Towards a Solvent Acidity Scale: The Calorimetry of the *N*-Methyl Imidazole Probe

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This paper reports a rather straightforward calorimetric method for the precise determination of the acidity of organic solvents. From the calculated enthalpies of solvation (ΔH_{solv}) of the probe compounds *N*-methylimidazole and *N*-methylpyrrole and the known relative permittivity (ε) of the solvent ΔH^{acid} is obtained through the equation:

$$\Delta H^{acid} = -[\Delta H^{0}_{solv}(N\text{-methylimidazole}) - \Delta H^{0}_{solv}(N\text{-methylpyrrole})] + 18.760\,f(\varepsilon) + 1.69.$$

The proposed method allowed us to determine the acidity of 36 solvents, including some slightly acidic ones, whose acidity is difficult to obtain by existing methods.

The existence of inert solvents is a subject of ongoing discussion and has fostered endeavours to quantify solute–solvent interactions in order to elucidate how given solvents influence the properties of some solutes. Such an influence can generally be exerted through[1] (*a*) the solvent ability to position the solute,[2] (*b*) acid–base interactions,[3,4] and (*c*) polarity/polarizability interactions.[5]

Once the acidity and basicity concepts had been unified,[6] the next major challenge was to find a quantifiable property of solvents that could be used as a measure of their acidity or basicity. Much effort in this direction has been made in the last few decades,[7] particularly by Kamlet, Taft *et al.*,[3–5,8–10] who gradually abandoned their former solvatochromic parameters in favour of those based on equilibrium constants.

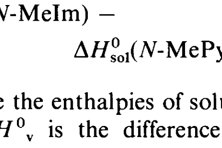
Acidity is more difficult to quantify than basicity, partly because of the difficulty in finding suitable probes and their corresponding reference compounds. For example, pyridine *N*-oxide has been used as a probe compound by Abboud *et al.*[11] in dilute solutions of acids in cyclohexane, and *N*-methylpyrrolidone in 1,1,1-trichloroethane solutions was recently used by Abraham *et al.*[12] for the same purpose. On the other hand, basicities can be determined more readily with the aid of such useful models as 4-fluorophenol/4-fluoroanisole,[7c,13] 4-nitrophenol/4-nitroanisole[2] or that recently reported by our group, pyrrole, toluene/*N*-methylpyrrole, benzene,[14] which we named the 'pure solvent method' and which can in principle be used with any type of solvent.

This paper reports a simple thermodynamic method for the determination of solvent acidity which does not require the use of an 'inert solvent', nor knowledge of the characteristics of the adduct formed, as with previous methods.[11,12] The method provides information on the acidity of solvents traditionally regarded as non acidic, and allows solvents to be classified according to their acid strength.

The solvent acidity scale (SA) presented here and the solvent basicity scale (SB) previously reported[14] appear to be a useful tool for the study of solvent-dependent processes such as chemical equilibria, reaction rates and spectral properties of solutes.

Acidity Quantification Scheme.—A reliable acidity probe should essentially meet the following requirements: (*a*) be a strong enough base to allow the acidity of very weakly acidic substances to be measured, (*b*) have a markedly localized basic site (preferably a single σ lone pair), (*c*) have a molecular structure posing no conformational problems, and (*d*) allow a reference compound with none of the basicity features of the probe to be employed.

In the gas-phase *N*-methylimidazole is 99.6 kJ mol^{-1} [15] more basic than ammonia, *i.e.* 25.5 kJ mol^{-1} [16] more basic than pyridine *N*-oxide. According to Kamlet *et al.*[17], its hydrogen-bond basicity is comparable to that of the last compound. In addition, the lone pair on the N_3 atom of its ring is unambiguously its one basic site.[18] In addition, it poses no conformational problems and its molecular structure allows the use of a reference compound such as *N*-methylpyrrole, which results from replacing the basic site of *N*-methylimidazole, namely its N_3 atom $(-\underset{\|}{N}:)$ by a non-basic site $(=\underset{|}{C}-H)$, with the consequent loss of the σ basicity. Thus the probes in question are *N*-methylimidazole/*N*-methylpyrrole (Scheme 1):



Scheme 1

The difference between the gas/solvent transfer enthalpies of *N*-methylimidazole and *N*-methylpyrrole is given by eqn. (1),

$$\delta\Delta H^{0}_{solv} = [\Delta H^{0}_{sol}(N\text{-MeIm}) - \Delta H^{0}_{sol}(N\text{-MePyr})]_s + \delta\Delta H^{0}_{v} \quad (1)$$

where $\Delta H^{0}_{sol}(i)$ are the enthalpies of solution of the probes in solvent s and $\delta\Delta H^{0}_{v}$ is the difference in the vaporization enthalpies between *N*-methylimidazole and *N*-methylpyrrole, which is -13.93 kJ mol^{-1} (see Table 1).

