Linear Solvation Energy Relationships. Part 1.[1] Solvent Polarity–Polarizability Effects on Infrared Spectra

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The linear solvation energy relationship (LSER) concept is shown to apply to i.r. spectra. Solvatochromic shifts of a variety of X = O, C–Cl, and O–H · · · B stretching frequencies and solvent effects on absorption intensities are linear with solvent π^*-values. Values of s in the solvatochromic equation, $\bar{\nu} = \bar{\nu}_0 + s\pi^*$, are related to chromophore structures.

IN an earlier paper,[2] we used solvatochromic comparisons of u.v.–visible spectral data to construct a π^* scale of solvent polarity–polarizabilities, so named because it derived from and was best fitted to correlate solvent effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions. This π^*-scale was intended to serve, together with an α-scale of solvent HBD (hydrogen bond donor) acidities [3] and a β-scale of solvent HBA (hydrogen bond acceptor) basicities,[4,5] toward rationalization of medium effects on many types of spectral and chemical properties and reactivity parameters (*XYZ*'s) through a general equation of the form,

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

a somewhat less general but frequently applicable equation,

$$XYZ = XYZ_0 + s\pi^* + a\alpha \qquad (2)$$

and an equation applicable in a few special cases,

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \qquad (3)$$

The s, a, and b terms in equations (1)—(3) are measures of the responses of *XYZ* to changing solvent polarity, HBD acidity and HBA basicity.

We reported that, when a number of simple strategems were used to exclude effects of hydrogen bonding to or by the solvents,† under which conditions equations (1)—(3) reduce to (4).

$$XYZ = XYZ_0 + s\pi^* \qquad (4)$$

Solvatochromic displacements of absorption maxima ($XYZ = \nu_{\text{max.}}$) for 47 $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of uncharged molecules showed very good to excellent linear regressions with solvent π^*-values. We also pointed out that equation (4) also applies to many other types of free-energy proportional *XYZ*'s including $n \rightarrow \pi^*$ electronic spectra, i.r., e.s.r., and n.m.r. spectral data, heats and free energies of solution and of transfer between solvents, and logarithms of rate and equilibrium constants.[2] With the linear solvation energy relationships involving these other *XYZ*'s, however, the r and SD measures of statistical fit were significantly better when the correlations were restricted to families of solvents with similar polarizability characteristics, *i.e.* (a) non-chlorinated aliphatic solvents, (b) polychlorinated aliphatics, and (c) aromatic solvents. In a subsequent communication,[6] we reported that correlations were better still (average $r > 0.985$) if restricted to a selected set of *ca.* 30 aliphatic solvents for which π^* values are very nearly proportional to molecular dipole moments.

Although they are now used to correlate all sorts of properties, equations (1)—(4) are referred to as the *solvatochromic equations*, α, β, and π^* as the *solvatochromic parameters*, *a*, *b*, and *s* as the *solvatochromic coefficients*, and the overall data analysis procedure as the *solvatochromic comparison method* to mark the fact that they were initially designed to correlate solvent effects on u.v.–visible spectra. In the present paper we use the solvatochromic comparison method to rationalize solvent polarity–polarizability effects on i.r. spectra.

The concept of linear solvation energy relationships (LSER'S) requires that solvents should exert parallel polarity–polarizability effects on different types of properties. That LSER's apply to i.r. spectra was first pointed out by Allerhand and Schleyer,[7] who reported that solvent shifts of various types of X=O stretching frequencies are proportional to solvent shifts of X–H · · · B stretching frequencies, *i.e.* of proton donor groups already engaged in inter- or intra-molecular hydrogen bonding. Based on this proportionality, they proposed an empirical linear free-energy relationship for the correlation of solvent sensitive i.r. vibration frequencies,

$$(\nu^\circ - \nu^s)/\nu^\circ = aG \qquad (5)$$

where ν° is the stretching frequency in the vapour phase, ν^s the observed frequency in a solvent, a a function of the particular i.r. vibration of a given molecule, and G a function of the solvent only. An arbitrary G value of 100 was assigned to methylene chloride to fix the scale, and values of G for 20 additional solvents were determined from the best fit of solvent shifts for a number of X=O and X–H · · · B stretching vibrations. In effect, although not used to correlate other types of *XYZ*'s, Allerhand and Schleyer's set of G values comprised an i.r.-based solvent polarity scale, similar in concept to our u.v.-based π^* scale. Values of G and π^* are compared in Table 1.

