

The effect of the anion on the physical properties of trihalide-based *N,N*-dialkylimidazolium ionic liquids

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Low viscosity, high density trihalide-based 1-*n*-butyl-3-methylimidazolium ionic liquids have been prepared and characterised. Key physical properties (density, conductivity, melting point, refractive index, surface tension and diffusion coefficient) of the ionic liquids have been determined and are compared with those of other 1,3-dialkylimidazolium molten salts. The relationship between anion identity and the physical properties of the ionic liquids under investigation is discussed.

Introduction

Room temperature ionic liquids (ILs) are currently attracting considerable attention as potentially benign solvents for electrochemical and chemical separations, as well as in material applications. A large number of reactions have been successfully performed in these solvents, showing their great potential as reaction media capable of maintaining, and in some cases enhancing, chemical reactivity and selectivity.¹ The importance of the anion in determining the physico-chemical properties of ILs has also been noted.²

Many polyhalide anions are known and have been studied, and they are prototypical examples of hypervalent bonding.³ In particular, trihalide anions are important because of their presence in many organic conductors and superconductors;⁴ several trihalide anions appear in charge-transfer complexes and trihalide anions (especially Br₃⁻) have been used as electrophilic halogenating agents in organic synthesis.⁵ In both solid and solution phases, the stability of a trihalide with respect to dissociation is greater when the cation is larger and more symmetrical; generally, inorganic trihalides are less stable than tetraalkylammonium salts.⁶ Trihalide anions may be defined as the addition products of a halide anion, acting as a base, to a halogen molecule, acting as a Lewis acid. X-ray diffraction data show⁶ that trihalide anions are linear, with size and shape depending on the molecular weight of the constituting atoms. Experimental data and theoretical calculations furthermore show that in heteronuclear trihalide anions (X₂Y⁻) the more stable isomers are those in which the heavier atom occupies the central position.⁷

During the investigation of new anions for the application of ILs as solvents and reagents in organic synthesis and in electrochemical devices, it became apparent that trihalide anions give hydrophobic and highly stable *N,N*-dialkylimidazolium ILs, having lower melting points and viscosities than other common anions. This family of ILs has been successfully used for the halogenation of alkenes, alkynes and aromatic compounds,⁸ but they also might be used for other non-synthetic applications, such as in analytical chemistry⁹ or for the preparation of novel molecular metals and superconductors based on cation-radical salts of organic donors.¹⁰ On the other hand, there are other promising potential applications of these ILs in materials

science, e.g. as gas absorbents or for the preparation of gels, and as electrolytes and redox couples in solar cells.¹¹

Trihalide anions combine a number of structural features that should provide the resulting salts with advantageous physical properties. The charge on the trihalide anions is diffuse and this should result in a decreased interaction between the cation and anion compared to ionic compounds bearing the more charge-localized halide anions. This is certainly an important factor in reducing the melting points of these salts. In any case, the relationship between anion and cation size, their interactions and the physico-chemical properties of ILs, is far from being well understood. In an effort to enhance the understanding of the correlation between IL structure and physico-chemical properties and to promote the application of trihalide ionic liquids, we report an analysis of the effect of the anion on the physical and spectroscopic properties of three 1-*n*-butyl-3-methylimidazolium (bmim) trihalide ILs, [bmim][Br₃], [bmim][ICl₂] and [bmim][IBr₂]. Comparison of the properties of these ILs with those of other [bmim]-based ionic liquids provides new insight into the effect of the anion on this class of ILs.

Experimental

Materials

Bromine (1 ml in sealed ampoules, >99.5%), ICl, IBr were used as supplied. [Bmim][Cl] and [bmim][Br] were prepared according to the reported procedures.^{8b}

Synthesis of trihalide based ILs

An appropriate amount of [bmim][Cl] or [bmim][Br] was weighed in a calibration flask under nitrogen and the ionic liquid was refrigerated at 0 °C. An equimolar amount of halogen (ICl, IBr or Br₂) was added at the same temperature and the trihalide ionic liquid was stored in the dark. Attention was paid to avoid the addition of a halogen excess: it is noteworthy that, even though a small amount of free halide does not affect the product distribution, when these ILs are used as reagent-solvents, it significantly varies the physico-chemical properties of these compounds.

