Relationship between hyperfine coupling constants of spin probes and empirical polarity parameters of some ionic liquids

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The polarity of 1-alkyl-3-methylimidazolium-based ionic liquids containing hexafluorophosphate, tetrafluoroborate, dicyanoimide, or bis(trifluoromethanesulfonyl)imide as anions and a variation of the alkyl-chain length of the cation are investigated by both solvatochromic dyes and spin probes. Two different polarity scales are used for discussion of the polarity of these ionic liquids. These polarity scales are the empirical Kamlet–Taft parameters α, β, and π^* and the hyperfine coupling constants $A_{\mathrm{iso}}(^{14}\mathrm{N})$ obtained for spin probes substituted either with an ammonio or a sulfate group at 4-position. The results show that both polarity scales are valid for description of the ionic liquid polarity although differences are found between the two polarity scales. The most clear trend is found in all ionic liquids investigated for the hydrogen-bond accepting ability (β) and the hyperfine-coupling constant of the anionic spin probe, where both parameters increase for all ionic liquids investigated until an alkyl chain length of eight carbon atoms and keep constant at longer alkyl chains.

Introduction

Ionic liquids have received interest as solvents for organic, inorganic, and polymer synthesis, as well as for extraction processes.[1–4] Furthermore, they have been useful as chromatographic materials for separation purposes in analytical chemistry.[5] Although the viscosity of ionic liquids is significantly higher in comparison with traditional organic solvents, there has been potential interest to apply these new materials because vanishing vapour pressure, broad liquid range, and superior dissolution properties favor the use for applications in a broad field.[1a]

Classification of solvents has been often done by their polarity. However, this is complicate because various polarity scales are discussed in literature.[6–27] Besides the relative permittivity, polarity is mostly expressed by interactions of the material under investigation with dissolved substances, such as solvatochromic, FTIR, and spin probes. Reichardt's dye has been one of the most used solvatochromic probes for the determination of solvent polarity.[16] A co-solvent is often used to dissolve this dye in ionic liquids. Removal of the co-solvent is necessary for UV measurements to obtain reliable data. This makes handling of this dye complicate for polarity investigation of ionic liquids. Furthermore, interactions between ionic liquid anions bearing stronger coordinating ability and the pyridinium moiety of Reichardt's dye may influence the UV/Vis absorption maximum of this dye.[25,26,28,29] Improved solvatochromic dyes that do not show UV/Vis absorption maxima shift caused by the electrostatic interaction between the anion of the ionic liquid and the pyridinium moiety have been used for determination of the polarity of ionic liquids as well.[14,25,26,28,29]

Systematic analysis of solvatochromic probes is possible using the Kamlet–Taft-equation shown in its simplified form in eqn (1).[6–11]

$$XYZ = (XYZ)_0 + a\alpha + b\beta + s(\pi^* + d\delta) \qquad (1)$$

XYZ is the value of a solvent-dependent physicochemical property measured in a given solvent, $(XYZ)_0$ represents the same value in the gas phase or a reference solvent. The parameters α, β, and π^* describe the hydrogen-bond donating (HBD) ability, the hydrogen-bond accepting (HBA) ability, and the dipolarity/polarisability of the solvent. The parameter δ represents a polarisability correction term that is 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents, and zero for aliphatic solvents. The coefficients a, b, s, and d are the solvent-independent regression coefficients reflecting the influence of the respective parameters on XYZ of the chemical process. A set of three well established solvatochromic probes sufficiently determines the α, β, and π^* values of commonly used solvents, surfaces, and ionic liquids.[24–26,28–32] The solvatochromic dye $[\mathrm{Fe(phen)_2(CN)_2}]\mathrm{ClO_4}$ (**3**) is reduced to $\mathrm{Fe(phen)_2(CN)_2}$ by dissolving in ionic liquids. The generated negative solvatochromic iron(II)-complex serves as an indicator to determine HBD abilities (α).[6,26] The HBA ability (β) can be determined by means of the positive solvatochromic dye 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b*′]-difuran-2,6-di-one (**4**).[24,25] 4-*tert*-Butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline (**5**) responds sensitively to the solvent dipolarity/polarisability. This is expressed by the π^* value reflecting both properties.[7,24] The solvatochromic dyes show UV/Vis absorption bands in the visible region from 500 to 700 nm when dissolved in a medium.

