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PAPER

Understanding the polarity of ionic liquids†

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The polarities of a wide range of ionic liquids have been determined using the Kamlet–Taft empirical polarity scales α, β and π^*, with the dye set Reichardt's Dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline. These have been compared to measurements of these parameters with different dye sets and to different polarity scales. The results emphasise the importance of recognising the role that the nature of the solute plays in determining these scales. It is particularly noted that polarity scales based upon charged solutes can give very different values for the polarity of ionic liquids compared to those based upon neutral probes. Finally, the effects of commonplace impurities in ionic liquids are reported.

Introduction

Ionic liquids are showing themselves to be solvents of ever greater interest and utility.[1] They have been the subject of widespread academic study[2] and have been applied in a number of commercial processes.[3] Since polarity is one of the most widely applied solvent concepts, its study for ionic liquids has been a major theme in their development.[2,4] Recently there has been much work on measurement of the dielectric constants of ionic liquids.[5] Other work has concentrated on effects ionic liquids on solvatochromic probe solutes,[6] or chromatographic techniques.[7,8]

The currently accepted definition of polarity is that it is the sum of all possible specific and non-specific intermolecular interactions between the solvent and any potential solute, excluding those interactions leading to chemical transformations of the solute.[9] While this is conceptually straight-forward, it is composed of several interacting components, including Columbic interactions, the various dipole interactions, both permanent and induced, hydrogen-bonding and electron pair donor–acceptor interactions. It is both a physical and a chemical phenomenon. Further to this, polarity is a description of the potential behaviors of the solvent in a relationship with the solute, not an absolute property of the pure liquid. Hence, there is no single measure of polarity; all polarity scales are estimates and different scales give different polarities for the same solvent and even different relative polarities can arise for the many different measurement techniques that have been used.[9,10] There is no useful concept of 'right' or 'wrong' when comparing these scales; rather whether the application of a particular polarity scale is more or less appropriate in a given circumstance is a more helpful approach. The test of an empirical polarity scale is its usefulness in explaining and/or predicting other solvent dependent phenomena.

Single parameter polarity scales are not capable of capturing the complexity of interactions that give rise to a solvent's polarity. Hence, Kamlet and Taft introduced multi-parameter polarity scales based upon Linear Solvation Energy Relationships (eqn (1)) composed of the complimentary scales of hydrogen bond acidity (α),[11] hydrogen bond basicity (β),[12] and dipolarity/polarizability effects (π^*).[13] These scales together provide greater sophistication when describing a solvent's polarity than single parameter scales. This methodology has been adapted for use with ionic liquids and sets of the three Kamlet–Taft parameters have been measured for a number of these.[14–21] However, it should be noted that none of these studies has used Kamlet and Taft's original methodology. The Kamlet–Taft LSER approach has had considerable successes in elucidating solvent dependent phenomena in ionic liquids, particularly in explaining and predicting the rates and selectivities of many chemical reactions,[15,16,22] including catalytic processes,[23] although not for all reactions for which this has been attempted.[19,24] However, their use has also received some criticism. In this paper, we report the use of derivatives of the Kamlet–Taft system, demonstrate their utility and explain their limitations.

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

Experimental

Syntheses of the ionic liquids used the accepted technique of first preparing the halide salt of the appropriate cation followed by anion metathesis.[1] The experimental details for

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the syntheses and characterizations of the ionic liquids are given in the ESI.†

All samples were dried under vacuum at 50 °C for 48 h before measurement. Dried ionic liquid (0.4 ml) was taken into a round-bottomed flask and the appropriate dye was added in DCM (*ca*. 0.9 mM, dry, 0.4 ml). The DCM was then removed at 50 °C under vacuum for 4 h before cooling and measuring the UV-vis spectrum of the sample at 25 °C on a Perkin-Elmer Lambda 25 machine.

Results

π* values

The π* value lies at the heart of the Kamlet–Taft system, yet it is in the measurement of the π* values for ionic liquids that there has been the greatest deviation from the original Kamlet–Taft methodology. It is recognised that when an empirical polarity scale is based upon the solvatochromism of a single probe molecule, idiosyncratic results can arise.[9,10] To avoid this, the Kamlet–Taft π* scale of solvent dipolarity/polarizability was first created using seven primary solvatochromic dyes with strong and symmetric solvatochromic absorption spectra.[13] The data used to calculate their π* values were then expanded, with a greater number of solvents investigated and more solvatochromic dyes used. In total, 45 dyes were used to generate π* values for over 200 solvents.[13] These π* values were an average of the values for all of the solvatochromic dyes, with a normalisation between 0 (cyclohexane) and 1 (dimethylsulfoxide). While the amount of data used allowed anomalies in the original set of dyes to be observed and to some extent corrected, it makes the measurement of solvent π* values using this original methodology impractical when new solvents are introduced. This is even more so when an entire new class of solvents with many members, such as ionic liquids, is made. Indeed, in subsequent studies of their own Kamlet and Taft did not use the full range of dyes.[25]

We therefore first sought to determine if a smaller number of dyes could be used to reliably calculate the Kamlet–Taft parameters of a given ionic liquid. In order to accomplish this, we first measured π* for a single ionic liquid ($[C_4C_1pyrr][NTf_2]$) and a single molecular solvent (dichloromethane, CH_2Cl_2) using the 12 dyes of those used by Kamlet and Taft in the creation of their polarity scales that are currently commercially available (these included all 7 of the original Kamlet–Taft dyes). The results of the π* measurements are shown in Table 1.

For both dichloromethane and the ionic liquid there is significant variation in the π* values derived from different dyes, with standard deviations greater than 20% of the average value for the 12 measurements. This result highlights one of the major weaknesses of the π* polarity scale, namely that dye selection can have a dramatic influence on the resulting measurement. For these probes the measurement arises from electronic transitions from a ground to an excited state. The relative stabilization of these two states by a solvent depends upon the difference in their two dipoles/polarisabilities, which in turn leads to the solvatochromism of the probes. Hence, it is possible for two structurally similar probes, such as *N*,*N*-diethyl-3-nitroaniline and *N*,*N*-diethyl-4-nitroaniline to give quite different π* values. The often-used literature

Table 1 π* values for $[C_4C_1pyrr][NTf_2]$ and CH_2Cl_2

	$[C_4C_1pyrr][NTf_2]$		CH_2Cl_2	
Dye	$\lambda_{max\ (nm)}$	π*[a]	$\lambda_{max\ (nm)}$	π*[a]
4-Dimethylaminobenzoate	338.0	0.830	337.0	0.774
Ethyl-4-aminobenzoate	283.8	1.279	277.7	0.670
3-Nitroaniline	373.9	1.278	361.8	0.738
Ethyl-4-dimethylaminobenzoate	309.7	0.727	303.2	0.231
N,*N*-Dimethyl-4-aminobenzophenone	350.5	0.932	346.4	0.765
2-Nitroaniline	402.6	1.116	394.3	0.774
N-Methyl-4-nitroaniline	384.8	1.006	374.2	0.786
N,*N*-Diethyl-3-nitroaniline	413.6	0.608	409.2	0.489
2-Nitroanisole	327.2	0.822	324.2	0.704
trans-4-Methoxy-*β*-nitrostyrene	354.1	0.755	354.6	0.774
1-Ethyl-4-nitrobenzene	279.4	0.849	277.9	0.759
N,*N*-Diethyl-4-nitroaniline	408.1	0.941	399.9	0.783
Mean	—	0.929	—	0.687
Standard deviation	—	0.21	—	0.17

[a] Calculated using formulae from ref. 13.