Table 1 Physical properties of trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim]⁺) ionic liquids^a

Ionic liquid	<i>n</i> ^b	<i>P</i> _m ^c	<i>ρ</i> ^d	<i>γ</i> ^e	<i>T</i> _m ^f	<i>η</i> ^g	<i>k</i> ^h	<i>D</i> ⁱ	<i>T</i> _d ^j
[Bmim][Cl] ₂	1.658	69.62	1.78	54.6		49.81	5.74	2.51	204.0
[Bmim][Br] ₃	1.659	82.04	1.702	51.5	8.2	92.53	8.93	3.83	251.0 (121.0)
[Bmim][IBr] ₂	1.610	95.50	1.547	57.3		57.28	6.16	3.36	196.0
[Hmim][IBr] ₂ ^k			1.75 ^o			17.0 ^o	40.0 ^o		
[Bmim][I]	1.572 ⁿ	60.79	1.44 ⁿ	54.7 ⁿ	-72.0 ⁿ	1110.0 ⁿ			258.0 ⁿ
[Bmim][Tf ₂ N] ^l	1.427 ⁿ	75.48	1.436 ^o	37.5 ⁿ	-9.0	52.0 ^m	3.9 ^m	3.38	
[Bmim][PF ₆] ^l	1.409 ⁿ	51.30	1.368 ^o	48.8 ⁿ	10.0 ⁿ	450.0 ⁿ			403.0 ⁿ
[Bmim][BF ₄]			1.17 ⁿ	46.6 ⁿ	-81.0 ⁿ	219.0 ⁿ	0.23 ^m		360.0 ⁿ

^a All data were recorded at room temperature, except where indicated. ^b Refractive index. ^c Molar polarizability in cm³ mol⁻¹ (see eqn. 1). ^d Density in g ml⁻¹. ^e Surface tension in dyn cm⁻¹. ^f Melting temperature in °C. ^g Viscosity in cP. ^h Electric conductivity in mS cm⁻¹. ⁱ Translational diffusion coefficient of the cation in 10⁻¹¹ m²s⁻¹ at 301 K; estimated errors are 0.01–0.06. ^j Degradation onset temperatures in °C. ^k [Hmim] = 3-methylimidazolium. ^l See also ref. 13 for comparison. ^m Ref. 1. ⁿ Ref. 2. ^o Ref. 20.

DSC analysis

Melting points were determined using Perkin-Elmer DSC-6 differential scanning calorimeter. Each sample was approximately 10 mg and was analysed in a hermetically sealed aluminium pan. For each experiment, an empty hermetically sealed pan was referenced as the blank. A ramp temperature of 10 °C min⁻¹ was employed over the temperature range -50 °C to 60 °C. Temperature calibration was performed with cyclohexane.

Density

The densities of each IL were determined by gravimetric analysis measuring the weight of the sample in a 1 cm³ calibrated flask. Each measurement was repeated in triplicate and the average values are recorded in Table 1. All measurements were taken at room temperature.

Refractive index

All measurements were made with an ATAGO (ATAGO Ltd.) 32476 series refractive index instrument. Deionized water was used as a reference for calibration. All measurements were taken at room temperature and repeated in triplicate; average values are reported in Table 1.

Surface tension.

Measured with a Fisher manual model tensiometer with a platinum–indium wire with a mean circumference of 6 cm and a ring/wire radius ratio of 53.6. A volume of 20 ml of sample in a beaker was determined to be sufficient to completely wet the probe and to prevent its interaction with the liquid meniscus. A correction factor for each measurement was determined by measuring the surface tension of deionized water, dividing the result by its established value and multiplying the data obtained for trihalide-based ILs by that value. Each sample was analysed in triplicate and the average values are reported in Table 1. All readings were taken at room temperature.

Conductivity.

Measured using a CON 510 bench meter supplied with conductivity/TDS electrode. This electrode comes with stainless steel rings, a cell constant of *K* = 1.0 and an inbuilt temperature sensor for automatic temperature compensation. The measurements were carried out with warming from 283 K to 343 K using a Haake D8 thermostat–cryostat and samples were thermally equilibrated at each temperature for at least 1 h before the readings were taken.

Viscosity

All dynamic viscosity measurements were carried out on a Physica viscosimeter. For each analysis a 10 ml sample was used and the measurements were performed in duplicate. The temperature of the sample was maintained to ±0.1 °C via a circulation-type thermo-regulated bath.

Thermal gravimetric analyses.