Structurally, the cavity effect should logically be similar for both compounds, and hence its contribution to $\delta\Delta H_{solv}$ should be negligible. On the other hand, according to Kamlet *et al.*,[17] *N*-methylimidazole is a non-acidic substance with $\alpha_2^{H} = (0)$; thus, if the acidity of *N*-methylpyrrole is also negligible, we may establish the working hypothesis that the contribution of the solvent basicity to the term $\delta\Delta H_{solv}$ will be negligible. The refractive indices of *N*-methylimidazole ($n_D^{20} = 1.4970$) and *N*-methylpyrrole ($n_D^{20} = 1.4875$) are so similar that the

Table 1 Enthalpies of solution of the two probes in the 36 solvents studied at 25 °C

		ΔH^0_{sol}/kJ mol^{-1}	
	Solvent	*N*-Methylimidazole	*N*-Methylpyrrole
1	Cyclohexane	16.71 ± 0.23	7.74 ± 0.25[b]
2	Carbon disulfide	11.58 ± 0.34	3.98 ± 0.08[b]
3	Hexamethylphosphoramide	−3.33 ± 0.13	−5.14 ± 0.08[b]
4	Cyclohexanone	1.57 ± 0.13	−0.43 ± 0.02[b]
5	1,2-Dichlorobenzene	2.73 ± 0.22	0.20 ± 0.01[b]
6	Propionitrile	1.35 ± 0.04	−0.11 ± 0.02[b]
7	Benzonitrile	0.65 ± 0.01	−0.83 ± 0.02[b]
8	Tetrahydrofuran	1.78 ± 0.16	−0.85 ± 0.03[b]
9	Nitrobenzene	1.20 ± 0.06	0.09 ± 0.02[b]
10	Methyl ethyl ketone	1.31 ± 0.14	−0.01 ± 0.01
11	1,1,3,3-Tetramethylurea	−0.96 ± 0.02	−1.82 ± 0.02[b]
12	Dimethyl ketone	0.94 ± 0.19	0.00 ± 0.03
13	Triethylamine	9.13 ± 0.40	3.65 ± 0.08[b]
14	Acetonitrile	1.25 ± 0.07	0.89 ± 0.02[b]
15	Chlorobenzene	2.11 ± 0.05	−0.10 ± 0.01[b]
16	Pyridine	0.75 ± 0.16[a]	−0.25 ± 0.04[a]
17	*N*,*N*-Dimethylformamide	−0.71 ± 0.16	−0.79 ± 0.08[b]
18	Ethyl acetate	1.86 ± 0.13	0.25 ± 0.04[b]
19	Dimethyl sulfoxide	−0.17 ± 0.13	0.54 ± 0.08[b]
20	Methoxybenzene	1.82 ± 0.04	0.14 ± 0.02[b]
21	Dichloromethane	−3.89 ± 0.19	−2.66 ± 0.07
22	1,4-Dioxane	2.08 ± 0.17	−0.21 ± 0.02[b]
23	Nitromethane	−1.38 ± 0.07	2.18 ± 0.02[b]
24	Trichloromethane	−9.37 ± 0.58[a]	−6.15 ± 0.08[a]
25	Propan-2-ol	−0.42 ± 0.02	5.73 ± 0.08[b]
26	Formamide	−3.38 ± 0.06	3.51 ± 0.06[b]
27	Ethanol	−3.33 ± 0.10	4.41 ± 0.08
28	Cyclohexanol	−0.09 ± 0.01	7.44 ± 0.07
29	Butan-1-ol	−1.86 ± 0.03	6.24 ± 0.05[b]
30	Aniline	−6.95 ± 0.09	0.09 ± 0.06[b]
31	Methanol	−6.86 ± 0.25	3.39 ± 0.08[b]
32	Water	−9.75 ± 0.13	1.05 ± 0.08[b]
33	Pyrrole	−12.82 ± 0.47	−0.45 ± 0.02[b]
34	2-Chloroethanol	−14.02 ± 0.34	2.13 ± 0.01
35	2,2,2-Trifluoroethanol	−20.76 ± 0.81	1.86 ± 0.03
36	2,2,2-Trichloroethanol	−24.78 ± 0.50	1.46 ± 0.01
		ΔH_{v}/kJ mol^{-1}	
		54.64 ± 0.46	40.71 ± 0.29

