Electronic Supplementary Information

Alternative probe for the determination of the hydrogen-bond acidity of ionic liquids and their aqueous solutions

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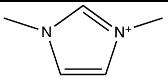
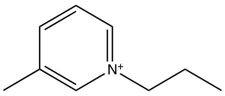
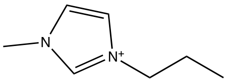
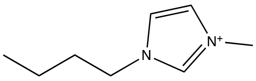
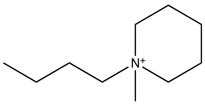
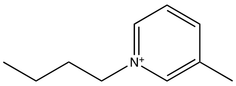
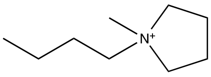
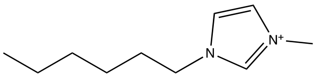
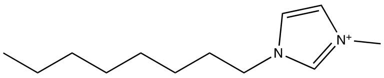
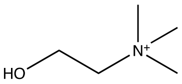
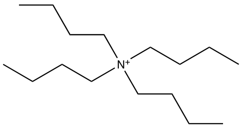
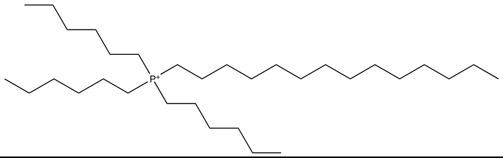
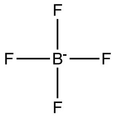
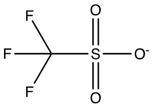
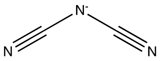
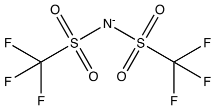
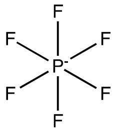
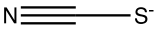
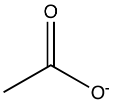
Materials

The following ionic liquids (ILs) were investigated in what concerns the determination of the hydrogen-bond acidity of neat compounds: 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_n$mim][Ntf$_2$], with n = 1, 3, 4, 6 and 8; all 99 wt% pure), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C$_4$mim][CF$_3$SO$_3$], 99 wt% pure), 1-butyl-3-methylimidazolium tetrafluoroborate ([C$_4$mim][BF$_4$], 99 wt% pure), 1-butyl-3-methylimidazolium dicyanamide ([C$_4$mim][N(CN)$_2$], 98 wt% pure), 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$], 99 wt% pure), 1-butyl-3-methyl-imidazolium thiocyanate ([C$_4$mim][SCN], 98 wt% pure), 1-butyl-3-methylimidazolium acetate ([C$_4$mim][CH$_3$CO$_2$], 98 wt% pure), 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ([C$_4$mpip][Ntf$_2$], 99 wt% pure), 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ([C$_4$mpyr][Ntf$_2$], 99 wt% pure), 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([C$_3$mpy][Ntf$_2$], 98 wt% pure), and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ([P$_{666,14}$][Ntf$_2$], 98 wt% pure). The hydrogen-bond acidity was determined for aqueous solutions of the following ILs at different concentrations: 1-alkyl-3-methylimidazolium chloride ([C$_n$mim]Cl, with n = 4 and 6, 99 and 98 wt % pure, respectively), tetrabutylammonium chloride ([N$_{4444}$]Cl, 97 wt% pure), cholinium chloride ([Ch]Cl, 98 wt% pure), 1-butyl-1-methylpyrrolidinium chloride ([C$_4$mpyr]Cl, 99 wt% pure), 1-butyl-3-methylpyridinium chloride ([C$_4$mpy]Cl, 98 wt% pure), [C$_4$mim][CF$_3$SO$_3$], [C$_4$mim][N(CN)$_2$], [C$_4$mim][SCN], and [C$_4$mim][CH$_3$CO$_2$]. All imidazolium-, pyridinium-, and pyrrolidinium-based ILs were purchased from Iolitec. [P$_{666,14}$][Ntf$_2$] was kindly offered by Cytec, and [N$_{4444}$]Cl and [Ch]Cl were purchased from Sigma Aldrich. The chemical structures of cations and anions that composed the studied ILs are presented in Table S1. In order to remove traces of water and volatile compounds, individual samples of each IL were dried at a moderate temperature (*ca*. 323 K) and at high vacuum (*ca.* 10^{-1} Pa), under constant stirring, and for a minimum period of 48 h, prior to the determination of the hydrogen-bond acidity of each neat IL and prior to the preparation of each aqueous solution. The water content was found to be below 0.1 wt%. ILs aqueous mixtures were prepared by weight with an uncertainty of $\pm 10^{-4}$ g. Pyridine-*N*-oxide (PyO) was commercially obtained from Sigma-Aldrich with a purity of 95%.

