A Unified Scale of Solvent Polarities for Specific and Non-specific Interactions

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A unified scale for predicting non-specific solvent polarity employs the physicochemical properties of solutes, such as NMR, EPR, electronic transitions, *etc.*, and the equation $\Delta\chi = S'P + W$ in order to produce a scale of non-specific solvating ability. This approach is successful due to the exclusion of data for systems where donor–acceptor interactions exist. In this paper, the Unified Scale is extended to include systems in polar acceptor solvents by using the equation $\Delta\chi = E_A'E_B^* + C_A'C_B^* + S'P + W$, which takes into account both the non-specific and specific donor–acceptor interactions of these solvents with donor solute probes. An experimental procedure which leads to the separation of solute solvation into non-specific and specific components is described.

In an earlier article,[1] a scale of solvent polarity was presented which enables one to estimate the influence of non-specific solvation on a wide variety of physicochemical properties for solutes of widely varying shapes and polarity. Eqn. (1) is used to

$$\Delta\chi = S'P + W \qquad (1)$$

treat non-specific solvation; where $\Delta\chi$ or χ is used for the value of the physicochemical property measured in the specified solvent; S' is a measure of the solvent's polarity; P is a measure of the susceptibility of the solute probe to solvation; and W is the value of $\Delta\chi$ at S' = zero. The S' values provide a scale of non-specific solvating ability. Substitution of a solvent's and a probe's parameters into eqn. (1) produces the value of the probe property observed in that solvent. Care was taken to exclude from the data set any systems in which there were contributions from specific donor–acceptor interactions. Donor probes are only measured in donor solvents, and data for acceptor or donor pi-solutes measured in pi-solvents are excluded. By eliminating specific interactions, all of the experimental data which, in the past, were used as the basis for several different scales of solvent polarity were found to be consistent with the one, new unified scale. The few exceptions involved measurements of polar probes in non-polar solvents and non-polar probes in polar solvents. These combinations lead to aggregation of the probe resulting in a molecular environment for the probe that is not entirely solvent. Exceptions to the model are also anticipated when a probe is studied whose dimensions are smaller than the dimensions of the cavities that can be created in the pure solvent. Ineffective solvation of the solute occurs in these circumstances.

With eqn. (1), we are in a position to predict non-specific solvation influences. Eqn. (2) has been used[2] to correlate the

$$-\Delta\chi = E_AE_B + C_AC_B + W \qquad (2)$$

donor–acceptor contribution of a variety of physicochemical properties in poorly solvating solvents where non-specific solvation contributions are minimal. Recently, the solvation model was extended[3] to systems in which the property $\Delta\chi$ involves probes that are acceptors involved in specific donor–acceptor, hydrogen bonding interactions in polar solvents. For example, changes in the electronic transition of the acceptor probe 4-nitroaniline were studied[4] in neat, polar donor solvents. The NH_2 group of aniline hydrogen bonds to the basic solvent,[4] and the adduct formed is non-specifically solvated by the polar solvent. For this situation, eqns. (1) and (2) are combined to accommodate both non-specific and specific interactions; eqn. (3) results. The E_B and C_B parameters for the

$$\Delta\chi = E_A^*E_B + C_A^*C_B + S'P + W \qquad (3)$$

solvent are those reported[2] for these donors reacting with a wide range of acceptors in poorly solvating solvents. The successful fit of physicochemical data for acidic probes in neat, polar donor solvents with eqn. (3) is reported.[3] The use of eqn. (3) and the reported solvent parameters for the analysis of physicochemical measurements on new acceptor solutes in polar donor solvents which both coordinate and non-specifically solvate the acceptor solutes is described.[3] Analyses of the data sets used[4] to establish the β–π^* parameters using eqns. (1) and (3) indicate[3] that these systems have complications from both π–π charge transfer interactions and incomplete complexation of the solute. These effects are averaged into the derived β and π^* parameters and limit their applicability.

In this article, the Unified Scale is extended to include the very important class of polar hydrogen bonding solvents. Since these solvents are capable of undergoing both non-specific and specific donor–acceptor interactions with donor solute probes, the relevant equation is (4). The prime values denote parameters

$$\Delta\chi = E_A'E_B^* + C_A'C_B^* + S'P + W \qquad (4)$$

that are consistent with the enthalpy based parameters of the ECW model[2] but are determined in the neat acceptor as the solvent. The specific interaction parameters of the neat solvent may differ slightly in some instances from parameters for the acceptor in the gas phase or in a dilute poorly coordinating solvent. For example, self-association of the acceptor in the pure acceptor solvent could lead to different parameters for the large aggregate than for the monomer or smaller aggregate in the gas phase or poorly solvating solvent. When uncertainty exists about the transferability of parameters measured in pure solvents to studies in the gas phase or in poorly solvating solvents, the prime symbol will be employed. It is to be emphasized that the E_A' and C_A' parameters are consistent with the enthalpy based parameters we have reported,[2] have units of (kcal mol^{-1})$^{\frac{1}{2}}$,† but are to be used to treat specific contributions to the interactions in the pure acceptor as the solvent.

This article provides the basis for extending the unified scale of solvent polarity to hydrogen bonding, polar acceptor solvents. Experiments are reported, and a set of E_A', C_A' and S' values are given, which, for the first time, enables one to

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† 1 cal = 4.184 J.

Table 1 S' Parameters for solvents

No.	Solvent	S'	No.	Solvent	S'
1	C_6H_{12}	1.11	24	$CH_3CO_2CH_3$[b,c]	(2.35)[e]
2	$(C_2H_5)_3N$	1.43	25	$CH_3COC_2H_5$	2.51
3	CCl_4[b]	1.49	26	C_5H_5N[a]	2.44
4	CS_2	1.51	27	$(C_2H_5O)_3PO$	2.55
5	$(C_4H_9)_2O$	1.58	28	$C_6H_5COCH_3$[a,b]	2.52
6	$C_6H_5CH_3$[a]	1.66	29	C_6H_5CN[a]	2.63
7	C_6H_6[a]	1.73	30	$C_6H_5NO_2$[a]	2.61
8	$(C_2H_5)_2O$	1.73	31	$(CH_3)_2CO$	2.58
9	$(CH)_4S$[c]	(1.83)[d]	32	$[(CH_3)_2N]_3PO$	2.52
10	$Cl_2C{=}CHCl$[b,c]	(1.90)[f]	33	$CH_3CON(CH_3)_2$	2.70
11	Cl_3CCH_3[b,c]	(1.93)[f]	34	$CH_2CH_2CH_2CONCH_3$	2.62
12	$C_6H_5N(CH_3)_2$[c]	(1.96)[d]	35	$[(CH_3)_2N]_2CO$[c]	(2.48)[d]
13	$CH_2[CH_2]_3S$[c]	(1.99)[d]	36	$C_2H_5NO_2$[c]	(2.78)[d]
14	$O(CH_2CH_2)_2O$	1.93	37	C_2H_5CN[c]	(2.80)[d]
15	$C_6H_5OCH_3$[a]	2.04	38	$(CH_3)_2NCN$[c]	(2.81)[d]
16	C_6H_5Cl[a]	2.07	39	$(CH_3O)_3PO$[c]	(2.79)[e]
17	$CH_2[CH_2]_4O$	1.98	40	$HCON(CH_3)_2$	2.80
18	$CH_2[CH_2]_3O$	2.08	41	$O[CH_2]_3CO$	2.86
19	1,2-$Cl_2C_6H_4$[b,c]	(2.13)[d]	42	$CH_2[CH_2]_3SO_2$[c]	(2.88)[e]
20	$CH_3CO_2C_2H_5$	2.15	43	$(CH_3)_2SO$	3.00
21	Quinoline[a,c]	(2.30)[d]	44	CH_3CN	3.00
22	$(C_4H_9O)_3PO$[c]	(2.30)[e]	45	CH_3NO_2	3.07
23	$CH_2[CH_2]_4CO$	2.35	46	$O[CH_2]_3OCO$	3.10

[a] π-Acceptor solutes must be avoided. [b] Strong donor nitrogen, sulfur and phosphorus solutes must be avoided. [c] Limited data is available on these solvents so an n-value of 1 is used in data fits compared to 0.2 for established solvents. [d] Not included in fit and calculated from $[E_T(30) - 19.63]/8.61$. [e] Not included in fit and average value calculated from $E_T(30)$ and $(\delta_{^{31}P} + 8.91)/5.09$. [f] Not included in fit and average value calculated from $E_T(30)$ and (Michler's ketone $- 31.38)/-1.18$.

determine non-specific and specific solvation components of the solvation of solutes in hydrogen bonding solvents.

Results and Discussion

Systems Involving Non-specific Interactions.—Eqn. (4), for acceptor solvents, contains a large number of unknown quantities. In order to facilitate finding the minimum for the best set of parameters to fit the solvent shift data, probes are employed for which P and W can be determined independently in non-specific solvating solvents. Donor probes are studied in donor solvents,[1] and these data are treated separately with eqn. (1) to determine P and W. Analysis of data for a probe whose P and W values are known in acceptor solvents leaves [in eqn. (4)] $E_B{}^*$ and $C_B{}^*$ to be determined for the probe and $E_A{}'$, $C_A{}'$ and S' to be determined for the solvents. The addition of new probes led us to refit the data set previously reported[1] for non-specific solvation of donor probes in donor solvents. Data for 366 spectral shifts lead to 366 simultaneous equations that are solved for 34 S' values and 82 probe parameters. The refined S' and P values are given in Tables 1 and 2, respectively. The agreement between the experimental shifts and the shifts calculated by substituting the parameters from Tables 1 and 2 into eqn. (1) is comparable to that reported earlier.[1] The symbol $\Delta\chi$ for the transition energy will be abbreviated as χ.