[a] Ref. 32. [b] Ref. 14.

interactions arising from the difference between the polarizability of the two probes and that of the solvent will make no significant contribution to $\delta\Delta H_{\text{solv}}$.

Consequently, $\delta\Delta H_{\text{solv}}$ will chiefly result from the contribution of the solvent acidity, followed by those interactions resulting from the potential polarity and polarizability of the solvent in question. The difference in dipole moments of the probes (μ_{NMI} = 3.70 D; μ_{NMP} = 1.98 D) does contribute to $\delta\Delta H_{\text{solv}}$ through the solvent polarity, *i.e.* through the well-known dipole–dipole interactions.[19] In principle, this interaction will be evaluated through the Onsager reaction field scheme[20] in which $f(\varepsilon)$ is, given by eqn. (2).

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

In summary, the $\delta\Delta H_{\text{solv}}$ value resulting from the contribution of the two probes should be a linear combination of the solvent acidity and polarity, as shown in eqn. (3), where

$$\delta\Delta H_{\text{solv}} = a\alpha_2^{\text{H}} + bf(\varepsilon) + c \qquad (3)$$

α_2^{H} is Kamlet and Taft's monomer acidity and $f(\varepsilon)$ is expressed by eqn. (2).

By solvent acidity we mean the net effect that the solvent produces on the lone pair of the *N*-methylimidazole N_3 nitrogen atom, which will mainly be the formation of hydrogen bonds.

Experimental

The enthalpies of solution of *N*-methylimidazole and *N*-methylpyrrole in the different solvents were determined with an LKB Batch Microcalorimeter equipped with a titration unit.[21] The experiments were carried out by addition of 2.6 or 5.2 cm^3 of solute to the reaction vessel, which contained 6–8 mm^3 of solvent. Ten to fifteen measurements per compound were typically made. The instrument was calibrated both electrically and by solution of propan-1-ol in water.

When the solubility of the probes was very low, in some of the solvents under study we used a new calorimeter system[22] especially designed for the dissolution of slightly soluble liquids. In these experiments the rate of solvent flow was normally *ca.* 8 mm^3 s^{-1} and the volume of injected solute was in the range of 1–8 mm^3. In all cases the solute was injected during a period of 100 s. The time for the dissolution process varied between 3 and 15 h.

All solutes and solvents used were of the highest available purity (>99.8%) and were supplied by Aldrich, Fluka and Merck. Immediately before use, the reagents were dried by

Table 2 Solvents and their physical parameters to evaluate the solvent acidity, (SA)[a]