Table 2 Values of π* obtained for the ionic liquids studied using four probes

Ionic liquid	π* (*N*,*N*-Diethyl-4-nitroaniline)	π* (4-Nitroanisole)	π* (*N*,*N*-Diethyl-3-nitroaniline)	π* (*N*-Methyl-2-nitroaniline)
$[C_4C_1im][SbF_6]$	1.039	0.905	0.706	1.022
$[C_4C_1im][BF_4]$	1.047	0.971	0.709	1.068
$[C_4C_1im][PF_6]$	1.032	0.927	0.696	1.038
$[C_4C_1im][OTf]$	1.006	0.927	0.662	1.009
$[C_4C_1im][NTf_2]$	0.984	0.839	0.623	0.949
$[C_4C_1C_1im][BF_4]$	1.083	0.996	0.820	1.081
$[C_4C_1C_1im][NTf_2]$	1.010	0.861	0.670	0.959
$[C_4C_1pyrr][NTf_2]$	0.954	0.813	0.586	0.892

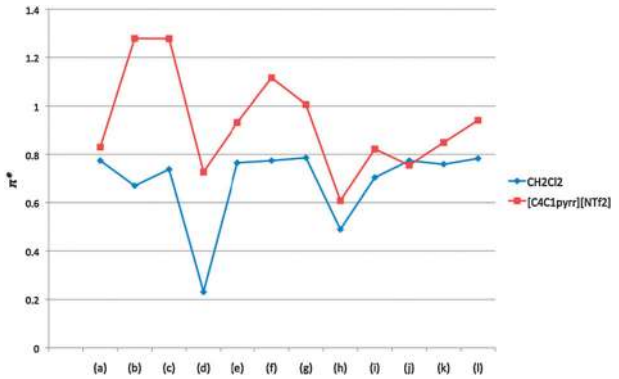

Fig. 1 π^* values for both $[C_4C_1pyrr][NTf_2]$ and dichloromethane. The dyes are as follows: (a) 4-dimethylaminobenzoate, (b) Ethyl-4-aminobenzoate, (c) 3-nitroaniline, (d) Ethyl-4-dimethylaminobenzoate, (e) *N*,*N*-dimethyl-4-aminobenzophenone, (f) 2-nitroaniline, (g) *N*-methyl-4-nitroaniline, (h) *N*,*N*-diethyl-3-nitroaniline, (i) 2-nitroanisole, (j) *trans*-4-methoxy-β-nitrostyrene, (k) 1-ethyl-4-nitrobenzene, (l) *N*,*N*-diethyl-4-nitroaniline.

equations that allow a π^* value to be calculated from any given dye are based on averaging values from many solvents and many dyes. This means that it is unlikely that the value calculated from the spectrum of one dye for any particular solvent will be the same as other values, either derived from another single dye measurement, or from an average of many measurements. Nor should it be expected that any averaged value should be the same as another, unless precisely the same set of dyes has been used to calculate it.

It is further worth noting that for dichloromethane the average π^* value resulting from the 12 dyes that we selected (0.687) was considerably lower than accepted literature values. This can be corrected to some extent by elimination of the two greatest outliers among our π^* results (ethyl-4-dimethylaminobenzoate and *N*,*N*-diethyl-3-nitroaniline each of which provided values outside the 90% confidence interval), which 'improves' the value to 0.753. However, not only is this somewhat arbitrary, but the literature values for dichloromethane are variable anyway, with the original Kamlet and Taft value[13] of 0.802 being revised to 0.82 by Marcus,[26] whereas Reichardt reports a value of 0.73.[9] This emphasises that π^* is in no way a fundamental property of the solvent, with a 'correct' value that different probes get closer to or farther from; but is an estimate of the relative propensity of the solvent to interact with particular solutes *via* dipolar/polarizability effects, which therefore varies with the probe used for its measurement. Consequently, when attempting to measure π^* for ionic liquids, the only practical way to avoid the variable results obtained from averaging different multiple dye measurements while simultaneously avoiding excessive synthetic work, is to use a single probe for all π^* measurements. This then raises the question of which to use.

The measured π^* values of $[C_4C_1pyrr][NTf_2]$ and dichloromethane with each dye is plotted in Fig. 1. The measured π^* values of $[C_4C_1pyrr][NTf_2]$ are all greater than those of dichloromethane, with only one exception (*trans*-4-methoxy-β-nitrostyrene). Further, the π^* values follow a similar trend for both solvents, indicating that the fluctuations in the measured π^* values result largely from differences inherent in the dyes themselves and not from any specific effect due to the ionic liquid.

The three more commonly used Kamlet–Taft dyes, *N*,*N*-diethyl-4-nitroaniline, *N*-methyl-2-nitroaniline and 2-nitroanisole, were then selected for more detailed examination. In our study we also included *N*,*N*-diethyl-3-nitroaniline, which gave one of the outlier values for $[C_4C_1pyrr][NTf_2]$ to ensure that this was a general result and not peculiar to this ionic liquid. All of these are from the original set of 7 Kamlet–Taft dyes and are commercially available.

The first point of note is that no two dyes give precisely the same π^* values for the same ionic liquid. In the cases of *N*,*N*-diethyl-4-nitroaniline, *N*-methyl-2-nitroaniline the π^* values are so similar that for some ionic liquids {$[C_4C_1im][SbF_6]$, $[C_4C_1im][NTf_2]$, $[C_4C_1C_1im][BF_4]$, $[C_4C_1C_1im][NTf_2]$ and $[C_4C_1pyrr][NTf_2]$} *N*,*N*-diethyl-4-nitroaniline gives the highest π^* values, whereas in others {$[C_4C_1im][BF_4]$, $[C_4C_1im][PF_6]$ and $[C_4C_1im][OTf]$} *N*-methyl-2-nitroaniline does so. For both 2-nitroanisole and *N*,*N*-diethyl-3-nitroaniline, the π^* values are sufficiently well separated for the order to always be the same. It can be seen from Fig. 2 that the same general trends for the π^* values of the different ionic liquids are followed. For any given dye, the π^* values of the ionic liquids studied are high in comparison to most molecular solvents and vary very little. For all of the dyes tested, the $[BF_4]^-$ ionic liquids gave the highest π^* values for any given cation, and the $[NTf_2]^-$ the lowest with $[OTf]^-$, $[PF_6]^-$ and $[SbF_6]^-$ having intermediate values. Upon closer inspection, it can be seen that for the ionic liquids the relative values do change with the dye used; for *N*,*N*-diethyl-4-nitroaniline and *N*,*N*-diethyl-3-nitroaniline $[C_4C_1C_1im][BF_4] > [C_4C_1im][BF_4] > [C_4C_1im][SbF_6] > [C_4C_1im][PF_6] > [C_4C_1C_1im][NTf_2] > [C_4C_1im][OTf] > [C_4C_1im][NTf_2] > [C_4C_1pyrr][NTf_2]$; for *N*-methyl-2-nitroaniline $[C_4C_1C_1im][BF_4] > [C_4C_1im][BF_4] > [C_4C_1im][PF_6] > [C_4C_1im][SbF_6] > [C_4C_1im][OTf] > [C_4C_1C_1im][NTf_2] > [C_4C_1im][NTf_2] > [C_4C_1pyrr][NTf_2]$; 4-nitroanisole $[C_4C_1C_1im][BF_4] > [C_4C_1im][BF_4] > [C_4C_1im][PF_6] = [C_4C_1im][OTf] > [C_4C_1im][SbF_6] > [C_4C_1C_1im][NTf_2] > [C_4C_1im][NTf_2] > [C_4C_1pyrr][NTf_2]$. However as can be seen, when inversions of relative polarity do occur it is between ionic liquids with very similar π^* values.

