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Extended Scale for the Hydrogen-Bond Basicity of Ionic Liquids

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In the past decade, ionic liquids (ILs) have been the focus of intensive research regarding their use as potential and alternative solvents in many chemical applications. Targeting their effectiveness, recent investigations have attempted to establish polarity scales capable of ranking ILs according to their chemical behaviours. However, some major drawbacks have been found since polarity scales are only 10 report relative behaviours because they depend on the set of probe dyes used, and they are sensitive to measurement conditions such as purity levels of the ILs and procedures employed.. Due to all these difficulties it is of crucial importance to find alternative and/or predictive methods and to evaluate them as *a priori* approaches able to provide the chemical properties of ILs. Furthermore, the large number of ILs available makes their experimental characterization, usually achieved by a trial and error 15 methodology, burdensome. In this context, we firstly evaluated COSMO-RS, Conductor-Like Screening Model for Real Solvents, as an alternative tool to estimate the hydrogen-bond basicity of ILs. After demonstrating a straight-linecorrelation between the experimental hydrogen-bond basicity values and the COSMO-RS hydrogen-bonding energies in equimolar cation-anion pairs, an extended scale for the hydrogen-bond accepting ability of IL anions is proposed here. This new ranking of the ILs chemical 20 properties opens the possibility to pre-screen appropriate ILs (even those not yet synthesized) for a given task or application.

Introduction

In the past few years, ionic liquids (ILs) have been proposed as promising liquids for the substitution of volatile organic solvents 25 widely used in industry.[1] ILs are typically composed of large and asymmetric organic cations and organic or inorganic anions. Due to their large ions, and thus delocalization of charge, ILs display lower melting temperatures in comparison toconventional salts – salts with melting temperatures below 100 °C are generally 30 recognised to be ILs. Their ionic nature also confers singular characteristics to most ILs, namely a negligible vapour pressure and low flammability at ambient conditions. In fact, these are the main features for their being widely described as "green solvents" and for much of the interest in these as potential solvents for 35 "clean" technologies. Nevertheless, it should be remarked that other properties, such as their toxicity and biodegradability,[2] should be investigated before such generalized assumptions can be confirmed. However, it is generally accepted that the use of non-volatile liquid solvents at ambient conditions is already a 40 major contribution to reduce the environmental human footprint.

In addition to the previously described characteristics, ILs are salts with a high solvation ability and selectivity.[3] In particular, the possibility to tune their properties, thereby creating "tailor made" compounds through the modification of their chemical 45 structures, has led to the synthesis of ILs with a wide variety of applications. ILs (as alternative solvents) have been largely used in catalysis and in a large assortment of organic/inorganic/organometallic reactions[4], in the treatment and/or dissolution of biomass[5] and in liquid-liquid extractions and 50 separations[6]. Nevertheless, an efficient and realistic use of ILs as solvents requires the previous knowledge of their physical and chemical properties. The main challenge consists therefore in the development of a "tailored solvent" for a target application. For that purpose, it is crucial to understand the solvation interactions 55 at a molecular level in order to further evaluate the performance of a given solvent. Among the most important features of an IL to be used as a solvent are the specific interactions occurring between the solvent and the dissolved substrate (solute-solvent interactions) which are usually related to the solvent polarity. It 60 has previously been demonstrated that the IL polarity influences its solvation ability, reaction rates, reaction mechanisms,product yields and enzyme activity, among others.[7]

One of the methods most often employed to estimate the polarity of ILs is the analysis of the UV-Vis spectral band shifts 65 of solvatochromic probes. Specific and nonspecific solute-solvent interactions are reflected in the respective absorbances of a suite of selected dyes.[8-9] A number of empirical solvatochromic parameters has been suggested to quantify the molecular-microscopic solvent properties of ILs.[8-9] For the sake of 70 simplicity only one indicator is frequently used to build the polarity scale and, amongst the various possibilities, the $E_T(30)$ Reichardt's betaine dye has been widely employed.[8] $E_T(30)$ is a measure of the solvent dipolarity/polarizability, though it is also sensitive to the solvents' hydrogen-bond donor ability. On the

other hand, a multiparametric approach was proposed by Kamlet, Taft and co-workers[9] and consists in the use of a set of solvatochromic probes which allow the assessment of different parameters for the same solvent.

The Kamlet-Taft equation[9], in its simple form of a Linear Solvation Energy Relationship (LSER), is given by the following equation,

$$XYZ = (XYZ)_0 + s(\pi* + \mathrm{d}\delta) + a\alpha + b\beta \qquad (1)$$

where XYZ is the result of a particular solvent-dependent process, $(XYZ)_0$ is the value for the reference system, $\pi*$ represents the solvent's dipolarity/polarizability, α is the hydrogen-bond donating ability, β is the hydrogen-bond accepting ability and δ is a correction term. The parameters a, b and s represent the solvent-independent coefficients.[9]

Different dyes and experimental approaches can result in diverse values of solvatochromic parameters for the same solvent.[8-9] In this context, different empirical techniques only provide uniquely defined scales of relative polarity. For instance, two structurally similar probes, N,N-diethyl-3-nitroaniline and N,N-diethyl-4-nitroaniline, lead to different values of $\pi*$ for the same IL.[10] This trend is a result of the diverse and complex interactions that occur between the solvent and a particular solute, i.e., the polarity scales are always solute-dependent. Published data for α, β and $\pi*$ for specific ILs are quite different and mainly depend on the set of solvatochromic dyes employed.[10-11]

