

Solvent–solute interactions in ionic liquids†

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A range of ionic liquids has been investigated using the Kamlet–Taft parameters α , β , and π^* . It was found that π^* is high for all of the ionic liquids studied and varies with both anion and cation, α is generally moderate and depends mainly on the cation, β is also moderate and depends mainly on the anion. Comparison is made with other polarity measurements in ionic liquids.

Introduction

Ionic liquids are becoming increasingly popular as solvents for a wide range of applications in synthesis and catalysis.¹ Although estimates vary, there is no doubt that the number of combinations of anions and cations that will give rise to potential ionic liquids is vast. This possibility for synthetic variation has led to ionic liquids being described as “Designer Solvents”.² However, in order to be able to realise this possibility it is necessary to know exactly what is being designed, which parameters are flexible and which are fixed. Further to this, although the large number of ionic liquids potentially available provides synthetic flexibility it also presents a problem, in that it is not possible to make every possible combination of ions and measure the properties of the resultant liquid. It is, therefore, necessary to link the feature that is being designed to more fundamental properties that can be predicted. Finally, it is also necessary to be able to compare ionic liquids to the molecular solvents that they may one day replace.

The key characteristics of a liquid that is to be used as a solvent are those that determine how it will interact with potential solutes. For molecular solvents, this is most commonly recorded as the polarity of the pure liquid, as expressed through its dielectric constant. The inability of this scale to provide adequate correlations with many experimental data has led to the use of empirically derived measurements of solvent properties.³ Kamlet and Taft⁴ have developed a system, based on the comparison of effects on the UV–vis spectra of sets of closely related dyes that were selected to probe particular solvent properties. These complimentary scales of hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity/polarizability effects (π^*) are the ones that we use here. There are several sets of dyes that can be used to derive the Kamlet–Taft parameters and many studies are quoted as an average of the values obtained for several of these dye sets. However, here we report the values obtained using a single set of dyes: Reichardt’s dye, 4-nitroaniline and *N,N*-diethyl-4-nitroaniline, which are shown in Fig. 1.

Results and discussion

The values of E_T^N , α , β , and π^* are listed in Table 1. The literature values included in the table (in parentheses) are those

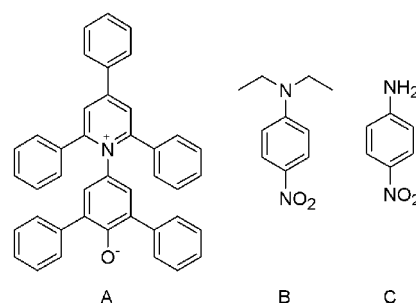


Fig. 1 The dyes used: Reichardt’s dye (A), *N,N*-diethyl-4-nitroaniline (B) and 4-nitroaniline (C).

Table 1 E_T^N and Kamlet–Taft values for a selection of ionic liquids

| Solvent | E_T^N (Lit.) | π^* (Lit.) | α (Lit.) | β (Lit.) | $\lambda_{c,u}/nm$ (Lit.) | $\Delta G_H^{19}/$ kJ mol ⁻¹ |
|--|-------------------|--------------------------------|--------------------------------|--------------------------------|------------------------------|--|
| [EtNH ₃][NO ₃] ¹¹ | (0.954) | (1.12) | (1.10 ^a) | (0.46 ^b) | | |
| [HO(CH ₂) ₂ -mim][Tf ₂ N] ¹⁰ | (0.929) | | | | | 1187.8 |
| [CH ₃ O(CH ₂) ₂ -mim][Tf ₂ N] ¹⁰ | (0.722) | | | | | 1187.8 |
| [bmim][SbF ₆] | 0.673 | 1.039 | 0.639 | 0.146 | 525.5 | 1069.7 |
| [bmim][BF ₄] ⁸ | 0.670 (0.673) | 1.047 | 0.627 | 0.376 | 565.0 | 1204.5 |
| [bmim][PF ₆] ⁸ | 0.669 (0.667) | 1.032 | 0.634 | 0.207 | 524.0 (516.5) | 1158.1 |
| [bmim][TfO] ⁸ | 0.656 (0.667) | 1.006 | 0.625 | 0.464 | 577.0 (601.5) | 1224.6 |
| [bmim][N(Tf) ₂] ⁸ | 0.644 (0.642) | 0.984 | 0.617 | 0.243 | 545.0 (546.0) | 1187.8 ²⁷ |
| [bm ₂ im][BF ₄] | 0.576 | 1.083 | 0.402 | 0.363 | 558.0 | 1204.5 |
| [bm ₂ im][N(Tf) ₂] | 0.544 | 0.954 | 0.427 | 0.252 | 545.0 | 1187.8 |
| [bm ₂ im][N(Tf) ₂] ⁸ | 0.541 (0.552) | 1.010 | 0.381 | 0.239 | 547.0 (547.5) | 1187.8 |
| Water ^{3,6,28} | (1.00) | (1.33) (1.13 ^b) | (1.12) (1.16 ^b) | (0.14) (0.50 ^b) | (591) | |
| Methanol ^{3,6,28} | (0.762) | (0.73) | (1.05) | (0.61) | (589) | |
| Acetonitrile ²⁸ | 0.460 | 0.799 | 0.350 | 0.370 | (575) | |
| Acetone ²⁸ | 0.350 | 0.704 | 0.202 | 0.539 | (571) | |
| Dichloro-methane ²⁸ | 0.309 | 0.791 | 0.042 | -0.014 | 497.5 (550) | |
| Toluene | 0.100 | 0.532 | -0.213 | 0.077 | | |
| Hexane ^{3,7} | (0.009) | (-0.12) | (0.07) | (0.04) | | |

