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HYDROGEN-BONDING. PART 4. AN ANALYSIS OF SOLUTE HYDROGEN-BOND BASICITY, IN TERMS OF COMPLEXATION CONSTANTS (LOG K), USING F_1 AND F_2 FACTORS, THE PRINCIPAL COMPONENTS OF DIFFERENT KINDS OF BASICITY*

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ABSTRACT

The principal components factors F_1 and F_2 in the equation

$$\log K = \mathrm{BDP}_0 + S_1F_1 + S_2F_2$$

have been used to obtain S_1 and S_2 values for sets of hydrogen-bond bases against 32 reference acid/solvent systems. The constants S_1 and S_2 define an angle $\theta = \tan^{-1} S_2/S_1$ that is a measure of the electrostatic:covalent bonding ratio in the hydrogen-bond complex. It is shown that θ can vary from 53 (4-fluorophenol in CH_2Cl_2) to 86 degrees (Ph_2NH in CCl_4) depending on the reference acid and solvent. This variation in θ can lead to family dependent behaviour in plots of log K for bases against a given reference acid system vs log K for bases against another reference acid system, and precludes the construction of any general scale of hydrogen-bond basicity using log K values. Amongst a quite wide range of reference acid/solvent systems θ varies only from 64 to 73 degrees, and for bases against these reference systems a 'reasonably general' scale could be set up. Such a scale could be extended to bases against reference acid/solvent systems outside the 64–73 degree range provided that certain classes of base (e.g. pyridines, alkylamines) were excluded from the additional reference acid/solvent systems.

Over the years there have been constructed numerous scales of basicity, both with respect to solutes and to solvents (see e.g. References 1–8). Because there are so many such scales, it is immediately clear that there is no completely general scale of basicity. However, it is still

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possible that within a given area it might be feasible to construct a basicity scale that has some, but not total, generality. Suppose we have a basicity dependent property (BDP) that might consist of a set of log K values for complexation of a series of bases against a reference acid, or of a set of spectral data for an indicator in a series of solvents acting as bases, etc. Then a qualitative criterion for a general scale of basicity is that a plot of this basicity dependent property, $(\mathrm{BDP})^{a}$, against any other BDP should yield a single line over the entire series of bases studied. Such behaviour is classified as 'family independent', in that all bases lie on the same line, no matter whether they are oxygen bases, nitrogen bases, etc. On the other hand if a plot of $(\mathrm{BDP})^{a}$ against $(\mathrm{BDP})^{b}$ resulted in a series of lines, one for each family of base, then no general basicity scale is possible, and the plot would be classified as 'family dependent'.

Although the above considerations are well understood, it has proved difficult to analyse these effects quantitatively, although the work of Panchenko and co-workers[9] represented a notable advance in the analysis of log K data. But recently, Maria, Gal and co-workers[10] have resolved this problem in a more general way. In essence, these workers analysed 10 sets of thermodynamic and spectroscopic basicity scales by principal component analysis (PCA) and showed that 95% of the total variance of the data could be accounted for by only two factors, F_1 and F_2. They suggested that F_1 represented a blend of electron delocalization (or covalent) and electrostatic effects and that F_2 represented essentially an electrostatic effect. Hence if some basicity property BDP, for a range of bases is correlated with F_1 and F_2 in the double regression equation (1), the constants S_1 and S_2 will reflect the sensitivity of the BDP to the covalent effect: electrostatic effect. Furthermore,

$$\mathrm{BDP} = \mathrm{BDP}_0 + S_1F_1 + S_2F_2 \tag{1}$$

an angle θ, defined as $\tan^{-1}(S_2/S_1)$, will provide a quantitative estimate of the relative amount of electrostatic:covalent character in the base–acid complex. Only if θ is the same for two basicity dependent properties, $(\mathrm{BDP})^{a}$ and $(\mathrm{BDP})^{b}$, will a plot of $(\mathrm{BDP})^{a}$ against $(\mathrm{BDP})^{b}$ be linear over all the bases, and show family independent character. The angle θ contains no more information than the ratio S_2/S_1, but it is a rather useful quantity for the description of electrostatic:covalent character, see Reference 10. But this is exactly the quantitative criterion needed to establish the generality or otherwise of basicity dependent properties. Maria, Gal and co-workers[10] then showed that over a wide range of basicity dependent properties, θ was not constant (values ranged from −61 to +77 degrees) and hence that no completely general scale of basicity can be set up.

