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Hydrogen-Bond Acceptance of Solvents: a ^{19}F Solvatomagnetic β_1 Database to Replace Solvatochromic and Solvatovibrational Scales

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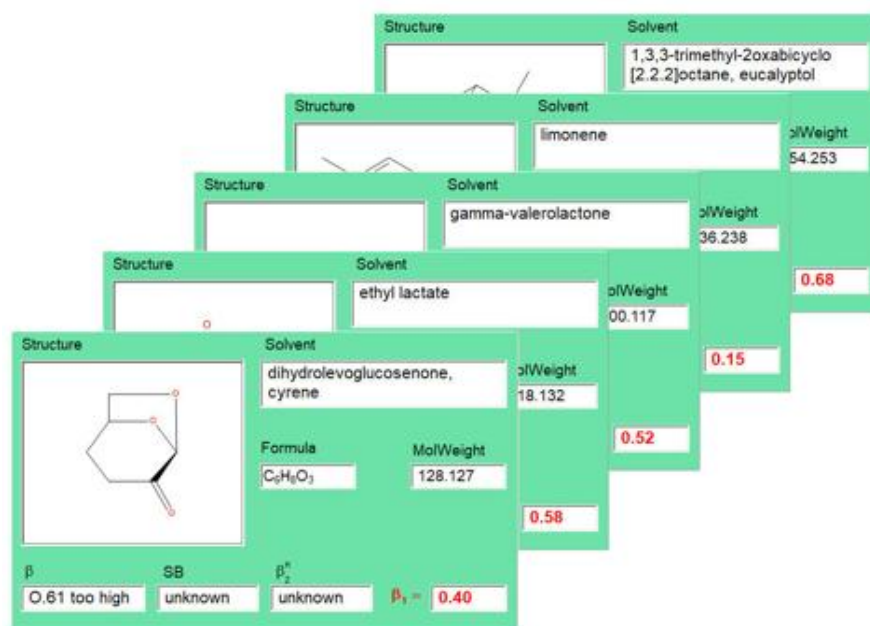
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Abstract: A variety of physicochemical properties and several hydrogen-bond donors have been used to define methods and to build scales aiming at measuring the hydrogen-bond acceptance of solvents. There is a great deal of confusion in these scales and methods. Solvatochromic, solvatocalorimetric, solvatovibrational, and ^{19}F solvatomagnetic comparison methods are critically reviewed. Only two methods, the solvatomagnetic and the solvatocalorimetric ones, are able to yield reliable solvent basicity scales. The solvatomagnetic β_1 scale defined from the ^{19}F chemical shift of 4-fluorophenol is extended to many solvents including ionic liquids and green solvents. The results for about 240 hydrogen-bond acceptor solvents are organized in a numerical β_1 database. The comparison of β_1 with

solvatochromic scales highlights their shortcomings, in particular for the important class of amphiprotic solvents. Therefore, the use of the ^{19}F solvatomagnetic comparison method and of the solvatomagnetic β_1 scale is recommended in solvent effect studies.

Graphical Abstract



The hydrogen-bond acceptance parameter of solvents, β_1 , is measured by the ^{19}F solvatomagnetic comparison method shown to be free of the shortcomings of the solvatochromic and solvatovibrational ones. About 240 β_1 values are organized in a numerical database. These values must be preferred to the β s in current use, in particular for the important class of amphiprotic solvents.

Keywords: Basicity; Empirical solvent parameters; Hydrogen bonds; Solvatochromism; Solvent Effects

Introduction

Most organic solvents are hydrogen-bond acceptors (HBAs) by virtue of nonbonding or π -bonding electron pairs in the electronic system of their molecules. When the solute is a hydrogen-bond donor (HBD), a solute HBD/solvent HBA molecular interaction -the hydrogen bond- takes place. This specific interaction inevitably influences the reactivity and physicochemical properties of organic solutes. Thus, in order to select the solvent appropriate to the process under study, a chemist must have a proper measure of the solvent HBA strength (among other solvent properties) for a comprehensive list of solvents. Also, if the solvent of interest is not yet parameterized, he must be able to determine its HBA strength by the most proper and the simplest method.

Today, there is a consensus to determine the HBA strength of molecules as solutes in an inert solvent by considering hydrogen bonding as a specific type of Lewis acid-base interaction¹ (where the HBD is the Lewis acid and the HBA the Lewis base) and extending the IUPAC definition of Lewis basicity² as follows: “*Hydrogen-bonding basicity: the thermodynamic tendency of a substance to act as a HBA. Comparative measures of this property are provided by the equilibrium constants for hydrogen-bonded complex formation for a series of HBAs with a common HBD*”. In this way, the hydrogen-bond basicity scale pK_{BHX} has been constructed³ for a thousand of HBAs against the reference HBD 4-fluorophenol in the quasi-inert solvent CCl_4 , and the measurement of the HB basicity of molecules as solutes can be considered as accomplished (see also references⁴⁻⁶ of previous works in Table 1).

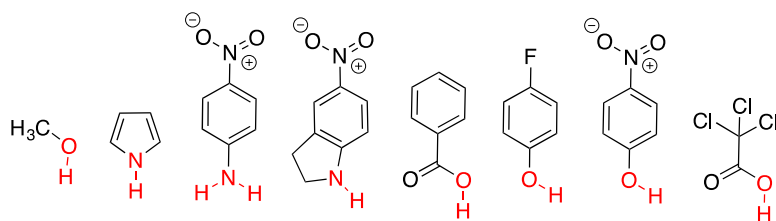
Measuring the HBA strength of molecules acting as solvents represents a much greater challenge. Complexation constants cannot be used since complete complexing of the reference HBD usually takes place in pure liquid HBA. Thus, other criteria of HBA strength must be looked for. Enthalpies of solution⁷⁻⁹ and spectroscopic shifts upon hydrogen

bonding^{1,10,11} have been studied. However, two terms are involved in the measured thermodynamic or spectroscopic property in the neat solvent: the desired term due to hydrogen bond formation and a contaminating term produced by nonspecific interactions. The latter contribution must be subtracted in order to isolate the hydrogen bonding contribution. To perform this task, a number of methods have been proposed. In 1970, Arnett et al. devised the “pure base calorimetric method”^{7,8}, modified in 1990 by Catalán et al. into a “pure solvent method”⁹. Hereafter, these methods will be called “Solvatocalorimetric Comparison Method”. In 1976, Kamlet and Taft proposed¹² the popular “Solvatochromic Comparison Method”, later improved in 1986 by Nicolet and Laurence¹³. In 1987, Nicolet et al. published¹⁴ an “infrared comparison method” (hereafter called Solvatovibrational Comparison Method). Lastly, in 2014, Laurence et al. conceived a “Solvatomagnetic Comparison Method”¹⁵. These methods and the corresponding solvent scales are summarized in Table 1, as well as: for comparison some solute HB basicity scales³⁻⁶, the $\Delta\nu(\text{OD})$ ¹⁰, $\Delta\nu(\text{OH})$ ¹¹ and $\Delta\nu(\text{CO})$ ¹⁴ infrared scales, the β statistical scale of Kamlet et al.^{12,16}, and the solvatochromic scales $\beta_1'(\text{NH}_2)$ ¹⁷, $\beta_1(\text{NH}_2)$ ^{18,19}, $\beta_1(\text{OH})$ ^{18,19}, and SB ²⁰. The corresponding probes used in these scales are depicted in Scheme 1.

Table 1. Scales measuring the HBA strength of HBA molecules as solvents (as solutes for comparison).

| Property measured | Symbol | Medium | N ^a | Ref |
|---|-------------------------------|----------------------------------|----------------|--------|
| <i>1. Solute basicity scales: equilibrium constants</i> | | | | |
| 1.1. OH, NH, CH HBDS + B \rightleftharpoons Complex | $\lg K_B^H$ | CCl ₄ | 215 | 4 |
| 1.2. 4-NO ₂ C ₆ H ₄ OH + B \rightleftharpoons Complex | $\lg K_\beta$ | CCl ₃ CH ₃ | 90 | 5 |
| 1.3. 4-FC ₆ H ₄ OH + B \rightleftharpoons Complex | pK_{BHX} | CCl ₄ | 1338 | 3 |
| <i>2. Solute basicity scale: retention in gas chromatography</i> | | | | |
| | β_2^C | | 87 | 6 |
| <i>3. Ill-defined scale: statistical average of miscellaneous solute and solvent properties</i> | | | | |
| | β | Pure base, CCl ₄ | ~160 | 12,16 |
| <i>4. Solvent scales: enthalpies of solution</i> | | | | |
| 4.1. Enhanced solution enthalpies of 4-FC ₆ H ₄ OH relative to 4-FC ₆ H ₄ OMe. | $\Delta H_f(\text{OH})^{[b]}$ | Pure base | 57 | 7,8 |
| 4.2. Enhanced solution enthalpies of pyrrole relative to <i>N</i> -methylpyrrole. | $\Delta H_f(\text{NH})^{[c]}$ | Pure base | 35 | 9 |
| <i>5. Solvent scales: infrared shifts</i> | | | | |
| 5.1. Infrared shift of the OD stretching of methan[² H]ol. | $\Delta\nu(\text{OD})^{[d]}$ | Pure base | 89 | 10 |
| 5.2. Infrared shift of the OH stretching of methanol | $\Delta\nu(\text{OH})$ | Pure base | 72 | 11 |
| 5.3. Enhanced infrared shift of the carbonyl stretching frequency of CCl ₃ COOH relative to CCl ₃ COOMe. | $\Delta\nu(\text{CO})$ | Pure base | 24 | 14 |
| <i>6. Solvent scales: enhanced bathochromic shift of the S₀→S₁ transition of:</i> | | | | |
| 6.1. 4-NO ₂ C ₆ H ₄ NH ₂ relative to 4-NO ₂ C ₆ H ₄ NEt ₂ | $\beta'_1(\text{NH}_2)^{[e]}$ | Pure base | 44 | 17 |
| 6.2. 4-NO ₂ C ₆ H ₄ NH ₂ relative to 4-NO ₂ C ₆ H ₄ NMe ₂ | $\beta_1(\text{NH}_2)$ | Pure base | 189 | 18,19 |
| 6.3. 4-NO ₂ C ₆ H ₄ OH relative to 4-NO ₂ C ₆ H ₄ OMe | $\beta_1(\text{OH})$ | Pure base | 191 | 18,19 |
| 6.4. 5-Nitroindoline relative to 1-methyl-5-nitroindoline | <i>SB</i> | Pure base | 202 | 20 |
| <i>7. Solvent scale: ¹⁹F chemical shift of 4-F-C₆H₄OH relative to 4-F-C₆H₄OMe</i> | | | | |
| | β_1 | Pure base | 113 | 15, 21 |

^a Number of bases. ^b Enthalpy of HB formation to 4-fluorophenol. ^c Enthalpy of HB formation to pyrrole. ^d For homogeneity, this symbol is preferred to the initial $\Delta\nu_D$ (where the subscript D stands for electron Donor). ^e For homogeneity, this symbol is preferred to the initial B_{KT} (where the subscript KT stands for Kamlet-Taft).



Scheme 1. Hydrogen-bond donors for the construction of hydrogen-bond acceptance scales depicted in Table 1, from left to right: methanol, pyrrole, 4-nitroaniline, 5-nitroindoline, benzoic acid, 4-fluorophenol, 4-nitrophenol, and trichloroacetic acid.

In solvent effect studies, there is a great deal of confusion on which HBA solvent scale to choose among the numerous ones available in the literature, and which method to select for the HBA characterization of new solvents. HBA scales and their determination methods will be critically examined in the first part of this paper.

The solvatomagnetic comparison method compares the ^{19}F chemical shifts of 4-fluorophenol (HBD) and 4-fluoroanisole (similar to 4-fluorophenol but non-HBD) in HBA solvents and yields the so-called solvatomagnetic β_1 parameter¹⁵. In the second part of this work, ^{19}F measurements and the deduced β_1 scale will be extended to 46 new solvents. Addition of the 113 primary β_1 values previously experimentally determined, and of 80 calculated secondary values (see below), yields a total of 249 β_1 values. For a convenient use of the scale, these values will be organized in a numerical database.

The most popular HB acceptance scale of solvents, the Kamlet-Taft β scale¹², has been defined by mixing basicity-dependent properties measured in the pure HBA solvent with other ones measured in CCl_4 . Because this procedure gives the chemists the fallacious feeling that the difference of medium measurement is negligible, we compare, in the third part, our solvent β_1 scale to a solute β_2^H scale (a linear transform of the $\text{p}K_{\text{BHX}}$ scale³ measured in CCl_4 , see below) in order to determine the degree of dissimilarity (or similarity) of the solute HB basicity scale and of the solvent HB acceptance scale.

