

Improvement of the Applicability of Taft–Kamlet Solvent Polarity Parameters to Chemical Reactivity

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Solvent effects on reaction rates (16 systems), equilibria (20 systems), and spectral properties (seven systems) are found to be better described by Taft–Kamlet solvent parameters divided by the $(n^2 - 1)/(2n^2 + 1)$ refractive index function than by the original Taft–Kamlet parameters.

In the past 25 years many solvent polarity parameters have been introduced and have had varying degrees of success in correlating solvent-dependent data. Great effort has also been devoted to studying the inter-relations of these polarity parameters.^{1–5} Moreover some attempts have been made to interpret some of these polarity scales theoretically.^{6–11}

These solvent effect studies are of use in the interpretation of various spectroscopic, kinetic, and equilibrium phenomena. The spectral studies have often been made with the aim of developing solvent polarity scales which could be applied generally to other properties. At present two such spectral polarity scales are popular, the solvent parameters of Taft and Kamlet (π^* , α , β) and the $E_T(30)$ parameters of Dimroth and Reichardt.

The purpose of this work is to show that the applicability of the Taft–Kamlet polarity parameters to chemical reactivity and some spectral data can be improved by dividing them by the refractive index (n) function $(n^2 - 1)/(2n^2 + 1)$ and to demonstrate the relation between the Taft–Kamlet and Dimroth–Reichardt solvent parameters. The initial framework of the study is the semitheoretical model of solvent effects on electronic and i.r. spectral band positions applied recently to the interpretation of the π^* solvent parameters.¹⁰

According to the model the solvent-induced shifts in electronic spectra of the Taft–Kamlet parameters are proportional to the product function $(D - 1)/(2D + 1) \cdot (n^2 - 1)/(2n^2 + 1) = f(D, n^2) = f(D) \cdot f(n^2)$. Here $f(D)$ characterizes the size of the equilibrium (total) polarization of cybotactic solvent molecules which is further considered to be a measure of the size of the cybotactic sphere and the distance between the solute and cybotactic solvent molecules. The $f(n^2)$ function characterizes only the additional deformational polarization of these cybotactic solvent molecules during solute excitation. In the case of the π^* solvent parameter the correlation equation between the π^* and $f(D, n^2)$ had the form (1)¹⁰ for the total solvent set and (2) for 29 selected solvents. The correl-

$$\pi^* = 15.24 f(D, n^2) - 0.570 \quad (r \ 0.841) \quad (1)$$

$$\pi^* = 14.65 f(D, n^2) - 0.573 \quad (r \ 0.989) \quad (2)$$

ation coefficient r obtained with the selected solvent set was not worse than those for other attempts^{6–9} at the interpretation of the π^* parameter.

Given our model the $f(n^2)$ part of the $f(D, n^2)$ term has no meaning for the chemical reactivity (equilibria and rates) as well as for spectral properties which do not depend on excitation process (*e.g.* e.s.r. hyperfine splitting constants or 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 $f(n^2)$ 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 $f(D)$ characterization. Let us define a new solvent dipolarity function, say π_n^* , which is related to the original spectral dipolarity parameter, π^* , by the simple equation (3). $\pi_n^* \cdot f(n^2) = \pi^*$ can now be used for

$$\pi_n^* = \pi^*/f(n^2) \quad (3)$$

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 the similar way as with π^* the modification of acidity (α) and basicity (β) parameters was carried out through them by $f(n^2)$ and corresponding α_n and β_n parameters were thus obtained.

A comparison of the applicability of the original and the modified Taft–Kamlet solvent parameters is presented in Table 2. Besides regression parameters of equation (4) (Y and

$$Y = Y_n + s_n \pi_n^* + a_n \alpha_n + b_n \beta_n \quad (4)$$

Y_n are the studied phenomena in a given solvent and in cyclohexane and s_n , a_n , and b_n are measures of the response of Y to changing the respective solvent property) there are the correlation coefficient and standard deviation for the correlation performed with the modified parameters (r_n , s.d. _{n}) and with the original parameters (r_{TK} , s.d. _{TK}). Systems studied as well as the solvents considered and source of the data are given in Table 1. The numbering of the solvents is the same as used by Taft and Kamlet.² The study was carried out with published data on solvent effects on 16 reaction rates, 20 equilibria, and seven spectral properties. The systems studied was selected according to the popularity of the systems in the field of solvent effect studies,^{2,3} *e.g.* systems 1, 23, 17, 19, 20, 37, and 42 were used as empirical 'polarity' scales and with the aim of employing the systems where only the dipolarity effect of solvents could be expected.