A rather special area of basicity dependent properties is that of hydrogen-bonding, and an even more particular area is hydrogen-bonding in terms of log K values for complexation of a series of bases against a reference acid in an inert solvent, equation (2). We therefore set out to examine the feasibility of setting up a 'general' scale of hydrogen-bond basicity, using only log K values, via the F_1 and F_2 methodology, equation (1). It has been known for

$$\mathrm{A{-}H} + \mathrm{B}^{i} \xrightleftharpoons[\text{inert solvent}]{K} \mathrm{A{-}H} - - - \mathrm{B}^{i} \tag{2}$$

some time that even within this restricted range of basicity dependent properties, family dependent character is found in plots of $(\mathrm{BDP})^{a}$ against $(\mathrm{BDP})^{b}$, where $\mathrm{BDP} = \log K$, in some instances especially when one of the reference acids is a weak acid.[11,12] Panchenko and co-workers[9] analysed log K values using the two parameter equation (3); $\log K_{\mathrm{PFP}}$ is the logarithm of the complexation constant against 4-fluorophenol in carbon tetrachloride and $\log K_{\mathrm{I}}$ is the corresponding constant against iodine in either *n*-heptane or carbon tetrachloride. The term in $C \log K_{\mathrm{I}}$ was taken as a measure of

$$\log K = \log K_0 + C \log K_{\mathrm{I}} + B \log K_{\mathrm{PFP}} \tag{3}$$

covalent interaction and the term in $B \log K_{PFP}$ as a measure of electrostatic interaction, so that equation (3) is very closely related to equation (1). We note that the β/ξ formalism,[13] or the *E*/*C* parameters of Drago *et al.*,[14] have also been used to investigate the problem of various basicity scales.

Panchenko and co-workers[9] also showed that when log *K* values for bases against reference acids 5-fluoroindole, chloroform, diphenylamine, and *N*-methylaniline were plotted against $\log K_{PFP}$, family dependent character was observed. However, use of the two parameter equation (3) gave good correlations.[9] Although this work demonstrates that the electrostatic: covalent ratio in complexes with the above few weak acids must be substantially different to that in complexes with 4-fluorophenol, Panchenko and co-workers[9] did not attempt to suggest any general area in solute hydrogen-bonding that might provide a hydrogen-bond basicity scale. Kamlet and co-workers[15] later analysed log *K* values for bases against the same four weak acids studied by Panchenko and co-workers, and concluded that log *K* values contained important contributions from dipole–dipole interactions. If we include these latter interactions in the long-range electrostatic interaction,[16] then this analysis follows closely that of Panchenko and co-workers.

We start with the F_1 and F_2 factors of Maria, Gal and co-workers; these are listed in Table 1 for the 22 recorded bases. (We omit 1,4-dioxane, because of confusion in the literature as to whether or not recorded log *K* values are statistically corrected, leaving 21 available bases.) In many cases, results for all the 22 bases in Table 1 will not be available. Whether or not equation (1) can usefully be employed will depend largely on the orthogonality of the resulting

Table 1. The F_1 and F_2 parameters used in this work[a]

Base	F_1	F_2
nitrobenzene	−0·89	0·01
acetonitrile	−0·57	−0·04
diethyl carbonate	−0·52	−0·02
1,4-dioxane	−0·37	−0·16
ethyl acetate	−0·44	−0·02
acetone	−0·37	−0·02
cyclohexanone	−0·34	0·01
diethyl ether	−0·29	−0·11
trimethyl phosphate	−0·08	0·24
tetrahydrofuran	−0·21	−0·04
2,6-dimethylpyridine	0·47	−0·10
2,4,6-trimethylpyridine	0·53	−0·07
dimethyl sulfoxide	0·15	0·20
tetramethylurea	0·20	0·11
N,*N*-dimethylaniline	0·11	−0·40
N,*N*-dimethylformamide	0·05	0·12
N,*N*-dimethylacetamide	0·18	0·15
N-methylpyrrolidone	0·15	0·16
hexamethylphosphoramide	0·48	0·38
pyridine	0·42	−0·08
4-methylpyridine	0·49	−0·05
triethylamine	0·85	−0·26

[a] All values taken from Reference 10.

