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## ARTICLE TYPE

## Task specific Ionic liquids as polarity shifting additives of common organic solvents

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The effect in polarity of addition of small quantities of room temperature ionic liquids (RTILs) to common organic solvents (acetonitrile, ethanol, tetrahydrofuran, isopropanol and chloroform) is explored. It is found that solvent polarity always increases with addition of RTILs following a linear increase until reaching a plateau. [C<sub>2</sub>OHMIM][PF<sub>6</sub>], [C<sub>10</sub>MIM][BF<sub>4</sub>] and [EMIM][NTf<sub>2</sub>] have a dramatic influence in the polarity of acetonitrile, displacing it by more than 0.15 in the normalized polarity scale ( $E_T^N$ ). When the same RTIL ([BMIM][BF<sub>4</sub>]) is added in the same quantity to different solvents, it is observed that the polarity obtained follows generically the same trend as the polarities of the pure solvents, with the exception of chloroform, which has a higher polarity than tetrahydrofuran when pure, but lower when [BMIM][BF<sub>4</sub>] is added.

## Introduction

According to IUPAC, polarity is defined as the “overall solvation capability (or solvation power) for (i) educts and products, which influences chemical equilibria; (ii) reactants and activated complexes (“transition states”), which determines reaction rates; and (iii) ions or molecules in their ground and first excited state, which is responsible for light absorptions in the various wavelength regions. This overall solvation capability depends on the action of all, nonspecific and specific, intermolecular solute–solvent interactions, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute”<sup>1</sup>.

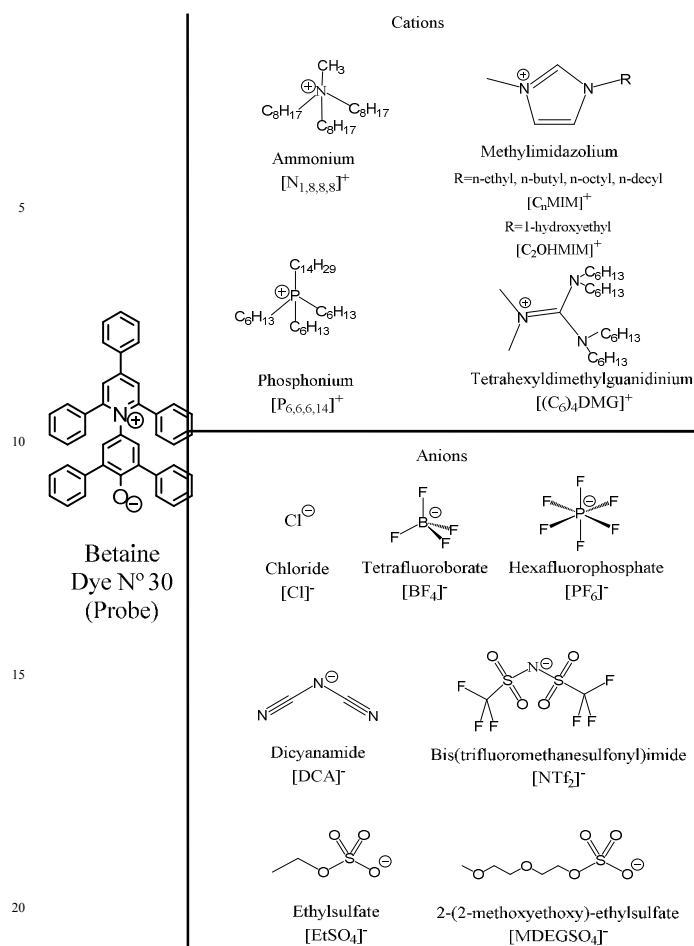
Polarity can be shifted with appropriate additives<sup>2,3,4,5</sup>. This effect can be explored for a variety of applications, such as separations<sup>2,3</sup> or reactions<sup>3,4</sup>. It is well known that extraction rates can be increased by addition of an appropriate co-solvent<sup>3,5</sup> or that the polarity of the solvent influences tautomeric equilibria and solvent change can be used to displace it<sup>3</sup>. Recently, solvent polarity was used to influence the cis-to-trans isomerization of 4-aminoazobenzene, being found that the rate of thermal isomerization is highly dependent on solvent polarity, with accelerated rates being observed in polar solvents<sup>6</sup>. However, to this date, there are only few examples of the application of ionic liquids for these purposes. It was reported that the addition of small quantities of [BMIM][PF<sub>6</sub>] to propylene carbonate results in a dramatic increase in polarity<sup>7</sup>. When using minute quantities of [BMIM][Cl] as co-solvent in acetonitrile for the extraction of mixed tocopherols dissolved in hexane it was found that the selectivity of  $\delta$ -tocopherol to  $\alpha$ -tocopherol was four times larger than when using pure acetonitrile and the distribution coefficients were at least eighteen times larger than when using pure [BMIM][Cl]<sup>8</sup>. Mellein and co-workers tested the inverse case,

i.e., the addition of small quantities of organic solvents to ionic liquids and found that the polarity of ILs is largely unaffected by the organic cosolvent<sup>9</sup>. Baker and co-workers showed equally that the addition of small quantities of water to [BMIM][PF<sub>6</sub>] has no significant effect in the polarity of the IL<sup>10</sup>. It was also shown that the presence in ILs of common impurities resulting from the synthetic pathways employed can influence the polarity of the IL<sup>11</sup>.