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This is a great advantage, because it opens the feasibility of a direct study by the molecular probe in the ionic liquid without any additional decolourising treatment of the ionic liquid. Many ionic liquids exhibit a slight yellow colour. The second advantage can be seen in the position of the UV/Vis absorption maximum of the dyes that is independent of probe concentration. Therefore, aggregation effects of the probes can be neglected. Each dye is highly specific with respect to a single Kamlet–Taft polarity parameter, as shown by eqn (2)–(4). The parameter n stands for the number of solvents, r is the correlation coefficient, sd represents the standard deviation, and F is the significance. Eqn (2)–(4) are used to calculate the α, β, and π^* values from UV/Vis absorption maximum of the longest wavelength of the solvatochromic dyes **3**, **4**, and **5**, respectively, dissolved in the ionic liquids.[29]

$$\alpha = -7.26 + 0.45\tilde{\nu}_{\max(\mathbf{3})}10^{-3}/\mathrm{cm}^{-1}$$
$$n = 19,\ r = 0.95,\ \mathrm{sd} = 0.18,\ F < 0.0001 \qquad (2)$$

$$\beta = 3.84 - 0.20\tilde{\nu}_{\max(\mathbf{4})}10^{-3}/\mathrm{cm}^{-1}$$
$$n = 26,\ r = 0.80,\ \mathrm{sd} = 0.18,\ F < 0.0001 \qquad (3)$$

$$\pi^* = 9.48 - 0.54\tilde{\nu}_{\max(\mathbf{5})}10^{-3}/\mathrm{cm}^{-1}$$
$$n = 27,\ r = 0.93,\ \mathrm{sd} = 0.22,\ F < 0.0001 \qquad (4)$$

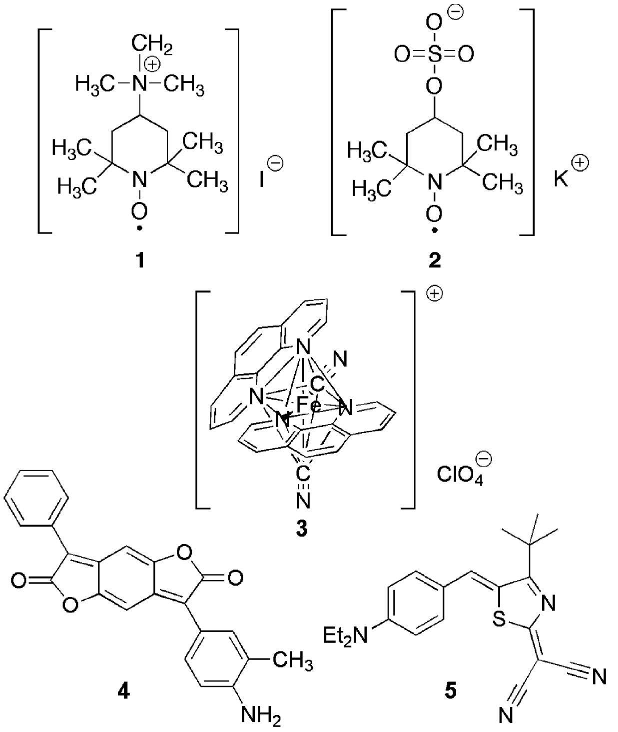
In general, solvatochromic probes work well in polarity studies as long as the matrix is transparent and does not show any intrinsic absorption in the Vis absorption window of the solvatochromic dye. These optical limitations can be overcome by the use of stable radicals, which are spin probes showing a response of their spectral properties upon change of solvent polarity. Although the concentration of spin probes in the matrix is also low, it is higher than the concentration of solvatochromic probes exhibiting large extinction coefficients.

Among the available spin probes 2,2,6,6-tetramethylpiperidine-1-yl-oxyl derivatives have received importance for the investigation of ionic liquids.[33–41] Modification of the substitution pattern of the probe molecule results in a variation of interactions between the spin probes and the ionic liquids. Strong interactions exist between ionic liquids and spin probes bearing an ionic substituent.[35,39–41] Therefore, spin probes substituted either with a cationic or an anionic substituent at 4-position are selected for polarity studies in this work.

