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Correlation between empirical solvent polarity scales and computed quantities derived from molecular surface electrostatic potentials

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Analysis of five empirical solvent polarity scales E_T^N, π^*, Py, S' and SPP is carried out by correlating them with Π and σ^2_{tot}, two computed quantities derived from molecular surface electrostatic potentials. Our results indicate (i) that the S' scale should be a good global solvent polarity scale, (ii) that it would be inappropriate to use the E_T^N and Py scales to describe non-specific solute–solvent interactions for protic solvents, and (iii) that the π^* and SPP scales are probably contaminated with charge-transfer effects for aromatic and polychlorinated solvents. The differences between our results and those obtained by the correlation of empirical scales with a theoretical thermodynamic analysis result (E_{PNA}) are discussed in the context of intermolecular interactions between the probe solutes and the solvent considered.

Introduction

The pronounced influences that solvents have on most physicochemical properties, *e.g.*, rates and equilibrium positions of chemical reactions, as well as the position and intensity of absorption bands in UV, IR, NMR, and EPR spectroscopy, have prompted extensive studies aimed at predicting solvent properties.[1–5] Generally speaking, solvent properties can be divided into acidity, basicity and polarity; of these solvent polarity has attracted the most attention and is the most difficult to deal with. A variety of empirical scales used to characterize solvent polarity have been developed since the advent of Kirkwood's approaches[6] (that of modeling this type of interaction by reaction field) and several reviews on this subject have been published.[1,2,5,7] Recently, in order to analyze these scales, their correlation with theoretical quantities have been investigated. Catalan[8] correlated a group of five representative scales (E_T^N,[2] π^*,[9] Py,[10] S'[11] and SPP[12]) with E_{PNA}, the energies for the first π–π^* electronic transition of 4-nitroanisole caused by non-specific solvent effects. Their values in individual solvents were evaluated by Matyushov[13] using molecular theories based on long-range solute–solvent interactions; this method was seen as providing a unique means of testing the purity of the description of the non-specific solvent effect. Katritzky[14] used a large number of descriptors programmed in CODESSA to develop correlation for 45 solvent scales (including several polarity ones). Although high quality correlations were obtained, the intrinsic meaning of many descriptors is not readily appreciated. Subsequently, Famini[15] used readily understandable theoretical linear solvation energy relationship (TLSER) descriptors to correlate eight solvent scales (including four polarity/polarizability ones, E_T^N, Y, P and MR). In addition to the above-mentioned theoretical quantities, a set of statistically-based indices has been devised by Murray[16] using molecular electrostatic potential, called general interaction properties function (GIPF) descriptors. These have been proven to be fairly effective for correlating and predicting the physicochemical properties that reflect solvent–solute interactions.[16–23] These computed quantities could also be used to test the empirical solvent polarity scales. In fact, one of them, V_{min}, has even been applied by Catalan to analyze the solvent basicity (SB) scale.[24]

Bearing this in mind, we set out to correlate the five representative empirical solvent polarity scales, E_T^N, π^*, Py, S' and SPP scales with the alternative computed GIPF parameters. To be comparable with Catalan's previous analyses,[8] we selected the same data set as used in his study, excluding iodobenzene for lack of the basis set of iodine, and especially, used two GIPF descriptors with explicit physical meaning, Π and σ^2_{tot}. The former is a measure of charge separation or local polarity, and the latter can be viewed as a measure of electrostatic interaction tendency. Both have been widely and successfully applied to describe the contribution of non-specific solvent–solute interactions.[16–18,23] The purpose of our work is to further (E_{PNA} is at the molecular level, whereas Π and σ^2_{tot} can be viewed at the electronic level), or in another sense, test whether these empirical solvent polarity scales are pure descriptors of non-specific solvent effects, or whether they are contaminated in any way with other specific solvent effects. Despite using the term "solvent polarity", in the light of its IUPAC recommended definition,[25] one need not be restricted to non-specific solute–solvent interactions.

Results and discussion

Table 1 lists a group of 59 solvents, their geometrical structures optimized at HF/6-31G* level by using Gaussian 98w software package.[26] Using these molecular structures, the electrostatic potentials on the isodensity 0.001 au molecular surfaces and subsequently Π and σ^2_{tot}, according to Murray,[16] have been calculated with the grid control option set to "cube = 100". The calculated Π and σ^2_{tot} values, along with the empirical solvent polarity scales E_T^N, π^*, Py, S', and SPP are also listed in Table 1. The correlations between them through linear regression analysis are summarized in Table 2, where n is the number of solvents submitted to the regression, r is the correlation coefficient, sd is the standard deviation, F is the overall statistical significance of the equation, and r_{cc} is the cross correlation for two independent variables. The predicted solvent polarity scales, as well as the residuals, are given in Table 3.