Table 1 lists the solvent polarity parameters for donor solvents under conditions where specific interactions with the probe are not involved. In some solvents, only a limited number of well-established probes have been studied, leading to tentative S' values. These solvents are also listed in Table 1, and the limited probes used in their determination are given in the footnote.

Table 2 lists the probe intercept (W) and susceptibility (P) values for 41 different probes. Abbreviations that are used for these probes in the discussion and computer fits are indicated in parentheses. Combining the probe parameters with S' in eqn. (1) enables one to calculate the spectral shift of the probe from non-specific solvation. The average absolute deviations, $\bar{x}$, of the various probes in the data fit are given in the footnotes to Table 2. The % fit gives the average deviation as a percentage of the range of shifts observed for the probe.[2e]

The S' values of new solvents, which only non-specifically solvate the probes, can be determined and added to the correlation by measuring the shifts of several probes in the solvent. A series of equations of the form of eqn. (1) is written for each probe and solved for S'. Alternatively, $\chi - W$ can be plotted *vs.* P, and the slope of the least squares line will give S'.

New probes can be added or physicochemical data can be analysed for non-specific solvation contributions by measuring χ in a series of non-coordinating solvents. The series of equations of the form of eqn. (1) is solved for P and W. A good fit of the data indicates that the measured changes of these probes with solvent variation are caused by non-specific solvation.

The addition of over 200 additional pieces of data in this fit compared to the earlier fit has not changed the trend in the S' values. The main difference is an increase in the S' values of solvents of low polarity (cyclohexane changes to 1.11 from 0.15) and a smaller percentage increase in solvents of high polarity. Most of this change is compensated for with increased P and decreased W values for the probes. Thus, the intercept ($S' = 0$) is better defined by the added data.

An Experimental Procedure for Factoring Specific and Non-specific Contributions to χ.—When solvent effects are measured in coordinating solvents, non-specific solvation and specific donor–acceptor interactions must be considered. This is accomplished for acceptor solvents by using eqn. (4). 205 Shifts induced by protonic solvents on the probes in Table 2 were used to write 205 equations of the form of eqn. (4), which were solved for E_B and C_B values of 25 probes and for $E_A{}'$, and $C_A{}'$ and S' values of ten solvents. A very shallow minimum exists for this

Table 2 P and W Parameters for Probes[aa] (tentative parameters in parenthesis)

Probe (Symbol)	P	W	n
ν; *N*,*N*-Diethyl-4-nitroaniline[a] (NNE4NO_2AN)	−1.69	29.31	0.22
ν; *N*,*N*-Dimethyl-2-nitroaniline[b] (NNM2NO_2AN)	−0.99	26.19	0.17
ν; *N*,*N*-Diethyl-3-methyl-4-nitroaniline[c] (NNE3M4NO_2AN)	−1.55	29.16	0.19
ν; *N*,*N*-Dimethyl-2-nitrotoluene[b] (NNM2NO_2TOL)	−0.95	25.60	0.13
ν; 4-Nitroanisole (4NO_2ANISOL)[a]	−1.29	35.51	0.18
ν; 4-(2,4,6-Triphenyl-1-pyridino)-2,6-diphenylphenoxide[d] (Betaine)	8.61	19.63	0.20
ν; Bis-2-[2-pyridylbenzylidine-3,4-dimethylaniline, biscyano iron(II)][e] (Burgess)	1.66	11.69	0.11
$\delta_{^{19}F}$; 1,4-Difluorobenzene[f] ($F_2C_6H_4$)	−0.36	7.26	0.11
$\delta_{^{19}F}$; 1-Fluoro-4-trifluoromethylbenzene[f] ($CF_3C_6H_4F$)	0.39	4.72	0.13
$\delta_{^{19}F}$; 1-Fluoro-4-nitrobenzene[f] ($NO_2C_6H_4F$)	0.59	8.61	0.12
$\delta_{^{19}F}$; 1-Cyano-4-fluorobenzene[f] (CNC_6H_4F)	0.49	8.42	0.08
$\delta_{^{15}N}$; 1-Methylsilatrane [$N(CH_2CH_2O)_3SiCH_3$] (N15)[g]	4.39	−4.88	0.22
ν; 1-Ethyl-4-methoxycarbonylpyridinium iodide (*Z*-value)[h]	13.23	31.38	0.20
A_N; Di-*tert*-butyl nitroxide[i] (ANTBUNO)	0.240	13.967	0.09
ν; *N*,*N*-(Dimethyl)thiobenzamide *S*-oxide [$C_6H_5CSO(NMe_2)$][j]	1.27	78.28	0.25
A_N; 4-Amino-2,2,6,6-tetramethylpiperidine-1-oxyl (ANPIPNO)[i]	0.229	14.072	0.09
ν; α-[4-(*N*,*N*-Dimethylamino)phenyl]aminoacetoacetanilide) ($Me_2NC_6H_4NCR_2$)[k]	−2.41	73.91	0.26
ν; Pyridine *N*-oxide (NUPYNO)[l]	0.36	35.00	0.15
νE; 1-Methyl-4-cyanoformylpyridinium oximate (OXIMATO-B)[m]*	3.90	39.46	0.34
Brookers IV[n]	8.42	28.24	0.24
$\delta_{^{13}C}$; *N*,*N*-Diethylbenzamide[o]	0.92	29.79	0.12
$\delta_{^{13}C}$; C_5H_5N[p]*	0.89	−16.53	0.16
$\delta_{^{13}C}$; C_5H_5NO[q]	1.92	−19.80	0.15
Isoquinolinium ylide (ISOQUIN-YLIDE)[r]	3.06	54.92	0.03
$\delta_{^{14}N}$; Pyridine N-oxide [N(14)PYNO][s]*	5.29	69.53	0.46
$\delta_{^{19}F}$; 1-Fluoro-4-fluorosulfonylbenzene ($FC_6H_4SO_2F$)[t]	0.79	11.20	0.19
$\delta_{^{19}F}$; 1-Fluoro-4-pentafluorothiobenzene ($FC_6H_4SF_5$)[t]	0.51	4.90	0.16
ΔE(s→t); Nickel *N*,*N*^{1}-di(*p*-tolyl)aminotroponeimineate (NiAmtrop)[t]	−0.60	4.10	0.13
ν; Ni(II) Bistrifluoromethyldithiolene-1,10-phenthroline [Ni(tfd)phen][u]	4.27	45.55	0.22
$\delta_{^{31}P}$; Triethylphosphine oxide [$^{31}P(C_2H_5)_3PO$][v]	5.09	−8.91	0.29
$\nu\ E_2$; 1-Methyl-4-cyanoformylpyridinium oxidmate (ν-4-Cyano-ox)[m]*	3.10	65.77	0.44
(Z')[h]*	14.65	23.96	0.46
ν(fl); 7-Amino-4-methylcoumarin (COUM)[w]*	−1.45	27.07	0.26
ν(fl); 7-*N*,*N*-Dimethylamino-4-methylcoumarin[w]*	−1.43	27.91	0.36
Brownstein's S' parameter[x] [S' bst)]	0.090	−0.392	0.08
1-C_2H_5-$NO_2C_6H_4$[b]	−0.99	38.57	0.20
ν; 4,4′-Bis(dimethylamino)benzophenone (Michler's ketone)[y]	−1.18	31.38	0.20
ν; *cis*-Dicyanobis-1,10-phenanthroline iron(II), Burgess (Sp)[z]	1.38	12.49	0.14

