Linear Solvation Energy Relationships. Part 4. Correlations with and Limitations of the α Scale of Solvent Hydrogen Bond Donor Acidities[1]

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The solvatochromic comparison method is employed to amend and expand the data base for the α scale of solvent HBD (hydrogen bond donor) acidities. In combination with the π^* scale of solvent polarities, the α scale serves to rationalize solvent effects on a number of chemical properties and reaction parameters (*XYZ*s) through equations of the form, $XYZ = XYZ_0 + s\pi^* + a\alpha$. Properties considered include electronic spectral data, free energies of transfer between solvents, ^{19}F and ^{31}P n.m.r. shifts, and log reaction rate constants. It is shown that Dimroth's $E_T(30)$ and Kosower's *Z* scales, intended as measures of solvent polarity (*i.e.* π^*-equivalent), and Gutmann's 'Acceptor Number (AN)' scale, intended as a measure of solvent electrophilicity (*i.e.* α-equivalent), correspond in fact to linear combinations of π^* and α.

In combination with the π^* scale of solvent polarities,[2] and sometimes with the β index of solvent HBA (hydrogen bond acceptor) basicities,[1,3,4] the α scale of HBD (hydrogen bond donor) acidities is intended to serve toward rationalization of solvent effects on many chemical and spectroscopic properties and reaction rate and equilibrium parameters. We wish now to amend and expand the data base for the scale of HBD acidities, and to report some correlations of solvent effects with solvent π^* and α values.

Where solvent effects include contributions from type-A but not type-B hydrogen bonding,[†] as when the solute species are non-proton donors, linear solvation energy relationships can take either of two forms. For $p\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic spectral transitions with all solvents considered together, and for other properties if families of solvents with similar polarizability characteristics[5] (*e.g.* non-chlorinated aliphatics, polychlorinated aliphatics, aromatic solvents) are considered separately, the form of the solvent effect equation is

$$XYZ = XYZ_0 + s\pi^* + a\alpha \qquad (1)$$

When, in the case of the other properties, solvents from the three families are considered together, an additional term needs to be added to equation (1) to give equations of the form

$$XYZ = XYZ_0 + s'(\pi^* + d\delta) + a\alpha \qquad (2)$$

The s (s') and a terms in equations (1) and (2) are measures of the responses of XYZ to changing solvent polarity and HBD acidity, respectively, and the d term is a measure of the polarizability susceptibility. The polarizability parameter, δ, is assigned a value of 0.00 for all non-chlorinated aliphatic solvents, 0.50 for polychlorinated aliphatics, and 1.00 for all aromatic solvents.

In our initial report on the formulation of the α scale,[6] we used six diverse properties and reaction parameters as indicators of combined solvent polarity and HBD acidity effects, while $\nu_{max.}$ values in the electronic spectra of 4-nitroanisole or *NN*-diethyl-4-nitroaniline were taken as comparison properties which reflected solvent polarity effects only. With the recent publication of the π^* scale,[2] a far more reliable comparison indicator of solvent polarity, based on averaged solvent effects on dozens of u.v.–visible spectra, has now become available.

Further, we have since found that, while solvent polarity–polarizability blends, as represented by the $d\delta$ term in equation (2), are remarkably similar ($d\delta = 0$) for large numbers of $p\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic spectral transitions (such as those for 4-nitroanisole and *NN*-diethyl-4-nitroaniline), the $d\delta$ term can differ markedly for other properties, including those considered in our earlier study.[6] It follows, therefore, that the earlier α values, especially that for the aromatic HBD solvent, benzyl alcohol, probably reflect intrinsic systematic errors due to neglect of the variable polarizability effect.

We have also encountered another complication which has sometimes led to incorrect rankings of apparent solvent HBD strengths. In extreme examples, stronger, HBD acids which can self-associate cause only minor solvatochromic effects, while larger effects are observed with weaker non-self-associating HBD solvents. Such a condition occurs when an indicator, which is a weak HBA base, has a property which is particularly sensitive to type-A hydrogen bonding interactions. The stronger HBD solvents achieve greater stability by remaining tied up with themselves, rather than by disrupting their self-association patterns to form hydrogen bonds to the solute. Thus, the aliphatic alcohols may remain as cyclic trimers or tetramers;[7] benzyl alcohol and phenylethanol (which behave particularly erratically, sometimes behaving in effect as non-hydrogen bond donor solvents)[8] may hydrogen bond to their own π systems;[9] and formamide and acetic acid may remain as cyclic dimers. The weaker HBD solvents, $CHCl_3$ and CH_2Cl_2,[10] do not have this self-association option, and self-association complexes of CH_3CN (if any) are probably not cyclic. These therefore associate weakly with the solute, and induce noticeable solvatochromic effects.[‡]

[†] In type-A hydrogen bonding the solvent acts as HBD acid and the solute as HBA base. In type-B hydrogen bonding the roles are reversed.

[‡] Although the equations have been extended to cover many non-spectroscopic properties, we find it convenient to continue to use the term *solvatochromic* to describe the effects, the comparison method, the equations, and the π^*, α, β, and δ parameters.

In more usual examples, frequently encountered where the solute undergoes type-A hydrogen bonding at multiple sites, the reversals of apparent solvent HBD strengths are not so dramatic. Moderately strong solvent-to-solute hydrogen bonds are sufficient to disrupt partially the solvent self-association patterns, but differing self association equilibrium constants[7] lead to certain of the amphiprotic solvents seemingly exhibiting proper relative HBD strengths, while others fall out of line in their solvatochromic effects. In such instances the aliphatic alcohols are usually well behaved, with benzyl alcohol, ethylene glycol, acetic acid, and water most likely to fall out of line.

