

Linear Solvation Energy Relationships. 12. The $d\delta$ Term in the Solvatochromic Equations^{1,2}

R. W. Taft,* Jose-Luis M. Abboud, and Mortimer J. Kamlet*

Contribution from the Department of Chemistry, University of California, Irvine, California 92717, Universite Cadi Iyad, Marrakech, Morocco, and Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910. Received July 28, 1980

Abstract: The solvatochromic equation, $XYZ = XYZ_0 + s(\pi^* + d\delta)$ is used to correlate nonhydrogen bonding solvent effects on a number of chemical properties. It is shown that $d = 0$ for two $p \rightarrow \pi^*$ electronic spectral transitions of uncharged indicators and that d is finite and negative in sign for the electronic spectral transition energy of a betaine indicator, a ^{19}F NMR shift, a nitrogen hyperfine splitting constant in an ESR spectrum, an infrared $\Delta\nu_{\text{P=O}}$ spectral shift (in solvent relative to gas phase), and ν_{max} in a fluorescence spectrum. It is suggested that $d = 0$ for $p \rightarrow \pi^*$ spectral transitions is a limiting condition (i.e., d is seldom, if ever, positive). The empirically derived solvatochromic parameters are related to more fundamental properties of the solvents.

In earlier papers of this series¹ we used the solvatochromic comparison method² to formulate three scales of intrinsic solvent properties. A π^* scale of solvent polarity-polarizabilities provides a measure of the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect.³⁻⁵ For most non-halogenated aliphatic solvents (specifically excluding dioxan and hexamethylphosphoramide), π^* values are very nearly proportional to molecular dipole moments.⁶ An α scale of solvent hydrogen bond donor acidities describes the solvent's ability to donate a proton in an intermolecular hydrogen bond,⁷⁻⁹ and a β scale of hydrogen bond acceptor basicities is an index of the solvent's ability to accept a proton (donate an electron pair) in a hydrogen bond.¹⁰⁻¹³

Our experience has been that where hydrogen-bonding effects are excluded, as when neither solvents nor solutes are hydrogen bond donors, solvent effects depend only on the π^* scale and solvatochromic equations can take either of two forms.² For $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic spectral transitions of uncharged molecules with all solvents considered together and for other properties if families of solvents with similar polarizability characteristics are treated separately (e.g., only nonchlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents),⁶ the form of the equation is

$$XYZ = XYZ_0 + s\pi^* \quad (1)$$

For the other properties, if all solvents need to be considered together, the equation becomes

$$XYZ = XYZ_0 + s(\pi^* + d\delta) \quad (2)$$

where δ , a polarizability correction term, is 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.¹⁴ The XYZ term in eq 1 and 2 may be a position or intensity of maximal absorption in a UV, IR, NMR, or ESR spectrum, an NMR coupling constant, a free energy or heat of solution or of transfer between solvents, or the logarithm of a rate or equilibrium constant or of a fluorescence lifetime.

We shall refer to the two types of correlational experience described above as (a) " π^* solvatochromic behavior" and (b) " $\pi^* + d\delta$ behavior". In the case of a, a single linear regression equation with π^* (eq 1) describes the effects of all nonhydrogen-bonding solvents on XYZ ; in b, incorporation of a $d\delta$ term (eq 2) or separate linear regression equations with π^* for the solvent families with differing polarizability characteristics are required to describe the solvatochromic effects.

It was demonstrated in part 6 of this series⁵ that the " $\pi^* + d\delta$ " pattern of correlational behavior was followed by solvent effects on $\log k$ for the Menschutkin reaction of tri-*n*-propylamine with methyl iodide ($d = -0.09$),¹⁴ $\log k$ for the pyridine-catalyzed ionic

decomposition of *tert*-butyl peroxyformate ($d = -0.07$), and ΔG of transfer between solvents of the $\text{Et}_4\text{N}^+\text{I}^-$ ion pair ($d = -0.17$). In this paper we report the patterns of solvatochromic behavior for several additional types of XYZ 's, including one fluorescence and three absorption spectra, a ^{19}F NMR shift, a $\text{P}=\text{O}$ band frequency in an IR spectrum, and an ESR nitrogen hyperfine splitting constant. The data used in the correlations, the majority of which were obtained from the literature, are assembled in Table I.

Brooker's Merocyanine. Two indicators which have served as the basis for earlier "solvent polarity" scales¹⁵ provide excellent examples of the contrasting patterns of solvatochromic behavior. Brooker and co-workers¹⁶ have based their χ_R scale on E_T values of the lowest energy band in the UV-visible spectrum of the merocyanine 1 [E_T (in kcal/mol) = $2.86 \nu_{\text{max}}$ (in $\times 10^3 \text{ cm}^{-1}$)]. This electronic transition derives from an extended conjugated system, with a p-electron donor amine nitrogen at one terminus

(1) Part 20 in the Solvatochromic Comparison Method series. See ref 3-13 for previous papers.

(2) Although the equations have been extended to cover many nonspectroscopic properties, we find it convenient to continue to refer to the method as the solvatochromic comparison method, the equations as the solvatochromic equations, the π^* , α , β , and δ terms as the solvatochromic parameters, and the s , a , b , and d terms as the solvatochromic coefficients.

(3) M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

(4) M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 337 (1979).

(5) M. J. Kamlet, T. N. Hall, J. Boykin, and R. W. Taft, *J. Org. Chem.*, **44**, 2599 (1979).

(6) J. L. Abboud, M. J. Kamlet, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 8327 (1977).

(7) R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976).

(8) M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 349 (1979).

(9) R. W. Taft and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, 1723 (1979).

(10) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

(11) T. Yokoyama, R. W. Taft, and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 3233 (1976).

(12) M. J. Kamlet, J. L. Abboud, M. E. Jones, and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 342 (1979).

