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PAPER

Distinct influence of the anion and ether group on the polarity of ammonium and imidazolium ionic liquids†

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The polarity of ionic liquids (ILs), usually denoted as $E_T(30)$ by the solvatochromic probe Reichardt's dye, is one of the most fundamental properties that remarkably affect the solvation and chemical reaction in ILs. It was generally accepted that the $E_T(30)$ of ILs was dominated by the nature of the cation. However, in this work, it was found that the common ammonium-based ILs showed strongly anion-dependent $E_T(30)$. For example, the $E_T(30)$ value for $[N_{1124}][DCA]$ and $[N_{1124}][NTf_2]$ is 49.0 and 59.0 kcal mol^{-1}, respectively, while the corresponding imidazolium ILs bearing the same anions possess nearly identical $E_T(30)$, the $E_T(30)$ value for [BMIm][DCA] and $[BMIm][NTf_2]$ is 51.4 and 51.6 kcal mol^{-1}, respectively. Moreover, introduction of an ether group was found to increase the $E_T(30)$ of imidazolium ILs while having no obvious effect on that of ammonium-based ILs. The Kamlet–Taft parameters and density functional theory (DFT) calculations indicated that the distinct result is related to different stabilization of the ground state of Reichardt's dye 30. In imidazolium ILs, the main interactions between ILs and zwitterionic dye involve both coulombic interaction (between the cation and the phenolate oxygen atom) and H-bonding interaction (between the acidic hydrogen on imidazolium ring and the phenolate oxygen atom). However, with the ammonium ILs lack of active hydrogen, the dye is only stabilized by the coulombic interaction between the cation and the phenolate oxygen atom. Interestingly, in both imidazolium and ammonium-based ILs, the spiropyran–merocyanine equilibrium exhibit obvious anion-dependent photochromism, solvatochromism, and thermal relaxation.

1. Introduction

Ionic liquids (ILs) are salts melting below 373 K, which have received increasing interest as suitable candidates in various areas, such as organic synthesis,[1–5] catalysis,[6–8] electrochemical devices,[9–12] and solvent extraction,[13–15] because of their attractive properties not available in molecular solvents. ILs are frequently referred to as 'tuneable', 'tailored', 'task-specific' or 'designer' solvents due to the ability to vary the ions, thereby modifying and optimizing a salt's physicochemical properties for specific applications, such as increasing reactivity, selectivity, catalyst recyclability, and so on.[2]

Polarity, as one of the most fundamental parameters for ILs, is of great importance for solvation and chemical reaction conducted in ILs,[16,17] especially for polarity-sensitive reaction and catalysis.[18,19] For example, the high polarity of a Brønsted acidic pyrrolidinium ILs was considered to be an important factor for the oxidative desulfurization of diesel fuel in the presence of H_2O_2.[19] Diels–Alder reactions processed in highly polar ILs produced a much higher *endo*/*exo* ratio as compared to others.[18] Solvatochromism, photochromism and thermal reversion of spiropyran indeed showed obviously polarity-dependence in ILs.[20,21] Polarity and hydrogen-bonding ability also play crucial roles in designing ILs as solvents for cellulose.[22]

Polarity is the sum of all possible interactions between the solvent and any potential solute, except for those that lead to a permenant chemical transformation, according to the IUPAC definition. Analogous to molecular solvents, the polarity of ILs has been intensively investigated using a series of solvatochromic dyes. Amongst all probes used, Reichardt's betaine dye 30 (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino) phenolate) betaine is the most common solvatochromic dye used in these experiments,[16] based on its large negative solvatochromic shift of the long-wavelength intramolecular π–π* charge transfer (CT) absorption band, and it has one of the most popular empirical solvent polarity scales ($E_T(30)$ or E_TN), which can be easily studied and compared with other solvents. Systematic and fundamental studies demonstrated that except protic ILs, common ILs exhibit lower polarity comparable to short chain alcohols, and the polarity of ILs varied according to the structure of ILs. It was previously suggested that $E_T(30)$ of general ILs appears to be dominated by the nature of the cation.[23,24] For instance, $E_T(30)$ for alkylimidazolium salts has mean values about 52 kcal mol^{-1},

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† Electronic supplementary information (ESI) available: structure parameters and atom coordinates calculated at the B3LYP/6-31+G(d,p) level of theory. see DOI: 10.1039/c2nj20965a

comparable with ethanol, replacing the proton at the 2-position of the ring with a methyl group resulted in lower values (48 kcal mol^{-1}). This is entirely consistent with the expected hydrogen-bond donor properties of these cations.[23,24] In 2005, Kaar and co-workers reported a series of 1-methyl-1-(2-methoxyethyl)-pyrrolidinium ([MOEMPy])-based ILs with anions including acetate, nitrate, trifluoroacetate, trifluoromethylsulfonate, and methanesulfonate,[25] which exhibit unexpectedly anion-dependent polarity with E_T^N (E_T^N = ($E_T(30)$ − 30.7)/32.4)[16] ranging from 0.37–0.91. Unfortunately, this unique anion-dependent polarity was not further investigated in detail. More recently, we have found that hydroxyl groups on imidazolium exhibit a significant effect on the $E_T(30)$ of ILs.[21] Although most of the nonhydroxyl 1-ethyl-3-methylimidazolium ILs exhibit anion-independent polarity with similar $E_T(30)$ in the narrow range of 49.7–52.6 kcal mol^{-1}, the $E_T(30)$ of the 1-(2-hydroxyethyl)-3-methylimidazolium ILs covers a rather wide range (51.2–61.7 kcal mol^{-1}) and is strongly anion-dependent.[21] Kamlet–Taft parameters and density functional theory calculations indicated that the greatly expanded range of $E_T(30)$ of hydroxyl ILs is correlated to an intramolecular synergistic solvent effect of the ionic hydrogen-bonded complexes between the anions and the hydroxyl group on cations, wherein the hydroxyl group exhibits a significant differentiating effect on the strength of H-bonding and thus the polarity. Lee *et al.* also investigated the effect of functional groups on the polarity of pyrrolidinium-based ILs, it was revealed that the presence of a cyano group on the pyrrolidinium cation slightly decreased the $E_T(30)$,[26] while a vinyl or disulfide group has a slight influence. Introducing an ether functional group into the alkyl chain on the cation was also found to increase the polarity of imidazolium ILs.[18]

