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Linear Solvation Energy Relationships. 13.[1] Relationship between the Hildebrand Solubility Parameter, δ_H, and the Solvatochromic Parameter, π^*

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Abstract: Free energies of solution of nondipolar solutes show better linear correlation with the Hildebrand solubility parameter, δ_H, than with the solvatochromic parameter, π^*. It is suggested that this is because the π^* parameter is a better measure of dipolar solute/solvent interactions, whereas the δ_H parameter is a better measure of the interactions between solvent molecules which must be disrupted to create a cavity for the solute. Slopes and intercepts in the correlations of ΔG_s°'s of nondipolar solutes with solvent δ_H values are linear with the solute molecular volumes. The parameters appear to be sufficiently "fine tuned" that multiple parameter correlations of ΔG_s°'s of dipolar solutes with solvent π^* and δ_H values allow (at least semiquantitative) discrimination between the solute/solvent interaction terms and the cavity terms.

In earlier papers of this series,[2-5] it was shown that, when solvent/solute hydrogen bonding interactions are excluded, as when neither solvents nor solutes are hydrogen bond donors, medium effects on many types of physicochemical properties and reactivity parameters (XYZ's) are well correlated by linear solvation energy relationships (LSER's) which may take either of two forms: For $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions with all solvents considered together, and for other properties when families of solvents with similar polarizability characteristics[2-6] are treated separately (e.g., only nonchlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents), the LSER's take the form

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

where the π^* parameter is a measure of solvent dipolarity/polarizability,[7] which describes the solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect. For other XYZ's, when all solvents need to be considered together, the preferred form of the LSER's becomes,

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

where δ, a "polarizability correction term", = 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. The π^* and δ terms in eq 1 and 2 have recently been related to more fundamental polarizability and dipolarity properties of the solvents, expressed in terms of functions of the solvent refractive index and either the dielectric constant or the molecular dipole moment, respectively.[2]

Numerous kinds of relatively precise correlations have been reported wherein the XYZ term in eq 1 or 2 is a position or intensity of maximal absorption in an IR, UV-visible, NMR, or ESR spectrum, an NMR coupling constant, a ΔG or ΔH of solution or of transfer between solvents, or the logarithm of a GLC partition coefficient, a reaction rate, or equilibrium constant, or a fluorescence lifetime.

Abboud and co-workers[8] have pointed out that correlations according to eq 1 are best when consideration is restricted to a set of nonprotic nonchlorinated aliphatic *select solvents*, which contain a single dominant bond dipole. For these *select solvents* (specifically excluding hexamethylphosphoramide), π^* values are roughly proportional to gas phase molecular dipole moments. They have also demonstrated that, when the analyses include only the data for these *select solvents*, many of the earlier "solvent polarity" scales show excellent linear correlations with the π^* parameters and with one another. The number of *select solvents* correlated, n, and the correlation coefficients, r, for the linear regression equations with π^* are as follows: (a) for Dimroth and Reichardt's $E_T(30)$ scale,[9] $n = 12$, $r = 0.987$; (b) for Brooker's χ_R,[10] $n = 16$, $r = 0.987$; (c) for Lassau and Junger's log $k(\mathrm{Pr_3N + MeI})$,[11] $n = 13$, $r = 0.985$; for Walther's E_K,[12] $n = 9$, $r = 0.977$; (e) for Knauer and Napier's A_N,[13] $n = 6$, $r = 0.978$; (f) for Allerhand and Schleyer's G,[14] $n = 8$, $r = 0.993$; (g) for Taft's P,[15] $n = 12$, $r = 0.989$; and (h) for Brownstein's S,[16] $n = 10$, $r = 0.981$. More recently, we have also shown that $n = 10$, $r = 0.960$ for the linear correlation of Gutmann's "Acceptor Numbers", AN,[17] with π^* values of *select solvents*.[18]

An important and widely used solvent property scale which did not conform well with this self-consistent and mutually supporting framework of intercorrelations was the Hildebrand *solubility parameter*, δ_H (we use the subscript to distinguish the Hildebrand parameter from the δ term in eq 2). The δ_H parameter, variously

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[1] Part 21 in the Solvatochromic Comparison Method series.

