The dipolarity/polarisability of 1-alkyl-3-methylimidazolium ionic liquids as function of anion structure and the alkyl chain length†

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Based on the developed tool to measure Kamlet–Taft polarity parameters α (hydrogen bond donating ability), β (hydrogen bond accepting ability), and π^* (dipolarity/polarisability) for ionic liquids (ILs), it is now possible to precisely determine the influence of both cation and anion structure on π^*. α, β, and π^* values of 38 1-alkyl-3-methylimidazolium ILs ([Rmim]X) are presented in this work to give a solid background for the discussion. The dipolarity/polarisability of [Rmim]X determined by means of the established π^*-sensitive solvatochromic probe 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-Δ^3-thiazoline is a blend of dipolarity and polarisability in equal parts. The large π^* parameters of ionic liquids are attributed to two cumulative effects: the ion pairing strength and the individual polarisabilities of both the cation and anion. This is shown by the influence of anion and cation structures (alkyl chain length of R) on the dipolarity/polarisability. For all studied ionic liquids we observed a general trend. The stronger the ion pairing effect, the greater is the determined π^* value.

Introduction

In previous works, we discussed in detail the importance and problems of empirical polarity parameters for ionic liquids in terms of their specific properties relating to hydrogen bond abilities of the 1-alkyl-3-methylimidazolium ([Rmim]) cation and corresponding anion, respectively.[1–3]

Kamlet–Taft empirical solvent parameters have been established for this purpose, which allow a differentiated polarity assignment to be made.[4–10] The Kamlet–Taft equation, in its simple form, is given in eqn (1).

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

(XYZ) is the result of a solvent-dependent process and $(XYZ)_0$ is the value for the reference system, for example the gas phase or a nonpolar solvent. α describes the hydrogen bond donating ability, β the hydrogen bond accepting ability, and π^* the dipolarity/polarisability of the solvent. δ is a polarisability correction term that is 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents, and zero for aliphatic solvents. This is a problem, as it does not permit a differentiated separation of the polarisabilities of solvents. *a*, *b*, *s*, and *d* are the solvent-independent correlation coefficients, which reflect predictions of the influence of the respective parameters on the result (XYZ) of the chemical process.

The above approach was used by several authors to determine the polarity parameters of various ionic liquid systems including binary solvent mixtures in recent years.[11–19] This methodology, as established for commonly used solvents, was not always applied to ILs with a critical point of view. The actual problems of empirical polarity parameters of ionic liquids were explained in former works by us.[1–3] Weingärtner *et al.* discussed related problems with respect to the dielectric properties of ILs in several recent articles.[20–23] However, it could be shown that the determination of independent α, β, and π^* parameters by means of specific solvatochromic probes seems really possible.[1–3] The results of these papers have demonstrated that a lot of empirical polarity parameters reported in the literature up to now were not precise enough, because the established probes used, especially Reichardt's dye for separating α, show ambiguous behaviour in ionic liquids.[3,8] We have found that a set of three different solvatochromic probes is sufficient to determine precise α, β, and π^* values of commonly used solvents, surfaces, and ionic liquids.[1–3,24–26]

The established solvatochromic probes are shown in Scheme 1. 4-*tert*-Butyl-2-(dicyanomethylene)-5-[4-(diethylamino)-benzylidene]-Δ^3-thiazoline (**1**) is mainly sensitive to the solvent dipolarity/polarisability.[1,25,26] The hydrogen bond accepting ability could be determined by means of the positive solvatochromic dye 3-(4-amino-3-methylphenyl)-7-phenylbenzo-[1,2-*b*::4,5-*b*′]difuran-2,6-dione (**2**).[1,2,26,27] [Fe(phen)$_2$(CN)$_2$]-ClO$_4$ (**3**) undergoes reduction to Fe(phen)$_2$(CN)$_2$ when dissolved in ionic liquids. The generated negative solvatochromic iron(II)-complex serves as an indicator to determine hydrogen bond donating abilities.[3,24,26] The dissolved solvatochromic dyes show UV/Vis absorption bands in the visible region from 500 to 700 nm. This is a great advantage,

