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Donor–acceptor and polarity parameters for hydrogen bonding solvents

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The acceptor parameters E_A' and C_A', as well as the unified solvation model solvent polarity parameters S' have been determined for 18 hydrogen bonding solvents enabling resolution of spectral shifts into specific and non-specific components. Equations are given which permit calculation of the E_A and C_A acceptor parameters for 77 substituted phenols. Alcohols are amphoteric solvents. This study also reports the donor parameters E_B and C_B to permit the calculation of the specific interaction for alcohols reacting as bases. Some of the well-known scales of solvent polarity and hydrogen bond acidity are examined and the claims made for the absence of specific or non-specific contributions in the scales evaluated. The ability of the unified solvation model to correlate a diverse set of solvation parameters shows the advantage of treating specific and non-specific solvation separately.

Introduction

There are numerous reports and excellent reviews[1] on the use of the solvatochromism of various probes to estimate solvent polarity. The more common probes, which include $E_T(30)$,[1a–e] Z-value,[2] π^*[3] and SPP^N[4] cover a wide range of solvent polarity. Work in this laboratory[5] has consolidated these and other solvatochromic data into the unified solvation model (USM), revealing a combination of specific and non-specific interactions in most of the reported scales. By eliminating systems involving specific interactions, a composite scale, S', of solvent polarity for non-specific interactions results, that encompasses most of the data from all of the more common scales. The influence of non-specific solvation on physico-chemical properties of solutes is estimated with USM using eqn. (1), where S' is the solvent polarity parameter, $\Delta\chi$ (with

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

units of energy) is the solvent dependent value of the physico-chemical property, P is the measure of the susceptibility of the solute to solvation and W is the value of $\Delta\chi$ when S' is zero. Because extrapolation of solvent polarity to $S' = 0$ may not remove the dispersion component, the W value is not necessarily the gas phase value. Values for S' have been established for over 50 donor solvents involved in non-specific interactions with more than 30 solute probes.[5c] Use of S' in correlations enables one to attribute deviations in data fits to specific interactions as opposed to looking for a good correlation by finding one of the several scales that will average in specific effects.

Alcohols and other protic solvents are widely used, but invariably cause problems in correlations to solvation parameters. These solvents were only briefly treated in the USM.[5c] An increased understanding of the specific and non-specific components of the reactivity of this important class of solvents is desired. Alcohol solvents are complicated by their amphoteric nature. In order to establish acceptor parameters, systems must be selected in which the probe is clearly an electron pair donor and the solvent alcohol the acceptor. An independent data fit to determine the alcohol donor parameters must use systems in which the probe is clearly an acceptor and the alcohol a donor.

Various attempts have been made to account for the specific acceptor interaction of protic solvents using one-parameter scales. Abraham's α_2^H scale of hydrogen bond acidity[6] is based on equilibrium constants measured in CCl_4. Taft and Kamlet[7] added an α term to their π^* scale for acceptor solvents capable of hydrogen bonding and a β term for donor solvents. Catalán's SPP^N scale has been extended in recent work[8] to include hydrogen bonding solvents.

The pitfalls associated with the use of one-parameter scales to describe donor–acceptor interactions[9] and the demonstrated[5] utility of USM to separate specific and non-specific interactions led to a reexamination of protic solvents by treating the non-specific donor–acceptor interaction with the USM model, and the specific interaction with the added terms in eqn. (2). In eqn. (2), $\Delta\chi$ is the physico-chemical property, E_A and C_A

$$\Delta\chi = E_AE_B^* + C_AC_B^* + S'P + W \qquad (2)$$

are the electrostatic and covalent acceptor parameters for the monomer, and E_B^* and C_B^* are the corresponding parameters for the response of the donor probe to electrostatic and covalent interactions. The W parameter is the value of $\Delta\chi$ when $P = E_B^* = C_B^* = 0$. In the case of alcohol solvents, the E' and C' parameters for the solution aggregates would differ from those of the monomer.

With the alcohol functioning as a donor solvent toward an acceptor probe, eqn. (2) takes the form shown as eqn. (3), where

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

E_B and C_B are the donor parameters. E_A^* and C_A^* are the acceptor probe response parameters. Analyses with eqns. (2) and (3) provide increased understanding of the solvation process by providing the specific and non-specific components. It is significant that many of the base E_B and C_B parameters, as well as acidic solvent E_A and C_A parameters used in these data fits, are obtained from independent[9a] enthalpy measurements in poorly solvating solvents and are not simply two more adjustable parameters to fit solvent shifts.

Experimental and calculations

Data fits

For each donor solute (probe) studied in donor solvents whose S' values are known, the physico-chemical data, $\Delta\chi$, are substi-

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tuted into eqn. (1) leading to several simultaneous equations for each solute. Using a least squares minimization routine, a *P* and *W* value are calculated for each solute and are referred to as probe parameters in Table 2. The above systems involve only non-specific interactions. For donor solutes studied in alcohol as well as donor solvents, the combined data are fit to eqn. (2). E_A and C_A are set at zero for the donor solvents and, if known,[9a] the reported values are entered and fixed for the protic solvents. Reported[5c] *P* and *W* probe parameters from non-specifically interacting donor solvents are entered and fixed in the data fit of these probes in protic solvents. The program solves for the unknown parameters giving best fit E_A, C_A and S' values for hydrogen bonding solvents and the best fit E_B*, C_B*, *P* and *W* for new probes.

The values reported[5c] for 7-amino-4-methylcoumarin (coum) and 7-dimethylamino-4-methylcoumarin (dmcoum) were incorrect. The revised *P* and *W* values used in this fit are −1.39 and 27.86 and −1.33 and 26.76, respectively.

An experimental procedure was reported earlier[5c] for the separation of specific and non-specific contributions to the observed shift of betaine. Results were obtained for non-specific solvation of this probe in the solvents methanol, ethanol, butan-1-ol, 2-methylpropan-2-ol, octan-1-ol and dichloromethane. The non-specific solvation shifts of betaine in these solvents were entered in the data fit with E_B* and C_B* fixed at zero because no specific interactions are involved.

In addition to spectral shifts, the enthalpies of interaction of alcohols with donors in non-solvating solvents were included in the fit. These results have no non-specific contributions so *P* is set at zero. In combining this and pure solvent data, the assumption is made that the alcohol aggregates that exist in the non-solvating solvents and in the neat alcohol have similar E_A and C_A values. The spectral probes and enthalpies of interaction for hydrogen bonding solvents lead to a total of 453 simultaneous equations, which were solved for 16 S' values, as well as E_A and C_A for 15 hydrogen bonding solvents (E_A and C_A values for 2,2,2-trifluoroethanol, CH_2Cl_2 and $CHCl_3$ were fixed at previously reported values[9a]). E_B* and C_B* values were determined for 43 donor probes.

