

Comparison of the $\pi^* + d\delta$ and $\pi^*/f(n^2)$ Methods for the Evaluation of Solvent Polarity Effect in Chemical Reactivity

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$\pi^* + d\delta$ and $\pi^*/f(n^2)$ formalisms are found to be of nearly the same effectiveness for the evaluation of solvent polarity effects on reaction rates and equilibria.

Two successful attempts have been made to improve applicability of the Kamlet-Taft solvent dipolarity-polarizability parameters π^* . Kamlet and Taft^{1,2} introduced an additional variable polarizability term $d\delta$ while we proposed^{3,4} the improvement of the applicability of the π^* in chemical reactivity through dividing the π^* by Onsager's refractive index (n) function $f(n^2) = (n^2 - 1)/(2n^2 + 1)$. We thus introduced π_n^* parameters [$\pi_n^* = \pi^*/f(n^2)$] which we have found to be more applicable than the original π^* for the evaluation of solvent polarity effects on reaction rate constants, equilibria, and even

21. log (solubility of tetramethylammonium iodide) in aprotic solvents,²¹ 14 solvents 7, 11, 15, 16, 18, 20, 21, 25, 28, 29, 31, 32, 47, 50
22. log (solubility of tetraethylammonium iodide) in aprotic solvents,²¹ 18 solvents 7, 11, 14–16, 18, 20, 21, 25, 29, 31–33, 37, 44, 47, 50, 58
23. log (solubility of nitromethane),²² 32 solvents 1–9, 11, 13–16, 18, 21, 23–25, 27–30, 33, 35, 36, 41, 50, 58, 62, 97, n-decane
24. Free energy of transfer of $\text{Et}_4\text{N}^+\text{I}^-$ from methanol to other solvent,²¹ 23 solvents 1, 2, 6, 7, 11, 14–16, 18, 20–22, 25, 28, 29, 31–33, 37, 44, 47, 50, 55
25. Octanol-water partition coefficients,²³ 57 solvents 1–3, 6–8, 10–16, 18, 20, 21, 23, 25, 26, 29, 30, 33, 35, 41, 43, 50, 52–54, 62, 64, 86, 97, 145, 146, 155, 226, 250, tetramethylsilane, neopentane, n-pentane, benzotrifluoride, cyclopentane, n-butane, fluorotrichloromethane, propane, n-propyl chloride, amphetamine, hexan-2-one, *N*-methylpiperidine, dimethylethylamine, n-propylamine, *NN*-diethylacetamide, trimethylamine, dimethyl ether, *o*-xylene, and ethylbenzene