Table 2. Log K values used in the analysis*

No.	Reference Acid	Solvent	Nitrobenzene	Acetonitrile	Ethyl Acetate	Acetone	Cyclohexane	Diethyl Ether	Trimethyl Phosphate	Tetrahydrofuran
1	Phenol	CCl_4	0·573^{a}‡	0·847^{b}	0·939^{c}	1·033^{c}	1·168^{c}	0·946^{d}	2·196^{e}	1·210^{d}
2	4-Fluorophenol	CCl_4^{m}		0·90	1·09		1·32	1·01	2·45	1·26^{n}
3	4-Fluorophenol	$C_6H_{12}^{m}$								
4	4-Fluorophenol	$C_6H_5Cl^{m}$								
5	4-Fluorophenol	o-$C_6H_4Cl_2^{m}$					1·02			
6	4-Fluorophenol	$ClCH_2CH_2Cl^{m}$					0·52			
7	4-Fluorophenol	$CH_2Cl_2^{m}$					0·50			
8	4-Chlorophenol	CCl_4			1·199^{o}	1·385^{p}		1·020^{q}		1·465^{q}
9	4-Bromophenol	CCl_4					1·423^{z}			
10	4-Iodophenol	CCl_4								
11	4-Methylphenol	CCl_4					1·049^{z}			
12	4-Methoxyphenol	CCl_4				0·986^{p}	1·037^{z}			
13	4-Nitrophenol	CCl_4	0·716^{af}							
14	4-Nitrophenol	$CH_3CCl_3^{ag}$		1·23	1·43	1·61	1·70			1·69
15	Meleimide	CCl_4^{ah}		0·398				0·602		
16	Succinimide	CCl_4^{ah}		0·301				0·602		
17	Methanol	CCl_4		0·101^{ai}	0·147^{aj}	0·257^{aj}		0·073^{ak}	0·999^{al}	
18	Ethanol	CCl_4			0·015^{aj}	0·088^{aj}		−0·126^{ak}		
19	*n*-Butanol	CCl_4				0·114^{aq}	0·263^{ar}	0·079^{aq}		0·041^{aq}
20	*t*-Butanol	CCl_4			−0·073^{aj}	0·015^{aj}		−0·152^{ak}		
21	1,1,1-Trifluoroethanol	CCl_4		0·743as	0·841as	0·950^{ao}		0·715as	2·170^{at}	1·002^{ao}
22	HFIP†	CCl_4		1·542^{ax}	1·568^{ay}	1·690^{ao}		1·432^{ax}		1·890^{ao}
23	Water	CCl_4^{az}				0·205		0·117	0·896	
24	Trichloromethane	CCl_4				−0·398^{bb}		−0·848^{bc}		−0·448^{bd}
25	Trichloromethane	$C_6H_{12}^{bj}$			−0·153	−0·107	0·028	−0·361^{bk}		−0·221^{bk}
26	Pyrrole	CCl_4				0·279^{aq}	0·362^{aq}			0·176^{aq}
27	Indole	CCl_4		0·249^{bq}	0·330^{bo}	0·421^{bq}				0·288^{bq}
28	5-Fluoroindole	CCl_4^{br}					0·75	0·23	1·49	0·34
29	4-Bromoaniline	CCl_4^{aq}		−0·031			0·145			
30	*N*-Methylaniline	C_6H_{12}			−0·051^{bl}	0·025^{bl}	0·053^{bl}			−0·148^{bl}
31	Diphenylamine	CCl_4		0·041^{aq}	−0·293^{bo}	0·342^{aq}	0·255^{aq}	−0·301^{aq}		
32	Bu_3NH^+	o-$C_6H_4Cl_2^{bv}$	1·410	2·410		2·398				2·182

*All values refer to 298 K, except set 29 which are at 293 K.

†Hexa fluoroisopropanol.

‡For all lettered References to this table see page following Table.

