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

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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 commonly used 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 \(^{13}\text{C}\) NMR chemical shifts, and the suitability of these values to appraise 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. \(^3\)-\(^4\) 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 “tunable”, “tailor”, “task-specific” or “designer” solvents. The versatility of these compounds has its roots 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 physicochemical properties can be further extended by mixing ILs with molecular liquids. Their aqueous solutions are particularly important, with applications in many fields.\(^5\)\(^6\) One particular sub-set 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, enzymes activities, reaction rates and 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.\(^11\) Solute–solvent interactions include multiple types, 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 can be 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), which has been used to correlate solvent effects (XYZ) on reaction rates, phase equilibria, and spectroscopic properties, through linear solvation energy relationships (LSER) equations of the form

\[
XYZ = (XYZ)_0 + s\pi^a + a\sigma + b\beta
\]  

where \((XYZ)_0\) is the value for the reference system, \(\pi^a\) represents the solvent’s dipolarity/polarizability, \(\sigma\) is the hydrogen bond donating ability (hydrogen-bond acidity), and \(\beta\) is the hydrogen-bond accepting ability (hydrogen-bond basicity). The parameters \(a\), \(b\) and \(s\) represent the solute coefficients, which characterize the respective influence of the \(\pi^a\), \(\sigma\), and \(\beta\) terms on the XYZ property under study.

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

Similarly to $\beta$, $\alpha$ values are obtained using the solvatochromic comparison method. However, no structurally similar pairs of probes are used, and amongst all the KT parameters, $\alpha$ also has been the most controversial parameter, particularly regarding their values for ILs. Generally, the KT solvatochromic probe used to obtain $\alpha$ values is based on the displacement of the solvatochromatic band observed in the spectrum of pyridinium $N$-phenolate betaine dye (Reichardt’s dye, Fig. 1). Although this dye has been used for long and known to be strongly dependent on the hydrogen bond donor ability of the solvent, it also shows a strong dependency on some other solvent properties. For molecular solvents, it has been reported that this probe is only 1.11 times more sensitive to $\pi^*$ than to $\pi^*$, and that it presents a slight dependence on $\beta$. This scenario is even worsened for ILs, since electrostatic interactions are also mapped by the dye. Other probe solutes have been used to evaluate the hydrogen bond donor properties by means of UV-visible spectroscopy or by $^{13}$C or $^{31}$P nuclear magnetic resonance (NMR), but all have shown dependences on others solvent properties. More importantly, the absorption spectrum of the Reichardt’s dye in concentrated salt solutions is extremely diffuse, while this dye is almost insoluble in water and aqueous 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, Fig. 1) was proposed as an alternative probe based on the replacement of the methoxyl group of 4-nitroanisole by a hydrogen-bond acceptor group. However, the solvatochromatic 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 $^{13}$C NMR chemical shifts measurements. Schneider et al. determined the $\alpha$ values of 26 molecular solvents by the $^{13}$C chemical shifts of PyO according to the following equations:

$$\alpha_{d_4} = 2.32 - 0.15 \times d_{d_4} \quad (2a)$$

$$\alpha_{d_4} = 0.40 - 0.16 \times d_{d_4} \quad (2b)$$

where $\alpha$ is the KT hydrogen bond donating ability of the solvent, $d_{d_4}$ and $d_{d_4}$ are the differences (in ppm) of the $^{13}$C NMR chemical shifts, $\delta$, of carbons 2 and 3, respectively, with respect to that of carbon 4 of PyO (cf. Fig. 1 with the carbons number identification). According to Marcus, the standard deviation of the $\alpha$ values obtained by Schneider et al. are estimated to be 0.07, while their dependence on other solvent properties, such as $\pi^*$ or $\beta$, are negligible. Based on this possibility, in the present work, we explored the applicability of this probe/method for the determination of the $\alpha$ parameter of ILs and of their aqueous solutions, being aqueous solutions particularly relevant since they could not be widely characterized by the common Reichardt’s dye probe, as previously highlighted.

