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PAPER

Do anions influence the polarity of protic ionic liquids?†

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Polarity studies in two classes of imidazolium-based protic ionic liquids (PILs) possessing $[HSO_4]^-$, $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions were carried out using a solvatochromic method from 298.15 to 353.15 K. For 1-methylimidazolium class of PILs, $E_T(30)$ was found to be independent over the entire range of temperature, while $E_T(30)$ was noted to decrease with a rise in temperature in the case of 1-butylimidazolium class of PILs containing $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions. The $E_T(30)$ value decreases in both the classes upon varying the anions ($[HSO_4]^-$, $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$). The $E_T(30)$ value is controlled by hydrogen bond acceptor basicity, β, and dipolarity/polarizability, π^*. The $E_T(30)$ value for PILs varies inversely to the strength of the coulombic interaction between ions in PILs. Strong interactions between ions lead to lower $E_T(30)$ values. Unlike the poor thermal effect on $E_T(30)$, the Kamlet–Taft parameters *i.e.* α, β and π^* have pronounced thermal effect in the imidazolium-based PILs. Variation in the Kamlet–Taft parameters is controlled by the stabilization of ions and the degree of proton transfer from Brønsted acid to Brønsted base.

Introduction

In the past decade or so, ionic liquids (ILs) have been the subject of intense study in the areas of organic synthesis, catalysis, electrochemical applications, solvent extraction, synthesis and stabilization of nanostructure materials to example a few.[1–3] The growing awareness of ILs is due to their insignificant vapour pressure, high thermal stability, low melting points, good solvating capabilities, wide electrochemical window, inflammability, intrinsic ionic conductivities, recyclability *etc.*[4,5] Since the use of volatile organic compounds (VOCs) leads to environmental pollution, ILs because of their beneficial properties may be a useful replacement for these VOCs.[6]

An IL consists of a poorly coordinating organic cation and an organic or inorganic anion. The physicochemical properties of ILs can easily be tailored by varying cations and anions, and thus are called as 'designers solvent'.[7] The variations in physicochemical properties of ILs, such as viscosity, conductivity, density and so on, were found to be more sensitive to the change in cation due to the various possible specific and non-specific interactions. Unfortunately, very little is known about the variation in properties upon varying anions.[4] The efficiency of an IL in diverse applications, *viz.*, chemical, biochemical, and electrochemical, lies in the accessibility of various parameters which makes them suitable as non-aqueous media.[8]

The era of ILs began with Protic Ionic Liquids (PILs) in 1914 with Walden, who discovered ethylammonium nitrate, (mp 12.5 °C).[9] PILs contain dissociable protons in their continuum medium. Currently, the PIL materials have been receiving a lot of interest towards their use as catalytic media for biological applications, explosive formulations and as lubricants.[10] PILs containing imidazolium cations have been used as catalytic media for many carbon–carbon bond, carbon–oxygen bond and carbon–nitrogen bond forming reactions.[11] High "turn over number" of PILs makes them useful catalysts for a variety of reactions.[12] They have been widely used in all kinds of chromatographic studies due to low cost, high polarity, elevated miscibility with water, air/moisture insensitivity and high selectivity to bind with polar solutes.[13] Their polarity can be easily monitored by changing either cations or anions, which makes them more useful in chromatographic studies.[13] PILs were known for their high dielectric conductivities, caused by extended hydrogen bonding, which makes them more polar.[14] While we are much aware about the thermal stability, density, molar volume, surface tension, viscosity and ionic conductivity of the PILs, insufficient data on the polarity of these materials make their use as a medium somewhat difficult.

Polarity of ILs is sensitive towards the nature of cations and anions. Strength of the coulombic and van der Waals interaction between ions decides the magnitude of polarity. Recent theoretical observations based on the principal component analysis for a number of aprotic ionic liquids (APILs) demonstrate the influence of structural variations on polarity.[15] Polarity of ILs can be measured by a multiparameter approach,

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electronic transition energy, $E_T(30)$, and Kamlet–Taft parameters, α hydrogen bond donor acidity, β hydrogen bond acceptor basicity and π^* dipolarity/polarizability.[8a,16] $E_T(30)$ is measured by using Reichardt's dye, while *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline have been used for the measurement of Kamlet–Taft parameters. The low volatility of solvatochromic dyes makes them useful over a wide range of temperatures. Polarity of ILs has been also measured by using microwave dielectric spectroscopy as studied by Weingartner *et al.*[17] However, for low viscous fluids, the fast elementary steps of solvation dynamics and solvent-controlled chemical reactions have been probed by using FTIR spectroscopy because dielectric spectroscopy is valid for slow diffusive processes.[18] The hyperpolarity of PILs as expected due to the extended hydrogen-bonding is also supported by the microwave dielectric spectroscopy, where strong orientational correlation between dipoles can enhance dielectric polarization.[18] The behavior of ILs and their solvation capability also depend upon the nature of the dissolved solute.[19] The polarity of ILs obtained using a polar solute differs significantly from that obtained by using a non-polar solute. The spectroscopically active salt [Py]I (1-ethyl-4-(methoxycarbonyl)pyridinium iodide) also indicates the higher polarity of ILs due to the lower concentration of ion-pairs while higher concentration was noted in the molecular solvents of higher polarity.[19]

A literature search reveals that a few studies exist on the thermosolvatochromism of ILs and their solutions.[20,21] The variation of alkyl chain length and the introduction of functional groups on cations alter the polarity.[20a,b] An earlier report from our group has shown the effect of cosolvents on the polarity of APILs using a preferential solvation model.[22] The strong synergism between an IL and methanol results into the positive deviation from ideal mixing.

