Use of Chemical Probes for the Characterization of Solvent Mixtures. Part 1. Completely Non-aqueous Mixtures

Yizhak Marcus
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

The use of chemical probes for the characterization of chemical properties (polarity, hydrogen bonding ability) is explored for solvent mixtures not involving water as a component. Preferential solvation is more important in such mixtures than in those that contain water. This implies that contrary to common practice, polarity indices *etc.* obtained in the mixtures with a given probe may not be generally valid for the solvation of other solutes. Still, approximate values of these properties can be obtained by judicious use of such probes.

Mixed solvents are ubiquitous in chemical practice, ranging in their use from chromatographic separations to organic chemical synthesis, to studies of the kinetics of reactions and to hydrometallurgical applications. In some cases liquid mixtures are the default medium obtained from nature, as, for example, crude oil or essential oil extracts, or due to the systems employed, as for liquid–liquid distribution with incompletely immiscible liquids. In other cases they are used by design, in order to improve physical characteristics, such as density, viscosity, vapour pressure, *etc.* In still other cases solvent mixtures are selected for their chemical characteristics, for improving solubility and for affecting the rate of formation and yield of desirable and side products, *via* the enhancement and suppression of reactivity.

The chemical characteristics of solvent mixtures are customarily determined in the same manner as those of neat solvents[1] by means of chemical probes (indicators). The properties of the solvents that are measured include their polarity, their interaction abilities by dispersive forces, their abilities to donate an electron pair to form a coordinative bond (donicity) and abilities to donate a hydrogen atom towards the formation of a hydrogen bond (or electron pair acceptance). Sometimes all these properties are included under the covering-term 'polarity'.[2]

It is generally tacitly, and in some cases overtly,[3,4] assumed that the expressions used to convert the raw measured data (*e.g.*, the wavelength of a light absorption peak) to the quantities describing polarity *etc.* for neat solvents[1] can be employed directly also for solvent mixtures. This assumption has rarely been put to the test, however. That this should not, perhaps, be the correct procedure becomes apparent when the phenomenon of preferential solvation is considered.

When preferential solvation is operative the chemical probe has in its environment more of the one solvent than the other, compared with the bulk composition, but this 'local' concentration may vary from one probe to another. Even if in a given solvent mixture different probes have similar environments in their ground states, the solvation of their excited states, hence the magnitude of the measured quantity, may differ.

In order to resolve this problem, it is necessary to examine the purpose for which the signals from chemical probes are measured in mixed solvents. One purpose is to study the preferential solvation of a given probe in the mixture, and the emphasis is then on that particular probe.[5] Another purpose is the determination of the nature and magnitude of solute–solvent interactions and the emphasis is then on the properties of the solvents and their mixtures, which should be measurable with appropriate probes. The interactions are obtained by means of linear free energy relationships (LFERs), provided that the corresponding properties of the solutes are known,[6] and, if there is a choice, the proper solvent or mixture for the chemical problem can be selected. For such purposes, however, the solutes in question need not be specified in advance, so that the listed solvent properties should be valid for the 'general solute'.

In the case of a neat solvent, all solutes have the same chemical environment, therefore a solvent property should be generally valid. It has been argued[7] that this can still hold practically for a mixed solvent, provided that several dissimilar probes produce convergent values of the property (at a given composition). The degree of convergence prescribed depends on the divergence allowed for this set of probes in neat solvents. For practical purposes this may be set as 5% of the total range of values encountered for this property in a large set of diverse solvents. In the case of 'polarity', measured by the Dimroth–Reichardt $E_T(30)$,[8] for example, this would be ± 0.8 kcal mol^{-1} (1 cal = 4.184 J), since the values range over 32.4 kcal mol^{-1}.

These abstract ideas are examined in this paper for completely nonaqueous binary mixtures. In a forthcoming paper mixtures involving water as one of the components will be dealt with, constrained with respect to the cosolvent because of the requirements of miscibility. Due to the limited availability of data in the literature, the property examined is mainly the 'polarity',[2] as measured with 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide, $E_T(30)$,[8] and 4-carbomethoxy- or 4-cyano-1-ethylpyridinium iodide, Kosower's Z and Z', respectively.[9] These two polarity indices are well linearly correlated[1] and measure different combinations of the ability of the solvent to donate a hydrogen atom towards the formation of a hydrogen bond and its actual polarity and polarizability.[1] Only the latter couple of properties is manifested in aprotic solvents and mixtures. The Kamlet–Taft[10] polarity/polarizability parameter π^*, measured with 4-nitro-*N*,*N*-diethylaniline, and their donicity parameter β (or the equivalent Koppel[11] B_{KT}), measured with 4-nitroaniline, are known for fewer nonaqueous mixtures. The former 'polarity' indices and the latter two parameters, π^* and β, are not well correlated with each other for neat solvents, provided protic solvents are included in the set tested,[1] since each depends on an independent property.

The data for systems that have been studied so far by various authors have been reported at a variety of compositions and composition scales (mole-, mass- and volume-fractions, and molar concentrations). In order to be able to compare the data it is expedient to recalculate them in a uniform manner, and the mole fraction scale is selected, x_A being the mole fraction of A, one of the components in the binary mixtures of solvents A + B

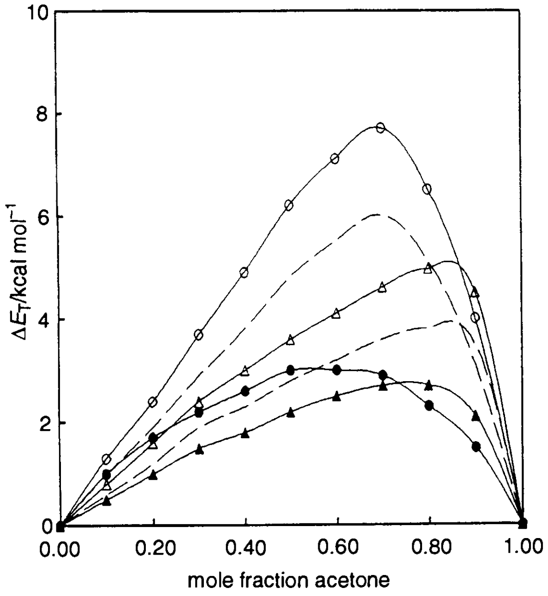

Fig. 1 The excess transition energies ΔE_T for betaine (**I**) [Dimroth–Reichardt's $E_T(30)$, empty symbols] and betaine (**II**) (Dawber's, filled symbols) for acetone + methanol (circles) and acetone + ethanol (triangles). The dashed curves represent $0.78\Delta E_T$(**I**).

