Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 3. The $E_T(30)$ polarity of binary mixtures of hydroxylic solvents

José Ortega, Clara Ràfols, Elisabeth Bosch * and Martí Rosés *

Departament de Química Analítica, Universitat de Barcelona, Avda. Diagonal 647, 08028 Barcelona, Spain

Solvent exchange models have been applied to the transition energy of the Dimroth–Reichardt $E_T(30)$ solvatochromic indicator in binary hydroxylic solvents at 25 °C. The models tested have been critically evaluated to show the simplifications and limitations inherent to each model. A general five-parameter model [two preferential solvation and three $E_T(30)$ parameters] has been selected as the most appropriate. This model fits well the 51 binary systems tested in this work and 19 different ones previously studied. It also allows a quantitative interpretation of the $E_T(30)$ behaviour of the binary systems in terms of solute–solvent and solvent–solvent interactions.

Solvent polarity has an important effect on chemical processes in solution.[1] There are several ways to measure solvent polarity, but one of the most convenient is by solvatochromic indicators. The transition energy of these solutes depends on the polarity of the solvent and therefore, this polarity can be easily ascertained from the maximum of the UV–VIS or near-IR spectrum of the indicator.[1] The most widely used solvatochromic indicator is the 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-io)phenolate or $E_T(30)$ dye, proposed by Reichardt and Dimroth.[1,2] The $E_T(30)$ parameter is defined as the excitation energy [kcal mol^{-1}; (1 cal = 4.184 J)] of the $E_T(30)$ dye [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 single and mixed solvents.[1,2] However, the interpretation of the measurements is different in a single solvent than in mixed solvents. A solvatochromic parameter measures the polarity of the solvent in its solvation sphere, which agrees with the polarity of the bulk solvent only for single solvents. In a mixed solvent, the solvatochromic indicator can interact to different degrees with the solvents of the mixture and in this instance the composition and polarity of the solvation sphere would be different from the ones of the bulk solvent. The term preferential or selective solvation is used to define this behaviour. Preferential solvation leads to non-linear relationships between solvatochromic polarity and solvent composition.[1] In addition to the solute–solvent interactions that determine preferential solvation, solvent–solvent interactions between the different solvents of the mixtures are usually present.

$E_T(30)$ values of mixed solvents can, therefore, provide information about the solute–solvent and solvent–solvent interactions present in the mixture. Dawber *et al.*[3] proposed the deviation from linearity of the $E_T(30)$ values of binary solvent mixtures as a measurement of the extent of preferential solvation and related it to several thermodynamic and kinetic properties.[4] The same approach was used by Chatterjee and Bagchi,[5,6] using *N*-alkylpyridinium instead of the $E_T(30)$ dye. These authors introduced the stepwise solvent exchange model of Covington *et al.*[7] to describe the preferential solvation of solvatochromic indicators.

Later, we derived an equation that related $E_T(30)$ values of binary solvent mixtures with solvent composition.[8] The equation is based on a one-step solvent exchange model defined by a preferential solvation parameter, which does not consider the solvent–solvent interactions. Because of this limitation, two equations were needed in many binary solvents to cover the whole range of solvent composition. For the same reason, the equation did not apply to synergetic mixtures, in which the two solvents interact to form a hydrogen bond complex, with polarity and E_T values higher than those of the two pure solvents mixed.

Skwierczynski and Connors[9] proposed two different solvent exchange models to describe the $E_T(30)$ values of binary aqueous mixtures. One of the solvent exchange models was the same as we used previously,[8] but the other included a solvent exchange equilibrium which can account for solvent–solvent interactions. The inclusion of this equilibrium allowed the $E_T(30)$ values of aqueous binary mixtures to be described using a unique equation. However, the restrictions included by Skwierczynski and Connors in their model did not allow application of the equation to synergetic mixtures.[10]

In recent studies,[10] we have derived a more general model based on a two-step solvent exchange model that can be effectively applied to synergetic mixtures.[10,11] For the mixtures studied, the proposed model could be simplified to the Skwierczynski and Connors' model but avoiding their restrictions. In this paper, we apply the model and equations to an extensive set of literature data of binary solvent mixtures containing water or alcohols.