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[7] The term *solvent dipolarity* is intended as a more specific description than the frequently misused *solvent polarity*, which has included as well the effects of hydrogen bonding interactions in varying combinations with the dipole/dipole effects.

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Table I. Free Energies of Solution of *n*-Octane and Nitromethane in *Select Solvents* Compared with Solvent π^* Values and with the Hildebrand Solubility Parameter, δ_H

no.[a]	solvent	π^* [b]	δ_H [c]	ΔG_s°,[d] kcal/mol: *n*-octane	ΔG_s°,[d] kcal/mol: nitromethane
1	hexane	−0.08	7.27	−2.36	0.19
2	cyclohexane	0.00	8.20	−2.42	0.35
3	triethylamine	0.14	7.45	−2.56	−0.57
5	di-*n*-butyl ether	0.24	7.62		
7	diethyl ether	0.27	7.50	−2.39	−0.95
11	ethyl acetate	0.55	8.90	−1.44	−1.80
13	tetrahydrofuran	0.58	9.30	−2.00	−1.71
16	2-butanone	0.67	9.21	−1.33	−1.92
18	acetone	0.68	9.60	−0.93	−1.94
23	*N,N*-dimethylacetamide	0.88	10.8[e]	−0.64	
25	dimethylformamide	0.88	11.76	−0.36	−2.25
28	*N*-methylpyrrolidone	0.92	11.3[e]	−0.35	
29	dimethyl sulfoxide	1.00	13.00	0.62	−2.19
32	nitromethane	0.80	12.61	0.47	−1.80[f]
41	cyclohexanone	0.76	9.90	−1.33	−1.99
50	acetonitrile	0.76	11.74	0.06	
52	methyl acetate	0.56	9.50		

[a] Solvent numbering is the same in all papers of this series. [b] Reference 3. [c] Calculated from most recent literature values of calorimetrically determined heats of vaporization. [d] Calculated from data of Rohrschneider.[32] Refer to gas as 1 atm and to solution at unit mol fraction. [e] Reference 20. [f] Calculated from vapor pressure.

described as the square root of the internal pressure or the square root of the cohesive energy density, is defined by,

$$\delta_H = (-E/V)^{1/2} \tag{3}$$

where $-E$ is the molal heat of vaporization to a gas at zero pressure, and V is the molal volume.[19,20] The δ_H scale has been used extensively by chromatographers and polymer chemists to correlate and predict solubility behavior of nonelectrolytes.[21-23]

Results and Discussion

Values of the δ_H and π^* parameters for 17 *select solvents* are assembled in Table I, and a plot of δ_H against π^* is shown in Figure 1. The least-squares regression equation, represented by the solid line in the figure, is,

$$\delta_H = 6.96 + 4.93\pi^* \tag{4}$$

$$n = 17,\ r = 0.886,\ \sigma = 0.89$$

By the standards which we have applied to linear solvation energy relationships, $r = 0.886$ represents quite poor correlation. Correlations of δ_H with the other solvent property scales mentioned above were of correspondingly poor quality.

The poor quality of the correlation of π^* with δ_H had for a number of years been a source of considerable puzzlement to us. However, the reason for this and the relationship between the solvent property scales became more evident to us when, in connection with a solvatochromic comparison study of gas/liquid partition coefficients,[24] we had occasion to attempt a correlation of free energies of solution of *n*-octane with the solvent π^* values. Our previous experience with free energies of solution or of transfer between solvents had been that ΔG° values for polar solutes like acetone or nitromethane or charged solutes like tetraethylammonium iodide showed good to excellent correlations with solvent π^* values.

