On the E_T (30), π^*, P_y, S', and SPP Empirical Scales as Descriptors of Nonspecific Solvent Effects

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The solvent where some physicochemical processes take place is a noninert medium that plays a prominent role in solution chemistry. For this reason, chemists are especially interested in anything that may expand available knowledge on solvent properties. Broadly speaking, the solvent effect can be divided into *specific* and *nonspecific solute−solvent interactions.*[1]

According to Drago,[2] *specific interactions* can be described in terms of localized donor−acceptor interactions involving specific orbitals by using electrostatic (E) and covalent parameters (C). On the other hand, Kamlet and Taft[3] used acid−base hydrogen-bonding interactions represented by their parameters α and β to describe this type of interaction.

In *nonspecific* interactions, the solvent is assumed to act as a dielectric continuum. The early attempts of Kirkwoord[4] and Onsager[5] at modeling this type of interaction were followed by empirical approaches aimed at characterizing solvent polarity and polarizability via an appropriate microscopic quantity.[1] A variety of empirical scales including $E_T(30)$,[6] π^*,[7] P_y,[8] S',[9] and SPP[10] have since then been developed; their success in accounting for medium effects on reactivity and a host of physicochemical properties is well-documented and widely perceived.[1,11−15]

An alternative approach to dealing with nonspecific solvent effects based on ideas derived from liquid state theories has emerged in the past few years. One prominent example is the recent paper by Matyushov et al.,[16] who carried out a theoretical thermodynamic analysis of solvent-induced shifts in the UV−vis spectra for chromophores; specifically, they studied *p*-nitroanisole (pNA), using molecular theories based on long-range solute−solvent interactions due to inductive, dispersive, and dipole−dipole forces. Table 1 gives the data evaluated by these authors for a wide range of solvents, as well as

Table 1. E_{pNA}, $E_T^N(30)$, π^*, P_y, S', **and SPP Values in the Different Solvents Examined**

solvent	E_{pNA}[a]	$E_T^N(30)$[c]	π^* [d]	P_y [e]	S' [f]	SPP[h]
n-pentane	99.23	(0.009)	−0.08		0.57[g]	0.507
n-hexane	99.62	(0.009)	−0.08	0.58	0.68[g]	0.519
n- heptane	99.38	(0.012)	−0.02		0.79[g]	0.526
n-octane	99.08	(0.012)	0.01			0.542
n-nonane	98.87	(0.009)			0.90[g]	0.552
n-decane	99.70	(0.009)	0.03		0.90[g]	0.562
n-undecane	98.42					0.563
n-dodecane	98.36	(0.012)		0.59		0.571
cyclohexane	99.00	(0.006)	0	0.58	1.11	0.557
benzene	98.76	0.111	0.59	1.05	1.73	0.667
toluene	98.43	0.099	0.54	1.04	1.66	0.655
m-xylene	98.30		0.47	1.01		0.616
p-xylene	98.32	0.074	0.43	0.95		0.617
fluorobenzene	96.74	0.194	0.62			0.769
chlorobenzene	96.16	0.188	0.71	1.08	2.07	0.824
bromobenzene	95.86	0.182	0.79	1.07		0.824
iodobenzene	95.69	0.170	0.81			0.835
nitrobenzene	92.22	0.324	1.01		2.61	1.009
benzonitrile	92.09	0.333	0.90		2.63	0.960
pyridine	94.29	0.302	0.87	1.42	2.44	0.922
Cl_4C	99.28	0.052	0.28		1.49	0.632
$CHCl_3$	98.02	0.259	0.58	1.25	1.74	0.786
CH_2Cl_2	96.34	0.309	0.82	1.35	2.08	0.876
1,1-DCE	94.58	0.269				
1,2-DCE	95.68	0.327	0.81	1.46		0.890
1,1,2,2-TCE	96.37	0.269	0.95			0.887
acetone	94.74	0.355	0.71	1.64	2.58	0.881
2-butanone	95.21	0.327	0.67	1.58	2.51	0.881
2-pentanone	93.78	0.321		1.50		0.883
2-hexanone	93.98	0.290				0.884
cyclohexanone	93.97	0.281	0.76	1.47	2.35	0.874
HCOOEt	95.16	0.315	0.61			0.812
MeOAc	96.54	0.287	0.60	1.48	2.35	0.785
EtOAc	96.96	0.228	0.55	1.37	2.15	0.795
PrOAc	95.75	0.210				0.782
BuOAc	95.90	0.241	0.46	1.35		0.784
acetonitrile	94.90	0.460	0.75	1.79	3.00	0.895
propionitrile	94.61	0.401	0.71	1.68	2.80	0.875
nitromethane	93.77	0.481	0.85		3.07	0.907
nitroethane	93.84	0.398	0.82		2.78	0.894
Et_3N	98.69	(0.043)	0.14		1.43	0.617
diethyl ether	98.71	0.117	0.27	1.02	1.73	0.694
THF	96.01	0.207	0.58	1.35	2.08	0.838
HMPA	94.32	0.315	0.87		2.52	0.932
DMF	93.10	0.404	0.88	1.81	2.80	0.954
DMA	92.83	0.401	0.88	1.79	2.70	0.970
NMP	92.54	0.355	0.92		2.62	0.970
PC	92.82	0.491	0.83		3.13	0.930
DMSO	92.63	0.444	1	1.95	3.00	1
methanol	95.79[b]	0.762	0.60	1.35	2.87	0.857
ethanol	96.12[b]	0.654	0.54	1.18	2.80	0.853
1-propanol	96.33[b]	0.617	0.52	1.09	2.68	0.847
1-butanol	96.51[b]	0.602	0.47	1.06	2.74	0.837
1-pentanol	96.61[b]	0.568	0.44	1.02		0.817
1-hexanol	96.69[b]	0.559	0.41			0.810
2-propanol	96.65[b]	0.546	0.48	1.09	2.66	0.848
i-butanol	96.74[b]	0.552		1.02		0.832
2-butanol	96.57[b]	0.506		1.03		0.842
tert-butyl alcohol	97.16[b]	0.389	0.41		2.46	0.829
H_2O	91.77[b]	1.00	1.09	1.87	3.53	0.962