In continuation, a kinetic investigation of Diels–Alder reaction in highly aqueous medium with IL as a cosolvent was reported in promoting the kinetics of the organic reaction.[23] The results indicated a pairwise interaction between the IL cosolvent and the initial states of reactants than that of the transition state, thereby lowering the rate constant (k_2) value. A comprehensive study of polarity of ILs and molecular solvents has been reported by Reichardt.[24]

PILs are considered to be 'hyperpolar' in nature due to the extensive hydrogen bonding between ions. The polarity of ILs decreases with the increase in distance between ions due to decrease in effective charge density between them. In this work, we present the polarity of some PILs with a view to ascertaining the role of anions. Herein, we represent another explanation based on the Kamlet–Taft parameters for the variation in polarity upon varying anions towards a particular cation. Polarity study using the solvatochromic technique depends on the preferential stabilization of well formed polar/apolar ground or excited states of the probe molecule. The probability of interaction between ions and the probe molecule directly depends on the extent of coulombic interactions between them. Strong coulombic forces between ions lead to weaker interaction with the probe molecule; thereby reducing the polarity on the solvatochromic scale.

Table 1 The acronyms of ILs employed in the present work

Acronyms	Names of ionic liquids
[BMIM][BF_4]	1-Butyl-3-methylimidazolium tetrafluoroborate
[BMIM][PF_6]	1-Butyl-3-methylimidazolium hexafluorophosphate
[HmIm][HSO_4]	1-Methylimidazolium bisulfate
[HmIm][HCOO]	1-Methylimidazolium formate
[HmIm][CH_3COO]	1-Methylimidazolium acetate
[HmIm][CH_3CH_2COO]	1-Methylimidazolium propionate
[HbIm][HSO_4]	1-Butylimidazolium bisulfate
[HbIm][HCOO]	1-Butylimidazolium formate
[HbIm][CH_3COO]	1-Butylimidazolium acetate
[HbIm][CH_3CH_2COO]	1-Butylimidazolium propionate

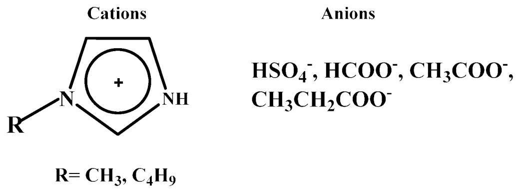

Fig. 1 Structures of the PILs used for thermosolvatochromic studies.

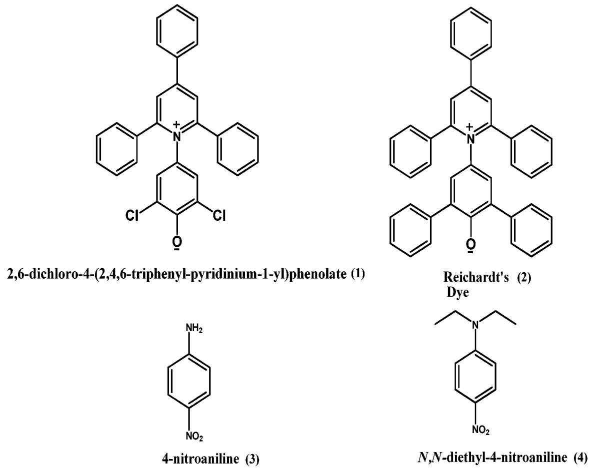

Fig. 2 Solvatochromic probe molecules.

In our laboratory, we have embarked upon an extensive research program on investigating the physicochemical properties of ILs and their implications on chemical and electrochemical processes.[21,22,25] As a part of this ongoing program, we now investigate the thermal effect on solvatochromism of probe molecules in 1-methylimidazolium and 1-butylimidazolium classes of PILs. We also address the question whether 'hyperpolarity' in PILs is anion-dependent. The acronyms and names of PILs used in this work have been collected in Table 1, while Fig. 1 depicts the structures of these PILs. In Fig. 2 are shown the solvatochromic probe molecules used in this investigation.

Experimental section

Materials

The spectroscopic indicator dye 2,6-dichloro-4-(2,4,6-triphenyl-pyridinium-1-yl)-phenolate (1) was obtained from Fluka Analytical (98.5% purity). Reichardt's dye (2) and 4-nitroaniline (3) were used as obtained from M/s Sigma Aldrich. *N*,*N*-Diethyl-4-nitroaniline (4) was purchased from Frinton laboratories

(99% purity) (shown in Fig. 2). 1-Methylimidazole, 1-butylimidazole and *n*-butyl bromide were distilled prior to their use. Formic acid, acetic acid, propionic acid, sulfuric acid solutions all obtained from Merck were used as obtained. Sodium tetrafluoroborate and potassium hexafluorophosphate were used as purchased from Merck.

Synthesis of protic ionic liquids

PILs were synthesized by an atom economic process by mixing equimolar amounts of acid and base.[26] Dropwise addition of base to acid was carried out for complete neutralization in an ice bath in order to avoid heat generation. The reaction mixture was stirred for 6 h at room temperature. The water formed in the neutralization was removed by using a rotavapor at 80 °C for 6 h. The last traces of water and other volatile impurities were removed from PILs under reduced pressure at 70 °C for 10 h. The characterization and their purities were determined by NMR spectroscopy. The water content of the pure and dried PILs as measured by Karl-Fischer coulometer analysis did not exceed 50 ppm. The halide contents were estimated using Volhard titration due to the lack of a sophisticated ion-chromatographic technique with us.[27] Note that the standard Volhard titration has been validated using a chloride-selective electrode.[28] The residual halide contents (bromides) were less, > 30 ppm.

Polarity measurements

The stock solutions of the required dyes were prepared in methanol prior to their use. The stock solution was added dropwise to a PIL, and the solvent was evaporated under vacuum. The PIL was then transferred to a quartz cuvette under a nitrogen atmosphere and sealed with a septum. The λ_{max} was measured at different temperatures using a UV-visible spectrophotometer. The temperature of the cell was controlled using the single cell accessory having an accuracy of ±0.1 K.

Determination of E_T^N and Kamlet–Taft parameters

The equations required to calculate various parameters for characterizing the polarity of ILs are given in Table 2. PILs have lower pK_a values, leading to the protonation of Reichardt's dye 30 (pK_a = 8.6) and therefore, the long-wavelength intramolecular charge transfer (ICT) absorption band disappears.

