Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 1. A comparison of several preferential solvation models for describing E_T (30) polarity of dipolar hydrogen bond acceptor-cosolvent mixtures

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The influence of solute–solvent and solvent–solvent interactions on the preferential solvation of solvatochromic indicators in binary solvent mixtures of dipolar hydrogen bond acceptors has been studied. Several equations based on solvent exchange models that relate the transition energy of the Dimroth–Reichardt E_T (30) indicator with the solvent composition are derived and compared. The models tested assume that the two solvents mixed interact to form a common structure with an E_T (30) value not always intermediate between those of the solvents mixed. The solvatochromic indicator can be preferentially solvated by any of the solvents mixed or by the mixed solvent obtained. The parameters obtained explain the strong synergism observed for some of the mixtures with strong hydrogen bond donors (alcohols and chloroform).

The study of physicochemical properties that depend on solute–solvent interactions is much more complex in mixed than in pure solvents. On one hand, the solute can be preferentially solvated by any of the solvents present in the mixture. On the other, solvent–solvent interactions can strongly affect solute–solvent interactions.

A simple and convenient method for studying solute–solvent interactions is by means of solvatochromic indicators, which in addition offer direct information about solvent properties such as polarity or hydrogen bonding capabilities.

The most used solvatochromic indicator is the 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-ium)-1-phenolate or E_T (30) dye, proposed by Reichardt and co-workers[1,2] for measuring solvent polarity. Thus, the E_T (30) polarity is defined as the excitation energy (kcal mol^{-1}) of the E_T dye in a particular solvent, which can be calculated from the wavenumber of the maximum of the absorption spectrum (ν) according to eqn. (1).

$$E_T(30) = hc\bar{\nu}N_A = 2.859 \times 10^{-3}\ \bar{\nu}/\text{cm}^{-1} \qquad (1)$$

The E_T (30) parameter has been measured for many solvents, pure or mixed. However, the interpretation of the E_T (30) values in pure or in mixed solvents is different. The E_T (30) value measures the polarity of the solvation microsphere surrounding the solvatochromic indicator. In a pure solvent the composition of this microsphere is the same as in the bulk solvent, but this is not necessarily true for mixed solvents. The indicator can interact to a different degree with the two solvents of a binary mixture and the solvation microsphere will reflect these interactions. On the solvation microsphere, the proportion of the solvent with the strongest interaction with the indicator will be larger than in the bulk solvent and the indicator will be preferentially solvated by this solvent. Dawber *et al.*[3] proposed the deviation from linearity of experimental E_T (30) values of binary solvents as a measurement of preferential solvation and related the preferential solvation of E_T with several thermodynamic and kinetic properties.[4]

In a previous work,[5] we derived an equation that relates E_T (30) values of binary solvent mixtures with solvent composition through a preferential solvation parameter. The same type of equation was also applied to dissociation pK values of ion pairs in binary mixtures.[6]

However, for many solvent mixtures two equations were needed to cover the whole range of solvent composition because each one of the equations applied to only one solvent rich zone. Nor was the proposed equation applicable to synergetic mixtures, which have E_T values higher than those of the two pure solvents mixed. These synergetic mixtures are composed of a hydrogen bond acceptor solvent with almost no hydrogen bond donor ability (*e.g.* dimethyl sulfoxide) and a hydrogen bond donor (*e.g.* an alcohol).

Several approaches to modify the equation in order to cover the whole range of solvent compositions have been made. On one hand, we have recently derived a new equation that considers the solvent–solvent interaction between the two solvents mixed and applied it to the dissociation pK_a values of acids in binary mixtures of water with propan-2-ol.[7] On the other, Skwierczynski and Connors[8] have proposed two equations to describe the E_T (30) values of binary aqueous mixtures. The two equations were derived from two preferential solvation models based on the solvent exchange theory that had been previously applied to several other parameters.[9–13] In fact, one of the equations proposed by Skwierczynski and Connors is the same as that which we derived, from another point of view, for the E_T (30) parameter[5] and dissociation pK values[6] of binary mixtures.

In this paper, we compare these preferential solvation equations and others that can be derived on the basis of the same solvent exchange theory, and apply them to the description of the E_T (30) values of binary mixtures of hydrogen bond acceptors with hydrogen bond donors.

Preferential solvation models

All the preferential solvation models compared here consider that the transition energy (E_T) of a solvatochromic indicator is an average of the transition energies in the solvents that compose the solvation microsphere of the indicator according to their mole fractions on this sphere.

Model 1

For a binary mixture composed of solvents 1 (S1) and 2 (S2) the observed E_T value, according to the preceding hypothesis, is given by eqn. (2) where x_1^s and x_2^s are the mole fractions of

$$E_T = \frac{x_1^s E_{T1} + x_2^s E_{T2}}{x_1^s + x_2^s} \quad (2)$$

solvents 1 and 2 in the microsphere of solvation of the indicator and E_{T1} and E_{T2} the transition energies of the solvatochromic indicator in the pure solvents 1 and 2.

We proposed a preferential solvation parameter, $f_{2/1}$ (previously named f_2/f_1), that measures the tendency of the indicator to be preferentially solvated by solvent 2 rather than solvent 1.[5,6] The solvation depends also on the mole fractions of the two solvents on the bulk mixed solvent (x_1^0 and x_2^0) and $f_{2/1}$ is the ratio

$$f_{2/1} = \frac{x_2^s/x_1^s}{x_2^0/x_1^0} \quad (3)$$

Considering that

$$x_1^0 + x_2^0 = x_1^s + x_2^s = 1 \quad (4)$$

Eqn. (2) becomes

$$E_T = E_{T1} + \frac{a x_2^0}{(1 - x_2^0) + f_{2/1} x_2^0} = E_{T1} + \frac{a x_2^0}{1 + b x_2^0} \quad (5)$$

with

$$a = f_{2/1}(E_{T2} - E_{T1}) \quad (6)$$

$$b = f_{2/1} - 1 \quad (7)$$

An alternative form of this equation has been derived by Skwierczynski and Connors[8] from the solvent exchange model. This model establishes an equilibrium between the mole fractions of a solvatochromic indicator (I) solvated by solvent 1 [I(S1)] and by solvent 2 [I(S2)].

$$\mathrm{I(S1)} + \mathrm{S2} \rightleftharpoons \mathrm{I(S2)} + \mathrm{S1}$$

Since the amounts of solvents 1 and 2 solvating the indicator are much lower than the amounts of the solvents in the bulk, the constant of the equilibrium is equal to our preferential solvation parameter $f_{2/1}$ of eqn. (3).