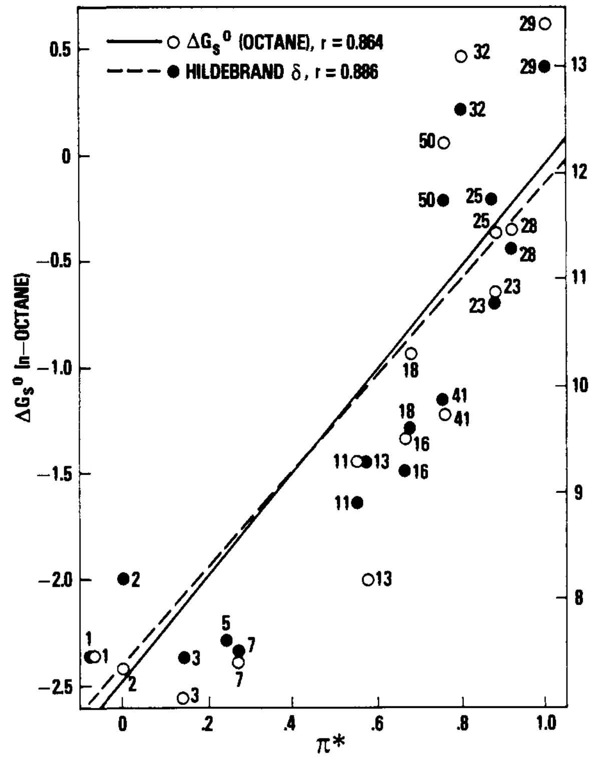

Figure 1. Free energies of solution of *n*-octane in select solvents and the Hildebrand solubility parameter, δ_H, plotted against solvent π^* values.

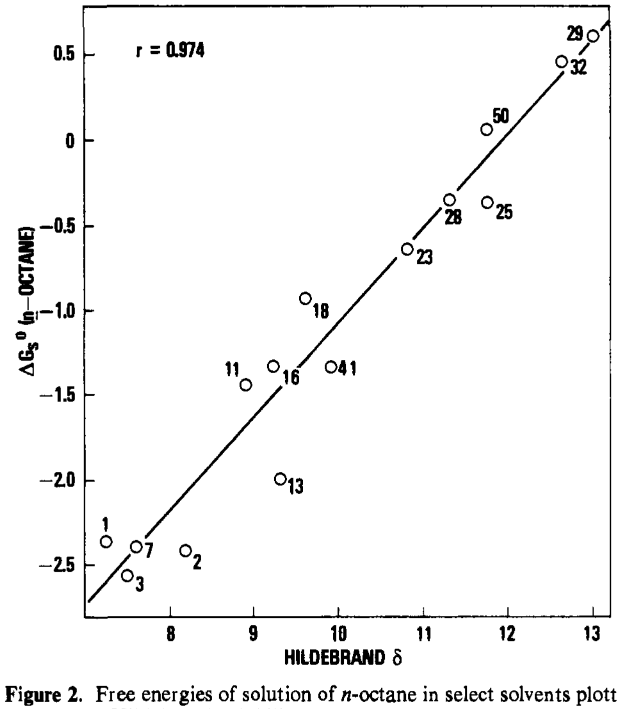

Figure 2. Free energies of solution of *n*-octane in select solvents plotted against the Hildebrand solubility parameter, δ_H.

Values of ΔG_s° (*n*-octane) in 15 of the select solvents are also assembled in Table I, and a plot of ΔG_s° against π^* is shown in Figure 1, superimposed on the earlier plot. The least-squares regression equation, represented by the dashed line in the figure, is

$$\Delta G_s^\circ(n\text{-octane}) = -2.72 + 2.70\pi^* \text{ kcal/mol} \tag{5}$$

$$n = 15,\ r = 0.864,\ \sigma = 0.56 \text{ kcal/mol}$$

On detailed examination of the results, it is seen that δ_H and ΔG_s°(*n*-octane) show strikingly similar solvatochromic behavior,

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(23) See, however: Herbrandson, H. F.; Neufeld, F. R. *J. Org. Chem.* **1966**, *31*, 1140.