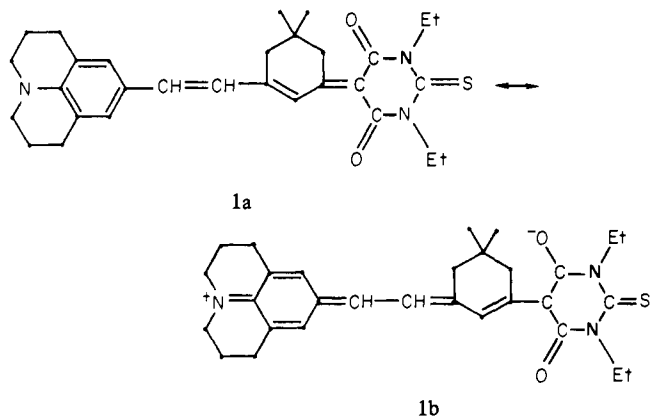
(13) M. J. Kamlet, A. Solomonovici, and R. W. Taft, *J. Am. Chem. Soc.*, **101**, 3734 (1979).

(14) The d term is estimated through the equation $d = 2\Delta XYZ/[s(a) + s(ar)]$, where ΔXYZ is the difference between values calculated through the aliphatic and aromatic solvent regression equations at $\pi^* = 0.7$ and $s(a)$ and $s(ar)$ are the slopes of those regression equations.

(15) We have shown in earlier papers^{3,10} that when protic solvents are included in the correlations, the χ_R and $E_T(30)$ indexes, often represented as solvent polarity scales, are in fact combined measures of solvent polarity and solvent hydrogen bond donor acidity.

(16) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965).

* Address correspondence as follows: R.W.T., University of California; M.J.K., White Oak Laboratory.



of the chromophore and two equivalent electron acceptor carboxamide oxygens at the other termini. The ground state more closely resembles canonical resonance structure **1a**, and the electronic excited state is more like **1b**. Characteristically of most $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of uncharged molecules, electron migration in the electronic excitation is in the direction of and very nearly coincident with the axis of the molecule's ground-state dipole. Since increased charge is generated in the electronic excitation, higher solvent polarities lead to lower transition energies, and the solvatochromic shifts are toward longer wavelengths.

$E_T(1)$ values have been reported in 30 nonhydrogen-bonding solvents for which π^* values are known. An $E_T(1)$ vs. π^* plot of the results is shown in Figure 1, where it may be seen that the data points for the three families of solvents are very nearly colinear.

Least-squares correlation equations are as follows: (a) for 16 nonchlorinated aliphatic solvents, ex dioxan (an obviously out-of-line point)¹⁷

$$E_T(1) = 50.6 - 8.07\pi^* \text{ kcal/mol} \quad (3a)$$

with r (the correlation coefficient) = 0.981 and σ (the standard deviation) = 0.56 kcal/mol; (b) for 29 solvents of all types, ex dioxan

$$E_T(1) = 50.8 - 8.03\pi^* \text{ kcal/mol} \quad (3b)$$

$$r = 0.977 \quad \sigma = 0.53 \text{ kcal/mol}$$

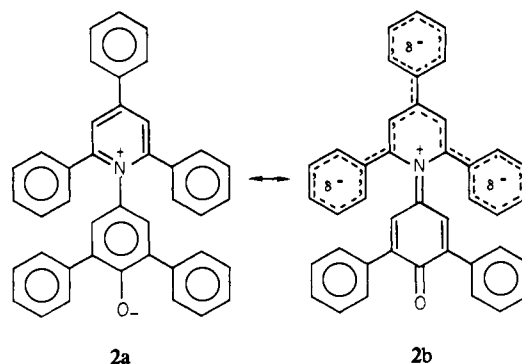
If the result for dioxan is included, r becomes 0.966 and $\sigma = 0.063$ kcal/mol.

The similar s and XYZ_0 values (slopes and intercepts) in eq 3a and 3b and the insignificant increase in the goodness of the statistical fit for the aliphatic solvent results compared with the "all solvent" results represent characteristic " π^* solvatochromic behavior".

Similar " π^* behavior" had been shown for 47 $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions reported earlier.³ Of the r values for the "all data" correlations, 19 were >0.99 , 21 were between 0.98 and 0.99, five were between 0.97 and 0.98, and two were between 0.95 and 0.97. The 47 indicators had in common that solvatochromic shifts were toward the red with increasing solvent polarity (negative s values). Indeed, there now seems enough evidence in this regard to suggest that UV-visible absorption spectral bands which show bathochromic shifts with increasing solvent polarity will most likely follow the " π^* pattern of behavior".

Dimroth and Reichardt's Betaine. In marked contrast to the above, typical " $\pi^* + d\delta$ behavior" is shown by 4-(2,4,6-tri-

phenylpyridinium) 2,6-diphenylphenoxide (**2**), the indicator used



by Dimroth and Reichardt¹⁸ as the basis for their " $E_T(30)$ " scale of solvent polarity.¹⁵ The "solvatochromiebande" for this indicator involves an electronic spectral transition from a ground state which is more like canonical structure **2a** to an excited state more like **2b**. Since there is charge delocalization in the electronic excitation, more polar solvents stabilize the ground state relative to the excited state and the solvent shift with increasing π^* is hypsochromic.

$E_T(2)$ values have been reported for 49 nonhydrogen bonding solvents for which π^* values are known (Table I). The results are plotted in Figure 2a, where it is readily seen that the data points representing the different solvent families cluster around three distinct regression lines.

The three regression lines are described by the following correlation equations: (a) for 26 nonchlorinated aliphatic solvents

$$E_T(2) = 31.1 + 13.5\pi^* \text{ kcal/mol} \quad (4a)$$

with $r = 0.955$ and $\sigma = 1.24$ kcal/mol [if the results for dioxan (solvent **9**), hexamethylphosphoramide (**26**), and acetic anhydride (**34**) are excluded,¹⁷ r becomes 0.972 and $\sigma = 1.01$]; (b) for six polychloroaliphatic solvents

$$E_T(2) = 27.1 + 17.9\pi^* \text{ kcal/mol} \quad (4b)$$

$$r = 0.995 \quad \sigma = 0.46 \text{ kcal/mol}$$

(c) for 17 aromatic solvents

$$E_T(2) = 25.3 + 16.9\pi^* \text{ kcal/mol} \quad (4c)$$

$$r = 0.967 \quad \sigma = 0.86 \text{ kcal/mol}$$

From eq 4a and 4c, the d value in eq 2 is calculated to be -0.24 ,¹⁴ and the "all solvent" correlation equation with $(\pi^* - 0.24\delta)$ becomes

$$E_T(2) = 30.5 + 14.5(\pi^* - 0.24\delta) \text{ kcal/mol} \quad (4d)$$

$$r = 0.959 \quad \sigma = 1.12 \text{ kcal/mol}$$

If results for **9**, **26**, and **34** are excluded, r becomes 0.969 and $\sigma = 0.98$. For comparison with the above, the "all solvent" correlation coefficient between $E_T(2)$ and π^* according to eq 1 is 0.891 and $\sigma = 1.8$ kcal/mol, i.e., significantly poorer statistical correlation when the three families of solvents are considered together. A plot of $E_T(2)$ vs. $(\pi^* - 0.24\delta)$ is shown in Figure 2b.