This approach cannot fully describe the behaviour of many solvent mixtures.[5,7,8] To explain the pK_a values of acids in water–propan-2-ol mixtures,[7] we assumed that the two solvents mixed (S1 and S2) interact to form a common structure (S12) with particular properties. For the sake of simplicity, it is considered that the two solvents interact in the ratio of 1:1, that is to say, the mixed structures formed contains the same number of molecules of solvents 1 and 2. This hypothesis will be assumed throughout the text. Mixed solvents with a structure stoichiometry other than 1:1 can be regarded, as a good approximation from a practical point of view, as mixtures of two structures: the 1:1 mixed structure and the structure of the solvent in excess. Therefore, the equilibrium for formation of the 'mixed solvent' is written as

$$\mathrm{S1} + \mathrm{S2} \rightleftharpoons 2\ \mathrm{S12}$$

where the coefficient 2 in the right hand of the equilibrium is necessary to keep the number of solvent molecules constant. This equilibrium should be considered an equilibrium between solvent structures more than between individual solvent molecules. The extent of the solvent 1–solvent 2 interaction is quantified by the equilibrium constant (K_{12}) defined in the mole fraction scale in eqn. (8) where x_1, x_2 and x_{12} are the mole

$$K_{12} = \frac{x_{12}^2}{x_1 x_2} \quad (8)$$

fractions of solvents S1, S2 and S12 in equilibrium. These mole fractions are related to the mole fractions of solvents mixed (x_1^0 and x_2^0) through eqns. (9)–(11).

$$x_1^0 = x_1 + \frac{x_{12}}{2} \quad (9)$$

$$x_2^0 = x_2 + \frac{x_{12}}{2} \quad (10)$$

$$x_1^0 + x_2^0 = x_1 + x_2 + x_{12} = x_1^s + x_2^s + x_{12}^s = 1 \quad (11)$$

The mole fraction of solvent S12 can be calculated by eqn. (12)

$$x_{12} = k - \sqrt{k^2 + 4k x_2^0 (x_2^0 - 1)} \quad (12)$$

where

$$k = \frac{K_{12}}{K_{12} - 4} \quad (13)$$

The E_T value of the mixture is

$$E_T = x_1^s E_{T1} + x_2^s E_{T2} + x_{12}^s E_{T12} \quad (14)$$

and if we define two different solvent exchange processes by

$$\mathrm{I(S1)} + \mathrm{S2} \rightleftharpoons \mathrm{I(S2)} + \mathrm{S1}$$

$$\mathrm{I(S1)} + \mathrm{S12} \rightleftharpoons \mathrm{I(S12)} + \mathrm{S1}$$

with the equilibrium constants defined by $f_{2/1}$ [eqn. (3)] and by $f_{12/1}$ [eqn. (15)] then eqn. (16) is obtained where a and b

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_{12}^0/x_1^0} \quad (15)$$

$$E_T = E_{T1} + \frac{a x_2^0 + c[k - \sqrt{k^2 - 4k(1 - x_2^0)x_2^0}]}{1 + b x_2^0 + d[k - \sqrt{k^2 - 4k(1 - x_2^0)x_2^0}]} \quad (16)$$

are defined by eqns. (6) and (7), and c and d are defined by eqns. (17) and (18).

$$c = f_{12/1}(E_{T12} - E_{T1}) - \frac{f_{2/1}(E_{T2} - E_{T1})}{2} \quad (17)$$

$$d = f_{12/1} - \frac{(1 + f_{2/1})}{2} \quad (18)$$

A simplified form of eqn. (16) (taking $K_{12} \longrightarrow \infty$) was successfully used for acid pK values in water–propan-2-ol mixtures.[7]

The main limitation of eqn. (16) is the choice of value of K_{12}. The E_T value is very sensitive to the proportions of solvents S1, S2 and S12 in the solvation microscphere, but not to their proportions in the bulk solvent. Therefore, a direct estimation of K_{12} from the E_T values of the mixture is very hazardous. In other words, a high proportion of S12 in the solvation sphere may come from a high $f_{12/1}$ value or from a high K_{12} value. Simultaneous estimation of both parameters is very difficult and usually leads to a large error in the estimations of the parameters.

An alternative to this preferential solvation model is to assume that the solvent 12 is formed in the microsphere of solvation of the indicator from solvents 1 and 2. This is one of the assumptions of Skwierczynski and Connors,[8] although their solvent exchange scheme is different and will be considered later (Model 2).

If we assume formation of the S12 solvent on the microsphere of solvation, the solvent exchange processes are written as

$$\mathrm{I(S1)} + \mathrm{S2} \rightleftharpoons \mathrm{I(S2)} + \mathrm{S1}$$

$$\mathrm{I(S1)} + \tfrac{1}{2}\,\mathrm{S2} \rightleftharpoons \mathrm{I(S12)} + \tfrac{1}{2}\,\mathrm{S1}$$

with the equilibrium constant $f_{2/1}$ defined in eqn. (3) and $f_{12/1}$ defined in eqn. (19).

$$f_{12/1} = \frac{x^s_{12}/x^s_1}{\sqrt{x^0_2/x^0_1}} \qquad (19)$$

The final equation obtained is given in eqn. (20) with parameters a and b defined by eqns. (6) and (7), and c and d by eqns. (21) and (22).