The least frequent instances of type-A solvation, but those which are best suited for the determination of the α_i values which are used in formulation of the α scale, are where the indicator or reactant is a sufficiently strong HBA base that competitive self-association has only a minor influence on the $\Delta\Delta$ terms attributable to hydrogen bonding.

The complication caused by competitive self-association has introduced serious uncertainties in the determination and use of the solvent α values, and is probably a main reason why linear solvation energy relationships involving type-A hydrogen bonding and the α scale have usually been less precise than those involving type-B bonding and the β scale. We shall often have occasion in this series of papers to point out examples of breakdowns in correlation due to this effect which, while a complication, can be quite a revealing phenomenon if properly recognized. In such instances, limited solvent effect relationships, involving only the monofunctional alkanols, have sometimes given satisfactory statistical correlations. A contributing factor here may be that self-association equilibrium constants may also be very nearly linear with solvent α values for the aliphatic alcohols.

Requirements for Indicators.—For the reasons cited above, we felt that more stringent requirements than before should be fulfilled by the properties and reactivity parameters used in constructing the α scale, and we have established the following criteria of suitability: (*a*) The properties should involve sufficiently strong HBA reactants or indicators that competitive solvent self-association should not materially influence the $\Delta\Delta$ terms (the enhanced solvatochromic effects due to hydrogen bonding). (*b*) Ratios of the a/s terms in equation (1) should not be too low (*i.e.* $a/s > 0.3$) so that uncertainties in the π^* values, which are necessarily less reliable for the HBD than for the non-HBD solvents,[2] should not introduce unacceptable uncertainties in the α_i values.

Of the properties treated in our earlier study,[6] the spectral data for Brooker's merocyanine indicator[11] failed to meet these criteria of acceptability. The other five sets of properties and the nine addition properties and reaction parameters analysed in the present paper do appear to fulfil both requirements.

TABLE 1

Properties correlated by the solvatochromic comparison method

XYZ No.	Property	Ref.
(1)	4-(2,4,6-Triphenylpyridinium)-2,6-diphenylphenolate transition energy, E_T, kcal mol^{-1}	14, 15
(2)	4-(2,4,6-triphenylpyridinium)-2,6-di-(t-butyl)-phenolate transition energy, E_T, kcal mol^{-1}	14 15
(3)	Bis[α-(2-pyridyl)benzylidine-3,4-dimethylaniline]bis(cyano)iron(II), charge transfer band, $\nu_{max.}$, kK	16
(4)	t-Butyl chloride solvolysis, 120 °C, $Y' = 1.800$ ($\log k^{120°}{}_{solvent} - \log k^{120°}{}_{gas\ phase}$), kcal mol^{-1}	17
(5)	t-Butyl chloride solvolysis 25 °C, $-\log k$	18
(6)	t-Butyl *o*-phenylthioperbenzoate thermal decomposition, 40 °C, $-\log k$	19
(7)	Tetra-n-hexylammonium iodide–1,3,5-trinitrobenzene charge-transfer complex, $\nu_{max.}$, kK	20
(8)	4-Fluoro-2-picoline ^{19}F n.m.r. shift, $-\delta$	21
(9)	$Et_4N^+I^-$ Ion pair, free energy of transfer from methanol, $\Delta G_c{}^t$, kcal mol^{-1}	18
(10)	Gutmann's Acceptor Number, AN, based on ^{31}P n.m.r. shift of Et_3PO, AN = 2.349 ($-\delta_\infty{}^{corr.}$)	22
(11)	Kosower's $Z = E_T$ *N*-ethyl-4-ethoxycarbonylpyridinium iodide, kcal mol^{-1}	13
(12)	Tropylium iodide charge-transfer band, E_T, kcal mol^{-1}	23
(13)	1-(2-Methacryloyloxyethyl)-4-(3-ethoxy-4-oxystyryl)pyridinium betaine, charge-transfer band, E_T, kcal mol^{-1}	24
(14)	1-(2-Methacryloyloxyethyl)-4-ethoxycarbonylpyridinium iodide, charge-transfer band, E_t, kcal mol^{-1}	24

We have also replaced Brownstein's S parameter[12] with Kosower's *Z* scale, based on transition energies in the electronic spectrum of *N*-ethyl-4-ethoxycarbonylpyridinium iodide.[13] This is because the use of multiple linear regression analysis with the solvatochromic comparison method now allows us to analyse properties with fewer available data in non-hydrogen bonding solvents than was required with the stepwise method used earlier. Brownstein's *S* scale was based on correlations of a number of properties with *Z*, and neglected (incorrectly) variable effects of solvent HBD acidity.

The *XYZ*s which we have analysed in terms of equation (1) are listed in Table 1, and the literature data employed in the correlations are assembled in Table 2, together with solvent π^* values and α_{1-6} results * from our earlier study. Table 2 includes all reported experimental information in non-chlorinated aliphatic solvents for which π^* values are known. For the few instances where we report correlations with aromatic solvent data, please refer to the cited references for the original experimental information. The properties studied are of four types and include: (*a*) electronic spectral band positions or transition energies for eight solvatochromic indicators; (*b*) a set of ^{19}F-n.m.r. shifts and a solvent 'Acceptor Number' scale based on a set of ^{31}P-n.m.r. shifts; (*c*) a set of free energies of transfer between solvents; and (*d*) three sets of reaction rate constants.

