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Alternative probe for the determination of the hydrogen-bond acidity of ionic liquids and their aqueous solutions†

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Abstract

Although highly relevant to *a priori* select adequate solvents for a given application, the determination of the hydrogen-bond acidity or proton donor ability of aqueous solutions of ionic liquids is a difficult task due to the poor solubility of the common probes in aqueous media. In this work, we demonstrate the applicability of the pyridine-*N*-oxide probe to determine the hydrogen-bond acidity of both neat ionic liquids and their aqueous solutions based on ¹³C NMR chemical shifts, and the suitability of these values to predict the ability of ionic liquids to form aqueous two-phase systems.

Due to their unique properties and enhanced performance, ionic liquids (ILs) have received increasing attention as suitable candidates for various applications, such as in organic synthesis, catalysis, polymerization, as solvent media for chemical reactions, and in separation/extraction processes.^{1–4} They are salts composed of bulk organic cations combined with either organic or inorganic anions, whose asymmetry and dispersed charge leads to low melting temperatures, by general definition below 100 °C. Important features associated to most ILs include their negligible vapour pressure, good thermal and chemical stabilities, and the ability to dissolve a wide variety of solutes. Furthermore, ILs are extremely versatile and often referred to as “tuneable”, “tailor”, “task-specific” or “designer” solvents. The versatility of these compounds has its root on the possibility of adjusting their physical and chemical properties by changing their constituting ions.

In addition to the large number of available ILs, the fine-tuning of their physico-chemical properties can be further extended by mixing ILs with molecular liquids. Their aqueous solutions are particularly important, with applications in many fields.^{4, 5} One particular subset of this strategy comprises IL-water mixtures for liquid-liquid phase separation and extraction processes.^{6, 7} In this field, a large interest has been given to IL-based aqueous biphasic systems (ABS) as alternative concentration and purification platforms of a wide variety of value-added compounds.⁴ However, to better predict their applicability at an industrial level, the physicochemical characterization of their coexisting phases is a crucial requirement.

An important criterion for choosing the most appropriate solvent for a particular application is the knowledge of its polarity, which encompasses all non-specific and specific interactions. It has been previously demonstrated that the IL polarity influences its solvation

ability, enzyme activity, reaction rates and reaction mechanisms, among others.^{4, 8–10} To appraise the polarity of solvents, several polarity scales are known and well-described in the literature, most of which are based on the interactions of solvatochromic dyes with the target solvent.¹¹ The solute–solvent interactions include multiple types of interactions, such as electrostatic, dipole–dipole, dipole-induced dipole, hydrogen bonding, and electron pair donor–acceptor interactions. A quantitative estimation of the solvent polarity aiming at explaining and/or predicting other solvent dependent phenomena is adequately obtained through a multi-parameter approach. The most widely accepted multiparametric polarity scale is the one proposed by Kamlet and Taft^{12–15} (KT), and that has been used to correlate the solvent effects (XYZ) on reaction rates, phase equilibria, and spectroscopic properties through linear solvation energy relationships (LSER) equations of the form

$$XYZ = (XYZ)_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where $(XYZ)_0$ is the value for the reference system, π^* represents the solvent's dipolarity/polarizability, α is the hydrogen bond donating ability (hydrogen-bond acidity), and β is the hydrogen-bond accepting ability (hydrogen-bond basicity). The parameters a , b and s represent the solute coefficients, which characterizing the respective influence of the π^* , α , and β terms on the XYZ property under study.

The determination of the β and π^* parameters by the identification of the solvatochromic peak maxima of selected probes is relatively straightforward. For example, the UV-Vis spectrum of the non-protonic indicators N,N-diethyl-4-nitroaniline (**1**) (Fig. 1) or 4-nitroanisole (**2**) (Fig. 1) in non-hydrogen bond acceptors solvents is shifted bathochromically by increasing the solvent dipolarity, and solvent effects on the peak shift depend only on π^* . For β , the magnitudes of the enhanced bathochromic displacements attributable to hydrogen bonding by 4-nitroaniline (**3**) relative to (**1**), and by 4-nitrophenol (**4**) relative to (**2**) (all chemical structures shown in Fig. 1,) are compared to the same solvent acceptors.

