melting points reported for the same ionic liquid, e.g., $[\text{C}_2\text{mim}][\text{BF}_4]$: 15 °C [17], 5.8 °C [18], 12.0 to 12.5 °C [19], 11 °C [20] and 14.6 °C [21]. It is clear that catalytic results reported will not be comparable, unless the purity of the medium is reported! Additionally, the difference of melting point shows that the physical properties depend strongly on the purity, and we will demonstrate this point with examples of viscosity and density later. Another point, which will be important to the process engineers, is the corrosive nature of chloride ions in ionic liquids.

In order to assess the relative merits of the various syntheses of ionic liquids, we were interested in identifying whether chloride impurities present in ionic liquids arise from unreacted starting material, dissolved NaCl or AgCl (metathesis), or HCl (acid-base reaction), and which methods of preparation yield the cleanest ionic liquids. Additionally, since the preparation is carried out in water, it appeared to be important to further investigate miscibility with water, and the effect this has on the physical properties.

DETERMINATION OF RESIDUAL SODIUM AND CHLORIDE IN IONIC LIQUIDS

Chloride measurements were conducted using a chloride-selective electrode (*ex*: Cole-Parmer). Calibration curves were obtained from aqueous solutions (1–1000 ppm) of the corresponding 1-alkyl-

3-methylimidazolium chloride, that is, if the chloride contents of ionic liquids containing the $[\text{C}_4\text{mim}]^+$ cation were to be measured, the calibration curve was obtained from $[\text{C}_4\text{mim}]\text{Cl}$. This was found to be necessary because the intercept and the slope of the calibration curves vary with the cation. Ionic liquids exhibit varying polarities depending on the cation present [22], and also varying degrees of hydrogen bonding [23], both effects that may contribute toward the cation dependency of the calibration curves. Measurements were performed at least in duplicate to determine reproducibility, and agreed within 3%.

In order to validate the results obtained with the chloride-selective electrode, the Vollhard procedure [24] was chosen as a wet-chemical method to measure chloride. The principle of this method is to precipitate all chloride ions present as silver(I) chloride by adding a known excess of silver(I) nitrate. The precipitate is collected by filtration, and the excess of silver present in the filtrate is back-titrated with a solution of potassium thiocyanate. Excess thiocyanate, in turn, forms a red-brown thiocyanato-iron(III) complex with the indicator iron(III) nitrate. The endpoint of the titration is determined visually. The results obtained with the Vollhard method were compared to those of the chloride-selective electrode. The student's *t*-test revealed that the difference between both sets of results were statistically insignificant, and can be ascribed to random, rather than systematic errors in the methodology.

In conclusion, it can be stated that both methods can be used to determine residual chloride. The advantage of Vollhard's method is that any halide is detected, and a qualitative determination can quickly be made by adding AgNO_3 to an aqueous solution of ionic liquid. The chloride-selective electrode, on the other hand, does not detect other halides, and is relatively expensive. However, the use of toxic thiocyanate is avoided.

Sodium measurements were performed with a sodium-selective electrode (*ex*: Cole-Parmer) in aqueous solution, with 1–1000 ppm NaCl solutions as calibration standards.

After establishing the methodology, measurements were conducted to determine the nature and amount of the chloride impurity of ionic liquids prepared by different methods. Some representative results are compiled in Table 1.

All the ionic liquids listed in Table 1 are fully water-miscible at room temperature, which makes it difficult to free them from chloride impurity. Clearly, all ionic liquids made by metathesis from the corresponding sodium salt have high chloride contents (see entries 2, 4, and 6), whereas those made from the silver salts yield ionic liquids with significantly lower levels of contamination (see entries 1 and 3). The same can be said for the sample of $[\text{C}_4\text{mim}][\text{NO}_3]$, which was prepared by the acid-base method (entry 5). It was now of interest to determine if the high chloride content of the sodium-derived ionic liquids was due to dissolved NaCl or unreacted starting material, and we therefore conducted measurements using a sodium-selective electrode. As can be seen from Table 1, the sodium content is very low in all instances (entries 2, 4, and 6), and thus it was concluded that the high chloride content is due to unreacted starting material, and that metathesis does not proceed to completion. Indeed, a study was conducted in which it was attempted to dissolve NaCl in $[\text{C}_4\text{mim}][\text{BF}_4]$, and it was found that its solubility is very low (<0.28% w/w Cl^- , 0.08 mol kg^{-1}) in dry (<200 ppm of water) $[\text{C}_4\text{mim}][\text{BF}_4]$ at room temperature.

