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On Solvent Basicity: Analysis of the SB Scale

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The solvent basicity (SB) scale, introduced by Catalán *et al.* in 1996, was compared with theoretical data ($V_{\min}$ and $\epsilon_{\mathrm{mo(Vmin)}}$), calculated at the HF-SCF 6-31G** level, and with experimental data (ΔH_f of Arnett, $\delta\Delta H_{\mathrm{solv}}$ of Laynez, $\Delta\Delta\tilde{\nu}(1)-(2)$ and $\Delta\Delta\tilde{\nu}(3)-(5)$ of Laurence, and $\Delta H^{\mathrm{g}\rightarrow\mathrm{solvent}}$ for SO_2 and I_2 of Benoit and Louis). The fact a SB scale is a family-independent scale results in no grouping of the solvents in parallel lines. As also shown by the results, a basicity scale constructed around a standard phenolic Brönsted acid (R-OH) such as 4-nitrophenol or 4-fluorophenol is more correct than one based on an unsubstituted amine such as 4-nitroaniline. The SB scale has a near-unity covalent-to-electrostatic ratio, so it is sensitive to both covalent and electrostatic interactions and hence approaches closely the requirements for a general basicity scale.

Introduction

The solvent in which a physicochemical process takes place is a noninert medium that plays a major role in solution chemistry. Thus, solvents modify the rate of chemical reactions, displace chemical equilibria, and alter the spectral features of solutes. This has aroused the interest of chemists in describing the effects of solvents in terms of their interactions with solutes, which can be of the *specific* or *nonspecific* type. For a comprehensive discussion of this topic, interested readers are referred to the book of Reichardt.[1]

Specific solvent−solute interactions are usually described in terms of localized donor−acceptor interactions. Ever since Lewis unified the acidity and basicity concepts in 1923,[2] chemists have been confronted with the challenge to find a quantifiable property of solvents that can be used as a general basicity indicator. Scales based on a straightforward basicity descriptor of solvent basicity such as the ΔH_f of Arnett *et al.*,[3] the $B_{(\mathrm{MeOD})}$ of Koppel and Palm,[4] the β of Kamlet and Taft,[5] and, more recently the authors' solvent basicity (SB),[6] were conceived for bulk solvents. In 1963, Pearson[7] introduced two descriptors which he designated "hardness" and "softness" and provided a qualitative description for interactions between donors and acceptors. However, it was Drago *et al.*[8,9] who developed a quantitative two-parameter model capable of predicting the enthalpy of formation of 1:1 complexes in a noninteracting solvent [see eq 1] based on their well-known covalent and electrostatic parameters C_A, C_D, E_A, and E_D, where subscript A denotes the acceptor

$$-\Delta H = C_A C_D + E_A E_D \qquad (1)$$

and D the donor.

Drago *et al.*[9,10] were also the first to point out that, based on their model, a basicity scale must be dependent on the acid used to construct it. Subsequently, Panchenco *et al.*[11] and Maria *et al.*[12] dwelled upon this issue and stated that one serious shortcoming of these basicity scales is that they are family-dependent as a result of the different electrostatic and covalent contributions to the specific solute−solvent interaction. This led Taft *et al.*[13] to introduce a coordinate covalency parameter, ξ [1 for an $N(sp^3)$ base, 0.60 for an $N(sp^2)$ base, 0.20 for an $O(sp^3)$ base, and 0.00 for an $O(sp^2)$ base if the oxygen atom is bonded to an N, C, or S atom and −0.20 if it is bonded to a P atom], in order to restore family-independent situations in combination with the parameter β; as a result, family-dependence reflects in parallel lines that join members of the same base family.[3b,13−15] More recently, Maria *et al.*[16] analyzed the difficulty of comparing basicity scales and showed that two basicity-dependent properties (BDP) can only vary linearly (i.e., exhibit a family-independent behavior) if the two acids used to define them result in similar electrostatic-to-covalent ratios in the BDP sets. This type of analysis also revealed that only unsubstituted amines are seemingly appropriate acids for this purpose and that, despite the apparently acceptable spectral features of phenol acids (Nicolet *et al.*[15−17]), they should be avoided in constructing basicity scales.

In this paper, we used theoretical (this work) and experimental data (from the bibliography) in order to analyze the SB scale is potential shortcomings as a general solvent basicity scale. The SB scale was derived from UV-vis measurements of the first electronic transition for the probe 5-nitroindoline (NI) and its homomorph 1-methyl-5-nitroindoline (MNI), and encompasses 202 solvents. It ranks the solvents studied from 1 for the most basic [tetramethylguanidine, TMG] to 0 for the gas phase (i.e., the absence of solvent). In addition, we report the SB values for six new solvents which we believed of interest to introduce in some of the analyses performed. Moreover, theoretical data for 53 different solvents (nitrogen- and oxygen-containing bases), spanning the whole basicity range and liable to reflect the family-dependence problem, were used to demonstrate that the SB scale is the closest approach to a general solvent basicity scale.

Experimental and Theoretical Section

5-Nitroindoline (NI) was purchased from Aldrich and carefully purified by column chromatography on silica gel, using 6:4 dichloromethane/*n*-hexane as eluent. Its derivative, 1-methyl-5-nitroindoline (MNI), was obtained as described elsewhere.[6]

The eight solvents studied were obtained in the highest available purity from either Aldrich or Fluka and redistilled in an inert atmosphere prior to use.

