Linear Solvation Energy Relationships. Part 31. On Bekárek's Modifications of the Solvatochromic Parameters

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Bekárek has proposed that the solvatochromic parameters, π^*, and α, and β, be modified to give $\pi_n^* = \pi^*/f(n^2)$, $\alpha_n = \alpha/f(n^2)$, $\beta_n = \beta/f(n^2)$, where $f(n^2) = (n^2 - 1)/(2n^2 + 1)$, and has suggested that, while the former parameter set is adequate to correlate some types of electronic spectral properties, the latter set is to be preferred for correlating most other type properties. It is shown that π^* and π_n^* correspond to single, unique dipolarity–polarizability blends in the solvent effects, and that the $(\pi^* + d\delta)$ formalism is better suited to correlate effects involving the full range of possible dipolarity–polarizability blends in the solute–solvent interactions.

During the past decade, we have been involved in the formulation and use of three scales of solvent properties, known collectively as the solvatochromic parameters.[1] A π^* scale of dipolarity–polarizabilities describes the ability of a solvent to stabilize a solute charge or dipole by virtue of its dielectric effect. For select solvents, non-polychlorinated aliphatic solvents with single dominant bond dipoles, π^* values are very nearly proportional to molecular dipole moments.[2] An α scale of HBD (hydrogen-bond donor) acidities measures the solvent's ability to share a proton in a solvent-to-solute hydrogen bond. A β scale of HBA (hydrogen-bond acceptor) basicities measures the solvent's ability to share a proton from an HBD solute.[1] (We have recently reported[3] that, for non-self-associating compounds, the solvatochromic parameters serve equally well to describe the dipolarity–polarizability and hydrogen-bonding properties of the same materials acting as solutes.)

When hydrogen-bonding effects are excluded, as when neither solutes nor solvents are hydrogen-bond donors, medium effects on a property, XYZ, can be described by expressions of the form (1), where XYZ_0 represents the regression value of the

$$XYZ = XYZ_0 + s(\pi^* + d\delta) \qquad (1)$$

property in the reference solvent, cyclohexane, and $d\delta$ is a variable polarizability term. The δ parameter has values of 0.00 for non-chlorinated aliphatic solvents, 0.50 for polychlorinated aliphatics, and 1.00 for aromatic solvents. The d coefficient is a measure of the polarizability contribution to the dipolarity–polarizability blend in the solvent effect studied. Where polarizability contributions are near maximal, as in solvent effects on bathochromically shifted electronic spectra, d takes a value of zero. For other properties the sign of d is usually negative, approaching -0.40 as the polarizability contribution falls to near nil.

Where hydrogen-bonding interactions also contribute to the solvent effects, XYZ is given by equation (2). Equations (1) and

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

(2) have been successfully applied to the correlation of medium effects of many types of properties, including positions of maximal absorption in u.v.–visible absorption and fluorescence spectra,[1a,4] n.m.r. shifts and coupling constants,[1b,5] i.r. spectra,[6] logarithms of reaction rate constants,[1b,7] and free energies of transfer of dipolar and charged solutes between solvents.[8] More

recently, an equation including terms in $(\pi^* - 0.40\delta)$ and β (and a further term in V, the solute molecular volume) has been used to correlate partition coefficients of aliphatic[3a] and aromatic[3b] non-HBD solutes between octanol and water.

Anticipating questions which will arise in the ensuing discussion, it is worth mentioning that the $(\pi^* + d\delta)$ formalism in (1) and (2) has been quite successful in accounting (in a reasonably simple way) for a wide range of dipolarity–polarizability blends in the solute–solvent interactions studied. Thus, polarizability contributions have varied from near maximal for solvent effects on $\pi \longrightarrow \pi^*$ electronic transitions of uncharged indicators ($d = 0$, r usually greater than 0.980),[1a] to near nil for solvent effects on ^{77}Se n.m.r. shifts of dimethyl selenide ($d - 0.36$, r 0.966),[9] and for the octanol–water partition coefficients mentioned above ($d -0.40$, r 0.991).[3] As we have mentioned earlier,[1a] and recently reiterated,[10] the fact that single values of δ for each of the three classes of solvents serve so effectively in the correlations simply reflects the fact that values of the refractive index function, $f(n^2) = (n^2 - 1)/(2n^2 + 1)$, are reasonably similar within each class. Thus, for a typical solvent set like that in the Table, values of $f(n^2)$ for the aliphatic select solvents range from 0.180 to 0.222 and average 0.195; values for the aromatic solvents range from 0.218 to 0.244 and average 0.236; values for the polychlorinated aliphatic solvents range from 0.200 to 0.230 and average 0.216.