Correlations with π^* and α.—Solvatochromic comparisons of the *XYZ*s with solvent π^* and α_{1-6} values were

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* The subscript indicates that α_i values from six correlations were averaged to arrive at these numbers. When the present correlations are completed, the final values will become α_{11-4}.

Table 2

Data used in solvatochromic comparisons (see Table 1 for property and unit of measurement corresponding to each number)

No.	Solvent [a] (aliphatics only)	π^*	α_{1-6}	(1) E_T	(2) E_T	(3) $\nu_{max.}$	(4) Y'	(5) $-\log k$	(6) $-\log k$	(7) $\nu_{max.}$	(8) $-\delta$	(9) ΔG_c^t	(10) AN	(11) Z	(12) E_T	(13) E_T	(14) E_T
(1)	Hexane	−0.081					4.9	16.0			7.24	14	0.0				
(2)	Cyclohexane	0.000					6.1		5.164		7.10	13					
(3)	Triethylamine	0.140					7.6										
(7)	Diethyl ether	0.273				14.29	8.1	12.74		20.7	7.52	8.9	3.9				
(9)	Dioxan	0.553		36.0	34.2			10.80								45.24	59.43
(11)	Ethyl acetate	0.545		38.1	35.4					21.0	8.00	5.3	10.8				
(13)	Tetrahydrofuran	0.576		37.4	35.1				4.523	21.1	7.69		8.0			45.95	
(16)	Butan-2-one	0.674										3.2				46.31	61.18
(18)	Acetone	0.683		42.2	37.9	14.81	11.3	9.90	3.913	21.2	8.08	2.3	12.5	65.7	53.0	46.47	65.24
(19)	Triethyl phosphate	0.715		40.3													
(23)	*NN*-Dimethylacetamide	0.882		43.7									13.6				
(24)	Dimethylformamide	0.875		43.8	39.4	14.86	13.4	8.48			[10.1] [d]	0.9	16.0	68.5		47.65	68.33
(26)	Hexamethylphosphoramide	0.871											[10.6] [f]				
(28)	*N*-Methylpyrrolidone	0.921						8.97				1.0	13.3				
(29)	Dimethyl sulphoxide	1.000		45.0	39.7	14.97	14.8		3.220	22.4	8.20	0.5	19.3	71.1		48.84	
(32)	Nitromethane	0.848	nyd			15.36	13.7	8.12	3.264	22.1	8.20	1.2	20.5			48.60	
(34)	Acetic anhydride	0.742		43.9													
(50)	Acetonitrile	0.713	0.29	46.0	41.4	15.11	13.2	8.73		23.1		1.4	19.3	71.3	58.3	48.80	71.13
(52)	Methyl acetate	0.556		40.0													
(61)	1,2-Dimethoxyethane	0.526		38.2	35.5												
(101)	2-Methylpropan-2-ol	(0.534) [g]	0.436	43.9	[37.4] [c]		12.9		3.489	23.5	9.15	3.8		71.3		[48.4] [e]	70.45
(102)	Propan-2-ol	0.505	0.687	48.6	[40.4] [c]	15.65	14.8		3.120	25.0	10.54	2.4	33.5	76.3	64.5	50.51	75.87
(103)	Butan-1-ol	0.503	0.710	50.2	45.0	15.67	15.2	7.39		25.9	10.73	2.1		77.7		50.70	77.50
(112)	Propan-1-ol	0.534	0.766	50.7	45.6	15.77	15.4			26.2	10.84	1.8		78.3		51.52	77.82
(104)	Ethanol	0.540	0.850	51.9	46.9	15.92	15.9	7.07	2.836	26.7	10.93	1.3	37.1	79.6	66.6	52.36	79.60
(105)	Methanol	0.586	0.990	55.5	50.8	16.16	17.4	6.10	2.323	26.8	11.46	0.0	41.3	83.6	70.9	54.11	83.48
(107)	Ethylene glycol	(0.932) [g]	0.792	56.3	51.1	16.21				27.5	11.50			85.1			
(109)	Benzyl alcohol [b]	[0.948]	[0.43] [b]	50.8	46.5		22.2				11.14						
(111)	Water	1.090	1.017	63.1		16.75		1.54				−7.5 [e]	54.8	94.6	82.7	59.17	
(201)	Acetic acid	0.664	0.79				17.3	6.71					[52.9] [f]	79.2			
(204)	Formamide	(1.118) [g]	nyd	56.6									39.8	83.3		53.88	82.45

[a] Solvent numbering is the same in all papers of this series. [b] Aromatic solvent; excluded from correlations. [c] Excluded from correlations; steric effect. [d] Excluded from correlations; out of line for unknown reason. [e] Personal communication, Prof. M. H. Abraham, University of Surrey. [f] Excluded from correlation; see text. [g] π^*-values in parentheses are subject to modification based on ^{13}C n.m.r. results with ααα-trifluorotoluene indicator; to be reported in a future paper..

carried out by the method of multiple linear regression analysis (multiple parameter least-squares analysis). Correlation equations are assembled in Table 3, together with the r (correlation coefficient) and SD (standard deviation) measures of the goodness of the statistical fits. For reasons cited above, correlations have been restricted to families of solvents with similar polarizability characteristics, *i.e.* only non-chlorinated aliphatic solvents or, in a few instances where sufficient data were available, only aromatic solvents. It is seen that the statistical fits are quite good, eleven of the r values for the aliphatic solvent correlations being $\geqslant 0.990$ and all fourteen being $\geqslant 0.978$.