$$E_T = E_{T1} + \frac{ax^0_2 + c\sqrt{(1 - x^0_2)x^0_2}}{(1 - x^0_2) + f_{2/1}x^0_2 + f_{12/1}\sqrt{(1 - x^0_2)x^0_2}} = E_{T1} + \frac{ax^0_2 + c\sqrt{(1 - x^0_2)x^0_2}}{1 + bx^0_2 + d\sqrt{(1 - x^0_2)x^0_2}} \qquad (20)$$

$$c = f_{12/1}(E_{T12} - E_{T1}) \qquad (21)$$

$$d = f_{12/1} \qquad (22)$$

An interesting property of eqns. (16) and (20) is that both give the simplified eqn. (5) if c and d are equal to zero. This occurs for eqn. (20) when $f_{12/1} \longrightarrow 0$, and for eqn. (16) when the solvent S12 has intermediate properties between those of solvents S1 and S2 according to eqns. (23) and (24).

$$f_{12/1} = \frac{1 + f_{2/1}}{2} \qquad (23)$$

$$E_{T12} = \frac{E_{T1} + f_{2/1}E_{T2}}{1 + f_{2/1}} \qquad (24)$$

Model 2

Skwierczynski and Connors[8] proposed two different solvent exchange models to fit the E_T (30) values of binary aqueous mixtures. Some of the mixtures fitted the simplifed form of Model 1 [eqn. (5)], but for the others they proposed solvent exchange processes with formation of the S12 solvent on the microsphere of solvation, that can be written as

$$\mathrm{I(S1)_2} + 2\,\mathrm{S2} \rightleftharpoons \mathrm{I(S2)_2} + 2\,\mathrm{S1}$$

$$\mathrm{I(S1)_2} + \mathrm{S2} \rightleftharpoons \mathrm{I(S12)_2} + \mathrm{S1}$$

The constants of these processes can be defined as

$$f_{2/1} = \frac{x^s_2/x^s_1}{(x^0_2/x^0_1)^2} \qquad (25)$$

$$f_{12/1} = \frac{x^s_{12}/x^s_1}{x^0_2/x^0_1} \qquad (26)$$

Substituting the constants in eqn. (14) and rearranging terms gives eqn. (27) with a and c defined by eqns. (6) and (21).

$$E_T = E_{T1} + \frac{a(x^0_2)^2 + c(1 - x^0_2)x^0_2}{(1 - x^0_2)^2 + f_{2/1}(x^0_2)^2 + f_{12/1}(1 - x^0_2)x^0_2} \qquad (27)$$

One inconvenience of eqn. (27) is it does not simplify to eqn. (5) when $f_{2/1} \longrightarrow 0$. In this instance, quadratic terms are obtained [eqn. (28)].

$$E_T = E_{T1} + \frac{a(x^0_2)^2}{(1 - x^0_2)^2 + f_{2/1}(x^0_2)^2} \qquad (28)$$

Skwierczynski and Connors[8] introduced a simplication to eqn. (27). They assumed

$$E_{T12} = \frac{E_{T1} + E_{T2}}{2} \qquad (29)$$

This hypothesis gave good results for the non-synergetic mixtures they studied, but it cannot be applied to the synergetic mixtures with E_T values higher than E_{T1} and E_{T2}, as it will be demonstrated later.

Model *m*

It can be easily observed that the models 1 and 2, defined by eqns. (20) and (27), are particular cases of a more general model defined by the solvent exchange processes

$$\mathrm{I(S1)}_m + m\,\mathrm{S2} \rightleftharpoons \mathrm{I(S2)}_m + m\,\mathrm{S1}$$

$$\mathrm{I(S1)}_m + \tfrac{m}{2}\,\mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_m + \tfrac{m}{2}\,\mathrm{S1}$$

The constants of these processes are defined by

$$f_{2/1} = \frac{x^s_2/x^s_1}{(x^0_2/x^0_1)^m} \qquad (30)$$

$$f_{12/1} = \frac{x^s_{12}/x^s_1}{\sqrt{(x^0_2/x^0_1)^m}} \qquad (31)$$

And the final equation obtained is eqn. (32) where a and c have been defined in eqns. (6) and (21).

$$E_T = E_{T1} + \frac{a(x^0_2)^m + c\sqrt{[(1 - x^0_2)x^0_2]^m}}{(1 - x^0_2)^m + f_{2/1}(x^0_2)^m + f_{12/1}\sqrt{[(1 - x^0_2)x^0_2]^m}} \qquad (32)$$

In this general model, m is the number of solvent molecules in the microsphere of solvation of the solvatochromic indicator affecting its transition energy. Models 1 and 2 are the same general model for the particular cases $m = 1$ and $m = 2$, respectively.

It can be also deduced that when $f_{12/1} \longrightarrow 0$, eqn. (32) becomes eqn. (33) which is equal to eqn. (5) only when $m = 1$.

$$E_T = E_{T1} + \frac{a(x^0_2)^m}{(1 - x^0_2)^m + f_{2/1}(x^0_2)^m} \qquad (33)$$

Table 1 Solvatochromic parameters of pure solvents at 25 °C [1,5]

Solvent	E_T^N	π^*	α	β
Group 1: dipolar strong hydrogen bond acceptors and poor hydrogen bond donors				
Trimethyl phosphate	0.398	0.72	0.00	0.77
Triethyl phosphate	0.340	0.72	0.00	0.77
Tripropyl phosphate	0.302	0.70 [a]	0.00	0.77 [b]
Tributyl phosphate	0.275	0.65	0.00	0.77
Dimethyl sulfoxide	0.444	1.00	0.00	0.76
Acetone	0.355	0.71	0.08	0.48
Acetonitrile	0.460	0.75	0.19	0.40
Group 2: strong hydrogen bond donors				
Water	1.000	1.09	1.17	0.47
Methanol	0.762	0.60	0.98	0.66
Ethanol	0.654	0.54	0.86	0.75
Propan-1-ol	0.617	0.52	0.84	0.90
Propan-2-ol	0.546	0.48	0.76	0.84
2-Methylpropan-2-ol	0.389	0.41	0.68	1.01
Dichloromethane	0.309	0.82	0.30	0.00
Chloroform	0.259	0.58	0.20	0.10
Group 3: poor hydrogen bond acceptors and poor hydrogen bond donors				
Tetrachloromethane	0.052	0.28	0.00	0.10
Benzene	0.111	0.59	0.00	0.10
Cyclohexane	0.006	0.00	0.00	0.00

[a] Calculated from the E_T^N value [$E_T(30) = 30.31 + 14.6\pi^* + 16.5\alpha$].[1]
[b] Estimated from the β values of the other phosphates.