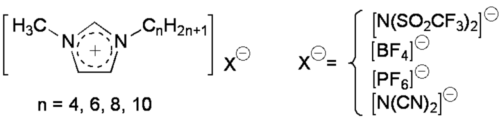
ESR spectroscopic investigation of spin probes results in the isotropic hyperfine-coupling constants $A_{\mathrm{iso}}(^{14}\mathrm{N})$, which are a measure for perturbation of the spin density distribution of the radical in solution.[42] This parameter sensitively responses to the local changes of the polarity of the surrounding matrix. This results in a change of the spin density at the nitrogen atom of the radical.[42–50] A more polar surrounding causes an increased spin density on the nitrogen, and thus, a larger interaction between the unpaired electron and the N-nucleus of the nitroxyl radical. This leads to higher hyperfine-coupling constants related to nitrogen.[42]

The Kamlet–Taft parameters distinguish between hydrogen-bond-donating and -accepting abilities and polarisability/dipolarity of the matrix.[6,24–32] In contrast to this, the hyperfine coupling constant is a single parameter for polarity determination. The use of spin probes bearing cationic or anionic substituents resulting in additional ionic interactions with the ionic liquids on the one hand and the comparison of the hyperfine-coupling constants with the Kamlet–Taft parameters may open a deeper insight into the probe/ionic liquid interactions.

Therefore, this paper focuses on comparison of hyperfine coupling constants obtained for spin probes bearing either a cationic (**1**) or an anionic (**2**) substituent (Scheme 1) with the Kamlet–Taft parameters α, β, and π^* received from investigation of the solvatochromic dyes **3–5** depicted in Scheme 1. Imidazolium-based ionic liquids are used for the polarity discussion containing various anions such as bis(trifluoromethanesulfonyl)imide, tetrafluoroborate, hexafluorophosphate, and dicyanoimide as well as a variation of the alkyl-chain length bound at one nitrogen atom of the imidazolium ring (Scheme 2).



Scheme 1 Chemical structures of the spin probes **1** and **2** and of the solvatochromic probes **3**, **4**, and **5** used for polarity investigation.



Scheme 2 Chemical structures of 1-alkyl-3-methylimidazolium-based ionic liquids with various anions.

Results and discussion

A variation of both the alkyl-chain length at one nitrogen atom of the imidazolium ring and the structure of the anion includes systematic changes of the interactions between the cation and the anion of the ionic liquid (Scheme 2). The variation of the length of the 1-alkyl group results in a modification of the ionic liquid polarity. Steric effects of longer alkyl groups contribute to a reduction of the anion/cation interactions in the case of imidazolium salts substituted with a longer alkyl group.[29,51] Furthermore, longer alkyl groups induce interionic van der Waals forces between the alkyl groups.[52] Moreover, the size and the charge density of the anion affects the cation/anion interactions as well.[53–56] We selected dicyanoimide, tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethanesulfonyl)imide as anions because of their differences in the bond strength between the anion and the cation. This bond strength decreases in the following order:

$N(CN)_2^- > BF_4^- > PF_6^- > NTf_2^-$ as discussed for the 1-butyl-3-methylimidazolium salts in the literature.[25,51] These anions were combined with 1-alkyl-3-methylimidazolium salts bearing 1-butyl, 1-hexyl, 1-octyl or 1-decyl groups as substituents at the imidazolium ring as additional factor of influence on polarity discussion in this work. The results are compiled in Table 1.

Influence of both the length of 1-alkyl-chain bound to the imidazolium ring and of the corresponding anion on the isotropic hyperfine coupling constants, $A_{iso}(^{14}N)$, of the spin probes used and on the Kamlet–Taft parameters (*α*, *β*, and *π**) obtained by solvatochromic probes

The spin probes **1** and **2** can interact with the ionic liquid *via* the radical structure. Furthermore, additional ionic interactions exist either between the trimethylammonio group of **1** and the anion of the ionic liquid or between the sulfate group of **2** and the cation of the ionic liquid. These additional Coulomb interactions are responsible for stronger interactions between the ionic spin probes and the ionic liquids in comparison with spin probes without substituent or substituted with a hydroxy group at the 4-position.[35–38]

Table 1 Hyperfine coupling constants, $A_{iso}(^{14}N)$, obtained for the spin probes **1** and **2** and Kamlet–Taft parameters (*α*, *β*, and *π**; data taken from ref. 29) of 1-alkyl-3-methylimidazolium salts