^a Recalculated, ^b Average value from more than one dye set.

† Electronic supplementary information (ESI) available: synthesis of ionic liquids. See <http://www.rsc.org/suppdata/cp/b3/b303095d/>

obtained using the aforementioned dye set. All spectra were recorded at 25 °C and we were, therefore, restricted in our selection of ionic liquids to those that are liquid at room temperature. The ionic liquids used in this work are shown (with abbreviations) in Fig. 2.

π^* values

All of the π^* values (Table 1) for the ionic liquids are high in comparison with non-aqueous molecular solvents.^{5–7} Although differences between the ionic liquids are small, both the cation and the anion can be seen to affect the value. All of the [Tf₂N][−] based ionic liquids lie at the low end of the range of values observed. The [bmim]⁺ ionic liquids have lower values than the [bm₂im]⁺ ionic liquids with a common anion and the [bmpy][Tf₂N] ionic liquid has the lowest value of all.

In molecular solvents, π^* reports the effects of the dipolarity and polarizability of the solvent. However, it should be noted that what is being measured is a property of the solute, namely the differential stabilization of the more polar excited state with respect to the ground state of the dye. Hence, π^* is derived from the change in the energy of the absorption maximum of the dye that is induced by the local electric field generated by the solvent. Therefore, it is no surprise that π^* has been greatly affected by the ion-dye interactions now possible in the ionic liquid. It can be seen that as the charge on the anions becomes delocalised over more atoms the value of π^* decreases due to the decrease in the strength of these Coulombic interactions. In the cations, on the other hand, it appears that the decrease in Coulombic interactions caused by delocalising the charge around the imidazolium ring is more than compensated for by the increased polarizability of the delocalised system. The effect of delocalized π -electron systems can be seen in the relatively high π^* value of toluene in comparison to hexane (Table 1).

It should be noted that the ionic liquids used in this study are all composed of relatively similar cations. Poole *et al.* have measured π^* for a series of alkylammonium nitrates and thiocyanates (Table 1), which have still higher values,¹¹ albeit with a different set of dyes. This probably reflects the closeness of approach to the charge centres of these salts that is possible and hence greater ion-dye Coulombic interactions.

The E_T^N scale

The E_T^N scale is considered to be a good general scale of the solvating ability of a liquid and is known for a wide range of

molecular solvents.³ It is also the scale that has been applied to the greatest number of ionic liquids.^{8–11} Measurement of the position of the absorption maximum of Reichardt's dye is a necessary part of the measurement of α as well as the source of the E_T^N scale. Hence we discuss the E_T^N values of the ionic liquids here.

Where the same ionic liquids have been used and so comparison is possible, it can be seen that the values here are in good agreement with those from the literature. As has been noted by others,⁸ the E_T^N values for the [bmim]⁺ ionic liquids lie in the range associated with polar hydrogen bond donor solvents such as alcohols.³ The E_T^N values are higher for [HO(CH₂)₂mim][Tf₂N],¹⁰ which contains its own alcohol functionality and [EtNH₃][NO₃],¹¹ which is an N–H hydrogen bond donor. However, the value for [CH₃O(CH₂)₂mim][Tf₂N]¹⁰ is also higher than for [bmim][Tf₂N], even though it contains a basic functionality (ether). While it also registers local electric field effects, the E_T^N scale is particularly sensitive to the hydrogen bond donor ability of the cation of the ionic liquid.⁸ This suggests that the electron withdrawing effect of the oxygen atom of [CH₃O(CH₂)₂mim][Tf₂N] is actually increasing the overall acidity of the ion. The [bm₂im]⁺ salts have significantly lower E_T^N values, as does [bmpy][Tf₂N]. Comparison of the [bmim]⁺ salts shows that there is also a clear effect of changing anion on E_T^N . These details will be discussed below in terms of their effects on the α values.