The three models defined here will be tested on their application to the E_T (30) values of mixtures of dipolar hydrogen bond acceptors in order to determine which model describes better the behaviour of these mixtures.

Computation methods

The E_{T1}, E_{T2}, E_{T12}, $f_{2/1}$, $f_{12/1}$ and m (for model m) parameters that minimize the square residuals of the E_T (30) values of each binary solvent system studied have been calculated by non-linear regression by means of computer programs written in BASIC. The programs use the Gauss–Newton–Marquardt algorithm as described by Valkó and Vajda.[14] The E_T data can be fitted to any of the equations describing the different models. Since non-linear regression is an iterative procedure, initial estimates of the parameters are obtained by the program from the shape of the E_T *vs.* x_2 curve. All the E_T data have been normalized (E_T^N) by reference to tetramethylsilane ($E_T^N = 0$) and water ($E_T^N = 1$) according to eqn. (34).[1]

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} \qquad (34)$$

Results and discussion

Table 1 presents the polarity and hydrogen bonding properties of several solvents, as measured by the Dimroth–Reichardt E_T^N and Kamlet–Taft π^*, α and β parameters. The solvents are divided into three groups. Trialkyl phosphates, dimethyl sulfoxide, acetone and acetonitrile have strong hydrogen bond acceptor (high β values) and poor hydrogen bond donor (low α values) capabilities. The mixtures of these solvents with the solvents of the second group (strong hydrogen bond donors) often present a high synergetic effect for the E_T (30) parameters.[15] That is to say, some intermediate compositions of the mixtures show E_T (30) values higher than the ones of the pure solvents. These solvent mixtures could not be fitted to eqn. (5).[5] On the contrary, the mixtures with the solvents of the third group of Table 1 (poor hydrogen bond acceptors and donors) and the mixtures between solvents of the first group (*e.g.* acetone–dimethyl sulfoxide) do not show the synergetic effect and could be fitted to eqn. (5).[5]

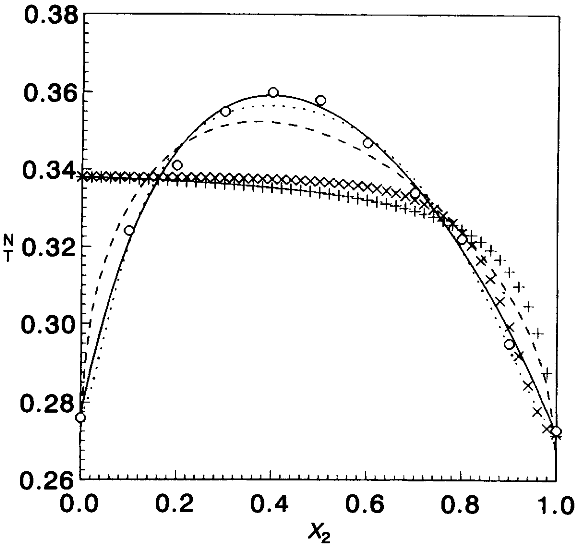

Fig. 1 Application of the different models and equations studied to the synergetic mixtures of tributyl phosphate (S1) with chloroform (S2); ○, experimental points; + + +, $m = 1$ and eqn. (5); — — —, $m = 1$ and eqn. (20); × × ×, $m = 2$ and eqns. (27) and (29); ——, $m = 2$ and eqn. (27); · · ·, $m = 3$ and eqn. (32). X_2 is the mole fraction of chloroform.

The different behaviour of the mixtures can be attributed to the strong hydrogen bonding between the strong hydrogen bond acceptors and the strong hydrogen bond donors. This interaction produces a hydrogen bond complex that often is more polar than any of the two pure solvents mixed. This high polar complex can only be produced by mixing the solvents of group 1 with the solvents of group 2.

The general eqns. (20), (27) and (32) consider the formation of an intermediate solvent structure with its own polarity (E_{T12}^N) and preferential solvation ability ($f_{12/1}$) and hence, they should apply to the synergetic mixtures. The point is to decide which of the models (or m value) gives a more accurate fit to the experimental values and a more reasonable description of the properties of the mixtures.

The mixtures of tributyl phosphate with chloroform[16] are a very good example of the application of the different models to the synergetic mixtures. In spite of the fact that tributyl phosphate and chloroform have very different hydrogen bond donor and acceptor capabilities, the two solvents present a very similar E_T^N value (see Table 1). However, their mixtures have E_T^N values higher than the values of the pure solvents, with a maximum of 0.360 for a mole fraction of chloroform of 0.4.

The results obtained on the application of the different equations to these mixtures are presented in Table 2 and Fig. 1. It can be observed that eqn. (5) does not describe well these mixtures because it cannot give E_T^N values higher than E_{T1}^N or E_{T2}^N. Nor can eqn. (27) with the assumption that Skwierczynski and Connors[8] [eqn. (29)] used for aqueous mixtures. According to this assumption, the E_T^N value of the chloroform–tributyl phosphate hydrogen bond complex should be the average of the E_T^N values of chloroform and tetrabutyl phosphate, and therefore the E_T^N values of the mixtures cannot be higher than the ones of the pure solvents.

The other models give good fits to the experimental data, but the best results are obtained for m values close to 2. In fact, iteration of the m parameter, together with the other parameters, gives the best value of $m = 2.1$ In addition, the values obtained for the model $m = 1$ [eqn. (20)] are very

Table 2 Application of the different preferential solvation models to the E_T^N values of the mixtures of tributyl phosphate (S1) with chloroform (S2)

Eqn.	m	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	SSR[a]	sd[b]/10^{-3}
(5)	1	0.338	0.271	—	6.4×10^{-2}	—	6.2×10^{-3}	28
(20)	1	0.273	0.266	87.8	1.5	2.4×10^{-3}	4.4×10^{-4}	8.6
(27) + (29)	2	0.338	0.272	0.305[c]	1.7×10^{-2}	4.1×10^{-6}	5.5×10^{-3}	28
(27)	2	0.277	0.272	0.417	2.2	4.3	5.0×10^{-5}	2.9
(32)	2.1[d]	0.277	0.272	0.410	2.2	4.9	5.0×10^{-5}	3.2
(32)	3	0.276	0.274	0.369	3.4	26	7.4×10^{-5}	3.5

[a] SSR = sum of squares of residuals. [b] sd = standard deviation. [c] E_{T12}^N calculated from eqn. (29). [d] m value iterated.