Preferential solvation models

The simplest of the proposed models[8–10] is based on the solvent exchange equilibrium in Scheme 1, where I(S1) and I(S2)

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

Scheme 1

indicate the solvatochromic indicator (I) solvated by solvents 1 and 2, respectively. S1 and S2 are the two solvents that compose the binary mixture. This model was used in a previous work to relate the $E_T(30)$ values of binary solvent mixtures with the solvent composition.[8] A normalized form of this equation was also used by Skwierczynski and Connors[9] for several aqueous–organic solvent mixtures. However, the model cannot predict E_T values higher than E_{T1} or E_{T2}, and therefore it cannot be applied to synergetic systems.[8] In addition, for some binary solvents it cannot cover the full range of solvent compositions. To solve the latter problem, Skwierczynski and Connors[9] proposed a two-step solvent exchange equilibrium, which to be consistent with our own work we will write as shown in Scheme 2. In a similar manner to Scheme 1, $I(S1)_2$ and $I(S2)_2$ represent

$$I(S1)_2 + 2\,S2 \rightleftharpoons I(S2)_2 + 2\,S1$$
$$I(S1)_2 + S2 \rightleftharpoons I(S12)_2 + S1$$

Scheme 2

the indicator fully solvated by solvent 1 and solvent 2, respectively, and $I(S12)_2$ represents the indicator solvated by the 'mixed solvent' formed by interaction of solvents 1 and 2.[10]

We have recently proposed a more general model[10] based on the solvent exchange processes (Scheme 3). The constants of

$$I(S1)_m + m\,S2 \rightleftharpoons I(S2)_m + m\,S1$$
$$I(S1)_m + m/2\,S2 \rightleftharpoons I(S12)_m + m/2\,S1$$

Scheme 3

these processes are defined by the preferential solvation parameters [eqns. (2) and (3)] that relate the ratio of mole

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

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{\sqrt{(x_2^0/x_1^0)^m}} \qquad (3)$$

fractions of solvents S1, S2 and S12 solvating the indicator (x_1^s, x_2^s and x_{12}^s, respectively) with the ratio of mole fractions of the two solvents in the bulk mixed solvent (x_1^0 and x_2^0, respectively).

The transition energy (E_T) of a solvatochromic indicator is taken as an average of the transition energies in the solvents that compose the solvation microsphere of the indicator according to their mole fractions in this sphere [eqn. (4)],[5,6,8–11] where

$$E_T = x_1^s E_{T1} + x_2^s E_{T2} + x_{12}^s E_{T12} \qquad (4)$$

E_{T1}, E_{T2} and E_{T12} are the transition energies of the solvatochromic indicator in the pure solvents S1, S2 and S12.

Substituting eqns. (2) and (3) in eqn. (4), eqn. (5) is obtained, where a and c are defined by eqns. (6) and (7).

$$E_T = E_{T1} + \frac{a(x_2^0)^m + c\sqrt{[(1-x_2^0)x_2^0]^m}}{(1-x_2^0)^m + f_{2/1}(x_2^0)^m + f_{12/1}\sqrt{[(1-x_2^0)x_2^0]^m}} \qquad (5)$$

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

$$c = f_{12/1}(E_{T12} - E_{T1}) \qquad (7)$$

In this general model, m is the number of solvent molecules in the microsphere of solvation of the solvatochromic indicator affecting its transition energy. The model Skwierczynski and Connors (Scheme 2) is the same model for the particular case where $m = 2$ and eqn. (8) is obtained in this instance.

$$E_T = E_{T1} + \frac{a(x_2^0)^2 + c(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \qquad (8)$$

However, Skwierczynski and Connors[9] introduced the simplification shown in eqn. (9).

$$E_{T12} = (E_{T1} + E_{T2})/2 \qquad (9)$$

It was observed that for many synergetic and non-synergetic mixtures, the best m values obtained from eqn. (5) were close to 2.[10] Therefore, in many instances the model of Skwierczynski and Connors defined by eqn. (8) is valid, although the simplification of taking E_{T12} as a simple average of E_{T1} and E_{T2} [eqn. (9)] cannot be of general validity. This simplification does not hold at all for synergetic mixtures because it cannot predict E_T values higher than E_{T1} or E_{T2}.[10]

Skwierczynski and Connors[9] divided the aqueous–organic solvent mixtures they studied into two different groups. Some of the binary solvents follow eqn. (10), which is the equation

$$E_T = E_{T1} + \frac{a x_2^0}{(1-x_2^0) + f_{2/1}x_2^0} \qquad (10)$$

derived from Scheme 1, but other binary solvents had to be fitted to eqn. (8), which is based on Scheme 2. Consequently, binary aqueous solvents were classified in one-step [eqn. (10) and Scheme 1] and two-step [eqn. (8) and Scheme 2] solvent exchange groups. Apparently, Scheme 1 is not related to Scheme 2 because they consider a different number of solvent molecules solvating the indicator. However, it can be easily observed that eqn. (8) simplifies to eqn. (10) if eqns. (11) and (12) are valid.

