

Investigations of solvent–solute interactions in room temperature ionic liquids using solvatochromic dyes

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Different measures of polarity and nucleophilicity of a range of ionic liquids have been investigated using two solvatochromic dyes; the polarity appears to be largely cation controlled, while the donor strength is entirely anion dependent.

Ionic liquids (ILs) based on the 1,3-dialkylimidazolium cation have generated a great deal of interest over the past few years as solvents in many different areas of chemistry. In particular, ILs have shown significant promise as media for organic synthesis,¹ biphasic catalysis,² and separations.³ Alteration of the cation or anion can cause changes in properties such as viscosity, melting point, water miscibility, and density.⁴ It has been noted that many substrates are insoluble, and some reactions give poor results or do not take place at all, in certain cation–anion combinations. Despite this, there are very few reports on how the cations and anions of these liquids interact with solutes. Bonhôte *et al.* showed that 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([emim][Tf₂N]) displayed a polarity similar to that of ethanol based on the fluorescence spectrum of pyrene.⁵ They also reported that the apparent relative permittivity value for this solvent was below 10, based on the fluorescence spectrum of pyrenecarbaldehyde. More recently, Carmichael and Seddon reported that a study of the absorption spectrum of the solvatochromic dye Nile Red in a range of 1-alkyl-3-methylimidazolium (Rmim) based ILs showed similar λ_{\max} values to those obtained in short chain alcohols.⁶ Alteration of the length of the alkyl substituent had little effect on the position of λ_{\max} . Finally, Brennecke *et al.* have investigated the polarity of four imidazolium- and pyridinium-based ILs using the fluorescent probes 4-aminophthalimide and 4-(*N,N*-dimethylamino)phthalimide. Their data indicated polarities lying between those of methanol and acetonitrile, depending on the cation present.⁷

In molecular solvents the exact meaning of “polarity” is complex, as many different interactions can be involved, for example hydrogen bonding, π -interactions or van der Waals forces. ILs are even more complicated, since both cations and anions can have their own distinct interactions. Most probes allow examination of only one major type of interaction with a solvent, so a range of different probes are usually required to give a full picture of the strength of different types of solute–solvent interaction. In this study we report the behaviour of two well-known solvatochromic systems that probe completely different interactions using a range of ILs. These systems are the Dimroth–Reichardt $E_T(30)$ scale based on the *N*-(4-oxido-phenyl)pyridinium dye **1**, and [Cu(acac)(tmen)][X] (X = BPh₄ or ClO₄), **2** (see Fig. 1).

The E_T scale is one of the most widely applied of empirical polarity scales.⁸ Compound **1** exhibits an extremely large solvatochromic shift in its charge transfer (CT) absorption band, from $\lambda_{\max} = 810$ nm in diphenyl ether to $\lambda_{\max} = 453$ nm in water. The solvatochromism arises from unequal, differential solvation of the highly dipolar zwitterionic ground state ($\mu_g = 15$ D) compared with the less dipolar first excited state ($\mu_e = 6$ D). The position of the CT absorption of the dye is

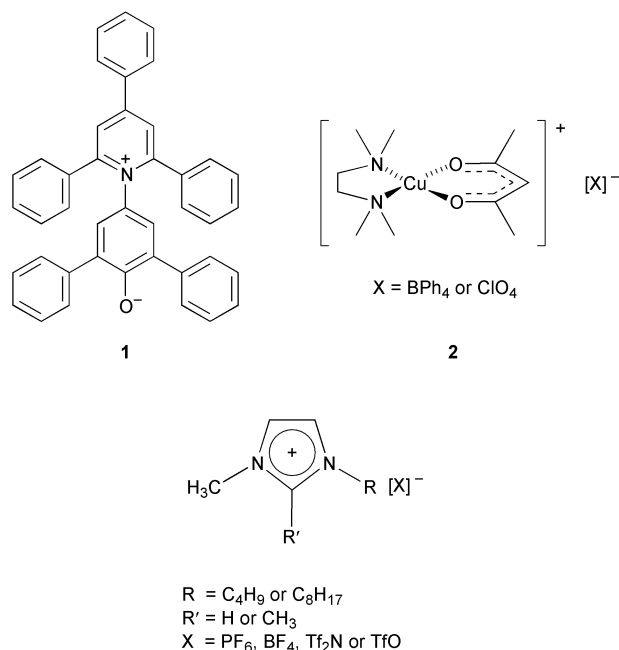


Fig. 1 Structures of solvatochromic probes and ionic liquids.

particularly strongly influenced by the ability of the solvent to act as a hydrogen bond donor (HBD) to the phenoxide oxygen atom. Taft and Kamlet calculated that *ca.* 68% of the shift in transition energy could be assigned directly to specific interactions involving the phenoxide oxygen atom.⁹ Their hypothesis was that for protic solvents the E_T scale is largely a measure of the hydrogen bond donor strength. The transition energy for the CT absorption may be calculated from the position of λ_{\max} using the relationship: $E_T(30)/\text{kcal mol}^{-1} \dagger = 28591/(\lambda_{\max}/\text{nm})$, giving a value referred to as $E_T(30)$. For convenience these values are often normalised to give a parameter E_T^N , where $E_T^N = 0.0$ for tetramethylsilane, and 1.0 for water.