In this work, NMR chemical shifts ($\delta$) were obtained in ppm using a Bruker Avance 300 spectrometer (operating at 300.13 MHz for $^1$H and 75.47 MHz for $^{13}$C NMR). Solutions containing 0.25 mol dm$^{-3}$ of PyO in each sample were characterized, and a solution of tetramethylsilane (TMS) in pure deuterated water (99.9% D) as internal standard, were used in NMR tubes adapted with coaxial inserts. The TMS/D$_2$O solution was always used as the inner part of the concentric tubes, while each sample was used in the outer part of the NMR tube. Using this approach it is possible to guarantee that the TMS standard and D$_2$O are not in direct contact with the sample, avoiding thus possible interferences or deviations in the $^{13}$C NMR chemical shifts. Further details on the NMR experimental procedure and spectra analysis are given in the ESI.$^\dagger$

The validity of the probe/method employed was firstly ascertained by the determination of the $\alpha$ parameter of pure ILs, which were compared against those obtained using 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 (the definition of the ILs acronym is provided as a footnote): $[\text{C}_4\text{mim}]\text{[Ntfs]}_2$ with $n = 1, 3, 4, 6$ and 8, $[\text{C}_4\text{mim}]\text{[CF}_3\text{SO}_3]$; $[\text{C}_4\text{mim}]\text{[BF}_4]$; $[\text{C}_4\text{mim}]\text{[N(CN)}_2]$; $[\text{C}_4\text{mim}]\text{[PF}_6]$; $[\text{C}_4\text{mim}]\text{[SCN]}$; $[\text{C}_4\text{mim}]\text{[CH}_3\text{CO}_2]$; $[\text{C}_4\text{mpyr}]\text{[Ntfs]}_2$; $[\text{C}_3\text{mpyr}]\text{[Ntfs]}_2$; $[\text{C}_4\text{mpy}]\text{[Ntfs]}_2$; $[\text{C}_4\text{mpy}]\text{[Ntfs]}_2$; $[\text{P}_{66614}]\text{[Ntfs]}_2$. Since the goal is to move further to the characterization of aqueous solutions, the following ILs were used in aqueous solutions at different concentrations: $[\text{C}_4\text{mim}]\text{Cl}$ with $n = 4$ and 6; $[\text{C}_4\text{mim}]\text{Cl}$; $[\text{C}_4\text{mpyr}]\text{Cl}$; $[\text{C}_4\text{mpy}]\text{Cl}$; $[\text{C}_4\text{mim}]\text{[CF}_3\text{SO}_3]$; $[\text{C}_4\text{mim}]\text{[N(CN)}_2]$; $[\text{C}_4\text{mim}]\text{[SCN]}$ and $[\text{C}_4\text{mim}]\text{[CH}_3\text{CO}_2]$. ILs chemical structures and further details on the probe and ILs purity, purification steps, and preparation of the aqueous solutions can be found in the ESI.$^\dagger$
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. Further details on the α values determination are given in the ESI†.

The analysis of the data illustrated in Fig. 2, which also considers the α values of molecular solvents, shows that α24 and α34 strongly correlate according to:

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

where n is the number of experimental points, r is the correlation coefficient, SD the standard deviation, and F is the ratio of variance. It should be noted that acetic acid, benzyl alcohol, and cyclohexane were considered as outliers. As shown, all ILs fit within the given equation which also comprises values for molecular solvents, meaning that the physicochemical information of all solvents (including ILs), i.e., the solvents ranking in terms of hydrogen-bond acidity provided by both scales, is in close agreement. This general correlation that includes both organic solvents and ILs show that electrostatic interactions are not mapped by the current probe.