$$f_{12/1} = 1 + f_{2/1} \qquad (11)$$

$$E_{T12} = \frac{E_{T1} + f_{2/1}E_{T2}}{1 + f_{2/1}} \qquad (12)$$

Therefore, the one-step solvent exchange group is a particular case of the two-step group, and the same solvent processes would be followed by all the binary systems. However, this does not mean that eqn. (8) must be used in all instances. For those binary systems classified as one-step, eqn. (10) may provide more accurate values of the preferential solvation parameters. If a particular system can be well fitted to eqn. (10), this means that the three parameters (E_{T1}, E_{T2} and $f_{2/1}$) are sufficient to describe it. In this instance, the five-parameters eqn. (8) is overparameterized and the mathematical fit can lead to different parameter combinations with similar standard deviations. Therefore, the best way to estimate the parameters of these systems is to fit the E_T data to eqn. (10), obtain E_{T1}, E_{T2} and $f_{2/1}$, and later $f_{12/1}$ and E_{T12} from eqns. (11) and (12).

Eqn. (12) shows that the simplification of Skwierczynski and Connors of calculating E_{T12} as a simple average of E_{T1} and E_{T2} cannot be valid for the one-step group solvents. Eqns. (9) and (12) do not agree unless $f_{2/1} = 1$. In this instance there is no preferential solvation, and the model would predict a linear relationship between E_T and solvent composition.

Ideal binary systems

It is interesting to check the validity of the different models for ideal mixtures. Ideal mixtures show a linear relationship between the solvatochromic parameter (E_T) and the solvent composition (x_2^0) [eqn. (13)].

$$E_T = x_1^0 E_{T1} + x_2^0 E_{T2} = E_{T1} + (E_{T2} - E_{T1})x_2^0 \qquad (13)$$

Ideal behaviour is usually observed when two solvents with very similar properties are mixed.

Eqn. (10) becomes (13) when $f_{2/1} = 1$. That is, the model of Scheme 1 predicts an ideal behaviour for those systems which do not present preferential solvation.

For Scheme 2 to represent an ideal system, the denominator of eqn. (8) must be 1. To fulfil this requirement, the $f_{2/1}$ parameter must be 1, as expected, but surprisingly the $f_{12/1}$ parameter must be 2. This is because the interaction of one molecule of solvent 1 with one molecule of solvent 2 gives two molecules of solvent S12. Therefore, the ratio $x_{12}^s : x_1^s$ must be twice the ratio $x_2^0 : x_1^0$. When these requirements are fulfilled, eqn. (8) becomes eqn. (14), which in turn will become eqn. (13) if eqn. (15) is valid.

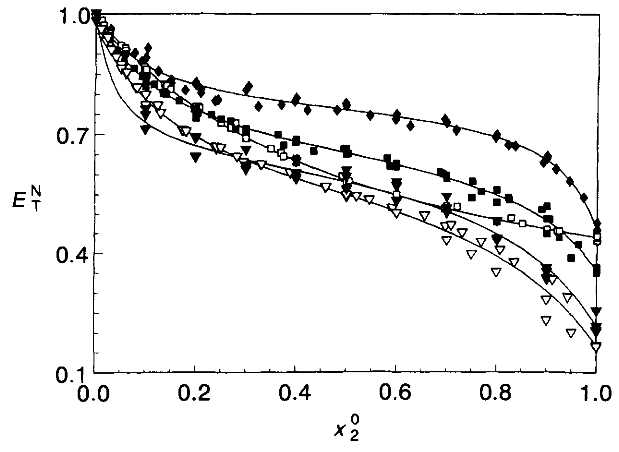

Fig. 1 Binary solvent mixtures of water (S1) with: ▼, tetrahydrofuran; ▽, 1,4-dioxane; ■, acetone; □, dimethyl sulfoxide; ◆, acetonitrile. Lines computed by eqn. (8) from the parameters of Table 1.

$$E_T = (1 - x_2^0)^2 E_{T1} + (x_2^0)^2 E_{T2} + 2x_2^0(1 - x_2^0)E_{T12} \quad (14)$$

$$E_{T12} = (E_{T1} + E_{T2})/2 \quad (15)$$

That is, for the model of Scheme 2, an ideal behaviour will be observed when there is no preferential solvation and in addition, the E_T value of the mixed solvent S12 formed is the simple average of the E_T values of the two solvents mixed. In this instance, eqns. (9) and (12) are equivalent and fulfilled. Eqn. (11) is also fulfilled and the one-step and the two-step models give the same eqn. (13).

However, it is not possible to derive an ideal system from the more complex model of Scheme 3, and this model does not seem to be valid in the simplest case of an ideal mixture. Therefore, the model of Scheme 2 defined by eqn. (8) will be used to fit the $E_T(30)$ data of the binary systems studied.