Our experience has been that " $\pi^* + d\delta$ " type behavior, similar to that of **2**, is shown by all UV-visible spectral bands which are shifted hypsochromically on going to more polar solvents. Indeed, we know of no examples to the contrary. With **1** and **2** as examples of the contrasting patterns of solvatochromic behavior where XYZ in eq 1 and 2 is E_T or ν_{\max} , we shall now consider how other XYZ 's vary with solvent π^* values.

¹⁹F NMR Spectra of 4-Nitrosofluorobenzene. ¹⁹F NMR shifts for $p\text{-F}-\text{C}_6\text{H}_4-\text{N}=\text{O}$ (**3**) relative to internal $\text{C}_6\text{H}_5\text{F}$ have been

(17) We have mentioned that dioxan (**9**) and hexamethylphosphoramide (**26**) were specifically excluded from the select set of aliphatic solvents for which $\pi^* = K\mu$.^{6,24} Our experience has been that these are the solvents which are most apt to be bad actors in solvatochromic comparison studies. Thus, it has been noted in the text that **9** is out-of-line in Figures 1, 2, and 6. In addition, it is the farthest out-of-line solvent in Figures 3 and 5. It may be that different indicators induce different chair/boat ratios for the dioxan molecules in their cybotactic environments (solvent shells). A further contributing factor may be that small amounts of hydroxylic impurities in dioxan can have pronounced solvatochromic effects with HBA base indicators like those considered here.

(18) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **18**, 98 (1979); K. Dimroth, C. Reichardt, T. Seipmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963); C. Reichardt, *ibid.*, **752**, 64 (1971).

(19) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

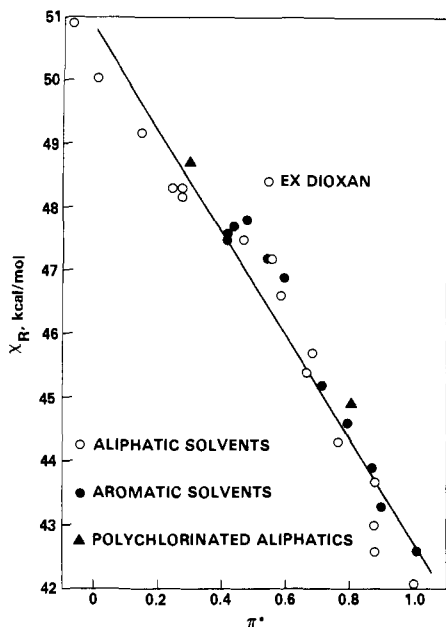


Figure 1. $\chi_R = E_T(1)$ plotted against solvent π^* values.

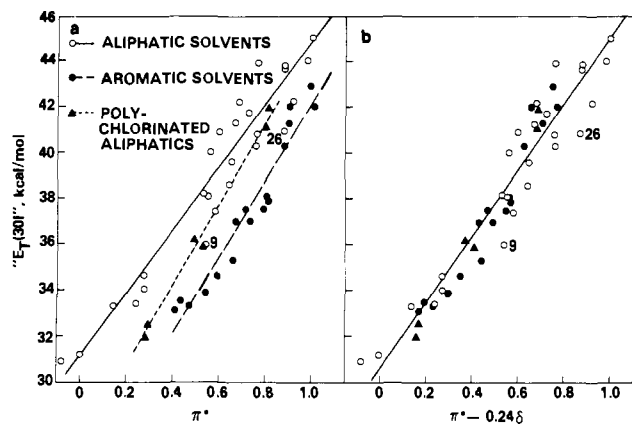


Figure 2. " $E_T(30)$ " = $E_T(2)$ plotted (a) against π^* and (b) against $(\pi^* - 0.24\delta)$.

determined in 28 solvents for which π^* values are known. Several of the \int_H^{p-NO} results in Table I have been changed somewhat from earlier published values on the basis of more recent experimental information which allowed better extrapolations to infinite dilution (especially in the less polar solvents, where 3 tends to self-associate). The table also includes some previously unpublished results.

A plot of $\int_H^{p-NO}(3)$ vs. π^* is shown in Figure 3a. It is seen that data points representing the nonchlorinated aliphatic and aromatic families of solvents clearly conform to separate regression lines. The least-squares correlation equations are as follows: (a) for 12 nonchlorinated aliphatic solvents

$$\int_H^{p-NO}(3) = 10.50 + 2.70\pi^* \text{ ppm} \quad (5a)$$

$$r = 0.987 \quad \sigma = 0.16 \text{ ppm}$$

(b) for 13 aromatic solvents

$$\int_H^{p-NO}(3) = 9.52 + 3.36\pi^* \text{ ppm} \quad (5b)$$

$$r = 0.945 \quad \sigma = 0.16 \text{ ppm}$$

The similar σ values in eq 5a and 5b indicate that, as with most of the examples cited here, the lower r value in eq 5b does not derive from a greater scatter of the data points but rather from the lower range between high and low π^* values among the aromatic solvents.

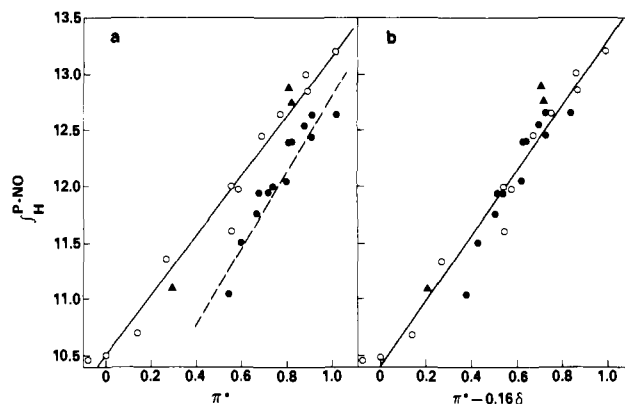


Figure 3. \int_H^{p-NO} for *p*-fluoronitrosobenzene plotted (a) against π^* and (b) against $(\pi^* - 0.16\delta)$. Symbols for the solvent families are as in Figure 1.