Based on the straight correlation between α24 and α34 shown in Fig. 2, and although the two scales could be used to characterize solvents, for the sake of simplicity it is pointless to use both scales. Recent reported studies on 13C and 1H NMR chemical shifts of H-bond complexes of derivatives of PyO in ILs showed that small interchange in positions of C3, C4 and C5 (cf. Fig. 1) signals can appear. Thus, α24 data result from a more straightforward analysis with less interferences of ILs as solvents, and on the following discussion we only call upon the α24 data. Moreover, the α-values obtained by the different probes have no fundamental physical meaning, but should be considered instead as a guide to rank a given set of solvents which are appraised at the same conditions and using the same probes.

The α24 values of pure ILs (Table 1) and molecular solvents (shown in the ESI†), determined from the 13C NMR data of PyO, are compared with the data obtained with the Reichardt’s dye (αRD) in Fig. 3. The straight correlation presented in Fig. 3 is given by the following equation,

$$\alpha_{24} = 0.88_{\pm 0.05} \alpha_{RD} \quad (4)$$

where n is the number of experimental points, SD the standard deviation, F the ratio of variance and p is the common statistic p-value based on the null hypothesis. The obtained straight correlation supports the suitability of PyO as an alternative 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.

Eqn (4) allows a backwards calculation and the determination of the widely used ET(30) (or E27) single parameter polarity scales, according to the following equations:

$$ET(30) = (\alpha_{RD} + 2.03 + 0.72\pi^*)/0.0649 \quad (5a)$$

Table 1 Solvatochromic parameters for the ILs studied in the present work.

<table>
<thead>
<tr>
<th>ILs</th>
<th>α24</th>
<th>α34</th>
<th>αRDa</th>
<th>βa</th>
<th>πa</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4mim][Ntf2]</td>
<td>0.58</td>
<td>0.51</td>
<td>0.82</td>
<td>0.20</td>
<td>0.97</td>
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<tr>
<td>[C5mim][Ntf2]</td>
<td>0.51</td>
<td>0.44</td>
<td>0.78</td>
<td>0.23</td>
<td>0.96</td>
</tr>
<tr>
<td>[C6mim][Ntf2]</td>
<td>0.48</td>
<td>0.39</td>
<td>0.69</td>
<td>0.27</td>
<td>0.94</td>
</tr>
<tr>
<td>[C7mim][Ntf2]</td>
<td>0.50</td>
<td>0.40</td>
<td>0.64</td>
<td>0.27</td>
<td>0.95</td>
</tr>
<tr>
<td>[C8mim][Ntf2]</td>
<td>0.44</td>
<td>0.37</td>
<td>0.64</td>
<td>0.28</td>
<td>0.94</td>
</tr>
<tr>
<td>[C4mim][CF3SO3]</td>
<td>0.39</td>
<td>0.32</td>
<td>0.62b</td>
<td>0.49b</td>
<td>1.00b</td>
</tr>
<tr>
<td>[C8mim][Ntf2]</td>
<td>0.48</td>
<td>0.39</td>
<td>0.69</td>
<td>0.27</td>
<td>0.94</td>
</tr>
<tr>
<td>[C4mim][BF4]</td>
<td>0.42</td>
<td>0.33</td>
<td>0.62b</td>
<td>0.49b</td>
<td>1.00b</td>
</tr>
<tr>
<td>[C8mim][N(CN)2]</td>
<td>0.39</td>
<td>0.32</td>
<td>0.54b</td>
<td>0.60b</td>
<td>1.05b</td>
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<tr>
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<td>0.36</td>
<td>0.68b</td>
<td>0.21b</td>
<td>1.02b</td>
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<tr>
<td>[C4mim][SCN]</td>
<td>0.40</td>
<td>0.31</td>
<td>0.43bd</td>
<td>0.71bd</td>
<td>1.06bd</td>
</tr>
<tr>
<td>[C4mim][CH3CO2]</td>
<td>0.25</td>
<td>0.19</td>
<td>0.43b</td>
<td>1.20b</td>
<td>0.96b</td>
</tr>
<tr>
<td>[C4mim][Pyridine]</td>
<td>0.36</td>
<td>0.26</td>
<td>0.44</td>
<td>0.26</td>
<td>0.94</td>
</tr>
<tr>
<td>[C4mim][Pyridine]</td>
<td>0.44</td>
<td>0.35</td>
<td>0.47</td>
<td>0.28</td>
<td>0.94</td>
</tr>
<tr>
<td>[C4mim][Pyridine]</td>
<td>0.79</td>
<td>0.80</td>
<td>0.51</td>
<td>0.26</td>
<td>0.98</td>
</tr>
<tr>
<td>[C4mim][Ntf2]</td>
<td>0.34</td>
<td>0.27</td>
<td>0.24</td>
<td>0.46</td>
<td>0.86</td>
</tr>
</tbody>
</table>