Clearly, the dye used to measure the π^* value affects both the absolute value and, for ionic liquids with very similar

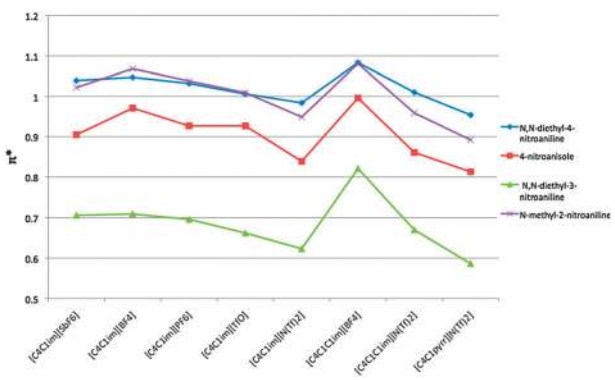

Fig. 2 π^* values for a range of ionic liquids obtained from four primary probes.

values, the relative ordering. It should be noted again that π^* is not a fundamental physical property of a solvent, but a guide to the effect of the solvent upon solute species that are sensitive to interactions with the solvent dipoles and, in the case of ionic liquids its ions. The precise π^* value has no fundamental physical meaning. It follows from this that when using only one dye the selection of the preferred π^* probe must be based upon some other criteria. *N*,*N*-diethyl-4-nitroaniline is the most commonly used π^* probe in the literature; it is readily commercially available and chemically robust. For these reasons, we have selected it as our preferred π^* probe. This does not mean that we believe that other choices are wrong, but it does mean that when using π^* values in LSERs (see ESI for method and worked example†) to analyse other solvent dependent phenomena π^* values arising from other probes cannot be used with these values.

Table 4 shows π^* values for a range ionic liquids, both measured by us and from the literature obtained with the dye *N*,*N*-diethyl-4-nitroaniline at room temperature. Since we are now using just one dye, modern spectrometers are sufficiently precise for these to be reported with several significant figures. However, we believe that this would give a false impression as to how these measurements should be applied when using them to explain other solvent-dependent phenomena. Hence, we report the values to two decimal places.

It can be seen that values for the same ionic liquid (*e.g.* $[C_4C_1im][NTf_2]$) from different reports can vary considerably, even when the same probe is used. It is well known that the low volatility of ionic liquids leads to an inability to purify these by distillation and that without the greatest care impurities can be present in these. Studies of Kamlet–Taft values for mixtures of ionic liquids with molecular liquids have shown that these generally (with the exception of water) lead to a reduction in π^* values.[17,27] However, these impurities should be readily removed from the ionic liquid during the vacuum drying step of the measurement. Of the other impurities that are commonly found in ionic liquids, unreacted alkylamines, in our case methylimidazole, reduce the ionic liquids' π^* values, whereas others have no impact upon these values.

Table 4 shows that the π^* values of ionic liquids are high in comparison to molecular solvents and depend upon both the anion and the cation of the ionic liquid. Alcohol functionalization of either the cation or anion can lead to high π^* values.[18g] Generally, π^* values vary with the cation such that morpholinium > imidazolium > pyridinium > pyrrolidinium > phosphonium ionic liquids sharing the same anion. Increasing the length of the alkyl substituent on the cation reduces the π^* value. Using a siloxane side chain further decreases the π^* value. For the anion, the π^* values appear to depend upon the size and basicity of the anion. These observations are all consistent with the expected effect of the introduction of solvent ion-solute dipole interactions in the ionic liquid solutions of the dye.

The π^* values of ionic liquids are higher than expected on the basis of dielectric constant measurements.[5] Spange *et al.*[28] generated π^* values for some ionic liquids using 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline as the probe. There is insufficient overlap of examples with the ionic liquids in Table 4 to be able to determine any quantitative correlation between the two sets of values, but for those ionic liquids that are present in both sets the π^* values are similar. In that study, the high π^* values were attributed to the ionic liquids being aromatic (they all had 1,3-dialkylimidazolium cations). However, this does not explain the high π^* values found for ionic liquids in general.

In a study using *N*,*N*-dimethyl-4-nitroaniline Kimura *et al.*[29] noted that the π^* values showed reasonable correlation with the molar concentrations of the ionic liquids, concluding that the consideration of the relative charge concentrations of the ionic liquids was a useful way of understanding the values. At the same time Kobrak[30] advanced the idea that the electrostatic part of ionic liquid interactions (the greatest of any interactions leading to π^* values) with a neutral dipolar solute should be determined primarily by the number density of the ionic liquid ions. These trends also appear to hold for values derived from measurements with *N*,*N*-diethyl-4-nitroaniline (Table 4) for ionic liquids with the same cation type, but different alkyl chain lengths. These trends probably arise because charge concentration is a good guide to the ability of the ions to closely approach the probe molecule, and/or for the probe molecule to align itself with the ionic liquid ions, so as to maximise the strength of the Coulomb interactions between the ionic liquid and the probe's dipole, which in turn leads to a greater effect upon its spectrum.

By combining all of the above it can be summarised that the π^* values of ionic liquids are generally high due to their ionic character. Their π^* values are increased by the presence of large permanent dipoles, often arising from the presence of functional groups, and also by the presence of delocalized bonds, which give rise to greater polarizabilities. Their π^* values are decreased by increased alkylation.

β values

The Kamlet–Taft β parameter describes the solvent's ability to donate electron density to form a hydrogen bond with protons of a solute. The β scale is generated by the solvatochromic comparison method.[12] This methodology compares solvent-induced shifts of the absorption bands of two probe molecules. They are selected to be structurally very similar pairs except that one is capable of hydrogen bond donation and the other is not and that have a good correlation of their spectra in non-hydrogen bond acceptor solvents, but with sufficient differences in their spectra in hydrogen bond accepting solvents for the construction of a scale based upon these differences to be possible. This approach is the most logically robust of all of those used to generate the Kamlet–Taft parameters; *i.e.*, if the only difference between the homomorphic pair is that one can hydrogen bond donate and the other cannot, then any solvent induced differences must arise from hydrogen bond acceptance by the solvent. The pairs that Kamlet and Taft selected were 4-nitroaniline/*N*,*N*-diethyl-4-nitroaniline, or 4-nitrophenol/4-nitroanisole, and the results normalised to $\beta = 1$ for hexamethylphosphoric acid triamide (HMPT). While these two sets of pairs gave rise to very similar β scales, the precise values for any given solvent with the two dye sets differed. Hence, we chose to measure the β values of a selection of ionic liquids with both of these probe sets (Table 3, Fig. 3).

Table 3 Kamlet–Taft β values for the homomorphic solvation probe pairs *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline and 4-nitroanisole/4-nitrophenol

Ionic liquid	4-Nitroanisole/ 4-nitrophenol β	*N*,*N*-Diethyl-4-nitroaniline/ 4-nitroaniline β
$[C_4C_1im][BF_4]$	0.45	0.38
$[C_4C_1im][PF_6]$	0.40	0.21
$[C_4C_1im][SbF_6]$	0.34	0.15
$[C_4C_1im][OTf]$	0.60	0.50
$[C_4C_1im][Tf_2N]$	0.41	0.24
$[C_4C_1C_1im][BF_4]$	0.46	0.36
$[C_4C_1C_1im][Tf_2N]$	0.51	0.24
$[C_4C_1pyrr][Tf_2N]$	0.41	0.25

It can be seen in Table 3 and Fig. 3 that the precise β values for these dye sets are different, with the 4-nitroanisole/4-nitrophenol pair giving consistently higher values than the *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline pair. However, the same general trends can be seen for both dye sets; the β value depends largely upon the anion. For the $[C_4C_1im]^+$ ionic liquids, the highest value obtained, for $[OTf]^-$, is similar to acetone, whilst acetonitrile is between $[BF_4]^-$ and $[NTf_2]^-$. The $[PF_6]^-$ and $[SbF_6]^-$ ionic liquids are the weakest hydrogen bond acceptor anions. It can be seen that the relative β values do change with dye set used; *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline $[C_4C_1im][OTf] > [C_4C_1im][BF_4] > [C_4C_1C_1im][BF_4] > [C_4C_1pyrr][NTf_2] > [C_4C_1C_1im][NTf_2] = [C_4C_1im][NTf_2] > [C_4C_1im][PF_6] > [C_4C_1im][SbF_6]$; 4-nitroanisole/4-nitrophenol $[C_4C_1im][OTf] > [C_4C_1C_1im][NTf_2] > [C_4C_1C_1im][BF_4] > [C_4C_1im][BF_4] > [C_4C_1pyrr][NTf_2] = [C_4C_1im][NTf_2] > [C_4C_1im][PF_6] > [C_4C_1im][SbF_6]$. While the differences in these two sets of results are generally between ionic liquids with a common anion, and therefore very similar β values, the result for $[C_4C_1C_1im][NTf_2]$ with the 4-nitroanisole/4-nitrophenol pair stands out. This value is considerably higher than those of other $[NTf_2]^-$ containing ionic liquids measured with this dye set. We have repeated this measurement on this ionic liquid prepared on three separate occasions by different group members and are reassured that it does not arise from experimental error. From simple inspection it appears that 4-nitrophenol is showing a greater solvatochromic shift than it's π^* homomorph, resulting in good trends in π^* and α values (see later), but an anomalously high β value. We do not have an explanation for this behaviour at this time.