It also deserves mention that in all instances where sufficient data in non-hydrogen bonding solvents were available, correlation equations by the multiple linear regression method corresponded closely to equations determined by the stepwise solvatochromic comparison method wherein: (*a*) the XYZ_0 and s terms in equation (1) were evaluated by linear correlation of XYZs in non-HBD solvents with solvent π^* values; (*b*) the a term in equation (1) was evaluated by correlating $\Delta\Delta XYZ$s (enhanced effects attributable to hydrogen bonding) with solvent α values; and (*c*) the goodness of the statistical fit was confirmed at every step.

Thus, using the free energy of transfer of the $Et_4N^+I^-$ ion pair from methanol to a variety of solvents as an example [XYZ No. (9) of Tables 1—4], as the first step in the stepwise method, the regression equation with π^* for the data in nine non-hydrogen bonding solvents is determined to be

$$\Delta G_c^t = -13.18\pi^* + 12.62 \text{ kcal mol}^{-1} \quad (3)$$

Table 3

Correlation equations (see Table 1 for property and unit of measurement corresponding to each XYZ)

$$XYZ = XYZ_0 + s\pi^* + a\alpha_{1-6}$$

No.	Solvents [a]	$XYZ =$	XYZ_0	s	a	r [b]	SD	n HBD	n NHB
(1)	Aliphatic	E_T	29.78	15.74	16.07	0.987	1.18	10	11
	Aromatic		22.93	19.69	(16.07) [c]	0.980	0.68	1	9
(2)	Aliphatic	E_T	28.90	11.51	14.48	0.993	0.68	6	7
	Aromatic		25.40	13.54	(14.48) [c]	0.988	0.30	1	5
(3)	Aliphatic	$\nu_{max.}$	14.06	0.946	1.599	0.997	0.054	9	4
(4)	Aliphatic	Y'	5.85	8.56	6.71	0.997	0.36	9	7
	Aromatic		4.66	7.24	(6.71) [c]	0.959	0.48	1	4
(5)	Aliphatic	$-\log k$	15.17	−7.42	−5.01	0.994	0.39	6	6
(6)	Aliphatic	$-\log k$	5.299	−1.963	−1.769	0.984	0.17	5	4
(7)	Aliphatic	$\nu_{max.}$	19.62	2.65	6.34	0.991	0.35	8	5
(8)	Aliphatic	$-\delta$	7.20	1.119	3.848	0.994	0.18	7	7
	Aromatic		6.58	1.847	(3.848) [c]	0.938	0.12	1	8
(9)	Aliphatic	ΔG_c^t	12.73	−13.39	−5.15	0.995	0.54	8	9
(10)	Aliphatic	AN	−0.10	17.05	33.73	0.994	1.83	5	9
(11)	Aliphatic	Z	52.64	18.37	20.42	0.995	0.83	11	3
(12)	Aliphatic	E_T	38.23	21.04	20.87	0.997	0.94	5	1
(13)	Aliphatic	E_T	39.29	9.55	9.32	0.978	0.87	8	6
(14)	Aliphatic	E_T	47.17	23.79	23.65	0.990	1.16	7	4

[a] Aliphatics do not include polychlorinated aliphatics. [b] From a least-squares correlation of XYZ (obs.) with XYZ (calc.). [c] Assumed to be the same as for aliphatic solvents.

with $r = 0.992$ and SD = 0.73 kcal mol^{-1}. Next, the $\Delta\Delta(\Delta G_c^t)$ values in eight HBD solvents [the enhanced values relative to those calculated through equation (3)] are shown to be nicely linear with α_{1-6},

$$\Delta\Delta(\Delta G_c^t) = -5.276\alpha_{1-6} + 0.077 \text{ kcal mol}^{-1} \quad (4)$$

with $r = 0.972$ and SD = 0.35 kcal mol^{-1}. Force fitted through the origin to reflect the necessary proportionality between the $\Delta\Delta$ terms and corresponding α values, this becomes

$$\Delta\Delta(\Delta G_c^t) = -5.16\alpha_{1-6} \pm 0.29 \text{ kcal mol}^{-1} \quad (5)$$

Combining the slope and intercept from equation (3) with the slope from equation (5), we obtain the stepwise solvatochromic equation,

$$\Delta G_c^t = 12.62 - 13.18\pi^* - 5.16\alpha_{1-6} \text{ kcal mol}^{-1} \quad (6)$$

which is in excellent agreement with the multiple linear regression solvatochromic equation (from Table 3),

$$\Delta G_c^t = 12.73 - 13.39\pi^* - 5.15\alpha_{1-6} \text{ kcal mol}^{-1} \quad (7)$$

