Toward a Solvent Basicity Scale: The Calorimetry of the Pyrrole Probe

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Abstract: The solution calorimetry of pyrrole, *N*-methylpyrrole, benzene, and toluene in 35 solvents has been investigated. The results obtained with an appropriate combination of the solvation enthalpies of these four compounds, used as probes, suggest a new hydrogen-bond basicity scale for solvents. The results have been tested against previously suggested scales. The "*pure solvent method*" proposed in this paper yields accurate basicity estimations for the 35 solvents tested. An additional practical advantage of this method is that ΔH°_{sol} can be accurately and easily measured.

It is well-known that solvents are not inert components; i.e., they contribute significantly to the properties of solutes in solution. Therefore, there has been a sustained effort[1] to identify those properties of solvents that control their interaction with the solutes.

It can be assumed that solute molecules modify solvents not only by direct solute–solvent interactions but also by affecting solvent–solvent interactions. Obviously, the solute–solvent interaction depends on the nature of both solvent and solute; it can be broken down into acid–base interactions, dipolar interactions, and dispersion forces. Solute-induced modifications of solvent–solvent interactions are due to the structural changes produced in the solvent by the creation of a cavity of suitable size to incorporate the solute, with the consequent reorganization of solvent molecules around it.

Ever since G. N. Lewis[2] unified the acidity and basicity concepts in 1923, it has been a constant challenge for chemists to find a single quantifiable property of solvents that could serve as a general basicity indicator. Among the efforts made in this direction we shall mention the following.

(i) The first effort concerns basicity studies in gas phase,[1h,11,3] in which contributions to solvation are absent. These studies lead to a better understanding of the following hypothetical process (1):

$$\mathrm{B{:}(g) + H^+(g) \rightarrow BH^+(g)} \qquad (1)$$

In this process the basicity of the "solvent molecule" is exalted since the acid is a bare unsolvated proton.

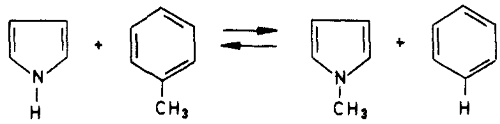
(ii) The second effort concerns basicity studies in condensed phase,[1c,h,j,o,3b,4] in which reported data of pK_a and ΔH_i values involve an important contribution to the solvation from a few of the solvent molecules solvating B:, H^+, and BH^+ (2):

$$\mathrm{B{:}(sol) + H^+(sol) \rightarrow BH^+(sol)} \qquad (2)$$

(iii) The third effort concerns studies of processes in which complexes are formed with different adducts (hydrogen bond,[1c] BF_3,[5] $SbCl_5$,[1e,6] I_2 and compounds of the IX type,[7] $HgBr_2$,[8] $CHCl_3$,[9] $AlMe_3$,[10] etc.) which have led to the introduction of different scales for the solvent basicity in terms of different magnitudes such as DN,[1e] ΔN,[1b] E/C,[1f,11] $\Delta H(BF_3)$,[5] B,[12] β,[13] etc. A major shortcoming of these basicity scales is that they are family dependent.[1c,5,14-17] This behavior probably arises from the fact that some of these magnitudes include, besides the basicity of the compound, other interactions due to the complex formation, such as dipole–dipole interactions, steric effects, etc.

The purpose of this article is to present a simple thermodynamic method of determining the hydrogen-bond basicity of solvents. This method does not require the use of an "inert solvent" nor a knowledge of the characteristics of the adduct formed, and it can be also used with protogenic or polyfunctional solvents. The main result of our study is the finding that the hydrogen-bond

Scheme I



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(1) (a) Hammett, L. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden Hutchinson and Ross: Strousburg, PA, 1973; *J. Org. Chem.* **1989**, *54*, 1423. (c) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875. (d) Benoit, R. L.; Louis, C. *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1978; Vol. IA. (e) Gutmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978. (f) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251. (g) Jensen, W. B. *The Lewis Acid–Base Concepts. An Overview*; Wiley: New York, 1980. (h) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247. (i) Stewart, R. *The Proton Applications to Organic Chemistry*; Academic Press: New York, 1985. (j) Taft, R. W.; Abboud, J. L. M.; Kamlet, M. J.; Abraham, M. H. *J. Sol. Chem.* **1985**, *14*, 153. (k) Hepler, L. G. *Thermochem. Acta* **1986**, *100*, 171, and references therein. (l) Meot-Ner, M. *J. Phys. Chem.* **1987**, *91*, 417. (m) Maria, P. C.; Gal, J. F.; Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483. (n) Reichardt, C. *Solvent Effects in Organic Chemistry*, 2nd revised and enlarged ed.; Verlag Chemie: Weinhein, 1988. (o) Bagno, A.; Scorrano, G. *J. Am. Chem. Soc.* **1988**, *110*, 4577 and references therein.

