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Christian Laurence, Sergui Mansour, Daniela Vuluga, Khadija Sraïdi, Julien Legros. Theoretical, Semiempirical, and Experimental Solvatochromic Comparison Methods for the Construction of the α 1 Scale of Hydrogen-Bond Donation of Solvents. *Journal of Organic Chemistry*, 2022, 87 (9), pp.6273-6287. 10.1021/acs.joc.2c00526 . hal-03838942

HAL Id: hal-03838942

<https://hal.science/hal-03838942>

Submitted on 3 Nov 2022

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**Theoretical, semi-empirical, and experimental
solvatochromic comparison methods for the construction
of the α_1 scale of hydrogen-bond donation of solvents**

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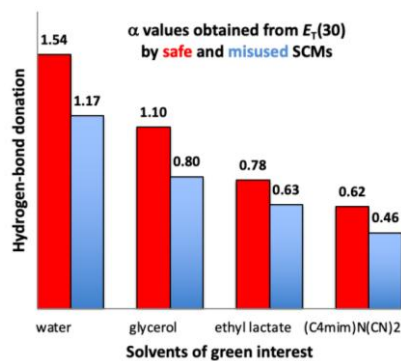
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Graphical Abstract

The misused Kamlet-Taft solvatochromic comparison method (SCM) must be replaced by theoretical (PCM-TD-DFT calculations) or semi-empirical (Mc Rae equation) or experimental (comparison of two betaine dyes) SCMs.



Keywords: Acidity; Empirical solvent parameters; Hydrogen bond; Solvatochromism; Solvent Effects.

Abstract: Today, the hydrogen bonding donation (HBD) ability parameter of new solvents, α , is generally determined either by the Kamlet-Taft solvatochromic comparison of two probes, Reichardt betaine dye B(30) and 4-nitroanisole, or by the measurement of a single probe (e.g. solvatochromism of an iron coordination complex). This work highlights the shortcomings of these probes, and recommends three replacement methods: (a) the theoretical comparison of the experimental and PCM-TD-DFT calculated transition energies $E_T(30)$ of B(30), (b) the semi-empirical comparison of the experimental and McRae calculated $E_T(30)$, and (c) for ionic liquids, the experimental comparison of $E_T(30)$ and $E_T(33)$ lying on the lower basicity of the betaine dye B(33) compared to B(30). These methods yield a new HBD parameter, α_1 , for 101 molecular solvents and 30 ionic liquids. The novelty is emblematic for water, with $\alpha_1 = 1.54$ instead of α (Kamlet-Taft) = 1.17. The solvent parameter α_1 is not equivalent to the solute hydrogen-bond acidity parameter α_2^H , partly because of the self-association of HBD solvents.

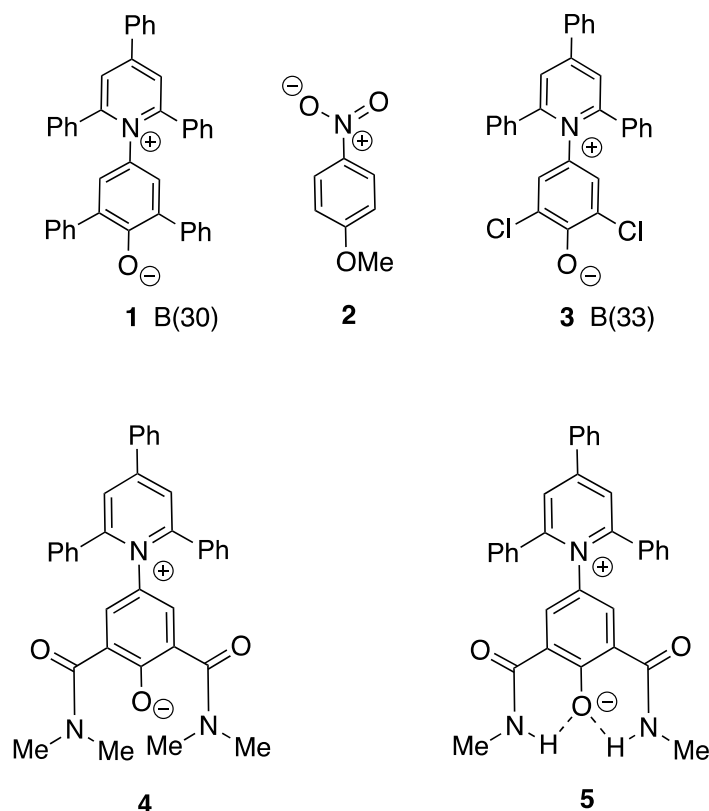
1 Introduction

One of the most important chemical properties of solvents, their effectiveness as hydrogen-bond donors (HBDs), is also one of the most difficult to determine. This difficulty arises from the many solute-solvent intermolecular forces at the origin of solvent effects.¹ For example, even a simple HBD like 1-octanol can interact with solutes not only in donating hydrogen bonds but also in interacting by three kinds of non-specific (van der Waals) forces: dispersion and induction because of its molecular polarizability and electrostatic forces because of its permanent dipole moment.

To isolate the specific hydrogen bond from non-specific solvent effects, Kamlet and Taft devised forty-six years ago a so-called “solvatochromic comparison method” (SCM)^{2,3} that yielded the Kamlet-Taft scales of hydrogen-bond acceptance (β)² and donation (α)³ ability of solvents. Shortly, the method consists in the comparison of the solvatochromism of two probes having similar non-specific effects, one capable, one incapable or less capable of hydrogen bonding. This comparison generates a pure hydrogen bonding scale if three important conditions are satisfied: (a) a good linear correlation must be observed between the solvatochromic shifts in a series of solvents of varying non-specific effects; (b) points in this correlation representing solvents in which hydrogen bonding occurs should show significant deviations from the comparison line (all in the same direction); and (c) the direction of deviations should be consistent with the solvatochromism involved and their magnitudes should reflect a reasonable order of solvent HBD strengths (for the α scale) or solvent hydrogen-bond acceptor (HBA) strength (for the β scale).

The method cannot suffer much criticism since it is based on the similarity principle, a fundamental principle in science successfully used in many fields of chemistry.⁴ But this important and original method has been misused by generations of chemists since 1975. Today, most chemists determine new α values from the solvatochromic comparison of the Reichardt pyridinium *N*-phenolate betaine dye B(30)⁵ (the probe capable to accept hydrogen bonds) and of 4-nitroanisole (the probe less capable to receive hydrogen bonds)(Scheme 1). In this work we show that the solvatochromic comparison of B(30) and 4-nitroanisole does not satisfy the above conditions (a)-(c) and yields unreliable α values not only for important molecular liquids such as glycol ethers,⁶ hydrofluoroethers,⁷

and alkanolamines⁸ but also for ILs. In order to avoid the difficulty to find two solvatochromic probes with similar non-specific effects but dissimilar HBA effects, we have proposed in 2014 to determine an α_1 scale by means of the solvatochromism of B(30) and PCM-TD-DFT (polarizable continuum model-time dependent-density functional theory) calculations (hence the name “theoretical SCM” used in this paper).⁹ The validity of these α_1 values will be confirmed in this work. However, PCM-TD-DFT calculations on such a large molecule as B(30) are not easily performed by non-computational chemists. So, we propose here to analyze the solvatochromism of B(30) by means of a simplified McRae equation¹⁰ of which the theoretical coefficients are adjusted to the experimental solvatochromic shifts (hence the name “semi-empirical SCM”). The α_1 values determined by the semi-empirical SCM agree so well with the theoretical ones that we have used the semi-empirical method as a secondary one to extend the α_1 database to many molecular liquids. Nevertheless, the PCM used in the theoretical and semi-empirical SCMs does not apply to ILs. We have therefore imagined to compare the solvatochromism of B(30) with that of the betaine dye B(33)⁵ (Scheme 1), having two chloro instead of two phenyl substituents in ortho of the phenolate oxygen. Because of the structural similarity of their chromophores the two betaines should interact with solvents similarly through non-specific effects but B(33) is much less capable to receive hydrogen bonds on its phenolate oxygen than B(30) by virtue of the electron-withdrawing effects of the chloro substituents. This method is called “experimental SCM” since two *experimental* solvatochromic shifts are now compared, those of B(30) and B(33). The agreement of the experimental SCM results with those of the theoretical SCM for molecular solvents leads to the application of the experimental SCM to ILs.



Scheme 1. Solvatochromic probes for the SCMs discussed in this work. The Kamlet-Taft comparison is between **1** and **2**. Our recommended comparison is between **1** and calculated values, or between **1** and **3** for ILs. The comparison between **4** and **5** is valuable but these probes are not commercially available.

The objective of this work is to put an end to the misuse of the solvatochromic comparison method and to provide chemists with reliable methods to determine the α parameter of molecular solvents and ionic liquids using commercially available probes and spectroscopic techniques available in any chemistry laboratory. 131 α_1 values of HBD solvents are thus obtained and their validity is tested on physicochemical properties mainly α -dependent. The validity of this comprehensive new α_1 scale makes it possible to statistically analyze many α -type scales proposed in the literature. This analysis aims to determine the purity of these scales, i. e. the presence or absence of non-specific contaminating effects. There are also scales in the literature measuring the HB acidity of molecules as solutes (e.g. the α_2^H scale¹¹); they will be compared with the solvent scale α_1 to study the possible equivalence of solute and solvent scales of hydrogen-bond donation.

2 Results and Discussion

The hundred of a_1 values determined by the theoretical SCM⁹ and the semi-empirical SCM (this work) are collected in Table 1(in bold for the semi-empirical values and in normal characters for the theoretical ones).

Table 1. a_1 scale of hydrogen-bond strength of HBD solvents (**in bold** 37 new values determined by the semi-empirical SCM).