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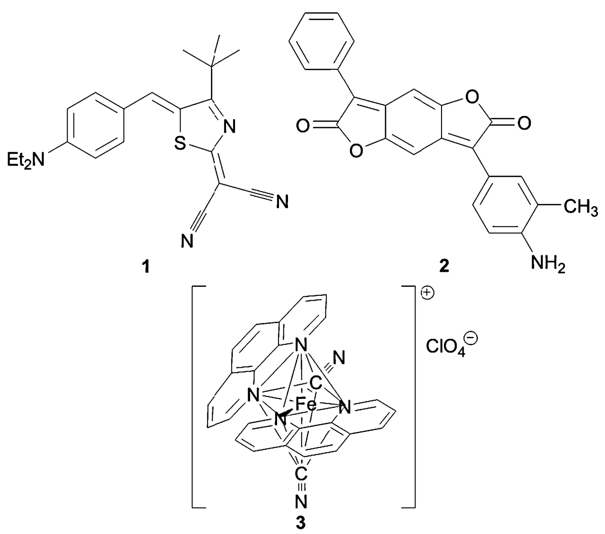


Scheme 1 Chemical structure of the established solvatochromic probes **1**, **2**, and **3** used in this work to determine the Kamlet–Taft polarity parameters α, β, and π*.

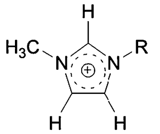
because it opens the feasibility of a direct study by dissolving the molecular probe in the ionic liquid without any additional decolourising treatment. Mostly, ILs exhibit a slight yellow colour. The second advantage is that the position of the UV/Vis absorption maximum of the dyes is independent from the used probe concentration. Therefore, aggregation effects can be excluded, leading to artificial conclusions. All of these probes are highly specific when solely concerning one of the three Kamlet–Taft polarity parameters, as shown by eqn (2)–(4) (n = number of solvents, r = correlation coefficient, sd = standard deviation and F = significance), respectively. These equations were used to calculate the α, β, and π* values from the longest wavelength UV/Vis absorption maximum of **1**, **2**, and **3** dissolved in the ionic liquids, respectively.

$$\pi^* = 9.48 - 0.54\tilde{\nu}_{\max(\mathbf{1})}/10^{-3}\ \mathrm{cm}^{-1}$$
$$n = 27,\ r = 0.93,\ \mathrm{sd} = 0.22,\ F < 0.0001 \qquad (2)$$

$$\beta = 3.84 - 0.20\tilde{\nu}_{\max(\mathbf{2})}/10^{-3}\ \mathrm{cm}^{-1}$$
$$n = 26,\ r = 0.80,\ \mathrm{sd} = 0.18,\ F < 0.0001 \qquad (3)$$

$$\alpha = -7.26 + 0.45\tilde{\nu}_{\max(\mathbf{3})}/10^{-3}\ \mathrm{cm}^{-1}$$
$$n = 19,\ r = 0.95,\ \mathrm{sd} = 0.18,\ F < 0.0001 \qquad (4)$$

A perpetual problem is that the π* parameter reflects two important properties of a solvent, the dipolarity as well as the polarisability. Various dipolar aromatic push–pull dyes have been used for the determination of π*. Both solvent properties are associated within the individual calculated π* value, but with different proportion depending on the molecular structure of the respective UV/Vis probe used.[28–30] Fortunately, Catalan *et al.* was able to show that dipolarity and polarisability effects of a solvent on a solvatochromic probe can be separated from each other using a special methodology.[31,32] We apply this improved concept to re-evaluate the solvatochromism of the π*-sensitive probe **1**.[25]



R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$
$X^{\ominus}$ = 17 various anions

Scheme 2 Chemical structure of the ionic liquids used in this study.

ESR Spin probes were also applied to get a rough image of the polarity of ionic liquids studying the hyperfine splitting constant as a function of the changing the nature of the IL.[33–37] In a forthcoming publication we are going to compare these results with the results obtained using the Kamlet–Taft equation.

The objective of this work is to demonstrate which molecular structural aspects of 1-alkyl-3-methylimidazolium ionic liquids affect the π* value. In our previous work we demonstrated that the hydrogen bond accepting ability of 1-alkyl-3-methylimidazolium-based ILs are mainly specified by the anion. Acidic protons in the 2-, 4-, and 5-positions of the imidazolium ring determine the hydrogen bond donating ability of such ionic liquids.[1–3] For this task a systematic variation of cation structure and anion nature was necessary. The chemical structures of the studied ILs are shown in Scheme 2. Especially, the effect of anion nature on π* was of interest because in a previous paper we discussed their charge-transfer contributions to the dipolarity/polarisability.[1] The interaction strength between the [Rmim] cation and the anion may be gradually altered by alkyl chain length, because of steric effects.