As follows further from the linear solvation energy relationship concept, we have found that, when hydrogen bonding effects are eliminated (by excluding the HBD

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† With hydrogen bond acceptor solvents ($\beta \neq 0$), correlations were limited to non-hydrogen bond donor indicators ($b = 0$); with hydrogen bond donor solvents ($\alpha \neq 0$) correlations were limited to non-hydrogen bond acceptor indicators ($a = 0$)

solvents, $CHCl_3$, and CH_2Cl_2, about which see below), Allerhand and Schleyer's G-values are nicely linear with our π^*-values (shown in the Figure). For the 15 non-HBD solvents for which G and π^* values have been reported, the regression equation is given by (6). If the

TABLE 1

Solvent π^* and G values

No [a]	Solvent [b,c]	π^*	G [d]
(1)	n-Hexane (SSS)	−0.081	44
(2)	Cyclohexane (SSS)	0.000	49
(3)	Triethylamine (SSS)	0.140	62
(5)	Di-n-butyl ether (SSS)	0.239	61
(6)	Carbon tetrachloride	0.294	69
(7)	Diethyl ether (SSS)	0.273	64
(8)	Toluene	0.535	74
(9)	1,4-Dioxan	0.553	86
(11)	Ethyl acetate (SSS)	0.545	
(14)	Benzene	0.588	80
(17)	Anisole	0.743	
(18)	Acetone (SSS)	0.683	
(20)	1,2-Dichloroethane	0.807	95
(21)	Dichloromethane	0.802	100
(24)	Pyridine	0.867	94
(29)	Dimethyl sulphoxide (SSS)	1.000	108 [e]
(30)	Chloroform	0.760	106
(32)	Nitromethane (SSS)	0.848	99
(43)	Tetrachloroethylene	0.277	64
(44)	1,1,2,2-Tetrachloroethane	0.948	
(50)	Acetonitrile (SSS)	0.713	93

[a] Solvent numbering is the same in all papers of this series. [b] Includes solvents used in all correlations in this paper. A more complete list of π^*-values is given in ref. 2. [c] SSS = selected solvent set; see text. [d] Ref. 7. [e] Not included in Table of G-values in ref. 7, but discussed in text.

$$G = 56.2\,\pi^* + 49.8,\ r = 0.986,\ \text{SD} = 3.4 \qquad (6)$$

correlation is limited to the eight solvents in the *selected solvent set* (for which π^* is proportional to μ) which are common to both scales, the goodness of statistical fit of the correlation improves significantly, the regression equation becoming that shown in (7).

$$G = 59.0,\pi^* + 49.4,\ r = 0.996,\ \text{SD} = 2.3 \qquad (7)$$

It is also seen in the Figure that the G-values for chloroform and methylene chloride are larger than called for by equation (6). A likely reason is that type-A hydrogen bonding † by these HBD solvents to the X=O and O–H $\cdots$ B oxygens of Allerhand and Schleyer's indicator compounds led to larger frequency shifts than required by the solvent polarity effects alone. The $\Delta\Delta G$ terms [the increases in the G-values attributable to hydrogen bonding; $\Delta\Delta G = G_{\text{obs}} - G_{\text{calc}}$ (eqn. 6)] are 13.5 for $CHCl_3$ and 5.1 for CH_2Cl_2.

As shown here with the G-scale, an important use of the solvatochromic comparison method and the solvatochromic equations and parameters has been in unravelling solvent polarity from hydrogen bonding effects. Similar separations of effects for HBD solvents have been reported [3] for Dimroth and Reichardt's $E_T(30)$-scale,[8] Brooker and his co-workers' χ_R-scale,[9] and Brownstein's S-scale of solvent polarities,[10] and will be demonstrated in a future paper [11] for Kosower's Z-scale,[12] Gutmann and Mayer's 'acceptor numbers' (AN),[13] and Napier and Knauer's e.s.r-based A_N-scale.[14] Although represented as 'solvent polarity' scales (except AN, which is represented as a measure of hydrogen bonding equivalent of Lewis acidity), all of these, when applied to HBD solvents, measure linear combinations of solvent polarity and type-A hydrogen bonding effects.

Individual Correlations.—Solvatochromic displacements of 25 single and double bond i.r. stretching frequencies of various types are correlated with solvent π^*-values in Table 2. Correlation equations are given for (a) all non-HBD solvents in which $\bar{\nu}$ values have been reported in the cited references and π^*-values are known, and (b) solvents of the *selected solvent set* (SSS in the Table) for which $\pi^* = K\mu$.[6] Together with the solvatochromic equations and measures of the goodness of the statistical fits, the Table contains $-\Delta\Delta\nu$ results (enhanced lower energy shifts relative to the correlation equations) for the two HBD solvents, chloroform and methylene chloride.