The systems in which the alcohols are acting as donors were treated in a separate fit. Systems were first chosen where non-specific interactions were minimized through the use of poorly solvating solvents such as cyclohexane or CCl_4. Several probes, whose E_A*, C_A* and *W* values were reported earlier,[9] were fixed. To fit new acceptor probes, bases whose E_B and C_B values are known were fixed and combined with the basic alcohol data. The data were fitted to eqn. (2) to determine the new probe E_A*, C_A* and *W* parameters, and the best fit E_B and C_B values for the alcohols.

Several solvents have only limited data available, leading to tentative parameters that are assigned low weights in Table 1. These weights should be used in subsequent analyses, and if large deviations occur, the solvent parameters should be redetermined by refitting all available data. The procedure for adding or revising probes or solvents is reported.[5c,9a]

The probe E_B* and C_B* parameters, listed in Table 2, have been determined using acceptors whose C_A/E_A ratio is limited to the range of 0.1 to 1. Applications should be limited to acceptors whose ratio falls in this range, and the parameters should be redetermined as new systems outside this range become available.

^{13}C NMR solvatochromism experiment

Approximately 0.1 M solutions of 4-nitrobenzoic acid (NBA) were prepared in the following solvents: methanol; ethanol; propan-1-ol; propan-2-ol; butan-1-ol; 2-methylpropan-2-ol; acetonitrile; *N*,*N*-dimethylacetamide; *N*,*N*-dimethylformamide; dimethyl sulfoxide; chloroform; dichloromethane and diethyl ether. All solvents were purified according to published methods,[31] and the ^{13}C spectra were obtained using a Varian VXR 300. An external lock and reference of deuterated acetone and TMS in a sealed capillary tube were used during each run. The chemical shifts (relative to TMS) of all carbons in the NBA–solvent adduct were recorded.

Table 1 Alcohol E_A, C_A and S' parameters

Solvent (C_A/E_A)	Wgt[a]	E_A	C_A	S'
H_2O[b] (0.58)	0.5	1.35	0.78	3.86
CH_3OH (0.58)	1	1.27	0.74	2.87
C_2H_5OH (0.58)	1	1.15	0.67	2.79
n-C_3H_7OH (0.58)	0.6	1.17	0.68	2.68
i-C_3H_7OH (0.58)	1	1.19	0.69	2.40
n-C_4H_9OH (0.70)	1	1.05	0.74	2.75
t-C_4H_9OH (0.58)	1	1.14	0.66	2.46
n-$C_5H_{11}OH$[c] (0.54)	0.2	1.27	0.68	2.35
n-$C_6H_{13}OH$ (0.61)	0.2	1.14	0.70	2.51
$C_6H_{11}OH$ (0.41)	0.6	1.23	0.50	2.22
n-$C_8H_{17}OH$[c] (1.0)	0.4	0.89	0.87	2.62
CF_3CH_2OH (0.51)	0.8	2.07	1.06	3.05
$HC(O)NH_2$[d] (0.16)	0.6	2.00	0.32	2.22
$HCONH(CH_3)$[d] (0.12)	0.2	1.25	0.15	2.56
CH_2Cl_2[d] (0.13)	1	0.86	0.11	2.03
$CHCl_3$[d] (0.28)	1	1.56	0.44	1.63
CH_3COOH (0.27)	0.2	3.39	0.91	1.28
$C_6H_5CH_2OH$ (0.46)	0.2	1.19	0.55	2.62

[a] Weight. Probes with measured enthalpies and 12 defined spectral probes are assigned a weight of one. If no enthalpies are reported, 0.2 is subtracted. If there are only 10 different types of spectral probes, 0.1 is subtracted; if only eight probes, 0.2 is subtracted; if only six probes, 0.4 is subtracted; and if only four probes, 0.6 is subtracted. [b] Hydrophobic probes give poor results in water, as do several other probes that are well-behaved in the alcohols studied, *e.g.* C_5H_5NO (PYNO). [c] The S' value is poorly defined because of limited data. [d] Lower weights may have to be used with weakly basic probes because of incomplete complexation in these solvents.

Results and discussion

Acceptor solvent and donor probe parameters

The resulting E_A, C_A and S' values for the protic solvents included in this data fit are listed in Table 1. All reported data for the solvents in Table 1 are included for each solute unless indicated in the discussion. The non-specific interactions in methanol and ethanol are characterized by S' values comparable to DMF. The polarity decreases with alkyl chain length and with chain branching. The solvent values of E_A and C_A in combination with the probe E_B* and C_B* give the specific donor–acceptor component of the property examined. Consistent with expectation, the exceptional solvent properties of alcohols for basic solutes are due to contributions from both specific and non-specific interactions. The parameters permit determination of the relative importance of these two effects for different solutes.

Table 2 lists the probe name and abbreviation as well as the intercept (*W*), susceptibility (*P*) and the electrostatic and covalent donor parameters (E_B* and C_B*). The *P* and *W* parameters include those previously reported[5c,d] and the new probes labelled as Fe2, Fe3, MoTp3, MoTp6, TEMPO and Nile Red. The sign of the *P* value gives the direction of the solvent influence.

Weak donor spectral probes dissolved in weak acceptor solvents sometimes deviate from the fit in a direction that suggests incomplete complexation. With a positive *P* value, incomplete complexation of a solute leads to an experimental value that is smaller than the calculated value. For probes with negative *P* values, the experimental value is larger than the calculated value. Weak donor probes in the solvents CH_2Cl_2, $CHCl_3$ and *N*-methylformamide (NMF), have been omitted from the data fit. When one considers the complexity from the existence of multiple donor sites in many probes, the fact that so many systems are well behaved is more surprising than finding that some