The $E_T(30)$ data for all PILs were derived from $E_T(33)$, a polarity scale of the less basic probe 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (pK_a = 4.78). For this purpose, a simple linear regression method was used, involving eight molecular solvents and one IL (see Fig. S1, ESI†).

$$E_T(30) = 0.9119(\pm 0.02956)\ E_T(33) - 3.80634(\pm 1.68048) \tag{1}$$

The calculated $E_T(30)$ values using the above formula were found to be in good agreement with the measured $E_T(30)$ values as shown in Table 3.

As suggested by earlier workers, Reichardt dye 30 (2) is not suitable for the polarity measurement of protic ILs.[29] They used Nile red, the least basic solvatochromic dye that has been extensively used for the polarity measurement of weak acids and protic molecular solvents. However in our study we used Reichardt dye 33 (1) and observed the long wavelength ICT absorption band, which is absent in the case of Reichardt dye 30 (2).

Table 2 Equations to determine the E_T^N and Kamlet–Taft parameters

Polarity parameters	Empirical equations
Normalized electronic transition energy (E_T^N)	$E_T(30)$ (kcal mol^{-1}) = $hc\nu_{max}$ = 28 591/$\lambda_{max(nm)}$ = 2.8591ν_{max} where λ_{max} is the maximum wavelength of the lowest energy band of Reichardt's dye (2) $E_T(30)$ can be normalized between water and TMS $E_T^N = [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{solvent}) - E_T(\text{water})] = [E_T(\text{solvent}) - 30.7]/32.4$
Hydrogen bond donor acidity (α)	$\alpha = 0.0649\ E_T(30) - 0.72\pi^* - 2.03$
Hydrogen bond acceptor basicity (β)	$\nu_{(3)max} = 1.035\nu_{(4)max} - 2.8\beta + 2.64$ where $\nu_{(3)max}$ and $\nu_{(4)max}$ are the maximum wave numbers of 4-nitroaniline (probe 3) and *N*,*N*-diethyl-4-nitroaniline (probe 4), respectively
Polarity index (π*)	$\nu_{(4)max} = 27.52 - 3.182\pi^*$

Table 3 Polarity parameters of aprotic ionic liquids, protic ionic liquids and molecular solvents at 298.15 K

Ionic liquids/solvents	$E_T(33)$/kcal mol^{-1}	$E_T(30)$/kcal mol^{-1}	E_T^N	π*	α	β
[HmIm][HSO_4]	73.89	63.6	1.02	1.17	1.225	0.61
[HmIm][HCOO]	65.62	56.0	0.78	1.10	0.812	0.81
[HmIm][CH_3COO]	59.50	50.5	0.61	1.03	0.506	0.85
[HmIm][CH_3CH_2COO]	55.70	47.0	0.50	1.50	−0.06	0.10
[HbIm][HSO_4]	76.04	65.5	1.07	1.12	1.415	0.58
[HbIm][HCOO]	66.20	56.6	0.80	0.97	0.945	0.73
[HbIm][CH_3COO]	65.01	55.5	0.77	0.88	0.938	0.73
[HbIm][CH_3CH_2COO]	64.35	54.9	0.75	1.01	0.806	0.63
[BMIM][PF_6]		53.64 (52.375)[a]	0.71 (0.669)[a]	1.04 (1.032)[a]	0.702 (0.634)[a]	0.241 (0.207)[a]
[BMIM][BF_4]	61.61	52.4 (53.6)[b]	0.67 (0.707)[b]	1.05 (1.047)[b]	0.615 (0.627)[b]	0.716 (0.376)[b]
Methanol	65.13	55.6 (55.4)[c]	0.77 (0.762)[c]	0.735 (0.730)[c]	1.049 (1.05)[c]	0.625 (0.610)[c]
Acetone	51.34	43.0 (42.04)[d]	0.38 (0.35)[d]	0.71 (0.70)[d]	0.250 (0.20)[d]	0.54 (0.54)[d]
Ethylene glycol	65.73	56.1 (56.30)[e]	0.78 (0.790)[e]	1.024 (0.932)[e]	0.874 (0.95)[e]	0.588 (0.51)[e]
Tetrahydrofuran	45.59	37.8 (38.11)[f]	0.22 (0.206)[f]	0.590 (0.60)[f]	−0.002 (0.0)[f]	0.609 (0.54)[f]

Reported values are given in the parentheses. [a] Ref. 21*b*. [b] Ref. 21*b*. [c] Ref. 20*a*. [d] Ref. 20*a*. [e] Ref. 2*c*. [f] Ref. 30.

Results and discussion

The polarity parameters $E_T(30)$, α, β, and π^* for 1-methylimidazolium and 1-butylimidazolium classes of PILs were initially determined at 298.15 K as shown in Table 3. The measured values are in good agreement with the reported data for some ILs and organic solvents. The trends in polarity for $[HmIm]^+$ and $[HbIm]^+$ classes of PILs were found to be:

$$[HmIm][HSO_4] > [HmIm][HCOO] > [HmIm][CH_3COO] > [HmIm][CH_3CH_2COO]$$

$$[HbIm][HSO_4] > [HbIm][HCOO] > [HbIm][CH_3COO] > [HbIm][CH_3CH_2COO]$$

A comparison of polarity in PILs and APILs

Polarity studies in APILs and PILs show opposite behavior with respect to Kamlet–Taft parameters. In APILs, hydrogen-bond donating (HBD) ability, α, has a major effect on the E_T^N value, while hydrogen-bond accepting (HBA) ability, β, has a negligible effect on the E_T^N.[22a,24] HBD ability is solely controlled by the cation while HBA ability depends on the nature of anion. Similar observations were obtained in the case of hydroxylic solvents and water, where HBD ability promotes high polarity (E_T^N). Introduction of an alkyl substituent greatly affects the HBD ability. In imidazolium-based ionic liquids, the polarity decreases as the length of alkyl chain increases from ethyl to octyl. From [EMIM][NTf_2] to [OMIM][NTf_2], E_T^N decreases from 0.658 to 0.630. This decrease in E_T^N is in the same order of decreasing HBD ability (0.627 for [EMIM][NTf_2] and 0.595 for [OMIM][NTf_2]).[20b] Similar observations were noted for the pyridinium, pyrrolidinium and phosphonium-based ionic liquids where E_T^N values vary as the HBD ability.[20b,22a] Influence of substituents on α was observed similar to the influence on polarity, indicating that α is a major contributor to polarity.[20a,21b] Hydrogen bond accepting tendency β depends on the anion. The presence of an alkyl substituent on the cation has a little effect on β value.[20b]

