New aspects on polarity of 1-alkyl-3-methylimidazolium salts as measured by solvatochromic probes

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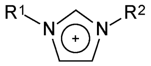
Kamlet–Taft solvatochromic polarity parameters β and π^* of ionic liquids with 1-alkyl-3-methylimidazolium cations are determined in two ways by the counter anion X^-: the β value represents the hydrogen bond basicity and the π^* value depends on the polarizability of X^-.

The solvent polarity of RTIL (room temperature ionic liquids) seems significantly determined by the nature of the anion and corresponding cation. Solvatochromism of suitable UV/Vis probes has been established to investigate the manifold aspects on solvent polarity of various RTIL.[1–5] It is crucial to use such types of solvatochromic indicators which reflect the portions of hydrogen bond donating (HBD) ability (α), hydrogen bond accepting (HBA) ability (β) and dipolarity/polarizability (π^*) adequately as well as reasonably. For this purpose the Kamlet–Taft LSER (linear solvation energy relationship) has been established to determine the separate parameters α, β, and π^*.[6] Eqn (1) shows the simplified form of the LSER of Kamlet–Taft used for the application of solvatochromic dyes.[6]

$$\nu_{\max}(\text{probe}) = \nu_{\max,0} + a\alpha + b\beta + s\pi^* \qquad (1)$$

$\nu_{\max}$(probe) is the position of the UV/Vis absorption band of the solvatochromic indicator measured in the respective environment. The factors a, b, and s are solvent-independent correlation coefficients. For reviews on polarity measurements of RTIL using solvatochromic dyes see the literature.[1,2]

The hydrogen bond donating strength of ionic liquids can be attributed to the hydrogen atom (Type I RTIL, comparable to non-quaternary ammonium ions) and to the polar α-CH-bond of alkyl groups (Type II RTIL) bound at the positively charged nitrogen atom (Scheme 1).[7]



Type I: R^1 = Alkyl; R^2 = H
Type II: R^1, R^2 = Alkyl

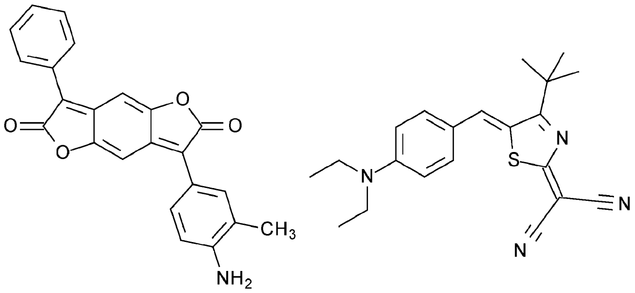
Scheme 1 Examples of two types of cations of imidazolium based RTIL.

The specific hydrogen bond donating ability of 1,3-dialkylimidazolium ions has been additionally explained by the weak acidity of the hydrogen atom in position 2 of the imidazolium cation due to the crystal structure analyses revealing hydrogen bond interactions between the ring and the anion.[8] However, α values of RTIL have been mainly determined using Reichardt's dye as the solvatochromic probe, because its sensitivity to HBD-sites is well established.[1] We fear that α values are also influenced by traces of water due to the formation of stoichiometric 1 : 1 water–probe complexes because Reichardt's dye and other HBD sensitive probes preferentially interact with water.[9] For this to occur, the required amount of water is below Karl–Fischer titration detection limits. Therefore, we see a difficulty in the determination of HBD ability parameters of RTIL, and the associated influence of water traces. We are also sensitive to the fact that very low concentrations of water cannot be exactly quantified, and we find it necessary to solve this important problem in future work.

To determine β as well as π^* values of HBD solvents, solvatochromic probes are required which show a significance of the UV/Vis shift to solely one of the Kamlet–Taft parameters. The HBD ability of the environment should not have an influence upon $\nu_{\max}$ of the solvatochromic probe.

Another topic in this communication will be the mismatch of the solvatochromically determined polarity parameter π^* to results from dielectric measurements,[10,11] which is still an open question in the literature.

In this communication we introduce 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b*′]-difuran-2,6-dione **1** as a solvatochromic indicator to determine β values for anions of RTIL (Scheme 2).[12] **1** possesses a large absorption coefficient ($\varepsilon \sim 10^4$ l mol^{-1} cm^{-1}) and it absorbs in the visible region from 400 to 700 nm.[12,13] Scheme 2 shows also the mainly sensitive π^* indicator 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline **2** which is used to determine the π^* parameter as independently as possible.[14]



1 **2**

Scheme 2 Structure of the two solvatochromic dyes **1** and **2** used in this study to determine independent β and π^* values of seven RTIL.

