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Review Commentary

Ionic liquids: solvent properties and organic reactivity

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ABSTRACT: Ionic liquids are a fascinating class of novel solvents, which are attracting attention as possible 'green' alternative to volatile molecular organic solvents to be applied in catalytic and organic reactions and electrochemical and separation processes. Over 200 room temperature ionic liquids are known but for most of them physico-chemical data are incomplete or lacking. Furthermore, despite the incredible number of potential ionic liquids (evaluated as $>10^{14}$), generally only a few imidazolium-based salts are used in synthesis. Moreover, most of the data reported to date were focused on the effect that these new solvents have on chemical reaction products; only a few reports evidence the effect on reaction mechanisms or rate or equilibrium constants. In this review, the physico-chemical properties of the most used ionic liquids, that are relevant to synthesis, are discussed and a decided emphasis is placed on those properties that most clearly illuminate the ability of ionic liquids to affect the mechanistic aspects of some organic reactions. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ionic liquids; solvent properties; organic reactivity; synthesis

INTRODUCTION

Ionic liquids (ILs) are a class of novel solvents with very interesting properties, which are attracting the attention of a growing number of scientists and engineers, as shown by the increasing number of papers published in recent years.[1] As a consequence of some of their peculiar properties, such as negligible vapour pressure, ability to dissolve organic, inorganic and polymeric materials and high thermal stability, ILs have also gained popularity as 'green' alternatives to volatile organic solvents (VOCs) to be applied in electrochemical, synthetic and separation processes.

'Ionic liquid' is now the commonly accepted term for low-melting salts (melting-point typically <100 °C) obtained by the combination of large organic cations with a variety of anions. Although estimates vary, there is no doubt that the number of combinations of anions and cations that can give rise to potential ILs is vast. The high possibility for synthetic variations has led to ILs being described as 'designer solvents'.[2] Since it is not possible to make every combination of ions and measure their properties (the number is $>10^{14}$), in order to be able to exploit their potential it is necessary to establish the physico-chemical properties of the already synthesized ILs and the correlation between these and molecular structure. Furthermore, it is also necessary to understand how the physico-chemical properties of ILs are able to affect organic reactivity. ILs can replace molecular solvents only if the chemist is able to compare ILs with generally used reaction media.

At present, most of the data available are focused on bulk physical properties, such as phase transitions, viscosity and density, and on the correlation between these properties and the molecular structure of the ILs. Relatively little is known about the microscopic physical properties of these new materials and how to predict the influence of these solvents on chemical reaction rates. Such understanding would give the information necessary to synthesize new ILs with precisely tailored properties for every chemical reaction.

Several excellent reviews on their synthesis and use are available.[1,3,4] Therefore, this paper, rather than attempting to give a comprehensive overview of IL chemistry, is focused on physico-chemical properties of ILs and on the microscopic solvent properties of these media, with a decided emphasis on those features that most clearly illuminate the ability of ILs to affect the mechanistic aspects of some organic reactions. The first part of the review is centred on the physico-chemical properties of ILs. In the second part, the stereochemical and kinetic behaviour of some organic reactions in ILs will be examined and compared with that characterizing the same reactions in molecular solvents.

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STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF ILs

Structural features

The simplest definition of an IL is a liquid composed exclusively of ions, with the forces overwhelmingly coulombic. The cation is generally a bulk organic structure with low symmetry. Those described so far are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, thiazolium, oxazolium and pyrazolium cations, differently substituted, although the more recent research has mainly focused on room temperature ionic liquids composed of asymmetric *N*,*N*′-dialkylimidazolium cations associated with a variety of anions (Scheme 1).[1,3,4]

Nomeclature of ILs

Anions. On the basis of the anion, ILs may be divided into four groups: (a) systems based on $AlCl_3$ and organic salts such as 1-butyl-3-methylimidazolium chloride, [bmim][Cl]; (b) systems based on anions like $[PF_6]^-$, $[BF_4]^-$ and $[SbF_6]^-$; (c) systems based on anions such as $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^- \equiv [Tf_2N]^-$ and similar; (d) systems based on anions such as alkylsulfates[5] and alkylsulfonates.[6]

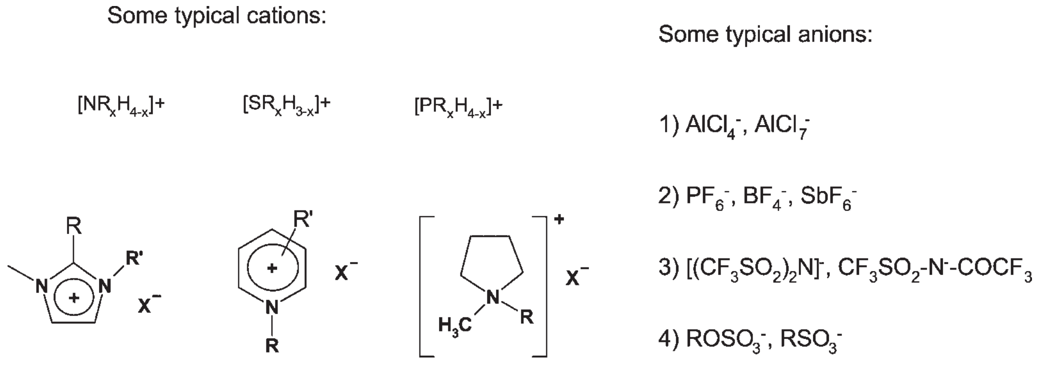
The first group represents the ILs of ‘first generation’, whose Lewis acidity can be varied by the relative amounts of organic salt/$AlCl_3$; with a molar excess of $AlCl_3$ these ILs are Lewis acidic, with an excess of organic salt they are Lewis basic, and Lewis neutral liquids contain equimolar amounts of organic salt and $AlCl_3$. These ILs are, however, extremely hygroscopic and handling is possible only under a dry atmosphere. The systems mentioned in (b) are nearly neutral and air stable, although they have the disadvantage of reacting exothermically with strong Lewis acids, such as $AlCl_3$, and with water. Moreover, slow hydrolysis of $[PF_6]^-$ in the presence of water, leading to detectable amounts of HF, has often been observed.[4] ILs based on anions mentioned in (c) are much more stable towards such reactions and are generally characterized by low melting-points, low viscosities and high conductivities. Furthermore, $[Tf_2N]^-$-based ILs are expected to behave as moderately coordinating solvents. Structural studies of organic $[Tf_2N]^-$ salts have shown only weak coulombic interactions between $[Tf_2N]^-$ and weak Lewis acids, attributable to delocalization of the negative charge within the S—N—S core. However, the possibility of this anion giving a stronger bonding interaction with Lewis acidic metal ions has been also evidenced.[7] Probably, the metal enhances the contribution of the resonance structure bearing the negative charge on the nitrogen atom.

Recently, the synthesis of several ILs based on the bis(methanesulfonyl)amide ($[Ms_2N]^-$) anion, has provided[8] new insights into the effect of anion fluorination on the properties of ILs. The substitution of the $[Tf_2N]^-$ anion with $[Ms_2N]^-$ produces a significant increase in hydrogen bonding, which determines a significant rise in the glass transition temperature and a concurrent increase in viscosity, which in turn produces a drop in conductivity. The lack of anion fluorination also results in decreased thermal and electrochemical stability of the corresponding salts.[8]

ILs bearing perfluorinated anions have, however, some disadvantages: (1) a high price, in particular those having $[Tf_2N]^-$ as counter anion; and (2) the presence of fluorine makes the disposal of spent ILs more complicated.[4] In addition, they may contain traces of halides (chlorides and bromides) arising from the preparation procedure. Generally, these salts are synthesized by exhaustive alkylation of the corresponding bases with an alkyl halide (chloride or bromide) followed by a metathesis reaction.

For these reasons, research on new ILs bearing inert low coordinating and none-fluorinated anions represents a field of intense investigation in the chemistry of ILs. Among the possible alternatives recently proposed are the ILs having as counter anions carboranes ($[CB_{11}H_{12}]^-$, $[CB_{11}H_6Cl_6]^-$, $[CB_{11}H_6Br_6]^-$)[9] and orthoborates (Scheme 2).[10]

However, also these latter none-fluorinated ILs have relatively high transition temperatures and room



Scheme 1

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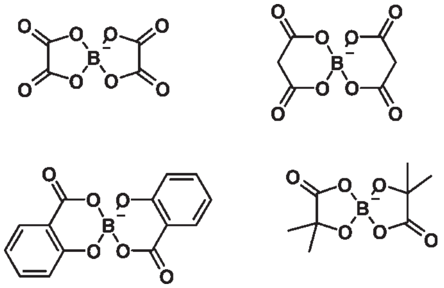


Scheme 2

temperature viscosities, two features that have been attributed to strong van der Waals interactions associated with their multi-atom unfluorinated character.

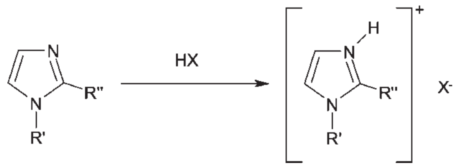
ILs based on anions mentioned in (d) may overcome at least some of the above-mentioned problems. These anions are relatively cheap, do not contain fluorine atoms and often the corresponding ILs can be easily prepared under ambient conditions by reaction of organic bases with dialkyl sulfates or alkyl sulfonate esters; they are therefore not contaminated by traces of halides.[4] Moreover, these new ILs are characterized by a wide electrochemical window and air stability.

Cations. Concerning the cation structure, it is generally assumed that non-symmetrical *N*,*N*-dialkylimidazolium cations give salts having low melting-points, even though dibutyl, dioctyl, dinonyl and didecylimidazolium hexafluorophosphates are liquid at room temperature.[11] 1-Butyl-3-methyl and 1-ethyl-3-methylimidazolium cations ($[bmim]^+$ and $[emim]^+$) are probably the most investigated structures of this class.

ILs having specific functional groups on the cation have also been prepared. For example, ILs bearing a fluorous tail have been synthesized to facilitate the emulsification of perfluorocarbons in ILs. These ILs act as surfactants and appear to self-aggregate within imidazolium ILs.[12] A free amine group or a urea or thiourea have been inserted to capture H_2S or CO_2 or heavy metals, respectively.[13] Moreover, ether and alcohol functional groups have been attached to imidazolium cations to promote the solubility of inorganic salts.[14] The presence of these extra potential complexing groups makes these latter ILs suitable for specific applications.

ILs able to act as catalysts

Finally, properly functionalized ILs, able to act as catalysts, have been synthesized. In particular, imidazolium salts containing anionic selenium species $[SeO_2(OCH_3)]^-$ have been prepared[15] and these salts have been used as selenium catalysts for the oxidative carbonylation of anilines. Analogously, ILs bearing acidic counter anions ($[HSO_4]^-$, $[H_2PO_4]^-$) have been used in catalyzed esterifications as recyclable reaction media.[16] Similar results have also been obtained using zwitterionic ILs bearing a pendant sulfonate group, which can be converted, by reaction with an equimolar amount of an acid having a sufficiently low pK_a (TsOH, TfOH), into the corresponding Brønsted acidic ionic liquids.[17] SO_3H-functionalized ionic liquids have recently been employed for the oligomerization of various alkenes, to produce branched alkene derivatives with high conversions and excellent selectivity.[18] Finally, protonated ionic liquids have been synthesized by direct neutralization of alkylimidazoles, imidazole and other amines with acids and their physical properties (thermal stability, conductance, viscosity) are currently under investigation.[19–22] However, NMR studies seem to indicate, at least in the case of 1-methylimidazolium bromide (Scheme 3), that the nitrogenic proton is not labile and, therefore, this latter salt cannot be viewed as a conventional Brønsted acid.[20]



Scheme 3

Although asymmetric synthesis of ILs is still at a preliminary stage, chiral ILs have been synthesized and their use in asymmetric synthesis is under investigation.[23]

Bulk physical and chemical properties

Before discussing the physical and chemical properties of ILs, it must be remembered that they can be dramatically altered by the presence of impurities. Purification of the ILs is essential not only to avoid possible interactions between reactants and impurities, but also because they can change the nature of these solvents. The main contaminants are halide anions and organic bases, arising from unreacted starting material, and water. The influence of water, organic solvents and other impurities, especially leftover chloride, on the viscosity and density of ILs has already been extensively discussed.[24]

In this section, we will examine some macroscopic properties of ILs, such as melting-point, viscosity and density.

Melting-point and crystal structure. The melting-point of ILs represents the lower limit of the liquid gap and together with thermal stability defines the interval of temperatures within which it is possible to use the ILs as solvents. Since this physical property can be adjusted through variations on the cation and/or anion, attempts have been made to correlate the structure of the already known ILs with their melting-points.

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Unfortunately, the melting-points of many ILs are very uncertain because they undergo considerable supercooling; the temperature of the phase change can differ considerably depending on whether the sample is heated or cooled. Anyway, by examining the properties of a series of imidazolium cation-based ILs, it has been established[25] that the melting-point decreases when the size and asymmetry of the cation increase. Further, an increase in the branching on the alkyl chain increases the melting-point.