It is expected that increasing alkyl chain length should have an intensifying effect on the polarisability. To have a better background for the discussion and for completion, α and β values for all studied ionic liquids were determined using the established methodology which is presented in our previous work.[1–3] π* values of ionic liquids ranged between 0.88 and 1.17, as reported in the literature. A selection of them are collected in Table 1.

The relatively large π* values compared to their dielectric constants were already the subject of intense discussions.[20–23] One argument considers the large polarisability of the

Table 1 π* values for a selection of ionic liquids (B = n-butyl, C_6 = n-hexyl, C_8 = n-octyl) as reported in literature

Ionic liquid	π*	Ref.
[Bmim]Cl	1.17	38
[Bmim]SbF_6	1.04	13
[Bmim]BF_4	1.05	13
[Bmim]PF_6	1.03	13
[Bmim]CF_3SO_3	1.01	13
[Bmim]NTf_2	0.98	13
[Bmim]SCN	1.06	1
[Bmim]CH_3OSO_3	1.06	1
[C_6mim]BF_4	0.95	1
[C_6mim]Br	1.09	1
[C_6mim]Cl	1.06	1
[C_6mim]PF_6	0.93	1
[C_6mim]CF_3SO_3	0.92	1
[C_8mim]Cl	1.08	38
[C_8mim]PF_6	0.88	38

imidazolium cation which associate ionic liquids to the group of aromatic solvents.[1]

Results and discussion

Correlation of the UV/Vis shift of 1 with the SP and SdP solvent parameters of Catalán

Catalán's multiparameter approach for the solvent-dependent UV/Vis absorption of a solvatochromic dye can be formulated as shown in eqn (5).[32]

$$(XYZ) = (XYZ)_0 + a\mathrm{SA} + b\mathrm{SB} + c\mathrm{SP} + d\mathrm{SdP} \qquad (5)$$

(XYZ) denotes a solvent-dependent physicochemical property in a given solvent, and $(XYZ)_0$ the statistical quantity corresponding to the value of the property in the gas phase. SA describes the acidity, SB the basicity, SP the polarisability, and SdP the dipolarity of a solvent. They represent independent and complementary solvent parameters accounting for various types of solute–solvent interactions. The parameters a, b, c, and d are regression coefficients describing the sensitivity of property (XYZ) to the different solute–solvent interaction mechanisms.[32]

Re-evaluation of the solvatochromic properties of **1** was performed to show to what extent the solvatochromic UV/Vis shift is a function of dipolarity and polarisability, respectively. For the multiple square analyses a set of 26 different UV/Vis absorption maximum data of **1** dissolved in commonly used solvents were taken from the literature and the novel empirical solvent parameters from Catalán were used.[25,32] Solvent parameter data and the UV/Vis absorption maxima of the dissolved dye **1** used for the correlation analyses are given in the ESI.† The crucial result is shown in eqn (6).

$$\tilde{\upsilon}_{\max(\mathbf{1})}/10^{-3}\ \mathrm{cm}^{-1} = 18.53 - 1.54\,\mathrm{SP} - 1.60\,\mathrm{SdP}$$

$$n = 26,\ r^2 = 0.96,\ \mathrm{sd} = 0.21,\ F < 0.0001 \qquad (6)$$

Both of the important solvent properties, dipolarity as well as polarisability, are reflected by the UV/Vis absorption maxima of **1** in equal parts as evidenced by the correlation coefficients c (1.54) and d (1.6). This knowledge is of importance for the discussion of the experimentally determined π^* values of ionic liquids. Another important advantage of this solvatochromic dye is that the hydrogen bond donor and acceptor ability of a solvent does not affect the position of the UV/Vis absorption maxima. Therefore, **1** can be applied to protic solvents within the scale of commonly used solvents and ionic liquids.

π^* values as function of the anion for 1-butyl-3-methylimidazolium ionic liquids

According to our previous work, 1-butyl-3-methylimidazolium was used as the reference cation to study the effect of anion nature on the dipolarity/polarisability. 17 different anions have been involved in this study. The results are compiled in Table 2, which also contains corresponding α and β values from our previous studies.