* Values taken from the ref. 32 unless otherwise indicated. † Data from ref. 16. ‡ Data from ref. 33. A different set of dyes was used (see ref. 33).
The experimental ET\textsubscript{(30)} values obtained with the Reichardt’s dye probe and those calculated with eqn (4) and (5) using the PyO probe to obtain the $z$ values are given in the ESI (both for molecular organic solvents and ILs).

Amongst the three KT solvatochromic parameters, given in Table 1, the $x$ and $\beta$ parameters are recognized to cover a wider range of values, being $\pi$ usually less divergent.\textsuperscript{16,32,35} The $\beta$ parameter of the ILs studied in the present work ranges from 0.20 (for [C\textsubscript{4}mim][CH\textsubscript{3}CO\textsubscript{2}]) up to 1.18 (for [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}]), $\pi^*$ varies between 0.89 (for [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}]) and 1.06 (for [C\textsubscript{4}mim][SCN]), and $z_{24}$ ranges between 0.25 (for [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}]) and 0.79 (for [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}]). The hydrogen bond donor strength of an IL is recognized to be dominated by the cation, depending only slightly upon the anion.\textsuperscript{16,32,35} This effect was also verified in the current work when evaluating the $x$ values obtained for the [C\textsubscript{4}mim]-based ILs ($z_{24}$ = 0.42 $\pm$ 0.03, [C\textsubscript{4}mim]+ combined with a wide variety of anions, such as [N\textsubscript{tf2}], [C\textsubscript{2}F\textsubscript{3}SO\textsubscript{3}], [BF\textsubscript{4}], [N(CN)\textsubscript{2}], [PF\textsubscript{6}] and [SCN]). The only exception was observed with [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}] that displays an extremely low $z_{24}$ value, and where similar trends were obtained with the Reichardt’s probe.\textsuperscript{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 the $x$ 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.\textsuperscript{32,33,36,37} For the ILs studied sharing the [N\textsubscript{tf2}] anion, their acidity increases in the order: [P\textsubscript{666,14}[N\textsubscript{tf2}] < [C\textsubscript{3}mpip][N\textsubscript{tf2}] < [C\textsubscript{4}mipyr][N\textsubscript{tf2}] < [C\textsubscript{4}mim][N\textsubscript{tf2}] < [C\textsubscript{4}mpyr][N\textsubscript{tf2}], as measured by the PyO probe. A slight different acidity ordering is obtained when using the Reichardt’s dye, and according to: [P\textsubscript{666,14}[N\textsubscript{tf2}] < [C\textsubscript{4}mipyr][N\textsubscript{tf2}] < [C\textsubscript{3}mpy][N\textsubscript{tf2}] < [C\textsubscript{4}mpyr][N\textsubscript{tf2}] < [C\textsubscript{4}mim][N\textsubscript{tf2}]. It is well-known that 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.\textsuperscript{38} The sensitivity of chemically distinct solvatochromic- or NMR-based probes are probe-specific, which could thus lead to slightly divergent polarity scales. In particular, PyO has been described to participate in very strong positive/negative charge-assisted H-bonding,\textsuperscript{28,40} which could be the reason behind the differences observed for the ranking on the $z$ values for [C\textsubscript{4}mpyr][N\textsubscript{tf2}] vs. [C\textsubscript{4}mim][N\textsubscript{tf2}].