It is apparent from the correlation characteristics that the modified Taft–Kamlet parameters obey the experimental data better than the original ones. The model used also explains the 'temperamental' behaviour of carbon disulphide² which is the result of the high refractive index of this solvent.

The improvement of the applicability of the modified parameters is also apparent for a property studied only in selected solvents.² Thus for a representative Menschutkin reaction (system 1 in Table 1) studied in 19 selected solvents the correlation equations have the forms (5) and (6).

$$\log k = -4.38 + 0.974 \pi_n^* \quad (r \ 0.993, \text{ s.d. } 0.19) \quad (5)$$

$$\log k = -4.23 + 4.640 \pi^* \quad (r \ 0.981, \text{ s.d. } 0.31) \quad (6)$$

As for the relation between the π_n^* and $E_T(30)$ solvent parameters a fairly good correlation can be obtained with the

Table 1. Solvent-dependent phenomena and solvents considered ^a

Kinetics	
1	Tri-n-propylamine with methyl iodide ^{12,13} (log <i>k</i> or ρ solvent polarity scale), 38 solvents 1—3, 5—11, 13—16, 18, 20—22, 24, 25, 29—34, 36—38, 41, 43, 44, 47, 50, 51, 53, 56
2	Triethylamine with ethyl bromoacetate, ¹³ 15 solvents 2, 6, 8, 14, 16, 18, 21, 26, 28, 31, 32, 35, 37, 50, 53
3	Triethylamine with ethyl iodoacetate, ¹³ 15 solvents as for system 2
4	Trimethylamine with <i>p</i> -nitrobenzyl chloride, ¹⁴ 11 solvents 1, 7, 11, 14, 18, 30—32, 47, 50, 58
5	Methoxycarbonylacetylene with piperidine, ¹⁵ 5 solvents 2, 7, 9, 14, 50
6	Diphenylketene with <i>n</i> -butyl vinyl ether, ¹⁶ 5 solvents 2, 11, 15, 37, 50
7	Chlorosulphonyl isocyanate with 2-ethylhex-1-ene, ^{17,18} 6 solvents 2, 7, 21, 30—32
8	Cyclohexene with 2,4-dinitrobenzenesulphonyl chloride, ¹⁹ 5 solvents 6, 20, 30, 31, 201
9	Solvolysis of <i>p</i> -methoxyneopentyl tosylate, ²⁰ 10 solvents 7, 11, 13, 18, 24, 25, 29, 32, 34, 50
10	Auto-oxidation of styrene, ²¹ 11 solvents 2, 6, 8, 14, 15, 31—33, 35, 50, 60
11	Thermal decomposition of <i>t</i> -butyl performate, ²² 14 solvents 1, 2, 5, 6, 8, 9, 13—15, 21, 30—32, 35
12	Thermolysis of α -chlorobenzyl methyl ether, ²³ 6 solvents 6, 8, 15, 30, 50, 56
13	Solvolysis of butyl chloride ²⁴ at 298 K, 11 solvents vapour state, <i>n</i> -pentane, 1, 7, 14, 18, 23, 25, 28, 31, 32, 50
14	Solvolysis of butyl chloride at 373 K, ²⁴ solvents as for system 13
15	Aniline with benzoyl chloride, ²⁵ 23 solvents <i>n</i> -octane, 5—9, 11, 13—16, 18, 21, 23, 30—33, 35, 37, 41, 50, 53
16	Isomerization of <i>cis</i> -1-azonorbornane to <i>trans</i> -1-azonorbornane, ²⁶ 6 solvents <i>n</i> -dodecane, <i>o</i> -xylene, 17, 25, 37, 41
Equilibria	
17	Eluant strength parameters ϵ^0 of Snyder ^{27,28} (adsorption chromatography), 20 solvents <i>n</i> -pentane, 2, 4, 6, 7—9, 11, 13—16, 18, 21, 24, 30, 29, 32, 35, 50, 52