Table S1. Acronyms, names and chemical structures of cations and anions of the ILs investigated.

Acronym	IL cations	Chemical structure
$[C_1mim]^+$	1,3-dimethylimidazolium	
$[C_3mpy]^+$	1-propyl-3-methylpyridinium	
$[C_3mim]^+$	1-methyl-3-propylimidazolium	
$[C_4mim]^+$	1-butyl-3-methylimidazolium	
$[C_4mpip]^+$	1-butyl-1-methylpiperidinium	
$[C_4mpy]^+$	1-butyl-3-methylpyridinium	
$[C_4mpyr]^+$	1-butyl-1-methylpyrrolidinium	
$[C_6mim]^+$	1-hexyl-3-methylimidazolium	
$[C_8mim]^+$	1-methyl-3-octylimidazolium	
$[Ch]^+$	cholinium	
$[N_{4444}]^+$	tetrabutylammonium	
$[P_{666,14}]^+$	trihexyl(tetradecyl)phosphonium	

Acronym	IL anions	Chemical structure
$[BF_4]^-$	tetrafluoroborate	
$[CF_3SO_3]^-$	trifluoromethanesulfonate	
$[N(CN)_2]^-$	dicyanamide	
$[Ntf_2]^-$	bis(trifluoromethylsulfonyl)amide	
$[PF_6]^-$	hexafluorophosphate	

$[SCN]^-$	thiocyanate	
Cl^-	Chloride	Cl^-
$[CH_3CO_2]^-$	Acetate	

^{13}C NMR spectra analysis

^{13}C NMR spectrum of both neat ILs and IL-water mixtures were determined. Whenever necessary the ^{13}C NMR assignments were taken by 2D Heteronuclear Single Quantum Coherence (HSQC) experiments to a better identification of the IL and PyO chemical shifts. The Mnova software (Santiago de Compostela, Spain) was used for data processing. The standard deviation of α values obtained is estimated to be 0.07. In Figs. S1 and S2 are shown two examples of the NMR spectra analysis.

