

A Unified Scale for Understanding and Predicting Non-specific Solvent Polarity: A Dynamic Cavity Model

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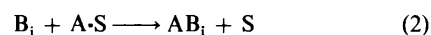
Data, which have provided the basis for several different solvation scales, are combined to produce a universal scale of solvent polarity. Over three hundred spectral shifts for 30 probe molecules and 31 solvents are fitted to an equation of the form $\Delta\chi = S'P + W$. Electronic transitions, NMR chemical shifts and EPR hyperfine coupling constants all fit to the same solvent S' values. The data fit a wide variety of probe shapes and sizes leading to the proposal of a dynamic cavity model. The success of the approach is attributed to the exclusion from the fit of data involving (i) concentrated solutions of polar probes in non-polar solvents, (ii) specific donor-acceptor interactions and (iii) polar solvents that exist as rotamers which solvate to different extents. A generalized scale of non-specific solvating ability is offered for use in the analysis of solvent effects. Deviations of results from those predicted by this scale signal unusual behaviour and experiments can be designed to identify the cause. Compared to the current practice of fitting results to one of the several 'solvation' scales now available, a scale of non-specific solvation can provide the basis for a more detailed understanding of reactivity and spectroscopy in solution.

The pronounced influences that solvents have on all areas of chemistry, *e.g.* reaction rates and physicochemical properties, have prompted extensive studies aimed at producing a scale of solvent polarity. In research from this laboratory,¹ solvation has been subdivided into specific and non-specific effects. Specific effects include localized donor-acceptor interactions involving specific orbitals. These interactions have been successfully correlated, predicted and understood with the E and C equation.² Non-specific effects involve the interactions modelled by the reaction field or Kirkwood approaches.³ Solvent reorganization occurs to form a cavity which accommodates the solute with stabilization resulting from the interaction of the solute dipole (and induced dipole) with the internal relative permittivity of the cavity. Solvent rearrangement and induced dipole moments tend to create an internal permittivity different from the bulk relative permittivity. In view of the difficulty in determining the radius of the cavity formed and the internal permittivity of the organized solvent region, the quantitative application of these models to the interpretation of solvent effects is not possible without making assumptions. Accordingly, empirical approaches have been employed to arrive at solvent polarity parameters to describe solvent effects.⁴⁻¹²

A large number of scales of solvent polarity have been offered in the literature.⁴⁻¹³ Most differ in significant ways so an investigator correlating complex chemical phenomena can usually find one that works. Unfortunately, this approach provides little insight about the system, *e.g.* why do the other scales not work. One reason for the diversity of scales arises from the fact that all reported studies include both specific and non-specific solvation effects. If one parameter can incorporate both effects, there would be no need to have two effects. In one of the more recent approaches three solvent parameters, which involve different physicochemical properties, are offered to treat solvation.¹³ In the work described here, we shall show that a common single parameter scale of solvent polarities can be derived, which incorporates data from most of the literature systems by excluding specific interactions. The resulting parameters allow one to predict non-specific solvation interactions for a wide variety of solutes and solvents.

The selection of systems that do not involve specific donor-acceptor interactions in the measurement is difficult because of

our incomplete understanding of weak interactions. One approach that has been used to detect subtle, specific interactions in solvents is referred to as EPS (Elimination of Solvation Procedure).¹⁴ A series of reactions [eqns. (1) and (2)]



is studied in poorly solvating media and then in basic, slightly polar solvents, S . The symbol $A \cdot S$, indicates that the acid is complexed by the solvent. Subtracting eqn. (2) from eqn. (1) leads to eqn. (3). The specific interaction of A with the solvent has



been subtracted from eqn. (3). Providing that B and B_i do not undergo specific donor-acceptor interactions with the solvent, only non-specific solvation remains. The experimental enthalpy of reaction for eqn. (3), for a given base pair, is a constant¹⁴ in a wide variety of solvents in which only non-specific interactions exist. Since dispersion interactions are a function of the molecular weight of the solute, non-specific solvation of the products equals that of the reactants and cancels.

An interesting result is obtained when the solvent is varied and the system does not produce the constant enthalpy expected for eqn. (3). This finding indicates that either specific interactions between B_i and the donor solvent exist or non-specific solvation enthalpies of the product and reactant fail to cancel. In this manner, specific interactions and unusual non-specific solvation are detected. Carbon tetrachloride forms weak adducts (*ca.* 1 kcal mol⁻¹)* with donors that have large C_B numbers, *e.g.* nitrogen or sulfur donors. Charge transfer complexes involving π -donor and π -acceptor interactions are observed^{1c} between solvents with π -systems *e.g.* C_6H_6 , or o - $Cl_2C_6H_4$ and solutes with π -systems. There is evidence to suggest that these donor-acceptor interactions involve pyridine with benzene and *o*-dichlorobenzene and even occur between pyridine molecules in liquid pyridine.¹⁵ These studies^{14c} also

* 1 cal = 4.184 J.

Table 1 S' parameters for solvents

No.	Solvent	S'	No.	Solvent	S'
1	$C_6H_{12}^a$	0.15	17	$(C_2H_5O)_3PO^c$	(2.25)
2	$(C_2H_5)_3N^c$	(0.4)	18	$C_6H_5C(O)CH_3^{a,b}$	2.34
3	CCl_4	0.87	19	$C_6H_5CN^{a,b}$	2.44
4	CS_2^c	(0.89)	20	$C_6H_5NO_2^{a,b}$	2.47
5	$(n-C_4H_9)_2O^d$	1.03	21	$(CH_3)_2CO$	2.47
6	$C_6H_5CH_3^{a,b}$	1.11	22	$[(CH_3)_2N]_3PO$ (HMPA)	2.56
7	$C_6H_6^{a,b}$	1.18	23	$CH_3CON(CH_3)_2$	2.67 ^e
8	$(C_2H_5)_2O$	1.21	24	$\underline{CH_2CH_2CH_2CONCH_3}$	2.68
9	$O(CH_2CH_2)_2O$	1.49	25	$HCON(CH_3)_2$	2.78
10	$C_6H_5OCH_3^{a,b,c}$	(1.66)	26	Butyrolactone ^{a,c}	(2.8)
11	$C_6H_5Cl^{a,b}$	1.67	27	$(CH_2)_4SO_2^{a,d}$	(2.8) ^d
12	$(CH_2)_5O$	1.68	28	$(CH_3)_2SO$	3.00
13	$(CH_2)_4O$	1.69	29	CH_3CN	3.12
14	$CH_3C(O)OC_2H_5$	1.80	30	CH_3NO_2	3.12
15	Quinoline ^a	(2.0) ^d	31	$CH_3C(H)OCO^{a,d}$	(3.2) ^d
16	$C_5H_5N^{a,b}$	2.16		$\begin{array}{c} \\ CH_2O \\ \end{array}$	

^a Not included in fit. See Table 4. ^b π -Acceptor solutes must be avoided e.g. p -NO₂C₆H₄X. ^c Limited data available. ^d Calculated from betaine shift only. ^e Adjusted by adding additional data. See Table 4.

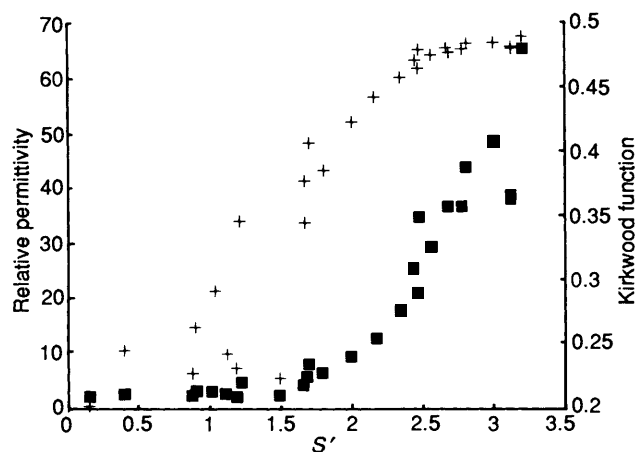


Fig. 1 Plot of S' vs. the relative permittivity (■) and the Kirkwood Function (+)

show that non-specific solvation of the products and reactants do not cancel when 1,2-dichloroethane is used as a solvent. Systems that are well behaved in *o*-dichlorobenzene are not when 1,2-dichloroethane is used as a solvent. The non-specific solvating properties of 1,2-dichloroethane are complicated by shifts in the equilibrium that exists between staggered and eclipsed forms of this solvent molecule when it solvates. This solvent is also capable of forming hydrogen bonds to donor solutes. It is best to avoid 1,2-dichloroethane for the quantitative determination of solvent effects. Keeping the above points in mind, systems are selected from extensive literature data to develop a scale of solvent polarities.