UV−Vis spectra were recorded as described in a previous paper.[6] Table 1 lists the absorption maxima (in cm^{-1}) for the

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TABLE 1: Wavenumbers of the Maximum of the First UV−vis Absorption Band of the Probe ($\tilde{\nu}_{NI}$) and the Homomorph ($\tilde{\nu}_{MNI}$). Differences between $\tilde{\nu}_{NI}$ and $\tilde{\nu}_{MNI}$ ($\Delta\tilde{\nu}$, cm^{-1}) and Their SB-Normalized Values[a]

solvent	$\tilde{\nu}_{NI}$	$\tilde{\nu}_{MNI}$	$\Delta\tilde{\nu}$	SB
N,*N*-dimethylaniline	25 420	24 385	1035	0.308 (0.305)[b]
dimethyl sulfite	25 302	24 323	979	0.341
1,3-dioxolane	25 596	24 717	879	0.398
2-bromopyridine	24 491	23 710	781	0.455
4-methylpyridine	24 700	24 147	553	0.586
2,3,3-trimethylindolenine	25 023	24 479	544	0.591
1-methylimidazole	23 891	23 481	410	0.668 (0.658)[b]
2,4,6-trimethylpyridine	25 229	24 956	273	0.748

[a] See text. [b] Values from ref 6.

probe and its homomorph in the eight solvents studied. These also includes the values for *N*-methylimidazole and *N*,*N*-dimethylaniline, which were remeasured on samples of these solvents dried over sodium and potassium hydroxide, respectively, and distilled at a low pressure. The SB values for the eight solvents studied were obtained from the following expression:

$$\mathrm{SB}_{\mathrm{solvent}} = \frac{\Delta\tilde{\nu}_{\mathrm{solvent}} - \Delta\tilde{\nu}_{\mathrm{gas\ phase}}}{\Delta\tilde{\nu}_{\mathrm{TMG}} - \Delta\tilde{\nu}_{\mathrm{gas\ phase}}}$$

where $\Delta\tilde{\nu}(\mathrm{cm}^{-1}) = \tilde{\nu}_{\mathrm{NI}} - \tilde{\nu}_{\mathrm{MNI}}$.

As can be seen from Table 1, the SB values for *N*-methylimidazole and *N*,*N*-dimethylaniline are virtually identical with those reported elsewhere.[6]

The molecular structures for the 53 solvents studied were fully optimized at the SCF 6-31G** level by using the Gaussian 94[18] program. They were confirmed to correspond to energy minima by analyzing the corresponding vibrational frequencies. Table 2 gives the values of the more interesting structural parameters (dipole moment μ, mean polarizability $\bar{\alpha}$, and Mulliken charge of the basic center q_x) for the isolated molecule of solvents.

In order to derive theoretical informations on the basicity of these solvents, we obtained $V_{\min}$ and $\epsilon_{\mathrm{mo(Vmin)}}$ for isolated molecules of solvent.

The electrostatic potential $V(r)$ created in the space around a molecule by its nuclei and electrons is defined in rigorous terms by

$$V(r) = \sum\nolimits_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|R_{\mathrm{A}} - r|} - \int \frac{\rho(r')\,\mathrm{d}r'}{|r' - r|}$$

where Z_A is the charge on nucleus A, located at R_A, and $\rho(r)$ is the molecular electronic density function. The sign of $V(r)$ in any particular region depends on whether the effects of nuclei or electrons are dominant there. The electrostatic potential $V(r)$ has proved particularly suitable for analyzing noncovalent interactions such as hydrogen bonding.[19−22] In an electrophilic approach, the hydrogen atom of the acid will initially be attracted to the more negative regions of $V(r)$ and, especially, to the points where the potential takes its most negative values (the local minima $V_{\min}$). Parameter $V_{\min}$ defines the relative liability of these zones to an electrophilic attack and has been successfully used to correlate experimental basicity parameters.[23] Table 3 gives the $V_{\min}$ values obtained at the 6-31G** level. $V_{\min}$ was found to lie in the zone of the lone electron pair of the active basic site of the molecule, specifically, in the zone of the lone electron pair of the nitrogen atom in *N* sites, whichever the type of hybridization, and in the zone of one or two (symmetric case) electron pairs for a basic oxygen site with O(sp^2) hybridization or an intermediate zone between the electron pairs for O(sp^3) hybridization. For a given basis set the magnitude of $V_{\min}$ depends on the nature of the basic atom and the prevailing molecular geometry, as well as on the presence of other heteroatoms, functional groups, aromatic fragments, *etc.*

TABLE 2: HF/6-31G-Calculated Dipole Moments (μ/Debye), Mean Polarizability ($\bar{\alpha}$/Fm^2), and Mulliken Charge of the Basic Center (q_x) for Isolated Solvents**

