The Properties of Organic Liquids that are Relevant to their Use as Solvating Solvents

Y. Marcus
Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K. *

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1 Introduction

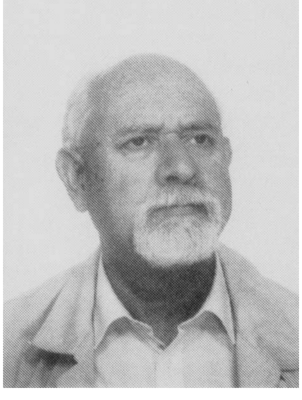
Organic liquids are characterized by several properties that make them suitable for dissolving and for providing reaction media for various types of solutes. These properties include physical quantities, such as the liquid range (freezing to normal boiling temperatures), vapour pressure, density, refractive index, relative permittivity, *etc.*, that are not further discussed here *per se*. The more 'chemical' properties to be discussed include polarity, ability to form hydrogen bonds, and structuredness, among others. Linear free energy relationships (LFER) or linear solvation energy relationships (LSER) have been proposed that relate such properties to divers processes in solution: solubility, distribution between two liquids, retention in chromatography, rates of reactions, free energy and enthalpy of equilibria, wavelengths of light absorption, NMR chemical shifts, *etc.* In most cases, the quantity that describes the intensity or extent of such a process (called XYZ in the following for the sake of generality) depends on more than one solvent property. Of the many expressions that have been proposed for the description of LSERs, one that was found to be very successful is the Kamlet–Taft[1] expression:

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

where XYZ_0, a, b, and s are (solvent-independent) coefficients characteristic of the process and indicative of its sensitivity to the accompanying solvent properties, α is the hydrogen bond donation (HBD) ability of the solvent, β is its hydrogen bond acceptance (HBA) or electron pair donation ability to form a coordinative bond, and π^* is its polarity/polarizability parameter. Further terms (involving products of coefficients and solvent properties) may be added as required for specific processes. For some processes any of the coefficients XYZ_0, a, b, and/or s may be negligibly small, so that the corresponding terms do not play a role in the characterization of the solvent effects for these processes.

The quantities α and β are solvatochromic properties of the solvents, *i.e.*, they are determined primarily by the energies of the longest wavelength absorption peaks of certain carefully selected probe solutes in the solvents in question, after subtraction of the effect that non-HBD and/or non-HBA solvents would have on the probe, determined in separate experiments. They have been designed and given numerical values so that ideally they describe exclusively the HBD and HBA properties of the solvents, not being affected by their other properties, such as polarity, polarizability, tightness of cohesion, *etc.* The solvatochromatic parameter π^*, on the other hand, describes a combination of properties, the polarity and the polarizability of the solvents. For certain processes a modification term, $- s\cdot d\cdot\delta$, has to be added to equation 1[1] in order to describe the solvent polarizability correctly, where $\delta = 1.0$ for aromatic solvents, 0.5 for polychlorinated (polyhalogenated?) aliphatic solvents, and 0 for all other aliphatic solvents, and $0 \leq d \leq 0.4$, depending on the process. This is a less desirable feature of the parameter π^*.

Yizhak Marcus received his M.Sc. in chemistry in 1952 and the Ph.D. in 1956 from the Hebrew University of Jerusalem. Until 1965 he was with the Israeli AEC, doing radiochemical research. In 1965 he was appointed as Professor of Inorganic and Analytical Chemistry at the Hebrew University. He has since been a visiting professor at universities in the U.S.A., Germany, Japan, and the U.K. He has authored three books and edited several more and published 200 research and review papers and book chapters.



A host of other solvent parameters have been proposed over the years to express solvent properties in this context. Some of these were called 'polarity indices', others 'donor-' and 'acceptor-numbers', *etc.* Survived and of widespread use are many of these, including Dimroth and Reichardt's $E_T(30)$,[2] Kosower's Z,[3] Mayer and Gutmann's AN,[4] Gutmann's DN,[5] and Swain *et al.*'s *Acity* and *Basity* (their symbols A and B are not employed here, to avoid confusion with other uses of these letters),[6] to mention but a few that describe various aspects of polarity and donor–acceptor behaviour. Also important with regard to the solvation abilities of the solvents are physical properties such as Hildebrand's solubility parameter δ_H,[7] and the relative permittivity (dielectric constant) ϵ, the dipole moment μ, and the refractive index n, among others. These quantities have been determined for a large number of solvents, whereas most other quantities are known for a limited number only.

There are several computational methods for relating experimentally observed quantities XYZ to solvent properties according to equation 1 or to equivalent expressions employing different solvent parameters. One is stepwise multiple linear regression (SMLR), where solvent parameters are offered one by one to the statistical computer program, being accepted, rejected, or exchanged until certain statistical criteria are met. These might be the explanation of a major fraction of the variance of the data (say, >98%) and a maximal Fisher-$F_{m,n}$ statistic for m independent parameters and $m + n$ data (solvent) points. Another method is principal component or factor analysis, in particular its target factor analysis (TFA) variant.[8] This, again on the basis of statistical criteria, determines first how many independent basic factors are required for the explanation of most of the variance of the data, and then selects that many among solvent property vectors that describe the data most adequately.

The former method (SMLR) has now been applied to a very extensive set of solvent properties that has not been considered previously for so many solvents of different classes, see Table 1. There are over 170 solvents for which the five parameters α, β, π^*, δ_H, and $E_T(30)$ have been established. (There are many more for which one, mainly $E_T(30)$ or δ_H, or two, both $E_T(30)$ and δ_H, are known.) There are 110 solvents for which DN, 52 for which AN, 61 for which Z, and 52 for which *Acity* and *Basity* are known in addition to the former five indices. (Each of these parameters is known for a few additional solvents, for which, however, most or all of α, β, π^*, and $E_T(30)$ are unknown.) Correlations among these parameters and between them and

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* Permanent address: Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

Table 1 The property parameters of organic solvents HBD ability α, HBA ability β, polarity/polarizability π^*, polarity $E_T(30)$, donor number *DN*, acceptor number *AN*, *Acity*, *Basity*, polarity *Z*, polarity *Z'*

