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On the π^* Solvent Scale

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The π^* scale, developed by Kamlet, Abboud, and Taft,[1] has been widely used as a solvent polarity[2] scale. The scale is based on the solvatochromic behavior of a number of indicator solutes (7 standards and about 40 auxiliary substances) rather than UV/vis spectral shifts for individual compounds. In this way, its proponents believed that any specific effects on estimated π^* values would be excluded.

The π^* scale, which measures a blend of dipolarity and polarizability solute/solvent interactions, has undergone two major modifications since it was proposed. In 1983, the proponents themselves[3] introduced the $d\delta$ term in order to correct for the contribution of polarizability according to various solvent families; thus, the parameter π^* was renamed $\pi^* - d\delta$ (where δ is 0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1 for aromatic solvents, the d value depending on the property described on the basis of the π^* scale). The other modification was introduced by Abe[4] in 1990 to circumvent the shortcoming that the π^* scale did not correlate to solvent spectral shifts for nonpolar and less polarized solutes; he developed the "supplementary π^*_2 scale". More recently, a new scale called the "π^*_{azo}" scale was reported by Buncel and Rajagopal.[5]

According to Drago[6] the fact that over 20 solvent polarity scales[7−9] exist and that the values they provide are inconsistent in many instances demonstrates that the parameters involved do not reflect nonspecific effects alone, but also specific effects of variable nature that are dependent on the type of probe used to develop each scale. Recently, Drago[6] analyzed selected data among those used to build the scales and proposed a new scale called "unified solvent polarity scale", which encompasses 31 nonprotic solvents and is allegedly contaminated with no specific effects. He subsequently used the new scale to examine the performance of the π^* scale and found the π^* values for some of the solvents studied to be contaminated with specific effects.[10] Recently, our group[11] introduced another pure polarity scale called the solvent dipolarity−polarizability (SPP) scale, based on the solvatochromism of the probe 2-(N,N-dimethylamino)-7-nitrofluorene (DMANF) and its homomorph 2-fluoro-7-nitrofluorene (FNF); we reported scale values for 100 solvents and found some π^* values to include contributions other than that of the solvent polarity. The SPP scale[11] has proved a powerful tool for rationalizing spectroscopic (UV-vis, IR, fluorescence, NMR), thermodynamic (equilibrium constants, differential solvation energies), and kinetic data.

Table 1. Wavenumbers of the Maximum of the First Absorption Band of the Probe DMANF($\tilde{\nu}_{DMANF}$) and Its Homomorph FNF($\tilde{\nu}_{FNF}$), Differences $\Delta\tilde{\nu}$ between $\tilde{\nu}_{DMANF}$ and $\tilde{\nu}_{FNF}$ for Three New Solvents, and the Respective SPP Values

solvent	$\tilde{\nu}_{DMANF}$/ cm^{-1}	$\tilde{\nu}_{FNF}$/ cm^{-1}	$\Delta\tilde{\nu}$/ cm^{-1}	SPP[a]
N,N-dimethylaniline	23295	29708[b]	6413	0.812
dibenzyl ether	23117	29544	6427	0.819
1,1,1-Trichloroethane	23817	30311	6494	0.850

[a] SPP = [$\Delta\tilde{\nu}$(solvent) − $\Delta\tilde{\nu}$(gas)]/[$\Delta\tilde{\nu}$(DMSO) − $\Delta\tilde{\nu}$(gas)], see text. [b] Calculated from $\tilde{\nu}_{FNF} = (0.494 \pm 0.016)\tilde{\nu}_{DMANF} + 18.21$; see ref 11.

