

As the F_S parameters are not true localized electrical effect parameters it follows that the treatment of SURS does not constitute a successful separation of electrical effects. No valid conclusions concerning the nature of substituent effects may be drawn from correlations with the revised F and R constants, and therefore the use of these constants serves no practical or useful purpose. That this is the case is hardly surprising in view of the large body

of data which has accumulated¹ indicating that the NMe_3^+ group, contrary to the statements of SURS, has a significant electron donor delocalized effect.

Supplementary Material Available: Tables of test and model data, calculated values of σ_I , and data correlated with eq 6, 8, and 17 (6 pages). Ordering information is given on any current masthead page.

Linear Solvation Energy Relationships. 28. An Analysis of Swain's Solvent "Acity" and "Basity" Scales

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Received December 14, 1983

From a computer correlation involving 1080 data sets for 61 solvents and 77 reactions and physicochemical properties, Swain and co-workers have concluded that all solvent effects can be rationalized in terms of two solvent property scales, A , measuring anion solvating ability or "acity", and B , measuring cation solvating ability or "basity". On this basis they assert that, in the three parameter Taft-Abboud-Kamlet correlations, the hydrogen bond acceptor (HBA) basicity parameter, β , is superfluous. It is shown that of Swain's 77 properties, 71 involve non-hydrogen bond donor (non-HBD) solutes and the other 6 involve only very weak or non-HBA solvents, so that conditions necessary for applicability of β are not met. For properties which do involve HBD solutes and HBA solvents, correlations with A/B are shown to be of substantially poorer quality than corresponding π^*/β correlations. Rather than being a "basity" measure, B is shown to measure solvent dipolarity/polarizability.

Swain, Swain, Powell, and Alluni (SSPA) have recently¹ described the formulation of two new solvent property scales: A , represented as a measure of anion-solvating ability or "acity" and B , represented as a measure of cation solvating ability or "basity". These scales were arrived by at least-squares fitting of the data for 77 reactions and physicochemical properties (for a total of 61 solvents) to equations of the form of eq 1, where A and B characterize

$$P = P_0 + aA + bB \quad (1)$$

the solvent and P , P_0 , a and b depend only on the reaction or property. They reported that the two unrelated parameters (A and B) alone account for over 98% of the effects from changing solvent in the set of 1080 typical rates, equilibria, and spectral energies that they examined. By any standards their effort represents a prodigious computational undertaking.

SSPA also reported comparisons of their correlations with those obtained for 18 of their reactions and properties using the present authors' (TAK)^{2,3} solvatochromic parameters π^* , δ , α , and β in equations of the generalized form of eq 2. Generally the regression eq 1 and 2 were said to

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (2)$$

be of comparable quality in spite of noninclusion of many data by TAK; 365 data gave an overall correlation coef-

ficient, r , of 0.987 for the 18 SSPA correlations, while 279 data gave an overall r value of 0.984 for the same 18 TAK correlations. The TAK correlations in the above comparisons were with π^* and α , and addition of the β term was said not to improve the fits.

That the two-parameter SSPA correlations showed slightly better goodness of fit than the TAK correlations, despite the fact that TAK were said to have the option of using any or all of four different solvent constants in eq 2, and despite the fact that TAK were said to have omitted from important reactions many solvents that SSPA retained, was cited as further evidence of the superiority of the A - B parameters over the π^* - δ - α - β parameters. Further, based on the above comparison, SSPA concluded that three or more solvent constants were superfluous in correlating solvent effects since the fits with two constants were already satisfactory ($r > 0.98$) and additional constants yielded no improvement. They concluded specifically that correlations of reactions with the β parameter are generally unsatisfactory and that the β parameter is superfluous.

We wish now to record our complete and unreserved agreement that, insofar as SSPA's 77 data sets are concerned, the β parameter which is the solvatochromic measure of solvent hydrogen bond acceptor (HBA) basicity, indeed, is superfluous. The reasons are as follows. Despite misconceptions set forth by SSPA, the solvatochromic parameters of TAK follow a quite rigid set of rules. Wherever solutes are hydrogen bond donor acids, (or certain nonprotonic Lewis acids) and solvents are HBA bases, the TAK correlations have always shown significant dependences on the β parameter. When these conditions are not fulfilled, the TAK correlations never included

(1) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* 1983, 105, 502.

