Acceptor Properties of Solvents: The Use of Isokinetic Relationships to Elucidate the Relationship Between the Acceptor Number and the Solvatochromism of N-Phenolate Betaine Dyes

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The thermochromism of the pyridinium N-phenoxide betaine dyes, betaine **1** and betaine **2**, has been studied in different solvents and over a range of temperatures and shown to yield isoparametric (isokinetic) relationships (IKR). (The use of the more lipophilic betaine **2** enabled the range of solvents to be extended to cover very apolar solvents in which betaine **1** is insoluble.) These IKRs led to the identification of five different groups of solvents, each group showing different solute–solvent and solvent–solvent mechanisms and being characterised by their functional groups. The corresponding T_{iso} values are, as demanded by theory, related to far-IR absorptions that are characteristic of reaction heat baths, which in these systems are found to be the betaines themselves. These groups are reflected in the relationship between Reichardt's E_T values and Gutmann's acceptor numbers (AN) which is reinvestigated and each group shown to lie on one of a series of parallel lines in the E_T vs. AN plot. It is demonstrated that acceptor parameters depend strongly on the donor properties of the probe used to obtain them.

The present paper is concerned with the close relationship between two well known solvent parameters, namely Reichardt's E_T-values [1][†] and Gutmann's acceptor numbers [2] (AN) and with the interpretation of these. The former is the energy associated with the longest wavelength charge transfer band of the betaine 1, expressed in kcal mol⁻¹, and the latter is obtained from the relative ³¹P-chemical shift of the 1:1 solvent adduct of Et₃PO in the particular solvent with hexane as reference solvent and using the SbCl₅–Et₃PO adduct in 1,2-dichloroethane to define 100 on the scale. A linear relationship between E_T and AN has been established by Mayer and Gutmann,[2-4] and this was later used for estimating E_T-based acceptor numbers (AN_E values) for solvents either not accessible by the NMR method or deviating markedly from the expected values.[5] This implies an interpretation of the E_T values, originally conceived as a means of describing solvent polarities, as providing an alternative scale of Lewis basicities (i.e. the acceptor properties) for solvents.

At first sight a plot of all available AN and E_T values (see Fig. 1) would suggest that the existence of such a relationship is of limited validity as many solvents deviate markedly from the linear relationship illustrated by the full line in the Figure.[5] This full line, which is defined by relationship (1), appears to

$$AN = 1.29E_T - 40.5 \qquad (1)$$

represent a lower limit of the given points. (The series of parallel lines is a result of the present investigation and is explained below.) In fact the relationship (1) was established after excluding various solvents, exclusion being supported by chemical or physical arguments. Although these arguments appear reasonable in many cases they are in general based on no more than chemical intuition.[5] The important question of whether it is possible to justify the exclusion of some solvents and not others remained open and led us to reexamine to what extent this relationship was in fact valid. Obviously further information about solvent–solvent and solvent–solute interactions was required.
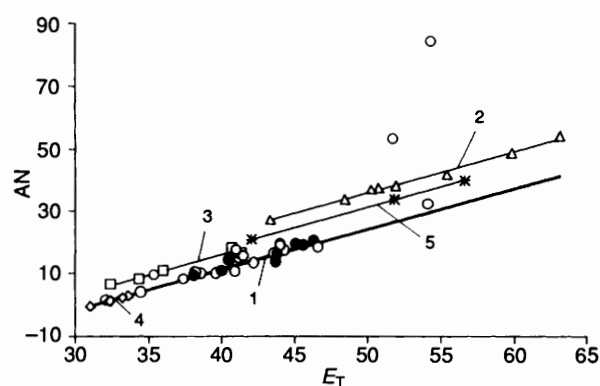

Fig. 1 Plot of E_T vs. AN for 56 solvents. The full line refers to the previously reported linear relationship (1) between E_T and AN: ● = group 1 ('well behaved solvents'); △ = group 2 (alcohols); ◇ = group 3 (aromatics); □ = group 4 (alkanes); ✳ = group 5 (amines); ○ = remaining solvents where no temperature dependent data are available.

From several thermodynamic and kinetic investigations it is known that isokinetic (isoequilibrium) behaviour can often be used to distinguish between different interaction mechanisms.[6,7] In general these effects are based on the occurrence of common points of intersection in Arrhenius- or van't Hoff-like plots. (In the case where neither kinetic nor equilibrium data have been employed directly these relationships might be called 'isoparametric relationships'. However, we use the term IKR in its widest generality since dynamic processes always govern chemical systems.) It has been shown that when a single point of intersection is found, the members of this group follow the same reaction (i.e. interaction) mechanism, and that a (generalized) linear free energy relationship (LFER) exists.[6,7] In other words, IKRs occur only when the reaction profile is essentially the same. This is the approach adopted in this study.