(ignoring the probe, assumed to be present at negligible concentrations). Density data are used to convert volume fractions and molar concentrations to mole fractions. A power series to the fourth power of x_A is used, but in the form shown in eqn. (1), where Y is the generalized symbol for the property

$$Y = x_A Y_A + (1 - x_A)Y_B + x_A(1 - x_A)[a + bx_A + cx_A^2] \quad (1)$$

reported and subscript B denotes the cosolvent. The last term on the rhs of eqn. (1) is the excess (or deficiency) of Y above (or below) the linear dependence of Y on the composition and given by eqn. (2). The value of ΔY itself is a measure of the

$$\Delta Y = Y - [x_A Y_A + (1 - x_A)Y_B] \quad (2)$$

preferential solvation, as realized by many authors (*e.g.*, refs. 12–14). However, different probes yield different values of ΔY, hence this measure cannot be unique.

Results

The failure of eqn. (2) to provide a definite measure of the preferential solvation is illustrated by the two probes studied by Dawber *et al.*,[13,15] the one (**I**) being the Dimroth–Reichardt betaine mentioned above and the other (**II**) being 1-methylpyridino-4-(2-ethenyl)phenoxide. For the 11 neat solvents with which both have been measured, there is an excellent correlation between the transition energies E_T of the two probes [eqn. (3)].

$$E_T(\mathbf{I}) = (1.282 \pm 0.029)E_T(\mathbf{II}) - (19.56 \pm 1.51)\ \text{kcal mol}^{-1}$$
$$r = 0.9969, \sigma[E_T(\mathbf{I})] = 0.7\ \text{kcal mol}^{-1} \quad (3)$$

However, for the acetone + methanol, + ethanol, and + propan-1-ol systems, ΔE_T(**II**) is systematically appreciably smaller than the value of $(1/1.282)\Delta E_T$(**I**) that it should have been, if the two probes had the same environment in the mixtures, see Fig. 1 for two of the mixtures. In the case of acetone + methanol, in fact, the maxima in the ΔE_T curves do not occur at the same composition. The two probes, which for neat solvents measure the same 'polarity' as shown by eqn. (3), show different preferential solvation according to eqn. (2). However, this mode of showing the data, ΔE_T, tends to enhance the differences between the probes.

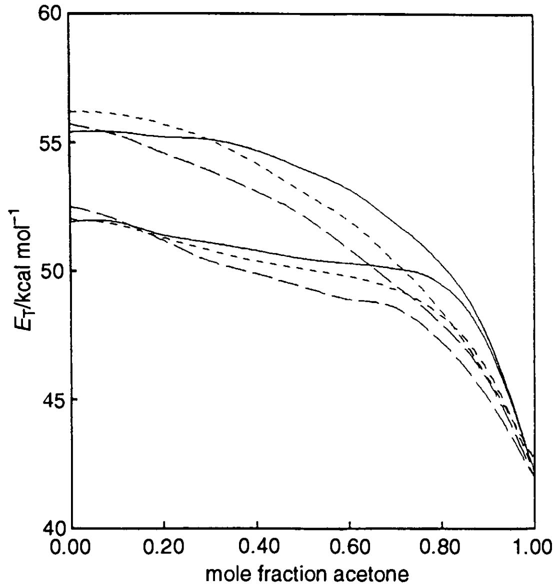

Fig. 2 The transition energies E_T for betaine (**I**) [Dimroth–Reichardt's $E_T(30)$, ——], betaine (**II**) (Dawber's, - - - -) and 4-cyano-1-ethylpyridinium iodide (Z', — — —). Upper set of curves: acetone + methanol, lower set: acetone + ethanol.

Even though these two probes do not measure exactly the same amount of 'polarity' in the mixtures, they may still provide a practically useful approximate measure of it. Another probe can be invoked at this point, 4-cyano-1-ethylpyridinium iodide, yielding Z' values. For the 26 neat solvents for which Z' values are known, they are well correlated[1] with the $E_T(30)$ values [called E_T(**I**) above] given by eqn. (4).

$$E_T(30) = (0.834 \pm 0.032)Z' - (10.3 \pm 1.4)\ \text{kcal mol}^{-1}$$
$$r = 0.9721, \sigma[Z'] = 1.7\ \text{kcal mol}^{-1} \quad (4)$$

The directly measured $E_T(30)$ values,[15] those obtained from eqn. (3) and data with the betaine **II**,[13] and those obtained from eqn. (4) with Z' and the pyridinium iodide ion pair[16] for acetone + methanol and acetone + ethanol mixtures are compared in Fig. 2. It is seen that fairly good agreement is obtained for the three probes in each mixture. The spread among the curves is barely more than the ± 0.8 kcal mol^{-1} uncertainty (*i.e.*, a maximal spread of 1.6 kcal mol^{-1}) suggested above, and is comparable with $\sigma(E_T)$ of eqn. (4).

