

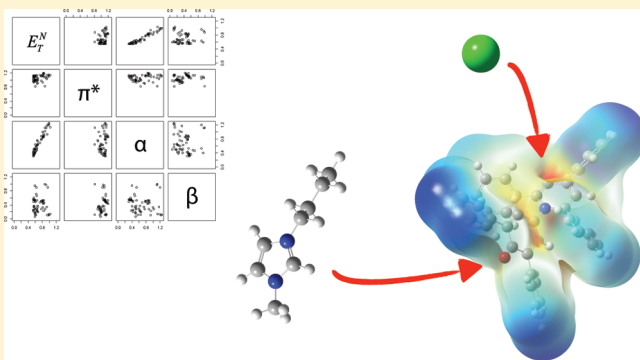
Influence of Structural Variations in Cationic and Anionic Moieties on the Polarity of Ionic Liquids

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Supporting Information

ABSTRACT: The polarity of a series of ionic liquids (ILs) arising from the quaternarization of *N*-methylmorpholine, *N*-methylpyrrolidine, *N*-methylpiperidine, *N*-methylazepane, 4-hydroxy-1-methylpiperidine, 1,2-dimethylimidazole, and 1-methylimidazole with simple alkyl chains and/or hydroxyl (mono- or dihydroxyl) functionalized alkyl chains and having bistriflimide, dicyanamide, or nitrate as counteranions has been investigated using solvatochromic dyes and expressed in terms of E_T^N and Kamlet–Taft parameters (dipolarity/polarizability (π^*), hydrogen bond donor acidity (α), and hydrogen bond basicity (β)). Significant variations of polarity were observed on changing the anion and cation combination. The resulting E_T^N and α values were strongly anion dependent; on going from bistriflimide to dicyanamide, a significant decrease in E_T^N and α values was observed. On the other hand, the alkyl chain length has only a moderate effect on these parameters; either an increase or decrease in E_T^N and α values was observed on increasing the alkyl chain length, depending on the cation core. In the case of cyclic onium salts, the size of the cation ring affected the α parameter; the ILs based on the seven-membered ring system *N*-methyl-*N*-butylazepanium (also named *N*-methyl-*N*-butylhexamethyleiminium, $[\text{HME}_{1,4}]^+$) have high polarity values, comparatively to the ILs based on analogous five- and six-membered cyclic cations (pyrrolidinium and piperidinium). The introduction of the OH groups on the cation alkyl chain increases the polarity; the effect is substantial for the first OH group and more moderate for the second. Also, the thermosolvatochromism (changes in solvatochromic properties with the change in temperature) was studied for four dihydroxyl functionalized ILs. Finally, the principal component analysis (PCA) carried out on 67 ILs has shown that there are only two statistically relevant parameters: PC1, a weighted sum of E_T^N and α , which is able to discern between the cation core structure, functionalization, and cation–anion association, and PC2, very close to β , which is related principally to the anion nature.



INTRODUCTION

There are few doubts that, at this moment, ionic liquids (ILs) show enormous potential as reaction media characterized by unusual and improved properties with respect to many molecular solvents.¹ Surely, the fact that they are composed of ions alone and are still liquid at ambient conditions has been reason enough to evoke the initial interest among researchers. However, the option of fine-tuning the physicochemical properties by an appropriate choice of cation and anion is the fact that has stimulated much of the current activity on these compounds, which are consequently defined as “designer solvents”.² However, for a rational application of ILs, it is fundamental to know the solvent properties of this extremely large class of compounds and how these properties change on changing IL structure. Most published work has focused on ILs containing the imidazolium cation. For these ILs, it is often reported that polarity is close to that of short-chained alcohols.³ Actually, this statement cannot be generalized⁴ because only some solvatochromic parameters characterizing a restricted number of ILs (such as $[\text{emim}][\text{Tf}_2\text{N}]$ and $[\text{bmim}][\text{Tf}_2\text{N}]$) are comparable to those of 2-butanol.³

Generally, the solvent effects can be split into the following two types of contributions: *nonspecific interactions*, related to the solvent acting as a bulk, and *specific interactions*, including all the possible interactions that can occur at microscopic level between solvent molecules and substrate. The first kind has been originally modeled by Kirkwood⁵ and Onsager⁶ on the basis of specific functions related to macroscopic physical parameters, such as relative permittivity, dipole moment, and refractive index. They have been empirically evaluated, analogously to the specific interactions, using solvatochromic dyes or probes and parametrized on the basis of well-known scales (e.g., Abboud–Kamlet–Taft, Drago’s S' , and Catalán scales).⁷ The UV/vis/near-IR absorption spectra of some specific compounds (probes) may be significantly influenced by the surrounding medium, and solvent can determine significant changes in the position, intensity, and shape of the absorption bands.⁸ This phenomenon, termed solvatochromism,