Bekárek's Modification of the Solvatochromic Parameters.—In a recent report in this journal,[11] Bekárek has suggested that the present solvatochromic parameters are adequate for correlating certain types of spectral solvent shifts, but that their applicability to most other types of solvent effects could be improved by dividing them by the refractive index function, and on this basis he has defined a modified set of parameters by equation (3).

$$\pi_n^* = \pi^*/f(n^2); \quad \alpha_n = \alpha/f(n^2); \quad \beta_n = \beta/f(n^2) \qquad (3)$$

As a rationale for this approach he has proposed a semi-theoretical model of solvent effects, according to which, quoting Bekárek, 'The solvent-induced shifts in electronic spectra which were used in the formulation of the π^* scale are proportional to the product function $(D - 1)/(2D + 1)\cdot(n^2 - 1)/(2n^2 + 1) = f(D,n^2) = f(D)\cdot f(n^2)$, where D is the bulk dielectric constant. Here $f(D)$ characterizes the size of the equilibrium (total) polarization of cybotactic solvent molecules, which is further to

Table. Values of π^*, π_n^*, and properties correlated

No.[b]Solvent	π^*	π_n^*	Properties correlated [a]					
			1	2	3	4	5	6
Select solvents, $\delta = 0.00$								
1 n-C$_6$H$_{14}$	-0.08	-0.43				25.51		48.9
2 c-C$_6$H$_{12}$	0.00	0.00	4.5			25.13	0.0	49.0
3 Et$_3$N	0.14	0.72	0.4	5.9				
4 (Pr^i)$_2$O	0.27	1.48				23.87		
5 (Bu^n)$_2$O	0.24	1.24				23.70		
7 Et$_2$O	0.27	1.52	-2.8	-0.2	19.05	23.36		53.7
11 CH$_3$COOEt	0.55	2.97				22.42	4.6	55.0
13 Tetrahydrofuran	0.58	2.94				22.37	4.4	55.4
16 CH$_3$COCH$_2$CH$_3$	0.67	3.56			20.62	22.17		
18 CH$_3$COCH$_3$	0.71	3.94	-9.8	-12.7	21.05	22.17	6.0	57.5
23 CH$_3$CON(CH$_3$)$_2$	0.88	4.25						
25 HCON(CH$_3$)$_2$	0.88	4.29	-11.9	-18.6	21.46		7.3	58.6
27 Butyrolactone	0.87	4.31						
28 N-Methylpyrrolidone	0.92	4.22						
29 CH$_3$–SO–CH$_3$	1.00	4.55	-14.9	-26.4	21.83		8.4	59.6
34 (CH$_3$CO)$_2$O	0.75	3.89						
38 CH$_3$COOC$_4$H$_9$-n	0.46	2.43						
41 Cyclohexanone	0.75	3.52			20.45	22.26		
42 (Bu^{n}O)$_3$PO	0.65	3.20						
51 Cyclopentanone	0.76	3.92						
52 CH$_3$COOMe	0.56	3.09						56.6
55 HCOOMe	0.60	3.43						
56 Sulpholane	0.99	4.55						
Other aliphatic solvents, $\delta = 0.00$								
9 Dioxane	0.55	2.72				22.73	6.2	54.6
20 ClCH$_2$CH$_2$Cl	0.81	4.05			20.80		6.2	
26 Hexamethylphosphoramide	0.87	4.07	-9.4				6.5	58.0
61 MeOCH$_2$CH$_2$OMe	0.53	2.82			20.34			
Polychloroaliphatic solvents, $\delta = 0.50$								
6 CCl$_4$	0.29	1.34	2.1	0.9		24.57	1.3	49.9
10 Cl$_2$C=CHCl	0.53	2.40						
12 CH$_3$CCl$_3$	0.49	2.33				23.53		
43 Cl$_2$C=CCl$_2$	0.28	1.22						
44 Cl$_2$CHCHCl$_2$	0.95	4.22						
253 Cl$_2$CHCH$_2$Cl	0.83	3.97						
Aromatic solvents, $\delta = 1.00$								
8 C$_6$H$_5$CH$_3$	0.54	2.29		0.0		23.58		52.8
14 C$_6$H$_6$	0.59	2.59	-3.2	-3.1	19.23	23.31	2.7	53.4
15 C$_6$H$_5$Cl	0.71	3.03			19.57	22.78	4.0	53.9
24 Pyridine	0.87	3.79	-5.5	-9.8				57.0
17 C$_6$H$_5$OCH$_3$	0.73	3.14			20.00	22.57		
31 C$_6$H$_5$NO$_2$	1.01	4.17	-5.4	-7.1	20.75		6.8	56.7
33 C$_6$H$_5$Br	0.79	3.26						53.9
35 1,4-C$_6$H$_4$(CH$_3$)$_2$	0.43	1.89						52.5
37 C$_6$H$_5$CN	0.90	3.81				22.07		
53 1,3,5-C$_6$H$_3$(CH$_3$)$_3$	0.41	1.81	0.3	5.8				
47 C$_6$H$_5$COOEt	0.74	3.23						
58 C$_6$H$_5$COCH$_3$	0.90	3.80			20.70			
63 C$_6$H$_5$CH$_2$CN	0.99	4.23	-7.0					
97 C$_6$H$_5$F	0.62	2.85		-5.9				