Experimental

Measurements.—Additional to already available measure-

† Often referred to as $E_T(30)$ values in the literature, but abbreviated to E_T in this paper for clarity.

ments on the thermochromism of N-phenolate-pyridinium betaine dyes 1 and 2, in different solvents[8-10] further measurements have been carried out using a Hitachi 2000 spectrophotometer equipped with a thermostatted cell holder. Temperatures were measured in the cell and are accurate within ±0.02 K. Solvents were purified according to usual procedures and contained (Karl-Fischer titration) less than 10^{-3} mol dm^{-3} water. Far-IR spectra of the betaines were measured with a Nicolet 20F FT-FIR spectrometer.

IKR-Analysis.—Changes in the visible absorption spectra do not directly yield rate or equilibrium constants for a solvation process, however, because the solvatochromism of betaines is related to an equilibrium distribution of solvent molecules around the betaine, we have adopted the analogy to the Arrhenius or van't Hoff plots in our investigation and used plots of E_T (betaine 1) and E'_T (betaine 2) vs. $1/T$ which were indeed found to be linear.[8-11] Statistical analysis of the occurrence of common points of intersection was carried out according to the literature.[6,12]

Results

Temperature Dependent E_T *Values.*—Betaine 1 is insoluble in very apolar solvents so the more lipophilic betaine 2 has been

1

2
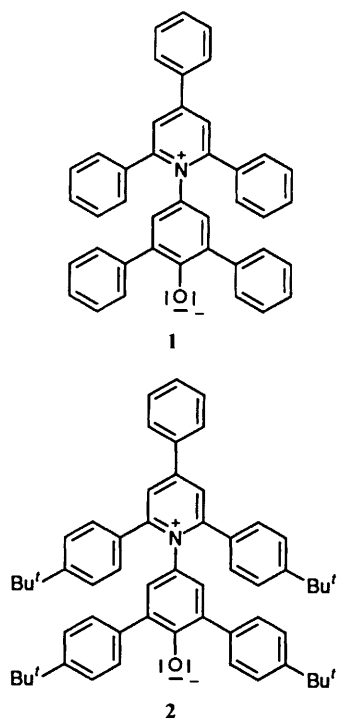
used as a probe for such solvents.[10] Its E'_T value, defined analogously to E_T, is linearly correlated to the latter eqn. (2). As

$$E'_T = 0.914E_T + 3.43 \text{ (at 25 °C)} \qquad (2)$$

far as possible both betaines have been investigated in parallel. Measurements of the thermochromism of the betaines have been reported for both molecules.[8,9] Temperature dependent E_T- and E'_T-values for solvents measured in this work are given in Table 1.

Based on both the already available and the newly measured values we investigated the E_T and the E'_T values for the occurrence of isoparametric relationships. As expected from the E_T vs. AN plot no single point of intersection that included all available solvents, was found. The available data do, however, divide unequivocally into different groups of solvents exhibiting

Table 1 Temperature dependence of absorption maxima and E_T (E'_T) values for various solvents

Betaine 1

CHCl$_3$			EtOH			Morpholine		
$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T
9.3	687.0	41.6	3.9	542.0	52.8	12.6	684.5	41.8
14.1	691.5	41.3	11.5	545.5	52.4	20.6	690.5	41.4
19.1	697.0	41.0	20.2	549.5	52.0	29.5	695.5	41.1
24.0	702.5	40.7	29.5	554.0	51.6	39.1	700.5	40.8
28.9	708.0	40.4	38.9	557.0	51.3	48.5	707.5	40.4
33.7	712.0	40.2	48.4	562.0	50.9	58.1	712.5	40.1
38.7	716.5	39.9	58.0	566.0	50.5	67.1	717.0	39.9
43.5	722.0	39.6	67.5	570.5	50.1	76.7	724.0	39.5
48.4	725.0	39.4	51.7	563.0	50.8	86.1	729.0	39.2
52.9	729.0	39.2	41.8	558.0	51.2	95.1	735.5	38.9
44.2	721.0	39.7	32.5	554.5	51.6	51.5	707.5	40.4
36.3	713.5	40.1	23.5	550.5	51.9	23.2	690.0	41.4
23.3	700.0	40.8						

Diethylamine			Nitrobenzene			Benzonitrile		
$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T
3.2	731.5	39.1	12.9	669.5	42.7	13.5	690.5	41.4
3.2	737.5	38.8	20.4	676.0	42.3	20.8	675.0	42.4
7.1	746.0	38.3	29.5	682.5	41.9	29.6	680.0	42.0
7.1	749.0	38.2	38.6	688.0	41.6	38.8	684.5	41.8
11.6	756.0	37.8	47.9	692.5	41.3	48.3	688.5	41.5
11.6	760.5	37.6	57.2	697.5	41.0	57.5	692.5	41.3
16.2	766.5	37.3	66.8	701.0	40.8	66.7	696.0	41.1
20.8	772.5	37.0	76.1	705.0	40.6	76.1	700.0	40.8
25.6	776.5	36.8	85.7	708.5	40.4	85.5	703.5	40.6
30.3	781.0	36.6	95.2	712.0	40.2	94.7	707.5	40.4
35.1	787.0	36.3	50.8	693.5	41.2	50.7	689.0	41.5
40.9	790.5	36.2	22.8	676.0	42.3	23.7	675.5	42.3
44.8	792.0	36.1						
49.5	795.0	36.0						
21.9	765.5	37.3						
21.9	770.0	37.1						