HBD Solvent	a_1	HBD Solvent	a_1
C-H donors		2-Propanol	0.53
1-Nonyne	0.03	2-Methyl-1-butanol	0.54
1,1,2,2-Tetrachloroethane	0.04	2-Methyl-1-propanol, <i>iso</i> -butanol	0.57
Acetone	0.04	1-Phenylethanol	0.57
Dibromomethane	0.07	3-Methyl-1-butanol	0.62
Trichloroethene	0.09	1-Pentanol	0.64
Pentachloroethane	0.09	1-Heptanol	0.64
Dichloromethane	0.10	1-Hexanol	0.65
Tribromomethane	0.14	1-Butanol	0.65
Bromo-trichloromethane (HalBD)	0.17	1-Octanol	0.66
(<i>E</i>)-1,2-Dichloroethene	0.19	1-Nonanol	0.66
Pentafluorobenzene	0.19	2-Ethoxyethanol	0.67
Trichloromethane	0.20	1-Propanol	0.68
(<i>Z</i>)-1,2-Dichloroethene	0.20	Monoethanolamine	0.70
Acetonitrile	0.23	1-Decanol	0.72
Phenylacetylene	0.26	2-Phenylethanol	0.72
3-Chloro-1-propyne, propargyl chloride	0.26	Pentane-1,5-diol	0.74
Nitromethane	0.28	Ethanol	0.75
Chloroacetonitrile	0.31	Butane-2,3-diol	0.77
Ethoxy-nonafluorobutane (HFE7200)	0.38	1,3-Dimethoxy-2-propanol	0.78
Methoxy-nonafluorobutane (HFE7100)	0.40	Ethyl lactate	0.78
Ethyl propynoate, ethyl propiolate	0.58	2-(<i>n</i> -Butoxy)ethanol	0.79
N-H donors		Benzyl alcohol	0.79
Piperidine	0.00	Allyl alcohol	0.79
Cyclohexylamine	0.02	Butane-1,3-diol	0.80
<i>N</i> -(<i>tert</i> -Butyl)-benzylamine	0.03	2-Methoxyethanol	0.83
Diethylamine	0.04	Butane-1,2-diol	0.83
<i>tert</i> -Butylamine	0.06	Butane-1,4-diol	0.85
Diallylamine	0.07	Diethanolamine	0.86
<i>n</i> -Butylamine	0.09	Diethylene glycol	0.87
<i>N</i> -Benzyl-methylamine	0.10	Triethanolamine	0.88
1,2-Diaminoethane	0.11	Diethylene glycol	0.88
Allylamine	0.12	2-Phenoxyethanol	0.89
Morpholine	0.17	Propane-1,2-diol	0.90
3-Amino-1-propyne, propargylamine	0.25	Triethyleneglycol	0.90
<i>N</i> -Methylaniline	0.38	3-Methoxy-1,2-propanediol	0.92
Pyrrolidin-2-one	0.44	2,2,2-Trichloroethanol	0.92
Aniline	0.47	Propane-1,3-diol	0.94
<i>N</i> -Methylpropionamide	0.55	1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-ol	0.95

<i>N</i> -Ethylacetamide	0.58	Methanol	1.00
<i>N</i> -Methylacetamide (32°C)	0.59	2-Chloroethanol	1.01
<i>N</i> -Methylformamide	0.81	1,1,1-Trifluoro-2-(trifluoromethyl)pent-4-en-2-ol	1.03
Pyrrole	0.93	Ethane-1,2-diol, Glycol	1.05
Formamide	0.97	1,1,1-Trifluoro-2-(trifluoromethyl)pentan-2-ol	1.07
O-H donors		2-Fluoroethanol	1.07
2-Methyl-2-propanol, <i>tert</i> -butanol	0.24	2,2,2-Trifluoro-1-phenylethanol	1.09
2-Methyl-2-butanol, <i>tert</i> -amyl alcohol	0.29	Glycerol	1.10
Pentan-3-ol	0.39	2-Propyn-1-ol, propargyl alcohol	1.10
Cyclopentanol	0.44	3-Methylphenol	1.22
Pentan-2-ol	0.45	2,2,2-Trifluoroethanol(TFE)	1.36
2-Butanol, <i>sec</i> -butanol	0.46	Water	1.54
Cyclohexanol	0.47	1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP)	1.86

2.1 Preliminary considerations

As most chemists, we have chosen as the source of our α_1 parameter the solvatochromism of B(30) measured by the parameter $E_T(30)$ defined⁵ as the molar electronic transition energy (historically in kcal mol⁻¹; 1 cal = 4.184 J) of the dye:

$$(1) \ E_T(30) = hcN_A\tilde{\nu} = 28591/\lambda$$

where h , c , and N_A are Planck's constant, speed of light, and Avogadro's constant, respectively, $\tilde{\nu}$ is the wavenumber (cm⁻¹), and λ the wavelength (nm) of the solvatochromic band attributed to an intramolecular charge-transfer transition from the phenolate moiety to the pyridinium ring. Indeed, (a) this dye shows an exceptional solvatochromism with $\Delta E_T(30) = 32.9$ kcal mol⁻¹ from CCl₄ to 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), (b) we have now at hand 270 $E_T(30)$ values carefully measured in the same laboratory with the same experimental conditions on purified solvents, (c) the charge-transfer transition of B(30) is accompanied by a loss of electron density at the phenolate oxygen, therefore by a decrease of its HBA character, hence $E_T(30)$ contains an important α_1

contribution. However, there is also a significant contribution of non-specific solvent effects that must be subtracted to isolate α_I .

This task will be accomplished by different kinds of SCMs (theoretical, semi-empirical, and experimental). One could also calculate the contribution of the non-specific interactions by applying the Kamlet-Abboud-Taft linear solvation energy relationship (LSER)¹² of eq 2 to $E_T(30)$:

$$(2) \quad E_T(30) = \mathbf{E}_T^0 + s \pi^* + d \delta + a \alpha + b \beta$$

wherein \mathbf{E}_T^0 is the intercept and π^* , α , and β , respectively, describe the solvent's dipolarity/polarizability, HBD ability, and HBA ability, while δ corresponds to a polarizability correction. The regression coefficients s , d , a , and b measure the sensitivity of $E_T(30)$ toward a change of the corresponding four parameters. This method is not to be encouraged since the α values obtained by eq 3 depend upon the quality of too many solvent parameters, and on the robustness of the regression coefficients.

$$(3) \quad \alpha = [E_T(30) - (\mathbf{E}_T^0 + s \pi^* + d \delta + b \beta)]/a$$

The LSER methodology will however be used for the statistical analysis of the many physicochemical properties claimed to be only α -sensitive, but we will prefer to use the LSER of eq 4:

$$(4) \quad P = P^0 + di DI + e ES + a \alpha_1 + b \beta_1$$

wherein P is the property, P^0 is the intercept, and DI , ES , α_1 , and β_1 , respectively, describe the dispersion-induction, electrostatic, solute HBA/solvent HBD, and solute HBD/solvent HBA interactions.¹³ The advantages of eq 4 over eq 2 have been explained elsewhere.¹³ The analysis will focus on the percent of contribution of the α_1 parameter to the variance of P in order to know if the determination of the HBD ability of solvents can be accomplished from a single probe.

To perform any SCM, it is necessary to classify solvents according to their capabilities to donate or not donate hydrogen bonds to the solute. The criterion on which this classification is accomplished lies on the IUPAC definition of the hydrogen bond¹⁴ as discussed in a previous paper.⁹ With this criterion, all solvents with O–H, N–H, and Csp–H groups are classified as HBDs. Solvents with Csp²–H and Csp³–H groups are classified as HBDs only when there is experimental (e.g. spectral, thermodynamic, and/or crystallographic) and/or theoretical evidence of hydrogen bond formation in ordinary conditions (liquid state, room temperature, and atmospheric pressure). This is the case of (non-exhaustively): pentafluorobenzene, trichloroethene, (*Z*)- and (*E*)-1,2-dichloroethene, trichloromethane, dichloromethane, pentachloroethane, tribromomethane, dibromomethane, acetonitrile, nitromethane, and acetone. The case of acetone is interesting since this solvent was found non-HBD (*SA* = 0) in the Catalán *SA* scale of HBD strength of solvents.¹⁵ However, there is spectroscopic and thermodynamic evidence of hydrogen bonding between acetone and pyridine *N*-oxide in cyclohexane.¹⁶ Therefore acetone must be classified as HBD solvent.

2.2 The solvatochromic comparison of the Reichardt's dye and of 4-nitroanisole does not fulfill the Kamlet-Taft conditions for a safe SCM

The initial construction (1976) of the Kamlet-Taft α scale³ involved the systematic application of the SCM to many processes strongly dependent on the HBD ability of solvents such as: (a) the solvatochromism of the Reichardt's dye, Brooker's merocyanine dye, and Burgess' dye (an iron coordination compound), (b) the Gibbs energy of transfer of the Et₄N⁺I[−] ion pair from methanol to solvents, and (c) the solvolysis of *tert*-butyl chloride. They were compared to the solvatochromism of 4-nitroanisole, and the results were averaged and given an origin ($\alpha = 0$ for non-HBD solvents) and a format ($\alpha = 1$ for methanol). New solvents are difficult to incorporate in this statistical framework, so chemists were obliged to determine new α values from a single reference solvatochromic comparison, and they often selected the comparison of B(30) with 4-nitroanisole. The equation of the line comparing the non-HBD solvents being³

$$(5) \quad \tilde{\nu} [\text{B(30)}] = -1.873 \tilde{\nu} (\text{4-nitroanisole}) + 74.58 \text{ k cm}^{-1}$$

and the displacement of methanol from this line being 6.24 k cm^{-1} , most new α values are calculated by means of the Kamlet-Taft eq 6:

$$(6) \quad \alpha = [\tilde{\nu} (\text{B30}) - (-1.873 \tilde{\nu}(\text{4-nitroanisole}) + 74.58)] / 6.24$$

However, a simple look at the structures of the two indicators in Scheme 1 casts doubt on their similar solvatochromism in non-HBD solvents, especially since the latter is negative for B(30) but positive for 4-nitroanisole (hence the negative slope of the comparison line). We have therefore reexamined the comparison of B(30) and 4-nitroanisole on a very large diversified sample of 150 non-HBD and 67 HBD solvents. These data originate from our laboratory and were published in 1991 and 1994 for 4-nitroanisole^{17,18} and 2014 for B(30).¹⁹ At the time of Kamlet and Taft much less experimental data were available since they could study only 17 non-HBDs and 13 HBDs. Our results are dramatically different of those of Kamlet and Taft since the requirement that the solvatochromic shifts of B(30) and 4-nitroanisole in non-HBD solvents should be similar is not observed, the determination coefficient r^2 being only 0.670 as illustrated in Figure 1. The second requirement for a reliable SCM that all data points representing HBD solvents should be displaced from the comparison line of non-HBD solvents in the same direction is also not fulfilled in Figure 1 since 16 HBD solvents out of 67 ones corresponding to Csp-H, Csp²-H, Csp³-H, and N-H donors (e.g. phenylacetylene, trichloroethene, trichloromethane, and diallylamine) deviate downwards from the comparison line whereas the other HBD solvents deviate upwards. Finally, the relative magnitudes of displacements are not always consistent with the chemistry involved. For example (a) the displacement of chloroacetonitrile (1.47 k cm^{-1}) is less than acetonitrile (2.30 k cm^{-1}) despite the electron-withdrawing effect of the chloro substituent that increases the HBD ability; (b) similarly the displacement of 2,2,2-trichloroethanol (3.00 k cm^{-1}) lower than that of ethanol (5.15 k cm^{-1}) does not take into account the electron-withdrawing effect of CCl₃, and (c) 3-methylphenol shows a displacement of 3.15 k cm^{-1}

inferior to those of most alcohols (between 4 and 6 k cm^{-1}) despite the well-known higher HBD ability of phenols compared to alcohols.¹¹

As a consequence, α values calculated by means of eq 6 must be considered cautiously. Thus, the α values of glycol ethers⁶ with $\alpha = 0.40$ for $\text{CH}_3\text{CH}(\text{OMe})\text{CH}_2\text{OMe}$, and those of hydrofluoroethers⁷ with $\alpha = 0.602$ for $\text{CH}_3\text{O}(\text{CF}_2)_3\text{CF}_3$ and $\alpha = 0.598$ for $\text{C}_2\text{H}_5\text{O}(\text{CF}_2)_3\text{CF}_3$ are clearly too high compared to those of the best $\text{Csp}^3\text{-H}$ donors ($\alpha_1 = 0.31$ for chloroacetonitrile). On the contrary, those of alkanolamines⁸ (from 0.40 to 0.64) appear too weak compared to that of ethanol (0.75).