Ionic liquid	$A_{iso}(^{14}N)$/G of spin probe **1**	$A_{iso}(^{14}N)$/G of spin probe **2**	*α*	*β*	*π**
$[Bmim]N(CN)_2$	15.74	15.94	0.44	0.64	0.98
$[C_6mim]N(CN)_2$	15.53	16.05	0.44	0.69	1.00
$[C_8mim]N(CN)_2$	15.67	16.28	0.43	0.71	0.97
$[C_{10}mim]N(CN)_2$	15.57	16.42	0.44	0.71	0.96
$[Bmim]BF_4$	15.68	15.98	0.52	0.55	0.96
$[C_6mim]BF_4$	15.49	16.08	0.44	0.60	0.96
$[C_8mim]BF_4$	14.23	16.25	0.45	0.63	0.93
$[C_{10}mim]BF_4$	14.06	16.25	0.47	0.65	0.90
$[Bmim]PF_6$	14.89	16.04	0.54	0.44	0.90
$[C_6mim]PF_6$	13.71	16.05	0.51	0.50	0.93
$[C_8mim]PF_6$	13.73	16.15	0.52	0.53	0.92
$[C_{10}mim]PF_6$	13.15	16.15	0.48	0.55	0.89
$[Bmim]NTf_2$	15.81	16.15	0.55	0.42	0.83
$[C_6mim]NTf_2$	15.74	16.76	0.51	0.44	0.86
$[C_8mim]NTf_2$	15.87	16.94	0.48	0.47	0.86
$[C_{10}mim]NTf_2$	15.84	16.90	0.48	0.49	0.86

Fig. 1a shows the influence of the alkyl-chain length on the hyperfine coupling constant of the spin probes dissolved in the ionic liquids bearing both a variation of the alkyl chain length bound at the imidazolium ion and a variation of the anion. The differences in the hyperfine coupling constants between the spin probes substituted either with an ammonio group or a sulfate group are attributed to the different charges at these spin probes.[37,38,57] Therefore, the dependence of the hyperfine coupling constants behaves oppositely for the trimethylammonio substituted spin probe and the spin probe bearing the sulfate group. The hyperfine coupling constant increases with increasing size of the alkyl chain length at the imidazolium ion for the spin probe substituted with the sulfate group whereas it decreases for the trimethylammonio substituted probe (Fig. 1a). Furthermore, some ionic liquids exist in which the hyperfine coupling constant is independent of the length of the alkyl chain. Interestingly, significant differences are observed comparing the hyperfine coupling constants for the spin probes as a function of the length of the alkyl chain bound at the imidazolium ion in the case of the ionic liquids with different anions. The largest increase of the hyperfine coupling constants of the spin probe bearing the anionic substituent with increasing alkyl chain length is found in the case of the imidazolium bis(trifluoromethanesulfonyl)imides. Comparing these hyperfine coupling constants with the data obtained for this spin probe in molecular solvents, such as *tert*-butyl methylether (15.1 G), dimethyl sulfoxide (15.7 G), ethanol (16.0 G), and water (16.9 G), would lead to the conclusion that the polarity of the imidazolium bis(trifluoromethanesulfonyl)imides would increase with increasing length of the alkyl chain bound at the imidazolium ion.[57] However, as already discussed, the anionic spin probe undergoes additional Coulomb interactions with the cation of the ionic liquid. The increased tendency of the ionic liquid to separate into polar and nonpolar domains on a molecular level with increasing alkyl chain length at the nitrogen atom of the imidazolium ring as concluded from X-ray diffraction measurement published in the literature may cause the increase in the hyperfine coupling constants of the anionic spin probe dissolved in the imidazolium bis(trifluoromethanesulfonyl)imide.[57] The delocalization of the charge in the case of the bis(trifluoromethanesulfonyl)imide results in weak interactions between the imidazolium ion and this anion and supports the preference of the place of residence of this spin probe at the imidazolium ion. In contrast to this, the influence of the alkyl chain length on the hyperfine coupling constant of this spin probe is weak and it is detected only at longer alkyl chain lengths if the ionic liquids contain hexafluorophosphate, tetrafluoroborate, or dicyanoimide as anions that strongly interact with the imidazolium ion.

Furthermore, the alkyl-chain length bound at the imidazolium ion has nearly no impact on the hyperfine coupling constants using ammonio substituted spin probes for the ionic liquids