The anion effect is more difficult to rationalize. For imidazolium ILs containing structurally similar anions, such as triflate ($[TfO]^-$) and bis(triflyl)imide ($[Tf_2N]^-$), the lower melting-points of the latter have been attributed to the electron delocalization and the relative inability of this anion to undergo hydrogen bonding with the proton(s) of the cation, in particular with that at C-2. A similar explanation has been given also comparing ILs having the same cation and $[CF_3COO]^-/[CH_3COO]^-$ or $[Ms_2N]^-/[Tf_2N]^-$ as the anions.[8]

The presence of hydrogen bonding between counter anions has often been invoked to explain the physicochemical properties of imidazolium ILs, even if the existence of such a type of interaction between anions and cations is still controversial. Actually, the presence of hydrogen bonding has been unambiguously established between the protons of the imidazolium ring and basic counter anions, such as halides and polyhalogenated metals (MCl_4, where M = Co or Ni).[26] Hydrogen bonding has been identified[27] in the crystal structure of $[emim][NO_3]$ and evidence has been obtained[28] by IR and NMR studies for $[bmim][BF_4]$ in the liquid state, whereas the results for ILs bearing anions such as $[PF_6]^-$ are inconclusive.

Recent data related to ILs having 1-butyl-2,3-dimethylimidazolium or 1-allyl-2,3-dimethylimidazolium ($[bm_2im]^+$, $[am_2im]^+$) as cation and hydrogensulfate, chloride, bromide or chloroferrate(II, III) as anion have given new insights in this field.[29] Although these cations are characterized by the absence of hydrogen at C-2, evidence for hydrogen bonding in the crystal lattice and in neat liquid has been obtained.[29] Moreover, it has been shown[29] that the contribution of the hydrogen bonds to lattice energies, and therefore to melting-points, can be correlated with the acceptor strength of the anion. However, a simple correlation between melting-points, the charge density of the anion, and the number of $C—H\cdots X$ contacts cannot be derived. For example, [bmim]Cl has three $C—H\cdots Cl$ contacts per formula unit, whereas $[bm_2im]Cl$ has only two contacts, but the melting-point of the latter is higher.

Consequently, it has been proposed[29] that the thermodynamic properties of ILs are strongly dependent on the mutual fit of the cation and anion, in term of size, geometry and charge distribution although, within a similar class of salts, small changes in the shape of uncharged, covalent regions of the ions may have an important influence.

It must be also remarked that the energy associated with melting is dominated by the entropy change from the order lattice to the liquid state. Accordingly, room temperature ILs showing low melting-points often contain ‘soft’ unsymmetrical ions which, ideally, possess internal degrees of rotational freedom which can become active in the liquid status. For example, in the case of 1-butyl-3-methylimidazolium ILs, having as counter anions substituted tetraphenylborates, the increasing bulk and orientational flexibility of the substituents on the aromatic rings of the anion depresses the melting-point of these salts.[30]

In view of the difficulty of rationalizing the dependence of the melting-point on chemical structure and the increasing need to predict the properties of yet unsynthesized ILs, calculations have been performed to predict melting-points. Only modest success was achieved[31] using computer-generated molecular descriptors in the case of imidazolium halides, whereas some promise has been gained[32] using *ab initio* calculations to evaluate the interaction energy of 1-alkyl-3-methylimidazolium halides. The calculated interaction energy was found to increase with decreasing alkyl chain length but no trend was found for the anion radius.

Strictly related to the melting-points are the crystal structures of the ILs. Although the structural organization is much lower in a liquid than in a crystal, the structural organization of the crystal lattice may provide a reasonable starting point for understanding structural features in the liquid phase. The crystal structures of several imidazolium ILs have been reported, including the widely used $[PF_6]^-$ salts.[29,30,33] In $[emim][PF_6]$, each $[PF_6]^-$ anion is surrounded by six imidazolium cations and each imidazolium by six anions. The close points of contact between the imidazolium cation and anion are the aromatic protons and the nitrogen atoms. The methyl and ethyl groups are oriented in alternating directions to give the most efficient packing while beginning to separate the charged and the neutral portions of the cation. In 1-dodecyl-3-methylimidazolium hexafluorophosphate, $[C_{12}mim][PF_6]$, this separation is more dramatic and a lamellar bi-layer type of organization can be evidenced. The bulk structural organization therefore consists of two alternating non-polar regions, the salt-like packing of anions and cation heads and the hydrocarbon-like regions of the alkyl tails. It is noteworthy that this salt-type packing of ions will result in a non-polar but polarizable medium.

The presence of polar (or polarizable) and non-polar domains has been recognized[34] also in the double-layer crystal structures of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate and hexafluorophosphate ($[bm_2im][BF_4]$ and $[bm_2im][PF_6]$), whereas no such domains have been evidenced in the structure of $[bm_2im][SbF_6]$. In these latter three non-hydrogen-bonded ILs (no evidence of hydrogen bonding between counter anions has been obtained for $[bm_2im][BF_4]$, $[bm_2im][PF_6]$ and $[bm_2im][SbF_6]$) packing is determined by anion size.

It has therefore been hypothesized[34] that, when a strong anion–cation hydrogen bonding is possible (for example, in imidazolium chlorides), this becomes the dominant force determining the packing of the ions in the crystal lattice and far exceeds the contribution of cation–cation repulsive interactions. The latter become important instead in the case of ILs containing the $[bm_2im]^+$ cation and small anions ($[BF_4]^-$ and $[PF_6]^-$), which are not hydrogen bonded. Finally, in $[bm_2im][SbF_6]$ also the cation–cation repulsive interactions are no longer influential owing to the lattice expansion.

It is evident from this brief summary that the reasons determining the low melting-points of ILs, and the nature and entity of the interactions present at the liquid state, are far from being completely understood and much more work, both experiment and theoretical, is necessary to obtain a more complete picture.

Thermal stability. Most ILs exhibit high thermal stability; the decomposition temperatures reported in the literature are generally >400 °C, with minimal vapour pressure below their decomposition temperatures. The onset of thermal decomposition is furthermore similar for the different cations but appears to decrease as the anion hydrophilicity increases. It has been suggested that the stability dependence on the anion is $[PF_6]^- > [Tf_2N]^- \sim [BF_4]^- >$ halides.[35] An increase in cation size, at least from 1-butyl to 1-octyl, $[bmim]^+$ to $[omim]^+$, does not appear to have a large effect.

The thermal stability of ILs has, however, been revised recently,[36] showing that high decomposition temperatures, calculated from fast thermogravimetric analysis (TGA) scans under a protective atmosphere, do not imply long-term thermal stability below these temperatures. After 10 h, even at temperatures as low as 200 °C, 1-alkyl-3-methylimidazolium hexafluorophosphates and 1-decyl-3-methylimidazolium triflate show an appreciable mass loss. On the other hand, 1-butyl-3-methylimidazolium triflate is stable under the same conditions, in the absence of silica. Carbonization generally occurs irrespective of the nature of the anion (hexafluorophosphate, triflate) but not for the salts with a shorter side-chain; the colour of these ILs does not change after conditioning for 10 h at 200 °C in air.

Viscosity[25,37]. One of the largest barriers to the application of ILs arises from their high viscosity. A high viscosity may produce a reduction in the rate of many organic reactions and a reduction in the diffusion rate of the redox species. Current research for new and more versatile ILs is driven, in part, by the need for materials with low viscosity.

The viscosity of ILs is normally higher than that of water, similar to those of oils, and decreases with increasing temperature. Generally, viscosity follows a non-Arrhenius behaviour but, sometimes, it can be fitted with the Vogel–Tammann–Fulcher (VFT) equation. Furthermore, viscosity remains constant with increasing shear rate and ILs can be classified in terms of Newtonian fluids, although non-Newtonian behaviours have been observed.

Examining various anion–cation combinations, the increase in viscosity observed on changing selectively the anion or cation has been primarily attributed[10] to an increase in the van der Waals forces. In agreement with this statement, in the 3-alkyl-1-methylimidazolium hexafluorophosphate and bis(triflyl)imide series ([Rmim] $[PF_6]$ and $[Rmim][Tf_2N]$), viscosity increases as n, the number of carbon atoms in the linear alkyl group, is increased.[25b] The trends are, however, different; a linear dependence has been found for the $[Tf_2N]^-$ salts whereas a more complex behaviour characterized the $[PF_6]^-$ salts. Branching of the alkyl chain in 1-alkyl-3-methylimidazolium salts always reduces viscosity. Finally, also the low viscosity of ILs bearing polyfluorinated anions has been attributed to a reduction in van der Waals interactions.

Hydrogen bonding between counter anions is, however, another factor considered to affect viscosity. The large increase in viscosity recently found[8] on changing the anion of several ILs (imidazolium, pyrrolidinium and ammonium salts) from $[Tf_2N]^-$ to $[Ms_2N]^-$ has been attributed to the combination of the decreased anion size, less diffuse charge and large increase in hydrogen bonding.

Finally, the symmetry of the inorganic anion has sometimes been considered[25] as an additional parameter; viscosity decreases in the order $Cl^- > [PF_6]^- > [BF_4]^- > [NTf_2]^-$.

Density[25]. Density is one of the most often measured properties of ILs, probably because nearly every application requires knowledge of the density. In general, ionic liquids are denser than water. The molar mass of the anion significantly affects the overall density of ILs. The $[Ms_2N]^-$ species have lower densities than the $[Tf_2N]^-$ salts,[8] in agreement with the fact that the molecular volume of the anion is similar but the mass of the fluorine is greater. In the case of orthoborates, with the exception of bis(salicylato)borate, the densities of the examined ILs having the $[bmim]^+$ cation decrease with increase in anion volume and this order is followed also when the densities of other salts, such as those having $[Tf_2N]^-$, $[TfO]^-$ or $[BF_4]^-$ as anion, have been included.[10] This behaviour has been attributed to the fact that packing may become more compact as the alternating positive and negative species become more even in size.

Ionic diffusion coefficients and conductivity. The transport properties are crucial when we consider the reaction kinetics in a synthetic process or ion transport in an electrochemical device. Despite this, the correlation

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between IL chemical structure and transport properties is still not completely understood. Probably, since ILs are concentrated electrolyte solutions, the interpretation of their transport properties is very complicated. Through pulse-gradient spin-echo NMR measurements, carried out on two 1-ethyl-3-methylimidazolium and two 1-butylpyridium ILs, in particular [emim][BF_4], [emim][Tf_2N], [bpy][BF_4] and [bpy][Tf_2N], it has been shown[38] that the two cations diffuse at almost the same rate as $[BF_4]^-$ but faster than $[Tf_2N]^-$. The sum of cationic and anionic diffusion coefficients for each IL follows the order [emim][Tf_2N] > [emim][BF_4] > [bpy][Tf_2N] > [bpy][BF_4].

The order of the magnitude of the diffusion coefficients contrasts well with that of the viscosity of each ionic liquid. The relationship between the self-diffusion coefficient, viscosity and molar conductivity was analyzed in terms of Stokes–Einstein and Nernst–Einstein equations, showing that, although the applicability of Stokes–Einstein equation [Eqn (1)] to ionic liquids has been questioned, the ionic diffusivity (D) of the above-mentioned ILs basically obeys the equation

$$D = kT/c\pi\eta r \qquad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, c is a constant (4–6) and r is the effective hydrodynamic or Stokes radius.

Furthermore, it has also been evidenced that the slopes of the relationships T/η versus D do not reflect the size of each species, suggesting that in these media the diffusion of an ion may depend on its counter-ion. In agreement with this hypothesis, the ratios between the molar conductivity, determined by impedance measurements, and the conductivity calculated from the NMR diffusion coefficients, applying the Nernst–Einstein equation without considering ion association, are smaller than unity. In particular, they range from 0.6 to 0.8 for [emim][BF_4] and [bpy][BF_4] and from 0.3 to 0.5 for [emim][Tf_2N] and [bpy][Tf_2N]. This behaviour has been considered as evidence that in $[BF_4]^-$ salts most of the individual ions contribute to the ionic conduction, whereas in the case of [emim][Tf_2N] and [bpy][Tf_2N] the presence of ion pairs and neutral ion aggregates has been proposed.[38] It is furthermore worth noting that these ratios do not vary much with temperature, showing that the structure of each IL does not change greatly with this parameter.

Partially in disagreement with the hypothesis of the presence of ion pairs in [emim][Tf_2N] is the comparative NMR study of [emim][TfO] and [emim][Tf_2N], which seemed to indicate the presence of relatively weak ionic interactions in the imide salt, whereas stronger interactions, resulting in ionic aggregation, occur in the case of [emim][TfO].[39]

The formation of ion pairs in ILs has often been invoked to explain the inconsistency between conductivity and diffusion coefficients. However, not all data support this hypothesis. When the relation of fluidity (η^{-1}) to conductance has been considered in terms of the Walden plot, it has been evidenced[40] that all the $[bmim]^+$ salts (the anions early examined were $[BF_4]^-$, $[Tf_2N]^-$, $[PF_6]^-$, $[TfO]^-$ and $[FeCl_4]^-$, but recently also chelated orthoborates have been included[10]) show a quasi-ideal behaviour, at variance with ILs based on the substituted ammonium cations. This behaviour has been considered as evidence of an ideal 'quasi' lattice structure, in which no ion pairs exist, at least for any statistically significant period of time.