In the current study, **1** was dissolved in a range of ILs based on the 1-butyl- and 1-octyl-3-methylimidazolium (bmim and omim respectively) as well as 1-butyl- and 1-octyl-2,3-dimethylimidazolium cations (bmmim and ommim), combined with the anions [PF₆]⁻, [Tf₂N]⁻, [BF₄]⁻ and [TfO]⁻ (Tf = CF₃SO₂), as illustrated in Fig. 1. ‡ Table 1 shows λ_{\max} values obtained for **1**, along with the corresponding $E_T(30)$ and E_T^N values. Comparative values for some conventional organic solvents are also included. The results fell into two general classes: the 1,3-dialkyl substituted salts (entries 1–4, 7 and 8) gave values similar to those obtained for short chain primary alcohols (entry 10), while the 1,2,3-trisubstituted salts had noticeably lower E_T values (entries 5, 6 and 9), similar to those obtained for secondary alcohols (entry 11).⁸ Our values for [bmim][PF₆] and [omim][PF₆] are also close to those estimated in a recent publication from fluorescence maxima and lifetimes of *N,N*-dimethylaminophthalimide.⁷ Alteration of the anion had

Table 1 Spectroscopic data obtained for solvatochromic probes **1** and **2** in a range of ionic liquids and some conventional solvents

Entry	Solvent	λ_{\max} (1)/nm ^a	$E_T(30)$ /kcal mol ⁻¹	E_T^N	λ_{\max} (2a)/nm
1	[bmim][PF ₆]	546.5	52.3	0.667	516.5
2	[omim][PF ₆]	558.0	51.2	0.633	516.5
3	[bmim][Tf ₂ N]	555.5	51.5	0.642	546.0
4	[omim][Tf ₂ N]	559.0	51.1	0.629	548.5
5	[bmmim][Tf ₂ N]	588.0	48.6	0.552	547.5
6	[ommim][Tf ₂ N]	599.5	47.7	0.525	549.5
7	[bmim][TfO]	547.0	52.3	0.667	601.5
8	[bmim][BF ₄]	545.0	52.5	0.673	—
9	[ommim][BF ₄]	592.0	48.3	0.543	—
10	Ethanol	551 ^b	51.9 ^b	0.654 ^b	585 ^c
11	Propan-2-ol	591 ^b	48.4 ^b	0.546 ^b	591.0 ^d
12	1,2-Dichloroethane	692 ^b	41.3 ^b	0.327 ^b	500 ^c
13	Acetone	678 ^b	42.2 ^b	0.355 ^b	569 ^c
14	<i>N,N</i> -Dimethylformamide	662 ^b	43.2 ^b	0.386 ^b	602 ^c

^a UV-visible spectra were recorded at 25 °C on a Shimadzu UV-2501PC with double monochromator in a thermostatted quartz cell, and are accurate to ± 0.5 nm. The samples were dried by heating under vacuum for 24 hours or until no further change in the value of λ_{\max} was observed. All results this work unless otherwise indicated. ^b Ref. 8; note that the λ_{\max} values have been calculated from quoted $E_T(30)$ values. ^c Ref. 14. ^d Value for **2b**.

very little effect on the E_T value, with the exception of [bmim]-[Tf₂N] which displayed a λ_{\max} value approximately 10 nm higher than those observed for the other salts containing the same cation. An increase in the length of the alkyl substituent caused only a small decrease in E_T value. A similarly small decrease in polarity has been reported on increasing chain length in primary alcohols, a result that was found to be similar to that of adding *n*-hexane to short chain alcohols.¹⁰ It was reported that this arose simply from a reduction in the relative concentration of -OH groups available for hydrogen bonding to the dye molecules.

These results suggest that the main influence on the position of λ_{\max} for **1** in ILs is the strength of interaction with the cationic head group, and that the strongest interaction is hydrogen bonding between the phenoxide group on **1** and the hydrogen atoms on the imidazolium ring. Crystal structure data obtained for a number of 1,3-dialkylimidazolium salts has revealed the existence of hydrogen bonding and other strong dipole-dipole interactions between the imidazolium ring and a range of anions. In most cases, the strongest interaction occurs at the 2-position on the ring.¹¹ The reduction in HBD ability of the solvents was quite evident when the hydrogen at the 2-position was replaced with a methyl group.

As indicated above, the E_T scale is most strongly influenced by the HBD ability of the solvent. Clearly, however, this is not the only interaction of importance. The lack of change in position of λ_{\max} for **1** with different anions shows that it is not a good probe of the hydrogen bond acceptor ability, or nucleophilicity of the ILs. An alternative solvatochromic system is therefore required to remedy this gap in the information. The square planar salt [Cu(acac)(tmen)][X] (acac = acetylacetonate, tmen = *N,N,N',N'*-tetramethylethylenediamine, X = [BPh₄]⁻ (**2a**) or [ClO₄]⁻ (**2b**)) has been shown to give a good correlation between the donor number (DN) of a solvent and the value of λ_{\max} for the lowest energy d-d band.¹² More recently, it has been shown that this salt can also be used to estimate the donor numbers of anions in solution.¹³ The solvatochromism arises from changes in the splitting of the d-orbitals of Cu²⁺ as the salt becomes five- or six-coordinated.