Table 1 Representative results for Na^+ and Cl^- contents in water-miscible ionic liquids.

| Entry | Ionic liquid | Preparation methods | $[\text{Na}^+] / \text{mol kg}^{-1}$ | $[\text{Cl}^-] / \text{mol kg}^{-1}$ |
|-------|---------------------------------------|---|--------------------------------------|--------------------------------------|
| 1 | $[\text{C}_2\text{mim}][\text{BF}_4]$ | $\text{Ag}[\text{BF}_4]$ | - | 0.01 |
| 2 | $[\text{C}_2\text{mim}][\text{BF}_4]$ | $\text{Na}[\text{BF}_4]$ | 0.06 | 1.75 |
| 3 | $[\text{C}_4\text{mim}][\text{NO}_3]$ | $\text{Ag}[\text{NO}_3]$ | - | 0.02 |
| 4 | $[\text{C}_4\text{mim}][\text{NO}_3]$ | $\text{Na}[\text{NO}_3]$ | 0.06 | 1.00 |
| 5 | $[\text{C}_4\text{mim}][\text{NO}_3]$ | acid/base | - | 0.01 |
| 6 | $[\text{C}_4\text{mim}][\text{BF}_4]$ | $\text{Na}[\text{BF}_4]$ | 0.05 | 0.43 |
| 7 | $[\text{C}_4\text{mim}][\text{BF}_4]$ | $\text{Na}[\text{BF}_4]$ (chilled water-extraction) | 0.03 | 0.01 |

On one occasion, an attempt to synthesize $[\text{C}_4\text{mim}][\text{NO}_3]$ (a liquid at room temperature) from NaNO_3 , yielded a liquid–solid mixture at room temperature. Chloride measurements of each phase revealed chloride contents of 1.73 mol kg^{-1} for the liquid and 3.66 mol kg^{-1} for the crystals. A single crystal was analyzed by single crystal X-ray crystallography. The X-ray results showed that the only species present in this crystal was $[\text{C}_4\text{mim}]\text{Cl}$. This confirms that the chloride contamination is due to unreacted $[\text{C}_4\text{mim}]\text{Cl}$. The crystallization of $[\text{C}_4\text{mim}]\text{Cl}$ from $[\text{C}_4\text{mim}][\text{NO}_3]$ is an interesting finding in itself, showing a limited solubility of the chloride salt in another ionic liquid.

It is worth noting that the metathetic reaction with the silver salt, on the other hand, proceeded to completion, due to the low solubility product of AgCl ($1.56 \times 10^{-10} \text{ mol l}^{-1}$ at 25°C) in aqueous solution [25].

For water-miscible ionic liquids, the removal of the unreacted chloride salt is not effectively feasible at room temperature. However, in the case of $[\text{C}_4\text{mim}][\text{BF}_4]$, which is soluble in water at room temperature, but forms a biphasic system with water at 5°C , extraction with chilled water (entry 7, Table 1) achieves very low chloride contents. However, the yields are low due to loss to the aqueous phase.

In summary, metathesis with a silver salt yields the cleanest ionic liquids, but produces a molar equivalent of silver chloride, and is comparatively expensive. The acid-base method also leads to chloride-free media but residual acidity can be a problem. For instance, in the case of the nitrates, it was found that they contain dissolved HNO_3 . The much-used $[\text{C}_4\text{mim}][\text{BF}_4]$ is generally made with NaBF_4 , and our study shows that great care needs to be taken to ensure purity. Additionally, the reaction conditions of the metathesis need to be validated to ensure quantitative conversion.

EFFECT OF CHLORIDE IMPURITY ON VISCOSITY, DENSITY, AND ^1H NMR CHEMICAL SHIFT

We were interested in the effect chloride salts would have on physical properties such as viscosity and density. Viscosity was measured by a LVDV-II Brookfield Cone and Plate Viscometer (1% accuracy, 0.2% repeatability). The sample cup of the viscometer was fitted with luer and purge fittings, so that a positive current of dry dinitrogen was maintained at all times during the measurements, thus avoiding absorption of atmospheric moisture. The density was measured using calibrated 10 cm^3 density bottles, with an experimental error of $\pm 0.0008 \text{ g cm}^{-3}$. The viscosity of chloride-contaminated batches of $[\text{C}_2\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{NO}_3]$, and $[\text{C}_8\text{mim}][\text{NO}_3]$ was compared to the viscosity of the batches with low chloride content in Table 2.