Table 3 Parameters of dimethyl sulfoxide (S1) binary mixtures

		$m = 2$								
Cosolvent (S2)	m	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	sd/10^{-3}	N[a]	Ref.
Water	—	0.441	0.994	0.542	0.57	2.0	3.4	9.2	50	8, 15, 17–19
Methanol	1.7	0.445	0.762	0.763	0.02	2.1	110	6.4	11	15
Ethanol	2.4	0.432	0.648	0.687	0.25	1.8	7.4	6.6	12	15
Propan-2-ol	2.4	0.437	0.545	0.614	0.51	1.6	3.1	4.7	18	15
2-Methylpropan-2-ol	1.6	0.444	0.400	0.548	0.72	1.6	2.3	3.9	23	15
Chloroform	2.1	0.450	0.319	0.473	0.19	0.31	1.6	1.6	11	3
Acetonitrile	0.6	0.435	0.454	0.450	0.02	5.9	254	2.5	14	20
Acetone	1.6	0.451	0.364	0.448	1.04	2.8	2.7	1.2	11	3
Benzene	1.3	0.442	0.123	0.393	0.38	3.6	9.4	5.9	24	20
Tetrachloromethane	—	0.455	0.056	0.327	0.01	0.91	88	1.5	11	16

[a] N is the number of data points.

Table 4 Parameters of acetonitrile (S1) binary mixtures

		$m = 2$								
Cosolvent (S2)	m	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	sd/10^{-3}	N	Ref.
Water	—	0.457	0.995	0.761	1.3	13	9.9	15	59	8, 17, 18, 21, 22
Methanol	0.8	0.468	0.769	0.777	0.003	20	7×10^3	6.5	28	15, 23
Ethanol	1.5	0.466	0.650	0.703	2.5	20	8.1	3.5	15	15
Propan-2-ol	2.6	0.463	0.545	0.630	2.6	20	7.5	3.9	11	15
2-Methylpropan-2-ol	2.6	0.463	0.396	0.558	7.0	22	3.1	5.5	12	15
Dimethyl sulfoxide	0.6	0.454	0.435	0.450	43	254	5.9	2.5	14	20
Benzene	—	0.463	0.123	0.419	1.3	4.7	3.8	6.9	13	20

unrealistic because the E_{T12}^N value obtained is too high to be credible. The results obtained with $m = 3$ seem quite logical, but they are not very different to the ones obtained for $m = 2$ and the fit is slightly worse.

These results are not an isolated case. Tables 3–6 present the m values that give best fits for the different mixtures studied. A (—) symbol is given for the mixtures that give different m values depending on the initial value used in the iterations. In general, these mixtures are not synergetic. Practically, for all the mixtures with synergetic behaviour (or close to synergetic, that is to say E_{T12}^N close to E_{T1}^N or E_{T2}^N) the best m value is *ca.* 2. For most of these mixtures a too high E_{T12}^N value (and usually a very small $f_{12/1}$ value) is obtained if m is taken to be equal to 1. m Values higher than 2 usually give fits slightly worse than for $m = 2$.

Therefore, the best model seems to be model 2 as defined by eqn. (27) or by eqn. (32) with $m = 2$. All the further calculations have been done for this model. The results obtained with $m = 2$ are presented in Tables 3–6 for the different mixtures studied, grouped according to the common solvents of group 1 in Table 1.

Dimethyl sulfoxide mixtures

The results of these mixtures are presented in Table 3. Fig. 2 presents the plots obtained for the mixtures of dimethyl

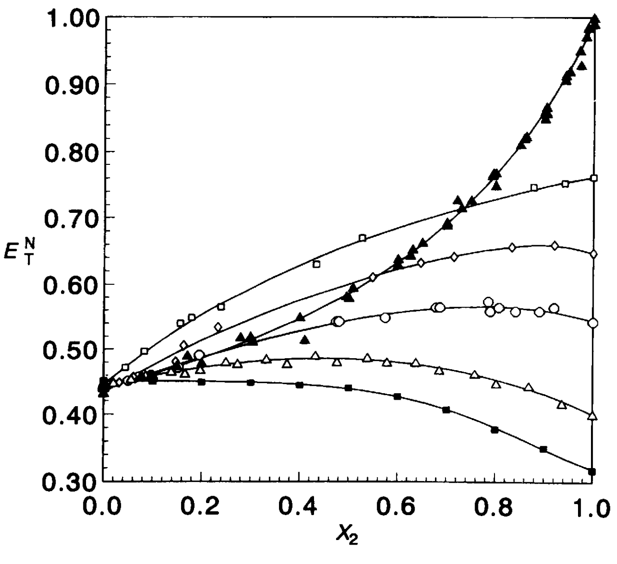

Fig. 2 Binary solvent mixtures of dimethyl sulfoxide (S1) with: ▲, water; □, methanol; ◇, ethanol; ○, propan-2-ol; △, 2-methylpropan-2-ol; ■, chloroform. Lines computed by eqn. (27) from the parameters of Table 3.

