Hydrogen Bonding. Part 26. The Calorimetric Acidity Scale of Laynez

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A new acidity scale based on calorimetric measurements of *N*-methylimidazole and *N*-methylpyrrole in bulk solvents has been reported by Laynez *et al.* Although this is claimed to be a solvent acidity scale, it has been incorrectly matched with the solute α_2^H hydrogen-bond acidity parameter of Abraham. When correctly matched to the Kamlet–Taft solvatochromic hydrogen-bond parameter for bulk solvents, α_1, a useful equation can be constructed for the determination of α_1 values by the calorimetric method.

In a recent paper, Laynez *et al.*[1] have described a new method for the determination of the hydrogen-bond acidity of bulk solvents. They measured the differential enthalpy of solvation of *N*-methylimidazole and *N*-methylpyrrole, $\delta\Delta H^\circ_{solv}$, in a series of bulk solvents and then attempted to relate $\delta\Delta H^\circ_{solv}$ to known hydrogen-bond acidities; $\delta\Delta H^\circ_{solv}$ is defined through eqn. (1).

$$\delta\Delta H^\circ_{solv} = \Delta H^\circ_{solv}(N\text{-methylimidazole}) - \Delta H^\circ_{solv}(N\text{-methylpyrrole}) \quad (1)$$

Now since hydrogen-bond acidities of bulk solvents are not so easy to obtain, any new method of determining these acidities would, in principle, be of considerable value. Unfortunately, Laynez *et al.*[1] have confused hydrogen-bond acidities of solutes with hydrogen-bond acidities of solvents, thus leading to a number of erroneous statements, and finally to a key regression equation in which $\delta\Delta H^\circ_{solv}$ is related to solute hydrogen-bond acidity and not to the required hydrogen-bond acidity of bulk solvents at all.

To put the matter straight, the hydrogen-bond acidity of bulk solvents can be obtained by the Kamlet–Taft solvatochromic method,[2] using values of the UV–VIS λ_{max} of indicators such as 4-nitro-*N*,*N*-dimethylaniline and Reichardt's dye in bulk solvents: this solvent scale is denoted as α or α_1. The hydrogen-bond acidity of monomeric solutes can be obtained from 1:1 hydrogen-bond complexation constants in tetrachloromethane, leading to the α_2^H solute acidity scale.[3] The α_1 and α_2^H scales are not interchangeable and relate to two different processes. Thus

Table 1 Solvent parameters used in the calculations

Solvent	π_1^*	α_1	$\delta_H^2/100$	$f(\varepsilon)$	$-\delta\Delta H^\circ_{solv}$
Cyclohexane	0.00	0.00	0.672	0.201	4.96
Carbon disulfide	0.55	0.00	0.978	0.261	6.33
Hexamethylphosphoric triamide	0.87	0.00	0.734	0.475	12.12
Cyclohexanone	0.76	0.00	0.980	0.460	11.93
1,2-Dichlorobenzene	0.80	0.00	—	0.428	11.40
Proprionoitrile	0.70	0.00	1.130	0.473	12.47
Benzonitrile	0.90	0.00	1.229	0.471	12.45
Tetrahydrofuran	0.58	0.00	0.864	0.407	11.30
Nitrobenzene	1.01	0.00	1.222	0.479	12.82
Butanone	0.67	0.06	0.860	0.460	12.61
Tetramethylurea	0.83	0.00	—	0.469	13.07
Propanone	0.71	0.08	0.906	0.464	12.99
Triethylamine	0.14	0.00	0.555	0.243	8.45
Acetonitrile	0.75	0.19	1.378	0.479	13.57
Chlorobenzene	0.71	0.00	0.936	0.377	11.72
Pyridine	0.87	0.00	1.113	0.441	12.93
N,*N*-Dimethylformamide	0.88	0.00	1.389	0.480	13.85
Ethyl acetate	0.55	0.00	0.792	0.385	12.32
Dimethyl sulfoxide	1.00	0.00	1.688	0.484	14.64
Methyl phenyl ether	0.73	0.00	0.929	0.345	12.25
Dichloromethane	0.82	0.30	0.977	0.421	15.16
1,4-Dioxane	0.55	0.00	1.000	0.223	11.64
Nitromethane	0.85	0.22	1.585	0.480	17.49
Trichloromethane	0.58	0.44	0.887	0.356	17.15
Propan-2-ol	0.48	0.76	1.331	0.462	20.08
Formamide	0.97	0.71	3.617	0.493	20.82
Ethanol	0.54	0.83	1.621	0.470	21.67
Cyclohexanol	0.45	0.75	1.344	0.452	21.46
Butan-1-ol	0.47	0.79	1.295	0.458	22.03
Aniline	—	—	—	0.399	20.97
Methanol	0.60	0.93	2.052	0.477	24.18
Water	1.09	1.17	5.490	0.491	24.73
Pyrrole	—	—	—	0.406	26.30
2-Chloroethanol	0.83	1.04	—	0.471	20.08
2,2,2-Trifluoroethanol	0.73	1.51	1.371	0.472	36.58
2,2,2-Trichloroethanol	—	—	—	0.474	40.17

Table 2 Comparison of observed α_1 values with those calculated through eqn. (3)