Received: May 17, 2011

Revised: July 1, 2011

Published: July 01, 2011

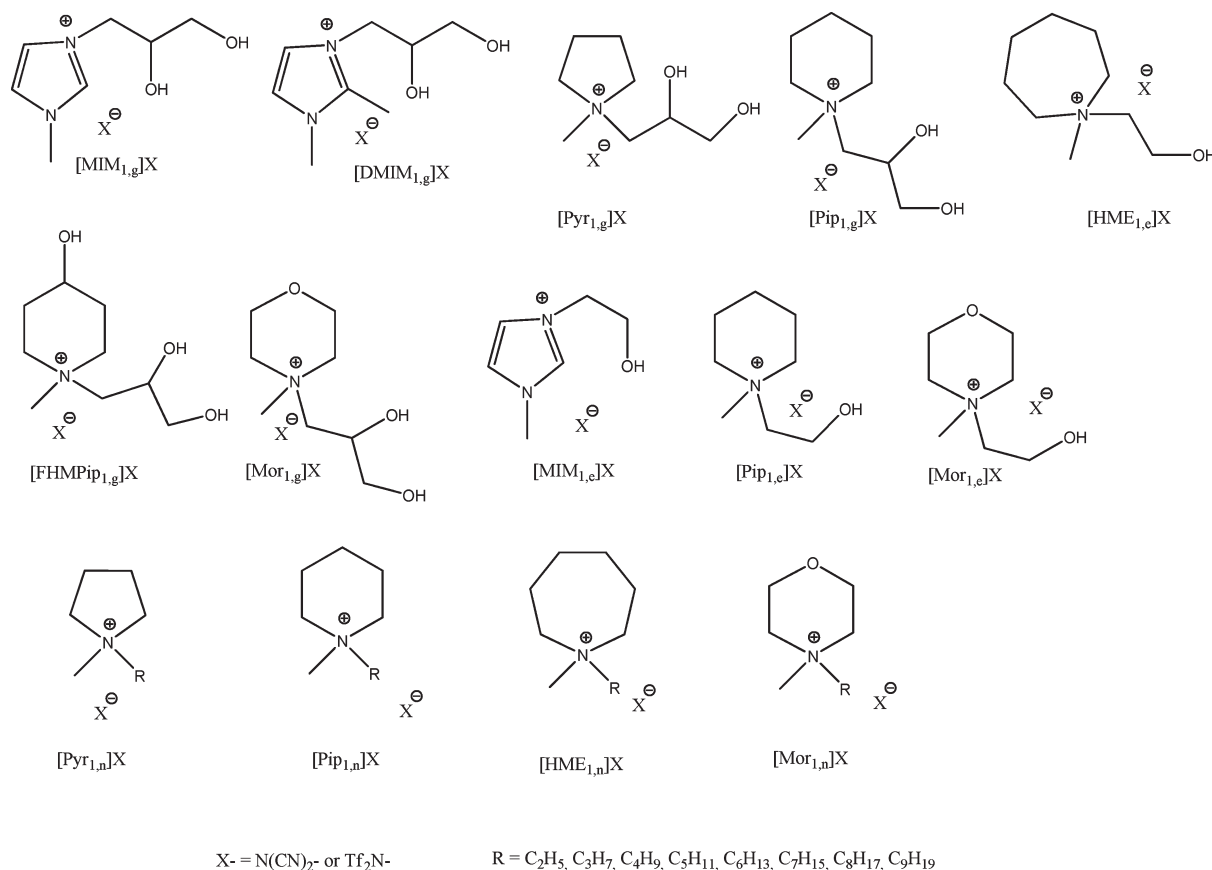


Figure 1. Investigated ILs.

is caused by the differential solvation of the ground and first excited state of the chromophore molecule. In solvatochromic absorbance and fluorescence probes, the changes in electronic transitions are systematic with respect to some property of the medium, for example, dipolarity/polarizability, static dielectric constant, hydrogen bond donating (HBD) acidity, hydrogen bond accepting (HBA) basicity.⁸

Although the changes in absorbance and/or fluorescence of a solvatochromic probe with solvent structure can be considered a direct consequence of the changes in nonspecific and specific solute–solvent interactions, a change in temperature and/or pressure can also affect solvatochromism. The temperature dependence of polarity parameters, or *thermosolvatochromism*, is reported in both molecular solvents and ILs. However, in ILs, it is generally much more pronounced than it is in molecular solvents, and therefore, it is more easily evaluable.⁹ Interesting results were found by Kumar et al.¹⁰ by contrasting thermosolvatochromic trends in three series of ILs in the temperature range 298–353 K. On the other hand, the temperature-dependent polarity of [bmim][PF₆] was previously studied by Baker et al.,¹¹ emphasizing that the hydrogen bond donor (HBD) strength of the imidazolium cation was strongly temperature dependent but hydrogen bond acceptor (HBA) abilities were weak functions of temperature and added water. Pandey et al.¹² have shown temperature-dependent behavior of some solvatochromic probes with [bmim][PF₆], [bmim][BF₄], and aqueous mixtures of [bmim][BF₄] whereas El Seoud et al.¹³ have investigated the thermosolvatochromism in binary mixtures of water and ILs to assess the relative importance of solute–solvent solvophobic interactions. Previously, the same group had reported the thermosolvatochromic

behavior of certain dyes in aqueous [bmim][BF₄] and compared it with behaviors of aqueous alcohols in the temperature range 10–60 °C.¹⁴

Although the extensive research performed in the last 10 years on dialkyl-substituted imidazolium salts has had a strategic role in the development of the IL chemistry, important information on the properties of these media is emerging nowadays, in part, also, as a consequence of the fact that other classes of salts that are liquid at room temperature have been taken into account. Data of dielectric constants at 25 °C, recently published¹⁵ for some ILs, including also aprotic, protic, and hydroxyl functionalized ammonium, pyrrolidinium, and pyridinium salts, have shown that the range of dielectric constants is substantially larger than expected ($10 < \epsilon < 85$) on the basis of data available a few years ago. In particular, it has been shown that aprotic ILs with anions of high symmetry possess low dielectric constants, on the order of $\epsilon = 10$ –16. The replacement of highly symmetric anions by some dipolar anions, such as [Tf₂N][−], has only a marginal effect. However, large anion effects have been found for oxyanions such as ethylsulfate; [emim][EtSO₄] is characterized by a dielectric constant of 35, although protic ILs exhibit higher values than aprotic ILs. The highest dielectric constant has been reported for (2-hydroxyethyl)ammonium lactate, $\epsilon = 85.6$. Nevertheless, it has been shown¹⁶ through solvatochromic measurements that ILs bearing an hydroxyl group on the cation possess a greatly expanded polarity, which is, moreover, anion dependent. Among all the investigated hydroxyl ILs, those based on anions such as [PF₆][−], [Tf₂N][−], and [ClO₄][−] are characterized by a *hyperpolarity* ($E_T(30) = 60.3$ –61.7 kcal/mol) close to those of protic solvents and water, which has been correlated to an intramolecular synergic solvent effect of the

hydrogen bonded HBD/HBA complexes generated by the association between an anion and the hydroxyl group on a cation.

To obtain further information on the possibility to tune the IL solvent power through structural modifications, we decided to investigate the polarity of some functionalized and alkyl-substituted ILs arising from the quaternarization of *N*-methylmorpholine, *N*-methylpyrrolidine, *N*-methylpiperidine, *N*-methylazepane, 4-hydroxy-1-methylpiperidine, 1,2-dimethylimidazole, and 1-methylimidazole, determining the solvatochromic Kamlet–Taft parameters at 25 °C and, for some ILs, also at higher temperatures.

Here, we report the collected data, which have been analyzed and discussed, also taking into account the literature data, on the basis of the IL cluster ability and the possible interactions of the IL cations and anions with the Reichardt's dye, the used probe having more interaction sites and steric requirements.

EXPERIMENTAL SECTION

All ILs with different cations and anions (Figure 1), namely, *N*-ethyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,2}][N(CN)₂]), *N*-propyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,3}][N(CN)₂]), *N*-butyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,4}][N(CN)₂]), *N*-pentyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,5}][N(CN)₂]), *N*-hexyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,6}][N(CN)₂]), *N*-heptyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,7}][N(CN)₂]), *N*-octyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,8}][N(CN)₂]), *N*-nonyl-*N*-methylmorpholinium dicyanamide ([Mor_{1,9}][N(CN)₂]), *N*-ethyl-*N*-methylmorpholinium bistriflimide ([Mor_{1,2}][Tf₂N]), *N*-butyl-*N*-methylmorpholinium bistriflimide ([Mor_{1,4}][Tf₂N]), *N*-octyl-*N*-methylmorpholinium bistriflimide ([Mor_{1,8}][Tf₂N]), *N*-ethanol-*N*-methylmorpholinium dicyanamide ([Mor_{1,e}][N(CN)₂]), *N*-ethanol-*N*-methylpiperidinium dicyanamide ([Pip_{1,e}][N(CN)₂]), *N*-ethanol-*N*-methylhexamethyleniminium dicyanamide ([HME_{1,e}][N(CN)₂]), 1-glyceryl-3-methylimidazolium dicyanamide ([MI-M_{1,g}][N(CN)₂]), 1-glyceryl-2,3-dimethylimidazolium dicyanamide ([DMIM_{1,g}][N(CN)₂]), *N*-glyceryl-*N*-methylpyrrolidinium dicyanamide ([Pyr_{1,g}][N(CN)₂]), *N*-glyceryl-*N*-methylpiperidinium dicyanamide ([Pip_{1,g}][N(CN)₂]), *N*-glyceryl-*N*-methylmorpholinium dicyanamide ([Mor_{1,g}][N(CN)₂]), *N*-glyceryl-*N*-methyl-4-hydroxypiperidinium dicyanamide ([FHMPip_{1,g}][N(CN)₂], a 1:1 mixture of two stereoisomers), *N*-glyceryl-*N*-methylpyrrolidinium bistriflimide ([Pyr_{1,g}][Tf₂N]), 1-glyceryl-2,3-dimethylimidazolium bistriflimide ([DMIM_{1,g}][Tf₂N]), *N*-glyceryl-*N*-methylpiperidinium bistriflimide ([Pip_{1,g}][Tf₂N]), *N*-glyceryl-*N*-methylmorpholinium bistriflimide ([Mor_{1,g}][Tf₂N]), *N*-glyceryl-*N*-methylimidazolium bistriflimide ([MIM_{1,g}][Tf₂N]), *N*-butyl-*N*-methylhexamethyleniminium bistriflimide ([HME_{1,4}][Tf₂N]), and *N*-glyceryl-*N*-methylpyrrolidinium nitrate ([Pyr_{1,g}][NO₃]), were prepared according to well-established synthetic procedures and confirmed by NMR analysis and electrospray ionization mass spectrometry (ESI-MS). All ILs were dried under vacuum (pressure 10^{−2} to 10^{−3} mbar) at 80 °C for 24 h prior to spectral analysis. The details of synthesis and characterization are available in the Supporting Information.