Contrary to APILs, for which the constituent cation governs polarity, the anion has a major contribution towards polarity (E_T^N) in PILs. In spite of very high α values, the E_T^N of PILs were observed to be low when compared to those of the molecular solvents, for which higher α values always resulted in higher polarity (E_T^N value). This indicated the partial reduction in the cationic control on polarity by the anion. The E_T^N value fluctuates according to their hydrogen bond accepting tendency (β). Variation in the polarity with anion is in the same order as that of the β value. The α has no direct effect on the polarity of PILs. However, [HmIm][HSO_4] and [HbIm][HSO_4] show high polarity due to the presence of oxyanions. HBA tendency for $[HSO_4]^-$, $[HCOO]^-$ and $[CH_3COO]^-$ anions was found as 0.61, 0.81 and 0.85, respectively, which is in the order of their decreasing polarity. In the case of the $[CH_3CH_2COO]^-$ anion the β value was noted as 0.10, which is against the order of E_T^N value. Probably, high π^* (1.50) value controls this behavior. A substitution of $-CH_3$ by $-C_4H_9$ on the imidazole ring favors high E_T^N values. It appears that the steric crowding around the cation plays down the influence of the anion on polarity. However, the thermo-solvatochromic trend mimics the thermal effect on α than on β. An increase in temperature from 298.15 to 353.15 K causes slight lowering in the α value leading to negligible or small effect on the E_T^N value.

E_T^N parameter

The E_T^N values for 1-methylimidazolium and 1-butylimidazolium classes of PILs show a similar trend with the variation in anion, but a slightly different trend with temperature. The E_T^N value for 1-methylimidazolium class of PILs remains unaffected with the change in temperature from 298.15 to 353.15 K. A strong stabilization of the dye molecule in the ground state cannot be weakened by an increase in temperature. A very small decrease in the α and β values in the temperature range of 298.15 to 353.15 K supports strong association between PILs and the dye molecule. The temperature dependence of the E_T^N parameter for several PILs is shown in Fig. 3(a) and (b). The polarity index (π^*) depends on the interaction of a dye molecule with its cybotactic environment. The strong interaction of a dye with its environment leads to a high value of π^*. The high π^* value stabilizes the charge of the dye molecule in the excited state; thereby influencing the polarity.

The π^* value for 1-methylimidazolium class of PILs was noted to be either constant or to decrease slowly with temperature from 298.15 to 353.15 K. The observed trends in the E_T^N values for 1-butylimidazolium class of PILs are found to be slightly different with increasing temperature. The E_T^N value for [HmIm][HSO_4] was noted to be 1.02 at 298.15 K. An increase in the basicity of anion from $[HSO_4]^-$ to $[HCOO]^-$ as indicated by the increased β value from 0.61 to 0.81, respectively, leads to strong coulombic interactions between ions in PILs, which lowers the E_T^N value from 1.02 for [HmIm][HSO_4] to 0.78 for [HmIm][HCOO] at 298.15 K. A further increase in the β value (0.85) for $[CH_3COO]^-$ anion lowers the E_T^N value to 0.61 at 298.15 K. The β value for $[CH_3CH_2COO]^-$ was observed to be lower than those for $[HCOO]^-$ and $[CH_3COO]^-$ suggesting that polarity should be higher for [HmIm][CH_3CH_2COO] than for [HmIm][HCOO] and [HmIm][CH_3COO]. However, the polarity for [HmIm][CH_3CH_2COO] was observed to be lower than for [HmIm][HCOO] and [HmIm][CH_3COO]. This anomalistic decrease in polarity (E_T^N value) in spite of a lower β value (0.10) for

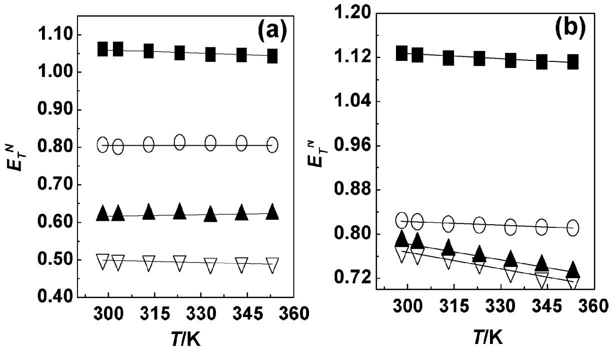

Fig. 3 The E_T^N–T plots of (a) [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽); (b) [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

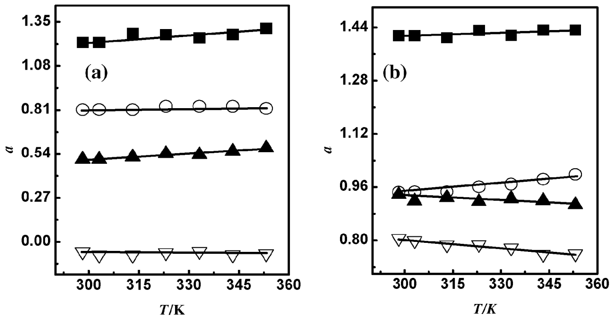

Fig. 4 The α–T plots for (a) [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽); (b) [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

[HmIm][CH_3CH_2COO] is quite surprising. However, a high π^* value (1.50) indicates higher polarity. We are currently carrying out these measurements on a variety of PILs to ascertain this behaviour.