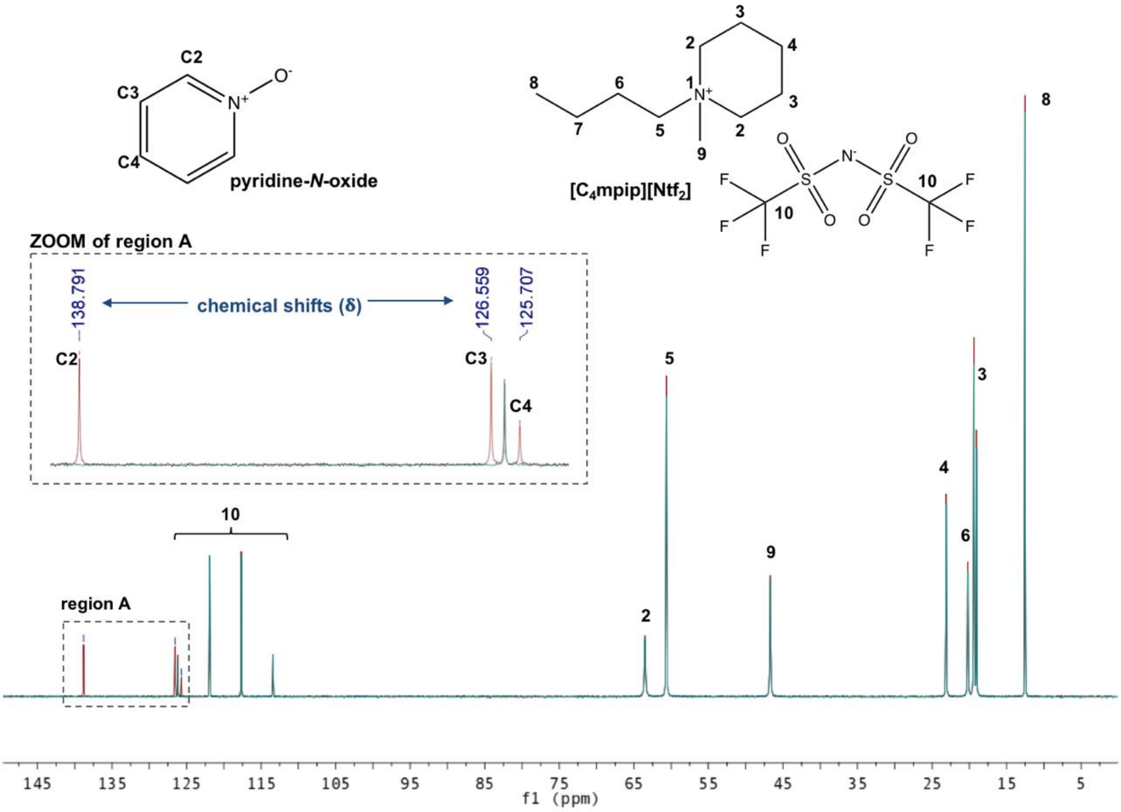


Fig. S1 Identification of the PyO probe ^{13}C NMR chemical shifts in presence of pure $[C_4mpip][Ntf_2]$.