Recently, the transport properties in a family of dialkylimidazolium ILs ([emim][Br], [emim][I], [emim][TfO], [emim][Tf_2N], [mmim][I], [pmim][I], [bmim][I], [hmim][I], [hpmim][I]) have been examined.[41] The four $[emim]^+$ salts bearing different anions presented very similar conductivities, despite the different melting-points. The diffusion coefficients, however, fell into two groups, with the halide salts showing considerably lower coefficients than the triflyl salts. In this case, the difference has been ascribed to differences in viscosity; halide salts have much higher viscosities. Although there is a correlation between viscosity and conductivity, the viscosity alone does not always account for the conductivity behaviour; ionic size and ion pairs can affect conductivity. For example, [emim][Tf_2N] and 1-butyl-3-ethylimidazolium bis(triflyl)amide [beim][Tf_2N] have similar viscosity but the former salt shows double the conductivity of the latter.

Surface tension. Surface tension may be an important property in multiphase processes. ILs are widely used in catalysed reactions, carried out under multiphase homogeneous conditions, that are believed to occur at the interface between the IL and the overlying organic phase. These reactions should therefore be dependent on the access of the catalyst to the surface and on the transfer of the material across the interface, i.e. the rate of these processes depends on surface tension.

In general, liquid/air surface tension values for ILs are somewhat higher than those for conventional solvents [$(3.3–5.7) \times 10^{-4}\,N\,cm^{-1}$], although not as high as for water, and span an unusually wide range. Surface tension values vary with temperature and both the surface excess entropy and energy are affected by the alkyl chain length, decreasing with increasing length. For a fixed cation, in general, the compound with the larger anion has the higher surface tension.[42] However, alkylimidazolium $[PF_6]^-$ salts have higher surface tensions than the corresponding $[Tf_2N]^-$ salts.

Refractive index. This parameter is related to polarizability/dipolarity of the medium and the excess molar refraction is used in the least-squares energy relationship of Abraham as a predictor of solute distribution. The values found for [bmim][X] salts are comparable to those

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Table 1. Density, viscosity, conductivity and refractive index for various ILs

	Density (25 ° C) (g ml^{-1})	Viscosity (cP) (T°C)	Conductivity (mS cm^{-1})	Refractive index, n
[emim][PF$_6$]	Solid			
[bmim][PF$_6$]	1.368[25a]	450 (25 °C)[25a]		
[hmim][PF$_6$]	1.292[25b]	585 (25 °C)[25a]		
[omim][PF$_6$]	1.237[25b]	682 (25 °C)[25a]		1.423[25]
[emim][Tf$_2$N]	1.519[25b]	28 (25 °C)[25a]	8.8[8]	1.423
[bmim][Tf$_2$N]	1.436[25b]	52 (25 °C)[25a]		1.427[25]
[hmim][Tf$_2$N]	1.372[25b]			
[omim][Tf$_2$N]	1.320[25b]			
[emim][NMs$_2$]	1.343[8]	787[8]	1.7[8]	
[bmim] [BF$_4$]	1.12[25a]	233 (25 °C)[25a]	1.7[25c]	1.429
[bmim] Cl	1.08[25a]	Solid	Solid	Solid
[hmim] Cl	1.03[25a]	716 (25 °C)[25a]		1.515[25a]
[omim] Cl	1.00[25a]	337 (25 °C)[25a]		1.505[25a]
[bmim] I	1.44[25a]	1110 (25 °C)[25a]		1.572[25a]
[bmim] [TfO]	1.29[25a]	90 (25 °C)[25a]	3.7[25c]	1.438[25c]
[bmim] [CF$_3$CO$_2$H]	1.21[25a]	73 (25 °C)[25a]	3.2[25c]	1.449[25c]
[em$_2$im][Tf$_2$N][a]	1.51[25c]	88 (20 °C)[25c]	3.2[25c]	1.430[25c]
[bmpyrr][Tf$_2$N][a]	1.41[8]	85 (25 °C)[8]	2.2[8]	
[bmpyrr][NMs$_2$]	1.28[8]	1680 (20 °C)[8]	0.07[8]	

[a] [em$_2$im] = 1-ethyl-2,3-dimethylimidazolium; [bmpyrr] = 1-butyl-1-methylpyrrolidinium.

for organic solvents.[25a] These data will be discussed later in more detail.

The above properties for various ILs are summarized in Table 1.

Solubility in water. The hydrophilic/hydrophobic behaviour is important for the solvation properties of ILs as it is necessary to dissolve reactants, but it is also relevant for the recovery of products by solvent extraction. Furthermore, the water content of ILs can affect the rates and selectivity of reactions. The solubility of water in ILs is, moreover, an important factor for the industrial application of these solvents. One potential problem with ILs is the possible pathway into the environment through wastewater.

Extensive data are available on the miscibility of alkylimidazolium ILs with water. The solubility of these ILs in water depends on the nature of the anion, temperature and the length of the alkyl chain on the imidazolium cation. For the [bmim]$^+$ cation the [BF$_4$]$^-$, [CF$_3$CO$_2$]$^-$, [NO$_3$]$^-$, [NMs$_2$]$^-$ and halide salts display complete miscibility with water at 25 °C. However, upon cooling the [bmim][BF$_4$]–water solution to 4 °C, a water rich-phase separates. In a similar way, 1-hexyl-3-methylimidazolium hexafluorophosphate, [hmim][PF$_6$], shows a low solubility in water even at 25 °C. [PF$_6$]$^-$, [SbF$_6$]$^-$, [NTf$_2$]$^-$, [BR$_4$]$^-$ salts are characterized by very low solubilities in water, but 1,3-dimethylimidazolium hexafluorophosphate is water soluble.[25]

Also, the ILs which are not water soluble tend to adsorb water from the atmosphere. On the basis of IR studies it has been established[43] that water molecules absorbed from the air are mostly present in the 'free' state, bonded via H-bonding with [PF$_6$]$^-$, [BF$_4$]$^-$, [SbF$_6$]$^-$, [ClO$_4$]$^-$, [CF$_3$SO$_3$]$^-$ and [Tf$_2$N]$^-$ with a concentration of the dissolved water in the range 0.2–1.0 mol dm^{-3}. Most of the water molecules should exist in symmetrical 1:2 type H-bonded complexes: anion$\cdots$HOH$\cdots$anion. The strength of H-bonding between anion and water increases in the order [PF$_6$]$^-$ < [SbF$_6$]$^-$ < [BF$_4$]$^-$ < [Tf$_2$N]$^-$ < [ClO$_4$]$^-$ < [NO$_3$]$^-$ < [CF$_3$CO$_2$]$^-$.

Voltammetric studies have furthermore suggested[3g] that nano-inhomogenity can be generated by the addition of controlled amounts of water to water-immiscible ILs. The presence of 'nano-structures' in the wet liquids could allow neutral molecules to reside in less polar regions and the ionic species in the more polar regions. Wet ionic liquids should not be considered as homogeneous structures (solvents) but have to be regarded as nano-structures with polar and non-polar regions.[3g]

A study of structure of [bmim][BF$_4$] and its interaction with water has recently been performed also through intermolecular nuclear Overhauser enhacement (NOEs) experiments.[28b] On the basis of the integration of ROESY cross peaks relating to water–imidazolium protons, it has been suggested that at low water content the interaction with water is specific and localized at H-2, H-4, and H-5. At higher water contents the interaction of water with all the other protons increases and the system seems to pass from a selective to a less defined, non-selective solvation. A small positive NOE was also detected on the water signal, suggesting that water can act as a hydrogen-bonding donor towards the [BF$_4$]$^-$ anion. These data are in agreement with a progressive change in the IL structure. The presence of water probably replaces progressively the cation–anion interaction with hydrogen

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bonds involving water as acceptor towards the cation and as a donor towards the anion. In the presence of water, the IL has a different organization characterized by a looser imidazolium–imidazolium association.

The interaction between water and ILs has been investigated also through theoretical calculations. Molecular dynamics simulations of mixtures of 1,3-dimethylimidazolium ILs ([mmim]Cl and [mmim][PF_6]) and water have been performed[44] as a function of the composition. In both liquids, calculations indicate that water molecules tend to be isolated from each other in mixtures with more ions than water molecules. Only when the molar proportion of water reaches 75% is a percolating network of water found as well as some isolated molecules and small clusters. Considering that similar results were obtained both for [mmim]Cl and [mmim][PF_6], the authors conclude[44] that calculations suggest that in ILs the difference between hydrophilic and hydrophobic behaviour is not reflected in microscopic properties.

Microscopic physical properties

Polarity. The key features of a liquid that is to be used as solvent are those which determine how it will interact with potential solutes. For molecular solvents, this is commonly recorded as the 'polarity' of the pure liquid, and is generally expressed by its dielectric constant. ILs can be classified, as all the other solvents, on the basis of their bulk physical constants, reported above. At variance with molecular solvents, however, dielectric constants cannot be used in the quantitative characterization of *solvent polarity*. Actually, this scale is unable to provide adequate correlations with many experimental data also in the case of molecular solvents, and the quantitative characterization of the 'solvent polarity' is a problem not completely solved even for molecular solvents.

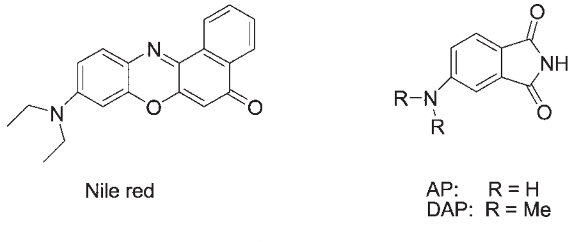
The exact meaning of 'solvent polarity' is complex, since this term takes into account all the possible microscopic properties responsible for all the interactions between solvent and solute molecules (e.g. Coulumbic, directional, inductive, dispersion, hydrogen bonding, electron pair donor and electron pair acceptor forces), excluding such interactions leading to definite chemical alterations on the solute.

For decades, in the case of molecular solvents, attempts have been made to develop empirical solvent polarity scales, which should help to to explain differences in solvent-mediated reaction pathways, reaction yields, synthesis product ratios, chromatographic retention and extraction coefficients. Empirical polarity parameter scales were described by observing the effect of the solvent on solvent-dependent processes, such as the rate of chemical reactions, the absorption of light by solvatochromic dyes and partition methods.[45] These approaches have been applied also to ILs and both solvatochromic and fluorescent dyes, and also partition coefficients, have been utilized to determine the polarity of these new solvents.

It is evident, from the data reported below, that the determination of the polarity of ILs is not easy, and the correlation between 'polarity' and IL structure and the comparison between ILs polarity and molecular solvents polarity are extremely difficult. At variance, these correlations may be extremely important considering the number of potential ILs. Generally, the chemist chooses a solvent on the basis of its polarity; ILs are often used in a completely casual fashion.

ILs–solvatochromic probe interactions. Studies of solute–solvent interactions by means of solvatochromic probes are generally easy to perform, and they may be convenient if the interpretation is carefully considered. Generally, each probe is sensitive to a particular kind of interaction (hydrogen bonding, dipolarity/polarizability, etc.) but solvent polarity arises from the sum of all possible intermolecular interactions, and therefore different probes can give different polarity scales.

Neutral probes: Nile red and aminophthalimides. The first experiment using a solvatochromic dye, in particular Nile red (Scheme 4), was carried out[46] by Carmichael and Seddon on a series of 1-alkyl-3-methylimidazolium ILs. The visible absorption band for Nile red displays one of the largest solvatochromic shifts known. This probe is most likely sensitive to changes in solvent dipolarity/polarizability, although exactly which factors dominate the shift in its absorption maximum is unclear. The values found for a number of 1-alkyl-3-methylimidazolium ILs show[30,46,47] that the polarity of these salts is comparable to that of short-chain alcohols. The range of values is narrow and the small variations in polarity seems to be determined by the anion in the case of ILs containing short 1-alkyl groups, and by the cation for those containing long 1-alkyl groups. For the [bmim]$^+$ ILs, the polarity decreases through the series $[NO_2]^- > [NO_3]^- > [BF_4]^- > [NTf_2]^- > [PF_6]^-$. The decrease in polarity correlates with anion size, i.e. with the effective charge density. The anomalous behaviour of $[Tf_2N]^-$ has been attributed to the partial charge delocalization within this anion. The presence of some functional groups (OH or OR) on the alkyl chain of the imidazolium cation[47] is able



Scheme 4

to vary the polarity of the corresponding salts over a wide range.