(2) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* 1981, 13, 1080.

(3) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* 1983, 48, 2877.

Table I. Correlations of Properties Depending on Solvent HBA Basicity with π^*/β and with A/B

compd	π^*/β			A/B		
	<i>n</i>	<i>r</i>	<i>sd.</i> kK	<i>n</i>	<i>r</i>	<i>sd.</i> kK
UV/Visible Spectral Solvent Shifts ^a						
ethyl 4-aminobenzoate	21	0.996	0.11	15	0.887	0.56
4-aminobenzo-phenone	28	0.995	0.10	22	0.905	0.43
3,5-dinitroaniline	32	0.995	0.10	25	0.861	0.52
3-nitroaniline	33	0.991	0.15	26	0.773	0.70
N-ethyl-3-nitroaniline	32	0.995	0.09	26	0.931 ^b	0.30
NMR Shifts and Coupling Constants ^c						
FC(NO ₂) ₂ H, ¹ H NMR shift	11	0.976 ^d		9	0.860	
Thioacetamide, ¹ H NMR shift	7	0.998		7	0.965	
CHCl ₃ , ¹³ C NMR shift	10	0.985		10	0.845	
CHCl ₃ , ¹ H NMR shift	10	0.984		10	0.880	
CHCl ₃ , <i>J</i> (¹³ C ¹ H) coupling constant	9	0.996 ^e		9	0.734	

^a Reference 5. ^b The higher *r* value for the A/B correlation for *N*-ethyl-4-nitroaniline compared with the other spectral A/B correlations is because this property has a lower *b/s* ratio (the ratio of the dependences on HBA basicity/dipolarity-polarizability) in eq 2. The higher the *b/s* ratio in eq 2, the more seriously will SSPA-type correlations break down. ^c Reference 6. ^d The correlation is with β alone. ^e The correlation is with π^*/β .

statistically significant dependence on β .

It is our position that the fatal flaw in both the SSPA procedure and reasoning is that, of their 77 data sets, 71 have involved only non-HBD reactants or indicators. The other six data sets involve distributions coefficients between water and immiscible organic solvents. Since most HBA bases with β values above 0.20 are at least partly miscible with water (which is a strong HBD acid) these six data sets have necessarily been restricted to non-HBA or very weak HBA base solvents. Specifically, the solutes in these six data sets were 2-nitrophenol, picramic acid, *o*-vanillin, benzoic acid, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol; the solvents were CCl₄, ClCH₂CH₂Cl, C₆H₅Br, C₆H₅Cl, C₆H₆, *c*-C₆H₁₂, *n*-C₆H₁₄, C₆H₅CH₃, *n*-C₇H₁₆, *m*-C₆H₄(CH₃)₂, and *p*-C₆H₄(CH₃)₂. The highest β value in this solvent set is 0.13 for the xylenes. It necessarily follows, therefore, that none of SSPA's 77 data sets satisfy the condition required for a significant dependence on β or any other solvent HBA basicity parameter.

It also follows necessarily that SSPA correlations by eq 1 should compare very unfavorably with TAK correlations by eq 2 ($\alpha = 0$) for reactions or properties wherein the solutes are HBD acids and the solvents are HBA bases. The selection of SSPA's 77 data sets is remarkable in the light of the fact that dozens of such β -dependent properties and data sets have been reported in the recent literature by TAK^{2,3} and other workers. Indeed, solvent effects on the UV/visible spectra of 4-nitrophenol and 4-nitroaniline (HBD, and hence β -dependent) were reported by TAK in the same paper⁴ with results for 4-nitroanisole and *N,N*-diethyl-4-nitroaniline (non-HBD, and hence β -independent). Citing that paper,⁴ SSPA included among their 77 data sets the β -independent, but not the β -dependent spectra. Their finding of the β parameter to be superfluous results from this data selection.

(4) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1976, 98, 377.