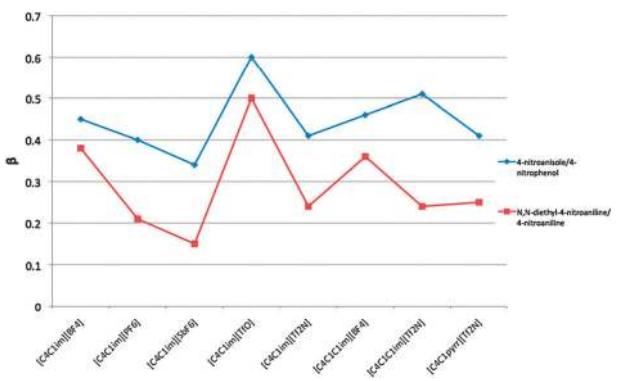

Fig. 3 Kamlet–Taft β values for the homomorphic solvation probe pairs *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline and 4-nitroanisole/4-nitrophenol.

Again, the question of which probe set should be used arises. When the π^* values are derived from the average of values measured using a wide range of probes, this choice is somewhat arbitrary. However, for measurements of ionic liquids we have selected *N*,*N*-diethyl-4-nitroaniline as the preferred π^* probe. Hence, using the *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline pair provides the greatest internal consistency in the polarity analysis. Its other advantage is that it is the most commonly used pair in the literature, which gives the greatest availability of comparisons with other solvents. Again it must be noted that when applying LSERs (see ESI for method and worked example†) to analyse other solvent dependent phenomena, β values derived from different dye sets should not be used together.

Table 4 shows β values measured by us for range ionic liquids and others from the literature obtained with the probe pair *N*,*N*-diethyl-4-nitroaniline/4-nitroaniline. It can be seen from Table 4 that different β values have been reported for the same ionic liquids. It has been shown that β values of ionic liquids can be affected by the presence of molecular solvents.[17,27] We also found (Table 5) that common impurities arising from the synthesis of the ionic liquids, such as alkylamines (which increase β), Li^+ (which decreases β) and Cl^- (which increases β), can have a significant effect on the β value obtained.

It can be seen that the β value is dominated by the anion of the ionic liquid, with the cation having a secondary effect. The trend in the β values shows an inverse relationship with the Gibbs free energy change on the deprotonation of the conjugate acid of the anion in the gas phase (ΔG_H).[14] The observed trend provides us with the ability to predict these values for the ionic liquids using calculated ΔG_H, which leads to the possibility to design ionic liquids with desired basicities.

α values

The Kamlet–Taft α parameter describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond, with the fixed reference point of $\alpha = 1$ for methanol.[31] Of all of the Kamlet–Taft parameters, α has generated the greatest amount of controversy in regard to its use with ionic liquids. As with β, α values are generated using the solvatochromic comparison method. However, no attempt was made to find structurally similar pairs of probes. Instead, the HBD ability of solvents is derived from Reichardt's E_T^{30} scale, which includes HBD and polarizability/polarity effects, with the latter being removed using the π^* value of the solvent as shown in eqn (2).

$$\alpha = 0.0649E_T^{30} - 2.03 - 0.72\pi^* \quad (2)$$

While the E_T^{30} value for any given solvent is unique, clearly its α value will depend upon the value of π^* used. The higher the value for π^* used the lower the value for α will be (Fig. 4). We have included α values for ionic liquids prepared by us and others from the literature calculated using the π^* values derived from measurements of *N*,*N*-diethyl-4-nitroaniline in Table 4. This provides the greatest logical consistency for when applying α values in LSERs (see ESI for method and worked example†).

Table 4 Kamlet–Taft parameters, using the dye set Reichardt's Dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline

Ionic liquid	Abbreviation	α	β	π^*	Ref.
1-Nonyl-1-methylmorpholinium dicyanamide	$[C_9C_1mor][N(CN)_2]$	0.36	0.54	1.11	18*g*
1-Octylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_8pyr][NTf_2]$	0.56	0.12	0.97	18*e*
1-Octylpyridinium tetrafluoroborate	$[C_8pyr][BF_4]$	0.54	0.34	0.97	18*e*
1-Octyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[C_8C_1pyrr][NTf_2]$	0.80	0.08	0.73	18*e*
1-Octyl-1-methylmorpholinium dicyanamide	$[C_8C_1mor][N(CN)_2]$	0.35	0.54	1.11	18*g*
1-Octyl-3-methylimidazolium tetrafluoroborate	$[C_8C_1im][BF_4]$	0.62	0.41	0.98	15
1-Octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_8C_1im][NTf_2]$	0.60	0.29	0.96	
1-Octyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_8C_1{}^4pyr][NTf_2]$	0.50	0.33	0.97	18*d*
1-Octylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_8C_1{}^3pyr][NTf_2]$	0.51	0.28	0.99	18*d*
1-Octyl-3-methylpyridinium tetrafluoroborate	$[C_8C_1{}^3pyr][BF_4]$	0.51	0.44	1.00	15
1-Octyl-3-methylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_8C_1{}^3pyr][NTf_2]$	0.50	0.33	0.97	18*d*
1-Octyl-2-methylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_8C_1{}^2pyr][NTf_2]$	0.48	0.35	0.95	18*d*
1-Heptyl-1-methylmorpholinium dicyanamide	$[C_7C_1mor][N(CN)_2]$	0.35	0.54	1.11	18*g*
1-Hexylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_6pyr][NTf_2]$	0.50	0.07	0.98	18*e*
1-Hexyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[C_6C_1pyrr][NTf_2]$	0.76	0.06	0.81	18*e*
1-Hexyl-1-methylmorpholinium dicyanamide	$[C_6C_1mor][N(CN)_2]$	0.38	0.55	1.11	18*g*
1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_6C_1im][NTf_2]$	0.65	0.26	0.97	18*b*
		0.59	0.25	0.98	
1-Hexyl-3-methylimidazolium chloride	$[C_6C_1im]Cl$	0.48	0.94	1.02	15
1-Hexyl-3-methylimidazolium bromide	$[C_6C_1im]Br$	0.45	0.74	1.09	15
1-Pentyl-1-methylmorpholinium dicyanamide	$[C_5C_1mor][N(CN)_2]$	0.38	0.54	1.11	18*g*
1-Pentyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[C_5C_1pyrr][NTf_2]$	0.44	0.26	0.95	
1-Pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_5C_1im][NTf_2]$	0.63	0.26	0.97	
1-Butylpyridinium bis(trifluoromethanesulfonyl)imide	$[C_4pyr][NTf_2]$	0.64	0.12	0.82	18*e*
		0.54	0.21	1.01	18*b*
1-Butylpyridinium tetrafluoroborate	$[C_4pyr][BF_4]$	0.53	0.21	1.08	18*e*
1-Butyl-1-methylmorpholinium dicyanamide	$[C_4C_1mor][N(CN)_2]$	0.38	0.53	1.12	18*g*
1-Butyl-1-methylpiperidinium dicyanamide	$[C_4C_1pip][N(CN)_2]$	0.31	0.49	1.13	18*g*
1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[C_4C_1pyrr][NTf_2]$	0.73	−0.11	0.89	18*e*
		0.57	0.23	0.87	19
		0.43	0.24	0.95	
1-Butyl-3-methylimidazolium tetrafluoroborate	$[C_4C_1im][BF_4]$	0.77	0.39	1.04	15
		0.63	0.37	1.05	
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_4C_1im][NTf_2]$	0.72	0.24	0.90	19
		0.64	0.25	0.97	18*b*
		0.61	0.23	0.99	
1-Butyl-3-methylimidazolium octanesulfonate	$[C_4C_1im][(C_8)OSO_3]$	0.69	0.79	0.89	15
1-Butyl-3-methylimidazolium hexafluorophosphate	$[C_4C_1im][PF_6]$	0.68	0.21	1.02	15
		0.65	0.25	1.02	18*b*
		0.63	0.24	1.02	15
		0.63	0.19	1.04	
1-Butyl-3-methylimidazolium hexafluoroantimonate	$[C_4C_1im][SbF_6]$	0.62	0.15	1.04	
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	$[C_4C_1im][OTf]$	0.62	0.49	1.00	
1-Butyl-3-methylimidazolium acetate	$[C_4C_1im][MeCO_2]$	0.57	1.18	0.89	16
		0.43	1.05	1.04	18*c*
		0.48	1.20	0.96	
1-Butyl-3-methylimidazolium dicyanamide	$[C_4C_1im][N(CN)_2]$	0.54	0.60	1.05	
1-Butyl-3-methylimidazolium methylsulfate	$[C_4C_1im][MeSO_4]$	0.53	0.66	1.06	
1-Butyl-3-methylimidazolium butyrate	$[C_4C_1im][PrCO_2]$	0.51	1.23	0.92	18*c*
1-Butyl-3-methylimidazolium glycolate	$[C_4C_1im][(HO)C_1CO_2]$	0.44	0.87	1.12	18*c*
1-Butyl-3-methylimidazolium propionate	$[C_4C_1im][EtCO_2]$	0.48	1.16	0.94	18*c*
1-Butyl-3-methylimidazolium dimethylphosphate	$[C_4C_1im][Me_2PO_4]$	0.45	1.13	0.98	
1-Butyl-3-methylimidazolium methanesulfonate	$[C_4C_1im][MeSO_3]$	0.44	0.77	1.02	
1-Butyl-3-methylimidazolium malate	$[C_4C_1im][O_2CCH_2CH(OH)CO_2]$	0.41	1.00	1.10	18*c*
1-Butyl-3-methylimidazolium succinate	$[C_4C_1im][O_2CCH_2CH_2CO_2]$	0.39	1.08	1.09	18*c*
1-Butyl-3-methylimidazolium maleate	$[C_4C_1im][O_2CCHCHCO_2]$	0.34	1.02	1.11	18*c*
1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	$[C_4C_1C_1im][BF_4]$	0.39	0.36	1.08	
1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_4C_1C_1im][NTf_2]$	0.38	0.26	1.02	
1-Butyl-1-methylpyrrolidinium dimethylphosphate	$[C_4C_1pyrr][Me_2PO_4]$	0.24	1.14	1.02	
1-(2-Ethoxyethyl)-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[(C_2OC_2)C_1pyrr][NTf_2]$	0.49	0.28	0.93	
1-Propyl-1-methylmorpholinium dicyanamide	$[C_3C_1mor][N(CN)_2]$	0.42	0.49	1.12	18*g*
1-Ethyl-1-methylmorpholinium dicyanamide	$[C_2C_1mor][N(CN)_2]$	0.31	0.51	1.12	18*g*
1-Ethyl-1-methylmorpholinium bis(trifluoromethanesulfonyl)imide	$[C_2C_1mor][N(CN)_2]$	0.50	0.19	1.01	18*g*
1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[C_2C_1im][NTf_2]$	0.71	0.23	0.98	18*b*
		0.42	0.10	1.02	19
		0.63	0.23	1.00	
1-Ethyl-3-methylimidazolium hexanesulfonate	$[C_2C_1im][(C_6)SO_4]$	0.65	0.71	0.98	15
1-Ethyl-3-methylimidazolium octanesulfonate	$[C_2C_1im][(C_8)SO_4]$	0.65	0.77	0.93	15
1-Ethyl-3-methylimidazolium acetate	$[C_2C_1im][MeCO_2]$	0.57	1.06	0.97	16

Table 4 (*continued*)

Ionic liquid	Abbreviation	α	β	π^*	Ref.
1,2,4-Trimethylpyrazolium triflate	$[C_1C_1C_1pyz][OTf]$	0.43	0.25	0.94	
1-Methyl-3-pentamethyldisiloxymethylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[(SiOSi)C_1C_1pyrr][NTf_2]$	0.59	0.28	0.89	
1-Methyl-3-pentamethyldisiloxymethylimidazolium bis(trifluoromethanesulfonyl)imide	$[(SiOSi)C_1C_1im][NTf_2]$	0.65	0.28	0.91	
1-Methyl-3-heptamethyltrisiloxymethylimidazolium bis(trifluoromethanesulfonyl)imide	$[(SiO)_2SiC_1C_1im][NTf_2]$	0.79	0.33	0.88	
1-Glyceryl-3-methylimidazolium chloride	$[(HO)^3(HO)^2C_3C_1im]Cl$	1.12	0.99	0.82	18*g*
1-Glyceryl-3-methylimidazolium dicyanamide	$[(HO)^3(HO)^2C_3C_1im][N(CN)_2]$	0.87	0.47	1.17	18*g*
1-Glyceryl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[(HO)^3(HO)^2C_3C_1im][NTf_2]$	1.20	0.13	1.15	18*g*
1-Glyceryl-2,3-dimethylimidazolium dicyanamide	$[(HO)^3(HO)^2C_3C_1\ C_1im][N(CN)_2]$	0.87	0.47	1.17	18*g*
1-Glyceryl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	$[(HO)^3(HO)^2C_3C_1\ C_1im][NTf_2]$	0.93	0.11	1.14	18*g*
1-Glyceryl-1-methylmorpholinium dicyanamide	$[(HO)^3(HO)^2C_3C_1mor][N(CN)_2]$	0.85	0.43	1.20	18*g*
1-Glyceryl-3-methylmorpholinium bis(trifluoromethanesulfonyl)imide	$[(HO)^3(HO)^2C_3C_1mor][NTf_2]$	1.25	0.12	1.11	18*g*
1-Glyceryl-1-methylpiperidinium dicyanamide	$[(HO)^3(HO)^2C_3C_1pip][N(CN)_2]$	0.86	0.53	1.12	18*g*
1-Glyceryl-3-methylpiperidinium bis(trifluoromethanesulfonyl)imide	$[(HO)^3(HO)^2C_3C_1pip][NTf_2]$	1.23	0.11	1.13	18*g*
1-Glyceryl-1-methylpyrrolidinium nitrate	$[(HO)^3(HO)^2C_3C_1pyrr][NO_3]$	0.87	0.53	1.19	18*g*
1-Glyceryl-1-methylpyrrolidinium dicyanamide	$[(HO)^3(HO)^2C_3C_1pyrr][N(CN)_2]$	0.90	0.46	1.18	18*g*
1-Glyceryl-3-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	$[(HO)^3(HO)^2C_3C_1pyrr][NTf_2]$	1.13	0.14	1.14	18*g*
1-Hydroxypropyl-3-methylimidazolium acetate	$[(HO)^3C_3C_1im][MeCO_2]$	0.51	0.99	1.08	18*c*
1-Hydroxyethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$[(HO)^2C_2C_1im][NTf_2]$	1.14	0.28	1.08	18*c*
1-Hydroxyethyl-3-methylimidazolium acetate	$[(HO)^2C_2C_1im][MeCO_2]$	0.53	0.90	1.04	18*g*
1-Hydroxyethyl-1-methylmorpholinium dicyanamide	$[(HO)^2C_2C_1mor][N(CN)_2]$	0.78	0.49	1.13	18*g*
1-Hydroxyethyl-1-methylpiperidinium dicyanamide	$[(HO)^2C_2C_1pip][N(CN)_2]$	0.78	0.51	1.11	18*g*
Trioctylmethylammonium bis(trifluoromethanesulfonyl)imide	$[(C_8)_3C_1N][NTf_2]$	0.35	0.37	0.91	15
		0.33	0.23	0.87	19
Trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide	$[(C_6)_3C_{14}P][NTf_2]$	0.37	0.27	0.83	19
Tetrapentylammonium 2-(cyclohexylamino)-ethanesulfonate	$[(C_5)_4N][CHES]$	0.50	0.91	0.95	18*a*
Tetrapentylammonium 2-[bis(2hydroxyethyl)amino]ethanesulfonate	$[(C_5)_4N][BES]$	0.47	1.00	0.95	18*a*
Tetrapentylammonium 2-hydroxy-4-morpholinepropanesulfate	$[(C_5)_4N][MOPSO]$	0.33	0.96	0.98	18*a*
Tetrabutylammonium 2-(cyclohexylamino)-ethanesulfonate	$[(C_4)_4N][CHES]$	0.56	0.98	0.97	18*a*
Tetrabutylammonium 2-[bis(2hydroxyethyl)amino]ethanesulfonate	$[(C_4)_4N][BES]$	0.31	0.81	1.06	18*a*
Tetrabutylammonium 2-hydroxy-4-morpholinepropanesulfate	$[(C_4)_4N][MOPSO]$	0.28	0.74	0.98	18*a*
Tetrabutylphoshonium valinate	$[(C_4)_4P][Val]$	0.96	1.46	0.93	18*e*
Tetrabutylphoshonium alanate	$[(C_4)_4P][Ala]$	0.88	1.04	0.98	18*e*
Tetrabutylphosphonium glycinate	$[(C_4)_4P][Gly]$	0.18	1.61	0.93	
Tetrapropylammonium 2-(cyclohexylamino)-ethanesulfonate	$[(C_3)_4N][CHES]$	0.54	0.80	1.02	18*a*
Tetrapropylammonium 2-hydroxy-4-morpholinepropanesulfate	$[(C_3)_4N][MOPSO]$	0.22	0.83	0.98	18*a*
Triethanolmethylammonium methylsulfate	$[((HO)^2C_2)_3C_1N][MeSO4]$	1.1	0.44	1.14	
Triethanolmethylammonium triflate	$[((HO)^2C_2)_3C_1N][OTf]$	1.06	0.29	1.16	