The Kamlet-Taft parameters are well established for traditional solvents and it is one of the most accepted (used) polarity scales.[12] Nevertheless, for more recent solvents such as ILs, these parameters are still not definitive and are undergoing continuous experimental measurements by several research groups.[10-11] One of the major reasons behind this is the sensitivity of the Kamlet-Taft values to impurities.[10,13] In ILs, many of these impurities come from their own synthesis. Improvements on the synthetic routes of ILs are also under constant development.[14] Recently, it was demonstrated that water, 1-methylimidazole, 1-chlorobutane and the ions of the salts precursors significantly influence the values of the solvatochromic parameters of ILs.[10,15] One of the major advantages of ILs over the traditional solvents is their lack of vapour pressure at ambient conditions. However, this low volatility doesn't allow their purification by simple distillation. Only volatile impurities can thus be removed by heating under vacuum. Furthermore, to simplify the experimental tasks, ILs should ideally be liquid at room temperature and non-coloured. Finally, the Kamlet-Taft parameters are obtained as average values of a series of selected probes requiring thus require a considerable experimental effort to derive the respective parameters for any new solvent. Still, and despite some divergences found between different authors and probe dyes, it is generally accepted that: (i) the dipolarity/polarizability ($\pi*$) values are similar amongst several ILs and are higher than those of most molecular solvents (Coulombic interactions as well as dipole and polarizability effects occur in ILs); (ii) the hydrogen-bond basicity values cover a large range, from similar to acetonitrile to lower values, and are mainly controlled by the IL anion; and (iii) the hydrogen-bond acidity values of ILs are comparable to or lower than that of aniline and are mainly

determined by the IL cation (although the anion also plays a secondary role since stronger cation-anion interactions further reduce the ability of the cation to interact with the substrate).[10-11]

Aiming at overcoming the difficulties encountered with common solvatochromic probes and the establishment of polarity scales in ILs, several attempts have been carried out in order to find suitable alternatives. For instance, Chiappe and Pieraccini[16] studied the formation of an electron donor-acceptor complex between 4,4'-bis(dimethylamino)benzophenone and tetracyanoethene and correlated its visible absorption maximum with the Kamlet-Taft parameters. Wu et al.[17] proposed a spectroscopic method based on the transition energy of spiropyran probes and demonstrated its correlation with the polarity of ILs by means of the $E_T(30)$ values. Lungwitz and co-workers[18] established that there is a close correlation between α and β. The same research group[18] proved that β also correlates with the ^{1}H NMR chemical shift of the most acidic proton of the imidazolium cation. More recently, Hunt and co-workers[19] proposed the use of different computational descriptors for predicting Kamlet-Taft parameters, namely α and β, in ILs.

Due to all the difficulties found hitherto to establish a polarity scale for ILs, it is of crucial importance to find alternative and/or predictive methods. Furthermore, the large number of ILs available from their structural flexibility also represents a major drawback in that it is unfeasible to experimentally determine the solvatochromic parameters for all the cation/anion combinations which may form an IL. Therefore, we provide here novel results on the use of COSMO-RS, Conductor-Like Screening Model for Real Solvents,[20] as a valuable tool to estimate the hydrogen-bond basicity, β, of ILs. COSMO-RS is based on unimolecular quantum calculations and is mostly used for the prediction of phase equilibrium.[21] COSMO-RS is also valuable in the prediction of the excess properties of binary mixtures composed of molecular solvents and ILs, as well as between ILs and gases or other volatile compounds.[22]

Results and discussion

Experimental Kamlet-Taft solvatochromic parameters

There are two major literature sources reporting the Kamlet-Taft parameters for 1-butyl-3-methylimidazolium-([C₄mim])-based ILs with the main goal of appraising the effect of the IL anion through its hydrogen-bond basicity.[10,18] To expand this database, additional Kamlet-Taft solvatochromic parameters were here determined for 4 ILs based on the [C₄mim]$^+$ cation. A list of the studied fluids, including a definition of their acronyms, is provided as an endnote.‡ There are several sets of dyes that can be used to determine the Kamlet-Taft parameters. In this work, the Reichardt's dye, 4-nitroaniline and N,N-diethyl-4-nitroaniline were used. All spectra were recorded at 25 ºC, and thus, only ILs that are liquid at room temperature were appraised. The values of the Kamlet-Taft solvatochromic parameters determined in this work are reported in Table 1.

The solvatochromic data for [C₄mim][CF₃SO₃] and [C₄mim][(CH₃O)₂PO₂] are in close agreement with previous published data[10,19] whereas novel results are presented for the [C₄mim][C₈H₁₇SO₄] and [C₄mim][CF₃CO₂].

The $\pi*$ values are high for all the ILs investigated in

comparison to non-aqueous molecular solvents[9] and slightly depend on the IL anion. π^* is a true measure of the ion-dye non-specific interactions (polarizability, and dipole-dipole and dipole-induced dipole interactions) and tends to decrease with the increase on the charge delocalization of the IL anion.[10] In fact, the octylsulphate-based IL is the one which presents the lowest π^* value – a consequence of the long aliphatic moiety present in this anion.