Formamide			Dimethylformamide			Dimethylacetamide		
$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T
11.7	509.0	56.2	11.3	654.5	43.7	12.0	669.5	42.7
20.6	511.0	56.0	20.3	657.0	43.5	20.2	672.5	42.5
30.2	512.5	55.8	29.8	660.0	43.3	29.3	675.0	42.4
40.0	516.5	55.4	39.3	663.5	43.1	38.7	678.5	42.1
49.7	516.5	55.4	49.0	666.0	42.9	48.1	682.0	41.9
59.5	518.0	55.2	58.4	668.0	42.8	57.4	685.5	41.7
69.1	520.0	55.0	67.8	671.0	42.6	66.8	688.5	41.5
79.0	523.5	54.6	77.2	674.0	42.4	76.0	691.0	41.4
79.0	527.5	54.2	86.4	677.0	42.2	85.1	694.5	41.2
88.7	530.0	53.9	96.0	680.0	42.0	93.4	698.5	40.9
51.1	517.0	55.3	50.4	666.0	42.9	50.5	682.0	41.9
22.1	511.0	56.0	22.4	657.0	43.5	23.9	672.0	42.5

Betaine 2

CHCl$_3$			EtOH			PrOH		
$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T	$T/°C$	λ/nm	E'_T
12.8	690.5	41.4	3.6	552.5	51.7	11.1	563.5	50.7
16.4	695.0	41.1	11.3	555.5	51.5	19.4	567.5	50.4
20.5	701.0	40.8	20.0	559.0	51.1	28.7	572.5	49.9
24.9	706.0	40.5	29.3	562.5	50.8	38.2	577.0	49.6
29.5	711.0	40.2	38.9	566.5	50.5	47.7	582.0	49.1
34.1	715.5	40.0	48.3	571.5	50.0	57.2	584.5	48.9
38.8	720.5	39.7	57.9	574.5	49.8	67.0	591.0	48.4
43.4	725.0	39.4	67.2	578.0	49.5	76.4	595.5	48.0
48.1	728.5	39.2	40.8	566.5	50.5	86.0	600.0	47.7
52.7	731.0	39.1	24.0	559.5	51.1	50.3	581.0	49.2
24.2	704.0	40.6				22.7	564.0	50.7

Table 2 Statistical analyses for the occurrence of isoparametric relationships.[a]

Group	Betaine	T_{iso}/K	ν_{iso}/cm^{-1}	E_{Tiso}	$F_{(f_1, f_2)}$	Solvents[c]
1	1	83	58	62.9	0.115$_{(7,41)}$	Ac, An, DMSO, DMF, DMA, EtOAc, NMF, Py, NM
	2	90	63	58.7	0.018$_{(4,14)}$	Ac, An, DMSO, EtOAc, Py
2	1	130	90	68.9	0.246$_{(5,11)}$	Gly, MeOH, EtOH, PrOH, BuOH, AmlOH
	2	164	114	61.5	2.72 *	MeOH, EtOH, PrOH, BuOH
3	1	749	521	32.2	0.041$_{(5,14)}$	PhH, PhMe, p-Me$_2$C$_6$H$_4$, PhC$_2$H, Ph$_2$O, dioxene, DCE
	2	670	466	32.0	3.23$_{(4,11)}$	PhH, PhMe, p-Me$_2$C$_6$H$_4$, PhC$_2$H, DCE
4	2	800	556	30.3	0.61$_{(3,11)}$	c-C$_6$H$_{12}$, decalin, C$_7$H$_{16}$, C$_{10}$H$_{22}$
5	1	118	82.6	64.5	b	Fa, Et$_2$NH, en