However, it is not simple to measure polarity and so far only indirect methods have been found to measure the polarity of a medium. By far the easiest method to achieve this measurement is through the addition of a solvatochromic probe, i.e., a probe which will change colour according to the polarity of the environment it is in. The most widely used is the negatively solvatochromic pyridinium N-phenolate betaine dye, also commonly known as Reichardt’s dye n° 30, for which it is possible to measure the wavelength of the highest absorption peak in the visible region of the spectra and correlate it with the polarity of the medium it is in<sup>12,13,14,15</sup>. A normalized scale (the  $E_T(30)$  scale) can be built based on the molar electronic transition energies (ET) of the dissolved probe, measured in kilocalories per mole (kcal/mol) at room temperature (25 °C) and normal pressure (1 bar).  $E_T(30)$  can be expressed as:

$$E_T(30)/(\text{kcal mol}^{-1}) = h c \tilde{\nu}_{\max} N_A = (2.8591 \times 10^{-3}) \tilde{\nu}_{\max}/\text{cm}^{-1} = 28591/(\lambda_{\max}/\text{nm}) \quad (\text{eq 1})$$

where  $\tilde{\nu}_{\max}$  is the wavenumber,  $\lambda_{\max}$  is the maximum wavelength and  $h$ ,  $c$ , and  $N_A$  are the Planck’s constant, the speed of light, and Avogadro’s constant, respectively<sup>13</sup>. Although this probe is not able to measure the least polar solvents, it is possible to use a



**Fig. 1** Molecular structures of ionic liquids cations and anions and probe used in this work.

more lipophilic betaine dye with five t-butyl groups in the 4-positions of the five peripheral phenyl groups of the standard betaine dye, which presents a linear correlation for the  $E_T$  values with the standard betaine dye<sup>14</sup>. It is thus possible to build a dimensionless normalized polarity scale,  $E_T^N$ , expressed in equation 2, ranging from 0 (the least polar molecule, tetramethylsilane, TMS) to 1 (the most polar molecule, water)<sup>13</sup>.

$$E_T^N = \frac{[E_T(\text{solvent}) - E_T(\text{TMS})]}{[E_T(\text{water}) - E_T(\text{TMS})]} = \frac{[E_T(\text{solvent}) - 30.7]}{32.4} \quad (\text{eq } 2)$$

However, this method when described for ILs has some limitations. In fact, each polarity scale is an estimate which depends largely on the probe being used, meaning there is no definitive probe for polarity measurements. Different polarity scales can even present different relative polarities between the same set of solvents being measured. In the case of the  $E_T(30)$  scale, when applied to ILs, the value measured will have a contribution resulting from an interaction of the phenoxide oxygen of the probe with the IL cation, which is not present when the probed solvent is molecular<sup>11</sup>. The solution normally employed to overcome this problem is to use different probes in order to assess the Kamlet-Taft parameters  $\alpha$ ,  $\beta$  and  $\pi^*$ , which

represent respectively hydrogen bond acidity, hydrogen bond basicity and dipolarity/ polarizability effects. But to do this it is needed to employ a large number of probes, which becomes impractical. Welton tried to overcome this problem by doing a systematic study in order to reduce the number of probes used<sup>11</sup> and later by using computational methods recurring to the aid of the COnductor-like Screening MOdel for Real Solvents (COSMO-RS)<sup>16</sup>.

In a previous work<sup>17</sup>, we proposed not to measure the ILs polarity directly, but to study the influence in the polarity of acetonitrile with the addition of small quantities of imidazolium ionic liquids using Reichardt's dye as a probe. It was shown that different ionic liquids can be used as additives, in small quantities, in order to shift the polarity of acetonitrile. Herein, we expand the range of ionic liquids studied in acetonitrile by adding imidazolium ionic liquids with a smaller or larger side chain (1-ethyl-3-methylimidazolium and 1-decyl-3-methylimidazolium, respectively) or with a side chain presenting an hydroxyl group (1-hydroxyethyl-3-methylimidazolium), as well as other classes of cations (such as ammonium, phosphonium and guanidinium). Molecular structures of RTILs anions and cations employed in this work, as well as of the probe used, are presented in Figure 1. Furthermore, we also explore the addition of ionic liquids to other common organic solvents, such as ethanol, isopropanol, tetrahydrofuran and chloroform.

## Materials and Methods

All RTILs used in this work are from Solchemar Lda (>98% purity), except  $[N_{1,8,8,8}][Cl]$  (Aldrich, >98%),  $[EMIM][MDEGSO_4]$  (Solvent Innovation, >98%) and  $[P_{6,6,6,14}][Cl]$  (Cytec, >98%). Acetonitrile was HPLC grade (Scharlau). Ethanol, tetrahydrofuran (THF), isopropanol and chloroform were all p.a. in purity and from Sigma Aldrich. Betaine dye n°. 30 was from Sigma-Aldrich (>90% purity). The water content of all ILs used in this work was measured by Karl Fischer titration with a Metrohm 831 KF Coulometer, and it was found to be between 9 and 200 ppm.

## UV/Visible Spectroscopy

A solution of 20 mg betaine dye n°. 30 in 100 mL of appropriate solvent was prepared as stock solution for the measurements. From this stock solution, 2.4 mL were placed in a quartz cell of 10 mm path length. The appropriate volume (2, 4, 6, 8 or 10  $\mu$ L) of the ionic liquid to be measured was added and the cell was agitated for complete dissolution. The exception was  $[(C_6)_4DMG][Cl]$  which had to be diluted with the solvent being studied before the addition, as very small amounts of this IL would completely decolorize the Reichardt's dye solution. Measurements were performed in a Perkin Elmer Lambda 35 UV/Vis Spectrometer. The results are the average of at least two measurements at 294 K.

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Table 1 Effects in polarity of the addition of ionic liquids to acetonitrile.†