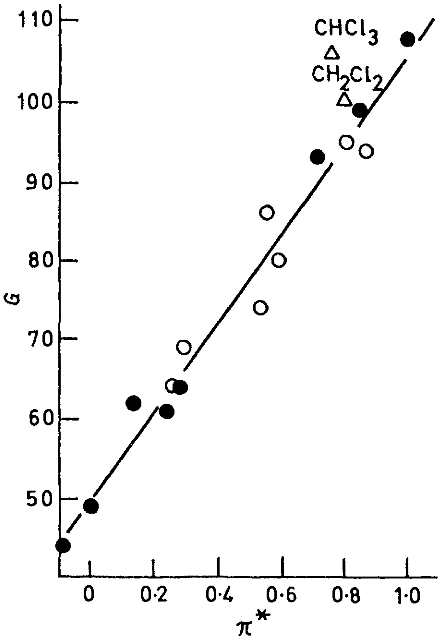

FIGURE Allerhand and Schleyer's G values plotted against solvent π^*-values. ● = Select solvent set, ○ = other solvents, and Δ = HBD solvents

It is seen that the statistical fits of the 'all data' correlations in Table 2 are quite respectable. All r-values are >0.90, 23 of the 25 are >0.95, and 15 are >0.97. Also, the two r-values which are <0.95 do not reflect lower SD's, but result instead from the lower s-values (slopes) in the regression equations (see Davis and Pryor's instructive discussion of measures of goodness of fit in linear free energy relationships).[15] It is also seen that the goodness of the fits improves significantly for the *select solvent set* (SSS) correlations. All r-values are >0.96, and 7 of 13 are >0.99.

Solvent Polarity Effects on Infrared Spectra.—Some interesting solvent effects on i.r. stretching frequencies

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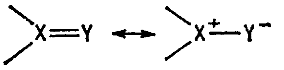
† In type-A hydrogen bonding, the solvent is HBD acid (electron acceptor) and the solute HBA base (electron donor); the converse applies in type-B hydrogen bonding.

are seen on intercomparison of the solvatochromic equations in Table 2. Most structure effects on i.r. stretching frequencies of X–Y and X=Y bonds have been rationalised in terms of canonical structures (I)—(IV), with factors which favour the charge-separated structures (II) and (IV) lowering the effective bond orders, hence ' loosening ' the linkages and shifting the absorption bands to lower frequencies (lower energies). Solvent effects can be rationalized in similar terms.



(I) (II)

$$\overset{\delta-}{\text{-X}}\text{—}\overset{\delta+}{\text{Y}} \longleftrightarrow \text{-X—Y} \longleftrightarrow \overset{\delta+}{\text{-X}}\text{—}\overset{\delta-}{\text{Y}}$$

(IVa) (III) (IVb).

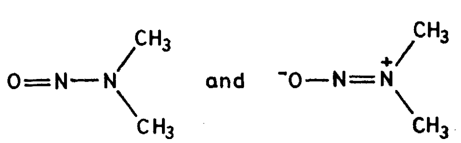
(e.g. O–H) (e.g. C—Cl)

Thus, dielectric stabilization of (II) and (IV) relative to (I) and (III) accounts for the shifts of most single and double bond stretching frequencies to lower energies in the more polar solvents (negative sign of *s*). Also, relative magnitudes of the —*s* values for acetone (19), dimethylformamide (20), and methyl acetate (21) carbonyl stretching frequencies are readily explained on the basis that polar solvents stabilize canonical structure (VI) relative to (V). This further lowers the C–O bond order and the vibration energy, with the effect increasing the greater the contribution of (VI) to the total resonance hybrid, *i.e.*, X = Me_2N > MeO > Me.

$$\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—X} \quad \text{—} \quad \text{-}\overset{\overset{\text{O}^-}{|}}{\text{C}}\text{=X}^+$$

(V) (VI)

The positive sign of *s* for the N–N stretching band of dimethylnitrosamine (15), although converse to the other frequency shifts, can be explained by similar considerations. Here the contributing canonical structures are,



(15a) (15b)

Increasing solvent polarity favours charge-separated canonical structure (15b) relative to (15a), hence increasing the N–N bond order, ' tightening ' the linkage, and shifting ν to higher frequencies. Such reasoning would also suggest a high negative *s*-value for the N=O bond of (15). Although insufficient data were available for inclusion in Table 2, the fragmentary results (r = 0.995 for four data points) [16] indicate that $s = -28.7$, appreciably higher than the —*s* values for the N=O stretching frequencies of methyl nitrite (13) and isopropyl nitrite (14).