Results and Discussion

Determination of the Basic Set of Parameters.—Using a least squares minimization program described in the literature,¹⁵ measured physicochemical properties (χ) of systems that cannot undergo a specific interaction with the donor solvent are fitted to eqn. (4) where S' is a solvent polarity parameter,

$$\Delta\chi = PS' + W \quad (4)$$

P a solute parameter that indicates the susceptibility of the solute probe to polarity and W a non-zero intercept at $S = 0$.

All the data used in the fit have been used to establish or support a variety of different solvation scales in the literature. This analysis differs from earlier literature analyses by omitting systems that consist of π -solutes in π -solvents, covalent donors, e.g. C_5H_5N , in halogenated solvents, e.g. CCl_4 , 1,2-dichloroethane and 1,2-dimethoxyethane. The complications encountered in these solvent systems were discussed above. In other analyses of solvent effects, *n*-alkanes are assumed to be nearly ideal non-solvating solvents with some scales anchored to this point. The alkanes are such poor solvents that aggregation of solutes can be a problem. Instead of the solute being solvated by alkane, it is solvated by another solute molecule. Accordingly, alkanes have been omitted from this fit and are assigned S' values below 0.2.

One hundred and sixty-two relevant literature values were found that conform to the above requirements. Sixteen solvents and eighteen probes were utilized. In order to obtain a solution for the forty P , S' and W values from the 162 simultaneous equations of the form of eqn. (4), one S' value must be fixed. Dimethyl sulfoxide is assigned a value of 3.00 to anchor the scale. The resultant best fit parameters P , S' and W are given in Tables 1 and 2. Substitution of these values into eqn. (4) yields the calculated values of the physicochemical measurements reported in Table 3. The experimental values are reproduced very well. The average deviation for most of the solvents is of the order of magnitude of the experimental error in the measurements.

The data fit encompasses electronic transitions (entries 1–7, 13, 15, 17, 18) that are red and blue shifted, ¹⁹F and ¹⁵N chemical shifts (8–12) and EPR coupling constants (14 and 16). It is most impressive that the same solvent, S' , parameters accommodate solutes with geometries that have cage structures, or are flat, pyramidal, or octahedral. The solvents cover a wide range of polarity as do the solutes.

Meaning of the Parameters.—The parameters show a general trend with relative permittivity, dipole moment and the Kirkwood function $(\epsilon - 1)/(2\epsilon + 1)$. The latter function is recommended by Chastrette *et al.*¹³ as a characteristic solvent parameter to account for polarity. Fig. 1 is a plot of S' vs. the relative permittivity and the Kirkwood function, with both of these quantities giving an equally poor quantitative fit. The relative permittivity correlates well with S' for values above $\epsilon = 9$ while the Kirkwood function correlates better for values below 0.45. Molar refraction and refractive index plot up

Table 2 *P* and *W* parameters for probes (tentative parameters in parentheses)

No.	Probe (Symbol)	<i>P</i>	<i>W</i>
1	ν ; <i>N,N</i> -diethyl-4-nitroaniline ^a (NNE4NO2AN)	-1.03	27.55
2	ν ; <i>N,N</i> -dimethyl-2-nitroaniline ^b (NNM2NO2AN)	-0.67	25.29
3	ν ; <i>N,N</i> -diethyl-3-methyl-4-nitroaniline ^c (NNE3M4NO2AN)	-1.07	27.80
4	ν ; <i>N,N</i> -dimethyl-2-nitrotoluene ^b (NNM2NO2TOL)	-0.65	24.73
5	ν ; 4-nitroanisole (4NO2ANISOL) ^a	-0.87	34.33
6	ν ; 4-(2,4,6-triphenyl-1-pyridyl)-2,6-diphenylphenoxide ^d (BETAINE)	6.01	27.23
7	ν ; Bis-2-[2-pyridylbenzylidene-3,4-dimethylaniline, biscyano iron(II)] ^e (Burgess)	(1.19)	(13.03)
8	$\delta^{19}\text{F}$; 1,4-difluorobenzene ^f (F2C6H4)	-0.26	6.95
9	$\delta^{19}\text{F}$; 1-fluoro-4-trifluoromethylbenzene ^f (CF3C6H4F)	0.27	5.07
10	$\delta^{19}\text{F}$; 1-fluoro-4-nitrobenzene ^f (NO2C6H4F)	0.41	9.14
11	$\delta^{19}\text{F}$; 1-cyano-4-fluorobenzene ^f (CNC6H4F)	0.34	8.85
12	$\delta^{15}\text{N}$; 1-methylsilatrane-N(CH ₂ CH ₂ O) ₃ SiCH ₃ (N15) ^g	2.70	-0.29
13	ν ; 1-ethyl-4-methoxycarbonylpyridinium iodide (<i>Z</i> value) ^{h,n}	8.74	44.05
14	<i>A_N</i> ; di- <i>tert</i> -butyl nitroxide ⁱ (ANTBUNO)	0.167	14.175
15	ν ; <i>N,N</i> -dimethylthiobenzamide <i>S</i> -oxide [C6H5CSO(NMe)2] ^j	(0.77)	(79.69)
16	<i>A_N</i> ; 4-amino-2,2,6,6-tetramethylpiperidine 1-oxide (ANPIPNO) ⁱ	0.167	14.251
17	ν ; α -[4-(<i>N,N</i> -dimethylamino)phenyl]iminoacetoacetanilide (Me2NC6H4NCR2) ^k	(-1.49)	(71.39)
18	ν ; Pyridine <i>N</i> -oxide (NUPYNO) ^l	0.20	35.42
19	$\delta^{31}\text{P}$; triethylphosphine oxide (C ₂ H ₅) ₃ PO ^{m,n}	-3.48	2.76
20	$\delta^{14}\text{N}$; pyridine 1-oxide C ₅ H ₅ NO ^{m,n}	3.12	75.82
21	ν ; 4-cyanoformyl-1-methylpyridinium oximate ^m	(2.05)	(68.7)
22	ν ; isoquinolinium ylides (CO ₂ Et) ^m	(2.13)	(57.6)
23	ν ; Brookers VII (Non-polar) ^m	-3.17	52.3
24	ν ; Ni(tfd)(phen) ^m	2.92	49.45
25	ΔE ; Nickel(II) <i>N,N</i> '-diazobenzene aminotroponeiminate (NiAmtrop) ^{m,n}	-0.543	3.76
26	$\delta^{19}\text{F}$; 1-fluoro-4-methoxybenzene	-0.088	11.67
27	$\delta^{19}\text{F}$; 4-fluorobenzaldehyde	0.300	8.30
28	$\delta^{19}\text{F}$; 1-fluoro-4-phenoxybenzene	-0.269	7.62
29	$\delta^{19}\text{F}$; 1-fluoro-4-methylthiobenzene	0.110	4.63
30	$\delta^{19}\text{F}$; 1-fluoro-4-methylbenzene	-0.065	5.52