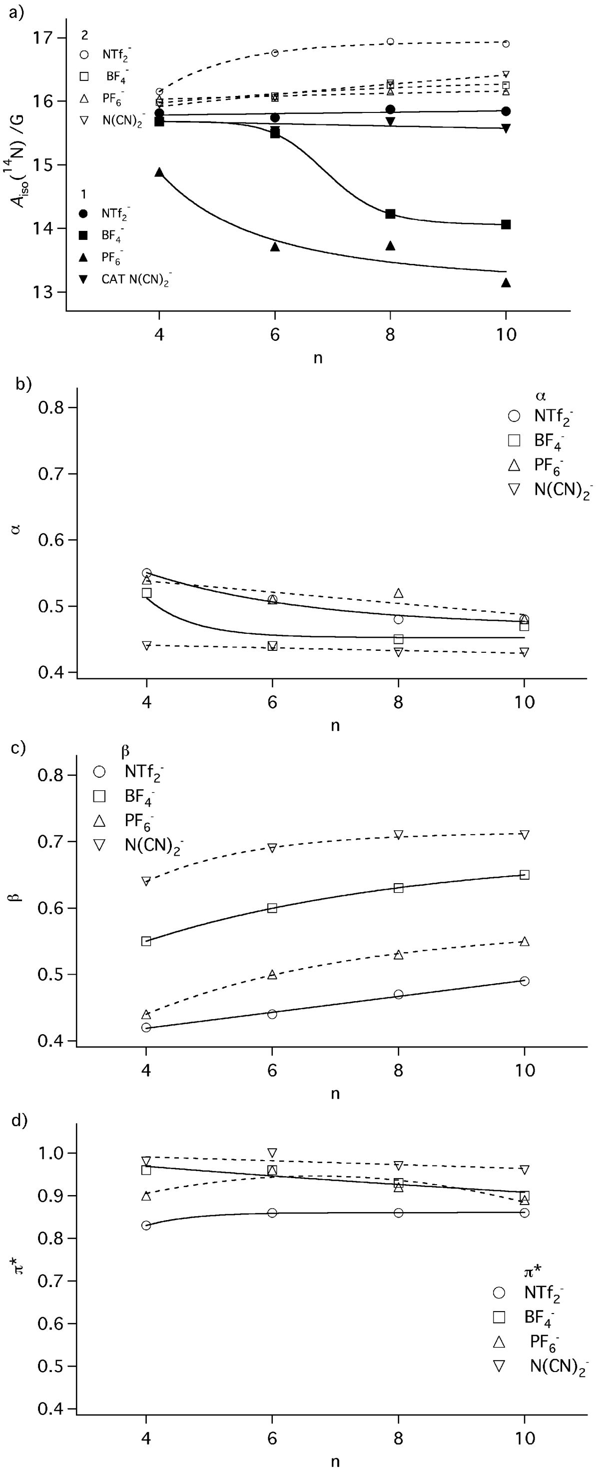


Fig. 1 Dependence of (a) the hyperfine coupling constants, $A_{\mathrm{iso}}(^{14}\mathrm{N})$, obtained for the spin probes **1** (full line) and **2** (dashed line) on the length of the alkyl chain bound at one nitrogen atom of 1-alkyl-3-methylimidazolium salts, and dependence of the Kamlet–Taft parameters (b) α, (c) β, and (d) π* on the length of the alkyl chain bound at one nitrogen atom of 1-alkyl-3-methylimidazolium salts bearing NTf_2^- (full line), BF_4^- (full line), PF_6^- (dashed line), or $N(CN)_2^-$ (dashed line).

bearing the bis(trifluoromethanesulfonyl)imide as anion. The spin probe bearing the cationic substituent undergoes strong additional interactions with the anion of the ionic liquid.

Delocalization of the charge at the bis(trifluoromethanesulfonyl)imide may result in reduced interactions between the trimethylammonio substituent of this spin probe and the bis(trifluoromethanesulfonyl)imide. In contrast to this, a strong decrease in the hyperfine coupling constants of this spin probe with increasing alkyl chain length is found for the imidazolium hexafluorophosphates and tetrafluoroborates. The charge is less delocalized in these anions relative to the bis(trifluoromethanesulfonyl)imide resulting in stronger interactions with both the imidazolium ion and the cationic substituent of the spin probe. As shown by ESI-MS measurements and solvatochromic studies, the dicyanoimide possesses a higher binding ability to the imidazolium ion than the tetrafluoroborate and the hexafluorophosphate ion.[25,51] In contrast to this, the decrease in the hyperfine coupling constant with increasing alkyl chain length at the imidazolium ion locates within the experimental error. Furthermore, the ESI-MS experiments and solvatochromic measurements indicate a stronger binding ability of the tetrafluoroborate to the imidazolium ion relative to the hexafluorophosphate although the hyperfine coupling constants are smaller for the imidazolium hexafluorophosphates compared to the imidazolium tetrafluoroborates. From this one can conclude that further factors of influence are necessary to explain these results. One approach is the comparison of the hyperfine coupling constants of the spin probes with the Kamlet–Taft parameters.