Table 1. Kamlet–Taft parameters using the following set of dyes: Reichardt's Dye, N,N-diethyl-4-nitroaniline and 4-nitroaniline.

IL	α	β	π^*
[C$_4$mim][CF$_3$SO$_3$]	0.62	0.48	0.98
[C$_4$mim][C$_8$H$_{17}$SO$_4$]	0.65	0.80	0.93
[C$_4$mim][(CH$_3$O)$_2$PO$_2$]	0.48	1.12	0.96
[C$_4$mim][CF$_3$CO$_2$]	0.57	0.84	0.94

As previously demonstrated in the literature, the hydrogen-bond acidity of ILs is mainly determined by the IL cation;[10] yet, there is also a clear dependence on the IL anion, as shown here and in agreement with literature data.[10] The data presented in Table 1 reveal that the ability of the IL to act as a hydrogen-bond donor (mainly arising from the IL cation) is moderated by the hydrogen-bond acceptor ability of the anion composing the respective IL. For instance, the dimethylphosphate-based IL, having an anion with the highest ability to accept a hydrogen bond, is the one with the lowest α value. The high ability of this anion to hydrogen-bond with the IL cation limits its availability to interact as a hydrogen bond donor to the dye.

The β value reflects the hydrogen-bond basicity of each IL acting as a solvent. As shown in Table 1, the β values are strongly dependent on the IL anion. Between the studied ILs, the dimethylphosphate-based fluid presents the highest ability to hydrogen-bond with the protons of the hydrogen bond donor group (-NH$_2$) of the 4-nitroaniline dye.

Estimation of the hydrogen-bond basicity of ILs

Taking into account all the difficulties in experimentally determining the Kamlet-Taft solvatochromic parameters we tested the COSMO-RS as a viable and expeditious tool to estimate the hydrogen-bond basicity of [C$_4$mim]-based ILs. The hydrogen-bond basicity was chosen in this work since it is one of the most important parameters reflecting the hydrogen-bond acceptor ability of the IL anion. Most of the relevant properties of ILs regarding this solute-solvent interaction are significantly determined by the nature of the anion rather than the cation.[23] In fact, the β parameter is widely used to explain (and indeed correlates with) diverse properties, such as solvation ability and phase equilibrium behaviour of ILs.[24] Within this perspective, the hydrogen-bond basicity was here correlated with the hydrogen-bonding interaction energy in the equimolar cation-anion mixture (E_{HB} / (kJ·mol^{-1})) obtained from COSMO-RS to infer a possible dependence. It should be remarked that other attempts were also carried out, namely the correlation of the hydrogen-bond basicity with the van der Waals and misfit energies derived from COSMO-RS. Although, and as expected, the enhanced correlations with the experimental β values were gathered with the COSMO-RS hydrogen-bonding energies and as shown hereinafter.

As previously mentioned, the solvatochromic parameters

values determined by different authors are slightly different. In general, each group of researchers provide one relative polarity scale. Therefore, the E_{HB} values for each IL were correlated with the Kamlet-Taft β parameters published by Welton and co-workers[10] and Lungwitz et al.[18]. These literature sources[10,18] were chosen since they represent the most complete databases found for [C$_4$mim]-based ILs. These experimental values allow the inspection on the IL anion effect and the comparison between the hydrogen-bond basicity and the E_{HB}. The β experimental data[10,18] and the respective COSMO-RS results are compiled in Table 2. The complete description of the IL anions is provided in Table 3.

Table 2. Hydrogen-bond basicity (β) data, experimental ^{1}H NMR chemical shift of the C2-proton (δ / ppm) and hydrogen-bonding interaction energy in the equimolar cation-anion mixture (E_{HB} / (kJ·mol^{-1})) taken from COSMO-RS calculations for [C$_4$mim]-based ILs.