[a] E_{pNA} values are taken from ref 16. [b] D. V. Matyushov, private communication. [c] E_TN (30) values are taken from ref 1; the E_TN (30)-values in parentheses are secundary values, determined by means of more lipophilic penta-*tert*-butylsbstituted betaine day. [d] π^* values are taken from refs 18 and 19. [e] Py values are taken from ref 8. [f] S′ values are taken from refs 9 and 20. [g] These S′ values are taken from ref 26. [h] SPP values are either taken from refs 10 and 21, or they been evaluated in this work(see Table 2).

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Table 2. Wavenumbers of the Maximum of the First Absoption Band of the Probe DMANF ($\tilde{\nu}_{\mathrm{DMANF}}$) and Its Homomorph FNF ($\tilde{\nu}_{\mathrm{FNF}}$), Differences ($\Delta\tilde{\nu}$) between $\tilde{\nu}_{\mathrm{DMANF}}$ and $\tilde{\nu}_{\mathrm{FN}}$ for Four New Solvents, and Respective SPP Values

solvent	$\tilde{\nu}_{\mathrm{DMANF}}$ (cm^{-1})	$\tilde{\nu}_{\mathrm{FNF}}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	SPP[a]
ethyl formate	23918	30330	6412	0.812
iodobenzene	22858	29320	6462	0.835
2-pentanone	23596	30159	6563	0.883
2-hexanone	23598	30164	6566	0.884

[a] SPP = [$\Delta\tilde{\nu}$(solvent) − $\Delta\tilde{\nu}$(gas)]/[$\Delta\tilde{\nu}$(DMSO) − $\Delta\tilde{\nu}$(gas)] = ($\Delta\tilde{\nu}$ − 4692)/2119.

those corresponding to some hydroxyl solvents (private communication).

The shifts in the first electron transition for *p*-nitroanisole caused by the nonspecific solvent effects evaluated by Matyushov et al. provide a unique means for determining whether the more relevant solvent polarity[17] scales [E_T(30), π^*, P_y, S' and SPP] are pure descriptors of nonspecific solvent effects or if they are contaminated in any way with specific effects arising from the donor or acceptor nature of the solvents. In this work, the above-mentioned scales were tested against the energy for the first π,π^* electron transition of *p*-nitroanisole, E_{pNA} (in kcal·mol^{-1}), which was evaluated by Matyushov et al. in 58 different solvents, in terms of long-range solute–solvent interactions solely. The SPP values for four new solvents (Table 2) that were studied by Matyushov et al. (viz., 2-pentanone, 2-hexanone, iodobenzene, and ethyl formate) are also reported. The solvent polarities on the different empirical scales studied are also given in Table 1. The following symbols are used to represent the different types of solvents in the figures below: nonprotic (●), aromatic (■), polychlorinated (▲), hydroxylic (×) and saturated hydrocarbons (■).