[a] Properties correlated are: (1) [77]Se n.m.r. shifts of Me$_2$Se, p.p.m.;[22] (2) [125]Te n.m.r. shifts of Me$_2$Te, p.p.m.;[22] (3) U.v.–visible v_{max} values of tungsten tetracarbonyl-1,10-phenanthroline, $\times 10^3$ cm^{-1};[22] (4) Fluorescence v_{max} of NN-dimethyl-4-(4,6-dichloro-1,3,5-triazinyl)aniline, $\times 10^3$ cm^{-1};[7] (5) [15]N n.m.r. shifts of 1-methylsilatrane, p.p.m.;[19] (6) Walther's E_K scale; based on E_T of 1,2-di-imine complex of molybdenum(0).[20b] Solvent numbering the same as in most other parts of the series.

be considered to be a measure of the size of the cybotactic sphere and the distance between the solute and the cybotactic solvent molecules. The f(n^2) function characterizes only the additional deformational polarization of these cybotactic molecules during solute excitation. In the case of the π^* solva-

tochromic parameter, the correlation equation between π^* and f(D,n^2) had the form of (4a) for the select solvents, (4b) for aromatic solvents, and (4c) for all solvents considered together (as reported in an earlier Bekárek paper).[12] The correlation coefficient obtained with the select solvent set was said to be no

$$\pi^* = 14.65\,\mathrm{f}(D,n^2) - 0.570, r = 0.989 \quad (4a)$$

$$\pi^* = 8.09\,\mathrm{f}(D,n^2) - 0.058, r = 0.963 \quad (4b)$$

$$\pi^* = 15.24\,\mathrm{f}(D,n^2) - 0.570, r = 0.841 \quad (4c)$$

worse than for other attempts[4,13] at the interpretation of the π^* parameter.

