Supplementary material

S1 Substituent Constants

Substituent Constants Employed

Substituent	σ_p [a]	σ_m [a]	σ_p^+ [a]	σ_m^0 [b]	σ_I [c]	σ_R^- [c]	σ_R^0 [c]	σ_R^{BA} [c]	σ_R^+ [c]
OMe	−0.27	0.12	−0.78	0.10	0.27	−0.45	−0.45	−0.61	−1.02
Me	−0.17	−0.07	−0.31	−0.06	−0.04	−0.11	−0.11	−0.11	−0.25
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.23	0.37	0.11	0.37	0.46	−0.23	−0.23	−0.23	−0.36
C(O)Me	0.50	0.38	−	0.36	0.28	0.47	0.16	0.16	0.16
CF_3	0.54	0.43	0.61	0.46	0.45	0.17	0.08	0.08	0.08
CN	0.66	0.56	0.66	0.62	0.56	0.33	0.13	0.13	0.13
NO_2	0.78	0.71	0.79	0.71	0.65	0.46	0.15	0.15	0.15
4-OMe-3-Me[d]	−0.34	−	−0.85	−	0.23	−0.56	−0.56	−0.72	−1.13

[a] Values from: C. Hansch, A. Leo and R. W. Taft, *Chem. Rev*., 1991, **91**, 165.

[b] Values from: S. Wold and M. Sjöström, *Chem. Scripta*, 1976, **9**, 200 quoted by S. Wold and M. Sjöström in *Correlation Analysis in Chemistry*, eds. N. B. Chapman and J. Shorter, Plenum Press, New York and London, 1978, p. 25.

[c] Values from: S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Progr. Phys. Org. Chem*., 1973, **10**, 1.

[d] Additivity assumed: 'σ_p' = $\sigma_p^{OMe} + \sigma_m^{Me}$; '$\sigma_p^+$' = $\sigma_p^{+OMe} + \sigma_m^{Me}$; '$\sigma_I$' = $\sigma_I^{OMe} + \sigma_I^{Me}$; '$\sigma_R$' = $\sigma_R^{OMe} - 0.11$ for each σ_R series.

S2 Relative Permittivities

Relative permittivities, ε_r, of binary mixtures of solvents were interpolated from published data fitted by appropriate polynomials. In all cases second order polynomials in φ were satisfactory: $\varepsilon_r = a_0 + a_1\varphi + a_2\varphi^2$ where φ is the fraction of a particular co-solvent in acetone.

Polynomials for interpolation of relative permittivities of binary solvent mixtures at 298.2 K

Entry	*Co-solvent in acetone*	*Fraction type*	*Points fitted*	*Coefficients, a_n, of polynomials in fraction, φ, of co-solvent*			R^2
				a_0	a_1	a_2	
1	Hexane[a]	v/v	11	21.068	−25.867	6.584	0.9998
2	Dimethylformamide[b]	mol. fr.	9	20.428	18.462	−1.232	0.9998
3	Water[c]	w/w	22	20.522	56.697	2.403	0.9998

[a] F. Mato and F. Fernandez-Polanco, *An. Quim*., 1976, **72**, 280.

[b] D. S. Gill and H. Schneider, *Indian J. Chem., Sect. A*, 1980, **19**, 313.

[c] P. S. Albright, *J. Am. Chem. Soc*., 1937, **59**, 2098; A. M. Nilsson, and P. Beronius, *Z. Phys. Chem*., 1972, **79**, 93; K. Singh and P. P. Sinha, *J. Indian Chem. Soc*., 1977, **54**, 975.

Citations *a–c* from the Detherm Database accessed *via* Chemical Data Service, http://cds.dl.ac.uk

Interpolated relative permittivities

Binary Solvent	φ	*Interpolated ε_r*
60% v/v Hexane in acetone	0.6000	7.92
80% v/v DMF in acetone	0.7922[a]	33.60
1% v/v Water in acetone	0.0126[b]	21.24
5% v/v Water in acetone	0.0625[b]	24.08
20% v/v Water in acetone	0.2405[b]	34.30

[a] Calculated as (80×0.944/73.10)/[(80×0.944/73.10) + (20×0.787/58.08)] where 0.944 and 0.787 g cm^{-3} are the respective densities of DMF and acetone at 298 K and 73.10 and 58.08 their respective relative molar masses. (Density of DMF at 298 K given in *CRC Handbook of Chemistry and Physics*, 84th edn. Ed.-in-Ch. D. R. Lide, CRC Press, Boca Raton, FL, 2003, Table **15**-16; density of acetone at 298 K given by G. W. C. Kaye and T. H. Laby in *Tables of Physical and Chemical Constants*, 12th edn., Longmans, London, 1962, p. 119).

[b] Calculated as (v×0.9970)/[v×0.9970 + (100−v)×0.787] where v is 1, 5 or 20 as appropriate and 0.9970 g cm^{-3} is the density of water at 298 K (given in *CRC Handbook of Chemistry and Physics*, 84th edn. Ed.-in-Ch. D. R. Lide, CRC Press, Boca Raton, FL., Table **6**-5).

S3 Evaluation of f_X and f_H for various $\Delta\rho$

Substituent	σ_p	$\Delta\rho = 0.5$		$\Delta\rho = 1.0$		$\Delta\rho = 1.5$		$\Delta\rho = 2.0$	
		f_X[a]	f_H[b]	f_X[a]	f_H[b]	f_X[a]	f_H[b]	f_X[a]	f_H[b]
4-OMe-3-Me	−0.34	−0.38	−0.556	−0.20	−0.428	−0.11	−0.370	−0.07	−0.048
4-OMe	−0.27	−0.35	−0.473	−0.18	−0.341	−0.11	−0.283	−0.07	−0.056
4-Me	−0.17	−0.27	−0.333	−0.15	−0.215	−0.09	−0.167	−0.06	−0.058
4-Cl	0.23	1.63	1.253	0.54	0.318	0.36	0.161	0.28	0.236
4C(O)Me	0.50	−6.25	−3.51	3.20	1.013	1.73	0.308	1.38	0.580
4-CN	0.66	−3.79	−1.77	12.36	2.704	4.13	0.423	3.15	0.700
4-NO_2	0.78	−3.36	−1.41	1170.20	194.537	8.41	0.569	5.99	0.732

		$\Delta\rho = 2.45$		$\Delta\rho = 3.0$		$\Delta\rho = 3.5$		$\Delta\rho = 4.0$	
		f_X[a]	f_H[b]	f_X[a]	f_H[b]	f_X[a]	f_H[b]	f_X[a]	f_H[b]
4-OMe-3-Me	−0.34	−0.05	−0.322	−0.03	−0.310	−0.02	−0.008	−0.01	−0.298
4-OMe	−0.27	−0.05	−0.234	−0.03	−0.221	−0.02	−0.013	−0.02	−0.207
4-Me	−0.17	−0.05	−0.126	−0.04	−0.114	−0.03	−0.021	−0.02	−0.101
4-Cl	0.23	**0.25**	**0.068**	0.22	0.045	0.21	0.135	0.20	0.024
4C(O)Me	0.50	**1.24**	**0.074**	1.17	0.037	1.13	0.151	1.11	0.011
4-CN	0.66	**2.86**	**0.069**	2.71	0.028	2.65	0.079	2.63	0.006
4-NO_2	0.78	**5.40**	**0.066**	5.14	0.023	5.06	0.038	5.02	0.004

[a] Calculated *via* eqn. (12). [b] Calculated *via* eqn. (10).