Table 2 Probe parameters

Probe (Symbol)	E_B*	C_B*	*P*	*W*	Wgt[a]
ν; *N*,*N*-Diethyl-4-nitroaniline (NNE4NO2AN)[b]	−1.43	3.23	−1.69	29.31	0.9
ν; *N*,*N*-Dimethyl-2-nitroaniline (NNM2NO2AN)[c]	−0.69	2.01	−0.99	26.19	1
ν; 4-Nitroanisole (4NO2ANISOL)[d]	−0.92	2.72	−1.29	35.51	0.9
ν; *N*,*N*-Dimethyl-2-nitrotoluidine (NNM2NO2TOL)[e]	−0.32	1.37	−0.95	25.60	1
ν; 4-(2,4,6-Triphenyl-1-pyridino)-2,6-diphenylphenoxide (betaine)[f]			8.61	19.63	0.8
ν; 2-(Dimethylamino)-7-nitrofluorene (DMANF)[g]			−1.10	26.20	1
ν; 2-Fluoro-7-nitrofluorene (FNF)[g]			−0.65	31.60	1
$\Delta\nu$; FNF − DMANF[h]			0.47	5.40	1
A_N; Di-*tert*-butyl aminoxyl (ANTBUNO)[i]	0.33	0.00	0.24	13.967	1
A_N; 4-Amino-2,2,6,6-tetramethylpiperidin-1-oxyl (ANPIPNO)[i]	0.21	0.16	0.229	14.072	1
ν; *N*,*N*-(Dimethyl)thiobenzamide *S*-oxide [C6H5CSO(NMe2)][j]	1.21	2.85	1.27	78.28	1
ν; Pyridine *N*-oxide (NUPYNO)[k]	0.92	0.92	0.36	35.00	0.8
δ ^{31}P; Triethylphosphine oxide (ET3PO)[l]	5.87	3.75	5.09	−8.91	0.9
δ ^{13}C; *N*,*N*-Diethylbenzamide (C13DEBZAM)[m]	1.49	1.43	0.92	29.79	0.8
ν; α-[4-(*N*,*N*-Dimethylamino)phenyl]iminoacetoacetanilide (Me2NC6H4NCR2)[n]	−3.02	4.38	−2.41	73.91	1
δ ^{13}C; Pyridine *N*-oxide (C13PYNO)[o]	1.17	3.25	1.92	−19.80	1
δ ^{13}C; Pyridine (C13PY)[p]	−0.28	3.69	0.89	−16.53	1
ν; 7-Amino-4-methylcoumarin (coum)[q]	−0.13	−1.12	−1.39	27.86	0.7
ν; 7-*N*,*N*-Dimethylamino-4-methylcoumarin (dmcoum)[q]	−0.41	−0.48	−1.33	26.76	1
Brownstein's *S* Parameter [*S* (bst)][r]	0.10	0.03	0.09	−0.392	1
ν; 4,4′-Bis(dimethylamino)benzophenone (Michler's ketone)[s]	−1.15	0.60	−1.18	31.38	0.8
ν; *cis*-Dicyanobis(1,10-phenanthroline)iron(II) (FePHEN)[s]	1.38	−0.08	1.38	12.49	1
In Tau[t]	−1.02	−0.33	−1.37	11.74	0.7
In TauNR[t]	−1.11	−0.55	−1.28	11.86	0.7
ν; *cis*-Dicyanobis(1,10-phenanthroline)ruthenium(II) (RuPHEN)[u]	1.33	0.30	1.11	16.99	0.9
ν; Bis(bipyridyl)dichloroplatinum (PtBPY2Cl2)[v]	1.37	−1.46	1.86	20.58	1
ν; Tetracarbonylbipyridinetungsten (WCO4BPY)[w]	0.95	−3.24	2.37	15.34	0.8
ν; Tetracarbonylbipyridinemolybdenum (MoCO4BPY)[w]	0.76	−2.77	2.15	16.51	0.8
ν; Tetracarbonylbipyridinechromium (CrCO4BPY)[w]	1.09	−3.86	2.36	14.68	1
ν; Tetracarbonylphenanthrolinetungsten (WCO4PHEN)[w]	1.45	−4.28	2.24	15.70	0.9
ν; $Fe(LL\ II)_2(CN)_2$ LL II = Schiff base ligand 2 (Fe2)[x]	0.75	0.12	0.56	13.40	1
ν; Bis(2,2′-bipyridyl)biscyanoiron(II) (Fe3)[y]	1.90	−1.00	1.57	12.32	0.8
ν; [{Mo(NO)Tp*Cl}0(L-L)] (L-L) = $4\text{-}NC_5H_4(CH{=}CH)_4C_5H_4N\text{-}4'$ (MoTp3)[z]	0.89	−1.17	1.13	15.15	0.9
ν; [{Mo(NO)Tp*I}0(L-L)] (L-L) = $4\text{-}NC_5H_4(CH{=}CH)_4C_5H_4N\text{-}4'$ (MoTp6)[z]	0.50	−0.53	0.88	15.93	0.5
ν; Nile Red[aa]	−0.85	0.82	−1.11	21.66	1
ν; 2,2,6,6-Tetramethylpiperidine-*N*-oxyl radical (TEMPO)[bb]	0.50	0.21	0.31	20.67	1

[a] Weight. The weight assigned here is equal to $1/[5(0.3x)^{\frac{1}{2}}]$. This is consistent with the scheme used in previous papers, where '*n*' was used as a weighting factor, and a smaller '*n*' value gave more weight. We have changed this so that a larger 'wgt' means more weight is given. [b] Electronic transition energy in 10^3 cm^{-1}. Data from ref. 10*a*. $x = 0.15$, %fit = 6. [c] Electronic transition energy in 10^3 cm^{-1}. Data from ref. 10*b*. $x = 0.05$, %fit = 4. [d] Electronic transition energy in 10^3 cm^{-1}. Data from ref. 10*a*. $x = 0.15$, %fit = 11. [e] Electronic transition energy in 10^3 cm^{-1}. Data from ref. 10*b*. $x = 0.07$, %fit = 5. [f] Transition energy in kcal mol^{-1}. Data from ref. 1. $x = 0.42$, %fit = 4. [g] Transition energy in cm^{-1}. Data from refs. 4, 8. DMANF: $x = 0.16$, %fit = 12. FNF: $x = 0.16$, %fit = 13. [h] Difference in the transition energies of FNF and DMANF in cm^1. [i] The nitrogen hyperfine coupling constant in 10^{-4} cm^{-1}. Data from ref. 11 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 10^{-4} cm^{-1}. The fit is run by multiplying the numbers by 10^4. ANTBUNO: $x = 0.04$, %fit = 9. ANPIPNO: $x = 0.04$, %fit = 10. [j] Transition energy in kcal mol^{-1}. Data from ref. 12. $x = 0.21$, %fit = 4. [k] Transition energy in 10^3 cm^{-1}. Data from ref. 13. $x = 0.07$, %fit = 3. [l] ^{31}P chemical shift in ppm. Data from ref. 14. $x = 0.08$, %fit = 1. [m] Difference in ^{13}C chemical shift (in ppm) of C=O and C(1) of the phenyl ring. Data from ref. 15. $x = 0.03$, %fit = 2. [n] Transition energy in kcal mol^{-1}. Data from ref. 16. $x = 0.09$, %fit = 3. [o] Difference in ^{13}C chemical shift (in ppm) between γ and α carbons. Data from ref. 17. $x = 0.25$, $r^2 = 0.99$. [p] ^{13}C chemical shift in ppm. Data from ref. 18. $x = 0.08$, %fit = 2. [q] Transition energy in kcal mol^{-1}. Data from ref. 19. coum: $x = 0.23$, %fit = 12. dmcoum: $x = 0.08$, %fit = 4. [r] Dimensionless reactivity scale. Data from ref. 20. $x = 0.03$, %fit = 10. [s] Transition energy in 10^3 cm^{-1}. Data from ref. 21. Michler's ketone: $x = 10$, %fit = 4. FePHEN: $x = 0.10$, %fit = 4. [t] Excited state lifetime of Rose Bengal. Data from ref. 22. Ln Tau: $x = 0.06$, %fit = 3. Ln TauNR: $x = 0.07$, %fit = 3. [u] Transition energy in 10^3 cm^{-1}. Data from ref. 23. $x = 0.16$, %fit = 5. [v] Transition energy in 10^3 cm^{-1}. Data from ref. 24. $x = 0.34$, %fit = 9. [w] Transition energy in kJ mol^{-1}. Data from ref. 25. WCO4BPY: $x = 0.09$, %fit = 8. MoCO4BPY: $x = 0.17$, %fit = 14. CrCO4BPY: $x = 0.13$, %fit = 10. WCO4PHEN: $x = 0.19$, %fit = 16. [x] Transition energy in 10^3 cm^{-1}. Data from ref. 26*a*. $x = 0.11$, %fit = 7. [y] Transition energy in 10^3 cm^{-1}. Data from ref. 27. $x = 0.16$, %fit = 10. [z] Transition energy in nm. Data from ref. 28. MoTp3: $x = 0.14$, %fit = 8. MoTp6: $x = 0.23$, %fit = 13. [aa] Transition energy in 10^3 cm^{-1}. Data from ref. 29. $x = 0.12$, %fit = 7. [bb] Transition energy in 10^3 cm^{-1}. Data from ref. 30. $x = 0.05$, %fit = 4.