In Table I we illustrate the corresponding SSPA and TAK correlations for several truly representative properties for which extensive data sets have been reported for HBD solutes in HBA solvents: (a) UV/visible spectra of a number of aniline indicators,⁵ and (b) NMR spectral shifts and coupling constants of some C-H and N-H hydrogen bond donors.⁶ The data and the correlations are included in the cited references. In contrast to the excellent π^*/β correlations (eq 2 with $\delta = \alpha = 0$) the A/B correlations (eq 1) are of poor statistical quality.⁷

It is also of interest to compare A/B and π^*/β correlations for some properties of cations and other nonprotonic Lewis acids. The data are given in Table II, together with the solvent parameters and correlation equations, and include all results for the properties cited in solvents for which the A/B and π^*/β parameters are known. The properties correlated are as follows: (a) the L_s parameter of Rakshys and Taft,⁸ which is an averaged solvent/cation complexation constant, obtained by normalizing and averaging effects of pure solvents on ¹⁹F NMR shieldings of some *m*- and (*p*-fluorophenyl)alkyl- and aryl-substituted "onium" ions (ammonium, carbonium, phosphonium, sulfonium), (b) *J* (¹¹⁹Sn-CH₃) coupling constants of trimethyltin chloride, reported by Bolles and Drago,⁹ and (c) ¹⁹F NMR shifts of bis(4-fluorophenyl)mercury, reported by Kravtsov and co-workers.¹⁰ Again it is seen that the correlations with π^*/β are significantly better than those with A/B .⁷

These, and many additional correlations such as the above, with the π^*/β correlations always outperforming the A/B correlation, provide abundant evidence that rather than being "superfluous", as suggested by SSPA, β is the quintessential measure of solvent "basity", by Swain's definition of that term, and is required to properly rationalize any solvent effect caused by the solute acting as a hydrogen bond donor to a hydrogen bond acceptor solvent. It is fair, therefore, to inquire, what then is the solvent property described by SSPA's *B* parameter, which correlated 77 properties and 1080 data points so well? The answer is readily at hand.

TAK have repeatedly pointed out that most of the earlier reported single solvent property scales differed from one another and from the π^* scale¹¹ mainly in the very important matter of how they disentangled or failed to disentangle solvent dipolarity from polarizability and hydrogen bonding effects.¹² We showed, however, that when consideration was restricted to a set of about 30 select solvents, nonprotonic aliphatic solvents with a single dominant bond dipole (i.e., solvents wherein hydrogen bonding is excluded and polarizability effects are similar),

(5) Kamlet, M. J.; Abboud, J. L. M.; Jones, M. E.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* 1979, 342.

(6) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* 1980, 14, 485.

(7) That the correlation coefficients are not still poorer is a consequence of the fact that for most non-chlorinated aliphatic solvents there is a rough parallelism between π^* and β . Where this parallelism does not hold, e.g., for triethylamine, $\pi^* = 0.14$, $\beta = 0.71$, the A/B correlation shows significantly poorer precision.

(8) Rakshys, Jr., J. W.; Taft, R. W. "Abstracts of Papers", 154th National Meeting of the American Chemical Society, Sept 1967; American Chemical Society: Washington, D.C., 1967; V-39; Taft, R. W.; Gurka, D.; Joris, L.; Schleye P. v. R.; Rakshys, J. W. *J. Am. Chem. Soc.* 1969, 91, 4801.

(9) Bolles, T. F.; Drago, R. S. *J. Am. Chem. Soc.* 1966, 88, 5730.

(10) Kravtsov, D. N.; Kvasov, B. A.; Fedin, E. N.; Faingor, B. A.; Golovchenko, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1969, 536.

(11) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* 197, 99, 6027.

(12) Abboud, J.-L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1977, 99, 8327.