As previously mentioned, the physicochemical properties of ILs can be further tuned by mixing these ionic species with molecular solvents, such as water or alcohols. Nevertheless, the a\textit{ priori} knowledge of the polarity of ILs and their mixtures with other solvents is a crucial requirement for carrying out reactions, as well as separation processes. Despite its relevance, there are however few data in the literature regarding the polarity of IL–water mixtures\textsuperscript{31–44} – a major consequence of the Reichardt’s dye almost null solubility in aqueous solutions. After addressing the potential of the PyO probe to determine the hydrogen-bond acidity of neat ILs, we further explored its applicability to determine the $z$ parameter of IL–water mixtures. Both IL–water mixtures of partial miscibility (mainly derived from the solid state of the ILs appraised at room temperature, Fig. 4) and complete miscibility (Fig. 5) were studied. All detailed data, including some examples of the obtained NMR spectra, are presented in the ESI.\textsuperscript{†}

For all studied IL–water mixtures, the hydrogen-bond acidity decreases as a function of the IL concentration, meaning that water has a higher ability to donate protons than aqueous solutions of ILs. In both sets appraised, the hydrogen-bond acidity of IL aqueous solutions follows the ILs ranking discussed above. For instance, at a fixed concentration of IL, aqueous solutions of [N\textsubscript{4444}]Cl display a lower ability to donate protons than aqueous solutions of [Ch]Cl – an expected trend given the more hydrophobic character of [N\textsubscript{4444}]Cl, afforded by the four butyl chains attached to the nitrogen central atom, when compared to the more hydrophilic [Ch]Cl, composed of shorter aliphatic moieties and an extra –OH group. For the first set of IL–water mixtures (Fig. 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. On the other hand, for the second set of IL–water mixtures (Fig. 5) investigated, an almost ideal behaviour is observed for the [C\textsubscript{4}mim][SCN], [C\textsubscript{4}mim][N(CN)\textsubscript{2}] and [C\textsubscript{4}mim][CF\textsubscript{3}SO\textsubscript{3}]-water mixtures, whereas for the [C\textsubscript{4}mim][CH\textsubscript{2}CO\textsubscript{2}]-water mixture a non-ideal behaviour is perceived. Khupse and Kumar\textsuperscript{41} also observed a non-linear behaviour of the $z$ parameter (measured with the Reichardt’s dye) in binary water–IL mixtures composed of [BF\textsubscript{4}]-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
The results illustrated in Fig. 6 reveal that the closer is the $\alpha_{24}$ 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 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.\textsuperscript{7,45–47} For the ILs evaluated, the immiscibility region in ABS decreases according to the series: $[N_{4444}]\text{Cl} > [C_{4}\text{mim}]\text{Cl} > [C_{4}\text{mpyr}]\text{Cl} > [C_{4}\text{mim}]\text{Cl}$, regardless of the salt.\textsuperscript{7,45–47} and thus the systems formed by $[N_{4444}]\text{Cl}$ require a lower amount of salt to undergo liquid–liquid demixing, whereas the opposite is observed with $[C_{4}\text{mim}]\text{Cl}$. In summary, the correlations shown in Fig. 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 \textsuperscript{13}C NMR chemical shifts of carbon 2 (or 3), with respect to that of carbon 4, of PyO 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 $\alpha$ values does not require the determination of other solvent properties, such as $\pi$ or $\beta$. 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 PyO probe and \textsuperscript{13}C NMR analysis. Taking into account the utility of polarity scales to predict other physicochemical 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.

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Notes and references