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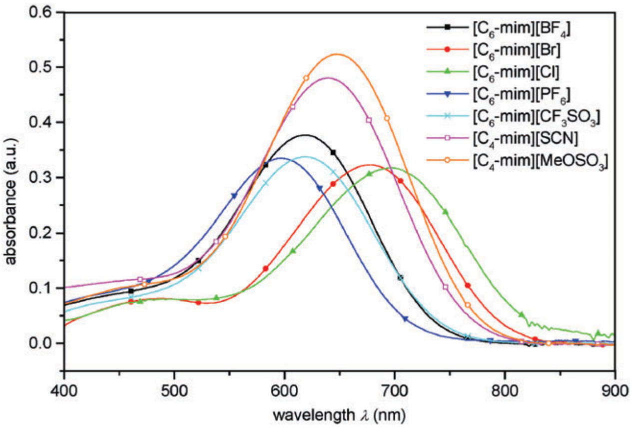

Fig. 1 UV/Vis absorption spectra of **1** measured in various RTIL.

The determination of the basicity of anions is not only of importance for RTIL. Basicity is one of the fundamental properties of molecules.[15] Up to now β parameters of anions have been measured using transition metal complexes with empty d-orbitals[16,17] or nitroanilines which contain HBD groups.[18,19] An established β indicator is Cu(tmen)(acac)$^+$ often used for RTIL[20] and other purposes, because the position of the solvent dependent UV/Vis absorption band is solely a function of β.[8] However, there is a dangerous problem arising from the change of coordination sphere of the copper atom by interacting with strongly coordinating anions, which makes the use of LSER derived from solvent scales likely unsuitable to parameterize anion basicity.[17] Perhaps, sometimes too large β values are reported for anions.[16] The use of nitroaniline probes, which are sensitive mainly to π^* and in the second instance to β, makes the separation of the β term from ν_{max}(probe) often less significant.[18]

In spite of the manifold response of $\nu_{max}(\mathbf{1})$ to solvent properties,[12,13] its β sensitivity is of highest significance as shown by eqn (2) (taken from the literature[13]).

$$\beta = 3.84 - 0.20\nu_{max}(\mathbf{1})10^{-3}\ (\mathrm{cm}^{-1})$$
$$n = 26;\ r = 0.8;\ sd = 0.18;\ F = 0.000 \qquad (2)$$

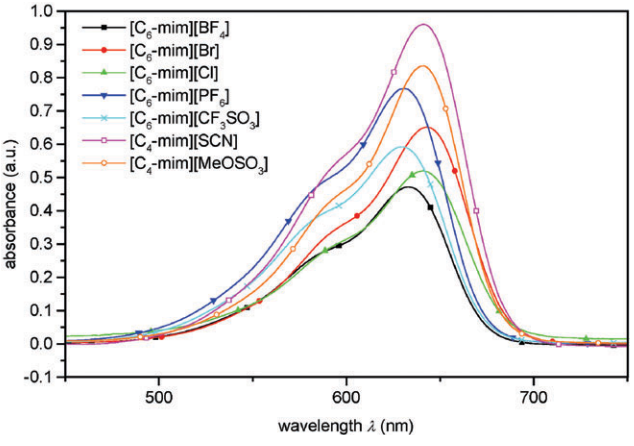

Fig. 2 UV/Vis absorption spectra of **2** measured in various RTIL.

Table 1 UV/Vis absorption maxima of **1** and **2** measured in 1-hexyl-3-methylimidazolium [C$_6$-mim]$^+$/1-butyl-3-methylimidazolium [C$_4$-mim]$^+$ salts at room temperature

	ν_{max} 10^{-3} (cm^{-1})	
Ionic liquid	**1**	**2**
[C$_6$-mim][BF$_4$]	16.16	15.80
[C$_6$-mim][Br]	14.73	15.55
[C$_6$-mim][Cl]	14.35	15.60
[C$_6$-mim][PF$_6$]	16.75	15.85
[C$_6$-mim][CF$_3$SO$_3$]	16.18	15.87
[C$_4$-mim][SCN]	15.65	15.60
[C$_4$-mim][MeOSO$_3$]	15.46	15.60