Solvent	α	β	π^*	$E_T(30)$	*DN*	*AN*	*Acity*	*Basity*	*Z*	*Z'*
perF-n-nexane	00	− 08	− 41							
perF-Me-c-hexane	00	− 06	− 40							
perF-decalin	00	− 05	− 32							
Me_4-silane	00	02	− 09	30 7						
2-Me-butane	00	01	− 08	30 9						
n-pentane	00	00	− 08	31 1						
n-hexane	00	00	− 04	31 0	0	0	01	− 01		
n-heptane	00	00	− 08	31 1	0	0	00	00		
n-octane	00	00	01	31 1						
n-decane	00	00	03	31 0						
n-dodecane	00	00	05	31 1						
c-hexane	00	00	00	30 9	0		02	06	60 1	
cis-decalin	00	08	11	31 2						
benzene	00	10	59	34 3	1	8 2	15	59	54 0	54 0
toluene	00	11	54	33 9	1		13	54		
m-xylene	00	12	47	33 3	5 0		04	50		
p-xylene	00	12	43	33 1	5 0		06	50		
mesitylene	00	13	41	32 9	10 0					
styrene	00	12		34 8	5 0					
water	1 17	47	1 09	63 1	18 0	54 8	1 00	1 00	94 6	89 6
methanol	98	66	60	55 4	30 0	41 3	75	50	83 6	79 4
ethanol	86	75	54	51 9	32 0	37 1	66	45	79 6	75 8
n-propanol	84	90	52	50 7		37 3	63	44	78 3	73 7
i-propanol	76	84	48	49 2	36 0	33 5	59	44	76 3	72 4
n-butanol	84	84	47	50 2	29 0	36 8	61	43	77 7	73 7
i-butanol	79	84	40	48 6					77 7	
s-butanol	69	80	40	47 1					75 4	
t-butanol	42	93	41	43 7	38 0	27 1	45	50	71 3	68 1
n-pentanol	84	86	40	49 1	25 0				77 6	72 9
i-pentanol	84	86	40	49 0	32 0				77 6	73 3
t-pentanol	28	93	40	41 1						66 6
n-hexanol	80	84	40	48 8					76 5	73 3
c-hexanol	66	84	45	46 9	25 0				75 0	
n-octanol	77	81	40	48 3	32 0					
n-decanol	70	82	45	47 7					73 3	
benzyl alcohol	60	52	98	50 4	23 0	36 8			78 4	
2-phenylethanol	64	61	88	49 5	23 0	33 8				
3-phenylpropanol	53	55	95	48 5						
allyl alcohol	84	90	52	52 1						
2-chloroethanol	1 28	53	46	55 5						
trifluoroethanol	1 51	00	73	59 8		53 8				
hexafluoroiPrOH	1 96	00	65	65 3		66 7				
ethanediol	90	52	92	56 3	20 0		78	84	85 1	
glycerol	1 21	51	62	57 0	19 0				82 7	
phenol	1 65	30	72	53 4	11 0					
m-cresol	1 13	34	68	52 4		50 4				
p-cresol	1 64	34	68	53 3						
m-chlorophenol	1 57	23	77	60 8						
diethyl ether	00	47	27	34 5	19 2		12	34		
di-n-propyl ether	00	46	27	34 0	18 0					
di-i-propyl ether	00	49	27	34 0	19 0					
di-n-butyl ether	00	46	27	33 0	19 0		06	28	60 1	
di-ClEt ether	00	40	82	41 6	16 0					
anisole	00	32	73	37 1	9 0		21	74		
phenethole	00	30	69	36 6	8 0				58 9	
dibenzyl ether	00	41	80	36 3	19 0					
diphenyl ether	00	13	66	35 5						
furan	00	14		36 0	6 0					
tetrahydrofuran	00	55	58	37 4	20 0	8 0	17	67	58 8	56 0
2-Me-THF	00	45		36 5	12 0				55 3	
tetrahydropyran	00	54	51	36 6	22 0					
dioxane	00	37	55	36 0	14 3	10 3	19	67	64 5	61 1
dioxolane	00	45	69	43 1						
dimethoxyethane	00	41	53	38 2	20 0	10 2	21	50	59 1	
bis-MeOEt ether	00	40	64	38 6		9 9				
18-cineole	00	61		34 0	24 0					
acetone	08	43	71	42 2	17 0	12 5	25	81	65 7	61 8
2-butanone	06	48	67	41 3	17 4		23	74	64 0	60 4
c-pentanone	00	52	76	39 4	18 0					
2-pentanone	05	50	65	41 1					63 3	
3-pentanone	00	45	72	39 3	15 0					
c-hexanone	00	53	76	39 8	18 0		25	79		
Me-i-Bu ketone	02	48	65	39 4					62 0	58 3
2-heptanone	05	48	61	41 1					65 2	