The magnitude of the determined π^* values range from 1.14 (bromide) to 0.83 (bis(trifluoromethylsulfonyl)imide). Thus, the dipolarity/polarisability of these Ionic Liquds are in the order of strong dipolar liquids such as aromatic alcohols (*e.g.* benzyl alcohol $\pi^* = 0.96$).[5]

Table 2 UV/Vis absorption maxima of **1** in pure ionic liquids (cation = [Bmim]), calculated π^*, α, and β values (from ref. 2 and 3), as well as the product of α with β

Anion	$\tilde{\upsilon}_{\max(\mathbf{1})}/10^{-3}$ cm^{-1}	π^*	α	β	$\alpha \times \beta$
Br^-	15.46[a]	1.14	0.36	0.87	0.313
I^-	15.48	1.13	0.41	0.75	0.308
Cl^-	15.48[a]	1.13	0.32	0.95	0.304
$CH_3CO_2^-$	15.60	1.06	0.36	0.85	0.306
SCN^-	15.60	1.06	0.43	0.71	0.305
NO_2^-	15.63	1.05	0.38	0.81	0.308
$CH_3OSO_3^-$	15.63	1.05	0.39	0.75	0.293
$CH_3SO_3^-$	15.65[a]	1.04	0.36	0.85	0.306
NO_3^-	15.65	1.04	0.40	0.74	0.296
$N(CN)_2^-$	15.75	0.98	0.44	0.64	0.282
ClO_4^-	15.75	0.98	0.50	0.55	0.275
BF_4^-	15.80	0.96	0.52	0.55	0.286
$C(CN)_3^-$	15.82	0.94	0.51[b]	0.54[b]	0.275
$CF_3SO_3^-$	15.90	0.90	0.50	0.57	0.285
PF_6^-	15.90	0.90	0.54	0.44	0.238
SbF_6^-	15.95	0.87	0.58[b]	0.42[b]	0.244
NTf_2^-	16.03	0.83	0.55	0.42	0.231

[a] Measured in the melt. [b] Determined in this work.

For the discussion we will apply the corresponding α and β values. There are good correlations of π^* with α and β, respectively, as shown by the results given in eqn (7) and (8). The values of $[Bmim]CF_3SO_3$ are excluded for some reasons which will be explained later. It is clearly observable that the dipolarity/polarisability of the ionic liquids is strongly associated with the hydrogen bond donating and accepting abilities.

$$\pi^* = 1.46 - 1.03\alpha$$

$$n = 16,\ r^2 = 0.82,\ \mathrm{sd} = 0.04,\ F < 0.0001 \qquad (7)$$

$$\pi^* = 0.67 - 0.50\beta$$

$$n = 16,\ r^2 = 0.85,\ \mathrm{sd} = 0.04,\ F < 0.0001 \qquad (8)$$

In the literature, the product of α with β of two components has been recommended by Jensen *et al.* as indicator of the strength of acid–base interactions between them.[39] This approach was successfully used to estimate the individual contributions of specific interactions for solvents able to dissolve cellulose or to explain acid–base interactions among adsorption of polymers on solid acids.[40,41] In the case of ionic liquids we have a similar scenario with the interaction between the basic anion and the acidic cation. For this reason we applied the approach of Jensen *et al.* for [Rmim] based ILs. π^* as a function of the product of α with β for 1-butyl-3-methylimidazolium ionic liquids is shown in Fig. 1.

Fig. 1 demonstrates the significant correlation between the π^* values and the product of α with β, which is shown mathematically by eqn (9). The outlying point of $[Bmim]CF_3SO_3$ was excluded from the correlations, because of the unexpectedly low π^* value. In our previous work we demonstrated that this ionic liquid could fit very well into the correlations between α and β, as well as α and β with the ^{1}H-NMR chemical shift of the proton in the 2-position of the imidazolium ring of [Bmim]

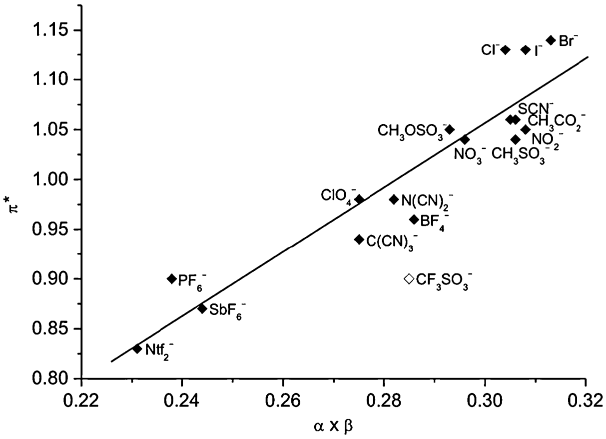


Fig. 1 Correlation of the determined π^* values with the product of α with β for [Bmim] ionic liquids using various anions.