In the following parts, the solvatomagnetic β_1 scale¹⁵ is compared to the solvocalorimetric⁷⁻⁹, solvatochromic¹⁷⁻²⁰, and solvatovibrational^{10,11,14} scales of solvent HB acceptance listed in Table 1. The comparison with the solvocalorimetric scales (numbered 4.1 and 4.2 in the list) is required to look for the thermodynamic status of β_1 . The differences between β_1 and the solvatochromic β -type values (numbered 6) are analyzed. Difficulties encountered with the trichloroacetic acid probe in the construction of the solvatovibrational $\Delta\nu(\text{CO})$ scale (numbered 5.3) are highlighted, and the replacement of CCl_3COOH by the less acidic $\text{C}_6\text{H}_5\text{COOH}$ is studied. Finally, the long-claimed status of the OH (OD) stretching infrared shift (numbered 5.1 and 5.2) as basicity parameter¹ is re-examined.

Results and Discussion

1. Definitions and methods

1.1. Hydrogen-bond basicity and affinity, and hydrogen-bond acceptance. According to IUPAC rules², hydrogen-bond basicity should be measured as an equilibrium constant K (as $\lg K$ or ΔG). So, only scales determined from equilibrium constants can be rigorously named HB basicity scales. If the enthalpic term of ΔG is used, the terminology should be “enthalpy of basicity”¹. However the current terminology for the enthalpy of basicity is “affinity” (for example proton affinity¹ and cation affinity¹). When the ability of a molecule to behave as a HBA is measured by a spectroscopic shift (UV-visible, NMR, or IR) or a retention in gas chromatography⁶, it is better to speak of hydrogen-bond acceptance or hydrogen-bond acceptor strength scale.

1.2. Solute and solvent scales. When the molecular property depending on HBA strength is measured on a series of HBAs against a reference HBD both diluted in an inert solvent, this series of results yields a *solute* scale. When the measurements are performed on the reference

HBD diluted in the pure HBAs as solvents, one obtains a *solvent* scale. The possible equivalence of solute and solvent scales is a matter of debate^{15,22}. It will be studied below.

1.3. Thermodynamic and spectroscopic scales. Because Lewis basicity is defined as the *thermodynamic* tendency of a substance to act as a Lewis base², and therefore HB basicity as the thermodynamic tendency of a substance to act as a HBA, HB acceptance scales are better determined from thermodynamic properties. The scales based on the enthalpy of HB formation to 4-fluorophenol^{7,8} and to pyrrole⁹ (Table 1) are thermodynamic, but they are well correlated to HB basicity scales only if an extrathermodynamic relationship between hydrogen-bond enthalpies and Gibbs energies exists¹. The existence of such an extrathermodynamic relationship depends on the type of bases¹ (for example oxygen bases, sulfur bases, nitrogen bases, etc) and is of little importance here since most HB acceptance scales of solvents in current use are spectroscopic. This arises from the ease with which spectroscopic measurements can be carried out. Spectroscopic scales are based on the change of a spectroscopic property (NMR, UV-visible, or IR) of the HBD probe upon hydrogen bonding to a series of HBAs, and on the assumption that this change is dominated by the strength of the hydrogen bond.

1.4. Comparison methods. When a HBD molecule Z-H is dissolved in a HBA solvent the solvent effect on a property P of ZH (solution enthalpy, IR, UV, or NMR spectral property) can be partitioned into two hypothetical terms: that due to the formation of a hydrogen-bonded complex Z-H...B and that due to nonspecific ZH/HBA molecular interactions. The latter term can be approximated by a model compound Z-Me which is as similar as possible in structure to Z-H save that it is incapable of hydrogen bonding donation. This similarity explains that plotting $P(\text{Z-H})$ against $P(\text{Z-Me})$ for the gas phase and (quasi) non-HBA and

(quasi)non-HBD solvents (e.g. perfluoroalkanes, alkanes, CCl₄, CS₂, and polychlorobenzenes) gives a reference line (comparison line) of eq 1:

$$(1) \quad P(\text{Z-H}) = a P(\text{Z-Me}) + b$$

with a slope and a determination coefficient r^2 close to unity.

HBA solvents (e.g. dimethyl sulfoxide, DMSO) are displaced (below or above according to the property P) from this comparison line because of the contribution of the hydrogen bond Z-H...B to the solvent effect on P . This contribution ΔP (HB) to the total solvent effect ΔP (total) is calculated, as shown in the figure 1, by eq 2:

$$(2) \quad \Delta P (\text{HB}) = [a P(\text{Z-Me}) + b] - P(\text{Z-H})$$

A HBA solvent scale denoted β_1 (the subscript 1 is generally given to solvent scales whereas 2 is for solute scales) can be created by setting ΔP (HB) = 0 for solvents obeying eq 1 and $\beta_1 = 1$ for the strong HBA solvent hexamethylphosphoric triamide (HMPT) that deviates from the comparison line by $\Delta P_{\text{HMPT}}(\text{HB})$. In this way, most β_1 values calculated by eq 3 ranges from 0 to 1:

$$(3) \quad \beta_1 = \Delta P (\text{HB}) / \Delta P_{\text{HMPT}}(\text{HB})$$

ΔP (HB) = 0 for all solvents obeying eq 1 implies that the property P of the HBD probe ZH is unable to reveal any HB acceptor character of these solvents. Most workers^{12,14,15,17,19} have generalized this observation and assumed $\beta_1 = 0$ for such solvents in the correlation analysis of solvent effects.

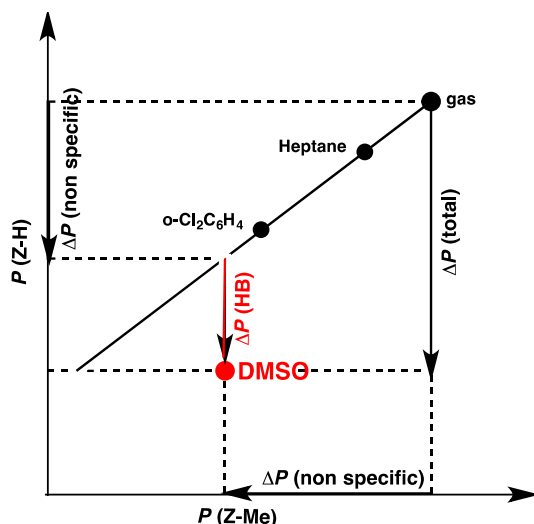


Figure 1. Illustration of comparison methods: solvocalorimetric (P : solution enthalpy), solvatochromic (P : UV-visible wavenumber), solvovibrational (P : IR wavenumber), and solvatomagnetic (P : chemical shift). Reference line equation: $P(\text{Z-H}) = a P(\text{Z-Me}) + b$. By comparing the properties P of the HBD probe ZH and of the non-HBD compound ZMe, the solvent effect of a HBA such as DMSO on the property P of the ZH probe, ΔP (total), is partitioned into a nonspecific part, ΔP (nonspecific), and a HB contribution, ΔP (HB), measuring the HBA strength of this solvent.

1.5. Solvocalorimetric comparison method. It must be understood that the “pure base calorimetric method” devised by Arnett et al.^{7,8} is nothing else than a solvocalorimetric comparison method with the assumption that the slope of the reference line is equal to 1. Indeed, these workers have measured the solution enthalpies of 4-fluorophenol, ΔH_s (FP), and of 4-fluoroanisole, ΔH_s (FA), both in the pure base and in the reference solvent CCl_4 . From these four solution enthalpies, they unravel the enthalpy of hydrogen bond formation to 4-fluorophenol, ΔH_f (OH), through eq (4):

$$(4) \quad \Delta H_f(\text{OH}) = [\Delta H_s(\text{FP}) - \Delta H_s(\text{FA})]_{\text{base}} - [\Delta H_s(\text{FP}) - \Delta H_s(\text{FA})]_{\text{CCl}_4}$$

The rearrangement of this equation gives eq (5):

$$(5) \quad \Delta H_f(\text{OH}) = [\Delta H_s(\text{FP})]_{\text{base}} - \{ \Delta H_s(\text{FA})_{\text{base}} + [\Delta H_s(\text{FP}) - \Delta H_s(\text{FA})]_{\text{CCl}_4} \}$$

In a plot of $\Delta H_s(\text{FP})$ against $\Delta H_s(\text{FA})$, $\Delta H_f(\text{OH})$ is nothing else than the displacement of a point representing the base from a reference line of slope unity passing through the point for CCl_4 with the co-ordinates $\Delta H_s(\text{FA})_{\text{CCl}_4}$ and $\Delta H_s(\text{FP})_{\text{CCl}_4}$ (see Figure 2A). In the Arnett solvent set, the magnitude of displacements varies from -4.9 kJ mol^{-1} for the weak HBA Cl_2SO to $-37.3 \text{ kJ mol}^{-1}$ for the strong HBA NEt_3 .

Later, Catalán et al. devised a so-called “pure-solvent method”⁹ using pyrrole as the reference HBD and *N*-methylpyrrole as a similar non-HBD model compound. They took into account the methylation effect using benzene and toluene. An appropriate combination of the solution enthalpies of these four compounds in the pure base, as well as of their vaporization enthalpies in order to anchor the scale to the gas phase, yields $\delta\Delta H^\circ_{\text{solv}}$, the solvent basicity. This combination yields non-zero $\delta\Delta H^\circ_{\text{solv}}$ values of 1.5, 1.8, 2.3, and 2.4 kJ mol^{-1} for cyclohexane, tetrachloromethane, trichloromethane, and carbon disulfide respectively, despite the fact that these solvents are generally recognized as non-HBA solvents. For comparison, the $\delta\Delta H^\circ_{\text{solv}}$ values for recognized HBA solvents range from 5.7 kJ mol^{-1} for benzene to 24.1 kJ mol^{-1} for NEt_3 . The data treatment in the “pure-solvent method” presents another difficulty, the necessity of *four* measurements of solution enthalpies for the determination of the HB acceptance of *one* solvent. Consequently, we have re-treated the calorimetric data of the pyrrole probe by the “solvatocalorimetric comparison method”. In a plot (figure 2B) of the solution enthalpy of pyrrole, $\Delta H_s(\text{pyrrole})$, against the solution enthalpy of *N*-methylpyrrole, $\Delta H_s(\text{N-methylpyrrole})$, the non- or very weak HBA solvents cyclohexane, tetrachloromethane, trichloromethane, and carbon disulfide draw a reference line of eq 6:

$$(6) \quad \Delta H_s(\text{pyrrole}) = 1.013 \Delta H_s(N\text{-methylpyrrole}) + 7.544$$

$$r^2 = 0.997 \quad s = 0.39 \text{ kJ mol}^{-1} \quad n = 4$$

where r^2 , s , and n are the determination coefficient, the standard error of the estimate, and the number of non-HBA solvents, respectively. The displacements of HBA solvents from this line yield the enthalpy of HB formation to pyrrole as eq 7:

$$(7) \quad \Delta H_f(\text{NH}) = \Delta H_s(\text{pyrrole}) - [1.013 \Delta H_s(N\text{-methylpyrrole}) + 7.544]$$

As expected, the solvocalorimetric $\Delta H_f(\text{NH})$ values are correlated to the “pure solvent method” values $\delta\Delta H_{\text{solv}}^\circ$ ($r^2 = 0.986$), but now the solvocalorimetric scale is anchored to recognized non or very weak HBAs and the determination of the HB acceptance of a new solvent requires the measurement of only *two* solution enthalpies.

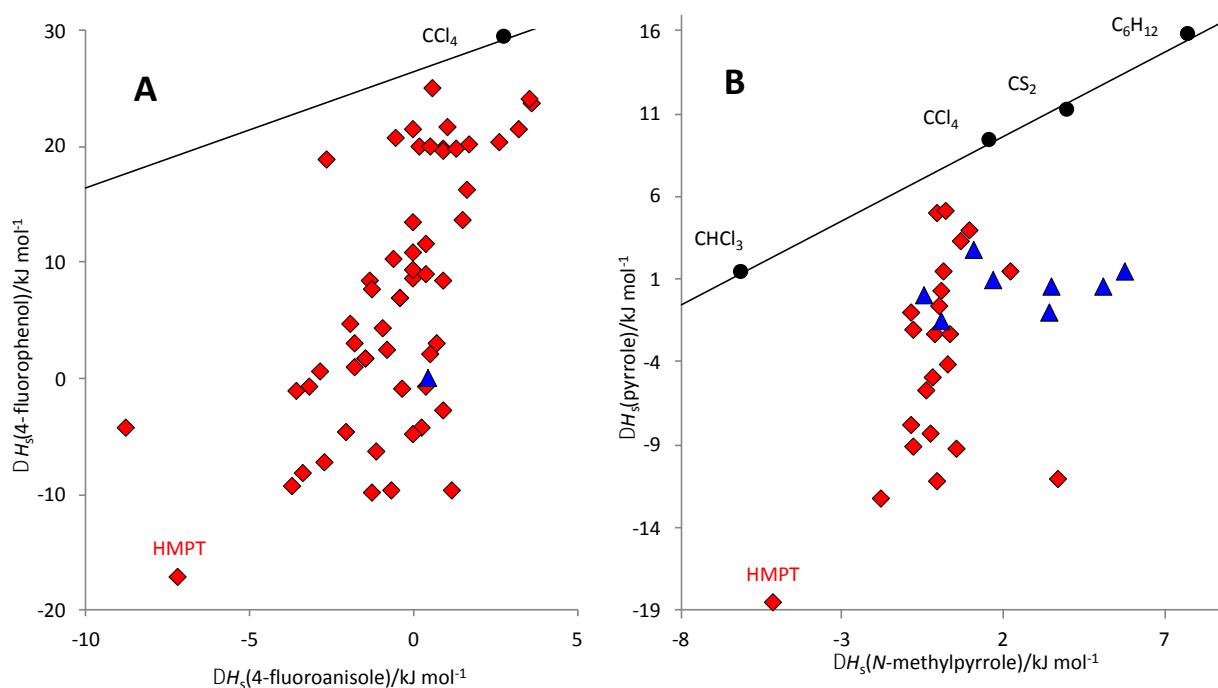


Figure 2. Solvocalorimetric comparison method. Black circles: non-HBA solvents fixing the reference line. Red diamonds: HBA solvents. Blue triangles: amphiprotic solvents. (A) Solution enthalpy of 4-fluorophenol

against the same quantity for 4-fluoroanisole (data from refs 7 and 8). (B) Solution enthalpy of pyrrole against the same quantity for *N*-methylpyrrole (data from ref 9).