Conducted using a Stanton-Redcroft TG-750 instrument (temperature range: 20–900 °C, heating rate: 10 °C min⁻¹, under a flow of N₂) and data collected on a PC using Pico Technologies “Dr. Daq” interface card.

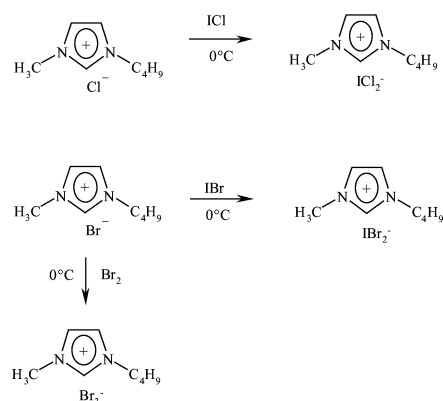
NMR analysis

NMR and diffusion measurements were carried out on a Bruker Avance DRX 300 spectrometer equipped with a 5 mm BBO *z*-gradient (53 G cm⁻¹ max) inverse probe. The samples were fitted into 5 mm coaxial inserts (60 µl internal volume) and externally locked to a D₂O signal. The temperature was set at 301 ± 0.1 K. Diffusion coefficients were determined through a standard ¹H BPPLIED sequence.¹² In dealing with the more viscous samples, the usual sine-shaped gradients were replaced by trapezoidal-ramped gradients, delivering an 80% integrated area with respect to their rectangular analogues. Typical timing values employed in the sequence were 1.7 ms for the pulsed-gradient duration, 700 ms for the diffusion delay and 5 ms for the eddy-current delay. For each sample, the integrated echo signals were firstly fitted as a function of the applied gradient strength and then averaged in order to obtain a better estimate of the diffusion coefficient. All the errors reported in Table 1 were estimated by the standard deviation of the sample mean, since these values were systematically higher than the standard errors of the single best fitting parameter.

Results and discussion

Preparation and physical properties

Air-stable 1-butyl-3-methylimidazolium trihalides ([bmim][Br]₃, [bmim][Cl]₂ and [bmim][IBr]₂) have been prepared from the corresponding 1,3-dialkylimidazolium halides (Cl, Br) by addition of an equimolar amount of ICl, IBr or Br₂ at 0 °C (Scheme 1).

**Scheme 1** Synthesis of trihalide-based ILs.

These ILs have been stored in the dark at 4 °C for several months without any degradation or loss of reactivity and selectivity. Purity grade (>98%) during storage was checked by NMR, ESI-MS and UV-vis analysis.

Polarity

Regardless of the counteranion, trihalide-based ILs are normally miscible with liquids of medium dielectric constant, like alcohols and ketones, acetonitrile and dimethyl sulfoxide. They are only slightly soluble in chlorinated solvents, whereas they are completely immiscible with water, alkanes, dioxane, toluene and diethyl ether. The polarity of these ILs cannot be determined through the use of solvatochromic dyes (due to the strong absorbance of trihalide anions in the UV-vis region); however, an estimate of their electronic polarizability can be obtained from their refractive index n . The refractive index at a specified frequency, typically that of visible light, is related to the molar volume polarizability of the medium (P_m) according to the Lorenz-Lorentz equation (eqn. 1), where ρ is the density and M the molecular weight:

$$P_m = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \quad (1)$$

Table 1 shows the values of n and P_m , as well as other physical quantities discussed hereafter, for the investigated trihalide salts and for other common ILs. It is noteworthy that the presence of a trihalide anion significantly enhances the refractive index of the corresponding ILs; the n -values (1.61–1.66) lie in the same range of iodobenzene (1.62), quinoline (1.63) and carbon disulfide (1.74), as might have been expected on the basis of the high atomic number of I and Br. Correspondingly, the trihalide-based ILs have quite high electronic polarizabilities and the order ($\text{IBr}_2 > \text{Br}_3 > \text{ICl}_2$) is also consistent with the increasing overall molecular weight of the anions.

Density

The densities of trihalide-based ILs do not seem to be related to anion size, although they are higher than those reported for other common imidazolium salts. This feature, together with the immiscibility with many organic solvents and compounds, is particularly important when these salts are used as reagent-solvents for the halogenation of unsaturated compounds, as they may improve the product recovery favoring the separation of the IL from the product(s) or from the solvent used for product(s) extraction.