n°	solvents	μ	$\bar{\alpha}$	q_x
1	tetramethylguanidine	2.63	69.07	−0.69
2	*N*-methylimidazole	4.18	46.37	−0.54
3	cyclohexylamine	1.35	65.43	−0.7
4	ethylenediamine	0.00	34.49	−0.71
5	pyrrolidine	1.43	44.98	−0.61
6	HMPA	4.00	96.17	−0.75
7	piperidine	1.25	55.35	−0.62
8	dimethyl sulfoxide	4.51	39.80	−0.79
9	2,4,6-trimethylpyridine	1.97	83.05	−0.61
10	4-methylpyridine	2.74	59.79	−0.55
11	2,3,3-trimethylindolenine	2.46	109.43	−0.54
12	2,6-dimethylpyridine	1.56	71.73	−0.6
13	pyridine	2.31	48.65	−0.54
14	1-methylpiperidine	0.60	66.11	−0.59
15	triethylamine	0.71	69.66	−0.6
16	*N*-methylacetamide	4.19	38.20	−0.6
17	quinoline	2.17	89.15	−0.58
18	*N*,*N*-dimethylacetamide	3.92	48.73	−0.61
19	*N*,*N*-dimethylformamide	4.10	39.22	−0.59
20	triethyl phosphate	0.99	86.23	−0.75
21	trimethyl phosphate	1.01	54.93	−0.74
22	tetrahydrofuran	1.94	41.77	−0.66
23	2-bromopyridine	3.73	66.24	−0.53
24	propylene carbonate	6.1	44.08	−0.55
25	cineole	1.44	97.26	−0.7
26	sulfolane	5.84	56.16	−0.68
27	aniline	1.52	60.51	−0.74
28	propionitrile	4.17	32.50	−0.46
29	tetrahydropyran	1.57	51.93	−0.64
30	diethyl ether	1.42	45.64	−0.64
31	acetonitrile	4.07	22.16	−0.45
32	acetophenone	3.25	75.73	−0.54
33	acetone	3.14	32.43	−0.52
34	ethyl acetate	2.14	45.16	−0.57
35	benzonitrile	4.85	66.97	−0.45
36	dimethyl sulfite	3.79	43.84	−0.7
37	2-chloroethanol	3.45	25.25	−0.62
38	benzaldehyde	3.47	65.97	−0.51
39	1,4-dioxane	0.00	44.46	−0.64
40	methyl benzoate	2.08	78.65	−0.58
41	dimethyl carbonate	0.38	37.06	−0.6
42	1,3-dioxolane	1.35	34.20	−0.65
43	nitrobenzene	5.07	66.59	−0.47
44	chloroacetonitrile	3.40	30.71	−0.43
45	nitromethane	4.03	23.89	−0.45
46	2,2,2-trifluoroethanol	1.87	24.00	−0.63
47	2,2,2-trichloroethanol	1.84	51.06	−0.62
48	anisol	1.35	67.59	−0.66
49	ethyl trifluoroacetate	3.23	44.57	−0.53
50	*N*,*N*-dimethylaniline	1.49	82.99	−0.7
51	perfluoropyridine	0.98	49.69	−0.61
52	furan	0.77	35.56	−0.54
53	hexafluoro-2-propanol	2.78	33.23	−0.62

If $V_{\min}$ allows one to describe the electrostatic contribution to basicity, the covalent contribution can be associated to the ease of local electron ionization at the position of $V_{\min}$, a role that we shall assign to the most labile occupied molecular orbital significantly contributing to the electron density in that zone, the energy of which we shall denote by $\epsilon_{\mathrm{mo(Vmin)}}$ (see Table 3). The molecular orbital (MO) of energy $\epsilon_{\mathrm{mo(Vmin)}}$ corresponds to the lone electron pair in the molecules with a nitrogen atom as the basic site and to one of the two lone electron pairs on an oxygen basic site. This MO is the highest occupied molecular orbital (HOMO) in saturated amines or a deeper orbital (e.g., in some aromatic systems such as benzonitrile, it is HOMO-

TABLE 3: Electrostatic Potential Local Minima (V_{min} 6-31G/Kcal/mol) and Energy of Molecular Orbital with More Electron Density on V_{min} ($\epsilon_{mo(Vmin)}$/hartree) Calculated at HF/6-31G** Level. Also Electrostatic Potential Local Minima (V_{min} STO-5G/Kcal/mol) Calculated with STO-5G Basis Set on 6-31G** Geometry**

n°	solvents	SB	V_{min} 6-31G**	$\epsilon_{mo(Vmin)}$	V_{min} STO-5G
1	tetramethylguanidine	1	−83.3	−0.4088	−106.1
2	*N*-methylimidazole	0.658	−81.7	−0.4223	−107.8
3	cyclohexylamine	0.959	−80.5	−0.3718	−103.4
4	ethylenediamine	0.843	−79.8	−0.3847	−101.5
5	pyrrolidine	0.99	−79.7	−0.3665	−96.0
6	HMPA	0.813	−79.0	−0.4447	−95.4
7	piperidine	0.933	−77.8	−0.3479	−98.0
8	dimethyl sulfoxide	0.647	−76.5	−0.5092	−97.7
9	2,4,6-trimethylpyridine	0.748	−73.6	−0.3946	−96.6
10	4-methylpyridine	0.587	−72.8	−0.4056	−92.7
11	2,3,3-trimethylindolenine	0.591	−72.4	−0.4014	−95.3
12	2,6-dimethylpyridine	0.708	−71.8	−0.3973	−94.9
13	pyridine	0.581	−70.5	−0.4091	−90.8
14	1-methylpiperidine	0.836	−69.9	−0.3436	−89.6
15	triethylamine	0.885	−69.4	−0.3401	−88.6
16	*N*-methylacetamide	0.735	−69.2	−0.4108	−70.4
17	quinoline	0.526	−68.8	−0.4066	−90.4
18	*N*,*N*-dimethylacetamide	0.65	−68.6	−0.4094	−70.1
19	*N*,*N*-dimethylformamide	0.613	−67.6	−0.4209	−68.6
20	triethyl phosphate	0.614	−67.3	−0.4387	−88.5
21	trimethyl phosphate	0.522	−66.2	−0.4484	−86.0
22	tetrahydrofuran	0.591	−61.9	−0.4581	−71.4
23	2-bromopyridine	0.455	−60.6	−0.4277	−81.9
24	propylene carbonate	0.341	−60.1	−0.4708	−62.9
25	cineole	0.737	−60.1	−0.4013	−72.6
26	sulfolane	0.365	−59.5	−0.4572	−76.9
27	aniline	0.264	−59.5	−0.4426	−76.1
28	propionitrile	0.365	−58.9	−0.5359	−76.8
29	tetrahydropyran	0.591	−58.8	−0.4409	−69.1
30	diethyl ether	0.562	−58.2	−0.4502	−70.5
31	acetonitrile	0.286	−57.9	−0.5491	−76.0
32	acetophenone	0.365	−57.8	−0.4102	−56.8
33	acetone	0.475	−57.8	−0.4063	−57.4
34	ethyl acetate	0.542	−57.6	−0.4387	−62.5
35	benzonitrile	0.281	−57.5	−0.5291	−76.6
36	dimethyl sulfite	0.341	−57.1	−0.4684	−87.4
37	2-chloroethanol	0.377	−56.5	−0.4666	−67.4
38	benzaldehyde	0.29	−55.3	−0.4211	−54.2
39	1,4-dioxane	0.444	−53.4	−0.45	−62.9
40	methyl benzoate	0.378	−53.1	−0.4442	−60.1
41	dimethyl carbonate	0.433	−51.2	−0.4648	−60.1
42	1,3-dioxolane	0.399	−50.1	−0.4994	−60.8
43	nitrobenzene	0.24	−49.0	−0.4889	−58.5
44	chloroacetonitrile	0.184	−48.6	−0.5731	−65.3
45	nitromethane	0.236	−46.9	−0.4887	−54.7
46	2,2,2-trifluoroethanol	0.107	−45.4	−0.5298	−60.0
47	2,2,2-trichloroethanol	0.186	−45.3	−0.5018	−53.8
48	anisol	0.299	−44.7	−0.4744	−59.1
49	ethyl trifluoroacetate	0.229	−43.8	−0.4804	−49.9
50	*N*,*N*-dimethylaniline	0.305	−42.8	−0.401	−53.1
51	perfluoropyridine	0.144	−37.9	−0.5087	−72.0
52	furan	0.107	−36.1	−0.531	−46.7
53	hexafluoro-2-propanol	0.014	−35.3	−0.5493	−50.7