Computation methods

The $E_T(30)$ data have been normalized (E_T^N) with reference to tetramethylsilane ($E_T^N = 0$) and water ($E_T^N = 1$) according to eqn. (16).[1] The E_{T1}^N, E_{T2}^N, E_{T12}^N, $f_{2/1}$, $f_{12/1}$ parameters that

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} \quad (16)$$

minimize the square residuals of the E_T^N values of each studied binary solvent system, have been calculated by non-linear regression as described in the previous work.[10]

Results and discussion

Eqn. (8) has been applied to $E_T(30)$ literature data at 25 °C for binary solvents containing alcohols and/or water. The data have been divided into different sets according to the solvent mixtures that contain water, methanol, ethanol, ethane-1,2-diol, methoxyethanol and propanols or butanols (Tables 1–6). Each one of these sets contains a common alcohol (or water) with at least three different cosolvents. In order to check if the model holds for non-hydroxylic mixtures, a last set (Table 7) has been formed with those available binary mixtures that were not included in the previous sets and that had not been studied in reference 10. As far as we know, the data sets analysed here and in reference 10 constitute all the literature $E_T(30)$ data available for binary solvents at 25 °C.

The data for the binary mixtures of dimethyl sulfoxide, acetonitrile and acetone with alcohols and water used in reference 10 have been reanalysed and the results are included in Tables 1–3 and 6 for comparison with the other hydroxylic systems. These results are essentially the same as those presented in reference 10, although the number of points (N) given in Table 1 for the aqueous mixtures of acetone, dimethyl sulfoxide and acetonitrile (65, 49 and 58) is slightly lower than the number of points given in reference 10 (69, 50 and 59). The reason is that there are several E_T literature data sets for these mixtures and most of them include the same E_T data point for pure water ($E_T^N = 1.000$). Owing to the fact $E_T(30)$ dye has a very low solubility in water, this solvent is not usually measured and the literature value given by Reichardt[1,2] is taken. In reference 10 we used all the data available, but in this work we prefer to use one unique data point for pure water in each binary solvent.

It is interesting to compare the E_{T1}^N and E_{T2}^N values obtained from the binary mixture analysis with the accepted literature values for pure solvents given in references 1 and 2. Among the 51 binary systems studied in this work, only the E_T^N value obtained for chloroform in methanol–chloroform and propan-1-ol–chloroform mixtures differs by more than 0.03 E_T^N unities from the literature value, as has been already pointed out.[3,8] A few other solvents present discrepancies with literature values of about 0.02–0.03 E_T^N unities. These solvents are: water, formamide, toluene, 2-methylpropan-2-ol and chloroform in water–ethanol, water–propan-2-ol, water–piperidine, water–formamide, methanol–toluene, ethanol–2-methylpropan-2-ol and tetrachloromethane–chloroform. All other E_{T1}^N and E_{T2}^N calculated values agree with the literature ones within 0.01 E_T^N unities or less. The few discrepancies have to be attributed to the experimental measurements of the original data and not to the calculation method. The calculation method gives E_{T1}^N and E_{T2}^N values that differ by 0.005 or less with the input data for the pure solvents 1 and 2. The only exception can be the calculated value for pure water. Apparently, the addition of small amounts of some cosolvents to pure water produces a reinforcement of the structure of water that may not be fully explained by the models presented here. This phenomenon is under study and we shall discuss it in future works.

It also has to be pointed out that the E_T^N values given in reference 2 for triethyl phosphate and tributyl phosphate, and also the $E_T(30)$ value for tributyl phosphate, are mistaken. These values were obtained from those in reference 28, but they do not agree with them, or with those of reference 1. The values calculated here and in the previous work[10] agree within 0.001 E_T^N unities with those given in references 1 and 28.

Water mixtures

The results obtained for water mixtures are presented in Table 1. The data sets can be subdivided into three other sets according to the type of solvent mixed with water: dipolar hydrogen bond acceptor solvents (Fig. 1), basic nitrogen solvents (Fig. 2) and alcoholic solvents (Fig. 3).

The mixtures of water with dipolar hydrogen bond acceptor solvents were previously analysed taking the dipolar hydrogen bond acceptor solvent as the reference solvent (solvent 1).[10] Here, we analyse them in reference to the common solvent water (taken as solvent 1). Fig. 1 presents the plots obtained for these systems; except for dimethyl sulfoxide mixtures, an S-shape curve is observed. This shape is caused by the strong preferential solvation of the $E_T(30)$ indicator by the intermediate species S12 ($f_{12/1}$ and $f_{12/2}$ much higher than unity) and the value of E_{T12}^N intermediate between the E_T^N values of water and the dipolar hydrogen bond acceptor cosolvent. In fact, the E_{T12}^N value (Table 1) is quite close to the simple average of E_{T1}^N and E_{T2}^N, and the simplification of Skwierczynski and Connors [eqn. (9)] holds for these binary systems. Therefore, the good fits obtained with the application of the two-step model of Skwierczynski and Connors to these mixtures are not surprising.