In u.v.–visible spectral correlations with solvent π*-values, we observed [2] that bulky substituents on the indicator served to insulate the chromophore from the solvent, thereby effectively increasing the size of the solvent cavity and decreasing the effect of π* on $\nu_{max.}$ (lower —*s* values). A similar steric effect seems to apply to solvatochromism in the i.r. region. Thus, we can rationalize the lower —*s* values for the C–Cl stretching frequencies of isobutyl chloride relative to n-propyl chloride, and for the S=O stretching frequency of diphenyl relative to dimethyl sulphoxide. Further, we can also explain the lower —*s* values for the *cis* relative to the *trans* N=O stretching frequency of methyl nitrite and for the *gauche* relative to the *trans* C–Cl frequencies in the alkyl halides. That we do not observe such a progression toward lower *s*-values for the C=O stretching frequencies of acetone, acetophenone, and benzophenone may result from competition of this effect with the (V)—(VI) effect.

As with the u.v.–visible spectral correlations,[2] these reasonable variations of *s* with systematic structural changes lend confidence that this solvatochromic parameter may come to serve as a useful and meaningful indicator of the interaction of an i.r. vibration with its cybotactic environment. For example, one would expect a greater solvent sensitivity for a symmetrical than for an antisymmetrical stretching frequency. Relative *s*-values could therefore be useful tools in band assignment.

It also deserves comment that, in contrast with the very good linear regressions of the C–Cl stretch frequencies of n-propyl and isobutyl chloride with solvent π*-values, the comparable bands for methylene chloride and chloroform show poor correlation with π*. For CH_2Cl_2 sym, $r = 0.74$, for asym, $r = 0.90$; for $CHCl_3$ sym, $r = 0.33$, for asym, $r = 0.66$.[17] This is readily explained by the fact that some of the solvents included in the correlations were HBA bases, and that these stretching frequencies for the HBD indicators probably depend on solvent β-values as well as π*-values.

Solvent Hydrogen Bonding Effects.—Charge delocalization from X or Y in canonical structures (II) and (IV) also serves toward stabilization of these contributors to the resonance hybrids, and results in shifts to lower energies for the stretching vibrations. Thus, type-B hydrogen bonding by indicator protons to HBA solvents leads to delocalization of the positive charge in structure (IV; X = H), with consequent lower energies for bonded relative to non-bonded Y–H stretching frequencies. Similarly, type-A bonding by protic solvents to –C–O–, C=O, S=O, and P=O oxygens leads to delocalization of the negative charges in structures (II; Y = O) and (IV; Y = O), again lowering the overall X–Y bond orders, and shifting the $\bar{\nu}$'s to lower frequencies (as is observed for *most* bands in Table 2).

The $\Delta\Delta\bar{\nu}$ terms for CH_2Cl_2 and $CHCl_3$ in Table 2 reflect the enhanced solvatochromic effects caused by type-A hydrogen bonding by these HBD solvents to the HBA indicators, with the relative magnitudes suggesting that chloroform is 2.5—3.5 times as strong an HBD acid as methylene chloride. Also, values of $-\Delta\Delta\bar{\nu}/\bar{\nu}$ can serve as rough measures of hydrogen bond acceptor strengths at the bonding sites. The $-\Delta\Delta\bar{\nu}(CHCl_3)/\bar{\nu}$ terms for the various types of stretching vibrations are (all values $\times 10^{-3}$): bonded O–H, 3—8; S=O, 5—6; P=O, *ca.* 5; and C=O, 1—3. These relative values are consistent with the rankings of compounds containing such substituents on the β [4,5] and pK_{HB} scales of HBA basicity.[18]

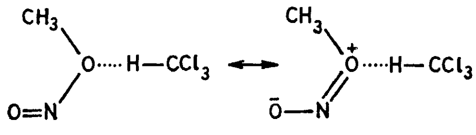
TABLE 2

Correlations of i.r. spectral data with the π^*-scale of solvent polarity–polarizabilities