Therefore, the determination of α values by comparing the solvatochromism of B(30) and 4-nitroanisole must be abandoned in favor of the theoretical SCM that we will recall and whose validity we will now confirm.

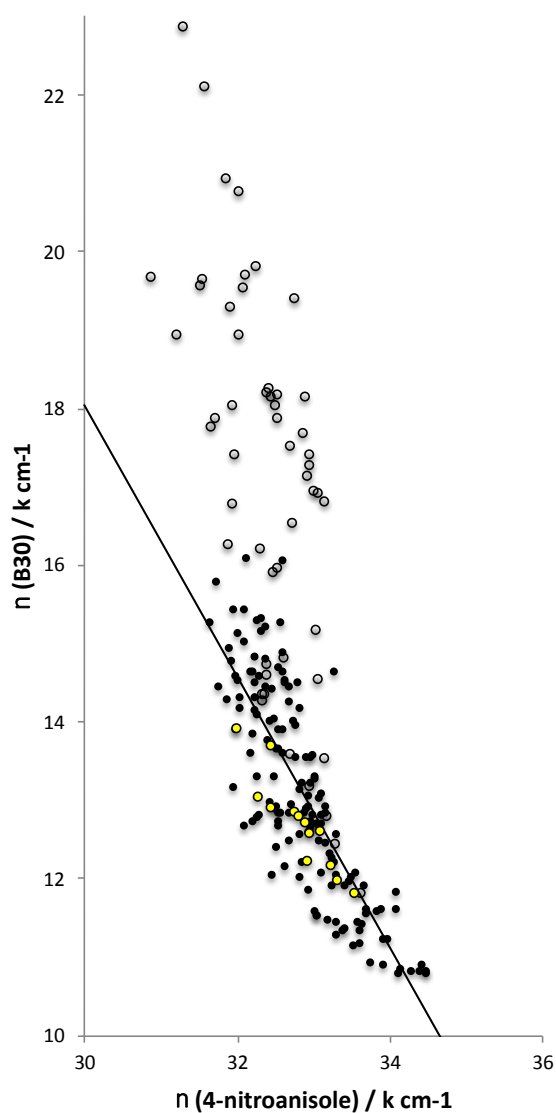


Figure 1. Kamlet-Taft solvatochromic comparison of the Reichardt betaine dye B(30) with 4-nitroanisole. Black circles: 150 non-HBDs fixing the reference line. Red circles: 51 HBDs displaced above the line. Yellow circles: 16 HBDs displaced abnormally below the line.

2.3 Validity of the theoretical solvatochromic comparison method

In this method⁹ $E_T(30)$ values were calculated by a PCM-TD-DFT method with the CAM-B3LYP exchange-correlation functional and the 6-31++G(d,p) atomic basis set. For the electronic excited

state, the linear-response PCM model in its non-equilibrium limit was used. The PCM model accounts only for non-specific effect. The method takes advantage of this limitation as follows.

Firstly, experimental $E_T(30)$ values are plotted against calculated $E_T(30)$ (PCM-TD-DFT) ones for a series of 31 non-HBD solvents from alkanes to DMSO. As shown on Figure 1 in ref 9, these solvents draw a comparison line of eq 7

$$(7) \quad E_T(30)(\text{experimental}) = 0.693 E_T(30) (\text{PCM-TD-DFT}) + 1.31$$

with $n = 31$, a determination coefficient $r^2 = 0.953$, and a standard deviation of the estimate $s = 1.0$ kcal mol⁻¹ (to be compared with a maximum experimental error of 0.5 kcal mol⁻¹). Because B(30) has a merocyanine-like electronic structure and that TD-DFT calculations overshoot the electronic transition energies of this family of cyanine dyes, the calculated $E_T(30)$ values are overestimated and the slope of the comparison line (0.693) is far from unity. However, we need only a *relative* agreement between experimental and calculated values. This agreement is excellent since r^2 is greater than 0.95.

Secondly, data points representing HBD solvents are added to this graphic. It is found that they are all displaced above this comparison line by an amount $\Delta E_T(30)$ ranging from 0.30 kcal mol⁻¹ for cyclohexylamine to 23.95 kcal mol⁻¹ for HFIP. These displacements are explained by the hypsochromic band shifts induced by hydrogen bonding to the phenolate oxygen atom of B(30) that are not accounted for in the PCM model. They are calculated by eq 8

$$(8) \quad \Delta E_T(30) = E_T(30)(\text{experimental}) - [0.693 E_T(30) (\text{PCM-TD-DFT}) + 1.31]$$

Lastly, to obtain a dimensionless scale of HBD ability, we take the $\Delta E_T(30)$ value of 12.87 kcal mol⁻¹ for methanol as the scaling factor and define an α_1 scale according to eq 9

$$(9) \quad \alpha_1 = \Delta E_T(30)/12.87$$

In this way $\alpha_1 = 0$ for non-HBD solvents and $\alpha_1 = 1$ for methanol and the α_1 scale has the same origin and format as the α scale of Kamlet and Taft.

PCM-TD-DFT calculations of the $E_T(30)$ values of 63 HBD solvents and 1 halogen-bond donor solvent⁹ yield the 64 theoretical α_1 values collected in Table 1. To test the validity of these values, we have applied eq 10 to varied physicochemical properties P known to depend almost only on the solvent's HBD ability.

$$(10) \quad P = P^0 + a \alpha_1$$

The results are given in Table 2 and illustrated by Figures 2 and 3. The satisfactory to excellent determination coefficients constitute a first validation of the α_1 scale.

Table 2. Correlations of thermodynamic, kinetic, and electrochemical properties P according to eq 10^a.

no.	property P	n	r^2	ref
1	Gibbs energy of transfer of Cl^- from water to solvents	11(11)	0.943	²⁰
2	rate of the $\text{S}_{\text{N}}2$ reaction $\text{Cl}^- + \text{CH}_3\text{I}$	10(7)	0.924	²¹
3	rate of <i>cis-trans</i> isomerization of $\text{Pt}(\text{PEt}_3)_2(3\text{-MeC}_6\text{H}_4)\text{Cl}$	8(8)	0.875 ^b	²²
4	proton-transfer time of 7-azaindole	12(12)	0.938	²³
5	redox potential of hexacyanoferrate(III)-hexacyanoferrate(II)	9(5)	0.971	²⁴

^a n = number of data points (number of HBD solvents in parentheses), r^2 = determination coefficient. ^b This coefficient rises to 0.986 when the outlier 2-methoxyethanol is excluded.

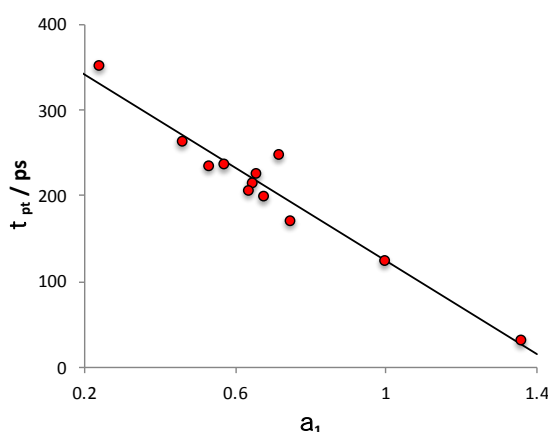


Figure 2. Plot of the proton-transfer time of 7-azaindole in 12 alcohols from *tert*-butanol to 2,2,2-trifluoroethanol against the theoretical α_1 scale. Data from ref ²³.

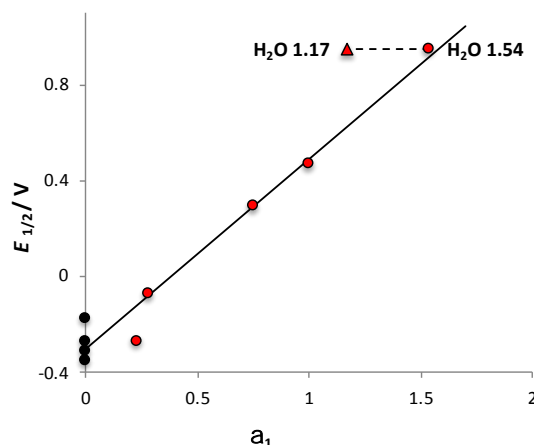


Figure 3. Plot of the redox potential of hexacyanoferrate(III)-hexacyanoferrate(II) in non-HBD (black circles) and HBD (red circles) solvents. Data from ref ²⁴. For water, the α_1 value (1.54) correlates the solvent effect much better than the Kamlet-Taft α (1.17).