The Dimroth–Reichardt's E_T(30) Scale. The E_T(30) scale[6] is based on the extremely solvatochromic character of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridiniumyl)phenoxide (A) and is defined by the position (in kcal·mol^{-1}) of the maximum of the first absorption band for this dye, which has marked intramolecular charge-transfer connotations and gives rise to an excited electronic state that is much less dipolar than the ground state. This results in strong hypsochromism with increased solvent polarity. Normalized E_T^N(30) values range from 0.000 for tetramethylsilane to 1.000 for water.[1]

Figure 1 compares E_T^N(30) and E_{PNA} values in various solvents. As can be seen, the two parameters are acceptably correlated for nonprotic polar solvents only (n = 23, r^2 = 0.700, SD = 0.06). Polychlorinated and aromatic solvents can be included in the previous correlation without making it worse. The strong basic character of probe A is known to cause marked shifts in hydrogen-bond donor (HBD) solvents,[1,10,13,15,16,22] thus revealing that parameter E_T^N(30) includes specific solvent acidity effects.

The Kamlet–Abboud–Taft π^* Scale. The π^* scale was established from the average solvatochromic behavior of a number of indicator solutes (standards pNA and B–G in the Chart 1 and about 40 auxilliary compounds) rather than from spectral shifts for individual compounds.[7] In this way, its proponents believed that any specific solvents would be excluded. π^* values range from −0.08 for *n*-hexane to 1.09 for water.[18]

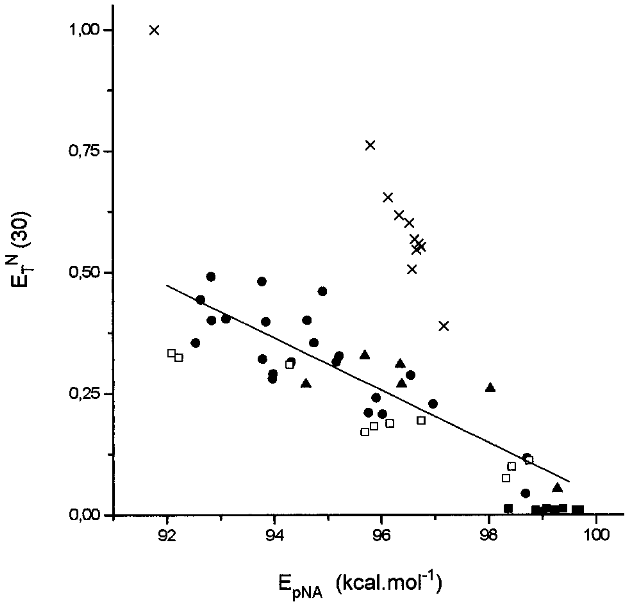

Figure 1. Comparative analysis of E_T^N(30) and E_{pNA} for the studied solvents: ●, nonprotic; □, aromatic; ▲, polychlorinated; ×, hydroxylic; and ■, saturated hydrocarbons.