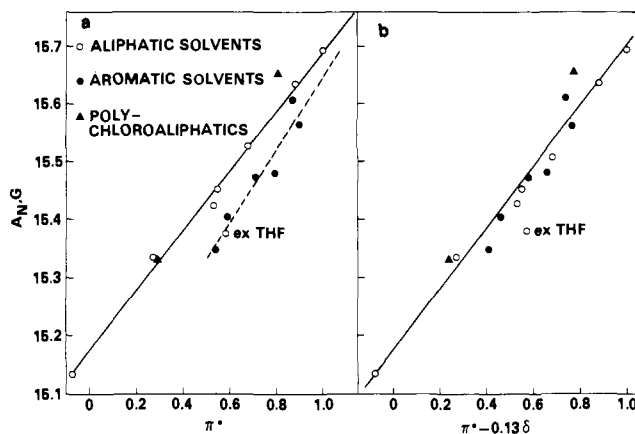


Figure 4. A_N for di-*tert*-butyl nitroxide plotted (a) against π^* and (b) against $(\pi^* - 0.13\delta)$.

From eq 5a and 5b, the d value is calculated to be -0.17 ,¹⁴ and the "all solvent" correlation according to eq 2 is

$$\int_H^{p-NO}(3) = 10.44 + 2.82(\pi^* - 0.17\delta) \text{ ppm} \quad (5c)$$

$$r = 0.970 \quad \sigma = 0.19 \text{ ppm}$$

For comparison with the above, the "all solvent" correlation of \int_H^{p-NO} with π^* according to eq 1 leads to $r = 0.928$ and $\sigma = 0.29$ ppm, i.e., again a significantly lower r and higher σ when the solvents from the three families are considered together. A plot of $\int_H^{p-NO}(3)$ vs. $(\pi^* - 0.17\delta)$ is shown in Figure 3b.

In the course of our investigations in the field of linear solvation energy relationships, we have examined solvent effects on about 25 sets of NMR spectral shifts and coupling constants, including ^1H , ^{13}C , ^{15}N , ^{19}F , ^{29}Si , ^{31}P , ^{119}Sn , and ^{199}Hg . We have found that, as with 3, they all exhibit " $\pi^* + d\delta$ " type behavior, with d values ranging from -0.05 to -0.40 [the latter value for the $J(^1\text{H}-^1\text{H})$ coupling constant of 1,1-difluoroethylene²⁰ being about the largest $-d$ term we have yet encountered].

The ESR Spectrum of Di-*tert*-butyl Nitroxide (4). Napier and Knauer²¹ have reported nitrogen hyperfine splitting constants of di-*tert*-butyl nitroxide, $A_N(4)$, in 16 nonprotic solvents for which π^* values are known (we have discussed the correlation of A_N of protic solvents with π^* and α in an earlier paper).⁸ The plots of A_N against π^* and against $(\pi^* + d\delta)$, are shown in Figure 4a,b.

Excluding the obviously out-of-line point for tetrahydrofuran (solvent 13), the correlation equation between $A_N(4)$ and π^* for seven nonchlorinated aliphatic solvents is

$$A_N(4) = 15.177 + 0.512\pi^* \text{ G} \quad (6a)$$

$$r = 0.998 \quad \sigma = 0.014 \text{ G}$$

(20) C. J. MacDonald and T. Schaefer, *Can. J. Chem.*, **45**, 3157 (1967).
 (21) B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, **98**, 439 (1976).

Table I. Data Correlated with Solvent π^* Values^a

no. ^b	solvent	π^*	1	2	3	4	5	6a	6b
Aliphatic Solvents									
1	hexane, heptane	-0.08	50.9	30.9 ^d	10.46	15.134	12	25.91 ^c	25.51 ^c
2	cyclohexane	0.00	50.0	31.2 ^d	10.50			25.74	25.13
3	triethylamine	0.14	49.3	33.3 ^d	10.70		16		
4	diisopropyl ether	0.27	48.6	34.0					23.87
5	di- <i>n</i> -butyl ether	0.24	48.6	33.4			18		23.70
7	diethyl ether	0.27	48.3	34.6	11.35	15.334	17	25.64	23.36
9	dioxan	0.54	[48.4] ^e	[36.0] ^e	11.60	15.452	25	25.51	22.73
11	ethyl acetate	0.55	47.2	38.1	12.00			25.32	22.42
13	tetrahydrofuran	0.58	46.6	37.4	11.98	[15.373] ^e	20	25.06	22.37
16	2-butanone	0.67	45.4	41.3					22.17
18	acetone	0.68	45.7	42.2	12.45	15.527	25		22.17
19	triethyl phosphate	0.72		41.7					
23	<i>N,N</i> -dimethylacetamide	0.88	43.0	43.7					
25	<i>N,N</i> -dimethylformamide	0.88	43.7	43.8	12.85	15.635	27		
26	hexamethylphosphoramide	0.87		[40.9] ^e					
27	butyrolactone	0.87	42.6		13.00				
28	<i>N</i> -methylpyrrolidone	0.92		42.2					
29	dimethyl sulfoxide	1.00	42.0	45.0	13.20	15.692	31		
34	acetic anhydride	0.76		[43.9]	12.65				
38	butyl acetate	0.46	47.5						
41	cyclohexanone	0.76	44.3	40.8			25		22.22
42	tri- <i>n</i> -butyl phosphate	0.65		39.6					
51	cyclopentanone	0.76		40.3					
56	sulfolane	0.98		44.0					
61	1,2-dimethoxyethane	0.53		38.2		14.356			
88	bis(2-methoxyethyl) ether	0.64		38.6					
52	methyl acetate	0.56		40.0					
138	ethyl formate	0.60		40.9					
Polychloroaliphatic Solvents									
6	carbon tetrachloride	0.29	48.7	32.5	11.10	15.331		25.51	24.57
10	trichloroethylene	0.53		35.9					
12	1,1,1-trichloroethane	0.49		36.2					23.53
20	methylene chloride	0.80	44.9	41.1	12.88				
21	1,2-dichloroethane	0.81		41.9	12.75	15.655			
44	tetrachloroethylene	0.28		31.9					
Aromatic Solvents									
8	toluene	0.54	47.2	33.9	11.05	15.347	20	25.32	23.58
14	benzene	0.59	46.9	34.6	11.50	15.404	21	25.19	23.31
15	chlorobenzene	0.71	45.2	37.5	11.95	15.472	24	25.06	22.78
17	anisole	0.73		37.0	12.00			24.94	22.57
24	pyridine	0.87	43.9	40.3	12.55	15.608			
31	nitrobenzene	0.01	42.6	42.0	12.65		26		
33	bromobenzene	0.79	44.6	37.5	12.05	15.479			
35	<i>p</i> -xylene	0.43	47.7	33.5					
37	benzotrile	0.90	43.3	42.0	12.65		27		22.07
53	mesitylene	0.41	47.5	33.1					
57	<i>N,N</i> -dimethylaniline	0.90					26		
58	acetophenone	0.90		41.3	12.45	15.562	28		
59	diphenyl ether	0.66		35.3	11.76				
60	<i>o</i> -dichlorobenzene	0.80		38.1	12.40				
90	cumene	0.41	47.6						
92	<i>m</i> -dichlorobenzene	0.67		37.0	11.95				
62	iodobenzene	0.81		37.9					
135	<i>m</i> -xylene	0.47		33.3					