Two new contributions recently reported may foster use of the π^* scale. Effenberger *et al.*[12] found the position solvatochromism of 5-(dimethylamino)-5′-nitro-2,2′-bithiophene ($Me_2NT_2NO_2$) to allow a reliable, straightforward, rapid estimation of π^* values by using a single indicator dye. The new probe meets the essential requirements for establishing solvent parameters, *viz.* good spectral sensitivity, absorption in the visible wavelength range where all solvents are transparent, a high intensity of the CT transition—not masked by any other electronic transitions—and good solubility in all organic solvents. On the other hand, Laurence *et al.*[13] used the position solvatochromism of 4-nitroanisole to redefine and critically examine the π^* scale for 229 solvents including nonhydrogen bond donors, weak hydrogen bond donors, and the gas phase. The changes in the π^* values for some of the solvents studied were quite significant—some were up to 0.15 units smaller relative to the original π^* scale.

In the light of the SPP scale, we analyze in this note whether the results reported by the previous two groups are contaminated with effects other than those inherent in nonspecific contributions from the solvent. We also report SPP values for three new solvents studied by these groups (Table 1).

Table 1 lists the $\tilde{\nu}_{DMANF}$ and $\tilde{\nu}_{FNF}$ values, the differences between both ($\Delta\tilde{\nu}$), and the corresponding SPP value for each solvent tested, calculated from the equation reported in ref 11:

$$\mathrm{SPP}_{\mathrm{solv}} = (\Delta\tilde{\nu} - 4692)/2119$$

Table 2 lists the SPP and π^* values as well as the wavenumbers of the maximum of the first absorption band of the chromophore ($Me_2NT_2NO_2$) in the solvents studied.

As can be seen from Figure 1, the solvatochromic data for $Me_2NT_2NO_2$ reported by Effenberger *et al.*[12,15] are poorly correlated with the SPP values for the solvents used. If the data for formamide, chloroform, and the five

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(1) Kamlet, J. M.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027−6038.

(2) In this paper solute−solvent interactions are referred to as *specific* when they are due to hydrogen bond or charge transfer complexation and as *nonspecific* when only the remaining van der Waals contributions are considered. The word *polarity* is used in this paper as referring only to nonspecific interactions. For a detailed description about the matter, see ref 7.

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Table 2. SPP Values, π^* Values, and Wavenumbers of the First UV/vis Absorption Maximum of the Chromophore $Me_2NT_2NO_2$ in the Different Solvents Examined