α values

The α values for the ionic liquids are listed in Table 1. The values are largely determined by the nature of the cation, but there is also a smaller anion effect. The values for the [bmim]⁺ are generally moderately high (*cf.*, *t*-BuOH).⁵ It has long been known that all three of the imidazolium ring protons are acidic,^{12,13} and it was predicted that hydrogen bonding to solutes would be significant in the absence of hydrogen bond accepting anions.¹⁴ The [bm₂im]⁺ ionic liquids have the lowest α values, reflecting the loss of the proton on the 2-position of the ring. [bmpy][Tf₂N] has a slightly higher α value than [bm₂im][Tf₂N]. Although one might have expected this latter relationship to be the reverse, since hydrogen bond donation increases with the increasing s-character of the C–H bond,¹⁵ hydrogen bonds to the α -carbons of alkyl chains in alkylammonium salts are well known.¹⁶ The higher than expected α value for [bmpy][Tf₂N] in comparison to [bm₂im][Tf₂N] probably reflects the number of protons that can be involved in the hydrogen bonding to the probe

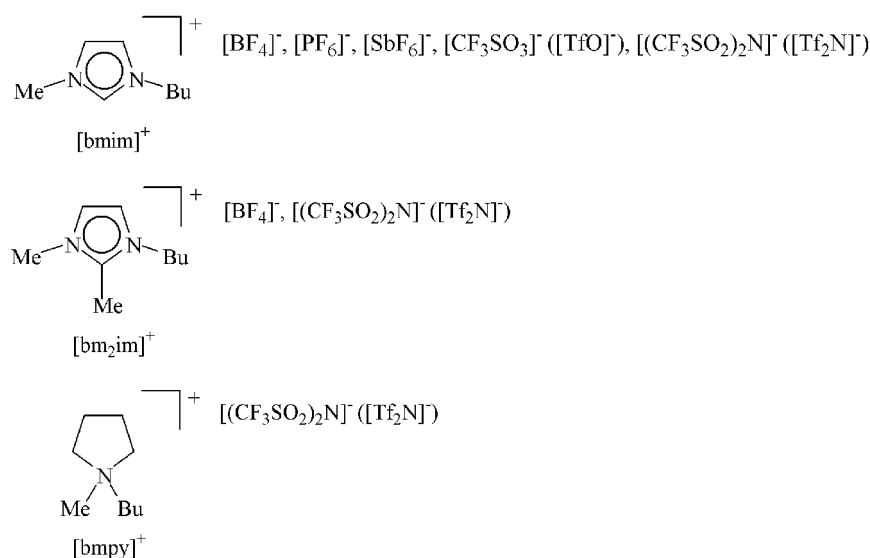
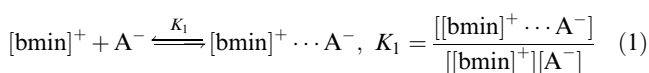


Fig. 2 The ionic liquids used in this study.

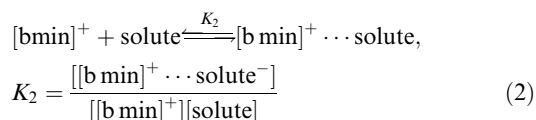
molecule in each case. The higher α value of [EtNH₃][NO₃], which is an N–H hydrogen bond donor, shows that the opportunity arises to prepare strongly hydrogen bond donating ionic liquids. The hydrogen bond donor abilities of ammonium cations are known to be higher than that of their neutral amines,¹⁷ hence the appearance of a large Coulombic contribution to the α value.

Focusing on the [bmim]⁺ salts, there is a clear anion effect seen. With the exception of the [N(Tf)₂]⁻ ion, which appears not to fit the simple trend, as the anion becomes more basic (increasing β) the hydrogen bond donor ability of the ionic liquid decreases. However, since the cation has been unchanged, its ability to act as a hydrogen-bond donor has been unchanged, so why is an effect seen at all?