1.6. Solvatovibrational comparison method. In this method, illustrated by Fig.3, Nicolet et al.¹⁴ plot the wavenumbers of the C=O stretching vibrations of the HB donor CCl₃COOH against those of its non-HBD model CCl₃COOMe for the gas phase and non-HBA solvents (perfluorohexane, perfluoro(*n*-tributylamine), alkanes, CCl₄, C₂Cl₄, CS₂, di- and tri-halogenobenzenes) in order to define a reference line of equation 8 demonstrating the similarity of nonspecific solvent effects:

$$(8) \quad \nu_{\text{CO}}(\text{CCl}_3\text{COOH}) = 1.1747 \nu_{\text{CO}}(\text{CCl}_3\text{COOMe}) - 298.6$$

$$r^2 = 0.9986 \quad s = 0.16 \text{ cm}^{-1} \quad n = 13$$

For HBA solvents B, the formation of the hydrogen bond CCl₃C(=O)OH...B results in a decrease in the C=O vibration wavenumber and causes the displacement of the points of these solvents from the reference line. These displacements $\Delta\nu(\text{CO})$ were calculated by equation 9:

$$(9) \quad \Delta\nu(\text{CO}) = [1.1747 \nu_{\text{CO}}(\text{CCl}_3\text{COOMe}) - 298.6] - \nu_{\text{CO}}(\text{CCl}_3\text{COOH})$$

They were claimed to reflect the solvent HBA strength; in the set studied in 1987, they ranged from 0.3 cm⁻¹ for chlorobenzene to 27.2 cm⁻¹ for trimethylphosphate.

In this work, we have extended the solvent set to 23 neat alcohols ROH. In spite that both type A and type B hydrogen bonds¹² are present in alcoholic solutions (scheme 2), it is possible to observe various carbonyl bands in the IR spectra of CCl₃COOH and CCl₃COOMe, thanks to small bandwidths and deconvolution of overlapping bands, and to attribute them to the various species shown in scheme 2. Only the carbonyl band of non-hydrogen-bonded

CCl_3COOMe (species 4), and the carbonyl band of $\text{CCl}_3\text{COOH}\dots\text{O(H)R}$ (type B hydrogen bond, species 1)) are used for the calculation by eq 9 of the hydrogen bond shift $\Delta\nu$ (CO).

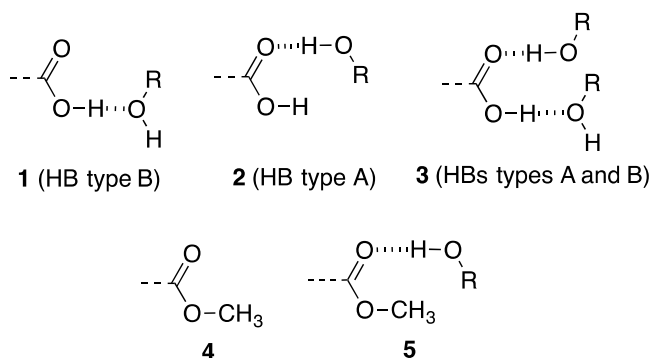
Because of proton-transfer reactions between CCl_3COOH and strongly basic solvents, we have turned in this work to a less acidic carboxylic acid, and studied the carbonyl vibration of the pair $\text{C}_6\text{H}_5\text{COOH}/\text{C}_6\text{H}_5\text{COOMe}$. The equation of the comparison line (obeyed by the gas phase, alkanes, CCl_4 , C_2Cl_4 , CS_2 , and dihalogenobenzenes) becomes:

$$(10) \quad \nu_{\text{CO}}(\text{C}_6\text{H}_5\text{COOH}) = 1.1116 \nu_{\text{CO}}(\text{C}_6\text{H}_5\text{COOMe}) - 178.7$$

$$r^2 = 0.9996 \quad s = 0.11\text{cm}^{-1} \quad n = 9$$

and the displacements $\Delta\nu'$ (CO) are calculated as:

$$(11) \quad \Delta\nu'(\text{CO}) = [1.1116 \nu_{\text{CO}}(\text{C}_6\text{H}_5\text{COOMe}) - 178.7] - \nu_{\text{CO}}(\text{C}_6\text{H}_5\text{COOH})$$



Scheme 2. Possible hydrogen bonding of neat alcohols (self-association not drawn for clarity) to carboxylic acids (species 1-3) and to the corresponding methyl esters (species 4 and 5) (the various importance of species 1-5 depends on R and on the carboxylic acid).

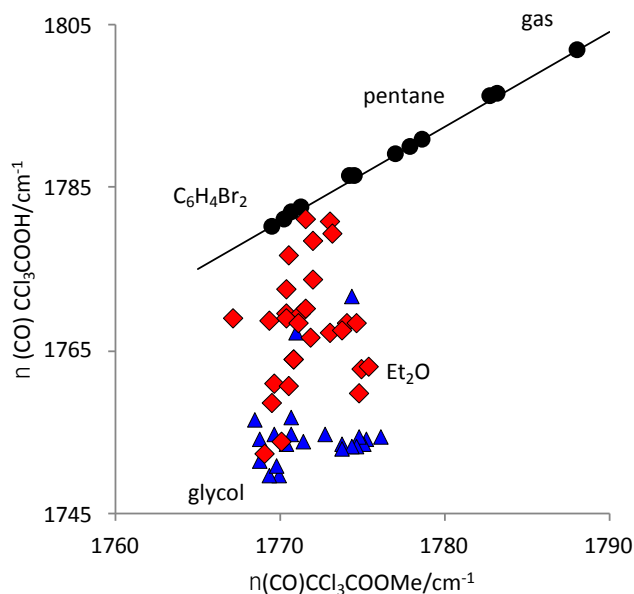


Figure 3. Solvatovibrational comparison method: plot of the carbonyl stretch of CCl_3COOH against the same property for CCl_3COOMe . Black circles: non-HBA solvents fixing the reference line. Red diamonds: HBA solvents. Blue triangles: amphiprotic solvents.

1.7. Solvatochromic comparison method. This method was proposed by Kamlet and Taft¹². It compares the wavenumbers of the $S_0 \rightarrow S_1$ electronic transition of 4-nitroaniline and 4-nitrophenol as HBD probes and of *N,N*-diethyl-4-nitroaniline and 4-nitroanisole as the non-HBD model compounds. The hydrogen-bond shifts of 4-nitroaniline, $\Delta\nu(\text{NH}_2\text{-NEt}_2)$, and of 4-nitrophenol, $\Delta\nu(\text{OH-OMe})$, were isolated, in the way outlined in Figure 1 (where P is the wavenumber of the $S_0 \rightarrow S_1$ transition), for 35 HBA solvents.

The method was later improved by Nicolet and Laurence¹³ and applied to a more comprehensive set of 190 HBA solvents^{1,18}. They choose *N,N*-dimethyl-4-nitroaniline as a better non-HBA model for 4-nitroaniline and use the gas phase and a much larger set of non- or very weak HBA solvents in order to better fix the reference lines of eqs 12 and 13:

$$(12) \quad \nu(\text{NH}_2) = 0.9752 \nu(\text{NMe}_2) + 3728$$

$$r^2 = 0.991 \quad s = 96 \text{ cm}^{-1} \quad n = 32$$

$$(13) \quad \nu(\text{OH}) = 1.0381 \nu(\text{OMe}) - 384$$

$$r^2 = 0.992 \quad s = 77 \text{ cm}^{-1} \quad n = 32$$

where $\nu(\text{NH}_2)$, $\nu(\text{NMe}_2)$, $\nu(\text{OH})$, and $\nu(\text{OMe})$ stand for the wavenumber in cm^{-1} of the $S_0 \rightarrow S_1$ electronic transition of 4-nitroaniline, *N,N*-dimethyl-4-nitroaniline, 4-nitrophenol, and 4-nitroanisole, respectively, in the various solvents. The $\Delta\nu$ shifts attributable to hydrogen bonding to the HBA solvents are extracted from the total solvatochromic shift by means of eqs 14 and 15:

$$(14) \quad \Delta\nu(\text{NH}_2\text{-NMe}_2) = [0.9752 \nu(\text{NMe}_2) + 3278] - \nu(\text{NH}_2)$$

$$(15) \quad \Delta\nu(\text{OH-OMe}) = [1.0381 \nu(\text{OMe}) - 384] - \nu(\text{OH})$$

$\Delta\nu(\text{NH}_2\text{-NMe}_2)$ and $\Delta\nu(\text{OH-OMe})$ values can be scaled in a range from 0 (solvents obeying eqs 12 or 13) to 1 by dividing by the shift of HMPT, 2760 cm^{-1} for 4-nitroaniline and 2030 cm^{-1} for 4-nitrophenol. This yields the solvatochromic parameters $\beta_1(\text{NH}_2)$ and $\beta_1(\text{OH})$ ^{18,19}:

$$(16) \quad \beta_1(\text{NH}_2) = \Delta\nu(\text{NH}_2\text{-NMe}_2) / 2760$$

$$(17) \quad \beta_1(\text{OH}) = \Delta\nu(\text{OH-OMe}) / 2030$$

1.8. Solvatomagnetic comparison method. The ¹⁹F chemical shift of 4-fluorophenol is quite sensitive to hydrogen bonding of the OH group to HBAs. This method exploits this sensitivity

for characterizing the HBA property of solvents¹⁵. The hydrogen bonding contribution to the ¹⁹F chemical shift of the 4-fluorophenol HBD probe is isolated from non-specific solvent effects thanks to 4-fluoroanisole (non-HBD but similar to 4-fluorophenol in non-HBA solvents) as illustrated in Fig 1, where P is the ¹⁹F chemical shift, ZH is 4-fluorophenol and ZMe 4-fluoroanisole. Eight non- or very weak HBA solvents draw a reference line of eq 16:

$$(16) \quad -\delta(^{19}\text{F})_{\text{OH}} = 1.009 [-\delta(^{19}\text{F})_{\text{OMe}}] - 1.257$$

$$r^2 = 0.9992 \quad s = 0.025 \text{ ppm} \quad n = 8$$

where $\delta(^{19}\text{F})_{\text{OH}}$ and $\delta(^{19}\text{F})_{\text{OMe}}$ stand for the fluorine chemical shifts of 4-fluorophenol and 4-fluoroanisole, respectively. The contribution $\Delta\delta$ of the hydrogen bond to the chemical shift of 4-fluorophenol can be calculated by eq 17:

$$(17) \quad \Delta\delta = [-\delta(^{19}\text{F})_{\text{OH}}] - \{1.009 [-\delta(^{19}\text{F})_{\text{OMe}}] - 1.257\}$$

The solvatomagnetic β_1 values can then be calculated by eq 18 setting $\beta_1 = 0$ for solvents such as alkanes obeying eq 16 and $\beta_1 = 1$ for HMPT that deviates from the reference line by 3.041 ppm:

$$(18) \quad \beta_1 = \Delta\delta / 3.041$$

1.9. Infrared shift $\Delta\nu(\text{ZH})$ scales. The Z-H stretching infrared wavenumber of HBDs is significantly lowered upon hydrogen bonding to HBAs, and this shift increases with the HB strength¹. Therefore a number of workers (for a review see ref¹⁹) have suggested that the $\nu(\text{ZH})$ shifts can be used as a spectroscopic measurement of the HBA strength of solvents. For

example, Kagya et al. have measured the wavenumbers of the O-D stretching of methan[²H]ol in 89 HBA solvents¹⁰. Taking benzene as the reference solvent they defined a $\Delta\nu$ (OD) scale as:

$$(19) \quad \Delta\nu(\text{OD}) = \nu_{\text{OD}}(\text{benzene}) - \nu_{\text{OD}}(\text{HBA solvent})$$

2. Extension of the β_1 scale to new solvents and organization of results in a database

We have extended the ¹⁹F measurements and the consecutive β_1 values to 46 new HBA solvents of which 8 imidazolium-based ionic liquids and the following green solvents: limonene, α -pinene, ethyl lactate, γ -valerolactone, dihydrolevoglucosenone (cyreneTM), and 2-methyltetrahydrofuran. Addition of the 113 β_1 values determined in previous works^{15,21} yield 159 primary values (β_1 values based directly on ¹⁹F NMR measurements are designated as primary).