Table 1 *contd*

Solvent	α	β	π^*	$E_T(30)$	*DN*	*AN*	*Acity*	*Basity*	*Z*	*Z'*
acetophenone	04	49	90	40 6	15 0		23	90		
formic acid	1 23	38	65	57 7	19 0	83 6	1 18	51		82 6
acetic acid	1 12	45	64	55 2	20 0	52 9	93	13	79 2	79 2
propanoic acid	1 12	45	58	55 0						79 0
butanoic acid	1 10	45	56	54 4						78 3
pentanoic acid	1 19	45	54	55 3						79 5
hexanoic acid	1 22	45	52	55 4						79 6
heptanoic acid	1 20	45	50	55 0						79 0
acetic anhydride	00	29	76	43 9	10 5					
methyl formate	00	37	62	45 0					70 3	66 6
ethyl formate	00	36	61	40 9						
methyl acetate	00	42	60	40 0	16 3	10 7				
ethyl acetate	00	45	55	38 1	17 1	9 3	21	59	64 0	58 7
propyl acetate	00	40		37 5	16 0					
butyl acetate	00	45	46	38 5	15 0					
methyl propanoate	00	27		38 0	11 0					
dimethyl carbonate	00	43		38 8	17 2				64 7	
diethyl carbonate	00	40	45	37 0	16 0				64 6	
ethylene carbonate	00	41		48 6	16 4					
propylene CO$_3$	00	40	83	46 6	15 1	18 3			72 4	
methyl benzoate	00	38		38 1	15 0					
ethyl benzoate	00	41	74	38 1	15 0					
diMe-phthalate	00	78	82	40 7						
ethyl Clacetate	00	35	70	39 4	13 0					
ethyl Cl$_3$acetate	00	25	61	38 7						
4-butyrolactone	00	49	87	44 3	18 0	17 3				
fluorobenzene	00	07	62	37 0	3 0				60 2	
p-difluorobenzene	00	03	58	36 4						
hexafluorobenzene	00	02	33	34 2						
1-chlorobutane	00	00	39	36 9						
chlorobenzene	00	07	71	36 8	3 3		20	65	58 0	
dichloromethane	13	10	82	40 7	1 0	20 4	33	80	64 7	59 3
1,1-dichloroethane	10	10	48	39 4		16 2			62 1	58 3
1,2-dichloroethane	00	10	81	41 3	0	16 7	30	82	64 3	
o-dichlorobenzene	00	03	80	38 0	3 0				60 0	
m-dichlorobenzene	00	03	75	36 7	2 0					
tr-diClethylene	00	00	44	41 9						
chloroform	20	10	58	39 1	4 0	23 1	42	73	63 2	57 8
1,1,1-Cl$_3$ethane	00	00	49	36 2						
trichloroethylene	00	05	53	35 9			16	54		
Cl$_4$methane	00	10	28	32 4	0	8 6	09	34		
Cl$_4$ethylene	00	05	28	31 9			10	25		
1,1,2,2-Cl$_4$ethane	00	00	95	39 4					64 3	
1-bromobutane	00	13	50	36 6						
dibromomethane	00	00	92	39 4					62 8	
1,2-dibromoethane	00	00	75	38 3					60 0	
bromoform	05	05	62	37 7						
bromobenzene	00	06	79	36 6	3 0		22	66	59 2	
1-iodobutane	00	23	47	34 9						
diiodomethane	00	00	65	36 5						
iodobenzene	00	06	81	36 2	4 0					
butylamine	00	72	31	37 6	42 0		15	1 17		
diaminoethane	13	1 43	47	42 0	55 0	20 9				
pyrrolidine	16	70	39	39 1						
piperidine	00	1 04	30	35 5	40 0					
morpholine	29	70	39	41 0		17 5				
diethylamine	03	70	24	35 4	50 0	9 4				
triethylamine	00	71	14	32 1	61 0	1 4	08	19		
tributylamine	00	62	16	32 1	50 0					
diMe benzylamine	00	64	45		21 0					
diMe cHexylamine	00	84	23	37 3						
aniline	26	50	73	44 3	35 0		36	1 19		
o-chloroaniline	25	40	83	45 5	31 0					
N-methylaniline	17	47	82	42 5	33 0		40	1 07		
dimethylaniline	00	43	73	36 5	27 0					
pyridine	00	64	87	40 5	33 1	14 2	24	96	64 0	60 3
4-methylpyridine	00	67	84	39 6	34 0					
2-fluoropyridine	00	51	84	42 4						
perfluoropyridine	00	16	53	36 3						
2-bromopyridine	00	53	1 00	41 3						
3-bromopyridine	00	60	89	39 7						
3,4-lutidine	00	78	73	38 9						
2,6-lutidine	00	76	80	36 9			18	81		
2-cyanopyridine	00	29	1 20	44 2						
quinoline	00	64	92	39 4	32 0					
acetonitrile	19	40	75	45 6	14 1	18 9	37	86	71 3	66 9

Table 1 *contd*

Solvent	α	β	π^*	$E_T(30)$	*DN*	*AN*	*Acity*	*Basity*	*Z*	*Z'*
propanitrile	00	39	71	43 6	16 1					
butanitrile	00	40	71	42 5	16 6				67 8	
Cl-acetonitrile	00	34	1 01	46 4	10 0					
benzyl cyanide	00	41	1 00	42 7	15 1					
benzonitrile	00	37	90	41 5	11 9	15 5	30	87	65 0	60 6
nitromethane	22	06	85	46 3	2 7	20 5	39	92	71 2	68 2
nitrobenzene	00	30	1 01	41 5	4 4	14 8	29	86		
formamide	71	48	97	56 6	24 0	39 8	66	1 00	83 3	
N-Me-formamide	62	80	90	54 1	27 0	32 1				
dimethylformamide	00	69	88	43 8	26 6	16 0	30	93	68 4	65 3
diethylformamide	00	79		41 8	30 9					
N-Me-acetamide	47	80	1 01	52 0					77 9	
dimethylacetamide	00	76	88	43 7	27 8	13 6	27	97	66 9	
diethylacetamide	00	78	84	42 4	32 2	13 6				
2-pyrrolidinone	36	77	85	48 3						
N-Me-pyrrolidinone	00	77	92	42 2	27 3	13 3				
N-Me-caprolactam	00	69		41 6	27 1					
tetraMe-urea	00	80	83	41 0	29 6	9 2				
tetraMe-guanidine	00	86	76	39 3						
diMe-cyanamide	00	64	72	43 8	17 0					
carbon disulfide	00	07	61	32 8	2 0		10	38		
dimethyl sulfide	00	34	57	26 8						
diethyl sulfide	00	37	46	35 7						
di-i-propyl sulfide	00	38	36	34 9						
di-n-butyl sulfide	00	38	36	34 9						
tetraCH_2 sulfide	00	44	62	36 7						
pentaCH_2 sulfide	00	36	61	35 9						
dimethyl sulfoxide	00	76	1 00	45 1	29 8	19 3	34	1 08	70 2	67 0
tetraCH_2 sulfoxide	00	81	1 06	43 6						
sulfolane	00	39	98	44 0	14 8	19 2			70 6	
dimethyl sulfate	00	36	78							
trimethyl phosphate	00	77	72	43 6	23 0	16 3				
triethyl phosphate	00	77	72	41 7	26 0				64 6	
tributyl phosphate	00	80	65	39 6	23 7	9 9			61 3	
Me_6 phosphoramide	00	1 05	87	40 9	38 8	10 6	00	1 07	62 8	

other relevant quantities have now been explored with the following results Certain recommendations can be made on the basis of these results for the use of such solvent parameters