Table 5 Parameters of acetone (S1) binary mixtures

		m = 2								
Cosolvent (S2)	m	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	sd/10^{-3}	N	Ref.
Water	2.2	0.355	1.000	0.657	0.78	6.3	8.1	12	69	3, 8, 17, 24, 25
Ethanol	1.3	0.365	0.657	0.663	1.0	9.0	9.0	5.7	21	26
Propan-1-ol	2.3	0.364	0.617	0.682	2.4	6.5	2.8	1.8	11	3
Dimethyl sulfoxide	1.6	0.364	0.451	0.448	0.96	2.7	2.8	1.2	11	3
Trimethyl phosphate	—	0.356	0.398	0.398	1.2	2.0	1.7	1.0	6	16
Dichloromethane	—	0.360	0.324	0.389	2.1	7.4	3.5	0.6	21	26
Chloroform	1.6	0.359	0.272	0.448	3.3	5.8	1.8	3.5	32	3, 26
Tetrachloromethane	—	0.358	0.056	0.235	0.10	1.2	13	1.4	10	16
Cyclohexane	—	0.353	0.006	0.267	0.15	2.7	18	4.3	11	27

Table 6 Parameters of trialkyl phosphates (S1) and chloroform (S2) binary mixtures

		m = 2								
Solvent (S1)	m	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	sd/10^{-3}	N	Ref.
Trimethyl phosphate	2.4	0.398	0.274	0.491	1.5	3.1	2.0	2.0	10	16
Triethyl phosphate	2.6	0.337	0.272	0.459	2.2	4.8	2.2	2.4	11	16
Tripropyl phosphate	2.1	0.303	0.274	0.439	2.3	4.8	2.1	1.1	11	16
Tributyl phosphate	2.1	0.277	0.272	0.417	2.2	4.3	2.0	2.9	11	16

sulfoxide with the good hydrogen bond donor solvents of group 2 in Table 1. Synergetic behaviour, with E^N_{T12} values higher than E^N_{T1} and E^N_{T2}, is obtained for some of these mixtures. The largest synergetic effect (as measured by the difference between the E^N_{T12} value and the highest E^N_{T1} or E^N_{T2}) is observed for 2-methylpropan-2-ol. Slightly less synergetic are the mixtures with propan-2-ol and even less the mixtures with ethanol and chloroform. The E^N_{T12} value of the dimethyl sulfoxide–methanol mixtures is practically identical to the E^N_T value of pure methanol and therefore these mixtures are on the verge of synergism. No synergism is observed for the mixtures with water.

In fact, the highest synergetic effects are observed for the mixtures of the solvents of group 1 with the solvents of group 2 that have similar E^N_T values, such as dimethyl sulfoxide–2-methylpropan-2-ol or tributyl phosphate–chloroform. If the polarities of the two solvents mixed are very different (as in many aqueous binary solvents), no synergism is observed. As explained earlier, the reason for the synergism is the formation of a solvent 1–solvent 2 hydrogen bond complex more polar than the pure solvents. However, if the two solvents mixed have polarities very different, the polarity of the complex is intermediate between those of the pure solvents.

Of course, no synergism is obtained for mixtures of solvents that do not interact by hydrogen bonding. Fig. 3 presents the plots obtained for the mixtures of dimethyl sulfoxide with poor hydrogen bond donors. The mixtures are clearly not synergetic, even for dimethyl sulfoxide–acetonitrile that have very similar E^N_T values.

The results obtained in the fit of the E^N_T data to the model proposed also give information about the solvation of the solvatochromic indicator. In general, the preferential solvation parameters $f_{12/1}$ and $f_{12/2}$ are higher than unity and this demonstrates that the indicator tends to be solvated by the dimethyl sulfoxide–cosolvent complex, rather than by the pure solvents. The $f_{12/1}$ parameter measures the tendency of the indicator to be solvated by the complex in preference to dimethyl sulfoxide [eqn. (19)]. The $f_{12/2}$ parameter measures the tendency of the indicator to be solvated by the complex in preference to the cosolvent (solvent 2), and it is the $f_{12/1}/f_{2/1}$ ratio. The $f_{2/1}$ parameter is lower than unity (except for acetone) and this indicates that the indicator is more solvated by pure dimethyl sulfoxide than by pure cosolvent. Also, a trend can be observed in the f values of related cosolvents. For the mixtures with alcohols, $f_{2/1}$ increases and $f_{12/1}$ and $f_{12/2}$ decrease as the length of the alcohol chain increases, demonstrating that the indicator is more solvated by the alcohol and less by the complex.

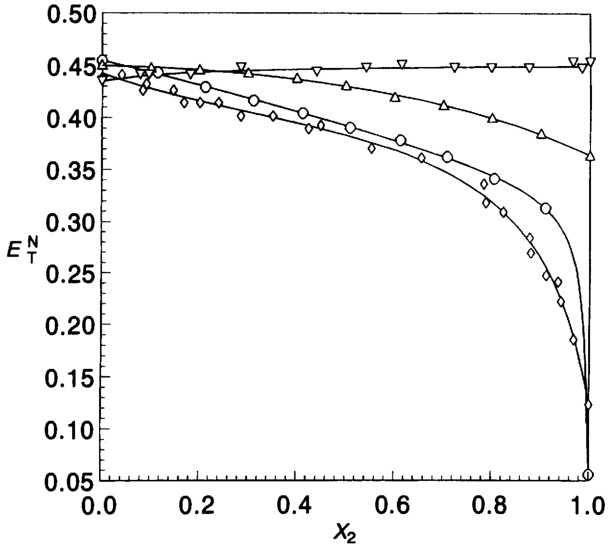

Fig. 3 Binary solvent mixtures of dimethyl sulfoxide (S1) with: ▽, acetonitrile; △, acetone; ○, tetrachloromethane; ◇, benzene. Lines computed by eqn. (27) from the parameters of Table 3.

Acetonitrile mixtures

Acetonitrile mixtures are presented in Table 4 and Fig. 4. The behaviour of these mixtures is similar to that of the dimethyl sulfoxide mixtures. Mixtures with alcohols are synergetic, with the greatest effect for 2-methylpropan-2-ol and propan-2-ol (with E^N_T values close to the one of acetonitrile) and the lowest for methanol (with a high E^N_T value). All the other mixtures are not synergetic.