Substitution of the $-CH_3$ group by $-C_4H_9$ remarkably increases the E_T^N value. In the 1-butylimidazolium class of PILs comparatively lower values of π^* and β while higher α value decide the extent of coulombic interaction between ions and hence polarity in PILs. This lowering in Kamlet–Taft parameters can only be attributed to the presence of the butyl chain.

Discrepancies in the E_T^N value for 1-butylimidazolium class of PILs were seen with an increase in the temperature from 298.15 to 353.15 K. There was no thermosolvatochromic change found in the E_T^N value for [HbIm][HSO_4] and [HbIm][HCOO], but the decreasing trend in the E_T^N value was observed for [HbIm][CH_3COO] and [HbIm][CH_3CH_2COO]. Thermosolvatochromic response for [HbIm][CH_3COO] and [HbIm][CH_3CH_2COO] may be due to high thermal sensitivity of the Kamlet–Taft parameter. The E_T^N value was found to decrease for [HbIm][CH_3COO] from 0.77 to 0.71 and for [HbIm][CH_3CH_2COO] from 0.75 to 0.70 in the temperature range from 298.15 to 353.15 K. Thus, [HbIm][CH_3COO] and [HbIm][CH_3CH_2COO] show positive thermosolvatochromic response.

α Parameter

In spite of very close similarity in the behavior of E_T^N and α in the temperature range of 298.15 to 353.15 K, it was noted that α had no direct hold on the polarity of PILs (Fig. 4). For 1-methylimidazolium class of PILs the α parameter was observed to be constant over the temperature change from 298.15 to 353.15 K. For 1-butylimidazolium class of PILs, a small increase in α was noted for [HbIm][HSO_4] and [HbIm][HCOO] with rise in temperature, while E_T^N remained constant. However, for [HbIm][CH_3COO] and [HbIm][CH_3CH_2COO], α decreased from 0.938 to 0.907 and 0.806 to 0.760, respectively, within the temperature range of 298.15 to 353.15 K. The exceptionally high α value for [HmIm][HSO_4] and [HbIm][HSO_4] may be due to the presence of oxyanions. The unusually higher α value makes them more polar than water. Surprisingly a negative α value for [HmIm][CH_3CH_2COO] was noted, which indicated the dominance of HBA basicity of anion over the HBD acidity of cation. Probably, retrotransfer of a quaternized proton to a more basic organic anion is responsible for this dramatic behavior.[31] Further, PILs form extensive hydrogen bonding which stabilizes both cation and anion, therefore, the probability of reverse proton transfer becomes low. Due to these opposing phenomena, a very small proportion of neutral moiety exists along with the PIL that leads to the lower α value, which is far beyond the α value for pure CH_3CH_2COOH *i.e.* 1.12.[31b]

The order of HBD tendency for 1-methylimidazolium class of ILs was found to be:

$$[\mathrm{HmIm}][\mathrm{HSO_4}] > [\mathrm{HmIm}][\mathrm{HCOO}] > [\mathrm{HmIm}][\mathrm{CH_3COO}] > [\mathrm{HmIm}][\mathrm{CH_3CH_2COO}]$$

Further, the HBD tendency for 1-butylimidazolium class of ILs was noted to be slightly higher than that for 1-methylimidazolium class of ILs as shown in Table 3. The presence of butyl chain in 1-butylimidazole surprisingly increases the HBD acidity. The order of HBD value for 1-butylimidazole class at 298.15 K was observed as:

$$[\mathrm{HbIm}][\mathrm{HSO_4}] > [\mathrm{HbIm}][\mathrm{HCOO}] > [\mathrm{HbIm}][\mathrm{CH_3COO}] > [\mathrm{HbIm}][\mathrm{CH_3CH_2COO}]$$

β Parameter

The hydrogen bond acceptor (HBA) basicity β was observed to decrease with an increase in temperature from 298.15 to 353.15 K. The β value increased with the increase in temperature from 298.15 to 353.15 K for [HmIm][HSO_4] and [HbIm][HSO_4]. Contrary to this, the β values for PILs containing $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions were found to be high and decreased with a rise in temperature (Fig. 5). Exceptionally low β values for [HmIm][CH_3CH_2COO] may be due to the presence of a neutral moiety along with the ionic species. However, β for [HmIm][CH_3CH_2COO] is very small than the β for pure CH_3CH_2COOH (0.45). Let us consider the following equilibria:

$$\mathrm{HA} + \mathrm{B} = [\mathrm{BH}^+] + \mathrm{A}^-$$

The strong acid (low pK_a) favors the equilibrium towards right due to complete transfer of proton showing high β value.

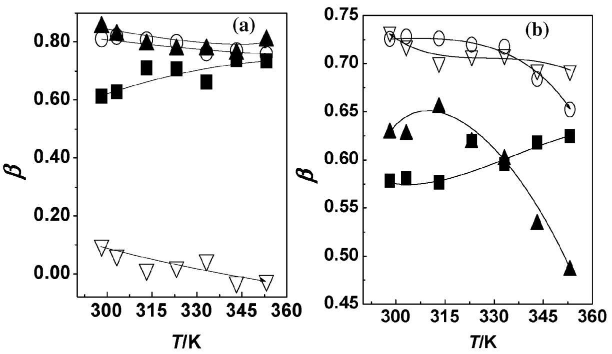

Fig. 5 The β–T plots for (a) [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽); (b) [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

However, the stabilization of cations and anions by hydrogen bonding opposes the formation of neutral species. Thus, it was assumed that the presence of ionic species favors high β value and a combination of neutral species *i.e.* solvents and ionic species favors low β value.

Further the observed trends for 1-methylimidazolium and 1-butylimidazolium classes of PILs were noted to be:

$$[\mathrm{HmIm}][\mathrm{HSO_4}] > [\mathrm{HbIm}][\mathrm{CH_3CH_2COO}] > [\mathrm{HbIm}][\mathrm{HCOO}] > [\mathrm{HbIm}][\mathrm{CH_3COO}]$$

$$[\mathrm{HbIm}][\mathrm{HSO_4}] > [\mathrm{HbIm}][\mathrm{CH_3CH_2COO}] > [\mathrm{HbIm}][\mathrm{HCOO}] > [\mathrm{HbIm}][\mathrm{CH_3COO}]$$

Thus, the anomalous trend in β values for PILs containing [HCOO], [CH_3COO] and [CH_3CH_2COO] anions is attributed only to the higher basicity (pK_a) and to the relative stability of these anions by hydrogen bonding.