miss. Many of the exceptions found in this data fit are also encountered in the solvent polarity literature and have been referred to as 'spectral anomalies' or 'spurious effects'.

The footnotes to Table 2 indicate the average deviation (*x*) and percent fit for each solute studied. The percent fit is the average deviation divided by the range of the values of the physicochemical property in that system times one hundred. The use of these quantities has been discussed earlier.[32]

Various probes and scales

In this section we shall examine in detail probes that form the basis for the more common scales of solvent polarity and hydrogen bond acidity. Analyses of these probes with eqn. (2) indicate the extent to which contributions from specific and non-specific interactions are included causing the different scales to provide different measures of 'solvation'. The resolution into specific and non-specific solvation provides a reinterpretation of the measurements and in most instances incorporates the data into the USM. The diversity of scales and the good fit of all this data to USM emphasizes the deficiencies in other models that combine specific and non-specific solvation into a single polarity parameter.

$(C_2H_5)_3PO$ and the acceptor number scale. The ^{31}P shift of $(C_2H_5)_3PO$ (ET3PO) is the basis for the acceptor number (AN)[14b] scale, which is proposed to be a measure of solvent acidity.[14b] The relationship between AN and the ^{31}P shift is given in eqn. (4), where δ_S is the ^{31}P shift in a given solvent and δ_H is the ^{31}P shift in hexane (−1.68 ppm).

$$AN = 2.348(\delta_S - \delta_H) \qquad (4)$$

The ^{31}P chemical shifts of $(C_2H_5)_3PO$ in donor and acceptor solvents were used in the master fit instead of AN and show an excellent correlation to E_A, C_A and S'. Both 2-methylpropan-2-ol and $CHCl_3$ were omitted from the fits. A steric interaction, involving the ethyl groups of the $(C_2H_5)_3PO$ and the *tert*-butyl group of the alcohol, may force a linear P–O · · · H–O geometry. This leads to a weaker interaction than bonding in an angular manner to an sp^2 oxygen lone pair of the phosphine oxide for which E_B* and C_B* apply. A larger shift is calculated than is observed. A similar steric problem is anticipated and found to cause the chloroform deviation. Propan-2-ol and CH_2Cl_2 are less bulky and well behaved. The resulting E_B* and C_B* parameters for the $(C_2H_5)_3PO$ chemical shift (Table 2) show an increased shift from both electrostatic and covalent bond interactions. Mayer reports[14a] that the 2-methylpropan-2-ol shift is smaller than expected and attributes the deviation to chain branching. $CHCl_3$ has a larger ^{31}P chemical shift than expected[14a] in many acceptor number correlations.

The ^{31}P chemical shifts of $(C_2H_5)_3PO$ in various donor solvents, in which a specific interaction is not expected ($E_A = C_A = 0$), show significant solvent dependent changes from non-specific solvation. Thus, attributing the shift in acceptor solvents solely to specific interactions, as suggested in the AN literature,[14a] leads to an overestimate of the acceptor properties of the solvent and in several instances, an assignment of acceptor properties to solvents that are not acceptors.

In a recent article,[14b] Riddle and Fowkes analyzed the AN scale and concluded that it contains both specific and non-specific solvation contributions. The non-specific contribution to the ^{31}P shift (and thus the AN) was calculated using surface and interfacial tensions. With ethanol, the USM estimation of the non-specific contribution to the ^{31}P chemical shift is 5.29 ppm, compared to −0.83 ppm from surface and interfacial tensions. Even the sign of the latter is contrary to expectations indicating USM provides a more reasonable estimate of specific and non-specific solvation.

NUPYNO and C13PYNO. As reported earlier, the energies of the electronic transition, NUPYNO, and the ^{13}C shifts of pyridine *N*-oxide[17] correlate well to eqn. (1) with basic solvents. When hydrogen bonding solvents are treated with eqn. (2), fixing P and W at their values from the basic solvent fit, a good correlation results giving $r^2 = 0.99$, with $x = 0.07$ for NUPYNO. Limited ^{13}C data for alcohols lead to the tentative values in Table 2. Water is omitted as the only system that deviates and does so in both measurements. The ^{13}C value employed is the chemical shift of the γ carbon minus the chemical shift of the α carbon. Contrary to the literature assumption,[17] the resulting solute P and basicity parameters given in Table 2 indicate that the shift difference contains both specific and non-specific interactions. The shift difference does provide an excellent probe of solvation employing eqn. (2).

FePHEN and RuPHEN. The electronic spectral shifts of bis(1,10-phenanthroline)dicyanometal complexes [iron(II) and ruthenium(II), FePHEN and RuPHEN, respectively] in basic solvents were previously treated by USM.[5c,d] In protic solvents, FePHEN is well behaved, with 2-methylpropan-2-ol deviating in the direction of a steric effect. This explanation is negated by $CHCl_3$, which is well behaved with appreciable contributions to the shift in the electronic spectra from specific and non-specific interactions. In the RuPHEN system, chloroform and water deviate. Water was not studied with FePHEN. More solvents need to be studied to detect patterns in these deviations. The deviant solvents are not included in the master fit. The tentative parameters for both probes are given in Table 2.

DMANF and FNF and the SPP^N scale. A fit of the DMANF shifts[4,8] to S' in basic solvents is reported.[5d] Significant deviations were found with the *n*-alkane solvents, and these are attributed to probe aggregation.[5d] Deviations with aromatic solvents are attributed to specific π-complexation to the probe. Alkane and aromatic solvents were omitted in these and the earlier correlations.[5d] With the inclusion of nitromethane (omitted earlier[5d]), the r^2 is found to be 0.91 (with an average deviation of 0.20). This gives a new P value of −1.10 and a new W value of 26.20. A similar fit adding CH_3NO_2 to FNF gave an r^2 of 0.86 (with an average deviation of 0.15), and $P = -0.65$ and $W = 31.60$, with parameters similar to those reported earlier.[5d] CH_3CN was omitted from both fits.