[a] Solvent groups found for the thermochromism of betaine 1 and betaine 2, isoparametric temperatures, T_{iso}, associated isokinetic vibrational frequencies, ν_{iso}, isoparametric E_T and E'_T-values, statistical F values, and the respective degrees of freedom f_1 and f_2. [b] Values estimated without detailed statistics which could not be performed due to lack of data. [c] Solvents used in this study: chloroform (CHCl$_3$); ethanol (EtOH); morpholine; diethylamine (Et$_2$NH); nitrobenzene (NB); benzonitrile (BN); formamide (Fa); dimethylformamide (DMF); dimethylacetamide (DMA); propanol (PrOH); acetone (Ac); acetonitrile (An); dimethylsulfoxide (DMSO); ethyl acetate (EtOAc); pyridine (Py); nitromethane (NM); glycol (Gly); butanol (BuOH); iso-amyl alcohol (AmlOH); benzene (PhH); toluene (PhMe); p-dimethylbenzene (PhMe$_2$); phenylacetylene (PhC$_2$H); diphenyl ether (Ph$_2$O); dichloroethane (DCE); cyclohexane; decalin; heptane (C$_7$H$_{16}$); decane; (C$_{10}$H$_{22}$); ethylenediamine (en); N-methylpyrrolidin-2-one (NMP); trimethylphosphate (TMP).
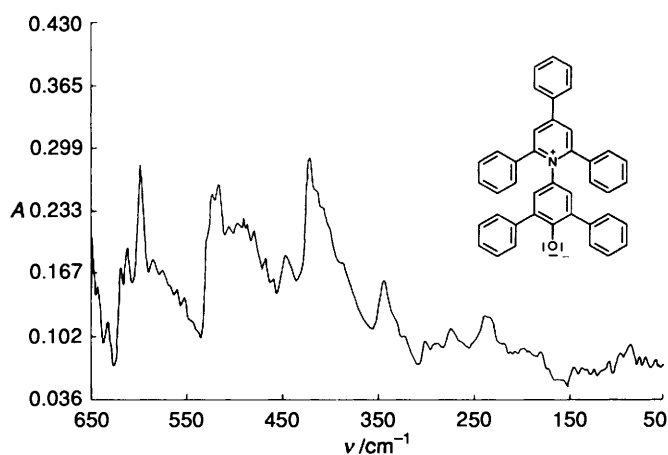
Fig. 2 Far-IR spectrum of betaine 1
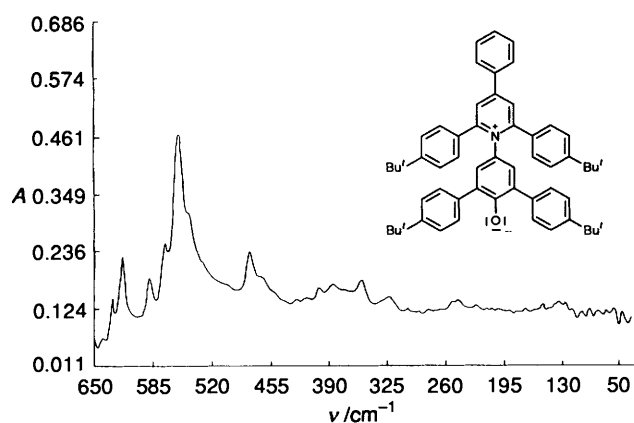
Fig. 3 Far-IR spectrum of betaine 2

independent, statistically significant points of intersection. These groups are listed in Table 2.

Table 2 contains E_{Tiso} values which refer to the ordinate position of the respective common points of intersection in the E_T (or E'_T) vs. $1/T$ plots. Using eqn. (1) E_{Tiso} can be transformed into E'_{Tiso} and vice versa emphasizing the accuracy of the method used to identify the common points of intersection.[7,13] It has been established that T_{iso} values are related to the vibrational spectra of the respective heat bath (i.e. the energy source required to overcome the reaction barrier on a molecular

level).[6,14] In the case of large molecules such as the betaines they are able to act as their own 'heat bath'.[6] This has also been found experimentally for the methylation of several betaines, where iso-solvent relationships occur,[11] and has been suggested to account for deviations in the observed rate constants of the intramolecular electron transfer within the betaine from theoretical predictions.[15] Cyclodextrins provide a further example of large molecules capable of acting as their own heat-bath.[16] Such a (theoretically demanded) relationship requires that the T_{iso} found for a reaction series should correspond to a resonant vibrational frequency (in cm^{-1}) given by $\nu_{iso} = kT_{iso}/(hc\ 100) \approx 0.695\ T_{iso}$ and this frequency must be present within the investigated reaction system. (If this resonant frequency is not available no IKR will be observed.[6]) We have therefore measured the far IR-spectra of both betaines to enable a comparison between T_{iso} and the actual IR-absorption frequencies to be made (see Figs. 2 and 3).

Correlation of AN with E_T.—As mentioned above the occurrence of an IKR is associated with a LFER. Different isokinetic groups are associated with different (generalized) LFERs and we have separately analysed the AN vs. E_T relationship for each of the five groups (see Table 2).

Group 1. Fig. 4 consists of what could be called the 'well-behaved' solvents, and includes some of the solvents previously included in the linear relationship[1] between E_T and AN. It consists of acetone (Ac), acetonitrile (An), ethyl acetate (EtOAc), nitromethane (NM), trimethylphosphate (TMP), dimethylsulfoxide (DMSO) and pyridine (Py) [but not N-methylformamide (NMF)]. The very low isokinetic temperatures of 83 K and 90 K would correspond to vibrational bands at 57 and 62 cm^{-1}. Unfortunately, the far-IR spectra obtained show insufficient detail in the region from 50 to 200 cm^{-1} to confirm the corresponding absorption bands in the betaines.