TABLE 4

Construction of the α-scale of solvent hydrogen bond donor (HBD) acidities

No.	Solvent	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9	α_{10}	α_{11}	α_{12}	α_{13}	α_{14}	Final α_{1-14}	SD	n
(101)	2-Methyl-propan-2-ol	0.356		0.485	0.370		0.438	0.389	0.351	0.345		0.433			0.447	[0.401] [c]	0.050	9
(102)	Propan-2-ol	0.676		0.696	0.691		0.679	0.687	0.721	0.693	0.738	0.704	0.750	0.603	0.706	0.695	0.037	12
(103)	Butan-1-ol	0.778	0.712	0.709	0.753	0.808		0.780	0.771	0.756		0.775		0.764	0.766	0.762	0.029	11
(112)	Propan-1-ol	0.778	0.728	0.753	0.743			0.814	0.791	0.734		0.776		0.752	0.759	0.763	0.027	10
(104)	Ethanol	0.848	0.814	0.843	0.810	0.817	0.801	0.891	0.812	0.815	0.827	0.834	0.815	0.808	0.828	0.826	0.023	14
(105)	Methanol	1.026	1.047	0.967	0.975	0.942	1.041	[0.89] [a]	0.936	0.948	0.929	0.989	0.974	1.020	0.946	0.980	0.041	13
(107)	Ethylene glycol	0.737	0.792	0.793				0.853	0.846			0.751				[0.796] [c]	0.047	6
(109)	Benzyl alcohol	0.529	0.537		0.613				0.712							(0.597) [b]	0.085	4
(111)	Water	1.006		1.037	1.048	1.106				1.094	1.074	1.074	1.032	1.126		1.068	0.036	9
(201)	Acetic acid				0.861	0.705						0.703				(0.756) [b]	0.091	3
(204)	Formamide	0.574									0.615	0.495		0.420	0.367	[0.494] [c]	0.103	5
(50)	Acetonitrile	0.310	0.296	0.234	0.187	0.229	0.370	0.251		0.346	0.212	0.272	0.242		0.296	(0.270) [b]	0.054	12
(32)	Nitromethane	0.197		0.311	0.090	0.151		0.037	0.013	0.034	0.179			0.130		[0.126] [c]	0.096	9

[a] Excluded from average. [b] Secondary values; see text. [c] α-Values in brackets are subject to modification based on ^{13}C n.m.r. results with phenyl methyl sulphoxide and dimethyl sulphoxide indicators. However all correlation equations remain essentially the same; to be reported in a future paper.

Such close correspondence in all instances with pairs of single parameter correlations lends statistical rigour to the multiple parameter least-squares correlations in Table 3.

The Revised and Expanded α Scale.—To construct the revised and expanded α scale, we have used our known π^* values [2] with the reciprocals of the correlation equations in Table 3 to determine α_i values from the reported *XYZ*s in HBD solvents [see equation (8)].

$$\alpha_i = (XYZ - XYZ_0 - s\pi^*)/a \quad (8)$$

The α_i results are assembled in Table 4 and averaged to give the α_{1-14} values which comprise the current version of the α scale of solvent HBD acidities.

Conforming with the categories established for the π^* and β scales,[2,3] criteria of reliability for the α_{1-14} values are as follows. (*a*) *Primary* α values are based on solvatochromic data for at least 6 well behaved indicators. These are considered to be satisfactory and are not to be modified further unless warranted by the weight of additional evidence. (*b*) *Secondary* α values are based on results for at least three indicators. They may be used in correlations, and are to be promoted to primary when sufficient data become available. (*c*) Because certain of the α values for which many results are available have not yet 'settled down', we have established the further requirement that the standard deviation for the mean of the α_i values for primary solvents must be $\leqslant 0.050$. As is seen in Table 4, this requirement has kept acetonitrile [solvent (50)] and nitromethane (32) in the secondary category.

A Rationale for the Ranking of the α Values.—It is of interest to compare the relative orderings of amphiprotic solvent HBD acidities and HBA basicities. The HBA basicities (β values) of R–OH solvents [3] are nicely linear with σ^* constants of the substituents,[25] the least-squares regression equation being

$$\beta = -1.056\sigma^* + 0.704 \quad (8)$$

$r = 0.986$, SD = 0.046.[26] As is seen in Figure 1, the results for water (111), ethylene glycol (107), 2-phenylethanol (106), and benzyl alcohol (109), on the one hand, and the aliphatic alcohols (101—105), on the other, fit the relationship equally well.

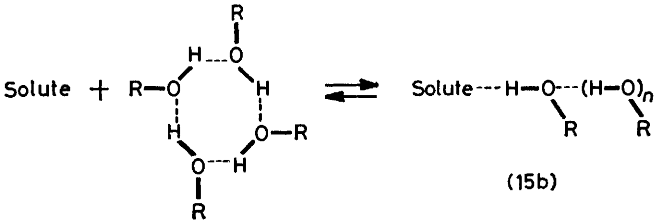
The situation differs markedly with the HBD acidities. As with β, the α values of the monofunctional alkanols (101)—(105) and (112) are nicely linear with substituent σ^* constants, the correlation equation being

$$\alpha_{1-14} = 1.903\sigma^* + 0.987 \quad (9)$$

$r = 0.987$, SD = 0.030. Here, however, water (111), benzyl alcohol (109), and ethylene glycol (107) have α values which are substantially lower than required by equation (9) (Figure 1). Also, acetic acid (201) and formamide (204), which might have been expected from *a priori* considerations to be stronger HBD acids than the alkanols have proven to have lower α values than (101)—(103) and (112).

We rationalize these seeming anomalies in terms of the differing structures of the associating solvent clusters. We have shown by solvatochromic dilution studies [27] that, in neat ROH solvents, $(ROH)_n$ dimers or polymers are the type-B solvating species, and it is likely that similar considerations apply with type-A hydrogen bonding. For example, for hydrogen bonding by the monofunctional alkanols, one can visualize an equilibrium of the form (10).