For no other non-aqueous systems could data for three probes be found, but there are several more, where data for $E_T(30)$ and Z' [or Z, $E_T(30) = 0.809Z - 11.9$, with the same statistical measures of the regression as eqn. (4)] are available. The latter were converted to the former by eqn. (4) and the resulting E_T values are compared in Table 1. The average differences are ± 1.0 kcal mol^{-1}, the worst case is 2.6 kcal mol^{-1}, but differences of ± 0.8 kcal mol^{-1} are noted also for values obtained with the same probe, the Dimroth–Reichardt betaine, by different authors. The conclusion that can be drawn from the examination of these cases is that a good idea, though not an exact value, of the 'polarity' of the mixtures can be gained from the use of any one of the probes.

This being the case, it is worthwhile to examine the many systems where only one probe, namely the Dimroth–Reichardt betaine, has been employed to yield $E_T(30)$ values for non-aqueous mixtures. Representative values are shown in Table 2; when data are available from more than one author, the unweighted averages are presented. Sources of $E_T(30)$ data for several more systems, that do not change the emerging picture, are mentioned at the bottom of Table 2.

'Polarity' data have been published for two further probes in non-aqueous mixtures: Winstein's Y[25] and Brooker's χ_R.[22] The former is linear with $E_T(30)$ over a part of the composition scale for aqueous mixtures (up to x_{H_2O} ~0.8), and was given for mixtures of formic acid with acetic acid and with dioxane.

Table 1 $E_T(30)$ values (in kcal mol^{-1}) obtained directly with the betaine probe (upper line) and those calculated from eqn. (4) with Z or Z' obtained with 4-substituted 1-ethylpyridinium iodide (lower line) for each mixture, at the specified values of x_A

A[a]	B[a]	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	Ref.
MeOH	Me_2CO	42.2	46.5	50.3	52.9	53.6	53.8	54.0	54.3	54.8	55.4	55.4	15
		42.0	45.8	48.0	49.5	50.9	52.2	52.9	53.5	54.1	55.3	55.7	16[b]
EtOH	Me_2CO	42.2	47.2	48.5	49.8	50.2	50.3	50.5	50.8	51.4	51.9	51.9	15
		42.0	45.7	47.9	49.2	49.9	50.4	50.9	51.4	52.2	53.0	53.0	16[b]
$CHCl_3$	Me_2CO	42.2	42.9	43.1	43.0	42.7	42.2	41.6	40.9	40.2	39.6	39.1	15
		42.1	43.3	44.1	44.2	44.3	44.5	44.3	43.6	42.6	41.5	41.2	18[c]
CH_2Cl_2	Me_2CO	42.4	42.8	42.9	42.9	42.9	42.8	42.6	42.4	42.2	41.8	41.2	18
		42.2	43.3	43.7	43.9	44.1	44.0	43.9	43.6	43.1	42.7	40.9	18[c]
EtOH	$CHCl_3$	39.5	44.2	45.6	46.4	47.2	47.8	48.6	49.5	50.3	51.2	51.9	18
		41.2	46.2	47.2	48.1	48.9	49.7	50.3	51.3	51.8	52.4	52.8	18[c]
EtOH	MeCN	45.7	50.7	52.9	53.6	53.6	53.5	53.5	53.4	53.4	53.4	51.8	11
		46.1	48.7	50.3	51.2	51.6	51.8	51.9	52.0	52.3	52.7	53.2	17[b]

[a] Abbreviations: MeOH, methanol; EtOH, ethanol; Me_2CO, acetone; MeCN, cyanomethane. [b] From values of Z'. [c] From values of Z.

Table 2 $E_T(30)$ values (in kcal mol^{-1}) obtained directly with the betaine probe in mixtures of solvents A and B as a function of x_A[a]