However, there is a difference in the preferential solvation parameters of acetonitrile–cosolvent and dimethyl sulfoxide–cosolvent mixtures. The $f_{2/1}$ parameters for acetonitrile–

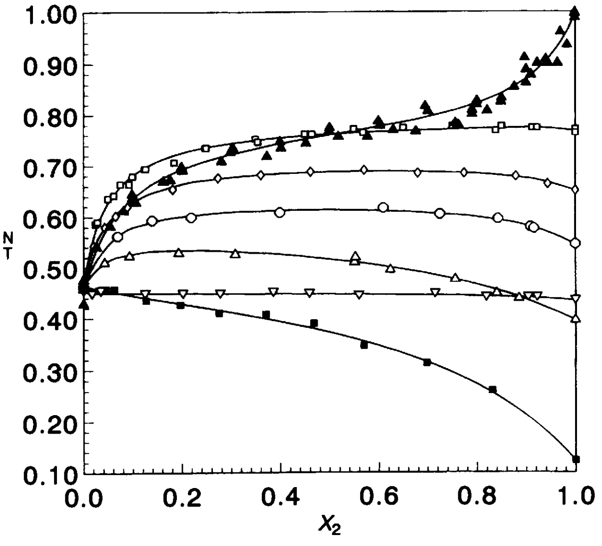

Fig. 4 Binary solvent mixtures of acetonitrile (S1) with: ▲, water; □, methanol; ◇, ethanol; ○, propan-2-ol; △, 2-methylpropan-2-ol; ▽, dimethyl sulfoxide; ■, benzene. Lines computed by eqn. (27) from the parameters of Table 4.

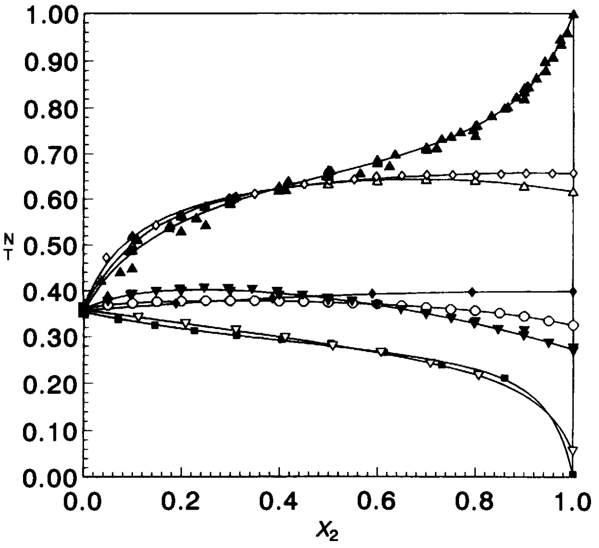

Fig. 5 Binary solvent mixtures of acetone (S1) with: ▲, water; ◇, ethanol; △, propan-1-ol; ◆, trimethyl phosphate; ○, dichloromethane; ▼, chloroform; ▽, tetrachloromethane; ■, cyclohexane. Lines computed by eqn. (27) from the parameters of Table 5.

cosolvent are, in general, higher than unity, whereas the ones for dimethyl sulfoxide–water are lower than unity. This means that the E_T solvatochromic indicator is poorly solvated by acetonitrile, but well solvated by dimethyl sulfoxide. In consequence, the $f_{12/1}$ parameter that measures the preferential solvation of the indicator by the acetonitrile–cosolvent complex in preference to acetonitrile, is larger than the same parameter for dimethyl sulfoxide–cosolvent mixtures.

The large preferential solvation of the solvatochromic indicator by the acetonitrile–water complex (high $f_{12/1}$ and $f_{12/2}$ values) and the fact that the E^N_{T12} value is almost in the middle of the E_T^N values of acetonitrile and water determines the S shape of these mixtures in Fig. 4. For dimethyl sulfoxide–water $f_{12/1}$ and $f_{12/2}$ are lower and the E^N_{T12} value is close to the E_T^N value of acetonitrile. In consequence, the S shape of this plot (Fig. 2) is not apparent in the dimethyl sulfoxide rich region.

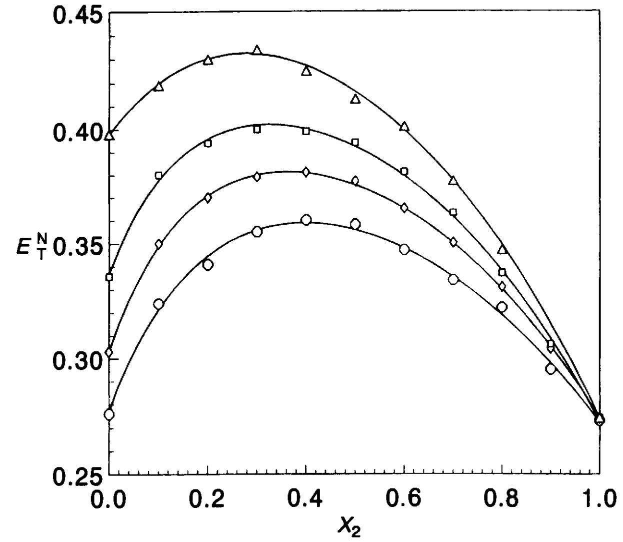

Fig. 6 Binary solvent mixtures of trialkyl phosphates (S1) with chloroform (S2); △, trimethyl phosphate; □, triethyl phosphate; ◇, tripropyl phosphate; ○, tributyl phosphate. Lines computed by eqn. (27) from the parameters of Table 6. X_2 is the mole fraction of chloroform.

Acetone mixtures

These results are presented in Table 5 and Fig. 5. Synergetic behaviour is observed in the mixtures of acetone with the hydrogen bond donors chloroform, dichloromethane, propan-1-ol and ethanol. The synergism for the latter cosolvent is very low because it has an E_T^N value much higher than the E_T^N value of acetone.

As for the previous mixtures, the indicator is preferentially solvated by the solvent 1–solvent 2 complex ($f_{12/1}$ and $f_{12/2}$ values higher than unity). The indicator is more solvated by propan-1-ol, trimethyl phosphate, dichloromethane and chloroform than by acetone ($f_{2/1} > 1$) and less solvated by water, tetrachloromethane and cyclohexane than by acetone ($f_{12/1} < 1$).