18	log <i>K</i> of dimerization of benzoic acid, ²⁹ 5 solvents 6, 8, 14, 15, 30
19	log <i>K</i> of tautomeric equilibrium in ethyl acetoacetate, ³⁰ 6 solvents 1, 7, 14, 29, 30, 50
20	Free energy difference between <i>cis</i> - and <i>trans</i> -isomers of 2-isopropyl-5-methoxy-1,3-dioxane, ^{31,32} 13 solvents 1, 2, 6—8, 13, 14, 18, 21, 30, 31, 50, 53
21	Free energy difference between <i>cis</i> - and <i>trans</i> -isomers of 2-isopropyl-5-ethoxy-1,3-dioxane, ^{31,32} 13 solvents as for system 20
22	log of solubility of tetramethylammonium iodide in aprotic solvents, ³³ 14 solvents 7, 11, 15, 16, 18, 20, 21, 25, 28, 29, 31, 32, 47, 50
23	log of solubility of tetraethylammonium iodide in aprotic solvents, ³³ 20 solvents 7, 11, 14—16, 18, 20—22, 25, 29, 31—33, 37, 44, 47, 50, 55, 58
24	log of solubility of tetrapropylammonium iodide in aprotic solvents, ³³ 10 solvents 11, 15, 18, 20, 22, 31, 32, 37, 44, 50
25	Free energy of solution of dissociated species $(\text{CH}_3\text{CH}_2)_4\text{N}^+ + \text{I}^-$, ³³ 15 solvents 7, 11, 15, 16, 18, 20—22, 25, 29, 31—33, 37, 44, 47, 50, 55, 58
26	Free energy of solution of dissociated species $(\text{CH}_3)_4\text{N}^+ + \text{I}^-$, ³³ 14 solvents 7, 11, 15, 16, 18, 20, 21, 25, 28, 29, 31, 32, 47, 50
27	Free energy of solution of dissociated species $(\text{C}_3\text{H}_7)_4\text{N}^+ + \text{I}^-$, ³³ 10 solvents 11, 15, 18, 20, 22, 31, 32, 37, 44, 50
28	Free energy of solution of ion pairs $(\text{CH}_3)_4\text{N}^+\text{I}^-$, ³³ 14 solvents 7, 11, 15, 16, 18, 20, 21, 25, 28, 29, 31, 32, 47, 50
29	Free energy of solution of ion pairs $(\text{C}_2\text{H}_5)_4\text{N}^+\text{I}^-$, ³³ 19 solvents 7, 11, 15, 16, 18, 20—22, 25, 29, 31—33, 37, 44, 47, 50, 55, 58
30	log of distribution coefficient of furfural between aprotic solvents and water, ³⁴ 11 solvents <i>n</i> -octane, 4, 6, 8, 14, 15, 33, 35, 38, 62, CH_2Br_2
31	log of distribution coefficient of methylfurfural between aprotic solvents and water, ³⁴ 12 solvents <i>n</i> -octane, 4, 6, 8, 14, 15, 33, 35, 38, 62, 135, CH_2Br_2
32	log of distribution coefficient of vanillin between aprotic solvents and water, ³⁴ 11 solvents 1, 2, 6, 8, 14, 15, 20, 30, 31, 33, 35
33	log of distribution coefficient of salicylaldehyde between aprotic solvents and water, ³⁴ 14 solvents 1, 2, 6, 8, 11, 14, 15, 20, 30, 31, 33, 35, 62, 135
34	log of distribution coefficient of isovanillin between aprotic solvents and water, ³⁴ 11 solvents 1, 2, 6, 8, 14, 15, 20, 30, 31, 33, 35
35	log of distribution coefficient of orthovanillin between aprotic solvents and water, ³⁴ 12 solvents 1, 2, 6, 8, 14, 15, 20, 30, 31, 33, 35, 38
36	log of distribution coefficient of acetylacetone between aprotic solvents and water, ³⁴ 19 solvents 1, 2, 5, 6, 8, 10, 14, 15, 20, 30, 31, 33, 35, 38, 42, 44, 62, 135, CH_2Br_2