(2) Lewis, G. N. *Valence and Structure of Atoms and Molecules*; The Chemical Catalog Co.: New York, 1923; p 142.

(3) (a) Beauchamp, J. L. *Ann. Rev. Phys. Chem.* **1971**, *22*, 517. (b) Kebarle, P. *Ibid.* **1977**, *28*, 445. (c) Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, p 1. (d) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (e) Lias, S. G. *Gas Phase Basicities and Proton Affinities*; additions and corrections 1987, personal communication. (f) Taft, R. W.; Topson, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. (g) Lias, S. G.; Bartmes, J. E.; Holmes, J. L.; Levin, R. D.; Liebman, J. F.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl. 1 to Vol. 17*; 1988.

(4) (a) Arnett, E. M.; Quick, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *22*, 1260. (b) Arnett, E. M.; Scorrano, G. *Adv. Phys. Org. Chem.* **1976**, *13*, 83. (c) Arnett, E. M. *J. Chem. Educ.* **1985**, *62*, 385 and references therein.

(5) Maria, P. C.; Gal, J. F. *J. Phys. Chem.* **1985**, *89*, 1296.

(6) Gutmann, V. *Coordination Chemistry in Non-Aqueous Solution*; Springer-Verlag: Wein, 1968; *Coord. Chem. Rev.* **1975**, *15*, 207.

(7) Laurence, C.; Queignec-Cabanetos, M.; Dziembowska, T.; Queinec, R.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1981**, *103*, 2567.

(8) (a) Persson, I. *Pure Appl. Chem.* **1986**, *58*, 1153. (b) Persson, I.; Sandtröm, M.; Goggin, J. L. *Inorg. Chem. Acta* **1987**, *129*, 183.

(9) Slejko, F. L.; Drago, R. S.; Brown, D. G. *J. Am. Chem. Soc.* **1972**, *94*, 9210. (b) Wiley, G. R.; Miller, S. I. *J. Am. Chem. Soc.* **1972**, *94*, 3287.

(10) (a) Herikson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461. (b) *Ibid.* **1968**, *7*, 1028.

(11) Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2772.

(12) Koppel, I. A.; Palm, V. A. *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972; Chapter 5.

(13) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377.

(14) Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* **1982**, *47*, 4557.

0002-7863/90/1512-1678$02.50/0

basicity can be mathematically expressed as a linear combination of the ΔH°_{solv} for the selected probes (pyrrole, *N*-methylpyrrole, benzene, and toluene), which provides a new and accurate hydrogen-bond basicity scale for all tested solvents.

Basicity Quantification Scheme

In order to determine the formation enthalpy, ΔH°_f, of hydrogen-bond complexes between *p*-fluorophenol and nonprotogenic bases, Arnett et al.[1c,18] proposed the *pure base method*. In this method ΔH°_f is evaluated by the following relation:

$$\Delta H^\circ_f = (\Delta H^\circ_{sol}(A) - \Delta H^\circ_{sol}(M))_{base} - (\Delta H^\circ_{sol}(A) - \Delta H^\circ_{sol}(M))_{ref\,sol} \quad (3)$$

where $\Delta H^\circ_{sol}(A)$ and $\Delta H^\circ_{sol}(M)$ are the solution enthalpies for the acid and the model compound, respectively, measured in both the pure base and the reference "inert" solvent. In this work we propose a variant of this *pure base method* that we shall designate as the "*pure solvent method*", since all solution enthalpies of the selected probe compounds (pyrrole, *N*-methylpyrrole, benzene, and toluene) are measured in the solvent under characterization only, *no measurements in a reference solvent being required.* As discussed below, the set of four probes has been selected, in order to cancel effects not directly related to the basicity of the solvent.