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

Kinetics	
1. Tri- <i>n</i> -propylamine with methyl iodide, ⁶ 50 solvents 1, 2, 5–11, 13–18, 20–22, 25, 30–33, 35–37, 41, 43, 44, 47, 50, 51, 53, 54, 58–60, 62, 63, 86, 89, 91–93, 96, 98, 131, 132, 135, 138	
2. Thermal decomposition of <i>t</i> -butyl performate, ⁷ 15 solvents 1, 2, 5, 6, 8, 9, 13–15, 21, 30–32, 35, 90	
3. Solvolysis of butyl chloride at 298 K, ⁸ 12 solvents n-pentane, 1, 7, 9, 14, 18, 23, 25, 28, 31, 32, 50	
4. Auto-oxidation of styrene, ⁹ 11 solvents 2, 6, 8, 14, 15, 31–33, 50, 60	
5. Triethylamine with ethyl bromoacetate, ¹⁰ 22 solvents 2, 6, 8, 14, 16–18, 20, 26, 28, 31, 32, 35, 37, 50, 53, 54, 58, 63, 89, 98, 131	
6. Triethylamine with ethyl iodoacetate, ¹⁰ 22 solvents as for system 5	
7. Solvolysis of <i>p</i> -methoxyneophyl tosylate, ¹¹ 10 solvents 7, 11, 13, 18, 24, 25, 29, 32, 34, 50	
8. 1,4-Diazabicyclo[2.2.2]octane with (2-chloroethyl)benzene, ¹² 17 solvents 8, 9, 11, 13–15, 18, 25, 29, 31–33, 37, 41, 50, 63	
9. 1,4-Diazabicyclo[2.2.2]octane with (2-bromomethyl)benzene, ¹² 19 solvents 4, 6, 8, 9, 11, 13–15, 17, 18, 25, 29, 31–33, 37, 41, 50, 63	
10. 1,4-Diazabicyclo[2.2.2]octane with (2-iodoethyl)benzene, ¹² 19 solvents as for system 9	
11. Trimethylamine with <i>p</i> -nitrobenzyl chloride, ¹³ 11 solvents 1, 7, 11, 14, 18, 30–32, 47, 50, 58	
12. Thermolysis of α -chlorobenzyl methyl ether, ¹⁴ 7 solvents 6, 8, 15, 30, 31, 50, 56	
13. Aniline with benzoyl chloride, ¹⁵ 23 solvents n-octane, 5–9, 11, 13–16, 18, 21, 23, 30–33, 35, 37, 41, 50, 53	
14. Methyl phenyl sulphide with dimethyl sulphate at 60 °C, ¹⁶ 12 solvents 6, 8, 9, 11, 14, 15, 17, 18, 32, 50, 56, 137	
15. Methyl phenyl selenide with dimethyl sulphate at 60 °C, ¹⁶ 12 solvents as for system 14	
16. <i>p</i> -Aminobenzenethiyl free radical with styrene, ¹⁷ 21 solvents 2, 3, 6, 8, 9, 11, 13, 14, 17, 20, 21, 24, 25, 29, 30, 37, 47, 48, 53, 60, 97	
Equilibria	
17. Free energy differences between <i>cis</i> - and <i>trans</i> -isomers of 2-isopropyl-5-methoxy-1,3-dioxane, ¹⁸ 13 solvents 1, 2, 6–8, 13, 14, 18, 21, 30, 31, 50, 53	
18. Free energy difference between <i>cis</i> - and <i>trans</i> -isomers of 2-isopropyl-5-ethoxy-1,3-dioxane, ¹⁸ 13 solvents as for system 17	
19. Free energy of the transition between <i>E</i> and <i>Z</i> conformers of methyl 2-fluorobenzoate, ¹⁹ 12 solvents 1, 2, 5, 6, 9, 14, 21, 29, 32, 43, 50, 56	
20. Free energy difference for mutarotation of <i>N</i> -(α -benzoylbenzylidene)-1-phenylethylamine, ²⁰ 11 solvents 4–6, 8, 9, 14, 18, 30, 40, 50, 61	

^a Solvent numbers correspond to those of Kamlet and Taft.¹

Table 2. Comparison of the applicability of the $\pi^* + d\delta$ and π_n^* terms

System	n	d	R_{KT}	R_n	Remark	
1	50	-0.086	0.982	0.984	Including CS ₂ , d determined by Kamlet and Taft without CS ₂	
	49	-0.086	0.988			
2	15	-0.074	0.989	0.978	d determined by Kamlet and Taft	
3	12	-0.246	0.987	0.988		
4	11	-0.183	0.985	0.992	Besides polarity terms basicity term also used	
5	22	-0.090	0.959	0.966		
6	22	-0.073	0.960	0.975		
7	10	-0.102	0.965	0.988		
8	17	-0.144	0.961	0.980		
9	19	-0.155	0.981	0.988		
10	19	-0.165	0.983	0.980		
11	11	-0.228	0.948	0.939		
12	7	-0.320	0.923	0.962		
13	23	-0.311	0.960	0.950		
14	12	-0.200	0.971	0.939		d determined by Kamlet and Taft, also basicity term used
15	12	-0.200	0.964	0.939		
16	21	-0.20	0.968	0.959		
17	13	-0.221	0.928	0.937	Besides polarity terms Hildebrand term used	
18	13	-0.202	0.911	0.951		
19	12	-0.236	0.942	0.961		
20	11	-0.192	0.891	0.927		
21	14	-0.222	0.971	0.978		
22	18	-0.169	0.929	0.972	Besides polarity terms Hildebrand term used	
23	32	-0.203	0.913	0.934		
24	23	-0.174	0.981	0.990		
25	57	-0.40	0.988	0.985	d determined by Kamlet and Taft; besides polarity terms, also basicity and molar volume terms used	

some spectral properties which do not depend on excitation processes, e.g. e.s.r. hyperfine splitting constants and n.m.r. chemical shifts. Abboud *et al.*⁵ recently performed a comparison of the applicability of their $\pi^* + d\delta$ and our π_n^* for the evaluation of solvent effects on spectral properties and we would like to complete this comparison for chemical reactivity systems.