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Table II. Free Energies of Solution of Nonpolar Solutes in *Select Solvents* Correlated with the Hildebrand Solubility Parameter, δ_H

$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H$ kcal/mol

no.	solute	$(R)^a$	$(\Delta G_s^\circ)_0$	h	r^b	σ^c	n	$r(\pi^*)^d$
1	He	(1.32)	3.51	0.203	0.980	0.13	5	0.891
2	Ne	(1.39)	3.16	0.216	0.977	0.14	5	0.888
3	Ar	(1.75)	1.69	0.258	0.984	0.14	5	0.927
4	Kr	(1.95)	1.01	0.264	0.990	0.11	5	0.934
5	Xe	(2.19)	0.05	0.282	0.996	0.07	5	0.938
6	CH_4	(1.90)	1.40	0.240	0.992	0.07	8	0.918
7	C_2H_6	(2.26)	0.24	0.251	0.988	0.08	7	0.928
8	C_3H_8	(2.47)	−1.09	0.318	0.991	0.12	5	0.938
9	n-C_4H_{10}	(2.70)	−1.90	0.334	0.992	0.12	4	0.933
10	n-C_5H_{12}	(2.89)	−3.64	0.440	0.966	0.21	11	0.729
11	n-C_6H_{14}	(3.11)	−4.13	0.434	0.978	0.19	9	0.770
12	n-C_7H_{16}	(3.32)	−5.22	0.482	0.985	0.15	4	0.934
13	n-C_8H_{18}	(3.52)	−6.63	0.555	0.974	0.26	15	0.860
14	c-C_6H_{12}	(3.24)	−4.52	0.416	0.978	0.22	6	0.852
15	$(CH_3)_4Sn$	(3.14)	−3.93	0.389	0.960	0.24	11	0.880

[a] R is a solute parameter related to the solute radius.[28] See text. [b] Correlation coefficient. [c] Standard deviation. [d] Correlation coefficient for the corresponding least-squares linear-regression equation with π^*.

both in the qualities of the correlations with π^* and in the coincidences of individual data points in the plots. For example, data points for solvents 3, 5, 11, 13, 16, 41, and 23 of Table I lie well below the regression lines in both instances, while points for 29, 32, and 50 lie well above the regression lines.

Accordingly, a good correlation is found between the ΔG_s°-(n-octane) values and the δ_H parameters of the 15 *select solvents*. As is shown in Figure 2, a plot of the data exhibits quite good linearity; the least-squares regression equation is,

$$\Delta G_s^\circ(n\text{-octane}) = -6.63 + 0.56\delta_H \text{ kcal/mol} \qquad (6)$$

$$n = 15,\ r = 0.974,\ \sigma = 0.26 \text{ kcal/mol}^{25}$$

In the light of the uncertainties in the experimental determinations of the δ_H terms which are evidenced by the spreads of published values,[19-23] $r = 0.974$ must be regarded as representing quite satisfactory correlation.[25]

The Relationship between π^* and δ_H. The relationship between the solvent property scales becomes more evident when we compare eq 5 and 6 with the solvatochromic equations for the free energy of transfer of the tetraethylammonium iodide ion pair from methanol to aliphatic *select solvents*. Based on the data of Abraham,[26] the correlation equation with π^* is,[5]