^a These parameters fit the electronic transition energy in kK (1kK = 1000 cm⁻¹). Data from ref. 4b. The average deviation is 0.11 and the percentage fit is 4.9% for NNE4NO₂AN and 0.06 and 3.4% for 4NO₂ANISOL. Estimated experimental error is 0.1 kK. ^b Parameters to calculate the transition energy in kK. Data from ref. 4b. The average deviation is 0.075 and the percentage fit is 5.0% for NNM2NO₂AN and 0.075 and 5.5% for NNM2NO₂TOL. Estimated experimental error is 0.1 kK. ^c Parameters to calculate the transition energy in kK. Data from ref. 4. The average deviation omitting acetone is 0.11 and the percentage fit is 4.7% and the experimental error is 0.1 kK. ^d Parameters to calculate ν kcal mol⁻¹. Data from ref. 5a. The ν value in hexane is 30.9, the average deviation is 0.15 and the percentage fit 1%. ^e Parameters to calculate ν kK. Data from ref. 6. The average deviation is 0.05, the percentage fit is 5.7% and the experimental error in 0.1 kK. ^f Parameters to calculate the ¹⁹F chemical shift relative to ¹⁹F as an internal standard. Average deviation 0.05 and percentage fit is 8.5% for F₂C₆H₄. Average deviation 0.08 and 13%; 0.06 and 6.4%; 0.03 and 4% for the CF₃, NO₂ and CN derivatives, respectively. The experimental error is 0.08 ppm.^g ^g Parameters to calculate the ¹⁵N chemical shift in ppm for 1-methylsilatrane relative to cyclohexane. Data from ref. 17, average deviation 0.29 and percentage fit 4.5%. ^h Transition energy in kcal mol⁻¹. Data from refs. 5a and 7. In most instances, the transition is concentration dependent and has been extrapolated to zero solute concentration. The average deviation is 0.1 and the percentage fit 0.8%. ⁱ The nitrogen hyperfine coupling constant in cm⁻¹ × 10⁻⁴. Data from ref. 18 where *A_N* is reported as the line separation in gauss which is actually *A_N*/*gβ*. Since *g* is not given, it is assumed to be 2.0047 and *β* = 4.6686 × 10⁻⁵ kcal mol⁻¹/G. Multiplying the line separation by 9.3591 × 10⁻⁵ gives *A_N* in units of cm⁻¹ × 10⁻⁴. The fit is run by multiplying the numbers by 10⁴. The average deviation is 0.035 and the percentage fit 9.7% and 0.038 and 10%. Estimated experimental error is 0.01 × 10⁻⁴ cm⁻¹. ^j Transition energy in kcal mol⁻¹. Data from ref. 20. The average deviation is 0.17 and the percentage fit 4.1%. ^k Transition energy in kcal mol⁻¹. Data from ref. 19. The average deviation is 0.17 and the percentage fit 5.9%. ^l Transition energy in kK. Data from ref. 20. The average deviation is 0.09 and the percentage fit 15%. ^m Not included in the fit. See Tables 6 and 7. ⁿ Probes not to be used in non-polar solvents (*S* = 0.2–2).

poorly with *S'*. Fig. 2 is a plot of the dipole moment vs. *S'*. A smooth curve results when gas phase values are employed but the relation is not linear. A general trend is evident when solution dipole moments are used with considerable scatter at the high dipole moment end. Dioxane is a much better solvating solvent than the overall dipole moment would suggest for its orientation toward a dipole puts a polar group close to it. Thus, even with the specific donor–acceptor interactions essentially eliminated, these bulk solvent properties do not provide quantitative measures of non-specific solvation. No linear combination of the Kirkwood function and refractive index (F1 and F2 of ref. 13) could be found to reproduce the *S'* values for solvents used in Table 2 data fit. The best combination gave an average deviation of 0.3 in the *S'* value.

The problem of estimating solvent polarity from a molecular property can be appreciated by considering what is involved in the process of solvation on the molecular level. The fact that the

same *S'* values can be used for a wide range of solute shapes and sizes suggests a dynamic cavity model. The solvent rearranges to form a cavity to accommodate the solute. The cavity forms so as to maximize the non-specific solvent–solute interactions at the expense of solvent–solvent interactions. The cavity size varies with solute dimensions as well as the strength of the non-specific interaction with strong interactions leading to short solute–solvent distances. As is the case for the *E* and *C* parameters, a solute–solvent distance function is also incorporated into the *P* and *S'* parameters. Solvent orientation and induced dipoles make up the effective internal relative permittivity, of the cavity. All of these factors cause *S'* and *P* to differ from the dipole moment or relative permittivity or any pure solvent property. When the solvent–solvent and/or solute–solute interactions are comparable to solute–solvent, aggregation of the solute occurs. When they are much larger, the solute is insoluble.

The excellent fit of data for solutes of widely varying dipole moments to a single *S'* parameter suggests that both the dipole

Table 3 Calculated and experimental frequencies for various solute molecules

Solute ^b	Solvent	ν_{expt}	ν_{calc}	Deviation	<i>n</i> value ^a	
NNE4NO2AN	(C ₂ H ₅) ₂ O	26.52	26.31	-0.21	1.0000	
	CH ₃ COOC ₂ H ₅	25.74	25.70	-0.04	1.0000	
	(CH ₃) ₂ CO	25.22	25.01	-0.21	0.5000	
	(CH ₂) ₅ O	25.74	25.82	0.08	1.0000	
	(CH ₂) ₄ O	25.61	25.81	0.20	1.0000	
	(C ₂ H ₅) ₃ N	27.14	27.16	0.02	1.0000	
	HCON(CH ₃) ₂	24.66	24.69	0.03	1.0000	
	CH ₃ CON(CH ₃) ₂	24.75	24.86	0.11	1.0000	
	(CH ₃) ₂ SO	24.30	24.47	0.17	1.0000	
	(C ₂ H ₅ O) ₃ PO	25.19	25.24	0.05	1.0000	
	O(CH ₂ CH ₂) ₂ O	25.77	26.02	0.25	1.0000	
	CH ₂ (CH ₂) ₂ CONCH ₃	24.60	24.65	0.05	1.0000	
	CCl ₄	26.70	26.65	-0.05	1.0000	
	HMPA	24.75	24.91	0.16	1.0000	
	NNM2NO2AN	CH ₃ COOC ₂ H ₅	24.27	24.08	-0.19	1.0000
(CH ₂) ₄ O		24.20	24.15	-0.05	1.0000	
HCON(CH ₃) ₂		23.41	23.42	0.01	1.0000	
(CH ₃) ₂ SO		23.18	23.27	0.09	1.0000	
(C ₂ H ₅ O) ₃ PO		23.83	23.78	-0.05	1.0000	
O(CH ₂ CH ₂) ₂ O		24.11	24.29	0.18	1.0000	
CH ₂ (CH ₂) ₂ CONCH ₃		23.40	23.39	-0.01	1.0000	
CCl ₄		24.67	24.70	0.03	1.0000	
NNE3M4MO2AN		(C ₂ H ₅) ₂ O	26.70	26.51	-0.19	1.0000
		CH ₃ COOC ₂ H ₅	26.01	25.88	-0.13	1.0000
	(CH ₃) ₂ CO	24.41	25.17	0.76	10.0000	
	(CH ₂) ₅ O	26.08	26.00	-0.08	1.0000	
	(CH ₂) ₄ O	25.91	25.99	0.08	1.0000	
	HCON(CH ₃) ₂	24.91	24.83	-0.08	1.0000	
	CH ₃ CON(CH ₃) ₂	24.97	25.01	0.04	1.0000	
	(CH ₃) ₂ SO	24.60	24.60	0.00	1.0000	
	(C ₂ H ₅ O) ₃ PO	25.38	25.40	0.02	1.0000	
	O(CH ₂ CH ₂) ₂ O	25.94	26.21	0.27	1.0000	
	CH ₂ (CH ₂) ₂ CONCH ₃	24.81	24.79	-0.02	1.0000	
	CCl ₄	26.85	26.87	0.02	1.0000	
	T-BASE	27.80	27.80	0.00	2.0000	
HMPA	25.00	25.06	0.06	1.0000		
NNM2NO2TOL	CH ₃ COOC ₂ H ₅	23.77	23.56	-0.21	1.0000	
	(CH ₂) ₄ O	23.66	23.63	-0.03	1.0000	
	HCON(CH ₃) ₂	22.87	22.92	0.05	1.0000	
	(CH ₃) ₂ SO	22.79	22.78	-0.01	1.0000	
	(C ₂ H ₅ O) ₃ PO	23.30	23.27	-0.03	1.0000	
	O(CH ₂ CH ₂) ₂ O	23.59	23.77	0.18	1.0000	
	CH ₂ (CH ₂) ₂ CONCH ₃	22.87	22.90	0.03	1.0000	
	CCl ₄	24.15	24.16	0.01	1.0000	
	4NO2ANISOL	(C ₂ H ₅) ₂ O	33.45	33.28	-0.17	1.0000
		CH ₃ COOC ₂ H ₅	32.79	32.76	-0.03	1.0000
(CH ₂) ₄ O		32.79	32.85	0.06	1.0000	
HCON(CH ₃) ₂		32.05	31.90	-0.15	1.0000	
CH ₃ CON(CH ₃) ₂		32.05	32.05	0.00	1.0000	
(CH ₃) ₂ SO		31.70	31.71	0.01	1.0000	
(C ₂ H ₅ O) ₃ PO		32.41	32.37	-0.04	1.0000	
O(CH ₂ CH ₂) ₂ O		32.89	33.04	0.15	1.0000	
CH ₂ (CH ₂) ₂ CONCH ₃		31.90	31.87	-0.03	1.0000	
CH ₃ CN		32.47	31.61	-0.86	10.0000	
CCl ₄		33.56	33.57	0.01	1.0000	
HMPA		31.90	32.09	0.19	1.0000	
BETAINE		(C ₂ H ₅) ₂ O	34.60	34.48	-0.12	1.0000
	CH ₃ COOC ₂ H ₅	38.10	38.04	-0.06	1.0000	
	(CH ₃) ₂ CO	42.20	42.06	-0.14	1.0000	
	(CH ₂) ₄ O	37.40	37.43	0.03	1.0000	
	HCON(CH ₃) ₂	43.80	43.97	0.17	1.0000	
	(CH ₃) ₂ SO	45.00	45.27	0.27	1.0000	
	O(CH ₂ CH ₂) ₂ O	36.00	36.17	0.17	1.0000	
	CH ₃ CN	46.00	46.00	0.00	1.0000	
	CCl ₄	32.50	32.50	0.00	1.0000	
	CH ₃ NO ₂	46.30	45.99	-0.31	1.0000	
	C ₅ H ₅ N	40.20	40.21	0.01	1.0000	