Similarly to β , α values are obtained using the solvatochromic comparison method. However, no structurally similar pairs of probes are used and of all of the KT parameters, α has been the most controversial parameter in regard to its use with ILs.¹⁶ Generally, the KT solvatochromic probe used to obtain α values is based on the displacement of the solvatochromic band observed in the spectrum of pyridinium *N*-phenolate betaine dye (Reichardt's dye, Figure 1). Although this dye has been used for long and known to be strongly dependent on the hydrogen bond donor ability of the solvent^{17–19}, it also shows a strong dependency on some other solvent properties. For molecular solvents, it has been reported²⁰ that this probe is only 1.11 times more sensitive to α than to π^* , and that it presents a slight dependence on β .²⁰ This scenario is even worsened for ILs, since electrostatic interactions are also mapped by the dye.^{21–26} Other probe solutes have been used to evaluate the hydrogen bond donor properties by means of UV-Vis spectroscopy or by ¹³C or ³¹P NMR²⁷, but all have shown dependences on others solvent properties.¹³ More importantly, the absorption spectrum of the Reichardt's dye in concentrated salt solutions is extremely diffuse^{28, 29}, and frequently the dye is insoluble in these salt solutions,

precluding its use in the characterization of aqueous solutions of ILs or in the characterization of the coexisting phases of IL-based ABS.

To overcome some of the aforementioned problems, pyridine *N*-oxide (PyO, Figure 1) was proposed as an alternative probe based on the replacement of the methoxyl group of 4-nitroanisole by a group that is capable of hydrogen-bond acceptance.³⁰ However, the solvatochromic effect observed (283-254 nm) falls within the absorption region of many solvents, including some ILs, thus detracting a widespread spectroscopic utility of this probe. A more adequate solution was further proposed using the same dye as a probe to characterize the hydrogen-bond acidity of 26 molecular solvents, yet through ¹³C NMR chemical shifts measurements.³¹ Schneider et al.³¹ determined the α values of 26 molecular solvents by the ¹³C chemical shifts of pyridine-*N*-oxide according to the following equations:

$$\alpha_{24} = 2.32 - 0.15 \times d_{24} \quad (2a)$$

$$\alpha_{34} = 0.40 - 0.16 \times d_{34} \quad (2b)$$

where α is the KT hydrogen bond donating ability of the solvent, d_{24} and d_{34} are the differences (in ppm) of the ¹³C NMR chemical shifts, δ , of carbons 2 and 3, respectively, with respect to that of carbon 4 of pyridine-*N*-oxide (*cf.* Figure 1 with the carbons number identification). According to Marcus²⁷, the standard deviation of the α values obtained by Schneider *et al.*³¹ are estimated to be 0.07, while their dependence on other solvent properties, such as π^* or β , are negligible. Based on this possibility, in the present work, we explored the applicability of this probe/method for the determination of the α parameter of ILs and of their aqueous solutions, being the aqueous solutions particularly relevant since they could not be widely characterized by the common Reichardt's dye probe.

In this work, NMR chemical shifts (δ) were obtained in ppm using a Bruker Avance 300 spectrometer (operating at 300.13 MHz for ¹H and 75.47 MHz for ¹³C NMR). Solutions containing 0.25 mol.dm⁻³ of the probe in neat solvent and tetramethylsilane in deuterated water as internal standard were used. ¹³C NMR assignments were taken by 2D Heteronuclear Single Quantum Coherence (HSQC) experiments. The validity of the probe/method was firstly evaluated by the determination of the α parameter of pure ILs, which were compared against those obtained with the Reichardt's dye, followed by its use to characterize aqueous solutions of ILs. The following ILs were investigated in what concerns the determination of the hydrogen-bond acidity of pure compounds: 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_{*n*}mim][Ntf₂], with *n* = 1, 3, 4 6 and 8); 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄mim][CF₃SO₃]); 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]); 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][N(CN)₂]); 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]); 1-butyl-3-methylimidazolium thiocyanate ([C₄mim][SCN]); 1-butyl-3-methylimidazolium acetate ([C₄mim][CH₃CO₂]); 1-butyl-1-methylpiperidinium

bis(trifluoromethylsulfonyl)-amide ([C₄mpip][Ntf₂]); 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][Ntf₂]); 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([C₃mpy][Ntf₂]); and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P_{66,14}][Ntf₂]). Since the goal is to move further to the characterization of aqueous solutions, the following ILs were used in aqueous solutions at different concentrations: 1-alkyl-3-methylimidazolium chloride ([C_{*n*}mim]Cl, with *n* = 4 and 6); tetrabutylammonium chloride ([N₄₄₄₄]Cl); cholinium chloride ([Ch]Cl); 1-butyl-1-methylpyrrolidinium chloride ([C₄mpyr]Cl); 1-butyl-3-methylpyridinium chloride ([C₄mpy]Cl); 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C₄mim][CF₃SO₃]); 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][N(CN)₂]); 1-butyl-3-methylimidazolium thiocyanate ([C₄mim][SCN]); and 1-butyl-3-methyl-imidazolium acetate ([C₄mim][CH₃CO₂]) (for chemical structures see ESI, Table S1). Further details on the probe and ILs purity, purification steps, and preparation of the aqueous solutions can be found in the ESI.