The E_T^N scale

The E_T^N scale is based on the solvatochromic absorption band

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Table 1 Empirical solvent polarity scales E_T^N, π^*, Py, S' and SPP and computed Π, σ^2_{tot} values in the different solvents

	Solvent	E_T^N	π^*	Py	S'	SPP	Π/eV	σ^2_{tot}/eV^2
1	*n*-Pentane	0.009	−0.08		0.57	0.507	0.096	0.006
2	*n*-Hexane	0.009	−0.08	0.58	0.68	0.519	0.096	0.006
3	*n*-Heptane	0.012	−0.02		0.79	0.526	0.095	0.006
4	*n*-Octane	0.012	0.01			0.542	0.093	0.006
5	*n*-Nonane	0.009			0.90	0.552	0.092	0.006
6	*n*-Decane	0.009	0.03		0.90	0.562	0.091	0.006
7	*n*-Undecane					0.563	0.091	0.006
8	*n*-Dodecane	0.012		0.59		0.571	0.089	0.006
9	Cyclohexane	0.006	0.00	0.58	1.11	0.557	0.086	0.006
10	Benzene	0.111	0.59	1.05	1.73	0.667	0.359	0.092
11	Toluene	0.099	0.54	1.04	1.66	0.655	0.320	0.091
12	*m*-Xylene		0.47	1.01		0.616	0.296	0.093
13	*p*-Xylene	0.074	0.43	0.95		0.617	0.290	0.101
14	Fluorobenzene	0.194	0.62			0.769	0.400	0.106
15	Chlorobenzene	0.188	0.71	1.08	2.07	0.824	0.421	0.094
16	Bromobenzene	0.182	0.79	1.07		0.824	0.408	0.092
17	Nitrobenzene	0.324	1.01		2.61	1.009	0.583	0.398
18	Benzonitrile	0.333	0.90		2.63	0.960	0.584	0.447
19	Pyridine	0.302	0.87	1.42	2.44	0.922	0.467	0.250
20	Tetrachloromethane	0.052	0.28		1.49	0.632	0.147	0.034
21	Trichloromethane	0.259	0.58	1.25	1.74	0.786	0.352	0.229
22	Dichloromethane	0.309	0.82	1.35	2.08	0.876	0.519	0.223
23	1,1-Dichloroethane	0.269					0.464	0.136
24	1,2-Dichloroethane	0.327	0.81	1.46		0.890	0.468	0.110
25	1,1,2,2-Tetrachloroethane	0.269	0.95			0.887	0.383	0.191
26	Acetone	0.355	0.71	1.64	2.58	0.881	0.508	0.419
27	Butan-2-one	0.327	0.67	1.58	2.51	0.881	0.440	0.443
28	Pentan-2-one	0.321		1.50		0.883	0.398	0.425
29	Hexan-2-one	0.290				0.884	0.370	0.455
30	Cyclohexanone	0.281	0.76	1.47	2.35	0.874	0.362	0.425
31	Ethyl formate	0.315	0.61			0.812	0.475	0.325
32	Methyl acetate	0.287	0.60	1.48	2.35	0.785	0.484	0.336
33	Ethyl acetate	0.228	0.55	1.37	2.15	0.795	0.405	0.338
34	Propyl acetate	0.210				0.782	0.391	0.337
35	Butyl acetate	0.241	0.46	1.35		0.784	0.341	0.362
36	Acetonitrile	0.460	0.75	1.79	3.00	0.895	0.869	0.302
37	Propionitrile	0.401	0.71	1.68	2.80	0.875	0.715	0.322
38	Nitromethane	0.481	0.85		3.07	0.907	0.957	0.251
39	Nitroethane	0.398	0.82		2.78	0.894	0.753	0.234
40	Triethylamine	0.043	0.14		1.43	0.617	0.174	0.101
41	Diethyl ether	0.117	0.27	1.02	1.73	0.694	0.236	0.181
42	Tetrahydrofuran	0.207	0.58	1.35	2.08	0.838	0.292	0.307
43	Hexamethylphosphoramide	0.315	0.87		2.52	0.932	0.448	0.660
44	*N*,*N*-Dimethylformamide	0.404	0.88	1.81	2.80	0.954	0.581	0.639
45	*N*,*N*-Dimethylacetamide	0.401	0.88	1.79	2.70	0.970	0.557	0.611
46	*N*-Methylpyrrolidone	0.355	0.92		2.62	0.970	0.518	0.588
47	Propylene carbonate	0.491	0.83		3.13	0.930	0.809	0.431
48	Dimethyl sulfoxide	0.444	1.00	1.95	3.00	1.000	0.710	0.799
49	Methanol	0.762	0.60	1.35	2.87	0.857	0.589	0.500
50	Ethanol	0.654	0.54	1.18	2.80	0.853	0.411	0.412
51	Propan-1-ol	0.617	0.52	1.09	2.68	0.847	0.372	0.426
52	Butan-1-ol	0.602	0.47	1.06	2.74	0.837	0.324	0.423
53	Pentan-1-ol	0.568	0.44	1.02		0.817	0.295	0.368
54	Hexan-1-ol	0.559	0.41			0.810	0.253	0.321
55	Propan-2-ol	0.546	0.48	1.09	2.66	0.848	0.392	0.423
56	Isobutanol	0.552		1.02		0.832	0.336	0.310
57	Butan-2-ol	0.506		1.03		0.842	0.335	0.323
58	*tert*-Butyl alcohol	0.389	0.41		2.46	0.829	0.337	0.417
59	Water	1.000	1.09	1.87	3.53	0.962	1.135	0.627

