A hydrogen bond accepting (HBA) scale for anions, including room temperature ionic liquids†

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A hydrogen bond accepting (HBA) ability scale for anions of room temperature ionic liquids (RTILs) has been determined by means of ^{1}H NMR spectroscopy and a solvatochromic UV/vis probe.

The relevant properties of room temperature ionic liquids (RTILs) for solute interaction and their effect on catalysis are significantly determined by the nature of the anion rather than the cation.[1,2] Therefore, knowledge of the effect of the anion on the properties of RTILs is of great importance for choosing the appropriate RTIL for a particular application.[3,4]

The interaction of the anion with the cation of 1,3-dialkylimidazolium salts is very complex in nature because of the protons in the two-, four- and five-positions of the imidazolium ring, the weakly CH-acidic protons of the two *N*-alkyl substituents and the aromatic ring system contribution. Basicity, geometry and polarizability of the anion play crucial roles for ion pair formation. Furthermore, the dielectric constant of RTILs are influenced in a complex manner by the anion.[1,5,6] Thus, it is still not clear whether ion pair formation is attributed preferentially to the basicity or also to the dipolarity/polarizability effects of the ion pair, and how the environment's dipolarity affects the cation–anion interaction.[7] Grätzel *et al.* showed for a series of 1,3-dialkylimidazolium RTILs that the ^{1}H NMR chemical shift of the ring proton in the two-position moves to lower field with the increasing anion basicity in acetone solvent.[8] Related effects of the anion on the chemical shift of the ring protons of 1,3-dialkylimidazolium ions were reported for several ionic liquids. The effects on NMR chemical shifts have been surveyed.[9] It seems clear that ion pair formation is very sensitive to both the solvent and the anion.[10]

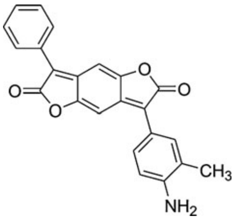
The β parameter, introduced by Kamlet and Taft, has been established in order to quantify the anionic nature of RTILs.[1,2] Originally, the β parameter was introduced as a measure of the hydrogen bond accepting (HBA) ability of a solvent.[11,12] Many related empirical parameters have been determined that relate to the ability of an anion to form a hydrogen bond with the CH, OH or NH acidic sites of organic molecules.[13,14] β can be determined by using solvatochromic dyes that contain acidic NH or OH groups, which can interact with an external base. The NH···anion interaction usually induces a bathochromic shift of the UV/vis absorption band of the chromophore.[11,15] The advantage of the solvatochromic method is its ease of use, high reproducibility and large sensitivity of the UV/vis spectrum of the probe to graduate changes in the environment under study. However, the response of the UV/vis probe is often not only sensitive to the HBA ability. The separation of the dipolarity/polarizability portions from the total shift of the UV/vis probe is not always accomplished.[11,12]

The motivation of this study is to determine whether a relationship exists between the β parameter and the interaction strength with the imidazolium ring for a series of RTILs that differ in base strength and polarizability of the anion.

Recently, for the rapid determination of the HBA nature of RTILs, we introduced the 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b*′]-difuran-2,6-di-one dye (**1**) (shown in Scheme 1), whose UV/vis band shift is strongly affected by the nature of the anion. This allows the accurate determination of the solvatochromic parameter, β, for RTILs.[16] **1** possesses a large UV/vis absorption coefficient ($\varepsilon \sim 10^4$ l mol^{-1} cm^{-1}) in the visible region from 460 to 700 nm.[17,18] For this reason, it is not necessary to decolorize the mostly slightly yellow RTIL, which shows a UV/vis absorption of at most 400 nm, as exemplified by intensely colored 1-butyl-3-methylimidazolium ([Bmim]) iodide.

However, differentiation must be made between the color due to anions (*e.g.* iodide, nitrite, thiocyanate) and impurities. UV/vis absorption maxima for **1** are independent of dye concentration from 0.05 to 0.6 mM. This is an indication that impurities have no significant effect on the determination of β values.

The impact of the anion on ion pair formation with [Bmim] has been investigated in deuterated dichloromethane (CD_2Cl_2) by means of ^{1}H NMR spectroscopy. This was undertaken because ion pair formation of 1,3-dialkylimidazolium salts



Scheme 1 Structure of dye **1** used in this work to determine the β values of RTILs.

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† Electronic supplementary information (ESI) available: Copies of UV/vis and ^{1}H NMR spectra for all the RTILs. See DOI: 10.1039/b714629a

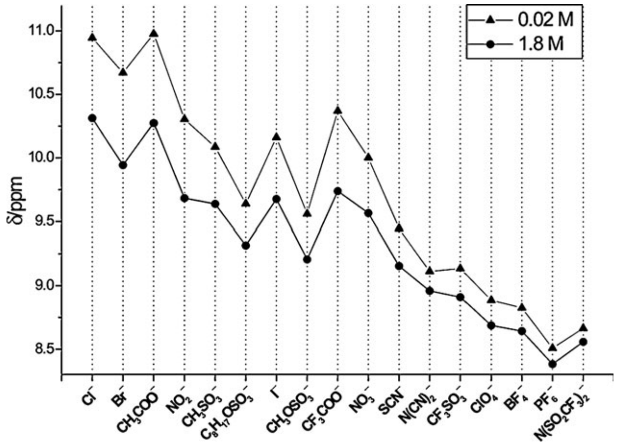

Fig. 1 Effect of salt concentration on the ^{1}H NMR chemical shift δ of the proton in the 2-position of the imidazolium ring for anions studied in CD_2Cl_2.