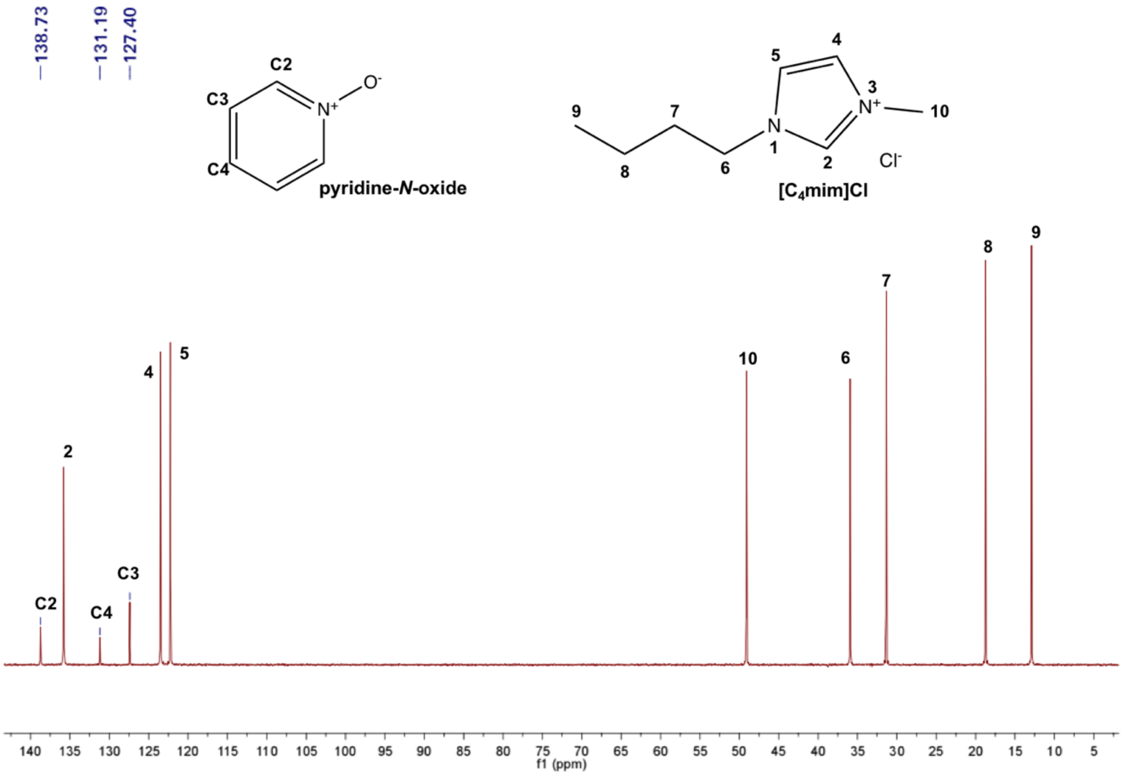


Fig. S2 Identification of the PyO probe ^{13}C NMR chemical shifts in presence of a [C$_4$mim]Cl aqueous solution at 10 % (mol/mol).

Results

Table S2. Solvatochromic parameters for molecular solvents.

Solvent	α_{24}[a]	α_{34}[a]	α_{RD}[b]	π^{*}[b]	$ET_{(30)exp.}$[b,c]	$E_{T\,exp.}^{N}$[b,c]	$ET_{(30)cal.}$[c]	$E_{T\,cal.}^{N}$[c]
Acetic acid	1.24	1.36	1.09	0.64	55.2	0.76	60.1	0.91
3-Methylphenol	1.34	1.25	0.88	0.68	52.4	0.67	62.3	0.97
Water	1.36	1.24	1.28	1.09	63.1	1.00	67.2	1.13
Hexafluoro-2-propanol	1.11	1.07	1.74	0.65	65.3	1.07	57.9	0.84
2,2,2-Trifluoroethanol	1.11	1.07	1.33	0.73	59.8	0.90	58.8	0.87
1,2-Ethanediol	1.06	0.98	0.96	0.92	56.3	0.79	60.1	0.91
Methanol	0.90	0.84	1.13	0.6	55.4	0.76	53.7	0.71
Formamide	0.86	0.79	0.94	0.97	56.6	0.80	57.1	0.81
Ethanol	0.81	0.74	0.95	0.54	51.9	0.65	51.5	0.64
1-Propanol	0.80	0.73	0.82	0.48	49.2	0.57	50.6	0.61
1-Butanol	0.78	0.72	0.84	0.4	48.6	0.55	49.4	0.58
2-Propanol	0.77	0.70	0.74	0.4	47.1	0.51	49.2	0.57
Benzyl alcohol	0.37	0.62	0.54	0.98	50.4	0.61	48.6	0.55
N-Methylformamide	0.57	0.52	0.83	0.9	54.1	0.72	51.2	0.63
Aniline	0.51	0.46	0.32	0.73	44.3	0.42	48.3	0.54
Nitromethane	0.25	0.22	0.36	0.85	46.3	0.48	45.1	0.44
Dichloromethane	0.19	0.21	0.02	0.82	40.7	0.31	43.7	0.40
Chloroform	0.27	0.16	0.09	0.58	39.1	0.26	42.4	0.36
Acetonitrile	0.19	0.16	0.39	0.75	45.6	0.46	42.9	0.38
Dimethylsulfoxide	0.22	0.13	0.18	1	45.1	0.44	46.2	0.48
N,*N*-Dimethylformamide	0.14	0.06	0.18	0.88	43.8	0.40	43.5	0.39
Acetone	0.10	0.05	0.20	0.71	42.2	0.35	40.9	0.32
Tetrachloromethane	0.00	0.02	-0.13	0.28	32.4	0.05	34.4	0.11
Hexamethyl phosphoric triamide	0.06	-0.03	0.00	0.87	40.9	0.31	42.0	0.35
Cyclohexane	-0.54	-0.40	-0.03	0	30.9	0.01	21.8	-0.27

[a] data from H. Schneider, Y. Badrieh, Y. Migron and Y. Marcus, *Z. Phys. Chem.*, 1992, **177**, 143–156;