The cations of choice are 1-hexyl-3-methylimidazolium [C$_6$-mim]$^+$ and 1-butyl-3-methylimidazolium [C$_4$-mim]$^+$, because a wide range of anions in conjunction to these cations are liquid at room temperature, including chloride. The excellent HBD-indicator Fe(phen)$_2$(CN)$_2$ [(*cis*-dicyano)-bis(1,10-phenanthroline)iron(II)],[21] is insoluble in the used 1-alkyl-3-methylimidazolium salts. It is possible that the higher lattice energy cannot be compensated by the weaker interaction in the RTIL or the HBD abilities of [C$_6$-mim]$^+$ and [C$_4$-mim]$^+$, respectively, are too weak. Dyes **1** and **2** are moderately soluble in these RTIL. UV/Vis spectra of **1** and **2** measured in RTIL are shown in Fig. 1 and 2. UV/Vis spectroscopic results are compiled in Table 1.

There is a significant influence of the anion observed on the shift of the solvatochromic UV/Vis band. The bathochromic shift of **1** increases in the following order, which responds to the HBA strength of the anion according to the thermodynamics of hydrogen bond complex formation with phenol (see the plot in Fig. 3):[22]

$$PF_6^- < CF_3SO_3^- \sim BF_4^- < SCN^- < MeOSO_3^- < Br^- < Cl^-$$

Thus, a simple UV/Vis spectroscopic method has been found suitable to determine the HBA strength of anions. Calculated

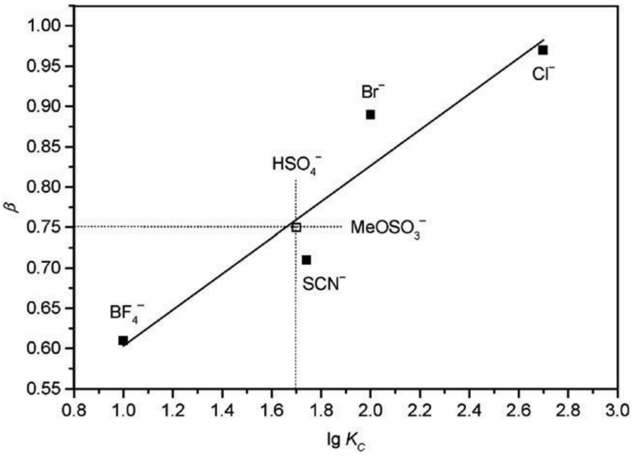

Fig. 3 β value of X$^-$ as a function of log K_C of (C$_2$H$_5$)$_4$N$^+$X$^-$ with phenol in CH$_2$Cl$_2$ from the literature.[22] Closed squares are implied into the regression. No value of log K_C is given for MeOSO$_3$$^-$, so the related value for HSO$_4$$^-$ was used from ref. 22 (indicated as open square).

Table 2 Calculated β and π^* values for RTIL using the LSERs of **1** and **2**

Ionic liquid	β from eqn (2)	π^* from eqn (3)	π^* from eqn (4)
[C_6-mim][BF_4]	0.61	0.95	0.90
[C_6-mim][Br]	0.90	1.09	0.96
[C_6-mim][Cl]	0.97	1.06	0.91
[C_6-mim][PF_6]	0.50	0.93	0.91
[C_6-mim][CF_3SO_3]	0.60	0.92	0.86
[C_4-mim][SCN]	0.71	1.06	0.99
[C_4-mim][$MeOSO_3$]	0.75	1.06	0.97

β values are given in Table 2. The values range from 0.5 (hexafluorophosphate) to 0.97 (chloride). The order of magnitude matches established values determined previously for RTIL and related data from the literature.[1,2,7] The values for PF_6^- and BF_4^- are larger than those reported in the literature.[5,20] That the large β value for BF_4^- or PF_6^- is caused by fluoride ions sourced from the dissociation of BF_4^- or PF_6^- can be excluded, as shown by a control experiment carried out with tetra-*n*-butylammonium fluoride (1.0 M in THF). It shows that naked fluoride interacts much more strongly with **1** than the other tested RTIL. A UV/Vis band from the strong bathochromic shift derived from the interaction of **1** with fluoride was never observed for BF_4^- or PF_6^-.[23] In ref. 20, even a too large β value for BF_4^- has been estimated using Cu(tmen)(acac)$^+$ as the solvatochromic probe. The authors thought that chloride impurities were responsible for this result. However, we think the β value of 0.61 for BF_4^- is reasonable, because it also fits well in the linear plot of Fig. 3 which is calculated using an independently determined thermodynamic data set for anions.[22]