The Kamlet–Taft parameters are influenced by a variation of the alkyl chain length at the imidazolium ion and by the anion in a different way. The α value behaves nearly independent of the alkyl chain length in the case of the imidazolium dicyanoimides, although it decreases with the length of the alkyl chain if the imidazolium salts contain either hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, or tetrafluoroborate as anion (Fig. 1b). Moreover, the α value is similar for the imidazolium salts bearing hexafluorophosphate, or bis(trifluoromethanesulfonyl)imide (NTf_2) as anion, and it decreases in the order of $NTf_2^- \approx PF_6^- > BF_4^- > N(CN)_2^-$.

The β value increases with the length of the alkyl chain in the case of all ionic liquids (Fig. 1c). It shows the highest values for the imidazolium dicyanoimides and it decreases in the following order: $N(CN)_2^- > BF_4^- > PF_6^- > NTf_2^-$. This result agrees qualitatively with the order of intrinsic bond strength between 1-butyl-3-methylimidazolium ions with various anions that was investigated by electrospray ionization mass spectrometry (ESI-MS).[51] As expected, the opposite order is obtained for the β value in comparison with the α value when comparing the imidazolium salts bearing different anions. Furthermore, differences are higher for the β values of these ionic liquids than for the α values. From this one can conclude that differences in the ionic liquid polarity are better expressed by the higher differences in the β values if the anions are changed, than the polarity changes of the ionic liquids by variation of the alkyl-chain length at the imidazolium ion, which is expressed by their α value.

Small differences are also found for the polarisability/dipolarity (π*) comparing the imidazolium salts (Fig. 1d). Although the π*-values differ in many examples when selecting different anions, only small differences are found in the π*-values of imidazolium salts bearing different alkyl chain lengths.

The exceptions are the imidazolium tetrafluoroborates and hexafluorophosphates, where similar π^*-values were obtained. The imidazolium dicyanoimides show the highest π^*-values and they are only slightly affected by the length of the alkyl chain (Fig. 1d). The π^*-values for the imidazolium salts decrease in the order $N(CN)_2^- > BF_4^- \approx PF_6^- > NTf_2^-$. The differences of polarisability/dipolarity are higher for variation of the anion structure compared to changes of the alkyl chain length. A similar trend is also found for the β values although π^*-values are similar for imidazolium salts bearing hexafluorophosphate or tetrafluoroborate as anions. These results demonstrate a description of ionic liquid polarity by both spin probes and solvatochromic dyes. It is interesting to compare these different parameters with each other to obtain more information about the polarity of ionic liquids. Because the hyperfine coupling constant of the spin probes is a single parameter and the Kamlet–Taft parameters are a combination of three values (α, β, and π^*), the hyperfine coupling constant will be compared with each Kamlet–Taft parameter.

Comparison of the isotropic hyperfine coupling constants, $A_{iso}(^{14}N)$, of the cationic spin probe with the Kamlet–Taft parameters (α, β, and π^*)

The HBD ability (α) and the hyperfine coupling constant, $A_{iso}(^{14}N)$, of **1** decrease with increasing length of the alkyl chain bound at the imidazolium ring in the case of the imidazolium hexafluorophosphates. Therefore, these parameters show the same trend in the case of the imidazolium hexafluorophosphates. One would expect a similar tendency also for the imidazolium tetrafluoroborates. However, data obtained do not allow us to draw a clear decision in the case of the imidazolium tetrafluoroborates. Furthermore, neither the $A_{iso}(^{14}N)$ values nor the α values describe polarity differences for the imidazolium dicyanoimides bearing a variation of the alkyl chain length. Although the α value detects differences in polarity of the imidazolium bis(trifluoromethanesulfonyl)imides as a function of the alkyl chain length, the $A_{iso}(^{14}N)$ value exhibits almost the same data for the cationic spin probe.

The relation between the two methods is more clear for the HBA ability β obtained by the solvatochromic dyes and the $A_{iso}(^{14}N)$ values of **1** (Fig. 2). Although the hyperfine coupling constants decrease with increasing length of the alkyl chain, the β values increase in the case of both imidazolium tetrafluoroborates and hexafluorophosphates. This allows us to draw the conclusion that both values reliably describe polarity differences of the ionic liquids bearing either tetrafluoroborate or hexafluorophosphate as anions. A similar trend was also found for the β values determined in imidazolium salts bearing either dicyanoimide or bis(trifluoromethanesulfonyl)imide although the cationic spin probe does not show significant changes in the hyperfine coupling constants, and therefore, this probe does detect these polarity differences.