Surface tension

Trihalide-based ILs are also characterized by high values of the surface tension γ (Table 1), similar to that of [bmim][I] but higher than those reported for the other common ILs.^{2,14} The principle of independent surface action formulated by Langmuir¹⁵ states that, 'each part of a molecule possesses a local surface free energy and therefore the measured surface tension should correspond to the part of the molecule that is actually present at the interface'. Considering that both the anion and the cation are present at the surface of ILs, both should contribute to the final value of surface tension. Nevertheless, as previously reported by Watson *et al.*,¹⁴ the values of the surface tension of ILs are generally close to that of imidazole, indicating that the surface tension is governed by the cation orientation and therefore varies mainly with the identity of the alkyl substituent on the cation and, to a lesser extent, with the nature of the anion. Since all the ILs under investigation share the same cation, the data reported in Table 1 show that γ -values increase somewhat with increasing anion size. This could suggest a change in average cation orientations in these ILs embodying a rotation that moves the methyl group deeper, as the size of the anion increases.

Melting point

The melting point of ionic liquids is strongly related to the strength of the crystal lattice, which in turn is determined by intermolecular forces, molecular symmetry and conformational degrees of freedom.¹⁶ It has been suggested by several authors that in the case of ILs packing inefficiency is responsible for their low melting points;¹⁷ however, the exact origin of the low melting points of imidazolium-based ILs still remains unclear. Even slight changes in molecular structure may give rise to very different melting points. The DSC analysis of trihalide-based ILs reveals that the anion identity significantly influences the melting point of these salts. In fact, only in the case of [bmim][Br₃] was a melting point detectable; neither [bmim][IBr₂] nor [bmim][ICl₂] crystallized upon fast cooling in liquid nitrogen, although [bmim][IBr₂] did crystallize after long standing at -30 °C. Furthermore, none of the ILs under investigation showed a detectable glass transition by DSC measurements.

Viscosity

A particularly significant effect of trihalide anions on the physical properties of the corresponding ILs is that on viscosity. The viscosities of the salts under investigation are constant from 100 to 1000 s⁻¹ and therefore they can be considered as Newtonian fluids. Furthermore, the values characterizing these ILs are appreciably low. Changes in viscosity observed on changing the anionic or cationic component of a given IL have been attributed primarily to an increase in van der Waals forces, although hydrogen bonding may also play some role.¹⁸ In agreement with this, the combination of the increased anion size, more diffuse negative charge and decreased hydrogen bonding between anion and cation should result in a decrease in viscosity on going from Cl⁻ to I⁻ in the halide-based ILs. It is however noteworthy that, within the trihalide ILs family, the viscosity increases in the order ICl₂ < IBr₂ < Br₃.

Since the three investigated trihalide ILs share the same cation, one can reasonably expect that the trends in viscosity arise mainly from the nature of the anion and on its interaction with the common cation. The main factor that characterizes the ILs studied herein (and indeed distinguishes them from other major IL types) is the very high polarizability of the anion. This leads to two, partly opposing, consequences: on one hand, their low charge density will render the electrostatic interaction weaker; on the other hand, dispersive forces will be enhanced. As a further consequence, the onset of strong dispersive interactions will cause the cation-anion interaction to take place in a less specific orientation, because strict matching of opposite poles is not required. Therefore, there is no simple criteria whereby one can rank dynamic bulk properties such as viscosities.

Further information about the structure of ILs can be derived from the change of viscosity with temperature. As in the case of [bmim][PF₆],¹⁹ the viscosity of trihalide based ILs is strongly dependent upon temperature (an increase of up to 29% is found upon going from 280 to 290 K). The relationship between viscosity and temperature has been studied over the temperature range 279–320 K and the plots were fitted using the logarithmic form of the Arrhenius equation, which describes the temperature dependence of viscosity for undissociated liquid electrolytes:

$$\ln \eta = \ln \eta_\infty + E_\eta / RT$$

where E_η is the activation energy for viscous flow, and η_∞ the viscosity at an infinite temperature. For all the ionic liquids under investigation this empirical equation was obeyed, as plotting $\ln \eta$ vs. T^{-1} always resulted in a straight line (Fig. 1).