It can be observed in Table 2 that the presence of even low concentrations of chloride in the ionic liquids substantially increases the viscosity. In order to assess the magnitude of the increase in viscosity with chloride content, known quantities of $[\text{C}_n\text{mim}]\text{Cl}$ were deliberately added to $[\text{C}_{4-6}\text{mim}][\text{BF}_4]$ and to $[\text{C}_{4-6}\text{mim}][\text{PF}_6]$. In all cases, the viscosity increased dramatically with the concentration of chlo-

Table 2 Comparison of the viscosity of chloride-contaminated and low chloride content batches of ionic liquids at 20°C .

| Ionic liquid | $[\text{Cl}^-] / \text{mol kg}^{-1}$ | $\eta / \text{mPa s}$ |
|---|--------------------------------------|-----------------------|
| $[\text{C}_2\text{mim}][\text{BF}_4]$ | 0.01 | 66.5 |
| | 1.8 | 92.4 |
| $[\text{C}_4\text{mim}][\text{BF}_4]$ | 0.01 | 154 |
| | 0.5 | 201 |
| $[\text{C}_4\text{mim}][\text{NO}_3]^a$ | 0.02 | 67 |
| | 1.7 | 222.7 |
| $[\text{C}_8\text{mim}][\text{NO}_3]$ | 0.01 | 1238 |
| | 2.2 | 8465 |

^a at 45°C .

ride. This is shown for $[\text{C}_4\text{mim}][\text{BF}_4]$ with added $[\text{C}_4\text{mim}]\text{Cl}$ in Fig. 3a. The addition of $[\text{C}_4\text{mim}]\text{Cl}$ to $[\text{C}_4\text{mim}][\text{BF}_4]$ also produced a nonlinear decrease of the density (see Fig. 3b). At chloride concentrations higher than 2.8 mol kg^{-1} , $[\text{C}_4\text{mim}]\text{Cl}$ is not soluble in $[\text{C}_4\text{mim}][\text{BF}_4]$ at room temperature.

The ^1H NMR spectra of $[\text{C}_n\text{mim}][\text{BF}_4]/\text{Cl}$ and $[\text{C}_n\text{mim}][\text{PF}_6]/\text{Cl}$ liquid mixtures dissolved in propan-2-one revealed that the presence of chloride causes a downfield shift for the signal corresponding to the H(2) proton of the imidazolium ring (for numbering, compare Fig. 1). A downfield shift was also observed, to a lesser extent, in the signals corresponding to the H(4) and H(5) protons (see Fig. 4).

It is well known that hydrogen bonding causes the proton chemical shift to move to lower field [23]. In previous ionic liquids studies, it has also been noticed that the shifts of the imidazolium ring protons depend on the concentration of the solvent used and on the anion [9,23]. This effect has been reported to be stronger for the more acidic H(2) proton, and weaker for the H(4) and H(5) protons [9,23]. Therefore, the downfield shifts with increasing concentration of chloride in $[\text{C}_4\text{mim}][\text{BF}_4]$ indicate that the increase of viscosity is related to an increase in the cohesive forces *via* hydrogen bonding between the chloride and the protons of the imidazolium ring.

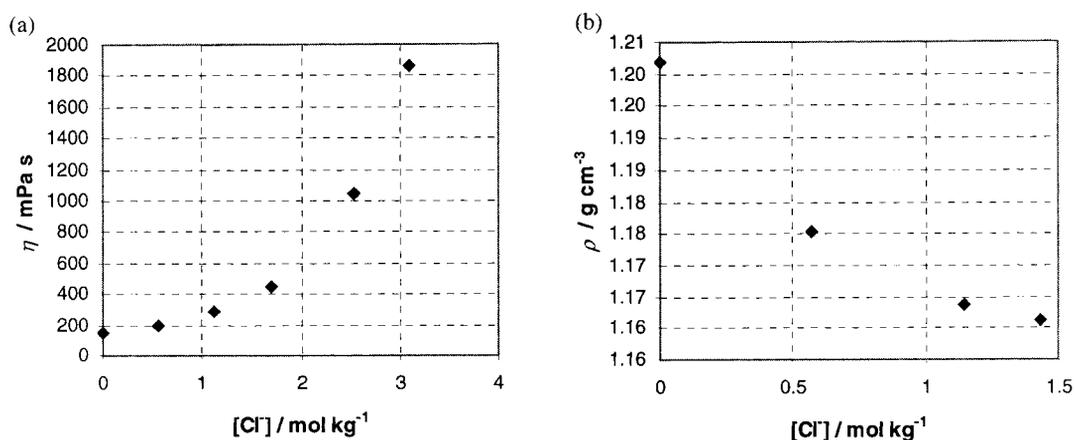


Fig. 3 Viscosity (a) at 20°C and density (b) at 30°C of $[\text{C}_4\text{mim}][\text{BF}_4]$ vs. molal concentration of chloride, mol kg^{-1} , added as $[\text{C}_4\text{mim}]\text{Cl}$.