Before our discovery of the solvatomagnetic comparison method, we argued for the use of an improved solvatochromic comparison method to define solvatochromic $\beta_1(\text{OH})$ and $\beta_1(\text{NH}_2)$ values¹³, on the condition to apply this method only to the 4-nitrophenol/4-nitroanisole *or* (and not *and*) 4-nitroaniline/4-nitro-*N,N*-dimethylaniline (and not 4-nitro-*N,N*-diethylaniline)²³. In a thesis¹⁸, 190 solvatochromic hydrogen-bonding shifts for each pair [$\Delta\nu(\text{OH-OMe})$ and $\Delta\nu(\text{NH}_2\text{-NMe}_2)$ defined by eqs 14 and 15 above] were obtained with this improved method. We then explained, from new experimental and theoretical studies¹⁵, that the 4-nitroaniline/4-nitro-*N,N*-dimethylaniline pair should be discarded, and that the 4-nitrophenol/4-nitroanisole should not be used for amphiprotic solvents¹⁵. We concluded¹⁵ that this last pair could however be useful for the determination of secondary β_1 values for *non*-amphiprotic solvents not yet measured by the solvatomagnetic comparison method. Indeed, we now find a good correlation between primary β_1 values and $\Delta\nu(\text{OH-OMe})$:

$$(20) \quad \beta_1 = 0.459 \Delta\nu(\text{OH-OMe}) + 0.026$$

For 30 non-amphiprotic HBA solvents, the determination coefficient r^2 is equal to 0.978 and the standard deviation of the β_1 estimate is 0.032 (to be compared to a β_1 values range from 0 to 1). The quality of this estimation allows then to calculate secondary β_1 values from $\Delta\nu(\text{OH-OMe})$ and eq 20 for 80 additional non-amphiprotic HBA solvents.

We have now at hand a comprehensive set of 239 β_1 values that are reported in Table 2. The HBAs are divided into chemical families (e.g. pyridines, ethers, ketones, nitriles, etc.) and arranged in order of increasing β_1 values within each family. In the Table S1 of the Supporting Information we have also added:

- β_2^H values of a solute HB basicity scale. The subscript 2 and the superscript H indicate that this scale is specific to the solute and the hydrogen bond, respectively. They are calculated from the $\text{p}K_{\text{BHX}}$ scale³ (defined from the hydrogen bond complexation constants of 4-fluorophenol with bases in CCl_4) by the Abraham procedure⁴ as follows:

$$(21) \quad \beta_2^H = (\text{p}K_{\text{BHX}} + 1.1)/4.70$$

Eq 21 allows to give to the scale the origin $\beta_2^H = 0$ for non hydrogen-bonding molecules ($\text{p}K_{\text{BHX}} = -1.1$ according to Abraham⁴) and the format $\beta_2^H = 1$ for HMPT ($\text{p}K_{\text{BHX}} = 3.60$)³. The reader is referred to the Abraham work⁴ for deeper explanations.

- SB values of the Catalán solvent basicity scale²⁰. They were given the origin $SB = 0$ for the gas phase and $SB = 1$ for tetramethylguanidine.

- the historical Kamlet-Taft β values. These values have unfortunately too much changed along the years since the first paper in 1976¹². We have retained the values contained in the “comprehensive collection of the solvatochromic parameters” published by Kamlet and al. in 1983¹⁶.

The success of the pK_{BHX} database in medicinal chemistry³, and the recent published use of the empirical solvent parameters database²¹ for directed discovery of greener cosolvents²⁴, encourages us to organize the above scales in a database. The spreadsheet data of Table S1 can be easily transformed into a searchable numerical database through various softwares. The 2-propanol entry of such a database is displayed in Figure 4. The solvent is identified by means of four fields: 2D structure, name, empirical formula, and molecular weight. Four other fields are devoted to the parameters β_1 , β_2^H , SB , and β . We do not intend here to provide an exhaustive database for all proposed solvent basicity scales. However, since the addition of a new column in the spreadsheet generates a new field in the entries, any additional scale can be easily added.

Table 2. Solvatomagnetic β_1 scale of hydrogen-bond acceptance for 239 HBA solvents

| Solvent | β_1 | Solvent | β_1 |
|--|-------------|------------------------------------|-----------|
| Alkanes | 0 | Esters | |
| Alkenes | | 4,5-dichloro-1,3-dioxolan-2-one | 0.21 |
| dicyclopentadiene | 0.10 | ethyl trichloroacetate | 0.31 |
| cyclohexene | 0.14 | methyl trifluoroacetate | 0.32 |
| α -pinene | 0.14 | methyl trichloroacetate | 0.33 |
| limonene | 0.15 | ethyl propynoate, ethyl propiolate | 0.36 |
| 1,4-cyclohexadiene | 0.16 | dimethyl carbonate | 0.40 |
| 1,5-cyclooctadiene | 0.24 | propylene carbonate | 0.40 |
| trans,trans,cis,1,5,9-cyclodecatriene | 0.26 | methyl formate | 0.41 |
| Aromatic π bases | | 1,2,3-triacetoxypropane, triacetin | 0.41 |

| | | | |
|--|------|---|------|
| 1,2,4-trichlorobenzene | 0 | methyl benzoate | 0.42 |
| 1,2,-dichlorobenzene | 0 | ethyl chloroacetate | 0.42 |
| (trifluoromethyl)benzene | 0.06 | methyl chloroacetate | 0.44 |
| chlorobenzene | 0.06 | diethyl carbonate | 0.45 |
| thiophene | 0.07 | γ -butyrolactone | 0.46 |
| bromobenzene | 0.08 | ethyl benzoate | 0.47 |
| iodobenzene | 0.09 | ethyl formate | 0.47 |
| fluorobenzene | 0.11 | methyl propanoate | 0.48 |
| diphenylmethane | 0.11 | triolein, glycerol trioleate | 0.50 |
| 1-methylnaphtalene | 0.12 | methyl hexanoate, methyl caproate | 0.50 |
| 2,6-di- <i>tert</i> -butylpyridine | 0.13 | methyl pentanoate, methyl valerate | 0.50 |
| benzene | 0.14 | methyl butanoate | 0.50 |
| methylbenzene, toluene | 0.15 | methyl acetate | 0.51 |
| 1,4-dimethylbenzene, p-xylene | 0.17 | methyl octanoate, methyl caprylate | 0.52 |
| 1,3,5-trimethylbenzene, mesitylene | 0.19 | ethyl acetate | 0.52 |
| 1,2,3,4-tetramethylbenzene, prehnitene | 0.24 | γ -valerolactone | 0.52 |
| Halogenoalkanes | | δ -valerolactone | 0.54 |
| 1-bromopropane | 0.11 | methyl(9Z,12Z)-octadeca-9,12-dienoate, methyl linoleate | 0.56 |
| bromoethane | 0.12 | <i>n</i> -butyl acetate | 0.58 |
| 1,4-dichlorobutane | 0.13 | ethyl lactate | 0.58 |
| iodoethane | 0.13 | <i>n</i> -propyl acetate | 0.60 |
| 1-bromobutane | 0.14 | methyl decanoate, methyl caprate | 0.61 |
| 1,10-dichlorodecane | 0.15 | methyl cis-9-octadecenoate, methyl oleate | 0.62 |
| 1-chlorobutane | 0.15 | Carboxylic acids | |
| 1-chloropropane | 0.18 | formic acid | 0.20 |
| chlorocyclohexane | 0.24 | acetic acid | 0.38 |
| Alcohols, water, phenol | | propanoic acid | 0.45 |
| perfluoro- <i>tert</i> -butanol | 0.09 | Amides, ureas | |
| 3-methylphenol | 0.10 | formamide | 0.45 |
| 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol | 0.13 | <i>N</i> -methylformanilide | 0.62 |
| 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP | 0.16 | <i>N</i> -methylformamide | 0.63 |
| 2,2,2-trichloroethanol | 0.22 | <i>N,N</i> -dimethylformamide | 0.69 |
| 2,2,2-trifluoroethanol | 0.23 | 1-formylpiperidine | 0.71 |

| | | | |
|---|-------------|--|-------------|
| 2,2,3,3,3-pentafluoro-1-propanol | 0.25 | pyrrolidin-2-one | 0.72 |
| 1,1,1-trifluoro-2-propanol | 0.29 | <i>N</i> -methylacetamide | 0.74 |
| water | 0.37 | <i>N,N</i> -diethylformamide | 0.75 |
| propane-1,2,3-triol, glycerol, | 0.38 | <i>N,N</i> -dimethylacetamide | 0.75 |
| 2-propyn-1-ol, propargyl alcohol | 0.38 | <i>N,N</i> -dimethylpropionamide | 0.76 |
| 2-chloroethanol | 0.39 | 1-methylpyrrolidin-2-one | 0.76 |
| 2-bromoethanol | 0.39 | 1,1,3,3-tetramethylurea | 0.76 |
| ethane-1,2-diol, glycol | 0.47 | 1,1,3,3-tetraethylurea | 0.77 |
| 2-phenoxyethanol | 0.48 | 1-ethylpyrrolidin-2-one | 0.78 |
| propane-1,3-diol | 0.48 | <i>N</i> -methylpropionamide | 0.79 |
| benzyl alcohol | 0.50 | <i>N</i> -ethylacetamide | 0.79 |
| 2-phenylethanol, phenethyl alcohol | 0.53 | <i>N,N</i> -diethylacetamide | 0.81 |
| butane-1,3-diol | 0.53 | 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)- pyrimidinone | 0.81 |
| propane-1,2-diol | 0.53 | Nitroalkanes, nitroarene | |
| butane-1,4-diol | 0.53 | nitroethane | 0.22 |
| methanol | 0.54 | nitromethane | 0.23 |
| allyl alcohol | 0.55 | nitrobenzene | 0.26 |
| 2-(2-hydroxyethoxy)ethanol, diethylene glycol | 0.55 | 2-nitropropane | 0.28 |
| butane-2,3-diol | 0.56 | 2-methyl-2-nitropropane | 0.32 |
| pentane-1,5-diol | 0.56 | Phosphorous compounds | |
| 1-phenylethanol | 0.58 | phosphoryl chloride | 0.33 |
| butane-1,2-diol | 0.58 | diethylchlorophosphate | 0.61 |
| triethylene glycol | 0.59 | trimethyl phosphate | 0.65 |
| ethanol | 0.62 | triethyl phosphate | 0.71 |
| 2-methoxyethanol | 0.63 | tri- <i>n</i> -butyl phosphate | 0.75 |
| 1-propanol | 0.65 | hexamethylphosphoric triamide, HMPT | 1 |
| 2-methyl-1-propanol, <i>iso</i> -butanol | 0.66 | Sulfinyl and sulfonyl compounds | |
| 1-butanol | 0.67 | dimethyl sulfate | 0.23 |
| 2-propanol | 0.68 | 1,3,2-dioxathiolan 2-oxide, ethylene sulfite | 0.32 |
| 1-pentanol | 0.70 | dimethyl sulfite | 0.34 |
| 2-ethoxyethanol | 0.70 | tetrahydrothiophene 1,1-dioxide, sulfolane | 0.34 |
| 2-methyl-2-butanol, <i>tert</i> -amyl alcohol | 0.71 | 3-methylsulfolane | 0.40 |
| cyclopentanol | 0.71 | diethyl sulfite | 0.45 |