We have recently reported[19] that N-methylation in azoles (pyrrole, imidazole, and pyrazole) involves the loss of an active solvation center. This effect was found to be proportional to the net positive charge on the pyrrolic hydrogen of the azole compound, to increase with increasing hydrogen-bond basicity of the solvent. These results directed our research toward considering the N-methylation enthalpy as a measure of the solvent basicity. The azolytic compound selected for characterizing the solvent basicity through its methylation was the pyrrole, due to the following characteristics: (1) low dipolar moment, only slightly modified by N-methylation; (2) planar structure that precludes conformational changes during interaction with the solvent; and (3) absence of electronic pairs in its σ skeleton, which minimizes significant basicity changes during N-methylation.

However, the use of the pyrrole/*N*-methylpyrrole pair, as a hydrogen-bond basicity scale probe, is not totally adequate, since N-methylation increase volume, basicity, and polarity of pyrrole. Fortunately, this problem can be solved by the inclusion of the toluene/benzene pair. C-methylation produces similar changes in benzene, which therefore must be considered in the reverse direction (Scheme I).

The pyrrole–*N*-methylpyrrole molar volume difference (19.5 cc) is very similar to the benzene–toluene molar volume difference (17.4 cc); the *slight increase* of *N*-methylpyrrole hydrogen-bond basicity can be approximately cancelled due to the *slight decrease* of the benzene basicity with respect to that of toluene. Furthermore, the polarizability change upon methylation of pyrrole and benzene is a perfect match as indicated by molar refractions.

In conclusion, all the characteristics of Scheme I suggest the following expression

$$\delta\Delta H^\circ_{solv} = (\Delta H^\circ_{solv}(P) + \Delta H^\circ_{solv}(T) - \Delta H^\circ_{solv}(MP) - \Delta H^\circ_{solv}(B))_{BASE} = (\Delta H^\circ_{sol}(MP) + \Delta H^\circ_{sol}(B) - \Delta H^\circ_{sol}(P) - \Delta H^\circ_{sol}(T))_{BASE} + K \quad (4)$$

is an excellent candidate for quantifying the basicity of any solvent (MP, *N*-methylpyrrole; P, pyrrole; B, benzene; T, toluene; BASE, any solvent under study). The constant *K* has the value 8.79 kJ mol^{-1}.

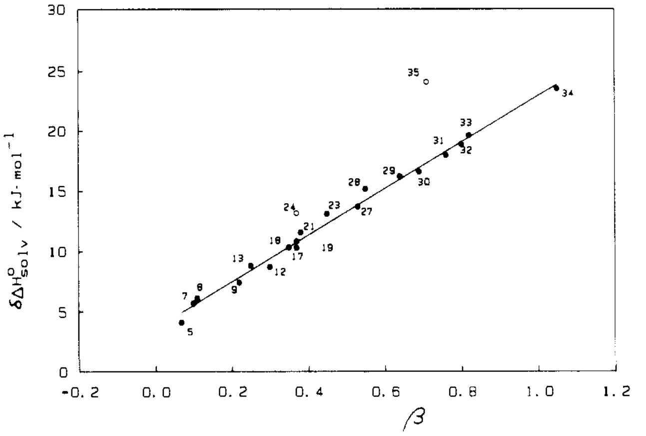

Figure 1. Plot showing the good correlation (r^2 = 0.991) between $\delta\Delta H^\circ_{solv}$ and β.

Experimental Section

The enthalpies of solution of pyrrole, *N*-methylpyrrole, benzene, and toluene in the different solvents were determined with an LKB batch microcalorimeter equipped with a titration unit.[20] The experiments were carried out by addition of 5.20 μL of solute to the reaction vessel, which contained 6 mL of solvent. Ten to 15 measurements were typically performed for each compound. The calibration of the instrument was done electrically, and also by the solution of *n*-propanol in water. The uncertainties in the values reported in Table I were calculated as twice the overall standard deviation.

All solutes and solvents used in this work were of the highest purity (>99.5%) available (Aldrich, Fluka, Merck) and stored with 4 Å molecular sieves. Furthermore, pyrrole, *N*-methylpyrrole, $CHCl_3$, aniline, formamide, 1,4-dioxane, and triethylamine were purified again by distillation just before use.