The situation complicates if one compares the $A_{iso}(^{14}N)$ values with the dipolarity/polarisability parameter π^*. A relation between these two parameters was found only in the case of the imidazolium tetrafluoroborates showing a decrease of both $A_{iso}(^{14}N)$ and π^* with increasing alkyl chain length. However, there are nearly no changes of both parameters in the case of imidazolium dicyanoimides and bis(trifluoromethanesulfonyl)imides. The imidazolium hexafluorophosphates show that the relation between $A_{iso}(^{14}N)$ and π^* cannot be understood in the same way using the cationic spin probe. The scattering of the data does not allow a deeper discussion in detail.

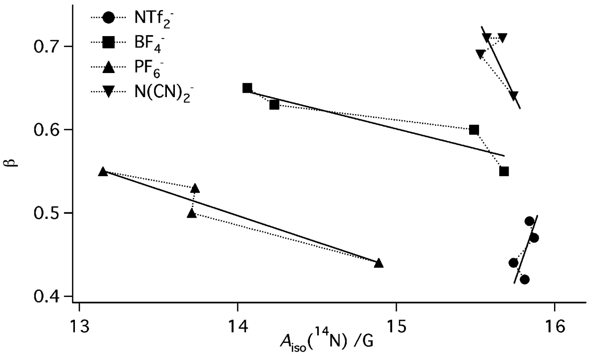


Fig. 2 Comparison of the Kamlet–Taft parameter β with hyperfine coupling constants, $A_{iso}(^{14}N)$, determined for the spin probe **1** dissolved in 1-alkyl-3-methylimidazolium salts bearing different anions.

Comparison of the isotropic hyperfine coupling constants, $A_{iso}(^{14}N)$, of the anionic spin probe with the Kamlet–Taft parameters (α, β, and π^*)

In contrast to the results obtained by the cationic spin probe, the relation is more clear comparing the hyperfine coupling constants of the anionic spin probe and the Kamlet–Taft parameters. The α values decrease while the $A_{iso}(^{14}N)$ values of the anionic spin probe increase in the case of imidazolium bis(trifluoromethanesulfonyl)imides with increasing alkyl-chain length bound at the imidazolium ion up to eight carbon atoms of the chain (Fig. 3).

A further increase in the alkyl chain length does not significantly influence neither the Kamlet–Taft parameter α nor the hyperfine coupling constant $A_{iso}(^{14}N)$ of the spin probe **2**. A slight decrease of the α value and an opposite behavior of the isotropic hyperfine coupling constant showing an increase is also found in the case of the imidazolium dicyanoimides. The use of imidazolium hexafluorophosphates and tetrafluoroborates indicates a stronger dependence between these polarity

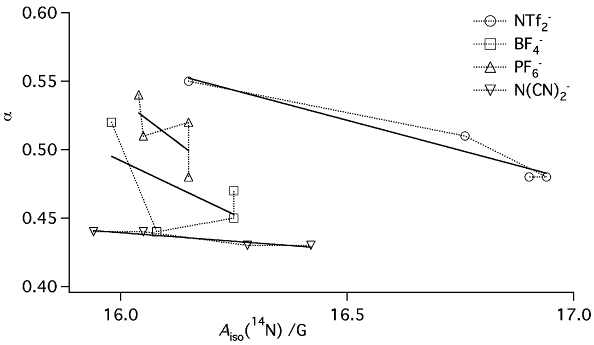


Fig. 3 Comparison of the Kamlet–Taft parameter α with hyperfine coupling constants, $A_{iso}(^{14}N)$, determined for the spin probe **2** dissolved in 1-alkyl-3-methylimidazolium salts bearing different anions.

parameters although the tendency is similar. Moreover, sufficient correlation exists between the HBA ability (β) and the hyperfine coupling constant of the anionic spin probe (Fig. 4). An increase of these parameters with increasing alkyl chain length is found in the case of all ionic liquids investigated although similar values are obtained for the 1-octyl and the 1-decyl-substituted imidazolium salts. From this one can conclude that the hyperfine coupling constant of the anionic spin probe does well response to the HBA ability of the ionic liquid.

Comparison of the hyperfine coupling constant with the polarisability/dipolarity data of the solvatochromic probes shows a more complex situation. Both values exhibit a similar increasing tendency only in the case of imidazolium bis(trifluoromethanesulfonyl)imides. An opposite tendency for π^* values and $A_{\text{iso}}(^{14}\text{N})$ values is found for the imidazolium salts bearing either dicyanoimide or tetrafluoroborate (Fig. 5) anion. However, no correlation between these parameters is found for the imidazolium hexafluorophosphates caused by scattering of the data.