Table 5 Effect on the Kamlet–Taft measurements of adding common synthetic impurities to $[C_4C_1im][NTf_2]$

Impurity	$\Delta\alpha$	$\Delta\beta$	$\Delta\pi^*$
1-methylimidazole 1%	+0.20	+0.25	−0.18
10%	+0.25	+0.25	−0.26
$Li[NTf_2]$ 1%	+0.10	−0.04	No change
10%	+0.13	−0.10	No change
$[C_4C_1im]Cl$ 1%	−0.03	+0.06	No change
10%	−0.05	+0.11	No change
$[HC_1im][NTf_2]$ 1%	No spectrum	No change	No change
10%	No spectrum	No change	No change

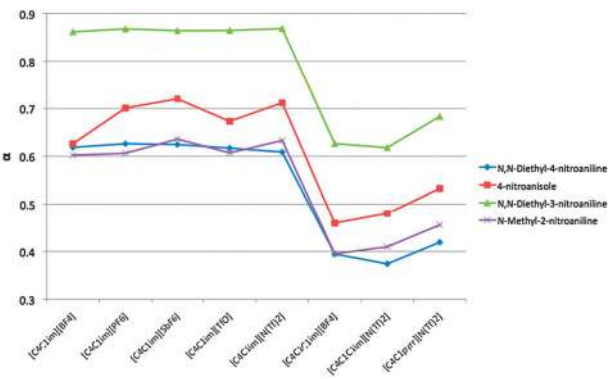

Fig. 4 α values for a range of ionic liquids, calculated using the spectral shift of Reichardt's dye coupled with a range of π^* dyes.

It can be seen from Table 4 that different α values have been reported for the same ionic liquids. It has been shown that α values of ionic liquids can be affected by the presence of molecular solvents.[17,27] The values would also be expected to be affected by other impurities that are commonly found in ionic liquids from the synthetic process, particularly Li^+ or other small cationic species from the metathesis step, and unreacted alkylamine, which both increase the α obtained (Table 5). Interestingly, when we tried to investigate the effect of the protonated product from the synthesis, $[HC_1im][NTf_2]$, it did not affect the α value at even 0.01% contamination, but instead bleached the Reichardt dye completely, making a direct measurement of α impossible.

It is recognised that the hydrogen bond donor ability of the ionic liquids can be mainly attributed to the nature of the cation, with the anion playing a secondary role. Cations with hydrogen-bonding substituents, such as –OH, have the highest α values. Of the other ionic liquids, α values for $[C_nC_1im]^+$

based ionic liquids are generally high and of the order of those values observed for molecular solvents such as *tert*-butanol or formamide (0.68 and 0.71 respectively).[9] This can be reduced by methylating at the C^2 position of the imidazolium ring, *e.g.*, $[C_4C_1C_1im]^+$. A similar effect can be seen for the substitution of alkylpyridinium cations. Pyrrolidinium and ammonium ionic liquids have lesser α values, with phosphonium ionic liquids having the lowest of all.

For ionic liquids with the same cation and different anions a secondary but measurable anion effect can be seen. As the anion becomes more basic (increasing β) the hydrogen bond donor ability of the ionic liquid decreases. We have previously attributed this to a competition between the Reichardt's dye probe and the ionic liquid for the hydrogen bonding site of the cation.[14] The cation may hydrogen bond to the ionic liquid anion, as indicated by the ^{1}H NMR spectra of $[C_4C_1im]^+$ ionic liquids (eqn (3)),[32] or it can hydrogen bond to the solute (eqn (4)). For any given solute, the stronger the hydrogen bond to the anion, then the weaker the hydrogen bond to the solute.

$$C^+ + A^-C^+ \cdots A^- \quad K' = \frac{[C^+ \cdots A^-]}{[C^+][A^-]} \qquad (3)$$

$$C^+ + \text{solute}C^+ \cdots \text{solute} \quad K'' = \frac{[C^+ \cdots \text{solute}]}{[C^+][\text{solute}]} \qquad (4)$$

There are sufficient examples of ionic liquids based on the $[C_4C_1im]^+$ cation to be able to analyse this effect further. Fig. 5 shows the α values for a range of $[C_4C_1im]X$ ionic liquids as a function of their β value. It can be seen that when the anion gives rise to a low (<0.5) β value the α values are similar ($0.60 < \alpha > 0.65$). Increasingly more basic anions lead to progressively lower α values until a minimum value of 0.45 is reached. This minimum value is similar to that found for ionic liquids methylated at the C^2 position of the ring. This suggests that for weakly basic anions, the Reichardt's dye is primarily hydrogen bonded to the C^2–H proton. As the anion becomes more basic, it competes more effectively for this proton and the Reichardt's dye is then displaced to the $C^{4,5}$-H protons. Recent simulations on the ionic liquid mixture $[C_2C_1im][NCS]_nCl_m$ ($n + m = 1$) has also shown the displacement of a weaker hydrogen bond acceptor ($[NCS]^-$) from the C^2–H proton to the $C^{4,5}$–H protons upon the addition of a stronger hydrogen bond acceptor (Cl^-),[33] confirming this possibility.