We propose that there is a competition between the anion and probe dye solute for the proton. So, the α values of the ionic liquids are controlled by the ability of the liquid to act as a hydrogen-bond donor (cation effect) moderated by its hydrogen-bond acceptor ability (anion effect). This may be described in terms of two competing equilibria. The cation can hydrogen bond to the anion (eqn. (1)):



The cation can hydrogen bond to the solute, in this case the probe dye (eqn. (2)):



Clearly the concentration of the hydrogen bonded [bmim]⁺...solute complex is dependent upon the availability of the cation for bonding which, in turn, is dependent on the value of K_1 . Hence, as the anion becomes a better hydrogen bond acceptor, K_1 increases and the concentration of free non-hydrogen bonded [bmim]⁺ decreases and, since for a given solute in the [bmim]⁺ based ionic liquids K_2 is fixed, the concentration of the [bmim]⁺...solute complex falls. We have previously used these equilibria to explain the change in selectivity of the Diels–Alder cycloaddition of cyclopentadiene and methyl acrylate in various ionic liquids.¹⁸

An alternative explanation is that the anions are interacting directly with the dye itself. However, the positive charge of Reichardt's dye is distributed around the aromatic system and there is no well-located site for interaction with the anions that would play the part that the lone pairs of the oxygen atom play for the cations.

β values

β is the hydrogen bond basicity of the solvent. The values for the ionic liquids studied here are moderate and dominated by the nature of the anion (Table 1). As the conjugate bases of strong acids, the anions of the ionic liquids might be expected to have low β -values in comparison to other solvents. However, although those found in this study are not as high as for acetone, they are comparable to acetonitrile, which is thought of as an electron pair donor solvent.⁵ This shows again that there is an important Coulombic contribution to the hydrogen bonds formed between the ionic liquid and solute species.

Table 1 also includes a measure of the gas phase basicity of the anions, given as the calculated Gibbs free energy change for the gas phase deprotonation of its conjugate acid, ΔG_{H} .¹⁹ Experimental measurement of the acidity of such strong Brønsted acids is extremely difficult, hence these calculated values are preferred and are available for all of the anions used here. Calculated values also have the advantage that they can be generated for hypothetical acids. However, it should be

noted that the calculated values increasingly over-estimate the acidity (under-estimate ΔG_{H}) as the acid gets stronger.¹⁹ It can be seen that the hydrogen bond basicity of the ionic liquids is generally inversely proportional to the acidities of the conjugate acid of the ionic liquid's anions. The deviation from linear behaviour is probably a result of the under-estimation of ΔG_{H} of the stronger acids.

The different β values obtained for the different [Tf₂N]⁻ ionic liquids show that the cation has an influence, but with the limited data set here no trend can be clearly discerned at this stage.

Comparisons with other polarity studies

A number of other methods have been used to investigate solvent behaviour of ionic liquids.^{20–22} Most of these have not involved a sufficient overlap with the range of ionic liquids used here to allow for comparison of the trends observed.

Gordon *et al.*⁸ have used the absorption maximum of (acetylacetonato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II)tetraphenylborate {[Cu(acac)(tmen)][BPh₄] λ_{Cu} } as a probe of the basicity of the anions of ionic liquids and correlated this value with the rates (TOF) of nickel catalysed oligomerization reactions.²³ We have extended this study to include all of the ionic liquids investigated here. It can be seen that there is excellent agreement between this measure of basicity and β and it can be concluded that the two measurements are reporting similar behaviour.

A study of multiple solvation interactions, based on GC measurements, that were used to characterise a range of ionic liquids has been recently reported.²⁴ Eight of the ionic liquids used are from the same samples as those as used in this study. The ionic liquids were prepared, purified and the sample split into two parts one of which was sent for the GC measurements and the other used for this Kamlet–Taft experiment, so a direct comparison can be made. The non-specific interactions are not directly comparable for the two methods, yet in both studies the ionic liquids were consistently found to be highly polar.

The hydrogen bonding effects would be expected to give similar results in both experiments. Indeed, the hydrogen bond basicities of the ionic liquids follow the same trend in both studies, are controlled by the anion and are moderate in value. Comparisons of hydrogen bond acidity are, however, not so clear-cut. In the solvation study the ionic liquids' hydrogen bond donation behaviour as a whole was found to be dominated by the hydrogen bond *basicity* of the anions, with a much lesser contribution from the hydrogen bond acidity of the cation. Low and even negative values were found for the hydrogen bond acidity function. The only ionic liquids to display significant hydrogen bond donor ability were those of the [Tf₂N]⁻ ion.²⁴ In contrast, this Kamlet–Taft study has strongly emphasised the role of the hydrogen bond acidity of the cation. A plot (Fig. 3) of the two functions, α from this study and b from the solvation study, reveals a complex relationship.