Solvent	α_1[a]	α_1(calc.)
Cyclohexane	0.00	−0.09
Hexamethylphosphoric triamide	0.00	−0.10
Cyclohexanone	0.00	−0.02
Proprionontrile	0.00	0.06
Benzonitrile	0.00	−0.04
Tetrahydrofuran	0.00	0.02
Nitrobenzene	0.00	−0.07
Butanone	0.06	0.05
Propanone	0.08	0.06
Triethylamine	0.00	0.04
Acetonitrile	0.19	0.13
Chlorobenzene	0.00	−0.01
Pyridine	0.00	0.00
N,*N*-Dimethylformamide	0.00	0.08
Ethyl acetate	0.00	0.09
Dimethyl sulfoxide	0.00	0.10
Methyl phenyl ether	0.00	0.01
Dichloromethane	0.30	0.15
1,4-Dioxane	0.00	0.07
Nitromethane	0.22	0.35
Trichloromethane	0.44	0.39
Propan-2-ol	0.76	0.68
Formamide	0.71	0.72
Ethanol	0.83	0.78
Cyclohexanol	0.75	0.79
Butan-1-ol	0.79	0.81
Methanol	0.93	0.96
Water	1.17	1.12
2,2,2-Trifluoroethanol	1.51	1.59

[a] From references 5 and 6.

when Laynez *et al.*[1] state that '... Kamlet, Taft *et al.* have gradually abandoned their former solvatochromic parameters in favour of those based on equilibrium constants,' this is not correct. The Kamlet–Taft solvatochromic solvent parameters are in current use,[4] and are the appropriate parameters to use when dealing with bulk solvents.

Laynez *et al.*[1] then constructed a number of equations relating $\delta\Delta H^\circ_{\text{solv}}$ to α_2^{H}, and on this basis suggested revised values of α_2^{H} for a number of compounds. This procedure is entirely incorrect, because the bulk solvent measurements giving $\delta\Delta H^\circ_{\text{solv}}$ have no relevance to the monomeric solute parameter α_2^{H}. We deal with this no further, but concentrate on a more useful procedure, *viz.* the correlation and connection of $\delta\Delta H^\circ_{\text{solv}}$ to solvent parameters.

In Table 1 are given the $\delta\Delta H^\circ_{\text{solv}}$ values reported by Laynez *et al.*,[1] together with a number of bulk solvent parameters,[5,6] π_1^* the Kamlet–Taft dipolarity/polarisability parameter, α_1 as above, δ_{H}^2 the Hildebrand cohesive energy density, and the Kirkwood relative permittivity function $(\varepsilon - 1)/(2\varepsilon + 1)$ denoted as $f(\varepsilon)$. There is a connection between $\delta\Delta H^\circ_{\text{solv}}$ and $f(\varepsilon)$ and α_1 given by eqn. (2) [*cf.* eqn. (4) of Laynez *et al.*[1]], where n

$$-\delta\Delta H^\circ_{\text{solv}} = 4.26 + 13.15\alpha_1 + 17.70f(\varepsilon) \qquad (2)$$

$$n = 33 \qquad \rho = 0.963 \qquad \text{sd} = 1.85$$

is the number of data points, ρ is the overall correlation coefficient and sd is the standard deviation. Although eqn. (2) seems reasonable, it is hardly good enough for any back-calculation of α_1, because the likely error in the calculated α_1 values is too large, around 1.85/13.15 = 0.14 units. A rather more useful correlation is that shown as eqn. (3) where now the expected error in any calculated α_1 values is 1.13/15.85 = 0.07 units. Note that carbon disulfide, which for some reason is a wild outlier, has been left out of eqn. (3).

$$-\delta\Delta H^\circ_{\text{solv}} = 7.54 + 8.60\pi_1^* + 15.85\alpha_1 - 1.81\delta_{\text{H}}^2/100 \qquad (3)$$

$$n = 29 \qquad \rho = 0.985 \qquad \text{sd} = 1.13$$

Interestingly, there is a small but significant term in the Hildebrand cohesive energy density, δ_{H}^2, in eqn. (3), even though the differential enthalpy of solution might be expected[1] to lead to a negligible cavity term. Various other equations involving $\delta\Delta H^\circ_{\text{solv}}$, α_1, and other solvent parameters were constructed, but none were better than eqn. (3).

Although eqn. (3) requires a knowledge of the Kamlet–Taft solvatochromic parameter π_1^*, and also the Hildebrand cohesive energy density δ_{H}^2, it might be useful for the determination of α_1 values. Inspection of Table 2 suggests that it is more likely to be useful for large α_1 values, rather than small values, always provided that no proton transfer to the calorimetric probes takes place. Interestingly, the calculated value for trichloromethane, 0.39, is quite close to the suggested value of 0.44 by Kamlet *et al.*[6] in 1983, rather than to the original[2] estimate of approximately zero.

In conclusion, the new calorimetric method of Laynez *et al.*[1] is not appropriate for the determination of *solute* α_2^{H} values and should not be used to amend any existing such values. It *is* appropriate for the determination of *solvent* α_1 values, and could be used to obtain α_1 values, especially for solvents that have large, rather than small, α_1 values.

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Paper 2/06234H
Received 23*rd November* 1992
Accepted 15*th December* 1992