| Mixture (ACN + RTIL) <sup>a</sup>                    | Volume RTIL (μL) <sup>b</sup> | X <sub>RTIL/ACN</sub> × 10 <sup>-4</sup> <sup>c</sup> | μ <sub>RTIL/Betaine</sub> <sup>d</sup> | Wavelength (nm) <sup>e</sup> | E <sub>T</sub> (30) <sup>f</sup> | E <sub>T</sub> <sup>g</sup> | Water content (ppm) <sup>h</sup> |
|------------------------------------------------------|-------------------------------|-------------------------------------------------------|----------------------------------------|------------------------------|----------------------------------|-----------------------------|----------------------------------|
| ACN                                                  | -                             | -                                                     | -                                      | 626.1                        | 45.67                            | 0.462                       | <10                              |
| [N <sub>1,8,8,8</sub> ][Cl]                          | 10                            | 4.94                                                  | 22.41                                  | 624.4                        | 45.79                            | 0.466                       | <20                              |
| [N <sub>1,8,8,8</sub> ][DCA]                         | 10                            | 4.45                                                  | 20.20                                  | 623.1                        | 45.89                            | 0.469                       | <20                              |
| [P <sub>6,6,6,14</sub> ][Cl]                         | 6                             | 2.22                                                  | 10.06                                  | 624.3                        | 45.80                            | 0.466                       | <15                              |
| [P <sub>6,6,6,14</sub> ][BF <sub>4</sub> ]           | 10                            | 3.54                                                  | 16.08                                  | 624.7                        | 45.77                            | 0.465                       | <20                              |
| [P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]          | 10                            | 2.99                                                  | 13.56                                  | 625.4                        | 45.72                            | 0.464                       | <15                              |
| [P <sub>6,6,6,14</sub> ][DCA]                        | 10                            | 3.56                                                  | 16.15                                  | 624.7                        | 45.77                            | 0.465                       | <15                              |
| [EMIM][NTf <sub>2</sub> ]                            | 4                             | 3.39                                                  | 15.37                                  | 531.9                        | 53.76                            | 0.712                       | <60                              |
| [EMIM][EtSO <sub>4</sub> ]                           | 4                             | 4.55                                                  | 20.65                                  | 623.1                        | 45.89                            | 0.469                       | <150                             |
| [EMIM][MDEGSO <sub>4</sub> ]                         | 4                             | 3.24                                                  | 14.72                                  | 621.7                        | 45.99                            | 0.472                       | <150                             |
| [C <sub>10</sub> MIM][BF <sub>4</sub> ]              | 2                             | 1.5                                                   | 6.84                                   | 625.6                        | 45.70                            | 0.463                       | <100                             |
| [C <sub>2</sub> OHMIM][PF <sub>6</sub> ]             | 4                             | 4.73                                                  | 21.46                                  | 564.0                        | 50.70                            | 0.617                       | <150                             |
| [C <sub>2</sub> OHMIM][BF <sub>4</sub> ]             | 4                             | 5.31                                                  | 24.12                                  | 623.0                        | 45.90                            | 0.469                       | <200                             |
| [(C <sub>6</sub> ) <sub>4</sub> DMG][Cl]             | 0.6                           | 0.26                                                  | 1.16                                   | 624.5                        | 45.78                            | 0.465                       | <100                             |
| [BMIM][Cl] <sup>17</sup>                             | 1.8 mg                        | 2.24                                                  | 10.17                                  | 622.6                        | 45.93                            | 0.470                       | 103                              |
| [BMIM][BF <sub>4</sub> ] <sup>17</sup>               | 4                             | 4.31                                                  | 19.55                                  | 620.9                        | 46.05                            | 0.474                       | 190                              |
| [BMIM][PF <sub>6</sub> ] <sup>17</sup>               | 4                             | 4.16                                                  | 18.89                                  | 621.3                        | 46.02                            | 0.473                       | 47                               |
| [BMIM][NTf <sub>2</sub> ] <sup>17</sup>              | 6                             | 4.51                                                  | 20.49                                  | 618.1                        | 46.26                            | 0.480                       | 56                               |
| [BMIM][DCA] <sup>17</sup>                            | 4                             | 4.50                                                  | 20.42                                  | 622.7                        | 45.91                            | 0.470                       | 36                               |
| [C <sub>8</sub> MIM][BF <sub>4</sub> ] <sup>17</sup> | 4                             | 3.42                                                  | 15.52                                  | 622.5                        | 45.93                            | 0.470                       | 53                               |

<sup>a</sup> All ionic liquids were added pure to acetonitrile, with the exception of [(C<sub>6</sub>)<sub>4</sub>DMG][Cl], which was first diluted in acetonitrile and then added to the solution with Reichardt's dye. <sup>b</sup> Except [BMIM][Cl] which is solid at room temperature. <sup>c</sup> Mole fraction of RTIL in acetonitrile. <sup>d</sup> Number of moles of RTIL per mole of betaine dye. <sup>e</sup> Wavelength refers to the value obtained after addition of the indicated quantity of RTIL. <sup>f</sup> Calculated by eq 1. <sup>g</sup> Calculated by equation 2. <sup>h</sup> Maximum value of water content measured by Karl Fischer titration.

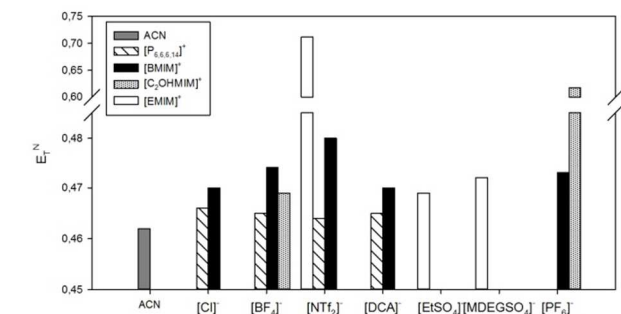


Fig. 2 Anion effect in E<sub>T</sub><sup>N</sup> values of acetonitrile. Values for [BMIM]<sup>+</sup> RTILs from a previous work<sup>17</sup>.

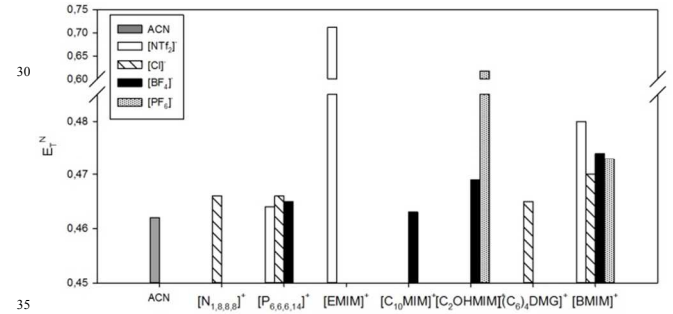


Fig. 3 Cation effect in E<sub>T</sub><sup>N</sup> values of acetonitrile. Values for [BMIM]<sup>+</sup> RTILs from a previous work<sup>17</sup>.