$\bar{\nu} = \bar{\nu}_0 + s\pi^*$			All data in cm^{-1}					$\Delta\Delta\bar{\nu}$		
	Stretch band	Solvents [a]	$\bar{\nu}_0$	*s*	*r*	SD	*n*	$CHCl_3$	CH_2Cl_2	Ref.
(1)	n-Propyl chloride, *trans* C–Cl	All	734.2	−18.70	0.981	1.2	10			17
		SSS	733.8	−18.47	0.997	0.6	7			
	gauche C–Cl	All	655.3	−14.19	0.972	1.0	10			
		SSS	654.7	−13.81	0.998	0.3	7			
(2)	Isobutyl chloride, *trans* C–Cl	All	734.6	−14.91	0.982	0.9	10			17
		SSS	734.1	−14.54	0.997	0.5	7			
	gauche C–Cl	All	691.5	−13.91	0.978	0.9	10			
		SSS	691.1	−13.62	0.997	0.4	7			
(3)	$CH_3OCH(CH_3)CH_2CH_2OH$, bonded O–H	All	3 552.0	−50.46	0.989	2.7	7 [b]	−17.6	−7.5	7
(4)	$CH_3CHOH{-}CH_2CHOH{-}CH_3$, bonded O–H	All	3 553.4	−54.90	0.992	2.6	7 [c]			7
(5)	Methanol–ether, bonded O–H	All	3 517.2	−49.81	0.994	1.9	7 [b]	−28.3	−8.3	7
(6)	Phenol–ether, bonded O–H	All	3 359.2	−75.86	0.993	3.0	7 [b]	−13.4	−7.4	7
(7)	Methanol dimer, bonded O–H	All	3 545.8	−70.49	0.995	2.2	5 [b]	−10.2	−4.7	7
(8)	Dimethyl sulphoxide, S=O	All	1 083.0	−29.59	0.983	2.0	11 [c]	−5.6		16
(9)	Diphenyl sulphoxide, S=O	All	1 056.4	−13.00	0.938	1.7	12 [c]	−6.5		16
		SSS	1 055.6	−11.16	0.981	1.1	5			
(10)	Thionyl chloride, S=O	All	1 041.2	−9.40	0.974	0.7	11 [d]			16
(11)	Phosphorus oxychloride, P=O	All	1 310.4	−16.89	0.981	1.2	8 [d]			16
(12)	$(CH_3)_2HPO$, P=O, band 1	All	1 291.2	−26.09	0.957	2.7	10 [c]	−6.4		16
		SSS	1 291.3	−30.48	0.992	1.6	6			
	band 2	All	1 271.8	−16.97	0.928	2.3	10 [c]	−4.9		
		SSS	1 272.8	−20.89	0.991	1.1	6			
(13)	Methyl nitrite, *trans* N=O	All	1 665.5	−22.48	0.961	2.6	6 [b,e]	+6.6	+2.5	16
	cis N=O	All	1 614.4	−10.12	0.962	1.1	6 [b,e]	+7.0	+3.7	
(14)	Isopropyl nitrite, trans N=O	All	1 650.0	−21.42	0.957	2.6	7 [c,e]	+3.4		16
(15)	$(CH_3)_2N{-}N{=}O$, $>$N–N	All	1 024.0	+31.72	0.961	2.9	9 [d]			16
(16)	Acetophenone, C=O	All	1 696.4	−13.23	0.960	1.3	16 [c]	−3.3		*g*
		SSS	1 696.2	−12.71	0.981	1.0	7			
(17)	Benzophenone, C=O	All	1 670.2	−12.20	0.982	0.8	16 [c]	−2.9		*g*
		SSS	1 670.3	−11.64	0.991	0.6	7			
(18)	Cyclohexanone, C=O	All	1 723.4	−18.68	0.973	1.4	17 [c,f]	−4.2		*h*
		All	1 725.2	−18.90	0.955	2.0	16 [c]	−5.8		*g*
		SSS	1 724.9	−19.40	0.960	2.1	7			
(19)	Acetone, C=O	All	1 723.3	−12.63	0.961	1.2	16 [c]	−1.7		*g*
		SSS	1 723.2	−12.15	0.978	1.2	7			
(20)	Dimethylformamide, C=O	All	1 694.5	−22.80	0.972	1.9	16 [c]	−4.2		*g*
		SSS	1 694.2	−23.55	0.993	1.1	7			
(21)	Methyl acetate, C=O	All	1 753.9	−16.63	0.957	1.7	16 [c]	−5.3		*g*
		SSS	1 754.2	−15.36	0.967	1.6	7			