ILs, respectively.[2,3] The unusually low π^* value is difficult to explain due to the complexity of molecular structural aspects of ionic liquids which can have an effect upon the dipolarity/polarisability. We assume that the contribution of the individual polarisability of the anion on π^* is unexpectedly low. Therefore, the values of [Bmim]CF_3SO_3 should not strongly interfere in this context.

$$\pi^* = 0.08 + 3.24\alpha\beta$$

$$n = 16, r^2 = 0.87, \text{sd} = 0.03, F < 0.0001 \qquad (9)$$

The result of the correlation shown in Fig. 1 and eqn (9) indicates that a strong anion–cation interaction (large product of α with β) has an increasing effect on the dipolarity/polarisability of the ion pair. It is also observable that the three anions chloride, bromide and iodide show similar products of α with β and π^* in spite of different β values. Thus polarisability effects should also play a role due to the large π^* value of the iodide ionic liquid. This result supports the argument from eqn (6) that π^* values measured by **1** as the solvatochromic probe reflects adequately solvent dipolarity and polarisability. In general we could say that the π^* value increases with increasing cation–anion interaction strength for the studied 1-alkyl-3-methylimidazolium ionic liquids.

π^* values as a function of the alkyl chain length for 1-alkyl-3-methylimidazolium ionic liquids

π^* as a function of the alkyl chain length for 1-alkyl-3-methylimidazolium ionic liquids with chloride, nitrate, trifluoromethanesulfonate, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, and dicyanamide as anions has been studied. These anions were chosen as they cover the complete range of β values. The n-alkyl chain lengths of the [Rmim] cation were varied with R = n-butyl, n-hexyl, n-octyl, and n-decyl. The results are collected in Table 3. UV/Vis absorption maxima of **2** and **3** in pure ionic liquids are given in the ESI.†

There are two remarkable results. Both the cation and the anion structure affect the dipolarity/polarisability of the studied ionic liquids. The change of the anion has a larger effect on the π^* values compared to the alteration of the alkyl chain length at the cation, except for anions with large β values (*e.g.* chloride and nitrate). The complexity of the influence of structural variations on the dipolarity/polarisability is demonstrated by Fig. 2. π^* is plotted as a function of the alkyl chain length R of [Rmim] ionic liquids for each anion separately.

Table 3 UV/Vis absorption maxima of **1** in pure ionic liquids, calculated π^*, α, and β values, as well as the product of α with β

Ionic liquid	$\tilde{\upsilon}_{\max(\mathbf{1})}/10^{-3}\ \mathrm{cm}^{-1}$	π^*	α	β	$\alpha \times \beta$
[Bmim]Cl	15.48[a]	1.13	0.32[b]	0.95[b]	0.304
[C_6mim]Cl	15.60	1.06	0.31	0.97	0.301
[C_8mim]Cl	15.67	1.03	0.31	0.98	0.304
[C_{10}mim]Cl	15.77	0.97	0.31	0.98	0.304
[Bmim]NO_3	15.65	1.04	0.40[b]	0.74[b]	0.296
[C_6mim]NO_3	15.70	1.01	0.40	0.76	0.304
[C_8mim]NO_3	15.75	0.98	0.36	0.80	0.288
[C_{10}mim]NO_3	15.80	0.96	0.36	0.81	0.292
[Bmim]$N(CN)_2$	15.75	0.98	0.44[b]	0.64[b]	0.282
[C_6mim]$N(CN)_2$	15.72	1.00	0.44	0.69	0.304
[C_8mim]$N(CN)_2$	15.77	0.97	0.43	0.71	0.305
[C_{10}mim]$N(CN)_2$	15.80	0.96	0.44	0.71	0.312
[Bmim]BF_4	15.80	0.96	0.52[b]	0.55[b]	0.286
[C_6mim]BF_4	15.80	0.96	0.44	0.60	0.264
[C_8mim]BF_4	15.85	0.93	0.45	0.63	0.284
[C_{10}mim]BF_4	15.90	0.90	0.47	0.65	0.305
[Bmim]PF_6	15.90	0.90	0.54[b]	0.44[b]	0.238
[C_6mim]PF_6	15.85	0.93	0.51	0.50	0.255
[C_8mim]PF_6	15.87	0.92	0.52	0.53	0.276
[C_{10}mim]PF_6	15.92[a]	0.89	0.48	0.55	0.264
[Bmim]CF_3SO_3	15.90	0.90	0.50[b]	0.57[b]	0.285
[C_6mim]CF_3SO_3	15.87	0.92	0.47	0.61	0.286
[C_8mim]CF_3SO_3	15.90	0.90	0.48	0.64	0.307
[C_{10}mim]CF_3SO_3	15.95	0.87	0.48	0.65	0.312
[Bmim]NTf_2	16.03	0.83	0.55[b]	0.42[b]	0.231
[C_6mim]NTf_2	15.97	0.86	0.51	0.44	0.224
[C_8mim]NTf_2	15.97	0.86	0.48	0.47	0.226
[C_{10}mim]NTf_2	15.97	0.86	0.48	0.49	0.235