of a pyridinium *N*-phenolbetaine and is defined by the transition energy of the intramolecular charge-transfer band of this dye.[2] As can be seen in Table 2, eqn. (1) gives a correlation with the computed Π and σ^2_{tot} values for 57 solvents. Although the correlation relationship of eqn. (1) is statistically significant, it is less than satisfactory because of the relatively low correlation coefficient and high standard deviation. Contrasting the literature values of E_T^N with the ones predicted by eqn. (1), large discrepancies can be seen for the protic solvents **49**–**59** (see Table 1). Excluding these eleven protic solvents, a subsequent regression analysis yields eqn. (1a), an excellent correlation with a correlation coefficient of 0.973 and a standard deviation of 0.0351. This indicates that the E_T^N scale is not an appropriate descriptor of non-specific solvent effects for protic solvents. In Catalan's previous study,[8] an acceptable correlation ($r = 0.837$ and sd = 0.06) for 23 nonprotic solvents was obtained; including protic solvents worsens the correlation. Here, our conclusion is consistent with that made by Catalan,[8] and both are supported by the fact that the E_T^N scale for the alcoholic solvents measures primarily their hydrogen-bond donor (HBD) acidity.[27] Similar conclusions have been drawn by Katritzky[14b] and Famini,[15] who correlated this scale with computed descriptors and found that $q+$ (maximum partial charge for a H atom) had a significant contribution. However, for which kinds of solvent are the E_T^N values contaminated with specific solute–solvent interactions is still not obvious from their studies.

Table 2 Statistics for the correlation equations between the five empirical solvent polarity scales and the computed Π, σ^2_{tot} values for the solvents given in Table 1

	Correlation equation[a]	n	r	sd	F	r_{cc}	Eqn.
E_T^N	$E_T^N = 0.3719\Pi\ (3.71) + 0.5252\sigma^2_{tot}\ (4.66) + 0.0019$	57	0.790	0.1327	44.804	0.607	(1)
	$E_T^N = 0.5028\Pi\ (16.47) + 0.2320\sigma^2_{tot}\ (7.15) - 0.0310$	46	0.973	0.0351	381.970	0.622	(1a)
π^*	$\pi^* = 0.8762\Pi\ (6.67) + 0.3925\sigma^2_{tot}\ (2.64) + 0.0934$	50	0.841	0.1677	56.997	0.602	(2)
	$\pi^* = 0.6639\Pi\ (9.05) + 0.8488\sigma^2_{tot}\ (9.19) - 0.0481$	35	0.964	0.0891	213.340	0.610	(2a)
	$\pi^* - 0.4\delta = 0.6927\Pi\ (7.63) + 0.8137\sigma^2_{tot}\ (7.95) - 0.0513$	50	0.931	0.1158	152.400	0.602	(2b)
Py	$\text{Py} = 1.0436\Pi\ (6.04) + 0.7059\sigma^2_{tot}\ (3.88) + 0.6154$	36	0.895	0.1633	66.168	0.624	(3)
	$\text{Py} = 1.1313\Pi\ (8.82) + 0.9660\sigma^2_{tot}\ (8.37) + 0.5791$	27	0.972	0.0923	206.130	0.641	(3a)
S'	$S' = 1.7467\Pi\ (8.22) + 1.6325\sigma^2_{tot}\ (6.55) + 0.9357$	40	0.942	0.2588	147.000	0.628	(4)
SPP	$\text{SPP} = 0.2754\Pi\ (5.81) + 0.3952\sigma^2_{tot}\ (7.43) + 0.5700$	58	0.901	0.0625	119.050	0.630	(5)
	$\text{SPP} = 0.1953\Pi\ (5.63) + 0.4929\sigma^2_{tot}\ (11.69) + 0.5540$	43	0.958	0.0430	223.750	0.656	(5a)