The E_{T12}^N value of water–dimethyl sulfoxide mixtures is much lower than the simple average of the E_T values of the two pure solvents and the plot does not show the S-shape. In fact, this system can be clearly fitted to the one-step model.

Table 1 Parameters of water (S1) binary mixtures

Cosolvent (S2)	Eqn.	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Methanol	10	1.002	0.769	0.817	3.9	4.9	1.3	6.9	46	3, 12–14
Ethanol	10	1.016	0.662	0.706	7.0	8.0	1.1	8.4	49	12–15
Propan-1-ol	8	1.001	0.606	0.673	10	27	2.7	8.2	20	14, 15
Propan-2-ol	8	1.023	0.546	0.620	2.9	12	4.0	12	41	12–14
Ethane-1,2-diol	10	1.001	0.790	0.842	3.1	4.1	1.3	1.1	12	16
Propane-1,2-diol	10	0.992	0.730	0.761	7.5	8.5	1.1	8.7	12	16
Propane-1,3-diol	10	0.998	0.750	0.779	7.6	8.6	1.1	2.8	12	16
Tetrahydrofuran	8	0.991	0.217	0.640	4.9	23	4.7	23	32	3, 14, 17
1,4-Dioxane	8	0.999	0.167	0.586	2.1	8.8	4.3	19	69	12–14, 18–20
Acetone	8	1.000	0.355	0.657	1.3	8.0	6.3	13	65	3, 9, 12–14
Dimethyl sulfoxide	10	0.993	0.441	0.587	2.8	3.8	1.4	9.1	49	9, 14, 17, 19, 21
Acetonitrile	8	0.994	0.457	0.760	0.77	9.7	13	15	58	9, 14, 19, 22, 23
Formamide	10	0.977	0.798	0.856	2.1	3.1	1.5	8.4	6	17
N,*N*-Dimethylformamide	8	0.990	0.398	0.646	3.6	7.0	1.9	8.4	22	14, 17
Pyridine	8	1.001	0.306	0.763	48	56	1.2	8.6	30	12, 13, 17
Piperidine	8	1.015	0.150	0.633	18	30	1.7	11	21	12
2-Picoline[a]	8	1.004	0.243	0.724	72	92	1.3	6.9	24	12
2,6-Lutidine[b]	8	1.001	0.193	0.688	85	138	1.6	8.5	24	12

[a] 2-Methylpyridine. [b] 2,6-Dimethylpyridine.

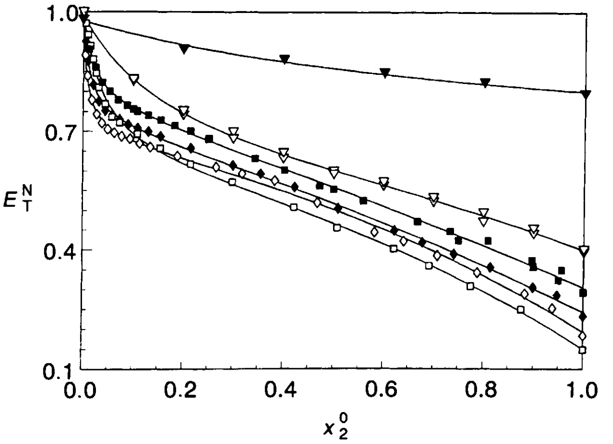

Fig. 2 Binary solvent mixtures of water (S1) with: ▼, formamide; ▽, *N*,*N*-dimethylformamide; ■, pyridine; □, piperidine; ◆, 2-picoline; ◇, 2,6-lutidine. Lines computed by eqn. (8) from the parameters of Table 1.

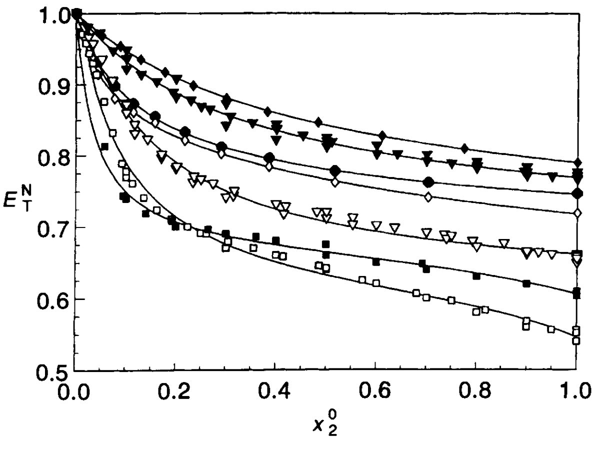

Fig. 3 Binary solvent mixtures of water (S1) with: ▼, methanol; ▽, ethanol; ■, propanol; □, propan-2-ol; ◆, ethane-1,2-diol; ◇, propane-1,2-diol; ●, propane-1,3-diol. Lines computed by eqn. (8) from the parameters of Table 1.