[a] Measured in the melt. [b] Data taken from ref. 2 and 3.

The π^* values for the bis(trifluoromethylsulfonyl)imide ILs increase slightly and remain constant going from n-butyl to n-decyl side chains. Obviously, the dipolarity/polarisability of the NTf_2^- ILs seem independent of the cation structure due to the weak cation–anion interaction strength, attributed to the weakly coordinating anion.

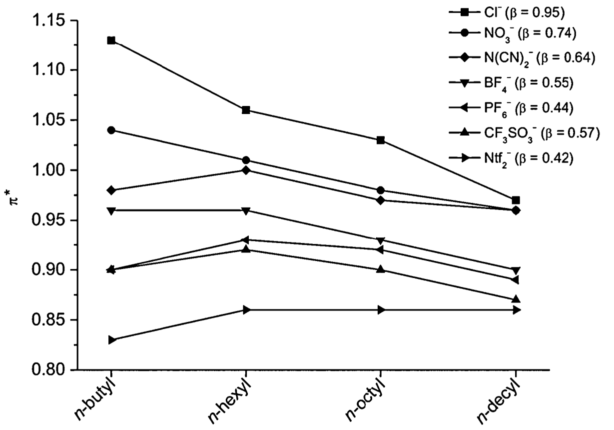


Fig. 2 π^* values as a function of the alkyl chain length R of [Rmim] ionic liquids using various anions. The β values given in the caption refer to the [Bmim] ILs.

π^* decreases with increasing alkyl chain length R for [Rmim] ionic liquids with strongly coordinating anions (large β values), such as chloride or nitrate, but the product of α with β does not alter. For moderately coordinating anions such as dicyanamide, tetrafluoroborate, hexafluorophosphate, and trifluoromethanesulfonate the function of π^* *versus* the alkyl chain length goes through a maximum at the [C_6mim] ILs and decreases going to longer chain length.

The decreasing π^* values are expected, because of a lowering of the interaction strength between cation and anion which is due to increasing size of the cation. This interpretation is supported by the fact that β values increase with the lengthening of the alkyl chain. The effect of alkyl chain length on the polarisability can not be determined using probe **1**. This is demonstrated by the fact that alkyl chain length of [Rmim]X has no effect on π^* since weakly coordinating anions such as bis(trifluoromethylsulfonyl)imide are used (see Fig. 2).

The product of α with β increases with increasing alkyl chain length. This would imply a stronger interaction strength and should lead to an increased π^* value. However, a different behaviour was observed. Obviously, the dipolarity/polarisability and the interaction strength between cation and anion could not be explained by the product of α with β in the case of longer alkyl chain lengths. Considering all studied anions, this fact is supported by Fig. 3.

There is no dependency observable when all data points from Table 3 are taken into account. Good-to-rough correlations were obtained, when the values of the ionic liquids with the four structurally different cations (n-butyl, n-hexyl, n-octyl, and n-decyl side chain) and various anions were correlated separately. The dispersion of data points increases with increasing alkyl chain length. The correlation coefficient r^2 decreases from 0.85 for the [Bmim] ILs to 0.64 for the [C_{10}mim] ionic liquids. The entire results of the multiple square analysis are given in the ESI†. Obviously, steric effects become more important by lengthening the alkyl chain. Therefore, the correlation of π^* with the product of α with β is only suitable when an equivalent cation is used and the anion is only varied for the same alkyl chain length.