A second validation is found in the agreement between the α_1 scale and the results of a solvatochromic comparison of the two 2,6-di(carbamoyl)-substituted pyridinium *N*-phenolate betaine dyes **4** and **5**²⁵ of Scheme 1. In **5** two intramolecular hydrogen bonds N–H...O[−] are formed so that the formation of intermolecular hydrogen bonds with added HBD solvents must be reduced.²⁵ Consequently, the solvatochromic comparison of **4** and **5** shows the following:

(a) in a plot of $E_T(\mathbf{4})$ vs $E_T(\mathbf{5})$ data points representing non-HBD solvents draw a comparison line of equation 11

$$(11) \quad E_T(\mathbf{4}) = 0.864 E_T(\mathbf{5}) - 3.27$$

with $n = 8$, $r^2 = 0.980$, and $s = 0.55 \text{ kcal mol}^{-1}$

(b) all HBD solvents are significantly displaced above this comparison line by an amount $\Delta E_T(\mathbf{4-5})$ calculated by eq 12

$$(12) \quad \Delta E_T(\mathbf{4-5}) = E_T(\mathbf{4}) - [0.864 E_T(\mathbf{5}) - 3.27]$$

ranging from 1.14 kcal mol⁻¹ for acetonitrile to 9.73 kcal mol⁻¹ for 2,2,2-trifluoroethanol (Table SI-1). Since these displacements are explained by the reduced ability of **5** to receive intermolecular hydrogen bonds from HBD solvents on its phenolate oxygen, they reflect the HBD ability of solvents. They are related to the α_1 scale by eq 13

$$(13) \quad \Delta E_T(\mathbf{4-5}) = 7.56 \alpha_1 + 0.13(\pm 0.45)$$

with $n = 14$, $r^2 = 0.915$, $s = 0.81$ kcal mol⁻¹, and an intercept not statistically different from zero (Figure 4). The fact that α_1 is able to explain 91.5% of the variance of an experimental measure of the HBD ability of solvents and is proportional to this quantity confirms the validity of the theoretical SCM and of the resulting α_1 scale.

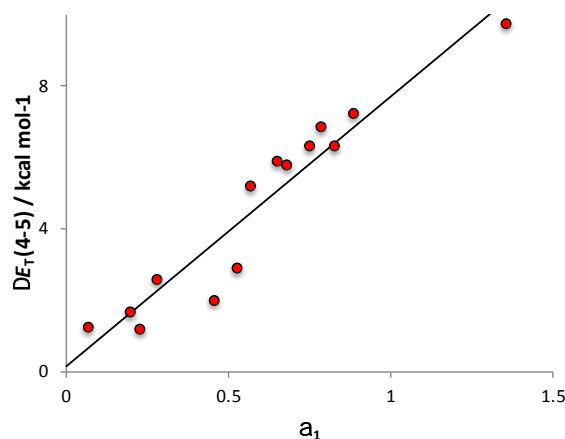


Figure 4. Enhanced hypsochromic band shifts induced by hydrogen bonding to the phenolate oxygen of the betaine dye **4** compared to betaine dye **5** against the theoretical α_1 scale for 14 HBD solvents from acetonitrile to 2,2,2-trifluoroethanol. Data from Table SI-1.

2.4 A semi-empirical solvatochromic comparison method

Thanks to commercial user-friendly packages and to computational details given in ref 9, the calculation of $E_T(30)$ (PCM-TD-DFT) values is straightforward for computational chemists. However, the task is harder for experimental chemists. So, we have devised an easier method based on the McRae formulation of solvatochromic shifts¹⁰ to partition $E_T(30)$ into a non-specific and an HBD part.

McRae has analysed the effects of electric dipole interactions on the electronic states of a solute and derived an expression for the corresponding solvatochromic shifts by means of the perturbation theory considering solvent effect as the perturbation. The introduction of a number of approximations regarding both the application of the second-order perturbation theory and the solute model (reduced to a point dipole in the centre of a spherical cavity) permits the relation of solvatochromic shifts to the refractive index n and static relative permittivity ε of the solvent. A simplified McRae's expression²⁶ for the $S_0 \rightarrow S_1$ transition energy of the dye B(30) can be written as eq 14:

$$(14) E_T(30) = E_T^0(30) + (A+B)\frac{n^2-1}{2n^2+1} + C\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + D\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)^2$$

$E_T^0(30)$ represents the transition energy in the gas phase and the parameters A-D are functions of the properties of the dye: oscillator strength, dipole moments and polarizabilities in the ground and excited states, and cavity radius. In this work, parameters A-D will be viewed as empirical constants evaluated from the multiple linear regression of experimental $E_T(30)$ values into the explanatory variables $f(n^2)$, $g(n^2, \varepsilon)$, and $h(n^2, \varepsilon)$ of eq 14. Each term of this equation represents a dye-solvent interaction as follows:

- A term: interaction between mutually induced dipoles of dye and solvent (London dispersion force)
- B term: interaction between permanent dye dipole and induced solvent dipole (induction force)

- C term: interaction between permanent dipoles of dye and solvent (electrostatic force)
- D term: interaction between induced dye dipole and permanent solvent dipole (Stark solvent effect).

This list does not contain the hydrogen bonding to the phenolate oxygen of B(30). Indeed, like the PCM, the McRae calculations only take into account non-specific interactions. This limitation is exploited to estimate the hydrogen-bonding contribution to $E_T(30)$ by the *semi-empirical* solvatochromic comparison method in a way similar to that of the *theoretical* one.

We start from our database¹⁹ of 248 solvents for which both $E_T(30)$, n , and ϵ have been carefully determined in our laboratory and divide these solvents in HBDs and non-HBDs. With the criterion used above, 176 solvents are considered non-HBDs. Their $E_T(30)$ values span from 30.8 (2-methylbutane) to 46.0 (propylene carbonate) kcal mol⁻¹, while their n values from 1.291 (methyl trifluoroacetate) to 1.702 (1-iodonaphtalene) and ϵ values from 1.84 (n -pentane) to 62.93 (propylene carbonate) vary in a very large range. This permits a satisfactory fit of $E_T(30)$ with $f(n^2)$, $g(n^2, \epsilon)$, and $h(n^2, \epsilon)$, with a determination coefficient $r^2 = 0.879$ and a standard deviation of the estimate $s = 1.30$ kcal mol⁻¹. The four more deviating solvents (by more than $2s$) are: 1,4-difluorobenzene, 1,4-dioxane, dimethyl carbonate, and diethyl carbonate. These molecules carrying several opposed bond dipoles appear more polar locally to the dye molecule than expected on the basis of their weak bulk relative permittivity. Their exclusion yields eq 15:

$$(15) \quad E_T(30) = 27.0 + 24.7 \frac{n^2-1}{2n^2+1} + 10.0 \left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right) + 9.4 \left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right)^2$$

with $r^2 = 0.904$ and $s = 1.17$ kcal mol⁻¹ for 172 non-HBD solvents. Each regression coefficient is significant at a confidence level greater than 99.99%. The C term (interaction between permanent dipoles of dye and solvent) is the greatest contributor (53%) to the variance of $E_T(30)$, as expected from the large dipole moment change (-7 D)²⁷ during the transition. Satisfactorily, the intercept of 27.0 kcal mol⁻¹ is found close to the value of 26 kcal mol⁻¹

range calculated²⁷ for the gas-phase vertical excitation energy at a high ab initio level (the experimental gas-phase value of $E_T(30)$ is not experimentally measurable⁵).

The second category of solvents consists of 72 HBD solvents. This set includes all molecules containing O–H, N–H, and Csp–H groups, as well as a number of molecules with Csp²–H and Csp³–H groups (vide supra). In the plot of experimental against calculated (by eq 15) $E_T(30)$ values shown in Figure 5, all (except the very weak HBD piperidine) data points representing HBD solvents are displaced above the line of slope unity corresponding to non-HBD solvents. These displacements are evidently the consequence of the hypsochromic shift caused by hydrogen bonding to the phenolate oxygen not taken into account by eq 15. They are calculated from eq 16:

$$(16) \quad \Delta E_T(30) = E_T(30)(\text{experimental}) - E_T(30)(\text{calculated by eq 15})$$

They are given in Table SI-2. They range from 12s of eq 15 for HFIP to 0.4s for acetone. A number of aliphatic amines, Csp²–H, and Csp³–H donors show displacements less than 2s, but this is inherent to their very weak HBD strength.

To assess the validity of the semi-empirical SCM, we have related the $\Delta E_T(30)$ values of Table SI-2 to the α_1 scale (Figure 6). The linear correlation is

$$(17) \quad \Delta E_T(30) = 12.47 \alpha_1 + 0.47 (\pm 0.10)$$

with $n = 58$ HBDs, $r^2 = 0.994$, and $s = 0.40 \text{ kcal mol}^{-1}$.

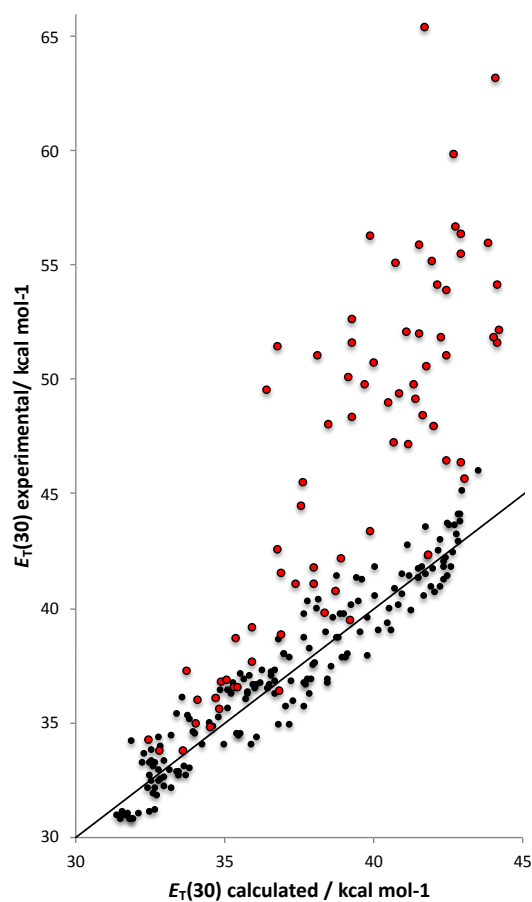


Figure 5. Semi-empirical solvatochromic comparison method. Plot of experimental $E_T(30)$ values against $E_T(30)$ calculated by the McRae equation. Black circles: non-HBD solvents. Red circles: HBD solvents.

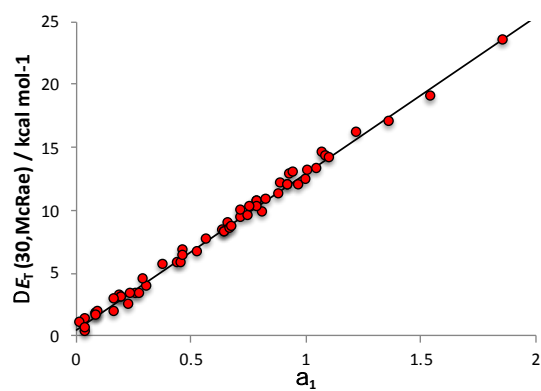


Figure 6. Correlation between the α_1 scale calculated from the theoretical SCM and the hydrogen bonding contribution to $E_T(30)$ calculated by the semi-empirical SCM for 58 HBD solvents from acetone to HFIP.