2 Correlations Among Parameters

Table 2 describes the results of the binary correlations, in which one parameter, XYZ ($= \alpha, \beta, \pi^*, E_T(30)$, *DN*, *AN*, *Z*, *Acity* and *Basity*) is tested against another, X (from the same list) in terms of the linear regression

$$XYZ = XYZ_0 + x \cdot X \qquad (2)$$

The quantity presented is $r(n)$, the correlation coefficient of the regression (equation 2), for $n - 2$ degrees of freedom, where n is the number of pairs (X,XYZ) available for a given pair of parameters It is seen that for most cases the correlation is very slight For our large set of data the parameters α, β, and π^* are essentially orthogonal to each other So are the donor number *DN* and the acceptor number *AN* (for the 45 solvents for which both are known) and the *Acity* and *Basity* (for all of the solvents for which both are known,^{6} excluding *o*-xylene, *iso*-octane, and trifluoroacetic acid, for which the other parameters are not known)

It should be noted that $E_T(30)$, *Z*, and *DN*, expressed in kcal mol^{-1}, and *AN*, expressed on a scale from 0 to 100, are not commensurate with α, β, and π^*, that range mainly from 0 to 1 The normalized $E_T^N = (E_T(30) - 30\ 7)/32\ 3$, where 30 7 is the $E_T(30)$ of tetramethylsilane and $32\ 3 = 63\ 1 - 30\ 7$, with 63 1 the $E_T(30)$ of water, has already been introduced by Reichardt, placing E_T^N also in the range of 0 to 1 Similarly, the normalized $DN^N = DN/38\ 8$, where 38 8 is the *DN* of hexamethyl phosphoric triamide, and $AN^N = AN/54\ 8$, where 54 8 is the *AN* of water, also place the normalized quantities mostly in the range 0 to 1 If these normalized quantities are employed in expressions such as equation 2 (or equation 3 below), the coefficient x (and y) has to be multiplied by 32 4, 38 8, and 54 8 for E_T^N, DN^N, and AN^N, respectively, and for the former also XYZ_0 must be modified Since most authors quote the non-normalized quantities $E_T(30)$, *DN*, and *AN*, however, these are reported in Table 1 and used in the correlations The readers should have no difficulties in using the normalized quantities instead

For those few cases in Table 2 where $r > 0\ 8$, Table 3 presents the values of XYZ_0 and x It is seen that α, $E_T(30)$, *AN*, *Z*, and *Acity* are interrelated, and so are *DN* with β and *Basity* with π^* For these cases it is worthwhile to explore correlations involving more than one independent variable Also shown in Table 3 are the results of the application of equation 2 to $XYZ = Z'$, the value of the longest wavelength transition energy of 4-cyano-1-ethylpyridinium iodide^9 (in kcal mol^{-1}, 1 kcal = 4 184 kJ) as a function of $X = Z$, the similar quantity for 4-methoxycarbonyl-1-ethylpyridinium iodide ^{3} In this case $XYZ_0 \approx 0$, so that Z' is practically proportional to Z For two further cases the correlation according to equation 2 is sufficiently good to claim that XYZ is linearly correlated with X for *Acity* with *AN* and for *Z* with $E_T(30)$

In a few cases there are outliers that are obviously based on faulty data (all the known data have been included in the correlations reported in Table 2) If these are excluded improved correlations according to equation 2 may be achieved, but this procedure should not be driven too far A few correlations with one independent variable but with data excluded are also known in Table 3 In the case of *AN* formic acid is an outlier, probably because it is a sufficiently strong acid to protonate, rather than hydrogen-bond to, the probe base, triethylphosphine oxide ^{4} In the case of *DN* the aliphatic amines diethyl-, triethyl-, and tributylamine are outliers, either because their *DN* values are too high or because their β values are too low^{10} (see also the

Table 2 Binary correlations of solvent parameters: the numbers in the first row of each entry are *r*, those in parenthesis in the 2nd row are *n*

X/*XYZ*	α	β	π^*	$E_T(30)$	*DN*	*AN*	*Z*	*Acity*	*Basity*
α	1	0.178	0.073	0.849	0.178	0.931	0.887	0.939	− 0.071
		(185)	(174)	(180)	(110)	(52)	(61)	(52)	(52)
β		1	0.246	0.342	0.871	−0.044	0.504	0.329	0.329
			(174)	(180)	(110)	(52)	(61)	(52)	(52)
π^*			1	0.436	−0.092	0.254	0.108	0.404	0.819
				(169)	(99)	(52)	(59)	(52)	(52)
$E_T(30)$				1	0.234	0.915	0.966	0.942	0.344
					(109)	(52)	(61)	(52)	(52)
DN					1	0.084	0.450	0.248	0.254
						(45)	(47)	(48)	(48)
AN						1	0.920	0.980	0.020
							(31)	(32)	(32)
Z							1	0.926	0.068
								(32)	(32)
Acity								1	0.152
									(52)