[a] The electronic transition energy in kK (1 kK = 1000 cm^{-1}). Data from ref. 4(*b*). $\bar{x}$ is 0.16 and % fit = 5.8 for NNE4NO_2AN and 0.11 and 4.5% for 4NO_2ANISOL. Estimated experimental error is 0.1 kK. [b] The transition energy in kK. Data from ref. 4(*b*). $\bar{x}$ = 0.10 and the % fit is 5.0 for NNM2NO_2AN, 0.13 and 6.6% for NNM2NO_2TOL and 0.13 and 6.7 for 1-ethyl-4-nitrobenzene. Estimated experimental error is 0.1 kK. [c] Transition energy in kK. Data from ref. 4. $\bar{x}$ Omitting acetone = 0.12, the % fit = 3.6 and the experimental error is 0.1 kK. [d] Transition energy ν kcal mol^{-1}. Data from ref. 5. The ν value in hexane is 30.9, the $\bar{x}$ = 0.14 and the % fit = 1. [e] Parameters to calculate ν/kK. Data from ref. 6. The $\bar{x}$ 0.04, the % fit = 1.9% and the experimental error is 0.1 kK. [f] The ^{19}F chemical shift in ppm relative to fluorobenzene as an internal standard. $\bar{x}$ = 0.04 and % fit = 6.2%. $\bar{x}$ = 0.06 and % fit = 7.5; $\bar{x}$ = 0.05 and % fit = 3.8; $\bar{x}$ = 0.02 and % fit = 2.4; $\bar{x}$ = 0.12 and % fit = 8.7; $\bar{x}$ = 0.9 and % fit = 10.5 for the F, CF_3, NO_2, CN, SO_2F and SF_5 derivatives, respectively. The experimental error is 0.08 ppm. Data from ref. 7. [g] The ^{15}N chemical shift in ppm for 1-methylsilatrane relative to cyclohexane. Data from ref. 8, $\bar{x}$ = 0.16 and % fit = 2.0. [h] Transition energy in kcal mol.$^{-1}$ Data from ref. 9. In most instances, the transition is concentration dependent and has been extrapolated to zero solute concentration. The $\bar{x}$ = 0.14 and the % fit = 1.1; $\bar{x}$ = 0.17 and % fit = 2.8. [i] The nitrogen hyperfine coupling constant in $cm^{-1} \times 10^{-4}$. Data from ref. 10 where A_N is reported as the line separation in gauss which is actually $A_N/g\beta$. Since g is not given, it is assumed to be 2.0047 and $\beta = 4.6686 \times 10^{-5}\ cm^{-1}\ G^{-1}$. Multiplying the line separation by 9.3591×10^{-5} gives A_N in units of $cm^{-1} \times 10^{-4}$. The fit is run by multiplying the numbers by 10^4. The $\bar{x}$ = 0.03 and the % fit = 6.7 and 0.03 and 7.1. Estimated experimental error is $0.01 \times 10^{-4}\ cm^{-1}$. [j] Transition energy in kcal mol^{-1}. Data from ref. 11. The $\bar{x}$ = 0.21 and the % fit = 8.7. [k] Transition energy in kcal mol^{-1}. Data from ref. 12. The $\bar{x}$ = 0.23 and the % fit = 5.5. [l] Transition energy in kK. Data from ref. 13. The $\bar{x}$ = 0.08 and the % fit = 8.9. Transition energy is 0.1 kK. [m] Transition energy in kcal mol^{-1}. Data from ref. 14. $\bar{x}$ = 0.1 and % fit = 5.7; $\bar{x}$ = 0.17 and % fit = 2.8. [n] Transition energy in kcal mol^{-1}. Data from ref. 15. $\bar{x}$ = 0.19 and % fit = 3.8. [o] Chemical shift in units of ppm. Data from ref. 16. $\bar{x}$ = 0.05 and % fit = 5.7. [p] Chemical shifts in units of ppm. Data from ref. 17. $\bar{x}$ = 0.02 and % fit = 1.6. [q] Chemical shift in units of ppm. Data from ref. 17 and 18. $\bar{x}$ = 0.08 and % fit = 6.3. [r] Transition energy in kcal mol^{-1}. Data from ref. 19. $\bar{x}$ = 0.003 and % fit = 0.1. [s] Chemical shift in units of ppm. Data from ref. 20. $\bar{x}$ = 0.17 and % fit = 2.5. [t] Chemical shift in units of ppm. Data from ref. 21. $\bar{x}$ = 0.06 and % fit = 6.7. [u] Transition energy in kcal mol^{-1}. Data from ref. 22. $\bar{x}$ = 0.16 and % fit = 2.2. [v] Chemical shift in units of ppm. Data from ref. 23. $\bar{x}$ = 0.29 and % fit = 4.1. [w] Transition energy in kcal mol^{-1}. Data from ref. 24. $\bar{x}$ = 0.06 and % fit = 3.6; $\bar{x}$ = 0.11 and % fit = 6.6. [x] Dimensionless reactivity scale. Data from ref. 25. $\bar{x}$ = 0.02 and % fit = 7.8. [y] Transition energy in kK. Data from ref. 26. $\bar{x}$ = 0.14 and % fit = 6.2. [z] Transition energy in kK. Data from ref. 26. $\bar{x}$ = 0.07 and % fit = 6.7. [aa] Asterisk indicates that limited data is available. The *n*-value is doubled to take this into account.

data set. A poor definition of the minimum is expected[2a] because all the specific interactions involve hydrogen bonding and these acceptors all have similar C_A'/E_A' ratios. Accordingly, experiments were designed to obtain an independent measure of the specific and non-specific contributions to the shift in acceptor solvents. This additional information will help define the minimum in the data fit to eqn. (4). The probe is dissolved in a weakly basic, slightly polar, non-coordinating solvent. Alcohol is added to this system, and the band maximum is plotted as a function of the alcohol concentration. The design of this experiment is critical. A weakly basic solvent is selected so the solvent will not compete effectively as a donor with the dilute probe molecule for the specific hydrogen bonding interaction to the alcohol. The solvent should be slightly polar so the probe does not aggregate at low alcohol concentrations. Data must be collected over the entire concentration range so

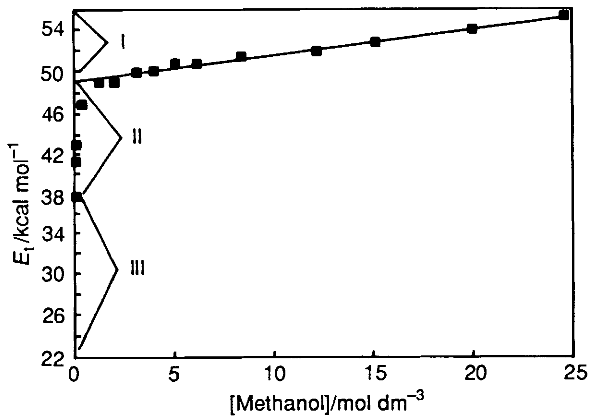

Fig. 1 Shift in the electronic transition of betaine with solvent composition in methanol–*o*-dichlorobenzene. The region labelled I is attributed to non-specific solvation of the betaine–methanol adduct by methanol. The region labelled II is the shift due to the specific interaction leading to betaine–methanol adduct formation. The region labelled III is the shift of betaine from non-specific solvation by *o*-dichlorobenzene. The lower limit of region III is the *W* value for betaine (19.63 kcal mol^{-1}). On this graph, region III was only extended to 22 kcal mol^{-1} for clarity.

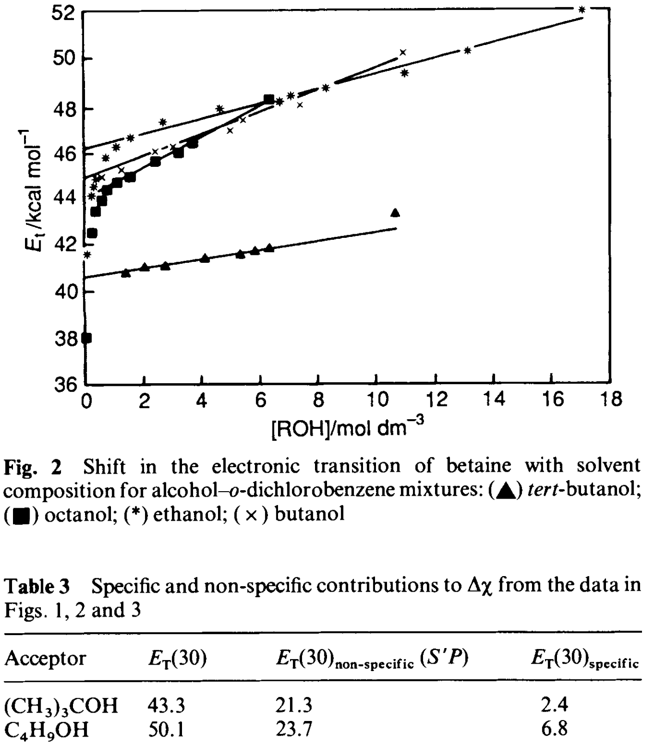

Fig. 2 Shift in the electronic transition of betaine with solvent composition for alcohol–*o*-dichlorobenzene mixtures: (▲) *tert*-butanol; (■) octanol; (*) ethanol; (×) butanol

Table 3 Specific and non-specific contributions to $\Delta\chi$ from the data in Figs. 1, 2 and 3

Acceptor	$E_T(30)$	$E_T(30)_{\text{non-specific}}$ $(S'P)$	$E_T(30)_{\text{specific}}$
$(CH_3)_3COH$	43.3	21.3	2.4
C_4H_9OH	50.1	23.7	6.8
$C_8H_{17}OH$	48.3	22.6	6.1
CH_3OH	55.4	24.6	11.2
C_2H_5OH	51.9	24.1	8.2
CH_2Cl_2	41.7	17.5	1.1

the non-specific solvation of the adduct can be extrapolated from concentrated to dilute alcohol solutions.

The change in frequency of the betaine transition[5] $E_T(30)$, upon the addition of methanol to a betaine solution (8.7×10^{-5} mol dm^{-3}) in *o*-dichlorobenzene is shown in Fig. 1. Separate peaks for the free and complexed betaine are not resolved. Instead, a gradual change in transition energy is observed because the varying relative contributions to the band from free and hydrogen bonded betaine add and shift the maximum. At low concentrations of methanol (CH_3OH), large shifts are observed for relatively small changes in solvent composition, as shown in region II, Fig. 1. These large shifts are attributed to the specific hydrogen bonding interaction of methanol with the oxygen donor functionality of betaine. At higher concentrations of methanol (> 3 mol dm^{-3}), the hydrogen bonded adduct is fully formed, and the change observed in $E_T(30)$ with further increase in alcohol concentration is due to non-specific solvation of the adduct, which is induced by a change in solvent composition. The positive slope of the linear portion of the curve in excess methanol indicates that non-specific solvation of the hydrogen bonded probe adduct is larger for methanol than for *o*-dichlorobenzene. The plot in Fig. 1 can be treated as two linear regions connected by a curved portion. Curvature occurs in the concentration range where both specific and non-specific solvation effects are contributing to the observed shift. The rapid change at low methanol concentration and the small region of curvature result because betaine is a better donor than *o*-dichlorobenzene. The difference in the probe and solvent donor strength is a key feature of this experiment, which permits factoring out the specific contribution to the shift.