Table 3 (continued)

Solute	Solvent	ν_{expt}	ν_{calc}	Deviation	n value ^a
BURGESS	(CH ₃) ₂ CO	16.00	15.97	-0.03	1.0000
	HCON(CH ₃) ₂	16.29	16.35	0.06	1.0000
	(CH ₃) ₂ SO	16.60	16.61	0.01	1.0000
	CH ₃ CN	16.78	16.75	-0.03	1.0000
F2C6H4	(C ₂ H ₅) ₂ O	6.65	6.63	-0.02	1.0000
	(CH ₃) ₂ CO	6.30	6.31	0.01	1.0000
	(CH ₂) ₄ O	6.40	6.51	0.11	1.0000
	HCON(CH ₃) ₂	6.20	6.23	0.03	1.0000
	(CH ₃) ₂ SO	6.15	6.17	0.02	1.0000
	CCl ₄	6.80	6.72	-0.08	1.0000
	CH ₃ NO ₂	6.25	6.14	-0.11	1.0000
	C ₅ H ₅ N	6.35	6.39	0.04	1.0000
CF3C6H4F	(C ₂ H ₅) ₂ O	5.45	5.40	-0.05	1.0000
	(CH ₃) ₂ CO	5.80	5.74	-0.06	1.0000
	(CH ₂) ₄ O	5.65	5.53	-0.12	1.0000
	HCON(CH ₃) ₂	5.90	5.83	-0.07	1.0000
	(CH ₃) ₂ SO	5.90	5.89	-0.01	1.0000
	CH ₃ CN	5.90	5.92	0.02	1.0000
	CCl ₄	5.15	5.31	0.16	1.0000
	CH ₃ NO ₂	5.75	5.92	0.17	1.0000
	C ₅ H ₅ N	5.70	5.66	-0.04	1.0000
NO2C6H4F	(C ₂ H ₅) ₂ O	9.65	9.63	-0.02	1.0000
	CH ₃ COOC ₂ H ₅	9.85	9.87	0.02	1.0000
	(CH ₃) ₂ CO	10.10	10.14	0.04	1.0000
	(CH ₂) ₄ O	9.75	9.83	0.08	1.0000
	HCON(CH ₃) ₂	10.30	10.27	-0.03	1.0000
	(CH ₃) ₂ SO	10.30	10.36	0.06	1.0000
	CH ₃ CN	10.35	10.41	0.06	1.0000
	CCl ₄	9.55	9.50	-0.05	1.0000
	CH ₃ NO ₂	10.55	10.41	-0.14	1.0000
CNC6H4F	(C ₂ H ₅) ₂ O	9.20	9.26	0.06	1.0000
	CH ₃ COOC ₂ H ₅	9.45	9.46	0.01	1.0000
	(CH ₃) ₂ CO	9.70	9.69	-0.01	1.0000
	(CH ₂) ₄ O	9.45	9.43	-0.02	1.0000
	HCON(CH ₃) ₂	9.80	9.80	0.00	1.0000
	(CH ₃) ₂ SO	9.85	9.87	0.02	1.0000
	CH ₃ CN	9.90	9.91	0.01	1.0000
	CCl ₄	9.20	9.15	-0.05	1.0000
	CH ₃ NO ₂	9.95	9.91	-0.04	1.0000
M15	CH ₃ COOC ₂ H ₅	4.60	4.56	-0.04	1.0000
	(CH ₃) ₂ CO	6.00	6.37	0.37	1.0000
	(CH ₂) ₄ O	4.40	4.29	-0.11	1.0000
	HCON(CH ₃) ₂	7.30	7.22	-0.08	1.0000
	(CH ₃) ₂ SO	8.40	7.81	-0.59	1.0000
	CH ₃ NO ₂	7.80	8.13	0.33	1.0000
	HMPA	6.50	6.63	0.13	1.0000
Z-VALUE	(CH ₃) ₂ CO	65.70	65.61	-0.09	1.0000
	(CH ₂) ₄ O	58.80	58.87	0.07	1.0000
	HCON(CH ₃) ₂	68.50	68.38	-0.12	1.0000
	CH ₃ CON(CH ₃) ₂	66.90	66.92	0.02	1.0000
	(CH ₃) ₂ SO	71.10	70.27	-0.83	10.0000
	CH ₃ CN	71.30	71.33	0.03	1.0000
	CH ₃ NO ₂	71.20	71.32	0.12	1.0000
ANTBUNO	(C ₂ H ₅) ₂ O	14.35	14.38	0.03	1.0000
	(CH ₃) ₂ CO	14.53	14.59	0.06	1.0000
	(CH ₂) ₄ O	14.39	14.46	0.07	1.0000
	HCON(CH ₃) ₂	14.63	14.64	0.01	1.0000
	(CH ₃) ₂ SO	14.69	14.68	-0.01	1.0000
	O(CH ₂ CH ₂) ₂ O	14.46	14.42	-0.04	1.0000
	CH ₃ CN	14.66	14.70	0.04	1.0000
	CCl ₄	14.35	14.32	-0.03	1.0000
	CH ₃ NO ₂	14.75	14.70	-0.05	1.0000
C ₅ H ₅ N	14.61	14.54	-0.07	1.0000	
C6H5C(SO) NMe 2	(CH ₃) ₂ CO	81.80	81.60	-0.20	1.0000
	(C ₂ H ₅) ₃ N	80.00	79.99	-0.01	1.0000
	HCON(CH ₃) ₂	81.70	81.85	0.15	1.0000
	(CH ₃) ₂ SO	81.70	82.01	0.31	1.0000
	O(CH ₂ CH ₂) ₂ O	80.80	80.84	0.04	1.0000
	CH ₃ CN	82.40	82.11	-0.29	1.0000

