

Polarity study of some 1-alkyl-3-methylimidazolium ambient-temperature ionic liquids with the solvatochromic dye, Nile Red

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ABSTRACT: The polarity of ambient-temperature ionic liquids based on the 1-alkyl-3-methylimidazolium cation was probed using the solvatochromic dye Nile Red. The polarity of these liquids was shown to be comparable to that of the lower alcohols. The effects on polarity with changing anion and 1-alkyl group are reported. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: polarity; ionic liquids; ambient temperature; 1-alkyl-3-methylimidazolium cation; solvatochromic dye; Nile Red

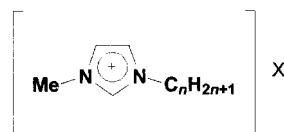
INTRODUCTION

Solvent polarity has a powerful influence on the outcome of chemical reactions and on the features observed with spectroscopic techniques. As a result, the choice of solvent for a particular application must be made with great care and thought. To aid such decisions, a number of parameters are available for guidance, e.g. dielectric constant, refractive index and dipole moment. However, solvent polarity cannot simply be defined using these terms, since specific solvent–solute interactions are not taken into account. This has led to the development of empirical scales of solvent polarity. A common approach to the development of such scales has been to use solvatochromic dyes, that is, compounds for which the absorption or emission band maxima shift according to the polarity of the medium in which they are dissolved.^{1–6}

Ambient-temperature ionic liquids based up the 1-alkyl-3-methylimidazolium cation (Fig. 1) were first reported in 1982 by Wilkes *et al.*⁷ These systems were based on the tetrachloroaluminate(III) anion but, although they possess many useful properties (e.g. wide liquidus, thermal stability and large electrochemical window), they are also reactive towards many materials and are very sensitive to moisture. In 1992, an air- and water-stable system was developed by Wilkes and Zaworotko, based on the tetrafluoroborate anion.⁸ Since that report, a wide range of ionic liquids containing

different anions have appeared in the literature.^{9–12} These solvents, which have been the subject of a number of reviews,^{13–20} have also received much popular attention.^{21–27} To give a sense of the scope for these solvents, it is worth mentioning that recent studies have shown that ambient-temperature ionic liquids can be used as media for a wide range of chemical reactions, including hydrodimerization,²⁸ hydrogenation,^{29–34} dimerization,³⁵ polymerization,³⁶ alkylation,³⁷ Friedel–Crafts reactions,^{38–41} Heck coupling,^{42,43} the Diels–Alder reaction^{44–46} and enzymatic catalysis of biotransformations.⁴⁷

As part of a programme aimed at understanding more about the nature of these ambient-temperature ionic liquids, and how they compare with conventional solvents, we have undertaken a study of their polarity using the solvatochromic dye Nile Red (Fig. 2). Nile Red is positively solvatochromic; thus, when dissolved in increasingly polar media, the wavelength of its visible absorption maximum (λ_{max}) moves to longer wavelengths (lower energies). In fact, amongst positively solvatochromic dyes, Nile Red displays one of the largest



$n = 4, 6, 8, 10$
 $X = [\text{NO}_2], [\text{NO}_3], [\text{BF}_4], [\text{PF}_6], [(\text{CF}_3\text{SO}_2)_2\text{N}]$

Figure 1. Molecular structure of 1-alkyl-3-methylimidazolium salts, $[\text{C}_n\text{-mim}]\text{X}$

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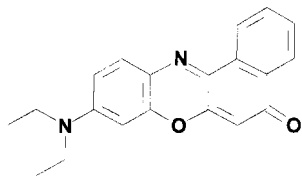


Figure 2. Molecular structure of the positively solvatochromic dye Nile Red

bathochromic shifts known. On changing the solvent from water to pentane, a change in λ_{\max} of 110 nm is observed.⁴⁸