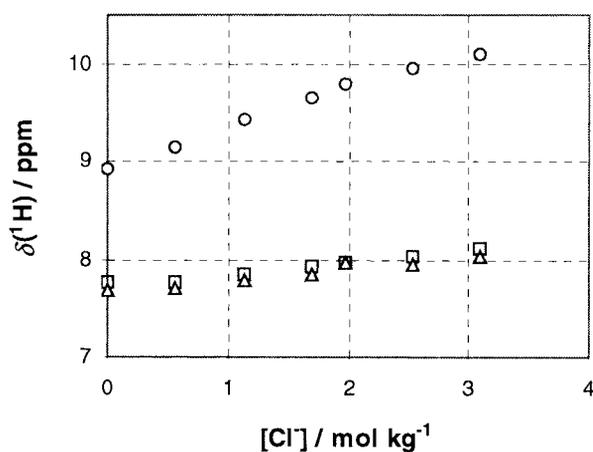


Fig. 4 ^1H -NMR chemical shift of $[\text{C}_4\text{mim}][\text{BF}_4]$ in d_6 -propan-2-one (0.25 g cm^{-3}) vs. molal concentration of chloride added as $[\text{C}_4\text{mim}]\text{Cl}$. (○) correspond to the H(2) position, (□) to the H(4) position and (△) to the H(5) position.

MISCIBILITY WITH WATER

Water contents for the following experiments were measured by coulometric Karl–Fischer titration [24]. Duplicate measurements were performed to determine reproducibility, and agreed within 100 ppm.

As indicated in Fig. 1, the choice of anion is one of the factors determining the solubility of the ionic liquid with water. At room temperature, all $[C_n\text{mim}][\text{PF}_6]$ and $[C_n\text{mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ionic liquids are insoluble in water, and all halide-, ethanoate-, nitrate-, and trifluoroacetate-based ionic liquids are fully water-soluble. However, ionic liquids based on $[\text{BF}_4]^-$ and $[\text{CF}_3\text{SO}_3]^-$ are positioned somewhere in between. Depending on the alkyl chain length on the cation, they are either fully miscible with water (e.g., $[\text{C}_2\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$) or form biphasic systems ($[\text{C}_n\text{mim}][\text{BF}_4]$, $n > 4$). Thus, the anion has a primary effect on water miscibility and the cation a secondary effect.

1-Alkyl-3-methylimidazolium hexafluorophosphate ionic liquids form biphasic systems with water, and are therefore commonly referred to as “hydrophobic” by ionic liquid researchers. This is in fact misleading: Fig. 5 shows the water-saturation of the so-called hydrophobic ionic liquids $[\text{C}_{4-8}\text{mim}][\text{PF}_6]$ and $[\text{C}_{6-10}\text{mim}][\text{BF}_4]$, which is a function of the alkyl chain length and the anion. As a rule, the $[\text{PF}_6]^-$ -based ionic liquids dissolve less water than the $[\text{BF}_4]^-$ ionic liquids, and the solubility of water decreases with increasing alkyl chain length.

Additionally, the so-called hydrophobic ionic liquids are in fact hygroscopic. Figure 6 shows the extent of the hygroscopicity of $[\text{C}_8\text{mim}]\text{Cl}$, $[\text{C}_8\text{mim}][\text{NO}_3]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}][\text{PF}_6]$, which was revealed in an experiment in which the absorption of water from atmospheric air at ambient temperature was measured as a function of time. Although the fully water-soluble chloride and nitrate ionic liquids absorb much more water than the corresponding hexafluorophosphate, an uptake of 1% w/w (0.16 mole fraction of water) over 3 h is significant. This should be kept in mind, especially when the ionic liquid is used as solvent in reactions with moisture-sensitive compounds, and efficient drying and anhydrous handling has to be ensured (i.e., under reduced pressure at 70 °C for 8 h). It should be also stressed that the presence of water in $[\text{PF}_6]^-$ ionic liquids has been reported to lead to decomposition reactions producing HF [26].

THE EFFECT OF WATER AND OTHER COSOLVENTS ON THE VISCOSITY AND DENSITY

In general, ionic liquids are miscible with liquids of medium- to high-dielectric constant and immiscible with liquids with low-dielectric constant [9,27]. For example, $[\text{C}_4\text{mim}][\text{BF}_4]$ is completely miscible

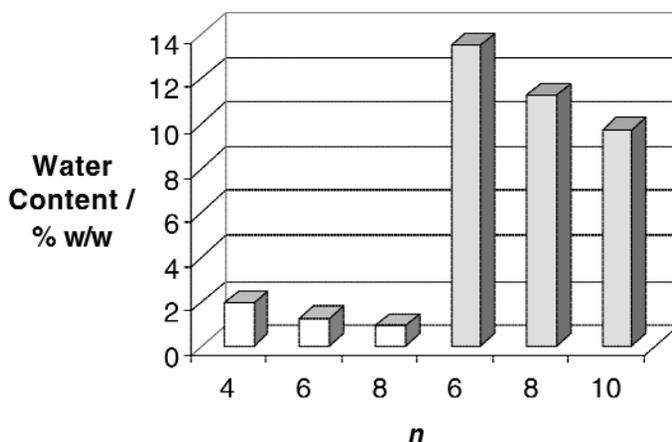


Fig. 5 Water content on saturation at ambient temperature (ca. 22 °C) for $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 4$ to $n = 8$) (white) and for $[\text{C}_n\text{mim}][\text{BF}_4]$ ($n = 6$ to $n = 10$) (gray).