The high statistical significance of this correlation enables to consider the semi-empirical SCM as a secondary method to determine new α_1 values (the primary method being the theoretical SCM). The linear regression of α_1 into $\Delta E_T(30)$ yields eq 18 that is used for 37 solvents: 1-alkynes, amides, amines, alcohols (mainly diols), ethyl lactate, alkanolamines, and hydrofluoroethers. These values are gathered in bold in Table 1.

$$(18) \quad \alpha_1 = 0.0797 \Delta E_T(30) - 0.033$$

The α_1 values of five classes of solvents are worthy of comments, the monosubstituted acetylenes $\text{HC}\equiv\text{CX}$, the solvolytic solvents, the green solvents, the alkanolamines, and the hydrofluoroethers.

When the theoretical α_1 value of phenylacetylene is added to the semi-empirical ones of 1-nonyne, propargyl chloride, and ethyl propiolate, it is found that the α_1 values of this set are closely related ($r^2 = 0.969$) to the hydrogen-bond acidity scale $\lg K$ of monosubstituted acetylenes,²⁸ where K is the hydrogen-bond formation constant of the hydrogen-bonded complex $\text{XC}\equiv\text{CH}\dots\text{OPPh}_3$ in CCl_4 . This excellent correlation lends confidence to the α_1 values of this class of organic liquids.

The α_1 values of hydroxylic solvolytic solvents are important to know since hydrogen-bond donating solvents stabilize developing anion in the transition state of the $\text{S}_{\text{N}}1$ solvolysis reaction.²⁹ It is satisfactory that the mixed semi-empirical and theoretical α_1 values of hydroxylic solvents correlate well a consistent set³⁰ of 23 solvolysis rates of *tert*-butyl bromide ($r^2 = 0.920$) and *tert*-butyl iodide ($r^2 = 0.929$) as illustrated by Figure 7.

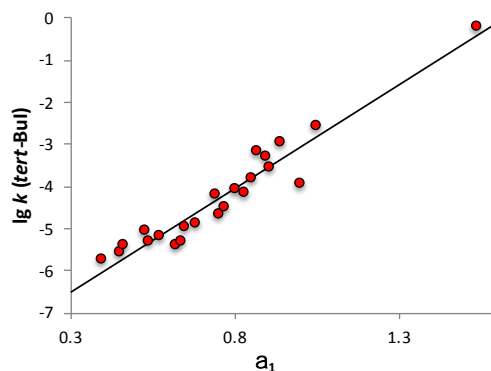


Figure 7. Correlation between the logarithm of the solvolysis rate (s^{-1}) of *tert*-butyl iodide and the theoretical and semi-empirical α_1 values of 23 solvolytic solvents from pentan-3-ol to water. Data from ref 30.

Concerning the green solvent ethyl lactate, it is found here an α_1 (0.78) significantly higher than the one determined³¹ by the Kamlet-Taft solvatochromic method (0.64). This situation is also encountered for other green HBD solvents³² as shown in Table 3. It is particularly dramatic that the α values of such important green solvents as water and glycerol have been so heavily underestimated for so many years. We insist that the α_1 value of water is 1.54 and not in the range 1.17-1.23 obtained³² by the misused Kamlet-Taft method.

Table 3 Comparaison of the α_1 values of green solvents, alkanolamines, and hydrofluoroethers determined by the semi-empirical solvatochromic comparison method to the α values determined by the misused Kamlet-Taft method.

Solvent		α	Ref	α_1	Ref
Green solvents					
ethyl lactate	CH ₃ CH(OH)COOEt	0.63	³¹	0.78	a
water	H ₂ O	1.17-1.23	³²	1.54	⁹
glycerol	HOCH ₂ CH(OH)CH ₂ OH	0.80-0.93	³²	1.10	⁹
glycerol monomethyl ether	MeOCH ₂ CH(OH)CH ₂ OH	0.83	³²	0.92	⁹
glycerol dimethyl ether	MeOCH ₂ CH(OH)CH ₂ OMe	0.72	³²	0.76	⁹
Alkanolamines					
2-aminoethanol	H ₂ NCH ₂ CH ₂ OH	0.40	⁸	0.70	a
diethanolamine	HOCH ₂ CH ₂ NHCH ₂ CH ₂ OH	0.59	⁸	0.86	a
triethanolamine	N(CH ₂ OH) ₃	0.64	⁸	0.88	a
Hydrofluoroethers					
methoxy-nonafluorobutane	CH ₃ O(CF ₂) ₃ CF ₃	0.60	⁷	0.40	a
ethoxy-nonafluorobutane	CH ₃ CH ₂ O(CF ₂) ₃ CF ₃	0.60	⁷	0.38	a

^a This work.

In the same vein, the Kamlet-Taft α values of alkanolamines⁸ are underestimated. For example, the Kamlet-Taft $\alpha = 0.59$ for diethanolamine is clearly too low compared to the $\alpha_1 = 0.87$ of the structurally similar diethylene glycol HOCH₂CH₂OCH₂CH₂OH.

Lastly, although seemingly high for Csp³-H donors, the α_1 values of hydrofluoroethers (0.38 and 0.40) are nevertheless more chemically significant than the Kamlet-Taft excessive values of 0.60.⁷

The addition of the theoretical and of the semi-empirical α_1 values gives a comprehensive list of 101 values for molecular solvents gathered in Table 1. There remains to characterize the HBD ability of ionic liquids. This will be accomplished in the next part by a method comparing the solvatochromism of two pyridinium *N*-phenolate betaine dyes, B(30) and B(33).

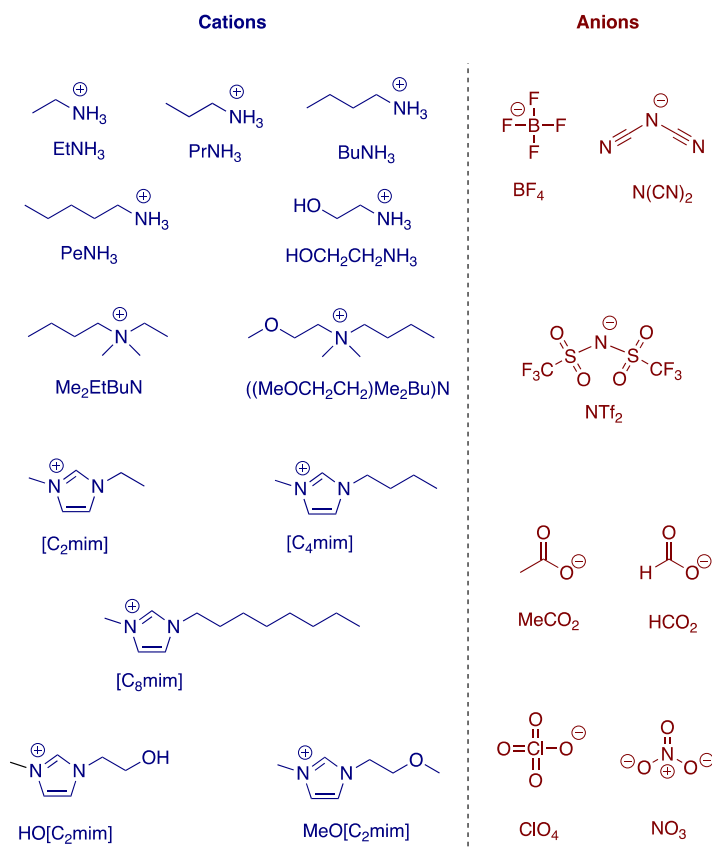
2.5 An experimental solvatochromic comparison method for ILs

Looking at the structures of Scheme 1, it is evident that B(33) is a much better model of non-specific effects for B(30) than 4-nitroanisole. Moreover B(33) is a worse proton acceptor ($pK_a = 4.78$)⁵ than B(30) ($pK_a = 8.64$)⁵ by virtue of the electron-withdrawing effect of the chloro substituents in B(33). Lastly, both B(30) and B(33) are commercially available. We have so been able to obtain $E_T(30)$ and $E_T(33)$ for 22 non-HBD and 24 HBD molecular solvents (Table SI-3) as well as for 30 ILs (from the literature,^{33–36} Table 4) with diversified cations and anions (Scheme 2).

Table 4. Literature $E_T(33)$ and $E_T(30)$ values (kcal mol^{−1}) of ionic liquids, enhancement of the hydrogen-bonding contribution in $E_T(30)$ compared to $E_T(33)$, $\Delta E_T(30-33)$ (kcal mol^{−1}), and HBD parameter α_1 .

IL	$E_T(33)$	$E_T(30)$	Ref	$\Delta E_T(30-33)$	α_1
[C8mim]Br	60.07	50.86	33	1.57	0.57
[C4mim]Cl	59.93	50.61	33	1.42	0.54
[C4mim]BF ₄	61.36	52.26	33	2.01	0.68
[C4mim]N(CN) ₂	60.18	51.15	33	1.77	0.62
[C4mim]NTf ₂	60.70	51.60	34	1.84	0.64
MeO-[C2mim]N(CN) ₂	60.60	52.40	34	2.71	0.84
MeO-[C2mim]NTf ₂	66.20	54.50	34	0.60	0.34
[(Me ₂ EtBu)N]N(CN) ₂	58.00	49.00	34	1.27	0.50
[(Me ₂ EtBu)N]NTf ₂	66.20	59.00	34	5.10	1.49
[(MeOCH ₂ CH ₂)(Me ₂ Bu)N]N(CN) ₂	58.70	49.00	34	0.74	0.22
[(MeOCH ₂ CH ₂)(Me ₂ Bu)N]NTf ₂	66.50	58.80	34	4.67	1.31
HO-[C2mim]NTf ₂	70.60	60.80	34	3.59	1.05
HO-[C2mim]MeCO ₂	60.80	51.20	35	1.36	0.52
HO-[C2mim]PF ₆	69.40	61.70	35	5.39	1.47
HO-[C2mim]ClO ₄	68.10	60.30	35	4.97	1.37
[C2mim]PF ₆	61.80	52.60	35	2.01	0.68
[C2mim]NTf ₂	61.80	52.00	35	1.41	0.54
[C2mim]ClO ₄	61.80	52.40	35	1.81	0.63
[C2mim]N(CN) ₂	61.10	51.70	35	1.63	0.59
[C2mim]NO ₃	61.90	51.50	35	0.83	0.40
[C2mim]MeCO ₂	58.70	49.80	35	1.54	0.57
[EtNH ₃]HCO ₂	67.75	59.81	36	4.74	1.32
[BuNH ₃]HCO ₂	65.28	57.99	36	4.78	1.33
[PeNH ₃]HCO ₂	64.98	56.96	36	3.97	1.14
[PrNH ₃]MeCO ₂	64.98	56.96	36	3.97	1.14

[PeNH ₃]MeCO ₂	63.68	55.73	³⁶	3.72	1.08
[EtNH ₃]NO ₃	70.08	61.75	³⁶	4.93	1.37
[HOCH ₂ CH ₂ NH ₃]NO ₃	71.30	62.02	³⁶	4.28	1.21
[PrNH ₃]NO ₃	69.57	61.36	³⁶	4.92	1.36
[BuNH ₃]NO ₃	68.40	60.32	³⁶	4.76	1.33



Scheme 2. Structures and abbreviations of the cations and anions of the studied ILs.