| | | | |
|---|-------------|--|-------------|
| 2-butanol, <i>sec</i> -butanol | 0.71 | dimethyl sulfoxide, DMSO | 0.71 |
| 1-hexanol | 0.72 | tetramethylene sulfoxide | 0.74 |
| 2-(<i>n</i> -butoxy)ethanol | 0.72 | Nitriles | |
| 2-methyl-2-propanol, <i>tert</i> -butanol | 0.73 | trichloroacetonitrile | 0.24 |
| cyclohexanol | 0.73 | chloroacetonitrile | 0.25 |
| 1-octanol | 0.74 | phenylacetonitrile | 0.33 |
| 1-heptanol | 0.75 | benzonitrile | 0.34 |
| 1-nonanol | 0.75 | acetonitrile | 0.37 |
| 1-decanol | 0.76 | propanenitrile | 0.40 |
| Ethers | | butanenitrile | 0.42 |
| furan | 0.11 | trimethylacetonitrile, pivalonitrile | 0.45 |
| diphenyl ether | 0.17 | pentanenitrile, valeronitrile | 0.46 |
| methoxybenzene, anisole | 0.23 | hexanenitrile | 0.47 |
| bis-(2-chloroethyl)ether | 0.32 | <i>N,N</i> -dimethylcyanamide | 0.49 |
| ethoxybenzene, phenetole | 0.39 | dodecanitrile | 0.55 |
| 1,4-dioxane | 0.44 | undecanitrile | 0.55 |
| dibenzyl ether | 0.47 | Pyridines | |
| 1,3-dioxolane | 0.47 | 2,6-difluoropyridine | 0.37 |
| dimethoxymethane | 0.48 | 2-fluoropyridine | 0.49 |
| tetrahydropyran | 0.57 | 2-bromopyridine | 0.54 |
| tetrahydrofuran | 0.58 | 2-chloropyridine | 0.55 |
| diethyl ether | 0.59 | 3-bromopyridine | 0.61 |
| 1,2-dimethoxyethane, monoglyme | 0.63 | pyridine | 0.69 |
| diethylene glycol dimethyl ether, diglyme | 0.63 | 4-methylpyridine, 4-picoline | 0.76 |
| cyclopentyl methyl ether | 0.63 | 3,4-dimethylpyridine | 0.82 |
| 2,5-dimethyltetrahydrofuran (cis+trans) | 0.64 | 2,4,6-trimethylpyridine | 0.82 |
| di- <i>n</i> -butyl ether | 0.64 | Amines | |
| di- <i>iso</i> -propyl ether | 0.65 | <i>N</i> -methylaniline | 0.43 |
| 2-methyltetrahydrofuran | 0.66 | aniline | 0.43 |
| <i>n</i> -butyl methyl ether | 0.66 | <i>N</i> -(<i>tert</i> -butyl)benzylamine | 0.87 |
| <i>tert</i> -butyl methyl ether | 0.67 | <i>N</i> -benzylmethylamine | 0.88 |
| 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane, eucalyptol | 0.68 | diisopropylamine | 0.90 |
| di- <i>tert</i> -butyl ether | 0.69 | diallylamine | 0.90 |

| | | | |
|--|-------------|---|-------------|
| 2,2,5,5-tetramethyltetrahydrofuran | 0.69 | triethylamine | 0.93 |
| Thioethers | | tri- <i>n</i> -butylamine | 0.93 |
| trimethylene sulfide | 0.34 | <i>N,N</i> -dimethylcyclohexylamine | 0.98 |
| diethyl sulfide | 0.34 | allylamine | 1.02 |
| dimethyl sulfide | 0.34 | diethylamine | 1.05 |
| tetrahydrothiophene | 0.37 | <i>N</i> -methylcyclohexylamine | 1.07 |
| pentamethylene sulfide | 0.38 | <i>tert</i> -butylamine | 1.08 |
| di- <i>iso</i> -propyl sulfide | 0.42 | piperidine | 1.12 |
| di- <i>n</i> -butyl sulfide | 0.43 | Ionic liquids | |
| Ketones | | 1-butyl-3-methylimidazolium hexafluorophosphate | 0.27 |
| hexachloroacetone | 0.17 | 1-butyl-3-methylimidazolium tetrafluoroborate | 0.36 |
| 1,1,1-trichloroacetone | 0.29 | 1-butyl-3-methylimidazolium iodide | 0.44 |
| dihydrolevoglucosenone, cyrene | 0.40 | 1-butyl-3-methylimidazolium thiocyanate | 0.64 |
| acetophenone | 0.48 | 1-butyl-3-methylimidazolium nitrate | 0.67 |
| acetone | 0.49 | 1-methyl-3-octylimidazolium chloride | 0.77 |
| 2,2,4,4-tetramethyl-3-pentanone, di- <i>tert</i> -butyl ketone | 0.53 | 1-hexyl-3-methylimidazolium chloride | 0.79 |
| cyclopentanone | 0.53 | 1-butyl-3-methylimidazolium acetate | 1.30 |
| 2-butanone, ethyl methyl ketone | 0.53 | | |
| 3-pentanone, diethyl ketone | 0.55 | | |
| cyclohexanone | 0.55 | | |
| 4-methyl-2-pentanone, iso-butyl methyl ketone | 0.58 | | |

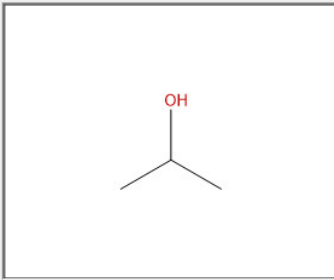
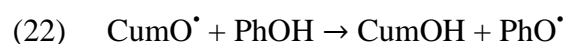
| Structure | | Solvent | |
|---|-------|---------------------------------|-------------|
|  | | 2-propanol | |
| | | Formula | MolWeight |
| | | C ₃ H ₈ O | 60.096 |
| β | SB | β_2^H | $\beta_1 =$ |
| 0.95 | 0.830 | 0.46 | 0.68 |

Figure 4. Screenshot of the β_1 database showing the 2-propanol entry. The order $\beta_1(\text{solvent}) > \beta_2^H(\text{solute})$ comes from the structuredness of the liquid alcohol, while the too high solvatochromic Kamlet-Taft β value results from shortcomings of the solvatochromic probe (vide infra).

The solute HBD/solvent HBA interaction is one of the four interactions that determine the solvent effect on reactivity (the other ones being the dispersion-induction interaction, the electrostatic interaction, and the solute HBA/solvent HBD interaction measured by parameters DI , ES , α_1 , respectively²¹). However, there are kinetic solvent effects depending almost only on the solvent HB acceptance. Two of them can illustrate the reliability of the β_1 scale: the rate constant k_1 for abstraction of the phenolic hydrogen atom from phenol by the cumyloxyl radical (CumO^\bullet) (reaction 22)²⁵ and the rate constant k_2 for the decomposition of 3-methyl-1-*p*-tolyltriazeno by benzoic acid (reaction 23)²⁶:



The satisfactory correlation between $\lg k_1$ and β_1 ($r^2 = 0.867$, $n = 14$ solvents, Figure 5) indicates that the kinetic solvent effect is determined by the strength of the hydrogen bond

between the HBD (PhOH) and the HBA solvent. Interestingly, the β_1 values of the amphiprotic solvents 2,2,2-trifluoroethanol (TFE), acetic acid, *tert*-butanol, and *tert*-amyl alcohol fit well the rates. The rate k_2 of reaction 23 is also well correlated with β_1 ($r^2 = 0.925$, $n = 12$ HBA solvents, Figure 6). Here rate decreases are attributable to increase in the strength of the hydrogen bond between PhCOOH and the HBA solvent.

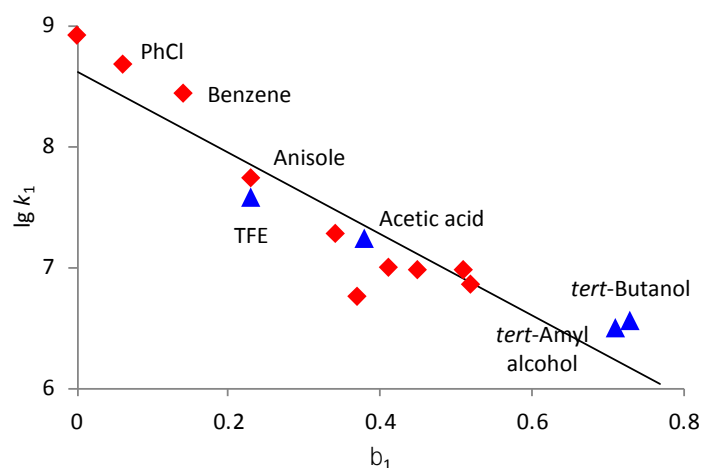


Figure 5. Correlation between the rate ($\text{L mol}^{-1} \text{s}^{-1}$) of reaction 22 and the HBA ability β_1 of solvents. Blue triangles represent amphiprotic solvents.

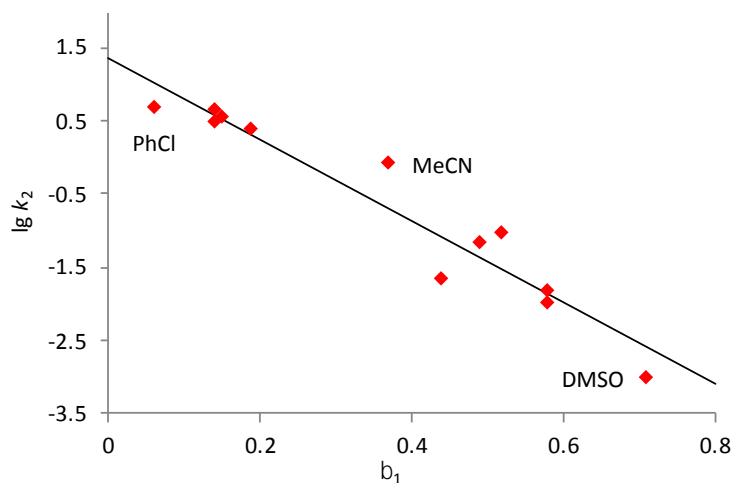


Figure 6. Correlation between the rate ($\text{L mol}^{-1} \text{min}^{-1}$) of reaction 23 and the HBA ability β_1 of solvents.

3. Comparison of the solvatomagnetic β_1 solvent scale and of the β_2^H solute scale

There are 152 HBAs in the database for which we have values both for the solute β_2^H scale and for the solvent β_1 scale. The regression equation against β_2^H is:

$$(24) \quad \beta_1 = 1.119 \beta_2^H + 0.006$$

$$r^2 = 0.806$$

$$s = 0.109$$

$$n = 152$$

There is a trivial statistically significant correlation between the two scales. However, only 80.6% ($100 r^2$) of the β_1 variance is explained by β_2^H . Moreover, the differences ($\beta_1 - \beta_2^H$) are not randomly distributed. On the graphical comparison of the two scales (Figure 7), all amines (red diamonds), all aliphatic non-cyclic ethers (green diamonds), and all aliphatic alcohols (blue triangles) stand above the line of equation $\beta_1 = \beta_2^H$. The differences ($\beta_1 - \beta_2^H$) are often greater than two times the standard deviation s . For amines, they range from +0.24 (di-*iso*-propylamine) to +0.38 (piperidine). For aliphatic ethers, they are as large as +0.30 and +0.22 for di-*tert*-butyl and di-*n*-butyl ether, respectively. For alcohols, the difference amounts to +0.22 and +0.28 for 1-butanol and 1-octanol, respectively.

For amines and ethers, a possible explanation of differences comes from the entropic contribution to β_2^H ($\beta_2^H \propto \text{p}K_{\text{BHX}} \propto \Delta G = \Delta H - T\Delta S$), whereas β_1 depends mainly on the enthalpy of 4-fluorophenol basicity (vide infra). It was found²⁷ that amines and ethers have higher entropies of 4-fluorophenol basicity than other families: on the mole fraction scale $-56 \text{ J K}^{-1} \text{ mol}^{-1}$ (average for 84 amines) and $-40 \text{ J K}^{-1} \text{ mol}^{-1}$ (average for 17 ethers), but between $-17 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-28 \text{ J K}^{-1} \text{ mol}^{-1}$ for other families. Therefore, the positive difference ($\beta_1 - \beta_2^H$) is more significant for amines and ethers than for other HBAs.

For alcohols, the differences ($\beta_1 - \beta_2^H$) are generally explained by higher β_1 values, because their self-association in the liquid state increases the HB acceptor character of oxygen

atoms, by virtue of the σ -bond cooperativity effect along the (mainly) linear chains of the self-association²⁸. On the contrary, in the liquid state formamide self-associates mainly as cyclic dimers wherein the still free oxygen lone pair has reduced electron density compared to free formamide in diluted CCl_4 solution¹⁵. Consequently, the β_1 formamide value (0.45) is now lower than the corresponding β_2^H one (0.61).

If all self-associated solvents, ethers, and amines are excluded from the sample of 152 HBAs, the regression equation against β_2^H becomes:

$$(25) \quad \beta_1 = 0.979 \beta_2^H + 0.019$$
$$r^2 = 0.909 \quad s = 0.067 \quad n = 97$$

Because of a still large s value, the prediction of unknown β_1 values (for other solvents than self-associated ones, ethers, and amines) from the more comprehensive $\text{p}K_{\text{BHX}} (\propto \beta_2^H)$ database remains a hazardous procedure. However, for this limited set of 97 HBA solvents 90.9% of the variance of β_1 is explained by β_2^H , the intrinsic HB basicity of the molecule. This correlation allows to look for structure-basicity relationships within families of bases pertaining to the limited set, since structural properties of isolated molecules can throw some light on the bulk behavior. As structural parameters we have used Hammett substituent constants σ_m and σ_p and Taft constants σ_F (measuring the field-inductive effect) and σ_R (measuring the resonance effect)(see ref ²⁹ for a review of Hammett-Taft substituent constants). Illustrative results are in Table 3 and Figure 8.