In this case, owing to the large electrostatic force acting between cation and anion, the activation energy E_η can be treated as the energy barrier that must be overcome to allow the ions to move past each other and hence can be correlated with structural information on ionic liquids. In the case of [bmim][PF₆], the high value E_η , associated with the large and negative value of $\ln \eta_\infty$,

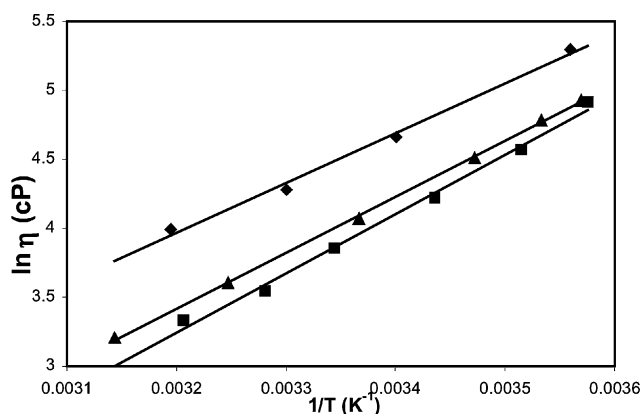


Fig. 1 Temperature dependence of viscosity for trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim]⁺) ionic liquids: ICl₂ (squares); Br₃ (diamonds); IBr₂ (triangles).

Table 2 Activation energies (E_a) and infinite-temperature viscosities (η_∞) for 1-*n*-butyl-3-methylimidazolium ([bmim]⁺) ionic liquids

Ionic liquid	$E_a/\text{kJ mol}^{-1}$	$\ln \eta_\infty$	Ref.
[Bmim][PF ₆]	37.60	-18.79	20b
[Bmim][Tf ₂ N]	25.40	-13.21	20b
[Bmim][BF ₄]	25.83	-5.07	20a
[Bmim][OTf]	26.17	-3.52	20a
[Bm ₂ im][Tf ₂ N] ^a	31.20	-14.91	20b
[Bmim][ICl ₂]	35.62	-10.47	
[Bmim][Br ₃]	33.73	-7.61	
[Bmim][IBr ₂]	30.07	-9.56	

^a [Bm₂im] = 1,2-dimethyl-3-butylimidazolium.

has been attributed to a high cross-linking and therefore to high-order degree. At an infinite temperature, coulombic interactions between ions are no longer effective and the viscosity (η_∞) is governed primarily by the geometry of the component ions. The E_a values found for trihalide-based ILs are reported in Table 2, together with literature data for other 1-butyl-3-methylimidazolium derivatives.²⁰

The activation energies for the ILs under investigation are among the highest values reported, significantly higher than those characterising ILs of similar viscosity at room temperature (for example, [bmim][Tf₂N]). In particular, [bmim][ICl₂] shows an activation energy similar to that of [bmim][PF₆] and is characterized by the most negative value of $\ln \eta_\infty$. This suggests that [bmim][ICl₂], better than the other trihalide salts, possesses a more ordered three-dimensional structure. This behavior may be a consequence of the smaller size of the anion, allowing the interaction with several of the surrounding cations.

Diffusion coefficients

Beginning with the pioneering work by Schröder *et al.*, who investigated the diffusion coefficient of an electrochemically active solute by cyclic voltammetry,²¹ the measurement of diffusion coefficients of ionic liquids is nowadays performed by PFGSE (pulsed field gradient spin-echo) NMR spectroscopy.^{22,13}

According to the improved form of the Stokes–Einstein equation embodied in Gierer–Wirtz’s microviscosity theory,²³ translational diffusion coefficients D are related to viscosities by an inverse relationship, $D \propto 1/\eta$, as in eqn. 2:

$$D = \frac{kT}{6\pi\eta r_0 f_t}; f_t = \frac{3r_s}{2r_0} + \frac{1}{1 + \frac{r_s}{r_0}} \quad (2)$$

where k is Boltzmann’s constant, T is the temperature, r_0 is the hydrodynamic radius of the diffusing species and f_t a translational microviscosity factor, which in turn depends on

the radii of solute (r_0) and solvent (r_s). On the contrary, bulk viscosities and diffusion coefficients of the ILs under study seem to be roughly proportional to each other: the IL with the highest viscosity, [bmim][Br₃], also exhibits the highest diffusion coefficient. This finding stands in contrast with both the Stokes–Einstein model and microviscosity theory, assuming that f_t and r_0 are the same for the cation. While a comprehensive model of the molecular dynamics of ILs has not yet been proposed, and within the small range of data investigated, this anomalous behaviour may be traced to several factors, like *e.g.* the single temperature investigated and possibly also to the complex structure of these liquids. Thus, we remark that the diffusion coefficient D has been measured on, and only pertains to, the cationic part of the IL (plus other ionic entities contributing to its hydrodynamic radius), whereas the viscosity η is a macroscopic quantity that contains combined effects from cation and anion. As a consequence, it is possible that small changes in ionic association affect D and η to different extents. This is further highlighted by conductivity studies below.