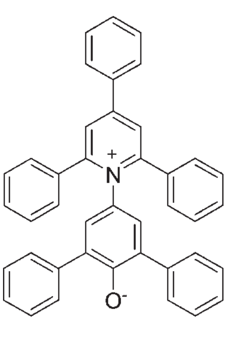
It is noteworthy, however, that the data on polarity obtained using other neutral solvatochromic dyes show some variability. For example, a different polarity trend has been found when two fluorescent neutral probes, 4-aminophthalimide (AP) and *N*,*N*′-dimethyl-4-aminophthalimide (DAP)(Scheme 4), have been used with a series of ILs.[48]

According to these latter probes, [bmim][PF_6] is more polar than acetonitrile and less polar than methanol. The imidazolium salts are more polar than pyridinium and the polarity of *N*-butylpyridinium tetrafluoroborate is near that of acetonitrile; furthermore, with these probes the replacement of the counter anion, $[PF_6]^-$ by $[NO_3]^-$ does not change the apparent polarity of the medium, in contrast to results with Nile red.

$E_{T(30)}$ values. Probably the most widely used empirical scale of polarity is the $E_{T(30)}$ scale, where $E_{T(30)}$ (in kcal mol^{-1}; 1 kcal = 4.184 kJ) = $28\,592/\lambda_{max}$ (in nm) and λ_{max} is the wavelength maximum of the lowest energy π–π^* absorption band of the zwitterionic Reichardt's dye. Often a normalized scale of $E_{T(30)}$ polarity, E_T^N, obtained by assigning water the value of 1.0 and tetramethylsilane zero, is used.

Because of its structure (Scheme 5), the solvatochromic shift of this probe is strongly affected by the hydrogen-bond donor ability of the solvent, which stabilizes the ground more than the excited state. The $E_{T(30)}$ scale is therefore largely, but not exclusively, a measure of hydrogen-bonding acidity of the solvent system.

The E_T^N values of several ILs are reported in Table 2. The alkyl chain length for the 1-alkyl-3-methylimidazolium ILs hardly affects the E_T^N values, which are similar to that for ethanol ($E_T^N = 0.65$), but the introduction of a methyl at C-2 reduces the solvent polarity.[49] These data are in agreement with the often proposed ability of the proton at C-2 to give hydrogen bonding and with the presumption that changes in E_T^N values are dominated by the hydrogen-bonding acidity of the solvent. The values for 1,2,3-trialkylimidazolium ILs are similar to those characterizing the pyrrolidinium salts and not very far from the value reported for acetonitrile ($E_T^N = 0.47$). Alteration of the anion ($[PF_6]^-$, $[BF_4]^-$, $[TfO]^-$) has very little effect on the E_T^N values, with the exception of [bmim][Tf_2N], which seems to be less polar than [bmim][PF_6].



Reichardt's dye

Scheme 5

Table 2. Kamlet–Taft solvent parameters for several ILs

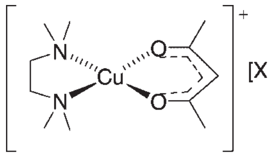
	E_T^N	π^*	α	β	Ref.
[bmim][BF_4]	0.67	1.047	0.627	0.376	52
[bmim][PF_6]	0.669	1.032	0.634	0.207	52
[bmim][TfO]	0.656	1.006	0.625	0.464	52
[bmim][Tf_2N]	0.644	0.984	0.617	0.243	52
[bm_2im][BF_4][a]	0.576	1.083	0.402	0.363	52
[bmpyrr] [Tf_2N]	0.544	0.954	0.427	0.252	52
[bm_2im] [Tf_2N]	0.541	1.010	0.381	0.239	52
[omim][PF_6]	0.633				49
[omim] [Tf_2N]	0.629				49
[om_2im] [Tf_2N][a]	0.525				49
[om_2im] [BF_4]	0.543				49

[a] [bm_2im] = 1-butyl-2,3-dimethylimidazolium; [om_2im] = 1-octyl-2,3-dimethylimidazolium.

Acetylacetonatotetramethylethyldiaminecopper(II) tetraphenylborate or perchlorate. Hydrogen bonding between the cation of IL and the solute is not however, the sole interaction of importance in these ionic media. The acetylacetonatotetramethylethyldiaminecopper(II) salts, [Cu(acac)(tmen)][X] (Scheme 6), are known to provide a good correlation between the donor number (DN) of a solvent and the value of λ_{max} for the lowest energy d–d band, arising from changes in the splitting of the d-orbitals as the solvent coordinates at the axial sites on the metal centre. It therefore gives a quantitative measure of the nucleophilic properties of electron pairs donor solvents.

Although only few ILs have been tested using this probe, the data show[49] that, for a given anion, there is no dependence of λ_{max} on the cation present. This suggests that the position of λ_{max} is in this case completely anion dependent and the cation plays no part in the nucleophilicity order, which is $[PF_6]^- < [Tf_2N]^- < [TfO]^-$. The nucleophilicity of these salts is, furthermore, much lower than that of alcohols.

Therefore, considering also the indications arising from Reichardt' dye, 1,3-dialkylimidazolium salts seem



X = BPh_4 or ClO_4

Scheme 6

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to have a hydrogen-bonding donor ability similar to that of short-chain alcohols but a much lower nucleophilic character.

Abboud–Kamlet–Taft parameters. It is evident from the data reported above that the determination of the polarity of ILs using a single solvatochromic probe is difficult. Evidence for the complexity in the interpretation of the values arising from solvatochromic measurements can be obtained by a recent investigation in which the behaviour of several well-established solvent polarity probes dissolved in an IL was evaluated.[50] In particular, the dipolarity of a representative IL, [bmim][PF_6], was measured using both absorbance (Reichardt's betaine dye) and fluorescence (pyrene, dansylamide, Nile red, 1-pyrenecarbaldehyde) solvatochromic probes. The results indicate that, in the case of pyrene and 1-pyrenecarbaldehyde, the [bmim][PF_6] microenvironment immediately surrounding the probe is similar to that of acetonitrile and DMSO. Dansylamide in the same IL senses a microenvironment similar to that of acetonitrile. However, calculated $E_T(30)$ values indicate a polarity similar to that of ethanol, while Nile red (in this experiment it was used as a fluorescence probe) shows that the polarity of the solvent in the immediate vicinity of the probe is similar to that of neat water and 90% glycerol in water.

More than 20 years ago, Abboud, Kamlet and Taft proposed an interesting system to separate non-specific effects of the local electrical fields from hydrogen-bonding effects. Based on the comparison of the effects on the UV–visible spectra of sets of closely related dyes, they evaluated some solvent properties, in particular, dipolarity/polarizability (π^*), H-bond basicity (β) and H-bond acidity (α).[51] Recently, Crowhurst *et al.* applied[52] the Abboud–Kamlet–Taft method, using three solvatochromic dyes (Reichardt's dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline), to determine the solvent parameters π^*, β and α of several imidazolium and pyrrolidinium ILs. In Table 2 are reported the normalized values; dimethyl sulfoxide for π^*, hexamethylphosphoramide for β and methanol for α have values of 1.

The π^* values found by Crowhurst *et al.* for the investigated ILs indicate that the dipolarity or polarizability of these salts is higher than that of alkyl chain alcohols. Although differences between the ILs are small, both the cation and anion affect this parameter. At variance, the H-bond basicity of the examined ILs covers a large range, from acetonitrile to lower β values. The anion nature dominates this parameter. Finally, the H-bond acidity is determined by the cation, even if a smaller anion effect is present. In particular, it has been suggested that the α values are controlled by the ability of the cation to act as an H-bond donor, moderated by the ability of the anion to act as an H-bond acceptor; a strong anion–cation interaction reduces the ability of the cation to hydrogen bond with the substrate. The H-bond acidity of the investigated ILs is generally less than those of water and of most short-chain alcohols but greater than those of many organic solvents, such as aniline.

Partition methods

Retention times in reverse GC. Starting from the consideration that a single 'polarity'/'solvent strength'/'interaction' parameter is not sufficient to explain the variation in experimental results in many IL-mediated processes, Anderson *et al.* recently applied[53] another 'multi-parameter–polarity approach' to quantify the polarity of ILs. In particular, 17 ILs (imidazolium and alkylammonium salts) where characterized on the basis of their distinct multiple solvation interactions with probe solute molecules using ILs as a GC stationary phase (inverse GC). The characterization of ILs, at relatively high temperatures (40, 70 and 100 °C), was performed applying the free energy relationship of Abraham [Eqn (2)]. This equation describes the solvation of a solute as a process occurring in three stages: (1) a cavity of suitable size is created in the solvent, (2) the solvent molecules reorganize around the cavity and (3) the solute is introduced in the cavity and various solute–solvent interactions are allowed to take place.

$$\log k = c + rR_2 + s\pi_2^{\mathrm{H}} + a\alpha_2^{\mathrm{H}} + b\beta_2^{\mathrm{H}} + l\log L^{16} \qquad (2)$$

where R_2 is an excess molar refraction calculated from the solute's refractive index; π_2^{H} is the solute dipolarity/polarizability; α_2^{H} and β_2^{H} are the solute hydrogen bond acidity and basicity; L^{16} is the solute gas–hexadecane partition coefficient; and k is the relative retention time, determined chromatographically. By multiple linear regression analysis the interaction parameter coefficients (r, s, a, b, l) were determined.

The experimental results showed that the dominant interactions are strong dipolarity (s), hydrogen-bond basicity (a) and dispersion forces (l). Whereas the dispersion forces are nearly constant for all ILs examined, the hydrogen-bond basicity (a) and dipolarity (s) seem to vary for each IL. Generally, when the hydrogen-bond basicity (a) is very high ([bmim][Cl], [bmim][SbF_6]) the hydrogen bond acidity (b) is negative. The anion controls the hydrogen bond basicity (a); ILs with the same cation $[\mathrm{bmim}]^+$ and different anions show different basicity and dipolarity, while ILs bearing different cations with the same anion $[\mathrm{Tf_2N}]^-$ are characterized by small differences in hydrogen-bond basicity and dipolarity. It is worth noting that this investigation seems also to indicate that only three ILs exhibit a significant hydrogen bond acidity (b), with [bmim][Tf_2N] having the higher value, and this parameter being affected by the nature of both the anion and cation. Furthermore, only three ILs {[bmim]Cl, 1-hexyl-2,3,4,5-tetramethylimidazolium bis(triflyl)imide [hm_4im][Tf_2N] and 1-octyl-2,3,4,5-tetramethylimidazolium bis(triflyl)imide, [om_4im][Tf_2N]} were able to interact with the probe via non-bonding or π-electrons, affecting the parameter r.

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In conclusion, with the present state of the art, the comparison between the polarities of ILs and molecular solvents is not easy. Although it is possible to state that the E_T^N values of the $[bmim]^+$ ILs are similar to those of short-chain alkyl alcohols, the values of π^*, α and β are different. Therefore, ILs are not solvents similar to alcohols. They are surely polar solvents, characterized by a high dipolarity/polarizability, that can act as hydrogen-bond donors and acceptors. All the methods used to investigate the polarity of ILs agree that the basicity of the investigated ILs depends on the anion. At variance, more controversial is the hydrogen-bond acidity of these salts. Surely it is a property of cation, but it is modulated by the anion. Furthermore, it is significantly affected by the presence of water and this aspect will be discussed later in more detail.

IL polarity in the presence of other 'solvents'

Effect of added water and ethanol. The use of ILs as solvents implies also the knowledge of their behaviour in the presence of other compounds, in particular water, other organic solvents and supercritical CO_2, the last often being used for product extraction. Furthermore, to increase the efficiency of the processes (syntheses, extractions, separations) carried out in ILs, sometimes cosolvents are added and these affect the physical properties of ILs.

Water is often present in ILs as an unwanted impurity, as a consequence of their hygroscopic nature, and the presence of even small amounts of water can modify not only the physical properties of ILs (viscosity, density, etc.) but also the polarity. The recently reported determination of the polarity of [bmim][PF_6] and [hmim][PF_6] (1-hexyl-3-methylimidazolium hexafluorophosphate) through the partition coefficients between water and the investigated ILs may be considered a determination of the polarity of these ILs in the presence of water. It should be noted that, under these conditions, the solvent parameters found for [bmim][PF_6] and [hmim][PF_6] were similar to, but not identical with, those obtained using GC retention times.[54] Both ILs are characterized by a small *s* coefficient, indicating that these salts have practically the same dipolarity/polarizability as that of water. However, they are less basic than water (about the same as a typical ester), while the *b* coefficient lies between those of ethylene glycol and trifluoroethanol, showing a strong hydrogen-bond acidity. In particular, these latter data are in disagreement with the results reported above, obtained using ILs as a GC phase, which showed that the H-bond acidity of [bmim][PF_6] was almost zero.