B[b]	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Ref.
A = MeOH E_T = 55.4											
EtOH	51.9	51.9	52.2	52.5	53.0	53.3	53.6	54.0	54.4	54.8	11
Bu^{s}OH	47.2	48.3	49.2	50.1	50.8	51.6	52.4	53.2	53.9	54.7	19
Pe^{t}OH	41.1	44.9	47.1	48.4	49.3	50.1	51.2	52.5	53.9	55.0	19
EG	56.9	56.9	56.9	56.7	56.5	56.4	56.2	56.1	55.9	55.7	20
THF	37.6	44.0	47.8	49.9	51.0	51.6	52.1	52.9	53.8	54.8	15
Diox	36.0	42.1	45.8	48.0	49.4	50.3	51.3	52.3	53.5		21
Me_2CO	42.2	48.1	51.3	53.1	54.0	54.1	54.7	55.1	55.6	55.6	15, 21
DMF	43.8	47.4	49.6	51.1	52.2	53.2	54.3	55.3	56.1		21
Py	40.2	42.8	44.8	46.9	47.5	48.4	49.3	50.3	51.6	54.6	19, 21
2,6-Lu	36.9	38.4	40.1	42.2	44.4	46.6	48.9	51.1	53.0	54.6	22[c]
MeCN	45.7	51.6	54.4	55.1	55.1	55.1	55.1	55.2	55.4	55.8	11, 15, 19, 21
$MeNO_2$	46.3	53.3	56.3	57.0	57.1	57.3	57.6	58.6	59.4	59.0	21
Me_2SO	45.1	47.2	48.8	50.0	51.0	51.8	52.6	53.3	54.1	54.8	11
$CHCl_3$	39.1	44.1	46.4	48.2	49.6	50.6	51.6	52.5	53.4	54.5	15
PhH	34.5	41.6	46.3	49.0	50.6	51.3	51.7	52.1	52.8	53.9	11
PhMe	34.7	42.6	47.0	49.0	49.8	49.9	50.1	50.8	51.9	53.6	19
A = EtOH E_T = 51.9											
Bu^{t}OH	43.7	45.7	47.0	47.8	48.4	48.9	49.5	50.1	50.8	51.4	11
TFE	59.8	59.1	58.6	58.2	57.8	57.3	56.7	55.9	54.8	53.5	19
EG	56.9	55.9	55.4	55.0	54.7	54.4	54.3	54.1	53.7	53.1	20
Diox	36.0	40.6	43.6	45.6	46.9	47.9	48.8	49.6	50.5	51.3	21
Me_2CO	42.2	46.5	48.7	50.0	50.6	50.9	51.3	51.5	51.8	51.9	15, 18, 21
DMF	43.8	46.8	48.6	49.7	50.3	50.9	51.4	52.0	52.5	52.6	21
TMU	41.0	43.5	45.2	46.5	47.5	48.3	49.0	49.7	50.5	51.2	21
Py	40.2	40.9	42.0	43.1	44.1	44.7	45.2	45.6	46.5	48.4	21
MeCN	45.7	51.0	53.0	53.5	53.4	53.4	53.8	53.5	53.7	53.4	11, 21
$MeNO_2$	46.3	51.7	53.6	53.8	54.0	54.1	54.3	55.4	56.3	55.7	21
Me_2SO	45.0	46.3	47.3	48.5	49.3	50.1	50.9	51.5	52.0	52.2	11, 21
$CHCl_3$	39.1	43.0	45.2	46.5	47.2	47.8	48.4	49.2	50.1	51.1	18
c-HxH	30.9	42.8	47.7	49.6	49.7	49.3	48.9	49.1	49.9	51.0	23
PhH	34.5	45.3	45.1	47.0	48.0	48.5	48.9	49.4	50.1	51.0	23
A = Me_2CO E_T = 42.2											
PrOH	50.7	51.1	51.3	51.2	51.2	51.1	50.8	50.3	48.9	46.4	15
Pr^{i}OH	49.7	49.2	48.7	48.2	47.7	47.1	46.5	45.7	44.6	43.1	16[c]
BuOH	50.2	50.9	50.5	49.7	49.2	48.9	49.1	49.2	48.8	46.8	21
Bu^{t}OH	46.5	44.7	43.6	43.0	42.6	42.3	41.9	41.6	41.2	41.0	16[c]
Py	40.2	40.3	40.5	40.7	40.9	41.0	41.0	41.1	41.2	41.5	21
Me_2SO	45.0	45.0	44.9	44.8	44.6	44.4	44.1	43.8	43.4	42.9	15
TMP	43.6	43.1	42.7	42.3	42.0	41.5	41.2	40.8	40.4	39.9	24
CH_2Cl_2	41.2	41.8	42.2	42.4	42.6	42.8	42.9	42.9	42.9	42.8	18
$CHCl_3$	39.1	40.2	40.8	41.4	42.1	42.6	43.0	43.3	43.4	43.2	15, 24
CCl_4	32.5	35.5	37.7	38.5	39.2	39.8	40.3	40.8	41.2	41.8	24

Table 2 (*continued*)

B[b]	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Ref.
A = Py E_T = 40.2											
Pe^{t}OH	41.1	42.2	42.6	42.5	42.3	42.0	41.8	41.7	41.5	41.0	21
HxOH	48.8	47.0	45.9	45.4	45.1	45.0	44.8	44.4	43.6	42.2	21
$MeNO_2$	46.3	45.2	44.5	44.0	43.5	43.0	42.5	42.0	41.4	40.7	21
PhH	34.5	35.7	36.6	37.3	37.8	38.4	38.9	39.5	40.0	40.4	11
A = MeCN E_T = 45.6											
Pr^{i}OH	48.4	49.7	50.0	50.0	50.0	50.1	50.6	51.0	50.8	49.4	11
Bu^{t}OH	43.7	44.9	45.7	46.2	46.7	47.3	47.8	48.2	48.3	47.6	11
HxOH	48.8	51.3	52.0	51.7	51.2	50.9	50.8	50.8	50.8	49.7	21
Diox	36.0	38.8	40.7	42.0	42.9	43.6	44.2	44.8	45.4	46.0	21
Me_2SO	45.0	45.0	45.0	45.1	45.1	45.2	45.3	45.3	45.4	45.6	11
PhH	34.5	37.2	39.2	40.8	41.9	42.7	43.4	44.0	44.6	45.1	11
A = Me_2SO E_T = 45.0											
Pr^{i}OH	48.3	49.0	49.3	49.3	49.0	48.5	47.9	47.2	46.4	45.7	11
BuOH	50.2	50.1	49.8	49.4	49.0	48.6	48.2	47.6	46.8	45.6	21
Bu^{t}OH	43.7	44.6	45.3	45.8	46.2	46.4	46.4	46.4	46.1	45.6	11
$CHCl_3$	39.1	41.4	42.6	43.5	44.1	44.6	44.9	45.1	45.3	45.3	24
CCl_4	32.5	41.0	41.8	42.4	42.9	43.5	43.7	44.1	44.5	45.1	24
PhH	34.5	38.8	41.2	42.4	42.9	43.1	43.3	43.6	44.1	44.6	11
A = $CHCl_3$ E_T = 39.1											
PrOH	50.7	49.7	48.8	47.9	47.1	46.2	45.3	44.2	42.9	41.2	15
TMP	43.6	44.3	44.6	44.7	44.4	44.1	43.6	42.9	41.9	40.9	24
TEP	41.5	43.0	43.5	43.7	43.7	43.5	43.1	42.6	41.8	40.8	24
TPP	40.5	42.0	42.7	43.1	43.1	43.0	42.6	42.1	41.6	40.8	24
TBP	39.7	41.3	41.8	42.3	42.4	42.4	42.0	41.6	41.3	40.5	24
CCl_4	32.5	34.2	35.8	36.6	37.1	37.8	37.9	38.5	39.0	39.2	24