Conductivity

Table 1 indicates that [bmim][Br₃] is the IL characterized by the highest conductivity even though it is the most viscous among the investigated trihalide-based ionic liquids. Although there is generally a correlation between viscosity and conductivity, the viscosity alone does not always account for the conductive behavior of ILs.²⁴ Yoshizawa and Ohno²⁵ highlighted that the degree of ion dissociation, as well as ion shape and radius, may play an important role in determining the transport properties of acidic imidazolium-based ionic liquids. On the other hand, Böhöte *et al.*^{18a} pointed out that a modified form of the Stokes–Einstein relation (eqn. 3), which takes in account also the molecular weight (F_w) and the ionic radii (r_a, r_c), should be used to correlate ionic transport to the viscosity of the ionic liquid:

$$\sigma = \frac{yF^2d}{6\pi N_A F_w \eta} [(\xi_a r_a)^{-1} + (\xi_c r_c)^{-1}] \quad (3)$$

where ξ_a and ξ_c are the anion and cation microviscosity factors, two correction factors which takes into account the specific interactions between the mobile ions in the melts.

In fact, considering the features of the ILs, it is not surprising that deviations from the Nerst–Einstein equation can be observed. The physical proximity of the ions in ILs creates the possibility of correlated ionic motions. This may simply imply that the random motion of an ion determines the motion of the counterion in the same direction or, depending on the ion’s structure, in conjunction with these correlated motions, bonded ion pairs or higher aggregates may also be present. Correlated motions, ion pairs and aggregates reduce conductivity. We finally remark that this anomalous behavior in fact matches the trend found for diffusion coefficients, which points out that bulk viscosities may not be good indicators of the molecular dynamics.

Therefore, considering all the physico–chemical data characterizing trihalide based ILs the relatively low conductivities of [bmim][ICl₂] and [bmim][IBr₂] as compared to [bmim][Br₃] can be attributed to the reduction of available charge carriers, mainly due to ion aggregates for the former salt (see, dependence of viscosity on temperature), whereas a reduced ion mobility resulting from the larger ion size and ion pairing (see NMR results), may be invoked in the case of [bmim][IBr₂].

The temperature dependence of conductivity for the ionic liquids under investigation exhibits classical linear Arrhenius behaviour (Fig. 2).

The change in conductivity with temperature depends also in this case on the nature of the ionic liquids: while a similar behavior has been found for bromide-containing species, a higher slope characterizes the straight line of [bmim][ICl₂]. The behavior is in agreement with a higher degree of ion aggregation

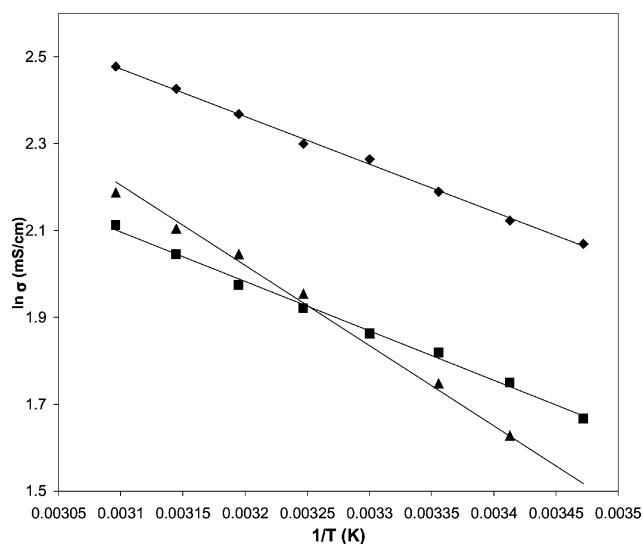


Fig. 2 Temperature dependence of conductivity for trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim]⁺) ionic liquids: ICl₂ (triangles); Br₃ (diamonds); IBr₂ (squares).

in the case of [bmim][ICl₂] with respect to the other two ILs, which could arise from the different size of ICl₂⁻ with respect to the other trihalides.