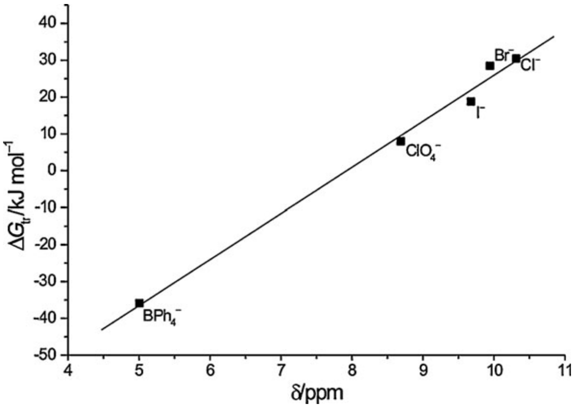

Fig. 2 Correlation of ΔG_{tr} (water/nitrobenzene, from ref. 19) with the ^{1}H NMR chemical shift of the proton in the 2-position of the imidazolium ring for five different anions.

preferentially occurs in this solvent, as shown by Seddon *et al.*[10] The advantage of this methodology is that other anions of general interest, *e.g.* tetraphenylborate or others, which do not form liquid salts with 1,3-dialkylimidazolium cations, can be considered as well. Since ion pair formation occurs in CD_2Cl_2, the chemical shift should be a function of the concentration of the salt used. This is because in dichloromethane (which has a moderate dielectric constant of 9.8), dissociation into solvated ions should take place only to a very low extent.[10] Thus, the observed ^{1}H signal is the average of all types of ion pair and dissociated ions. As expected, there is a clear dependence of the chemical shift on concentration, which provides evidence of ion pair formation. The proportion of ion pairs increases the larger the concentration of dissolved RTIL. It is of great importance that the effect of the anion on the chemical shift is the same for each anion at two significantly different concentrations, as shown in Fig. 1.

Therefore, the chemical shift is a measure of the interaction strength with the cation when similar concentrations are used. The thermodynamic reason for the chemical shift change is attributable to hydrogen bond formation in the ion pair. This conclusion is strongly supported by the correlation of the chemical shift with the free energy of transfer of the anion from water to nitrobenzene, ΔG_{tr}, as shown in Fig. 2.[19]

The excellent fit of the tetraphenylborate anion, which serves as a non-HBA anion, is clear evidence that the ^{1}H NMR chemical shift of the proton in the 2-position of the imidazolium ring can be used coherently as a measure of hydrogen bond strength. The β parameters of the pure RTILs have been determined using **1** for [Bmim] cations with 17 different anions. The data have been calculated from eqn (1) (n = number of solvents, r = correlation coefficient, sd = standard deviation and F = significance) using the UV/vis absorption maxima of dye **1**:[16]

$$\beta = 3.84 - (0.20 \times \tilde{\nu}_{\max(\mathbf{1})} \times 10^{-3})$$
$$n = 26;\ r = 0.80;\ \mathrm{sd} = 0.18;\ F < 0.0001. \qquad (1)$$

The UV/vis spectra of **1** dissolved in the RTILs are shown in the ESI.† The UV/vis absorption maxima ($\tilde{\nu}_{\max(\mathbf{1})}$) of the appropriate UV/vis bands are collected in Table 1.

The β values determined with **1** in this work are greater than those of several sets of literature data, which were measured using substituted nitroaniline dyes.[1,2] Nitroaniline UV/vis probes are mainly sensitive to dipolarity/polarisability, and in the second instance to β, which makes the separation of the β term from $\tilde{\nu}_{\max(\mathrm{probe})}$ often less significant.[11,12,18] This fact obviously explains the lower β values of the RTILs from the literature.

There is evidently correlation between the β parameter determined using **1** and the ^{1}H NMR chemical shift of the proton in 2-position of the imidazolium ring, δ, as shown in Fig. 3 and eqn (2).

$$\beta = -1.571 + (0.244 \times \delta)$$
$$n = 17;\ r = 0.94;\ \mathrm{sd} = 0.05;\ F < 0.0001 \qquad (2)$$

Table 1 UV/vis absorption maxima of **1** in pure RTILs (cation = [Bmim]), determined β values, ^{1}H NMR chemical shift of the proton in the 2-position of the imidazolium ring measured in CD_2Cl_2 at a concentration of 1.8 M, and normalized β^N-values calculated from eqn (3)