Although polarity of ILs has been widely investigated, the conclusion to date was generally stemmed from the commonly used imidazolium ILs. In contrast, the case of ammonium ILs remains poorly understood, mostly because of their relatively high melting points. Based on our previous work on the synthesis and characterization of dialkoxy functionalized quaternary ammonium ILs,[27] we further investigated the polarity behavior of ether functionalized ILs by $E_T(33)$, $E_T(30)$ and Kamlet–Taft parameters in-depth in this work, together with the results of imidazolium ILs for comparison. The solvation behavior, including polarity and hydrogen bonding ability of ammonium-based ILs with or without an ether group were investigated to understand the effect of anion and ether group on the $E_T(33)$, $E_T(30)$, hydrogen-bond acidity α, hydrogen-bond basicity β, and dipolarity/polarizability π^*. In contrast to the imidazolium ILs, it was interestingly found that the ammonium-based ILs exhibited strongly anion-dependent polarity, while the ether function has no obvious effect. Moreover, the [NTf$_2$]-based ammonium ILs possess higher polarity (close to glycol) that can fill the polarity gap between water and general molecular solvents, and can be used as a single aprotic ionic solvent for polarity-specific reaction and synthesis.

2. Experimental

2.1. Synthesis and characterization of ILs

All ILs with different cation and anion structures (Fig. 1), namely, cations: 1-butyl-3-methylimidazolium ([BMIm]), 1-(2-methoxyethyl)-3-methylimidazolium ([1O2MIm]), *N*-butyl-*N*-ethyl-*N*,*N*-diethylammonium ([N$_{1124}$]), *N*-(2-methoxyethyl)-*N*-butyl-*N*,*N*-diethylammonium ([N$_{114,1O2}$]); anions: nitrate ([NO$_3$]), dicyanamide ([DCA]), tetrafluoroborate ([BF$_4$]), hexafluorophosphate ([PF$_6$]), bis(trifluoromethanesulfonyl)amide ([NTf$_2$]), were synthesized according to a typical two-step protocol[27,28] and the purity was confirmed by ^{1}H-NMR, elemental analysis, water content, and AgNO$_3$ test (for details, see supporting information†).

2.2. Determination of polarity and Kamlet–Taft Parameters

The polarity and Kamlet–Taft parameters were determined by using the following solvatochromic probes, *i.e.*, Reichardt's dye, *N*,*N*-dimethyl-4-nitroaniline, 4-nitroaniline, and spiropyran (Fig. 2), according to our previous work.[21]

2.3. Computational analysis (DFT calculations)

All the calculations were performed with the Gaussian 03 programs using the B3LYP/6-31+G(d,p) method.[29] No restrictions on symmetries were imposed on the initial structures. Therefore the geometry optimization for the saddle points occurred with all degrees of freedom. The presence of a minimum amount of energy was ensured by the lack of imaginary vibrational frequencies. A scaling factor was not applied to the calculated frequency in the calculations. The gas-phase energy of the ion-pair formation (ΔE) has been estimated using eqn (1), according to Turner *et al.*[30]

$$\Delta E(\mathrm{kJ\ mol^{-1}}) = 2625.5[E_{\mathrm{AX}}(\mathrm{au}) - (E_{\mathrm{A+}}(\mathrm{au}) + E_{\mathrm{X-}}(\mathrm{au}))] \qquad (1)$$

where ΔE is the energy of the ion-pair formation, and E_{AX}, $E_{\mathrm{A+}}$, $E_{\mathrm{X-}}$ are the energy of ion pair, the isolated cation and anion, respectively.

3. Result and discussion

3.1. Effect of anion on the polarity of ILs

Polarity scales ($E_T(33)$ and $E_T(30)$, kcal mol^{-1}) of all ILs investigated were listed in Table 1, where comparative values for some conventional organic solvents are also included. For all ammonium and imidazolium ILs, there is indeed a linear relationship in polarity scales between $E_T(33)$ and $E_T(30)$ (Fig. S1†), as described in the following equation:

$$E_T(30) = 0.99382(\pm0.1109)\cdot E_T(33) - 8.74797(\pm7.04428),\ n = 10,\ r = 0.95363 \qquad (2)$$

where n is the number of solvents employed and r is the correlation coefficient. The result verified the feasibility of both

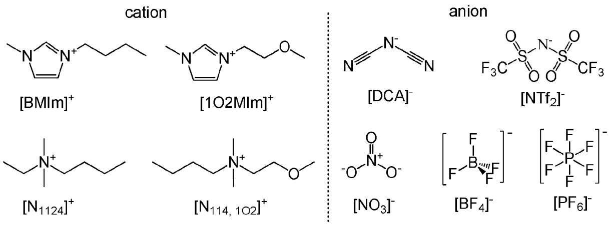


Fig. 1 Structures and abbreviations of the cations and anions.