Table 3 The coefficients of equation 2

XYZ	*X*	XYZ_0	*x*	$\sigma(XYZ)$	*r*	*n*
$E_T(30)$	α	38.2 ± 0.3	14.6 ± 0.7	3.9	0.8490	180
AN	α	12.1 ± 1.1	33.6 ± 1.9	6.4	0.9312	52
Z	α	63.2 ± 0.3	19.5 ± 1.3	4.0	0.8870	61
Acity	α	0.171 ± 0.015	$0.67 \pm 0.03_5$	0.09	0.9389	52
DN	β	0.25 ± 1.18	40.4 ± 2.2	6.2	0.8710	110
Basity	π^*	0.086 ± 0.061	0.91 ± 0.09	0.18	0.8188	52
AN	$E_T(30)$	− 65.9 ± 5.6	2.00 ± 0.12	7.1	0.9149	52
Acity	$E_T(30)$	− 0.99 ± 0.07	0.0317 ± 0.0016	0.09	0.9423	52
Z	$E_T(30)$	14.7 ± 1.9	1.236 ± 0.043	2.2	0.9661	61
Acity	*AN*	0.034 ± 0.017	0.0158 ± 0.0006	0.06	0.9795	32
Z	*AN*	53.3 ± 5.6	0.727 ± 0.079	3.8	0.9199	31
Z	*Acity*	53.6 ± 5.2	40.3 ± 7.4	3.7	0.9260	32
Z'	*Z*	− 0.03 ± 0.08	0.944 ± 0.002	0.5	0.9999	26
		Improved correlations with (presumably faulty) data excluded				
AN	α	12.2 ± 0.8	31.1 ± 1.4	4.7	0.9537	51
AN	$E_T(30)$	− 59.9 ± 4.1	1.850 ± 0.092	5.1	0.9441	51
			(formic acid was excluded)			
DN	β	0.5 ± 0.8	38.2 ± 1.5	4.3	0.9247	107
			(diethyl-, triethyl-, and tributylamine were excluded)			
Z	$E_T(30)$	13.0 ± 1.8	1.27 ± 0.04	2.0	0.9721	60
			(cyclohexane was excluded)			
Acity	$E_T(30)$	− 0.91 ± 0.05	0.0297 ± 0.0011	0.06	0.9662	50
Acity	*AN*	0.02 ± 0.01	0.0171 ± 0.0004	0.03	0.9943	30
			(formic acid and hexamethyl phosphoramide were excluded)			

Discussion). In the case of *Z* the reported value for cyclohexane is obviously too high, causing it to be an outlier.[11] Formic acid, again, is an outlier in the case of the *Acity*, but so also is hexamethyl phosphoramide, to which the arbitrary value of *Acity* = 0 was assigned, whereas a value of *Acity* ≈ 0.2 is expected in view of the values for *N*,*N*-dimethyl-formamide and -acetamide.[6]

Correlations with a constant and two independent variables according to equation 3 are shown in Table 4.

$$XYZ = XYZ_0 + x.X + y.Y \qquad (3)$$

The quantities listed beside the explicit equation 3 are $\sigma(XYZ)$ (the standard deviation of the dependent variable), the range of *XYZ* values, r^2 (the adjusted multiple correlation coefficient squared), the number *n* of data points (excluded were those listed in the lower part of Table 3 as well as further ones), and the $F_{3,n-3}$ statistic, for 3 and $n - 3$ degrees of freedom. Listed in Table 4 are only those correlations for which $r^2 > 0.90$. The scatter around the correlation vector in the 3-dimensional variable space is measured by $\sigma(XYZ)$, that should be minimal, but has to be compared with the range of the *XYZ* values. The higher *F*, the better is the correlation, but it should be remembered that it depends on the availability of data points, as counted by *n*.

The adequacy of the correlations depends on their purpose. If that is to learn what physical or chemical interactions are responsible for and contribute to a composite solvent parameter, then correlations that explain 98 or even 93% of the variance may be adequate. If the purpose is to use the correlation for the prediction of 'missing' values of a parameter, then the value of $\sigma(XYZ)$ ought to be comparable with the expected error in the experimental values of *XYZ*. For the values obtained spectroscopically as a transition energy expressed in kcal mol^{-1} [$E_T(30)$, *Z*] this error would be ± 0.4. For the statistically derived parameters *Acity* and *Basity* this error would be ± 0.04. For the thermochemical value *DN* it is ± 1.0 kcal mol^{-1}, and for *AN* derived from NMR chemical shifts but normalized on a scale of 0 to 100 this would be ± 0.5. The correlations in Table 4 do not quite meet this criterion, since their $\sigma(XYZ)$ are a few times

Table 4 Correlations according to equation 3 with $r^2 > 0\ 90$

$XYZ = XYZ_0 + x \cdot X + y \cdot Y$	$\sigma(XYZ)$	range of XYZ	r^2	n	F
$E_T(30) = 31\ 2 + 15\ 2 \cdot \alpha + 11\ 5 \cdot \pi^*$	2 1	31 1—63 1	0 9585	166	921
	(phenol *m* cresol and dimethylsulfide excluded)				
$AN = -30\ 0 + 15\ 3 \cdot \alpha + 1\ 01 \cdot E_T(30)$	2 4	0 0—54 8	0 9724	48	792
$AN = 2\ 9 + 29\ 7 \cdot \alpha + 14\ 0 \cdot \pi^*$	2 7	0 0—54 8	0 9667	48	652
	(formic acid acetic acid *m* cresol and chloroform excluded)				
$Z = 55\ 9 + 20\ 6 \cdot \alpha + 10\ 2 \cdot \pi^*$	2 9	54 0—91 4	0 9429	55	212
	(methyl formate propylene carbonate and benzene excluded)				
$Acity = 0\ 03 + 0\ 64 \cdot \alpha + 0\ 25 \cdot \pi^*$	0 05	0 00—1 00	0 9594	51	411
	(hexamethyl phosphoramide excluded)				
$Basity = 0\ 04 + 0\ 94 \cdot \pi^* + 0\ 035 \cdot \beta$	0 07	0 00—1 08	0 9260	47	275
	(acetic acid 1 butylamine aniline and carbon disulfide excluded)				

larger than the expected experimental errors The addition of a further variable was found to increase r^2 and decrease $\sigma(XYZ)$ somewhat $E_T(30)$ benefits most from this with the term $3\ 4 \cdot \beta$ in addition to those in α and π^* [reducing $\sigma(XYZ)$ to 1 6 and increasing r^2 to 0 9755] An alternative would be the discarding of even more outliers, where now the justification is not the exclusion of expected faulty data but the further improvement of the fit

It should be realized that according to the definition of α as the measure of the ability of a solvent to donate a hydrogen atom towards the formation of a hydrogen bond, only protic and protogenic solvents have non-zero α values These constitute only *ca* 30% of the solvents listed in Table 1, whereas the correlations with α shown in Tables 2 and 3 pertain to the entire set If only the subset of solvents with non-zero α values were employed, somewhat different results could be expected, but then the correlations would have been skewed by the non-inclusion of zero values in the cases where the other parameters themselves have zero or low values