Table 1 presents the KT parameters for the pure ILs studied in this work, while Table S2 in the ESI shows those for common molecular solvents.

The analysis of the data illustrated in Figure 2, also considering the α values of molecular solvents, shows that α_{24} and α_{34} are strongly correlated according to:

$$\alpha_{24} = 0.061_{\pm 0.009} + 1.01_{\pm 0.02} \alpha_{34} \quad (3)$$

$$(n = 37; r^2 = 0.992; SD = 0.033; F = 4188)$$

where *n* is the number of experimental points, *r* is the correlation coefficient, SD the standard deviation, and *F* is the ratio of variance.

As shown in Figure 2 all the ILs fit within the equation comprising also the molecular solvents, meaning that the physico-chemical information provided by both scales is in agreement. Based on this straight correlation it is pointless to use the two scales, and therefore, for the sake of simplicity, on the following discussion we only call upon the α_{24} data.

It should be noted that the α -value itself has no fundamental physical meaning¹⁶, but should be considered instead as a guide and as a relative value for a given set of solvents which were appraised at the same conditions and using the same probes. The values of α_{24} of pure ILs (Table 1) and molecular solvents (Table S2 in the ESI), determined from the ¹³C NMR data of pyridine-*N*-oxide, are compared with the data obtained with the Reichardt's dye (α_{RD}) in Figure 3. The straight correlation presented in Fig. 3 shows that pyridine-*N*-oxide is a suitable probe to characterize the hydrogen-bond donor properties of molecular solvents as well as of ILs, and that it can be used as an individual probe/method capable of ranking the hydrogen-bond acidity of a given set of solvents.

Amongst the three KT solvatochromic parameters, the α and β parameters are recognized to cover a wider range of values, being π usually less divergent.^{16, 32, 34} The β parameter of

the ILs studied in the present work ranges from 0.20 (for [C₁mim][Ntf₂]) up to 1.18 (for [C₄mim][CH₃CO₂]), π varies between 0.89 (for [C₄mim][CH₃CO₂]) and 1.06 (for [C₄mim][SCN]), and α_{24} ranges between 0.25 (for [C₄mim][CH₃CO₂]) and 0.79 (for [C₃mpy][Ntf₂]). The hydrogen bond donor strength of an IL is recognized to be dominated by the cation, depending only slightly upon the anion.^{16, 32, 34} This effect was also verified in the current work when evaluating the α values obtained for the [C₄mim]-based ILs ($\alpha_{24} = 0.42 \pm 0.03$, for [C₄mim]⁺ combined with a wide variety of anions, such as [Ntf₂]⁻, [CF₃SO₃]⁻, [BF₄]⁻, [N(CN)₂]⁻, [PF₆]⁻ and [SCN]⁻). The only exception was observed with [C₄mim][CH₃CO₂] that displays an extremely low α_{24} value, and where similar trends were obtained with the Reichardt's probe.^{16, 23} The reason behind the low hydrogen-bond acidity of the acetate-based IL is not yet clear, but could have its origin on the strong hydrogen-bond interactions occurring between the imidazolium cation and the acetate anion, as a result of this anion high hydrogen-bond basicity, reducing consequently its α value. On the other hand, the hydrogen-bond acidity of imidazolium-based ILs, as measured with the PyO probe, decreases with the increase in the number of carbon atoms at the alkyl side chains, in agreement with the literature data obtained with different probes/methods.^{32, 33, 35, 36}

For the ILs studied sharing the same [Ntf₂]⁻ anion, their acidity increases in the order: [P_{666,14}][Ntf₂] < [C₄mpip][Ntf₂] < [C₄mpyr][Ntf₂] < [C₄mim][Ntf₂] < [C₃mpy][Ntf₂], as measured by the pyridine-*N*-oxide probe. A slight different acidity ordering is obtained when using the Reichardt's dye, and according to: [P_{666,14}][Ntf₂] < [C₄mpip][Ntf₂] < [C₄mpyr][Ntf₂] < [C₃mpy][Ntf₂] < [C₄mim][Ntf₂]. The characteristics of hydrogen-bonding (H-bonding) in ILs cover an extremely wide and diverse range. These comprise conventional H-bonding and blue-shifted H-bonding, dihydrogen H-bonding, inverse H-bonding, resonance assisted H-bonding, charge-assisted H-bonding, ionic H-bonding, among others.³⁷ The sensitivity of chemically distinct solvatochromic- or NMR-based probes are probe-specific, which could lead to slightly divergent polarity scales. In particular, pyridine-*N*-oxide has been described to participate in very strong positive/negative charge-assisted H-bonding^{38, 39}, and that might be the reason behind the differences observed for the ranking on the α values of [C₃mpy][Ntf₂] and [C₄mim][Ntf₂].