Results and Discussion

For the polarity studies were selected thirteen commercially available RTILs, to expand the previous studies made in acetonitrile, based on trioctylmethylammonium ([N<sub>1,8,8,8</sub>]<sup>+</sup>), trihexyltetradecylphosphonium ([P<sub>6,6,6,14</sub>]<sup>+</sup>), alkylmethylimidazolium ([C<sub>n</sub>MIM]<sup>+</sup> (n = 2, 4, 8 or 10) or [C<sub>2</sub>OHMIM]<sup>+</sup>) and tetrahexyldimethylguanidinium ([[(C<sub>6</sub>)<sub>4</sub>DMG]<sup>+</sup>) cations combined with ethylsulfate ([EtSO<sub>4</sub>]<sup>-</sup>), 2-(2-methoxyethoxy)-ethylsulfate ([MDEGSO<sub>4</sub>]<sup>-</sup>), chloride ([Cl]<sup>-</sup>), tetrafluoroborate ([BF<sub>4</sub>]<sup>-</sup>), hexafluorophosphate ([PF<sub>6</sub>]<sup>-</sup>), dicyanamide ([DCA]<sup>-</sup>) and bis(trifluoromethanesulfonyl)imide ([NTf<sub>2</sub>]<sup>-</sup>) anions. For ease of representation, the 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations will be represented as [EMIM]<sup>+</sup> and [BMIM]<sup>+</sup>, respectively. This

selection of RTILs included more hydrophobic or hydrophilic cations and anions in order to elucidate its influence in the polarity studies.

In Table 1 are presented the values obtained by UV/Vis spectroscopy of the addition of RTILs to a solution of betaine dye (0.36 mM) in acetonitrile. This table includes the mole fraction of RTIL in acetonitrile (X<sub>RTIL/ACN</sub>), the number of moles of RTIL per mole of betaine dye (μ<sub>RTIL/Betaine</sub>), the wavelength of the maximum of the intramolecular CT absorption band of the betaine dye, and the respective E<sub>T</sub><sup>N</sup> and E<sub>T</sub>(30) values. Here are also included values for RTILs with [BMIM]<sup>+</sup> as cation, which were published previously<sup>17</sup>, for comparison purposes.

Figure 2 plots the effects in E<sub>T</sub><sup>N</sup> values of acetonitrile of the

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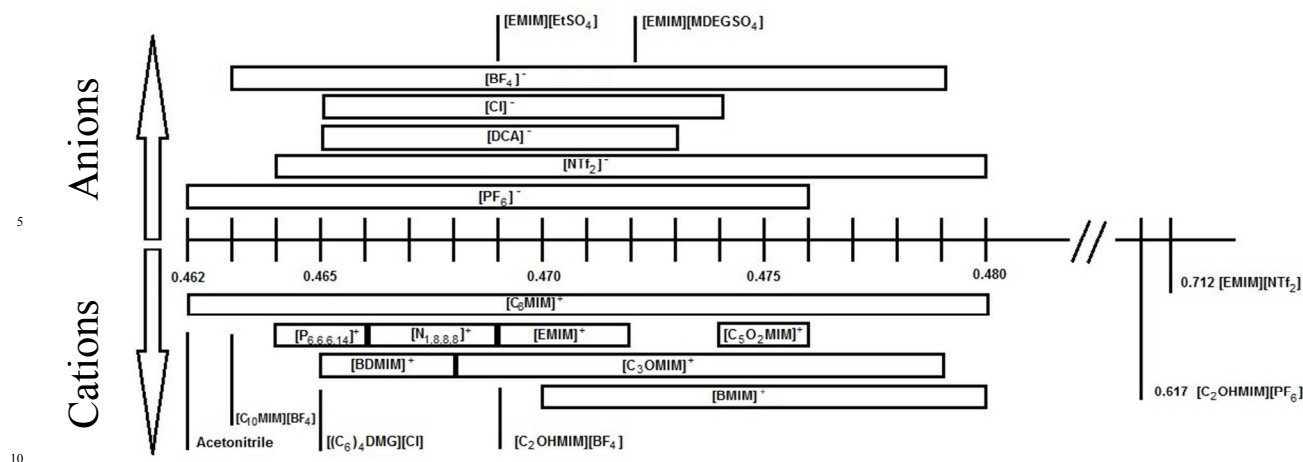


Fig. 4 Range of effects in acetonitrile polarity for individual anions and cations, in  $E_T^N$  values, including values from this work and our previous work<sup>17</sup>.

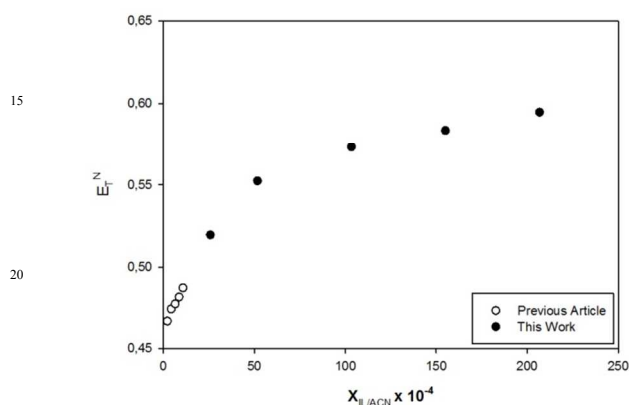


Fig. 5 Effect in  $E_T^N$  values of continuous addition of [BMIM][BF<sub>4</sub>] to acetonitrile. Values from this work and previous article<sup>17</sup>.

addition of RTILs by anion, for the cations [P<sub>6,6,6,14</sub>]<sup>+</sup>, [EMIM]<sup>+</sup>, [BMIM]<sup>+</sup> and [C<sub>2</sub>OHMIM]<sup>+</sup>, whereas Figure 3 plots the effects in  $E_T^N$  values of acetonitrile by the addition of RTILs by cation, for the anions [Cl]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup> and [NTf<sub>2</sub>]<sup>-</sup>. In both figures are shown values of RTILs tested in a previous work (those with [BMIM]<sup>+</sup> as cation)<sup>17</sup>, for comparison.