In a plot of $E_T(30)$ vs $E_T(33)$ (Figure 8) 22 non-HBD molecular solvents spanning a large range of $E_T(30)$ values from benzene (34.3 kcal mol⁻¹) to propylene carbonate (46.0 kcal mol⁻¹) draw a comparison line of eq 19

$$(19) \quad E_T(30) = 0.752 E_T(33) + 4.08$$

with $r^2 = 0.995$, and $s = 0.25$ kcal mol⁻¹. The very high determination coefficient testifies to the similarity of non-specific effects on the solvatochromism of the two betaines. On the contrary, because B(30) is more capable of hydrogen bonding acceptance than B(33), HBD molecular solvents stand systematically above this comparison line as shown in Figure 8. Their deviations $\Delta E_T(30-33)$ are calculated by eq 20

$$(20) \quad \Delta E_T(30-33) = E_T(30) - [0.752 E_T(33) + 4.08]$$

They range from 0.14 kcal mol⁻¹ for the very weak HBD acetone to 7.41 kcal mol⁻¹ for the strong HBD HFIP. Their relative magnitudes are chemically significant since well related to the reliable theoretical α_1 scale ($r^2 = 0.904$, $n = 24$).

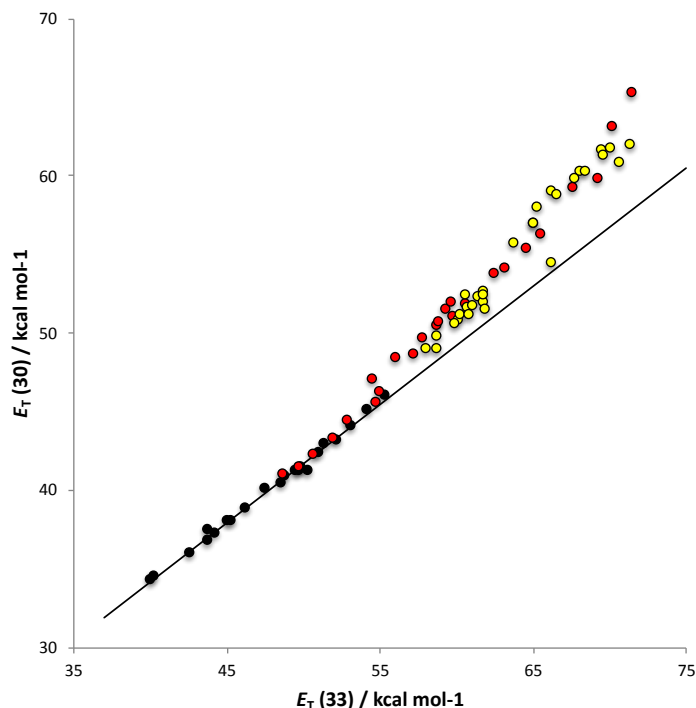


Figure 8. Solvatochromic comparison of betaine dyes B(30) and B(33). The line fits the non-HBD solvents (black circles). The molecular HBDs (red circles) and the ILs (yellow circles) stand above this line. Data from Table SI-3 for molecular solvents and Table 4 for ILs.

The validity of the solvatochromic comparison of $E_T(30)$ with $E_T(33)$ for molecular solvents leads us to extend it to ILs. On the graph of Figure 8, we now report the E_T values of 30 ILs. They are all displaced upwards from the comparison line by statistically significant amounts ranging from $\Delta E_T(30-33) = 0.60$ kcal mol⁻¹ (2.4 σ of eq 19) for 1-(2-methoxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide to $\Delta E_T(30-33) = 5.39$ kcal mol⁻¹ (21.6 σ of eq 19) for 1-hydroxyethyl-3-methylimidazolium hexafluorophosphate. These $\Delta E_T(30-33)$ values of ILs can be translated into α_1 values of ILs by means of eq 21 established from molecular solvents:

$$(21) \quad \alpha_1 = 0.236 \Delta E_T(30-33) + 0.20 (\pm 0.05)$$

with $n = 24$ molecular HBDs, $r^2 = 0.904$, and $s = 0.14$. The results are reported in Table 4.

Their reliability is strongly dependent on the purity and dryness of the ILs, so that the E_T values reported by various authors for the same IL are sometimes different from each other. In this case, Machado et al⁵ recommend choosing the lower value since acidic impurities and water increase E_T . Thus, the $E_T(33)$ value of $60.18 \text{ kcal mol}^{-1}$ from Spange et al³³ was preferred to that of 61.40 from Zhang et al³⁵ for $[\text{C4mim}]^+ [\text{N}(\text{CN})_2]^-$ and consequently an α_1 value of 0.62 was deduced instead of 0.32 from the Zhang datum.

The variation of the α_1 values of studied ILs is quite important (from 0.34 to 1.47). It depends on the strength of the dye-IL interactions. These are hydrogen bonding to the phenolate oxygen and charge-charge interaction between the IL cation and the anionic oxygen. For the cations of the studied ILs, the positive charge is either delocalized in an imidazolium aromatic ring or sterically hindered in tetraalkylammonium cations, so that the charge-charge interaction must be less important than hydrogen bonding. It is seen in Table 4 that α_1 values depend not only on the structure of the IL cation but also on the basicity of the anion.

Concerning the cation, the α_1 order is:

monoalkylammonium (1.08 - 1.37) \approx hydroxyethylmim (1.05 - 1.37 , excluding the acetate) \gg alkylmim (0.40 - 0.68)

Unsurprisingly, the OH group of hydroxyl ILs and the NH_3^+ group of ammonium ILs are much better HB donating than the C(2)-H group of imidazolium ILs. The importance of $\text{O}-\text{H}\cdots\text{O}^-$ hydrogen bonds can be confirmed if one compares the α_1 value of [hydroxyethylmethylimidazolium][NTf₂] with that of [methoxyethylmethylimidazolium][NTf₂]: the methylation of the OH group decreases α_1 by 0.71 unit.

The range of α_1 variation of alkylimidazolium ILs (0.40-0.68) is generally explained by the basicity order of the anions X^- . Indeed, imidazolium ILs are structured through C(2)–H... X^- hydrogen bonds. Such hydrogen bonds disadvantage the hydrogen bond C(2)–H... O^- all the more the more basic the anion.³⁷ So, for the [C4mim] and [C8mim] ILs, the α_1 values increase from 0.54 for the very basic anion Cl^- to 0.68 for the poorly basic anion BF_4^- in the regular order of β_1 values of HBA basicity of anions:



The influence of the anion basicity is less regular in the [C2mim] ILs, although it is also found that the more acidic IL corresponds to the less basic anion PF_6^- . Surprisingly, the anion influence is dramatic in tetraalkylammonium ILs, since α_1 increases from 0.50 for $[Me_2EtBuN]^+[N(CN)_2]^-$ to as much as 1.49 for $[Me_2EtBuN]^+[NTf_2]^-$ and from 0.22 for $[Me_2Bu(CH_2CH_2OMe)N]^+[N(CN)_2]^-$ to 1.31 for $[Me_2Bu(CH_2CH_2OMe)N]^+[NTf_2]^-$.

Whatever the chemical significance of these results, the standard deviation of the estimate of α_1 values from eq (21) is rather high (0.14 unit). Thus, we have looked for a more accurate method. Many groups have proposed methodologies to determine α values using a single solvent-dependent process, such as the solvatochromism of the dicyano-bis(1,10-phenanthroline)iron(II) complex³⁸ or the solvent effect on the difference d_{24} between the ^{13}C chemical shifts of the C(2) and C(4) carbons of pyridine *N*-oxide.³⁹ These methods are attractive since, for a given solvent, they require a single measurement on a single probe. Nevertheless, their validity lies on the assumption that the chosen property depends only on the HBD strength of solvents and is not contaminated by non-specific effects. The validity of this assumption is studied in the following part.

2.6 Critical analysis of single probe methods for the determination of α -like scales

A (non-exhaustive) list of physicochemical properties P claimed to be only α -dependent is given in Table 5, with the structures of the corresponding probes in Scheme 3. This assertion will be checked by correlating P through the LSER $P = P^0 + d_i DI + e ES + a \alpha_1 + b \beta_1$ and calculating the % variance of P explained by α_1 . The higher this percentage, the better the property will be to determine an α scale. However, this percentage is highly dependent on the number and variety of solvents available for the correlation. In particular the number of non-HBD and HBD solvents must be well-balanced in the sample. Since this is not always the case, and since a solely α -dependent property should remain constant for non-HBD solvents ($\alpha_1 = 0$), we chose a second criterion. It consists in calculating the ratio of the P variation for non-HBDs to the P variation for HBDs:

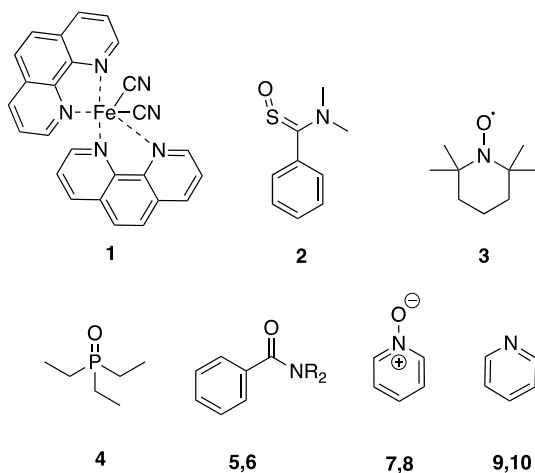
$$(22) \quad \% R = 100[\Delta P(\text{non-HBDs}) / \Delta P(\text{HBDs})]$$

The lower this percentage, the more we can consider that the property depends only on α . The results given in Table 5 show that there is no property exclusively α -dependent (with 100% α_1 and 0% R). This conclusion is justified in the following.

