Calorimetric quantification of the hydrogen-bond acidity of solvents and its relationship with solvent polarity

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A new solvent polarity–polarizability scale (SPP) has been used to reevaluate the hydrogen-bond acidity scale of organic solvents previously reported and has been extended to a new set of solvents. The hydrogen-bond acidity, expressed as the enthalpy term $\Delta_{acid}H$, has been evaluated by measuring the differences between the solvation enthalpies of *N*-methylimidazole and *N*-methylpyrrole in these solvents along with the solvent polarity–polarizability (SPP) values. The $\Delta_{acid}H$ values for 63 solvents are reported.

It has been previously reported[1] that the hydrogen-bond acidity of a given solvent can be quantified as the difference between the enthalpies of solvation of two solute probes, such as *N*-methylimidazole and *N*-methylpyrrole, which differ in their hydrogen-bond acceptor (HBA) strength. The large difference in basicity between these structurally similar solute molecules means that the expected difference in their enthalpies of transfer from the gas phase (where no intermolecular interaction is present) to solution, $\delta\Delta_{solv}H$, will mainly reflect the hydrogen-bond acidity of the solvent, as expressed in the enthalpy term $\Delta_{acid}H$, and to a lesser extent its polarity due to the very different dipolar moments of the solutes. To a first approximation, the relative permittivity[2] function of Kirkwood [eqn. (1)] was used in order to correct for the polarity

$$f(\varepsilon) = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \qquad (1)$$

contribution to $\delta\Delta_{solv}H$. Eqn. (2) so obtained allows the

$$-\Delta_{acid}H = \delta\Delta_{solv}H + 18.76\,f(\varepsilon) + 1.69 \qquad (2)$$

experimental quantification of the hydrogen-bond acidity of any solvent if its relative permittivity, ε, is known.[3]

More recently, a new solvent polarity–polarizability scale (SPP) based on the UV–VIS spectra of 2-dimethylamino-7-nitrofluorene (DMANF) and its homomorph 2-fluoro-7-nitrofluorene (FNF) has been proposed.[4] It allows reevaluation of the previously reported data as well as the application of this calorimetric approach to a wider group of solvents. The possible partial protonation of *N*-methylimidazole upon transfer from the gas phase to solution in a strongly acidic solvent (which would produce an enthalpic contribution to $\delta\Delta_{solv}H$ not directly related to the hydrogen-bond acidity of the solvent), will be discussed by comparing these results with those obtained with a less basic probe (*N*-methylpyrazole).

Experimental

N-Methylpyrazole was prepared by methylation of pyrazole using phase-transfer catalysis without solvent, as described by Diez-Barra *et al.*[5] but using much larger quantities. Starting from 100 g of pyrazole, 93 g (81% yield) of *N*-methylpyrazole with small amounts of water and pyrazole was obtained. The product was purified by repeated distillation at atmospheric pressure until the HPLC trace showed only the peak of *N*-methylpyrazole. All solutes and solvents used in this work were of the highest purity (⩾99.5%) and were supplied by Aldrich, Fluka and Merck. When necessary the solvents were purified by fractional distillation through a spinning band column under nitrogen followed by sequential drying with 4 Å molecular sieves. The purity and water content were checked by gas chromatography.

The enthalpies of solution of *N*-methylimidazole, *N*-methylpyrrole and *N*-methylpyrazole in different solvents were determined as follows.

For those compounds in which the solubility of the probes is high either an LKB batch microcalorimeter equipped with a titration unit[6] (6 cm^3 of solvent in the vessel) or a 2277 Thermal Activity Monitor System (Thermometric AB, Järfälla, Sweden) with a microcalorimetric vessel[7] (3 cm^3 volume) inserted in one of the channels were used. For those solvents, such as benzene, toluene, cyclohexane, acetonitrile, in which the solubility of the probes is low, a microcalorimeter based on the same principle as those of the Thermal Activity Monitor but with wider vessel holders to accommodate vessels of 9 or 20 cm^3 volume[8] was used. In order to achieve efficient mixing, turbine type stirrers with a stirring speed of about 120 rpm were used.