^a The following expressions correspond to the numbers in the headings: 1, $\chi_R = E_T(1)$ (kcal/mol); 2, " $E_T(30)$ " = $E_T(2)$ (kcal/mol); 3, $f_H^{p-NO} = {}^{19}F$ NMR shift for 4-nitrosobenzene (3) relative to internal C_6H_5F (ppm); 4, $A_N(4)$ = nitrogen hyperfine splitting constant (in G) for di-*tert*-butyl nitroxide; 5, $\Delta\nu(5)$ = infrared spectral shift (in cm^{-1}) in solvent relative to the gas phase of $(MeO)_2P(O)CH_3$; 6a, $\nu(6)_{max}^{abs}$ (μcm^{-1}); 6b, $\nu(6)_{max}^{fluor}$ (μcm^{-1}). ^b Solvent numbering is the same in all papers of this series. ^c Isooctane. ^d These values are probably derived from correlations of $E_T(30)$ with other properties rather than by direct measurement of the spectrum of 2 and are hence less reliable. ^e Excluded from correlations.

If the result for 13 is included, r becomes 0.977 and $\sigma = 0.041$ G. The corresponding equation for six aromatic solvents is

$$A_N(4) = 15.018 + 0.627\pi^* G \quad (6b)$$

$$r = 0.956 \quad \sigma = 0.032 G$$

The d term is calculated to be -0.13 ,¹⁴ and the correlation according to eq 2 for 15 solvents (ex 13) becomes

$$A_N(4) = 15.175 + 0.527(\pi^* - 0.13\delta) G \quad (6c)$$

$$r = 0.972 \quad \sigma = 0.036 G^{22}$$

The latter result compares with $r = 0.947$ and $\sigma = 0.051$ G for the "all solvent" (ex 13) correlation of $A_N(4)$ with π^* . Thus, it is again seen that, although the δ value of 0.5 for the polychloroaliphatic solvents does not normalize the results for CCl_4 and $ClCH_2CH_2Cl$ as well as in the earlier instances, the A_N property exhibits typical " $\pi^* + d\delta$ " behavior. (4-Amino-2,2,6,6-tetramethylpiperid-1-yl)oxy and (3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yl)oxy, for which solvent effects on ni-

(22) If the result for 13 is included, $r = 0.956$ and $\sigma = 0.044$. If the result for 1,2-dichloroethane is also excluded, $r = 0.985$ and $\sigma = 0.026$.

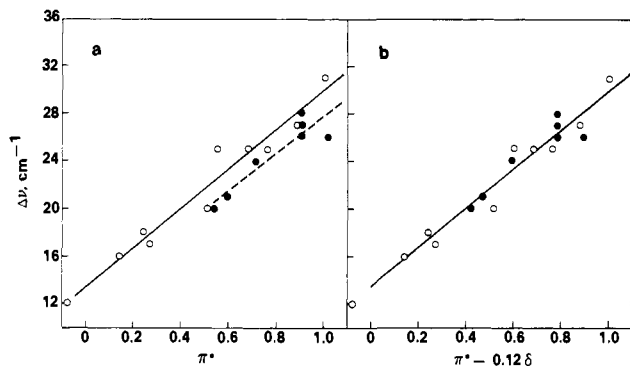


Figure 5. $\Delta\nu_{\text{P=O}}$ for dimethyl methylphosphonate plotted (a) against π^* and (b) against $\pi^* - 0.12\delta$. Symbols for the various solvent families are as in Figure 1.

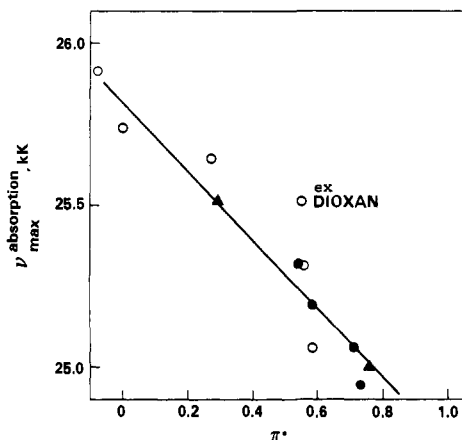


Figure 6. $\nu(6)_{\text{max}}^{\text{abs}}$ plotted against π^* . Symbols for the various solvent families are as in Figure 1.

trogen hyperfine splitting constants have also been reported by Knauer and Napier, show similar solvatochromic patterns, albeit with slightly poorer r values in all correlations.