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye 30) and 4-nitroaniline were purchased from Aldrich; *N,N*-diethyl-4-nitroaniline was purchased from Alfa Aesar.

Determination of $E_T(30)$ and Kamlet–Taft Parameters. UV–vis absorption spectra of three solvatochromic dyes (Reichardt's betaine dye, *N,N*-diethyl-4-nitroaniline, and 4-nitroaniline)^{8,17} dissolved in ILs were taken in a quartz cell with a light path length

of 1 mm on a Cary 2200 spectrophotometer (300–800 nm). Individual stock solutions of Reichardt's betaine dye, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline were prepared in dichloromethane. To prepare a given dye/IL solution, the appropriate amount of the dye stock solution was micropipetted into a clean dry quartz cuvette. Residual dichloromethane was evaporated under a gentle stream of argon gas. The IL was then added to the cuvette. The cuvette was then capped and sealed and the sample was mixed for an appropriate time before the experimental measurements.

Solvatochromic Measurements and Polarity. The $E_T(30)$ and E_T^N values have been determined on the basis of the absorption maximum of the Reichardt's dye 30, with the polarity scale $E_T(30)$ being defined as reported in eq 1:

$$E_T(30) \text{ (kcal mol}^{-1}\text{)} = 28\,591.5/\lambda_{\max} \text{ (nm)} \quad (1)$$

where λ_{\max} is the wavelength maximum of the lowest energy band, the intramolecular charge-transfer (CT) $\pi - \pi^*$ absorption band of the zwitterionic phenolate molecule.

The solvent dipolarity/polarizability, π^* , which was initially normalized by taking dimethyl sulfoxide ($\pi^* = 1.00$) and cyclohexane ($\pi^* = 0.00$) as references, is correlated to the wavelength maximum of the lowest energy band of *N,N*-diethyl-4-nitroaniline, a nonhydrogen bond donor solute.¹⁸

$$\pi^* = (8.649 - 0.314\nu_1) \quad (2)$$

The hydrogen bond donating (HBD) acidity, α , is calculated using the $E_T(30)$ and π^* values as follows:

$$\alpha = 0.0649(E_T(30)) - 0.72\pi^* - 2.03 \quad (3)$$

Finally, the hydrogen bond accepting (HBA) basicity, β , is determined on the basis of the absorption of 4-nitroaniline and *N,N*-diethyl-4-nitroaniline by using eq 4:

$$\beta = (1.035\nu_1 - \nu_2 + 2.64)/2.80 \quad (4)$$

$$\nu_1 = 10^4/\lambda_{4\text{-nitroaniline}} \text{ and } \nu_2 = 10^4/\lambda_{N,N\text{-diethyl-4-nitroaniline}}$$

RESULTS AND DISCUSSION

Because IL polarity is water-sensitive,^{11,19} before every test each IL was kept in a vacuum (pressure 10^{−2} to 10^{−3} mbar) at 80 °C for 24 h prior to spectral analysis. The estimated values of $E_T(30)$, E_T^N , dipolarity/polarizability (π^*), hydrogen bond acidity (α), and hydrogen bond basicity (β) for the presently investigated ILs have been reported in Table 1, together with the values characterizing other ILs and some molecular solvents.

As expressed in eqs 1–4, the polarity parameters $E_T(30)$, E_T^N , and α are related to the possible interactions of the solvent with the Reichardt's dye whereas π^* and β are related to two differently substituted 4-nitroanilines. Considering the structure of these probes (Figure 2) and the ILs peculiarities, some doubts have been expressed²⁵ about the fact that the empirical polarity parameters of the Kamlet–Taft equation can be determined for ILs independently of the probe molecule used, as well as about which thermodynamic parameters are really included. Surely, the fact that ILs are constituted by a 1:1 mixture of positively and negatively charged species may determine the insurgence of interactions with the Reichardt's dye not necessarily comparable to those occurring in molecular solvents, reducing the possibility to develop universal scales that include ILs and molecular solvents. Nevertheless, we think that the determination of the