[b] data from Y. Marcus, Chem. Soc. Rev., 1993, **22**, 409–416;

[c] $ET_{(30)exp.}$ values are based on the negatively solvatochromic pyridinium N-phenolate betaine dye (Reichardt's dye) as probe, and calculated according to Equation 5a; $E_{T\,exp.}^{N}$ are the normalized values defined according to Equation 5b; $ET_{(30)cal.}$ and $E_{T\,calc.}^{N}$ are the same quantities calculated through Equations 4, 5a and 5b, where α_{24} correspond to the ^{13}C NMR chemical shifts of carbon 2, with respect to that of carbon 4, of PyO.

Table S3. Differences d_{24} and d_{34} in ppm of the ^{13}C NMR chemical shifts, δ, of carbons 2 and 3, respectively, with respect to that of carbon 4 of PyO in the ILs studied in this work.

IL	d_{24}	d_{34}
$[C_1mim][Ntf_2]$	11.591	-0.697
$[C_3mim][Ntf_2]$	12.051	-0.237
$[C_4mim][Ntf_2]$	12.280	0.070
$[C_6mim][Ntf_2]$	12.155	0.005
$[C_8mim][Ntf_2]$	12.531	0.173
$[C_4mim][CF_3SO_3]$	12.900	0.490
$[C_4mim][BF_4]$	12.690	0.450
$[C_4mim][N(CN)_2]$	12.860	0.510
$[C_4mim][PF_6]$	12.520	0.280
$[C_4mim][SCN]$	12.800	0.550
$[C_4mim][CH_3CO_2]$	13.797	1.292
$[C_4mpip][Ntf_2]$	13.089	0.857
$[C_4mpyr][Ntf_2]$	12.511	0.323
$[C_3mpy][Ntf_2]$	10.190	-2.512
$[P_{666,14}][Ntf_2]$	13.194	0.782

Table S4. Solvatochromic parameters of the investigated ILs.

IL	$ET_{(30)exp.}$[a]	E_T^N exp.[a]	$ET_{(30)cal.}$[a]	E_T^N cal.[a]
$[C_1mim][Ntf_2]$	54.67	0.74	52.20	0.66
$[C_3mim][Ntf_2]$	53.95	0.72	50.86	0.62
$[C_4mim][Ntf_2]$	52.34	0.67	50.11	0.60
$[C_6mim][Ntf_2]$	51.68	0.65	50.57	0.61
$[C_8mim][Ntf_2]$	51.57	0.64	49.41	0.58
$[C_4mim][CF_3SO_3]$	51.93	0.66	49.20	0.57
$[C_4mim][BF_4]$	51.93	0.66	49.73	0.59
$[C_4mim][N(CN)_2]$	51.25	0.63	49.76	0.59
$[C_4mim][PF_6]$	53.07	0.69	50.30	0.60
$[C_4mim][SCN]$	49.66	0.59	50.04	0.60
$[C_4mim][CH_3CO_2]$	48.55	0.55	46.31	0.48
$[C_4mpip][Ntf_2]$	48.49	0.55	48.01	0.53
$[C_4mpyr][Ntf_2]$	48.95	0.56	49.41	0.58
$[C_3mpy][Ntf_2]$	50.01	0.60	55.98	0.78
$[P_{666,14}][Ntf_2]$	44.52	0.43	46.77	0.50

[a] $ET_{(30)exp.}$ values are based on the negatively solvatochromic pyridinium N-phenolate betaine dye (Reichardt's dye) as probe, and calculated according to Equation 5a; E_T^N exp. are the normalized values defined according to Equation 5b; $ET_{(30)cal.}$ and E_T^N calc. are the same quantities calculated through Equations 4, 5a and 5b, where α_{24} correspond to the ^{13}C NMR chemical shifts of carbon 2, with respect to that of carbon 4, of PyO.