[a] Further data are available from (for abbreviations of solvent names see *b* below): Ref. 15, BuOH + CS_2, Me_2SO + formamide; ref. 17, EtOH + cyanoethane, EtOH + 1-cyanopropane; ref. 18, 1,2-dibromoethane + 1,2-dibromopropane; ref. 21, EtOH + decan-1-ol, BuOH + $MeNO_2$, BuOH + Diox, BuOH + DMF, BuOH + CS_2, BuOH + TMU, octan-1-ol + CS_2, dodecan-1-ol + Py, Diox + $MeNO_2$, Diox + cyanoethane, MeCN + butane-1,4-diol, pinacolone + CS_2, *N-tert*-butylformamide + PhH, *N-tert*-butylformamide + Me_2CO; ref. 24, CCl_4 + TMP, CCl_4 + TEP, CCl_4 + TPP, CCl_4 + TBP, TMP + TBP; ref. 25, Winstein's *Y* values for HCO_2H + CH_3CO_2H, HCO_2H + Diox; ref. 26, PhH + nitrobenzene; ref. 27 for DMF + c-HxH (with phase separation). [b] Abbreviations: Bu^{s}OH, butan-2-ol; Pe^{t}OH, 2-methylbutan-2-ol; EG, ethane-1,2-diol; THF, tetrahydrofuran; Diox, 1,4-dioxane; DMF, *N,N*-dimethylformamide; Py, pyridine; 2,6-Lu, 2,6-dimethylpyridine; $MeNO_2$, nitromethane; Me_2SO, dimethyl sulfoxide; PhH, benzene; PhMe, toluene; Bu^{t}OH, 2-methylpropan-2-ol; TFE, 2,2,2-trifluoroethanol; TMU, *N,N,N',N'*-tetramethylurea, c-HxH, c-hexane; PrOH, propan-1-ol, Pr^{i}OH, propan-2-ol; BuOH, butan-1-ol; TMP, trimethylphosphate; HxOH, hexan-1-ol; TEP, triethylphosphate; TPP, tripropyl phosphate; TBP, tributyl phosphate. [c] The *Z'* data from ref. 16 were converted to $E_T(30)$ by means of the inverse of eqn. (4); the χ_B data from ref. 22 were converted by means of $E_T(30) = 1.03\chi_B - 8.9$ $\{\sigma[E_T(30)] = 1.1, r = 0.991$ for $n = 12$ solvents$\}$.

Table 3 The values of π^* in non-aqueous mixtures of solvents A and B as a function of x_A, calculated from data in ref. 28

A[a]	B[a]	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Me_2SO	CCl_4	0.26	0.59	0.73	0.77	0.77	0.78	0.81	0.88	0.96	1.02	1.00
Me_2SO	PhCl	0.67	0.75	0.80	0.84	0.86	0.88	0.90	0.93	0.95	0.98	1.00
Me_2SO	1,2-DCE	0.79	0.82	0.84	0.86	0.88	0.90	0.92	0.94	0.96	0.98	1.00
Me_2SO	CH_2Cl_2	0.80	0.83	0.85	0.86	0.88	0.89	0.91	0.93	0.95	0.97	1.00
THF	CCl_4	0.26	0.32	0.37	0.42	0.46	0.49	0.52	0.54	0.55	0.57	0.58
MeOH	CCl_4	0.26	0.37	0.46	0.53	0.58	0.63	0.66	0.69	0.72	0.74	0.75
Bu^{t}OH	CCl_4	0.26	0.32	0.35	0.38	0.41	0.44	0.47	0.51	0.55	0.59	0.61

[a] Abbreviations for solvents not given in Tables 1 and 2: PhCl, chlorobenzene; 1,2-DCE, 1,2-dichloroethane.

The latter is poorly correlated with $E_T(30)$ and was given for mixtures of dioxane with isooctane and of 2,6-lutidine with methylcyclohexane.

Of more interest is Kamlet and Taft's π^* polarity/polarizability parameter. Although the prescription for its determination involves the average between values for several probes,[10] the data for non-aqueous mixtures are available for only one probe: *N,N*-diethyl-4-nitroaniline.[28] This appears to be a 'well-behaved' probe for neat solvents, so that the results obtained for it are considered to represent π^* values [eqn. (5)] where ν(probe) is the wavenumber expressed in 1000 cm^{-1}.

$$\pi^* = 0.314\,[27.52 - \nu(\text{probe})] \qquad (5)$$

These π^* values are shown in Table 3. (The entries for x_A = 0 and x_A = 1 differ slightly from the published values for neat solvents,[1,10] that are averages of data from several probes.) Most other probes that are generally used for the determination of π^* are also nitro-substituted aromatic compounds with some other functional group (methoxy, ethyl, *etc.*). However, some less often used probes do not contain a nitro group, but have the *N,N*-dialkylamino substituent *para* to a cyano, benzoyl or methylcarboxylate group.[29] It should be interesting to see whether π^* values are obtained with these probes that agree with those in Table 3 for the mixtures included there.

A similar situation holds for the Kamlet–Taft electron pair donicity (hydrogen bond acceptance) parameter β. This quantity, again, was obtained from the spectral data with just one probe, 4-nitroaniline,[28] instead of as the average for several probes. The expression given by eqn. (6) was employed, with

Table 4 The values of β in non-aqueous mixtures of solvents A and B as a function of x_A