[a] The values in parentheses are the *t*-score.

The π^* scale

π^* is an empirical solvent polarity scale proposed by Kamlet and Taft, who introduced it on the basis of averaging the solvatochromic behavior of a large number of probe solutes, rather than a single one.[9] Our correlation equation of the π^* values of 50 solvents with Π and σ^2_{tot} is shown in eqn. (2). The quality of this equation is not as good as one might expect it to be; solvents poorly predicted by eqn. (2) are the aromatic solvents **10**–**19**, and the polychlorinated solvents **20**, **21**, **22**, **24** and **25**. If these 15 solvents are omitted, a significantly improved correlation relationship [eqn. (2a)] with a correlation coefficient of 0.964 and a standard deviation of 0.0891 is obtained. This implies that it is not appropriate to use the π^* scale to describe the non-specific solute–solvent interactions of aromatic and polychlorinated solvents; most probably it is contaminated with solute–solvent charge-transfer (CT) effects. This analysis is supported by the fact that π^* is usually used in combination with a correction term $d\delta$,[3,28–30] where $\delta = 1.0$ for aromatic solvents and 0.5 for polychlorinated solvents, and d depends on the property to which ($\pi^* + d\delta$) is being related. In Brinck's previous work,[31] a good correlation ($r = 0.97$) between ($\pi^* - 0.4\delta$) and a single computed quantity, Π, has been found for 25 solvents. Here, we obtain a similar relationship [eqn. (2b)] between ($\pi^* - 0.4\delta$) and the two computed quantities, Π and σ^2_{tot}, for our data set of 50 solvents; the correlation coefficient is 0.931 and the standard deviation is 0.1158 (if σ^2_{tot} is excluded, the correlation coefficient is only 0.829). Again, our analysis is in good agreement with that of Catalan's, which shows that the inclusion of aromatic and polychlorinated solvents would make the correlation worse. It should be mentioned that the π^* scale of Kamlet and Taft is actually a combination of polarity and polarizability effects. The two GIPF descriptors, Π and σ^2_{tot}, are excellent at correlating polarity effects, but are unable to account for polarizability effects in terms of their intrinsic meaning.

The Py scale

Similarly, testing the Py scale, which is based on the ratio between the intensities of components (0,0) I_1 and (0,2) I_3 of the fluorescence of pyrene in various solvents,[10] we obtain the correlation eqns. (3) and (3a) (in the latter, the nine protic solvents **49**–**53**, **55**–**57** and **59** are excluded). The significant improvement in correlation quality of eqn. (3a) relative to eqn. (3) reveals, as Catalan has pointed out, the presence of specific solute–solvent interactions in the Py values of these protic solvents. This has been substantiated by Lianos,[32] who found from infrared studies that pyrene forms weakly-bound 1 : 1 molecular complexes with simple alcohols in dilute solution in CCl_4. The aromatic solvents are also considered as outliers in Catalan's study,[8] but further improvement is not found in the correlation by removing these solvents in the present work.