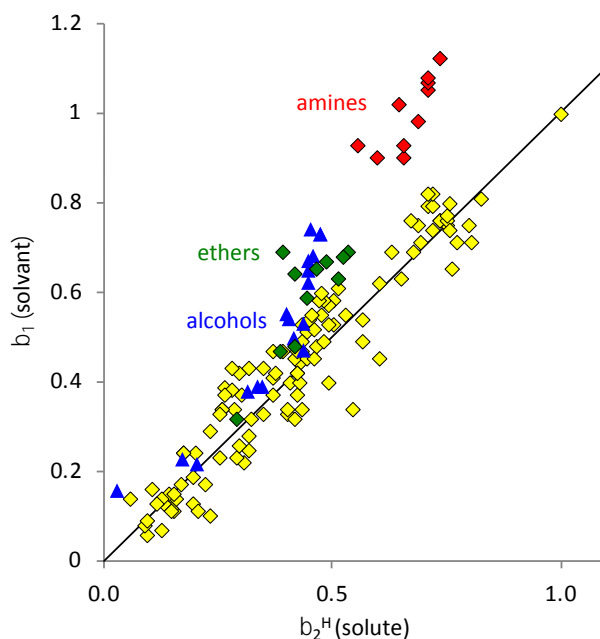


Figure 7. Comparison of the solvent β_1 scale and of the solute β_2^H scale. The line corresponds to $\beta_1 = \beta_2^H$. Three families of HBAs stand systematically above the line: amines (red diamonds), aliphatic ethers (green diamonds), and alcohols (blue triangles). Other HBA families (yellow diamonds) stand randomly near the line.

Table 3. Relationships between the HB acceptance of solvents β_1 and Hammett-Taft substituent constants for the families of substituted pyridines, π bases, and ketones.

| Family | Equation | β_1 unsubstituted | r^2 | n |
|--|--|-------------------------|-------|-----|
| <i>o</i> -XC ₅ H ₄ N | $\beta_1 = -0.406 \sigma_F + 0.716$ | 0.69 | 0.931 | 7 |
| <i>m,p</i> -XC ₅ H ₄ N | $\beta_1 = -0.309 \sigma_{m,p} + 0.718$ | 0.69 | 0.926 | 4 |
| X _n C ₆ H _{6-n} | $\beta_1 = -0.216 \sigma_F - 0.256 \sigma_R + 0.137$ | 0.14 | 0.950 | 9 |
| XCOMe | $\beta_1 = -0.513 \sigma_F - 0.520 \sigma_R^+ + 0.463$ | – | 0.946 | 9 |

All these correlations are good ($0.90 < r^2 < 0.95$). It is noteworthy that the intercepts of equations are close to the experimental β_1 value of the unsubstituted base (pyridine and benzene). It is interesting that the relationship for substituted benzenes predicts β_1 values for fluorobenzene, chlorobenzene, bromobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene in excellent agreement with experimental values (between parentheses):

0.11(0.11), 0.08(0.06), 0.08(0.08), 0.03(0), and $-0.02(0)$, respectively. So, the solvatomagnetic comparison method is able to measure fairly well the weak basicity of monohalogenobenzenes and the situation of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene experimentally found on the comparison line agrees with their very weak and zero calculated β_1 values, respectively.

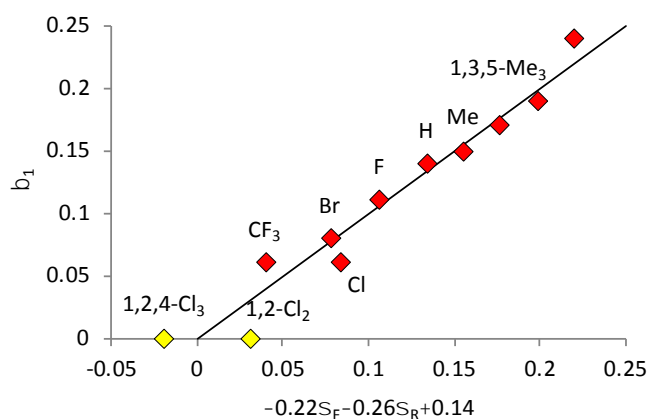


Figure 8. Relationship between the β_1 values of substituted benzenes $C_6H_{6-n}X_n$ and the substituent constants σ_F and σ_R of substituents X predicting (yellow diamonds) a quasi-zero value for 1,2-dichlorobenzene and a negative (therefore zero) value for 1,2,4-trichlorobenzene.

4. Comparison of the solvatomagnetic β_1 scale to thermodynamic affinity scales

The regression equation of β_1 against the Arnett 4-fluorophenol solvent affinity scale ΔH_f (OH)^{7,8}(see eq 5 above) measured by calorimetry is:

$$(26) \quad \beta_1 = 0.0246 \Delta H_f(\text{OH}) - 0.022$$

$$r^2 = 0.966$$

$$s = 0.045$$

$$n = 46$$

There is a large variety of oxygen, nitrogen, π carbon, sulfur, chlorine, and bromine bases in the comparison, the deviations are randomly distributed (i.e. they are not related to a type of base), and 96.6% of the β_1 variance are explained by the thermodynamic scale (and vice-versa) (Figure 9). Interestingly, the self-associated amphiprotic solvent *N*-methylformamide obeys well eq (26). This gives a thermodynamic (enthalpic) status to the spectroscopic β_1 scale. Also the two scales support themselves as excellent candidates to a reliable HB acceptance scale of solvents, and the two methods as reliable ones for the determination of the HB acceptance of new solvents.

The enthalpic status of β_1 is confirmed by the rather good correlation of β_1 with the pyrrole solvent affinity scale ΔH_f (NH) deduced from Catalán calorimetric measurements⁹:

$$(27) \quad \beta_1 = 0.0467 \Delta H_f (\text{NH}) - 0.044$$

$$r^2 = 0.923 \quad s = 0.071 \quad n = 27$$

The sample of bases is less numerous and less varied (only oxygen, nitrogen, and π carbon bases) than in eq (26), but has the advantage to contain 7 amphiprotic solvents (water, aniline, acetic acid, formamide, and 3 alcohols). This indicates that the solvatomagnetic comparison method applies not only to non-amphiprotic, but also to amphiprotic solvents. Such is not the case of the solvatochromic comparison method considered below.

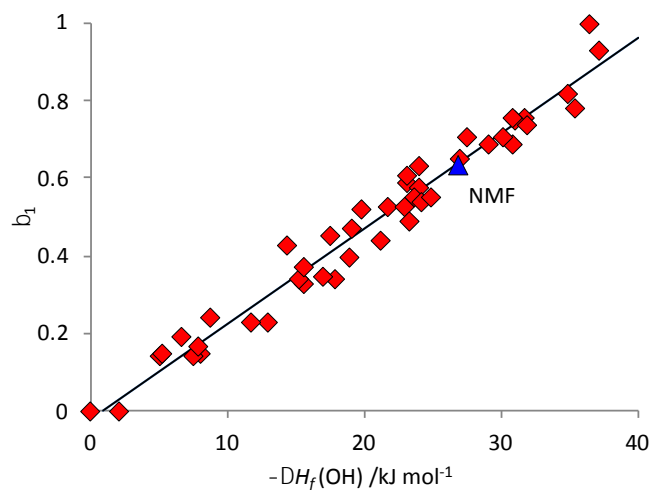


Figure 9. Correlation between the solvatomagnetic β_1 scale and the negative of the enthalpy of formation of the hydrogen bond of 4-fluorophenol to the HBA solvent. The amphiprotic solvent *N*-methylformamide (NMF, blue triangle) behaves similarly to non-amphiprotic solvents (red diamonds).

5. Comparison of the solvatomagnetic β_1 scale to solvatochromic scales.

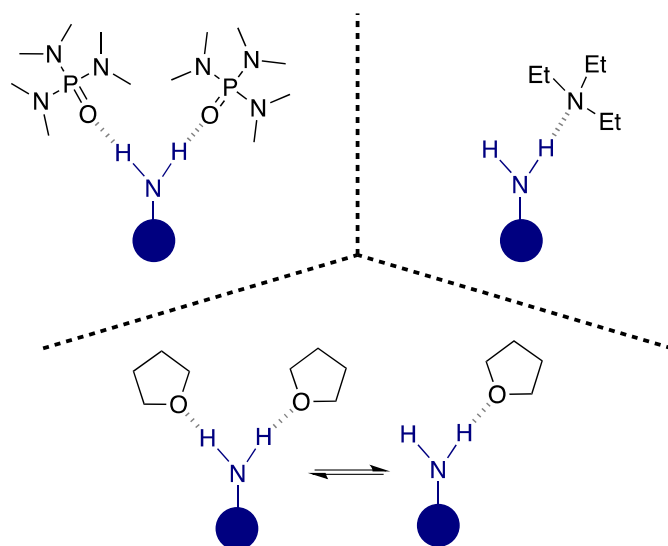
Before undertaking these comparisons, it is necessary to recall three important limitations to the choice of solvatochromic probes when applying the solvatochromic method to the determination of HB acceptance solvent parameters:

a) the effect of vibronic structure of the solvatochromic band of many indicators on the precision and sensitivity of the method¹³. Because of this effect, the historical indicator 4-NO₂C₆H₄NEt₂ used by Kamlet and Taft in their seminal work¹² must be avoided, and replaced by 4-NO₂C₆H₄NMe₂ as the non-HBD indicator having non-specific solvent effects similar to the HBD probe 4-NO₂C₆H₄NH₂.

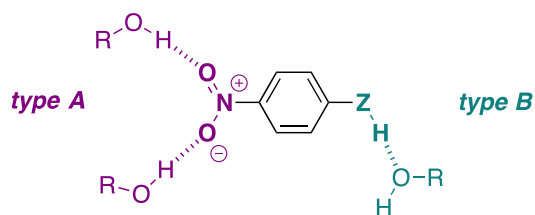
b) the presence of the NH₂ group in the structure of indicators, because there is experimental evidence (through infrared studies of the NH₂ stretching vibration)¹⁵ that the hydrogen-bonded complex of stoichiometry 1:2 (scheme 3) is not always the only species found in a

solution of 4-NO₂C₆H₄NH₂ in basic solvents. For example, 4-nitroaniline was shown to exist as (i) mainly 1:1 complex in triethylamine, or (ii) a mixture of 1:1 and 1:2 complexes in tetrahydrofuran, or (iii) mainly 1:2 complex in HMPT (scheme 3). Since 1:1 complexation produces much lower bathochromic shifts than 1:2 complexation¹⁵, the bathochromic shifts of 4-nitroaniline depend not only on the strength of the hydrogen bond(s) but also on the varying proportion of complexes of different stoichiometries and cannot be considered as a safe basicity-dependent property for the determination of basicity solvent scales¹⁵. It must be noted that 5-nitroindoline (the HBD indicator for the *SB* scale²⁰, scheme 1) with a single NH bond is a safe indicator from this point of view (however, see below).

c) the presence of the NO₂ group in the structure of indicators. Indeed, amphiprotic solvents such as alcohols, are able not only to receive the desired type B hydrogen bond (scheme 4) on the alcoholic oxygen atom, but also to give an undesired type A hydrogen bond (scheme 4) to the oxygen atoms of the nitro group¹². We have elsewhere experimentally and theoretically explained¹⁵ how type A hydrogen bonds may yield, for amphiprotic solvents, unreliable β_1 (OH), β_1 (NH₂), and *SB* values, all determined from nitro indicators (4-nitrophenol, 4-nitroaniline, and 5-nitroindoline, respectively).



Scheme 3. Various states of hydrogen-bond complexation of the amino group of 4-nitroaniline: 1:2 complex in HMPT, 1:1 complex in triethylamine, and mixture of 1:2 and 1:1 complexes in tetrahydrofuran.



Scheme 4. Type-A (undesired) and type-B (desired) hydrogen bonds for 4-nitrophenol ($Z = O$) and 4-nitroaniline ($Z = NH$) in alcohols (for the sake of clarity, the self-association of liquid alcohol is not drawn). Both types of hydrogen bond produce bathochromic shifts on the $S_0 \rightarrow S_1$ electronic transition of these indicators.

The low determination coefficient between the solvatochromic $\beta^*_1(\text{NH}_2)$ Krygowski scale¹⁷ and the solvatomagnetic β_1 scale ($r^2 = 0.702$, $n = 29$) is caused by the use of the $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2/4\text{-NO}_2\text{C}_6\text{H}_4\text{NET}_2$ pair of solvatochromic indicators. This pair unfortunately cumulates the three shortcomings above: vibronic structure of the solvatochromic band of $4\text{-NO}_2\text{C}_6\text{H}_4\text{NET}_2$, variable stoichiometry of complexation because of the two NH bonds of $4\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$, and type A hydrogen bonds to the nitro groups of both indicators. Because of vibrational anomalies, this pair of indicators lacks sensitivity as illustrated by its inability to

reveal the weak basicity of fluoro-, chloro-, and bromobenzene, all having $\beta'_1(\text{NH}_2) = 0$, whereas $\beta_1 = 0.11$, 0.06 , and 0.08 , respectively. The difficulty of the amino group to form 1:2 complexes is shown for *tert*-butylamine with a much lower value of $\beta'_1(\text{NH}_2)$ (0.69) compared to β_1 (1.08).