Table II. Correlations of Solvent Effects on Properties of Nonprotonic Lewis Acids with π^*/β and with A/B

solvent	π^*	β	A	B	Me_3SnCl $J(^{119}\text{Sn}-\text{CH}_3)^a$	L_s^b	$(4\text{-F-C}_6\text{H}_4)_2\text{Hg}$ $^{19}\text{F NMR } \Delta^c$
cyclohexane	0.00	0.00	0.02	0.06			-1.21
carbon tetrachloride	0.29	0.00	0.09	0.34	57.6		-1.17
benzene	0.59	0.10	0.15	0.59			-0.55
toluene	0.54	0.11	0.13	0.54	57.6		
diethyl ether	0.27	0.47	0.12	0.34	60.6		
dioxane	0.55	0.37	0.19	0.67			0.00
1,2-dimethoxyethane	0.53	0.41	0.21	0.50			0.43
ethyl acetate	0.55	0.45	0.21	0.59			0.32
chloroform	0.50	0.00	0.42	0.73			-1.09
pyridine	0.87	0.64	0.24	0.96	67.0	3.75	0.94
acetone	0.71	0.48	0.25	0.81	66.1		0.50
tetrahydrofuran	0.58	0.55	0.17	0.67	64.5		0.51
acetonitrile	0.75	0.31	0.37	0.86	64.2	2.85	0.45
nitromethane	0.85	0.20	0.39	0.92			0.00
dimethylformamide	0.88	0.69	0.30	0.93		4.23	
dimethylacetamide	0.88	0.76	0.27	0.97	68.8	4.40	
dimethyl sulfoxide	1.00	0.76	0.34	1.08	69.2	4.55	1.06
hexamethylphosphoramide	0.87	1.05	0.00	1.07	71.6	5.22	1.93
$XYZ = XYZ_0 + s\pi^* + b\beta$						L_s^b	$(4\text{-F-C}_6\text{H}_4)_2\text{Hg}$ $^{19}\text{F NMR } \Delta^c$
XYZ_0					54.4	0.81	-1.21
s					7.78	1.37	0.71
b					9.90	3.04	2.44
r					0.979 ^d	0.990	0.979
sd					0.95	0.10	0.18
$XYZ = XYZ_0 + aA + bB$						L_s^b	$(4\text{-F-C}_6\text{H}_4)_2\text{Hg}$ $^{19}\text{F NMR } \Delta^c$
XYZ_0					53.0	-1.77	-1.41
a					-7.27	-1.99	-3.28
b					17.17	6.58	3.30
r					0.935	0.912	0.881
sd					1.62	0.30	0.43

^a Coupling constant in cps. Reference 9. ^b Cation/solvent complexation parameter obtained from fluorine NMR shieldings of *m*- and *p*-alkyl- and aryl-substituted "onium" ions (ammonium carbonium, phosphonium, and sulfonium). Reference 8. ^c Shifts in ppm relative to fluorobenzene. Reference 10. ^d The *r* value for the correlation with $(\pi^* - 0.20\beta)$ and β is 0.987.

the various solvent property scales were nicely linear with one another and with the solvent molecular dipole moments μ .¹³

The correlation coefficients for the linear regression equations of the other single solvent property scales with the π^* scale are as follows: (a) dipole moment, μ , $r = 0.985$; (b) Dimroth and Reichardt's $E_T(30)$ scale, $r = 0.987$; (c) Brookers x_R scale, $r = 0.987$; (d) Lassau and Junger's $\log k(\text{Pr}_3\text{N} + \text{MeI})$ scale, $r = 0.985$; (e) Walther's E_K scale, $r = 0.977$; (f) Knauer and Napier's A_N scale, $r = 0.987$; (g) Taft's P scale, $r = 0.989$; (h) Brownstein's S scale (an extension of Kosower's Z), $r = 0.981$; (i) Allerhand and Scheleyer's G scale $r = 0.993$. More recently,¹⁴ we have reported the following additional correlations with π^* : (j) Dong and Winnick's Py scale,¹⁵ based on band intensities in the fluorescence spectrum of pyrene, $r = 0.989$; (k) Snyder's P' scale¹⁶ of "solvent chromatographic strength", based on Rohrschneider's gas/liquid partition coefficients, $r = 0.991$; (l) Gutmann's "Acceptor Number" scale, AN ,¹⁷ $r = 0.960$; (m) $\log \epsilon_B$ (solvent bulk dielectric constant), $r = 0.961$.