Table 1. $E_T(30)^a$ and Kamlet–Taft Parameters of ILs^b

run	salt	$E_T(30)$	E_T^N	π^*	α	β	ref
1	[emim][N(CN) ₂]	51.7	0.648	1.08	0.53	0.35	16
2	[bmim][N(CN) ₂]	51.4	0.629	1.13	0.464	0.708	20
3	[hmim][N(CN) ₂]	51.1	0.630	1.05	0.514	ND	21
4	[Pyr _{1,2}][N(CN) ₂]	48.7	0.556	1.03	0.37	ND	20
5	[Pip _{1,4}][N(CN) ₂]	48.6	0.552	1.13	0.31	0.49	
6	[HME _{1,4}][N(CN) ₂]	54.5	0.735	1.14	0.69	0.47	
7	[Mor _{1,2}][N(CN) ₂]	50.3	0.605	1.12	0.43	0.51	
8	[Mor _{1,3}][N(CN) ₂]	50.2	0.603	1.12	0.42	0.49	
9	[Mor _{1,4}][N(CN) ₂]	49.5	0.580	1.12	0.38	0.53	
10	[Mor _{1,5}][N(CN) ₂]	49.5	0.581	1.11	0.38	0.54	
11	[Mor _{1,6}][N(CN) ₂]	49.6	0.583	1.11	0.38	0.55	
12	[Mor _{1,7}][N(CN) ₂]	49.2	0.572	1.11	0.36	0.54	
13	[Mor _{1,8}][N(CN) ₂]	49.1	0.568	1.11	0.35	0.54	
14	[Mor _{1,9}][N(CN) ₂]	49.2	0.570	1.11	0.36	0.54	
15	[C ₅ DABCO][N(CN) ₂]	48.4	0.546	1.11	0.31	0.55	22
16	[C ₆ DABCO][N(CN) ₂]	48.5	0.549	1.08	0.32	0.56	22
17	[C ₈ DABCO][N(CN) ₂]	48.7	0.557	1.05	0.36	0.60	22
18	[C ₁₀ DABCO][N(CN) ₂]	48.5	0.549	1.06	0.34	0.55	22
19	[HOemim][N(CN) ₂]		0.784	1.11	0.80	0.51	16
20	[Pip _{1,e}][N(CN) ₂]	55.65	0.77	1.11	0.78	0.51	
21	[Mor _{1,e}][N(CN) ₂]	55.80	0.775	1.13	0.78	0.49	
22	[HME _{1,e}][N(CN) ₂]	57.44	0.825	1.12	0.89	0.52	
23	[MIM _{1,g}][N(CN) ₂]	57.6	0.831	1.17	0.87	0.47	
24	[DMIM _{1,g}][N(CN) ₂]	57.0	0.813	1.15	0.84	0.46	
25	[Pyr _{1,g}][N(CN) ₂]	58.28	0.851	1.18	0.90	0.46	
26	[Pip _{1,g}][N(CN) ₂]	57.0	0.811	1.12	0.86	0.53	
27	[Mor _{1,g}][N(CN) ₂]	57.8	0.836	1.20	0.85	0.43	
28	[FHMPip _{1,g}][N(CN) ₂]	59.2	0.879	1.09	1.02	0.28	
29	[bmim][Tf ₂ N]		0.840	1.09	0.940	0.23	23
30	[C ₂ mim][Tf ₂ N]	52.0	0.657	0.90	0.76	0.28	16
31	[C ₂ mim][Tf ₂ N]		0.658	0.998	0.627	0.225	23
32	[C ₄ mim][Tf ₂ N]		0.645	0.984	0.617	0.243	23
33	[C ₄ m ₂ mim][Tf ₂ N]		0.541	1.010	0.381	0.239	23
34	[C ₈ mim][Tf ₂ N]		0.630	0.961	0.595	0.291	23
35	[C ₄ Py][Tf ₂ N]		0.603	0.816	0.643	0.123	10
36	[C ₆ Py][Tf ₂ N]		0.593	0.984	0.500	0.065	10
37	[C ₈ Py][Tf ₂ N]		0.617	0.965	0.564	0.115	10
38	[C ₈ Py][Tf ₂ N]		0.588	0.99	0.51	0.28	9a
39	[2-C ₁ C ₈ Py][Tf ₂ N]		0.554	0.95	0.48	0.35	9a
40	[3-C ₁ C ₈ Py][Tf ₂ N]		0.576	0.97	0.50	0.33	9a
41	[4-C ₁ C ₈ Py][Tf ₂ N]		0.588	0.98	0.51	0.29	9a
42	[4-C ₁ C ₈ Py][Tf ₂ N]		0.576	0.97	0.50	0.33	9a
43	[Pyr _{1,3}][Tf ₂ N]		0.669	0.91	0.74	0.34	9a
44	[Pyr _{1,4}][Tf ₂ N] ^c		0.672	0.890	0.734	−0.108	10
45	[Pyr _{1,4}][Tf ₂ N]		0.566	0.93	0.52	0.37	9a
46	[Pyr _{1,4}][Tf ₂ N]		0.544	0.954	0.427	0.252	3c
47	[Pyr _{1,6}][Tf ₂ N] ^c		0.657	0.811	0.759	0.058	10
48	[Pyr _{1,8}][Tf ₂ N]		0.813	0.93	1.00	0.33	9a
49	[Pyr _{1,8}][Tf ₂ N] ^c		0.651	0.733	0.801	0.084	10
50	[HME _{1,4}][Tf ₂ N]	55.76	0.773	0.976	0.880	0.28	
51a	[Mor _{1,2}][Tf ₂ N] ^d	50.16	0.600	1.012	0.497	0.186	
51b	[Mor _{1,2}][Tf ₂ N] ^e	50.08	0.598	1.003	0.498	0.179	
51c	[Mor _{1,2}][Tf ₂ N] ^f	49.97	0.595	0.992	0.499	0.161	
52	[Mor _{1,4}][Tf ₂ N] ^f	48.98	0.564	1.002	0.427	0.205	

Table 1. Continued

run	salt	$E_T(30)$	E_T^N	π^*	α	β	ref
53	[Mor _{1,8}][Tf ₂ N] ^f	48.89	0.562	1.006	0.419	0.251	
54	[HOemim][Tf ₂ N]	60.8	0.929	1.03	1.17	0.34	16
55	[MIM _{1,g}][Tf ₂ N]	62.6	0.985	1.15	1.20	0.13	
56	[DMIM _{1,g}][Tf ₂ N]	61.2	0.941	1.14	0.93	0.11	
57	[Pyr _{1,g}][Tf ₂ N]	64.1	1.030	1.14	1.13	0.14	
58	[Pip _{1,g}][Tf ₂ N]	62.8	0.991	1.13	1.23	0.11	
59	[Mor _{1,g}][Tf ₂ N]	62.9	0.993	1.11	1.25	0.12	
60	[HOemim][NO ₃]		0.769	1.11	0.77		16
62	[Pyr _{1,g}][NO ₃]	57.86	0.838	1.19	0.87	0.53	
63	[C ₂ mim][NO ₃]	51.5	0.642	1.13	0.48	0.66	16
64	[C ₂ mim]PF ₆	52.6	0.676	0.99	0.66	0.20	16
65	[C ₄ mim]PF ₆		0.669	1.032	0.634	0.207	3c
66	[C ₂ mim][OAc]	49.8	0.590	1.09	0.40	0.95	16
67	[HOemim][OAc]	51.2	0.633	1.04	0.53	0.90	
68	[C ₄ mim]BF ₄		0.67	1.047	0.627	0.376	3c
69	[C ₂ m ₂ mim][BF ₄]		0.57	1.083	0.40	0.363	3c
70	[C ₆ mim]Br	61.80	0.96	1.09	1.20	0.90	9b
71	[C ₆ mim]Cl	60.18	0.91	1.06	1.11	0.97	9b
72	[MIM _{1,g}]Cl	59.0	0.875	0.82	1.12	0.99	
73	water		1.000	1.33	1.12	0.50	24
74	methanol		0.760	0.73	1.05	0.61	24
75	acetone		0.350	0.70	0.20	0.54	24
76	acetonitrile		0.460	0.75	0.19	0.40	24
77	DMSO		0.444	1.00	0.00	0.76	24

^akcal/mol. ^bDetermined at 25 °C. ^cThese ILs are characterized by β values significantly different from those of all the other bistriflimide salts; therefore, they have not been included in the plots of Figures 4 and 5. ^dThe measurement was carried out at 35 °C. ^eThe measurement was carried out at 45 °C. ^fThe measurement was carried out at 50 °C.

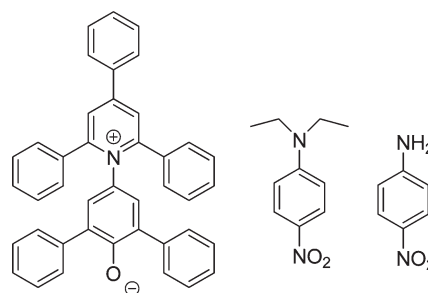


Figure 2. Solvatochromic probes.