Given our (Bekárek's) model, the $\mathrm{f}(n^2)$ part of the $\mathrm{f}(D,n^2)$ term has no meaning for the chemical reactivity (equilibria and rates) as well as for spectral properties which do not depend on the excitation process (e.g., e.s.r. hyperfine splitting constants and fluorescence lifetimes). That is why there is an inconsistency between these reactivity data and the common spectral solvent polarity parameters. Let us assume, now, that the additional polarization during excitation obeys the $\mathrm{f}(n^2)$ function (which behaves ideally according to the model), while all non-ideality in the solvent effects is due to equilibrium polarization which deviates from the $\mathrm{f}(D)$ characterization.'

Bekárek then defined π_n^* by (3) and stated that, '$\pi_n^*\cdot\mathrm{f}(n^2) = \pi^*$ can now be used for the evaluation of solvent effects on spectral properties which are connected to the excitation process, but π_n^* can be used for the evaluation of solvent effects on equilibria, reaction rates, and spectral properties which do not depend on the excitation process. In a similar way as with π^*, the modification of acidity (α) and basicity (β) parameters was carried out by dividing them by $\mathrm{f}(n^2)$ and the corresponding α_n and β_n parameters were thus obtained.' Bekárek then went on to propose equation (5) as a substitute for (2) and compared a series of correlations by (5) with corresponding correlations by (2), not as (2) was intended to be used, but with d arbitrarily set equal to zero. The case made by Bekárek was that, for most non-

$$XYZ = XYZ_0 + s\pi_n^* + a\alpha_n + b\beta_n \quad (5)$$

spectral properties, π_n^* correlated the results better than π^*.

We do not disagree that, for most non-spectral properties, (5) correlates the results better than (2; $d = 0.00$). Indeed, we shall show why this is the case. We do question, however, whether the comparisons made by Bekárek were appropriate or fair. In comparing the statistical goodness of fit of a new computational method with earlier literature methods, it is natural for a scientist to portray his own results in the most favourable possible light. However, one should adhere to some basic rules of equity if, in making one's own method look good, one makes the earlier method look poor. If Bekárek wished to compare R_n with R_{TK} (the correlation coefficients using the two sets of parameters) he should have taken R_{TK} for the correlational method recommended by Taft and Kamlet. For all examples involving aliphatic and aromatic solvents together, and a non-spectral property, this is the correlation with $(\pi^* + d\delta)$, where d is a finite, negative number. The R_n values might not have compared so favourably with the R_{TK} values, but Bekárek could have pointed out that (5) has the advantage of requiring one fewer parameter.

Some Comments regarding Bekárek's Model.—Several aspects of the Bekárek model deserve comment. (1) The other workers who have analysed the π^* scale in terms of fundamental physicochemical properties[4,13] have related π^* to the sum rather than the product of dielectric constant (or dipole moment) and refractive index functions, and Ehrenson[13b] has explicitly pointed out that in any general analysis of the π^* scale, a 'cross term', such as $\mathrm{f}(D,n^2)$ should appear only as a second-order term. (2) Bekárek's statement that the $\mathrm{f}(n^2)$ part of the $\mathrm{f}(D,n^2)$ term has no meaning for chemical reactivity is strongly at odds with most of the informed current thinking on the subject,[4,13] and amounts to ignoring a

major contributor to ground-state intermolecular interactions: London's dispersion forces. While the $\mathrm{f}(D)$ term does, indeed, originate in the electrostatic reaction field models of Kirkwood[14a] and Onsager,[14b] the dispersion reaction field is omnipresent and is determined by $\mathrm{f}(n^2)$.[15] We have recently dealt with this matter in some detail.[10] (3) The intercepts of -0.57, -0.06, and -0.57 in equations (4a—c) should correspond in principle to the value of π^* in the gas phase. This is an experimentally accessible number, recently estimated to be -1.15 to -1.20.[10,16] Further, the large difference in slopes in (4a) and (4b) suggests that they are just local parameterizations of the experimental π^* values. (4) Even if one accepts Bekárek's rationale for π_n^*, there seems to be absolutely no justification for α_n or β_n. The published α and β parameters[1b,c] were obtained by averaging multiple α_i and β_i values, which were obtained from both excitation-dependent (u.v.–visible spectral shifts)[17] and non-excitation-dependent properties (formation constants, [19]F n.m.r. shifts, and hydroxyl i.r. shifts of hydrogen-bonded complexes).[17a,18] The results obtained from the u.v.–visible spectra showed no discernible differences from those deriving from the other properties.