no.	solvent	SPP[a]	π^*[b]	$\tilde{\nu}$[c](kK)	no.	solvent	SPP[a]	π^*[b]	$\tilde{\nu}$[c](kK)
0	gas	0	−1.23		39	1-butanol	0.837	–	19.357
1	perfluorohexane	0.214	−0.48		40	1-chlorobutane	0.837	0.40	
2	2-methylbutane	0.479	−0.15		41	tetrahydrofurane	0.838	0.55	19.208
3	*n*-pentane	0.507	−0.15	21.46	42	pyrrole	0.838	1.00	
4	*n*-hexane	0.519	−0.11	21.45	43	2-propanol	0.848	–	19.38
5	*n*-heptane	0.526	−0.06		44	1,1,1-trichloroethane	0.850	0.44	
6	cyclohexane	0.557	0	21.186	45	ethanol	0.853	–	19.238
7	methylcyclohexane	0.563	–	21.19	46	methanol	0.857	–	19.055
8	*n*-dodecane	0.571	−0.01		47	(trifluoromethyl)benzene	0.857	0.50	
9	mesitylene	0.576	0.45	19.928	48	cyclohexanone	0.874	0.71	
10	*cis*-decalin	0.601	0.09		49	propiononitrile	0.875	0.64	
11	triethylamine	0.617	0.09	20.699	50	dichloromethane	0.876	0.73	18.688
12	*p*-xylene	0.617	0.45	19.833	51	2-butanone	0.881	0.60	
13	1-methylpiperidine	0.622	0.20		52	acetone	0.881	0.62	18.907
14	tri-*n*-butylamine	0.624	0.06		53	3-pentanone	0.883	0.57	
15	hexafluorobenzene	0.629	0.27		54	1,1,2,2-tetrachloroethane	0.887	0.88	
16	tetrachloromethane	0.632	0.21	20.433	55	trimethyl phosphate	0.889	0.73	
17	*o*-xylene	0.641	–	19.68	56	1,2-dichloroethane	0.890	0.73	18.636
18	di-*n*-butyl ether	0.652	0.18	20.35	57	acetonitrile	0.895	0.66	18.73
19	toluene	0.655	0.49	19.694	58	chloroacetonitrile	0.896	0.93	
20	benzene	0.667	0.55	19.60	59	valeronitrile	0.900	0.63	
21	diethyl ether	0.694	0.24	20.161	60	triethyl phosphate	0.908	0.69	
22	1,4-dioxane	0.701	0.49	19.732	61	1,2-dichlorobenzene	0.911	0.77	
23	dimethyl carbonate	0.711	0.47		62	butyronitrile	0.915	0.63	
24	fluorobenzene	0.769	0.59		63	pyridine	0.922	0.87	
25	tetrahydropyran	0.778	0.48		64	propylene carbonate	0.930	0.83	
26	*n*-butyl acetate	0.784	–	19.566	65	*N,N*-diethylacetamide	0.930	0.85	
27	methyl acetate	0.785	0.49		66	hexamethylphosphoramide	0.932	0.87	
28	chloroform	0.786	0.69	18.857	67	acetophenone	0.932	0.81	
29	ethyl acetate	0.795	0.45	19.489	68	*N,N*-diethylformamide	0.939	0.80	
30	methyl formate	0.804	0.55		69	1,1,3,3-tetramethylurea	0.952	0.79	
31	*N,N*-dimethylaniline	0.812	0.76		70	*N,N*-dimethylformamide	0.954	0.88	18.216
32	dibenzyl ether	0.819	0.80		71	benzonitrile	0.960	0.88	
33	anisole	0.823	0.70		72	*N,N*-dimethylacetamide	0.970	0.85	
34	chlorobenzene	0.824	0.68	18.936	73	γ-butyrolactone	0.987	0.85	
35	bromobenzene	0.824	0.84		74	dimethyl sulfoxide	1	1	17.756
36	2-methyl-2-propanol	0.824	–	19.49	75	sulfolane	1.003	0.90	
37	formamide	0.833	–	17.325	76	nitrobenzene	1.009	0.86	17.992
38	ethyl benzoate	0.835	0.68						

[a] SPP values are either taken from refs 11 and 14, or they have been evaluated in this work. [b] π^* values are taken from ref 13. [c] Wavenumbers of the first absorption maximum of $Me_2NT_2NO_2$ are taken from refs 12 and 15.

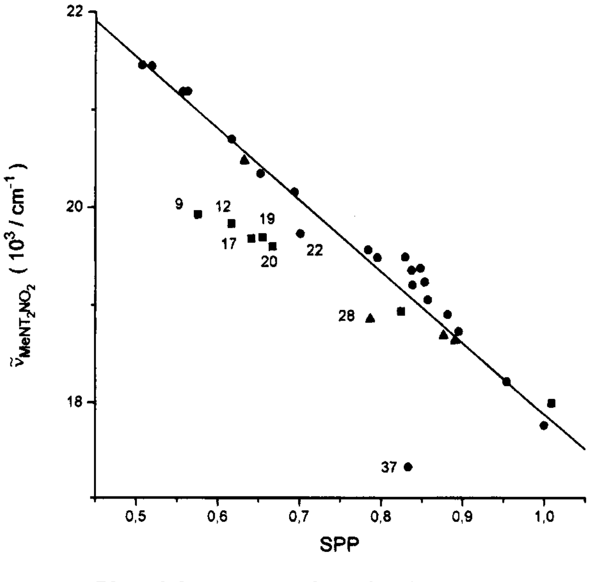

Figure 1. Plot of the wavenumbers for the maximum of the first UV/vis absorption band of $Me_2NT_2NO_2$ in various solvents against the SPP value for the solvent, listed in Table 2. (■) Aromatic solvents. (▲) Polychlorinated solvents. (●) Miscellaneous solvents.

least polar benzene derivatives studied are excluded, the fit is dramatically improved ($n = 25$, $r = 0.985$, SD = 0.170 kK). The HBD-acidity of formamide and chloroform cannot account for the divergent behavior as both fit the distribution of solvents of similar acidity (*e.g.* alcohols) quite well. Also, the deviations of the four low-polarity aromatics excluded suggest that their interactions with such a highly dipolar chromophore as $Me_2NT_2NO_2$ ($\mu = 7.9$ and 21.9 D for the ground and excited state, respectively[16]) are controlled by specific interactions between their π clouds.