As previously mentioned, the physico-chemical properties of ILs can be further tuned by mixing them with molecular solvents, such as water or ethanol. Nevertheless, the *a priori* knowledge of the polarity of ILs and their mixtures with other solvents is a crucial requirement for carrying out reaction, separation and extraction processes. There are however few data in the literature regarding the polarity of IL-water mixtures 40–43 – a major consequence of the Reichardt's dye low solubility in aqueous solutions. After addressing the potential of the PyO probe to determine the hydrogen-bond acidity of ILs, we further explored its applicability to determine the α parameter of IL-water mixtures. Both IL-water mixtures of partial miscibility (mainly derived from the solid state at room temperature of the ILs appraised, Figure 4) and complete miscibility (Figure 5) were studied. All detailed data are presented in the ESI (Table S3).

For all studied IL-water mixtures there is the decrease of the hydrogen-bond acidity as a function of the IL concentration, meaning that water has a higher ability to donate protons than aqueous solutions of ILs. For the first set of IL-water mixtures (Figure 4), where

concentrations up to 25% of IL (in mole fraction) were investigated, there is a linear correlation between the hydrogen bond donor acidity and the IL concentration. For the second set of IL-water mixtures (Figure 5) an almost ideal behaviour is observed for the [C₄mim][SCN]-, [C₄mim][N(CN)₂]- and [C₄mim][CF₃SO₃]-water mixtures, whereas for the [C₄mim][CH₃CO₂]-water mixture a non-ideal behaviour is observed. Khupse and Kumar⁴⁰ also observed a non-linear behaviour of the α parameter (measured with the Reichardt's dye) in binary water-IL mixtures composed of [BF₄]-based ILs, and interpreted the results based on preferential solvation models, in which the deviations from the ideal behaviour result from a different tendency of the probe to be solvated by the several solvents. However, it should be highlighted that no such extreme non-ideal behaviour, as reported by these authors⁴⁰, was here observed. This suggests that the probe used in this work could be better solvated by IL-water mixtures, further confirming the applicability of PyO to determine the hydrogen-bond donor properties of ILs and of IL aqueous solutions.

Ultimately, the practical outcome of a polarity scale is to explain or predict solvent effects on diverse types of physico-chemical phenomena. In this regard, we used the hydrogen-bond acidity data obtained in the current work for aqueous solutions of ILs along with data of phase equilibria of ternary IL-water-salt mixtures reported in the literature^{7, 44–46} to obtain new insights on the molecular-level phenomena ruling the phase splitting of IL-salt ABS. A strong correlation between the α values of the IL-water mixtures and the ability of each IL to create ABS was observed (Figure 6). The capability of each IL to create ABS was addressed by the IL/salt concentrations required to form two aqueous phases, *i.e.* by taking the values at each binodal curve in which the concentration of IL ([IL], in mol·kg⁻¹) is equal to the concentration of the salt ([Salt], in mol·kg⁻¹). Two salts (K₃PO₄ and K₃C₆H₅O₇) that are able to form ABS with a large variety of ILs^{7, 44–46} were used as examples. The α values presented in Figure 6 correspond to an IL concentration of 20% (in mole fraction). It should be mentioned however that similar correlations are obtained for different IL-water compositions, as would be expected from the linear behaviour of the α values of IL-water mixtures illustrated in Figures 4 and 5. All the ILs presented in Figure 6 share the same chloride anion. The effect of the IL anion was not considered in this type of correlations since the studied [C₄mim]-based ILs, all have, within the experimental uncertainty, the same α_{24} value, with the exception of [C₄mim][CH₃CO₂]. This is a main result of the hydrogen-bond acidity being governed by the IL cation as discussed before.