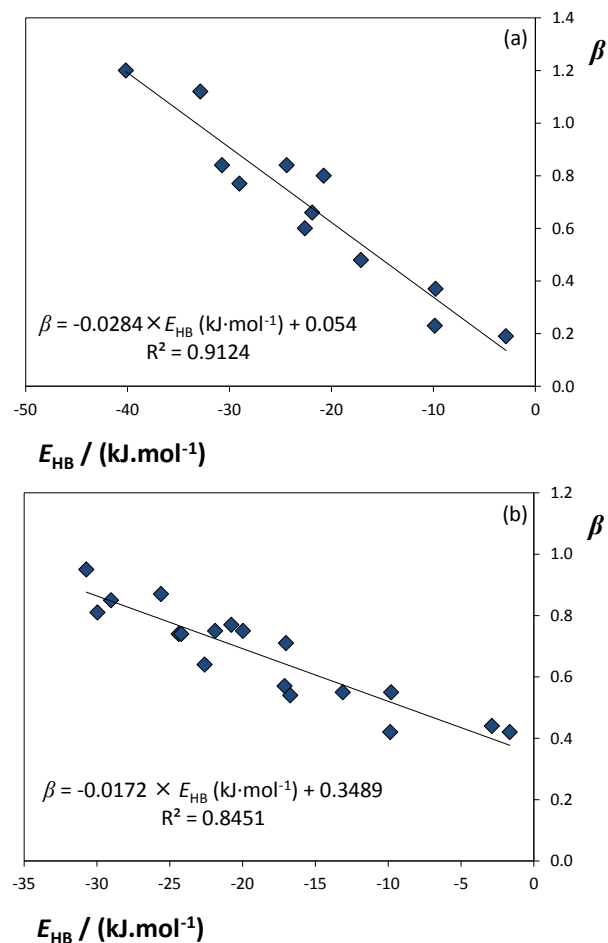| IL	β^{10}	β^{18}	δ^* / ppm	E_{HB} / (kJ·mol^{-1})
[C$_4$mim][N(CF$_3$SO$_2$)$_2$]	0.23	0.42	8.39049	-9.86
[C$_4$mim][PF$_6$]	0.19	0.44	8.10815	-2.88
[C$_4$mim][BF$_4$]	0.37	0.55	8.37390	-9.79
[C$_4$mim][CF$_3$SO$_3$]	0.48*	0.57	8.72675	-17.11
[C$_4$mim][ClO$_4$]	n.a.	0.55	n.a.	-13.11
[C$_4$mim][C(CN)$_3$]	n.a.	0.54	8.81457	-16.73
[C$_4$mim][N(CN)$_2$]	0.60	0.64	8.99083	-22.60
[C$_4$mim][SCN]	n.a.	0.71	9.04029	-17.01
[C$_4$mim][NO$_3$]	n.a.	0.74	n.a.	-24.21
[C$_4$mim][CF$_3$CO$_2$]	0.84*	0.74	n.a.	-24.38
[C$_4$mim]I	n.a.	0.75	n.a.	-19.97
[C$_4$mim][CH$_3$SO$_4$]	0.66	0.75	n.a.	-21.88
[C$_4$mim][C$_8$H$_{17}$SO$_4$]	0.80*	0.77	n.a.	-20.76
[C$_4$mim][CH$_3$SO$_3$]	0.77	0.85	n.a.	-29.03
[C$_4$mim]Br	n.a.	0.87	n.a.	-25.60
[C$_4$mim]Cl	0.84	0.95	n.a.	-30.72
[C$_4$mim][(CH$_3$O)$_2$PO$_2$]	1.12*	1.12	10.12070	-32.85
[C$_4$mim][CH$_3$CO$_2$]	0.85	1.20	10.58690	-40.17

*experimental data from this work

In general, the hydrogen-bond basicity values reported by Lungwitz et al.[18] are higher than those published by Welton and co-workers[10]. These differences are a main result of the different solvatochromic dyes used by the two research groups.[10,18]

Anions such as acetate, dimethylphosphate and halogens present high hydrogen-bond basicities and thus an expected strong coordinating ability in aqueous solutions or in other media able to donate protons. At the other extreme of the ILs β ranking, the fluorinated IL anions are found, such as [N(CF$_3$SO$_2$)$_2$]$^-$, [PF$_6$]$^-$, [BF$_4$]$^-$ and [CF$_3$SO$_3$]$^-$. These IL anions are weak hydrogen bond acceptors, and when combined with the imidazolium cation, result in non-coordinating ILs. Structural changes to the IL anion, such as the introduction of electron withdrawing atoms or groups, also have a considerable influence on the hydrogen-bond basicity values. For instance, considering the cyano-based ILs, [SCN]$^-$, [N(CN)$_2$]$^-$ and [C(CN)$_3$]$^-$, there is a decrease in the IL anion's ability to accept hydrogen bonds with the increase number of –CN groups attached to the central atom, despite the growing number of possible sites for interaction. The more –CN groups are present, the smaller is the overall charge of the end group, and thus the electron density that is required for hydrogen-bonding. The introduction of fluorinated groups, from [CH$_3$CO$_2$]$^-$ to [CF$_3$CO$_2$]$^-$ and [CH$_3$SO$_3$]$^-$ to [CF$_3$SO$_3$]$^-$, also leads to a decrease in the IL's hydrogen-bond basicity. The low polarizability of the fluorinated groups and their electron withdrawing effect weakens the hydrogen-bonding ability with the hydrogen bond donor

protons of the solvatochromic probe. Finally, there is an increase in the hydrogen-bond basicity with the increase of the alkyl side chain length attached to the IL anion, resulting from the electron-donating effect of the fatty groups – *cf.* data for methylsulphate- and octylsulphate-based ILs. In summary, a large range of β values are achievable by the structural modification of the IL anion. This pattern opens the door to the creation of ILs with defined hydrogen-bond basicity capable of reproducing the chemical behaviour of typical molecular solvents for specific applications.