The linear relationship found between AN and E_T using these solvents alone [eqn. (3)] is virtually identical to the general

$$AN = 1.29E_T - 39.9\ (r = 0.973) \qquad (3)$$

relationship (1) quoted above and it is this group of solvents which enable the interpretation of E_T values as a measure of acceptor properties to be made. Indeed the solvents involved are typical representatives for donor–acceptor interactions. The solvents act as acceptors towards the phenolate oxygen of the two betaines forming 1:1 complexes which indeed may characterise this group.
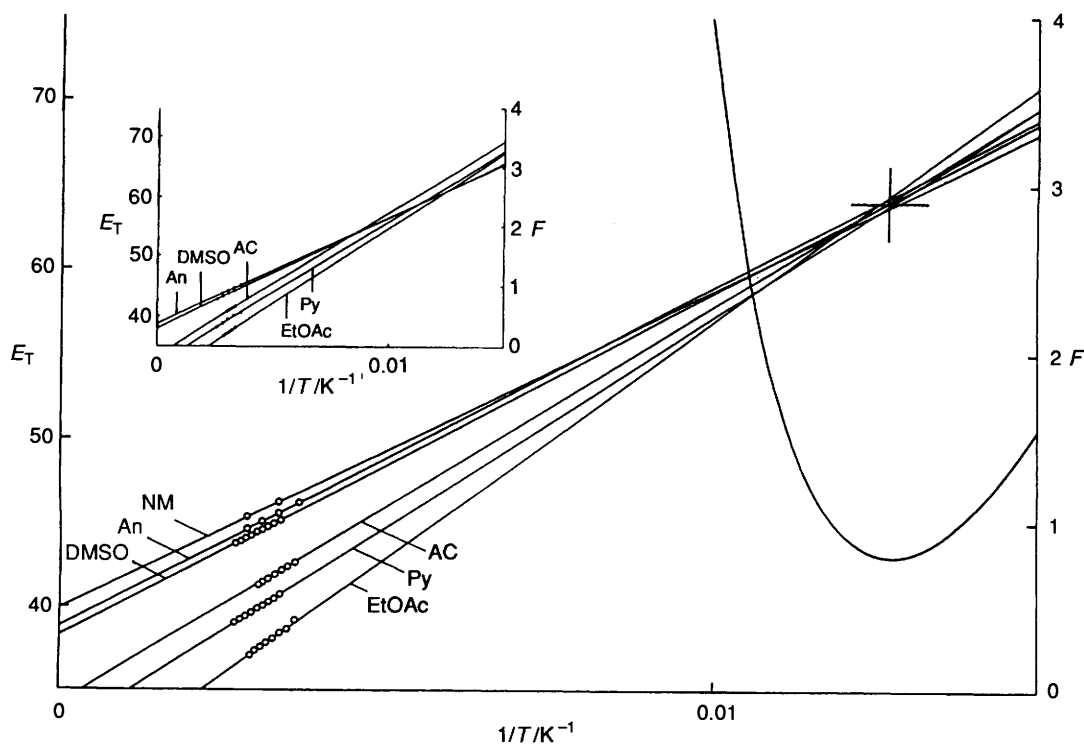
Fig. 4 Isoparameter plot (E_T vs. $1/T$) for betaine **1** in solvents of group 1. (The respective plot for betaine **2** is given as an insert.) Curved lines refer to statistical F-values (for details see refs 6 and 12).
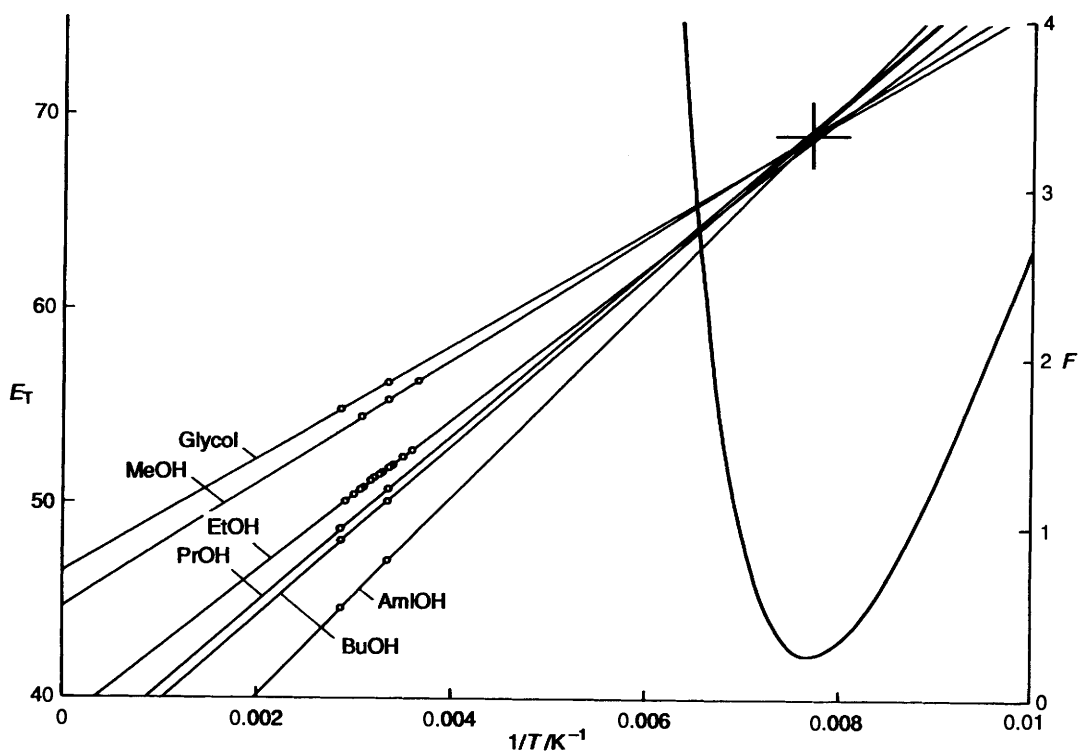