The calorimetric titration experiments consisted of 10 to 15 consecutive additions of the liquid solutes into the solvent in the calorimetric vessel. The additions were made from a gas-tight Hamilton syringe attached to a computer operated-syringe driver. The injection volumes were of 2.6 mm^3 in the LKB batch microcalorimeter. In the other calorimeters the injection volumes were between 1 and 5 mm^3, and the rate of injection varied between 1 and 0.1 mm^3 min^{-1}, depending on the solubility of the sample. The instruments were calibrated both electrically, using an insertion heater, and by dissolution of pure propan-1-ol in water.[9]

If the enthalpies of solution depended on the concentration, the data were extrapolated to infinite dilution.

Results and discussion

The molar enthalpies of solution at infinite dilution of the different probes in a total of 63 solvents together with the molar enthalpies of vaporization of the solutes at 25 °C are presented in Table 1. The uncertainties were calculated as twice the standard deviation of the mean. The molar enthalpies of transfer from the gas phase to an infinitely dilute solution were calculated as the difference between the molar enthalpy of solution and the molar enthalpy of vaporization [eqn. (3)].

Table 1 Enthalpies of solution of the three probes in 63 solvents at 25 °C

	$\Delta_{sol}H^\circ$/kJ mol^{-1}		
Solvent	*N*-Methylpyrrole	*N*-Methylimidazole	*N*-Methylpyrazole
1 Cyclohexane	7.90 ± 0.35	15.81 ± 0.47	19.46 ± 0.56
2 Nitrobenzene	0.09 ± 0.02[a]	1.20 ± 0.06[a]	
3 1,2-Dichlorobenzene	0.20 ± 0.01[a]	2.73 ± 0.22[a]	4.06 ± 0.15
4 Benzonitrile	−0.83 ± 0.02[a]	0.65 ± 0.01[a]	1.25 ± 0.07
5 Hexamethylphosphoramide	−5.14 ± 0.13[a]	−3.33 ± 0.13[a]	−4.71 ± 0.35
6 Tetrahydrofuran	−0.85 ± 0.03[a]	1.78 ± 0.16[a]	0.42 ± 0.03
7 Tetramethylurea	−1.82 ± 0.02[a]	−0.96 ± 0.02[a]	−2.40 ± 0.26
8 Cyclohexanone	−0.43 ± 0.02[a]	1.57 ± 0.13[a]	1.02 ± 0.11
9 Tetrahydropyran	0.03 ± 0.01	3.27 ± 0.62	
10 Triethylamine	3.65 ± 0.09[a]	9.13 ± 0.40[a]	
11 Pyridine	−0.25 ± 0.04[a]	0.75 ± 0.16[a]	
12 Propionitrile	−0.11 ± 0.02[a]	1.35 ± 0.04[a]	1.22 ± 0.10
13 Chlorobenzene	−0.10 ± 0.01[a]	2.11 ± 0.05[a]	3.48 ± 0.15
14 Butan-2-one	−0.01 ± 0.01[a]	1.31 ± 0.14[a]	
15 *N*,*N*-Dimethylformamide	−0.79 ± 0.08[a]	−0.71 ± 0.16[a]	−1.20 ± 0.13
16 Dimethyl sulfoxide	0.54 ± 0.08[a]	−0.17 ± 0.13[a]	−0.58 ± 0.03
17 Tributylamine	3.00 ± 0.44	7.83 ± 0.26	