The IR Spectrum of Dimethyl Methylphosphonate (5). Shagidullin and co-workers²³ have reported aprotic solvent IR shifts (relative to the gas phase) for the P=O stretching band of $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$, the $\Delta\nu$ values being estimated for the low-frequency component of a $\nu_{\text{P=O}}$ doublet (Table I). The $\Delta\nu(5)$ results in ten nonchlorinated aliphatic and seven aromatic solvents are plotted against π^* and against $\pi^* + d\delta$ in Figure 5a,b, where again we observe the characteristic pattern of " $\pi^* + d\delta$ " behavior.

The individual regression equations are as follows: for the aliphatic solvents

$$\Delta\nu(5) = 13.4 + 16.6\pi^* \text{ cm}^{-1} \quad (7a)$$

$$r = 0.977 \quad \sigma = 1.3 \text{ cm}^{-1}$$

for the aromatic solvents

$$\Delta\nu(5) = 12.2 + 15.6\pi^* \text{ cm}^{-1} \quad (7b)$$

$$r = 0.919 \quad \sigma = 1.3 \text{ cm}^{-1}$$

The d term is calculated to be -0.12 ,¹⁴ and the "all solvent" correlation according to eq 2 is

$$\Delta\nu(5) = 13.5 + 16.5(\pi^* - 0.12\delta) \text{ cm}^{-1} \quad (7c)$$

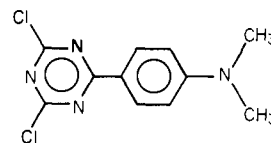
$$r = 0.971 \quad \sigma = 1.2 \text{ cm}^{-1}$$

For comparison, the "all solvent" correlation according to eq 1 leads to $r = 0.956$ and $\sigma = 1.5 \text{ cm}^{-1}$.

The report by Shagidullin et al. is also of particular interest to us in that these workers described linear dependences of $\Delta\nu_{\text{P=O}}$ on molecular dipole moments of the media. Separate regression

lines were observed for the aliphatic and aromatic solvents, with the dependence of $\Delta\nu$ on μ being significantly greater for the aliphatics than for the aromatic solvents. This accords quite well with our incorporation of a $d\delta$ term to accommodate aromatic solvents in the solvatochromic equations and with our observation^{6,24} that solvent π^* values for most nonchlorinated aliphatic solvents are very nearly proportional to molecular dipole moments. The Russian workers also anticipated our present findings in the astute comment, "thus, an investigation of phosphoryl compounds by IR spectroscopy shows a pronounced weakening of the dipole-dipole interaction if either the dissolved substance or the solvent includes aromatic fragments".

Absorption and Fluorescence Spectra of *N,N*-Dimethyl-4-(dichloro-1,3,5-triazinyl)aniline (6). Our two final sets of solvent



6

effect correlations involve different properties of the same indicator. Results reported by Cowley and Healy²⁵ allow us to compare solvatochromic behavior of the fluorescence spectrum and the $p \rightarrow \pi^*$ band in the absorption spectrum of **6** (ν_{max} values are given in Table I).

As is seen in the plot of $\nu(6)_{\text{max}}^{\text{abs}}$ vs. solvent π^* values in Figure 6, the absorption spectrum shows characteristic " π^* behavior"; i.e., as was observed earlier for $p \rightarrow \pi^*$ transition of para-substituted aniline indicators,¹² the data points for the aromatic and aliphatic solvents conform to the same regression line (within the precision of the measurements). The regression equation for five aliphatic solvents [ex dioxan (**9**), again an obviously out-of-line point]¹⁷ is

$$\nu(6)_{\text{max}}^{\text{abs}} = 25.82 - 1.065\pi^* \times 10^3 \text{ cm}^{-1} \quad (8a)$$

$$r = 0.949 \quad \sigma = 0.12 \times 10^3 \text{ cm}^{-1 26}$$

Equation 8a is almost coincident with the "all solvent" least-squares regression equation ($n = 11$, ex **9**)

$$\nu(6)_{\text{max}}^{\text{abs}} = 25.82 - 1.082\pi^* \times 10^3 \text{ cm}^{-1} \quad (8b)$$

$$r = 0.970 \quad \sigma = 0.08 \times 10^3 \text{ cm}^{-1 26}$$

The seemingly large spread of the data points in Figure 6 is primarily a consequence of the low s value (slope) in the solvent dependence, which allows an expanded ν_{max} scale. The σ values of 0.12 and $0.08 \times 10^3 \text{ cm}^{-1}$ for eq 8a and 8b should properly be compared with our earlier estimate of $0.10 \times 10^3 \text{ cm}^{-1}$ as a reasonable precision limit for ν_{max} of "well-behaved" absorption spectral bands.²⁷

In marked contrast with the above, the fluorescence spectrum of **6** shows characteristic " $\pi^* + d\delta$ behavior" (Figure 7), the individual correlation equations being as follows: for 11 nonchlorinated aliphatic solvents

$$\nu(6)_{\text{max}}^{\text{flu}} = 24.92 - 4.12\pi^* \times 10^3 \text{ cm}^{-1} \quad (9a)$$

$$r = 0.977 \quad \sigma = 0.27 \times 10^3 \text{ cm}^{-1}$$

for five aromatic solvents

$$\nu(6)_{\text{max}}^{\text{flu}} = 25.74 - 4.17\pi^* \times 10^3 \text{ cm}^{-1} \quad (9b)$$

$$r = 0.989 \quad \sigma = 0.10 \times 10^3 \text{ cm}^{-1}$$

for nineteen solvents of all types

$$\nu(6)_{\text{max}}^{\text{flu}} = 25.00 - 4.15(\pi^* - 0.19\delta) \times 10^3 \text{ cm}^{-1} \quad (9c)$$

$$r = 0.972 \quad \sigma = 0.25 \times 10^3 \text{ cm}^{-1}$$

(24) J. L. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

(25) D. J. Cowley and P. J. Healy, *J. Chem. Soc., Perkin Trans. 2*, 484 (1979).

(26) If the result for **9** is included, $r = 0.885$ and $\sigma = 0.16 \mu\text{cm}^{-1}$ for the aliphatic solvents correlation and $r = 0.934$ and $\sigma = 0.12$ for the "all solvent" correlation.

(27) See footnote 16 of ref 3.

(23) R. R. Shagidullin, V. E. Bel'skii, and L. Kh. Ashrafullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2034 (1974).