Results and Discussion

In Table I we give the solution enthalpies, ΔH°_{sol}, for benzene, toluene, pyrrole, and *N*-methylpyrrole in 35 solvents. Selected values from the literature[21-29] are also included as well as the enthalpies of vaporization,[19,30,31] ΔH_v, of the four solutes. With these values we have calculated $\delta\Delta H^\circ_{solv}$ according to eq 4. The results, ordered and numbered by increasing basicity, are presented in Table II. In order to test the validity of the proposed *pure solvent method* to quantify hydrogen-bond solvent basicities, we have compared our results with those of different basicity scales already in the literature as follows.

It seems appropriate to start the comparison with the basicities of the isolated solvent molecules measured in the gas phase.[3d,33-37]

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(15) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(16) Kamlet, M. J.; Gal, J. F.; Maria, P. C.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1985**, 1583.

(17) Kamlet, M. J.; Doherty, R. M.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *Chemtech* **1986**, 566.

(18) (a) Arnett, E. M.; Murty, T. S. S. R.; Schleyer, R. v. R.; Joris, L. *J. Am. Chem. Soc.* **1967**, *89*, 5955. (b) Arnett, E. M.; Joris, L.; Mitchell, E.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365.

(19) Catalán, J.; Cabildo, P.; Elguero, J.; Gómez, J.; Laynez, J. *J. Phys. Org. Chem.* **1989**, *2*, 646.

(20) Chen, A.; Wädso, I. *J. Biochem. Biophys. Methods* **1982**, *6*, 307.

(21) Fuchs, R.; Stephenson, W. K. *Can. J. Chem.* **1987**, *65*, 2624.

(22) Fuchs, R.; Young, T. M.; Rodewald, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 4705.

(23) Spencer, J. N.; Gleim, J. E.; Hachman, M. L.; Blevins, C. H.; Garrett, R. C. *J. Phys. Chem.* **1978**, *82*, 563.

(24) Stephenson, W. K.; Fuchs, R. *Can. J. Chem.* **1985**, *63*, 2529.

(25) Spencer, J. N.; Gleim, J. E.; Blevins, C. H.; Garrett, R. C.; Mayer, F. J.; Merkle, J. E.; Smith, S. L.; Hachman, M. L. *J. Phys. Chem.* **1978**, *83*, 2615.

(26) Spencer, J. N.; Berger, S. K.; Powell, C. R.; Henning, B. D.; Furman, G. S.; Loffredo, W. M.; Rydberg, E. M.; Neubert, R. A.; Shoop, C. E.; Blauch, D. N. *J. Sol. Chem.* **1981**, *10*, 50.

(27) Gill, S. J.; Nichols, N. F.; Wädso, I. *J. Chem. Thermodyn.* **1976**, *8*, 445.

(28) Fuchs, R.; Rodewald, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 5897.

(29) Nillsson, S. O.; Wädso, I. *J. Chem. Thermodn.* **1984**, *16*, 317.

(30) Pedley, J. B.; Rylance, J. *Sussex-NPL Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, Brighton, 1977.

(31) Mayer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell Scientific Publications: Oxford, 1985.

(32) Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Marcus, Y.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 5244.

Table I. Enthalpies of Solution, ΔH°_{sol}, of the Four Probes in the 35 Solvents Studied[m]