Table 1 (continued)

Spectral properties	
37	Nitrogen hyperfine splitting constant of di- <i>t</i> -butyl nitroxide (e.s.r.), ³⁵ 26 solvents 1, 6–9, 13–15, 18, 20, 21, 24, 25, 29, 30, 32, 33, 36, 50, 61, 103–105, 107, 111, 201
38	Nitrogen hyperfine splitting constant of 4-amino-2,2,6,6-tetramethylpiperidin-1-yloxy (e.s.r.), ³⁵ 26 solvents as for system 37
39	Nitrogen hyperfine splitting constant of 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (e.s.r.), ³⁵ 26 solvents as for system 37
40	Molecular ellipticity of the 2-benzoylbenzoic acid–amphetamine system, ³⁶ 9 solvents 6, 8, 9, 13–15, 21, 30, 50
41	Fluorescence life-time of Rose Bengal dye, ³⁷ 12 solvents 18, 25, 50, 101–105, 107, 111, 112, 202
42	Polarity scale P (¹⁹ F n.m.r.), ² 28 solvents 1–3, 6–8, 11, 13–15, 17, 18, 20, 21, 24, 25, 29, 31–34, 37, 40, 50, 55, 56, 92, CH ₂ I ₂
43	Polarity scale $E_T(30)$, ³ 55 aprotic solvents 1–18, 20, 21, 23–38, 41–44, 47, 50, 51–53, 56, 58, 60–63, 89, 97
44	Polarity scale E_K , ³⁸ 23 solvents 1, 2, 6–9, 11, 13–15, 18, 20, 21, 24–26, 29–31, 33, 36, 50, 55

^a Solvent numbers correspond to those of Taft and Kamlet.²

Table 2. Comparison of the applicability of the original and modified Taft–Kamlet solvent parameters

System	Y_n	s_n	b_n	a_n	r_n	S.d. _n	r_{TK}	S.d. _{TK}
1	–4.35	0.980			0.992	0.17	0.972	0.31
2	–4.00	0.731			0.975	0.23	0.929	0.35
3	–3.47	0.684			0.984	0.17	0.938	0.33
4	–4.41	0.317			0.933	0.48	0.866	0.66
5	–0.36	0.734			0.922	0.54	0.870	0.68
6	–0.05	0.502			0.961	0.27	0.851	0.52
7	–0.01	0.846			0.971	0.42	0.939	0.60
8	–1.65	1.242			0.990	0.23	0.960	0.46
9	–4.37	1.212			0.986	0.20	0.939	0.42
10	0.67	0.127			0.986	0.20	0.939	0.42
11	–2.75	0.430			0.982	0.13	0.980	0.13
12	12.56	–1.675			0.947	0.71	0.806	1.30
13	15.11	–1.440			0.992	0.50	0.971	0.93
14	37.67	–1.888			0.980	1.05	0.972	1.25
15	–0.86	0.595	0.575		0.957	0.33	0.889	0.49
16	0.89	0.095			0.915	0.07	0.909	0.08
17	0.03	0.104	0.077		0.966	0.05	0.948	0.07
18	4.94	–0.587	–4.76		0.917	0.28	0.880	0.33
19	–0.18	–0.273			0.962	0.16	0.955	0.17
20	1.32	–0.213			0.930	0.14	0.882	0.18
21	1.13	–0.226			0.936	0.14	0.889	0.18
22	–13.53	2.639			0.975	0.51	0.829	1.27
23	–11.97	2.526			0.965	0.51	0.791	1.19
24	–10.37	2.431			0.925	0.53	0.672	1.03
25	36.28	–7.265			0.926	2.13	0.728	3.86
26	40.70	–7.900			0.958	1.98	0.804	4.10
27	36.53	–7.812			0.888	2.15	0.556	3.89
28	17.04	–2.972			0.978	0.53	0.840	1.38
29	15.37	–3.056			0.955	0.69	0.791	1.43
30	–0.43	0.431			0.928	0.18	0.850	0.26
31	–0.12	0.448			0.946	0.15	0.887	0.22
32	–0.57	0.491			0.986	0.15	0.949	0.27
33	1.39	0.267			0.966	0.11	0.949	0.14
34	–0.68	0.484			0.991	0.12	0.980	0.17
35	0.76	0.409			0.987	0.11	0.966	0.19
36	0.06	0.261			0.888	0.19	0.855	0.23
37	15.04	0.155		0.151	0.965	0.12	0.891	0.21
38	13.96	0.151		0.143	0.977	0.09	0.963	0.12
39	15.16	0.138		0.125	0.982	0.07	0.903	0.16
40	3.55	–0.218	–1.01		0.945	0.10	0.890	0.15
41	3.86	–0.126		–0.146	0.980	0.08	0.967	0.10
42	–0.193	0.581			0.966	0.21	0.923	0.32