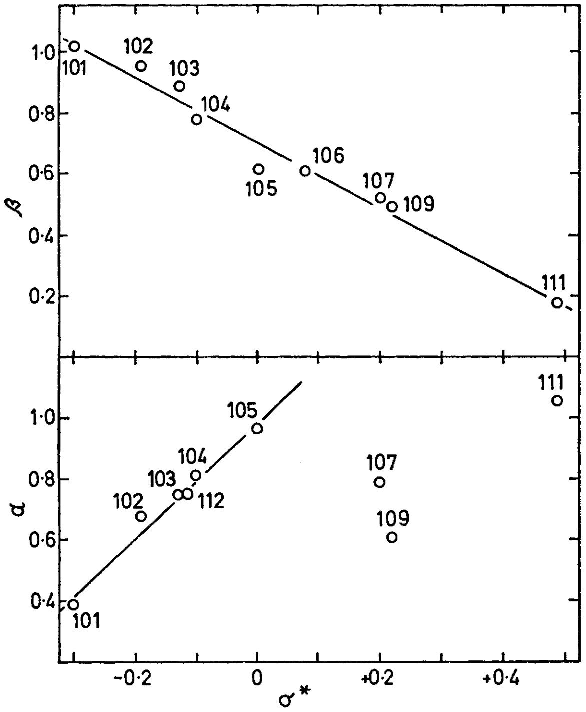
The important aspect of structure (15b) is that the oxygen of the hydroxy group whose proton serves as a donor to the solute acts as acceptor in a hydrogen bond with another ROH molecule. Huyskens[28] has recently shown that, when an amphiprotic molecule acts simultaneously as a hydrogen bond acceptor and donor at the same site, both the donor and acceptor strengths are enhanced substantially relative to the same species acting only as donor or only as acceptor.



(15a) (15b) (10)

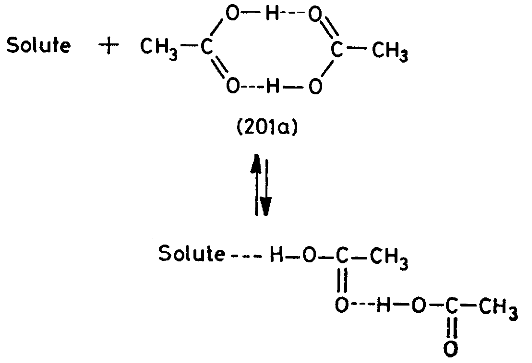
In the case of acetic acid, the equilibrium can probably be represented by (11) with the self-association complex of acetic acid (201a) substantially stronger than the alkanol self-association complex (15a). Again the acetic acid molecule acting as a hydrogen bond donor to the solute in (201b) is also simultaneously acting as an acceptor. Here, however, the acceptor site is two additional atoms removed from the donor site, with a consequently lessened HBD strengthening effect than in (15b). We attribute the greater proclivity of (201) to fall out of line in solvatochromic comparisons to the stronger self-association in (201a) relative to (15a), and the lower α to less HBD strengthening by the neighbouring hydrogen bond in (201b) relative to (15b).

With benzyl alcohol (109), the equilibrium may be as in (12),[8,9] with the weaker than expected HBD acidity again resulting from the fact that the donor solvent molecule is an acceptor at a position somewhat removed from the donor site. Here there is also the alternative possibility that the donor species is actually a monomer, *e.g.* (13).

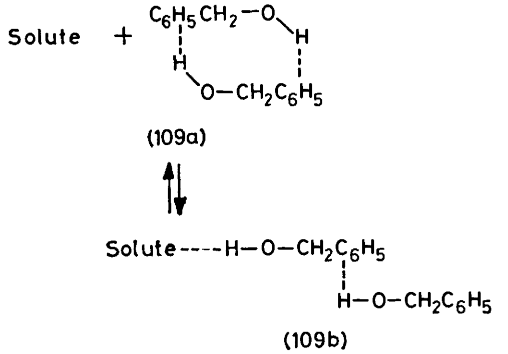


Correlation of α and β-values of ROH solvents with σ* of R

With water (111) and formamide (204), considerations of solvent structure suggest an entirely different rationale for the lower than expected α-values. Here, minimization of free energy *in the total system* may be achieved by *retaining the primary solvent structure*, and having the solvent molecule form a second hydrogen bond to the solute [*e.g.* equilibria (14) and (15)].



(201a) (201b) (11)

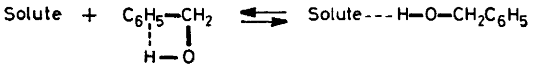


(109a) (109b) (12)

Huyskens[28] has also shown that when a molecule forms two donor or acceptor hydrogen bonds at the same site, the second hydrogen bond is weaker than it would have been in the absence of the first such bond. Such a situation would very neatly explain the relative hydrogen bond strengths of (111), (204), and (101)—(105) to HBA solutes.

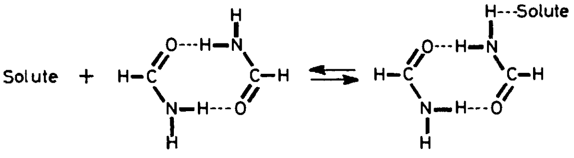
Solvent Effects on t-Butyl Chloride Solvolysis.—To this point we have attempted to deduce what we could about the properties of the solvents from the solvatochromic behaviour of the indicators. We now address ourselves to the converse question. What do the solvent effects tell us about the indicator compounds and reactions?

The *XYZ*s Nos. (4) and (5) of Tables 1—4 are of considerable interest to us in the light of the large amount of attention devoted to t-butyl chloride solvolysis in the 1950s,[29] as well as the fact that Winstein and Grunwald, in their pioneering LSER studies,[30] had based their *Y* scale of solvent ionizing power on solvent effects on the rate of this reaction. The solvatochromic coefficients in Table 3 confirm that there is significant rate acceleration in HBD solvents due to type-A hydrogen bonding to the leaving chlorine atom (in the terminology used by workers in this field,[29] this corresponds to *electrophilic assistance* of S_N1 solvolysis). The *a*/*s* ratios of 0.78 for *Y'* and 0.68 for log *k* (25 °C) provide measures of the relative sensitivities of this reaction to solvent polarity and solvent HBD acidity.