Because the $f_{12/1}$ and $f_{12/2}$ parameters are quite high for the water mixtures and the E^N_{T12} value is intermediate between the ones of acetone and water, an S shape, similar to the one of acetonitrile–water mixtures, is obtained for acetone–water mixtures. The same shape is obtained for acetone–tetrachloromethane and acetone–cyclohexane, but the lower $f_{12/1}$ values determine that the S shape is not so apparent for the actone-rich region.

Trialkyl phosphate mixtures

The mixtures of these phosphates with chloroform are presented in Table 6 and Fig. 6. The mixtures with tetrachloromethane are in Table 7 and Fig. 7.

The mixtures with chloroform present a high synergism because of the formation of hydrogen bond complexes. The highest synergism is observed for tributyl phosphate, which has an E_T^N value very similar to the one of chloroform. The order of preferential solvation of the solvatochromic indicator measured by the f parameters is phosphate–chloroform complex > chloroform > phosphate. The f values for the different phosphates are similar.

The mixtures of phosphates with tetrachloromethane are not synergetic because no hydrogen bond complex can be formed. The E^N_{T12} value is intermediate between the ones of tetrachloromethane and phosphate, but closer to the one of the phosphate. In general, the preferential solvation of the indicator is phosphate > phosphate–tetrachloromethane complex $\gg$ tetrachloromethane. The exception is that the indicator is

Table 7 Parameters of trialkyl phosphates (S1) and tetrachloromethane (S2) binary mixtures

		m = 2								
Solvent (S1)	m	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	sd/10^{-3}	N	Ref.
Trimethyl phosphate	—	0.396	0.056	0.288	0.1	1.5	15	1.1	10	16
Triethyl phosphate	—	0.340	0.057	0.192	0.009	0.51	56	0.85	11	16
Tripropyl phosphate	—	0.302	0.056	0.215	0.03	0.55	17	1.2	11	16
Tributyl phosphate	—	0.276	0.057	0.187	0.03	0.51	18	1.2	10	16

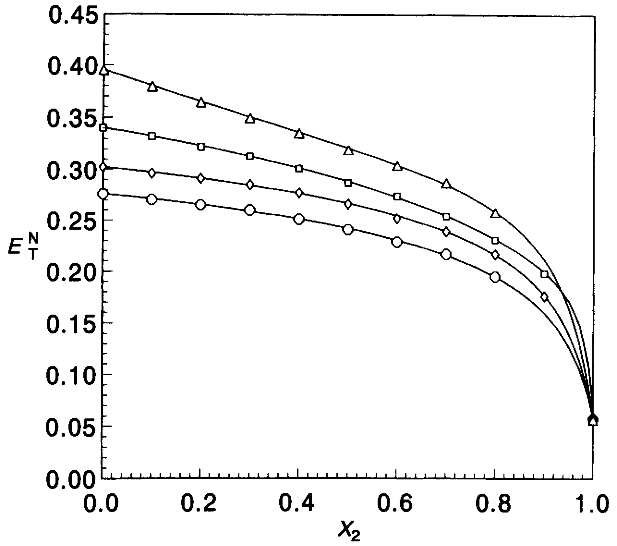

Fig. 7 Binary solvent mixtures of trialkyl phosphates (S1) with tetrachloromethane (S2): △, trimethyl phosphate; □, triethyl phosphate; ◇, tripropyl phosphate; ○, tributyl phosphate. Lines computed by eqn. (27) from the parameters of Table 6. X_2 is the mole fraction of tetrachloromethane.

slightly more solvated by the trimethyl phosphate–tetrachloromethane complex than by trimethyl phosphate ($f_{12/1} = 1.5$). These characteristics determine the shape of the plots of Fig. 7.

General trends

From the analysis of the results for the common solvents of Tables 3–7, some general trends in the preferential solvation of the Dimroth–Reichardt indicator can be deduced. On one hand, the indicator tends to be preferentially solvated by the solvent 1–solvent 2 complex (high $f_{12/1}$ and $f_{12/2}$ values) and also it is quite solvated by dimethyl sulfoxide ($f_{2/1} < 1$ in Table 3 where dimethyl sulfoxide is solvent 1). On the other hand, the indicator tends to avoid solvation by tetrachloromethane, water and acetonitrile. The $f_{2/1}$ values lower than 1 for tetrachloromethane and water in Tables 3, 5 and 7 demonstrate that the indicator is more solvated by the solvent 1 than by the solvent 2 (tetrachloromethane or water). In general, the $f_{2/1}$ values of Table 4 (acetonitrile) are lower than unity, and this indicates that the solvatochromic indicator is more solvated by the solvent 2 than by acetonitrile (solvent 1). Apparently, the indicator is poorly solvated by methanol (very low $f_{2/1}$ values in Tables 3 and 4), but the two methanol binary systems studied have E_{T12}^N values very close to the E_T^N value of pure methanol and this leads to high uncertainties in the estimation of the parameters.

The preferential solvation behaviour of the Dimroth–Reichardt indicator can be explained from its solute properties. The E_T (30) betaine is a large hydrophobic dipolar molecule with a good hydrogen bond acceptor capability. Therefore, it is poorly solvated by highly structured solvents, such as water, because of the high energy needed to create a cavity in the solvent. Nor is the betaine well solvated by non-polar solvents, such as tetrachloromethane, because these cannot interact with it by hydrogen bonding or dipole–dipole interactions.

Conclusions

Although some of the implicit assumptions have been recently questioned,[28] preferential solvation models based on the solvent exchange theory can be successfully applied to describe the E_T polarity of binary mixtures of dipolar hydrogen bond acceptor solvents.

The models based on one unique solvation molecule type does not describe well the E_T variation because they do not consider the formation of hydrogen bond complexes on the solvation shell. Nor can models that consider the formation of these hydrogen bond complexes, but assume that the E_T polarity of the complex is an average of the E_T polarities of the solvents mixed[8,28] [eqn. (29)]. Some of these hydrogen bond complexes have a high dipole moment that yields a high E_T value, even higher than the E_T values of the pure solvents mixed.

The model that gives the best fits and the most reasonable parameters for the studied mixtures is the one defined by eqn. (27) or by the general eqn. (33) with $m = 2$.

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