Table 3 (continued)

Solute	Solvent	ν_{expt}	ν_{calc}	Deviation	n value ^a
ME2NC6H4NCR2	(C ₂ H ₅) ₂ O	69.90	69.59	-0.31	2.0000
	CH ₃ COOC ₂ H ₅	68.80	68.71	-0.09	2.0000
	(CH ₃) ₂ CO	67.70	67.71	0.01	2.0000
	(CH ₂) ₄ O	68.50	68.86	0.36	2.0000
	(C ₂ H ₅) ₃ N	70.90	70.82	-0.08	2.0000
	O(CH ₂ CH ₂) ₂ O	68.90	69.17	0.27	2.0000
	CH ₃ CN	66.90	66.74	-0.16	2.0000
	CH ₃ NO ₂	66.70	66.74	0.04	2.0000
	HMPA	67.60	67.57	-0.03	2.0000
	ANPIPNO	(C ₂ H ₅) ₂ O	14.43	14.45	0.02
(CH ₃) ₂ CO		14.62	14.66	0.04	1.0000
(CH ₂) ₄ O		14.48	14.53	0.05	1.0000
HCON(CH ₃) ₂		14.67	14.72	0.05	1.0000
(CH ₃) ₂ SO		14.76	14.75	-0.01	1.0000
O(CH ₂ CH ₂) ₂ O		14.54	14.50	-0.04	1.0000
CH ₃ CN		14.75	14.77	0.02	1.0000
CCl ₄		14.42	14.40	-0.02	1.0000
CH ₃ NO ₂		14.84	14.77	-0.07	1.0000
C ₅ H ₅ N		14.66	14.61	-0.05	1.0000
NUPYNO		(C ₂ H ₅) ₂ O	35.60	35.65	0.05
	CH ₃ COOC ₂ H ₅	35.84	35.77	-0.07	1.0000
	(CH ₂) ₄ O	35.71	35.75	0.04	1.0000
	(C ₂ H ₅) ₃ N	35.52	35.49	-0.03	1.0000
	HCON(CH ₃) ₂	35.91	35.97	0.06	1.0000
	CH ₃ CON(CH ₃) ₂	35.91	35.93	0.02	1.0000
	(CH ₃) ₂ SO	35.97	36.01	0.04	1.0000
	(C ₂ H ₅ O) ₃ PO	35.92	35.86	-0.06	1.0000
	O(CH ₂ CH ₂) ₂ O	35.78	35.71	-0.07	1.0000
	CH ₂ (CH ₂) ₂ CONCH ₃	35.78	35.97	0.19	2.0000
	CH ₃ CN	36.28	36.03	-0.25	1.0000
	HMPA	35.71	35.92	0.21	1.0000

^a Values of n are assigned to give different weights to three data points that are obviously out of line. An error could have been made in recording the value, solvents switched or some unusual solvation effect exists. ^b Solute abbreviations are defined in Table 2.

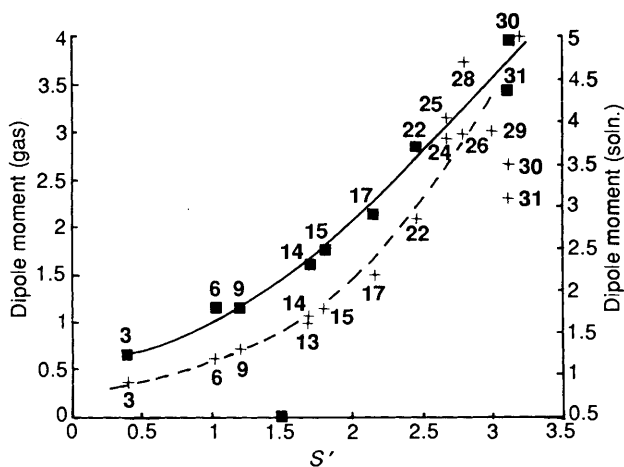


Fig. 2 Plot of S' vs. dipole moment. Gas phase values + CCl₄ or C₆H₆ solution.

and induced dipole contributions to non-specific solvation are incorporated in the parameters. The product term PS' enables the parameters to accommodate an induced moment. Thus, the individual parameters are viewed as reflecting a tendency to solvate, S' , and a susceptibility to respond in P . No single measured ground state property of the pure solute or solvent is expected to reflect this, just as no single molecular property is found to parallel the E and C parameters.

The value of W for the probes is the gas-phase value of the probe modified by any non-zero intercept contributions to the spectral shift at $S' = 0$. Most W values are close to the frequency in cyclohexanes plus $0.15 P$.

The understanding of solvation contributions to spectroscopic probes is simpler than understanding solvation contributions to enthalpies or free energies of solution. The energy required to rearrange the solvent to accommodate the solute does not contribute to the spectroscopy but does contribute to ΔG and ΔH . Thus, a different approach will be needed for this type of data which should include the SP term.

Application of the Model to New Solvents.—The model developed here is readily extended to new solvents. The measured properties are substituted into eqn. (4), with the probe parameters from Table 2. A least squares fit produces the S' value. The results for several solvents not included in the fit shown in Table 3 are given in Table 4. The results for cyclohexane ($S' = 0.15$), dibutyl ether ($S' = 1.03$) butyrolactone ($S' = 2.77$) and CS₂ ($S' = 0.89$) are satisfactory, with only limited data available on the latter three solvents.

The problems associated with referencing scales to a zero value for hexane is immediately evident. The average deviations of the probe fits, are contained in parentheses under hexane solvent in Table 4. Most of the hexane systems miss by more than the average deviation. In most instances, ν_{calc} in hexane does not agree with the $S' = 0$ intercept (W values) from the data fit. The complications are attributed to solute aggregation. This behaviour is in contrast to cyclohexane which gives an excellent fit to eqn. (4). The solvent 1,2-dimethoxyethane exists in *trans* and *gauche* isomers and fits poorly. A polar solute is expected to increase the *gauche* fraction and increase the effective S' value. This is consistent with a larger experimental Z value than calculated and smaller values for the other less polar probes.