From Figures 2 and 3 it is apparent that the influence in polarity is linked mainly to the cation, which is in perfect accordance with what we had previously observed<sup>17</sup>. The cation [P<sub>6,6,6,14</sub>]<sup>+</sup> has consistently the lowest polarity with the four anions plotted in Figure 2. This is an obvious consequence of its structure with four long arms without any functionalization. It also shows a polarity effect trend inverse to that of the [BMIM]<sup>+</sup> cation, i.e., while for [BMIM]<sup>+</sup> polarity increases in the sequence [Cl]<sup>-</sup> < [DCA]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [NTf<sub>2</sub>]<sup>-</sup>, for [P<sub>6,6,6,14</sub>]<sup>+</sup> the sequence is [NTf<sub>2</sub>]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [DCA]<sup>-</sup> < [Cl]<sup>-</sup>. The cation [N<sub>1,8,8,8</sub>]<sup>+</sup> presents similar values in the polarities changes as [P<sub>6,6,6,14</sub>]<sup>+</sup>. It should be noticed

that these cations are structurally similar, being composed of a central atom (nitrogen or phosphorus), with four unfunctionalized carbon chains (one methyl and three octyl for [N<sub>1,8,8,8</sub>]<sup>+</sup>, three hexyl and one tetradecyl for [P<sub>6,6,6,14</sub>]<sup>+</sup>). However, lower molar fractions of [P<sub>6,6,6,14</sub>]<sup>+</sup> were used, due to the longer carbon chains.

Polarity is, however, a broad concept which includes several parameters. Thus, the shifts in polarity which are observed can be explained by the cumulative contributions of individual parameters. In this context, it is also important to consider the acidity of selected RTILs in these studies<sup>11,18</sup>. As can be seen for RTILs of the [BMIM] cation type the polarity behaves in the order: [Cl]<sup>-</sup> ~ [DCA]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> < [NTf<sub>2</sub>]<sup>-</sup>. This can be directly related to the order of acidity, with the strongly coordinating chloride reducing the acidity of the cation. High resonance stabilized anions (e.g. [NTf<sub>2</sub>]<sup>-</sup>) can influence a weak coordination of anion and cation, therefore the acidity of these RTILs is higher. For RTILs without acidic protons, such as tetraalkyl phosphonium or ammonium salts, the order [NTf<sub>2</sub>]<sup>-</sup> < [BF<sub>4</sub>]<sup>-</sup> ~ [DCA]<sup>-</sup> < [Cl]<sup>-</sup> can be interpreted as the order of dipolarity of these compounds.

Different authors already described the importance of organic cations to tune physical and chemical properties of final RTIL. Many studies using solvatochromic polarity probes have described higher polarity effect for selected organic cation than anions. It is known that different kinds of strong interactions of each organic cation and other molecules (e.g. organic solvents) can be established. RTILs based on Tetra-alkylammonium and tetra-alkylphosphonium cations only establish electrostatic interactions but several RTILs based on alkylmethylimidazolium can also establish H-bonding interactions (acidic H-2 from methylimidazolium ring) and  $\pi$ - $\pi$  interactions (with other aromatic compounds). As it is also known that Reichardt's dye has a higher sensitivity to the acidity of the medium, the trends observed can be a result of these interactions.



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Table 2 Effects in polarity of the addition of ionic liquids to ethanol. †

| Mixture (EtOH + RTIL) <sup>a</sup>       | Volume RTIL (μL) | X <sub>RTIL/EtOH</sub> × 10 <sup>-4</sup> <sup>b</sup> | μ <sub>RTIL/Betaine</sub> <sup>c</sup> | Wavelength (nm) <sup>d</sup> | E <sub>T</sub> (30) <sup>e</sup> | E <sub>T</sub> <sup>f</sup> | Water content (ppm) <sup>g</sup> |
|------------------------------------------|------------------|--------------------------------------------------------|----------------------------------------|------------------------------|----------------------------------|-----------------------------|----------------------------------|
| EtOH                                     | -                | -                                                      | -                                      | 550.5                        | 51.94                            | 0.655                       | <0.5                             |
| [EMIM][EtSO <sub>4</sub> ]               | 4                | 5.08                                                   | 20.65                                  | 548.5                        | 52.13                            | 0.661                       | <150                             |
| [EMIM][MDEGSO <sub>4</sub> ]             | 6                | 5.44                                                   | 22.09                                  | 546.5                        | 52.32                            | 0.667                       | <150                             |
| [BMIM][PF <sub>6</sub> ]                 | 4                | 4.65                                                   | 18.89                                  | 548.5                        | 52.13                            | 0.661                       | 47                               |
| [BMIM][BF <sub>4</sub> ]                 | 4                | 4.81                                                   | 19.55                                  | 549.5                        | 52.03                            | 0.658                       | 190                              |
| [BMIM][NTf <sub>2</sub> ]                | 6                | 5.05                                                   | 20.49                                  | 548.5                        | 52.13                            | 0.661                       | 56                               |
| [BMIM][DCA]                              | 4                | 5.03                                                   | 20.42                                  | 549.5                        | 52.03                            | 0.658                       | 36                               |
| [C <sub>8</sub> MIM][PF <sub>6</sub> ]   | 6                | 5.29                                                   | 21.47                                  | 548.0                        | 52.17                            | 0.663                       | 19                               |
| [C <sub>8</sub> MIM][BF <sub>4</sub> ]   | 6                | 5.73                                                   | 23.28                                  | 548.5                        | 52.13                            | 0.661                       | 53                               |
| [C <sub>10</sub> MIM][BF <sub>4</sub> ]  | 6                | 5.06                                                   | 20.53                                  | 545.5                        | 52.41                            | 0.670                       | <100                             |
| [C <sub>2</sub> OHMIM][BF <sub>4</sub> ] | 3                | 5.94                                                   | 24.12                                  | 551.0                        | 51.89                            | 0.654                       | <200                             |

<sup>a</sup> All ionic liquids were added pure to ethanol <sup>b</sup> Mole fraction of RTIL in ethanol. <sup>c</sup> Number of moles of RTIL per mole of betaine dye. <sup>d</sup> Wavelength refers to the value obtained after addition of the indicated quantity of RTIL. <sup>e</sup> Calculated by eq 1. <sup>f</sup> Calculated by equation 2. <sup>g</sup> Maximum value of water content measured by Karl Fischer titration.