The SSPA concept is refuted by the fact that the B parameter fits very neatly into this fundamentally satisfying and mutually supporting¹⁸ framework of intercor-

relations. Their supposed "basity" measure correlates very well with π^* alone, and hence with the other solvent property scales. The linear regression equation with π^* for the 13 select solvents is given by eq 3a; if the correlation

$$B = 0.057 + 1.014\pi^* \quad (3a)$$

$$n = 13; r = 0.998$$

$$B = 0.056 + 1.033\pi^* \quad (3b)$$

$$n = 19; r = 0.992$$

$$B = 0.064 + 0.959\pi^* \quad (3c)$$

$$n = 35; r = 0.972$$

$$B = 0.073 + 1.001(\pi^* - 0.09\delta) \quad (3d)$$

$$n = 35; r = 0.998$$

$$B = 0.076 + 1.005(\pi^* - 0.09\delta) - 0.14\alpha \quad (3c)$$

$$n = 43 \text{ (ex AcOH)}; r = 0.977^{20}$$

(13) Specific references to the various property scales are cited in ref 12.

(14) Abboud, J.-L. M.; Taft, R. W.; Kamlet, M. J., *J. Chem. Res.*

(15) Dong, D. C.; Winnick, M. A. *Photochem. Photobiol.* 1982, 358 17.

(16) Snyder, L. R. *J. Chromatogr. Sci.* 1973, 16, 223.

(17) Gutmann, V. *CHEMTECH* 1977, 255.

(18) The solvent property scales included in the correlations derive from UV/visible spectra [$E_T(30)$, π^* , X_R , Z , S , E_K], fluorescence spectra (Py), infrared spectra (G), ESR spectra (A_N), NMR spectra (P and AN), reaction rates [A , B , and $\log k(\text{Pr}_3\text{N} + \text{MeI})$], and gas/liquid partition coefficients (P'). This serves as strong confirmation that these scales measure properties that are intrinsic to the solvents and independent of the methods and indicators used in their determination.

is extended to include 19 non-HBD select and nonselect aliphatic solvents, the linear regression is given by eq 3b; if further extended to also include 16 aromatic and polychloroaliphatic solvents, the correlation is given by eq 3c; if a $\delta\delta$ term is included to take into account the differing polarizability characteristics of the three families of solvents,¹⁹ the correlation is given by eq 3d; if the HBD solvents are included and a dependence on α is also allowed, the total solvatochromic equation for 43 solvents (excluding AcOH) is given by eq 3e. On the basis of the excellent r values for the above correlations, it seems fair to say that SSPA's 77 data sets, involving many diverse types of properties, confirm the precision of the π^* scale, which was formulated from electronic spectral data for 7 primary and 40 secondary indicators.

The above analysis raises the further important question. If π^* and B measure essentially the same property, is that property dipolarity/polarizability or cation solvating ability? Most of the earlier workers have regarded their solvent property scales (which are linear with π^* for the select solvents) as measures of "solvent polarity" or "solvent ionizing power". This, and the fact that six separate groups of workers^{12,21-25} have with varying degrees of success correlated the π^* parameters with various combinations of functions of the solvent dipole moments, dielectric constants, and refractive indexes, indicate that the property is dipolarity/polarizability rather than "basicity".

Further, the following simple progression of solvent B values, with triethylamine at the bottom of the list, argues

solvent	B	solvent	B
CH ₃ NO ₂	0.92	EtOEt	0.50
CH ₃ CN	0.86	CCl ₄	0.34
ClCH ₂ CH ₂ Cl	0.82	(CH ₃ CH ₂) ₃ N	0.19
CHCl ₃	0.73		

conclusively against that parameter as a measure of solvent "basicity".

To complete our analysis of the SSPA correlational method, we next direct our attention to the A parameter, the supposed measure of solvent "acidity". SSPA have also criticized the TAK parameters on the basis that π^* is significantly correlated with α with a correlation coefficient of 0.52.²⁶ By way of contrast, they claim that A and B are completely uncorrelated (with r imaginary). We have found the latter statement not to be true when solvent hydrogen bond donor contributions are excluded by comparing only non-HBD solvents. For example, for the 13 select solvents, the correlation between A and B has a correlation coefficient of 0.971, eq 4. For all non-HBD

$$A = 0.016 + 0.29B \quad (4)$$

$$n = 13; r = 0.971$$

solvents, the regression A with B has an r value of 0.769;

if one excludes hexamethylphosphoramide (whose A value was arbitrarily anchored at 0.0 by SSPA), the r value becomes 0.911; if one also excludes the xylenes, r becomes 0.942. The linear regression of A with π^* for the select solvents has an r value of 0.987, eq 5a.