The question remains, what role is played by the counterion on the dipolarity/polarizability of the RTIL. For this purpose we applied dye **2** (eqn (3)).[14]

$$\nu_{max}(\mathbf{2})10^{-3}\ (\mathrm{cm}^{-1}) = 17.5710 - 1.8544\pi^*$$
$$n = 27;\ r = 0.93;\ sd = 0.223;\ F < 0.0001 \qquad (3)$$

The α term has no influence on $\nu_{max}(\mathbf{2})$, as shown previously by investigating the adsorption of **2** on solid acids,[14] so the content of water can be ignored. However, the influence of β on $\nu_{max}(\mathbf{2})$ cannot completely be ignored taking into account the results of multiple square analyses.[14] Eqn (4) has been recalculated from previous data.[14] Thus we used eqn (4) to show the influence of β upon π^* of RTIL.

$$\nu_{max}(\mathbf{2})10^{-3}\ (\mathrm{cm}^{-1}) = 17.6908 - 0.5167\beta - 1.7474\pi^*$$
$$n = 27;\ r = 0.96;\ sd = 0.167;\ F < 0.0001 \qquad (4)$$

Calculated π^* values are shown in Table 2. The result is of importance, because it shows that the π^* term of Type II RTIL is independent of the β value of the anion.

The dielectric constant (ε) of 1-alkyl-3-methylimidazolium RTIL range from 10 to 15.[10,11] For the solvents considered for calculating eqn (3), a rough correlation of π^* as a function of the dielectric parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ results since aromatic solvents are excluded (eqn (5)).

$$\pi^* = 0.2182 + 0.288\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)$$
$$n = 24\ \text{(excluding benzene and toluene)}; \qquad (5)$$
$$r = 0.85;\ sd = 0.056;\ F < 0.0001$$

Using eqn (5), the mismatch of the calculated π^* values with the order of magnitude of the dielectric constant ε continues for ionic liquids. We think RTIL with 1-alkyl-3-methylimidazolium cations belong to aromatic solvents which show larger values of π^* than would be expected from their dielectric constants. Therefore, the seeming mismatch can be obviously explained by the strong additional influence of the polarizability of the ionic liquid on the bathochromic UV/Vis shift of the probe **2** and, perhaps, on similar π^* sensitive probes.[1,2,7] This interpretation is strongly supported by the fact that π^* values determined from eqn (4) for the ionic liquids (Table 2) show a clear dependence on the Swain–Scott "soft nucleophilicity" parameter, *n*,[24] and the polarizability,[25] respectively, of the anion.

Values of *n* are available for SCN^-, Br^-, and Cl^-.[24] The other anions fit scientifically soundly (Fajans' rules) in the range of π^* as a function of *n* for 1-alkyl-3-methylimidazolium X^-:

SCN^- (n = 4.77) > $MeOSO_3^-$ > Br^- (n = 3.89) > Cl^- (n = 3.04) ~ BF_4^- ~ PF_6^- ≫ $CF_3SO_3^-$
← increasing π^* of 1-alkyl-3-methylimidazolium X^-

It is possible that charge transfer interactions contribute to π^*, because *n* correlates with the frontier orbital energy (HOMO) of the anion. This theory informally explains that the lowest π^* value is measured for that RTIL with $CF_3SO_3^-$ as counterion. Further studies in this field are in progress.

Experimental

All the following ionic liquids were purchased in the highest available grade from commercial sources and used without further purification: 1-hexyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium tetrafluoroborate, 1-hexyl-3-methylimidazolium hexafluorophosphate (Merck), 1-hexyl-3-methylimidazolium bromide, 1-hexyl-3-methylimidazolium triflate (Acros), 1-butyl-3-methylimidazolium thiocyanate, 1-butyl-3-methylimidazolium methylsulfate (BASF).

The synthesis and purification of the solvatochromic probes **1** and **2** was described previously.[12–14] UV/Vis absorption spectra of freshly prepared solutions of the solvatochromic probe in the ionic liquids were measured under exclusion of moisture by means of an MCS 400 diode-array spectrometer from Carl Zeiss Jena with a resolution of 1 nm.

Multiple regression analysis were performed with the Origin 5.0 statistic program from Microcal Software.

Acknowledgements

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