In addition to the solvent parameters that measure the uncorrelated solvent properties 'polarity' (*e g* , π^*), electron-pair donicity (HBA ability, *e g* , β) and acceptance (HBD ability, *e g* , α) that are compared above, there are some other properties with which these parameters may be correlated These include properties obtained from physical measurements, such as the 'tightness' of the solvent, expressed as the Hildebrand solubility parameter δ_H or its square, the cohesive energy density $\delta_H^2 = (\Delta_{vap}H^* - RT)/V^*$, where $\Delta_{vap}H^*$ is the enthalpy of vaporization and V^* is the volume, both per mole of the pure liquid at 298 15 K Also included are the relative permittivity (the dielectric constant) ϵ or some function of it, *e g* , the polarization $P = (\epsilon - 1)/(2\epsilon + 1)$, and the polarizability, expressed as a function of the refractive index n_D (for the sodium D-line), $R = (n_D^2 - 1)/(2n_D^2 + 1)$

Table 5 shows that the solubility parameter and its square, which measures the work required to produce a cavity of unit volume in the solvent, are poorly correlated with any of the previously discussed parameters, so that this work is an independent property of the solvent The only exceptions are $E_T(30)$, which is somewhat correlated with δ_H, and α, that is also slightly related to it It is not surprising that HBD solvents may be associated in the neat liquid form, hence have large cohesive energy densities, but this does not suffice for an acceptable correlation It has been claimed[12] that the product of the HBD and HBA parameters, $\alpha \cdot \beta$, can substitute for δ_H^2 in certain correlations of processes with solvent properties As Table 5 shows, this might be true only for a limited set of selected solvents but the product $\alpha \cdot \beta$ is even less correlated with δ_H^2 than α is for our large set of very divers solvents

Table 5 Non-correlations of solvent polarity and hydrogen bonding parameters with their structuredness, measured by the solubility parameter or its square

Parameter	α	β	π^*	$E_T(30)$	DN	AN	$\alpha \cdot \beta$
n	121	121	121	121	85	50	121
$r(\delta_H)$	0 583	0 225	0 540	0 779	0 147	0 539	0 549
$r(\delta_H^2)$	0 533	0 225	0 475	0 712	0 122	0 495	0 493

The solvatochromic parameter π^* that describes in a composite manner the polarity and polarizability of the solvents has been said to be well correlated with the product of the polarization P and the polarizability R by means of equation 2 ($XYZ = \pi^*$, $X = P \cdot R$), albeit for certain limited sets of solvents [13] For an extensive set, 115, of divers solvents the value of r for equation 2 is only 0 780 and $\sigma(\pi^*)$ is 0 16 Application of equation 3 with $X = P$ and $Y = R$ yields similar results [$r^2 = 0\ 632$, $\sigma(\pi^*) = 0\ 16$] If water, dioxane, and the alkanols are excluded, then equation 2 yields for 90 solvents $r = 0\ 879$ and $\sigma(\pi^*) = 0\ 13$ The use of modified functions of ϵ and n_D, such as having $(\epsilon + 2)$ instead of $(2\epsilon + 1)$ or $(n_D^2 + 2)$ instead of $(2n_D^2 + 1)$ or the bulk quantities $V^* \cdot P$ or $V^* \cdot R$ did not improve the correlations However, the use of Kirkwood's[14] modified polarization function, $X = P' = 9 \cdot g \cdot \epsilon/(\epsilon - 1)(\epsilon + 2)$ (where g is the Kirkwood angular dipole correlation parameter) did produce with $Y = R$ in equation 3 for 84 solvents for which π^* and g[15] are known the value $r^2 = 0\ 780$ with $\sigma(\pi^*) = 0\ 10$, which is more promising, in view of the large variety of solvents included in the set Excluded, of course, are the non-polar solvents for which g cannot be obtained since the dipole moment is zero

3 Solvatochromic Parameters

Solvatochromic parameters, such as α, β, and π^* [also $E_T(30)$, Z and Z'] have certain advantages over other parameters in that they are readily measurable by equipment to be found in most laboratories Of these, π^* is measured directly, and is the mean of results for several probe (indicator) solutes 4-nitro-*N N*-diethylaniline (1), 3-nitro-*N N*-diethylaniline (2), 4-nitroanisole (3), 4-nitro-1-ethylbenzene (4), and 4-(2-nitroethenyl)anisole (5) [17] These probes are supposed to be insensitive to HBD and HBA properties of the solvents and to respond only to their polarity/polarizability The conversion expressions from the wavenumber ν (in 1000 cm^{-1}) of the longest wavelength absorption peak of a dilute solution of the probe in the solvent to π^* values have been given[17,18] (see also Table 6)

The solvatochromic HBA-ability parameter β can also be obtained from measurements with probe solutes, however, a knowledge of the π^* of the solvents is generally required Suitable probes are 4-nitro-aniline (6), 4-nitrophenol (7), and tetramethylethylenediaminoacetylacetonato-copper(II) perchlorate (8) (for the latter, knowledge of π^* is not required) The conversion expressions from the measured wavenumber ν to β values, given π^* values, have been presented[18] (see also Table 6) Failing this direct measurement, provided the DN values,[5,10] and the π^* and $E_T(30)$ values [19] are known or can be estimated, the expression given in Table 4 can be inverted to give β values as shown in Table 6, the sensitivity to *DN* being much larger than to the other two parameters

The determination of α has, until recently, depended on the knowledge of certain other quantities (π^* and in some cases also β), in addition to the solvatochromic or NMR data[20] Spectrometry in the UV-visible region has been applied with 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide (9) [*i e* , the $E_T(30)$ probe], 4-carbomethoxy-1-ethylpyridinium iodide (10) (*i e* , the *Z* probe), 4-cyano-1-ethylpyridinium iodide (11) (*i e* , the *Z*′ probe), bis(1,10-phenanthroline)-dicyano-iron(II) (12), among others NMR with ^{31}P was applied to triethylphosphine oxide (13) (*i e* , the *AN* probe) and with ^{13}C to *N,N*-dimethyl- or *N N*-diethylbenzamide [(14) and (15)] With the latter, large *a*/*s* (compare equation 1) were achieved, up to 4 74, depending on the chemical shift of which ring carbon was compared with that of the carbonyl one[21] Even much larger sensitivities to α with respect to π^* ($a/s \to \infty$) were recently achieved with ^{13}C NMR of pyridine-*N*-oxide (16) as the probe[22] The conversion expressions are shown in Table 6