5).[24] The molecular structure and nature of the basic site influences the relative energy of this MO within the system concerned.

In order to expand the contributions of Politzer *et al.*[23] to solvent basicity and compare them with the results of this work, V_{min} was calculated for the 53 solvents studied, in the way proposed by Politzer using STO-5G basis set (see Table 3) at the optimized 6-31G** geometries.

For simplicity, and in order to facilitate identification of family-dependent trends, solvents were labeled as follows (unless otherwise stated): sp nitrogen-containing bases (◬), sp^2 nitrogen-containing bases (△), sp^3 nitrogen-containing bases (▲), sp^3 oxygen-containing bases (●), sp^2 oxygen-containing bases (○), sulphur-containing bases (▽), halogen-containing bases (+), and aromatic bases (◇).

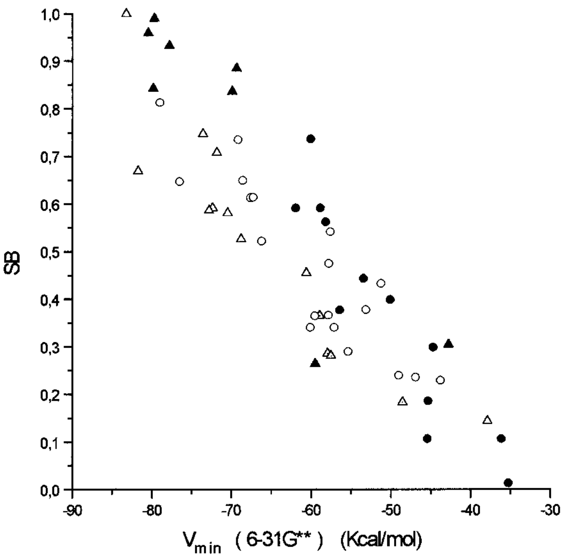


Figure 1. SB values of solvents *vs* calculated HF/6-31G** electrostatic potential local minima (V_{min} 6-31G**) for 53 solvent molecules studied. For this and subsequent figures see text for symbols.

TABLE 4: Least-Squares Statistical Analysis of SB *vs* V_{min} in Global and by Family Terms

$SB = A + BV_{min}$	*A*	*B*	*R*	sd
global (53 molecules)	−0.591	−0.018 (±0.001)	0.896	0.112
N(sp3) (8 molecules)	−0.630	−0.020 (±0.004)	0.887	0.146
N(sp2) (10 molecules)	−0.486	−0.016 (±0.002)	0.909	0.097
N(sp) (4 molecules)	−0.503	−0.014 (±0.004)	0.910	0.038
O(sp3) (12 molecules)	−0.812	−0.023 (±0.003)	0.932	0.087
O(sp2) (19 molecules)	−0.528	−0.016 (±0.002)	0.901	0.079

Experimental data for solvent basicity scales used in this work is collected in Supporting Information.

We used the CIS method[25] as implemented in the software package Gaussian 94 to examine excited states (UV−vis spectra) at the CIS/6-31G** level on HF/6-31G** geometries.

Results and Discussion

SB versus Theoretical Data. Let us first analyze the performance of SB against theoretical parameters obtained from *ab initio* calculations using a 6-31G** base.

Figure 1 shows the V_{min} values obtained at the 6-31G** level against the corresponding SB values for the 53 solvents studied. Note that the SB basicity and electrostatic potential V_{min} are proportional but in a highly diffuse manner ($r = 0.896$, sd = 0.11). More important, there is no evidence of family-dependence. Table 4 shows the results of the statistical processing of SB *vs* V_{min} data, both in global terms and by family.

These results contradict those obtained by Politzer *et al.*[22] in their pioneering work where they showed V_{min} data at the STO-5G level to be correlated with solvent basicity β for base families only (i.e., amines, ethers, and molecules containing double-bonded oxygen). In order to identify the origin of this divergence, we obtained V_{min} values by using the STO-5G base function and found that a plot against SB (Figure 2) made things worse: solvents gathered in two broad groups consisting of nitrogen-containing bases [and molecules containing O(sp^2) atoms bonded to P or S atoms] on the one hand and of oxygen-containing bases on the other. We can thus conclude that the flexibility of the basis set used is crucial because it influences the accuracy with which the electrostatic potential is described.