[a] All includes non-chlorinated aliphatics, polychlorinated aliphatics, and aromatic solvents. SSS = Selected solvent set; see text and ref. 6. [b] CH_2Cl_2 and $CHCl_3$ excluded from correlations; behave as HBD solvents. [c] $CHCl_3$ excluded from correlations and/or CH_2Cl_2 included. [d] $CHCl_3$ and $CHCl_3$ included in correlations. Do not behave as HBD acid solvents as indicator is evidently an insufficiently strong HBA base. [e] Ether excluded; spectrum obviously influenced by an impurity. [f] Tetrahydrofuran result obviously in error and excluded from correlation. Also, it is assumed that the ether and dioxan data are inverted due to a misprint. [g] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 14. [h] K. C. James and M. Ramgoolan, *Spectrochim. Acta*, 1975, 31A, 599.

The positive signs of the $\Delta\Delta\bar{\nu}$ terms for the N=O stretching bands of methyl and isopropyl nitrite in CH_2Cl_2 and $CHCl_3$ (converse to the signs for all other bands in Table 2 and converse to the directions of polarity effects) are of particular interest in that they may provide evidence regarding the sites of hydrogen bonding in these compounds. The nitrite esters contain two possible HBA sites, one at the R–O–N oxygen, the other at the N=O oxygen. As with the other X=O stretching frequencies, association at the double bonded oxygen should lower the N=O bond order and shift ν to lower energies. If hydrogen bonding were at the single bonded oxygen, however, it would be expected to stabilize solvated canonical structure (13a) relative to (13b), hence raising the N=O bond order and shifting ν to *higher* energies (as is observed).



(13a) (13b)

The relative $-\Delta\Delta\bar{\nu}$ values for (3)—(7) of Table 2 are also of some interest in that they seem to illustrate an effect transmitted through a number of σ and hydrogen bonds, *i.e.* the HBA basicity of the oxygen of the hydrogen bond donor hydroxy-group in $R'{-}O{-}H \cdots OR_2$ (the italicized oxygen) depends not only on R′ ($\Delta\Delta\bar{\nu}$ greater for methanol–ether than for phenol–ether), but also on R ($\Delta\Delta\bar{\nu}$ greater for methanol–ether or 3-methoxybutan-1-ol than for methanol dimer), with alkyl groups exerting their normal base-strengthening effects.

Solvent Effects on Absorption Intensities.—In addition to shifting the position of $\bar{\nu}$, the solvent used also influences the absorption intensity (AI) of an i.r. band, the AI usually increasing with increasing solvent polarity, and sometimes changing by more than a factor of two. We have found that the linear solvation energy relationship concept also applies to logarithmic absorption intensities.

Solvent effects on AI's for several nitriles and acetone have been reported by Tanaka, Tanabe, and Kamada.[19] For propionitrile in 11 solvents whose π^*-values are known

$$\log \mathrm{AI} = 0.519\,\pi^* + 2.560, \quad r = 0.955, \ \mathrm{SD} = 0.058 \quad (8)$$

and in five solvents of the selected solvent set

$$\log \mathrm{AI} = 0.556\,\pi^* + 2.579, \quad r = 0.997, \ \mathrm{SD} = 0.021 \quad (9)$$

For acetone in 10 solvents (ex $CHCl_3$)

$$\log \mathrm{AI} = 0.100\,\pi^* + 1.179, \quad r = 0.932, \ \mathrm{SD} = 0.015 \quad (10)$$

and in five SSS solvents

$$\log \mathrm{AI} = 0.095\,\pi^* + 1.184, \quad r = 0.961, \ \mathrm{SD} = 0.013 \quad (11)$$

Again the lower r-values in equations (10) and (11) relative to equations (8) and (9) do not arise from lesser precision of the correlations, but rather from lower s-terms (slopes).[15] Why the five-fold variation between the solvent sensitivity of the acetone absorption intensity and that for propiononitrile is a question which merits further study.

In concluding this discussion, we wish to acknowledge that certain of the effects we have described in our correlations with π^* were observed earlier by Allerhand and Schleyer [7] in their correlations with G. Thus, these workers commented that bulky substituents seem to lessen solvent sensitivity ' by diminishing access of the solvent to the chromophore group.'

It also deserves mention (and we are grateful to a referee for directing our attention to the fact) that Kagarise [20] had shown earlier that methylene chloride forms weak hydrogen bonded complexes with HBA bases. Further, Whetsel and Kagarise have demonstrated that chloroform forms 1 : 1 and 2 : 1 complexes with carbonyl compounds.[21]

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