Thermal stability

Since ionic liquids have no significant vapour pressure, the upper limit of their liquid range is defined by their stability. Table 1 shows the degradation onset temperatures for the trihalide salts as established by thermal gravimetric analysis. This onset temperature is defined as the point where significant mass loss initiates during a thermal gravimetric analysis experiment. For both the heterogeneous ICl₂ and IBr₂ salts, clean onset phenomena are observed and lead to >80% mass loss by 500 °C with a heating rate of 10 °C min⁻¹, followed by slow cleaning of the sample pan, suggesting low volatility residues remained. The onset temperatures of the salts of these heterogeneous anions are lower than those of the analogous halide salts²⁶ and also salts of the more complex, non-nucleophilic anions. The data for the tribromide salt is less clear as some slow degradation is observed at temperatures as low as 121 °C, although only *ca.* 15% mass loss occurs prior to the more significant mass loss onset at 251 °C and the mass loss profile subsequently displayed similar behaviour to the salts of the heterogeneous anions *i.e.* *ca.* 80% mass loss by 500 °C.

The mechanism for degradation of the *N,N'*-dialkylimidazolium halide salts has been established as nucleophilic attack of the halide anion at one of the *N*-alkyl groups.²⁶ Given that trihalides are less nucleophilic than halide anions and act as efficient halogenating agents for even deactivated aromatics,²⁷ it seems likely that the mode of degradation is halogenation of the aromatic ring, rather than nucleophilic substitution of the *N*-alkyl group. Whether the halogenation might involve an electrophilic or radical mechanism is unclear at this stage.

Analysis of ¹H NMR chemical shifts

It is known that the hydrogen atoms of the 1,3-dialkylimidazolium cations ILs can act as hydrogen bond (HB) donors and that the relative strength of such interaction, leading to an ion pair, is related to the nature of the anion.²⁸ The analysis of ¹H NMR chemical shifts, especially those of the ring protons, has been employed to probe this interaction. Thus, in order to obtain more insight on the degree of ion pairing we compared the chemical shifts of the imidazolium protons for pure trihalide-based ionic liquids.

Table 3 ¹H chemical shifts of imidazolium ring protons in neat trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim]⁺) ionic liquids

Proton	ICl ₂	Br ₃	IBr ₂
H-2	8.970	9.087	9.141
H-5 ^b	7.680	7.754	7.748
H-4 ^b	7.736	7.718	7.712
H-6	4.321	4.382	4.357
H-10	4.067	4.128	4.109
H-7	1.959	1.976	1.973
H-8	1.397	1.415	1.403
H-9	0.949	0.957	0.951

^a All data are referred to TMS as internal standard. ^b The relative assignment of H-4 and H-5 is based on ref. 30.

Several authors have shown that the chemical shifts of imidazolium protons are solvent and concentration dependent and that these two factors may exert opposite effects.^{29,18a} In the case under study, we have the additional complication that the very large polarizability of the anions, all containing heavy atoms such as Br and I, may exert further effects which are difficult to predict and model.

¹H NMR spectra were recorded on the pure ILs with D₂O external lock, to avoid the concentration and solvent dependence. According to our previous analysis of trihalide-based ILs,^{8b} the addition of ICl to [bmim][Cl] and IBr or Br₂ to [bmim][Br] causes an upfield shift of the H-2 signal. This may be considered as an indication of a significantly decreased hydrogen bonding in these trihalide ILs, which is consistent with the discussion of the physico-chemical properties above and with the immiscibility of these salts with water.

The experimental data for the neat ionic liquids, reported in Table 3, show that the chemical shift of the butyl protons and H-5 decrease in the order Br₃ > IBr₂ > ICl₂. H-2 and H-4 show a somewhat different trend (IBr₂ > Br₃ > ICl₂ and ICl₂ > Br₃ > IBr₂, respectively). Since H-2 is the strongest hydrogen-bond donor, within the scope of this comparison, IBr₂⁻ appears to be the best HB acceptor among the trihalide ions. However, one should keep in mind the small changes involved ($\Delta\delta = 0.17$ at most). Moreover, the inconsistent trend among the various protons indicates that other factors, like the anion polarizabilities, may be important in determining the chemical shift in the pure liquid. This is further analyzed below.