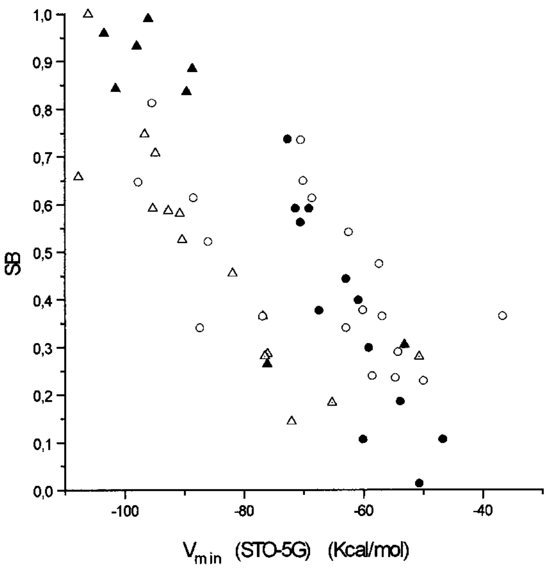


Figure 2. SB values of solvents *vs* calculated HF/STO-5G//HF/6-31G** electrostatic potential local minima (V_{min} STO-5G) for 53 solvent molecules studied.

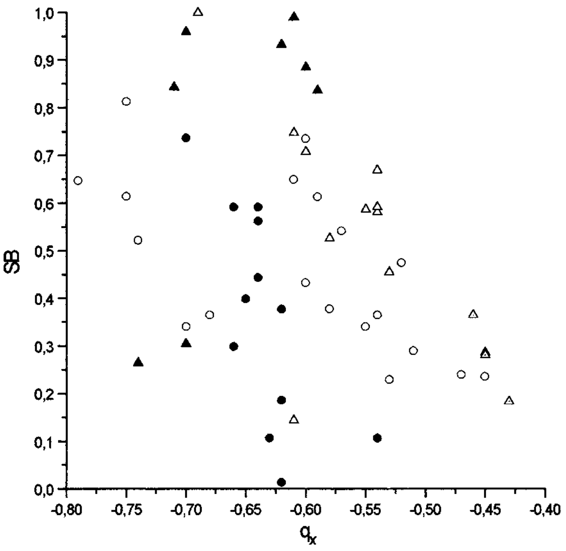


Figure 3. SB values of solvents *vs* charge of the basic center calculated by Mulliken population analyisis (q_x) for 53 solvent molecules studied.

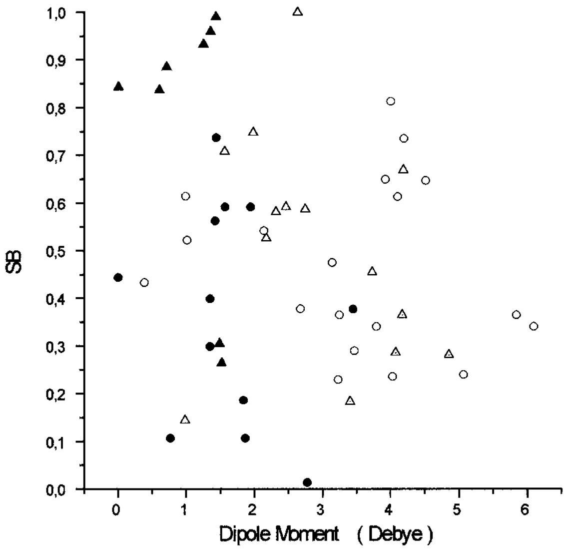


Figure 4. SB values of solvents *vs* calculated HF/6-31G** dipole moment (μ) for 53 solvent molecules studied.

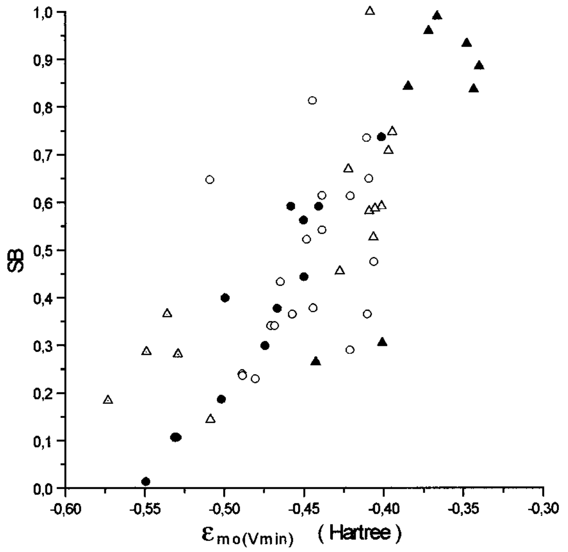


Figure 5. SB values of solvents *vs* energy of the molecular orbital with more electron density on V_{min} ($\epsilon_{mo(Vmin)}$) for 53 solvent molecules studied.

We should also note that SB values are not correlated with the charge on the basic site (Figure 3), expressed according to Mulliken population analysis; also, it exhibits no family grouping. As expected, a plot of SB against the dipole moment revealed no marked trend (see Figure 4).

Figure 5 shows a plot of SB *vs* $\epsilon_{mo(Vmin)}$. As can be seen, the two quantities are related, albeit in a highly diffuse manner ($r = 0.793$, sd $= 0.15$). Obviously, as higher is the energy of the orbital as higher is the basicity. More important, the plot exhibits no clear grouping into compound families.

If V_{min} and $\epsilon_{mo(Vmin)}$ are representative of electrostatic and covalent contributions to solvent basicity and the two were scarcely correlated ($r = 0.669$, sd $= 9.38$), the next logical step was to analyze the dependence of SB on both. Obviously, the correlation coefficient increased (to 0.933) and data dispersion was slightly lower (sd $= 0.09$). Interestingly, this analysis, which involved the prior normalization of both variables V'_{min} and $\epsilon'_{mo(V_{min})}$ between the absolute values 0 and 1, revealed that SB is made up of quite a homogeneous combination of electrostatic and covalent contributions ($0.634/0.366 = 1.73$):

$$SB = (0.634 \pm 0.066)V'_{min} + (0.366 \pm 0.072)\epsilon'_{mo(V_{min})} + 0.326$$

with $n = 53$, $r = 0.933$, and sd $= 0.09$.