It can be seen for the imide ionic liquids, that the hydrogen bond acidity does indeed vary with cation with [bmim]⁺ being the most acidic followed by [bmpy]⁺ and finally [bm₂im]⁺ in both studies. However, changing to more basic anions leads to a dramatic drop in the acidity measurements in the solvation study, whereas it has only a limited effect in the study reported here. That is, the solvation measurement is anion dominated, whereas the Kamlet–Taft measurement is cation dominated.

We propose that this is not a simple matter of one of the measurements being right while the other is wrong, but rather more about what is actually being measured. The intimate relationship that exists between solute and solvent is such that the nature of the solute strongly influences which solvent

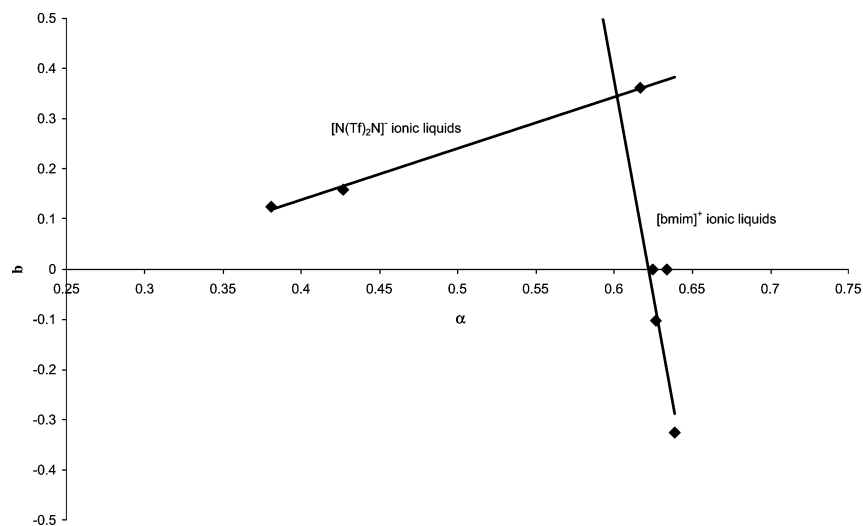


Fig. 3 Comparison of the hydrogen bond donor β vs. α functions for the ionic liquids.†

properties will be expressed. In the solvation study the set of probes has been deliberately selected to provide a broad range of interactions.²⁴ Some of the probes can act as hydrogen bond acceptors, others do not, some will interact strongly with the cation, others with the anion and yet others with neither. Whereas Reichardt's dye, key in the measurement of α , has a strongly hydrogen-bond-accepting phenoxide oxygen, which is anionic and will strongly and exclusively interact with the cation of the ionic liquid. Hence, this Kamlet–Taft study reveals the interactions of which the ionic liquids are capable in the presence of a strongly and specifically interacting solute and how they are influenced by the nature of the two competing ions, whereas the solvation study reveals the value when the nature of any particular solute has been deliberately down-played by averaging over many solutes and how that is influenced by the nature of the ions.

Conclusions

Comparison of the values with those of molecular solvents show that care must be taken in claims of similarities between ionic liquids and such solvents. While it can be said that the E_T^N values of the [bmim]⁺ ionic liquids are similar to those of short chain alcohols, all of the values of π^* , α and β are quite different. Therefore, it would not be sensible to state that ionic liquids are “like” short chain alcohols, without specifying the narrow respect in which this might be considered to be true. This will be true of many possible comparisons.

The results presented here suggest that ionic liquids are indeed polar solvents that can, under appropriate circumstances, act as both hydrogen bond donors and hydrogen bond acceptors. The π^* values are uniformly high and characteristic of ionic liquids and there is unlikely to be very much synthetic flexibility in this parameter. α and β vary more widely with the selection of the ions composing the ionic liquid and can be deliberately manipulated. It is particularly exciting that the relationships between DFT calculations of gas phase acidity, β , [Cu(acac)(tmen)]⁺ basicity measurements and the rates of transition metal catalysed reactions opens the possibility for designing the chemical function of the ionic liquids from scratch for the first time.

† We now believe that the unexpectedly high basicity of the [bmim][SbF₆] ionic liquid in the solvation study is the result of decomposition of the ionic liquid during transport and it has been removed from this comparison.

Experimental

The syntheses of the ionic liquids used in this research have been reported elsewhere,^{25,26} and are available as electronic supplementary information (ESI).† The dyes were used as received. All spectra were recorded using a PC-controlled Perkin-Elmer Lambda 2 spectrophotometer, fitted with a thermostatted sample holder.

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