The fit of the data for π -solvents is poor, supporting earlier¹

Table 4 Data fits for miscellaneous solvents

Solvent	Probe ^a	Average deviation	ν_{expt}	ν_{calc}	W
n-Hexane ($S' = \text{None}$) ^b	1	(0.11)	27.71	26.94	27.51
	2	(0.07)	25.38	24.95	25.26
	3	(0.11)	27.78	27.26	27.80
	4	(0.07)	24.88	24.40	24.70
	5	(0.06)	34.31	33.89	34.28
	6	(0.15)	30.90	30.28	27.43
	9	(0.08)	4.95	5.21	5.07
	10	(0.06)	9.00	9.35	9.15
	11	(0.03)	8.65	9.03	8.86
	14	(0.035)	14.164	14.260	14.175
	16	(0.030)	14.244	14.336	14.251
	17	(0.17)	71.20	70.63	71.32
	18	(0.09)	35.40	35.52	35.42
$\text{C}_5\text{H}_5\text{N}$ ($S' = 2.16$) ^c	1	—	(24.78)	(25.33)	—
	3	—	(24.97)	(25.64)	—
	5	—	(32.00)	(32.45)	—
	6	—	40.2	40.2	—
	8	—	6.35	6.39	—
	9	—	5.70	5.66	—
	10	—	(10.25)	(10.01)	—
	11	—	(9.80)	(9.59)	—
	13	—	(64.0)	(62.9)	—
	14	—	14.608	14.536	—
	16	—	14.609	14.610	—
C_6H_{12} ($S' = 0.15$)	1	—	27.40	27.38	—
	2	—	25.23	25.19	—
	3	—	27.62	27.65	—
	4	—	24.81	24.64	—
	5	—	34.13	34.21	—
	8	—	6.80	6.91	—
	9	—	5.05	5.11	—
	10	—	9.20	9.20	—
	11	—	8.95	8.90	—
	12	—	0.0	0.10	—
	15	—	79.90	79.81	—
	17	—	71.0	71.2	—
	18	—	35.37	35.45	—
$\text{C}_6\text{H}_5\text{C(O)CH}_3$ ($S' = 2.34$)	6	—	41.3	41.3	—
	14	—	14.565	14.563	—
	16	—	14.637	14.639	—
$(\text{C}_4\text{H}_9)_2\text{O}$ ($S' = 1.03$)	1	—	26.85	(26.49)	—
	5	—	33.56	33.44	—
	6	—	33.3	33.4	—
	18	—	35.6	35.6	—
	23	—	48.6	48.8	—
Butyrolactone ($S' = 2.77$)	1	—	24.67	24.70	—
	3	—	24.84	24.84	—
	5	—	31.95	31.91	—
$\text{CH}_3\text{C(O)N(CH}_3)_2$ ($S' = 2.67$)	1	—	24.75	24.80	—
	3	—	24.97	24.94	—
	5	—	32.05	32.01	—
	6	—	43.50	43.3	—
	13	—	66.90	67.4	—
	18	—	35.91	35.95	—
	23	—	43.0	44.1	—
$\text{C}_6\text{H}_5\text{Cl}$ ($S' = 1.67$) ^c	1	—	(25.38)	(25.54)	—
	6	—	37.5	37.3	—
	7	—	14.64	15.0	—
	9	—	5.50	5.53	—
	10	—	(10.05)	(9.82)	—
	11	—	(9.60)	(9.42)	—
	12	—	4.0	4.2	—
	14	—	14.480	14.454	—
	16	—	14.565	14.529	—
$\text{C}_6\text{H}_5\text{CN}$ ($S' = 2.44$) ^c	6	—	42.0	42.0	—
	8	—	6.35	6.32	—
	10	—	(10.45)	(10.13)	—
	11	—	(9.90)	(9.68)	—

Table 4 (continued)

Solvent	Probe ^a	Average deviation	ν_{expt}	ν_{calc}	W
$\text{C}_6\text{H}_5\text{OCH}_3$ ($S' = 1.66$) ^c	1	—	(25.31)	(25.84)	—
	3	—	(25.61)	(26.03)	—
	5	—	(32.41)	(32.89)	—
	6	—	37.2	37.2	—
	25	—	2.95	2.86	—
C_6H_6 ($S' = 1.18$) ^c	1	—	(25.60)	(26.13)	—
	2	—	(24.13)	(24.49)	—
	4	—	(23.67)	(23.96)	—
	5	—	(32.84)	(33.30)	—
	6	—	34.50	34.42	—
	7	—	14.47	14.44	—
	8	—	6.60	6.64	—
	9	—	(5.15)	(5.39)	—
	10	—	(9.45)	(9.62)	—
	11	—	(9.05)	(9.25)	—
	12	—	2.7	2.9	—
	13	—	(54.0)	(54.3)	—
	14	—	14.417	14.373	—
16	—	14.537	14.449	—	
$\text{C}_6\text{H}_5\text{NO}_2$ ($S' = 2.47$) ^c	6	—	42.0	42.2	—
	8	—	6.30	6.31	—
	9	—	5.70	5.74	—
	10	—	(10.50)	(10.14)	—
	11	—	(9.90)	(9.69)	—
12	—	6.8	6.4	—	
$\text{C}_6\text{H}_5\text{CH}_3$ ($S' = 1.11$) ^c	1	—	(25.87)	(26.41)	—
	2	—	(24.39)	(24.54)	—
	4	—	(23.80)	(24.01)	—
	6	—	33.9	33.9	—
	14	—	14.363	14.360	—
	16	—	14.470	14.436	—
25	—	3.16	3.16	—	
$\text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$ ($S' = \text{none}$) ^b	6	—	38.2	39.2	—
	13	—	62.1	61.4	—
	14	—	14.435	14.508	—
	16	—	14.530	14.581	—
CS_2 ($S' = 0.89$)	6	—	32.6	32.6	—
	14	—	14.309	14.325	—
	16	—	14.389	14.399	—

^a The probe number refers to the compound in Table 2. ^b The fit is so poor that no value is indicated. ^c Values in parentheses were omitted from the fit because of possible specific charge transfer interactions.

enthalpy-based conclusions of specific interactions, *i.e.* charge-transfer complexes, in these systems. Accordingly, the S' values on these systems are determined by omitting probes with π -systems. When the probes 1–5 are measured in π -solvents, they all have experimental values that are smaller than those calculated with parameters from the non- π -solvents fit. Betaine shows no complications from charge-transfer interactions in these solvents. Apparently, it is a poor π -acceptor and a poor π -donor. This is part of the reason that the S' parameters correlate well with $E_T(30)$, but poorly with π^* .

Probes 8–11 are π -solutes whose ^{19}F chemical shifts vary with solvent. 1,4-Difluorobenzene is the best behaved of these toward π -solvents, apparently being a weak donor and weak acceptor. The solvents ClC_6H_5 , CNC_6H_5 and $\text{NO}_2\text{C}_6\text{H}_5$ cause deviations in the NMR probes 9–11 in a direction opposite to benzene, pyridine, toluene and anisole. The role of the donor and acceptor may be reversed in these two solvent groups. This analysis serves as an illustration of the advantages of the S' and P approach. The lack of correlation with S' has detected a problem and signals the need for further study to understand the solution chemistry. These deviations are lost in the noise when parameters are

determined that average everything into one best-fit parameter.⁴

A quantitative test of specific π -complex formation can be provided by modifying eqn. (4) to incorporate specific donor–acceptor interactions with the E and C model leading to eqn. (5).

$$\Delta\chi = E_A^*E_B + C_A^*C_B + SP + W \quad (5)$$

Here $\Delta\chi$ is a general symbol for a physicochemical property and the asterisk indicates that the acceptor parameters are for a physicochemical property, while the E_B values are from the enthalpy scale. Of the π -systems in Table 4, E_B and C_B are known only for benzene. The number of systems that deviate are not extensive enough to attempt a data fit to determine the unknown E_A^* , C_A^* , E_B and C_B parameters needed to calculate the contribution from the specific interaction. However, since all the π -acceptors are expected to have similar C/E ratios, the conditions for a one-parameter treatment are met²¹ and eqn. (5) can be approximated by eqn. (6). The only unknowns are E_A^*

$$\Delta\chi = E_A^*B + SP + W \quad (6)$$

and B . Since $\Delta\chi - SP - W$ corresponds to the deviations

Table 5 Matrices of experiments and calculated (in parentheses) specific π -interactions
(a) π -Donor solvents

E_A^*	Probe	$B_{0.15}^\pi$				
		C_6H_6 0.77	C_5H_5N 0.78	$C_6H_5CH_3$ 0.77	$C_6H_5OCH_3$ 0.78	C_6H_5Cl 0.3
0.71	1	0.53 (0.55)	0.55 (0.55)	0.54 (0.54)	0.53 (0.55)	0.16 (0.21)
0.34	2	0.36 (0.27)	—	0.15 (0.26)	—	—
0.7	3	—	0.67 (0.55)	—	0.42 (0.55)	—
0.34	4	0.29 (0.27)	—	0.21 (0.26)	—	—
0.60	5	—	0.45 (0.47)	—	0.48 (0.47)	—
2.1	23	1.6 (1.6)	1.6 (1.6)	1.6 (1.6)	—	—