We carried out a correlation of solvent-induced changes of 25 kinetic and equilibrium parameters with above solvent parameters by equations (1) and (2). The studied properties (Y) as

$$Y = A + B(\pi^* + d\delta) \quad (1)$$

$$Y = A + B\pi_n^* \quad (2)$$

well as the solvents and sources of the data are given in Table 1. The numbering of the solvents is the same as used by Kamlet and Taft.¹

The comparison of the applicability of equations (1) and (2) is carried out by correlation coefficients in Table 2. In Table 2 n , d , and R_{KT} and R_n stand for the number of solvents, Kamlet-Taft polarizability coefficient, and correlation coefficients for correlations carried out by the equations (1) and (2), respectively. In the case of five systems equations (1) and (2) were extended for a basicity term (Kamlet-Taft β constant) (systems 13, 16, 25), Hildebrand's solubility parameter term (systems 20 and 23), and a molar volume term (system 25).

Comparison of the correlation coefficients shows that effectiveness of the both formalisms considered is, in the case of the systems studied, nearly the same regardless of the size of the polarizability parameter d .

References

- 1 M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, **13**, 485.

- 2 R. W. Taft, J. L. M. Abboud, and M. J. Kamlet, *J. Am. Chem. Soc.*, 1981, **103**, 1080.
- 3 V. Bekárek, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1293.
- 4 V. Bekárek, *Collect. Czech. Chem. Commun.*, 1984, **49**, 2332.
- 5 J. L. M. Abboud, R. W. Taft, and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, 1985, 815.
- 6 C. Lassau and J. O. Jungers, *Bull. Soc. Chim. Fr.*, 1968, 2678.
- 7 R. E. Pincock, *J. Am. Chem. Soc.*, 1964, **86**, 1820.
- 8 M. H. Abraham and R. J. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1974, 47.
- 9 J. A. Howard and K. W. Ingold, *Can. J. Chem.*, 1964, **42**, 1044.
- 10 Y. Drougard and D. Decrooq, *Bull. Soc. Chim. Fr.*, 1969, 2972.
- 11 S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, 1961, **83**, 618.
- 12 M. Auriel and E. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 7433.
- 13 M. H. Abraham, *J. Chem. Soc. B*, 1971, 299.
- 14 H. Kwart and P. A. Silver, *J. Org. Chem.*, 1975, **40**, 3019.
- 15 R. G. Makitra and Yu. N. Pirig, *Reakts. Sposobn. Org. Soedin.*, 1978, **15**, 352.
- 16 E. Maccarone and G. Perrini, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1605.
- 17 O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 568.
- 18 E. L. Eliel and O. Hofer, *J. Am. Chem. Soc.*, 1973, **95**, 8041.
- 19 Z. Fried, P. Fiedler, and O. Exner, *Collect. Czech. Chem. Commun.*, 1980, **45**, 1351.
- 20 Carmen Lopez-Mardomingo, R. Pérez-Ossorio, and J. Plumet, *J. Chem. Res. (S)*, 1983, 150.
- 21 M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1343.
- 22 L. Rohrschneider, *Anal. Chem.*, 1973, **45**, 265.
- 23 (a) C. Hansch and A. Leo, 'Substituent Constants for Correlation Analysis in Chemistry and Biology,' Wiley-Interscience, New York, 1979, (b) M. J. Kamlet, M. H. Abraham, R. M. Doherty, and R. W. Taft, *J. Am. Chem. Soc.*, 1984, **106**, 464.

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