$$\Delta G_t^c(Et_4N^+I^-) = 12.48 - 13.3\pi^* \text{ kcal/mol} \qquad (7)$$

$$n = 10,\ r = 0.985,\ \sigma = 0.73 \text{ kcal/mol}$$

The corresponding correlation equation with δ_H has now been found to be,

$$\Delta G_t^c(Et_4N^+I^-) = 27.14 - 2.25\delta_H \text{ kcal/mol} \qquad (8)$$

$$n = 9,^{27}\ r = 0.848,\ \sigma = 2.98 \text{ kcal/mol}$$

Comparing now the solvatochromic behavior of n-C_8H_{18} and $Et_4N^+I^-$, we see two major differences: (a) For n-octane the correlation with δ_H is significantly better than that with π^*, whereas for tetraethylammonium iodide the very much better correlation is with π^*. (b) For $Et_4N^+I^-$ the signs of the coefficients of π^* and δ_H in eq 7 and 8 are negative, the ΔG term becoming more *exogenic* in the more dipolar solvents because of the increased dielectric stabilization of the solute charge; for n-octane the signs of the coefficients of π^* and δ_H in eq 5 and 6 are positive, the ΔG term becoming more *endogenic* in the more dipolar solvents. The latter effect is evidently caused by the zero-dipole solute interfering with increasingly stronger solvent dipole/solvent dipole interactions.

Thus, the difference between the types of properties well correlated by π^* and by δ_H becomes more evident. The π^* parameter is a better measure of the ability of the medium to stabilize a charged or dipolar solute by virtue of solvent dipole/solute charge or solvent dipole/solute dipole interactions, whereas δ_H is a better index of the solvent dipole/solvent dipole interactions which are interrupted in forming a cavity for the nondipolar solute.

This picture is consistent with the methods and indicators used to derive the π^* and δ_H scales. The π^* values are based on UV/visible spectroscopic probes of the cybotactic (solvent) environments of a number of highly dipolar indicator solutes.[4] The δ_H parameter is derived from the solvent vaporization enthalpy and molal volume, i.e., involving no solute, but measuring only interactions between the solvent molecules.

A molecular structural example of why the measures of solvent/dipolar solute and solvent/solvent interactions do not parallel one another is illustrated by diethyl ether solvent. When the nondelocalized nonbonded electrons on the oxygen atom of diethyl ether are adjacent to the oxygen of another ether molecule, there is a destabilizing (endogenic) repulsion effect between pairs of nonbonded electrons, which is not offset by an attraction to the positive end of the weak ether dipole. When adjacent to a dipolar solute, however, there is no corresponding repulsion effect, and the nonbonded electrons help to stabilize the positive end of the stronger solute dipole. Thus diethyl ether (and di-n-butyl ether and triethylamine) have larger π^* values but smaller δ_H values than cyclohexane.

Correlations for Other Nondipolar Solutes. If the above rationale is correct, other nondipolar solutes should show patterns of solvatochromic behavior similar to n-octane, with the ΔG_s° values governed primarily by the δ_H values of the solvents and the molecular dimensions of the solutes. We have therefore compared correlations of free energies of solution of 14 additional nondipolar solutes with solvent π^* and δ_H values through equations of the forms,

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* \qquad (9)$$

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + h\delta_H \qquad (10)$$

and we have related the slopes and intercepts in eq 10 to solute molecular volumes. The solutes considered include the rare gases from helium to xenon, the straight chain hydrocarbons from C_1 to C_7, cyclohexane, and tetramethyltin. As before, the ΔG_s° values used in the correlations are primarily those published earlier by one of the present authors,[28] but include also free energies of solution in some additional solvents.[29] The δ_H and π^* values used in the correlations are listed in Table I.

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(25) If the datum for tetrahydrofuran (solvent no. 13) is excluded, the r value becomes 0.982.

(26) Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1343.

(27) Methyl formate is excluded as there was no known δ_H value.

(28) Abraham, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5477.

(29) Additional values are: solute (solvent, ΔG; solvent, ΔG): CH_4 (Et_2O, 3.20; MeOAc, 3.70; DMF, 4.09); C_2H_6 (MeOAc, 2.68; EtOAc, 2.53); n-C_5H_{12} (THF, 0.09; MEK, 0.49; cyclohexanone, 0.48; DMF, 1.35; DMA, 1.13); n-C_6H_{14} (MEK, −0.14; cyclohexanone, −0.18; DMF, 0.72); c-C_6H_{12} (cyclohexanone, −0.67); Me_4Sn (Et_2O, −0.80; n-Bu_2O, −0.91; THF, −0.73; MeOAc, −0.35; DMF, 0.47).