On the basis of Figure 2, there is a good linear correlation between the new π^* values and the SPP values for 70% of the solvents examined. Also, the π^* values for the scarcely polar aromatics are clearly contaminated with specific effects, with the notable exception of hexafluorobenzene, which conforms to the above-mentioned linear behavior. Introduction of the $d\delta$ polarizability correction factor is unwarranted since the compound families do not lie in parallel lines[3]—nor do they when comparing parameter $E_T(30)$ with SPP values.[11]

One possible explanation for the special π^* values for the aromatic solvents is that the solvatochromic behavior of the dipolar aromatic solvents is dictated by the probe dipolarity, whereas that of the nondipolar aromatic solvents is determined by specific interactions involving their π clouds. This may account for the differential

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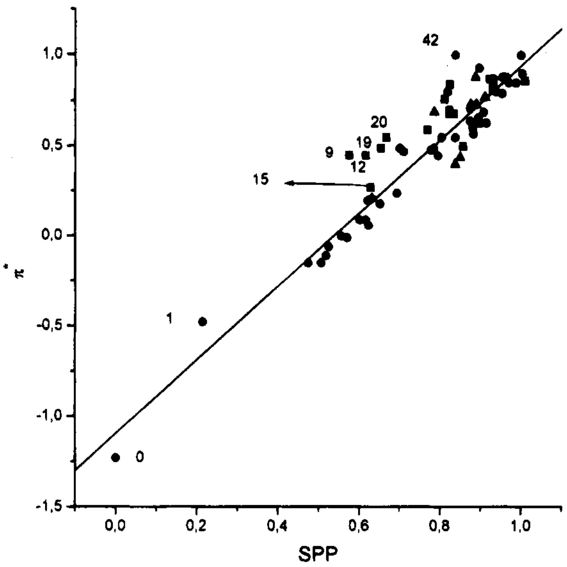

Figure 2. Comparison of the π^* values reported by Laurence *et al.*[12] and the SPP values for the solvents listed in Table 2. (■) Aromatic solvents. (▲) Polychlorinated solvents. (●) Miscellaneous solvents.

solvatochromic behavior of two aromatic solvents with zero dipole moment, *viz.* benzene and hexafluorobenzene; while the former, with a more polarizable π cloud (IP = 9.20 eV) is one of the most deviant from the linear trend, the latter, with a less polarizable cloud (IP = 9.90 eV), conforms to it.

Among the solvents which deviate from the linear behavior shown in Figure 2, pyrrole warrants a special note. On the basis of data reported by Laurence *et al.*,[13] this compound is one of the most polar within the π^* scale (it has a π^* value of 1, identical with that for DMSO). The SPP value for pyrrole is 0.837, based on which it is much less polar than DMSO and comparable to 1-chlorobutane (see Table 2), which seems to be more logical.

The results allow one to conclude that, while the use of both $Me_2NT_2NO_2$[12] and 4-nitroanisole[13] as new solvatochromic probes improves previous methods for determination of solvent π^* values,[2] they are inadvisable inasmuch as they provide contaminated polarity values. Also, introduction of the $d\delta$ correction[3] is unwarranted.

Experimental Section

Absorption 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 measurement were made at 25 °C by using a matched pair of quartz cells of 1 cm pathlength. A cell of 0.05 mm pathlength was used in those cases where the solvent cut-off was troublesome.

The maximum wavelength of the first UV/vis absorption 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 11. All the solvents studied (*N,N*-dimethylaniline, 1,1,1-trichloroethane, and dibenzyl ether) were obtained from Aldrich in the highest available purity and used as supplied.

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