Kamlet–Taft parameters on a representative set of ILs can give important information on the IL solvation ability and on the possibility to tune IL polarity.

Considering specifically the structure of Reichardt's dye, we can observe that this probe presents a quite easily accessible electron pair donor (or hydrogen bond acceptor) center, represented by the phenolate oxygen, and a more hindered electron pair acceptor center, the positively charged nitrogen, which is “buried” by its surrounding phenyl rings (Figure 3).

Consequently, we suppose that the IL cation will be strongly localized near the Reichardt's dye oxygen. The interaction between the IL cation–Reichardt's dye oxygen can take advantage of some of the chemical features of the cation (such as the

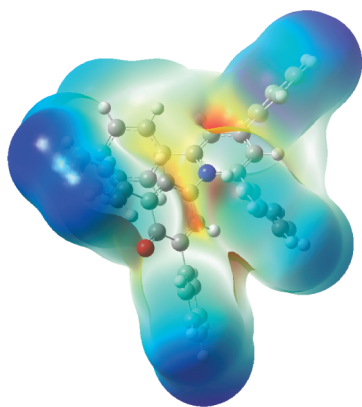


Figure 3. Optimized three-dimensional structure of the Reichardt's dye.

availability of the hydrogen on C(2) in 1,3-dialkyl substituted imidazolium ILs, the presence of the hydrogen on nitrogen in Brønsted acidic imidazolium salts, and specific functional groups on the side chain), although the charge–charge interaction should have a dominant effect. At variance, the interaction of the IL anion with this probe is probably less specific and depends mainly on steric effects. Monoatomic ions, like chloride, can approach closer to the positive charge of Reichardt's dye and, specifically, interact with it. Probably, linear anions are also able to interact in a similar way. On the other hand, for large spherical anions, such as $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$, steric hindrance results in a less close interaction. This feature should reduce the strength of the specific Coulombic interaction according to the inverse distance law.

Starting from these considerations, we can observe that the data reported in Table 1 and graphically represented using the scatter plots of Figures 4 and 5 show that the π^* values for ILs are generally high, at least in comparison with those for molecular solvents, and confined in a relatively limited range (0.8–1.20). Pyrrolidinium salts having as counteranion $[\text{Tf}_2\text{N}]^-$ show lower π^* values whereas morpholinium salts and dihydroxyl functionalized ILs are characterized by the highest π^* values.

Nevertheless, the E_T^N values lie in the range associated with the polar aprotic and protic solvents; the values extend from 0.55 to 1.03. The highest values have been found in the case of $[\text{Pyr}_{1,g}][\text{Tf}_2\text{N}]$, $[\text{Pip}_{1,g}][\text{Tf}_2\text{N}]$, and $[\text{Mor}_{1,g}][\text{Tf}_2\text{N}]$, which contain two hydroxyl groups on the cation alkyl chain and the bistriflimide anion. It is notable (Figure 4) that there is an evident correlation between E_T^N and α values, which, however, vary in a larger range (0.31–1.25), whereas no apparent correlation can be evidenced between E_T^N and π^* values. This suggests that, in the case of ILs, the Reichardt's dye is less sensitive to dipolarity/polarizability.

The values of E_T^N and α are determined by the cation but significantly affected by the anion. Glyceryl functionalized ILs, $[\text{Pip}_{1,g}][\text{Tf}_2\text{N}]$, $[\text{Mor}_{1,g}][\text{Tf}_2\text{N}]$, and $[\text{MIM}_{1,g}][\text{Tf}_2\text{N}]$ present the highest α values (these values are higher than that of water); however, it is notable that α values close to 1 (1.05 if the value reported for methanol) have been found also for nonhydroxyl functionalized ILs, such as $[\text{Pyr}_{1,8}][\text{Tf}_2\text{N}]$ and $[\text{HME}_{1,4}][\text{Tf}_2\text{N}]$. Nevertheless, it is worth mentioning that, in the case of pyrrolidinium salts, the α values appear to be strongly affected by the alkyl chain length; the value increases on going from $[\text{Pyr}_{1,4}][\text{Tf}_2\text{N}]$ to $[\text{Pyr}_{1,8}][\text{Tf}_2\text{N}]$.²⁶ This behavior, together with the role exerted by the ring size (compare azepanium and pyrrolidinium salts), suggests the possibility that the interaction between the IL cation and the Reichardt's dye may be affected in

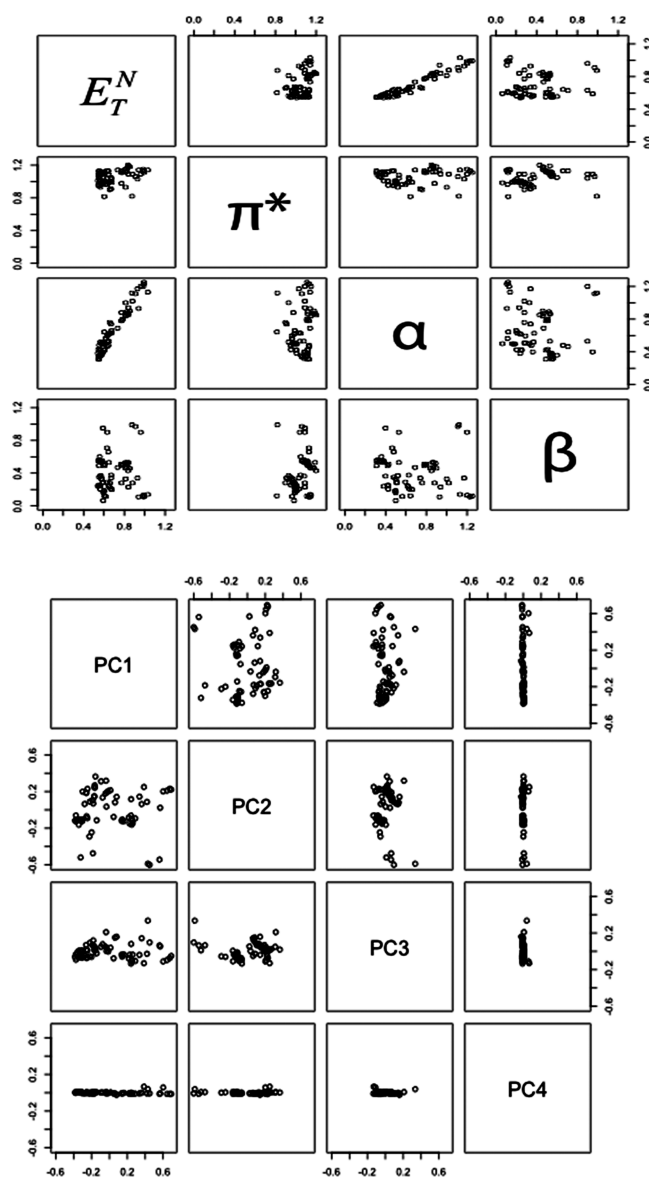


Figure 4. (a) Scatter plot matrix for any complete and eligible set of solvatochromic parameters reported in Table 1 (see notes in table title). (b) Scatter plot matrix of the principal components ordered by decreasing variance (and thus quantity of contained information). Principal components related quantities are reported in Table 2.

the case of cyclic onium salts by conformational and steric effects that determine the distance between the cation and anion and, consequently, as explained below, between the IL cation and Reichardt's dye.