	solvent	ΔH°_{sol} (kJ/mol)			
		benzene	toluene	*N*-Me-pyrrole	pyrrole
1	c-C_6H_{12}	3.81 ± 0.08[a]	3.22 ± 0.08[b]	7.74 ± 0.25[c]	15.65 ± 0.54[c]
2	CCl_4	0.54 ± 0.00[d]	−0.17 ± 0.00[d]	1.59 ± 0.08[c]	9.29 ± 0.08[c]
3	$CHCl_3$	−2.01 ± 0.08	−3.05 ± 0.08	−6.15 ± 0.08[c]	1.38 ± 0.08
4	CS_2	2.59 ± 0.08[a]	1.88 ± 0.08[a]	3.98 ± 0.08	11.11 ± 0.22
5	C_6H_5Cl	−0.02 ± 0.04	−0.45 ± 0.02	−0.10 ± 0.01	5.00 ± 0.08
6	1,2-$C_6H_4(Cl_2)$	0.48 ± 0.01	−0.18 ± 0.02	0.20 ± 0.01	5.06 ± 0.08
7	C_6H_6	0.00 ± 0.00[a]	0.50 ± 0.21[b]	0.69 ± 0.02	3.25 ± 0.08
8	$C_6H_5CH_3$	0.25 ± 0.17[a]	0.00 ± 0.00[a]	0.92 ± 0.09	3.86 ± 0.08
9	$C_6H_5OCH_3$	0.19 ± 0.02	0.30 ± 0.02	0.14 ± 0.02	1.41 ± 0.02
10	water	2.22 ± 0.02[i]	1.73 ± 0.04[g]	1.05 ± 0.08	2.72 ± 0.08
11	pyrrole	2.29 ± 0.02	2.75 ± 0.09	−0.45 ± 0.02	0.00 ± 0.00
12	$C_6H_5NO_2$	1.19 ± 0.05	1.10 ± 0.05	0.09 ± 0.02	0.26 ± 0.02
13	CH_3NO_2	4.67 ± 0.08	5.35 ± 0.08	2.18 ± 0.02	1.46 ± 0.06
14	*N*-Me-pyrrole	0.41 ± 0.05	0.72 ± 0.02	0.00 ± 0.00	−0.67 ± 0.05
15	$C_6H_5NH_2$	2.53 ± 0.02	3.67 ± 0.02	0.09 ± 0.06	−1.56 ± 0.02
16	CH_3COOH	1.81 ± 0.02	1.42 ± 0.08	1.70 ± 0.02	0.87 ± 0.04
17	C_6H_5CN	0.22 ± 0.02	0.06 ± 0.02	−0.83 ± 0.02	−2.17 ± 0.02
18	CHCN	2.66 ± 0.06	3.13 ± 0.02	−0.89 ± 0.02	−1.11 ± 0.03
19	*n*-C_3H_7CN	0.64 ± 0.02	0.83 ± 0.02	−0.11 ± 0.02	−2.34 ± 0.04
20	H-CO-NH_2	4.85 ± 0.13	5.39 ± 0.12	3.51 ± 0.06	0.56 ± 0.02
21	H-$COOC_3H_7$	0.76 ± 0.02	0.66 ± 0.02	0.34 ± 0.02	−2.35 ± 0.03
22	CH_3OH	1.51 ± 0.08[h]	1.88 ± 0.08[h]	3.39 ± 0.08	−1.13 ± 0.08
23	$CH_3COOC_2H_5$	0.38 ± 0.05[d]	0.50 ± 0.08[d]	0.25 ± 0.04[a]	−4.18 ± 0.08[e]
24	1,4-dioxane	0.21 ± 0.02	0.67 ± 0.02	−0.21 ± 0.02	−5.03 ± 0.06
25	2-C_3H_7OH	3.89 ± 0.08	3.72 ± 0.08	5.73 ± 0.08	1.46 ± 0.08
26	*n*-C_4H_9OH	2.30 ± 0.08	2.09 ± 0.08	5.10 ± 0.08	0.50 ± 0.08
27	cyclohexanone	−1.06 ± 0.02	−0.61 ± 0.02	−0.43 ± 0.02	−5.78 ± 0.03
28	THF	−1.44 ± 0.08	−0.77 ± 0.02	−0.85 ± 0.03	−7.91 ± 0.09
29	pyridine	−0.17 ± 0.08	0.56 ± 0.02	−0.25 ± 0.05[e]	−8.41 ± 0.21
30	DMF	0.17 ± 0.08[h]	0.67 ± 0.08[h]	−0.79 ± 0.08[e]	−9.12 ± 0.33[e]
31	DMSO	3.14 ± 0.25[d]	3.81 ± 0.29[d]	0.54 ± 0.08	−9.33 ± 0.12
32	TMU	−1.40 ± 0.02	−1.06 ± 0.05	−1.82 ± 0.02	−12.27 ± 0.08
33	*N*-Me-imidazole	1.18 ± 0.02	1.72 ± 0.09	−0.07 ± 0.02	−11.31 ± 0.08
34	HMPA	−2.52 ± 0.08	−3.90 ± 0.07	−5.14 ± 0.08	−18.54 ± 0.12
35	Et_3N	1.13 ± 0.05[d]	0.54 ± 0.04	3.65 ± 0.08	−11.09 ± 0.03
	ΔH°_v	33.85 ± 0.06[j]	37.99 ± 0.06[j]	40.71 ± 0.29[l]	45.35 ± 0.08[k]

[a] Reference 21. [b] Reference 22. [c] Reference 24. [d] Reference 25. [e] Reference 25. [f] Reference 26. [g] Reference 27. [h] Reference 28. [i] Reference 29. [j] Reference 30. [k] Reference 31. [l] Reference 19. [m] Values in kJ/mol.