In the same vein, the $4\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2/4\text{-NO}_2\text{C}_6\text{H}_4\text{NMe}_2$ pair yields a solvatochromic $\beta_1(\text{NH}_2)$ scale^{18,19} able to explain only 84.6 % of the variance of the solvatomagnetic β_1 scale ($r^2 = 0.846$, $n = 155$, see Figure 10A). Particularly, $\beta_1(\text{NH}_2)$ is heavily underestimated for hindered ethers and hindered amines (e.g. the differences are 0.29 and 0.45 for di-*tert*-butyl ether and tri-*n*-butylamine, respectively). This is another illustration of the stoichiometric difficulties with indicators having *two* N-H bonds.

The stoichiometric problem is avoided for the couple of indicators 5-nitroindoline/1-methyl-5-nitroindoline used for defining a solvent basicity scale SB ²⁰. The regression equation of the solvatomagnetic β_1 parameter against the solvatochromic parameter SB is:

$$(28) \quad \beta_1 = 0.903 SB + 0.058$$

$$r^2 = 0.858$$

$$s = 0.090$$

$$n = 106$$

SB is also an unsatisfactory solvatochromic parameter, since it can explain only 85.8% of the β_1 variance. This is probably caused by the amphiprotic solvents of the solvent set (3-methylphenol, 24 alcohols, acetic acid, 3 primary and secondary amides, aniline, *N*-methylaniline), since they can hydrogen bond to the nitro group of the indicators. Indeed the exclusion of these 31 amphoteric solvents yields eq 29 with a better determination coefficient:

$$(29) \quad \beta_1 = 1.134 SB - 0.027$$

$$r^2 = 0.938 \quad s = 0.064 \quad n = 75$$

We conclude that the 5-nitroindoline/1-methyl-5-nitroindoline pair is a good indicator for non-amphiprotic solvents, but is not a general pair of indicators, since it cannot satisfactorily deal with the important families of amphiprotic solvents such as alcohols and primary and secondary amides (see Figure 10B). For solubility reasons, it cannot also deal with water, the most important solvent. By an unclear procedure a SB value of 0.025 was attributed to water³⁰. This value seems inconceivably low compared to SB values for perfluorohexane (0.057) and alkanes (from 0.053 to 0.086)²⁰. Other unsatisfactory SB values are obtained for halogenobenzenes²⁰. They yield the surprising order ($>$ for “better HBA than”): iodo-, bromo-, chloro-benzene $>$ benzene and toluene. This SB order does not agree with both the solvatomagnetic¹⁵ β_1 and the solvatothermodynamic $\Delta H_f(\text{OH})$ ^{7,8} and $\Delta H_f(\text{NH})$ ⁹ chemically expected order: benzene, toluene $>$ halogenobenzenes.¹

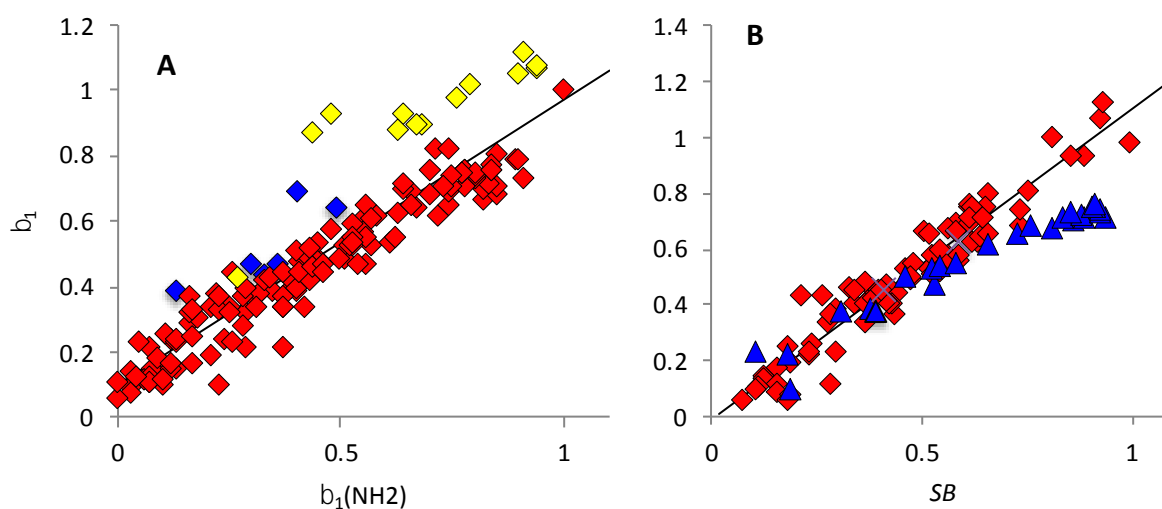


Figure 10. Comparison of the solvatomagnetic β_1 scale with solvatochromic scales:(A) $\beta_1(\text{NH}_2)$ scale; all amines (yellow diamonds) and most ethers (blue diamonds) have too low $\beta_1(\text{NH}_2)$ values because of their difficulty to

form 1:2 HBed complexes. (B) *SB* scale; amphiprotic solvents (blue triangles) have too high *SB* values because they form type-A hydrogen-bonds to the nitro group of the pair of indicators.

6. Comparison of the solvatomagnetic β_1 scale to the Kamlet-Taft β scale.

The historical β Kamlet-Taft parameter is often called solvatochromic. Actually, it is a statistically averaged scale defined not only from the bathochromic shifts of 4-nitroaniline and 4-nitrophenol measured in the pure base, but also from the logarithms of the formation constants of 4-fluorophenol and phenol hydrogen-bonded complexes and from the shift upon hydrogen bonding of the ^{19}F NMR signal of 4-fluorophenol, measured in CCl_4 ¹². Other solvatochromic shifts of aniline indicators, correlations with numerous literature basicity-dependent properties, as well as β estimation rules have allowed the definition of 162 β values¹⁶. Thus the β scale has been determined by mixing (i) numerous OH, NH, and NH_2 HBD probes (and even non-HBD Lewis acids), (ii) numerous physicochemical properties (solvatochromic shifts, infrared shifts, NMR shifts, equilibrium constants, and enthalpies), and (iii) two different measurement media: the pure base and the base diluted in an “inert” solvent. This method of definition has been qualified as “fuzzy” by Marcus³¹. So, in order to easily extend solvent basicity scales to new solvents, we propose here as a first choice (i) a single HBD probe, 4-fluorophenol, (ii) one property, the ^{19}F NMR shift, and (iii) one measurement medium, the pure base (in second choice, for limited classes of solvents, the bathochromic shifts of 4-nitrophenol).

This “wide-range” Kamlet-Taft scale is necessarily correlated to β_1 ($r^2 = 0.822$, $n = 72$), $\Delta H_f(\text{OH})(r^2 = 0.875$, $n = 31$), and $\Delta H_f(\text{NH})(r^2 = 0.794$, $n = 24$). However, this scale is also a “low-resolution” one, because constructed from many correlations not so general as claimed by Kamlet and Taft^[23]. Consequently a significant part (from 21 to 13%) of the variance of β_1 , $\Delta H_f(\text{OH})$, and $\Delta H_f(\text{NH})$ cannot be explained by β . The differences $\beta_1 - \beta$, as large as -0.28 for *tert*-butanol or $+0.31$ for tri-*n*-butylamine, are illustrated in Figure 11.

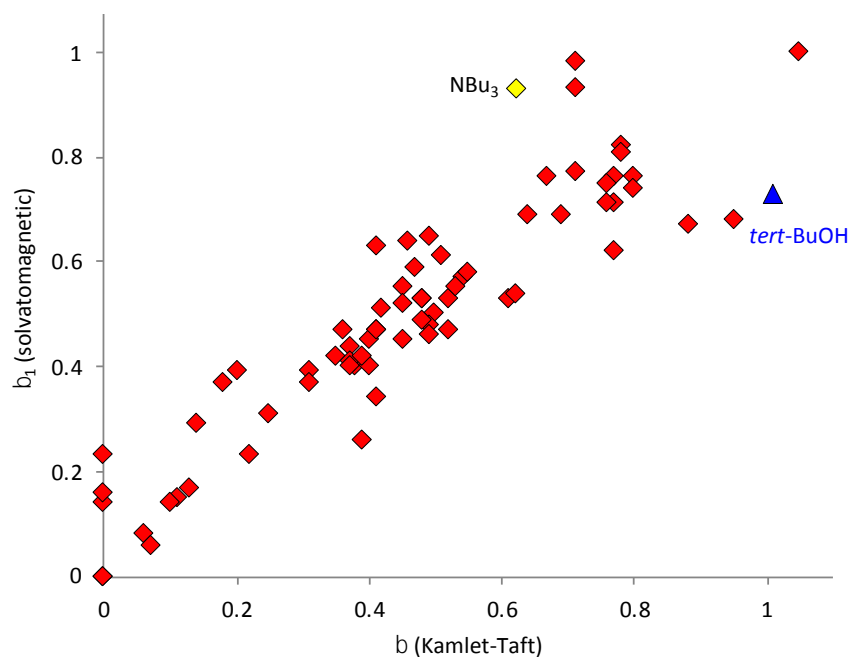


Figure 11. Comparison of the solvatomagnetic β_1 scale with the statistical β scale of Kamlet and Taft.

7. Comparison of the solvatomagnetic β_1 scale to solvatovibrational scales.

In the way described above, we have built two solvatovibrational scales, $\Delta\nu(\text{CO})$ (published elsewhere¹⁴ and extended here) and $\Delta\nu'(\text{CO})$ (constructed for this work), from the lowering, upon hydrogen bonding of the carboxylic OH group to HBA solvents, of the carbonyl stretching vibration of trichloroacetic acid and benzoic acid, respectively. Both scales are given in Table 4. Unfortunately, water could not be studied because of ionization, proton transfer reaction occurs for amines and most pyridines, and decarboxylation is observed in strong polar aprotic solvents such as DMSO and HMPT³². Also, most carbonyl-containing solvents are insufficiently transparent to be studied.

In Table 4, the value $\Delta\nu(\text{CO}) = 0$ for perfluorobutylamine; 1,2-dichlorobenzene; 1,2-dibromobenzene; 1,2,4-trichlorobenzene results from the position of these solvents on the comparison line, showing that CCl_3COOH behaves similarly to the non-HBD CCl_3COOMe in these solvents and consequently that these solvents may be considered as non-HBA solvents towards CCl_3COOH . Since this acid is a very strong HBD, one can conclude that the

hydrogen-bond acceptance of these solvents is zero in ordinary chemical conditions. On the contrary, the significant non-zero $\Delta\nu(\text{CO})$ value of pentafluoropyridine, reveals a residual HB acceptance of this compound in spite of its perfluorination. This results from the electron-donating resonance effect of the fluorine substituent ($\sigma_{\text{R}} = -0.25$)²⁹ compensating partially its electron-withdrawing field-inductive effect ($\sigma_{\text{F}} = +0.44$)²⁹; in the perfluorinated amine $\text{N}(\text{C}_4\text{F}_9)_3$, only the electron-withdrawing field-inductive effect operates and reduces the HB acceptance of the nitrogen atom to zero. A poor correlation is observed between β_1 and $\Delta\nu(\text{CO})$:

$$(30) \quad \beta_1 = 0.0172 \Delta\nu(\text{CO}) + 0.096$$

$$r^2 = 0.800 \qquad s = 0.090 \qquad n = 52$$

In fact, this relationship is family-dependent, i.e. different linear correlations are obtained for different classes (families) of HBA solvents. This family-dependence is illustrated in Figure 12A where only π bases ($n = 7$, $r^2 = 0.625$), ethers ($n = 8$, $r^2 = 0.918$), and alcohols ($n = 20$, $r^2 = 0.830$) are shown for the sake of clarity.

The family-dependence is less pronounced in the relationship (eq 31) between β_1 and $\Delta\nu'(\text{CO})$:

$$(31) \quad \beta_1 = 0.0287 \Delta\nu'(\text{CO}) + 0.022$$

$$r^2 = 0.914 \qquad s = 0.058 \qquad n = 22$$

Indeed, π bases, thioethers, nitriles, ethers, *N,N*-dimethylacetamide, and diethylchlorophosphate, pertaining to six different families, draw a common regression line on the Figure 12B. This can be attributed to a HB acidity³³ of 4-fluorophenol ($\alpha_2^{\text{H}} = 0.629$)

closer to that of benzoic acid ($\alpha_2^H = 0.588$)³³ than to that of trichloroacetic acid ($\alpha_2^H = 0.947$)³³. However, the addition of four substituted pyridines and of *N,N*-dimethylaniline to the sample of solvents lowers the determination coefficient to 0.762 ($n = 27$). Clearly, on Figure 12B the pyridines and the amine behave differently of carbon, sulfur, oxygen, and Nsp bases.