Table 5 Properties P used for the definition of α -type scales, contribution of α_1 to the variance of P (% α_1), and ratio of the P variation for non-HBDs to the P variation for HBDs % $R = 100[\Delta P(\text{non-HBDs}) / \Delta P(\text{HBDs})]$.

no.	P	% α_1	% R	ref
1	$v(t_{2g} \rightarrow \pi^*)$ (cis-dicyano)bis(1,10-phenanthroline)iron II	80	20	⁴⁰
2	$E_T(n \rightarrow \pi^*)$ <i>N,N</i> -(dimethyl)thiobenzamide <i>S</i> -oxide (E_T^{SO})	74	20	41
3	$E_T(n \rightarrow \pi^*)$ 2,2,6,6-tetramethylpiperidine <i>N</i> -oxyl radical (E_B)	73	26	42
4	³¹ P chemical shift triethylphosphane oxide (<i>AN</i>)	83	32	43,44
5	¹³ C chemical shifts <i>N,N</i> -diethylbenzamide $d_1 = \delta(C1) - \delta(C=O)$	100	11	45
6	¹³ C chemical shifts <i>N,N</i> -dimethylbenzamide $d_1 = \delta(C1) - \delta(C=O)$	100	17	46
7	¹³ C chemical shifts pyridine <i>N</i> -oxide $d_{24} = \delta(C4) - \delta(C2)$	78	46	47
8	¹³ C chemical shifts pyridine <i>N</i> -oxide $d_{34} = \delta(C4) - \delta(C3)$	73	36	47
9	¹³ C chemical shifts pyridine $d_{24} = \delta(C4) - \delta(C2)$	78	28	^a
10	¹³ C chemical shifts pyridine $d_{34} = \delta(C4) - \delta(C3)$	80	26	^a

^a This work.



Scheme 3. Structures of HBA probes claimed for the determinations of α scales. The numbers under structures correspond to the property number of Table 5.

Property 1. HBD solvents form hydrogen bonds with the cyano groups of $\text{Fe}(\text{LL})_2(\text{CN})_2$ complexes and shift their $t_{2g} \rightarrow \pi^*$ transition to higher wavenumbers. Spange et al³⁸ chose the Fe complex with 1,10-phenanthroline as the ligand L to determine the α values of ILs. However, eq 23 indicates that, for molecular solvents, this transition is not only sensitive to HB donation (80%) but also to HB acceptance (13%) and to electrostatic interactions (7%):

$$(23) \quad \tilde{\nu}(\text{Fe complex}/\text{k cm}^{-1}) = 16.10 + 0.62(\pm 0.21) ES + 2.03(\pm 0.06) \alpha_1 - 0.61(\pm 0.10) \beta_1$$

with $n = 47$ (29 HBDs), $r^2 = 0.969$, and $s = 0.18 \text{ k cm}^{-1}$. Migron and Marcus⁴⁸ find similar results with the Kamlet-Taft parameters π^* , α , and β , and conclude that this Fe complex “is not an exclusively α indicator”. The data of Burgess⁴⁹ on this Fe complex confirm this conclusion with α_1 contributions to the solvatochromism of 76% ($n = 20$) and of 78% ($n = 18$) when L is a Schiff base.⁵⁰

Property 2. Walter and Bauer⁴¹ claim that the transition energies of the long-wavelength band of *N,N*-(dimethyl)thiobenzamide *S*-oxide (E_T^{SO}) “are thought to be useful empirical solvent

parameters for characterizing the protic character of solvent”. However, eq (24) indicates that this transition is not only sensitive to HB donation (74%) but also to electrostatic interactions (26%):

$$(24) \quad E_T^{SO} / \text{kcal mol}^{-1} = 80.06 + 2.17(\pm 0.60) ES + 3.64(\pm 0.36) \alpha_1$$

with $n = 27$ (17 HBDs), $r^2 = 0.898$, and $s = 0.71 \text{ kcal mol}^{-1}$. Moreover, the transition energy is clearly not constant for non-HBDs ($R = 20\%$ from CCl_4 to DMSO).

Property 3. The negative solvatochromism of the $n \rightarrow \pi^*$ absorption band of the 2,2,6,6-tetramethylpiperidine *N*-oxyl radical was used by Janowski et al⁴² “to introduce a new scale of Lewis acidity of solvents E_B ”, because HBD solvents (Lewis acids) stabilize the nonbonding orbital more than the antibonding π^* orbital. The parameter E_B is defined as the transition energy of the $n \rightarrow \pi^*$ band. From the standardized regression coefficients of eq 25 it is found that only 73% of the variance of E_B is explained by α_1 :

$$(25) \quad E_B / \text{kcal mol}^{-1} = 60.25 + 1.48(\pm 0.17) ES + 3.29(\pm 0.14) \alpha_1$$

with $n = 45$ (18 HBDs), $r^2 = 0.959$, and $s = 0.30 \text{ kcal mol}^{-1}$. The significant contribution (27%) of ES to the variance of E_B is confirmed by the significant variation of E_B for non-HBD solvents from pentane to propylene carbonate ($R = 26\%$).

Property 4. The oxygen of triethylphosphane oxide is a strong HBA and forms hydrogen-bonded complexes in HBD solvents, with a consequent downfield shift in the NMR chemical shift δ of the ^{31}P atom.⁴³ The acceptor number scale, AN , was defined by Mayer et al⁴³ from δ (^{31}P) by setting up $AN = 0$ for hexane and $AN = 100$ for the adduct $\text{Et}_3\text{PO}-\text{SbCl}_5$. The standardized regression coefficients of eq 26 indicate that 83% of the variance of AN is explained by α_1 :

$$(26) \quad AN = 5.8 + 11.5(\pm 2.6) ES + 26.5(\pm 1.2) \alpha_1$$

with $n = 37$ (17 HBDs), $r^2 = 0.945$, and $s = 3.7$. With the significant contribution (17%) of the electrostatic parameter ES to the variance of AN , and a R value of 32%, it is clear that AN does not exclusively measure the HBD strength of solvents. This was already demonstrated by Riddle and Fowkes.⁴⁴ According to Marcus,⁵¹ “it is clear that AN includes a non-specific polarity effect” since non-HBD solvents have “non-vanishing acceptor numbers” and that this

acceptor number can reach values as high as 19 for DMSO. Shortcomings of the Kamlet-Taft α parameters and contamination of the AN parameter by non-specific effects might explain the absence of correlation between AN and α for ILs.⁵²

Properties 5 and 6. The ^{13}C NMR chemical shifts of the ipso carbon atom of N , N -diethyl-(or dimethyl)-benzamide relative to the carbonyl carbon atom, i.e. the quantity $d_1 = \delta(\text{C1}) - \delta(\text{C=O})$, are very sensitive to the HBD strength of solvents,⁴⁵ as indicated by eqs 27 and 28:

$$(27) \quad d_1(\text{PhCONEt}_2) = 32.1 + 3.76 (\pm 0.26) \alpha_1$$

with $n = 21$ (17 HBDs), $r^2 = 0.918$, and $s = 0.62$ ppm.

$$(28) \quad d_1(\text{PhCONMe}_2) = 33.4 + 3.51 (\pm 0.28) \alpha_1$$

with $n = 25$ (13 HBDs), $r^2 = 0.873$, and $s = 0.64$ ppm.

The parameters ES and DI are not statistically significant at the 95% confidence level in these equations, but (a) in eq (27) the sample of solvents is not well-balanced since only 4 non-HBD solvents out of 21 are present, (b) only 87.3% of the variance of d_1 is explained by α_1 in eq 28, and (c) the ratio R is far from zero for both set of data.

Properties 7 and 8. According to Schneider et al,⁴⁷ the ^{13}C NMR chemical shifts of the C2 and C3 atoms of pyridine N -oxide relative to the C4 atom, i.e. the quantities $d_{24} = \delta(\text{C4}) - \delta(\text{C2})$ and $d_{34} = \delta(\text{C4}) - \delta(\text{C3})$, are independent of non-specific solvent effects and are sensitive only to the HBD ability of solvents. Madeira et al³⁹ have exploited this finding to determine the Kamlet-Taft α parameter of 15 ILs with various cations and anions. However, only 78% and 73% of the variance of, respectively, d_{24} and d_{34} are explained by α_1 in eqs 29 and 30:

$$(29) \quad d_{24} = 16.85 - 3.04 (\pm 1.21) ES - 4.77 (\pm 0.53) \alpha_1$$

with $n = 24$ (19 HBDs), $r^2 = 0.850$, and $s = 1.30$ ppm.

$$(30) \quad d_{34} = 7.12 - 4.47 (\pm 2.22) DI - 2.15 (\pm 0.89) ES - 4.80 (\pm 0.41) \alpha_1$$

with $n = 24$ (19 HBDs), $r^2 = 0.904$, and $s = 0.94$ ppm.

Moreover, there is a large variation of d_{24} and d_{34} for non-HBD solvents from cyclohexane to DMSO. Therefore, it does not appear that d_{24} and d_{34} of pyridine N -oxide are totally independent of non-specific effects.

Properties 9 and 10. Schneider et al⁴⁷ also reported that the ¹³C NMR chemical shifts of the C2 and C3 atoms of pyridine relative to the C4 atom, i.e. $d_{24} = \delta(C4) - \delta(C2)$ and $d_{34} = \delta(C4) - \delta(C3)$, depend only on the HBD ability of solvents. This finding was based on literature data from different laboratories on 11 solvents. To make more significant the multiple linear regression analysis with DI , ES , α_1 , and β_1 and more consistent the NMR data, we have recorded the ¹³C NMR spectra of pyridine in 17 solvents (results in Table SI-4). It turns out that neither d_{24} nor d_{34} depend only on α_1 , since the variable ES is significant in eqs 31 and 32 at a confidence level greater than 99%.

$$(31) \quad d_{24} = -15.26 + 1.47 (\pm 0.40) ES + 2.82 (\pm 0.22) \alpha_1$$

with $n = 17$ (11 HBDs), $r^2 = 0.950$, and $s = 0.50$ ppm.

$$(32) \quad d_{34} = 11.66 + 0.44 (\pm 0.15) ES + 0.96 (\pm 0.08) \alpha_1$$

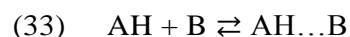
with $n = 17$ (11 HBDs), $r^2 = 0.942$, and $s = 0.18$ ppm.

In conclusion, there is, until now, no unambiguous *single* physicochemical property for α_1 .