Extrapolation to the E_T axis of the straight line portion of the curve that occurs at the higher concentrations of MeOH to 0% methanol gives the shift expected for the hydrogen bonded, betaine–methanol adduct in *o*-dichlorobenzene. The difference between this extrapolated point and the value of betaine in *o*-dichlorobenzene at $E_T = 38.0$ gives the specific contribution to the betaine shift from its hydrogen bonding to methanol. The shift from the specific interaction of betaine with methanol is the same in any solvent in which the adduct is formed. Different shifts observed in different solvents in which the methanol adduct is intact are attributed to non-specific solvation.

The $E_T(30)$ value of 55.5 for pure methanol (25 mol dm^{-3}) consists of contributions from a non-zero intercept (W), specific, and non-specific solvation, as shown in eqn. (5).

$$\chi - W = \chi_{\text{specific}} + \chi_{\text{non-specific}} \qquad (5)$$

The $E_T(30)$ axis of Fig. 1 shows the shift of betaine in *o*-dichlorobenzene [$E_T(30) = 38.0$], the shift attributed to specific interaction forming the methanol adduct in *o*-dichlorobenzene [$E_T(30) = 49.2$] and the shift of the hydrogen bonded betaine adduct in methanol. The intersection of the extrapolated line from pure methanol with the E_T axis divides the increased solvation by methanol (over the solvation by *o*-dichlorobenzene) into specific and non-specific components, labelled as II and I, respectively, on Fig. 1.

The experiment described above for methanol was extended to several other alcohols. Fig. 2 and Table 3 summarize the results. Recall that the non-specific solvation of betaine has a W value of 19.63, which corresponds to an S' value of zero. Thus, the non-specific contribution to solvation listed as $E_T(30)$ non-specific in Table 3, is given by eqn. (6). Eqn. (6) is simply a

$$E_T(30)_{\text{non-specific}} = E_T(30)_{\text{alcohol}} - 19.63 - E_T(30)_{\text{specific}} \qquad (6)$$

rearrangement of eqn. (5) with $E_T(30)_{\text{alcohol}}$ substituted for χ. $E_T(30)_{\text{non-specific}}$ is attributed to the $S'P$ term.

Fig. 3 shows the results for betaine in the binary solvent system methylene chloride and *o*-dichlorobenzene. In contrast to Fig. 1, where most of the shift from adduct formation occurs before the alcohol concentration reaches 1 mol dm^{-3}, specific contributions to the shift are still clearly evident in Fig. 3 at 3 mol dm^{-3} concentrations of CH_2Cl_2. Contributions from the specific interaction could exist all the way to pure CH_2Cl_2 and these contributions simply influence the slope of the line in concentrated CH_2Cl_2. Thus, the contribution to $E_T(30)$ from coordination, obtained for CH_2Cl_2 with the extrapolation procedure described for methanol, provides a lower limit on the

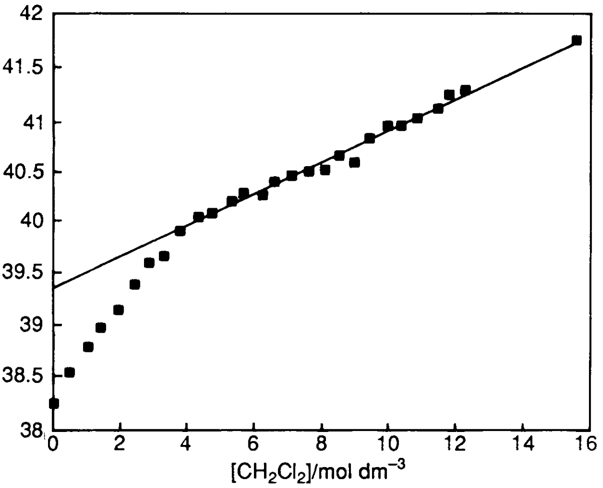

Fig. 3 Shift in the electronic transition of betaine with solvent composition for methylene chloride–*o*-dichlorobenzene mixtures

magnitude of the specific hydrogen bonding interaction in CH_2Cl_2 solvent.

It is to be emphasized that when designing this experiment, it was critical that the solvent not compete effectively with the probe in the acid–base interaction. This requires a very weakly basic solvent. Several studies of mixed solvent systems have been made[27,28] but in most cases, the solvent is basic enough to compete with or even dominate the specific interaction with the probe. Equations are reported[28] to describe these shifts with high precision, but at present, these investigators have made no attempt to separate the total solvation of the mixed solvent system into specific and non-specific contributions. The prediction of the polarity of a mixed solvent system is not the intent of this article and the reader is referred to ref. 28 for a treatment of mixed solvent polarity.

Basic probes undergo competition with the basic solvent causing the fraction of the probe that is hydrogen bonded to change over a wide range of mixed solvent composition. Competition would cause the curved portion of Fig. 1 to cover a wide range of solvent composition in donor solvents. Furthermore, the adduct formed by the donor solvent and protic solvent is more polar than either solvent and has a different S' than the pure solvents. Therefore, the mixed donor solvent case is a three component solvent mixture (protic solvent, donor solvent, adduct) that non-specifically and specifically solvates the probe.

Probe shifts for the addition of alcohols to weak donor solvents have been reported[26] and demonstrate the large shifts at low alcohol concentration, as seen in Fig. 1. Unfortunately, data were not reported at high alcohol concentration in order to permit extrapolation to obtain both the specific and non-specific components of solvation.

Data Fit for Acceptor Solvents.—Factoring the betaine shift into specific and non-specific components provides additional information to help define better the shallow minimum obtained in the fit of acceptor solvents. The betaine $E_T(30)_{\text{non-specific}}$ values (betns) are entered into the fit by setting E_A and C_A equal to zero for these quantities, *i.e.* the equation betns $= S'P$ is added to the series of simultaneous equations that is solved. Over 225 data points are solved for 48 probe unknowns and 38 solvent unknowns. The quality of the fit is illustrated by the agreement of the calculated and experimental data in Table 4. The calculated values of $\chi - W$, in Table 4 are obtained by substituting the best fit E_A', C_A', S', E_B^*, C_B^* and P parameters given in Tables 5 and 6 into eqn. (3). These best fit parameters from this data base provide a set of parameters for acceptor solvents and probes that characterizes the probe's ability to undergo specific and non-specific solvation. A wide variety of probe shapes, donor strengths and polarities is involved in the data fit. Unfortunately, the C_A'/E_A' ratio of the acceptor solvents only varies from about 0.05 to 1.2. This small range limits the applicability of the C_B^* and E_B^* parameters for the probes in data analysis or for the addition of new solvents to acceptor solvents that fall in the C_A'/E_A' range of the solvents reported. Fortunately, most of the common organic acceptor solvents that contain acceptor O–H, C–H, S–H or N–H functionalities are expected to have C_A'/E_A' ratios that fall in this range. Measurements of spectral shifts in more covalent solvents such as SO_2, $(C_A/E_A = 3.0)$[3] are needed badly to define better the division of the specific interaction into its electrostatic and covalent contributions and to provide a test of the more general applicability of this model.

The E and C model pertains to 1:1 adducts. Thus, it is somewhat surprising that the data for the specific interaction in the pure acceptor as the solvent fit the E and C model as well as it does. In spite of these complications, the analyses of shifts in polar acceptor solvents is as precise as those in non-polar solvents.[2a,b,3] Percentage fits[2d,e] (average deviation divided by the range in the values of χ for a particular donor or acceptor) are usually 2–3% or better for the established probes. This fit would seem to suggest that the adducts formed with a given probe have the same stoichiometry in all solvents. Of over 225 data points employed in the least squares fit, only three of the calculated values differed significantly from the experimental values. Two of the systems where deviations occurred involved water where the stoichiometry of the adducts formed in solution is uncertain. The other exception occurs for betaine dissolved in *tert*-butanol, where steric effects may prevent complete complexation.

Eqn. (4) can be used to calculate the specific and non-specific contributions to a solvent shift. In a recent article,[23c] Riddle and Fowkes analysed acceptor numbers [based on $\delta_{^{31}P}(C_2H_5)_3PO$] in terms of specific and non-specific solvation contributions. The non-specific component was estimated from measurements of surface and interfacial tensions. Our estimate of the non-specific contribution, which is obtained by multiplying S' for the alcohols with the P value for triethylphosphine oxide, is considerably larger than those estimated by surface and interfacial tensions approximations. The ^{31}P shifts should be measured under the conditions described in Fig. 1.

In addition to spectral shifts, our parameters can be applied to the understanding of the influence of solvent on the excited state lifetime of Rose Bengal.[29] The data fits require obtaining a best fit E_B^*, C_B^*, P and W on a system where limited data in non-interacting solvents are available (see Experimental). The E_B^*, C_B^* and P parameters from the fit of available data suggest that non-specific solvation and the tendency of the acceptor solvent to interact electrostatically in a specific fashion lead to the decrease in the excited state lifetime. Covalency in the specific interaction increases the lifetime.