(13)

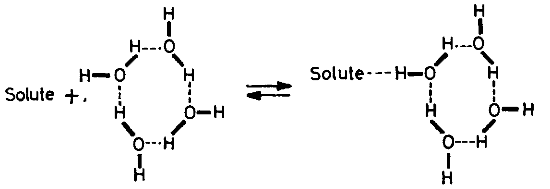
(109c) (109d)



(14)

(204a) (204b)

and



(15)

(111a) (111b)

While the participation of *electrophilic assistance* in S_N1 and S_N2 solvolyses has long been known,[30] most treatments of solvent effects on solvolysis reactions, including that of Schleyer and his co-workers as recently as 1976,[29] have been on the implicit assumption that a single *mY* term accounts adequately for each reactant's sensitivity to both general solvent power and specific electrophilic solvation of the leaving group. Schleyer *et al.* have expressed concern that this assumption might not be justified,[29] and our findings offer reason for such concern.

Indeed, we have found that for t-butyl bromide solvolysis, based on Abraham's collection of rate data (5 HBD solvents, 3 non-HBD),[18] the total solvatochromic equation for aliphatic solvents is as given in equation (16) with $r = 0.983$ and SD = 0.40 log unit. The *a*/*s* value of 0.45 in equation (16) compared with 0.68 for t-butyl chloride at 25 °C, is consonant with the leaving bromide ion being a weaker HBA base than chloride.

For *p*-methoxyneophyl tosylate solvolysis at 75 °C, based on Smith, Fainberg, and Winstein's data for 5 HBD and 7 non-HBD aliphatic solvents,[31] the total solvatochromic equation is as given in (17) with $r =$

$$\log k = 7.95\pi^* + 3.604\alpha_{1\text{-}14} - 12.81 \quad (16)$$

$$\log k = 5.137\pi^* + 3.163\alpha_{1\text{-}14} - 8.707 \quad (17)$$

0.984 and SD = 0.23 log unit. That the correlation is quite acceptable without introduction of the β parameter confirms the fact that nucleophilic participation plays a negligible role in this solvolysis reaction. The lower *s* value than for the t-butyl halide solvolyses is partially a temperature effect, but also reflects charge delocalization in the leaving group as well as in the forming carbonium ion (through anchimeric assistance by the *p*-methoxyphenyl group).

The varying *a*/*s* ratio for these three reactions suggest strongly that solvent effects on S_N1 and S_N2 solvolyses need to be reconsidered, with greater attention paid to the variable role of electrophilic assistance. The existence of the π*, α, and β scales now makes such a study in pure solvents feasible, and we will no doubt have more to say on this subject in future papers.

Free Energy of Transfer of $Et_4N^+I^-$.—When these data [18] were used in the formulation of our earlier version of the α scale,[6] we expressed puzzlement about an anomalous data point for water, which did not fit the correlation. Dr. M. H. Abraham of the University of Surrey has kindly written to us: ' The $\Delta G_t°$ values include not only an electrostatic term, but also a non-electrostatic part. For transfer from methanol to non-aqueous solvents, the non-electrostatic term is essentially zero, so that the observed $\Delta G_t°$ values can be equated with the electrostatic contribution. However, for transfer from methanol to water there is a very large non-electrostatic effect that depends only on the size (or volume) of the species transferred. We have estimated this term for the ion pair $Et_4N^+I^-$ as +7.1 kcal mol^{-1}, so that for transfer from methanol to water:

$$\begin{array}{rcll} \Delta G_t^\circ & = & \Delta G_n^\circ + & \Delta G_e^\circ \\ -0.4 & = & 7.1 & -7.5 \end{array}$$

These data on the molar scale are from *J. Chem. Soc.* (*A*), 1971, 1610.'

' Thus,' Dr. Abraham continues, ' the electrostatic free energy of transfer of the $Et_4N^+I^-$ ion pair from methanol to water is actually −7.5 kcal mol^{-1}. This value (published in 1971) is almost exactly the value you suggest in your footnote (26), that is −7 kcal mol^{-1}. Hence, when the contribution to $\Delta G_t°$ from the non-electrostatic or " volume " effect is taken into account, everything becomes consistent.' We have used Abraham's suggested −7.5 kcal mol^{-1} value for H_2O in the present correlation and, as is seen in Table 3 (*XYZ* No. 9), the statistical fit is excellent.

Gutmann's Acceptor Number (*AN*). Mayer, Gutmann, and Gerger[22] have used infinite dilution ^{31}P n.m.r. shifts of triethylphosphine oxide as the basis for what they describe as 'Acceptor Number (AN), A Quantitative Empirical Parameter for the Electrophilic Properties of Solvents' (the conversion factor is $-\delta_{\infty}^{\text{corr.}} = \mathrm{AN}/2.349$). For protic solvents, AN is intended to serve as a measure of HBD acidity; for non-protic solvents, it is seemingly intended to represent a sort of Lewis acid equivalent of HBD acidity. Compared with values which range from 33.5 to 41.3 for the aliphatic alcohols, AN values of representative non-HBD solvents are: 8.0 for THF, 12.5 for acetone, and 19.3 for Me_2SO. Thus, the latter type solvents are considered to have reasonably strong Lewis acid type electron acceptor properties. Together with a scale of 'Donor Numbers (DN),' measures of solvent nucleophilicity which, for most solvents, correlate reasonably well with our β scale, the AN scale was intended to correlate solution properties through a generalized two-parameter equation.