Anion	$\tilde{\nu}_{\max(\mathbf{1})}/10^{-3}$ cm^{-1}	β	δ/ppm	β^N
Cl^-	14.45	0.95[a]	10.31	1.00
Br^-	14.86	0.87[a]	9.94	0.93
$CH_3CO_2^-$	14.93	0.85	10.27	0.99
$CH_3SO_3^-$	14.95	0.85[a]	9.64	0.87
NO_2^-	15.15	0.81	9.68	0.88
$OctylOSO_3^-$	15.34	0.77	9.32	0.81
I^-	15.43	0.75	9.68	0.88
$CH_3OSO_3^-$	15.46	0.75	9.21	0.79
$CF_3CO_2^-$	15.48	0.74	9.74	0.89
NO_3^-	15.50	0.74	9.57	0.86
SCN^-	15.63	0.71	9.15	0.78
$N(CN)_2^-$	16.00	0.64	8.96	0.75
$CF_3SO_3^-$	16.34	0.57	8.91	0.74
ClO_4^-	16.45	0.55	8.69	0.69
BF_4^-	16.47	0.55	8.64	0.69
PF_6^-	17.01	0.44	8.38	0.64
$N(SO_2CF_3)_2^-$	17.21	0.42	8.56	0.67
$B(C_6H_5)_4^-$	—[b]	—[b]	5.00	0.00

[a] Measured in the melt. [b] Not determinable.

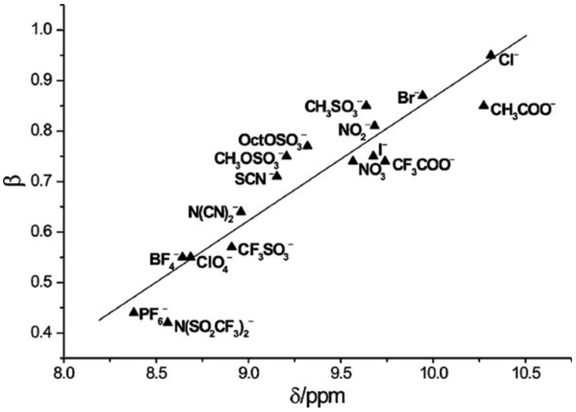

Fig. 3 Correlation of the β parameter determined with **1** in pure RTILs with the ^{1}H NMR chemical shift of the proton in the 2-position of the imidazolium ring measured in CD_2Cl_2.

The correlation shows that the solvatochromically-determined β value of the anion represents adequately its HBA property. Therefore, a normalized β^N scale can be predicted using solely the NMR data. β^N is defined according to eqn (3) using chloride and tetraphenylborate as the extreme reference anions:

$$\beta^N = \frac{\delta_{\text{anion}} - \delta_{\text{BPh}_4}}{\delta_{\text{Cl}} - \delta_{\text{BPh}_4}} = \frac{\delta_{\text{anion}} - 5.00}{5.31} \qquad (3)$$

Hence, the corresponding β^N scale ranges from 0.00 for the least HBA anion, tetraphenylborate, to 1.00 for chloride, the most HBA anion. The introduced ^{1}H NMR scale can be applied to determine β parameters by means of eqn (2) or eqn (3) if solvatochromism is not suitable.

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Experimental

General

1-Butyl-3-methylimidazolium ([Bmim]) tetraphenylborate, perchlorate, nitrite, iodide, trifluoroacetate, nitrate and bis(trifluoromethanesulfonyl)imide were synthesized according to established literature procedures.[8,20–24] All other chemicals were purchased in their highest available grade from commercial sources. The synthesis and purification of dye **1** has been described previously.[17,18] 1-Butyl-3-methylimidazolium acetate was washed five times with ethyl acetate (distilled over P_2O_5) because of the lack of purity of the commercially available substance. All [Bmim] salts were dried by dissolving in CH_2Cl_2 (dried and distilled over CaH_2), adding 4 Å molecular sieve, stirring overnight and evaporating the solvent. Basic alumina from ICN Biomedicals GmbH was added to the CH_2Cl_2 solutions of the bromide, methanesulfonate and tetrafluoroborate salts, respectively, to remove acid traces, which would otherwise cause an additional UV/vis absorption band of dye **1** to appear in the 400–500 nm region (see ESI†). Therefore, this UV/vis band can be used as an indicator for residual acid traces.

To reduce residual water traces, the ionic liquids were evaporated for 8 h at 60 °C and 24 h at room temperature under a pressure of 3 mbar.

Instrumentation

^{1}H NMR spectra were recorded with a Varian Gemini-300 spectrometer. Chemical shifts were reported as δ values in parts per million (ppm) relative to $Si(CH_3)_4$ as the reference (δ = 0 ppm), and to CD_2Cl_2 as the solvent and internal reference. UV/vis absorption spectra of freshly prepared solutions of dye **1** in ionic liquids were measured under exclusion of moisture by means of an MCS 400 diode array spectrometer from Carl Zeiss Jena GmbH, with a resolution of 1 nm. The longest wavelength absorption maximum was used to calculate β values. Analyses of the spectra were performed with Win-Aspect (version 1.31, Carl Zeiss Jena GmbH). The ^{1}H NMR and UV/vis spectra are shown in the ESI.† Multiple regression analyses were performed with the Origin 5.0 statistical program from Microcal™ Software.

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