Catalán *et al.* claim[4,8] that the differences in the shifts of DMANF and FNF ($\Delta\nu$) in a given solvent subtract out spurious solvation effects and specific interactions to provide a measure of non-specific solvation. The SPP^N scale is based on this premise. In order to evaluate this suggestion, $\Delta\nu$ was first fitted to eqn. (1) for basic solvents, giving $r^2 = 0.90$ and an average deviation of 0.08 (with acetonitrile and dioxane removed in all cases). Removal of all π and alkane solvents from the fit improves the r^2 to 0.92 ($x = 0.05$). Adding only the π-solvents back into the fit gives $r^2 = 0.89$ ($x = 0.07$). Putting only the alkane solvents back into the fit improves the r^2 value to 0.93 ($x = 0.06$). The π-solvents, omitted from this latter fit, all miss by greater than the average deviation. The improved average deviation with π-solvents excluded shows that the difference in the DMANF and FNF transition energies cancels the aggregation problems in alkane solvents but only partially corrects for the π-complexation in aromatic solvents. The differences in the shift of the extensive set of solvents studied by Catalán *et al.*[4,8] provide an excellent probe of non-specific solvation for basic, non-aromatic solvents.

Next the evaluation of the cancellation of specific hydrogen bonding with the shift difference was evaluated. When the alcohols were added to the difference fit reported above, the r^2 decreases to the unacceptable value of 0.77. Specific interactions are different in the two probes and are not cancelled with the transition energy difference. The transition energy difference in DMANF and FNF in hydrogen bonding solvents were fitted to eqn. (2) to determine E_B* and C_B* parameters for the specific interaction. Even with the omission of acetic acid and CH_2Cl_2, a poor r^2 of 0.67 resulted. Similar fits of the transition energies of DMANF and FNF individually gave r^2 values of 0.82 and 0.75, respectively. These poor fits of the individual probes and their differences indicate that these measurements cannot be used to evaluate solvation effects when specific hydrogen bonding interactions exist.

Taft and Kamlet systems. Taft and Kamlet have studied a series of nitro-substituted anilines, anisoles and toluidines as probes for their polarity, π*, acidity, α, and basicity, β, scales.[10] Two of the more extensively studied compounds, labelled NNE4NO2AN and 4NO2ANISOL, were included in the master fit. Weakly acidic CH_2Cl_2 misses in both systems, in a direction that suggests incomplete complexation. As suggested earlier[5b] for weak acceptor probes in weak donor solvents, incomplete complexation leads to free and complexed species in solution, giving an average band position that leads to an experimental shift that is smaller than that calculated with the fit parameters. With the even weaker donor probe 4NO2-ANISOL, $CHCl_3$ and formamide both miss in the same direction as CH_2Cl_2. The 4NO2ANISOL probe also is poorly behaved in water, possibly due to probe aggregation.

With NNM2NO2AN and NNM2NO2TOL, the nitro group is positioned *ortho* to the substituted aniline group. These probes are well behaved in the USM analysis for alcohols, with only CH_2Cl_2 missing because of incomplete complexation. All of the above probes are included in the master fit with the deviant solvents omitted. The resulting E_B* and C_B* parameters are given in Table 2.

In the design of the π*, α and β scales, more than one probe is used as a measure of solvent properties to average the solvatochromic effect of the solvent and to remove 'spectral anomalies' that may exist for one probe, but not for another. The π^* scale, referenced to cyclohexane as zero, is reported to treat non-specific interactions. The probes are assigned s values, which are the counterparts of P in the USM, with $s\pi^*$ corresponding to PS'. The π^* scale was extended to protic solvents with the addition of an a term to include specific acceptor interactions. Using the most recent π^*/a parameters,[3f] the alcohols were analyzed with USM to determine the correlation of π^* to S' and a to E_A and C_A for the alcohols in this report. Eqns. (5) and

$$\pi^* = 0.08\ (\pm\ 0.11)\ S' + 0.43\ (\pm\ 0.30) \qquad (r^2 = 0.04, n = 11, x = 0.18, F = 0.46) \quad (5)$$

$$a = 0.03\ (\pm\ 0.14)\ E_A + 1.14\ (\pm\ 0.28)\ C_A \qquad (r^2 = 0.94, n = 11, x = 0.21, F = 68.28) \quad (6)$$

(6) result. As shown by r^2, a large deviation is found for the limited range of π^* and S' for alcohols. r^2 is excellent for the correlation of a to E_A and C_A.

It is noted that for all the red-shifted (negative P), nitro-substituted aromatics (Kamlet, Taft and Catalán probes), the electrostatic contribution from the specific interaction to the shift is in the same direction as the non-specific interaction, but the covalent contribution is in the opposite direction indicating a stronger covalent contribution in the ground state than excited state.

Betaine and the $E_T(30)$ scale. Solvent shifts in the electronic spectra of the basic probe pyridinium *N*-phenoxide [betaine, $E_T(30)$] have been measured in many solvents.[1] For non-specific solvation in donor solvents, $E_T(30)$ values correlate[5c] extremely well to S'. If there were no specific contributions to the betaine shift in alcohols, $E_T(30)$ would correlate to S'. The poor correlation of $E_T(30)$ for all hydrogen bonding solvents to S' ($r^2 = 0.73$, with an average deviation of 3.10) shows $E_T(30)$ is not a non-specific solvent polarity probe for alcohols.

Holding the P and W for betaine fixed at the values from the donor solvent fit, the shifts in alcohols (weighted as in Table 1) are fit to E_A, C_A and S' giving poor results ($r^2 = 0.77$, with an average deviation of 3.94). Chloroform, CH_2Cl_2, and 2-methylpropan-2-ol have experimental $E_T(30)$ values considerably smaller than the calculated values. The reported shift for betaine in methanol is much larger than in other alcohols and is much larger than calculated with USM. Water also causes problems with this solute, not only in USM but also in the $E_T(30)$ correlations, giving a value smaller than expected. Hydrolysis, aggregation, and low solubility in water (2×10^{-6} mol dm^{-3}) are reported[1] problems.

When CH_2Cl_2, $CHCl_3$, 2-methylpropan-2-ol, water and methanol were omitted from the data fit to solve for E_B^* and C_B^* for betaine (fixing the P and W values to that of the donor solvent fit), a poor correlation still resulted ($r^2 = 0.86$, with an average deviation of 3.14). The poor correlations can be rationalized. Limited access to the betaine oxygen donor center could lead to steric problems of varying degrees with all alcohols except CH_3OH which forms strong hydrogen bonds utilizing the sp^2 oxygen lone pairs. Linear chain alcohols form weaker, linear $N{-}O\cdots H{-}OR$ hydrogen bonds because of steric effects, and branched-chain alcohols interact weakest by accessing only the largely oxygen π molecular orbital. Each donor type requires a different E_B^* and C_B^* value and, in some systems, mixtures of adducts could exist. Though betaine is an excellent probe for non-protic solvents, it is a poor probe for acceptor solvents.