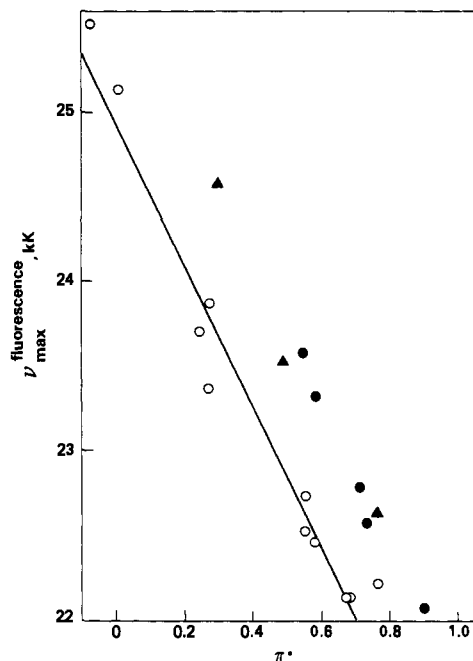


Figure 7. ν_{\max}^{fluo} plotted against π^* . Symbols for the various solvent families are as in Figure 1.

For comparison, the "all solvent" correlation with π^* according to eq 1 gives $r = 0.917$ and $\sigma = 0.47 \times 10^3 \text{ cm}^{-1}$.

The above results are consistent with our general experience that whether solvent effects conform with eq 1 or eq 2 depends on the type property being considered rather than the nature of the indicator. As has been mentioned, the case of $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ spectral transitions, where charged and uncharged indicators show differing behavior patterns, is an exception to this generalization. It may be that these should be considered as different type transitions on the basis of their differing responses to increasing solvent polarity (hypsochromic for charged, bathochromic for uncharged indicators). Further, the above considerations also apply where the property shows multiple dependences on π^* and α or π^* and β . Thus, the more general "all solvent" equation takes the form

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (10)$$

where the $s\pi^*$, the $d\delta$, the $a\alpha$, or the $b\beta$ term, or any combination thereof may equal zero.

Concerning the δ Values for Polychloroaliphatic and Aromatic Solvents. On detailed examination of Figures 2–5 and 7, it becomes evident that $\delta = 0.5$ is not a completely satisfactory approximation for polychloroaliphatic solvents. Thus, while $\delta = 0.5$ does appear to normalize the results in Figure 2, the results in Figures 3 and 4 could better accommodate a value near 0.0, and those in Figure 7 would be more consistent with $\delta = 1.0$. We have no ready solution for this problem. A possible alternative to eq 2 would be to have separate terms corresponding to d for polychloroaliphatic and aromatic solvents,²⁸ but this would detract from the simplicity of the solvatochromic equations.

Further, it has been of continuing concern in the present series of papers that increasing the number of adjustable parameters would detract from the statistical rigor of the correlations. With the fixed δ values of 0.0, 0.5, and 1.0 for the three families of solvents and with the fixed method of calculating the d term,¹⁴ we consider that the r values near 0.97 for eq 4d, 5c, 6c, 7c, and 9c lend greater credence to the correlations than would have been the case if optimal δ values had been determined for each solvent (in the same way that π^* values had been optimized by averaging

(28) It would, however, be consistent with the concept that different properties put different demands on π - and σ -electron mobility. To pursue this possibility, however, would involve "fine tuning" the solvatochromic equations too precisely.

π^* values from many correlations)³ or if the d terms had been least-squares values, chosen to maximize the correlation coefficients.

Relationship between the ($\pi^* + d\delta$) Term and More Fundamental Properties of the Solvents. Where the sign of d in eq 2 is positive, the polarizability correction term reinforces the π^* dipolarity–polarizability effect of the solvent; where negative, the $d\delta$ term lessens the π^* effect. Thus far, of well over 60 correlations which we have carried out according to eq 2 or 10, $d\delta \neq 0$, we have encountered a positive d coefficient in only one ambiguous instance;²⁹ all other d values have been negative. On this basis, $d = 0$ for $p \rightarrow \pi^*$ electronic spectral transitions appears to represent an extreme or limiting condition.

We have attempted to relate the empirically derived solvatochromic dipolarity–polarizability parameters to more fundamental properties of the solvents by comparing linear solvation energy relationships of the form of eq 2 with equations of the form

$$XYZ = XYZ_0 + fD + pP \quad (11)$$

The D term in eq 11 is a descriptor of the ability of the solvent to participate in solute dipole–solvent dipole interactions. For simplicity we shall refer to D as a measure of solvent dipolarity.³⁰ P is a measure of the ability of the solvent to participate in solute dipole–solvent induced dipole interactions, which we shall continue to refer to as solvent polarizability. As indexes of the dipolarity effect, we have examined the molecular dipole moment, μ , the dielectric constant function, $(\epsilon - 1)/(2\epsilon + 1)$,³¹ and the modified Onsager reaction field θ parameter of Abboud and Taft.³² As the polarizability measure, we have considered mainly variants of the refractive index function $(n^2 - 1)/(2n^2 + 1)$. An attempt was made to modify the latter term in such a manner that polarizability contributions to the dipolarity–polarizability blend would be largest for the less dipolar, more polarizable aromatic solvents and smaller for both the less polarizable aliphatic solvents and the more dipolar aromatic solvents.

We shall discuss the various measures of dipolarity and polarizability in greater detail in future papers; in the present introductory discussion, we shall take for the D term in eq 11 the molecular dipole moment, μ , and for the P term the following function

$$P = [f(n) - 0.19][1 - 0.23\mu] \quad (12)$$

$$f(n) = (n^2 - 1)/(2n^2 + 1)$$

The $[1 - 0.23\mu]$ term in eq 12 is near unity for very slightly dipolar aromatic solvents like benzene and the alkylbenzenes and approaches zero for more dipolar aromatic solvents like nitrobenzene and benzonitrile. The $[f(n) - 0.19]$ term is near zero for the less polarizable aliphatic solvents and larger for the more polarizable aromatic solvents.