2,6-Dimethyl-Pyridine	2,4,6-Trimethyl Pyridine	Dimethyl Sulfoxide	Tetramethyl-Urea	*N,N*-Dimethyl-Aniline	*N,N*-Dimethyl-Formamide	*N,N*-Dimethyl-Acetamide	*N*-Methyl-Pyrrolidone	Hexamethyl-Phosphoramide	Pyridine	4-Methyl-Pyridine	Triethylamine
1·892^{f}	2·043^{f}	2·262^{g}	2·134^{h}		1·832^{i}	2·104^{h}	2·138^{j}	3·185^{k}	1·690^{f}	1·821^{f}	1·886^{l}
		2·53^{n}	2·30	0·45	2·06^{n}	2·38^{n}		3·56^{n}	1·88^{n}	2·03^{n}	1·93^{n}
		2·56			2·30			3·80	2·03		1·99
		2·20			1·74			3·06	1·60		1·84
		2·18			1·70			3·06	1·63		1·93
		1·65			1·27			2·55	1·29		1·70
		1·44			1·18			2·37	1·26		1·67
		2·703^{r}	2·624^{s}		2·156^{t}	2·522^{u}	2·688^{v}	3·785^{w}	2·086^{x}		2·204^{y}
		2·769^{r}	2·656^{s}			2·573^{u}	2·736^{v}	3·924^{aa}	2·076^{ab}		2·176^{ac}
		2·826^{r}	2·658^{s}				2·676^{v}	3·955^{aa}	1·934^{x}		2·272^{ac}
		2·176^{r}	2·029^{s}			1·913^{u}	2·097^{v}	3·158^{ad}	1·563^{x}		1·726^{ac}
		2·176^{r}	2·033^{s}			1·972^{u}	2·130^{v}	3·137^{aa}	1·544^{x}		1·633^{ae}
		3·558^{r}	3·483^{s}			3·423^{u}	3·157^{v}				2·863^{ac}
		3·06	3·19		2·81		3·12		2·52	2·78	
		1·778				1·505		2·407	1·255	1·342	
		1·813				1·342		2·225	1·342	1·312	
0·505^{am}	0·521^{am}	0·910^{ai}			0·740^{aj}			1·591^{an}	0·467^{am}	0·490^{am}	0·759^{f}
			0·732^{ao}		0·542^{aj}	0·657^{h}		1·484^{an}	0·381^{aj}		0·594^{ap}
									0·322^{aq}		0·398^{aq}
					0·462^{aj}			1·204^{an}	0·161^{aj}		
	1·781^{au}	2·170^{av}	2·001^{ao}		1·613as	1·999^{ao}		3·090^{an}	1·548^{aw}		
	3·036^{ax}	3·156^{ao}	3·114^{ao}			3·182^{ao}		4·370^{an}	2·784^{aw}		
		0·911			0·555	0·787	0·963^{ba}		0·415		0·686
		0·077^{be}			−0·058^{be}	−0·058^{bf}		0·446^{bg}	−0·415^{bh}		−0·444^{bi}
−0·074^{bd}						0·732^{bi}	0·537	1·075^{bg}	−0·039^{bd}		−0·342
0·442^{bm}	0·612^{bm}	1·217^{bn}			0·865^{bo}				0·423^{bm}	0·599^{bm}	0·406^{bp}
		1·340^{bn}			1·085^{bo}				0·559^{bq}		
		1·49	1·43	0·17	1·25	1·47		2·31	0·75		0·53
0·041		0·653			0·398		0·511		0·000		
				−0·337^{bs}		0·867^{bl}			0·117^{bs}		−0·495^{bl}
		0·836^{bt}	0·672^{aq}		0·396^{bo}	0·621^{bt}		1·288^{bt}	0·176^{aq}	0·246^{bu}	−0·432^{aq}
		4·568				4·491		6·352	3·140	3·510	

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set of F_1 and F_2 factors. By definition, the correlation coefficient, r, between the original set of 22 F_1 and F_2 factors is zero (and for the 21 bases excluding 1,4-dioxane $r = -0{\cdot}040$), but if the six nitrogen bases in Table 1 are left out, the F_1 and F_2 factors for the remaining 16 bases are now well correlated with $r = 0{\cdot}764$, and nothing useful can be obtained through equation (1). For reasons we have outlined before, we consider only log K values, equation (2), in our BDP's, and list in Table 2 values for as many sets of bases against reference acids as we could find, excluding all sets of bases for which the log K values for the nitrogen bases were missing. In many cases, more than one experimentally determined log K value was available for a given complexation reaction: all the log K values given in Table 2 were taken from a much larger database and are known to be reasonably self-consistent. We include in Table 2 values for 4-fluorophenol in various solvents as separate sets, since we must consider each reference acid-solvent system as a separate 'reference acid'.