A[a]	B[a]	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Me_2SO	CCl_4[b]	0.10	0.65	0.86	0.89	0.85	0.84	0.84	0.91	0.98	0.98	0.79
	PhCl[b]	0.06	0.71	0.90	0.90	0.74	0.70	0.60	0.69	0.84	0.93	0.79
	1,2-DCE[b]	0.10	0.60	0.78	0.78	0.72	0.66	0.66	0.72	0.81	0.87	0.79
	CH_2Cl_2[b]	0.00	0.57	0.76	0.75	0.68	0.64	0.66	0.75	0.87	0.92	0.79
	MeCN[c]	0.46	0.58	0.67	0.71	0.73	0.73	0.74	0.75	0.75	0.75	0.75
	$MeNO_2$[c]	0.02	0.55	0.67	0.70	0.71	0.72	0.73	0.74	0.75	0.75	0.75
Py	MeCN[c]	0.46	0.54	0.59	0.63	0.66	0.70	0.71	0.73	0.76	0.77	0.80
	$MeNO_2$[c]	0.02	0.42	0.58	0.66	0.72	0.74	0.75	0.77	0.78	0.79	0.80
MeCN	$MeNO_2$[c]	0.02	0.22	0.31	0.36	0.41	0.42	0.43	0.45	0.46	0.46	0.46
HMPT	$MeNO_2$[c]	0.02	0.66	0.80	0.84	0.87	0.89	0.91	0.93	0.95	0.95	0.95
THF	CCl_4[b]	0.10	0.32	0.45	0.52	0.55	0.57	0.57	0.57	0.58	0.58	0.58
MeOH	Me_2CO[d]	0.45	0.49	0.52	0.55	0.57	0.58	0.60	0.61	0.62	0.63	0.65
	Me_2CO[e]	0.54	0.55	0.55	0.56	0.57	0.58	0.60	0.61	0.62	0.62	0.62
	MeCN[d]	0.52	0.53	0.54	0.55	0.56	0.57	0.59	0.61	0.63	0.65	0.68
	MeCN[e]	0.38	0.40	0.41	0.43	0.46	0.48	0.50	0.52	0.55	0.58	0.62
	CCl_4[b]	0.10	0.39	0.58	0.68	0.74	0.75	0.74	0.72	0.69	0.68	0.66
EtOH	Me_2CO[d]	0.45	0.46	0.48	0.50	0.52	0.54	0.57	0.59	0.62	0.64	0.66
	DMF[d]	0.78	0.78	0.78	0.78	0.78	0.78	0.77	0.76	0.74	0.72	0.68
	MeCN[d]	0.52	0.54	0.55	0.56	0.57	0.58	0.60	0.61	0.63	0.66	0.70
Pr^iOH	Me_2CO[d]	0.45	0.46	0.48	0.49	0.50	0.50	0.52	0.53	0.55	0.57	0.60
	MeCN[d]	0.52	0.53	0.53	0.53	0.53	0.53	0.53	0.55	0.57	0.60	0.65
Bu^tOH	CCl_4[b]	0.10	0.29	0.43	0.54	0.64	0.71	0.78	0.84	0.89	0.94	0.98

[a] For abbreviations of solvent names see Tables 1, 2 and 3; HMPT, hexamethyl phosphoric triamide. [b] From ref. 28. [c] From ref. 31. [d] From ref. 33. [e] From ref. 30.

the π^* from eqn. (5). The resulting β values are shown in

$$\beta = 0.358\,[31.10 - \nu(\text{probe}) - 1.125\pi^* \qquad (6)$$

Table 4. Similar results, of $B_{KT} \approx \beta$, were presented by Krygowsky *et al.*[30] for mixtures of methanol with 13 non-aqueous solvents: diethyl ether, tetrahydrofuran, 1,4-dioxane, ethyl acetate, acetone, propylene carbonate, formamide, *N*,*N*-dimethylformamide, cyanomethane, nitromethane, dimethyl sulfoxide, chloroform and benzene. For these 14 neat solvents, β, the tabulated average for several probes[1] is given by eqn. (7).

$$\beta = (0.002 \pm 0.040) + (0.975 \pm 0.060)B_{KT}$$
$$r = 0.9615,\ \sigma(\beta) = 0.06 \qquad (7)$$

The B_{KT} data complement those in Table 4, but are not shown except for two mixtures, see below, since they were tabulated at 0.1-spaced values of x_{MeOH} in the original paper.[30]

Further systems were studied with regards to their donicity, but with a different probe and method: the NMR chemical shift δ/ppm of ^{23}Na from a sodium perchlorate probe.[31] They are cyanomethane + dimethyl sulfoxide and + pyridine, and nitromethane + cyanomethane, + pyridine, + dimethyl sulfoxide and + hexamethyl phosphoric triamide. The regression line for the five neat solvents from this list unfortunately has a relatively large standard deviation which is given in eqn. (8).

$$\beta = (0.75 \pm 0.07) - (0.0415 \pm 0.0080)\delta$$
$$r = -0.9547,\ \sigma(\beta) = 0.13 \qquad (8)$$

This expression produces the β values in Table 4, if taken to apply to the mixtures.

The data obtained with an acetylacetonato ethylenediamine copper(II) perchlorate complex as the probe[32] for nitromethane + dimethylformamide pertain only to dilute solutions ($x_{DMF} \leqslant 0.174$), but the β of the better donor solvent has already been attained by the maximal concentration used. A very recent paper[33] contains further data obtained with this copper complex. The reported wave numbers are converted into β values by eqn. (9)[1] obtained for 17 neat solvents with

$$\beta = 0.358\,[18.76 - (\bar{\nu}/1000\ \text{cm}^{-1})] \qquad (9)$$

$\sigma(\beta) = 0.05$.[34] The β values for seven non-aqueous mixtures[32] calculated by eqn. (9) are shown in Table 4, but, again, pertain to solvent mixtures for which no other data are available, except for the methanol + acetone and methanol + cyanomethane systems.[30]

In fact, these are the only two non-aqueous solvent mixtures for which β values (as calculated in the present work) from two different chemical probes are available. The agreement is fair, taking into account the spread in values for the neat solvents and the small β interval for the mixtures involved. It remains to be seen whether these and other probes, such as 4-nitrophenol, that are well established for neat solvents,[1] yield β values for all the mixtures presented in Table 4 and in the paper by Krygowski *et al.*,[30] that are in agreement with those tabulated there.