with ethanenitrile ($\epsilon = 35.94$), 2-propenenitrile ($\epsilon = 33$), methanol ($\epsilon = 32.66$), dichloromethane ($\epsilon = 8.93$), or 1,2-dimethoxyethane ($\epsilon = 7.2$), whereas toluene ($\epsilon = 2.38$) is only miscible to up to 50 mol % and 1,4-dimethylbenzene ($\epsilon = 2.27$) up to 25 mol %. The effect of water and other solvents (ethanenitrile, trimethylethanenitrile, 2-propenenitrile, 1-methylimidazole, toluene, 1,4-dimethylbenzene, and 1,2-dimethoxyethane) on the viscosity of $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ has been investigated. When the viscosity of the ionic liquid–cosolvent mixtures is plotted against the molar fraction of cosolvent (see Fig. 7), all the above-mentioned solvents appear to have a surprisingly similar effect on the viscosity of the ionic liquid. In fact, a single exponential equation can be fitted to this data, which can be used for estimation of viscosity at 20 °C of such mixtures, with correlation coefficients >0.97 . In other words, eq. 1

$$\eta = \eta_s \exp(-x_{cs}/a) \quad (1)$$

can be used to predict the viscosity of a reaction mixture as a function of the concentration of the dissolved reactants and/or products, independent of their polarity! In the equation, η_s is the viscosity of the pure ionic liquid at 20 °C, x_{cs} is the mole fraction of the cosolvent and a is a constant with values 0.23 for $[\text{C}_4\text{mim}][\text{BF}_4]$ ($r^2 = 0.98$) and 0.19 for $[\text{C}_4\text{mim}][\text{PF}_6]$ ($r^2 = 0.97$).

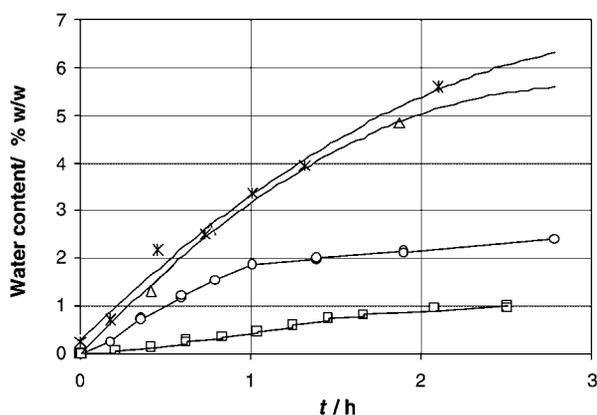


Fig. 6 Absorption of water from atmospheric air at ambient temperature and moisture, with constant stirring as a function of time of exposure. (Δ) corresponds to $[\text{C}_8\text{mim}][\text{NO}_3]$, ($*$) to $[\text{C}_8\text{mim}]\text{Cl}$, (\circ) to $[\text{C}_4\text{mim}][\text{BF}_4]$ and (\square) to $[\text{C}_4\text{mim}][\text{PF}_6]$.

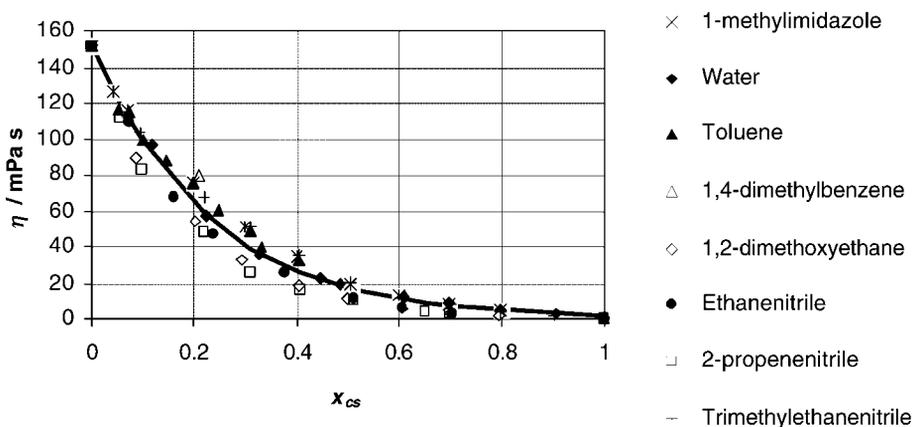


Fig. 7 Viscosity at 20 °C of cosolvent- $[\text{C}_4\text{mim}][\text{BF}_4]$ mixtures vs. mole fraction of cosolvent; the solid line represents the theoretical fit of these data to eq. 1, $r^2 = 0.98$.