Our analysis of the 32 sets in Table 2, using the F_1 and F_2 parameters in equation (1) is given in Table 3. The standard deviations of the constants log K_0 (equivalent to BDP$_0$), S_1 and S_2 are given, together with our estimated standard deviation in θ. The latter is calculated through equations (4) and (5), where σ_1 and σ_2 are the standard deviations in S_1 and S_2 as given in Table 1.

$$\sigma(S_2/S_1) = \frac{/S_2/}{/S_1/}\sqrt{\frac{\sigma_1^2}{S_1^2} + \frac{\sigma_2^2}{S_2^2}} \tag{4}$$

$$\sigma(\theta) = \frac{\sigma(S_2/S_1)}{1 + (S_2/S_1)^2}\,\frac{180}{\pi} \tag{5}$$

Since the right hand side of equation (5) is the first term only in a Taylor expansion, the equation will yield reasonable estimates of $\sigma(\theta)$ for cases in which $\sigma(S_2/S_1)$ is small. However, inspection of Table 2 shows that our computed values of $\sigma(\theta)$ are usually only around 2 or 3 degrees. In but two sets, no.s 19 and 30 the overall standard deviation in log K and the correlation coefficient are not at all good, and lead to very large computed errors in θ. In the case of *n*-butanol, this is of little consequence, and in the case of *N*-methylaniline the set is so important that a larger-than-usual error in θ can be tolerated. Maria, Gal and co-workers[10] listed a number of θ values for hydrogen-bond complexations. In general, our values agree well, however we find a θ value of 78 for $CHCl_3$ in CCl_4 whereas Maria and Gal record a much lower value of 56. We have traced the source of this discrepancy to the data used by Maria and Gal, taken from the compilation of log *K* values by Benoit and Louis.[17] These workers give log *K* values for complexation some of which are based on molar *K* values, and some on mol fraction *K* values, so that the overall set of log *K* values given by Benoit and Louis cannot be used as such. There is also a difference for $CHCl_3$ in cyclohexane, we find $\theta = 83$ for $n = 11$ whereas Maria and Gal found $\theta = 60$ for $n = 6$.

Before dealing with hydrogen-bond complexation constants as such, we first compare θ values obtained from log *K* for various BDP's, see Table 4. Values of θ for the I_2 complexation or the H_3O^+ proton transfer are far more negative than any of the hydrogen-bond θ values we have obtained, and show that for both of these acids, there is a much larger covalent character in their adducts than with the hydrogen-bond complexes. The difference in θ between BDP's against 4-fluorophenol ($\theta = 70$) and H_3O^+ ($\theta = -52$) is extremely large, and leads to family dependent behaviour in plots of log K_{PFP} vs pK_A values in water, as observed many years ago by Taft *et al.*[18,19]

Our analysis of the hydrogen-bond complexation constants follow on from the above results. We know that a substantial difference in θ for two BDP's leads to family dependent behaviour in plots of $(BDP)^a$ against $(BDP)^b$. We know also that a criterion for a general scale of hydrogen-bond basicity using log *K* values is that all the relevant BDP's should be linearly related and should show family independent behaviour. Hence we are now in a position to answer the fundamental question, 'Is it possible to construct a completely general scale of solute hydrogen-bond basicity using log *K* values for complexation in inert solvents, and, if not, is it possible to construct a scale that would still cover a wide area without being completely general?' In Table 5 are given θ values for BDP's against reference acids in the inert solvents CCl_4, cyclohexane, and 1,1,1-trichloroethane (TCE). These values range from 64 up to 86, that is a much smaller range than that encountered in the 4-fluorophenol/H_3O^+ plot mentioned above. Thus, although in principle it is clear that θ alters over the hydrogen-bond BDP's and hence that no completely general scale of solute hydrogen-bond basicity can be set up, in practice the loss of chemical information in setting up a general scale may be small enough to be tolerated. For example, in a plot of log *K* against a reference acid with $\theta = 80$ vs log *K* against a reference acid with $\theta = 70$, the family dependent behaviour, although not very pronounced, is apparent and indicates that if a completely general scale of hydrogen-bond basicity were to be set up over the reference acids in Table 5, the scale could not reproduce experimental log *K* values to less than about 0·2 or 0·3 units. An analysis we have carried out on published log *K* values suggests that the so-called level of exhaustive fit is about 0·07 units, so that there would be quite a loss in chemical information if a general hydrogen-bond scale was set up. Inspection of Table 5 indicates that, somewhat arbitrarily, the reference acids can be divided into two groups, with the dividing line between methanol and 5-fluoroindole. For the large group of reference acids from hexafluoroisopropanol (HFIP) in CCl_4 to methanol in CCl_4, θ varies by only 9 degrees, and plots of $(BDP)^a$ vs $(BDP)^b$ within this set of acids yield essentially family independent behaviour. (Thus Taft *et al.*[19] showed that BDP using log *K* values for 4-fluorophenol were strictly linear with BDP's using log *K* for ethanol, methanol, l-naphthol, TFE, phenol and HFIP.) Hence a solute hydrogen-bond basicity scale covering quite a large number of reference acids can be set up; in a subsequent publication we shall describe the construction of such a 'reasonably general' scale,[20] and will