The results illustrated in Figure 6 reveal that the closer is the α_{24} value of the IL-water mixture to that of water (1.36) or the higher the ability of a given IL-water mixture to donate protons, which further translates into a higher affinity of a given IL for water, the larger is the value of the respective binodal curve or the larger is the amount of IL and salt required to create an ABS. In an ABS, IL and salt ions compete for the water molecules, being well-accepted that this type of systems is formed due to the salting-out ability of the salt over the IL in aqueous media.^{7, 44–46} For the ILs evaluated, the immiscibility region in ABS decreases according to the series: [N₄₄₄₄][Cl] > [C₆mim][Cl] > [C₄mpyr][Cl] > [C₄mim][Cl], regardless of the salt ^{7, 44–46}, and thus the systems formed by [N₄₄₄₄][Cl] require a lower amount of salt to undergo liquid-liquid demixing whereas the opposite is observed with [C₄mim][Cl]. In summary, the correlations shown in Figure 6 reveal that the higher the hydrogen-bond acidity of a given IL-water mixture (which ranks the IL in terms of affinity

for water) the more difficult it is to create an ABS, confirming thus the usefulness of hydrogen-bond acidity data to predict the ability of ILs to create aqueous two-phase systems.

In this work we demonstrated that the differences of the ^{13}C NMR chemical shifts of carbon 2 (or 3), with respect to that of carbon 4 of pyridine-*N*-oxide, can be used to determine the hydrogen bond acidity or hydrogen bond donation ability of neat ILs and of their aqueous solutions. Furthermore, this approach to obtain the α values does not require the determination of other solvent properties, such as π or β . Compared to the current available scales, a wider scale for the hydrogen-bond acidity of ILs and of their aqueous solutions can be established with the pyridine-*N*-oxide probe and ^{13}C NMR analysis. Taking into account the utility of polarity scales to predict other physico-chemical phenomena, it was here demonstrated that the hydrogen-bond acidity of aqueous solutions of ILs closely correlates with the ILs ability to create ABS or to be salted-out by conventional salts in aqueous ternary mixtures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Solvatochromic dyes.

Figure 2.

Values of α_{24} plotted against the α_{34} values obtained from ^{13}C NMR of PyO for various molecular solvents (●) and ionic liquids (⊕).

Figure 3.

Values of α_{24} obtained from ^{13}C NMR of PyO plotted against the α values obtained with the Reichardt's probe (α_{RD}) for various molecular solvents (●) and ionic liquids (⊕).

Figure 4.
 α_{24} values for partially miscible IL-water mixtures as a function of the IL concentration.

Figure 5.
 α_{24} values for the completely miscible IL-water mixtures as a function of the IL concentration.

Figure 6.

α_{24} values for IL-water mixtures (chloride-based ILs) versus the capability of each IL to create ABS (addressed by the values at each binodal curve in which the concentration of IL is equal to the concentration of salt).

Table 1

Solvatochromic parameters for the ionic liquids studied in the present work (for chemical structures see Table S1 in the ESI).

Ionic liquid	α_{24}	α_{34}	α_{RD}^a	β^a	π^{*a}
[C ₁ mim][Ntf ₂]	0.58	0.51	0.82	0.20	0.97
[C ₃ mim][Ntf ₂]	0.51	0.44	0.78	0.23	0.96
[C ₄ mim][Ntf ₂]	0.48	0.39	0.69	0.27	0.94
[C ₆ mim][Ntf ₂]	0.50	0.40	0.64	0.27	0.95
[C ₈ mim][Ntf ₂]	0.44	0.37	0.64	0.28	0.94
[C ₄ mim][CF ₃ SO ₃]	0.39	0.32	0.62 ^b	0.49 ^b	1.00 ^b
[C ₄ mim][BF ₄]	0.42	0.33	0.62 ^b	0.49 ^b	1.00 ^b
[C ₄ mim][N(CN) ₂]	0.39	0.32	0.54 ^b	0.60 ^b	1.05 ^b
[C ₄ mim][PF ₆]	0.44	0.36	0.68 ^b	0.21 ^b	1.02 ^b
[C ₄ mim][SCN]	0.40	0.31	0.43 ^{c,d}	0.71 ^{c,d}	1.06 ^{c,d}
[C ₄ mim][CH ₃ CO ₂]	0.25	0.19	0.43 ^b	1.20 ^b	0.96 ^b
[C ₄ mpip][Ntf ₂]	0.36	0.26	0.44	0.26	0.94
[C ₄ mpyr][Ntf ₂]	0.44	0.35	0.47	0.28	0.94
[C ₃ mpy][Ntf ₂]	0.79	0.80	0.51	0.26	0.98
[P _{666,14}][Ntf ₂]	0.34	0.27	0.24	0.46	0.86

^a values taken from the literature³² unless otherwise indicated

^b data from reference¹⁶

^c data from reference³³

^d a different set of dyes was used (see reference³³)