Table 3 Effects in polarity of the addition of ionic liquids to tetrahydrofuran, chloroform and isopropanol. †

| Mixture (Solvent + RTIL)                | Volume RTIL (μL) | X <sub>RTIL/Solvent</sub> × 10 <sup>-4</sup> | μ <sub>RTIL/Betaine</sub> | Wavelength (nm) | E <sub>T</sub> (30) | E <sub>T</sub> <sup>f</sup> | Water content (ppm) |
|-----------------------------------------|------------------|----------------------------------------------|---------------------------|-----------------|---------------------|-----------------------------|---------------------|
| Tetrahydrofuran                         |                  |                                              |                           |                 |                     |                             |                     |
| THF                                     | -                | -                                            | -                         | 759.0           | 37.67               | 0.215                       | <0.2                |
| [BMIM][PF <sub>6</sub> ]                | 4                | 6.47                                         | 18.89                     | 640.7           | 44.62               | 0.430                       | 47                  |
| [BMIM][BF <sub>4</sub> ]                | 4                | 6.70                                         | 19.55                     | 660.1           | 43.31               | 0.389                       | 190                 |
| [C <sub>8</sub> MIM][PF <sub>6</sub> ]  | 6                | 7.35                                         | 21.47                     | 643.3           | 44.45               | 0.424                       | 19                  |
| [C <sub>10</sub> MIM][BF <sub>4</sub> ] | -                | -                                            | -                         | forms emulsion  |                     |                             | <100                |
| CHCl <sub>3</sub>                       | -                | -                                            | -                         | 703.2           | 40.66               | 0.307                       | <0.1                |
| Chloroform                              |                  |                                              |                           |                 |                     |                             |                     |
| [BMIM][PF <sub>6</sub> ]                | -                | -                                            | -                         | forms emulsion  |                     |                             | 47                  |
| [BMIM][BF <sub>4</sub> ]                | 4                | 6.65                                         | 19.55                     | 667.0           | 42.87               | 0.376                       | 190                 |
| [C <sub>8</sub> MIM][PF <sub>6</sub> ]  | 6                | 7.30                                         | 21.47                     | 649.5           | 44.02               | 0.411                       | 19                  |
| [C <sub>10</sub> MIM][BF <sub>4</sub> ] | -                | -                                            | -                         | forms emulsion  |                     |                             | <100                |
| i-PrOH                                  | -                | -                                            | -                         | 593.0           | 48.21               | 0.541                       | <0.3                |
| Isopropanol                             |                  |                                              |                           |                 |                     |                             |                     |
| [BMIM][PF <sub>6</sub> ]                | 4                | 6.10                                         | 18.89                     | 585.9           | 48.80               | 0.559                       | 47                  |
| [BMIM][BF <sub>4</sub> ]                | 4                | 6.31                                         | 19.55                     | 588.2           | 48.61               | 0.553                       | 190                 |
| [C <sub>8</sub> MIM][PF <sub>6</sub> ]  | 6                | 6.93                                         | 21.47                     | 580.2           | 49.28               | 0.573                       | 19                  |
| [C <sub>10</sub> MIM][BF <sub>4</sub> ] | 6                | 6.63                                         | 20.53                     | 577.4           | 49.52               | 0.581                       | <100                |

<sup>a</sup> All ionic liquids were added pure to the solvent. <sup>b</sup> Mole fraction of RTIL in solvent. <sup>c</sup> Number of moles of RTIL per mole of betaine dye. <sup>d</sup> Wavelength refers to the value obtained after addition of the indicated quantity of RTIL. <sup>e</sup> Calculated by eq 1. <sup>f</sup> Calculated by equation 2. <sup>g</sup> Maximum value of water content measured by Karl Fischer titration.

[EMIM][NTf<sub>2</sub>] presents the highest polarity value measured (0.712), which could be a consequence of the high electronegativity of the [NTf<sub>2</sub>]<sup>-</sup> anion, which is not sufficiently counterbalanced by the relatively small cation [EMIM]<sup>+</sup>. In fact, when the less electronegative anions ([EtSO<sub>4</sub>]<sup>-</sup> and [MDEGSO<sub>4</sub>]<sup>-</sup>) are used in conjunction with this cation, considerably lower values are obtained (0.469 and 0.472, respectively). [C<sub>2</sub>OHMIM] is a particular case in which the anion seems to play a determinant role in the polarity change observed. In fact, when the anion [BF<sub>4</sub>]<sup>-</sup> is used, a polarity only slightly lower than [BMIM][BF<sub>4</sub>] is observed, while for the anion [PF<sub>6</sub>]<sup>-</sup> a very high value of polarity is observed (0.617).

For [(C<sub>6</sub>)<sub>4</sub>DMG][Cl] the addition of only a very small quantity of RTIL (X<sub>RTIL/ACN</sub> = 0.26 × 10<sup>-4</sup>) has the same impact as other RTILs which have [Cl]<sup>-</sup> as anion for which it is needed to add

considerably more quantity (X<sub>RTIL/ACN</sub> = 2.2 × 10<sup>-4</sup> for [P<sub>6,6,6,14</sub>][Cl] and 4.94 × 10<sup>-4</sup> for [N<sub>1,8,8,8</sub>][Cl]).