Fig. 1 depicts the correlation between the experimental β parameter of each IL[10,18] and the respective E_{HB} COSMO-RS values.

$$\beta = -0.0284 \times E_{HB} \text{ (kJ·mol}^{-1}) + 0.054$$
$$R^2 = 0.9124$$

E_{HB} / (kJ.mol^{-1})

$$\beta = -0.0172 \times E_{HB} \text{ (kJ·mol}^{-1}) + 0.3489$$
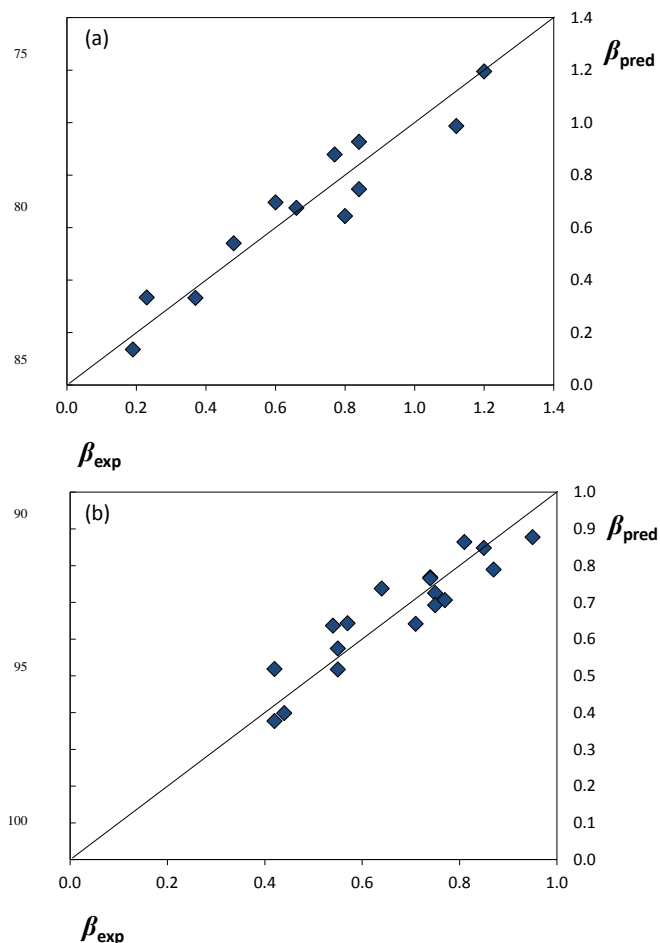$$R^2 = 0.8451$$

E_{HB} / (kJ.mol^{-1})

Fig. 1. Correlation between the experimental values of hydrogen-bond basicity (β) and the E_{HB} predicted by COSMO-RS: (a) experimental data from Welton and co-workers[10]; (b) experimental data from Lungwitz et al.[18].

At a first sight, it can be seen that there is a close relationship between the experimental hydrogen-bond basicity of [C$_4$mim]-based ILs and the hydrogen-bonding energy of the pure cation-anion pairs estimated by COSMO-RS. This correlation indicates that anions with an absolute lower hydrogen-bonding interaction with the corresponding imidazolium cation are also those that are less able to accept hydrogen bonds when acting as the solvent environment. However, a closer look at Fig. 1 also points out to the existence of two different correlations for the experimental

data taken from the two research groups.[10,18] Higher correlation coefficients and a higher dependence on the E_{HB} values are observed with the experimental results from Welton and co-workers.[10] This discrepancy can be ascribed to the different sets of dyes used by both groups and to the respective hydrogen-bonding dependency of the IL anion with a given dye.[10,18] However, both correlations depicted in Fig. 1 reveal a good agreement between the experimental hydrogen-bond basicity and the estimated hydrogen-bonding energies of the IL ions pairs. Based on this linear dependence and on the respective correlations it seems plausible to predict of the experimental β values.

Fig. 2 shows the relationship between the experimental and estimated β parameters.
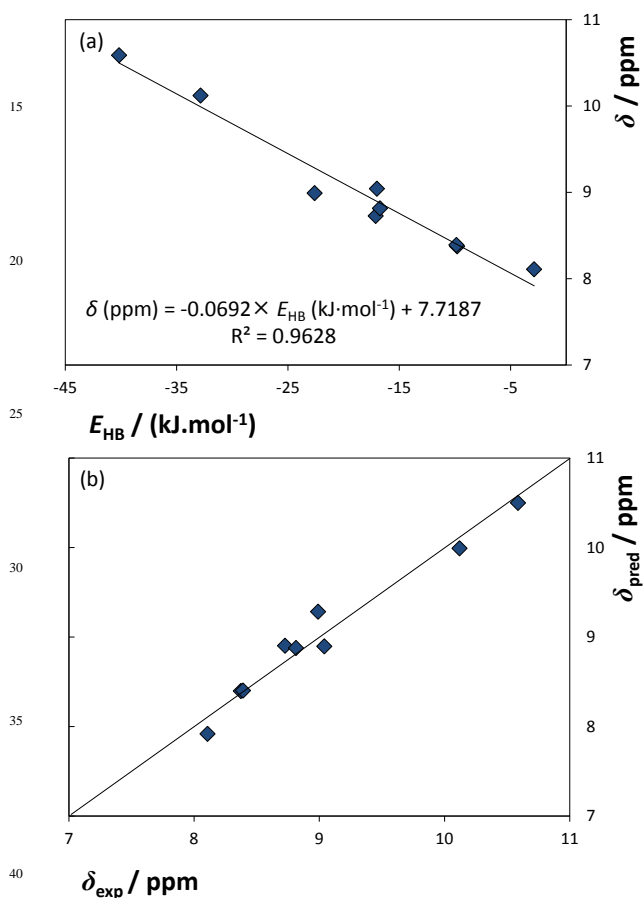

Fig. 2. Correlation between the predicted and experimental values of hydrogen-bond basicity (β_{pred} and β_{exp}, respectively) based on the equations provided by the E_{HB} estimated by COSMO-RS: (a) experimental data from Welton and co-workers[10]; (b) experimental data from Lungwitz et al.[18].