18 Acetone	0.00 ± 0.03[a]	0.94 ± 0.19[a]	−0.89 ± 0.16
19 Dibutyl ether	3.49 ± 0.09	7.70 ± 0.26	
20 Anisole	0.14 ± 0.02[a]	1.82 ± 0.04[a]	2.62 ± 0.31
21 Tetrachloromethane	1.59 ± 0.08[b]	2.35 ± 0.10	
22 *N*-Methylimidazole	0.07 ± 0.02		
23 Acetonitrile	1.58 ± 0.12	1.79 ± 0.12	
24 Ethyl acetate	0.25 ± 0.04[a]	1.86 ± 0.13[a]	0.76 ± 0.06
25 *N*-Methylpyrrole		0.14 ± 0.02	
26 Fluorobenzene	−0.37 ± 0.05	1.52 ± 0.18	
27 Butyl acetate	0.39 ± 0.06	1.72 ± 0.18	
28 1,4-Dioxane	−0.21 ± 0.02[a]	2.08 ± 0.17[a]	1.93 ± 0.21
29 Dibutylamine	2.96 ± 0.10	6.38 ± 0.42	
30 Toluene	0.92 ± 0.09	3.75 ± 0.18	
31 2-Methyltetrahydrofuran	−0.05 ± 0.02	1.75 ± 0.05	
32 *tert*-Butyl methyl ether	1.34 ± 0.07	3.25 ± 0.14	
33 Benzene	0.69 ± 0.02[b]	3.56 ± 0.10	
34 Propyl formate	0.34 ± 0.02[b]	−1.69 ± 0.20	
35 Dichloromethane	−2.66 ± 0.07[a]	−3.89 ± 0.19[a]	−0.65 ± 0.14
36 Nitromethane	2.18 ± 0.02[a]	−1.38 ± 0.07[a]	2.43 ± 0.20
37 Chloroform	−6.15 ± 0.08[a]	−9.37 ± 0.58[a]	−5.34 ± 0.27
38 Aniline	0.09 ± 0.06[a]	−6.95 ± 0.09[a]	−2.99 ± 0.21
39 Propan-2-ol	5.73 ± 0.08[a]	−0.42 ± 0.02[a]	2.28 ± 0.27
40 Formamide	3.51 ± 0.06[a]	−3.38 ± 0.06[a]	−0.15 ± 0.05
41 Prop-2-ynyl alcohol	1.41 ± 0.09	−6.69 ± 0.06	
42 Cyclohexanol	7.44 ± 0.07[a]	−0.09 ± 0.01[a]	
43 Ethanol	4.41 ± 0.08[a]	−3.33 ± 0.10[a]	0.95 ± 0.11
44 Propan-1-ol	5.59 ± 0.12	−2.65 ± 0.04	
45 Butan-1-ol	6.24 ± 0.05[a]	−1.86 ± 0.03[a]	2.48 ± 0.16
46 Pentan-1-ol	6.40 ± 0.11	−1.76 ± 0.04	
47 Cyclopentanol	7.96 ± 0.11	−0.92 ± 0.07	
48 Cyclooctanol	8.25 ± 0.23	−0.39 ± 0.03	
49 Octan-1-ol	6.71 ± 0.06	−1.39 ± 0.05	
50 Cycloheptanol	8.02 ± 0.15	−0.92 ± 0.07	
51 Water	1.05 ± 0.08[a]	−9.75 ± 0.13[a]	−6.17 ± 0.09
52 Methanol	3.39 ± 0.08[a]	−6.86 ± 0.25[a]	−1.77 ± 0.09
53 Ethylene glycol	3.88 ± 0.18	−7.84 ± 0.06	
54 Allyl alcohol	4.10 ± 0.07	−7.98 ± 0.14	
55 Pyrrole	−0.45 ± 0.02[a]	−12.82 ± 0.47[a]	
56 Phenethyl alcohol	2.85 ± 0.02	−11.51 ± 0.11	
57 Acetic acid	1.70 ± 0.02	−43.13 ± 0.38	−8.28 ± 0.42
58 Benzyl alcohol	2.42 ± 0.08	−12.83 ± 0.25	
59 2-Chloroethanol	2.13 ± 0.01[a]	−14.02 ± 0.34[a]	−8.27 ± 0.16
60 2,2,2-Trifluoroethanol	1.86 ± 0.03[a]	−20.76 ± 0.81[a]	−17.79 ± 0.37
61 2,2,2-Trichloroethanol	1.46 ± 0.05[a]	−24.78 ± 0.50[a]	−22.93 ± 0.75
62 *m*-Cresol	4.06 ± 0.03	−26.20 ± 0.05	−18.30 ± 0.96
63 Hexafluoropropan-2-ol	−6.46 ± 0.09	−89.52 ± 1.02	−32.74 ± 1.07
	$\Delta_{vap}H^\circ$/kJ mol^{-1}		
	40.71 ± 0.29	54.64 ± 0.46	41.84 ± 0.17

[a] Ref. 1. [b] Ref. 10.