	Solvent	$\delta\Delta H_{solv}$	ε	ΔH^{acid}	$\alpha_2{}^H$	SA
1	Cyclohexane	−4.96	2.02	−0.52	0.00	0.00*
2	Carbon disulfide	−6.33	2.64	0.26		0.02
3	Hexamethylphosphoramide	−12.12	29.60	1.52	(0.0)	0.04
4	Cyclohexanone	−11.93	18.30	1.60	(0.0)	0.04
5	1,2-Dichlorobenzene	−11.40	9.93	1.67	(0.0)	0.05
6	Propionitrile	−12.47	27.20	1.90	(0.0)	0.05
7	Benzonitrile	−12.45	25.20	1.92	(0.0)	0.05
8	Tetrahydrofuran	−11.30	7.58	1.97	(0.0)	0.05
9	Nitrobenzene	−12.82	34.82	2.16	(0.0)	0.06
10	Methyl ethyl ketone	−12.61	18.51	2.28	0.03	0.06
11	1,1,3,3-Tetramethylurea	−13.07	23.60	2.60	(0.0)	0.07
12	Dimethyl ketone	−12.99	20.70	2.58	0.04	0.07
13	Triethylamine	−8.45	2.42	2.77	(0.0)	0.07
14	Acetonitrile	−13.57	36.00	2.88	(0.09)	0.07
15	Chlorobenzene	−11.72	5.62	2.94	(0.0)	0.07
16	Pyridine	−12.93	12.30	2.96	(0.0)	0.07
17	*N*,*N*-Dimethylformamide	−13.85	37.00	3.15	(0.0)	0.08
18	Ethyl acetate	−12.32	6.02	3.40	(0.0)	0.08
19	Dimethyl sulfoxide	−14.64	46.70	3.86	(0.0)	0.09
20	Anisole	−12.25	4.33	4.09	(0.0)	0.10
21	Dichloromethane	−15.16	8.93	5.58	0.13	0.13
22	1,4-Dioxane	−11.64	2.21	5.76	(0.0)	0.13
23	Nitromethane	−17.49	35.87	6.55	0.12	0.15
24	Trichloromethane	−17.15	4.81	8.73	0.20	0.20
25	Propan-2-ol	−20.08	19.92	9.70	(0.31)	0.22
26	Formamide	−20.82	111.0	9.87		0.22
27	Ethanol	−21.67	24.55	11.16	0.33	0.25
28	Cyclohexanol	−21.46	15.00	11.30	0.31	0.25
29	Butan-1-ol	−22.03	17.51	11.74	0.33	0.26
30	Aniline	−20.97	6.89	11.80	0.26	0.26
31	Methanol	−24.18	32.70	13.53	0.35	0.30
32	Water	−24.73	78.30	13.83	0.35	0.30
33	Pyrrole	−26.30	7.48	16.99	0.39	0.37
34	2-Chloroethanol	−30.08	25.8	19.54	(0.346)	0.42
35	2,2,2-Trifluoroethanol	−36.58	26.14	26.03	0.560	0.56*
36	2,2,2-Trichloroethanol	−40.17	28.84	29.58	(0.500)	0.63

[a] ΔH values are in kJ mol^{-1} at 25 °C. ΔH_{solv} from eqn. (1), ΔH^{acid} from eqn. (5), Kamlet and Taft acidity $\alpha_2{}^H$ from refs. 7*j*, 10 and 25. [b] The $\alpha_2{}^H$ values between brackets are assumed to be zero or under discussion.

standard methods as described in the literature.[23] The reagents were then purified by fractional distillation through a spinning band column under dry nitrogen followed by sequential drying with 4 Å molecular sieves, except methanol, nitromethane, acetonitrile, ethanol and its halogen derivatives for which 3 Å molecular sieves were used. Prior to use the molecular sieves were activated at 300–320 °C overnight. Since hydration occurs rapidly on cooling of these dessicants, cooling was carried out in a vacuum dessicator and the molecular sieves then used immediately. The distilled reagents were stored and manipulated in a dry box. Purities of all solvents and solutes were checked by gas chromatography using an OV-17 column. The water content (always less than 80 ppm) was also determined by gas chromatography by means of a Porapak Q column.

Results and Discussion

Table 1 lists the enthalpies of solution (ΔH^0_{sol}/kJ mol^{-1}) of *N*-methylimidazole and *N*-methylpyrrole measured in the 36 solvents studied. It also includes selected literature values and the enthalpies of vaporization of the two probes.[24] To be consistent the compounds are listed in the same order of acidity in all the Tables.

Table 2 lists the $\delta\Delta H_{solv}$ values calculated from eqn. (1) for all solvents studied, in addition to their relative permittivity function $f(\varepsilon)$ and the corresponding literature $\alpha_2{}^H$ values.

As can be seen from Table 2, most of the solvents studied were considered to be non-acidic. Only those with $\alpha_2{}^H$ values for which there exists quite good agreement in the literature were used for the fitting. The acidic nature of the compounds studied arose from O–H groups (*e.g.* 2,2,2-trifluoroethanol, water, methanol, ethanol, cyclohexanol and butan-1-ol), N–H groups (*e.g.* pyrrole and aniline), or C–H groups (*e.g.* chloroform, dichloromethane, acetonitrile, nitromethane, acetone, butan-2-one and cyclohexane). Hydroxylic acids 2,2,2-trichloroethanol, 2-chloroethanol, and propan-2-ol were excluded from the fitting as they deviated significantly from the general behaviour of the 15 acids — they will now be discussed.