Maria *et al.*[12] used principal component analysis to examine electrostatic and covalent contributions to solvent basicity scales by estimating the variable θ, assimilated to the arc tangent of the ratio of the scale sensitivity to the principal factors F_2 and F_1. For the SB scale, θ is close to 14° because it conforms to the following expression:

$$SB = (0.317 \pm 0.035)F_1 + (0.081 \pm 0.106)F_2 + 0.56$$

with $n = 21$, $r = 0.91$, and sd $= 0.07$. *N*,*N*-dimethylaniline was excluded from the fitting because it resulted in significantly worse results ($n = 22$, $r = 0.87$). According to Maria *et al.*,[12] such a small SB value means that the SB scale is a balanced combination of electrostatic and covalent components.

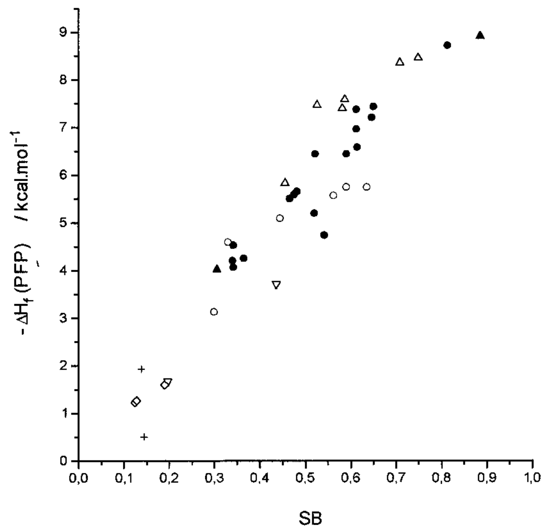


Figure 6. Enthalpies of formation for the hydrogen bonding (ΔH_f) of the 4-fluorophenol for the pure solvent method[3] *vs* the SB values of the solvents.

A comparison of SB values against the C_B and E_B values of Drago *et al.*[8] led to

$$SB = (0.195 \pm 0.028)E_B + (0.098 \pm 0.014)C_B - 0.002$$

with $n = 22$, $r = 0.922$, and sd = 0.09.

Therefore, the resulting electrostatic-to-covalent ratio is 1.97.

Based on the previous results, the SB scale is a balanced scale encompassing electrostatic and covalent interactions.

SB versus Experimental Data. One way of assessing the potential general nature of the SB scale is, for example, by applying it to data from R-OH and NH acids or to data from largely electrostatic or covalent scales. We analyzed the following situations studied for bulk solvents: (1) a calorimetric scale constructed from a phenolic acid (R-OH) and based on the ΔH_f of Arnett *et al.*,[3] (2) a calorimetric scale based on an N$-$H acid, (such as pyrrole) which poses no conformational problems and based on the $\delta\Delta H_{solv}$ of Laynez *et al.*,[26] (3) a spectroscopic scale constructed from a phenol acid such as that of $\Delta\Delta\tilde{\nu}(1)-(2)$ of Laurence *et al.*,[15] (4) a spectroscopic scale based on an N$-$H acid (4-nitroaniline), such as that of $\Delta\Delta\tilde{\nu}$-$(3)-(5)$ of Laurence *et al.*,[15] and (5) the $\delta\Delta H^{g\rightarrow solv}$ values for SO_2 and I_2 reported by Benoit and Louis.[27]

In 1970, Arnett *et al.*[3] developed a new calorimetric method for estimating solvent basicity, the "pure base method", which involves injecting a small amount of an acid probe into a base (a pure solvent). The resulting heat obviously consists of two different contributions, namely: that from the hydrogen bonding interaction between the acid and base (solvent) and that from the remaining heat exchanged. The latter contribution is subsequently subtracted as the measured heat of dissolution for an appropriate homomorph of the acid probe used. Specifically, Figure 6 shows the enthalpies of hydrogen bonding measured by Arnett *et al.*[3] for a series of nonprotic solvents in 4-fluorophenol (PFP) and its homomorph 4-fluoroanisole (PFA). As can be seen, correlation is quite good ($n = 38$, $r = 0.951$, sd = 0.7 kcal/mol). Also, no family grouping is observed—note that the solvent series included 2 N(sp^3) bases, 6 N(sp^2) base, 6 O(sp^3) bases, 17 O(sp^2) bases, 2 halogen-containing bases, 2 sulfur-containig bases, and 3 aromatic bases). We must emphasize the absence of family gatherings, which, according to Maria *et al.*,[12] is the result of Arnett's ΔH_f scale having a θ value of 42° (i.e., its electrostatic component is more substantial than in the SB scale).

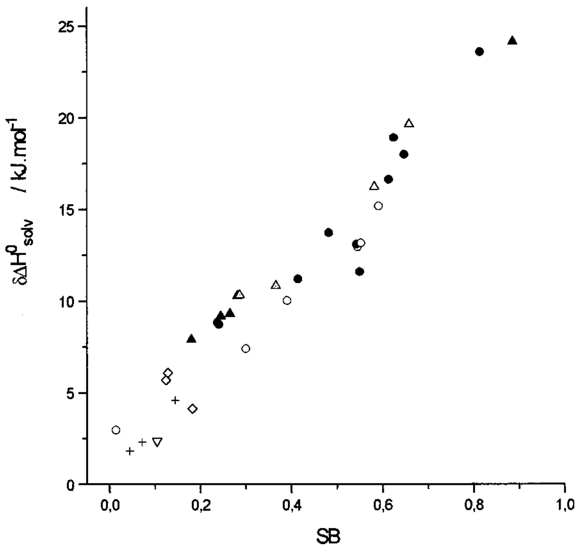


Figure 7. Variation of the enthalpy of the solvation of the couples pyrrole/*N*-methylpyrrole and toluene/benzene[26] *vs* the SB values of the solvents.