A good linear relationship is found between the gas-phase basicities values (PA) and $\delta\Delta H^\circ_{solv}$

$$PA = 628.41 + 14.41\delta\Delta H^\circ_{solv} \qquad (5)$$

with a correlation coefficient $r^2 = 0.909$. The linear fit includes the 20 aliphatic solvents in Table II (compounds **4**, **10**, **13**, **16**, **18–28**, **30–32**, **34**, and **35**) for which gas-phase values are available and for which polarizability effects are minor or negligible.

Since Kamlet and Taft[13] suggested the β basicity scale in 1976, this has become the most widespread magnitude used to quantify hydrogen-bond basicities. We also compare in Table II the results of the *pure solvent method* with the β values provided by the Kamlet and Taft scale. In Figure 1 we plot $\delta\Delta H^\circ_{solv}$ versus β. There is an excellent linear correlation, given by

$$\beta = -0.18 + 0.05\delta\Delta H^\circ_{solv} \qquad (6)$$

$$n = 19,\ r^2 = 0.991,\ SD = 0.02$$

In this correlation we have included 19 solvents from different types, such as π bases (compounds **5**, **7**, and **8** in Table II), ethers (**9** and **28**), carbonyls (**27**, **30**, and **32**), nitriles (**17**, **18**, and **19**), nitroderivatives (**12** and **13**), esters (**21** and **23**), heterocycles (**29** and **34**), and also P = O (**34**) and S = O (**31**) groups. Compounds for which β values are assumed to be zero (**1**, **2**, and **3**), those for which β values are still under discussion[38] (water and alcohols), and compounds for which β values have been estimated rather than calculated are not included in the correlation.

The compounds 1,4-dioxane and triethylamine are not included in the correlation since they do not fit in the regression line, as can be seen in Figure 1, but no significant deviation was observed for these two compounds in the correlation between PA and $\delta\Delta H^\circ_{solv}$ (eq 5). Maria et al.[5] have shown that the measured values of $\Delta H(BF_3)$ were family dependent with respect to β, but a good correlation was established for members within the same family. However, they found that the β value for 1,4-dioxane was too low to fit their regression line for ethers. We have found a similar disagreement by using literature data of ν_{OH} and $\Delta G_f(BH^+)_{aq}$ for 1,4-dioxane.[16] All this suggests that the 1,4-dioxane accepted β value is too low.

We shall now analyze the possible effects which may have led to a rather low β value for Et_3N from the free-energy relationship between a number of bases and *p*-fluorophenol (PFP) in CCl_4. Spencer et al.[39] have recently presented a detailed work on hydrogen-bond complexes between *n*-butyl alcohol and trialkylamines. They concluded that the equilibrium constants of these processes mainly depend on dipole–dipole interactions,[40] so, in the case of Et_3N–*n*-butyl alcohol the equilibrium constant is reduced by 33% when CCl_4 ($\pi^* = 0.28$) is used as solvent, instead of cyclohexane ($\pi^* = 0.00$). However, the difference in the ΔH°_f

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(33) Bollinger, J. C.; Houriet, R.; Yuernault, T. *Phosphorus and Sulfur* **1984**, *19*, 379.

(34) Anvia, F.; Taft, R. W. Unpublished results. Cited in Taft, R. W.; Gal, J. F.; Garibaldi, G.; Maria, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 861.

(35) Marriott, S.; Topson, R. D.; Lebrilla, C. B.; Koppel, I.; Mishima, M.; Taft, R. W. *J. Mol. Struct.* (*THEOCHEM*) **1986**, *137*, 133.

(36) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612.

(37) Scarlett, M.; Taylor, P. R. *J. Chem. Phys.* **1986**, *101*, 17.

(38) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Taft, R. W.; Morris, J. J.; Taylor, P. J.; Laurence, C.; Berthelot, M.; Doherty, R. M.; Kamlet, M. J.; Abboud, J. L. M.; Sraidi, K.; Guihéneuf, G. *J. Am. Chem. Soc.* **1988**, *110*, 8534.

(39) Spencer, J. N.; Modarress, K. J.; Nachlis, W. L.; Hovick, J. W. *J. Phys. Chem.* **1986**, *90*, 4443.