The same authors, however, found evidence[54] that the physico-chemical properties of pure ILs, as determined by GC analysis, may not be the same as those of ionic liquids in water systems because, in the latter case, the ionic liquids are saturated with water and water is able to change markedly the properties of these media. In agreement with this latter hypothesis are also the 'energy of transition' $E_T(30)$ values and the Abboud–Kamlet–Taft solvent parameters recently determined for [bmim][PF_6] as a function of temperature (10–70 °C) and water content [from 50 ppm or less, 'dry', to 2% (v/v), 'wet'].[55]

This study showed that dry [bmim][PF_6] exhibits a hydrogen-bond donor strength in the range of short-chain alcohols, with a linear temperature dependence. Addition of water (2%) significantly alters the solvent's hydrogen-bond donor capacity and the temperature dependence is nearly double. At variance, for both dry and wet [bmim][PF_6], the parameter β is not significantly affected by the addition of water, and in both cases the H-bond acceptor ability (intermediate between water and acetonitrile) is slightly dependent on temperature. Finally, the π^* parameters for wet and dry [bmim][PF_6] are higher than those of short-chain alcohols but lower than that of water, and they show a strong temperature dependence.

The study of the physico-chemical properties that depend on solute–solvent and solvent–solvent interactions is, however, much more complex in mixed solvent systems than in pure solvents. On the one hand, the solute can be preferentially solvated by any of the solvents present in the mixture; on the other, solvent–solvent interactions can affect the solute–solvent interactions. Preferential solvation may arise whenever the bulk mole fraction solvent composition is different from the solvation microsphere solvent composition. The response of spectroscopic probes is dependent on the composition in the solvation microsphere and therefore they are able to measure eventual preferential solvation phenomena occurring in the solvent mixtures. Despite the difficulties arising from the use of spectrophotometric probes to determine IL polarity, these probes offer a versatile mean to investigate the local microenvironments, dynamics and organization within ILs.

When the behaviour of four solvatochromic probes [pyrene, Reichardt's dye, 1-pyrenecarboxaldehyde and 1,3-bis(1-pyrenyl)propane] was investigated[56] in [bmim][PF_6] containing increasing small amounts of water, it was found that, although the presence of water has a profound effect on the last three probes, the spectrum of pyrene was not affected. Pyrene lacks any functional group other than the fused benzene rings and the polarity scale based on this probe is related to the static dielectric constant and the refractive index of the solvent. It is therefore possible that the presence of water within [bmim][PF_6] cannot be evidenced using this probe; the pyrene cybotactic region is probably rich in [bmim][PF_6] compared with the bulk. The aldehyde functional moiety on 1-pyrenecarbaldehyde and the zwitterionic nature of Reichardt's dye may instead favour a water-rich cybotactic region and significant shifts on addition of water may be observed using these probes. At variance, the non-polar 1,3-bis(1-pyrenyl)propane should be preferentially solvated by [bmim][PF_6] but in this case the reduction in the bulk viscosity of [bmim][PF_6], due to the presence of the cosolvent may

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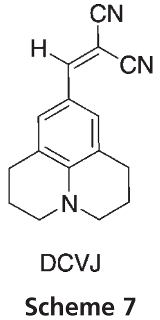
result in an increased intramolecular excimer formation efficiency of this probe.

A preferential solvation by IL, or by the other component of the mixture, was observed also when the same four solvatochromic probes were used to study the behaviour within binary [bmim][PF_6] and ethanol systems.[57] Also in this case, while pyrene is probably surrounded by more [bmim][PF_6] than that being present in the bulk solution, 1-pyrenecarboxyaldehyde and 1,3-bis(1-pyrenyl)propane are preferentially solvated by the other component, ethanol.

Effect of supercritical CO_2. On the basis of the previously discussed data, it is evident that the addition of appropriate amounts of water, or other cosolvents, can modulate the properties of ILs. In this context, it is worth noting the recent spectrophotometric study of Lu *et al.* on the solvent properties of mixtures of [bmim][PF_6] and supercritical CO_2.[58] The solvatochromic behaviour of *N*,*N*-dimethyl-4-nitroaniline has been used to measure the π^* parameter and the extent of volume expansion in mixtures of [bmim][PF_6] and supercritical CO_2 as function of temperature and CO_2 pressure. The effects of added CO_2 on the microviscosity of [bmim][PF_6] were evaluated using 9-(dicyanovinyl)julonilide (DCVJ), (Scheme 7).

The insignificant effect that substantial amounts of CO_2 have on the apparent polarity of [bmim][PF_6], given by the π^* parameter, suggests a preferential solvation of the probe solute, *N*,*N*-dimethyl-4-nitroaniline, by the IL. The molecular interaction between the IL and the polar solute appears to be dominant over the weak solute–CO_2 interaction, suggesting that the competitive IL–solute interaction might result in selective aggregation of [bmim][PF_6] around the indicator molecules. On the other hand, spectrophotometric measurements carried out using 9-(dicyanovinyl)julolidine as the fluorescent probe show that the microviscosity in the vicinity of the solute is dramatically reduced on increasing the CO_2 pressure. The addition of CO_2 seems, therefore, to have little impact on the polarity of [bmim][PF_6] when polar solutes are dissolved, owing to the preferential solvation of the solutes by [bmim][PF_6], yet it results in a strong reduction in microviscosity. This latter effect may be significant for promoting mass transport and facilitating separation for normal viscous ILs.



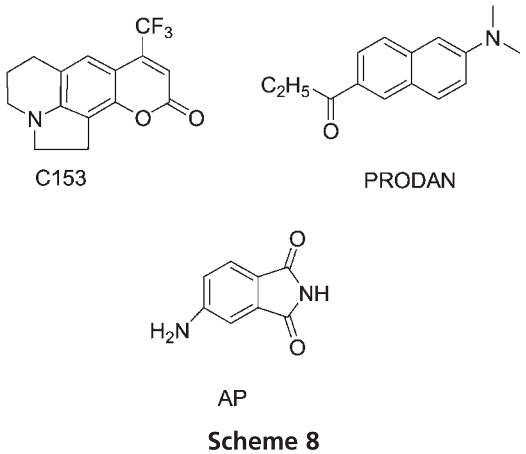
DCVJ

Scheme 7

Different, however, is the situation in the presence of no polar solutes. Mixtures of [bmim][PF_6] and CO_2 show a moderate decline in the value of I_1/I_3, determined using the fluorescent non-polar pyrene, as the pressure of CO_2 is increased,[59] which suggests a decrease in the local dipolarity surrounding pyrene on increasing the CO_2 pressure. The discrepancy between these two studies may be easily explained considering the existence of a solute-specific solvent effect; a polar solute is characterized by a cybotactic region rich in [bmim][PF_6], and a non-polar solute by a region rich in CO_2.

Solvent interactions within binary ILs mixtures. Several attempts have been made to improve the properties of ILs, including the search for new and unusual ILs in addition to the addition of 'green' cosolvents, such as water, ethanol and supercritical CO_2. However, the use of binary IL mixtures has hardly been investigated, although it has been shown that mixing two or more different ILs may confer on the mixture improved and unexpected properties.[60] Using several solvatochromic probes [pyrene, 1-pyrenecarboxaldehyde, Reichardt's dye, 4-nitroaniline, *N*,*N*-dimethyl-4-nitroaniline and 1,3-bis(1-pyrenyl)propane], it has been found that IL mixtures present some features, such as prevalence of H-bond donor and anion coordinating effects, which are not readily apparent from those of the individual components. Unfortunately, no data have been reported on the ability of these mixtures to affect organic reactivity.

Solvation dynamics and liquid structure. All the data mentioned above are focused on static aspects of solute solvation; however, a complete understanding of the effect of ILs on chemical reactions requires also an understanding of the microscopic dynamics of these materials. Recently, several papers on time-dependent solvation in ILs have appeared.[61,62] In particular, the time-resolved fluorescence behaviour of electron donor–acceptor (EDA) probe molecules, such as coumarin 153 (C153), 6-propionyl-2-dimethylaminonaphtalene (prodan) and 4-aminophtalimide (AP) (Scheme 8), has been studied in several ILs.



Scheme 8

Since the time-dependent changes in the fluorescence spectra of these systems are the result of solvent-induced relaxation of the fluorescent state of the molecules, these experiments are able to provide useful information on how molecules reorganize after an instantaneous change in the dipole moment of the solute upon absorption of photons. The studies carried out on ILs have indicated that, first, the measured rotation times of the investigated probes in ILs are considerably slower than those in polar molecular solvents, and the difference may be completely accounted for by the higher viscosity of these solvents. Furthermore, all examined ILs ([bmim][BF_4], [bmim][Tf_2N], [emim][Tf_2N], [emim][BF_4], [bmim][PF_6]) show biphasic dynamics occurring on picosecond and nanosecond time-scales. It has therefore been proposed that the process of solvation of a dipolar species in ILs is fundamentally different from that in conventional molecular solvents. In polar solvents, solvation arises owing to the rearrangement of the solvent molecules around an instantaneously created dipole upon absorption of photon. In ILs the solvation is possible owing to the motions of the ions. The ionic solvation is very slow and depends on the viscosity of the media. Related to the biphasic dynamics, two different explanations have been given contemporaneously by two different groups working in this field. An initial motion of anions and a collective motion of anions and cations were proposed by Karmar and Samanta,[61] whereas Maroncelli's group[62] considers that both the fast and slow components of solvation dynamics involve primarily translational motions of both cations and anions. The fast component should entail motions that do not require significant structural rearrangements of the neighbouring molecules, whereas the slow component does. Molecular dynamics studies have further confirmed that the solvation dynamics in ILs are multimodal and they occur over a remarkably wide time window (femtoseconds to nanoseconds).[63]

Recently, Maroncelli's group extended[64] the study of solvation dynamics by measuring the steady-state and the time-resolved fluorescence spectra of coumarin 153 in four ILs differing in cation structure, [bmim][Tf_2N], 1,2-dimethyl-3-propylimidazolium bis(trifyl)imide, [pm_2im][Tf_2N], methyltributylammonium bis(trifyl)imide, [N_{4441}][Tf_2N], and trihexyl(tetradecyl)phosphonium chloride, [$P_{666(14)}$]Cl. This investigation showed that 'the ultrafast component, which appeared to be ubiquitous in previous work, was absent in the two ILs that are not based on the imidazolium cation'. Considering these new results, the authors conjecture that the ultrafast component in imidazolium ILs is due to small-amplitude motions of one or more cations in close contact with the solute, facilitated by coplanar arrangements of the solute with the imidazolium moiety. At variance, the slower component is correlated with solvent viscosity. This interpretation has found further experimental support in a recent study of the solvation dynamics of coumarin 153 in several alkylphosphonium ILs. This investigation, moreover, suggested that the solvation time may be set by the slowest moving species present, which just happens to be the cation in all of the systems studied so far.[65]

A key to the comprehension of the molecular dynamics of these materials is generally considered[66] to be their liquid structure. NMR measurements indicate that the chemical shifts of imidazolium cations are anion and concentration dependent, suggesting the formation of ion pairs and the presence of a high degree of order. Kinetic data, related to some photoelectronic reactions (these data will be discussed in more detail later), show large values of the entropy of activation, suggesting that solvent ions are freed up on formation of the encounter complex and, in turn, that ILs are highly ordered.

Consistent with a high degree of order, which increases on increasing the length of the alkyl chain on the imidazolium cation, are also the data arising from a recent investigation carried out on several 1-alkyl-3-methylimidazolium bis(trifyl)imides at room temperature and ambient pressure, using heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES). OHD-RIKES is a non-linear optical technique that is widely used to study liquid-state dynamics. The OHD-RIKES response of a liquid can be used to calculate a dipolar solvation–time correlation function that can be compared with the solvent response obtained from in time-dependent fluorescence spectra, reported above. Alternatively, the OHD-RIKES response can be converted to a spectral density, that gives the polarizability-weighted distribution of low-frequency modes in the liquid. The spectral densities obtained from OHD-RIKES experiments in ILs are in general higher in frequency, broader and slightly more structured than in simple molecular liquids, suggesting a high degree of association or local order in these liquids. Furthermore, they appear to be composed of overlapping bands. The presence of two bands has been proposed[66a] by Hyun *et al.* on the basis of a fitting procedure for the reduced spectral densities of five [Rmim][Tf_2N] salts (R = ethyl, butyl, pentyl, hexyl and octyl). On the other hand, more recently, three bands have been identified in the reduced spectral densities of [bmim][TfO], [bmim][Tf_2N], [bmim][PF_6], [bm_2im][Tf_2N], [omim][Tf_2N].[66b] The relative contributions of these bands depend in the series of 1-alkyl-3-methylimidazolium salts on the alkyl chain and counter anion. Based on a theoretical analysis, the three bands have been attributed[66b] to librational motions of the imidazolium ring in three structures differing from each other in the location of the anion. The most representative structure should be that having the anion lying on the C—H bond between the two nitrogen atoms of imidazolium ring. Furthermore, considering that the three peaks are completely separated, the authors suggest[66b] that any eventual change in the position of the anion with respect cation must occur on time-scales longer that 2 ps. Therefore, if a typical chemical reaction takes place on a time-scale of ~1 ps, the position of the anion with respect to the cation can be considered stable during this interval of time.

IONIC LIQUIDS AND REACTION RATES

Although one of the classical methods to determine the microscopic physical properties of a solvent is to measure quantitatively the ability of the medium to affect the organic reactivity, few kinetic data have been reported for reactions carried out in ILs, at least in comparison with the large number of papers published on ILs overall. Below are discussed a few examples in which quantitative data (kinetic or equilibrium constants) have been reported.