$$A = 0.018 + 0.311\pi^* \quad (5a)$$

$$n = 13; r = 0.987$$

Thus, for the non-HBD solvents, the a parameter is also seen to be a measure of solvent dipolarity/polarizability, just as is the B parameter. However, when the HBD and non-HBD solvents are taken together, the A parameter is seen in the total solvatochromic equation, eq 5b, to mea-

$$A = 0.02 + 0.26\pi^* + 0.60\alpha \quad (5b)$$

$$n = 43; r = 0.979$$

sure a blend of about 30% solvent dipolarity/polarizability and 70% hydrogen bond donor ability. By similar analyses, we had shown² earlier Gutmann's AN scale, Kosower's Z scale, and Dimroth and Reichardt's $E_T(30)$ scale also to be blends of the same properties, albeit with somewhat different a/s ratios in eq 2 than for the A parameter.

The demonstration that A and B measure the same property of non-HBD solvents might be regarded by some as a *reductio ad absurdum* of the SSPA findings. It should not be taken as such, but rather as an example of how a sophisticated computer program, fed a prodigious amount of relatively accurate information, can provide seriously misleading results if the input assumptions are flawed. SSPA assume that solvent effects can be rationalized by means of specific anion and cation solvation terms, but that there is no general dipolarity/polarizability term that applies in varying degrees to both anion and cation solvation. The present authors assume that α is relevant to specific anion/HBD solvent interactions, that β (alone or in combination with the ξ parameter)³ measures specific cation (HBD acid) solvating ability, and that π^* and δ measure those nonspecific dielectric effects which further apply to the solvation of weakly basic anions or weakly acidic nonprotonic cations.²⁷ Which concept better accommodates the available and future experimental information can be decided only if each is fairly and critically tested.

We want finally to address briefly the serious allegation by SSPA to the effect that the present authors are guilty of selective deletion of many data, presumably to improve our fits. We assert categorically that in our studies of solvent effects we have never knowingly excluded a pertinent datum without making specific mention of the fact (and usually telling why the datum was excluded and what the r value would have been if the datum had been included). There are several reasons why an SSPA correlation may have involved more solvents than the corresponding TAK correlation: (a) The additional data were from a secondary correlation. As an example, for solubility reasons, $E_T(30)$ values could not be determined directly with Reichardt's betaine for the less dipolar solvents. Reichardt therefore estimated $E_T(30)$ values for these solvents from correlations with spectral data for another indicator (the 2,6-di-*tert*-butyl betaine). SSPA included these data; TAK did not because $E_T(30)$ is a blend of π^* and α , and the secondary indicator may have involved yet

(19) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* 1981, 103, 1080.

(20) If acetic acid were included, the r value would be 0.939.

(21) Bekarek, V. J. *Phys. Chem.* 1981, 85, 722; *Collect. Czech. Chem. Commun.* 1980, 45, 2063.

(22) Brady, J. E.; Carr, P. W. *Anal. Chem.* 1982, 54, 1751; *J. Phys. Chem.* 1982, 86, 3053.

(23) Kolling, O. W. *Trans. Kans. Acad. Sci.* 1981, 84, 32.

(24) Ehrenson, S. J. *Am. Chem. Soc.* 1981, 103, 6036.

(25) Samoshin, V. V.; Zeferov, N. S. *Dokl. Akad. Nauk SSSR* 1982, 264, 873.

(26) That HBD (and HBA) solvents are frequently dipolar is a readily understandable fact of nature. It is our assertion (backed by the correlational results herein and elsewhere^{2,3}) that for a truly representative solvent set, there is sufficient nonlinearity between each of the α, β and π^* scales that eq 2 can be applied to usefully disentangle the respective contributions to observed solvent effects.