Table 3. Analysis of log K values in terms of the parameters F_1 and F_2

No.	Reference Acid	Solvent	log K_0	S.D.	S_1	S.D.	S_2	S.D.	S_2/S_1	θ°	S.D.	n	Overall S.D.	Corr. Coeff.
1	Phenol	CCl_4	1·547	0·018	1·147	0·040	2·733	0·119	2·38	67	1	19	0·076	0·994
2	4-Fluorophenol	CCl_4	1·683	0·014	1·200	0·036	3·347	0·072	2·79	70	1	15	0·053	0·998
3	4-Fluorophenol	C_6H_{12}	1·724	0·086	1·418	0·170	3·603	0·215	2·54	69	3	5	0·088	0·997
4	4-Fluorophenol	C_6H_5Cl	1·337	0·098	1·401	0·195	2·839	0·246	2·03	64	4	5	0·101	0·993
5	4-Fluorophenol	o-$C_6H_4Cl_2$	1·395	0·057	1·353	0·120	2·632	0·219	1·95	63	3	6	0·105	0·993
6	4-Fluorophenol	$ClCH_2CH_2Cl$	0·957	0·046	1·491	0·095	2·258	0·174	1·51	57	3	6	0·083	0·995
7	4-Fluorophenol	CH_2Cl_2	0·901	0·047	1·430	0·098	1·918	0·179	1·34	53	3	6	0·085	0·994
8	4-Chlorophenol	CCl_4	1·857	0·030	1·368	0·077	3·306	0·173	2·42	68	2	12	0·098	0·994
9	4-Bromophenol	CCl_4	1·866	0·047	1·426	0·102	3·621	0·181	2·54	69	2	8	0·088	0·995
10	4-Iodophenol	CCl_4	1·809	0·169	1·576	0·347	3·764	0·420	2·39	67	5	6	0·167	0·982
11	4-Methylphenol	CCl_4	1·390	0·051	1·238	0·113	2·988	0·200	2·41	67	2	8	0·097	0·991
12	4-Methoxyphenol	CCl_4	1·414	0·031	1·130	0·070	3·045	0·146	2·69	70	1	9	0·075	0·995
13	4-Nitrophenol	CCl_4	2·429	0·052	1·966	0·096	4·673	0·315	2·38	67	2	6	0·113	0·997
14	4-Nitrophenol	CH_3CCl_3	2·227	0·036	1·551	0·099	3·934	0·368	2·54	68	2	11	0·110	0·992
15	Maleimide	CCl_4	1·061	0·033	0·891	0·086	2·435	0·194	2·73	70	2	7	0·079	0·996
16	Succinimide	CCl_4	1·027	0·068	0·971	0·182	2·035	0·406	2·10	64	6	7	0·167	0·979
17	Methanol	CCl_4	0·474	0·038	0·604	0·084	1·973	0·219	3·27	73	3	13	0·130	0·960
18	Ethanol	CCl_4	0·337	0·033	0·769	0·077	1·855	0·180	2·41	67	3	9	0·094	0·986
19	*n*-Butanol	CCl_4	0·261	0·079	0·352	0·159	0·742	0·834	2·11	65	26	6	0·097	0·855
20	*t*-Butanol	CCl_4	0·181	0·013	0·391	0·039	2·188	0·086	5·60	80	1	6	0·029	0·999
21	TFE*	CCl_4	1·382	0·026	1·030	0·074	3·179	0·179	3·08	72	2	13	0·085	0·994
22	HFIP†	CCl_4	2·377	0·031	1·581	0·089	3·230	0·232	2·04	64	2	11	0·099	0·996
23	Water	CCl_4	0·463	0·048	0·652	0·131	1·697	0·285	2·60	69	5	9	0·125	0·938
24	Trichloromethane	CCl_4	−0·356	0·040	0·364	0·098	1·758	0·203	4·83	78	3	9	0·111	0·968
25	Trichloromethane	C_6H_{12}	0·055	0·032	0·315	0·074	2·606	0·190	8·27	83	2	11	0·103	0·981
26	Pyrrole	CCl_4	0·497	0·030	0·602	0·081	2·809	0·270	4·67	78	2	10	0·084	0·970
27	Indole	CCl_4	0·616	0·026	0·460	0·073	3·397	0·254	7·38	82	1	7	0·061	0·993
28	5-Fluoroindole	CCl_4	0·863	0·058	0·633	0·162	2·777	0·253	4·38	77	3	12	0·184	0·967
29	4-Bromoaniline	CCl_4	0·153	0·016	0·152	0·041	2·219	0·130	14.6	86	1	7	0·038	0·993
30	*N*-Methylaniline	C_6H_{12}	0·176	0·107	0·192	0·246	2·144	0·650	11·17	85	7	8	0·265	0·834
31	Diphenylamine	CCl_4	0·199	0·049	0·215	0·115	2·775	0·310	12·91	86	2	13	0·173	0·946
32	Bu_3NH^+	o-$C_6H_4Cl_2$	3·065	0·103	1·594	0·214	6·639	0·693	4·16	76	2	9	0·281	0·987