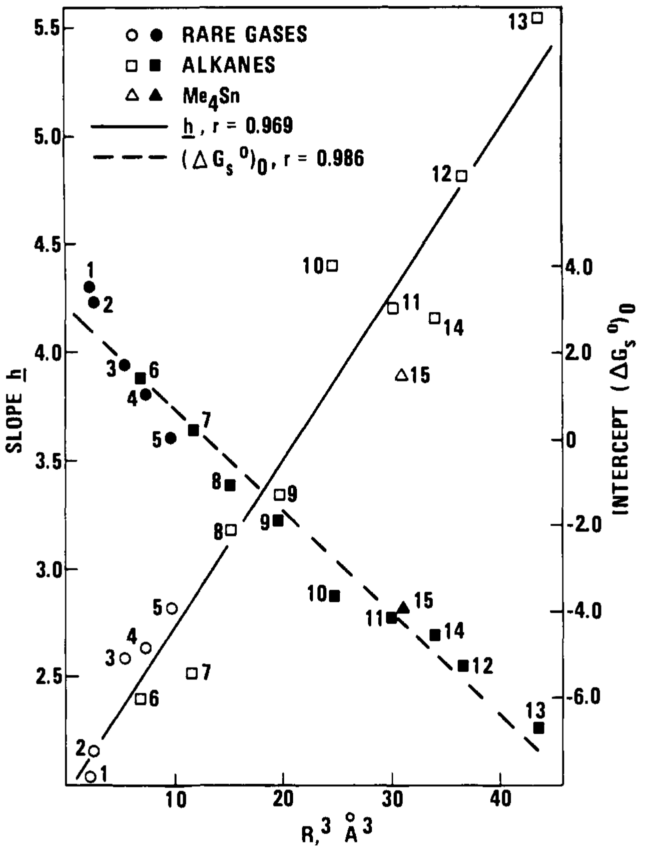

Figure 3. Slopes and intercepts in Table I plotted against $(R)^3$. Divide numbers on left-hand scale by 10.

The results of the correlations with δ_H as well as the earlier correlation for *n*-octane are summarized in Table II in terms of h and $(\Delta G_s^\circ)_0$ values (slopes and intercepts) in eq 10, together with the r and σ measures of the goodness of the statistical fits. For comparison of eq 9 and 10, the table also includes the r values for the corresponding correlations with π^*. The values of (R) in the third column of the table are empirical parameters related to the solute radius, designed earlier by one of us[28] to provide best fits to the relationship $\Delta G_s^\circ = a(R) + b$ for the present solutes in the 25 hydroxylic and nonhydroxylic solvents studied earlier.

It is seen in Table II that, as with *n*-octane, the ΔG_s° terms for all of the nondipolar solutes show much better linear regression with the solvent δ_H values than with the corresponding π^* parameters. Correlation coefficients for the regressions with δ_H are all higher than 0.960 and 13 of the 15 are higher than 0.975. For the corresponding correlations with π^*, the r values range from as low as 0.73 to no higher than 0.94. Further, the signs of the coefficients of δ_H are positive in all instances, indicating that for all of the solutes the ΔG_s° term becomes increasingly endogenic with increasing solvent dipolarity.

We have also found that the $(\Delta G_s^\circ)_0$ and h terms in eq 10 for the 15 solutes in Table II are in both cases linear with the solute molecular volumes, if we use as measures of the latter term the solute $(R)^3$ values. Plots of the data are shown in Figure 3. The least-squares regression equations are,

$$(\Delta G_s^\circ)_0 = 3.01 - 0.23(R)^3 \text{ kcal/mol} \qquad (11)$$

$$n = 15, r = 0.985, \sigma = 0.56 \text{ kcal/mol}$$

$$h = 0.195 + 0.0077(R)^3 \qquad (12)$$

$$r = 0.969, \sigma = 0.022$$

Correlations would have been equally good if other published estimates of the solute radii had been used. For example, the radii of Cramer[30] lead to $n = 10$, $r = 0.956$ in eq 12; the radii of de Ligny[31] lead to $n = 12$, $r = 0.985$.