π^* Parameter

The dipolarity/polarizability parameter, π^*, is based on the π–π^* electronic transition of *N*,*N*-diethyl-4-nitroaniline. Its magnitude depends upon the interactions of a chromophore with its cybotactic environment. With a rise in temperature the interaction weakens, giving rise to a decrease in π^* values. The high value of dipolarity/polarizability for 1-methylimidazolium class of PILs reveals that strong interaction occurs between the probe and PILs. With increasing temperature, non-linear decrease in the π^* values was observed as shown in Fig. 6. As evident, the trend in π^* value is:

$$[\mathrm{HmIm}][\mathrm{CH_3CH_2COO}] > [\mathrm{HmIm}][\mathrm{HSO_4}] > [\mathrm{HmIm}][\mathrm{HCOO}] > [\mathrm{HmIm}][\mathrm{CH_3COO}]$$

An exceptionally high dipolarity/polarizability ratio for [HmIm][CH_3CH_2COO] was recorded. A very low β value (0.10) and a moderate α value (0.66) can be attributed to the strong interactions between the dye and [HmIm][CH_3CH_2COO].

The π^* values for 1-butylimidazolium class of PILs were found to be slightly lower than those of the 1-methylimidazolium class of PILs. The introduction of a butyl chain on the imidazolium ring makes it more asymmetric, allowing a close approach of the cation to create the nanoscale regions with aliphatic character in which the probe molecule may partition.[32] This leads to the lower dipolarity/polarizability ratio for 1-butylimidazolium class of PILs. With a rise in temperature, π^* values decrease linearly. The observed trend in π^* values for 1-butylimidazolium class of PILs is as:

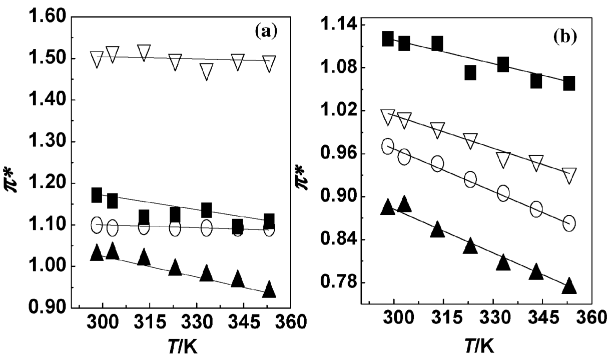

Fig. 6 The plots of π^*–T for (a) [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽); (b) [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

$$[\mathrm{HbIm}][\mathrm{CH_3CH_2COO}] > [\mathrm{HbIm}][\mathrm{HSO_4}] > [\mathrm{HbIm}][\mathrm{HCOO}] > [\mathrm{HbIm}][\mathrm{CH_3COO}]$$

Thus, polarity measurement (E_T^N value and Kamlet–Taft parameters) in PILs depends on the coulombic interaction which is governed by the basicity of anion and dipolarity/polarizability. The cation has a very small effect on the polarity of PIL.

Fajans' rule and polarity of ILs: reverse polarization

In 1923 Fajans developed his quanticule theory called as "Fajans' rule" to explain the development of partial covalent character in ionic bonds.[33] According to this theory a small, highly charged cation pulls the electron cloud of an anion, thereby developing covalent character in ionic bonds. Interaction of a cation of high charge density (hard) with an anion of high polarizability (soft) generates a covalent character between the ions in which the cation penetrates the electron cloud of the anion. Polarization of a large anion by a small cation is a very frequent phenomenon. However, is it possible to see the polarization of a large cation by a small anion? This turnaround of interaction between ions leading to covalent character is known as reverse polarization. However, practically it seems difficult because a soft cation holds its electron cloud, while a hard anion cannot repel its electron cloud to become a nucleus. For reverse polarization both the requirements are essential.

ILs are composed entirely of bigger ions and there is always a possibility to develop covalent character between them. Polarity study in different classes of APILs suggests them to be of low polarity, comparable to short chain alcohols. In all these classes of ILs it is difficult to correlate the polarity with cations and anions. In order to make an IL, it is desirable to incorporate a bulky cation having diffuse positive charge with various kinds of anions. A bulky cation with diffused charge behaves as a polarizable cation that can be easily distorted by an anion. In this condition there is a possibility of reverse polarization in IL. Hardness of anions, therefore, acts as a guiding criterion to develop the covalent character in ILs changing polarity. A strong interaction between ions creates more covalent character and therefore changes the polarity as measured by the solvatochromic method. Among various classes of ILs it was observed that soft anions such as [NTf_2]$^-$, [PF_6]$^-$ interact weakly with soft cations (such as alkylimidazolium) while hard anions such as [BF_4]$^-$, [$N(CN)_2$]$^-$ approach much closer towards the soft cations. The magnitude of this interaction governs the development of covalent character and thereby polarity of ILs. The E_T^N values for [BMIM][NTf_2] and [BMIM][PF_6] were measured as 0.645 and 0.669, respectively, while for [BMIM][$N(CN)_2$] as 0.629.[34] This small difference in E_T^N value arises due to the strong interactions of [$N(CN)_2$]$^-$ towards [BMIM]$^+$ as compared to those of [NTf_2]$^-$ and [PF_6]$^-$

offering less interactions for $[BMIM]^+$. Similarly, for [EMIM][NTf_2], [EMIM][PF_6] and [EMIM][$N(CN)_2$], the E_T^N values were observed as 0.658, 0.676 and 0.648, respectively.[34a,35] In the pyridinium-based ILs *i.e.* [BP][BF_4] and [BP][NTf_2], the E_T^N values recorded were 0.639 and 0.648, respectively.[22a] This again confirms the role of anion as a guiding factor to determine the polarity. An increase in the alkyl chain length has a similar effect on the E_T^N value for [OP][BF_4] and [OP][NTf_2], 0.606 and 0.617, respectively.[22a]