Chart 1

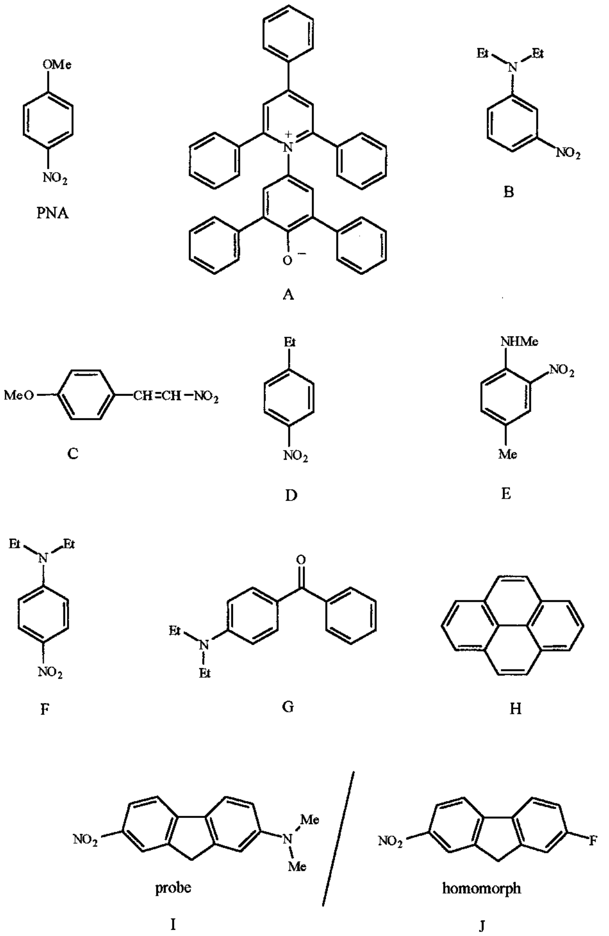

Figure 2 compares π^* and E_{pNA} values in various solvents. As can be seen, the two are acceptably well-

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[17] The word *polarity* is used in this paper as referring only to nonspecific solute–solvent interactions. The *solvation power* is assigned with the total solvation capability of solvent.

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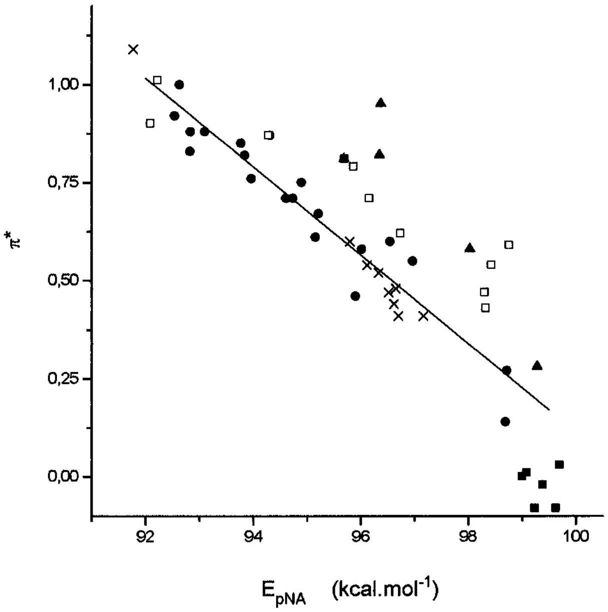

Figure 2. Comparative analysis of π^* and E_{pNA} for the studied solvents: ●, nonprotic; □, aromatic; ▲, polychlorinated; ×, hydroxylic; and ■, saturated hydrocarbons.

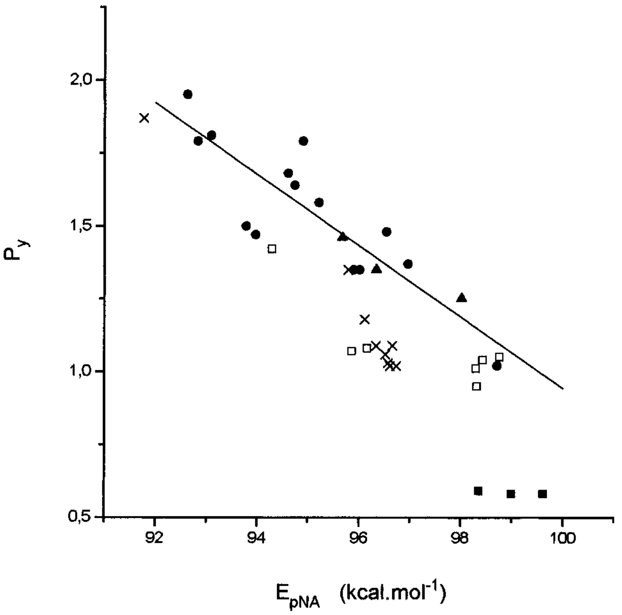

Figure 3. Comparative analysis of P_y and E_{pNA} for the studied solvents: ●, nonprotic; □, aromatic; ▲, polychlorinated; ×, hydroxylic; and ■, saturated hydrocarbons.

correlated for nonprotic polar solvents ($n = 20$, $r^2 = 0.906$, SD = 0.07). HBD solvents can be included in the previous correlation without making it worse. However, polychlorinated and aromatic solvents—strongly dipolar compounds such as nitrobenzene and benzonitrile excluded—exhibit a behavior that reflects contamination with CT effects.[16,23,24]

The Dong–Winnick P_y Scale. The P_y scale[8] is based on the ratio between the intensities of components (0,0) I_1 and (0,2) I_3 of the fluorescence of pyrene (H) in various solvents. P_y values (I_1/I_3) range from 0.58 for *n*-hexane to 1.95 for DMSO.