The S' scale

Correlation of the S' scale[11] with the computed descriptors Π and σ^2_{tot} for all available solvents in Table 1 leads to eqn. (4). The correlation relationship is satisfactory, the correlation coefficient is 0.942 and the standard deviation is 0.2588; no statistical improvement of the correlation quality is obtained by removing any one kind of solvent from the data set. The excellence of eqn. (4) demonstrates that S' should be a good global solvent polarity scale, whereas, in Catalan's previous study, the protic solvents were pointed out to exhibit strong specific solvent effects. According to Drago[11] (proponent of the S' scale), the S' scale was a parameter not directly measured, but established by using statistical methods, and specific interactions between the probe solute and the solvent were precluded before the data of previous polarity scales were used to construct them. More recently, Drago and his group[33] corroborated further the reasonability of their unified non-specific solvent polarity scale (S') by developing a successful correlation using two theoretical descriptors, the dipolar density and the reciprocal of the HOMO–LUMO energy gap. Thus, it seems that our analysis is more reasonable.

The SPP scale

SPP is a solvent polarity scale advocated by Catalan himself, based on the solvatochromic behaviors of 2-(*N*,*N*-dimethylamino)-7-nitrofluorene and its homomorph, 2-fluoro-7-nitrofluorene.[12] Correlation of this scale with Π and σ^2_{tot} for 58 solvents results in eqn. (5). In comparison to eqns. eqn (1)–(3) (all available data included), eqn. (5) shows a larger correlation coefficient and a smaller standard deviation. This result indicates that the SPP scale has the greatest applicability among the four solvent polarity scales (E_T^N, π^*, Py, and SPP) based directly on solvatochromic comparison methods. In spite of the advantages of the SPP scale over the others, eqn. (5) is not an excellent correlation in itself (the correlation coefficient is only 0.901); the differences between the literature SPP values and the ones predicted by eqn. (5) for aromatic and polychlorinated solvents are still rather large. With these solvents excluded, an improved correlation [eqn. (5a)] (correlation coefficient 0.958) is obtained. This implies that the SPP scale probably involves a component of CT interactions for aromatic and polychlorinated solvents. This differs from Catalan's analysis, where the SPP scale is believed to be a global descriptor of non-specific solvent effects for all kinds of solvents. Indeed, upon examining the molecular structures of the probe solutes used to construct