Equation 12 confirms that, as might be expected on the assumption that there is little or no solute/solvent interaction effect, the magnitude of the h term (slope) in eq 10 increases linearly with increasing size of the solvent cavity which must be created to enclose the solute. The decreasing $(\Delta G_s^\circ)_0$ with increasing solute molecular volume in eq 11 derives in part from the increasing h term (a calculational artifact), but also reflects in part the fact that, from Abraham's standard state definition (see footnote 38 of ref 28), the ΔG's are from gas phase to solution, and include an increasingly exogenic gas phase → pure liquid phase term.

Multiple Parameter Correlations with δ_H and π^*. Based on the above findings, it is reasonable to conclude that free energies of solution or of transfer of solutes to pure solvents involve one or both of two distinct dependences: an exogenic term in π^* as a measure of dipolar solute/solvent interaction effects, and an exogenic term in δ_H as a measure of the work in separating the solvent molecules to create a cavity for the solute (this latter term evidently including significant contributions from the solvent dipole/solvent dipole interactions which are disrupted). With the nondipolar solutes of Table II, the dominant term, by far, is that involved in cavity formation, whereas for a charged solute like $Et_4N^+I^-$ the solute/solvent interaction term dominates.

It follows logically that solvatochromic equations for ΔG_s°'s of solutes of intermediate dipolarity should be expected to include statistically significant terms in both π^* and δ_H. We have therefore carried out single and multiple parameter correlations for nitromethane solute in 12 *select solvents* (data in Table I)[32] and obtained the following regression equations:

$$\Delta G_s^\circ(\text{NM}) = 1.79 - 0.33\delta_H \text{ kcal/mol} \qquad (13)$$

$$r = 0.740, \alpha = 99^{33}$$

$$\Delta G_s^\circ(\text{NM}) = -0.095 - 2.47\pi^* \text{ kcal/mol} \qquad (14)$$

$$r = 0.962, \alpha = 99.999^{33}$$

$$\Delta G_s^\circ(\text{NM}) = -1.72 + 0.23\delta_H - 3.65\pi^* \text{ kcal/mol} \qquad (15)$$

$$r = 0.992, \alpha_{(\delta_H)} = 99.9, \alpha_{(\pi^*)} = 99.99, \alpha_{\text{Ehr}} = 99.999^{33}$$

One of us had earlier reported[34] a correlation of a related property of nitromethane (gas/liquid partition coefficients) with π^* of select solvents. The correlation coefficient was about like that in eq 14. It is therefore particularly noteworthy that eq 15 shows a highly significant improvement in the goodness of fit (as measured by α_{Ehr})[33] over either single parameter correlation. Further, as required by the above rationale, the term in $*\pi$ in eq 15 is exogenic and that in δ_H is endogenic. As an example of the magnitudes involved, for transfer of nitromethane solute from hexane to Me_2SO [$\Delta\Delta G_s^\circ$(calcd) = −2.62 kcal/mol, $\Delta\pi^* = 1.08$, $\Delta\delta_H = 5.73$], the calculated solute/solvent interaction term is −3.94 kcal/mol and the cavity term is +1.32 kcal/mol.

It is also noteworthy in view of their similar molecular volumes (NM, $\bar{V} = 54$ mL/mol; C_2H_6, $\bar{V} = 55$ mL/mol) that the h value of 0.23 for nitromethane in eq 15 is quite close to that of 0.25 for ethane in Table II. This leads us to believe that the π^* and δ_H parameters may be sufficiently "fine tuned" to allow (at least semiquantitative) discrimination between the important contributing terms to ΔG_s°. In a future paper we shall describe additional multiparameter correlations with π^* and δ_H of solution properties of a large number of solutes of varying dipolarity.