Effect of cation–anion association and of the presence of cavities in the ILs on organic reactivity

Electron-transfer reactions. At variance with other organic reactions, electron transfer processes in ILs have been widely investigated and several quantitative studies have been published in recent years.[67] The high yield of electrons and holes generated by radiolysis of pure ILs and further trapping by cations and anions has shown that these solvents may be excellent media for the generation of radical ions. Moreover, as the ILs show a tendency for supercooling, resulting in the formation of more viscous liquids and finally transparent glasses without crystallization, they have been used for the generation and spectroscopic characterization of unstable solute radical ions and then, after thermal annealing of the solvent up to ambient temperature, to study the reactivity of these transient species.[67a]

Nevertheless, the reaction kinetics in several ILs, as studied by pulse radiolysis, have provided[67] important information about the properties of these new reaction media. First, the rate constants for the investigated electron transfer reactions in ILs are generally lower than those in water and in common organic solvents and this behaviour was attributed, in the case of diffusion-controlled reactions, to their high viscosity. On the other hand, also when the examined processes are slower than the diffusion constants,[67b,68] the experimental rate constants in ILs are lower than rate constants for the same reactions in acetonitrile and aqueous solutions. This seems to suggest that ILs do not behave as highly polar solvents. However, the activation parameters are closer to those measured in aqueous solution than in alcohols. On this basis, the authors suggest that polarity is not the sole parameter that determines the solvent effect on the rate constant; because reaction requires separation and reassembly of solvent molecules, the rate constants are better correlated with the solvent cohesive energy densities. ILs are highly ordered reaction media, and the activation energies for reactions carried out in ILs can be high because it is necessary to break the order of the medium to bring all the components to the reaction site.

The electron transfer reactions may, however, be affected by the solvent also through the change in the energy of solvation of the charged species. In this respect, on the basis of an extensive study on the formation and reaction of $Br_2^{\cdot -}$ radicals, the same authors found[67e] that ILs behave like aprotic organic solvents, with the energy of solvation of small ions being lower than in water and alcohols. The stability of $Br_2^{\cdot -}$ is indeed much higher in the examined IL ($[N_{4441}][Tf_2N]$) than in water and the rate constant for oxidation of chlorpromazine by $Br_2^{\cdot -}$ decreases on changing the solvent from water to IL.[67e] Furthermore, the rate constants show a poor correlation with typical solvent polarity parameters, but a reasonable correlation with hydrogen-bond donor acidity and with anion-solvation tendency parameters, suggesting that the change of energy of solvation of Br^- is the main factor that affects the rate constant of the reaction through its effect on the reduction potential of $Br_2^{\cdot -}$.

Another important feature, evidenced by these studies, is that the rate constants measured for the electron transfer processes in ILs are often higher than the diffusion-controlled rate constants, estimated from the viscosity of the employed IL ($k_{\mathrm{diff}} = 8000RT/3\eta$). Different explanations have been given for this experimental result. For example, the rate constants for electron transfer from *N*-butylpyridinyl radical ($BuPy^{\cdot}$) to methylviologen, 4-nitrobenzoic acid and duroquinone (DQ) were considerably higher than the estimated limits. In this case, since the $BuPy^{\cdot}$ radical was derived from the solvent cation by one-electron reduction, it was speculated[67b] that the increased rate of reaction was due to electron hopping through solvent cations.

However, rate constants that are higher than the diffusion limits have also been found for reactions that cannot involve such a mechanism, e.g. quenching of benzophenone triplet by naphthalene,[69] the reaction of solvated electrons with aromatic compounds[70] and the reaction of pyridinyl radicals ($bpy^{\cdot}$) with duroquinone (DQ) in $[N_{4441}][Tf_2N]$ (Scheme 9).[71]

$$\mathrm{bpy}^{\cdot} + \mathrm{DQ} \rightarrow \mathrm{bpy}^{+} + \mathrm{DQ}^{\cdot -}$$

Scheme 9

On the basis of these latter data, it has therefore been proposed[71] that the viscosity of ionic liquids, which determine the diffusion of whole molecules or ions, does not adequately represent the diffusion of reactants within ILs. It has therefore been suggested that the highly ordered structure of these salts may contain voids, and these voids can accommodate small solute molecules. Furthermore, since the chains present on the cations are flexible, they can move more rapidly than the whole

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cation, permitting rapid diffusion of solutes from one void to another.[71] Practically, ILs behave as polymer matrices.[72]

The formation of cavities (voids) in ILs has recently been studied via Monte Carlo simulations.[73] Analysis of cavity size distribution functions shows that ionic liquids exhibit a high tendency to form cavities, a property which seems to be correlated with the attractive interactions between ions and, in particular, with the tendency of ions to associate in ion aggregates. The tendency to form cavities that can accommodate solute molecules may also find experimental support in the formation of liquid clathrate phases. These latter have been observed in mixtures of aromatic hydrocarbons (benzene, toluene and xylenes) and common 1-alkyl-3-methylimidazolium salts.[74]

The presence of voids and the ability of small molecules to move within them have also been proposed recently to explain the reactivity of $H^{\cdot}$ atoms with aromatic solutes in ILs. Indeed, it has been shown[75] that the rate constants for reactions of pyrene and phenanthrene with $H^{\cdot}$ atoms are 10 times higher than for the corresponding solvated electron reactions, implying that the diffusion-limited rate constant for the $H^{\cdot}$ atom reaction is higher by one order of magnitude. Furthermore, for both substrates the trend in the examined IL, $[N_{4441}][Tf_2N]$, is opposite to that observed in water, suggesting that a small neutral species, such as the $H^{\cdot}$ atom, can move easily between voids within the IL, whereas the diffusion of solvated electron, being a charged species, is limited by its interaction with the ionic charges of the medium.

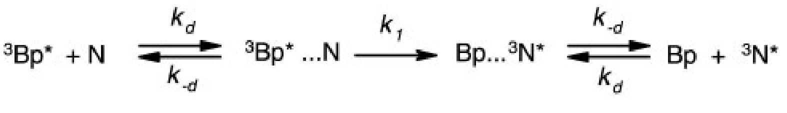
The high degree of order characterizing ILs has been invoked[69] also to explain the kinetic behaviour and the activation parameters characterizing the exothermic triplet energy transfer from benzophenone triplet (^{3}Bp*) to naphthalene (N). According to Scheme 10, at least three steps can be evidenced for this process. Initially, an encounter complex is formed with a bimolecular rate constant corresponding to diffusion control, k_d. This complex can then undergo an irreversible energy transfer, k_1, or can regenerate the reagents with a unimolecular rate constant, k_{-d}. Finally, ^{3}N* and Bp can diffuse apart with a rate constant k_{-d}. The overall bimolecular rate constant for ^{3}Bp* quenching by N is given by $k_q = k_d k_1/(k_{-d} + k_1)$. Provided $k_1 \gg k_{-d}$, this expression becomes $k_q = k_d$ and the reaction is diffusion controlled. In all the examined ILs the k_q values determined at several temperatures give activation energies within 10% of the activation energies for viscous flow, indicating that k_q values and activation parameters are those of a diffusion-controlled process. The reactions are, however, characterized by kinetic constants (k_d) which are an order of magnitude higher than those estimated from viscosity. Determination of Arrhenius parameters in the examined ILs and two conventional solvents, along with Andrade parameters for the same solvents (E_η and $\ln\eta$), has suggested that the differences between measured and estimated k_d are mostly due to the very large, solvent-dependent pre-exponential factors, A, which compensate for the large E_a values found in ILs.

The correlation between pre-exponential factors and activation energies for both kinetic constants, k_d, and viscosity values (η) gives rise to isokinetic behaviour, which has been interpreted as evidence that the probability of a diffusional jump is correlated with the amount of energy required to create a hole. This energy depends on the IL structure. Both E_a and A values show a significant dependence on the cation and anion; for any cation the E_a values are 12–15 kJ mol^{-1} higher for the $[PF_6]^-$ salts than the $[Tf_2N]^-$ salts and this behaviour has been considered to reflect the higher extent of ionic cross-linking characterizing the ILs bearing the smaller and more symmetrical $[PF_6]^-$ anion. On the other hand, this enhanced ionic cross-linking would result in a greater diffusing mass, and therefore a greater A, whilst creating large cavities for solutes to jump into. Finally, the increase in E_a associated with [omim]$^+$ vs [bmim]$^+$ substitution seems to indicate an important role of van der Waals interactions in the diffusion processes in these liquids, despite of the presence of strong electrostatic interactions between ions.

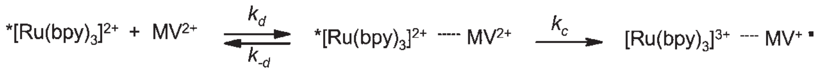
A large and positive entropy of activation, showing that the solvent ions are freed up on formation of an encounter complex, has also been found for the photoelectronic transfer from ruthenium tris(4,4′-bipyridyl), $[Ru(bpy)_3]^{2+}$, to methylviologen, MV^{2+} (Scheme 11).[76]

Once again, this behaviour has been considered as evidence that ionic liquids are highly ordered systems.

In conclusion, in agreement with other experimental measurements (see the first part), the kinetic and thermodynamic data arising from the electron-transfer reactions suggest highly ordered structures for ILs, also above their



Scheme 10



Scheme 11

melting-points. Furthermore, the presence of voids, able to contain substrates, makes these reaction media more similar to polymeric matrices than molecular solvents.

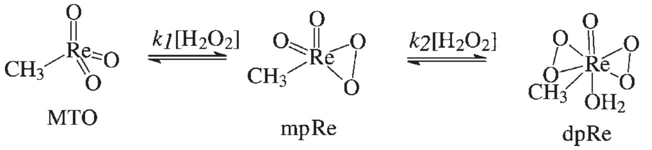
Effect of viscosity, H-bonding ability and ion-pairing on organic reactivity

MTO-catalyzed alkene oxidation. Kinetic investigations have been carried out also in the case of the reaction of methyltrioxorhenium (MTO) with hydrogen peroxide. MTO reacts with excess hydrogen peroxide to form two η_2-peroxo complexes, which are able to transfer an oxygen atom to suitable substrates.[77]

Solvent purity is of utmost importance for this type of kinetic measurement since the starting material, 1-alkylimidazole or pyridine, reacts with MTO to form yellow complexes, while bromide is oxidized by both peroxy complexes to hypobromite and then to Br_2.

The rate constants for the formation of the second complex (dpRe) from the first one (mpRe) (Scheme 12) have been determined in several ILs ([emim][BF_4], [bmim][BF_4], [bmim][NO_3], [bmim][OTf], [bpy][BF_4]) having different properties. The values found are, however, very similar and this behaviour has been attributed to the combination of several factors, including viscosity, coordination ability of the anion and hydrogen-bonding ability of the anion and cation. Furthermore, these solvents behave like acetonitrile at low water concentration. As [H_2O] increases, the reaction rate increases and the liquids behave more like aqueous solutions with high salt concentrations.

When dpRe was prepared in THF using urea hydrogen peroxide (UHP) as the oxidant, it was possible to determine the kinetic constants, k_4 and k_3, related to the reactions of two complexes with a serie of alkenes (Scheme 13).



Scheme 12

$$\begin{aligned} \text{dpRe} + \text{alkene} &\rightarrow \text{mpRe} + \text{epoxide} \quad k_4 \\ \text{mpRe} + \text{alkene} &\rightarrow \text{MTO} + \text{epoxide} \quad k_3 \\ \text{dpRe} &\rightarrow \text{mpRe} + H_2O_2 \quad k_{-2} \end{aligned}$$

Scheme 13

The values of k_4, measured in several ionic liquids, exceeded those observed in acetonitrile by one order of magnitude and were similar to those obtained in acetonitrile-water mixtures. The reactivity of styrenes in [bmim][BF_4] followed the expected trends for electrophilic oxygen transfer from rhenium complexes: styrene $<$ *trans*-β-methylstyrene $<$ α-methylstyrene. It is worth noting that the values of k_3 were only slightly higher than those in acetonitrile; therefore, in all examined ILs, at variance with aqueous acetonitrile, k_4 was higher (4.5 times) than k_3. The relative reactivity of mpRe and dpRe was, however, apparently dependent on the water content of the solvent; water contributes to the hydrogen bonding more with dpRe than with mpRe, because of the two peroxy groups, rendering dpRe less reactive.

Nucleophilic substitution reactions. The effect of solvent on nucleophilic substitution reactions has been widely investigated in molecular solvents starting from the fundamental studies of Hughes and Ingold.[78] A simple qualitative solvation model, considering only pure electrostatic interactions between ions or dipolar molecules in initial and transition states, was proposed by the authors to rationalize the solvent effect. Based on this model, the effect of the solvent on reactions of different charge types may be summarized as follows:

1. An increase in solvent polarity results in an increase in the rates of those reactions in which the charge density is greater in the transition states than in the initial reaction molecule(s).
2. An increase in solvent polarity results in a decrease in the rates of those reactions in which the charge density is lower in the transition state than in the initial reactants molecule(s).
3. A change in solvent polarity will have a negligible effects on the rates of those reactions that involve little or no change in the charge density on going from reactants to transition state.