Nile Red has been used to determine the polarity of conventional solvents and binary mixtures^{48–51} and of supercritical fluids^{48,52} and used to probe the microenvironment of polymers,⁴⁹ xerogels,⁵³ liquid crystals⁵⁴ and zeolites.⁵⁵ It has also been incorporated, as the sensing element, in fibre-optic devices capable of identifying and quantifying a range of organic vapours.^{56,57}

EXPERIMENTAL

Nile Red was purchased from ICN Biochemicals and used as received. The 1-alkyl-3-methylimidazolium ionic liquids were prepared using established literature procedures and dried *in vacuo* immediately prior to use.^{9,12,58}

Absorption spectra were recorded on a Perkin-Elmer Lambda 9 electronic absorption spectrophotometer. Solutions were examined using stoppered quartz cells of 1 mm pathlength. Absorption spectra of Nile Red in several conventional solvents were obtained and found to be in good agreement with published data.⁴⁸ The ionic liquids examined have no absorption bands in the region of interest.

To investigate whether aggregation of Nile Red in the ionic liquid would be a potential problem, several solutions were made up over an absorption range of 0.2–3.0. No change in λ_{\max} or spectral shape was observed over this range. For polarity measurements, a Nile Red concentration was chosen such that absorbances would fall in the range 0.5–1.0. This was achieved by preparing a stock solution of Nile Red in methanol (spectroscopic grade), of which 0.5 cm³ was transferred to a vial; the methanol was removed by heating *in vacuo*. Ionic liquid (2 cm³) was transferred into the vial by syringe and stirred under an atmosphere of dry dinitrogen until complete dissolution of the dye was achieved.

RESULTS AND DISCUSSION

A wide range of salts based on the dialkylimidazolium cation have been prepared; we estimate that there are potentially 10¹⁸ ionic liquid systems.⁵⁹ The alkyl groups in the 1- and 3- positions on the ring can be varied or

Table 1. Wavelengths of maximum absorption (λ_{\max}) and molar transition energies (E_{NR}) for Nile Red dissolved in [C_n-mim]⁺X⁻ ionic liquids

Ionic liquid	λ_{\max} (nm)	E_{NR} (kJ mol ⁻¹) ^a
[C ₄ -mim] ⁺ [NO ₂] ⁻	556.0	215.1(1)
[C ₄ -mim] ⁺ [NO ₃] ⁻	555.7	215.3(1)
[C ₄ -mim] ⁺ [BF ₄] ⁻	550.8	217.2(1)
[C ₄ -mim] ⁺ [PF ₆] ⁻	547.5	218.5(1)
[C ₄ -mim] ⁺ [(CF ₃ SO ₂) ₂ N] ⁻	548.7	218.0(1)
[C ₄ -mim] ⁺ [BF ₄] ⁻	550.8	217.2(1)
[C ₆ -mim] ⁺ [BF ₄] ⁻	551.9	216.8(1)
[C ₈ -mim] ⁺ [BF ₄] ⁻	549.5	217.7(1)
[C ₁₀ -mim] ⁺ [BF ₄] ⁻	545.7	219.2(1)
[C ₄ -mim] ⁺ [PF ₆] ⁻	547.5	218.5(1)
[C ₆ -mim] ⁺ [PF ₆] ⁻	551.7	216.8(1)
[C ₈ -mim] ⁺ [PF ₆] ⁻	549.8	217.6(1)
[C ₄ -mim] ⁺ [NO ₃] ⁻	555.7	215.3(1)
[C ₆ -mim] ⁺ [NO ₃] ⁻	552.9	216.3(1)
[C ₈ -mim] ⁺ [NO ₃] ⁻	550.1	217.4(1)

^a $E_{\text{NR}} = (hcN_A/\lambda_{\max}) \times 10^6$, where h is Planck's constant c is the speed of light, N_A is Avogadro's number and λ_{\max} is the wavelength of maximum absorption (nm).

altered to contain different functional groups, the 2-, 4- and 5- ring positions can be substituted and for each of these combinations the anion can be changed. Many of these alterations have the effect of raising the melting-point of these salts, but often by only a small amount above ambient temperature.