Relationship between π_n^*, π^*, and β.—Before discussing the relationship between the Taft–Abboud–Kamlet and Bekárek parameters, it is necessary to comment on the special cases of acetonitrile (AN) and nitromethane (NM). When we first defined 'select solvents' as non-hydrogen-bond donor aliphatic solvents with a single dominant bond dipole, and drew up the original list,[2] we were not aware that AN and NM had sufficiently strong hydrogen-bond donor properties (currently preferred α values[1c] are 0.19 for AN and 0.22 for NM) to influence XYZs with non-zero a values in (2). When it became evident to us that AN and NM were to be treated as HBD solvents, we no longer included them in later select solvent correlations,[2] but we were perhaps remiss in not pointing this out explicitly. We now take the opportunity to correct this oversight.

Before comparing correlations with π_n^*, π^*, and $(\pi^* + d\delta)$, it is useful to examine the relationship between these parameters. Values of the parameters for 44 representative non-HBD aliphatic, polychloroaliphatic, and aromatic solvents are assembled in the Table. The multiple linear regression equation of π_n^* with π^* and δ is given by (6a), which can be rewritten as (6b).

$$\pi_n^* = 0.26 + 4.58\pi^* - 0.478\delta$$
$$(n = 47, r = 0.990, \text{s.d.} = 0.18) \quad (6a)$$

$$\pi_n^* = 0.26 + 4.58(\pi^* - 0.10\delta) \quad (6b)$$

It follows from (6b) and from the fact that we have encountered d values ranging from 0.00 to -0.40 in equation (2) that, just as π^* corresponds to a single discrete dipolarity–polarizability blend with a near maximal polarizability contribution, π_n^* corresponds to another single discrete blend with a polarizability contribution which is near 75% of maximal. It reduces the Bekárek *versus* Taft–Abboud–Kamlet differences to the question of whether Bekárek's two discrete dipolarity–polarizability blends in the solute–solvent interactions [*i.e.*, π_n^* and $\pi_n^*\cdot\mathrm{f}(n^2) = \pi^*$] are to be preferred over the $(\pi^* + d\delta)$ formalism, which allows for the full range of polarizability contributions from near maximal ($d = 0$) to near nil ($d -0.40$). It also follows from (6b) that π_n^* will perform better than π^* for any XYZ with d greater than 0.05 in (2), but that $(\pi^* + d\delta)$ will perform better than π_n^* for any XYZ whose d value differs significantly from 0.10.

Comparison of Correlations with π_n^* and with $(\pi^* + d\delta)$.—To demonstrate the latter relationship, we have chosen six

properties with d values in (1) ranging from -0.20 to -0.36. The data used in the correlations are included in the Table. The properties correlated are: (a) solvent effects on ^{77}Se n.m.r. shifts of dimethyl selenide[9] [correlation equation (7)],

$$^{77}\text{Se n.m.r.-}\Delta = 2.65 - 16.0\,(\pi^* - 0.36\delta) \text{ p.p.m.,}$$
$$n = 13, r = 0.966, \text{s.d.} = 1.6 \text{ p.p.m.} \quad (7)$$

For corresponding correlation with π^*,
$$r = 0.847, \text{s.d.} = 3.2 \text{ p.p.m.}$$

For corresponding correlation with π_n^*,
$$r = 0.909, \text{s.d.} = 2.5 \text{ p.p.m.}$$

(b) solvent effects on the ^{125}Te n.m.r. shifts of dimethyl telluride[9] [equation (8)], (c) solvent effects on the u.v.–visible

$$^{125}\text{Te n.m.r.-}\Delta = 9.26 - 33.2\,(\pi^* - 0.24\delta) \text{ p.p.m.,}$$
$$n = 11,^* r = 0.983, \text{s.d.} = 2.1 \quad (8)$$