In order to further investigate the nature of the interactions that exists between the anion and the aromatic hydrogens in trihalide-based ILs, ¹H NMR analyses in several deuterated solvents were performed (Table 4). The concentrations were kept constant so that the chemical shifts of the aromatic protons should only be solvent-dependent. The H-2 signal undergoes larger chemical shift variations (*ca.* 2 ppm) than H-4 and H-5 (0.6 ppm). A graph of these chemical shifts against the $\Sigma\beta_2^H$ parameter, which measures the ability of a given species to act as hydrogen-bond acceptor,³¹ shows a trend that, again, differentiates H-2 from H-4,5 (Fig. 3). Thus, for the latter two sets the signals are roughly deshielded (by *ca.* 0.5 ppm) with increasing HB acceptor strength of the solvent. On the other hand, the H-2 signal undergoes more complex changes: (a) pyridine causes a much larger deshielding than expected on the basis of its $\Sigma\beta_2^H$ value, which is most likely due to a specific

Table 4 ^1H chemical shifts of trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim] $^+$) ionic liquids dissolved (0.1 M) in deuterated solvents at 298 K

Solvent	$\Sigma\beta_2^{\text{H}^a}$	ICl_2			Br_3			IBr_2		
		H-2	H-4	H-5	H-2	H-4	H-5	H-2	H-4	H-5
CDCl_3	0.02	9.106	7.305	7.305	8.913	7.349	7.349	9.020	7.300	7.300
CD_2Cl_2	0.05	8.967	7.306	7.299	8.841	7.350	7.342	8.406	7.413	7.406
CD_3CN	0.32	8.420	7.390	7.360	8.405	7.371	7.333	8.371	7.356	7.322
DMF-d_6	0.74	9.152	7.754	7.702	9.254	7.903	7.840	9.253	7.894	7.833
DMSO-d_6	0.78 ^b	9.084	7.731	7.667	9.104	7.758	7.691	9.087	7.745	7.680
Pyridine	0.52	9.925	7.818	7.771						

^a As defined in ref. 30. ^b Value of β_2^{H} .

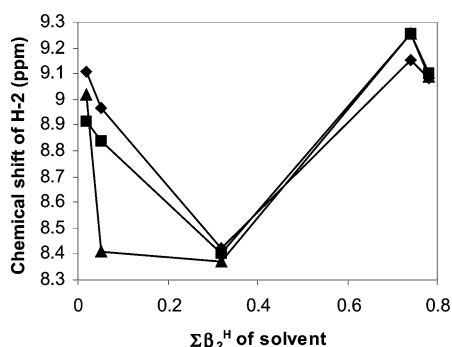


Fig. 3 Correlation between the solvent hydrogen-bond acceptor ability $\Sigma\beta_2^{\text{H}}$ and the chemical shift of the H-2 signal in trihalide-based 1-*n*-butyl-3-methylimidazolium ([bmim] $^+$) ionic liquids, dissolved in various solvents: ICl_2 (diamonds); Br_3 (squares); IBr_2 (triangles).

HB and (b) all ILs exhibit a minimum in acetonitrile, more pronounced for IBr_2 .

Within the limited range of data examined, we propose that in solvents having low or high HB strength the cation is hydrogen-bonded (*via* the H-2 site) to the counteranion or to the solvent, respectively, whereas at intermediate strengths the solvent polarity is sufficient to isolate the cation from the anion but not to act as a HB acceptor. [Bmim][IBr_2] is peculiar in that this situation is realized even in dichloromethane. This may be related to the very high polarizability and low charge density of the anion, entailing a relatively weak cation–anion interaction that is easily broken down by a very weak HB acceptor solvent.

Conclusions

Ionic liquids based on imidazolium cation and having trihalides as anion have been studied. Key physical properties of these salts have been determined and compared with those of related 1,3-dialkylimidazolium molten salts. Trihalide-based ILs show lower melting point and viscosity and higher density and hydrophobicity with respect to many other common imidazolium ionic liquids, including chlorides, bromides or iodides. Despite the very similar nature of the ILs, the physical properties vary significantly. The potential for forming ion pairs or ion aggregates, depending on the anion size, strongly affects the refractive index, electronic polarizability, viscosity and conductivity. Deviations from linearity have been observed plotting $\ln \eta$ vs. $\ln \sigma$, suggesting that the viscosity alone does not account for the conductive behaviour of these ILs.

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