The difference in the enthalpy of solvation between the probes was found to obey eqn. (4), with $n = 15$, $r^2 = 0.962$ and $SD =$

$$\delta\Delta H_{solv} = -41.388\alpha_2{}^H - 18.760f(\varepsilon) - 1.69 \quad (4)$$

1.56. Taking into account the considerable differences between the different solvents included in the fitting in $\alpha_2{}^H$ (up to 0.56 units for the 2,2,2-trifluoroethanol/cyclohexane pair), and $f(\varepsilon)$, (up to 0.278 units for the water/cyclohexane pair), eqn. (4) accurately describes the phenomenon.

We must point out that the existence of this correlation relating enthalpy ($\delta\Delta H_{solv}$) and free energy ($\alpha_2{}^H$) data may allow us to suppose that the corresponding ΔS values are constant. There are other reasons for supporting this assumption: on one hand, in a recent paper about the hydrogen bond basicity of solvents,[14] we found that the enthalpy [the defined solvent basicity parameter (SB)] and free energy ($\beta_2{}^H$) values are proportional. On the other hand, in a paper dealing with hydrogen bond formation between *N*-methylpyrrolidinone

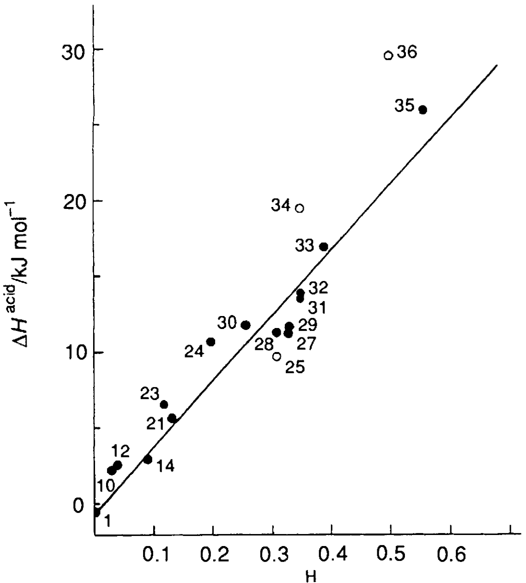


Fig. 1 Plot of ΔH^{acid} *vs.* α_2^H. Note the good correlation ($r^2 = 0.955$).

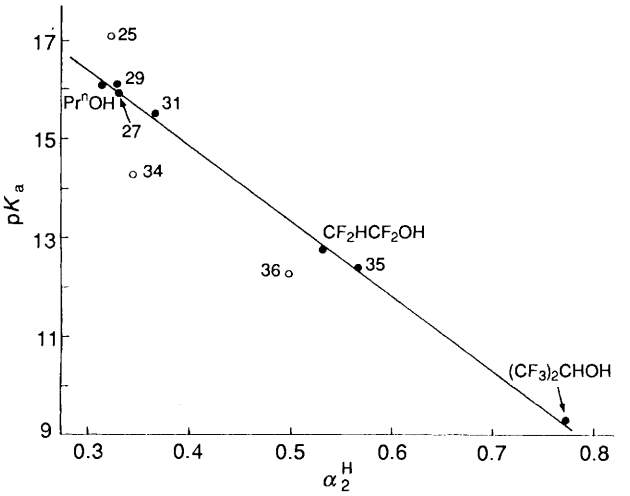


Fig. 2 Variation of pK_a with α_2^H ($r^2 = 0.9986$) for the solvents studied, after excluding nos. 25, 34 and 36, which are represented by empty circles

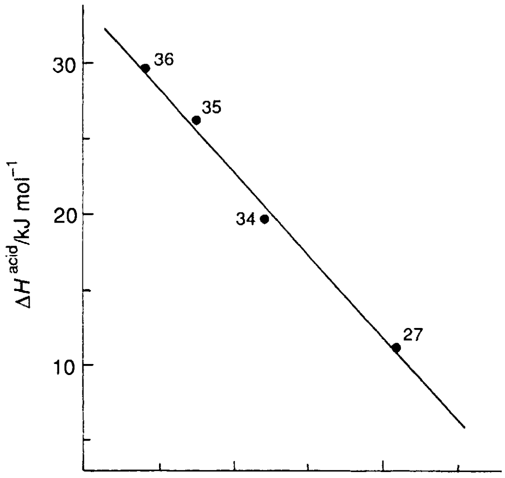


Fig. 3 Plot of ΔH^{acid} *vs.* ΔG_H for ethanol and three halogen derivatives

and 72 monomeric hydrogen bond acids, Abraham *et al.*[25] indicate that 'surprisingly, even when compared to the α_{SP} values of Sherry and Purcell[26] which are enthalpy related, there is a much better correlation with ΔG than there is with ΔH'.