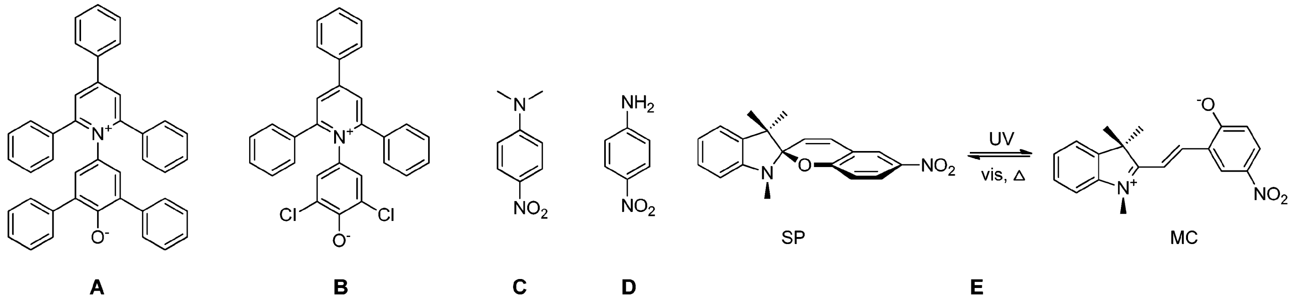


Fig. 2 Dyes and probe reaction used for probing polarity and Kamlet–Taft parameters of ILs: Reichardt's dye 30 (**A**), Reichardt's dye 33 (**B**), *N*,*N*-dimethyl-4-nitroaniline (**C**), 4-nitroaniline (**D**), and spiropyran (SP) ↔merocyanine (MC) (**E**).

Table 1 $E_T(30)$ and $E_T(33)$ scales,[a] and Kamlet–Taft parameters of ILs

ILs	$E_T(33)$	$E_T(30)$	E_T^N	π^*	α	β
[BMIm][DCA]	61.4	51.4	0.640	1.06	0.53	0.57
[BMIm][NTf$_2$]	60.7	51.6	0.645	0.97	0.60	0.24
[1O2MIm][DCA]	60.6	52.4	0.669	1.11	0.51	0.56
[1O2MIm][NTf$_2$]	66.2	54.5	0.733	0.96	0.78	0.29
[N$_{1124}$][DCA]	58.0	49.0	0.563	0.97	0.43	0.58
[N$_{1124}$][NTf$_2$]	66.2	59.0	0.868	0.89	1.16	0.27
[N$_{114,1O2}$][DCA]	58.7	49.0	0.563	0.99	0.42	0.61
[N$_{114,1O2}$][NTf$_2$]	66.5	58.8	0.867	0.87	1.16	0.38
[HOEMIm][DCA][b]	65.1	56.1	0.784	—	—	—
[HOEMIm][NTf$_2$][b]	70.6	60.8	0.929	—	—	—
1-propanol[c]	—	49.2	0.571	0.48	0.76	0.84
Ethanol	—	51.9	0.654	0.54	0.86	0.75
Methanol	—	55.4	0.762	0.60	0.98	0.66
Glycerol	—	57.0	0.812	0.62	1.21	0.51
Water	—	63.1	1.000	1.09	1.17	0.47

[a] kcal mol^{-1}. [b] Data from ref. 21. [c] Data of molecular solvents from ref. 39.

Reichardt's dye probes in studying the polarity of ILs. The coefficients in eqn (2) were further compared with those for conventional molecular solvents and other series of ILs, as listed in the following equations:

$$E_T(30) = 0.979 \times E_T(33) - 7.461 \qquad (3)$$

$$n = 32 \text{ molecular solvents, } r = 0.9905^{31}$$

$$E_T(30) = 0.9986 \times E_T(33) - 8.6878 \qquad (4)$$

$$n = 10 \text{ molecular solvents}^{32}$$

$$E_T(30) = 0.9953 \times E_T(33) - 8.1132 \qquad (5)$$

$$n = 20 \text{ (19 molecular solvents + 1 IL), } r = 0.9926^{33}$$

$$E_T(30) = 1.09396 \times E_T(33) - 15.15814 \qquad (6)$$

$$n = 10 \text{ ILs, } r = 0.9926^{21}$$

Obviously, excellent linear correlations between $E_T(30)$ and $E_T(33)$ scales were obtained for both molecular solvents and ILs. The coefficients in eqn (2) are comparable to the case of molecular solvents (eqn (3)–(5)) while exhibiting some deviation over the results from other ILs. This indicated that ILs maybe exhibit different solvation behavior towards the probe compared to molecular solvents, and thus a substantial correlation derived from the specific ILs is necessary.