However, when the concentration is expressed in % w/w, different trends become obvious. Selected results are shown in Fig. 8. The effect of 1,4-dimethylbenzene and 2-propenenitrile on the viscosity of $[\text{C}_4\text{mim}][\text{BF}_4]$ have been omitted from Fig. 8 for clarity, but as can be seen for $[\text{C}_4\text{mim}][\text{PF}_6]$ in Fig. 9, the effects follow the same trend as toluene and ethanenitrile, respectively.

Figures 8 and 9 show that the decrease of the viscosity of ionic liquids by the addition of cosolvents follows a different pattern depending on the nature of the cosolvent, possibly due to differences in polarities which lead to different interactions with the ions in the ionic liquids. Poole *et al.* [27] found that, upon addition of solvents with low dielectric constant to alkylammonium nitrate and thiocyanide ionic liquids, the logarithm of the viscosity decreased linearly with increasing volume percent of the organic solvent. However, addition of solvents with higher dielectric constant lead to a decrease in viscosity, which is best described by a third polynomial equation [27]. Perry *et al.* [28] also reported that the decrease in viscosity (and increase in conductivity) of basic $[\text{C}_2\text{mim}]\text{Cl}-\text{AlCl}_3$ by the addition of ethanenitrile, dichloromethane and benzene was greatest for the solvent with highest dielectric constant

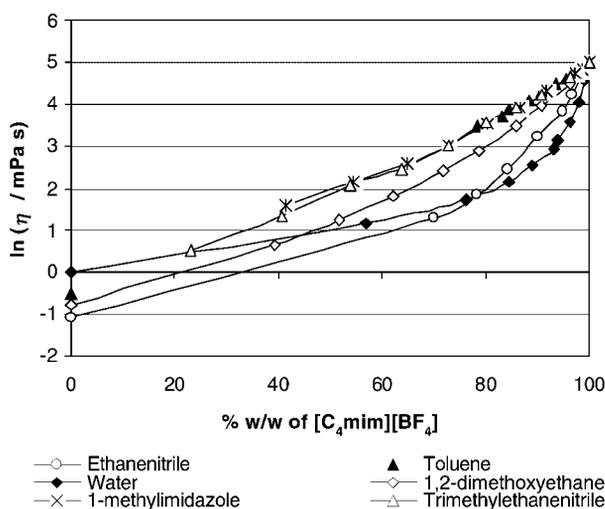


Fig. 8 Viscosity at 20 °C of cosolvents- $[\text{C}_4\text{mim}][\text{BF}_4]$ mixtures vs. % w/w of $[\text{C}_4\text{mim}][\text{BF}_4]$.

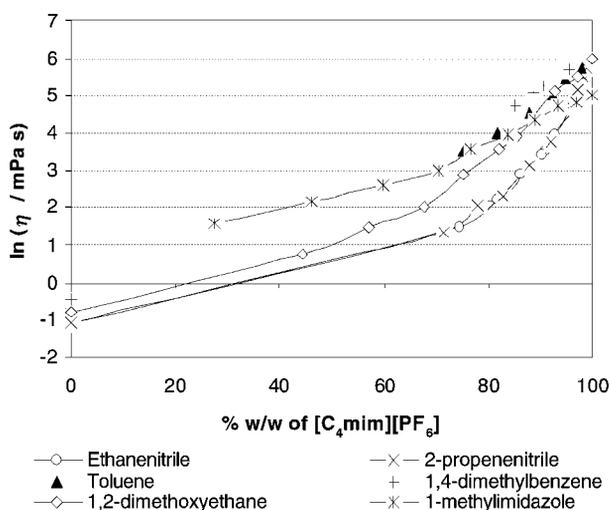


Fig. 9 Viscosity at 20 °C of cosolvents- $[\text{C}_4\text{mim}][\text{PF}_6]$ mixtures vs. % w/w of $[\text{C}_4\text{mim}][\text{PF}_6]$.

(i.e., ethanenitrile), while the least effect corresponded to the cosolvent with lower dielectric constant (i.e., benzene). Similarly, in this study, the magnitude of the decrease of viscosity of $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ is greatest for water, ethanenitrile, and 2-propenenitrile, and lowest for 1,4-dimethylbenzene, toluene, and 1-methylimidazole.