2.7 Solvent and solute α scales

There are two types of α scale. The solvent α_1 scale⁹ (subscript 1 for solvent) corresponds to compounds in bulk, acting as solvents. The solute α_2^H scale¹¹ (subscript 2 for solute and superscript H for hydrogen bonding) corresponds to compounds in dilute solutions, acting as solutes. It is useful to study the relationship of α_1 with α_2^H since it can throw some light on the bulk behavior.

The solute HB acidity scale α_2^H is constructed from equilibrium constants for the 1:1 hydrogen bond complexation, eqs 33 and 34, in CCl₄ at 25°C



$$(34) \quad K_c = [AH \cdots B] / [AH][B]$$

where AH is the HBD and B the HBA. A special statistical treatment of the equilibrium constants (as $\lg K_c$) for the complexation of a series of HBDs with 45 reference HBAs yields a $\lg K_A^H$ scale of HB acidity for some 190 HBDs. The observation that $\lg K_A^H = -1.1$ corresponds

to a quasi-absence of complexation enables a HB acidity parameter, α_2^H , to be defined with an origin of zero, via eq 35

$$(35) \quad \alpha_2^H = (\lg K_A^H + 1.1)/4.636$$

The scaling factor of 4.636 serves to yield a suitable spread of α_2^H .

Another solute HB acidity scale, $\lg K_a$, has been constructed⁵³ against a single reference HBA, *N*-methylpyrrolidin-2-one, in CCl_3CH_3 . Cyclohexane was used as the measurement solvent for the construction of a third solute HB acidity scale,^{16,54,55} $\lg K_{\text{PyO}}$, against pyridine *N*-oxide as the reference HBA in equilibrium (33). This very inert solvent permits to determine the complexation constants K_{PyO} even of very weak HBDs such as acetone¹⁶ and, consequently, from this experimental evidence for the formation of hydrogen bonding, to classify acetone as a HBD solvent according to the IUPAC definition of the hydrogen bond.

Table 6 summarizes the results of the correlations of the solvent α_1 scale with these three solute scales of HB acidity. From 78% to 86% of the variance of the solvent α_1 scale are explained by the solute scales. Thus, the solute and solvent scales of HBD strength are not entirely equivalent. A probable origin of this difference comes from the self-association of HBDs in the liquid state into cyclic dimers or linear and cyclic aggregates.^{51,56,57} The self-association of alcohols into aggregates $(\text{ROH})_n$ is particularly important compared to the self-association of C–H donors or amines.⁵⁸ Indeed, for all 24 HBDs having both α_1 and α_2^H known, the determination coefficient is 0.775 but it falls to 0.597 when only the O–H donors are considered. On the contrary, r^2 rises to 0.898 when only the amines and the C–H donors are taken into account. The weak self-association of 1-alkynes⁶¹ *permits* a high determination coefficient (0.969) between their solvent α_1 scale and their solute scale of HB acidity (*vide supra*). In the same vein, the important self-association of ROH molecules *prevents* a high correlation of their α_1 values with the Taft constant⁶⁰ σ^* of the R substituent ($r^2 = 0.747$, $n = 18$ from $\text{R} = \textit{tert}\text{-Bu}$ to $\text{R} = (\text{CF}_3)_2\text{CH}$), a molecular descriptor of the free molecule.

Table 6. Determination coefficients r^2 for the correlation of the solvent α_1 scale with the solute scales α_2^H , $\lg K_\alpha$, and $\lg K_{PyO}$.

Solute scale	n	r^2
α_2^H	24(all HBDs)	0.775
	15(OH HBDs)	0.597
	9(NH and CH HBDs)	0.898
$\lg K_\alpha$	12	0.858
$\lg K_{PyO}$	27	0.836

3 Conclusion

The solvatochromic comparison method devised by Kamlet and Taft in 1976 is probably the most appropriate method to yield pure (i.e. not contaminated by non-specific solvent effects) hydrogen-bond parameters. Because the parameter $E_T(30)$ (a) is very sensitive to the HB donation of solvents, (b) is available for a very large number of diversified solvents, and (c) can be easily determined by recording the visible-near IR spectrum of a commercially available probe, the Reichardt's dye B(30), in the solvent of interest, this dye is generally chosen as the reference HBA probe for the determination of α -like scales. But there is no evident structurally similar probe non or less capable of accepting hydrogen bonds. Kamlet and Taft used many such probes to establish an averaged α scale, and among them 4-nitroanisole. Today, the majority of chemists who want to know the α parameter of a new solvent, such as a green solvent or an ionic liquid, choose the pair of B(30)/4-nitroanisole indicators to perform a solvatochromic comparison. In this work we have shown that this choice is unfortunate and most often yields incorrect α values. Instead, we propose here three reliable comparison methods.

The first one, called “theoretical solvatochromic comparison method” is mainly intended for computational chemists. It compares experimental $E_T(30)$ values to PCM-TD-DFT calculated ones. With the CAM-B3LYP functional, the 6-31++G(d,p) basis set, and, for the excited state, the linear-response PCM model in its non-equilibrium limit, the α_1 values are obtained by eq 36:

$$(36) \quad \alpha_1 = \{E_T(30)(\text{experimental}) - [0.693 E_T(30) (\text{PCM-TD-DFT}) + 1.3]\}/12.87$$

They correlate well a number of thermodynamic, kinetic, and electrochemical properties depending mainly on the HBD strength of solvents. They also correlate with the solvatochromic displacements $\Delta E_T(\mathbf{4-5})$ attributable to enhanced hydrogen bonding by the HBD solvents to the strong HBA solute 2,6-bis(dimethylaminocarbonyl)-4-(2,4,6-triphenylpyridinium-1-yl)phenolate **4**, relative to the weaker HBA solute 2,6-bis(*N*-methylaminocarbonyl)-4-(2,4,6-triphenylpyridinium-1-yl)phenolate **5**. Here, the two intramolecular hydrogen bonds N–H...O[–] in this latter betaine dye disadvantage the intermolecular hydrogen bonds of HBD solvents. Since betaine dyes **4** and **5** are not commercially available we cannot recommend the calculation of new α_1 values from $\Delta E_T(\mathbf{4-5})$.

The second one, called “semi-empirical comparison method”, compares experimental $E_T(30)$ values to calculated ones by the McRae simplified equation 14 in which the coefficients A,B,C, and D are adjusted to experimental data by a multiple linear regression. The α_1 values are calculated from the experimental $E_T(30)$ value, the refractive index n , and the relative permittivity ε of the solvent by eq 37

$$(37) \quad \alpha_1 = 0.0797 \{ (E_T(30)(\text{experimental}) - [27.0 + 24.7 f(n^2) + 10.0 g(\varepsilon, n^2) + 9.4 h(\varepsilon, n^2)]) - 0.033 \}.$$

The last one, intended for ILs, called “experimental comparison method”, exploits the difference of basicity of the commercially available betaine dyes B(30) and B(33). The α_1 values are calculated by eq 21 from the solvatochromic displacements $\Delta E_T(30-33)$ attributable to enhanced hydrogen bonding by the HBD solvents to the strong HBA solute B(30) relative to the weaker HBA solute B(33).

At the end, a comprehensive list of 131 α_1 values is obtained. These values must be preferred to the Kamlet-Taft α ones.

A critical analysis of methods based on a *single* process shows that the physicochemical properties chosen are not exclusively α -dependent. Such is particularly the case of the solvatochromism of an iron complex Fe(LL)(CN)₂ and of the ¹³C NMR chemical shifts of pyridine *N*-oxide. On the contrary, solvatochromic comparison methods are able to

deliver physicochemical quantities such as $\Delta E_T(30)(\text{exp.-calc.})$, $\Delta E_T(4-5)$, or $\Delta E_T(30-33)$ that are free from non-specific solvent effects and only dependent on the HBD strength of solvents.

The comparison of the solvent α_1 scale to solute HB acidity scales shows that they are not entirely equivalent. The ROH HBDs are the most dissimilar because of their self-association in the liquid state.

4 Experimental section

4.1 Chemicals

The betaine dyes B(30), B(33), and the two 2,6-di(carbamoyl)-substituted pyridinium *N*-phenolate betaine dyes were generously given by Pr Reichardt (Marburg). Solvents were purified as already described.¹⁹

4.2 Visible/near IR spectra

Because of the thermosolvatochromism of betaine dyes, the cell temperature was regulated at 25°C. The cell length was 1 cm or 10 cm for the betaine dyes soluble with difficulty.

4.3 ¹³C NMR spectra

Carbon 13 NMR spectra were recorded at 300 K on a Bruker spectrometer operating at 75 MHz for ¹³C. Chemical shifts were referenced internally to acetone *d*-6 at $\delta = 206.26$ ppm.

4.4 Statistical calculations

They were performed by a least-squares linear method when there is one explanatory variable, or a multiple linear method when there are several explanatory variables (LSER eq 4 and McRae eq 14). For the LSER the statistically significant solvent parameters are found by a downward stepwise procedure. Solvent parameters are accepted or rejected one by one by means of a Student two-sided *t* test on each regression coefficient at the 95% confidence level.

The quality of prediction is judged by means of the determination coefficient r^2 , since $100r^2$ yields the percent of variance of the dependent variable P explained by the explanatory variables. The relative contribution of each solvent parameter to the explained variation of the dependent variable P is obtained by calculating the *standardized* regression coefficients by the following equation:

$$(38) \quad a' = |a| * (\sigma_{\alpha_1}/\sigma_P)$$

for the example of the regression coefficient a of the α_1 parameter in the LSER of eq 3, where the apostrophe means “standardized”, the bars denote absolute magnitude, σ_{α_1} represents the standard deviation of α_1 , and σ_P the standard deviation of P . The magnitudes of standardized regression coefficients can now be compared since they are on the same scale. For convenience di' , e' , a' , and b' are normalized⁶¹ in the way shown in eq 39 for the example of the coefficient a' :

$$(39) \quad \% \alpha_1 = 100 a'/(di' + e' + a' + b')$$

Thus % DI , % ES , % α_1 , and % β_1 may be regarded⁶¹ as estimates of the percentage contribution from dispersion-induction, electrostatic, HBD, and HBA interactions.

Supporting Information

Detailed physico-chemical data for all solvents.

Acknowledgements

Prof. H. Oulyadi is thanked for his kind assistance. This work has been partially supported by the European Regional Development Fund (ERDF), Labex SynOrg (ANR-11-LABX-0029), Carnot Institute I2C, the graduate school for research XL-Chem (ANR-18-EUR-0020 XL CHEM), and by Région Normandie.

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