(40) Kamlet, M. J.; Dickinson, C.; Gramstad, T.; Taft, R. W. *J. Org. Chem.* **1982**, *47*, 4971.

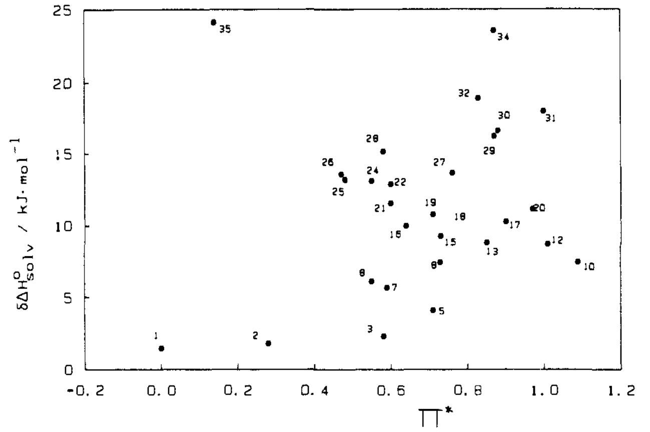

Figure 2. Plot showing the lack of correlation ($r^2 = 0.08$) between $\delta\Delta H^\circ_{solv}$ and π^*.

for these two processes is less than 5%. These results would indicate that the basicity of Et_3N will be underestimated if the reported ΔG°_f (Et_3N–*n*-butyl alcohol) value is used for the estimation of the corresponding β value. One could also expect ΔG°_f to be higher than the reported value if an interaction between Et_3N and CCl_4 is taken into account, as has been suggested.[41,42] Moreover, the omission of steric effects[43] and entropy losses in the formation of Et_3N complexes[39,43] will also lead to an underestimation in the basicity of this compound. This is a subject currently under study in our laboratory.

We have also investigated a possible interference of the π^* solvent parameter in the basicity values, $\delta\Delta H^\circ_{solv}$, provided by the pure solvent method. In Figure 2 we have plotted $\delta\Delta H^\circ_{solv}$ versus the π^* solvent parameter for all the solvents we have studied. The lack of correlation ($r^2 = 0.08$) is clear. In the same line, we have investigated a possible interference of the α acidity parameter in the basicity values $\delta\Delta H^\circ_{solv}$. The results were also conclusive, since the inclusion of an α term in eq 6 did not significantly improve the statistical fit. The probes used in this work have a basicity difference of 0.04 β units (*N*-methylpyrrole − pyrrole, $\Delta\beta = 0.06$; benzene − toluene, $\Delta\beta = -0.02$). Although this difference is small, a question can arise about the validity of our method for determining the basicity of acidic solvents. As the hydrogen-bond acidity of pyrrole is large ($\alpha = 0.41$)[38] the calculated β value (β_{calc}) will be underestimated, and consequently the β of Scheme I will be less than 0.04, i.e., our method is unaffected by solvent acidity. In the case of very acidic solvents, $\alpha \approx 1$, a small correction ($\approx$0.04) would be necessary to apply to β_{calc}.

All the above considerations suggest that the $\delta\Delta H^\circ_{solv}$ scale yields a direct measurement of hydrogen-bond basicity of solvents and can be used, as an example, to check the consistency of the β scale proposed by Kamlet and Taft. The β scale has been established from linear free-energy relationships which imply (1) the existence of an 1:1 equilibrium between the base and a number of acids in a solvent which must be "inert" toward both the reactants and the complex and (2) a stability of the complex governed exclusively by hydrogen-bond interactions. As these two conditions are often difficult to fulfill, especially in the case of protogenic and amphiprotic solvents, Kamlet et al.[32] were forced to propose different methods for estimating β.

The regression line in eq 6 has been used to calculate values of the hydrogen-bond basicity (β_{calc}) in agreement with the pure solvent method scale. Normalized hydrogen-bond basicity values, SB (solvent basicity), corresponding to the $\delta\Delta H^\circ_{calc}$ values were calculated such that SB = 0.0 for the gas phase and SB = 1.0 for the hexamethylphosphoramide (HMPA). The values for β_{calc} and SB are included in Table II. We have not found hydrogen-bond basicity values in the literature for some of the solvents included in Table II. For these cases we think that the β_{calc} and SB values reported in Table II could serve as an accurate estimation.