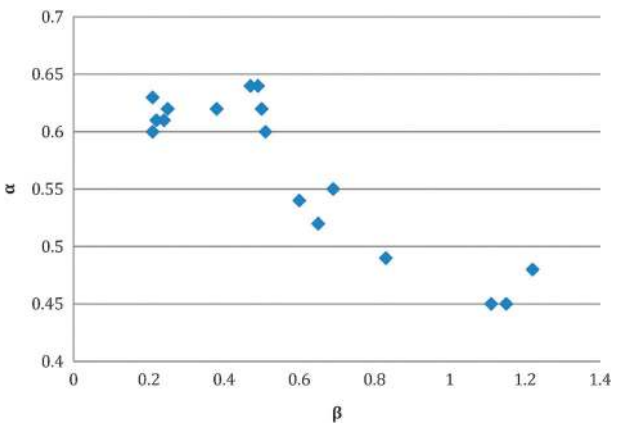

Fig. 5 α values for a range of $[C_4C_1im]X$ ionic liquids as a function of their β value.

It must be recognised that there has been some disagreement in the estimation of the abilities of ionic liquids to act as hydrogen bond donors. From the outset of the application of this methodology to the study of ionic liquid polarities, we noted that the Kamlet–Taft α values of the ionic liquids did not agree with measurements of their hydrogen bond donor abilities derived from GC measurements.[8,14] Not only were the latter values lower, but the HBD ability of the ionic liquid was far more sensitive to changing the anion than the cation. At the time we suggested that the discrepancy might arise from differences in the probes, but had no suggestion as to what those differences might be.

The Raman spectra of diphenylcyclopropane and phenol blue were shown to be far less affected by a change of ionic liquid from $[C_4C_1im][BF_4]$ to $[C_4C_1C_1im][BF_4]$ than would be expected on the basis of the α values of these ionic liquids.[34] This suggests that hydrogen bond donation to these solutes is not as significant as to Reichardt's dye. The UV-vis spectra of $Fe(phen)_2(CN)_2$ {generated by the reduction of $[Fe(phen)_2(CN)_2][ClO_4]$ upon dissolving, phen = 1,10-phenanthroline} also describe ionic liquids as considerably poorer hydrogen bond donors than suggested by their α values.[32] These probes are both uncharged molecules, as were all of those used in the GC studies.[7,8] Reichardt's dye is, in contrast, zwitterionic and has an anionic phenoxide oxygen hydrogen bond acceptor site. We propose that this is the explanation for the disparity of the results of these different polarity measures.

There are two implicit assumptions when attempting to use and compare empirical solvent polarity scales. The first is that if the response of the probe solute is the same in two solvents solvent then the polarities of the two solvents are the same. The second is that the effect of transferring from a solvent with a known value to one for which the value is not known is the same (or at least sufficiently similar) for all probes and therefore all polarity scales. It is this second assumption that we believe is breaking down here.

When transferring Reichardt's dye from a molecular solvent to an ionic liquid the interaction of its phenoxide oxygen will include a contribution from the Columbic interaction with the ionic liquid's cation. This Columbic component of the hydrogen bond between a cation and anion[35] is not present in the interaction with the neutral polarity probes that have been used with ionic liquids, nor is it present when the solvent is molecular. Consequently, the transfer from a molecular solvent to an ionic liquid solvent will have a far greater effect upon Reichardt's dye than for these neutral probes. This emphasizes that polarity is about a relationship between the solvent and solute and that it is as important to consider the nature of the solute as that of as the solvent when using empirical polarity scales. This is not to say that the Kamlet–Taft approach overemphasizes the importance of the Columbic component of the hydrogen bond compared to neutral probes, or vice versa. It is also true that small molecules with large permanent dipoles have been demonstrated to have their hydrogen bonds dominated by a

Coulombic component.[36] However, it is true that solvent polarity scales based upon charged probes are more likely to aid the understanding of processes involving charged solutes in ionic liquids, and solvent polarity scales based upon neutral probes are more likely to aid the understanding of processes involving neutral solutes in ionic liquids.

Effect of common synthetic impurities on Kamlet–Taft measurements

It is well established that the purification of ionic liquids is more difficult than for common volatile organic solvents and that ionic liquids can be contaminated with by-products of their synthesis and/or unreacted starting materials.[1] Hence, we tested the effect of the various impurities that might be present from the most common ionic liquids synthesis route, including water, 1-methylimidazole, 1-chlorobutane, Li[NTf_2], [C_4C_1im]Cl and, [HC_1im]$^+$, the by-product potentially formed by the possible competing elimination reaction in the synthesis of [C_4C_1im]Cl. It is particularly important to be aware of this for the ionic impurities, which cannot be easily detected using standard spectroscopic analytical techniques. The results are shown in Table 5.

The addition of water has surprisingly little effect on the Kamlet–Taft values, although this is likely due to the water-immiscible nature of this ionic liquid. It can be seen that α and β measurements are readily affected by the presence of many impurities, with residual Li[NTf_2] and [C_4C_1im]Cl having large effects on the final value obtained, even with only 1% or less of the impurity present. The π^* value of the ionic liquid, however, is not easily altered, with only the addition of 1-chlorobutane having a significant effect on values. Since 1-chlorobutane is highly volatile, it is unlikely that this will remain in the final ionic liquid sample without omitting the drying step of the procedure.

While not being designed to act as an analytical technique, deviation of Kamlet–Taft values from those of pristine samples do indicate which of the common ionic liquid impurities may be present and so what further purification techniques are appropriate. Decolourization of Reichardt's dye with no change in either π^* or β indicates the presence of protonated cations, in our case [HC_1im]$^+$. These can be removed by passing the ionic liquid through a pad of basic alumina. A notable increase in β with a small change in α and no change in π^* indicates the presence of halide ions, which requires further aqueous washing of the ionic liquid, or its solution in a solvent such as dichloromethane, until a negative silver nitrate test is achieved. A notable increase in α with a smaller decrease in β and no change in π^* indicates the presence of Li^+ salts, which can also be removed by washing the ionic liquid. Most workers prefer to use an excess of the chloride salt, so that that the only lithium salt present after metathesis is LiCl and not the reactant salt, in our case Li[NTf_2], which is more difficult to observe. A significant decrease in π^* accompanied by increases in both α and β indicates the presence of unreacted alkylamine, which although molecular tend to have high boiling points and so are not as easily removed *in vacuo* as other possible contaminants, such as chlorobutane. Alkylamines can be removed by passing the ionic liquid first through a plug of acidic alumina followed by a plug of basic alumina. However, it has been noted that the use of sorbents can lead to contamination of ionic liquids.[37] Hence, these are better removed by washing the ionic liquid precursor salt with ethyl acetate.

Conclusions

The Kamlet–Taft solvent polarity scales α, β, π^* have been adapted for use with ionic liquids. The necessary changes in the methodology that have been made limit the ability for quantitative comparison of ionic liquids to those that for which a common dye set have been used. However, with this *proviso* these scales provide a very useful set of solvent descriptors. Used together these scales allow complex solvent dependent behavior to be explained using the LSER methodology. Differences between the α values derived from measurements with Reichardt's dye and measurements of hydrogen bond donation with neutral dyes, can be explained by the presence or absence of the Columbic component of the hydrogen bond. Neither set of measurements is either right or wrong, rather one should ask which is more appropriate in a given set of circumstances. We propose that phenomena dominated by Coulombic interactions are be better modeled using polarity scales based upon charged probes, whereas those for which Coulomic interactions are not significant are better modeled using polarity scales based upon charged probes.