In both examples displayed in Fig. 2 there is a close agreement between the predicted and experimental β values meaning that the equations provided in Fig. 1 can be used to predict the hydrogen-bond basicity of [C$_4$mim]-based ILs with reasonable accuracy.

Aiming at further evaluating the capability of COSMO-RS for the prediction of the IL anions to accept hydrogen bonds,

additional ^{1}H NMR data were also determined in this work for pure ILs. The chemical shiftspresented here were measured for pure ILs, using an internal capillary containing the solvent and reference, to avoid the influences of solvent-IL interactions and the concentration of the salt itself upon the chemical shifts. In this way, the chemical shifts of pure ILs represent the Differences in their ability to hydrogen-bond with the IL cation and as a function of the respective anion.

The correlation between the ^{1}H NMR chemical shift of the proton in the C2-position of the imidazolium ring against the E_{HB} estimated by COSMO-RS is depicted in Fig. 3.

$$\delta \text{ (ppm)} = -0.0692 \times E_{HB} \text{ (kJ·mol}^{-1}) + 7.7187$$
$$R^2 = 0.9628$$

Fig. 3. (a) Correlation between the experimental values of ^{1}H NMR chemical shift of the C2-proton of the imidazolium ring and the E_{HB} estimated by COSMO-RS and (b) correlation between the predicted and experimental values of the ^{1}H NMR chemical shift of the proton in the C2-position of the imidazolium (δ_{pred} and δ_{exp}, respectively).

The interaction of IL anions with [C$_4$mim]$^+$ is complex in nature with preferential hydrogen-bonding with the most acidic hydrogen at the imidazolium cation, in the C2 position. Bonhôte et al.[25] demonstrated that the ^{1}H NMR chemical shift of the most acidic proton in 1,3-dialkylimidazolium moves to lower field with the increase of the anion basicity (in acetone solvent), and later on, Lungwitz and Spange[18] revealed that the same chemical shift closely correlates with the hydrogen-bond basicity (β) of ILs with a common anion and can be used as a measure of its hydrogen-bonding strength. According to Fig. 3, there is a close relationship between the interaction strength of the IL anion with the imidazolium ring (represented by the ^{1}H NMR chemical shift)

and E_{HB} estimated by COSMO-RS for a series of [C$_4$mim]-based compounds. The linear function depicted in Fig. 3 indicates that COSMO-RS is also able to predict the ^{1}H NMR chemical shift of the most acidic proton in the imidazolium ring as a result of the cation-anion hydrogen-bonding strength.

Extended scale of the hydrogen-bond basicity of ILs

Table 3. Hydrogen-bonding interaction energy in the equimolar cation-anion mixture (E_{HB} / (kJ·mol^{-1})) taken from COSMO-RS calculations for [C$_4$mim]-based ILs as a new and extended scale of hydrogen-bond basicity. The anions list is presented in a decreasing order of hydrogen-bond basicity of the IL anion.