The fitting obtained allows the acidity of a given solvent to be predicted from its $\delta\Delta H_{solv}$ value, provided ε is known beforehand, with a precision comparable to the best reported so far, through eqn. (5), obtained from eqn. (4), in which the α_2^H

$$-\Delta H^{acid} = \delta\Delta H_{solv} + 18.760f(\varepsilon) + 1.69 \qquad (5)$$

term has been substituted by ΔH^{acid}. Thus, the more positive is ΔH^{acid}, the greater the solvent acidity will be.

The ΔH^{acid} values obtained for the 36 solvents studied according to eqn. (5) are listed in Table 2. Fig. 1 shows the variation of ΔH^{acid} with the acidity α_2^H of 18 solvents. Three are represented by empty circles and will be discussed later. The identity between the terms α_2^H and ΔH^{acid} leads to correlation, eqn. (6).

$$\alpha_2^H = 0.0231\Delta H^{acid} + 0.0105$$
$$(n = 15;\ r^2 = 0.955;\ SD = 0.035) \qquad (6)$$

Eqn. (6) (see Fig. 1) can be used to transform our ΔH^{acid} values into Taft/Kamlet α_2^H values, thereby permitting transportation to that scale of the acidity of a number of compounds which were formerly given an $\alpha_2^H = 0$ on account of the difficulty involved in establishing equilibria reflecting their acidity.

Abraham *et al.*[27] recently showed that the values of log K^A in Cl$_4$C and in 1,1,1-trichloroethene are related to the pK_a values in aqueous solution of acids from homologous families, such as alkanols. Fig. 2 shows the pK_a[28] *vs.* α_2^H plot for the following compounds: methanol, ethanol, propan-1-ol, butan-1-ol, 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol, 2-chloroethanol, propan-2-ol, 2,2,3,3-tetrafluoropropan-1-ol and 1,1,1,3,3,3-hexafluoropropan-2-ol. As can be seen, there is an excellent linear correlation, provided the date corresponding to 2-chloroethanol, 2,2,2 trichloroethanol and propan-2-ol are excluded. The correlation equation is eqn. (7).

$$\alpha_2^H = -0.066\text{p}K_a + 1.38$$
$$(n = 6;\ r^2 = 0.9986;\ SD = 0.007) \qquad (7)$$

It is interesting to note that the three solvents excluded from the fitting, also represented by empty circles in Fig. 1, showed the same deviations seen in this Figure.

Consistent with the findings of Abraham *et al.*[12], we found no general relationship between the hydrogen-bond acidity and the intrinsic acidity (gas phase) in the solvents studied, which appears to be an effect of the polarizability, of such great significance to gas-phase acid–base processes.[29,30] However, if we consider aliphatic compounds which should show inductive-effect controlled acidity, as is the case with ethanol and its derivatives studied here, there is a clear correlation between their ΔH^{acid} values and their gas-phase acidities[31] (Fig. 3). The gas-phase free energies of deprotonation of 2-chloroethanol and 2,2,2-trichloroethanol were calculated from the expression reported by Taft *et al.*[32] relating such energies, ΔG^0_H, and the intrinsic effects of the substituent.[29,33] The existence of this correlation between the gas phase and solution acidities is further evidence for the constancy of ΔS.

The above findings allow us to conclude that the α_2^H values reported by Abraham *et al.*[27] for 2-chloroethanol and 2,2,2-trichloroethanol are too low despite the fact that, as stated by these authors, they might be subject to conformational problems arising from the occurrence of intramolecular hydrogen bonds in these compounds. However, this should also affect 2,2,2-trifluoroethanol. We would like to emphasize the unusually high value shown by dioxane, which warrants further investigation. The pseudo-polar behaviour of this solvent has previously been seen in spectroscopic studies, hence 'the dioxane anomaly'.[19]

All the above considerations suggest that the proposed model allows the ready, precise determination of the acidity of any solvent. Table 2 shows a solvent acidity scale (SA) obtained by normalizing the ΔH^{acid} values to zero for cyclohexane and 0.56 for 2,2,2-trifluoroethanol.

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