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References

1 (*a*) *Ionic Liquids in Synthesis*, ed. P. Wasserschied and T. Welton, VCH Wiley, Weinheim, 2nd edn, 2007.
2 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508.
3 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
4 C. F. Poole, *J. Chromatogr., A*, 2004, **1037**, 49.
5 H. Weingärtner, *Angew. Chem., Int. Ed.*, 2008, **47**, 654.
6 (*a*) C. Reichardt, *Green Chem.*, 2005, **7**, 339; (*b*) A. J. Carmichael and K. R. Seddon, *J. Phys. Org. Chem.*, 2000, **13**, 591; (*c*) W. Ogihara, T. Aoyama and H. Ohno, *Chem. Lett.*, 2004, **33**, 1414; (*d*) C. J. Drummond and D. N. Furlong, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3613; (*e*) M. J. Muldoon, C. M. Gordon and I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2*, 2001, 433; (*f*) J. Bartosik and A.-V. Mudring, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4005; (*g*) Y. Kimura, M. Fukuda, T. Fujisawa and M. Terazima, *Chem. Lett.*, 2005, **34**, 338; (*h*) T. Fujisawa, M. Fukuda, M. Terazima and Y. Kimura, *J. Phys. Chem. A*, 2006, **110**, 6164.
7 (*a*) S. K. Poole and C. F. Poole, *Analyst*, 1995, **120**, 289; (*b*) Z. S. Breitbach and D. W. Armstrong, *Anal. Bioanal. Chem.*, 2008, **390**, 1605; (*c*) T. Payagala, Y. Zhang, E. Wanigasekara, K. Huang, Z. S. Breitbach, P. S. Sharma, L. M. Sidisky and D. W. Armstrong, *Anal. Chem.*, 2009, **81**, 160; (*d*) Q. Zhao, J. Eichhorn, W. R. Pitner and J. L. Anderson, *Anal. Bioanal. Chem.*, 2009, **395**, 22.
8 J. L. Anderson, J. Ding, T. Welton and D. W. Armstrong, *J. Am. Chem. Soc.*, 2002, **124**, 14247.
9 *Solvents and Solvent Effects in Organic Chemistry*, ed. C. Reichardt and T. Welton, WILEY-VCH, Weinheim, 4th edn, 2010.

10 A. R. Katritzky, D. C. Fara, H. Yang and K. Tämm, *Chem. Rev.*, 2004, **104**, 175.
11 R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
12 (*a*) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377; (*b*) T. Yokoyama, R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 3233.
13 M. J. Kamlet, J. L. Abboud and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027.
14 L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.
15 A. Jeličić, N. Garcia, H.-G. Löhmannsröben and S. Beuermann, *Macromolecules*, 2009, **42**, 8801.
16 T. V. Doherty, M. Mora-Pale, S. E. Foley, R. J. Linhardt and J. S. Dordick, *Green Chem.*, 2010, **12**, 1967.
17 S. N. Baker, G. A. Baker and F. Bright, *Green Chem.*, 2002, **4**, 165.
18 (*a*) S. K. Poole, P. H. Shetty and C. F. Poole, *Anal. Chim. Acta*, 1989, **218**, 241; (*b*) C. Chiappe and D. Pieraccini, *J. Phys. Chem. A*, 2006, **110**, 4937; (*c*) Y. Wu, T. Sasaki, K. Kazushi, T. Seo and K. Sakurai, *J. Phys. Chem. B*, 2008, **112**, 7530; (*d*) J.-M. Lee, S. Ruckes and J. M. Prausnitz, *J. Phys. Chem. B*, 2008, **112**, 1473; (*e*) N. D. Khupse and A. Kumar, *J. Phys. Chem. B*, 2010, **114**, 376; (*f*) A. Jeličić, F. Köhler, A. Winter and S. Beuermann, *J. Polym. Sci. A*, 2009, **42**, 8801; (*g*) C. Chiappe, C. S. Pomelli and S. Rajamani, *J. Phys. Chem. B*, 2011, **115**, 2000 ''Just Accepted''.
19 S. Coleman, R. Byrne, S. Minkovska and D. Diamond, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5608.
20 S. Zhang, X. Qi, X. Ma, L. Lu and Y. Deng, *J. Phys. Chem. B*, 2010, **114**, 3912.
21 M. M. Waichigo, B. M. Hunter, T. L. Riechel and N. D. Danielson, *J. Liq. Chromatogr. Relat. Technol.*, 2007, **30**, 165.
22 (*a*) L. Crowhurst, N. L. Lancaster, J. M. Pérez-Arlandis and T. Welton, *J. Am. Chem. Soc.*, 2004, **126**, 11549; (*b*) L. Crowhurst, R. Falcone, N. L. Lancaster, V. Llopis-Mestre and T. Welton, *J. Org. Chem.*, 2006, **71**, 8847; (*c*) I. Newington, J. M. Perez-Arlandis and T. Welton, *Org. Lett.*, 2007, **9**, 5247; (*d*) G. Ranieri, J. P. Hallett and T. Welton, *Ind. Eng. Chem. Res.*, 2008, **47**, 638; (*e*) R. Bini, C. Chiappe, V. Llopis Mestre, C. S. Pomelli and T. Welton, *Org. Biomol. Chem.*, 2008, **6**, 2522; (*f*) T. Wells, J. P. Hallett, C. K. Williams and T. Welton, *J. Org. Chem.*, 2008, **73**, 5585; (*g*) P. Illner, S. Begel, S. Kern, R. Puchta and R. Van Eldik, *Inorg. Chem.*, 2009, **48**, 588; (*h*) J. C. Schleicher and A. M. Scurto, *Green Chem.*, 2009, **11**, 694; (*i*) S. M. Nabavizadeh, H. R. Shahsavari, H. Sepehrpour, F. N. Hosseini, S. Jamali and M. Rashidi, *Dalton Trans.*, 2010, **39**, 7800.
23 (*a*) V. Cimpeanu, V. Pârvulescu, V. I. Pârvulescu, J. M. Thompson and C. Hardacre, *Catal. Today*, 2006, **117**, 126; (*b*) M. Khodadadi-Mohaddam, H. Habibi-Yangjeh and M. R. Gholami, *Appl. Catal., A*, 2008, **341**, 58; (*c*) J. Teixeira, A. R. Silva, L. C. Branco, C. A. M. Afonso and C. Freire, *Inorg. Chim. Acta*, 2010, **363**, 3321.
24 S. Coleman, R. Byrne, S. Minkovska and D. Diamond, *J. Phys. Chem. B*, 2009, **113**, 15589.
25 M. J. Kamlet, T. N. Hall, J. Boykin and R. W. Taft, *J. Org. Chem.*, 1979, **44**, 2599.
26 Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409.
27 (*a*) B. R. Mellein, S. N. V. K. Aki, R. L. Ladewski and J. F. Brennecke, *J. Phys. Chem. B*, 2007, **111**, 131; (*b*) S. Trivedi, N. I. Malek, K. Behera and S. Pandey, *J. Phys. Chem. B*, 2010, **114**, 8118; (*c*) N. D. Khuspse and A. Kumar, *J. Phys. Chem. B*, 2011, **115**, 711.
28 A. Oehlke, K. Hofmann and S. Spange, *New J. Chem.*, 2006, **30**, 533.
29 Y. Kimura, T. Hamamoto and M. Terazima, *J. Phys. Chem. A*, 2007, **111**, 7081.
30 (*a*) M. N. Kobrak, *J. Phys. Chem. B*, 2007, **111**, 4755; (*b*) M. N. Kobrak, *Green Chem.*, 2008, **10**, 80.
31 M. T. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
32 R. Lungwitz, M. Friederich, W. Linert and S. Spange, *New J. Chem.*, 2008, **32**, 1493.
33 M. Brüssel, M. Brehm, T. Voigt and B. Kirchner, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13617.
34 T. Fujisawa, M. Fukuda, M. Terazima and Y. Kimura, *J. Phys. Chem. A*, 2006, **110**, 6164.
35 P. A. Hunt, B. Kirchner and T. Welton, *Chem.–Eur. J.*, 2006, **12**, 6762.
36 X. Li, L. Liu and H. B. Schlegel, *J. Am. Chem. Soc.*, 2002, **124**, 9639.
37 B. R. Clare, P. M. Bayley, A. S. Best, M. Forsyth and D. R. MacFarlane, *Chem. Commun.*, 2008, 2689.