For the corresponding correlation with π^*,
$$r = 0.901, \text{s.d.} = 4.7$$

For the corresponding correlation with π_n^*,
$$r = 0.931, \text{s.d.} = 4.0^*$$

spectrum of tungsten tetracarbonyl-1,10-phenanthroline[9] [equation (9)], (d) solvent effects on the fluorescence spectrum of

$$10^3\,\nu_{\text{max.}}/\text{cm}^{-1} = 18.1 + 3.64\,(\pi^* - 0.26\delta),$$
$$n = 13, r = 0.962, \text{s.d.} = 0.25 \quad (9)$$

For the corresponding correlation with π^*,
$$r = 0.766, \text{s.d.} = 0.55$$

For the corresponding correlation with π_n^*,
$$r = 0.921, \text{s.d.} = 0.33$$

NN-dimethyl-4-(4,6-dichloro-1,3,5-triazinyl)aniline[4] [equation (10)], (e) solvent effects on ^{15}N n.m.r. shifts of 1-methyl-

$$10^3\,\nu_{\text{max.}}\ \text{fluo/cm}^{-1} = 25.0 - 4.22\,(\pi^* - 0.20\delta),$$
$$n = 18, r = 0.975, \text{s.d.} = 0.25 \quad (10)$$

For the corresponding correlation with π^*,
$$r = 0.913, \text{s.d.} = 0.44$$

For the corresponding correlation with π_n^*,
$$r = 0.963, \text{s.d.} = 0.29$$

silatrane[19] [equation (11)], (f) Walther's E_{K} solvent 'polarity'

$$^{15}\text{N n.m.r.-}\Delta = -0.19 + 8.32\,(\pi^* - 0.21\delta) \text{ p.p.m.,}$$
$$n = 12, r = 0.993, \text{s.d.} = 0.32 \quad (11)$$

For the corresponding correlation with π^*,
$$r = 0.945, \text{s.d.} = 0.87$$

For the corresponding correlation with π_n^*,
$$r = 0.973, \text{s.d.} = 0.62$$

scale, based on transition energies in u.v.–visible spectrum of a 1,2-di-imine complex of molybdenum(0)[20] [equation (12)].

$$E_{\text{K}}/\text{kcal mol}^{-1} = 49.7 + 10.03\,(\pi^* - 0.26),$$
$$n = 19, r = 0.967, \text{s.d.} = 0.84 \quad (12)$$

For the corresponding correlation with π^*,
$$r = 0.881, \text{s.d.} = 1.50$$

For the corresponding correlation with π_n^*,
$$r = 0.945, \text{s.d.} = 1.04$$

The d term in (1) and (2) is zero for $\pi \longrightarrow \pi^*$ transitions in the electronic spectra of uncharged indicators, wherein there is no change in the direction of the molecular dipole on going from the ground state to the electronic excited state. The d term has also been near zero for several solubility properties which we have correlated with solute π^* values. For most other physico-chemical properties and reactivity parameters studied, however, d has been finite, and usually more negative than -0.10. The XYZs correlated by equations (7)—(12) are representative of the latter type properties, and we feel that it is fair to say that, as a general rule, the $(\pi^* + d\delta)$ formalism will allow more precise and more meaningful correlations than π_n^* (meaningful in that the d term provides information regarding solvent polarizability effects on the property studied).

Correlations of E_{K} and $E_{\text{T}}(30)$ by π_n^* and $(\pi^* + d\delta)$.—There exists an interesting ambiguity regarding Bekárek's correlations of the E_{K} and $E_{\text{T}}(30)$ solvent 'polarity' scales, the latter being based on transition energies for the 'solvatochromiebande' of 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenoxide.[21] According to our methodology, these are u.v.–visible spectra whose maxima are shifted hypsochromically with increasing solvent dipolarity–polarizability (because the dipoles change direction in the electronic excitation, and solvent molecules best orientated to solvate the ground state are no longer best orientated to solvate the electronic excited state), and are thus best correlated with $(\pi^* + d\delta)$. Thus, we found that the linear regression of E_{K} with $(\pi^* - 0.26\delta)$ according to (12), above, gave $r = 0.967$, and we have recently reported[1c] that $E_{\text{T}}(30)$ for non-HBD solvents was correlated as follows.