With two exceptions ([EMIM][NTf<sub>2</sub>] and [C<sub>2</sub>OHMIM][PF<sub>6</sub>] with E<sub>T</sub><sup>f</sup> values of 0.712 and 0.617, respectively), the range of polarities plotted in Figures 2 and 3 is very limited (from 0.464 to 0.480), about 2% of the total polarity scale range. So, it is seen that although the addition of RTILs to acetonitrile leads to measureable deviations in polarity, these are still considerably low for most cases, as would be expected, since acetonitrile is much more abundant in the solutions prepared.

Figure 4 presents the range of effects in acetonitrile polarity arranged by anions and cations, to help visualize the observed effects, for all the RTILs studied both in this work and in our previous paper<sup>17</sup>. Again, it is apparent that the deviations in acetonitrile polarity are mainly dictated by the cation present in

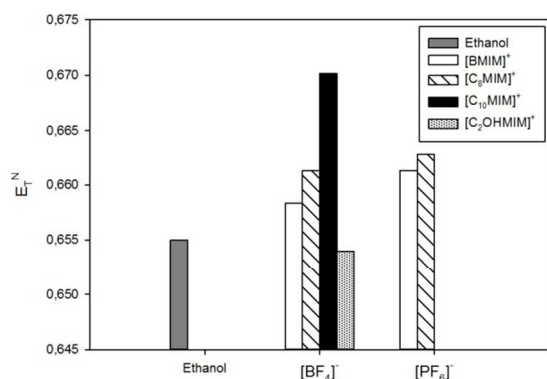


Fig. 6 Anion effect in  $E_T^N$  values of ethanol.

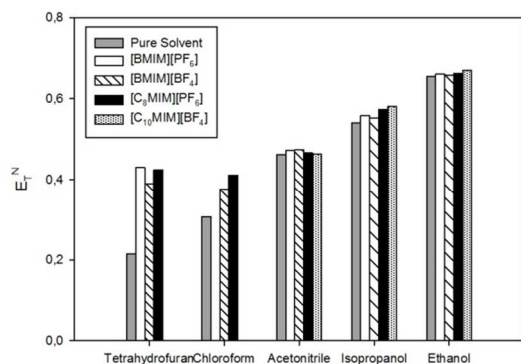


Fig. 8 Effect in  $E_T^N$  values of the addition of RTILs to tetrahydrofuran, chloroform, acetonitrile, isopropanol and ethanol.

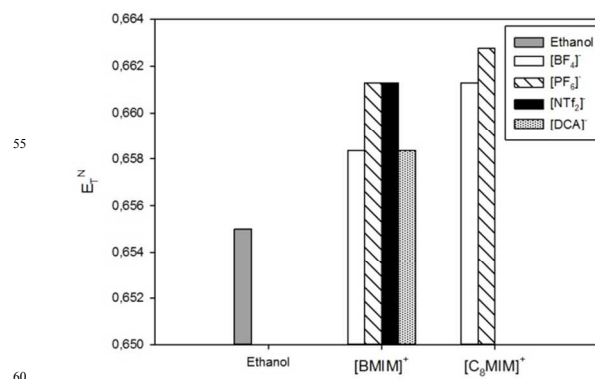


Fig. 7 Cation effect in  $E_T^N$  values of ethanol.

spectroscopy of the addition of RTILs to a solution of betaine dye (0.36 mM) in ethanol. This table includes the mole fraction of RTIL in ethanol ( $X_{\text{RTIL/EtOH}}$ ), the corresponding volume of RTIL added, the number of moles of RTIL per mole of betaine dye ( $\mu_{\text{RTIL/Betaine}}$ ), the wavelength of the maximum of the intramolecular CT absorption band of the betaine dye, the respective  $E_T^N$  and  $E_T(30)$  values.

When comparing the  $E_T^N$  values obtained for the addition of RTILs to ethanol with those obtained for the addition of RTILs to acetonitrile, it is clearly seen that the values of polarities in ethanol are always higher than in acetonitrile. This is directly related to the higher polarity of ethanol.

Figure 6 plots the effects in  $E_T^N$  values of ethanol by the addition of RTILs by anion, for the cations [BMIM]<sup>+</sup>, [C<sub>8</sub>MIM]<sup>+</sup>, [C<sub>10</sub>MIM]<sup>+</sup> and [C<sub>2</sub>OHMIM]<sup>+</sup> whereas Figure 7 plots the effects in  $E_T^N$  values of ethanol by the addition of RTILs by cation, for the anions [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup>, [NTf<sub>2</sub>]<sup>-</sup> and [DCA]<sup>-</sup>.

As with acetonitrile, the effect in polarity is more linked to the cation than to the anion. Specifically, we can see that the effect in polarity increases with the increase of the alkyl side chain for the imidazolium ring, as can be seen in the sequence [BMIM]<sup>+</sup> < [C<sub>8</sub>MIM]<sup>+</sup> < [C<sub>10</sub>MIM]<sup>+</sup> for the anion [BF<sub>4</sub>]<sup>-</sup>. The order of polarity effects introduced by the anions is slightly different than the one found in acetonitrile<sup>17</sup>. Now, the polarity effect increases in the sequence [DCA]<sup>-</sup> ≈ [BF<sub>4</sub>]<sup>-</sup> < [PF<sub>6</sub>]<sup>-</sup> ≈ [NTf<sub>2</sub>]<sup>-</sup>.