The effect of water on the viscosity of $[\text{C}_4\text{mim}][\text{BF}_4]$ showed a distinct trend from the rest of cosolvents. Thus, the interactions of water and $[\text{C}_4\text{mim}][\text{BF}_4]$ were further investigated by density measurements.

In Fig. 10a, the linear variation in density with weight composition is shown. However, when the mole fraction ratio is considered (Fig. 10b), a nonlinear relationship is clearly established.

The plots suggest that these mixtures can be divided into two different regions: the water-rich ($x_s < 0.5$) and salt-rich regions ($x_s > 0.5$). For example, the density does not vary a great deal in the salt-rich region on increasing the water concentration, up to 1 mole equivalent ($x_s = 0.5$) (see Fig. 10b). However, when $x_s < 0.5$, and thus water is in excess of the salt, the density decreases rapidly towards that of pure water.

Abraham *et al.* [29] also identified these two distinct regions in the viscosity and electrical conductance of mixtures of the eutectic $(\text{Ag/Tl})\text{NO}_3$ (and other similar low-melting nitrate salts) and water. These authors stated that from the pure ionic liquid ($x_s = 1$) to $x_s = 0.4 \pm 0.1$, water is in a "special state,

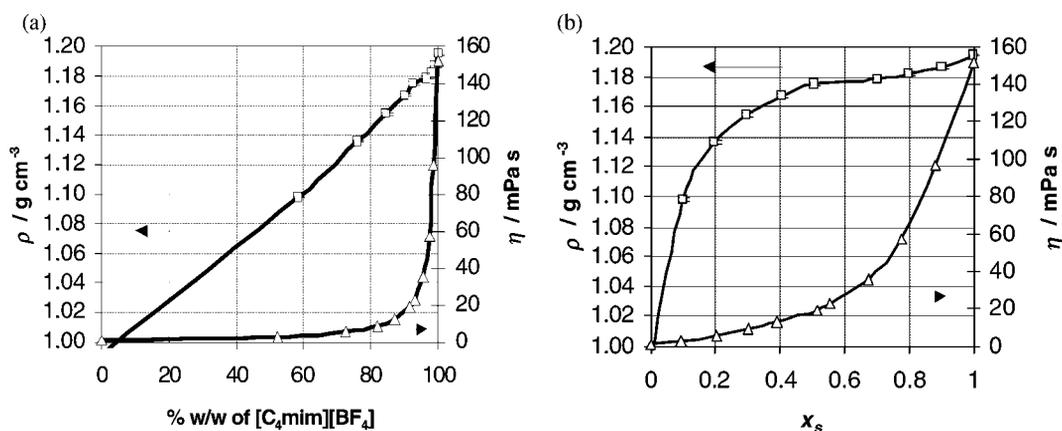


Fig. 10 Density (squares) at 40 °C and viscosity (triangles) at 20 °C of water- $[\text{C}_4\text{mim}][\text{BF}_4]$ mixtures vs. % w/w of $[\text{C}_4\text{mim}][\text{BF}_4]$ (a) and molar fraction of $[\text{C}_4\text{mim}][\text{BF}_4]$ (b).

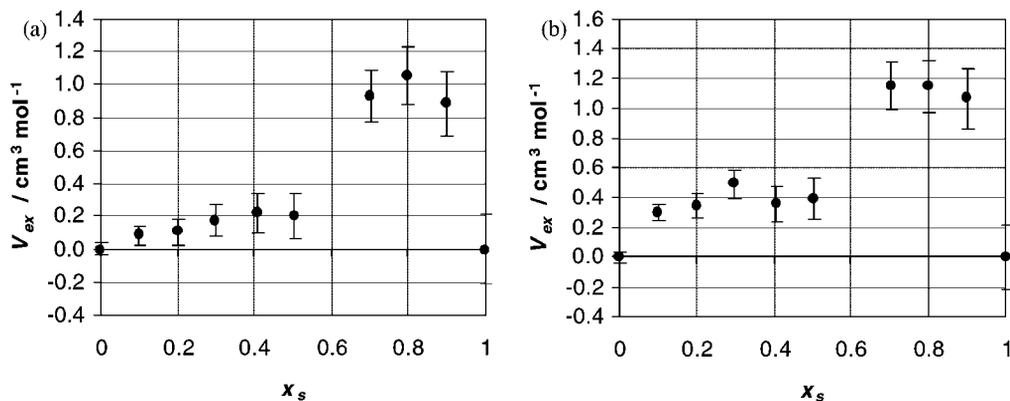


Fig. 11 Excess molar volume of water- $[\text{C}_4\text{mim}][\text{BF}_4]$ mixtures at 40 °C (a) and at 80 °C (b) vs. molar fraction of $[\text{C}_4\text{mim}][\text{BF}_4]$.

linked to the salt, with perturbation of the hydrogen bonds in water or even breaking of some of these, by the strong electrostatic field of ions" [29]. At lower x_s , an appreciable fraction of the water may be regarded as free water, in the sense that is not linked to the salt, so that the structure of the mixtures tends progressively to that of pure water [29].