The λ_{\max} values obtained for **2** in a range of ILs and for some conventional solvents by way of comparison (entries 10–14) are listed in Table 1. The [BPh₄]⁻ salt was employed where possible as this anion is assumed to be entirely non-coordinating.[§] Two major conclusions may be drawn from these results. (1) For a given anion, there is virtually no dependence of λ_{\max} on the cation present. This suggests that the position of λ_{\max} is entirely anion dependent, and also that the cations play no part in the nucleophilicity of the salts. (2) The order of nucleophilicity is [PF₆]⁻ < [Tf₂N]⁻ < [TfO]⁻.

The low nucleophilicity of the [PF₆]⁻ salts (entries 1 and 2) is not unexpected, given the symmetrical shape and low charge density of this anion, and these may be thought of as effectively

non-coordinating solvents. The [Tf₂N]⁻ salts (entries 3–6) appear to be more strongly coordinating, a result that is supported by a crystal structure of an imidazolium [Tf₂N]⁻ salt,¹⁴ which suggested that the negative charge is localised across the S–N–S moiety. The value obtained for [bmim][TfO] (entry 7) is slightly higher than that recorded previously for [NBu₄][TfO] in dichloroethane solution (581 nm),¹³ but clearly indicates that this anion coordinates to the Cu(II) centre much more strongly than the other two anions. Furthermore, the colour of **2** in [bmim][TfO] faded rapidly unless an excess of tmen was present. This behaviour has been noted previously for more strongly donating solvents, and has been ascribed to ligand displacement.^{12b} No values are reported for the [BF₄]⁻ salts as these gave variable λ_{\max} values that were far larger than expected. The expected value would be around 526 nm based on results gained by Linert *et al.*,¹³ indicating a coordination strength between that of [PF₆]⁻ and [Tf₂N]⁻. We believe that these high values were due to the presence of residual Cl⁻ in the [BF₄]⁻ salts. Being much more water soluble than the hydrophobic [PF₆]⁻ and [Tf₂N]⁻ salts, the removal of traces of Cl⁻ is more difficult. These results suggest that **2** could be used as an indicator for the presence of Cl⁻ ions in ILs. At this stage, however, we do not wish to assign donor numbers to the ILs until a wider range has been investigated.

The results reported in this paper allow possible explanations for many observations made on reactions catalysed by transition metal complexes in ILs. We have recently reported a study of the oligomerisation of ethene using a cationic Ni complex in a range of [PF₆]⁻ based ILs, and compared the results with the same reaction in CH₂Cl₂ and butane-1,4-diol.¹⁵ The degree of coordination indicated by [Cu(acac)(tmen)][BPh₄] in different solvents could be correlated to the turnover frequency (TOF) for the reaction. For example butane-1,4-diol coordinated strongly to the Cu probe and resulted in a much lower TOF value. This can be explained by the fact that more coordinating solvents block the active site of the cationic Ni catalyst. Another example is the hydrogenation of pent-1-ene catalysed by [Rh(nbd)(PPh₃)₂][PF₆] in [bmim][X] (nbd = η^4 -norbornadiene, X = [SbF₆]⁻, [PF₆]⁻, and [BF₄]⁻).¹⁶ In this study the TOF for formation of pentene was in the order [SbF₆]⁻ > [PF₆]⁻ \gg [BF₄]⁻. Although we have not studied ILs based on [SbF₆]⁻, one would anticipate that this anion would be even more weakly coordinating than [PF₆]⁻ owing to its larger size.

In conclusion, our results suggest that the ILs in this study can all be regarded as displaying hydrogen bond donor abilities similar to those of alcohols, while their nucleophilicities are much lower and entirely anion dependent. In this respect they are quite unique materials, since most solvents of such low nucleophilicity are generally regarded as non-polar. This behaviour probably accounts for the excellent properties of some ILs as solvents for transition metal complex catalysed organic reactions. In due course we will report the results

for a greater range of ILs and using further solvatochromic probes.

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Notes and references

† 1 kcal mol⁻¹ = 4.814 kJ mol⁻¹.

‡ The ionic liquids were prepared following literature methods, and their purity confirmed by ¹H NMR spectroscopy and CHN micro-analysis.^{3,5} All solutions were dried by heating at 70 °C under vacuum for several hours, or until no further change in the position of λ_{max} was observed. Absorbances of 0.2–2.0 were employed for all measurements; no dependence of band shape or the position of λ_{max} on concentration was observed for either probe molecule.

§ The [ClO₄]⁻ salt is not suitable for solvents of very low DN, owing to competitive coordination of the anion. In the present study, **2a** was employed for all salts.

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