S_N2 reactions between anions and neutral molecules are characterize by dispersal of charge on going from reactants to transition state and, in agreement with the above-mentioned model, generally the reaction rate decreases with increasing solvent polarity. Furthermore, the reaction rate is affected by the properties of the attacking anion, by its polarizability and its nucleophilicity (or basicity). The latter property is strongly dependent by the solvent. In the course of the activation process, the solvent shell of the nucleophile must be removed at the place of the attack, while a new solvent shell around the activated complex is formed. Hence, the activation energy will be higher, and the rate lower, the more strongly the molecules of the solvent shell are bound to the nucleophile. When considering the solvation of anions, molecular solvents are distinguished in two classes; protic and dipolar aprotic solvents. The main difference between these two classes lies in their ability to solvate ions. The traditional order of halide nucleophilicities,

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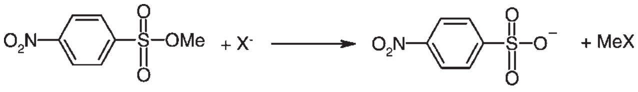


Scheme 14

$I^- > Br^- > Cl^-$, applies only when the nucleophile is deactivated through solvation by protic solvents, whereas the order $Cl^- > Br^- > I^-$ is observed in dipolar nonprotic solvents.

The relative nucleophilicities of chloride, bromide and iodide in ILs, and in particular in [bmim][Tf_2N], [bm_2im][Tf_2N] and [bmpyrr][Tf_2N] ([bmpyrr] = butylmethylpyrrolidinium), have been determined recently through the reaction of methyl *p*-nitrobenzenesulfonate with halides (Scheme 14).[79]

In molecular solvents this reaction can proceed either through discrete anions or through ion pairs. In ILs the reaction of discrete anions can be excluded; only anions coordinated by one or cations are present. The reactions in ILs are, however, greatly decelerated in comparison with dichloromethane, whether this is by the free ion or ion pairs, but they are much faster than in 2-hexafluoropropanol.

The experimental data show also that the reaction rates are not dependent on the viscosity of ILs alone. Furthermore, in [bmpyrr][Tf_2N] the nucleophilicity scale is $Cl^- > Br^- > I^-$, in agreement with the known gas-phase nucleophilicity trend. This behaviour suggests that the three halides interact similarly with IL. In [bmim][Tf_2N] the scale is $I^- > Br^- > Cl^-$, indicating that some influence of the IL is acting differentially on the three halides. [bm_2im][Tf_2N] is in some way intermediate, with nucleophilicity changing as $Cl^- > I^- > Br^-$.

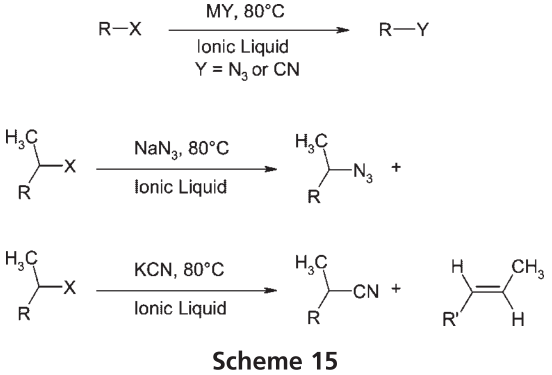
It is also noteworthy that the second-order rate constants for bromide are similar in the three ILs, and those of iodide are the same in the two imidazolium salts and only marginally lower in [bmpyrr]. However, those of chloride show a larger variation: the reaction rate increases in the order [bmim][Tf_2N] < [bm_2im][Tf_2N] < [bmpyrr][Tf_2N]. Clearly there is some interaction between the IL and the Cl^- ion that decreses the nucleophilicity of the anion in [bm_2im][Tf_2N] and more so in [bmim][Tf_2N]. Since chloride is the best hydrogen-bond acceptor of the halides, the change in nucleophilicity can be explained by the degree of stabilization of the chloride ion via hydrogen bonding to the cation of the ionic liquid.

The activation enthalpies for the reaction of chloride are furthermore very similar to those of ion pairs in dichloromethane, and the effect of IL should arise from the association of chloride with one or more cations of the IL.[79] The activation entropies (fairly large and negative) are, however, more similar to those of free ions than ion pairs (positive). This different behaviour between entropy and enthalpy has been explained[79] considering that the reaction occurs through an S_N2 mechanism, i.e. through a pentacoordinated transition state. The activation step is an association process, which should have negative entropy. In dichloromethane it has a positive value because, when the activated complex is formed, the cation of this ion pair is liberated as a free solvated cation and the leaving group cannot be stabilized by ion pairing. In ILs, the leaving group does associate with the cations of the IL. It has therefore been proposed that the entropy gained by liberating a cation is cancelled out by the association of another cation with the leaving group.

Finally, Lancaster *et al.* proposed[79] that in the IL an equilibrium exists between fully coordinated ‘unavailable’ chloride and a one face ‘available’ chloride which can associate with the substrate. This loose association of available chloride with the substrate should represent the ground state. It has been demonstrated by neutron diffraction that a Cl^- ion is surrounded by six cations. For the reaction to occur, the Cl^- ion must first come into close proximity with the substrate. To do this, the Cl^- anion must dissociate from at least one cation. The kinetic and thermodynamic data seem to suggest that the order of availability of chloride to react is [bmim][Tf_2N] < [bm_2im][Tf_2N] < [bmpyrr][Tf_2N], which is the reverse order of the strength of the cation–chloride interaction.

Recently, also the competition between S_N2 and S_N1 reactions in ILs ([bmim][PF_6], [bmim][Tf_2N] and [hpy][Tf_2N]), has been investigated,[80] examining the reactions of primary, secondary and tertiary halides or tosylates with KCN and NaN_3 (Scheme 15).

The observed ability of Cl^-, Br^-, I^- and tosylate to act as leaving groups in the substitution reaction of NaN_3 was similar to that reported for the same process in cyclohexane, exactly corresponding to that calculated for S_N2 reactions in the gas phase, suggesting also in this case the absence of strong specific interactions between the examined ILs and the activated complex. Related to this reaction, the reactivity of secondary substrates was comparable to or higher than those of the corresponding primary substrates and led to the exclusive formation of the corresponding substitution products. At variance, elimination products were obtained by reaction of KCN with secondary substrates. The different reactivity of the secondary substrates towards the two nucleophiles (N_3^-,



Scheme 15

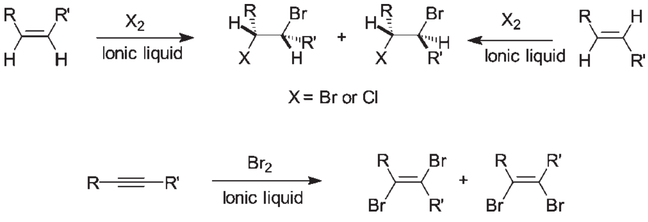
CN^-) when the reactions were carried out under identical conditions excluded a rate-determining diffusion-controlled trapping of a free secondary carbocation. In agreement with this latter hypothesis, no racemization was observed when optically active secondary substrates were used in the reaction with NaN_3.

On the other hand, 2-bromoadamantane, a typical secondary alkyl substrate for which an S_N2 mechanism is precluded by the cage structure, practically did not react with NaN_3 in all three ILs under reaction conditions that gave a conversion $>50\%$ from 2-bromoheptane.

On this basis, the involvement of a free carbocation intermediate in the reaction of secondary substrates with NaN_3 has been excluded in favour of a more concerted mechanism.

More in particular, it has been proposed that the reaction proceeds through the rear-side nucleophilic attack of N_3^- with an S_N2 mechanism in the case of primary substrates. This mechanism should, however, gradually shift towards pure S_N1, surely occurring in the case of the bridgehead cage 1-iodoadamantane, passing through the nucleophilically assisted formation of an ion pair intermediate in the case of secondary uncaged substrates. Finally, it is not possible to exclude that the reaction of primary and secondary substrates might occur even with preassociation.[81] Theoretical calculations indicate the presence of a nucleophile–substrate (or–product), encounter complex corresponding to an energy minimum before and after the energy maximum, on the reaction coordinate for the S_N2 substitution process in gas phase.[82] In solution, generally, the complexes become less important with increasing solvent polarity owing to the solvation of the anion. However, if the energy of 'solvation' of the N_3^- anion is much smaller in the IL than in water or in protic solvents, the formation of the encounter complex, and therefore the preassociation mechanism, might become much more favourable in these solvents than in molecular solvent.

Finally, it has been shown that 2-bromoheptane reacts more slowly with CN^- than with N_3^-, whereas octan-2-yl tosylate gives with CN^- exclusively the corresponding elimination product(s). The reactivity order of 2-bromoheptane ($N_3^- > CN^-$) is opposite to that observed[83] in molecular solvents for displacement reactions on methyl halides (pure S_N2 reaction), but the same as for nucleophilic reactions with carbocations. This behaviour therefore seems to indicate a larger amount of carbocation character in the transition state of this secondary substrate, or in other words further supports the formation of a nucleophilically assisted ion-pair intermediate. Moreover, the different elimination/substitution ratio found in the reaction of 2-bromoheptane and octan-2-yl tosylate with CN^- is in agreement with the involvement of ion-pair intermediates in the reaction of secondary substrates. For the first-order S_N1 reaction the leaving group has nothing to do with the competition between elimination and substitution. Analogously in S_N2 reactions, the elimination/substitution ratio is not greatly dependent on the leaving group.[84] Only in the case of ion-pair intermediates can the leaving group affect this ratio. Despite their polarity, ILs therefore seem to behave as ionizing but not dissociating solvents.



Scheme 16

Electrophilic additions. ILs have also been used efficiently for the synthesis of vicinal dihaloalkanes and dihaloalkenes by electrophilic addition of halogens to double and triple bonds (Scheme 16).[85–87]

Bromine addition in [bmim][PF_6] and [bmim][BF_4] is stereospecifically *anti* with dialkyl-substituted alkenes, alkyl-substituted alkynes and *trans*-stilbenes; *cis*-stilbenes and arylalkynes give instead mixtures of *syn* and *anti* addition products, although in the case of *cis*-diaryl-substituted alkenes the stereoselectivity *anti* is generally higher than in chlorinated solvents. In the case of diaryl-substituted alkenes, such as stilbenes, stereoselectivity in molecular solvents depends primarily on two factors: (1) the nature of the intermediate and (2) the lifetime of the ionic intermediates.[88] Bridged bromiranium ions give exclusively *anti* addition products, whereas open β-bromocarbenium ions give generally mixtures of *syn* and *anti* addition products (Scheme 17). The nature of the intermediate is determined by the nature of the substituents on the phenyl ring, electron-withdrawing groups favour bridged intermediates and electron-donating groups open β-bromocarbenium ions. Open β-bromocarbenium ions give the *syn* addition products mainly through an attack *anti* of the counter anion, after rotation around the C—C bond (k_θ). If the lifetime of the intermediate is sufficiently short the rotation around the C—C bond is not able to compete with the nucleophilic attack of the counter anion and almost exclusively the *anti* addition product can be obtained.

In molecular solvents, the nature of the ionic intermediate is not dependent on the properties of the solvent; in contrast, the lifetime of the ionic intermediates depends on the solvent. Probably also in ILs the nature of the intermediates is not affected by the medium, whereas the latter can affect the lifetime of these intermediates, affecting the stability of the ionic intermediates or modifying the nucleophicity of the attacking Br^- (or Br_3^-) anion. Furthermore, it can also affect the *syn/anti* ratio, decreasing the rate of isomerization of the ionic intermediates through rotation around the C—C bond.

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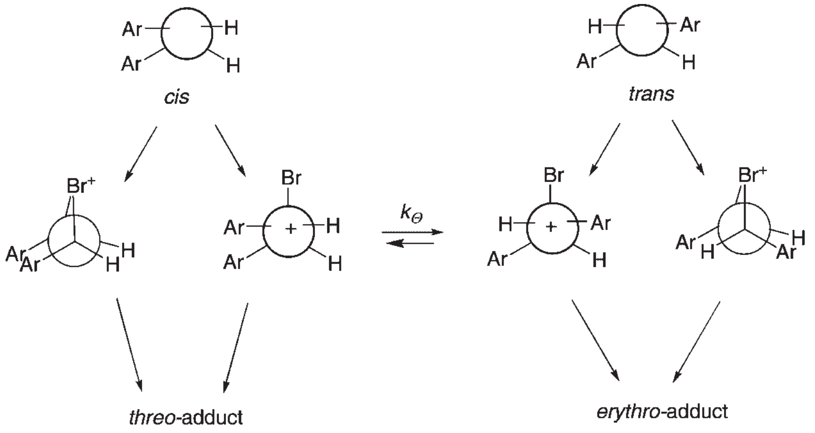
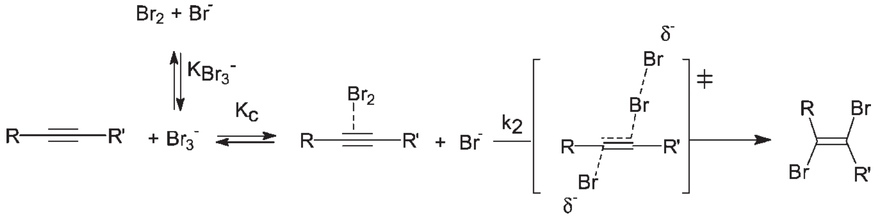
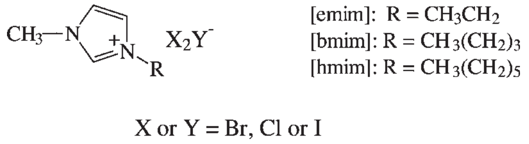


Scheme 17



Scheme 18



Scheme 19

It is also worth noting that, in [bmim][PF$_6$], the Br$_2$ reaction follows a second- or third-order rate law, depending on bromine concentration, a behaviour that generally in conventional media characterizes the bromine addition in protic solvents.