Discussion

Several parameters purport to describe the chemical properties of solvent mixtures, such as π^* for polarity/polarizability, β for hydrogen bond acceptance ability, and $E_T(30)$ and Z for a combination of the hydrogen bond donation ability (expressible by the Kamlet–Taft α) with a measure of the polarity (expressible by π^*). There is no doubt that preferential solvation of the chemical probes plays a dominant role in determining the size of the parameters measured by them in solvent mixtures. There is only one case among the many summarized in Tables 1–4, where preferential solvation does not take place: the $E_T(30)$ of 1,2-dibromoethane + 1,2-dibromopropane[18] is strictly linear with the (mole fraction) solvent composition. In a few other cases, where the solvents are similar, the deviations of $E_T(30)$ from linearity are slight (ΔE_T is small): methanol + ethanol or + ethane-1,2-diol and dimethyl sulfoxide + acetone or + cyanomethane. The same applies to the B_{KT} of methanol + acetone, + formamide, + *N*,*N*-dimethylformamide, + cyanomethane, and + dimethyl sulfoxide, $|\Delta\beta|$ being $\leqslant 0.03$.[30] These cases are exceptions and preferential solvation of the $E_T(30)$ betaine and other probes is the rule.

The question posed, however, is not whether preferential solvation of the probes takes place, but whether this obviates their use as stand-ins for the 'general solute'. The procedure suggested for answering this question, the use of multiple probes, can hardly be tested at present for non-aqueous solvent mixtures, due to the lack of sufficient data. The data for aqueous mixtures, dealt with in a forthcoming paper, tend to permit a negative answer, *i.e.*, that preferential solvation need not preclude the practical use of chemical probes in mixtures. The few data in Tables 1 and 3 and Fig. 2 are consistent with this more optimistic view also for non-aqueous systems, but are far from establishing this firmly.

The shapes of the parameter *vs.* x_A curves in mixtures of solvents A and B have been commented on by many authors. Fig. 3 shows a number of typical curves of $E_T(30)$ *vs.* x_A and Fig. 4 shows similar curves for β. The nearly linear curves, horizontal or with a minimal slope, are obtained when solvents A and B are associated to nearly the same extent and interact mutually to form similar associates. Association may be by means of hydrogen bonds, as in the case of methanol + ethanol, or of dipole–dipole interactions, as in the case of dimethyl sulfoxide + acetone, that have similar shapes (or even + cyanomethane, that has a different shape).

When association interferes with the property (donicity, 'polarity') and the mutual attraction is weaker than the self-association, then a maximum in the curve results. The $E_T(30)$ of chloroform + trialkyl phosphates and the β of methanol + tetrachloromethane are instances of such cases. However, a maximum is not obtained, when the non-associated component, having a low value of the property under discussion, does not interact appreciably with the associated one (that has a relatively high value of it), but only dilutes it. Then the mixture attains a considerable value of this property even when only a small amount of the latter component is added, so that the curve shows a steep portion, followed by one of much lower slope. It is then difficult to fit the curve with even a fourth degree power series, eqn. (1). Examples are the curves for $E_T(30)$ of ethanol + benzene and for β of dimethyl sulfoxide + nitromethane. In the latter case, although both components are polar, their mutual dipole interactions are possibly antagonistic, and both being aprotic, the mutual attraction is minimal, and the component of high donicity, dimethyl sulfoxide, manifests this property, β, already in dilute solutions.

Finally, curves with an initial moderate slope and a final large slope, as the associated component is approached, are typical for mixtures of a hydrogen-bonded solvent such as an alkanol with a polar aprotic solvent, if the latter has a lower value of this property, $E_T(30)$ or β. The mixtures of ethanol + pyridine and of methanol + nitromethane are examples of such behaviour. Such behaviour indicates that the mutual association of the components, by hydrogen bonding, is strong, but that the associate has a lower value of the property than the protic solvent.

The above shows that even if different probes produce non-ideal but convergent values for a property such as $E_T(30)$, Z, π^* or β, these values arise not only from preferential solvation of the probes but also from rather complicated self- and mutual-interactions of the solvents. This, again, has been noted by many previous authors, but the discussion of the notion of a 'property of a mixed binary solvent', and whether such a property can be defined, not to say be measured, by means of chemical probes, is the novel aspect of this paper. Probes which interact with the components of the binary mixed solvent less strongly than these self- or mutual-interactions would have similar environments and provide convergent values for the properties with the expressions employed for neat solvents. They can then act as stand-ins for the 'general solute', provided, again, that the latter does not have extremely strong interactions with one component of the mixture, interfering with the self- and mutual-interactions.

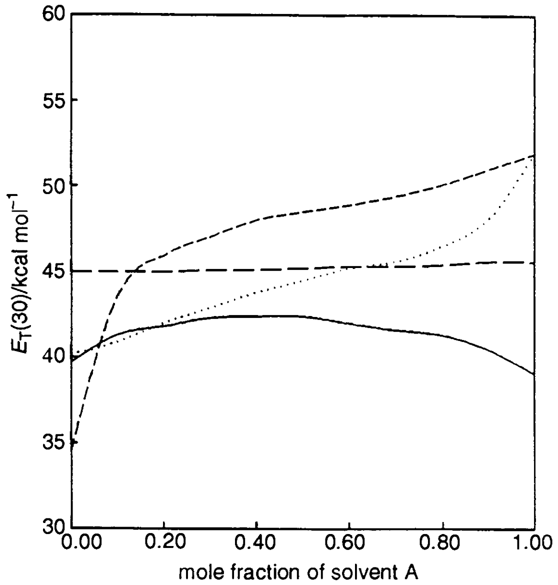

Fig. 3 Typical curves for the transition energies $E_T(30)$ for A + B solvent mixtures: tributyl phosphate + chloroform ——, cyanomethane + dimethyl sulfoxide — — —, benzene + ethanol – – – – and pyridine + ethanol · · · ·, as functions of the mole fraction of solvent A