This study is concerned with 1,3-dialkylimidazolium salts that are liquid at room temperature. Several of the salts based on the 1-alkyl-3-methylimidazolium cation (henceforth shortened to [C_n-mim]⁺, where n is the number of carbon atoms in the 1-alkyl chain; see Fig. 1) meet this requirement, and form the basis of this study. The effects on the polarity of these liquids by varying the anion and by varying the 1-alkyl chain are reported, and the results are compared with known polarity scales.

The wavelengths of maximum absorption (λ_{\max}) and the molar transition energies (E_{NR}) for Nile Red dissolved in the ionic liquids are summarized in Table 1. All absorption spectra taken in the ionic liquids gave a single maximum in the visible region, the norm for medium-to-high polarity solvents. In contrast, solvents of low polarity (e.g. cyclohexane) cause splitting of the main absorption band, giving double maxima.⁶⁰

For the [C₄-mim]⁺ ionic liquids, the polarity decreases through the anion series of nitrite, nitrate, tetrafluoroborate and hexafluorophosphate. This decrease in polarity correlates with increasing anion size, hence a reduction in the effective anion charge density, i.e. the negative charge becomes more spread out and there is less available for interactions with solutes, in this case Nile Red. There is no obvious correlation with, say, miscibility with water, but that is perhaps not surprising.

The [C₄-mim]⁺[(CF₃SO₂)₂N]⁻ ionic liquid contains an anion larger than the cases just mentioned. However, it is

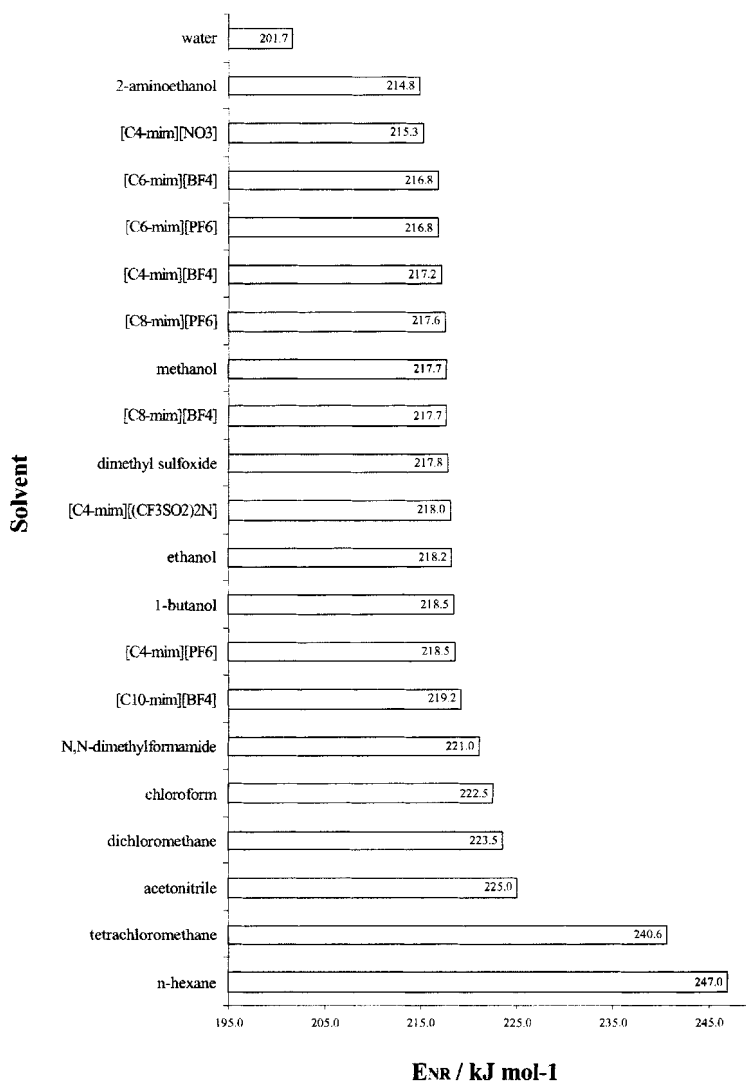


Figure 3. E_{NR} values for $[C_n\text{-mim}]X$ ionic liquids and common conventional solvents