*Trifluoroethanol.
†Hexafluoroisopropanol.

Table 4. Comparison of θ values for some hydrogen-bond complexation reactions, with those for other processes, all based on log *K* values

Reference Acid	Solvent	θ
Diphenylamine	CCl_4	86
4-Fluorophenol	CCl_4	70
HFIP	CCl_4	64
4-Fluorophenol	CH_2Cl_2	53
I_2	heptane/CCl_4	−21[a]
H_3O^+	H_2O	−52[a]

[a] Reference 10.

Table 5. Calculated values of θ for various reference acids in some nonpolar solvents

Reference Acid	Solvent	θ
Diphenylamine	CCl_4	86
4-Bromoaniline	CCl_4	86
N-Methylaniline	C_6H_{12}	~85
Trichloromethane	C_6H_{12}	83
Indole	CCl_4	82
t-Butanol[a]	CCl_4	80
Pyrrole	CCl_4	78
Trichloromethane	CCl_4	78
5-Fluoroindole	CCl_4	77
Methanol	CCl_4	73
TFE	CCl_4	72
Maleimide	CCl_4	70
4-Methoxyphenol	CCl_4	70
4-Fluorophenol	CCl_4	70
Water	CCl_4	69
4-Fluorophenol	C_6H_{12}	69
4-Bromophenol	CCl_4	69
4-Chlorophenol	CCl_4	68
4-Nitrophenol	CH_3CCl_3	68
Phenol	CCl_4	67
4-Iodophenol	CCl_4	67
4-Methylphenol	CCl_4	67
4-Nitrophenol	CCl_4	67
Ethanol	CCl_4	~67
n-Butanol	CCl_4	65
Succinimide	CCl_4	64
HFIP	CCl_4	64

[a] Over a large set of bases, this hydrogen-bonded acid behaves as though it was in the lower set of acids.