Table 3 Predicted solvent polarity scales E_T^N, π^*, Py, S' and SPP

	E_T^N		π^*		Py		S'		SPP	
	(Calcd) Eqn. (1a)	Residual	(Calcd) Eqn. (2a)	Residual	(Calcd) Eqn. (3a)	Residual	(Calcd) Eqn. (4)	Residual	(Calcd) Eqn. (5a)	Residual
1	0.019	−0.010	0.02	−0.10			1.11	−0.54	0.576	−0.069
2	0.019	−0.010	0.02	−0.10	0.69	−0.11	1.11	−0.43	0.576	−0.057
3	0.018	−0.006	0.02	−0.04			1.11	−0.32	0.575	−0.049
4	0.017	−0.005	0.02	−0.01					0.575	−0.033
5	0.017	−0.008					1.11	−0.21	0.575	−0.023
6	0.016	−0.007	0.02	0.01			1.10	−0.20	0.575	−0.013
7									0.575	−0.012
8	0.015	−0.003			0.69	−0.10			0.574	−0.003
9	0.014	−0.008	0.01	−0.01	0.68	−0.10	1.10	0.01	0.574	−0.017
10	0.171	−0.060			1.07	−0.02	1.71	0.02		
11	0.151	−0.052			1.03	0.01	1.64	0.02		
12					1.00	0.01				
13	0.138	−0.064			1.00	−0.05				
14	0.195	0.001								
15	0.203	−0.015			1.15	−0.07	1.82	0.25		
16	0.196	−0.014			1.13	−0.06				
17	0.354	−0.030					2.60	0.01		
18	0.366	−0.033					2.69	−0.06		
19	0.262	0.040			1.35	0.07	2.16	0.28		
20	0.051	0.001					1.25	0.24		
21	0.199	0.060			1.20	0.05	1.92	−0.18		
22	0.282	0.027			1.38	−0.03	2.21	−0.13		
23	0.234	0.035								
24	0.230	0.097			1.21	0.25				
25	0.206	0.063								
26	0.322	0.033	0.64	0.07	1.56	0.08	2.51	0.07	0.860	0.021
27	0.293	0.034	0.62	0.05	1.50	0.08	2.43	0.08	0.858	0.023
28	0.268	0.053			1.44	0.06			0.841	0.042
29	0.261	0.029							0.851	0.033
30	0.250	0.031	0.55	0.21	1.40	0.07	2.26	0.09	0.834	0.040
31	0.283	0.032	0.54	0.07					0.807	0.005
32	0.290	−0.003	0.56	0.04	1.45	0.03	2.33	0.02	0.814	−0.029
33	0.251	−0.023	0.51	0.04	1.36	0.01	2.19	−0.04	0.800	−0.005
34	0.244	−0.034							0.796	−0.014
35	0.224	0.017	0.49	−0.03	1.31	0.04			0.799	−0.015
36	0.476	−0.016	0.79	−0.04	1.85	−0.06	2.95	0.05	0.873	0.022
37	0.403	−0.002	0.70	0.01	1.70	−0.02	2.71	0.09	0.852	0.023
38	0.508	−0.028	0.80	0.05			3.02	0.05	0.865	0.042
39	0.402	−0.004	0.65	0.17			2.63	0.15	0.816	0.078
40	0.080	−0.037	0.15	−0.01			1.40	0.03	0.638	−0.021
41	0.130	−0.013	0.26	0.01	1.02	0.00	1.64	0.09	0.689	0.005
42	0.187	0.020	0.41	0.17	1.21	0.14	1.95	0.13	0.762	0.076
43	0.347	−0.032	0.81	0.06			2.80	−0.28	0.967	−0.035
44	0.409	−0.005	0.88	0	1.85	−0.04	2.99	−0.19	0.983	−0.029
45	0.391	0.010	0.84	0.04	1.80	−0.01	2.91	−0.21	0.964	0.006
46	0.366	−0.011	0.79	0.13			2.80	−0.18	0.945	0.025
47	0.476	0.015	0.85	−0.02			3.05	0.08	0.925	0.005
48	0.511	−0.067	1.10	−0.10	2.15	−0.20	3.48	−0.48	1.087	−0.087
49			0.77	−0.17			2.78	0.09	0.916	−0.059
50			0.57	−0.03			2.33	0.47	0.837	0.016
51			0.56	−0.04			2.28	0.40	0.837	0.010
52			0.53	−0.06			2.19	0.55	0.826	0.011
53			0.46	−0.02					0.793	0.024
54			0.39	0.02					0.762	0.048
55			0.57	−0.09			2.31	0.35	0.839	0.009
56									0.772	0.060
57									0.779	0.063
58			0.53	−0.12			2.20	0.26	0.825	0.004
59			1.24	−0.15			3.94	−0.41	1.085	−0.123

these empirical scales, we find that similarities exist between the probe solutes for the SPP scale and those for the π^* scale, *e.g.*, almost all of them are composed of an aromatic system bearing both an electron-withdrawing and an electron-releasing substituent group. Hence, one might expect similar solute–solvent interactions (CT interactions) to be involved, which to some degree supports our analysis.

It is necessary to point out that all saturated hydrocarbon solvents are excluded from Catalan's study because of their low values on all the empirical scales, but we imposed no such limit on our analysis. Also, it should be noted is that Π and σ^2_{tot} are introduced at the same time and their coefficients are positive in all of our correlations; they have middle but tolerable cross correlation (the correlation coefficients range from 0.602 to 0.656). Therefore, increasing the values of Π and (or) σ^2_{tot} of a molecule would favor the polarity of the corresponding solvent. Although the other computed quantities derived from molecular surface electrostatic potentials, such as the "balance" parameter ν, have also been used successfully to describe non-specific solute–solvent interactions,[16,34] however, either they are statistically insignificant or they represent opposite contributions to different empirical solvent polarity scales in this work.

Conclusion

The above analyses suggest (i) that the S' scale should be a good global solvent polarity scale, (ii) that it would be inappropriate to use the E_T^N and Py scales to describe the non-specific solvent effects of protic solvents, and (iii) that the π^* and SPP scales should not be used to describe the solvent polarity of aromatic and polychlorinated solvents. It should be mentioned that the five solvent polarity scales discussed here are not of equal origin and quality. The scales E_T^N, Py and SPP are directly measured and the π^* values are averaged results calculated from experimentally observed values for a series of probe solutes. The S' values are based on a manifold of other solvent-dependent processes, and they depend on the proper subjective selection of the appropriate solvent-dependent processes used to calculate them. Katritzky[14b] has developed similar correlations to each of the five solvent polarity scales, and Famini[15] one (E_T^N), using different methods. However, direct comparison of their methods with the present treatments is difficult because of the different data sets used to correlate them.

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