The molar volume of the mixtures can be expressed as $V = V_{id} + V_{ex}$, where V_{ex} is the excess molar volume, and V_{id} is the ideal molar volume of the mixtures defined as $V_{id} = V_s x_s + V_w x_w$. Thus, V_{ex} represents the deviation from ideal behavior of the mixtures, and it provides an indication of the interactions between both liquids. The excess molar volume of the $[C_4mim][BF_4]$ -water mixtures is plotted against molar fraction of the salt in Fig. 11.

The plots of the excess molar volume in Fig. 11 also reveal a structural change on going from the salt-rich region ($x_s > 0.5$) to the water-rich region ($x_s < 0.5$). The same pattern was observed at different temperatures on the temperature range 30–90 °C, although increasing temperatures produced higher volumetric expansion from ideal behavior (compare (a) and (b) in Fig. 11). Another finding supporting a structural change at the equimolar concentration was revealed in our study of the hygroscopic nature of $[C_4mim][BF_4]$. The ionic liquid absorbs water from the atmosphere at a fast rate until it reaches a plateau after 48 h, corresponding to approximately 6–8 % w/w of water ($x_s = 0.5$ –0.6).

The results of our study suggest that water is accommodated in the ionic liquid structure in the salt-rich region ($x_s = 1$ to $x_s < 0.5$), possibly by forming hydrogen bonds with both the anion and the cation. The dramatic decrease of the viscosity on going from the pure ionic liquid ($x_s = 1$) to $x_s = 0.5$ (see Fig. 10) indicates that the presence of the water molecules reduces the electrostatic attractions between the ions. Thus, the overall cohesive energy of the system is lowered, and hence its viscosity is lowered too. The reduced cohesive energy is likely to be the cause of the volumetric expansion of the system from the pure ionic liquid to $x_s = 0.6$. If water is present in equimolar amounts ($x_s = 0.5$), this order become unstable, and the ionic liquid rearranges into a different internal order, in which more water can be accommodated. Further addition of water ($x_s < 0.5$) may be the starting point of completely solvated ions and the appearance of the water molecules not hydrogen-bonded to the salt (the so-called "free water" by Abraham *et al.* [29]).

CONCLUSION

In conclusion, we have shown that it is of the utmost importance to assess the purity of ionic liquids. The Vollhard method or an ion-selective electrode can be used to measure chloride, and the later method can be applied for the measurement of sodium. Water was found to be present in ionic liquids either due to ineffective drying after preparation or due to absorption from the atmospheric air. This can be explained by their hygroscopicity, even of the hydrophobic ionic liquids. Indeed, $[C_4mim][PF_6]$ can absorb up to 0.16 mole fraction of water from atmospheric air. Both water and chloride impurities alter physical properties considerably. The presence of chloride contamination, for example, increases the viscosity of the ionic liquids, whereas the presence of water, or other cosolvents, reduces the viscosity. Thus, careful consideration must be given to the selected synthetic routes to ionic liquids, especially when physical parameters are to be determined. Purity measurements should always accompany reported physical data.

The effect of the addition of cosolvents has been studied and fitted to equations that can be used predictively for engineering design. In general, the addition of cosolvents notably reduces the viscosity, with the effect being stronger the higher the dielectric constant of the cosolvent. Nevertheless, the viscosity of a reaction mixture with known concentration of ionic liquid and reactants/products can be predicted using eq. 1, regardless of the polarity of the cosolvent. Interesting water-ionic liquid interactions have been identified and discussed. The structural change at the equimolar concentration of water and ionic liquid indicates the possible formation of a hydrogen-bonded complex with water.

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LIST OF ABBREVIATIONS

| | |
|-------------|--|
| V | molar volume / $\text{cm}^3 \text{mol}^{-1}$ |
| V_s | molar volume of pure salt / $\text{cm}^3 \text{mol}^{-1}$ |
| V_w | molar volume of pure water / $\text{cm}^3 \text{mol}^{-1}$ |
| V_{id} | ideal molar volume of mixture / $\text{cm}^3 \text{mol}^{-1}$ |
| V_{ex} | excess molar volume of mixture / $\text{cm}^3 \text{mol}^{-1}$ |
| ρ | Density / g cm^{-3} |
| x_{cs} | molar fraction of cosolvent |
| x_s | molar fraction of salt |
| x_w | molar fraction of water |
| η_s | Viscosity of pure salt / mPa s |
| η_{cs} | Viscosity of the cosolvent / mPa s |
| η | Viscosity / mPa s |

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