Electrophilic addition of Br$_3^-$, generated by bromine addition to [bmim][Br], can also be carried out[85–87] in ILs; in this case both [bmim][Br] and other ILs, bearing non-nucleophilic anions, can be used as solvents. The reaction is always *anti* stereospecific, independent of the alkene or alkyne structure. It follows a second-order rate law, suggesting a concerted mechanism of the type reported for Br$_3^-$ addition in aprotic molecular solvents, involving a product- and a rate-determining nucleophilic attack by bromide on the initially formed alkene or alkyne–Br$_2$ π-complex (Scheme 18).

However, the comparison of the kinetic constants and the activation parameters for the addition of Br$_3^-$ to triple bonds in [bmim][Br] with those related to the second-order reaction of the same alkynes with tetrabutylammonium tribromide in 1,2-dichloroethane suggests a possible effect of solvent viscosity, at least when the alkyne structure favours early transition states.

Other rather uncommon trihalide-based ILs (Scheme 19) have been prepared[87] by mixing equimolar amounts of halogens (ICl, or IBr, or Cl$_2$ or Br$_2$) to suitable 1-alkyl-3-methylimidazolium halides, and the structures of the trihalide ions formed have been investigated by electrospray ionization mass spectrometry (ESI-MS) and NMR. Despite the non-equilibrium conditions that relate to the analyser used for the ESI-MS measurements, the relative abundances of the different ionic species showed that the various trimeric anions are characterized by two distinct levels of stability.

Derivatives such as [Br$_3$]$^-$, [I$_3$]$^-$, [IBr$_2$]$^-$ and [ICl$_2$]$^-$ may be classified as fairly stable species, whereas [Br$_2$Cl]$^-$, [I$_2$Cl]$^-$ and [I$_2$Br]$^-$ are rather unstable, giving the above-mentioned more stable trihalogenide species. Although the dissociation constants of these trihalide anions have been never determined in ILs, spectroscopic measurements and reactivity data suggest that trihalide species are stable in these solvents. At variance with protic molecular solvents, which favour dissociation, owing to the very high energy of solvation of the small Br$^-$ or Cl$^-$ anions, ILs disfavour this process. The behaviour of ILs is therefore significantly different from that of alcohols or water.

The mixed trihalide ILs, in particular [Rmim][IBr$_2$] and [Rmim][ICl$_2$], have been proved to be excellent iodine-donor cosolvents for the stereoselective *anti* iodination of alkenes and alkynes in [bmim][PF$_6$].[87] Very good to almost quantitative yields of vicinal iodochloro or iodobromo adducts were observed for all the substrates examined. Furthermore, kinetic measurements carried

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out in several ILs, using [bmim][ICl_2] as the reactant, have shown that the ability of the cation of the IL to undergo hydrogen bonding plays an important role on the reactivity.[89]

Diels–Alder reactions. The Diels–Alder reaction is one of the most useful carbon–carbon bond-forming reactions in organic chemistry. Although highly efficient, this reaction suffers from being an addition process with a negative reaction entropy. As such, the use of high temperatures to give useful reaction rates has a detrimental effect on the position of the reaction equilibrium. Therefore, different strategies have been tried to accelerate the reaction at low temperature. Studies on solvent effects on the Diels–Alder reaction have evidenced the importance of the cohesive energy density, together with the hydrogen-bonding donor capacity.[90] The cohesive energy density essentially should quantify solvophobicity, underlining the importance of hydrophobic interactions in rationalizing the effect of solvents such as water on Diels–Alder reactions. Recently, ILs have attracted attention as possible reaction media for this kind of reaction. The molecular origin of how ILs influences this reaction is, however, still a matter of controversy. A solvophobic effect, able to generate an 'internal pressure' and to promote the association in a cavity of the solvent, was initially invoked to explain the kinetic and stereochemical behaviour of Diels–Alder reactions carried out in ILs.[91,92] The reactions in ionic liquids are indeed marginally faster than in water but are considerably faster than in diethyl ether. Furthermore, it has been shown that in analogy with molecular solvents the presence of a Lewis acid greatly accelerates the reaction and improves selectivity; for this purpose, the acidity of chloroaluminate ILs[93] or ILs containing $ZnCl_2$ and $SnCl_2$[94] have been used. In [bmim][PF_6] the selectivities of some isomers improves from 4:1 to 20:1 in the presence of $ZnCl_2$.

However, a recent study on the reaction of cyclopentadiene with methyl acrylate in several ILs has provided new insights into the mechanism(s) that determine reactivity and selectivity in ILs.[95] In all the examined ILs the reaction of cyclopentadiene with methyl acrylate followed a second-order rate law and the values of k_{obs} slightly increased with increasing viscosity. The increase in the rate of the reaction was concurrent with an increase in *endo* selectivity. The greatest selectivity (6.7) was found in [$HO(CH_2)_2$mim][Tf2N], the IL having an OH group and higher hydrogen-bonding ability. However, even in [$MeO(CH_2)_2$mim][Tf2N] the reaction occurred with a high *endo* selectivity (5.1), and also in [bmim][BF_4] (4.6), whereas it decreased in [bm_2im][BF_4], where the presence of the methyl group at C-2 deleted the hydrogen-bonding ability of the hydrogen present at C-2 in the [bmim] series. To investigate this phenomenon in more detail, the selectivity in five ILs having the same cation was evaluated, showing that in $[bmim]^+$ salts the nature of the anion affects the selectivity, and higher selectivity characterized ILs having the smaller hydrogen-bonding interactions between the cation and anion. The *endo* selectivity was therefore explained considering the ability of the cation to hydrogen bond to methyl acrylate, a process which is, however, determined by two competing equilibria. Since both anion (A) and solute (S) can be hydrogen bonded to the cation (see Scheme 20), the concentration of the bonded methyl acrylate is inversely proportional to the equilibrium constant for the formation of the cation–anion hydrogen-bonded adduct.

$$[\mathrm{bmim}]^+ + \mathrm{A}^- \rightleftharpoons [\mathrm{bmim}]\cdots\mathrm{A}$$
$$[\mathrm{bmim}]^+ + \mathrm{S} \rightleftharpoons [\mathrm{bmim}]\cdots\mathrm{S}$$

Scheme 20

The *endo/exo* ratio, and associated acceleration, of the Diels–Alder addition of cyclopentadiene to methyl acrylate in ILs seems, therefore, to be controlled by the ability of the cation of the IL to act as a hydrogen-bond donor, a property which is modulated by the ability of the counter anion to act as an hydrogen-bond acceptor.

Effect of dipolarity/polarizability of the ILs on the nature of the transition states

Electrophilic substitutions. Electrophilic aromatic substitution chemistry is of critical importance in a wide variety of industrial, fine chemical and academic processes. Several electrophilic aromatic substitution reactions have therefore been carried out[3,4] in ILs but, to the best of our knowledge, no systematic kinetic study has been reported.

Substrate selectivity ($k_{\mathrm{mesitylene}}$:k_{durene}) measured in competitive experiments carried out for the electrophilic fluorination of arenes, using F-TEDA-BF_4 (Selectfluor$^{\mathrm{TM}}$) as halogenating agent, has suggested,[96] however, that the reaction occurs through a polar mechanism, involving an ionic intermediate (σ-complex) and an ionic transition state in the rate determining step. The comparison with the reaction in acetonitrile has furthermore evidenced a slightly greater degree of polar character in the ionic liquid. The same reagent, F-TEDA, in the presence of iodine in imidazolium and pyridinium ILs has also been used[97] for the regioselective iodination of aromatic compounds. The reaction is *para*-directed when possible, otherwise it occurs in the *ortho*-position. Also in this case, competitive experiments suggested a polar mechanism for this process, as in molecular solvents.

Solvent effects on equilibria

Acid–base equilibria in ILs. Acidic chloroaluminated ILs containing protons may be superacids (Hammett function down to -18) and they are widely used as

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reaction media for acidic reactions.[98] However, since they are very sensitive to hydrolysis and also small amounts of water can change the salt composition and the proton concentration, it is generally difficult to control the acidity of these ILs. Therefore, even non-chloroaluminate ILs have been applied in acidic reactions.[99] The miscibility of water has been proposed as a guide to the chemical behaviour of Brønsted acids in ILs.[100] However, recently a determination of an acidic scale in ILs has been reported. The Brønsted acidity of two strong acids ($HNTf_2$ and HOTf) and a weak acid (CH_3COOH) in [bmim][Tf_2N], [bmim][BF_4], [bm_2im] [BF_4] has been evaluated from the determination of the acidity functions, using UV–visible spectroscopy.[101]

To determine the pK_a values, Eqn (4), arising from the Hammett function H_0, Eqn (3), was applied using 2,4-dinitroaniline as the indicator base. The method consisted of evaluating the protonation extent of the uncharged indicator (named I), in terms of a measurable ratio [I]/[IH^+]. It was first assumed that the indicator solutions were diluted enough to consider the activity coefficients (γ) to be unity. Second, it was assumed that the ratio of the transfer activity coefficients (Γ) of both I and IH^+ was unity and solvent independent.

$$H_0 = \mathrm{p}K_\mathrm{a}(\mathrm{I})_\mathrm{aq} + \log([\mathrm{I}]_\mathrm{S}/[\mathrm{IH}^+]_\mathrm{S}) \tag{3}$$

$$H_0 = -\log a(\mathrm{H}^+_\mathrm{aq}) - \log\gamma(\mathrm{I})/\gamma(\mathrm{HI}^+) - \log\Gamma(\mathrm{I})/\Gamma(\mathrm{HI}^+) \tag{4}$$

On the basis of the comparison of the Hammett functions of the different acids in the above-mentioned ILs, the authors[101] concluded that it is possible in these solvents to reach acidity levels ranging from −3.35. to −7.00, depending on the IL and on the acid. In [bmim][Tf_2N], HOTf shows practically the same acidity as $HNTf_2$, a behaviour much more similar to water than to acetic acid; in the latter solvent HOTf is more acidic (p$K_a = 4.2$) than $HNTf_2$ (p$K_a = 7.0$) owing to the less dissociative character of this solvent. Acetic acid is less acidic than both HOTf and $HNTf_2$ in [bmim][Tf_2N]. Water has a basic character in ionic liquids, and the absorbance of the unprotonated form of the indicator increases with increasing water concentration; it is not acidic enough to protonate 2,4-dinitroaniline. The acidity of HOTf and $HNTf_2$ increased when [bmim][BF_4] was used as the solvent, suggesting that the $[BF_4]^-$ anion is less solvating than the $[Tf_2N]^-$ anion towards H^+, leading to an increased acidity of the proton. Nevertheless, the presence of the methyl group at the 2-position of the imidazolium cation has practically no effect; the possible H-bond between $[BF_4]^-$ and the hydrogen at the 2-position does not seem to affect the acidic properties of these systems.

In contrast, no data on amine basicity have yet been reported. Recently it has been shown that, in agreement with a different basicity order of primary, secondary and tertiary amines in ILs, direct *N*-alkylation of primary amines can be performed to prepare secondary amines.[102] In contrast to molecular solvents, in ionic liquids overalkylation of the initially produced secondary amines is generally markedly reduced: the observed selectivities between mono- and dialkylation are typically of the order of 9:1, or higher.

CONCLUSION

Interest in the properties of ILs is rapidly expanding. Although there have been numerous studies concerning their preparation, use as reaction media and their physical properties, little is known about how, and to what extent, the unusual physico-chemical properties of these media can affect reactivity.

One important feature of these liquids is the possibility of tuning their physical and chemical properties by varying the nature of the anion and cation. If we consider all the possible combinations of the anions and cations, including the possibility of using mixtures of ILs, it is evident that the number of these ‘new solvents’ is extremely high and at least in principle it should always be possible to tailor the best ionic liquid for any application.

Understanding how chemical reactivity is influenced by different classes of ionic liquids is probably the key to obtaining the technological improvements for a safer, more secure society and substantially benefit the environment and the economy.

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