We first focused on the nonether ILs with a [DCA] or [NTf$_2$] anion. Clearly for the [BMIm]-based ILs, comparable polarity that similar to ethanol (E_T^N = 0.654) was observed between the two anions, [DCA] and [NTf$_2$], with E_T^N 0.640 and 0.645, respectively, which is also comparable to the previous result ([BMIm][DCA]: 0.639,[34] [BMIm][NTf$_2$]: 0.642,[23] 0.645[35]). In fact, it was reported that alteration of the anion has very little effect on the polarity of imidazolium ILs,[21,23,36] [BMIm]-based ILs for other anions typically have $E_T^N \approx 0.65$ at room temperature (trifluoroacetate: 0.630,[25] tetrafluoroborate: 0.680,[37] hexafluorophosphate: 0.667[38]). The result is consistent with the previous conclusion that the polarity of general ILs appears to be largely cation controlled.[23,24] However, it did not hold true for ammonium-based ILs with the same [DCA] or [NTf$_2$] anion. Both the $E_T(33)$ and $E_T(30)$ values are indicative of the significant influence of anion on the polarity of nonether ammonium ILs. $E_T(30)$ value of [N$_{1124}$][NTf$_2$] is 58.9 kcal mol^{-1}, comparable with that of glycerol, and much higher than those of most imidazolium ILs, while [N$_{1124}$][DCA] still possess $E_T(30)$ of 49.0 kcal mol^{-1}, slightly lower than general imidazolium ILs and comparable to 1-propanol.[39] Taking into account of the lack of suitable conventional solvents with polarity range of $E_T(30)$ = 55–63 kcal mol^{-1},[39] the [NTf$_2$]-based ammonium ILs, possessing relatively high polarity, will act as a single aprotic ionic solvent filling the polarity gap between water and general molecular solvents.

The longest wavelength intramolecular charge-transfer π–π* absorption bands of Reichardt's betaine dye 30 in the four ILs are shown in Fig. 3. Obviously, Reichardt's dye 30 in [BMIm][NTf$_2$] and [BMIm][DCA] showed UV-vis absorption both around 555 nm, while that of quaternary ammonium-based ILs exhibit distinct absorption for different anions, 584 nm for [N$_{1124}$][DCA] and 485 nm for [N$_{1124}$][NTf$_2$], respectively. Since the solvatochromic absorption band of this betaine dye lies within the visible region of the spectrum, the drastic anion-dependent polarity for ammonium-based ILs can be easily seen colorimetrically and a visual estimate of solvent polarity can often be made: the solution colour is violet in [BMIm][NTf$_2$] and [BMIm][DCA], while [N$_{1124}$][DCA] and [N$_{1124}$][NTf$_2$] are cyan and orange, respectively.

3.2. Effect of the ether group on the polarity of ILs

After ether functionalization, the polarity of [NTf$_2$]-based imidazolium ILs, [1O2MIm][NTf$_2$], was enhanced compared to nonether ILs and are comparable with that of methanol,

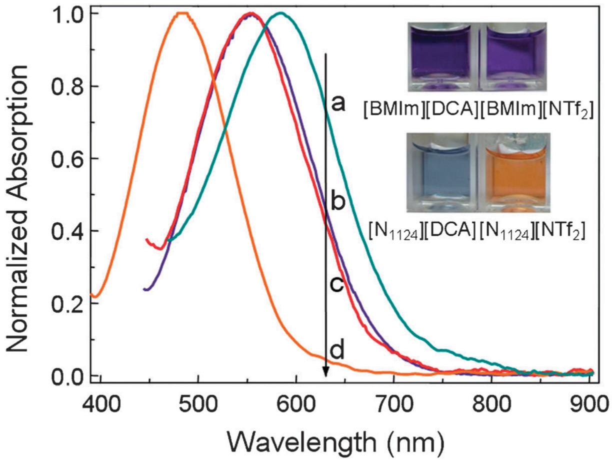


Fig. 3 Longest wavelength intramolecular charge-transfer π–π* absorption bands of Reichardt's betaine dye 30 in [N$_{1124}$][DCA] (a), [BMIm][NTf$_2$] (b), [BMIm][DCA] (c) and [N$_{1124}$][NTf$_2$] (d). Inset is a photograph illustrating the appearance of IL solutions of Reichardt's dye 30.

which is also consistent with the previous result.[18] However, polarity of [1O2MIm][DCA] is nearly constant, as indicated by both $E_T(33)$ and $E_T(30)$. This is somewhat similar to the effect of hydroxyl on imidazolium ILs but is of a smaller magnitude,[21] the anion-dependent polarity of hydroxyl ILs relative to [BMIm]-based ILs increased by 4.7 and 9.2 kcal mol^{-1} for [HOEMIm][DCA] and [HOEMIm][NTf$_2$], respectively, which was ascribed to the fact that OH in the imidazolium cation is a better hydrogen bond donor than C2–H to differentiate the (anion···HO) H-bonding strength.[21] In contrast, for quaternary ammonium-based ILs, introduction of an ether group has no obvious influence on their polarity, although it was reported that the ether group lead to significant ion crystal packing of ILs and notable differences in their thermal properties and viscosity,[40,41] and the location of ether oxygen showed significant influence on their reductive stability of ammonium ILs.[42]

To further investigate the distinct influence of anions and ether groups on the polarity, $E_T(33)$ scales of a series of ammonium and imidazolium ILs, including anions with different hydrogen bond accepting (HBA) ability were measured. The results are given in Table 2 and plotted in Fig. 4. Obviously, the above rule still hold true for all ILs. In detail, for the imidazolium ILs with anions [NO$_3$], [DCA], [BF$_4$], [PF$_6$] and [NTf$_2$], comparable $E_T(33)$ scales (60.7–61.6 kcal mol^{-1}) were obtained, which is in good agreement with the previous result,[21,23,36] and suggested little effect of the anion on the polarity. Introduction of an ether group on the cation, however, greatly expanded the $E_T(33)$ scales (59.2–66.2 kcal mol^{-1}) with the following trend: [1O2MIm][NO$_3$] < [1O2MIm][DCA] < [1O2MIm][BF$_4$] < [1O2MIm][PF$_6$] < [1O2MIm][NTf$_2$]. As for ammonium ILs, a comparable study of ammonium ILs with and without ether groups strongly suggested the significant effect of the anion rather than the ether group on the $E_T(33)$ scales. The changed trend in $E_T(33)$ scales is roughly similar to the case of [1O2MIm]-based imidazolium ILs, wherein an IL with an anion of lower HBA ability gives a higher $E_T(33)$ value. Note that $E_T(33)$ scales of [N$_{1124}$][NO$_3$], [N$_{1124}$][BF$_4$] and [N$_{1124}$][PF$_6$] were not determined because of their solid state at room temperature. For convenience, we will only discuss the comparable cases of [DCA] and [NTf$_2$]-based ILs in the next context.