Fig. 2 presents the plots obtained for the mixtures of water with the amides, 2-picoline and pyridine derivatives. The plots are not very different from those of Fig. 1, but the lower $f_{12/2}$ value determines that the curvature in the solvent 2 rich region is less defined. The E_{T12}^N value of the binary solvents of Fig. 2 is also close to the average of E_{T1}^N and E_{T2}^N, and Skwierczynski and Connors could fit these mixtures well to their two-step solvent exchange model.

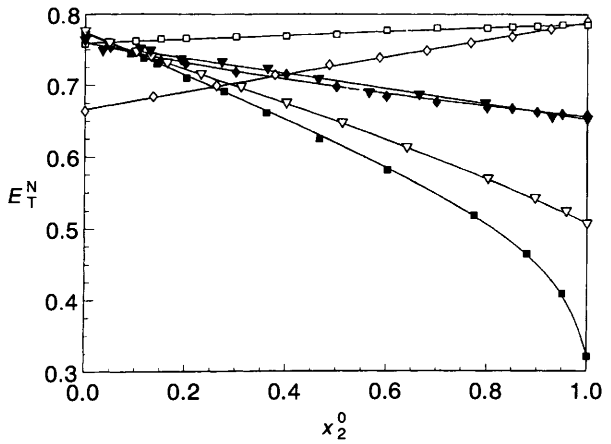

Fig. 4 Binary solvent mixtures of methanol (S1) with: ▼, ethanol; ▽, butan-2-ol; ■, 2-methylbutan-2-ol; □, ethane-1,2-diol; ◆, 2-methoxyethanol and ◇, binary solvent mixtures of 2-methoxyethanol (S1) with ethane-1,2-diol (S2). Lines computed by eqn. (8) from the parameters of Table 2.

The plots of mixtures of water with alcohols are presented in Fig. 3. Skwierczynski and Connors fitted these mixtures to the one-step solvent exchange model. However, propan-1-ol and propan-2-ol aqueous mixtures show a soft curvature in the alcohol rich region that the one-step model [eqn. (10)] cannot explain, and they must be fitted to the general two-step model. It can be easily observed in Fig. 3, that when the E_T^N value of the alcohol decreases, the curvature in the alcohol rich region increases. Therefore, the change in the shape of the plots from the one-step to the two-step models is gradual and all the binary systems should be regarded as belonging to the same general model.

Methanol mixtures

The results obtained for the binary solvents containing methanol are given in Table 2. The plots of mixtures of methanol with other alcohols are presented in Fig. 4. The mixtures of methanol with water and other alcohols, except 2-methylbutan-2-ol, can be fitted to the one-step model [eqn. (10)]. The mixtures of methanol with the most similar alcohols (ethane-1,2-diol and ethanol) can be considered ideal. The mixtures of methanol with 2-methylbutan-2-ol (the alcohol with the E_T^N value most different from that of methanol) must be fitted to eqn. (8). According to the $f_{2/1}$ values, the $E_T(30)$ indicator tends to be preferentially solvated in the order: 2-methoxyethanol > ethanol = methanol = ethane-1,2-diol > butan-2-ol > water > 2-methylbutan-2-ol.

Table 2 Parameters of methanol (S1) binary mixtures

Cosolvent (S2)	Eqn.	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Water	10	0.769	1.002	0.817	0.26	1.3	4.8	6.9	46	3, 12–14
Ethanol	10	0.759	0.652	0.705	1	2	2	3.7	28	24, 25
Butan-2-ol	10	0.771	0.510	0.649	0.88	1.9	2.1	2.2	14	26
2-Methylbutan-2-ol	8	0.773	0.321	0.483	0.06	1.0	18	1.7	14	26
Ethane-1,2-diol	10	0.759	0.786	0.772	1	2	2	1.3	15	24
2-Methoxyethanol	10	0.760	0.656	0.698	1.5	2.5	1.7	3.1	15	24
Acetonitrile	8	0.769	0.468	0.777	333	7000	20	6.5	28	21, 26
Dimethyl sulfoxide	8	0.762	0.445	0.763	50	110	2.1	6.4	11	21
Pyridine	8	0.762	0.294	0.425	0.03	0.72	23	3.3	15	26
Tetrahydrofuran	8	0.775	0.212	0.686	0.74	5.1	6.9	6.7	11	3
Chloroform	8	0.777	0.315	0.671	1.6	5.7	3.5	8.9	11	3
Dichloromethane	8	0.766	0.313	0.606	0.06	1.9	30	4.7	8	20
Benzene	8	0.761	0.123	0.564	0.05	2.2	41	3.5	17	25
Toluene	8	0.774	0.121	0.573	0.08	2.9	37	1.9	11	26