Finally, it is notable that the α values are affected by the anion structure; for each specific cationic system (1,3-dialkyl substituted imidazolium salts, *N,N*-dialkyl morpholinium, and alkyl pyridinium), with few exceptions (chlorides and bromides salts), an inverse relationship may be found between the α and β values.

To explain the effect of anion structure on α value, we have to consider that the anion can influence this parameter through the following two independent mechanisms: (i) the interaction among anions and cations inside the IL, which is a function of anion basicity. This property can modify the ability of the IL cation to interact with the dissolved probe, in the specific case

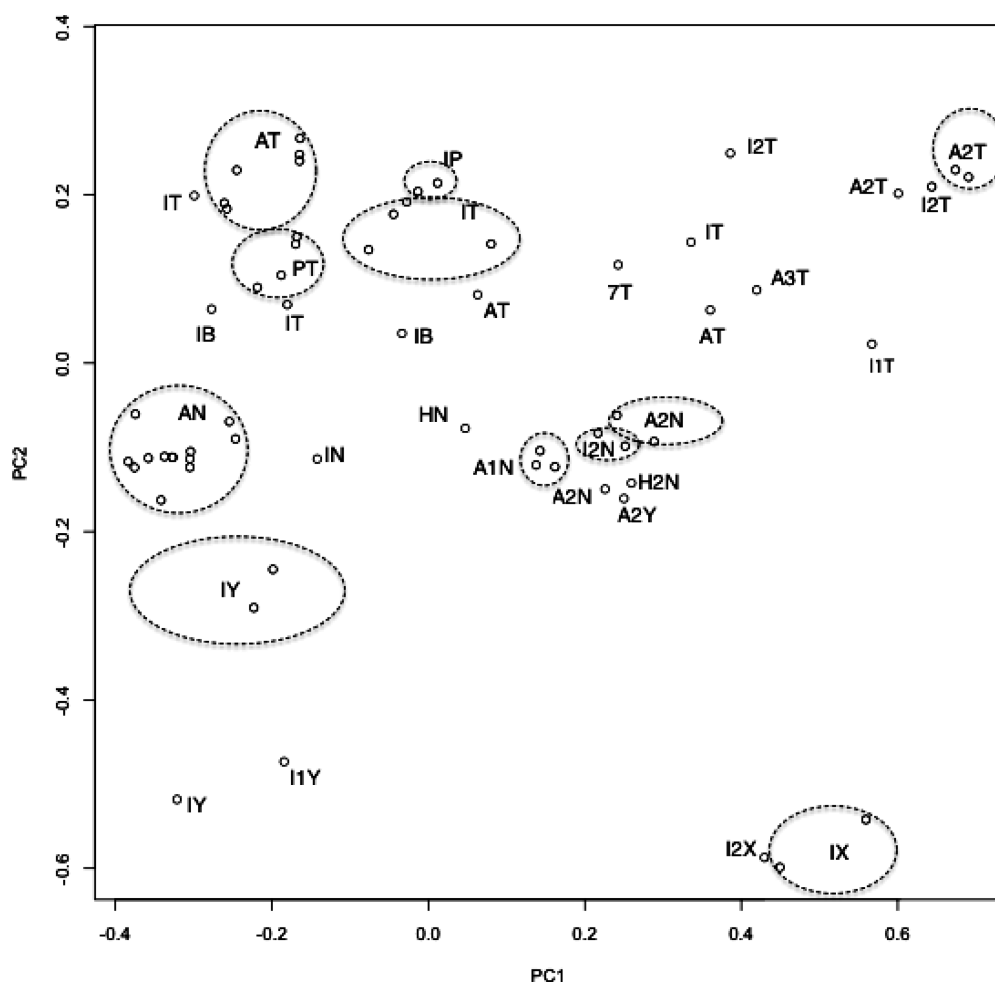


Figure 5. Principal component analysis; plot of the first two components. The cloud of points is partitioned according to chemical nature of cations and anions. Nearby groups of ILs of identical chemical nature are surrounded by a dashed ellipsoid with the label inside. Isolated points are identified by nearby label. The first label character corresponds to the cation; the last corresponds to the anion. The eventual central character defines the cation functional group. Cations: I, imidazolium; A, pyrrolidinium, piperidinium, and morpholinium; 7, azepanium; P, pyridine. Anions: X, halogen; Y, acetate and nitrate; N, dicyanamide; T, bistriflimide; B, tetrafluoroborate; P, hexafluorophosphate. Functional groups: 1, single OH; 2, two OH; 3, three OH.

with the oxygen atom of the Reichardt's dye. (ii) The IL anion direct interaction with the Reichardt's dye (in particular, with the positively charged nitrogen atom), which depends on the structure and size and stabilizes the ground state. As a result of the first effect, strong basic anions may reduce the α values, determining a destabilization of the ground state, whereas through the second mechanism they can increase the same parameter. The low ability of the bistriflimide anion to give cation–anion aggregates, previously shown through experimental measurements²⁷ and theoretical calculations,²⁸ allows the relatively “free” cations to interact with the electron donor site of the Reichardt's dye; $[\text{Tf}_2\text{N}]^-$ based ILs have values of α significantly higher than those of the corresponding dicyanamide-based ILs, independently of the cation core and substituents on the cation. An analogous behavior also characterizes $[\text{PF}_6]^-$ based ILs, which, on the basis of ESI-MS measurements, have been included²⁷ together with bistriflimides in the class of ILs bearing “loosely interacting anions”. Apparently, the effect of tightly coordinating anions such as Br^- , $[\text{N}(\text{CN})_2]^-$, $[\text{BF}_4]^-$, and $[\text{CF}_3\text{CO}_2]^-$ appears more complex. In this case, the stronger anion–cation interactions reducing the cation ability to interact with the Reichardt's dye should determine a reduction of $E_{\text{T}}(30)$,

E_{T}^{N} , and α . However, when small spherical anions, such as Br^- and Cl^- , are involved, it is possible to hypothesize that the coordination of the anion to the pyridinium nitrogen of the Reichardt's dye determines a decrease in the electron affinity of the pyridinium cation site and, consequently, an increase in the intramolecular CT transition energy of the dye. In other words, anion coordination can result in an increase in $E_{\text{T}}(30)$, E_{T}^{N} and α , which, however, is not due to the IL hydrogen bonding donor ability.

Data reported in Table 1 also show some other interesting features. As already partially discussed, the statement “an increase in the alkyl length determines a decrease in the IL polarity” is strictly true only for some classes of ILs. This behavior can be observed in imidazolium, pyridinium, and morpholinium based ILs but not in pyrrolidinium.