(27) Koppel, I. A. Palm, V. A. In "Advances in Linear Free Energy Relationships"; Chapman, N. B. Shorter, J. Eds.; Plenum: London, 1972; Chapter 5.

a different blend. (b) The pertinent π^* , α , and β values might not yet have been determined at the time TAK carried out their correlation. (c) The TAK correlation may have involved data from an earlier literature reference, where the SSPA correlation took data from a later paper in which the data base had been expanded. Again, this appears to be the case with the $E_T(30)$ results. (d) TAK may have specifically mentioned that we were using a limited data set, e.g., only select solvents or only non-protonic aliphatic solvents, to exclude hydrogen bonding or variable polarizability effects.

Fortunately, the information necessary to test the above allegation is readily at hand. As a specific instance, SSPA state in their footnote 60, "As a typical example, in Table II, we (SSPA) retain E_T data for triethylamine, methyl ethyl ketone, nitromethane, ethyl ether, hexane, and cyclohexane, all omitted by Kamlet et al. We (SSPA) use 47 E_T data whereas they use only 31." It is true that we (TAK) excluded these data. The reasons were (a-c) above. However, we have now repeated the correlation including all the additional solvents for which the solvatochromic parameters are known; n becomes 39, and the multiple linear regression equation is given by eq 6. The above

$$E_T(30) = -0.51 + 14.3(\pi^* - 0.23\delta) - 15.5\alpha \quad (6)$$

$$n = 39; r = 0.986$$

correlation coefficient compares with $r = 0.985$ for our earlier correlation involving the 31 solvents.

The free energies of transfer of the $\text{Et}_4\text{N}^+\text{I}^-$ ion pair is another example. SSPA commented that their 21 solvents gave $r = 0.984$, while our 10 solvents gave $r = 0.987$. Here, the reason for the exclusion of data was (d) above. Accordingly, we have rerun our correlation using the same 21 data as SSPA. The result is given in eq 7. Thus, in

$$\Delta G_t(\text{Et}_4\text{N}^+\text{I}^-) = 3.15 - 12.8(\pi^* - 0.17\delta) - 4.60\alpha \quad (7)$$

$$n = 21; r = 0.988$$

both cases, inclusion of the additional data have not worsened but very slightly improved the statistical goodness of fit of the TAK correlations. We consider this to be prime facie evidence that the SSPA allegation was incorrect.

Acknowledgment. The work by R.W.T. was supported in part by a grant from the Public Health Service. The work by M.J.K. was done under NSWC Independent Research Task IR-210.

Substituent and Solvent Effects on Chemical Reactivity

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Received February 21, 1984

This is a comparison of the procedures of five research groups using multiple correlation analyses for assessing the components of substituent and solvent effects. Advantages and problems of each procedure are indicated.

In 1983 our papers reevaluating components of substituent effects¹ and solvent effects² were published. After three papers³⁻⁵ critical of the first and one⁶ critical of the second were submitted, editors F. D. Greene and W. J. le Noble generously invited us to contribute this paper. The four omit any mention of the weaknesses of the approach being promoted; therefore, we shall try to put all five approaches into perspective and compare their strengths and weaknesses.

General Problems with Multiple Linear Free-Energy Relationships

Linear free-energy relationships are based on the fact that free-energy differences (or spectral frequencies or

logarithms of rate or equilibrium constants) for numerous reactions denoted by i can be expressed as linear functions ($a_i x_j + b_i$) of a common set of constants (a vector x_j) when common structural modifications denoted by j are made in a reactant or solvent. The first ones were the Brønsted laws for catalysis by acids ($\alpha_i(\text{p}K_A)_j + c_i$)⁷ or bases ($\beta_i(\text{p}K_B)_j + d_i$)⁸. The best known is the Hammett equation ($\rho_i \sigma_j + e_i$)⁹. We first suggested the use of *multiple*, e.g., dual ($a_i x_j + b_i y_j + c_i$), linear free-energy equations when structural changes influence the overall effect in multiple but nearly independent ways, as when both electrophilic (x_j) and nucleophilic (y_j) properties of a solvent affect logs of solvolytic rate constants.¹⁰ Such dual vector representations were subsequently adopted by Edwards and Pearson,¹¹ Winstein,¹² Yukawa and Tsuno,¹³ and many others. It often does happen that two factors are important and

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