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In conclusion, we wish to suggest that we may have succeeded in unravelling the contributions of the cavity term and the dipolar solute/solvent interaction term to the free energy of solution by the procedure of restricting consideration to the nonprotonic aliphatic *select solvents*.[8] Others taking a similar approach may have failed because they encountered complications of hydrogen bonding by protonic solvents, and variable solute dipole/solvent induced dipole (polarizability) effects in the case of aromatic solvents. However, Abraham and Reisse[35] have succeeded in subtracting out the cavity term contributions to a number of processes in hydroxylic solvents by direct calculation.

We also wish to point out that many earlier correlations (generally of poor precision) with the Hildebrand solubility parameter have been for properties which include important dipolar solute/solvent interaction effects. We suggest that such properties are likely to be much better correlated by the π^* parameter, by dual solvent parameter equations in π^* and δ_H, or, where solute/solvent hydrogen bonding effects also apply, by equations involving linear combinations of π^*, δ_H, α, and β, as appropriate (α and β being measures of solvent hydrogen bond donor acidity and hydrogen bond acceptor basicity).[3] Thus, we have recently demonstrated[36] that solvent effects on some fluorescence probes, which had been related to solvent δ_H values by Coosemans and co-workers[37] and by Reeves and co-workers,[38] were much better correlated by multiple linear regression equations in π^*, α, and β.

We are grateful to a referee for pointing out that Krishnan and Friedman[39] have calculated enthalpies of solution of gaseous nondipolar solutes by using an equation that contains an electrostatic term in μ and a term derived from solubility parameter theory; compare our two-term equation in π^* (also proportional to μ in the case of the select solvents)[8] and δ_H. We acknowledge that this earlier approach of Krishnan and Friedman is conceptually not dissimilar to ours. Unfortunately, it is not possible to make any direct comparison between the two methods because Krishnan and Friedman dealt with enthalpies of solution, whereas in the present work it is the free energy of solution that is the relevant thermodynamic parameter. It does deserve comment, however, that the earlier workers had suggested that solute/solvent electrostatic interaction terms account for ca. 15–30% of the $\Delta H_s°$ values for *n*-hexane solute in dipolar solvents, whereas our analysis indicates that the contributions of solute/solvent interactions to $\Delta G_s°$ values of the alkanes are essentially nil.

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Electronic Structure of Free-Base and Transition-Metal Tetraazaporphyrins

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Abstract: Electronic energy levels and charge distribution for metal-free tetraazaporphyrin (H_2TAP) and transition-metal tetraazaporphyrins (MTAP, M = Fe and Cu) have been calculated in the one-electron Hartree–Fock–Slater model. Spin densities were obtained for CuTAP and FeTAP. Optical transitions, photoelectron binding energies, and hyperfine fields are presented for comparison with available data and previous theoretical works. Density difference contour maps and a Mulliken atomic orbital population analysis are used to discuss similarities to the related porphine systems. Most bonding features expected on the basis of semiempirical calculations and chemical intuitive arguments are observed in the electron density maps. A transition-state procedure was used to investigate several optical transitions as well as one-electron binding energies. Spectroscopic features are in fair agreement with experiment and with extended-Hückel model results of Gouterman et al.

A variety of metallophthalocyanines (MPc) exist, consisting of essentially planar molecules of D_{4h} symmetry having the central metal ion coordinated to four nitrogen ligands. MPc's differ from the chemically similar porphyrins in replacing four carbon atoms of the porphin ring by nitrogen. The substitution of N (and other species) on the carbon skeleton modifies the interaction between the metal ion d electron and valence-electron states of the ring to a significant degree. One goal of the present work is to begin a systematic study of these metal d/ring interactions. These studies have some relevance to experimental interest in one-dimensional conducting stacks of MPc's, as found in "molecular metals" like $NiPcI_x$.[1]

The phthalocyanines are valuable as commercial pigments, due to intense absorption bands in the visible region. Theoretical models based upon semiempirical calculations have been able to explain most features of the optical spectra, but require the use of adjustable parameters.[2-5] Recently, good quality gas-phase photoelectron spectra for a number of Pc's have become available.[6]

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