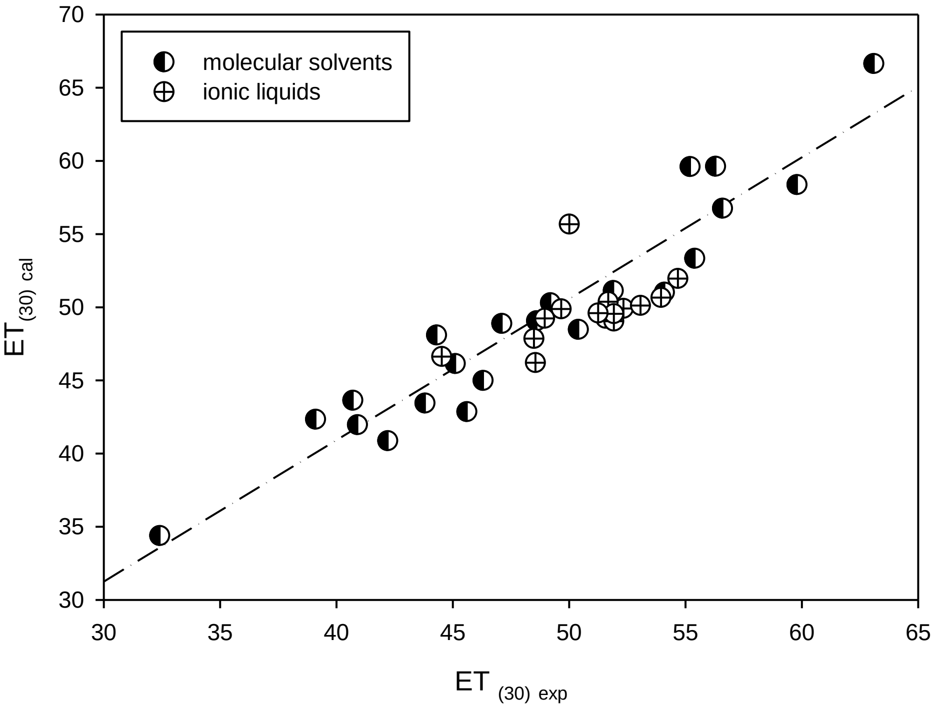


Fig. S3 $ET_{(30)cal.}$ values calculated with Equations 4 and 5, where the α values were obtained with the PyO probe, versus experimental values of $ET_{(30)exp.}$ obtained with the Reichardt's dye: molecular solvents (◑) and ILs (⊕). Similar results are obtained for E_T^N values (data not shown). 3-Methylphenol, hexafluoro-2-propanol and cyclohexane were found as outliers.

Table S5. α_{24} values and compositions of the studied IL-water mixtures.

IL	**[IL] / (mol.mol^{-1}) %**	**α_{24}**
[C$_4$mim]Cl	0.0	1.36
	5.1	1.28
	9.9	1.19
	19.9	1.01
	25.0	0.93
[C$_6$mim]Cl	5.1	1.24
	10.1	1.14
	19.8	0.97
	25.5	0.87
[N$_{4444}$]Cl	5.2	1.20
	9.7	1.08
	19.3	0.84
[Ch]Cl	5.2	1.33
	9.9	1.27
	20.3	1.18
	24.9	1.11
[C$_4$mpyr]Cl	5.0	1.30
	9.9	1.20
	19.8	1.00
	24.8	0.90
[C$_4$mpy]Cl	5.2	1.28
	10.1	1.19
	19.8	1.02
	0.90	0.90
[C$_4$mim][SCN]	0.0	1.36
	19.2	1.04
	38.9	0.84
	57.2	0.67
	77.3	0.53
	100	0.40
[C$_4$mim][N(CN)$_2$]	0.0	1.36
	18.3	1.04
	37.5	0.81
	56.3	0.64
	76.5	0.53
	100	0.39
[C$_4$mim][CF$_3$SO$_3$]	0.0	1.36
	20.1	1.03
	39.6	0.85
	58.0	0.66
	79.0	0.58
	100	0.39
[C$_4$mim][CH$_3$CO$_2$]	0.0	1.36
	19.4	0.92
	39.8	0.60
	59.4	0.41
	75.4	0.32
	100	0.25