Figure 3 compares P_y and E_{PNA} values in various solvents. As can be seen, correlation between the two is acceptable for nonprotic polar solvents only ($n = 14$, $r^2 = 0.745$, SD = 0.13). Polychlorinated solvents can be included in the previous correlation without making it worse. Protic and aromatic solvents exhibit strong shifts that reflect the presence of specific interactions in their P_y values.

***The Drago S′* Scale.** The “unified solvent polarity scale”, or S' scale, was established by Drago[9] using a least-squares minimization program.[25] Measured physicochemical properties (χ) of systems for which specific interactions with the solvent are precluded are fitted to the following equation:

$\Delta\chi = \mathrm{PS}' + \mathrm{W}$ where S' is a solvent polarity parameter, P is a solute parameter that represents the susceptibility of the solute probe to polarity, and W is a nonzero intercept at $S' = 0$. The scale is based on carefully selected data used to construct the previous polarity scales corresponding to solvents that exhibit no specific interactions with the probes used to construct them. S' values range from 0.57 for *n*-pentane[26] to 3.53 for water.[20] S' values cannot be measured directly; rather, they are estimated by statistical analysis of experimental data.

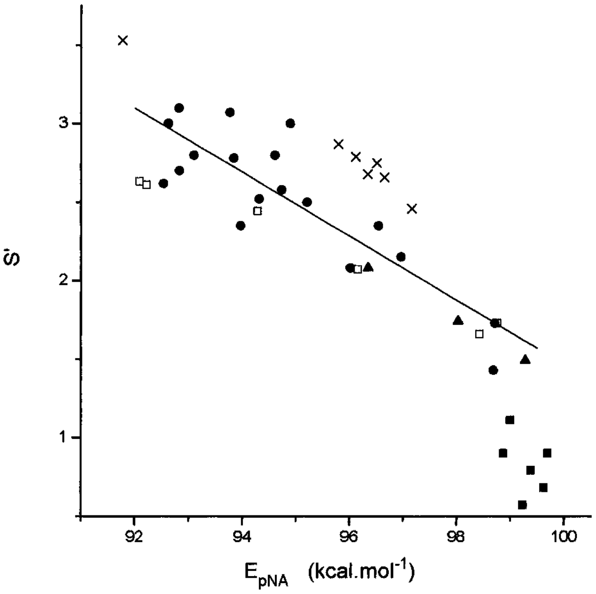

Figure 4. Comparative analysis of S' and E_{pNA} for the studied solvents: ●, nonprotic; □, aromatic; ▲, polychlorinated; ×, hydroxylic; and ■ saturated hydrocarbons.

Figure 4 compares S' and E_{pNA} values in various solvents. As can be seen, the two are acceptably correlated for nonprotic polar solvents only ($n = 18$, $r^2 = 0.734$, SD = 0.24). Polychlorinated and aromatic solvents can be included in the previous correlation without making it worse. By contrast, protic solvents exhibit strong shifts that reflect specific effects on S'.

The SPP Scale. The solvent polarity/polarizability (SPP) scale[10] is based on the solvatochromism of the probe 2-(*N*,*N*-dimethylamino)-7-nitrofluorene (I) and its

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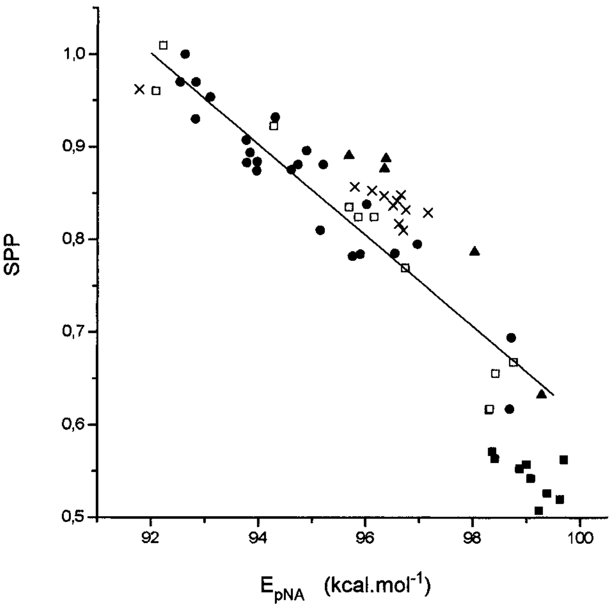