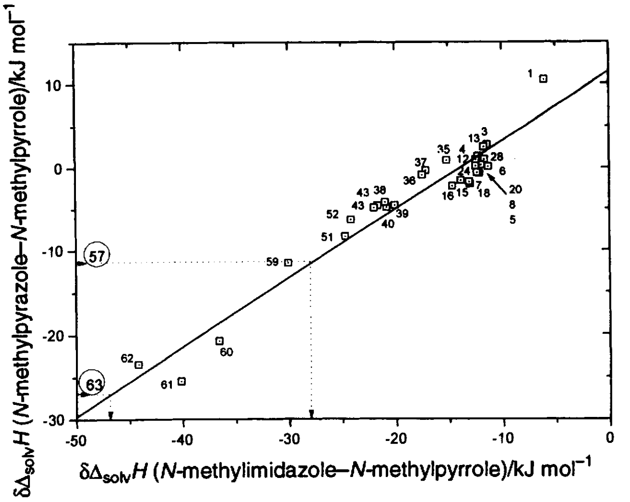

Fig. 1 Comparison of the differences between the enthalpies of solvation for the two pairs of probes

$$\Delta_{solv}H = \Delta_{sol}H - \Delta_{vap}H \qquad (3)$$

In principle, it seems possible that the interaction of *N*-methylimidazole, a potent hydrogen bond acceptor (HBA), with some strongly acidic solvents could lead to its partial or total protonation, adding a contribution to $\Delta_{sol}H$(*N*-methylimidazole) not directly related to the hydrogen bond acidity of the solvent. In order to check this possibility, we have evaluated the acidity of several solvents, substituting the basic probe *N*-methylimidazole by *N*-methylpyrazole, a much weaker hydrogen bond acceptor. *N*-methylimidazole has a solvent basicity value, SB, of 0.83.[10] Using the pure solvent method with the same four probes as in ref. 10, we obtained an SB value of 0.65 for *N*-methylpyrazole. The differences in the enthalpy of solvation for the two pairs of probes (*e.g.* *N*-methylimidazole–*N*-methylpyrrole and *N*-methylpyrazole–*N*-methylpyrrole) for the 63 solvents studied are presented in Table 2. As might be expected, the enthalpy difference is smaller when *N*-methylpyrazole is used as the basic probe due to its weaker HBA character. A plot of $\delta\Delta_{solv}H$(*N*-methylimidazole–*N*-methylpyrrole) *vs.* $\delta\Delta_{solv}H$(*N*-methylpyrazole–*N*-methylpyrrole) is shown in Fig. 1 and from it, it is possible to estimate the solvation enthalpy for those strongly acidic solvents which can protonate the *N*-methylimidazole probe and therefore are shifted horizontally to the left in Fig. 1, as is the case for acetic acid and hexafluoropropan-2-ol, with a protonation contribution to $\delta\Delta_{solv}H$(*N*-methylimidazole–*N*-methylpyrrole) of -31.27 and -49.75 kJ mol^{-1}, respectively.

As discussed above, this difference between the solvation enthalpies reflects not only the hydrogen-bond acidity strength of the solvent but also the polarity–polarizability interaction between the solvent and the residual polarity–polarizability of the combined probes. Fig. 2 shows the dependence of $\delta\Delta_{solv}H$ on the polarity-polarizability parameter (SPP) of the solvents studied. Two different behaviours are observed: for the non-hydrogen bond donor solvents the difference between the enthalpy of solvation of the two probes $\delta\Delta_{solv}H$, increases (in absolute value) linearly with the polarity–polarizability of the solvent, whereas for the hydrogen bond donor (HBD) solvents a deviation from this behaviour is observed.

For the 33 non-HBD solvents, marked with circles in Fig. 2, we have found the relation shown in eqn. (4) between

$$\delta\Delta_{solv}H = (-14.59 \pm 0.25)\,\mathrm{SPP} \qquad (4)$$

$\delta\Delta_{solv}H$ and the polarity–polarizability parameter, SPP, with

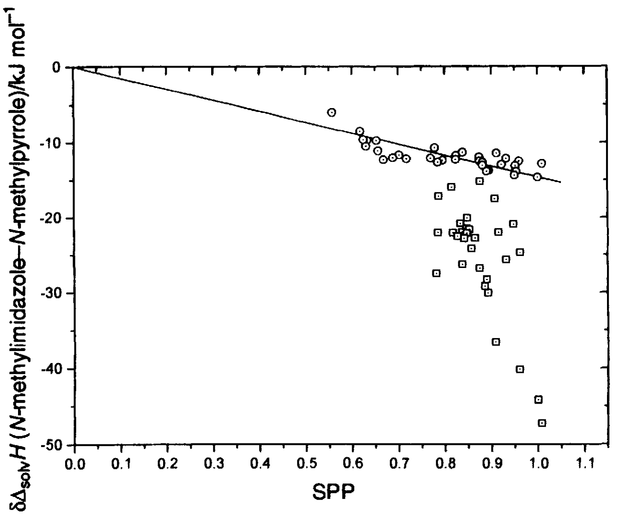

Fig. 2 Dependence of the difference between the enthalpies of solvation of the solvents on the polarity parameter

($n = 33$, $\chi^2 = 1.35$), where χ^2 is given by eqn. (5), N and n

$$\chi^2 \equiv \frac{\Sigma[f(X_i) - Y_i]}{N - n} \qquad (5)$$

being the number of parameters of the equation and the number of points, respectively, Y_i the experimental value of the solvation enthalpy in the solvent i, and $f(X_i)$, the solvation enthalpy calculated from eqn. (4).