Table 6 Expressions for the calculation of π^*, β, and α and their standard deviations σ Where applicable, the number of *n* of data and the ratio of the coefficients *a*, *b*, and *s* of equation 1 are also given

Probe	expression		n	2σ
(1)	$\pi^* = 0\ 314\cdot(27\ 52 - \nu)$			0 06
(2)	$\pi^* = 0\ 452\cdot(25\ 52 - \nu)$			0 06
(3)	$\pi^* = 0\ 427\cdot(34\ 12 - \nu)$			0 06
(4)	$\pi^* = 0\ 444\cdot(29\ 96 - \nu)$			0 06
(5)	$\pi^* = 0\ 443\cdot(37\ 67 - \nu)$			0 06
(6)	$\beta = 0\ 358\cdot(31\ 10 - \nu) - 1\ 125\cdot\pi^*$,	$b/s = 0\ 89$		0 09
(7)	$\beta = 0\ 346\cdot(35\ 045 - \nu) - 0\ 57\cdot\pi^* - 0\ 12\cdot\delta,^c$	$b/s = 1\ 76$	46	0 09
(8)	$\beta = 0\ 358\cdot(\nu - 18\ 76)$,	$b/s \to \infty$	17	0 09
DN	$\beta = 0\ 26\cdot DN - 0\ 00037\cdot E_T(30) - 0\ 019\cdot\pi^*$		90	0 10
(9)	$\alpha = 0\ 0649\cdot E_T(30) - 2\ 03 - 0\ 72\ \pi^*$,	$a/s = 1\ 39$	138	0 13
(10)	$\alpha = 0\ 0485\cdot Z - 2\ 75 - 0\ 46\cdot\pi^*$,	$a/s = 2\ 19$	55	0 12
(11)	$\alpha = 0\ 0514\cdot Z' - 2\ 75 - 0\ 46\cdot\pi^*$			0 13
(12)	$\alpha = 0\ 375\cdot(\nu - 15\ 636) - 0\ 45\cdot\pi^* + 0\ 27\cdot\beta$,	$a/s = 2\ 20$	14	0 06
(13)	$\alpha = 0\ 0337\cdot AN - 0\ 10 - 0\ 47\cdot\pi^*$,	$a/s = 2\ 12$	48	0 09
(14),(15)	$\alpha = 0\ 346\cdot(d_1^a - 32\ 40) - 0\ 42\cdot\pi^*$,	$a/s = 2\ 39$	34	0 13
(14),(15)	$\alpha = 0\ 356\cdot(d_2^a - 42\ 42) - 0\ 53\cdot\pi^*$,	$a/s = 1\ 87$	34	0 09
(14) (15)	$\alpha = 0\ 541\cdot[d_3^a - 41\ 98) - 0\ 21\cdot\pi^*$,	$a/s = 4\ 74$	34	0 18
(14),(15)	$\alpha = 0\ 694\cdot(d_4^a - 41\ 07) - 0\ 31\cdot\pi^*$,	$a/s = 3\ 18$	34	0 13
(16)	$\alpha = -0\ 162\cdot d_{24}^a + 2\ 43$,	$a/s = \to\infty$	27	0 15
(16)	$\alpha = -0\ 174\cdot d_{34}^b + 0\ 40$,	$a/s = \to\infty$	27	0 14

d are the differences in chemical shifts δ(C) − δ(C = O) in p p m of the ^{13}C NMR signals of the *i*th ring carbon and the carbonyl carbon atoms in *N N* dimethyl or *N N* diethylbenzamide [b] d_{24} is the difference in chemical shifts δ(C) − δ(C_4) and d_{34} is the difference δ(C_3) − δ(C_4) in p p m for ^{13}C NMR in pyridine *N* oxide The polarizability correction δ is 1 0 for aromatic 0 5 for polychlorinated aliphatic and 0 for all other aliphatic solvents

4 Discussion

The results presented above show that there are four more or less independent solvent parameters that describe solvent properties relevant to the present discussion One is the hydrogen bond donation (HBD) ability, that is accounted for best by α, but is also described (along with a measure of the solvent polarity) by $E_T(30)$, *Z* or *Z*, *AN*, and the *Acity* The second is the hydrogen bond acceptance (HBA) or electron pair donation ability, that is accounted for best by β, but with which *DN* is also correlated It is interesting to note that, although *DN* is a measure of enthalpy, it is well correlated with Gibbs free energy quantities, such as β, as also with others (*e g* , IR frequency shifts), a fact that was already commented upon[10] The third is the polarity and polarizability of the solvent, measured π^*, with which the *Basity* is correlated, and also, for a limited list of solvents, the modified polarization *P*′ and the polarizability *R* The fourth is the solvent stiffness,[15 16] measured by its cohesive energy density, δ_H^2, the work required to produce in the solvent a cavity of unit volume This is one measure of its structuredness[16]

Some or all of these four solvent property parameters should be adequate for LSERs or QSARs (quantitative structure/activity relationships) similar to equation 1 in all the 77 processes listed by Swain *et al*[6] and the 560 processes listed by Taft *et al*[23] (some of which appear also on the former list[6]) or the very numerous processes discussed by Reichardt[19] as far as solvent effects are concerned The processes include reaction kinetics and equilibria (*i e* , differences in solvent effects on initial and transition states and reactants and products, respectively) and spectroscopic processes (*i e* , differences in solvent effects on the ground and excited states) for light absorption in the ultraviolet, visible, and infrared regions, and NMR chemical shifts and similar quantities