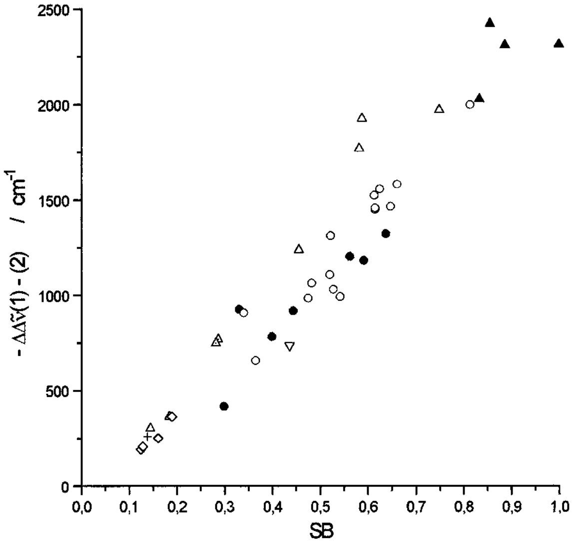


Figure 8. Solvatochromic shift $-\Delta\Delta\tilde{\nu}$ attributable to hydrogen-bonding for a couple 4-nitrophenol/4-nitroanisole by Laurence *et al.*[14] *vs* the SB values of the solvents.

Recently,[26] our group applied the pure solvent method to various probes (pyrrole, *N*-methylpyrrole, benzene, and toluene) in order to avoid effects other than those from hydrogen bonding (e.g., small cavity and dipolarity/polarizability effects) as far as possible. In addition, the acid probe used was of the N$-$H type rather than the O$-$H type employed by Arnett *et al.*[3] Figure 7 compares the results obtained and the corresponding SB values. Correlation is quite good ($n = 33$, $r = 0.970$, sd = 0.37 kcal/mol). Again, there was no family grouping among the solvents studied, *viz.* 4 N(sp^3) bases, 2 N(sp^2) bases, 3 N(sp) bases, 6 O(sp^3) bases, 10 O(sp^2) bases, 1 sulphur-containing base, 4 halogen-containing bases, and 3 aromatic bases.

Laurence *et al.*[15] applied the solvatochromic method to carefully made UV$-$vis measurements of the probe 4-nitrophenol and its homomorph 4-nitroanisole. They established the $\Delta\Delta\tilde{\nu}(1)-(2)$ scale, which is obviously of the O$-$H type. Figure 8 shows a plot of these values against the SB values for the same solvents. As can be seen, correlation between the two data sets is quite good ($n = 40$, $r = 0.959$, sd = 179 cm^{-1}). Also, no family grouping is observed. This can be ascribed to the small θ value (2°) assigned by Maria *et al.*[12] to this scale,

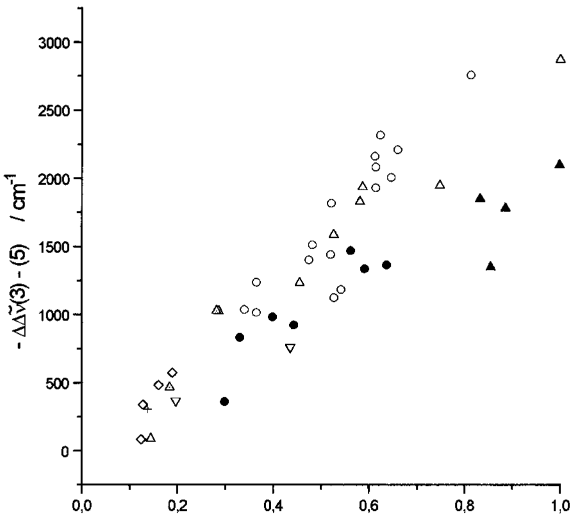
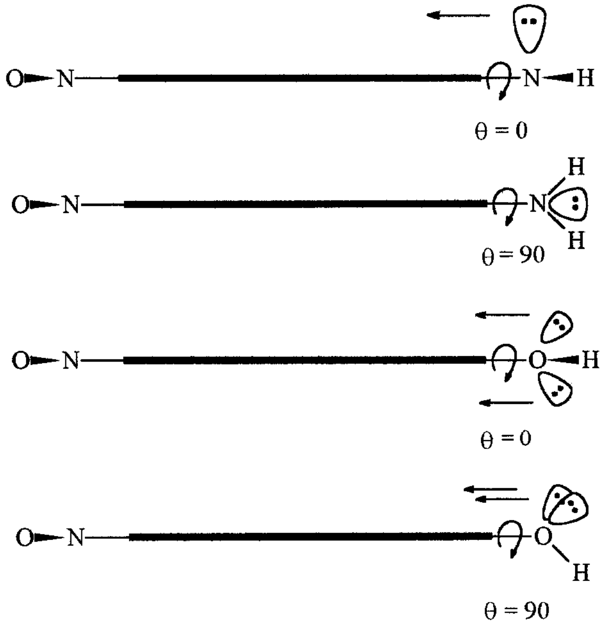


Figure 9. Solvatochromic shift $-\Delta\Delta\tilde{\nu}$ attributable to hydrogen-bonding for a couple 4-nitroaniline/4-nitro-*N*,*N*-dimethylaniline by Laurence *et al.*[15] *vs* SB.