The alcohols are an important class of solvents in sol gel applications. Some general trends are detected in the non-specific solvating and acceptor properties of these solvents. The C_A'/E_A' ratio decreases with the length of the straight chain alkyl substituent in the order CH_3OH (1), C_2H_5OH (0.9), C_3H_7OH (0.8), C_4H_9OH (0.7). The magnitude of C and E also decrease in this order indicating a decrease in acceptor strength toward all solutes. Chain branching decreases the C/E ratio to a greater extent than the corresponding straight chain alkyl. The solvent *tert*-butanol is the weakest acceptor and poorest solvating solvent of the alcohols studied. Comparing ethylene glycol to ethanol, the two solvents have the same C/E ratio, but the glycol is a stronger acceptor and better non-specific solvating solvent than ethanol.

Table 4 Data fit for acceptor solvents[a]

	CH_3OH			C_2H_5OH			i-C_3H_7OH			$(CH_3)_3COH$		
Base	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.
Betaine	35.77	35.85	0.08	32.27	32.80	0.53	28.77	28.95	0.18	23.67	26.23	2.56
N14PYNO	28.00	30.33	2.33	27.53	27.19	-0.34						
Z-Value	52.17	51.71	-0.46	48.17	48.36	0.19	44.87	44.87	0.00	39.87	40.48	0.61
ANTBUNO	1.20	1.19	-0.01	1.03	1.10	0.06	0.98	1.03	0.05	0.88	0.91	0.03
$C_6H_5C(SO)(NMe)_2$	7.62	7.32	-0.30	6.82	6.69	-0.13	6.52	6.36	-0.16	6.02	5.55	-0.47
$Me_2NC_6H_4NCR_2$	-7.71	-8.17	-0.46	-7.31	-7.72	-0.41				-6.41	-6.49	-0.08
ANPIPNO	1.09	1.10	0.01	0.97	1.01	0.03	0.94	0.92	-0.02	0.82	0.82	0.00
NUPYNO	2.97	3.07	0.10	2.66	2.74	0.08	2.59	2.61	0.02	2.48	2.22	-0.26
E-Base	1.80	1.55	-0.25	1.40	1.33	-0.07	1.20	1.28	0.08	1.07	1.04	-0.03
C-Base										0.70	0.69	-0.01
IQYL	13.57	13.82	0.25	12.77	12.50	-0.27	10.77	10.87	0.10			
Brooker's IV	34.76	34.24	-0.52	32.16	31.48	-0.68	27.86	28.04	0.18			
$CF_3C_6H_4F$	1.18	1.06	-0.12									
$(C_2H_5)_3PO$	24.90	25.23	0.33	23.37	23.16	-0.21	21.54	21.56	0.02	18.77	19.06	0.29
C13DEBZAM	5.64	6.01	0.37				4.91	4.85	-0.06			
C13PY	4.89	4.99	0.10	4.77	4.43	-0.34						
C13PYNO				9.00	9.49	0.49						
z′	55.40	55.48	0.08	52.00	51.98	-0.02	48.40	48.08	-0.32	44.10	43.53	-0.57
n,ndmcoum	-4.76	-4.54	0.22	-4.65	-4.50	0.15	-4.44	-4.64	-0.20	-4.54	-4.18	0.36
s′(bst)	0.44	0.44	0.00	0.39	0.40	0.01	0.35	0.36	0.01	0.29	0.32	0.03
Betns	24.57	24.68	0.11	24.07	24.07	0.00				21.27	21.19	-0.08
Coum	-5.05	-4.99	0.06	-4.85	-4.75	0.10	-4.39	-4.48	-0.09	-4.21	-4.08	0.13
4Cyano-ox	20.14	20.18	0.04	17.74	17.80	0.06	15.64	15.51	-0.13			
N15	12.98	13.18	0.20							10.48	10.58	0.10
Mitchketone	-4.30	-4.43	-0.13	-4.06	-4.21	-0.15	-3.74	-4.06	-0.32	-3.26	-3.64	-0.38
Burgess(Spange)	5.86	5.71	-0.15	5.46	5.36	-0.10	4.99	5.12	0.13	4.51	4.57	0.06
ln Tau	-5.44	-5.41	0.03	-5.13	-5.19	-0.06	-4.86	-5.18	-0.32	-4.62	-4.60	0.02
ln TauNR	-5.48	-5.53	-0.05	-5.14	-5.23	-0.09	-4.83	-5.15	-0.32	-4.54	4.55	-0.01

	H_2O			C_4H_9OH			CH_2Cl_2			$HCONH_2$		
Base	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.
Betaine	43.47	43.06	-0.41	30.47	30.10	-0.37	18.61	19.01	0.40	36.27	36.30	0.03
N14PYNO	36.97	36.56	-0.41				16.13	15.78	-0.35			
Z-Value	63.17	63.12	-0.05	46.27	46.37	0.10	32.77	32.41	-0.36	51.87	52.05	0.18
ANTBUNO				1.02	1.06	0.04	0.78	0.74	-0.03			
$C_6H_5C(SO)(NMe)_2$	9.12	8.99	-0.13	6.42	6.56	0.14	3.72	4.60	0.88	6.22	6.66	0.44
$Me_2NC_6H_4NCR_2$	-9.81	-9.94	-0.13							-10.01	-8.60	1.41
ANPIPNO				0.94	0.96	0.02	0.69	0.64	-0.05			
NUPYNO	4.28	3.76	-0.52	2.57	2.69	0.12				2.85	2.61	-0.24
E-Base	1.90	1.91	0.01	1.30	1.32	0.02						
C-Base	0.78	1.78	1.00							0.30	1.35	1.05
IQYL				11.57	11.32	-0.25				13.97	13.81	-0.16
Brooker's IV	40.66	41.25	0.59	28.56	29.13	0.57	19.26	18.80	-0.46			
$CF_3C_6H_4F$												
$(C_2H_5)_3PO$	30.57	30.81	0.24	22.90	22.29	-0.61	15.90	15.26	-0.64	24.18	23.94	-0.24
C13DEBZAM	7.57	7.27	-0.30	5.13	5.03	-0.10				5.48	5.48	0.00
C13PY	5.81	5.95	0.14									
C13PYNO	13.20	12.73	-0.47				5.60	5.31	-0.29			
z′				49.50	49.70	0.20	35.00	34.69	-0.31			
n,ndmcoum	-5.39	-5.75	-0.36									
s′(bst)	0.55	0.53	-0.02	0.38	0.37	-0.01	0.24	0.24	-0.01	0.44	0.43	-0.01
Betns				23.67	23.57	-0.10	17.50	17.88	0.38			
Coum	-5.84	-6.13	-0.29									
4Cyano-ox	26.24	24.13	-2.11				9.34	9.41	0.07			
N15	16.18	15.96	-0.22									
Mitchketone				-4.02	-4.17	-0.15	-3.30	-3.12	0.18	-4.74	-4.43	0.31
Burgess(Spange)				5.05	5.27	0.22	4.13	3.84	-0.29	5.79	5.59	-0.20
ln Tau	-6.97	-6.77	0.20	-5.09	-5.31	-0.22				-5.21	-5.24	-0.03
ln TauNR	-7.07	-6.89	0.18	-5.09	-5.29	-0.20				-5.23	-5.27	-0.04

Uses of the Unified Solvation Model.—The main purpose of this correlation is to provide a reactivity scale that can be used to interpret physicochemical measurements in polar acceptor solvents. In the course of this application, the need may also arise to add either a new solvent or a new probe to the model. The approach to be used to accomplish these three objectives will be discussed in this section.

Adding new acceptor solvents. New solvents are readily incorporated into the model. Solvents that are not acceptors are best studied with probes in Table 1 that have large *P* values and

Table 4 (*continued*)

	HOC_2H_4OH			$CHCl_3$			C_3H_7OH		
Base	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.
Betaine	36.67	36.58	−0.09	19.47	18.58	−0.89	31.07	30.99	−0.08
N14PYNO				17.25	19.01	1.76			
Z-Value	53.72	53.84	0.12				46.87	46.60	−0.27
ANTBUNO	1.35	1.25	−0.10	0.88	0.87	−0.01			
$C_6H_5C(SO)(NMe)_2$	7.73	7.68	−0.05	4.22	5.79	1.57			
$Me_2NC_6H_4NCR_2$									
ANPIPNO	1.18	1.14	−0.04	0.69	0.72	0.03			
NUPYNO	3.20	3.21	0.01				2.66	2.75	0.09
E-Base							1.30	1.38	0.08
C-Base									
IQYL	13.98	14.02	0.04				11.57	11.78	0.21
Brooker's IV									
$CF_3C_6H_4F$									
$(C_2H_5)_3PO$				17.92	17.72	−0.20			
C13DEBZAM	6.01	6.18	0.17						
C13PY				2.63	2.65	0.02			
C13PYNO				6.10	6.20	0.10			
z′				33.80	34.19	0.39	49.70	49.93	0.23
n,ndmcoum	−4.97	−4.95	0.02						
s′(bst)	0.46	0.45	−0.01	0.19	0.26	0.07	0.38	0.38	0.01
Betns									
Coum	−5.42	−5.23	0.19						
4Cyano-ox									
N15									
Mitchketone	−4.98	−4.69	0.29	−3.34	−3.23	0.11	−3.94	−4.12	−0.18
Burgess(Spange)	5.99	6.01	0.02	4.31	4.16	−0.15	5.27	5.25	−0.02
ln Tau							−5.13	−5.18	−0.05
ln TauNR							−5.14	−5.21	−0.07