3.3. Photochromism, solvatochromism and thermal reversion of spiropyran in ammonium and imidazolium ILs

Spiropyran was proposed as a multi-parameter probe for its immediate molecular environment, based on photochromic behavior, solvatochromism of the MC, and rate of thermal relaxation of MC to SP form (Fig. 2). Recently, photochromism of spiropyran in ILs were found to be sensitive to the solvation environments. Some distinctive features, including polarity and hydrogen bonding basicity-dependent photochromism, negative activation entropies, and good linear shape between $E_T(30)$ scales and the E_{SP} scales were obtained.[20,44] Here the photochromism of spiropyran was investigated in these ammonium and imidazolium ILs.

As can be seen from Table 3, positive photochromism was observed for all ILs investigated, which agree with the conclusion drawn by Wu *et al.*[20] that spiropyran showed positive photochromism with the E_{sp} ($28591/\lambda_{max}$) < 53.9 kcal mol^{-1}, while negative ones with the E_{sp} > 53.9 kcal mol^{-1} (when the thermodynamically less stable state of spiropyran is the more deeply coloured form, the system is called a "positive photochromism", otherwise it is called a "negative (or inverse) photochromism"[46]). Unlike the case in hydroxyl imidazolium-based ILs,[21] no significant polarity-dependent E_{sp} but an unexpected anion-dependence was found in these ILs, irrespective of the nature of the cation. For example, E_{sp} of [NTf$_2$]-based ILs are nearly constant (52.1–52.3 kcal mol^{-1}) although their $E_T(30)$ scales changed from 51.4 to 58.8 kcal mol^{-1} with cations of [BMIm], [1O2MIm], [N$_{114,1O2}$] and [N$_{11,1O2,1O2}$]. This anion-dependent E_{sp} still hold true for imidazolium ILs such as [EDMIm][NTf$_2$] and [EMIm][DCA] (Table 3). Similar to the case of solvatochromism, the rate constants (k) and half-lifetimes ($t_{1/2}$) for MC thermal isomerization tabulated in Table 3 exhibit no polarity dependence, but slight anion-dependence. $t_{1/2}$ for ILs containing [NTf$_2$] is obviously larger than that of [DCA] for each common cation, indicating that the MC was more stablized in [DCA]-based ILs. The obvious anion-dependent solvatochromism and thermal relaxation of MC is rather similar to the case of [Cu(acac)(tmen)][X] (X = BPh$_4$ or ClO$_4$), as reported by Gordon *et al.*,[23] where its λ_{max} values are significant anion-dependent, irrespective of the nature of cation. The anion-dependent response of spiropyran in both imidazolium and tetraalkylammonium ILs may be caused by the zwitterionic form in these ILs with short alkyl chain or non-function groups preferentially positioning itself near the anion, thus not being significantly influenced by the cation. Although both probes have similar zwitterionic structures, the above result indicated that spiropyran in ILs undergo different

Table 2 $E_T(33)^a$ scales of ammonium and imidazolium ILs with [NO$_3$], [BF$_4$] and [PF$_6$] anion

	[NO$_3$]	[BF$_4$]	[PF$_6$]
[BMIm]	61.2	61.6^c	61.4
[1O2MIm]	59.2	65	66.0
[N$_{1124}$]	—^{b}	—^{b}	—^{b}
[N$_{114,1O2}$]	63.2	63.3	65.4

[a] kcal mol^{-1}. [b] Data of [N$_{1124}$][NO$_3$], [N$_{1124}$][BF$_4$] and [N$_{1124}$][PF$_6$] were not determined since they are solid at room temperature. [c] Data from ref. 43.

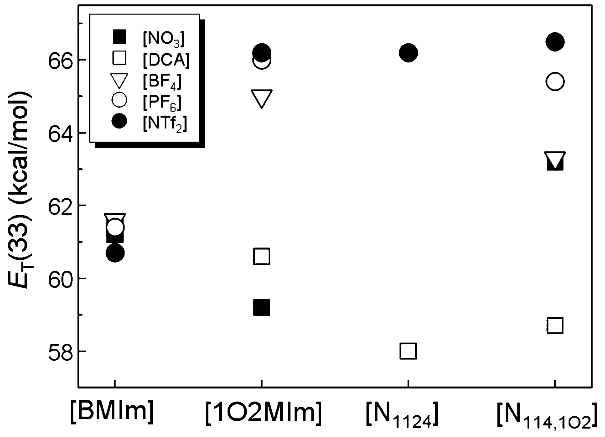


Fig. 4 Comparison of E_T(33) scales for ammonium and imidazolium ILs with different anions.