Table II. Values of $\delta\Delta H^\circ_{solv}$ (in kJ/mol) from Eq 5, Kamlet and Taft Basicity (β), Estimated Basicity from Eq 6 (β_{calc}), and Solvent Basicity (SB) of the 35 Solvents Studied

	solvent	$\delta\Delta H^\circ_{solv}$	β^a	β_{calc}	SB
	gas phase	0.00		−0.18	0.00
1	c-C_6H_{12}	1.46		−0.11	0.06
2	CCl_4	1.80		−0.09	0.08
3	$CHCl_3$	2.30		−0.06	0.10
4	CS_2	2.36		−0.06	0.10
5	C_6H_5Cl	4.12	0.07	0.03	0.17
6	1,2-$C_6H_4(Cl_2)$	4.58		0.05	0.19
7	C_6H_6	5.67	0.10	0.11	0.24
8	$C_6H_5CH_3$	6.09	0.11	0.13	0.26
9	$C_6H_5OCH_3$	7.41	0.22	0.20	0.31
10	water	7.46		0.20	0.32
11	pyrrole	7.88		0.22	0.33
12	$C_6H_5NO_2$	8.71	0.30	0.27	0.37
13	CH_3NO_2	8.82	0.25	0.27	0.37
14	*N*-Me-pyrrole	9.16		0.28	0.39
15	$C_6H_5NH_2$	9.29		0.30	0.39
16	CH_3COOH	10.01		0.33	0.42
17	C_6H_5CN	10.28	0.37	0.35	0.44
18	CH_3CN	10.32	0.35	0.35	0.44
19	*n*-C_3H_7CN	10.82	0.37	0.37	0.46
20	H-CO-NH_2	11.19		0.39	0.47
21	H-$COOC_3H_7$	11.59	0.38	0.41	0.49
22	CH_3OH	12.93	0.43	0.48	0.55
23	$CH_3COOC_2H_5$	13.09	0.45	0.49	0.56
24	1,4-dioxane	13.15	0.37	0.49	0.56
25	2-C_3H_7OH	13.22	0.52	0.50	0.56
26	*n*-C_4H_9OH	13.60	0.49	0.52	0.58
27	cyclohexanone	13.70	0.53	0.52	0.58
28	THF	15.17	0.55	0.60	0.64
29	pyridine	16.22	0.64	0.65	0.67
30	DMF	16.61	0.69	0.67	0.71
31	DMSO	17.99	0.74	0.74	0.76
32	TMU	18.90	0.80	0.79	0.80
33	*N*-Me-imidazole	19.62	0.82	0.82	0.83
34	HMPA	23.56	1.05	1.03	1.00
35	Et_3N	24.11	0.71	1.05	1.02

[a] See ref 15, 32, and 44.

It is worthwhile to comment on the interesting case of the self-associated solvents, such as water and alcohols. By using eq 6 we have estimated for the water a β_{calc} value of 0.20, in excellent agreement with the value suggested.[1j] Similarly, for methanol, 2-propanol, and *n*-butanol we obtain 0.48, 0.50, and 0.52, respectively, in good agreement with the suggested[44] values 0.43, 0.52, and 0.49, respectively.

It must be stressed that the basicity scale proposed in this article does not need any arbitrary zero ("inert" solvent). Obviously, $\delta\Delta H^\circ_{solv} = 0$ corresponds to the gas phase where no interactions are present. A value of $\beta_{calc} = -0.18$ is assigned to this situation in the Kamlet and Taft scale.

The results presented in this article allow us to conclude that with the calorimetry of the "pyrrole probe" we are in the right path toward the development of a general solvent basicity scale. The *pure solvent method* has served to determine accurate SB values not only for nonprotogenic solvents but also for protogenic and amphiprotic solvents.

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(41) (a) Collins, H. F. *Chem. Ind. London* **1957**, 704. (b) Lauterberger, W. J.; Jones, E. N.; Miller, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 1110.

(42) Stephenson, W. K.; Fuchs, R. *Can. J. Chem.* **1985**, *63*, 2540.

(43) Kasende, O.; Zeegers-Huyskens, T. *Spectrosc. Lett.* **1980**, *13*, 493.

(44) Abboud, J. L. M.; Roussel, C.; Gentric, E.; Sraidi, K.; Lauransan, J.; Guihéneuf, G.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1988**, *53*, 1545.