The increase of both π^* and $A_{\text{iso}}(^{14}\text{N})$ values in the case of the imidazolium bis(trifluoromethanesulfonyl)imides indicates that also interactions between the cation and the anion expressed by polarisability/dipolarity may influence the interactions between the spin probe bearing the anionic substituent and the ionic liquid.

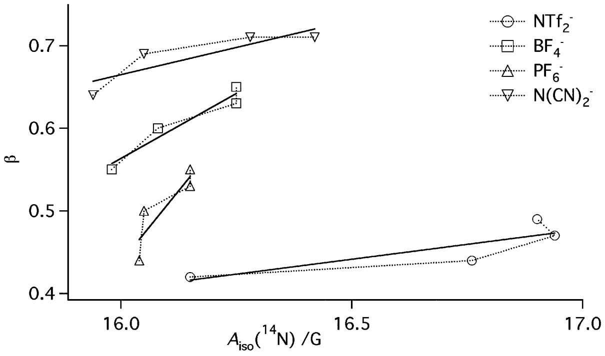


Fig. 4 Comparison of the Kamlet–Taft parameter β with hyperfine coupling constants, $A_{\text{iso}}(^{14}\text{N})$, determined for the spin probe **2** dissolved in 1-alkyl-3-methylimidazolium salts bearing different anions.

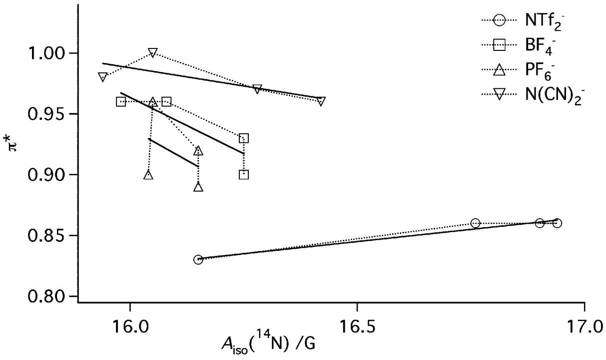


Fig. 5 Comparison of the Kamlet–Taft parameter π^* with the hyperfine coupling constant $A_{\text{iso}}(^{14}\text{N})$ determined for the spin probe **2** dissolved in 1-alkyl-3-methylimidazolium salts bearing different anions.

Conclusions

Comparing different polarity scales for ionic liquids, which are the empirical Kamlet–Taft parameters (α, β, and π^*) obtained from solvatochromic probes and the isotropic hyperfine coupling constants received by investigation of ionic liquids with spin probes, shows both similarities and differences in describing the polarity of ionic liquids. A clear trend is only found for the HBA ability (β) and the hyperfine coupling constant of the anionic spin probe for all ionic liquids investigated. The HBD ability (α) shows an opposite tendency to the hyperfine coupling constant in the case of most ionic liquids. The range of the α scale is smaller than the range of the β scale resulting in a higher contribution of data scattering in the case of the α scale. Furthermore, the spin probe bearing the anionic substituent is more valid for comparison with the Kamlet–Taft parameters than the spin probe substituted with the cationic group.

Experimental

General

The synthesis of imidazolium dicyanoimides, tetrafluoroborates, hexafluorophosphates and bis(trifluoromethanesulfonyl)imides from 1-methylimidazole and the corresponding haloalkanes followed by anion metathesis using sodium dicyanoimide, tetrafluoroboric acid, hexafluorophosphoric acid or lithium bis(trifluoromethanesulfonyl)imide is described elsewhere.[3c,29,57] The ionic liquids were dried *in vacuo* (1–4 mbar) at a temperature between 70 and 90 °C for 3 days. All ionic liquids do not contain halide. The water content is different for the single ionic liquids. The imidazolium bis(trifluoromethanesulfonyl)imides contain less than 1000 ppm water, whereas the water content is between 0.01 and 0.3 wt% for the imidazolium hexafluorophosphates, between 0.02 and 1.6 wt% for the imidazolium tetrafluoroborates, and between 0.04 and 1.3 wt% for the imidazolium dicyanoimides. Furthermore, all ionic liquids were colourless or only slightly yellow.

The synthesis of the spin probes **1** and **2** is described elsewhere.[39–41] The synthesis and purification of the dyes **3**, **4**, and **5** was described previously as well.[24,25,50]

Measurements

UV/Vis absorption measurements are described elsewhere.[28,29] ESR spectra of the spin probes were measured in X-band with a CW spectrometer ELEXSYS E500 (Bruker) at 9.4 GHz. The concentration of the spin probes in the ionic liquid is about 2×10^{-3} M.

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