Fig. 5 Isoparameter plot (E_T vs. $1/T$) for betaine **1** in solvents of group 2

Group 2. Fig. 5 is made up of the alcohols (with the exception of isopropanol and *tert*-butanol which can be explained on the basis of the large steric hindrance of these two compounds when forming coordinated species). T_{iso} refers to a v_{iso} of 90 cm^{-1} for betaine **1** and for betaine **2**. v_{iso} is 114 cm^{-1}, both of which would again fall into an inaccessible range of the available far-IR spectra.

Fig. 1 shows that a linear relationship between AN and E_T in fact also exists for this group (and the other groups) but that the line is parallel to that of group 1 and shifted towards higher AN-values. In other words the alcohols appear to be better acceptors towards Et_3PO than towards the betaines and an explanation of this appears in the Discussion. The correlation is given by eqn. (4).
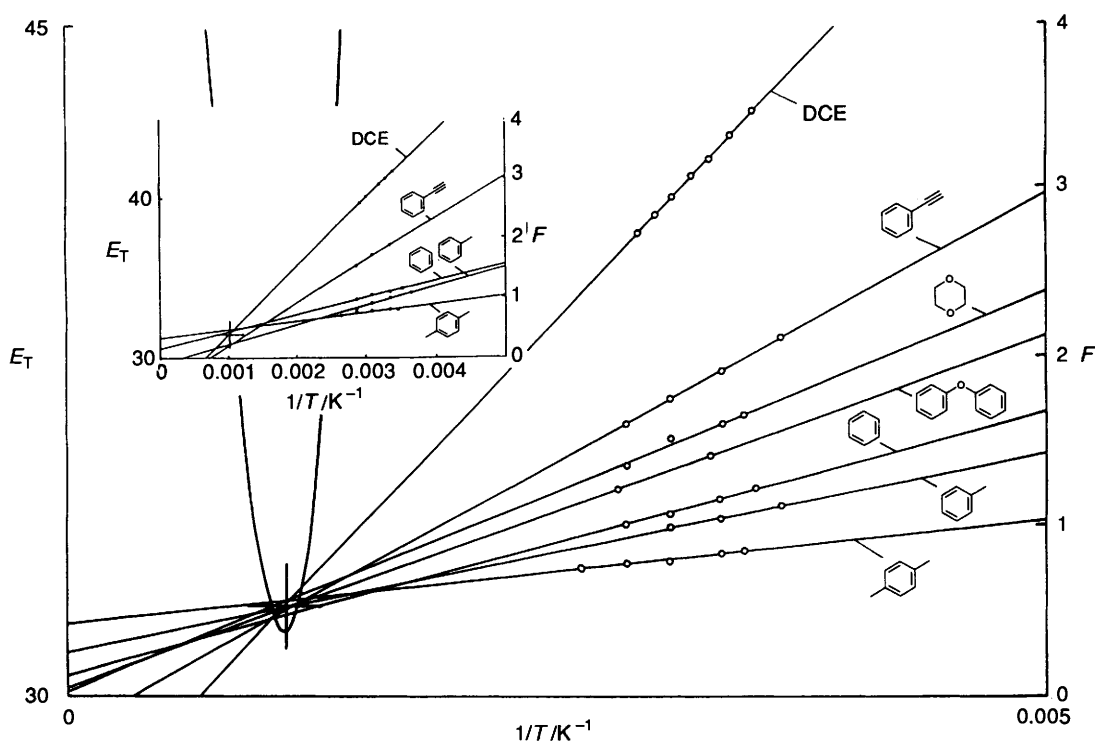
Fig. 6 Isoparameter plot (E_T vs. $1/T$) for betaine 1 in solvents of group 3 (the respective plot for betaine 2 is given as an insert)

$$AN = 1.31E_T - 29.6 \quad (r = 0.985) \qquad (4)$$

Group 3. Fig. 6 includes aromatic hydrocarbons such as benzene, toluene or phenylacetylene, ethers, and 1,2-dichloroethane. The members of this group appear to interact not *via* the phenolate oxygen but *via* weak interactions with the π-electron systems of the betaines. For steric reasons this should be less pronounced for betaine 1 and indeed a less clear cut common point of intersection is found for this group (*c.f.* the *F*-parameter of 3.24 compared to Table values $F_{4,11} = 3.36$ for $\alpha = 0.05$). This might also suggest that the solvent interactions with betaine 2 are not based on π-interactions although they certainly are weak. The well defined T_{iso} for betaine 1 corresponds to a vibrational band at 520 cm^{-1} which is indeed found in the far-IR spectrum of the betaine 1 (Fig. 2). The IR-spectrum of the betaine 2 (Fig. 3) shows an absorption at 478 cm^{-1} with a shoulder at 464 cm^{-1} which corresponds well with the required v_{iso}-value of 466 cm^{-1}.