Table 3 Photochromism and thermal reversion of spiropyran in ILs (10^{-4} M) at 298 K.[a]

ILs	$E_T(30)^b$	$\lambda_{max}{}^c$	$E_{sp}{}^b$	$10^3\ k/s^{-1}$	ln k	$t_{1/2}$/min	Photo[d]
[BMIm][DCA]	51.4	550	52.0	0.367	−7.91	31.4	P[e]
[BMIm][NTf$_2$]	51.6	549	52.1	1.010	−6.90	11.4	p
[1O2MIm][DCA]	52.4	552	51.8	0.548	−7.51	21.1	p
[1O2MIM][NTf$_2$]	54.5	547	52.3	0.911	−7.00	12.7	p
[N$_{1124}$][DCA]	49.0	552	51.8	0.694	−7.27	16.6	p
[N$_{1124}$][NTf$_2$]	59.0	547	52.3	0.711	−7.25	16.3	p
[N$_{114,1O2}$][DCA]	49.0	552	51.8	0.611	−7.40	18.9	p
[N$_{114,1O2}$][NTf$_2$]	58.8	547	52.3	0.828	−7.10	13.9	p
[EMIm][DCA][f]	51.6	551	51.9	0.382	−7.87	30.2	p
[EDMIm][NTf$_2$][g]	51.8	548	52.2	—	—	—	p

[a] Detailed measurement see our previous work.[44] [b] kcal mol^{-1}. [c] The wavelength corresponding to maximum absorption, nm. [d] Photochromism. [e] Positive photochromism. [f] [EMIm] = 1-ethyl-3-methylimidazolium, data from ref. 21. [g] [EDMIm] = 1-ethyl-2,3-dimethylimidazolium, data from ref. 45.

specific and non-specific interactions between ionic solute within ILs compared to Reichardt's dye, probably due to its more flexible conformation.

Further LSER (Linear Solvation Energy Relationships) analysis of ln k was conducted according to the established procedures,[47] using the Kamlet–Taft data in Table 1 (Kamlet–Taft data of [EMIm][DCA] is $\pi^* = 1.08$, $a = 0.53$, $\beta = 0.35$ from ref. 44). In the simplest Kamlet–Taft LSER's ($XYZ = XYZ_0 + a^*\alpha + b^*\beta + s^*\pi^*$), there are four parameters: a, b, s, and the intercept (XYZ_0). The standard procedure for LSER analysis is as follows:

If we perform a linear regression using all variables {α, β, π*}, we obtain:

$$\ln k = -2.33(\mathit{0.3198}) - 0.69(\mathit{0.2708})^*\alpha - 0.99(\mathit{0.2642})^*\beta - 4.18(\mathit{0.0656})^*\pi^*$$

The numbers in italics represent the p-values for each coefficient. Since nearly all coefficients proved significant ($p < 0.05$ is typical for smaller data sets to indicate significance[47]), we must then perform a regression using each pair of variables {α, β}, {β, π*}ss,[29]

$$\ln k = -7.10(\mathit{7.09 \times 10^{-5}}) + 0.22(\mathit{0.6988})^*\alpha - 0.95(\mathit{0.3963})^*\beta$$

$$\ln k = -4.49(\mathit{0.0102}) - 0.54(\mathit{0.4834})^*\beta - 2.66(\mathit{0.0947})^*\pi^*$$

$$\ln k = -3.01(\mathit{0.2073}) - 0.37(\mathit{0.5025})^*\alpha - 4.14(\mathit{0.0683})^*\pi^*$$

Since not all coefficients proved significant, we next test all three variables individually {α}, {β}, {π*}

$$\ln k = -7.71(\mathit{4.08 \times 10^{-8}}) + 0.52(\mathit{0.2572})^*\alpha$$

$$\ln k = -6.84(\mathit{2.17 \times 10^{-7}}) - 1.21(\mathit{0.1618})^*\beta$$

$$\ln k = -4.27(\mathit{0.0073}) - 3.12(\mathit{0.0305})^*\pi^*$$

It is clear that only the third relationship contains significant parameter. This indicates that the rate constants depend only upon {π*}.

3.4. Kamlet–Taft parameters and DFT calculation

Empirical Kamlet–Taft parameters (dipolarity/polarizability, π*; HBD acidity, α; HBA basicity, β) were determined and the result is shown in Table 1 and plotted in Fig. 5. The π* values of all ILs are high in comparison with molecular solvents (except water) because the effect of Coulombic interactions from the ions is incorporated as well as dipole and polarizability effects.[24,48] For all ILs, no matter ammonium or imidazolium-based, and no matter ether group functionalized, the [DCA]-based ILs possess higher π* and β than [NTf$_2$] but lower α. This was due to the higher electronegativity and nucleophilicity of [DCA] than that of [NTf$_2$]. Introduction of an ether group on both cations was found to somewhat expand the π* difference between the two anions, while narrowing the β difference.