	CH_3CO_2H			CH_3CO_2H			NMF		
Base	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.	$\chi - W$ (exp)	$\chi - W$ (calc)	Dev.
Betaine	40.17	40.14	−0.03				34.47	34.44	−0.03
N14PYNO	37.07	34.57	−2.50						
Z-Value				47.77	47.80	0.03			
ANTBUNO				1.40	1.40	0.00			
$C_6H_5C(SO)(NMe)_2$				10.52	9.77	−0.75	5.12	5.16	0.04
$Me_2NC_6H_4NCR_2$									
ANPIPNO				1.08	1.08	0.00			
NUPYNO				4.60	4.58	−0.02			
E-Base	2.07	1.93	−0.14	2.00	2.97	0.97			
C-Base	1.06	1.31	0.25	0.20	0.15	−0.05	0.30	0.47	0.17
IQYL									
Brooker's IV									
$CF_3C_6H_4F$							0.98	1.40	0.42
$(C_2H_5)_3PO$	29.93	30.29	0.36	27.84	27.96	0.12			
C13DEBZAM							4.41	4.02	−0.39
C13PY									
C13PYNO	11.70	11.88	0.18						
z′									
n,ndmcoum									
s′(bst)				0.40	0.37	−0.03			
Betns									
Coum									
4Cyano-ox									
N15									
Mitchketone	−5.62	−5.57	0.05						
Burgess(Spange)	6.82	7.09	0.27						
ln Tau	−7.40	−7.14	0.26				−4.81	−5.05	−0.24
ln TauNR	−7.50	−7.15	0.35				−4.77	−4.81	−0.04

[a] The specific contribution to the shift from experiments like those in Fig. 2 were added and fit to $E_A'E_B + C_A'C_B$. The experimental (calculated) values are: octanol–betaine 6.10 (6.13); CH_2Cl_2–betaine 1.11 (1.12); $SbCl_5$–$(C_2H_5)_3PO$ 35.47 (35.46).

good percentage fits. Betaine, *Z*-values, $\delta_{^{31}P}$ and 4-nitroanisole are recommended. Probes should be selected to provide a variety of shapes and polarity. Those probes that undergo large changes relative to the accuracy of the measurement are preferred.

Dry acceptor solvents should be studied with at least six dry

Table 5 Parameters for estimating specific and non-specific solvating properties of acceptor solvents

Solvent	E_A'	C_A'	S'	n^a
H_2O	1.91	1.78	3.53	0.28
CH_3OH	1.55	1.59	2.87	0.24
C_2H_5OH	1.33	1.23	2.80	0.23
C_3H_7OH	1.38	1.11	2.68	0.38
i-C_3H_7OH	1.28	0.83	2.66	0.21
t-C_4H_9OH	1.04	0.69	2.46	0.23
C_4H_9OH	1.32	0.90	2.74	0.25
CF_3CH_2OH	1.93	1.31	3.55	0.56
$HC(O)NH_2$	1.13	1.35	3.13	0.26
$HCONH(CH_3)$	0.22	0.47	3.63	1.00
CH_2Cl_2	0.86	0.11	2.08	0.32
$CHCl_3$	1.56	0.44	1.74	0.32
CH_3CO_2H	2.97	0.15	2.39	0.52
$HOCH_2CH_2OH$	1.63	1.49	3.02	0.38

[a] The *n*-value is calculated from the formula $n = (\bar{x} \times 0.3)^{\frac{1}{2}}$. If Betaine, $\delta_{^{31}P}$, *Z* and at least one probe with a small E_B and C_B are not studied, the *n*-value is doubled. If more than one of this group of probes has not been studied, a value of $n = 1$ is assigned.

Table 6 Probe acceptor parameters

Probe (C_B^*/E_B^*)	E_B^*	C_B^*	% Fit	n^a
Betaine (14)	0.46	6.59	0.92	0.26
N(14)PYNO	4.97	4.69	6.1	0.62
Z-value (0.67)	5.29	3.52	0.71	0.25
ANTBUNO	0.276	0.0482	5.9	0.2
$C_6H_5C(SO)(NMe_2)$	2.27	0.097	6.2	0.36
$Me_2NC_6NCR_2$	−0.019	−0.78	13	0.38
ANPIPNO	0.176	0.107	4.5	0.2
NUPYNO	1.25	0.06	4.5	0.2
IQYL	0.195	2.99	5.7	0.23
Brooker's IV	0.80	5.58	2.3	0.39
$CF_3C_6H_4F$	−0.005	−0.036	97	0.24
ln Tau[b]	−1.60	0.64	5.9	0.22
$(C_2H_5)_3PO$ (0.30)	5.25	1.57	1.4	0.29
C(13)DEBZAM	1.36	0.80	6.3	0.24
C(13)PY	0.38	1.17	4.7	0.21
Burgess, Sp (−0.002)	1.13	−0.002	5.4	0.21
C(13)PYNO	1.29	1.95	4.0	0.30
Z′ (0.94)	4.42	4.17	1.2	0.28
NNDMCOUM	(−1.29)	(0.99)	23	0.26
S′(bst)	0.048	0.068	6.8	0.2
COUM	−0.42	−0.12	8.8	0.21
4-Cyano-ox	2.91	4.27	0.61	0.2
Michket (−0.14)	−0.79	0.11	8.7	0.25
ln TauNR[c]	−1.64	0.43	4.8	0.21

[a] The *n*-value is determined with the formula $n = (\bar{x} \times 0.3)^{\frac{1}{2}}$. No system is assigned a value less than 0.2. [b] Ln excited state lifetime $P = -1.37$ and $W = 11.74$, data from ref. 29. [c] Ln excited state lifetime for the non-radiactive decay process. $P = -1.28$ and $W = 11.86$, data from ref. 29.

probes of varying donor strength and C_B^*/E_B^* ratios. The probes can be grouped into the following categories: (1) large C_B^*/E_B^*, large C_B^*; (2) small C_B^*/E_B^*, large E_B^*; (3) $C_B^*/E_B^* \sim 1$ with a large E_B^* and C_B^*; (4) $C_B^*/E_B^* \sim 1$ with a small E_B^* and C_B^*. One probe from each class should be selected. Betaine (for sterically accessible acceptors), Burgess, *Z*-value, NUPYNO, C(13)DEBZAM and $\delta_{^{31}P}$ of Et_3PO are recommended. The χ values for these probes are measured in the new solvent and can be substituted for $\Delta\chi$ into eqn. (4) along with the probe parameters to produce a series of simultaneous equations that is solved for E_A', C_A' and S'. The use of the probe parameters in Table 6 to add a new solvent is illustrated for benzyl alcohol. Since this alcohol has a π-substituent that could form charge transfer complexes with the probes, it was not used in the master fit (Table 4). The χ values that were measured and the corresponding χ-*W* values for various probes in this solvent are given in Table 7. Substituting these χ-*W* values into eqn. (3) along with the corresponding probe parameters from Table 6 leads to seven simultaneous equations. Solution of these equations, weighted with the *n* values in Table 6, leads to $E_A' = 1.51$; $C_A' = 1.00$; $S' = 2.78$. The good fit of the data to eqn. (4) indicates that the hydrogen bonding interactions in this solvent dominate the specific interaction, and π-complexation makes a minor, if any, contribution to the observed shifts. Benzyl alcohol can be added to the acceptor solvents listed in Table 5.

Table 7 Fit of reported data for benzyl alcohol to eqn. (3)

Probe	v	$v - W$(expt)[a]	$v - W$(calc)[b,c]
$C_6H_5C(SO)N(Me)_2$	84.7	6.4	7.07
Betaine	50.8	31.17	31.21
Michler's Ketone	26.48	−4.90	−4.37
BURGESS (Spange)	17.860	5.37	5.55
ANTBUNO/cm^{-1}	15.223	1.256	1.137
ANPIPNO/cm^{-1}	15.242	1.170	1.010
$_{13}$CDEBZAM	35.56	5.77	5.42

[a] *W* values from Table 2. [b] Calculated with $E_A' = 1.51$, $C_A' = 1.00$ and $S' = 2.78$. [c] $\bar{x} = 0.29$.

Adding new probes. The addition of new probes can be accomplished by measuring the spectral shift of a probe molecule in a series of solvents. The χ values in non-interacting solvents of varying polarity should be measured first. These data are fit to eqn. (1) to determine *P* and *W*. The data in acceptor solvents are treated next. *W* is subtracted from the χ values in acceptor solvents, and a series of equations of the form of eqn. (4) is written with χ-*W* replacing χ and the value of *P* fixed. Using solvents whose E_A', C_A' and S' values are known leads to simultaneous equations that are solved for the unknown quantities E_B^* and C_B^*. Literature systems that have been suggested as probes are examined in Table 8.

The UV shifts for nitroaniline and nitroanisole and $\delta_{^{19}F}$ shifts for the probes in Table 8 form the basis for the Kamlet–Taft π^* and corresponding, α-acceptor probe parameters.[4] Good fits to data in non-coordinating solvents are obtained. The resulting *P* and *W* values are given in Table 2. Very poor fits are obtained in acceptor solvents even when any one of the solvents is excluded from the data fit. We conclude that the shifts of these probes in acceptor solvents are poor indicators of donor–acceptor interactions. These probes work well in non-interacting solvents, so the deviation in Table 8 can be attributed to complications in the specific interaction. The probes are probably coordinated incompletely in some solvents, or they contain a variety of coordination sites that are coordinated to different extents in different acceptor solvents.