Again this group exhibits a highly significant linear relationship between AN and E_T, again parallel but shifted to higher AN values than that of group 1. The correlation is given by eqn. (5)

$$AN = 1.30E_T - 36.0 \quad (r = 0.985) \qquad (5)$$

Group 4 consists of alkanes. Since betaine 1 is insoluble in very apolar solvents, only E'_T could be measured. Although the thermochromism is not very pronounced the v_{iso} value of 556 cm^{-1} (calculated from T_{iso}) corresponds extremely well with the strong absorption band of betaine 2 found at 556.6 cm^{-1}. The correlation of AN with E_T is given by eqn. (6).

$$AN = 1.29E_T - 40.5 \quad (r = 0.999) \qquad (6)$$

Group 5 consists of the amines and amides. Unfortunately lack of temperature dependent data makes the characterisation of this group less successful. However, it seems reasonable to include it as separate group on two grounds: firstly, regression analysis leads to eqn. (7) and secondly this line approaches that

$$AN = 1.39E_T - 33.5 \quad (r = 0.999) \qquad (7)$$

representing the alcohols, and in both of these series hydrogen bonding is important (see Discussion).

Further groups. It seems highly unlikely that other groups (depending on other functional groups) do not exist, but lack of temperature dependent data makes further analysis impossible. For example, in Fig. 1 the two points exhibiting the greatest deviation from the basic correlation line represent ethanoic and methanoic acid in that order and one might well expect to find that ethanoic acid lies on a straight line representing a whole series of carboxylic acids with methanoic acid as an exception.

Discussion

It was suggested by Reichardt[17] that betaine 1 forms 1:1 complexes with alcohols *via* a hydrogen bond and this could be the characteristic mode of interaction for these compounds. A comparison with the thio-betaines (which it can safely be assumed do not take part in such bonding) suggests,[17] however, that the hydrogen bond, if it exists, is very weak.

For interactions between the alcohols and Et$_3$PO, however, 1:2 and even 1:3 interactions certainly contribute to the NMR measured numbers. Correction of the acceptor numbers to refer to 1:1 interactions can be achieved by making use of an IR-method.[18] When this is done the ANs are indeed brought into coincidence with the basic linear relation derived from group 1 solvents. (The points in Fig. 7 are linked when values derived by both methods are known.) We suspect that this will also hold true for other solvents that can involve hydrogen bonding, but no IR data are available at present. However, another way of looking at this effect is as follows. If the probe is a strong donor (and this is certainly true of Et$_3$PO) then the attached species will be affected in such a way as to encourage the binding of a second molecule to the site (*e.g.* by hydrogen bonding). This, in turn, will lead to an increase in the effective acceptor properties of the species [*c.f.* the effect of this phenomenon in increasing the donor and acceptor properties of bulk water (solvent) over that of an isolated H$_2$O (solvent) molecule].[2,19] This is, therefore, a
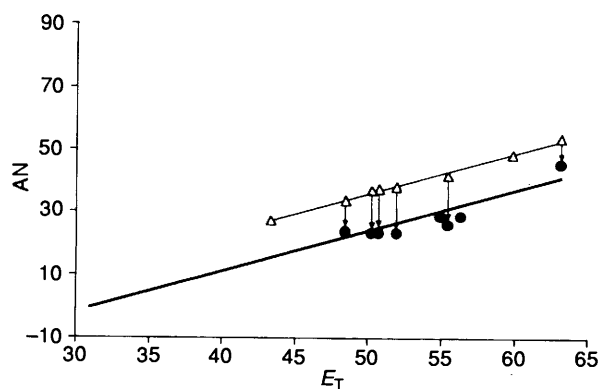
Fig. 7 Plot of E_T vs. AN for group 2 solvent (alcohols). Open symbols ($\triangle$) refer to acceptor numbers corrected to 1:1 interactions between solvent molecules and Et_3PO.[18] The lower regression line is that for the previously reported linear relationship between E_T and is identical to that of group 1 solvents ('well behaved solvents').
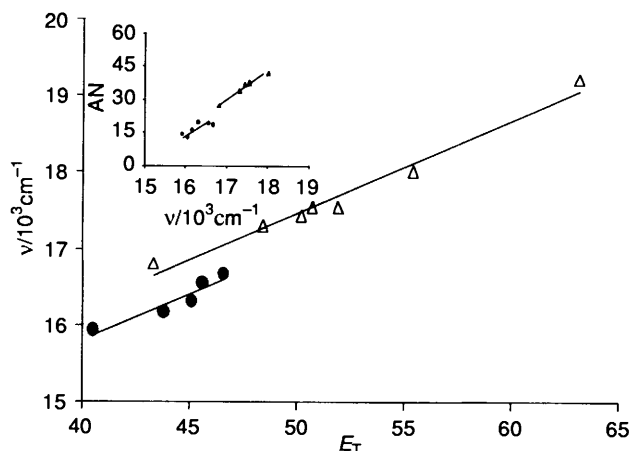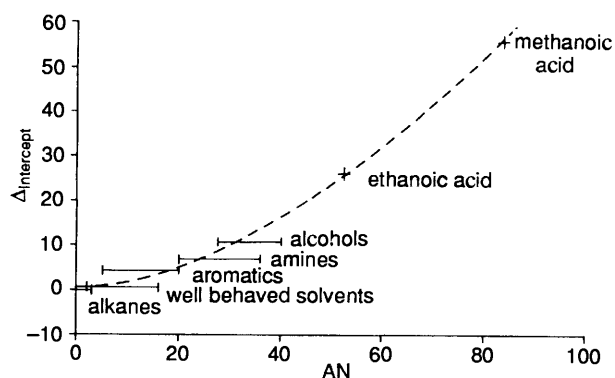