then concentrate on chemical aspects. The generality of such a scale can be extended to the reference acids with $\theta > 73$, provided that bases such as pyridines, aliphatic amines, and some ethers are excluded. Alternatively, a second, independent, solute basicity scale could be constructed based just on log K values against the reference acids from 5-fluorindole to diphenylamine. The great advantage of the use of the F_1 and F_2 factors, equation (1), is that sets of bases against various reference acids can be assembled in a quantitative order and grouped in terms of the electrostatic:covalent ratio, as in Table 5, where the dashed line is intended to separate categories. The varying nature of this ratio, quantitatively given by θ, explains why, for example, plots of log K against 4-fluorophenol show family dependent behaviour with respect to log K against diphenylamine.[9]

Solvent effects on log K values for sets of bases against the reference acid 4-fluorophenol were first examined by Taft *et al.*[21] These workers showed that as the solvent became more polar, there arose systematic deviations in log K values for pyridines and triethylamine ascribed to an increased stretching of the OH bond in the 4-fluorophenol/pyridine and 4-fluorophenol/Et_3N complexes brought about by the more polar solvents. Later work[15] by the same group suggested that these solvent effects were due to various solute/solute and solute/solvent dipole/dipole interactions. We have mentioned earlier that in the overall electrostatic:covalent ratio, the former effect included long range interactions of the dipole/dipole type (betwen dipolar hydrogen-bond acid and dipolar hydrogen-bond base). For nonassociated solvents, these interactions are proportional to $\mu_A\ \mu_B/\varepsilon_r$ where μ_A and μ_B are the dipole moments of the acid and base, and ε_r is the solvent dielectric constant. Now if, say, DMSO(μ_B = 4·1 D) and Et_3N(μ_B = 0·7 D) complex with 4-fluorophenol partly by long range dipole/dipole interactions, the effect of a more polar solvent will be to reduce log K for DMSO more than log K for Et_3N. If the covalent effect is the same in the two solvents, the decrease in the electrostatic interaction will lead to a reduction in the value of θ on transfer to a more polar solvent. In Table 6 is a comparison of the relevant values of θ and also of S_2/S_1 with solvent dielectric constant. Bearing in mind that θ is only good to about ±4 degrees for the various base sets in Table 6, there is a quite reasonable connection between θ or S_2/S_1 and the quantity $100/\varepsilon$. Thus the same analysis that explains the variation of θ amongst different reference acids, serves also to explain the variation with the same reference acid and different solvents. (Values of θ for 4-nitrophenol in CCl_4 (ε_r = 2·015) and TCE (ε_r = 7·53) are almost identical, but this is probably due to the two sets of bases not being well matched.) Although couched in other terms, the analyses of Taft *et al.*[15,21] can probably be reworded using our concepts of electrostatic:covalent ratios. The results given in Table 6 lead to another important conclusion, namely that in the construction of even a 'reasonably general' scale of hydrogen-bonding basicities, reference acids that give rise to θ between about 64–73 degrees in solvents CCl_4 or cyclohexane may have to be excluded when used in other solvents where they yield very different θ values. Thus a set of bases against 4-fluorophenol in chlorobenzene would be included in a 'reasonably general' scale, Table 5, but would be excluded in dichloromethane, at least with regard to bases such as pyridines and alkylamines, (see Table 6).

We conclude by stating that no completely general scale of solute hydrogen-bonding basicity can be constructed, but that it is possible to devise a 'reasonably general' scale that could be used to reproduce and to predict log K values of all bases against reference acid/solvent systems with θ between 64 and 73 degrees, and of certain classes of base against reference acid/solvent systems with θ outside these limits, see Table 5. We note also that the results of this investigation into basicity scales has considerable implications with regard to the construction of a general scale of solute hydrogen-bond acidity based on log K values. Thus log

Table 6. Comparison of θ and S_2/S_1, for 4-fluorophenol reference acid in various solvents with solvent dielectric constant

Solvent	θ	S_2/S_1	$100/\varepsilon_r$
Tetrachloromethane	70	2·79	44·88
Cyclohexane	69	2·54	49·63
Chlorobenzene	64	2·03	17·79
o-Dichlorobenzene	63	1·95	10·07
1,2-Dichloroethane	57	1·51	9·78
Dichloromethane	53	1·34	11·20

K values for acids with $64 < \theta < 73$ against all reference bases (at least in solvents CCl_4 and cyclohexane) can be used to define a 'reasonably general' hydrogen-bond acidity scale for solutes, but log *K* values for acids with $\theta > 77$ against particular bases such as pyridines and alkylamines cannot be included in this 'reasonably general' scale.

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