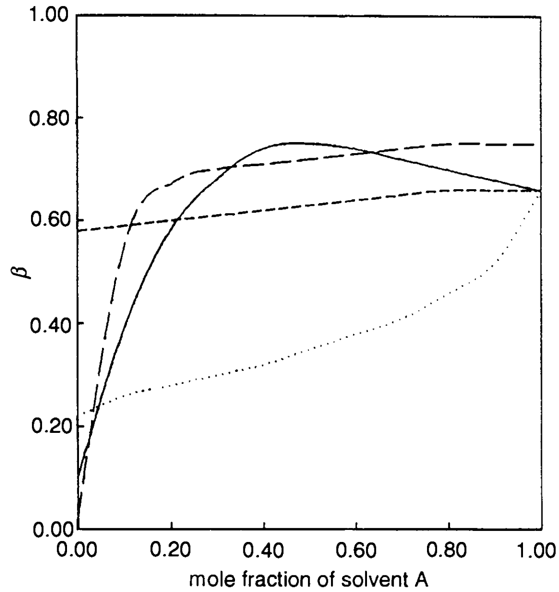

Fig. 4 Typical curves for the donicities β for A + B solvent mixtures: methanol + tetrachloromethane ——, dimethyl sulfoxide + nitromethane — — —, methanol + acetone – – – – and methanol + nitromethane · · · ·, as functions of the mole fraction of solvent A

Acknowledgements

A preliminary form of this work was presented at the 23rd International Conference on Solution Chemistry, Leicester, August 1993. Prof. M. J. Blandamer and Prof. G. T. Hefter are thanked for their hospitality at the Universities of Leicester (UK) and Murdoch (Australia), respectively, where some of the work was done during the author's sabbatical leave.

References

1 Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409.
2 C. Reichardt, *Solvent Effects in Organic Chemistry*, 2nd edn., 1988, VHS, Weinheim (Germany), p. 60, 339.
3 W. J. Cheong and P. W. Carr, *Anal. Chem.*, 1988, **60**, 820.
4 E. Casassas, G. Fonrodona and A. de Juan, *J. Solution Chem.*, 1992, **21**, 147.
5 M. C. R. Symons, *Pure Appl. Chem.*, 1986, **58**, 1121.
6 M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73.
7 H. Schneider, Y. Migron and Y. Marcus, *Z. Phys. Chem.*, NF, 1992, **175**, 145.
8 K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Ann. Chem.*, 1963, **661**, 1.
9 E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253.
10 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
11 I. A. Kopel and J. B. Kopel, *Org. React.*, (*USSR*), 1983, **20**, 523, 547.
12 J. R. Haak and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 307.
13 J. G. Dawber, S. Etemad and M. A. Beckett, *J. Chem. Soc.*, *Faraday Trans. 1*, 1990, **86**, 3725.
14 P. Chatterjee, A. K. Laha and S. Bagchi, *J. Chem. Soc.*, *Faraday Trans. 1*, 1992, **88**, 1675.
15 J. G. Dawber, J. Ward and R. A. Williams, *J. Chem. Soc.*, *Faraday Trans. 1*, 1988, **84**, 713.
16 P. Chatterjee and S. Bagchi, *J. Chem. Soc.*, *Faraday Trans.*, 1991, **87**, 587.
17 P. Chatterjee and S. Bagchi, *J. Phys. Chem.*, 1991, **95**, 3311.
18 S. Balakrishnan and A. J. Easteal, *Aust. J. Chem.*, 1981, **34**, 933.
19 H. Elias, G. Gumbel, S. Neitzel and H. Voltz, *Fresenius' Z. Anal. Chem.*, 1981, **306**, 240.
20 L. M. P. C. Albuquerque, A. M. N. Simoes, M. C. M. Ventura and R. M. C. Goncalves, *23rd Int. Conf. Solution Chem.*, Leicester, 1993, to be published.
21 H. Langhals, *Angew. Chem.*, *Int. Ed. Engl.*, 1982, **21**, 724.
22 L. G. S. Brooker, A. C. Craig, D. W. Hesletine, P. W. Jenkins and L. L. Lincoln, *J. Am. Chem. Soc.*, 1965, **87**, 2443.
23 P. Nagy and R. Herzfeld, *Acta Phys. Chim.* (*Szeged*), 1985, **31**, 735.
24 Z. B. Maksimovic, C. Reichardt and A. Spiric, *Fresenius' Z. Anal. Chem.*, 1974, **270**, 100.
25 A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.
26 K. Tamura, Y. Ogo and T. Imoto, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2988.
27 H. Langhals, *Z. Phys. Chem.* (*Leipzig*), 1987, **268**, 91.
28 M. J. Kamlet, E. G. Kaiser, M. E. Jones, J. L. Abboud, J. W. Easter and R. W. Taft, *J. Phys. Chem.*, 1978, **82**, 2477.
29 P. Nicolet and C. Laurence, *J. Chem. Soc.*, *Perkin Trans. 2*, 1986, 1071; C. Laurence, P. Nicolet and M. Helbert, *J. Chem. Soc.*, *Perkin Trans. 2*, 1986, 1081.
30 T. M. Krygowsky, C. Reichardt, P. K. Wrona, C. Wyszomirska and U. Zielkowska, *J. Chem. Res.* (*S*), 1983, 116.
31 V. Gutman, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978, p. 132; M. S. Greenberg and A. I. Popov, *Spectrochim. Acta*, *Part A*, 1975, **31**, 697.
32 D. Bourdin, D. Lavabre, J. P. Beteille, G. Levy and J. C. Micheau, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2985.
33 M. Scremin, S. P. Zanotto, V. G. Machado and M. C. Rezende, to be published, 1994, communicated to the author.
34 Y. Migron and Y. Marcus, *J. Phys. Org. Chem.*, 1991, **4**, 310.

Paper 3/07117K
Received 1*st December* 1993
Accepted 15*th December* 1993