(b) π -Acceptor solvents

B	Probe	$E_{A\pi}^*$			
		C_5H_5N -0.28	C_6H_5Cl -0.26	C_6H_5CN -0.25	$C_6H_5NO_2$ -0.3
0	8	0.04 (0.0)	—	-0.03 (0.0)	+0.01 (0.0)
0	9	-0.03 (0.0)	+0.03 (0.0)	—	+0.04 (0.0)
1	10	-0.24 (-0.28)	-0.23 (-0.26)	-0.32 (-0.25)	-0.36 (-0.3)
0.79	11	-0.21 (-0.22)	-0.23 (-0.21)	-0.22 (-0.20)	-0.21 (0.12)
5.3	23	1.6 (1.5)	—	1.3 (1.3)	1.9 (1.6)
0.2	26	—	—	0.0 (-0.05)	-0.10 (-0.06)
2	27	-0.61 (-0.56)	—	—	-0.51 (-0.6)
0.14	28	0.04 (-0.04)	—	—	(-0.04)
0.41	30	-0.07 (-0.11)	—	—	-0.19 (-0.12)

shown for π - π systems in Table 4, these can be fitted to E_A^*B setting $B = 0.77$ for benzene. This corresponds²¹ to an estimated C/E ratio of 0.15 expected² for this type of complex. As seen in Table 5(a), the deviations in all instances can be calculated to within experimental error using the B values given for the donor solvents and the E_A^* values for the acceptor probes. Since benzene, toluene and anisole are donor solvents toward the fluorobenzenes, they are treated with the solvent π -donor parameters in Table 7(a).

In part (b) of Table 5, the ^{19}F NMR data is treated for acceptor solvents. Different parameters are needed for π -solvents when they behave as donors than apply when they behave as acceptors. Unfortunately, the ^{19}F solutes have only been studied in one donor solvent. These systems all show positive deviations but a second or third ^{19}F data point to provide a check on the calculated E_A^* value is not available.

The ^{19}F systems in Table 5(b) do not fit with the solvent π -donor parameters. These systems involve acceptor solvents and donor probes. Within experimental error, all show negative deviations in Table 4. The deviations can be reproduced using the E_A^* values derived for π -acceptor solvents and the B values derived for the π -donor probes. Probe 23 also gives evidence of a reversal of donor acceptor roles in these π -solute- π -solvent systems. The observed deviations for this probe are incompatible with the π -donor solvent parameters

in Table 5(a). They correlate well with the π -acceptor solvent parameters.

Since the deviations in Table 4 are small and the errors large, the E_A^* and B values reported for the specific donor-acceptor interaction parameters are tentative. The main purpose of this analysis is to illustrate that the deviations from non-specific solvation can be consistently interpreted with a quantitative donor-acceptor model for these π -systems.

Applications of the Model to New Probes.—There is a large amount of literature on systems that have been suggested as probes of solvation. Some show large variations in the measurement with probe concentration. Others involve NMR shifts employing an external standard. Still others use proton chemical shifts in which neighbour anisotropic contributions play a large role. The possible existence of factors other than solvation that could contribute to the measurement resulted in these systems not being used in Table 3 to derive parameters. They can be analysed, if interested, by employing the S' values reported here. New probes can be added to this correlation by studying them in solvents whose S' values are known. The S' values and measured properties are substituted into eqn. (4) to produce a series of simultaneous equations that are solved for P and W . Table 6 contains data fits for several systems, illustrating the application of the S' parameters to new probes. These

Table 6 Fit of other physicochemical probes to eqn. (4)

Probe	Solvent	Expt.	Calc.	Probe	Solvent	Expt.	Calc.	
19 ^a	(C ₂ H ₅) ₂ O	-1.6	-1.5	26 ^h	(CH ₃) ₂ SO	58.3	58.2	
	(CH ₂) ₄ O	-3.4	-3.1		HCON(CH ₃) ₂	57.8	57.6	
	O(CH ₂ CH ₂) ₂ O	(-4.6)	(-2.4)		(CH ₃) ₂ CO	57.0	56.7	
	(CH ₃) ₂ CO	-5.3	-5.8		C ₆ H ₅ N	56.8	(55.8)	
	CH ₃ C(O)N(CH ₃) ₂	-5.8	-6.5		(CH ₂) ₄ O	54.2	54.4	
	CCl ₄	-3.6	(-0.3)		CH ₃ CO ₂ C ₂ H ₅	54.7	54.7	
	HC(O)N(CH ₃) ₂	-6.8	-6.9		(C ₂ H ₅) ₂ O	(51.5)	(53.0)	
	CH ₃ CN	-8.0	-8.1		C ₆ H ₅ CH ₃	(50.8)	(52.7)	
	(CH ₃) ₂ SO	-8.22	-7.7		O(CH ₂ CH ₂) ₂ O	53.8	53.8	
	CH ₃ NO ₂	-8.7	-8.1					
	CH ₂ CH ₂ CH ₂ CONCH ₃	-5.7	-6.6					
	20 ^b	C ₆ H ₁₂ (saturated)	76.47		76.29	C ₆ H ₁₂	11.70	11.65
		(C ₂ H ₅) ₂ O (saturated)	78.78		79.60	O(CH ₂ CH ₂) ₂ O	11.45	11.54
CCl ₄ (saturated)		(80.84)	(78.54)	CCl ₄	11.50	11.59		
Dioxane		81.40	80.47	(CH ₃) ₂ CO	11.45	11.45		
(CH ₃) ₂ CO		82.85	83.54	(CH ₄) ₂ SO	11.35	11.30		
(CH ₃) ₂ SO		85.64	85.19	HCON(CH ₃) ₂	11.50	11.42		
21 ^c	CH ₃ CO ₂ C ₂ H ₅	72.5	72.4	(C ₂ H ₅) ₂ O	11.65	11.56		
	(CH ₃) ₂ CO	73.6	73.8	27 ⁱ	C ₆ H ₁₂	9.15	(8.67)	
	(CH ₃) ₂ SO	75.3	74.9		(CH ₂) ₄ O	9.15	9.14	
	CH ₃ CN	74.9	75.1		O(CH ₂ CH ₂) ₂ O	9.10	9.08	
			(CH ₃) ₂ CO		9.30	9.37		
22 ^d	CH ₃ CO ₂ C ₂ H ₅	61.5	61.5	(CH ₃) ₂ SO	9.50	9.53		
	(CH ₃) ₂ CO	62.8	62.9	HCON(CH ₃) ₂	9.45	9.46		
	HC(O)N(CH ₃) ₂	63.5	63.5	CH ₃ CN	9.65	9.56		
	(CH ₃) ₂ SO	64.1	64.0	28 ^j	C ₆ H ₁₂	7.45	(7.58)	
23 ^e	CH ₃ CN	45.7	(42.4)		(CH ₂) ₄ O	7.20	7.17	
	(CH ₃) ₂ CO	45.7	44.5		O(CH ₂ CH ₂) ₂ O	7.40	7.39	
	CH ₃ NO ₂	44.0	(42.4)		(CH ₃) ₂ CO	6.90	6.96	
	CCl ₄	48.7	49.5	(CH ₃) ₂ SO	6.85	6.82		
			(C ₂ H ₅) ₂ O	7.25	7.30			
			29 ^k	C ₆ H ₁₂	4.40	4.64		
O(CH ₂ CH ₂) ₂ O	48.4	47.6		(CH ₂) ₄ O	4.75	4.81		
CH ₃ CON(CH ₃) ₂	43.0	43.8		O(CH ₂ CH ₂) ₂ O	4.95	4.79		
HC(O)N(CH ₃) ₂	43.7	43.5		HCON(CH ₃) ₂	4.95	4.93		
(CH ₃) ₂ SO	42.0	42.8	(C ₂ H ₅) ₂ SO	4.80	4.76			
(C ₂ H ₅) ₂ O	48.3	48.5	30 ^l	(CH ₂) ₄ O	5.40	5.41		
CH ₃ CO ₂ C ₂ H ₅	47.2	46.6		O(CH ₂ CH ₂) ₂ O	5.50	5.42		
(CH ₂) ₄ O	46.6	46.9		CCl ₄	5.40	5.46		
				(CH ₃) ₂ SO	5.30	5.32		
Brookers IV (Polar) ^f	CH ₃ CN	53.7	53.6	(C ₂ H ₅) ₂ O	5.45	5.44		
	(CH ₃) ₂ CO	50.1	50.6					
	HCON(CH ₃) ₂	51.5	51.7					
24 ^g	CH ₃ CN	58.1	58.6					
	CH ₃ NO ₂	58.6	58.6					