PILs due to the extensive hydrogen bonding act as hyperpolar media. A transfer of proton from Brønsted acid to Brønsted base generates the conjugate counterpart of acid and base. The relative basicity of an anion for a cation controls the development of covalent character. However, oxyanions such as $[HSO_4]^-$, $[NO_3]^-$, $[H_2PO_4]^-$ *etc.* due to the extensive network of hydrogen bonding generate highly polar PILs. The current polarity study in 1-methylimidazolium and 1-butylimidazolium classes of PILs with $[HSO_4]^-$, $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ as counter anions shows exceptionally low E_T^N values except for [HSO_4^-]. The lower polarity arises due to the increasing polarizability of anions. The stronger interaction of 1-methylimidazolium with the increasing polarizability of anions ($[HCOO]^-$, $[CH_3COO]^-$ and [$CH_3CH_2COO]^-$)) leads to the greater degree of polarization and hence, the E_T^N value becomes exceptionally low. The E_T^N values for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] were noted as 0.78, 0.61 and 0.50, respectively. The lowest value for [HmIm][CH_3CH_2COO] is close to that of dimethylsulfoxide (0.444), acetonitrile (0.46) and 2-propanol (0.50) acting as non-polar media. Similarly, for 1-butylimidazolium-based PILs with $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions, the E_T^N values were found to be 0.80, 0.77 and 0.75, respectively. The presence of $–C_4H_9$ lowers the polarizing power of the cationic core thereby decreasing the E_T^N value due to partial development of covalent character.

A correlation between the polarity (E_T^N value) and polarization of ions prompts us to develop a concept dealing with the polarizing power and polarizability of cation/anion. However, it is difficult to discuss the Kamlet–Taft parameters (α, β and π*) and polarization of ions on similar grounds. Only hydrogen bond donor tendency (α) was observed to depend on the nature of anion. More polarizable anions lead to lower α values than less polarizable anions. The α value for [BMIM][$N(CN)_2$] was observed to be 0.464, while for [BMIM][NTf_2] and [BMIM][PF_6] the values were 0.617 and 0.634, respectively.[34]

Conclusions

In conclusion, the polarity in PILs is anion specific. The PILs having organic anions play a crucial role in deciding the interaction of dye and ions in ILs due to their large hydrogen bond acceptor tendency β. The relative stabilization of the ions *via* hydrogen bonding and the reverse proton transfer between cations and anions control the α and β. The thermosolvatochromic study shows a constant polarity for PILs over a wide range of temperatures. It suggests that PILs can be used as media for those processes, where constant polarity is needed at higher temperatures. Further investigations are required to explore the data on the thermosolvatochromic study in other classes of PILs.

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Notes and references

1 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*b*) R. Sheldon, *Chem. Commun.*, 2001, 2399; (*c*) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag, Stuttgart, Germany, 2002; (*d*) J. Dupont and P. A. Suarez, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2441; (*e*) V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; (*f*) H. Weingartner, *Angew. Chem., Int. Ed.*, 2008, **47**, 654.
2 (*a*) T. Fischer, A. Sethi, T. Welton and J. Woolf, *Tetrahedron Lett.*, 1999, **40**, 793; (*b*) M. J. Earle, P. B. McCormac and K. R. Seddon, *Green Chem.*, 1999, **23**, 517; (*c*) M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877; (*d*) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, Germany, 3rd edn, 2003.
3 (*a*) H. Ohno, *Electrochemical Aspects of Ionic Liquids*, Wiley Interscience, New York, 2005; (*b*) S. A. Forsyth, J. M. Pringle and D. R. MacFarlane, *Aust. J. Chem.*, 2004, **57**, 113; (*c*) J. Esser, P. Wasserscheid and A. Jess, *Green Chem.*, 2004, **6**, 316; (*d*) J. G. Huddleston, A. E. Visser, W. M. Reichardt, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
4 (*a*) J. Fuller, A. C. Breda and R. T. Carlin, *J. Electrochem. Soc.*, 1997, **144**, 67; (*b*) W. Peter and K. Wilhelm, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*c*) J. Salminen, N. Papaiconomou, R. A. Kumar, J. M. Lee, J. Kerr, J. Newman and J. M. Prausnitz, *Fluid Phase Equilib.*, 2007, **261**, 421.
5 (*a*) N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; (*b*) M. Smiglak, A. Metlen and R. D. Rogers, *Acc. Chem. Res.*, 2007, **40**, 1182; (*c*) T. L. Merrigan, E. D. Bates, S. C. Dorman and J. H. Davis, *Chem. Commun.*, 2000, 2051; (*d*) D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth and G. B. Deacon, *Chem. Commun.*, 2001, 1430; (*e*) H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 19593.
6 (*a*) M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391; (*b*) R. D. Rogers and K. R. Seddon, Ionic Liquids as Green Solvents: Progress and Prospects, *ACS Symp. Ser.*, 2003, **856**, 599; (*c*) K. R. Seddon and R. D. Rogers, *ACS Symp. Ser.*, 2005, **901**, 334; (*d*) M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831; (*e*) C. Hardacre, J. B. Holbrey, N. Nieuwenhuyzen and T. G. A. Youngs, *Acc. Chem. Res.*, 2007, **40**, 1106.
7 M. Freemantle, Designer Solvents, *Chem. Eng. News*, 1998, **76**, 32.
8 (*a*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*b*) J. Dupont, R. F. De Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667; (*c*) D. R. MacFarlane and M. Forsyth, *Adv. Mater.*, 2001, **13**, 957; (*d*) M. C. Buzzeo, R. G. Evans and R. G. Compton, *ChemPhysChem*, 2004, **5**, 1106; (*e*) R. Hagiwara and Y. Ito, *J. Fluorine Chem.*, 2000, **105**, 221.
9 P. Walden, *Bull. Acad. Imper. Sci.*, 1914, 1800.
10 (*a*) Z. Y. Du, Z. P. Li, S. Guo, J. Zhang, L. Y. Zhu and Y. Q. Deng, *J. Phys. Chem. B*, 2005, **109**, 19542; (*b*) H. Schneider and J. Stroka, *Pol. J. Chem.*, 1994, **68**, 795; (*c*) R. M. Lau, M. J. Sorgedrager, G. Carrea, F. Van Rantwijk, F. Secundo and R. A. Sheldon, *Green Chem.*, 2004, **6**, 483.
11 (*a*) Y. Du and F. Tian, *J. Chem. Res.*, 2006, **8**, 486; (*b*) R. V. Hangarge, D. V. Jarikote and M. S. Shingare, *Green Chem.*, 2002, **4**, 266.
12 T. Jiang, H. X. Gao, B. X. Han, G. Y. Zhao, Y. H. Chang, W. Z. Wu, L. Gao and G. Y. Yang, *Tetrahedron Lett.*, 2004, **45**, 2699.
13 (*a*) C. F. Poole, *J. Chromatogr.*, 2004, **1037**, 49; (*b*) J. L. Anderson, J. Ding, T. Welton and D. W. Armstrong, *J. Am. Chem. Soc.*, 2002, **124**, 14247.
14 C. J. F. Boettcher, *Theory of Dielectric Polarization*, Elsevier, Amsterdam, 1973, vol. 1.
15 (*a*) C. Chiappe, C. S. Pomelli and S. Rajamani, *J. Phys. Chem. B*, 2011, **115**, 9653; (*b*) E. S. Giray, C. Chiappe, Z. Tunal and S. Rajamani, *Phys. Chem. Chem. Phys.*, 2011, **1**, 761.