This AN solvent parameter scale is of some interest to us in that, whereas in many other instances we have found that solvent property scales intended to serve as measures of solvent polarity, *i.e.*, π^*-equivalent, correspond in fact to linear combinations of π^* and α [as has been shown for $E_T(30)$, χ_R, S, Z, and AN], here we have a property intended to serve as an electrophilicity measure, *i.e.* α-equivalent, which also corresponds in fact to a linear combination of π^* and α.

Thus, when only data for aliphatic non-HBD solvents are considered, the AN results show statistically acceptable linear regression with solvent π^* values:

$$\mathrm{AN} = 15.51\pi^* + 0.64,\ r = 0.933,\ \mathrm{SD} = 0.21 \qquad (17)$$

If the datum for hexamethylphosphoramide [solvent (26)] is excluded, the r value goes up to 0.960, and the SD goes down to 0.17. The latter result may illuminate some effect which we have not yet taken into account, since for most non-halogenated aliphatic solvents, but not (26), π^* values are proportional to molecular dipole moments.[5]

Note added in proof: Based on more recent ^{13}C n.m.r. results with benzotrifluoride, phenyl methyl sulphoxide, and diphenyl sulphoxide indicators, it appears that the π^* and α values need to be modified somewhat for certain of the HBD solvents. The tentative preferred values are: t-butyl alcohol [solvent (101)], $\pi^* = 0.40$, $\alpha = 0.63$; ethylene glycol (107), $\pi^* = 0.73$, $\alpha = 0.98$; formamide (204), $\pi^* = 0.85$, $\alpha = 0.80$; nitromethane (32), $\pi^* = 0.80$, $\alpha = 0.31$ (unpublished data of B. Chawla and M. Fujio). The conclusions and correlations in this paper and the earlier Part 3[1] remain the same using these alternative values. Indeed the correlation coefficients are improved somewhat.

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REFERENCES

[1] Part 3, M. J. Kamlet and R. W. Taft, *J.C.S. Perkin II*, 1979, 349.

[2] M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Amer. Chem. Soc.*, 1977, **99**, 6027.

[3] M. J. Kamlet and R. W. Taft, *J. Amer. Chem. Soc.*, 1976, **98**, 377.

[4] T. Yokoyama, R. W. Taft, and M. J. Kamlet, *J. Amer. Chem. Soc.*, 1976, **98**, 3233.

[5] J. L. Abboud, M. J. Kamlet, and R. W. Taft, *J. Amer. Chem. Soc.*, 1977, **99**, 8325.

[6] R. W. Taft and M. J. Kamlet, *J. Amer. Chem. Soc.*, 1976, **98**, 2886.

[7] C. Duboc, *Spectrochim. Acta, Part A*, 1974, **30**, 431, 440.

[8] See, for example, M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Amer. Chem. Soc.*, 1973, **95**, 5210.

[9] For a discussion of the HBA properties of the benzene π-system see G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' W. H. Freeman, San Francisco, 1960, pp. 22—24; also B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, 1964, **86**, 5240.

[10] For examples of hydrogen bonding by CH_2Cl_2, see M. J. Kamlet and R. W. Taft, *J.C.S. Perkin II*, 1979, 337; E. F. Meyer and F. A. Baiocchi, *J. Amer. Chem. Soc.*, 1977, **99**, 6206.

[11] L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Amer. Chem. Soc.*, 1965, **87**, 2443.

[12] S. Brownstein, *Canad. J. Chem.*, 1960, **38**, 1590.

[13] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 5253; E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, p. 301.

[14] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1; C. Reichardt, *ibid.*, 1971, **752**, 64.

[15] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[16] J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1957.

[17] I. A. Koppel and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, 1969, **6**, 504.

[18] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[19] D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Amer. Chem. Soc.*, 1963, **85**, 1938.

[20] K. M. C. Davis, *J. Chem. Soc.* (*B*), 1963, 1128.

[21] C. S. Giam and J. L. Lyle, *J. Amer. Chem. Soc.*, 1973, **95**, 3253.

[22] U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235; V. Gutmann, *Electrochim. Acta*, 1976, **21**, 661.

[23] E. M. Kosower, *J. Org. Chem.*, 1964, **29**, 957.

[24] P. Strop, F. Mikes, and J. Kalal, *J. Phys. Chem.*, 1976, **80**, 694.

[25] R. W. Taft in 'Steric Effects in Organic Chemistry,' M. S. Newman, ed. Wiley, New York, 1965, ch. 13.

[26] See also R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, 1971, **36**, 1342.

[27] M. J. Kamlet, E. G. Kayser, M. E. Jones, J. L. Abboud, J. W. Eastes, and R. W. Taft, *J. Phys. Chem.*, 1978, **82**, 2477.

[28] P. L. Huyskens, *J. Amer. Chem. Soc.*, 1977, **99**, 2579.

[29] For a recent discussion see T. W. Bentley and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1976, **98**, 7658; F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *ibid.*, 1976, **98**, 7667.

[30] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770; see also E. Grunwald and S. Winstein, *ibid.*, 1948, **70**, 848; S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 1951, **73**, 2700; S. Winstein and A. H. Feinberg, *ibid.*, 1957, **79**, 5937; A. H. Fainberg and S. Winstein, *ibid.*, 1957, **79**, 1597; *ibid.*, 1957, **79**, 1608.

[31] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 618. The data point for water, which the authors rightly considered questionable, is excluded.