more polar than its hexafluorophosphate analogue. A crystallographic study of an analogous imidazolium bis[(trifluoromethyl)sulfonyl]imide salt reveals that the negative charge is only partially delocalized within the anion.⁶¹ This study shows that the negative charge is spread across the S—N—S moiety, which is larger than the tetrafluoroborate anion but smaller than the hexafluorophosphate anion. This correlates with the observed polarity of the $[C_4\text{-mim}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ ionic liquid, fitting it to the series on the basis of its effective anion charge.

A similar trend in the polarity of both the tetrafluoroborate and hexafluorophosphate ionic liquids was observed due to variation of the 1-alkyl chain. In both cases, the polarity rises upon changing from $n = 4$ to $n = 6$, and after this point polarity falls with further increases in the length of the alkyl chain. The observed polarity maximum at $n = 6$ correlates with the melting-points for these liquids. For the two series of ionic liquids ($n = 2\text{--}18$) the melting-points reach a minimum at

$n = 6$ ^{9,58} (M. J. Torres and K. R. Seddon, Unpublished work, 1998–99). As mentioned above, the polarity for the $[C_4\text{-mim}]^+$ ionic liquids varies with the anion. However, for the $[C_6\text{-mim}]^+$ and $[C_8\text{-mim}]^+$ ionic liquids, there are no differences in polarity, within experimental error, between the tetrafluoroborate and hexafluorophosphate series.

Therefore, for 1-alkyl-3-methylimidazolium ionic liquids, the polarity is apparently determined by the anion for those containing short 1-alkyl groups and by the cation for those containing long 1-alkyl groups. The nitrate series, in contrast, do not follow the same trend. Hence these conclusions must be considered tentative, pending a more extended study.

CONCLUSIONS

The results from this study do not give a complete answer regarding the polarity of the 1-alkyl-3-methylimidazo-

lium ionic liquids, but they do give information about their relative polarity and trends within the series. The values of E_{NR} observed for the 1-alkyl-3-methylimidazolium ionic liquids position them in the middle to upper half of the polarity table generated by Deye *et al.*⁴⁸ According to this scale, the ionic liquids are in the same polarity region as 2-aminoethanol (214.8 kJ mol⁻¹) and the lower alcohols, methanol (217.7 kJ mol⁻¹), ethanol (218.2 kJ mol⁻¹) and butan-1-ol (218.5 kJ mol⁻¹). Figure 3 displays these data, along with the values for several widely used solvents for comparison.⁴⁸ Bonhôte *et al.* probed the polarity of [C₂-mim][(CF₃SO₂)₂N] using the fluorescent compound pyrene.¹² Our results on a range of ionic liquids are in good agreement with their measurement, which showed that [C₂-mim][(CF₃SO₂)₂N] had a polarity similar to that of ethanol. We are also aware of a related independent study (C. M. Gordon, University of Strathclyde, unpublished work) using Reichardt's dye, and these results are very similar to ours. Given the complexity of the extended three-dimensional liquid structure of ionic liquids (currently under active investigation in our laboratories, using computational, neutron and x-ray techniques), with a supramolecular structure influenced by hydrogen bonds, it is not surprising that this study does not yield definitive answers on the question of polarity. Indeed, this study raises many interesting questions for the future, not least of which is the role of the hydrophobic cationic hydrocarbon chain, and the validity of using a dye molecule which may disrupt the very environment which it is attempting to probe.

As these materials increasingly become alternatives for conventional solvents, data such as these, which are taken for granted for most systems, will become important to the synthetic chemist. There is a paucity of good reproducible physical data on these systems, and a strong impetus to create a reliable database of ionic liquid properties.

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