$$E_{\text{T}}(30) = 30.31 + 14.7\,(\pi^* - 0.23\delta) \text{ kcal mol}^{-1} \quad (13)$$
$$n = 32, r = 0.972, \text{s.d.} = 0.94$$

According to Bekárek's methodology, on the other hand, these are spectral properties which depend on the excitation process and, correspondingly, should be well correlated by π^* or $\pi_n^*\cdot\text{f}\,(n^2)$. The above notwithstanding, however, he has reported[11] the following correlation equations, with no explanation of why certain spectral properties should require the term in $\pi_n^*\cdot\text{f}(D)$, and others not.

$$E_{\text{K}}(\text{kcal mol}^{-1}) = 50.11 + 10.61\,\pi_n^*\cdot\text{f}(D) -$$
$$10.85\pi_n^*\cdot\text{f}(n^2) \quad (14)$$
$$n = 23,\dagger r = 0.903, \text{s.d.} = 1.36$$

$$E_{\text{T}}(30) = 32.09 + 8.27\,\pi_n^*\cdot\text{f}(D) - 6.00\,\pi_n^*\cdot\text{f}(n^2) \quad (15)$$
$$n = 55,\dagger r = 0.974, \text{s.d.} = 0.93$$

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* Excluding the point for nitrobenzene. If this point is included, the r value for the correlation with $(\pi^* + d\delta) = 0.954$, and that for the correlation with $\pi_n^* = 0.892$.

† There are two reasons why Bekárek's data sets are larger than ours. He includes CH_3CN, CH_3NO_2, CH_2Cl_2, and $CHCl_3$, which we exclude because we consider them to be hydrogen-bond donors. Also, in his $E_{\text{T}}(30)$ data set, he includes a large number of secondary values, obtained from correlations of Dimroth and Reichardt's original $E_{\text{T}}(30)$ scale with Kosower's Z scale and other properties. We have excluded these secondary values because we were not certain that the other properties had the same dipolarity–polarizability blend as the original $E_{\text{T}}(30)$ betaine indicator.

It is seen that the statistical goodness of fit is significantly poorer for (14) than for (12), and about the same for (13) and (15). This would scarcely seem to justify the increased complexity of (14) and (15) compared with (12) and (13), with no physical significance attributed to the fact that one term in (14) and (15) does not appear in correlations of other types of properties and reactivity parameters.

This points up another important difference between Bekárek's approach and our own. We have set forth a rather stringent set of 'ground rules' according to which we have carried out our correlations, and in some 40-odd papers on the subject we have never knowingly deviated from these rules. Bekárek, on the other hand, seems in recent papers[11,22] to be using whatever combination of parameters gives the best statistical goodness of fit, with no explanation or apparent physical basis for that choice of parameters.

In so doing, he does no service to the new or potential investigator into solvent effects, who is already faced with an almost overwhelming choice between a large number of published solvent property scales, and has no immediately obvious basis for choosing which scale or scales to use. We are perhaps unique among proponents of solvent property scales in that we have related our solvatochromic parameters to every solvent property scale which has come to our attention, including, *inter alia*, $E_T(30)$, E_K, AN, DN, Z, S, A_N, A (acity), B (basity), P(Taft), P(Snyder), P(Koppel–Palm), Y, E, B(Koppel–Palm), G, P_y, C_A, E_A, $\log k$ (Pr$_3$N + MeI), *etc.* We have related our parameters to functions of dipole moments, bulk dielectric constants, and refractive indexes, and we have used them, with better than fair success, to correlate and rationalize almost every type of phenomenon that involves a solute–solvent interaction. We therefore suggest that no new solvent property scales be introduced into the literature, unless they show real and obvious advantages over existing scales. We do not feel that π_n^*, α_n, and β_n meet such a requirement.

Acknowledgements

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