Figure 5. Comparative analysis of SPP and E_{pNA} for the studied solvents: ●, nonprotic; □, aromatic; ▲, polychlorinated; ×, hydroxylic; and ■, saturated hydrocarbons.

homomorph 2-fluoro-7-nitrofluorene (J) and has been extended to 145 solvents and the gas phase.[10,21,23,27,28] This scales encompasses values between 1 for DMSO and 0 for the gas phase.

Figure 5 compares SPP and E_{pNA} values in various solvents. As can be seen, the two are well-correlated for nonprotic polar solvents ($n = 23$, $r^2 = 0.895$, SD = 0.03). Polychlorinated, aromatic, and protic solvents can be included in the previous correlation without making it worse.

In light of the previous results, the following cautions should be exercised in rationalizing solute properties on the basis of the different solvent polarity scales: (a) If the substance concerned has a basic character, including protic and nonprotic solvents simultaneously in the $E_T(30)$, P_y, and S' scales should be avoided because they are contaminated with specific HBD solvent effects (see Figures 1, 3, and 4). (b) If the substance in question can readily form CT complexes via its π electron cloud, aromatic and nonaromatic solvents should not be included simultaneously in the π^* and P_y scales because they are significantly contaminated with specific interactions of the CT type (see Figures 2 and 3).

We should note that saturated hydrocarbons as solvents exhibit lower polarity on all the empirical scales than what one would assign them on the basis of long-range interactions with pNA (see Figures 1−5). Table 3 offers a global analysis of the behavior of the solvents remaining after saturated hydrocarbons are excluded (i.e., nonprotic polar, protic, polychlorinated, and aromatic solvents) on the different scales against the corresponding values for E_{pNA}. As can be seen, the SPP scale is the most consistent (viz., that exhibiting the highest r^2 and lowest sd). Because this scale provides a correct description of interactions throughout the range of solvents considered, including SPP data in saturated hydrocarbons in the fit does not detract from its goodness ($n = 55$, $r^2 = 0.839$, SD = 0.058).

Table 3. Coefficients of the Equation $y = y_0 + aE_{pNA}$ for all Solvents (Saturated Hydrocarbons Excluded)

y	y_0	x	n	r^2	SD
$E_T^N(30)^a$	4.34 ± 1.23	−0.042 ± 0.013	50	0.18	0.17
π^*	9.30 ± 0.84	−0.090 ± 0.009	45	0.71	0.12
P_y	14.84 ± 1.50	−0.141 ± 0.016	33	0.72	0.16
S'	19.92 ± 2.36	−0.183 ± 0.025	34	0.62	0.31
SPP	5.22 ± 0.30	−0.046 ± 0.003	50	0.81	0.04

[a] If the hydroxylic solvents were excluded, $n = 39$, $r^2 = 0.69$, and SD = 0.07.

In conclusion, from the analyses made in this work, it follows that the SPP scale is an appropriate solvent polarity scale. This is thus a resounding success of the chemical intuition behind the probe/homomorph model used by this scale to evaluate general solvent effects. Also some cautions are proposed that should be exercised in understanding solute properties on the basis of contaminations of specific effects. These specific effects are present in some of the most frequently used solvent polarity scales.

Experimental Section

Absoption spectra of DMANF and FNF were recorded on a Shimadzu 2100 UV−vis spectrophotometer. The monochromator was calibrated with respect to wavelength by using the 486.0- and 656.1-nm lines from a deuterium lamp and holmium oxide and didymium filters. All spectra measurements were made at 25 °C by using a matched pair of quartz cells of 1-cm path length. A cell of 0.05-mm path length was used in those cases where the solvent cutoff was troublesome.

The maximum wavelength of the first UV−vis absoption band of DMANF and FNF was determined from the derivative function. The results given are the arithmetic means of at least eight spectra whose maxima were shifted by less than 0.2 nm. The tabulated wavenumbers are direct conversions of the λ_{max} values.

The DMANF and FNF samples used were of the same purity as that employed in ref 10. All the solvents studied (iodobenzene, 2-pentanone, 2-hexanone, and ethyl formate) were obtained from Fluka in the highest available purity and used as suplied.

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