This dependence of the differences between the enthalpies of solvation in non-HBD solvents for the two probes [eqn. (4) and Fig. 2] is smaller than that expected from the difference in the dipolar moments of the probes for the *N*-methylimidazole (μ = 3.77 D)[11] and for *N*-methylpyrrole (μ = 1.91 D),[11] but consistent with their slightly different polarity–polarizability parameters (SPP = 0.950 and 0.890 respectively).[4]

On the other hand, the small scatter of the points in the linear correlation presented in Fig. 2 for the non-HBD solvents clearly indicates that no other term, such as the molar volume or Hildebrand parameter, is needed to account for the interaction between these solvents and the combination of the two probes. According to these results, acetonitrile (solvent 23) behaves calorimetrically as a non-HBD solvent and the same is true for some carbonyl compounds such as acetone (solvent 18) and butan-2-one (solvent 14), whereas propyl formate (solvent 34), usually considered as non-HBD, behaves as a weak hydrogen bond donor (HBD).

The contribution of the polarity–polarizability term to the difference between the enthalpy of solvation of the two solute probes, $\delta\Delta_{solv}H$, for the HBD solvents can be evaluated through eqn. (4) in the same way as for the non-HBD solvents. Consequently the enthalpic contribution of the interaction between the hydrogen bond acidity of the solvent and the hydrogen bond basicity of the combined probes, $\Delta_{acid}H$, can be easily obtained from eqn. (6).

$$\Delta_{acid}H = \delta\Delta_{solv}H + 14.59\mathrm{SPP} \qquad (6)$$

In fact, this equation is a quantification of the displacement from the linear behaviour shown by the non-HBD solvents in a plot of $\delta\Delta_{solv}H$ *vs.* SPP for an HBD solvent from its SPP value.

The hydrogen-bond acidities of the 63 solvents studied, $\Delta_{acid}H$, are gathered in the 5th column of Table 2, where the following structural dependencies can be observed. (*a*) For linear chain alcohols, an increase in hydrocarbon chain length does not pronouncedly decrease the acidity. This is valid except

Table 2 Thermodynamic and polarity parameters for the evaluation of $\Delta_{acid}H$. All enthalpy values in kJ mol^{-1}