Fig. 9 Variation of the intercepts on the AN vs. E_T plot (Fig. 1) with the AN of the solvents

Table 3 The relationship between the intercepts on the AN vs. E_T plots and the acceptor number of the solvents.

Solvent	Intercept	Δintercept	AN-range
Alkanes	−40.5	0	0–3
'Well behaved'	−39.9	0.6	2–16
Aromatics	−36.0	4.5	5–20
Amines	−33.5	7.0	20–36
Alcohols	−29.6	10.9	28–40
Carboxylic acids [a]	−14.5	26.0	53
(Methanoic acid) [b]	15.5	56.0	84

[a] Based on ethanoic acid alone. [b] Assumed to be unique.

Fig. 8 Relationship of an acceptor scale based on the interaction of $[Fe(bipy)_2(CN)_2]$ with various solvents with E_T. The insert shows its relationship to AN. ($\triangle$ = alcohols; ● = group 1).

plausible explanation for the increase of the ANs obtained by the NMR method (dependent on bonding to a strong acceptor!) over those obtained via Reichardt's method (which depends on a weak donor). Furthermore, since the interaction depends on the donor properties of the probe, it will also depend upon the type of interaction involved and hence, in general to the functional group present on the solvent.

It is important to note that the extent to which solvents are separated into groups in the AN vs. E_T plot c.f. Fig. 1) is a function of the strength of the donor probe, and as such is in no way unique to Et_3PO as a strong donor or to the NMR method used.[2] If for example we look at the solvatochromism of $[Fe(bipy)_2(CN)_2]$ (bipy = bipyridine) in solvents of group 1 and group 2 we can use the data of Toma and Takasugi[21] and treat the shift in frequency of the absorption band as another acceptor scale and plot these vs. E_T (Fig. 8). The shift in frequency observed for this compound arises from solvent interaction with the cyanide ligand which is a strong donor, and thus the separation of the solvents into two well separated groups is observed (Fig. 8). (The same would be the case for $[Fe(phen)_2(CN)_2]$ (phen = 1,10-phenanthroline), well known as a colour indicator[22] for the AN, but insufficient data using this compound are available for this purpose.) Furthermore, since the donor properties of Et_3PO differ from those of $[Fe(bipy)_2(CN)_2]$, a plot of AN vs. the absorption band frequency also demonstrates an analogous (but much smaller) separation into the two groups.

In Table 3 the various groups are presented in order of their intercepts on the AN vs. E_T plot (these are then referred to the alkanes as zero) together with the range of ANs observed for each group. When the differences in intercept are plotted against AN (Fig. 9) we see that the deviation of the parallel lines from the limit of that for solvents with almost zero donor and acceptor strengths (i.e. the alkanes, Fig. 1) increases fairly smoothly with increase of acceptor number of the solvent. This is to be expected from the discussion above, and explains the failure of previous attempts to fully correlate acceptor number with Reichardt's E_T value.

Because the betaines are poor donors, any acceptor scale based on these measurements will be internally consistent as long as it is applied to weak donor systems. However, for strong donor systems, using the appropriate scale would mean allowing for the donor properties of the species being investigated (Figs. 1, 7, 8 and 9). Thus we propose, as a compromise, that the AN values should only be adopted as a working acceptor number scale whenever a strong donor species is involved, using the AN_E values for weak donor species. This is supported by the fact that many correlations such as that of the second-order rate constants for the substitution of fluoride in p-nitrofluorobenzene by azide[4,5,20] with acceptor properties of the solvents are far better when using AN_E values (or available AN values corrected so as to involve only 1:1-interactions) precisely because the species involved are poor donors.

In a recent study of the donor properties of anions[23] it was demonstrated that the effective donor numbers obtained depended strongly on the acceptor properties of the solvent concerned. This is the converse of the effect noted in this work and leads to the firm conclusion that both donor and acceptor numbers must be related to the contrary attribute and that internally consistent scales using only one parameter (i.e. an invariant order) can only be obtained when the contrary attribute is of low value.

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