***Z*-value and *Z'*.** Kosower has outlined[2c] some of the problems involved in the determination of *Z*-values. The scale is based on the transition energy for the longest-wavelength band observed in 1-ethyl-4-methoxycarbonylpyridinium iodide (pyridinium iodide **214**). A negative solvatochromism is reported for this probe (consistent with the reported positive P value of 13.23). In the more polar solvents, this transition is shifted into the region of the stronger $\pi \rightarrow \pi^*$ transition of the pyridinium ion, and *Z*-values are obtained by extrapolating transitions in solvent mixtures. Because pyridinium iodide **214** is not soluble in non-polar solvents, it is necessary to use an alternate probe (1-ethyl-4-*tert*-butoxycarbonylpyridinium iodide **360**). The measurements in non-polar solvents are extrapolated to zero ionic strength because ion-pair aggregation leads to a shift that is too large.

Because of these complications, *Z*-values were not included in the master fit of the solvation data. The solvent E_A, C_A and S' parameters and weights in Table 1 were correlated to the *Z*-value for alcohol solvents using P and W values from Table 2 [eqn. (7)]. The average deviation of 1.22 kcal mol^{-1}, which

$$Z - PS' - W = 6.66\ (\pm\ 1.46)\ E_A + 5.46\ (\pm\ 2.55)\ C_A \qquad (r^2 = 0.99, n = 7, x = 1.22) \quad (7)$$

translates to a 426 cm^{-1} miss, gives an excellent r^2 because of the large shifts observed for this probe.

Griffiths and Pugh[33] suggested a change of water's *Z*-value from 94.6 to 91.8 but this would lead to a larger deviation for water in our fit. Medda *et al.*[34] chose a derivative of **214** for their Z' scale. Z and Z' give comparable correlations to E_A, C_A and S' [eqn. (8)].

$$Z' - PS' - W = 9.56\ (\pm\ 1.31)\ E_A + 5.93\ (\pm\ 2.31)\ C_A \qquad (r^2 = 0.99, n = 8, x = 1.23) \quad (8)$$

NMP. The enthalpies for hydrogen bonding to *N*-methylpyrrolidinone (NMP)[35] were included in our data fit fixing E_B and C_B at the reported values ($E_B = 2.12$, $C_B = 1.65$).[9a] Because the measurements were taken in 1,2-dichloroethane (DCE), a constant enthalpy contribution, W, from solvation of the NMP could exist, so eqn. (2) was used with PS' set at zero to fit enthalpies of hydrogen bonding to several substituted phenols whose E_A and C_A values are known. The constant W value (calculated to be 1.54 kcal mol^{-1}) was subtracted from the reported enthalpies for all the alcohols and $CHCl_3$ and these systems were included in the master fit with S' set at zero to determine E_A' and C_A' for the aliphatic alcohols. An excellent fit results ($r^2 = 0.96$, $x = 0.14$).

Abraham's a_2^H scale. Abraham *et al.* have developed a scale[6b] of hydrogen bond acidity to treat specific interactions using equilibrium constants, K^i, for complexation of a series of acids with a series of bases in dilute solutions in CCl_4. The a_2^H scale arises from a fit of hydrogen bonding equilibrium constants to eqn. (9), where L_B and D_B are empirical base parameters and

$$\log K^i = L_B \log K_A^{Hi} + D_B \quad (9)$$

$\log K_A^{Hi}$ is an acid parameter. The acid parameter is converted into a hydrogen bond acidity parameter, a_2^H, using eqn. (10).

$$a_2^H = (\log K_A^{Hi} + 1.1)/4.636 \quad (10)$$

Some of the acids show family-dependent behavior toward a series of bases as do some families of bases toward acids. These family dependent combinations were eliminated from the systems used to determine a_2^H.

As claimed, the a_2^H scale measures the specific interaction as shown by an excellent correlation to ECW. Using the E_A, C_A and weights given in Table 1 eight aliphatic alcohols, pyrrole and 17 substituted phenols were correlated to E_A and C_A. The correlation is given in eqn. (11). Acetic acid, $CHCl_3$ and CH_2Cl_2

$$a_2^H = 0.07\ (\pm\ 0.06)\ E_A + 0.59\ (\pm\ 0.15)\ C_A - 0.16\ (\pm\ 0.05) \qquad (r^2 = 0.95, n = 26, x = 0.03) \quad (11)$$

Table 3 Data fits for benzyl alcohol and acetic acid solvents

Probe	Benzyl alcohol $(\chi - W)_{exp}$	Benzyl alcohol $(\chi - W)_{cal}$[a]	Acetic acid $(\chi - W)_{exp}$	Acetic acid $(\chi - W)_{cal}$[b]
NNE4NO2AN	−3.06	(−4.35)		
NNM2NO2AN	−3.76	(−2.98)		
4NO2ANISOL	−2.92	(−2.30)	−2.88	−2.94
NNM2NO2TOL	−2.92	(−2.12)		
DMANF	−3.80	(−3.15)	−2.59	−2.36
FNF	−2.49	(−1.80)	−1.50	−1.68
Betaine	31.17	31.25		
Z-value			47.82	(41.42)
ANTBUNO	1.26	1.03	1.40	1.49
ANPIPNO	1.17	0.94	1.08	1.26
NUPYNO			4.60	4.44
ET3PO			29.76	29.77
S (bst)			0.40	0.49
C13DEBZAM	5.77	(4.97)		
Michler's ketone	−4.90	(−4.12)		
C6H5CSO(NMe2)	6.40	6.35	10.52	(8.10)
FePHEN	5.37	5.22		
WCO4BPY	5.48	5.56		
MoCO4BPY	5.03	5.01		
Fe2	2.40	2.43		
Fe3	5.86	5.82		
CrCO4BPY	5.31	5.35		
WCO4PHEN	5.43	5.24		
MoTp3			2.74	(3.55)

[a] Calculated with 1.19 (±0.07) $E_B{}^*$ + 0.55 (±0.02) $C_B{}^*$ + 2.62 (±0.07) P, using W values from Table 2, $r^2 = 0.9998$, $x = 0.10$. Systems with values in parentheses were not included in the overall fit. [b] Calculated with 3.39 (±0.20) $E_B{}^*$ + 0.91 (±0.05) $C_B{}^*$ + 1.28 (±0.20) P, using W values from Table 2, $r^2 = 0.9999$, $x = 0.12$. Systems with values in parentheses were not included in the overall fit.

deviate and were omitted. The $\alpha_2{}^H$ scale is an acidity scale that can be used as reference scale to correlate data for alcohols and phenols subject to the limitations discussed for one parameter scales.[9b]