Solvent	$\delta\Delta_{solv}H$ (MeIm–MePyrr)	$\delta\Delta_{solv}H$ (MePyrz–MePyrr)	SPP	$\Delta_{acid}H$	α^c	AN^d
1 Cyclohexane	−6.02	10.43	0.557^a	2.10		
2 Nitrobenzene	−12.82		1.009^a	1.89		14.8
3 1,2-Dichlorobenzene	−11.40	2.73	0.911^a	1.88		3.0
4 Benzonitrile	−12.45	0.95	0.960^a	1.55		15.5
5 Hexamethylphosphoramide	−12.12	−0.70	0.932^a	1.47		10.6
6 Tetrahydrofuran	−11.30	0.14	0.838^a	0.92		8.0
7 Tetramethylurea	−13.07	−1.71	0.952^a	0.81		9.2
8 Cyclohexanone	−11.93	0.32	0.874^a	0.81		
9 Tetrahydropyran	−10.69		0.778^a	0.65		
10 Triethylamine	−8.45		0.617^a	0.55		1.4
11 Pyridine	−12.93		0.922^a	0.51		14.2
12 Propionitrile	−12.47	0.20	0.875^a	0.29		
13 Chlorobenzene	−11.72	2.46	0.824^a	0.29		
14 Butan-2-one	−12.61		0.881^a	0.23	0.06	
15 *N*,*N*-Dimethylformamide	−13.85	−1.54	0.954^a	0.06		16.0
16 Dimethyl sulfoxide	−14.64	−2.25	1.000^a	0.06		19.3
17 Tributylamine	−9.61		0.624^a	−0.00		
18 Acetone	−12.99	−2.02	0.881^a	−0.15	0.08	12.3
19 Dibutyl ether	−9.72		0.652^a	−0.21		
20 Anisole	−12.25	1.35	0.823^a	−0.25		
21 Tetrachloromethane	−9.69		0.632^a	−0.48		0.0
22 *N*-Methylimidazole	−14.36		0.950^a	−0.51		
23 Acetonitrile	−13.72		0.895^a	−0.67	0.19	18.9
24 Ethyl acetate	−12.32	−0.62	0.795^a	−0.73		9.3
25 *N*-Methylpyrrole	−13.79		0.890^a	−0.81		
26 Fluorobenzene	−12.04		0.769^a	−0.83		
27 Butyl acetate	−12.60		0.784^a	−1.17		
28 1,4-Dioxane	−11.64	1.01	0.701^a	−1.27		10.3
29 Dibutylamine	−10.51		0.630^b	−1.32		
30 Toluene	−11.10		0.655^a	−1.55		
31 2-Methyltetrahydrofuran	−12.13		0.717^a	−1.68		
32 *tert*-Butyl methyl ether	−12.02		0.687^a	−2.13		
33 Benzene	−12.27		0.667^a	−2.55		8.2
34 Propyl formate	−15.96		0.815^a	−3.99		
35 Dichloromethane	−15.16	0.88	0.876^a	−4.00	0.30	20.4
36 Nitromethane	−17.49	−0.88	0.907^a	−4.17	0.22	20.5
37 Chloroform	−17.15	−0.32	0.786^a	−5.60	0.44	4.0
38 Aniline	−20.97	−4.21	0.948^b	−7.04		
39 Propan-2-ol	−20.08	−4.58	0.848^b	−7.62	0.76	33.5
40 Formamide	−20.82	−4.79	0.833^a	−8.58	0.71	39.8
41 Prop-2-ynyl alcohol	−22.03		0.915^b	−8.59		
42 Cyclohexanol	−21.46		0.847^b	−9.02		
43 Ethanol	−21.67	−4.59	0.853^a	−9.14	0.83	37.1
44 Propan-1-ol	−22.17		0.847^a	−9.73	0.78	37.3
45 Butan-1-ol	−22.03	−4.89	0.837^b	−9.73	0.79	36.8
46 Pentan-1-ol	−22.09		0.817^b	−10.09		
47 Cyclopentanol	−22.81		0.865^b	−10.10		
48 Cyclooctanol	−22.57		0.827^b	−10.42		
49 Octan-1-ol	−22.03		0.785^b	−10.50		
50 Cycloheptanol	−22.87		0.841^b	−10.52		
51 Water	−24.73	−8.35	0.962^b	−10.60	1.17	54.8
52 Methanol	−24.18	−6.29	0.857^a	−11.59	0.93	41.3
53 Ethylene glycol	−25.65		0.932^a	−13.43	0.90	
54 Allyl alcohol	−26.81		0.875^b	−13.96		
55 Pyrrole	−26.30		0.838^a	−13.99		
56 Phenethyl alcohol	−28.29		0.890^b	−15.22		33.8
57 Acetic acid^e	−27.49	−11.11	0.781^a	−15.96	1.12	52.9
58 Benzyl alcohol	−29.18		0.886^b	−16.16		36.8
59 2-Chloroethanol	−30.08	−11.53	0.893^b	−16.96		
60 2,2,2-Trifluoroethanol	−36.58	−20.78	0.908^b	−23.24	1.51	53.3
61 2,2,2-Trichloroethanol	−40.17	−25.52	0.960^b	−26.07		
62 *m*-Cresol	−44.19	−23.59	1.000^b	−29.50		50.4
63 Hexafluoropropan-2-ol^e	−47.24	−27.41	1.007^b	−32.47	1.96	66.7

[a] Ref. 4. [b] Ref. 12. [c] Ref. 14. [d] Ref. 15. [e] $\delta\Delta_{solv}H$(MeIm–MePyrr) value is obtained from Fig. 1 with data of $\delta\Delta_{solv}H$(MePyrz–MePyrr).