Plot of the dipolarity/polarizability, HBD acidity, and HBA basicity *vs.* the E_T(30) scale for all ILs investigated, respectively, is also shown in Fig. 5. Obviously, no significant correlation between π* or β and the E_T(30) scale was obtained according to least squares analysis. Although α value increased with E_T(30) value, with good linearity ($r = 0.98$), it is not unexpected because hydrogen bonding acidity is known to contribute mainly to polarity (*ca.* two thirds as reported by Taft and Kamlet[49]), and for protic solvents the E_T(30) scale is largely a measure of the hydrogen bond donor strength. Moreover, the α parameter was determined indirectly, from the measurements of E_T(30) and polarizability of the solvent.[21] In light of this, it is clear that since a significant change is not observed in the π* values as the anion of the ammonium ILs is varied from [DCA] to [NTf$_2$], thus α of these ILs will reasonably change as the E_T(30) values and the unusual polarity behavior of ammonium ILs cannot be simply explained by the hydrogen bonding acidity.[50]

The reason for the outstanding negative solvatochromism of Reichardt's dye 30 in ILs stems from the unequal, differential solvation of the dipolar electronic ground and less dipolar excited state of the probe with increasing solvent (ILs) polarity, according to its inherent molecular structure.[16] Since the phenolate oxygen atom exhibits a highly basic EPD (electron pair donor) centre, suitable for the interaction with H-bonding donors and Lewis acids (EPA = electron pair acceptor),[16] the zwitterionic probe in ILs is thus suitable for the registration of

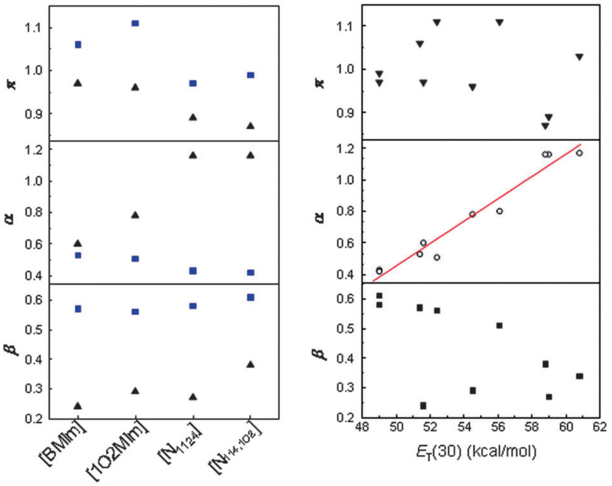


Fig. 5 (Left) Comparative study of the Kamlet–Taft parameters between $[DCA]^-$ (■) and $[NTf_2]^-$ (▲)-based ILs, (Right) Plot of π^*, α, β *vs.* $E_T(30)$ scale, respectively. The result of correlation analysis is the following: $E_T(30) = -3.07885 + 0.07068\alpha$, $r = 0.98$.

(i) the coulombic interaction between the cation and the phenolate oxygen atom (EPA/EPD interaction); (ii) the H-bonding interaction between acidic hydrogen on cation and the phenolate oxygen atom. In contrast, as confirmed by the experimental results,[51] coulombic interaction between the pyridinium moiety and anion was small and practically not registered because the positive charge is delocalized and sterically somewhat shielded, thus the betainic dye is neither a hydrogen-bond donor (HBD) nor an electron-pair acceptor (EPA).[52]

In imidazolium ILs, the strong delocalization of positive charge on the imidazolium ring caused weak coulombic interaction with the negative phenoxide oxygen, while the hydrogen bonding donor acidity of the imidazolium cation (for example, $pK_a = 21–23$ for the C2-H[53]) suggested that the ground state of Reichardt's dye 30 was dominantly stabilized by the H-bonding interaction between hydrogen (mainly C2-H) and the phenolate oxygen. It has long been recognized by experiment and molecular dynamics study that the E_T^N scale for ILs is directly related to the specific interactions involving the phenoxide oxygen atom.[54] However, for ammonium ILs, the stabilization of the dipolar electronic ground state mainly originated from the coulombic interaction between the cation and the phenolate oxygen atom (Scheme 1), since the tetraalkylammonium is a poor H-bonding donor by the lack of acidic hydrogens, and moreover, its positive charge is less delocalized than the imidazolium ring.

Based on the suggested interaction between ILs and Reichardt's dye probe, DFT computation of four typical imidazolium and tetraalkylammonium ILs with the B3LYP method and basis set 6–31+g(d,p) was conducted to get optimized structure and ionic energy and to deeper understand the different polarity behavior at the molecular level. Shown in Fig. 6 are the optimized structures for the calculated ion pairs. In the case of the imidazolium cation, the anion was located in front of the imidazolium ring, where its atoms of more negative charge are close to the methyl, ethyl, in particular C2-H (Fig. 6). In detail, $[DCA]^-$ nearly located in the plane of the imidazolium ring and $[NTf_2]^-$ located its S–N–S core in the plane of the imidazolium ring with each CF_3 group above or below the plane. In the case of the tetraalkylammonium cation, the optimized strutures are that the anion is located on top of the two methyl groups, which are about 4.0 (for $[N_{1124}][NTf_2]$) and 3.41 kJ mol^{-1} (for $[N_{1124}][DCA]$) stabilized as compared to the cases that the anion located on top of the two methylene groups, due to the extra stabilization by the other two methylene groups. The optimized geometries for these ILs are similar to the previous theoretical reports at different levels.[55]

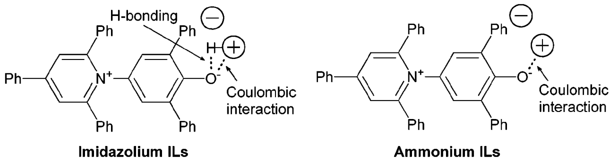
According to Welton's proposition,[47] the ability of the cation in ILs to interaction with a probe appears to come from an antagonistic relationship between its anions, as described below:

$$[\mathrm{Cation}]^+ + [\mathrm{Anion}]^- \rightleftharpoons [\mathrm{Cation}]^+\text{---}[\mathrm{Anion}]^-$$

$$[\mathrm{Cation}]^+ + \mathrm{solute} \rightleftharpoons [\mathrm{Cation}]^+\text{---}\,\mathrm{solute}$$