[C$_4$mim]-based ILs		
Anion	Abbreviation	E_{HB} / (kJ.mol^{-1})
Acetate	[CH$_3$CO$_2$]$^-$	-40.17
Decanoate	[C$_9$H$_{20}$CO$_2$]$^-$	-38.64
Bis(2,4,4-trimethylpentyl)phosphinate	[C$_{16}$H$_{34}$O$_2$P]$^-$	-38.45
Benzoate	[(C$_6$H$_5$)CO$_2$]$^-$	-34.35
Diethylphosphate	[(C$_2$H$_5$O)$_2$PO$_2$]$^-$	-33.41
Dimethylphosphate	[(CH$_3$O)$_2$PO$_2$]$^-$	-32.85
Dibutylphosphate	[(C$_4$H$_9$O)$_2$PO$_2$]$^-$	-32.46
Chloride	Cl$^-$	-30.72
Nitrite	[NO$_2$]$^-$	-29.96
Methanesulfonate	[CH$_3$SO$_3$]$^-$	-29.03
Bromide	Br$^-$	-25.60
Salicylate	[C$_7$H$_5$O$_3$]$^-$	-25.46
Toluene-4-sulfonate (tosylate)	[C$_7$H$_8$SO$_3$]$^-$	-25.05
Trifluoroacetate	[CF$_3$CO$_2$]$^-$	-24.38
Nitrate	[NO$_3$]$^-$	-24.21
Heptafluorobutanoate	[C$_3$F$_7$CO$_2$]$^-$	-22.64
Dicyanamide	[N(CN)$_2$]$^-$	-22.60
2-(2-methoxyethoxy)ethylsulphate	[C$_5$OC$_1$SO$_4$]$^-$	-22.12
Ethylsulfate	[C$_2$H$_5$SO$_4$]$^-$	-22.10
Methoxyethylsulphate	[C$_3$H$_7$OSO$_4$]$^-$	-21.92
Methylsulphate	[CH$_3$SO$_4$]$^-$	-21.88
Ethoxyethylsulphate	[C$_4$H$_9$OSO$_4$]$^-$	-21.78
Butylsulphate	[C$_4$H$_9$SO$_4$]$^-$	-21.56
Octylsulphate	[C$_8$H$_{17}$SO$_4$]$^-$	-20.76
Bis(malonato)borate	[C$_6$H$_4$BO$_8$]$^-$	-20.33
Iodide	I$^-$	-19.97
Tri(fluoromethane)sulfonate	[CF$_3$SO$_3$]$^-$	-17.11
Bis(pentafluoroethyl)phosphinate	[PO$_2$(C$_2$F$_5$)$_2$]$^-$	-17.09
Thiocyanate	[SCN]$^-$	-17.01
Tricyanomethane	[N(CN)$_3$]$^-$	-16.73
Bis(salicylato)borate	[BC$_{14}$H$_8$O$_6$]$^-$	-16.50
Bisbiphenyldiolatoborate	[BC$_{24}$H$_{16}$O$_4$]$^-$	-14.42
Perclorate	[ClO$_4$]$^-$	-13.11
Tetracyanoborate	[B(CN)$_4$]$^-$	-12.48
Bis(trifluoromethylsulfonyl)methane	[CH(CF$_3$SO$_2$)$_2$]$^-$	-11.16
Bis(oxalate)borate	[B(C$_2$O$_4$)$_2$]$^-$	-10.88
Bis(trifluoromethanesulfonyl)imide	[N(CF$_3$SO$_2$)$_2$]$^-$	-9.86
Tetrafluoroborate	[BF$_4$]$^-$	-9.79
Bis(pentafluoroethylsulfonyl)imide	[N(C$_2$F$_5$SO$_2$)$_2$]$^-$	-8.27
Tris(trifluoromethylsulfonyl)methide	[C(SO$_2$CF$_3$)$_3$]$^-$	-7.20
Boron tetrachloride	[BCl$_4$]$^-$	-4.13
Triiodide	[I$_3$]$^-$	-2.99
Hexafluorophosphate	[PF$_6$]$^-$	-2.88
Hexafluoroarsenate	[AsF$_6$]$^-$	-1.72
Hexafluorostibate	[SbF$_6$]$^-$	-1.65
Tetrachloroferrate	[FeCl$_4$]$^-$	-0.99
Tris(pentafluoroethyl)trifluorophosphate	[(C$_2$F$_5$)$_3$PF$_3$]$^-$	-0.74
Bis(nonafluorobutyl)trifluorophosphate	[(C$_4$F$_9$)$_2$PF$_3$]$^-$	-0.69

A single "polarity" parameter is not sufficient to explain all the variations in experimental results in solvent-mediated processes. Simple solvents, like *n*-alkanes, are limited in the number and type of interactions with the dissolved molecule. On the other

hand, more complex solvents, with additional functional groups, are capable of having additional interactions, and ILs tend to fall within this category. Given their chemical structure and diversity of functional groups, ILs are able to establish dispersive, $\pi\cdots\pi$, $n\cdots\pi$, hydrogen-bonding and electrostatic interactions. The experimental polarity scales are a weighted average of solute-solvent interactions, and are thus more complex in nature for ILs. In this work we focused essentially on the hydrogen-bond basicity of ILs, which is strongly dominated by their anions, while maintaining a fixed cation ($[C_4mim]^+$). The β value is a numerical description of the hydrogen-bond basicity of ILs and describes the importance of the individual ability of each IL anion to accept hydrogen bonds. Table 3 lists the COSMO-RS hydrogen-bonding interaction energies for an extended number of IL anions in a decreasing order of hydrogen-bond basicity.

The information provided in Table 3 henceforward can be used to understand the effect of different IL anions towards chemical-mediated processes. This extended polarity scale of the ability of the IL anion to hydrogen-bond can provide *a priori* information to select an improved IL for a specific application before extensive and time-consuming experiments.

Conclusions

The great complexity of ILs to act either as hydrogen-bond donors or acceptors has resulted in great efforts in the literature aimed at characterizing these fluids according to a polarity scale. Furthermore, this complexity, achieved by innumerable chemical structural variations, is valuable for the creation of "tailor-made" compounds. However, an efficient and realistic employment of ILs in scientific research, or even in industrial applications, requires the accurate knowledge of their physical and chemical properties. One of the most important aspects of ILs when envisaging their use for replacing typical molecular solvents relies on the specific interactions occurring between the solvent and the dissolved solute. The reactivity of dissolved substrates, reaction rates and reaction mechanisms are dependent on the solvent-solute interactions. The quantification of these solvent characteristics is thus an important tool to understand the physicochemical phenomena and chemical behaviour of systems involving ILs. For that purpose, several solvent parameters and relative polarity scales for ILs have been proposed in the past few years. Nevertheless, these polarity scales are dependent on the set of solvatochromic dyes used, on the experimental procedure adopted and also on the purity of the ILs. Therefore, a proper comparison amongst different groups of research is not viable and we are always limited to a relative polarity scale for a restricted number of ILs.