for the first term of the series where $\Delta_{acid}H$ is −11.59 kJ mol^{-1} for methanol and −9.4 kJ mol^{-1} for ethanol. (*b*) Cyclization has no significant effect on acidity, which is −10.09 kJ mol^{-1} for pentan-1-ol and −10.10 kJ mol^{-1} for cyclopentanol, and −10.50 kJ mol^{-1} and −10.42 kJ mol^{-1} for octan-1-ol and cyclooctanol, respectively. (*c*) Halogenation of an alcohol dramatically increases its acidity. In the ethanol series this value increases from −9.14 kJ mol^{-1} for ethanol to −16.96 kJ mol^{-1} for 2-chloroethanol and to −26.07 kJ mol^{-1} for 2,2,2-trichloroethanol. Similarly, the acidity increases from −7.62 kJ mol^{-1} for propan-2-ol to −32.47 kJ mol^{-1} for hexafluoropropan-2-ol. (*d*) The acidity value per hydrogen bond of pyrrole (−13.99 kJ mol^{-1}) underlines its potential use as a basicity environment probe.

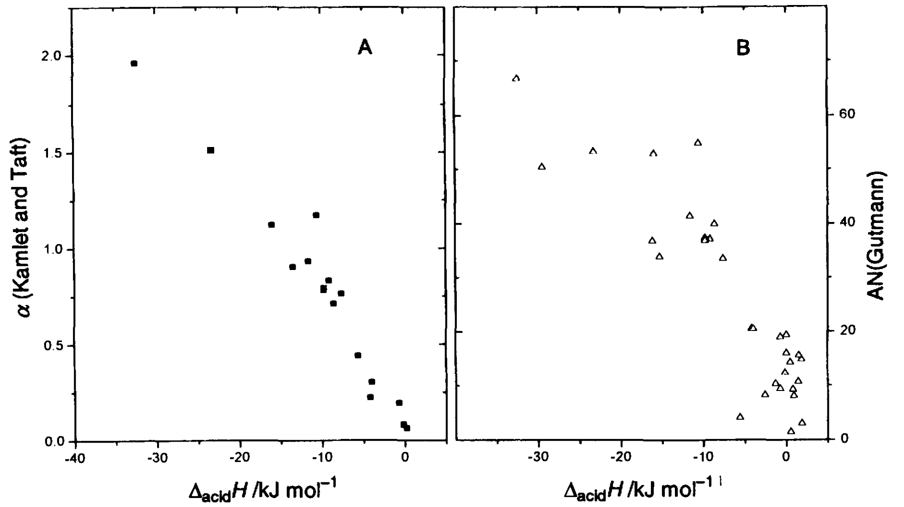

Fig. 3 (A) Correlation between the α scale of Taft and Kamlet and $\Delta_{acid}H$ values of 17 solvents shown in the 6th column of Table 2. (B) Correlation between AN scale of Gutmann and $\Delta_{acid}H$ values for 32 solvents shown in the 7th column of Table 2

Finally, we will compare our $\Delta_{acid}H$ values with data from two acidity scales, the α scale obtained from UV–VIS measurements and the AN scale derived from NMR measurements. The solvent acidity scale more frequently used is the solvatochromic α scale proposed by Taft and Kamlet[13] in 1976. In Fig. 3(A) we have plotted α values[14] *vs.* $\Delta_{acid}H$ for 17 solvents. There is a fair correlation between the two scales given by eqn. (7), where $n = 17$, $r = 0.967$ and sd $= 0.136$.

$$\alpha = (-0.060 \pm 0.004)\,\Delta_{acid}H + 0.166 \qquad (7)$$

Aiming to quantify the electrophilic properties of electron pair acceptor solvents, Mayer *et al.*[15] derived the acceptor number scale (AN). This was obtained from the ^{31}P NMR chemical shifts produced by the electrophilic action of acceptor solvents on triethylphosphate oxide, according to reaction (8), where S is the solvent under study.

$$\mathrm{Et_3P{=}O + S \rightleftharpoons Et_3P{-}O{-}S} \qquad (8)$$

The plot of the AN *vs.* the $\Delta_{acid}H$ scale for 32 solvents is shown in Fig. 3(B). The correlation obtained is given in eqn. (9), where $n = 32$, $r = 0.884$ and sd $= 8.68$.

$$\mathrm{AN} = (-1.748 \pm 0.0169)\,\Delta_{acid}H + 13.55 \qquad (9)$$

In conclusion, the proposed calorimetric $\Delta_{acid}H$ scale is suitable for estimating the acidity of solvents.

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