In summary, the solvatovibrational comparison method, based on the same similarity principle as the solvatochromic, solvatothermodynamic, and solvatomagnetic ones, is a safe method on paper. But its application comes up against technical (solvent transparency) and chemical (protonation, decarboxylation) problems that limit its use to a restricted set of solvents. Moreover, the too large differences in HB acidity between CCl_3COOH and 4-fluorophenol prevents a family-independent good correlation between the solvatomagnetic β_1 and the solvatovibrational $\Delta\nu(\text{CO})$ scale. Currently, we do not see a future for this method.

Table 4. Infrared shifts $\Delta\nu(\text{CO})$ and $\Delta\nu'(\text{CO})(\text{cm}^{-1})$ of the carbonyl stretching vibrations of CCl_3COOH and $\text{C}_6\text{H}_5\text{COOH}$ upon hydrogen bonding to HBA solvents, calculated from eqs 9 and 11.

| Solvent | $\Delta\nu(\text{CO})$ | $\Delta\nu'(\text{CO})$ | Solvent | $\Delta\nu(\text{CO})$ | $\Delta\nu'(\text{CO})$ |
|--|------------------------|-------------------------|------------------------------------|------------------------|-------------------------|
| Aromatic π bases | | | ethoxybenzene | 12.6 | 10.5 |
| 1,2,4-trichlorobenzene | 0 | | 1,4-dioxane | 20.7 | 15.9 |
| 1,2-dichlorobenzene | 0 | 0 | dibenzyl ether | 21.4 | 16.8 |
| 1,2-dibromobenzene | 0 | | diethyl ether | 23.7 | |
| chlorobenzene | 0.3 | 1.1 | dibutyl ether | 24.0 | |
| 1-methylnaphtalene | 1.3 | 2.1 | 2,2,5,5-tetramethyltetrahydrofuran | 26.5 | 20.3 |
| benzene | 1.4 | | Thioethers | | |
| thiophene | 1.8 | 2.0 | methyl disulfide | 8.5 | 7.0 |
| phenylacetylene | 2.7 | 2.8 | ethyl disulfide | 9.2 | 7.4 |
| 1,4-dimethylbenzene | 3.4 | | thioanisole | 11.4 | 7.6 |
| 1,2,3,4-tetramethylbenzene | 5.0 | 6.0 | methyl sulfide | 16.2 | 13.2 |
| Alcohols | | | ethyl sulfide | 16.9 | 14.1 |
| 3-methylphenol | 14.0 | | <i>iso</i> -propyl sulfide | 17.0 | 14.6 |
| 2,2,2-trifluoroethanol | 14.0 | | butyl sulfide | 17.6 | 15.4 |

| | | | | | |
|-------------------------|------|------|-----------------------------------|------|------|
| 2,2,2-trichloroethanol | 14.4 | | tetrahydrothiophene | 17.6 | 15.5 |
| 2-propyn-1-ol | 22.1 | | <i>tert</i> -butyl sulfide | 17.7 | 15.6 |
| 2-cyanoethanol | 24.6 | | Amide, Sulfite, phosphates | | |
| 2-bromoethanol | 25.0 | | Diethyl sulfite | 12.4 | |
| 2-chloroethanol | 25.4 | | diethylchlorophosphate | 17.7 | 20.0 |
| 2-fluoroethanol | 26.6 | | <i>N,N</i> -dimethylacetamide | | 23.8 |
| 2-methoxyethanol | 27.5 | | trimethyl phosphate | 27.2 | |
| 2-phenoxyethanol | 27.5 | | Nitriles | | |
| 2-ethoxyethanol | 28.3 | | chloroacetonitrile | 8.4 | |
| allyl alcohol | 29.2 | | benzonitrile | 11.0 | 10.8 |
| benzyl alcohol | 29.6 | | acetonitrile | 11.6 | 11.4 |
| ethane-1,2-diol | 30.6 | | trimethylacetonitrile | 11.7 | 10.8 |
| 2-phenylethanol | 30.9 | | <i>N,N</i> -dimethylcyanamide | 19.3 | 14.6 |
| methanol | 31.9 | | Pyridines | | |
| <i>iso</i> -propanol | 32.5 | | pentafluoropyridine | 4.7 | |
| cyclohexanol | 32.5 | | 2,6-difluoropyridine | 13.6 | |
| 1-propanol | 32.7 | | 2-bromopyridine | 26.2 | 23.6 |
| ethanol | 32.7 | | 2-fluoropyridine | 27.0 | 21.6 |
| 1-butanol | 32.8 | | pyridine | | 32.0 |
| 1-octanol | 33.1 | | 2,6-dimethylpyridine | | 33.2 |
| <i>tert</i> -butanol | 33.4 | | Amines | | |
| Ethers | | | Perfluorobutylamine | 0 | |
| furan | 4.6 | 3.1 | <i>N,N</i> -dimethylaniline | | 28.5 |
| methoxybenzene, anisole | 12.2 | 10.3 | | | |

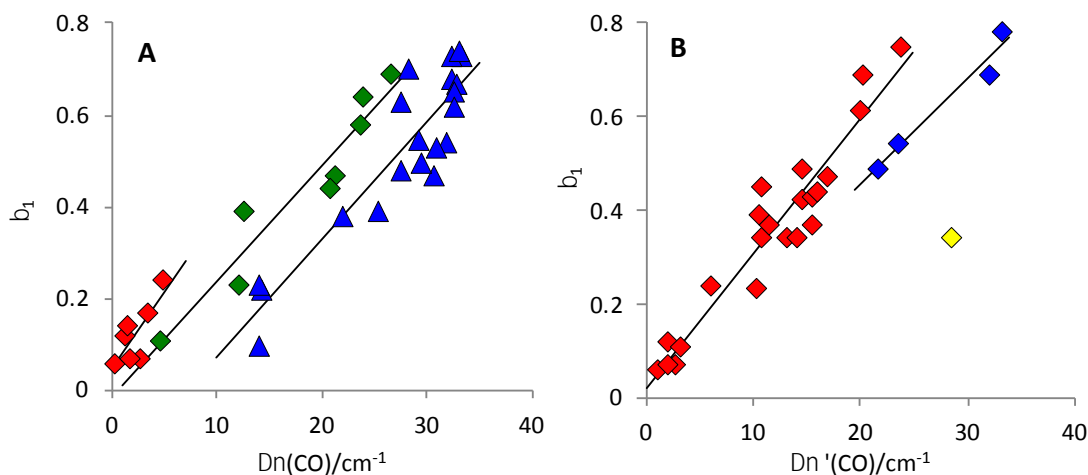


Figure 12. Family-dependent relationships between β_1 and solvatovibrational scales: (A) $\Delta\nu(\text{CO})$ of CCl_3COOH with π bases (red diamonds), ethers (green diamonds), and alcohols (blue triangles); (B) $\Delta\nu'(\text{CO})$ of $\text{C}_6\text{H}_5\text{COOH}$ with all bases (red diamonds) except pyridines (blue diamonds) and *N,N*-dimethylaniline (yellow diamond).

A vibrational probe more sensitive to hydrogen bonding than the carbonyl stretch of carboxylic acids is the OH (or OD) stretch of alcohols¹ (water is not easy to study and phenols give too large shifts). From its spectacular shift to lower frequencies upon hydrogen bonding, many more or less equivalent scales have been proposed along the years (for a review see ref [19]). For a comparison with the solvatomagnetic β_1 scale, we have selected the scales based on the OD stretch of methan[²H]ol, $\Delta\nu(\text{OD})$ ¹⁰ (vide supra), and on the OH stretch of methanol, $\Delta\nu(\text{OH})$ ¹¹, because they have been measured for sets of varied solvents.

The correlation between β_1 and $\Delta\nu(\text{OD})$ is poor ($r^2 = 0.722$, $n = 37$). In fact, the choice of methan[²H]ol is technically unfortunate because deuterium can be exchanged with the hydrogen atoms of wet solvents and HOD molecules are formed leading to spurious bands, and consequently uncertainties on the results. The correlation between β_1 and $\Delta\nu(\text{OH})$ is better ($r^2 = 0.824$, $n = 45$), but remains poor for two main reasons. Firstly, the vibrational shift registers all the molecular interactions between CH_3OH and the solvent, i. e. not only the (desired) effect of the hydrogen bond between the OH group and the solvent but also the (undesired) nonspecific effects. This contamination of the $\Delta\nu(\text{OH})$ scale may be significant

for a number of solvents. Secondly, scales provided by OH infrared shifts are not generally related to thermodynamic properties of the hydrogen bond. For example, the methanol $\Delta\nu(\text{OH})$ solute scale is weakly related to the Gibbs energy of HB formation to methanol ($r^2 = 0.543$ for 42 HBAs)¹. The correlation is better with the enthalpy of HB formation ($r^2 = 0.837$ for 41 HBAs)¹ but nevertheless much less successful than with other HBA scales. For example, the solvatomagnetic β_1 scale and the enthalpy of hydrogen-bond formation of 4-fluorophenol are excellently correlated ($r^2 = 0.966$, $n = 46$, see eq 26 above). For the above reasons, we discourage the use of scales based on OH infrared shifts, especially as better solvent HBA scales are now available.

Conclusion

Many physicochemical properties such as electronic transitions, NMR chemical shifts, vibrational frequencies, and enthalpies of solution are sensitive to solute HBD/solvent HBA interactions. Many HBD probes were chosen, on the basis of technical reasons, to measure the solvent effect on these properties: 4-fluorophenol and pyrrole for heats of solution, 4-fluorophenol for ¹⁹F NMR, 4-nitroaniline, 4-nitrophenol, and 5-nitroindoline for the $S_0 \rightarrow S_1$ electronic transition, carboxylic acids for the carbonyl stretch, and methanol for the OH stretch. To isolate the hydrogen-bond contribution to the overall solvent effect, all the corresponding physicochemical data (except the OH shift) have been treated on the basis of the similarity principle by comparison methods pioneered by Arnett (solvocalorimetric comparison method) and Kamlet and Taft (solvatochromic comparison method). They were followed by the solvatovibrational comparison method and, recently, by the solvatomagnetic comparison method. These methods yield a variety of scales aiming at measuring the

hydrogen-bond strength of solvents, the most popular being the (partly) solvatochromic β scale of Kamlet and Taft, and the most recent the solvatomagnetic β_1 scale.

Because of its fuzzy definition, it is difficult to extend the Kamlet-Taft β scale to new solvents such as ionic liquids and green solvents. Solvatochromic scales are contaminated either by varying stoichiometries of complexation (when the HBD donor group is an amino one) or/and by hydrogen bonding of amphiprotic solvents to the nitro group of nitroaromatic indicators, so that the important class of amphiprotic solvents cannot be safely parameterized by such solvatochromic indicators (or similar ones such as the ABF dye)³⁴. Solvatovibrational studies are limited to a restricted range of solvents because of the chemical reactivity of carboxylic acids and of the lack of infrared transparency of the important class of carbonyl solvents. Finally, only the solvatomagnetic β_1 scale, requiring the measurement of the ^{19}F NMR spectra of 4-fluorophenol and 4-fluoroanisole, and the solvocalorimetric scale, based on the enthalpies of solution of these two compounds, are free of shortcomings. In fact, they are strongly correlated and this correlation shows that the shift upon hydrogen bonding of the ^{19}F NMR signal is dominated by the strength of the hydrogen bond, and so gives to the NMR β_1 scale the thermodynamic status required for considering this spectroscopic scale as an “enthalpy of basicity” scale.

Because NMR spectrometers are more widely available than calorimeters in chemistry laboratories, and that ^{19}F NMR spectra are more quickly measured than enthalpies of solution, we consider that the ^{19}F solvatomagnetic comparison method is the method of choice to characterize the HB acceptance of new solvents. There is indeed a need of robust HBA parameters for solvents such as ionic liquids and green solvents³⁵. For the moment, we propose here a database giving the chemist homogeneous β_1 values for unprecedented range and variety of HBA solvents and for previously un-parameterized HBAs.

Experimental Section

Chemicals. The purification and drying of 4-fluorophenol, 4-fluoroanisole, and solvents were achieved as previously described¹⁵. Trichloroacetic and benzoic acids and corresponding methyl esters are high-purity commercial compounds.

¹⁹F NMR spectroscopy. The NMR spectra were obtained on a 400 MHz spectrometer as already described¹⁵.

Infrared spectra of carboxylic acids and esters. The IR spectra of carboxylic acids and esters were recorded from 1800 to 1600 cm⁻¹ with a FTIR spectrometer at a resolution of 0.5 cm⁻¹. Overlapping carbonyl bands of various present species were deconvoluted. To overcome difficulties arising from the dimerization of acids and low solvent transparency, the thickness of cells varied from 0.1 to 50 mm. Solutions were thermoregulated at 20°C and prepared in a dry glove-box.

Statistical treatment. The relationship between a dependent variable and an explanatory variable is established by the least-squares method. The degree of correlation between two variables is given by the determination coefficient r^2 (square of the correlation coefficient r) since $100 r^2$ yields the percentage of variance of one variable explained by the other.

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