Addition of new solvents to the USM

The addition of new solvents to the USM will be illustrated using data for benzyl alcohol and acetic acid. These acceptor solvents were not included in the master fit because of potential complications from π-solute–π-solvent charge transfer interactions in the former and acid dimerization in the latter. These interactions would distort the master fit introducing error in the parameters. Benzyl alcohol was subsequently analyzed using eqn. (2). The $\Delta\chi$ for the probes studied in this solvent, and their $E_B{}^*$, $C_B{}^*$, P and W values reported in Table 2 are used to generate a series of equations that are solved for E_A, C_A and S' for benzyl alcohol. Table 3 reports the results after several probes that gave large deviations (2.5 times the average deviation) were removed from the fit. The deviant systems include NNE4NO2AN, NNM2NO2AN, 4NO2ANISOL, NNM2NO2TOL, DMANF, FNF, C13DEBZAM and Michler's ketone. The omitted probes show a pattern of π–π* interactions dominating hydrogen bonding because of the weak probe basicity. Benzyl alcohol is reported[36] to give poor fits to π* and α in many analyses. The fit of the remaining systems to eqn. (2) gives $E_A = 1.19$, $C_A = 0.55$ and $S' = 2.62$, with an $r^2 = 0.99$ and $x = 0.10$. Inclusion of some probes where π complexation is possible suggests that the donor sites in these probes are strong enough that the hydrogen bonding interaction dominates the potential π complexation. The parameters for benzyl alcohol should be used with caution toward weakly basic π solutes.

Acetic acid forms cyclic dimers in solution and the gas phase, which are broken when the carboxy proton undergoes a specific interaction with a donor to form an adduct. Dimerization is offered[7b] as the reason when acetic acid does not fit in solvatochromic comparisons. Weak donor probes would be incompletely complexed in acetic acid and the observed shift would be less than calculated. Table 3 shows the fit of acetic acid with the probes that are well behaved in this study.

Table 4 Alcohol E_B and C_B parameters

Solvent (C_B/E_B)	Wgt[a]	E_B	C_B
H_2O (0.86)	0.3	1.34	1.15
CH_3OH (0.44)	1.0	1.95	0.86
C_2H_5OH (0.44)	1.0	2.00	0.88
n-C_3H_7OH (0.44)	1.0	2.03	0.89
i-C_3H_7OH (0.44)	1.0	2.05	0.90
n-C_4H_9OH (0.44)	1.0	2.03	0.89
i-C_4H_9OH (0.44)	0.5	2.03	0.89
t-C_4H_9OH (0.44)	1.0	2.10	0.93
$CH_2{=}CHOH$ (0.92)	0.5	1.59	1.47
$C_6H_{11}OH$ (0.85)	0.5	1.74	1.48
n-$C_8H_{17}OH$ (0.44)	0.7	2.04	0.90
CF_3CH_2OH (4.2)	0.2	0.50	2.09

[a] Weight based on number of acceptors studied.

The solution of this data set gives $E_A = 3.39$, $C_A = 0.91$ and $S' = 1.28$ ($r^2 = 0.99$, $x = 0.12$). The *Z*-value, C6H5CSO(NMe2), and MoTp3 probes were omitted from this fit.

Data fit for alcohols as donors

Toward strong acid solutes, alcohols behave as donors whose specific interaction is characterized by E_B and C_B. In these systems, care has to be taken to be certain that the alcohol is not the acceptor. The donor parameters for alcohols (Table 4) were determined from a separate master fit of the data for the acidic probes listed in Table 5. All of the systems listed in Table 5 were fitted very well to eqn. (2), with a few exceptions.

The enthalpies of donor alcohol interaction with iodine were fitted poorly. The enthalpies reported[47] for methanol, ethanol and 2-methylpropan-2-ol are smaller than calculated. These data were assigned low weights in the master fit giving 1 kcal mol^{-1} deviations but with predicted enthalpies in the range expected by comparison to ethers.[9]

The fit of $\Delta\nu(OH)$ for $(CF_3)_3COH$, was poor for donor solvents with known E_B and C_B values. No logical pattern could be found in the misses so the systems were not used to determine alcohol basicity.

The log *K* for 4-fluorophenol, which includes a wide range of donors, was fitted with an average deviation of 0.32. These are

Table 5 Parameters for systems in alcohol basicity

Shift or reaction	E_A*	C_A*	W	Wgt[a]
log K 4-nitroaniline[b]	1.8	1.1	−5.1	0.8
log K_1 3,4-dinitrophenol[c]	4.4	0.8	−6.0	0.7
$\Delta\nu$ (OH) $(CF_3)_3COH$[d]	229	152	−172	0.5
$\Delta\nu$ (OH) 4-fluorophenol[e]	163	101	−171	0.3
$\Delta\nu$ (OH) phenol[f]	167	109	−205	0.3
log K 3,5-dichlorophenol[g]	72	−158	−0.9	1
log K 3-nitrophenol isooctane[h]	187	−423	1.5	1
log K 3-nitrophenol C_6H_{12}[i]	118	−264	−0.4	1
log K 4-fluorophenol[j]	1.1	0.4	−1.3	0.6
log K phenol[k]	−119	281	−9.0	1
pK_{HB}[l]	1.69	1.12	−3.46	1
pK_{BH^+}[m]	74	−165	−4.5	1
log k ROH_2^+[n]	−11.3	−7.0	31.2	1
Δ ^{13}C CF_3COOH[o]	−1543	3495	0	1
Δ ^{13}C CF_3COOH[p]	−1941	4396	0	1
log K_b[q]	0.69	−0.84	−0.07	1
−ΔH phenol[r]	2.27	1.07	0	—
−ΔH n-C_3H_7OH[r]	1.17	0.68	0	—
−ΔH I_2[s]	0.50	2.00	0	—
^{13}C 4-nitrobenzoic acid[t]	0.15	0.73	160.5	1