Aiming at overcoming the difficulties encountered with the establishment of a polarity scale for ILs, we proposed here the use of the hydrogen-bonding interaction energies, occurring in the equimolar cation-anion mixtures (E_{HB} / (kJ·mol^{-1})), estimated from COSMO-RS calculations. Reasonable linear correlations between the experimental hydrogen-bond basicity values and the E_{HB} estimated from COSMO-RS were found, thus underlining the validity of the proposed methodology. Based on this dependence, we provided an extended polarity scale capable of characterizing the IL anions' abilities to hydrogen-bond when acting as solvent media. The E_{HB} values estimated from COSMO-RS can be adequately used for routine screening, before extensive and time-consuming experimental measurements by a trial and error approach, and allow for the correct choice of an improved IL for a specific application.

Experimental

Materials

The ILs experimentally investigated were $[C_4mim][CF_3SO_3]$ (99 wt% purity from Iolitec), $[C_4mim][C_8H_{17}SO_4]$ (97 wt% purity form Merck), $[C_4mim][(CH_3O)_2PO_2]$ (98 wt% purity from Iolitec) and $[C_4mim][CF_3CO_2]$ (97 wt% purity from Iolitec). All the ILs investigated are transparent, colourless and liquid at room temperature. The purity of each IL was also checked by ^{1}H, ^{13}C, and ^{19}F (whenever applicable) NMR spectra and found to be in accordance with the purity levels given by the suppliers.

The dyes used were N,N-Diethyl-4-nitroaniline, 99% purity from Fluorochem, Reichardt dye, 90% purity from Sigma-Aldrich, and 4-nitroaniline, 99% purity from Aldrich.

The deuterium oxide used was acquired at Aldrich with > 99.96 % D atoms. The 3-(trimethylsilyl)propionic-2,2,3,3-d4 acid sodium salt (TSP) was from Aldrich with >98 % D atoms.

Methods

Solvatochromic assays. All the IL samples were dried under vacuum, at 50ºC for 48 h, before use. The dried IL (0.5 mL) was taken and placed into an appropriate round-bottom flask and each dye was further added (Reichardt dye, *N*, *N*-diethyl-4-nitroaniline or 4-nitroaniline) in a dichloromethane solution. Dichloromethane was then removed under vacuum at 50ºC (for 3 h). After cooling the UV-Vis spectra of all samples were recorded at 25 ºC (thermostated sample holder) using a PC-controlled Perkin-Elmer Lambda 2 spectrophotometer. Further details on the experimental procedure can be found elsewhere.[10]

Nuclear magnetic resonance (**NMR**). The ^{1}H NMR spectra were obtained with pure IL samples (and after drying under vacuum) placed in NMR spectroscopy tubes containing sealed reference capillaries with D_2O and TSP (3-(trimethylsilyl)propionic-2,2,3,3-d4 acid sodium salt) as the internal reference, and at 25 ºC. The ^{1}H NMR measurements were performed on a Bruker Avance 300 spectrometer operating at 300.13 MHz.

COSMO-RS

COSMO-RS[20] is a thermodynamic model that combines quantum chemistry, based on the dielectric continuum model known as COSMO (COnductor-like Screening MOdel for Real Solvents), with statistical thermodynamics calculations. COSMO calculations are performed in an ideal conductor, meaning that molecules are assumed as surrounded by a virtual conductor environment, and the interactions are completely made on the conductor interface, taking into account the electrostatic screening and the back-polarization of the solute molecule. Therefore, COSMO gives a discrete surface around the solute molecule which is characterized by its geometry and screening charge density (σ) that iteratively corresponds to a minimum energetic state at the conductor. COSMO-RS treats the surface

around the solute molecule as segments, and it also similarly treats the screening charge density of the respective segment, σ'.

In the molecular interaction approach, the most significant molecular interaction energy modes are the electrostatic misfit energy, and the hydrogen-bonding energy, E_{HB}, defined according to the following equation,

$$E_{HB} = a_{eff}\, c_{HB}\, min(0; min(0; \sigma_{donor} + \sigma_{HB}) \times max(0; \sigma_{acceptor} - \sigma_{HB})) \quad (2)$$

described as a function of the polarization charges of the two interacting segments, ($\sigma_{acceptor}, \sigma_{donor}$) and where a_{eff} is the effective contact area between two surface segments, c_{HB} is the hydrogen-bond strength and σ_{HB} is the threshold for hydrogen-bonding. The van der Waals energy is also accounted but in an approximate way; yet, it only depends on element specific van der Waals interaction parameters.

A number of conformations are available for the IL ions studied. In all the studied examples the lowest energy conformer was employed in the COSMO-RS calculations. Moreover, independent files for the IL cation and anions were used. An equimolar cation-anion mixture was used to specifically determine the E_{HB} values of a pure IL. The quantum chemical COSMO calculation was performed in the Turbomole program package[26] with the BP density functional theory, giving the surface charge density and the Ahlrichs-TZVP (triple-ζ valence polarized large basis set). [26] The COSMOtherm program with the parameter file BP_TZVP_C2.1_1301 were used in all the calculations.[26]

Notes and references

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§Acronyms of the ILs experimentally investigated: 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [C₄mim][CF₃SO₃]; 1-butyl-3-methylimidazolium octylsulphate, [C₄mim][C₈H₁₇SO₄]; 1-butyl-3-methylimidazolium dimethylphosphate, [C₄mim][(CH₃)₂PO₂]; 1-butyl-3-methylimidazolium trifluoroacetate, [C₄mim][CF₃CO₂].

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