Finally, some considerations have to be made related to the effect of hydroxyl groups. Generally, the presence of a hydroxyl group significantly increases the ability of the solvent to act as a hydrogen bond donor, but the introduction of a second hydroxyl group on the alkyl chain only moderately affects this ability. Nevertheless, the presence of the hydroxyl groups reduces the effect of the cation core on the Kamlet–Taft α parameter; for

Table 2. Definition of Principal Components with Respect to Solvatochromic Parameters and Related Statistical Quantities

	PC1	PC2	PC3	PC4
E_T^N	0.4539	−0.0745	−0.2694	0.8461
π^*	0.0451	−0.1224	−0.9341	−0.3323
α	0.8852	−0.0572	0.1985	−0.4168
β	−0.0911	−0.9880	0.1245	0.0015
σ	0.3067	0.2206	0.0855	0.0138
σ^2	0.0941	0.0486	0.0073	0.0002
% σ^2	62.63	32.38	4.87	0.13

example, [DMIM_{1,g}][N(CN)₂] and [Pip_{1,g}][N(CN)₂], having different cations but the same functional groups and the same counteranion, have almost all of their solvatochromic parameters as the same. At variance, the anion structure affects the $E_T(30)$, E_T^N , π^* , and α parameters; in the case of [Pyr_{1,g}][N(CN)₂], [Pyr_{1,g}][Tf₂N], and [Pyr_{1,g}][NO₃], we can observe that the ILs bearing the more basic [N(CN)₂][−] and [NO₃][−] anions, as in the case of unfunctionalized ILs, have lower α values, whereas ILs having [Tf₂N][−] as the counteranion are characterized by very high $E_T(30)$, E_T^N , and α values.

A more quantitative analysis of the solvatochromic parameters as a function of IL structure can be carried out using the principal component analysis (PCA).²⁹ This statistical analysis has also been applied previously to molecular solvents.³⁰ Because $E_T(30)$ and E_T^N are linearly correlated by definition, we have considered only E_T^N . Nevertheless, with E_T^N and the Kamlet–Taft parameters being dimensionless and normalized to a 0–1 scale, this choice allowed us to avoid any rescaling. The analysis has been performed using the R statistical package,³¹ and as usually reported, values were shifted to obtain a zero average value. The results of this analysis are reported in Table 2 and graphically represented in Figures 4b and 5.

The first principal component (PC1), which accounts for 62.63% of the total variance, is a linear combination with sign concordance of E_T^N and α (two parameters that are linearly correlated, as already observed in Figure 4a) and thus can be related to the solvent hydrogen bond donor ability. In contrast, PC2 is essentially the β parameter (with a minus sign), and its variance share is 32.38%. PC3 corresponds roughly to π^* but accounts for 4.87% of the total variance. This component corresponds to the previously discussed small spreading of the values of this parameter. Finally, PC4 (only 0.13% of the total variance) is a weighted difference between E_T^N and α and accounts for the spread of the points around their linear correlation. The amount of information related to each component is quantitatively expressed by its variance and graphically shown in Figure 4b. PC3 and, in particular, PC4 are characterized by narrow clouds of points. Both these components and, consequently, the parameters that they represent give only a small contribution to the change of the solvent properties of the ILs on the structure modification. In contrast, PC1 and PC2 (together describe 95% of the total variance) show a well spread scatter plot, from which it is possible to obtain information on the relationship of ILs structure–solvent properties. In Figure 5, a labeled version of this scatter plot is reported. This plot is characterized by a horizontal organization with respect to the anions. Halides and oxyanions (acetates and nitrates) lie in the lower part of the plot, according to their high β values. In the lower-left corner are arranged acetate- and nitrate-based ILs

whereas in the lower-right are chlorides and bromides. In the case of chlorides, the presence of an alcoholic moiety on the cation is not relevant. Dicyanamides are assembled in a narrow central region ($-0.2 < PC2 < 0.0$). In particular, dicyanamide-based ILs having aliphatic cations (with the exception of azepanium salts) show relatively low PC1 values and are accumulated in the left part of this region. The hydrogen bond donor ability of these ILs is, however, strongly increased by the introduction of a hydroxyl group on the cation moiety, and the points related to the corresponding ILs are in the central part of the plot. The second hydroxyl group leads to a further small drift. Imidazolium dicyanamides show an analogous shift after the addition of one or two hydroxyl groups; however, because the hydrogen atoms of the imidazolium-based ILs are more acidic, the starting points of the unfunctionalized imidazolium salts are at higher PC1 values with respect to the aliphatic ones. Azepanium dicyanamides lie in the same region as imidazolium salts. Presently, the limited number of data available for this class of ILs allows only some hypotheses to rationalize this unexpected “high” hydrogen bond donor ability. One hypothesis is that steric and conformational effects can favor the interaction between Reichardt’s dye and the more acidic hydrogen atoms of the cation. The only functionalized nitrate salt, [Pyr_{1,g}][NO₃], lies near the dicyanamide-based ILs bearing the same class of cations. In this case, the presence of two hydroxyl groups appears to overrule the anion effect. The position of [Pyr_{1,g}][NO₃] in Figure 5 is shifted toward the upper-right corner, outside the nitrate group. An analogous shift can also be observed in the case of the sole IL bearing three OH groups, ([FHMPip_{1,g}][N(CN)₂]).

The limited number of tetrafluoroborates and hexafluorophosphates, as well as of pyridines, reduces the possibility to perform any kind of analysis on these classes of ILs. At variance, the relevant number of data on bistriflimide-based ILs, which are spread on a large range of PC2 values (twice that of dicyanamides) allows us to establish that the poor coordination ability of the bistriflimide anion, reducing the effect of the anion–cation association, makes more relevant the cation effect on the solvent properties. It is notable that, on increasing anion basicity, the ILs bearing the same cations shift toward the left part of the plot, in agreement with a lower hydrogen bond donor ability (PC1 component). The plot is therefore characterized by a triangular distribution of the points. The peculiar position of chlorides and bromides (completely outside of this triangular distribution), together with their insensitivity to the introduction of a hydroxyl group on the cation, suggests that interactions different from hydrogen bonding determine the E_T^N and α values. As previously discussed, we suppose that an important role may be exerted by the interaction of the small spherical chloride anion with the positively charged nitrogen atom of the Reichardt’s dye that determines a further stabilization of the ground state. This interpretation is in agreement with the fact that, when retention times in reverse gas-chromatography (reverse GC) have been used to determine polarity of the IL, [bmim]Cl resulted, characterized by a high hydrogen bond basicity but by a negative value of hydrogen bond acidity, that is, a very low (if any) hydrogen bond acidity.³²

Thermosolvatochromism. Because it has been shown that pyridinium-, pyrrolidinium- and phosphonium-based ILs present a substantial temperature dependence on polarity parameters, we decided to investigate the thermosolvatochromism of four dihydroxyl functionalized ILs ([Pip_{1,g}][N(CN)₂], [DMIM_{1,g}][N(CN)₂], [DMIM_{1,g}][Tf₂N], and [Pyr_{1,g}][Tf₂N]), determining