For K_2TNS, the data in non-acceptor solvents are fit to eqn. (1). The resulting *P* and *W* values are used to analyse the data in acceptor solvents in a subsequent fit of acceptor systems to eqn. (4). The probe K_2TNS fails to qualify as a probe of non-specific or specific solvation. The average deviation in the non-acceptor solvent fit is 0.28 for systems that range over only 1.3 units for a percentage fit of 21%. The potassium ion is an acceptor centre that could lead to specific interactions of the donor solvents with the probe. Solvent coordination could lead to varying extents of ion-pairing causing the probe to fail as an indicator of non-specific solvation. The fit in acceptor solvents is equally poor giving an average deviation of 0.78 and a percentage fit of 18%. Hydrogen bonding of the acceptor to the anion and coordination of the oxygen donor centres in the acceptor solvents to K^+ can lead to complications. Cation solvation, a complicating factor in the K^+TNS^- analysis, does not appear to influence the lifetime of Rose Bengal in the polar solvents that have been studied.

Table 8 Fit of literature data for reported probes to eqn. (3)

	$\delta_{^{19}F}$, $NO_2C_6H_4F$[a,c]			$\delta_{^{19}F}$, $FC_6H_4SO_2F$[a,d]			NNE4NO_2AN[a,e]		
Solvent	v	$v - W$ (expt)	$v - W$ (calc)	χ	$- W$	$\chi - W$ (calc)	v	$v - W$	$v - W$ (calc)
CH_3OH	10.35	1.74	2.06	13.50	2.30	2.44	25.16	−4.15	−4.44
CH_2Cl_2	10.85	2.24	2.11	13.60	2.40	2.36	24.96	−4.35	(−2.93)
$CHCl_3$	11.05	2.44	2.42	13.70	2.50	2.48			
CH_3CO_2H	10.00	1.39	(4.67)	13.05	1.85	(4.54)			
$HCONHCH_3$	10.30	1.69	1.98	13.40	2.20	2.70			
$HCONH_2$	11.00	2.39	1.95	13.85	2.65	2.45			
i-C_3H_7OH							25.35	−3.96	−3.94
C_4H_9OH							25.51	−3.80	−4.07
C_2H_5OH							25.48	−3.83	4.32
HOC_2H_4OH							24.10	−5.21	4.59
H_2O							23.23	−6.08	−5.38
$(CH_3)_3COH$							25.61	−3.70	−3.71
C_3H_7OH							25.35	−3.96	−4.03
CF_3CH_2OH							23.70	−5.61	−5.18
$O[CH_2]_2CH_2CH_2$									
$CH_3CO_2C_2H_5$									
$(CH_3)_2CO$									
$CH_3CON(CH_3)_2$									
$HCON(CH_3)_2$									
$(C_3H_7O)_2CO$									

	4NO_2ANISOL[a,f]			$K_2{}^+TNS^-$[b,g]			Ni(tfd)(phen)[a,h]		
Solvent	v	$v - w$	$v - w$ (calc)	v	$v - w$	$v - w$ (calc)	v	$v - w$	$v - w$ (calc)
CH_3OH	32.79	−2.72	−3.03	22.52	−3.77	−4.95	56.80	11.25	10.4
CH_2Cl_2							55.30	9.75	8.9
$CHCl_3$							53.70	8.15	7.2
CH_3CO_2H	32.63	−2.88	(−0.15)				55.80	10.25	10.8
$HCONHCH_3$									
$HCONH_2$	31.65	−3.86	−3.66	20.70	−5.59	−5.27			
i-C_3H_7OH	32.94	−2.57	−2.60	23.70	−2.59	−2.92	55.20	9.65	10.15
C_4H_9OH	32.89	−2.62	−2.71	23.58	−2.71	−3.14			
C_2H_5OH	32.89	−2.62	−2.96				55.70	10.15	10.6
HOC_2H_4OH	31.95	−3.56	−3.09						
H_2O	31.55	−3.96	−3.63	19.42	−6.87	−5.55			
$(CH_3)_3COH$	32.94	−2.57	−2.51	23.47	−2.82	−2.73			
C_3H_7OH	32.89	−2.62	−2.69				55.50	9.95	10.2
CF_3CH_2OH	31.75	−3.76	−3.36	20.41	−5.88	−4.09			
$O[CH_2]_2CH_2CH_2$				23.98	—	24.29			
$CH_3CO_2C_2H_5$				24.33	—	24.06			
$(CH_3)_2CO$				23.87	—	23.62			
$CH_3CON(CH_3)_2$				23.64	—	23.49			
$HCON(CH_3)_2$				23.36	—	23.39			
$(C_3H_7O)_2CO$				22.99	—	23.32			

[a] P and W were determined from data in non-protic solvents and fixed in the protic solvent fit. [b] K. Medda, M. Pal and S. Bagchi, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 1501. [c] $E_B{}^* = 1.14$, $C_B{}^* = -0.88$, $P = 0.59$; $\bar{x} = 0.24$, % fit = 34. [d] $E_B{}^* = 0.93$, $C_B{}^* = -0.80$, $P = 0.79$; [e] $E_B{}^* = 0.74$, $C_B{}^* = -0.46$, $P = -1.69$; $\bar{x} = 0.32$, % fit = 14. [f] $E_B{}^* = 1.02$, $C_B{}^* = -0.57$, $P = -1.29$; [g] $E_B{}^* = 1.86$, $C_B{}^* = -3.05$, $P = -1.04$, $W = 26.29$; [h] $E_B{}^* = 0.26$, $C_B{}^* = -1.41$, $P = 4.27$; $\bar{x} = 0.54$, % fit = 19.

This poor result for $K_2{}^+TNS^-$ illustrates a positive feature of the Unified Solvation Model. The poor fit indicates that the model is not parameterized to the point where almost any data set can be fit. Furthermore, rather than fit another set of data to accommodating parameters, the connection of the parameters to eqn. (2) enables the model to recognize a data set in which the donor–acceptor interactions are more complicated than the interactions for the probes in Table 6.

The probe Ni(tfd)phen is a viable indicator of non-specific solvation. However, the data in acceptor solvents indicate that the specific interactions in this system are complex. Good fits do not result when either one or two solvents are eliminated from the data fit.

Future research in this area should be directed toward finding probes whose properties are easy to measure and which possess different shapes and polarity than those afforded by the systems in Table 2. Covalent solvents and small probes are of particular interest. It is anticipated that bulky solvents may not form cavities small enough to effectively solvate small solutes, which will lead to a poor fit to eqn. (1).

Using the parameters to interpret reactivity. The Brownstein parameters (bst) are reactivity parameters that have been optimized to fit a variety of IR spectral shifts and rates of reactions. These parameters correlate well with S' parameters for donor solvents ($\bar{x} = 0.02$). They also correlate very well in the acceptor solvent data fit. The fit of the Brownstein scale

Table 9 Solvation model estimation of enantiomeric excess[a]

Solvent	ee	ln (ee)(exp)	ln (ee) − *W*(exp)	ln (ee) − *W*(calc)[b]	ee(calc)[c]
$C_6H_5CH_3$	7	1.95	1.31	2.06	15
$CH_3CO_2H_5$	9	2.20	1.56	2.59	25
$(CH_2)_4O$	31	3.43	2.79	2.51	23
$HCON(CH_3)_2$	51	3.93	3.29	3.37	55
CH_2Cl_2	53	3.97	3.33	3.30	51
CH_3OH	72	4.28	3.64	3.65	73
C_2H_5OH	79	4.37	3.73	3.66	74
i-C_3H_7OH	88	4.48	3.84	3.79	84
t-C_4H_9OH	83	4.42	3.78	3.43	59
CF_3CH_2OH	69	4.22	3.59	(5.11)	—

[a] $E_B{}^* = 1.03$, $C_B{}^* = -0.89$, $P = 1.21$ and $W = 0.64$. [b] $\bar{x} = 0.29$, % fit = 12. [c] $\bar{x} = 8$, % fit = 9.9.

indicates that the solvent parameters in Tables 1 and 5 can be used with confidence in analysing solvent effects on chemical reactivity in a wide variety of systems. The Brownstein parameters are adjusted to fit a variety of physicochemical measurements with varying *C*/*E* ratios to a one parameter scale.[26] This average scale will not fit the data as well as the dual parameter data fit of eqns. (3) or (4). Thus, the good fit of the Brownstein scale to eqn. (4) suggests an even better fit of the individual data sets that form the basis for the Brownstein parameters to eqns. (3) and (4). The procedure used to analyse reactivity data is similar to that described above for adding a new probe. Though any measured physicochemical property can be analysed with eqn. (4), it is important to realize that $\Delta\chi$ must have energy (kcal mol^{-1}) or energy related (*e.g.* kK, cm^{-1}) units.

The use of our solvation model in reactivity studies can be illustrated with a study[30] of the influence of solvent on the enantiomeric excess (ee) obtained in the hydrogenation of *N*-acylhydrazone. The ee is considered to be the consequence of two competing paths for the hydrogenation reaction. For the purposes of the correlation, the relative energies of activation should be employed and not the relative rate constants. A fit of this data is shown in Table 9. In view of the complexity of the chemical reaction being considered, the fit is good. The mechanisms whereby solvation leads to an increased ee are not known. At low ees, the activation energies for the two paths are not very different and small errors in predicted activation energy differences lead to large errors in the ee values. The general trend is reproduced except for the solvents *tert*-butanol and trifluoroethanol. For the former, the bulkiness of this solvent may lead to high ees by a mechanism other than the mechanism involved in solvent specific and non-specific interactions. In the case of trifluoroethanol, intramolecular hydrogen bonding of the hydroxy group to fluorine may lead to error in the estimate of the specific interaction. Polarity in the non-specific interaction ($P = 1.21$) and electrostatic bonding ($E_B{}^* = 1.03$) in the specific interaction lead to an increased ee. Covalency in the interaction ($C_B{}^* = -0.9$) leads to a decreased ee.