We shall refer to functions such as that in eq 12 as *reducing functions of n* (and we shall point out in future papers that the various reducing functions of n in combination with the various measures of solvent dipolarity, normalize aliphatic and aromatic solvent effects on many types of XYZ 's to unitary linear relationships such as have not hitherto been demonstrated with fundamental dipolarity–polarizability measures). *In concept, reducing functions of n take into account the fact that the ability of the external dipole of a dipolar solute molecule to induce displacement of charge in the σ and π bonds of a solvent molecule is reduced substantially if those bonds are already polarized by*

(29) The lowest energy band in the spectrum of $C_6H_5CH=C(CN)_2$ [P. Jacques and J. Faure, *J. Chim. Phys.*, **70**, 653 (1973)] appears to show $d = +0.44$ in eq 2, but this may result from specific π -donor/ π -acceptor interactions shifting ν_{\max} bathochromically in aromatic solvents.

(30) The term *solvent dipolarity* is intended as a more specific description than the often misused term *solvent polarity*, which frequently has included as well the effects of hydrogen bonding interactions in varying combinations with the dipole–dipole effects.

(31) F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc. B*, 460 (1971).

(32) J.-L. M. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

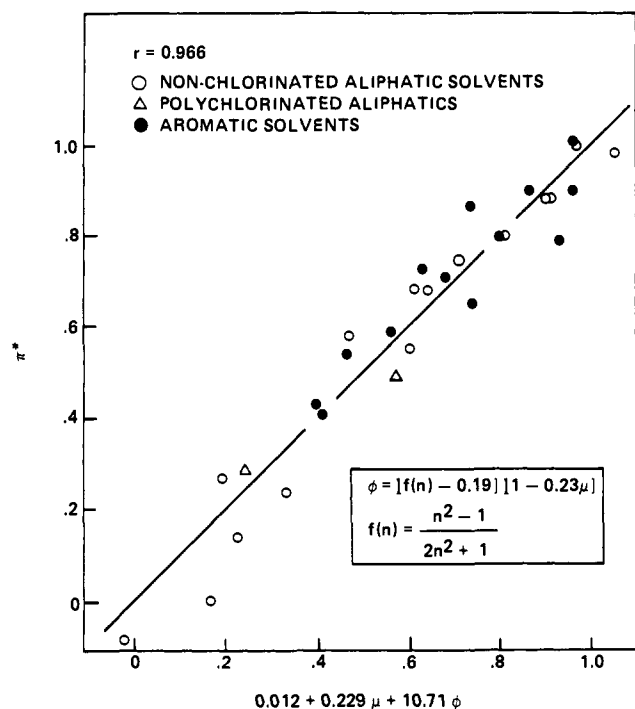


Figure 8. Correlation of π^* with μ and ϕ .

an internal dipole within the solvent molecule.

Since ν_{\max} values of $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of all sorts of uncharged indicator molecules are linear with π^* values for all nonhydrogen-bonding solvents (i.e., in eq 2, $d = 0$), we can estimate the relative dipolarity and polarizability contributions to solvent effects on such transitions by a multiple parameter least-squares correlation of solvent π^* values with μ and P (eq 12). The multiple linear regression equation is

$$\pi^* = 0.012 + 0.229\mu + 10.71P \quad (13)$$

$$n = 30 \quad r = 0.966 \quad (p/f)_{\text{eq 11}} = 46.8$$

That the correlation coefficient for eq 13 is only fair by the standards which we have applied to linear solvation energy relationships, we attribute to the many sources and variable reliabilities of the dipole moment data used in the correlation. The more important aspect of eq 13 is that, as is shown in Figure 8, the distributions of data points on both sides of the regression line are similar for the aliphatic, polychloroaliphatic, and aromatic solvents.

For comparison with eq 13, we have also carried out a correlation of Dimroth's " $E_T(30)$ " parameter for nonhydrogen bond donor solvents with μ and P (eq 12). As was shown in eq 4a-d,

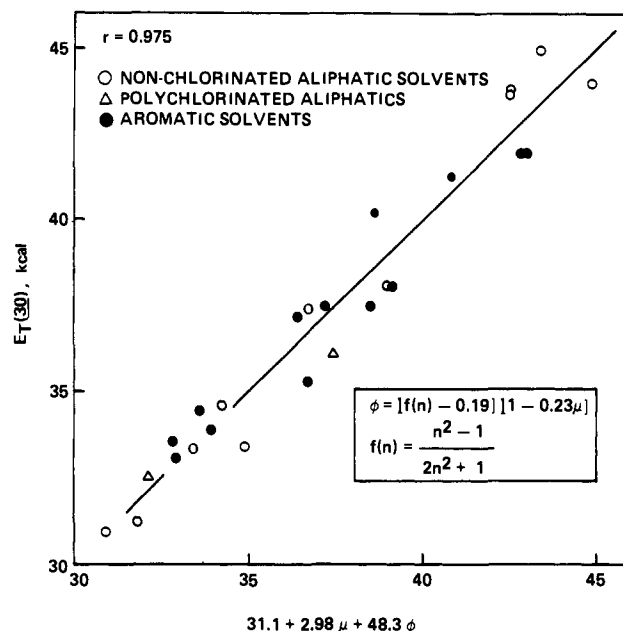


Figure 9. Correlation of $E_T(30)$ with μ and ϕ .

this property shows pronounced " $\pi^* + d\delta$ solvatochromic behavior", the d value being -0.24 . The multiple linear regression equation is

$$E_T(30) = E_T(2) = 31.1 + 2.98\mu + 48.3P \text{ kcal/mol} \quad (14)$$

$$n = 26 \quad r = 0.975 \quad (p/f)_{\text{eq 11}} = 16.2$$

As is seen in Figure 9, there is again an equal distribution of aromatic and aliphatic data points about the regression line.

It is also seen on comparing eq 13 and 14 that the $(p/f)_{\text{eq 11}}$ ratio for " $E_T(30)$ " is only about one-third of that for π^* . This suggests that the polarizability contribution to the dipolarity-polarizability blend in solvent effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (in which the molecular dipolar moment increases on electronic excitation) is significantly greater than is the case with the "solvatochromiebande" of Dimroth's betaine (in which the dipole moment decreases). In a future paper we shall show that relative polarizability contributions for a number of XYZ 's grow smaller as the $-d$ terms (eq 2) grow larger and that there is an approximate linear relationship between $(p/f)_{\text{eq 11}}$ and $-d$. Thusly, we appear to provide a more fundamental basis for the solvatochromic parameters, which have hitherto been considered as semiempirical.

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