The addition of the RTIL [C<sub>2</sub>OHMIM][BF<sub>4</sub>] to ethanol is the only case observed in which the polarity of the solvent decreased. This is quite probably due to the presence of hydroxyl groups both in ethanol and the cation. However, with continued addition, the polarity value surpasses that of pure ethanol. This RTIL was considered in this study as the most hydrophilic example because of the contribution of the methylimidazolium cation with ethanol pendant group and BF<sub>4</sub> as anion. Contrarily of other organic cations, in this case two specific contact points are available (acidic H-2 of methylimidazolium ring and OH group) and a similar ethanol structure is present in the cation structure and organic solvent. These observations can contribute to understand this specific interaction but in order to prove it additional studies will be required.

the RTIL studied. All the anions studied seem to cover practically the whole range of values of polarities obtained, with the exception of [EtSO<sub>4</sub>]<sup>-</sup> and [MDEGSO<sub>4</sub>]<sup>-</sup>, for which there is only one example of each. The cations studied seem to increase the effect in polarity deviation in the order [P<sub>6,6,6,14</sub>]<sup>+</sup> < [BDMIM]<sup>+</sup> < [N<sub>1,8,8,8</sub>]<sup>+</sup> < [EMIM]<sup>+</sup> < [BMIM]<sup>+</sup>. [C<sub>8</sub>MIM]<sup>+</sup> and [C<sub>3</sub>OMIM]<sup>+</sup> cover a range too wide to be included in this generalization, while [(C<sub>6</sub>)<sub>4</sub>DMG]<sup>+</sup> and [C<sub>10</sub>MIM]<sup>+</sup> are present in only one example of each. [C<sub>5</sub>O<sub>2</sub>MIM]<sup>+</sup> presents an effect greater than [EMIM]<sup>+</sup>, but it is not clear if it should be considered in the same range or higher than [BMIM]<sup>+</sup>.

In our previous work<sup>17</sup>, we reported that the continued addition of RTIL to acetonitrile had a linear increasing effect on the polarity of acetonitrile. However, this is only true up until a certain mole fraction of RTIL in acetonitrile. In Figure 5 we enlarged the range of [BMIM][BF<sub>4</sub>] to acetonitrile molar composition, and it is visible that the first points follow a linear trend until a mole fraction of [BMIM][BF<sub>4</sub>] in acetonitrile of  $25.8 \times 10^{-4}$  is reached, after which the slope decreases, reaching a plateau. Probably, initial additions can change acidity of the media (in particular after addition of methylimidazolium based RTILs), until a point where an equilibrium can be established where the solvatochromic probe is not sensible enough to detect the small variations involved.

In Table 2 are presented the values obtained by UV/Vis

It is interesting to notice that the only two cases of the cation [EMIM]<sup>+</sup> studied – [EMIM][EtSO<sub>4</sub>] and [EMIM][MDEGSO<sub>4</sub>] – have effects in polarity similar to [BMIM][PF<sub>6</sub>], [BMIM][NTf<sub>2</sub>] and [C<sub>8</sub>MIM][BF<sub>4</sub>] in the case of the anion [EtSO<sub>4</sub>]<sup>−</sup> or to [C<sub>10</sub>MIM][BF<sub>4</sub>] in the case of the anion [MDEGSO<sub>4</sub>]<sup>−</sup>. This leads us to conclude that these two anions are very polar and thus present effects similar to imidazolium RTILs with longer alkyl side chains and less polar anions.

In Table 3 are presented the values obtained by UV/Vis spectroscopy of the addition of RTILs to solutions of betaine dye (0.36 mM) in tetrahydrofuran, chloroform and isopropanol. This table includes the mole fraction of RTIL in the solvent ( $X_{\text{RTIL/Solvent}}$ ), the corresponding volume of RTIL added, the number of moles of RTIL per mole of betaine dye ( $\mu_{\text{RTIL/Betaine}}$ ), the wavelength of the maximum of the intramolecular CT absorption band of the betaine dye, the respective  $E_T^N$  and  $E_T(30)$  values. Apart from the solvents presented in Tables 1, 2 and 3 toluene and dioxan were also tested, but these presented no measurable band in the region considered for the  $E_T^N$  scale and were thus discarded from this study.

Figure 8 plots the effects in  $E_T^N$  values of tetrahydrofuran, chloroform and isopropanol of the addition of all RTILs tested in these solvents, as well as the effects of addition of the same RTILs to acetonitrile and ethanol, for comparison.

It is seen that, despite chloroform having a higher  $E_T^N$  value, the values obtained after addition of RTIL are practically identical to those obtained with tetrahydrofuran. Isopropanol, on the other hand, has higher  $E_T^N$  values for all the RTILs tested. For all the cases studied, the polarity of the solvent increased with the addition of RTIL, with the exception noted previously of the addition of [C<sub>2</sub>OHMIM][BF<sub>4</sub>] to ethanol. It was observed for every solvent tested that the continuous addition of small volumes of RTIL results in a linear increase in polarity, as with acetonitrile (up until  $25 \times 10^{-4} X_{[\text{BMIM}][\text{BF}_4]/\text{Solvent}}$ ).

From Figure 8 we can also observe the effects of the addition of the same quantity of one specific RTIL to all the solvents tested in this work. We can see that the increase in polarity with the addition of RTIL follows generically the same trend as the polarities of the pure solvents, with the exception of chloroform, which has a higher polarity than tetrahydrofuran when pure, but lower when [BMIM][BF<sub>4</sub>] is added. Also, the general tendency observed in polarity shift is a decrease with increasing original polarity of the solvent tested, which is probably indicative of a closer polarity between solvent and RTILs.

## Conclusions

This work intended to explore the changes in polarity of common organic solvents by the addition of small quantities of room temperature ionic liquids (RTILs). It was seen that the influence in solvent polarity is more linked to the cation than the anion. For all the cases studied, the polarity of the solvent increased with the addition of RTIL and continued addition is linearly correlated to the increase in polarity in a first phase, followed by a plateau. The only exception is [C<sub>2</sub>OHMIM][BF<sub>4</sub>], which decreases the polarity

of ethanol with the first addition, but with further additions it also increased the value of polarity. It was observed that three ionic liquids ([C<sub>2</sub>OHMIM][PF<sub>6</sub>], [C<sub>10</sub>MIM][BF<sub>4</sub>] and [EMIM][NTf<sub>2</sub>]) have a dramatic influence in the polarity of acetonitrile, displacing it by more than 0.15 in the normalized polarity scale. The increase in polarity with the addition of the same quantity of [BMIM][BF<sub>4</sub>] to different solvents follows generically the same trend as the polarities of the pure solvents, with the exception of chloroform, which has a higher polarity than tetrahydrofuran when pure, but lower when [BMIM][BF<sub>4</sub>] is added.

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## Notes and references

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