The range in the $C_A{}'/E_A{}'$ ratios of the solvents used to obtain $E_B{}^*$ and $C_B{}^*$ for the reaction is not very large. This leads to uncertainty in the prediction of the magnitude of the ees on new systems. For example, ethylene glycol is predicted to give an ee over 100%. Our objective in analysing a complex reaction is not to obtain a high quality fit, but to detect patterns in solvent influences. In this reaction, the trend predicted with the parameters is expected to prevail leading to the conclusion that butanol is expected to give an ee equal to or slightly larger than isopropanol, while benzyl alcohol and ethylene glycol are expected to give the largest ee value and be the best of the alcohols. This type of application, which guides the selection of solvents for synthetic or other practical applications, is one of the most important consequences of this correlation.

The Cavity Term in Solvation Effects.—Measurements of the enthalpies of solution of one liquid in another has formed the basis for regular solution theory.[31] Though the *E* and *C* parameters should provide an estimate of the specific interaction of donor or acceptor molecules in donor or acceptor solvents, enthalpy data should not be analysed with the Unified Solvation Model. In contrast to spectral shifts, enthalpies contain an endothermic contribution from the energy that must be expended to create a cavity in the solvent to accommodate the solute. Additional solvent parameters are needed to correlate this energy contribution. The same is true for reactions whose transition states require extensive solvent rearrangement to provide a cavity of appropriate size. This cavity term does not contribute to any of the data for the probes contained in Table 2. This problem is discussed in detail in a recent article,[32] where a model has been offered to analyse enthalpy data using *E* and *C* to account for specific interactions.

A One Donor Parameter Fit of the Specific Interaction.—Earlier work[33] has shown that when the C_A/E_A ratio of a series of acceptors is constant, physicochemical measurements can be interpreted with a one parameter basicity scale. Since the $C_A{}'/E_A{}'$ ratios of the acceptor solvents only vary from 0.05 to 1.2, it was of interest to determine if the specific interaction for the probes studied could be accommodated with a one parameter scale. The data in Table 4 were fit to the eqn. (6),

$$\chi = A_iB_i + S'P + W \qquad (6)$$

where A_i is a one parameter, solvent acceptor scale and B_i a parameter, probe donor scale. The S' value of CH_2Cl_2 was set at 2.08; *P* and *W* for the probes were fixed at the values from the non-interacting solvent fit. The least squares program was allowed to find the best fit A_i, B_i and S' values for all other probes and solvents. An unacceptable fit results. Compared to the fit to eqn. (4), the $\bar{x}$ values for the various solvents were almost twice as large, and twice as many systems deviated by more than the experimental error in the measurement. We conclude that a two parameter equation is needed to accommodate specific interaction with solutes whose $C_B{}^*/E_B{}^*$ ratios vary from 0.05 to 14 in solvents whose $C_A{}'/E_A{}'$ ratios vary from 0.05 to 1.2.

Experimental and Calculations

Purification of Reagents.—*o*-Dichlorobenzene (Fisher Scientific) was distilled over CaH_2 under N_2. Betaine 95% (Aldrich) was used without any further purification. The alcohols were distilled over CaO under N_2. The CH_2Cl_2 was distilled over P_2O_5 under N_2.

Betaine Shifts with Solvent Composition.—A stock solution of betaine dissolved in *o*-dichlorobenzene ($\sim 2 \times 10^{-4}$ mol dm^{-3}) was prepared. The alcohol was weighed into a 5 cm^3 volumetric flask by difference. The betaine stock solution (2 cm^3) was delivered by pipette into the flask. Then, the volumetric flask was filled with *o*-dichlorobenzene. This procedure was repeated for a range of weights of alcohols, making solutions from very dilute to very concentrated solutions of alcohol. The UV/VIS spectrum of each solution was taken using a Perkin Elmer Lambda 6 spectrophotometer. The longest wavelength absorption maximum was monitored.

Calculations.—The spectral data for the various probe solutes listed in Table 2, measured in the solvents listed in Table 1, were fit to eqn. (1) using a least squares minimization routine.[2b] The resulting fit is of the quality reported earlier and is shown in the supplementary material. The P and W values of the donor probes determined in the fit of polar donor solvents (Table 2) are fixed in the subsequent fit of hydrogen bonding solvents. The W value for these probes is subtracted from χ, and $\chi - W$ of eqn. (3) is minimized.

In addition to the measured shifts ($\chi - W$), the specific interaction of betaine with octan-1-ol was entered as one of the simultaneous equations to be solved in the data fit using the reported[2] E_A and C_A values for octanol. For the solvents CH_2Cl_2 and $CHCl_3$, the reported E_A and C_A values were used. The specific interaction of $SbCl_5$ with $(C_2H_5)_3PO$ was entered with reported E_A and C_A values for $SbCl_5$. The values for the non-specific contribution to the $E_T(30)$ shift were also entered as additional simultaneous equations for the data fit. This entry is labelled 'betns' and is assigned an E value and C value of zero. The P value of betaine is known and fixed for the betns equations. This entry provides for a more accurate determination of the S' values for the alcohols. A weight is given for each $\chi - W$. The weight assigned to each data point in the fit is given by $1/n$. The values used for n are reported in the supplementary material. For most $\chi - W$ values, the value of n is 1. The exceptions are described below. In the case of N14PYNO, the values of $\chi - W$ were given an n value of 3 (corresponding to one third of the weight) due to quadrupolar interactions. Since the $\chi - W$ value for Antbuno, Anpipno and S'(bst) are small compared to other probes, the n-values for these systems were set at 0.3.

Some of the probes that were studied only with a limited set of solvents ($CF_3C_6H_4F$ and $Me_2NC_6H_4NCR_2$) settled into meaningless minima. This is usually characterized by a very large negative value of $E_B{}^*$ (or $C_B{}^*$) or a large positive value of $C_B{}^*$ (or $E_B{}^*$). In order to eliminate this problem, a construct was devised called 'E-acid' and 'C-acid'. 'C-Acid' is defined as an acid which has parameters, $E_A = 0$, $C_A = 1$, and $S' = 0$. When C-acid was entered into the fit with a value assigned to it, C-acid was treated by the program as an additional shift. Doing this allowed the program to find the best fit of the data with the added constraint that the $C_B{}^*$ will have to fall in a range near the value assigned as a shift with C-acid. The extent to which $C_B{}^*$ is allowed to miss the assigned value is a function of the n assigned to the C-acid shift. For $Me_2NC_6H_4NCR_2$, a C-acid shift was added with a value of -0.40 and $n = 2.0$. The quantity called 'E-acid' is a similar construct for the E_B value with $E_A = 1$, $C_A = 0$ and $S' = 0$. For $CF_3C_6H_4F$, an E-acid shift was added with a value of -0.03 at a value of $n = 0.01$.

There are several alcohols for which E_A and C_A are known. Therefore, the E_A' and C_A' for the alcohol solvents should be in the same range. To make the E_A' and C_A' values close to E_A and C_A, the constraint of E-base of C-base is used. As above, E-base has $E_B = 1$, $C_B = 0$, $P = 0$; C-base has $E_B = 0$, $C_B = 1$, and $P = 0$. In this instance, the knowledge of parameters for the dilute acceptor can be introduced to help define the parameters for the neat acceptor as solvent. Again, the value E-base assigned to an alcohol is treated as an additional shift by the program. These constructs allow the best fit of the data to result and eliminate the possibility that some random error in the experimental data will cause the program to select an E_A value which does not conform with known systems.

For the fit of LnTau and LnTauNR, the following procedure was used. An earlier data fit of the large data base which did not include LnTau and LnTauNR was used to calculate an initial $E_B{}^*$, $C_B{}^*$, P and W. The W value was then varied to yield an optimal value for $E_B{}^*$, $C_B{}^*$ and P. At this point, it was decided that LnTau and LnTauNR should be included in the large data fit. The $\chi - W$ data was entered using the optimized W calculated above. To allow for an optimal P value, the donor solvent $\chi - W$ was entered also. For these solvents, $E_A' = 0$ and $C_A' = 0$, so the program calculated the $\chi - W$(calc) using only the solvent S' value and the P for the probe.

The fit in Table 7 was done using the P and W values from Table 2 and the E_B and C_B and n values from Table 6. A smaller computer program which is designed for this type of fit was used. The W was subtracted from the χ values, and the best E_A, C_A and S' was found. The fit of the probes in Table 8 was done in the same manner. The W given in Table 2 was subtracted from $\Delta\chi$. The P value was also fixed at the value reported in Table 2. The E_A, C_A and S' and n values found in Table 5 were used to find the best E_B and C_B. For $K_2{}^+$TNS, the donor solvents were fit first using the values found in Table 1. The P and W found were used as described above to gain the E_B and C_B value from the acid solvent systems.

For the fit in Table 9, the four non-hydrogen bond solvents were used to find a P and W. The weight assigned to tetrahydrofuran (THF) and dimethylformamide (DMF) was 0.2. The weight of ethyl acetate and toluene was set at 0.5 due to the potential error in ee. The W was subtracted and a best fit for E_B, C_B and P obtained for the hydrogen bonding solvents with eqn. (4). The donor solvents were used in eqn. (4) to redetermine P as described above for Rose Bengal.

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