^a Data from V. Mayer, V. Gutmann and W. Gerger, *Z. Chem.*, 1975, **106**, 1235. Calculated with $P = -3.48$, $W = 2.76$. Average deviation is 0.35 and the percentage fit is 5%. ^b Data from Witanowski *et al.*, *J. Magn. Reson.*, 1989, **83**, 351. Calculated with $P = 3.12$, $W = 75.82$. Average deviation is 0.6, fit 6.6%. ^c Data from R. A. Mackay and E. Z. Poziomek, *J. Am. Chem. Soc.*, 1972, **94**, 6107. Calculated with $P = 2.06$, $W = 68.7$. ^d Data from D. Dorohoi *et al.*, *An. Stiint. Univ. Al. Cuza Sect. 16*, 1974, **20**, 147. $P = 2.13$, $W = 57.6$. ^e Data from ref. 9. $P = -3.17$, $W = 52.3$, average deviation 0.6, fit 9%. ^f Data from ref. 9. $P = 5.54$, $W = 36.30$. ^g Data from T. R. Miller and I. G. David, *J. Am. Chem. Soc.*, 1973, **95**, 6970. The transition is mainly dithidene to phenanthroline in bis(trifluoromethyl)dithiolene 1,10-phenanthroline nickel(II). $P = 2.92$, $W = 49.45$, average deviation 0.16, fit 3.4%. ^h Data from ref. 8. $P = 0.088$, $W = 11.67$. ⁱ Data from ref. 8. $P = 0.300$, $W = 8.30$. ^j Data from ref. 8. $P = -0.269$, $W = 7.62$. ^k Data from ref. 8. $P = 0.110$, $W = 4.627$. ^l Data from ref. 8. $P = -0.065$, $W = 5.519$.

systems turn out to be well behaved but are limited in terms of data available or solute aggregation in certain solvents.

Triethylphosphine oxide has served as the basis for Gutmann's Acceptor number scale. By selecting solvents that are not expected to behave as acceptors, the probe is shown to have a sizable non-specific solvation component with a P value of 2.61, giving a standard deviation of 0.35 and a percentage fit of 5%. Non-polar solvents with P values below 2 had to be omitted from the fit. Aggregation of the triethylphosphine oxide is probably a problem in these solvents. The other probes in Table 6 also fit well and can be used with confidence over the range of S' values studied. In most instances, the literature data is limited or the fit is not quite as good as indicators with similar geometries in Table 2. Brookers VII is the interesting case of a non-polar probe that may be aggregating in polar solvents (S

> 3). The shift observed is not as large as expected in polar solvents. Such a deviation would result if a polar solvent were replaced, because of aggregation by another non-polar probe molecule.

Application of S' Parameters to Reactivity and Infrared Spectroscopy.—In view of the many potential complicating factors involved when a solvent is changed in a chemical reaction or in IR spectroscopy, these measurements have not been used in parameter determination. However, S' values can be used to analyse the extensive amount of data of this sort and if complications exist they can be detected. Experiments can then be designed to determine the cause of the unusual behaviour. The Brownstein Parameters,¹¹ χ , were derived mainly from reactivity and IR spectroscopy. Table 7 illustrates

Table 7

(a) Brownstein solvation parameters

Solvent	χ_{expt}^a	χ_{calc}^b	Solvent	χ_{expt}^a	χ_{calc}^b
CH ₃ CN	-0.104	-0.115	C ₆ H ₅ NO ₂	-0.218	(-0.156)
CH ₃ COOC ₂ H ₅	-0.210	-0.198	C ₆ H ₅ OCH ₃	-0.214	-0.207
(C ₂ H ₅) ₂ O	-0.277	-0.236	C ₆ H ₅ Cl	-0.182	-0.207
(C ₂ H ₅) ₃ N	-0.285	-0.287	C ₆ H ₅ CH ₃	-0.237	-0.242
CS ₂	-0.240	-0.256	C ₆ H ₆	-0.215	-0.238
CH ₃ NO ₂	-0.134	-0.115	C ₆ H ₁₂	-0.324	-0.303

(b) Ni Amtrop

Solvent	ΔE_{expt}^c	ΔE_{calc}^d	Solvent	ΔE_{expt}^c	ΔE_{calc}^d
CS ₂	2.34	(3.28)	C ₆ H ₅ CH ₃	3.16	3.16
C ₅ H ₅ N	2.64	2.59	CCl ₄	3.28	3.29
C ₆ H ₆	2.89	3.12	C ₆ H ₁₂	3.77	3.68
C ₆ H ₅ OCH ₃	2.95	2.86			

^a Ref. 11. ^b Calculated with $P = 0.063$ and $W = -0.312$. The average deviation is 0.02 and the percentage fit is 9%. ^c Ref. 22. ^d Calculated with $P = -0.543$ and $W = 3.76$. Average deviation is 0.08 and the percentage fit is 7%.

the fit of S' -values to χ . The percentage fit is large (9%), but indicative of a good general trend. Since the Brownstein parameters average in systems involving specific interactions better correlations are to be expected when S' values are used to fit the individual systems comprising this data set. For example, the larger χ value for CH₃CN than for CH₃NO₂ arises because the former solvent is a better donor and has systems averaged in that involve acceptor solutes.

Interesting solvent dependency is shown on the singlet-triplet equilibrium in nickel(II) N,N' -diazobenzene aminotropone-imineate.²² The energy difference as a function of solvent is fitted to the S' parameters in Table 7. An excellent fit results with the small solvent polarity range studied causing a 1.1 kcal mol⁻¹ difference in the singlet-triplet energy gap. Considering that solvents of only moderately strong solvating strength (S ranges from 0.15 to 2.16) were studied, this is a large energy change.

Application of the SP Model.—The model presented can be applied to (i) characterize new solvents, (ii) characterize new probes and (iii) analyse physicochemical data for non-specific solvation contributions. To characterize new solvents one or two probes selected from probes 1–5, as well as probes selected from 6, 7, 14 (or 16), 18, 19, 21, 22 and 24 are recommended subject to the limitations discussed earlier. With polar probes in non-polar solvents or non-polar probes in polar solvents it is recommended that a Beer's law study be carried out to probe solute aggregation. The EPR probes in the literature utilize ' A_N ' values that correspond to peak separation in the EPR spectra. Future investigations should use the proper energy, dividing the peak separation by $g\beta$.

In applications (ii) and (iii) above, a range of solvents of differing polarity and donor strength (E_B and C_B of ref. 2) should be selected to probe the existence of specific interactions. A range of π -solvents can be studied to probe the existence π -charge-transfer interactions. It is anticipated that difficulties will arise when small probe molecules are studied in solvents in which bulky groups are attached to a polar functional group. Steric effects can make the solvent cavity large. When it is much larger than the solute, the solute is not as effectively solvated.

With a unified scale of non-specific solvating ability, effort can be directed to looking for unusual effects and devising experiments to demonstrate their nature instead of searching the literature for a one parameter scale to fit data. This approach should significantly increase our understanding of solvation. The next steps will involve understanding and

treating the specific interactions of acceptor probes in polar solvents and donor probes in protic solvents.

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