16 M. J. Muldoon, S. Aki, J. L. Anderson, J. K. Dixon and J. F. Brennecke, *J. Phys. Chem. B*, 2007, **111**, 9001.

17 C. Wakai, A. Oleinikova, M. Ott and H. Weingartner, *J. Phys. Chem. B*, 2005, **109**, 17028.

18 (*a*) M. Kruger, E. Brundermann, S. Funkner, H. Weingartner and M. Havenith, *J. Chem. Phys.*, 2010, **132**, 101101; (*b*) M. M. Huang and H. Weingartner, *ChemPhysChem*, 2008, **9**, 2172.

19 (*a*) M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831; (*b*) M. Y. Lui, L. Crowhurst, J. P. Hallett, P. A. Hunt, H. Niedermeyer and T. Welton, *Chem. Sci.*, 2011, **2**, 1491.

20 (*a*) J. M. Lee, S. Ruckes and J. M. Prausnitz, *J. Phys. Chem. B*, 2008, **112**, 1473; (*b*) J. M. Lee and J. M. Prausnitz, *Chem. Phys. Lett.*, 2010, **492**, 55; (*c*) A. Sarkar, S. Trivedi, G. A. Baker and S. Pandey, *J. Phys. Chem. B*, 2008, **112**, 14927; (*d*) C. T. Martins, B. M. Sato and O. A. EI Seoud, *J. Phys. Chem. B*, 2008, **112**, 8330.

21 (*a*) B. R. Mellein, S. N. V. K. Aki, R. L. Ladewski and J. F. Brenneck, *J. Phys. Chem. B*, 2007, **111**, 131; (*b*) L. Crowhurst, P. R. Mawdsley, J. M. Parez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.

22 (*a*) N. D. Khupse and A. Kumar, *J. Phys. Chem. B*, 2010, **114**, 376; (*b*) N. D. Khupse and A. Kumar, *J. Phys. Chem. B*, 2011, **115**, 711.

23 N. D. Khupse and A. Kumar, *J. Phys. Chem. A*, 2011, **115**, 10211.

24 C. Reichardt, *Green Chem.*, 2005, **7**, 339.

25 (*a*) S. Tiwari and A. Kumar, *Angew. Chem., Int. Ed.*, 2006, **45**, 4824; (*b*) S. Tiwari, N. D. Khupse and A. Kumar, *J. Org. Chem.*, 2008, **73**, 9075; (*c*) N. D. Khupse and A. Kumar, *J. Solution Chem.*, 2009, **38**, 589; (*d*) G. S. Rai and A. Kumar, *Chem. Phys. Lett.*, 2010, **496**, 143; (*e*) G. S. Rai and A. Kumar, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14715.

26 H. Ohno and M. Yoshizawa, *Solid State Ionics*, 2002, **303**, 154.

27 For example see: A. Stark, P. Behrend, O. Braun, A. Muller, J. Ranke, B. Ondruschka and B. Jastorff, *Green Chem.*, 2008, **10**, 1152.

28 K. R. Seddon, A. Stark and M. J. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275.

29 W. Ogihar, T. Aoyama and H. Ohno, *Chem. Lett.*, 2004, 11.

30 L. H. Lee, *Langmuir*, 1996, **12**, 1681.

31 (*a*) M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411; (*b*) J. Stoimenovski, E. I. Izgorodina and D. R. MacFarlane, *Phys. Chem. Chem. Phys.*, 2008, **10**, 80.

32 M. N. Kobrak, *Green Chem.*, 2008, **10**, 80.

33 K. Fajans, *Nature*, 1923, **11**, 165.

34 (*a*) R. Bini, C. Chiappe, V. Lioplis Mestre, C. S. Pomelli and T. Welton, *Org. Biomol. Chem.*, 2008, **6**, 2522; (*b*) L. Crowhurst, P. R. Mawdsley, J. M. Parez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192; (*c*) C. Chiappe and D. Pieraccini, *J. Phys. Chem. A*, 2006, **110**, 4937.

35 S. Zhang, X. Qi, X. Ma, L. Lu and Y. Deng, *J. Phys. Chem. B*, 2010, **114**, 3912.