SCHEME 1



which, however, is inconsistent with the high $E^{*}_{\rm A}/C^{*}_{\rm A}$ ratio (5) obtained by Drago *et al.*[28]

Similarly, Laurence *et al.*[15] established their $\Delta\Delta\tilde{\nu}(3)-(5)$ scale, of the N−H type, by applying the solvatochromic method to UV−vis measurements of the probe 4-nitroaniline and its homomorph *N*,*N*-dimethyl-4-nitroaniline. Figure 9 shows the data for this scale against the SB values for the same solvents. If the data for trisubstituted amines (▲) are excluded (see later), correlation between the two data sets is quite good ($n = 40$, $r = 0.933$, $sd = 260$ cm^{-1}); however, the resulting dispersion is obviously higher relative to Figure 8. In any case, Figure 9 shows no family grouping. This is worth special note since Maria *et al.*[12] assigned this scale a θ value of 66° (and hence a markedly electrostatic character) in their principal components analysis.

One plausible explanation for the special behavior of the probes 4-nitrophenol and 4-nitroaniline toward tertiary amines is that, in interacting *via* hydrogen bonding, the tertiary amine causes both the hydroxyl and the amino groups in the probes to rotate; however, while a rotating hydroxyl group still allows the lone electron pairs on the oxygen atom to interact with the π electron density of the aromatic ring, a rotating amino group reaches a point where its lone electron pair is normal to the π density of the ring and disrupts its conjugation (see Scheme 1). The consequent loss of resonance of the amino group resulting from the steric hindrance of the trisubstituted amine displaces the electron transition of the probe 4-nitroaniline to a higher energy level, thereby substantially decreasing the $\Delta\Delta\tilde{\nu}(3)-(5)$ value and leading to the deviation observed in Figure 9. Table 5 shows the energy for the first UV transition $(\pi, \pi^*)^1$ of both probes, based on CIS/6-31G** calculations. The results support the above hypothesis.

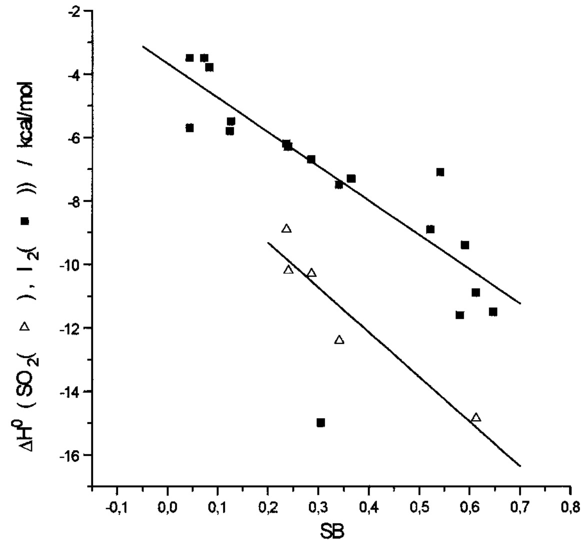


Figure 10. Enthalpies of gas phase-to-bulk solvent transfer by Benoit and Louis[27] *vs* SB.

TABLE 5: Transition Energies $(\pi,\pi^*)^1$ (λ/nm) of 4-Nitrophenol and 4-Nitroaniline Probes for Different Torsion Angles (θ) of −OH and $-NH_2$ Groups. Geometries were Generated from the Starting Point $\theta = 0$ which Corresponds to the HF/6-31G-Optimized Geometry**

θ (deg)	4-nitroaniline	4-nitrophenol
0	218.2	207.1
15	218.6	207.1
45	219.8	206.8
67	215.7	205.9
90	208.7	205.2

The principal component analysis of the Lewis acids sulphur dioxide and iodine carried out by Maria *et al.*[12] revealed that both possess a charge-transfer character (i.e., that the two act in an essentially covalent manner) with large, negative θ values of −45° and −51°, respectively. Figure 10 shows the enthalpies of gas phase-to-bulk solvent transfer reported by Benoit and Louis[26] as a function of the SB values for the solvents considered. As can be seen, both data sets are correlated with SB values; thus, $n = 17$, $r = 0.925$, and sd = 1.01 kcal/mol for SO_2 while shown in Figure 10, the data for *N*,*N*-dimethylaniline was excluded from the fitting, and $n = 5$, $r = 0.946$, and sd = 0.87 kcal/mol for I_2. Both data sets show no signs of compound grouping in families. This is especially relevant taking into account that the two basicity scales (SO_2 and I_2) possess the lowest electrostatic-to-covalent ratio studied.[12]

Conclusions

SB data are proportional to both theoretical values for the molecular electrostatic potential ($V_{\rm min}$) and $\epsilon_{\rm mo(Vmin)}$ for the isolated molecule of solvents. In addition, neither relationship is family-dependent.

The different analyses performed revealed that the SB scale is sensitive to both electrostatic and covalent interactions, the ratio of which is close to unity.

The above results clearly indicate that, contrary to the assertion of Nicolet *et al.*, phenolic acids such as 4-nitrophenol are no doubt more appropriate to describe solvent basicity than unsubstituted amines acids such as the widely used 4-nitroaniline and its derivatives.

Plotting SB data against values from other basicity scales (e.g., Figures 6−8 and 10, and others in ref 6) reveals the absence of data gathering in parallel lines according to base families. Therefore, the SB scale meets the requirements for a general basicity scale.

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Supporting Information Available: Table of experimental data for solvent basicity studies (3 pages). Ordering information is given on any current masthead page.

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(24) $\epsilon_{\mathrm{mo(Vmin)}}$ for molecules containing N(sp^3), N(sp^2), and N(sp) corresponds to the orbital of the lone pair of N; specifically, it is HOMO for N(sp^3) and HOMO-2 for N(sp^2) and N(sp). In oxygen-containing molecules, this term corresponds to one of the orbitals of the lone pairs of the oxygen atom, *viz.* the orbital distributed among the pairs in molecules with O(sp^3) and that with lobes on both sides of the oxygen atom in molecules with O(sp^2). As a rule, the corresponding orbital for the former is HOMO-1 and that for the latter is the HOMO. When the oxygen atom is bonded to P, S, or N, these orbitals are somewhat deeper.

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