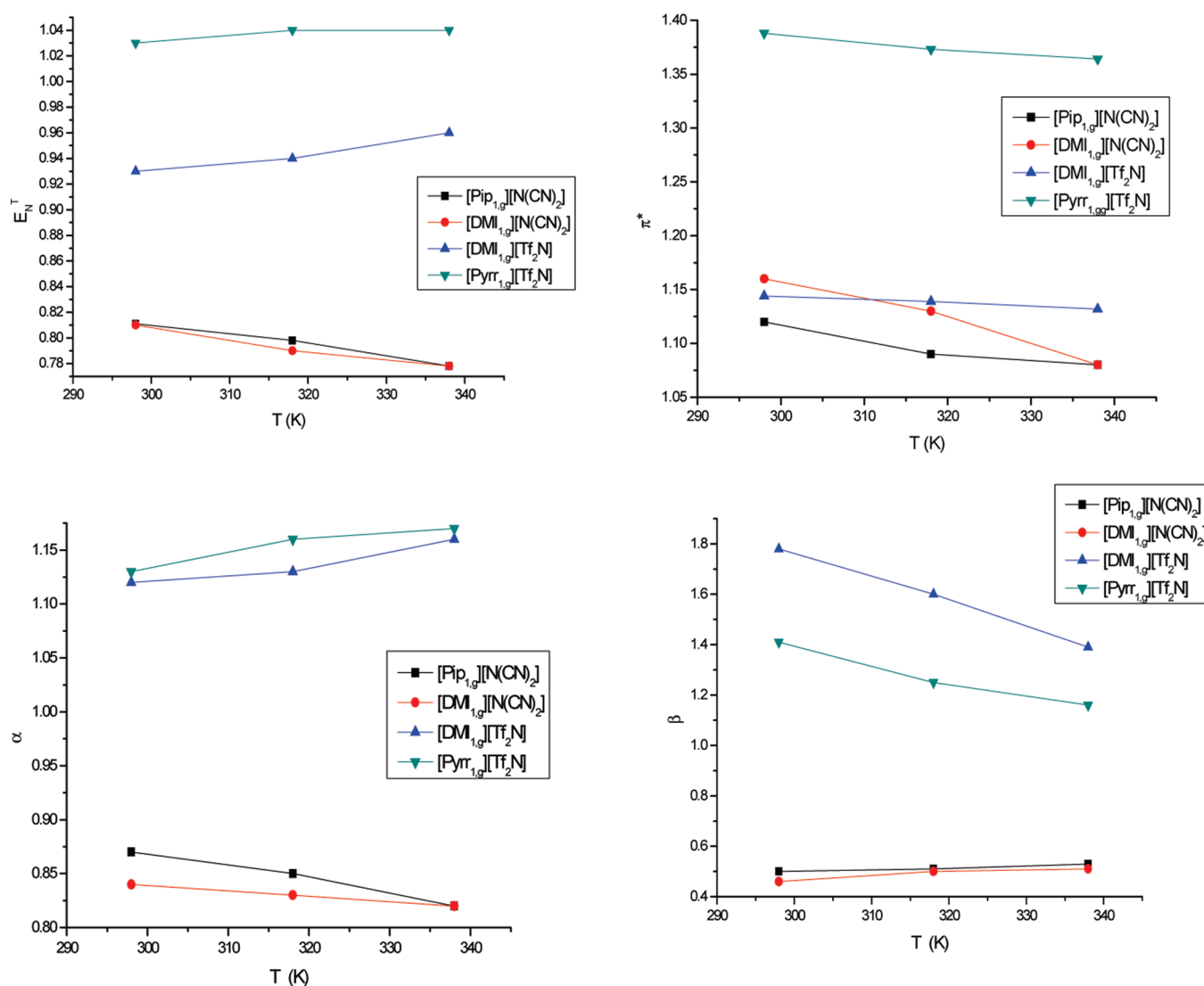


Figure 6. Variations of solvatochromic parameters with temperature. Top left, E_T^N variation for four ILs with temperature; top right, π^* variation for four ILs with temperature; bottom left, α variation for four ILs with temperature; and bottom right, β variation for four ILs with temperature.

the Kamlet–Taft solvatochromic parameters at three different temperatures, 25, 45, and 65 °C. Although the overall changes in the polarity parameters increasing or decreasing the temperature in the interval 25–65 °C were moderate, a dependence on the IL structure was observed. In particular, the E_T^N values decrease linearly with increasing temperature in the case of the two dicyanamide-based ILs ([Pip_{1,g}][N(CN)₂] and [DMIM_{1,g}][N(CN)₂]) but moderately increase with temperature for [DMIM_{1,g}][Tf₂N] and practically remain constant for [Pyr_{1,g}][Tf₂N] (see Figure 5).

Interestingly, the Kamlet–Taft parameters are also affected in different ways by temperature in the case of dicyanamide and bistriflimide salts. From Figure 6, we can see that the polarizability parameter π^* decreases with increasing temperature for all the investigated ILs. However, this effect is more pronounced in the case of dicyanamides and associated with a decrease in hydrogen bonding donor ability; for these salts, the α parameter decreases with increasing temperature. At variance, an increase in α parameter can be observed for bistriflimides. On the other hand, the hydrogen bonding acceptor ability (β) always has an

opposite trend with respect to α ; in particular, it decreases significantly in the case of bistriflimides and moderately increases for dicyanamides. Dicyanamide-based ILs present, therefore, the typical behavior of polar solvents. When the temperature is increased, the ground state interactions between solvent and betaine dye are weakened, thus reducing the gap between the ground and excited state of the betaine dye. Contemporaneously, the hydrogen bond donor acidity also decreases. The opposite effect of temperature, in the case of bistriflimide-based ILs, appears to be related to a decrease in the anion basicity (β) of this anion upon increasing the temperature, which could favor more efficient interactions between the IL cation and the zwitterionic dye, thus determining an increase in the α parameter.

CONCLUSIONS

In summary, through the analysis of the E_T^N and Kamlet–Taft parameters of a large number of ILs synthesized by the quaternarization of *N*-methylmorpholine, *N*-methylpyrrolidine, *N*-methylpiperidine, *N*-methylazepane, 4-hydroxy-1-methylpiperidine,

1,2-dimethylimidazole, and 1-methylimidazole, with simple alkyl chains and/or hydroxyl (mono- or dihydroxyl) functionalized alkyl chains, it has been possible to verify that IL polarity varies in a large interval. In particular, the principal component analysis has shown that there are only two statistical relevant parameters: (i) PC1, a weighted sum of E_T^N and α , which is able to discern among the cation core structure, functionalization, and cation–anion association; and (ii) PC2, very close to β , which is related principally to the anion nature. Generally, for all the investigated cations from bistriflimide to more basic anions (with the exception of chloride and bromide), a significant decrease in PC1 can be observed. On the other hand, the alkyl chain length has only a moderate effect on these parameters whereas the introduction of the OH groups on the cation alkyl chain increases polarity. The effect is significant for the first OH group and more moderate for the second. A triangular distribution characterizes the plot of PC1 vs PC2. This behavior can be rationalized by taking into account both the structural organization of ILs and the possible interactions of anions and cations with the Reichardt's dye. Highly polar ILs can be obtained by associating weakly coordinating anions to properly functionalized cations. Finally, the peculiar position of chlorides and bromides in this plot strongly supports the hypothesis that meaning of E_T^N and α in the case of chlorides and bromides does not conform with that of the other ILs and molecular solvents, being that they are at least partially determined by other interactions.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details of synthesis and characterization of ILs. Numerical values of all measured absorption maxima. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ ACKNOWLEDGMENT

The authors thank Fondazione CARIFI for the financial support.

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