[a] Weight. The weight assigned here is equal to $1/[5(0.3x)^{\frac{1}{2}}]$. This is consistent with the scheme used in earlier papers, where 'n' was used as a weighting factor, and smaller 'n' value gave more weight. We have changed this so that a larger 'wgt' means more weight is given. [b] log K for the reaction between p-nitroaniline and the alcohol in aqueous solution. Data from ref. 37. $x = 0.20$, %fit = 20. [c] log K for the reaction between 3,4-dinitrophenol and the alcohol in highly dilute C_6H_{12} solution. Data from ref. 38. $x = 0.28$, %fit = 8. [d] Change in the O–H stretching frequency of $(CF_3)_3COH$ upon adduct formation in the solvent FC75. Data from refs. 39 and 40. [e] Change in the O–H stretching frequency of 4-fluorophenol upon adduct formation in CCl_4. Data from ref. 39. $x = 2.16$, %fit = 2. [f] Change in the O–H stretching frequency of phenol upon adduct formation in CCl_4. Data from ref. 39. $x = 1.60$, %fit = 5. [g] log K for the reaction between 3,5-dichlorophenol and the alcohol in C_6H_{12}. Data from ref. 39. $x = 0.02$, %fit = 4. [h] log K for the reaction between 3-nitrophenol and the alcohol in isooctane. Data from ref. 39. $x = 0.02$, %fit = 4. [i] log K for the reaction between 3-nitrophenol and the alcohol in C_6H_{12}. Data from ref. 39. $x = 0.02$, %fit = 4. [j] log K for the reaction of 4-fluorophenol with the alcohol in CCl_4. Data from ref. 39. $x = 0.32$, %fit = 11. [k] log K for the reaction between phenol and the alcohol. Data from ref. 41. $x = 0.08$, %fit = 14. [l] pK based on the OH shift of $(CF_3)_3COH$ and the log K value for 4-fluorophenol. Data from ref. 39. $x = 0.03$, %fit = 1. [m] pK based on the ^{13}C shift of two carbons in the alcohol. Data from ref. 42. $x = 0$, %fit = 0. [n] log of the rate constant for protonation of the alcohol by HBr at 163 K. Data from ref. 43. $x = 0.14$, %fit = 6. [o] Change in ^{13}C chemical shift of the primary carbon upon addition of a 1 M solution of CF_3COOH in CCl_4. Data from ref. 44. $x = 0.16$, %fit = 4. [p] Difference in the shift of C-1 and C-2 in the alcohols upon addition of CF_3COOH in CCl_4. Data from ref. 44. $x = 0.03$, %fit = 1. [q] log K_b for 5% v/v solutions in dilute HCl at ionic strength = 1.0 and 25 °C. Data from ref. 45. $x = 0.17$, %fit = 17. [r] Enthalpy (in kcal mol^{-1}) of dimerization in CCl_4. Data from ref. 46. [s] Enthalpy (in kcal mol^{-1}) of interaction with I_2 in CCl_4 or n-heptane. Data from ref. 47. [t] ^{13}C chemical shift of the carboxylate carbon of 4-nitrobenzoic acid in neat solvents. This probe is not to be used with alcohols. The P value calculated for this system is 1.58. Data from this work. $x = 0.1$, $r^2 = 0.97$.

Table 6 Spectroscopic data for 4-nitrobenzoic acid in various solvents

Solvent	$^{13}C_{exp}$[a]	$^{13}C_{cal}$[b]	S'[c]
CH_3OH	167.6	(165.9)	2.86
C_2H_5OH	167.0	(165.9)	2.79
n-C_3H_7OH	166.3	(165.7)	2.67
i-C_3H_7OH	166.2	(165.4)	2.52
n-C_4H_9OH	166.3	(165.8)	2.75
t-C_4H_9OH	166.3	(165.4)	2.46
DMA	166.0	166.1	2.70
DMF	166.4	166.2	2.80
Acetone	166.0	165.8	2.58
CH_3CN	166.0	166.0	3.00
NMP	165.8	166.1	2.62
DMSO	166.7	166.7	3.00
Pyridine	167.2	167.2	2.44

[a] ^{13}C chemical shift relative to TMS in pure solvent of the carboxylate carbon at 25 °C. [b] Calculated using eqn. (12). Values in parentheses were not included in the overall fit. [c] S' values from this work and from ref. 9a.

the largest misses that are seen with any of the log K systems studied.

NMR solvatochromism experiment. Limited data are available for systems in which the alcohol is clearly the donor, so a series of measurements were carried out using the ^{13}C of the carboxylate carbon of 4-nitrobenzoic acid as a basic solvent probe. The experimental values in several donor solvents are given in Table 6. The NMR data in non-protic basic solvents were fitted to the USM with the results given [eqn. (12)]. An excellent fit

$$^{13}C = 0.15\ (\pm\ 0.19)\ E_B + 0.73\ (\pm\ 0.10)\ C_B + 1.58\ (\pm\ 0.47)\ S' + 160.5 \quad (12)$$

with $r^2 = 0.97$ and an average deviation of 0.1 ppm resulted. Both specific and non-specific interactions contribute to the observed shift. The calculated coefficients and error in E_B suggest that the shifts are dominated by covalency. Next, the alcohols were added to the fit using the procedure described in the calculations section. A poor fit results, with $r^2 = 0.14$. The ^{13}C chemical shift of NBA is an excellent measure of specific and non-specific solvation properties for non-protic basic solvents but not for protic donors. The problem could arise from amphoteric alcohols acting as bases to hydrogen bond the carboxy proton and also as acceptors to hydrogen bond to the carboxylate conjugate base.

E_A and C_A parameters for substituted phenols

It has been shown[48] that the substituent constants ΔE^X and ΔC^X can be used to calculate E_A and C_A values for families of acceptors. The formulae are given by eqns. (13) and (14), where

$$E_A{}^X = s_A{}^E\ \Delta E^X + E_A{}^H \quad (13)$$

$$C_A{}^X = s_A{}^C\ \Delta C^X + C_A{}^H \quad (14)$$

$E_A{}^H$ and $C_A{}^H$ are the E and C values for the parent hydrogen compound. Using eqns. (13) and (14), one can calculate the $E_A{}^X$ and $C_A{}^X$ parameters for any of the 77 3- or 4-substituted phenols whose X-substituent constants, ΔE^X and ΔC^X, are known. The proportionality constants $s_A{}^E$ and $s_A{}^C$ measure the sensitivity of the E and C values to substituent change relative to $s_B{}^E = 1$ and $s_B{}^C = 1$ for the pyridine family. Using the latest ΔE^X and ΔC^X values that have been reported[48d] and those phenols whose E_A and C_A values have been determined from enthalpy studies, $s_A{}^E$ and $s_A{}^C$ have been redetermined for the phenol family to be −0.817 (±0.014) and −0.225 (±0.003), respectively. Calculating the $E_A{}^X$ and $C_A{}^X$ for reported ΔE^X and ΔC^X substituent constants with eqns. (13) and (14), one can estimate enthalpies of reaction for 77 3- and 4-substituted phenols with the more than 80 bases in the ECW correlation.

Conclusions

This work reports parameters for alcohols and other hydrogen bonding solvents that enable one to factor the specific and non-specific components of solvent influences. The reported solvent polarity parameters for protic solvents afford a quantitative assessment of the solvent influence on chemical reactions, providing information about the basicity and polarity of transition states. A wide variety of systems, including enthalpies of interaction and spectral shifts, have been correlated providing new insights about the relative importance of specific and non-specific solvent influences. The protic solvent parameters are used to analyze several common solvent polarity scales and the limitations of these scales are determined. The USM detects a variety of specific interactions contributing to reported non-specific solvation scales and non-specific effects in reported specific solvation scales. The variations in reported scales is attributed to combining these solvation components into a single parameter.

Procedures are given for analyzing new probes and adding new solvents to the model. Several probes, such as ET3PO, Michler's ketone, the ^{13}C and ν(NO) for pyridine *N*-oxide, *Z*-values and FePHEN have shown great utility in the characterization of both specific and non-specific components of hydrogen bonding solvents. The enthalpies of hydrogen bonding to NMP, and the $a_2{}^H$ parameters are useful measures of the specific interaction. DMANF, FNF and betaine are excellent probes for non-specific solvation by basic solvents. These probes are recommended for use in the determination of donor–acceptor and polarity parameters of new solvents.

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