use of the old model. In order to relate the $E_T(30)$ parameters with the relative permittivity and refractive index functions we recently established equation (7).¹¹ Upon replacing one $f(D)$ function in each term by the characteristic π_n^* of the

$$E_T(30) = 29.87 + 72.02 f^2(D) - 29.16 f(D, n^2) \quad (r 0.957) \quad (7)$$

cybotactic sphere we obtain for the set of 55 aprotic solvents equation (8) and for 24 selected solvents for which $E_T(30)$ are known, equation (9). In a similar way the correlation

$$E_T(30) = 32.09 + 8.27 \pi_n^* \cdot f(D) - 6.00 \pi_n^* \cdot f(n^2) \quad (r 0.974, \text{ s.d. } 0.93) \quad (8)$$

$$E_T(30) = 31.84 + 10.61 \pi_n^* \cdot f(D) - 10.85 \pi_n^* \cdot f(n^2) \\ (r\ 0.984, \text{ s.d. } 0.86) \quad (9)$$

between the π_n^* and the E_K scale of Walther³⁸ (excitation of the indicator is also a charge-transfer process) has for 23 aprotic solvents form (10) and for 10 selected solvents (11).

$$E_K = 50.11 + 4.40 \pi_n^* \cdot f(D) - 1.24 \pi_n^* \cdot f(n^2) \\ (r\ 0.903, \text{ s.d. } 1.36) \quad (10)$$

$$E_K = 49.86 + 3.42 \pi_n^* \cdot f(D) - 2.67 \pi_n^* \cdot f(n^2) \\ (r\ 0.981, \text{ s.d. } 0.80) \quad (11)$$

As far as one of the basic problems in the field of empirical evaluation of media effects is concerned, *viz.* whether to use one-parameter [*e.g.* $E_T(30)$] or multiparameter (*e.g.* Taft-Kamlet) equations we consider the multiparameter equations to be more convenient. Apart from the commonly known advantages and disadvantages of the both processes^{2,3} the one-parameter methods hide greater uncertainties in interpretation. Thus for example in their recent work Schmittel and his co-workers²⁶ evaluated solvent effects on the rate of isomerization of *cis*-1-azonobornane. They found a good correlation of the experimental data with $E_T(30)$ for aprotic solvents but the data obtained in alcohols deviated highly from the regression line. The authors interpreted the deviations as resulting from the hydrogen bonding ability of the alcohols and the role of hydrogen bonding in the rate-determining process. $E_T(30)$ values are known to contain dipolarity as well as acidity contributions.^{1,2} The π^* values of the alcohols used are not known but from π^* values of similar alcohols it seems probable that the effect of these alcohols on the isomerization rate is mainly due to their dipolarity effect while the hydrogen bonding donor effect of the alcohols in the reaction is rather problematic.

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Received 20th August 1982; Paper 2/1454