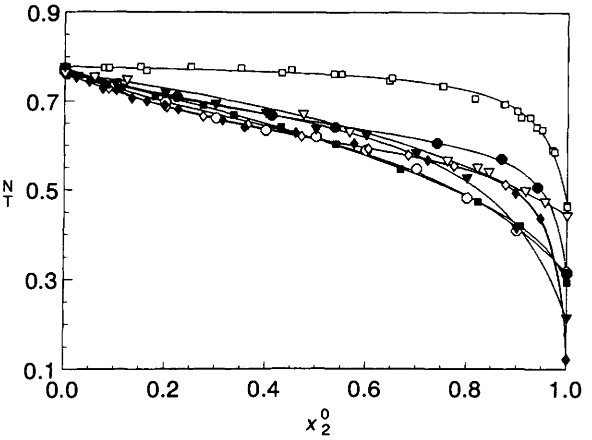

Fig. 5 Binary solvent mixtures of methanol (S1) with: ▼, tetrahydrofuran; ▽, dimethyl sulfoxide; ■, pyridine; □, acetonitrile; ◆, benzene; ◇, toluene; ●, dichloromethane; ○, chloroform. Lines computed by eqn. (8) from the parameters of Table 2.

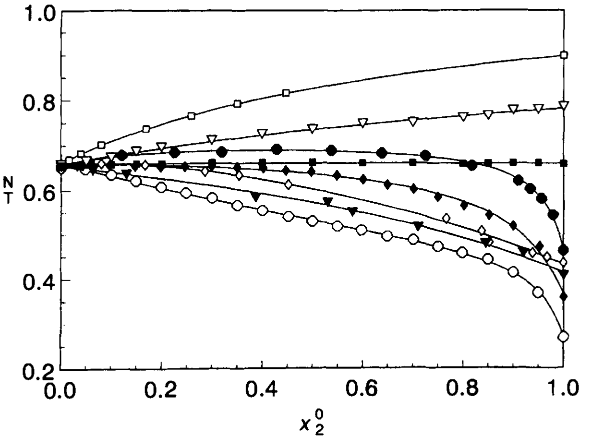

Fig. 6 Binary solvent mixtures of ethanol (S1) with: ▼, 2-methylpropan-2-ol; ▽, ethane-1,2-diol; ■, 2-methoxyethanol; □, 2,2,2-trifluoroethanol; ◆, acetone; ◇, dimethyl sulfoxide; ●, acetonitrile; ○, chloroform. Lines computed by eqn. (8) from the parameters of Table 3.

The plots of mixtures with non-hydroxylic solvents are shown in Fig. 5. The E_{T12}^N values of all these mixtures are quite far from the value defined by eqn. (12) and these data sets must be fitted to the two-step model of eqn. (8).

As already explained,[10] the mixtures of methanol with dimethyl sulfoxide and acetonitrile present a small synergism (E_{T12}^N value slightly higher than the E_T^N value of methanol). The small difference in these two E_T values previously[8] induced us to classify the two binary solvents as non-synergetic and to fit the two systems to eqn. (10), although this was later corrected.[10] The preferential solvation of the indicator by the methanol–acetonitrile hydrogen bond complex is much higher than the preferential solvation by the methanol–dimethyl sulfoxide complex, as reflected in the $f_{12/1}$ values. Apparently, the indicator is more solvated by acetonitrile and dimethyl sulfoxide than by methanol ($f_{2/1} \gg 1$), but an E_{T12}^N value close to the E_T^N value of methanol introduces a high error in the calculation of the $f_{2/1}$ parameter.[10]

The $f_{2/1}$ values of pyridine, tetrahydrofuran, dichloromethane, benzene and toluene shown in Table 2 are clearly mainly lower than unity and this demonstrates that the solvatochromic indicator is preferentially solvated by methanol, rather than by those low polarity solvents. However, the $f_{2/1}$ value for chloroform is higher than unity indicating that the $E_T(30)$ indicator is more solvated by chloroform than by methanol. This was also observed for acetone–chloroform and acetone–dichloromethane mixtures,[10] where the $f_{2/1}$ parameter for chloroform was higher than that for dichloromethane.

The mixtures of methanol with benzene and toluene give practically the same equation and plot because the two cosolvents have almost identical properties.