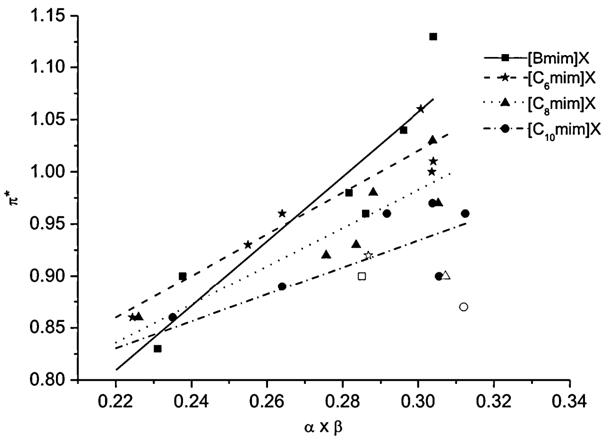


Fig. 3 Correlation of the determined π^* values with the product of α with β for [Rmim] ionic liquids using various anions (X, omitted for clarity). The trend lines were fitted without the triflate ILs (unfilled symbols).

Conclusions

In this work we demonstrated the use of the solvatochromic dye **1** to determine the dipolarity/polarisability (π^*) of 1-alkyl-3-methylimidazolium based ionic liquids ([Rmim]X). Both of the important solvent properties are reflected by the UV/Vis absorption maxima of **1** in equal parts. The π^* values were determined as a function of 17 different anions and of the alkyl chain length R with n-butyl, n-hexyl, n-octyl, and n-decyl. Altogether, the results clearly indicate that the dipolarity/polarisability is a function of cation–anion interaction strength rather than only a function of individual anion or cation properties. With the weakly coordinating anion bis(trifluoromethylsulfonyl)imide the resulting cation effect on π^* is completely different compared to the strongly coordinating chloride anion. For all studied ionic liquids a general trend is observed. The stronger the ion pairing effect, the greater the determined dipolarity/polarisability. In the case of the [Bmim] ILs we obtained a very good correlation of the π^* values with the product of α with β, which serves as an indicator for the interaction strength between cation and anion.

Experimental

General

The 1-alkyl-3-methylimidazolium ionic liquids with nitrite, nitrate, iodide, dicyanamide, perchlorate, tetrafluoroborate, trifluoromethanesulfonate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide anions were synthesised from the respective chloride salt according to established literature procedures.[42–49] 1-Butyl-3-methylimidazolium bromide, chloride, tricyanomethane, and hexafluoroantimonate, $AgNO_2$, $AgNO_3$, $NaN(CN)_2$, $AgClO_4{\cdot}H_2O$, HBF_4 (50 wt.% aq. solution), HPF_6 (65 wt.% aq. solution), $LiN(SO_2CF_3)_2$, dichloromethane, and CaH_2 were purchased in the highest available grade from commercial sources. [Bmim] acetate, thiocyanate, methansulfonate, and methylsulfate were provided by the BASF SE. The synthesis and purification of the dyes **1**, **2**, and **3** has been described previously.[24,25,27,50] All ionic liquids were dried by dissolving in dichloromethane (dried and distilled over CaH_2), adding molecular sieves (4 Å), stirring overnight, and evaporation of the solvent. Basic alumina from ICN Biomedicals GmbH was added to the dichloromethane solutions of the bromide, methansulfonate, acetate, andtrifluoromethanesulfonate ILs to remove acid traces. To remove residual water traces, the ionic liquids were evaporated for 8 h at 60 °C and 24 h at room temperature under a reduced pressure of 3 mbar. All studied ILs were colourless or at most slightly yellow except for the iodide, nitride, and thiocyanate, where the colour is due to the anion.

UV/Vis measurements

A few crystals of each dye was completely dissolved in the ionic liquid. The UV/Vis absorption spectra were recorded using precision quartz cells with a light path of 2 mm under exclusion of moisture by means of a MCS 400 diode-array spectrometer from Carl Zeiss (Jena) with a resolution of 1 nm. Spectral analyses were performed with Aspect Plus

(Version 1.76, Carl Zeiss Jena GmbH). The longest wavelength absorption maximum was used for the calculation of the α, β, and π^* values. Multiple regression analysis was performed with the Origin Pro G8 SR6 statistic program from OriginLab Corporation.

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