It should be noted that the terms ‘acidity’ and ‘basicity’ as applied to solvents (to be distinguished from *Acity* and *Basity*[6]) are not employed in the present context They pertain to the complete transfer of a proton from the solvent to the solute (acidity) or from the solute to the solvent (basicity), forming new species that are charged Such a process goes beyond solvation by the solvent which should be confined to adduct formation and hydrogen bonding or dipole – (induced) dipole interactions The assignment, sometimes found in the literature, of (Lewis) acidity to aprotic and non-protogenic solvents such as dimethylsulfoxide, *N N*-dimethylformamide, or hexamethyl phosphoric acid triamide implies the formation of a coordinative bond between an electron pair of a donor atom of a solute and the positive end of the dipole of the solvent molecule The evidence is against this, the positive end of the dipole being well shielded It is more expedient to assign the solute–solvent interactions to dipole attraction In the present context, this is the responsibility of the π^* term rather than that of the α term, and aprotic solvents therefore rightly have zero α values

The question of whether quantities based on a single indicator probe, on the average of results from several probes, or as a statistical parameter derived from a large number of results (including reaction kinetics and equilibria as well as spectroscopic data) are the best descriptors of solvent properties has been argued in the literature[6 23 24] Strictly speaking, the solvent effects observed for a given probe should not be readily transferable to any other solute, in particular one that has different functional groups A case in point is the different HBA properties of solvents measured with 4-nitroaniline and with 4-nitrophenol[25] Practically, however, the main consideration should still be that the purpose of obtaining numerical values for solvent properties is their use as descriptors or predictors of the solvent effects on the behaviour of divers kinds of solutes and transition states The probes should thus act as stand-ins or substitutes for the ‘general solute’ Hence, if several probes of rather different chemical constitution provide concordant results for a given property (within a few percent of the total range of the quantity for the entire set of solvents), this would mean that they do indeed measure the property in a useful manner The average of the numerical values obtained from such probes is, therefore, a more meaningful quantity than the value obtained from any single probe, such as, *e g* , antimony pentachloride for the donor number *DN*[5] or 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide for the polarity index $E_T(30)$[2 19] This is one advantage of the Kamlet–Taft α, β, and π^* solvent parameters,[1] which are averages of results from several probes, although this has also been regarded as one of their weaknesses[24 25] The uncertainties of the parameters quoted in Table 6 (2σ) reflect the spread of the values for the individual probes around the mean (Some other parameters used in physical organic chemistry, such as the Hammett acidity functions H_0, are also based on averages of several probes, with comparable uncertainties) On the other hand, driving this procedure to the extreme of the statistical analysis of Swain *et al*[6] has the disadvantage that new solvents are not readily added to the list of 61 considered by these authors without the use of their particular statistical program and the many kinds of results (including reaction kinetics and equilibria as well as spectroscopic data) they have employed

There are many additional probe molecules that have found limited use for the determination of polarity, HBA, and HBD properties of solvents by means of UV-visible spectrometry (solvatochromatic indicators) or, say, IR band position and NMR chemical shift measurements Only a few can be mentioned here

Nicolet and Laurence, for instance, provided data from which π^* of solvents can be obtained with indicators such as 2,4-dinitro-*N,N*-diethylaniline, 4-cyano-*N,N*-dimethylaniline, 4-acetyl-*N,N*-dimethylaniline, and 4-carbomethoxy-*N,N*-dimethylaniline, in addition to (1) and (3) mentioned above [25] They also provided data from which β can be obtained with the indicator 4-aminoacetophenone, in addition to the indicators (6) and (7) listed above The HBA ability can be determined by the shift between the lowest and the second-lowest energy absorption peaks of diacetylacetonatooxovanadium(IV), $\Delta_{\text{I II}}$[26] and the NMR chemical shift of ^{23}Na in dilute solutions of sodium iodide [10 27] In particular, the shift of the O–D stretching frequency of CH_3OD in various solvents, forming the basis of Koppel and Palm's well-known *B* scale[28] was shown to be linear with *DN*, hence also with β [10] The lowest energy absorption peak of Michler's ketone, 4,4′-bis(dimethylamino)benzophenone, was shown[29] to conform very well to equation 3 with $X = \alpha$ and $Y = \pi^*$ The combination of Drago's earlier *E–C* enthalpy-based specific interaction approach with his more recent spectroscopically-based non-specific interaction approach led him to a four-parameter expression[30] similar in form to equation 1, but stressing other aspects of the solute–solvent interactions than the α–β–π^* treatment stressed here The averaging of results obtained with several probes of different natures, shapes, and sizes, however, was recommended These are just examples of such correlations, reference 19 gives a wealth of further information

5 Summary

The more widely used solvent parameters that have been proposed for the description of the polarity and the hydrogen bond and electron-pair donation and acceptance properties of more than 180 solvents have been compared and correlated These properties contribute to the *exoergic* solute–solvent interactions that are required for the solute to be soluble in the solvent in the first place and to solvent effects on spectra and reactions in the second place Three mutually independent quantities play roles in this respect these are measured by the solvatochromic parameters α (for HBD), β (for HBA), and π^* (for polarity/polarizability) of the solvent

The main *endoergic* contribution to solute–solvent interactions is the formation of a cavity in the solvent to accommodate the solute This is a chemical property of the solvent, depending on the association of its molecules in the liquid state It is measured by the cohesive energy density, δ_H^2, which is independent of the former three parameters when all the solvents are considered together This measure of the stiffness or tightness of the solvent is related indirectly to its 'structuredness', which is measured by the entropy deficiency of the liquid solvent relative to the solvent in the ideal gas state, corrected for its compression [15] This quantity, however, has not been calculated so far for most solvents at room temperature

When only a small set of related solvents is considered, mutual correlations of the solvent parameters may arise, and this must be guarded against when causes for solvent effects are sought, since not all the four parameters need be operative for a given process The mutual orthogonality of the parameters employed must be tested and confirmed

It must also be stressed that certain physical properties of solvents, such as the relative permittivity (dielectric constant, ϵ) may be very important where charged solute species are concerned Low ϵ values lead to solute–solute interactions (ion pairing of unlike charged species) even in dilute solutions, but this effect is outside the scope of this paper Also, certain chemical properties of solvents, such as hydrophobicity and miscibility or mutual solubility with water are not directly relevant to the solvation ability of solvents, although they play important roles in chromatography or liquid–liquid distribution The solvating ability of solvents is described by the HBA and HBD abilities, the polarity, and tightness, without having to invoke their behaviour towards water However, when interaction takes place with a very 'soft' solute, the softness of the solvent should also be taken into account as an additional solvent property [31]

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