The nature of the anion will lead to different degrees of interaction with a cation and thus different degrees of interaction of a cation with the solute. With changing the anion from $[DCA]^-$ to $[NTf_2]^-$, the negative charge of the anion is delocalized and the distance between the cation and anion is increased, thus the interaction energy between cation and anion decreased. As can be seen from Table 4, ion pairs $[N_{1124}][DCA]$ are more strongly bound than $[N_{1124}][NTf_2]$ by 25.33 kJ mol^{-1}, indicating a tendency for very strong ion pairing in the former ILs, thus the residue effective cation charge to interact with the phenolate oxygen atom increased and the dipolar electronic ground of Reichardt's dye 30 in $[N_{1124}][NTf_2]$ is much more stabilized than that in $[N_{1124}][DCA]$. Taking into account the above conclusion that the polarity of ammonium ILs was controlled by coulombic interaction between cation and the phenolate oxygen (Scheme 1), the resulting strong coulombic interaction in $[N_{1124}][NTf_2]$ gives higher $E_T(30)$. This change of polarity of tetraalkylammonium ILs is rather similar to that observed in acetonitrile solution with addition of metal salts, where the long-wavelength CT absorption band of Reichardt's dye 30 hypsochromic shifted with increasing effective cation charge (*i.e.* ion charge/ion radius).[51]

In contrast, the difference in binding energy with changing anion from [DCA] to $[NTf_2]$ (ΔE_{disp}) for imidazolium ILs is about half of the ammonium ILs (Table 4). Moreover, due to the presence of C2-H, polarity of imidazolium ILs experienced by Reichardt's dye 30 resulted mainly from H-bonding interaction with phenolate oxygen but less affected by the Coulombic interaction.[23] However, for general imidazolium ILs the difference in intensity of hydrogen bonds for various anions is not enough to differentiate their polarities, since the C2-H is less acidic and free to interact with the phenolate oxygen of



Scheme 1 A cartoon illustrating plausible interaction between Reichardt's dye 30 and ILs.

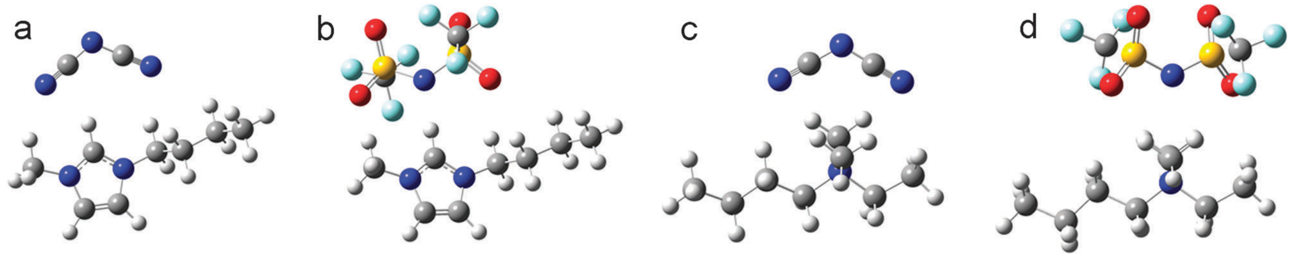


Fig. 6 Optimized geometries of ion-pair conformations of ILs in this work: (a) [BMIm][DCA], (b) [BMIm][NTf_2], (c) [N_{1124}][DCA] and (d) [N_{1124}][NTf_2].

Table 4 Bonding energy (ΔE) and displacement energies (ΔE_{disp}) calculated for four imidazolium and ammonium ILs.[a]

ILs	ΔE (kJ mol^{-1})	ΔE_{disp}[b] (kJ mol^{-1})
[BMIm][DCA]	−327.08	−13.12
[BMIm][NTf_2]	−313.96	0.0
[N_{1124}][DCA]	−314.86	−25.33
[N_{1124}][NTf_2]	−289.53	0.0

[a] Atom coordinates see supporting information.† [b] For displacement energy [BMIm][NTf_2] and [N_{1124}][NTf_2] was denoted as reference, respectively.

Reichardt's dye, as indicated by their comparable hydrogen bond donating ability (α values in Table 1).[21] Thus imidazolium ILs with the two anions give comparable polarity scales.

Introduction of an ether group resulted in different effects on the polairty of imidazolium and ammonium ILs. The increase in polarity of [1O2MIm][NTf_2], although less significant than 1-(2-methoxyethyl)-1-methylpyrrolidinium-based ILs,[25] was ascribed by Crowhurst *et al.* to the electron withdrawing effect of the oxygen atom, which actually increases the overall acidity of the ion.[48] In contrast, the ether group affected the coulombic interaction between ammonium cation and anions less.

4. Conclusion

In conclusion, a distinct influence of anion and ether group on the polarity of ammonium and imidazolium ILs was found. The polarity of the ammonium ILs appears to be strongly anion dependent, but less affected by the ether group, unlike the case of imidazolium ILs. The polarity of imidazolium ILs was much more affected by the ether group than the anions. The possible reason is that the polarity of imidazolium ILs experienced by Reichardt's dye 30 resulted mainly from H-bonding interaction with the phenolate oxygen, while the polarity of ammonium ILs is controlled by coulombic interaction between cation and the phenolate oxygen. Note that the [NTf_2]-based ammonium ILs possess higher polarity (close to glycol) that can fill the polarity gap between water and general molecular solvents, and can be used as a single aprotic ionic solvent for polarity-specfic reaction and synthesis.

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