Ethanol mixtures

The results obtained for the data available for ethanol mixtures are presented in Table 3. The plots obtained with water and methanol have already been given in Figs. 3 and 4, and the rest of the plots are presented in Fig. 6. Ethanol–methanol and ethanol–2-methoxyethanol are ideal binary systems. The mixtures with other alcohols and water can be fitted to the simplified eqn. (10), whereas the mixtures with less polar solvents (acetone, dimethyl sulfoxide, acetonitrile and chloroform) must be fitted to the general eqn. (8).

A synergetic behaviour already explained[10] is observed for the mixtures of ethanol with acetone, dimethyl sulfoxide and acetonitrile.

Ethane-1,2-diol mixtures

The results for these mixtures are presented in Table 4 and the plots distributed between Figs. 3, 4 and 6. The $E_T(30)$ values of the cosolvents studied are not far from the $E_T(30)$ value of ethane-1,2-diol and the mixtures could be fitted to the one-step model [eqn. (10)].[24] The solvation of the $E_T(30)$ indicator by ethane-1,2-diol is the same as by methanol and 2-methoxyethanol which form ideal binary systems with ethane-1,2-diol. It is also equally solvated by the hydrogen bond complexes ethane-1,2-diol–methanol and ethane-1,2-diol–2-methoxyethanol ($f_{12/1} = 2$). However, the indicator is more solvated by ethane-1,2-diol than by ethanol and water ($f_{2/1} < 1$) and less than by the respective hydrogen bond complexes ($f_{12/1} < 2$).

Table 3 Parameters of ethanol (S1) binary mixtures

Cosolvent (S2)	Eqn.	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Water	10	0.662	1.016	0.706	0.14	1.1	8.0	8.4	49	12–15
Methanol	10	0.652	0.759	0.705	1	2	2	3.7	28	24, 25
2-Methylpropan-2-ol	10	0.654	0.414	0.570	0.53	1.5	2.9	6.6	11	25
Ethane-1,2-diol	10	0.659	0.781	0.734	1.6	2.6	1.6	3.4	15	24
2-Methoxyethanol	10	0.660	0.659	0.659	1	2	2	1.1	15	24
2,2,2-Trifluoroethanol	10	0.654	0.897	0.825	2.4	3.4	1.4	2.7	9	26
Acetone	8	0.657	0.365	0.663	1.0	9.0	9.0	5.7	21	23
Dimethyl sulfoxide	8	0.648	0.432	0.687	4	7.4	1.8	6.6	12	21
Acetonitrile	8	0.650	0.466	0.703	0.4	8.1	20	3.5	15	21
Chloroform	8	0.662	0.267	0.460	0.08	1.5	20	3.2	21	27

Table 4 Parameters of ethane-1,2-diol (S1) binary mixtures

Cosolvent (S2)	Eqn.	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Water	10	0.790	1.000	0.842	0.32	1.3	4.1	1.1	12	16
Methanol	10	0.786	0.759	0.772	1	2	2	1.3	15	24
Ethanol	10	0.781	0.659	0.735	0.61	1.6	2.6	3.4	15	24
2-Methoxyethanol	10	0.788	0.666	0.727	1	2	2	2.0	11	24

Table 5 Parameters of 2-methoxyethanol (S1) binary mixtures

Cosolvent (S2)	Eqn.	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Methanol	10	0.656	0.760	0.698	0.65	1.6	2.5	3.1	15	24
Ethanol	10	0.659	0.660	0.659	1	2	2	1.1	15	24
Ethane-1,2-diol	10	0.666	0.788	0.727	1	2	2	2.0	11	24

Table 6 Parameters of propanol or butanol (S1) binary mixtures

Solvent (S1)–solvent (S2)	Eqn.	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Propan-1-ol–water	8	0.606	1.001	0.673	0.10	2.7	27	8.2	20	14,15
Propan-1-ol–acetone	8	0.617	0.364	0.682	0.43	2.8	6.5	1.8	11	3
Propan-1-ol–chloroform	8	0.618	0.318	0.542	1.2	3.8	3.2	1.6	11	21
Propan-2-ol–water	8	0.546	1.023	0.620	0.34	4.0	12	12	41	12–14
Propan-2-ol–acetonitrile	8	0.545	0.463	0.630	0.38	7.5	20	3.9	11	21
Propan-2-ol–dimethyl sulfoxide	8	0.545	0.437	0.614	2.0	3.1	1.6	4.7	18	21
2-Methylpropan-2-ol–ethanol	10	0.414	0.654	0.570	1.9	2.9	1.5	6.6	11	25
2-Methylpropan-2-ol–acetonitrile	8	0.396	0.463	0.558	0.14	3.1	22	5.5	12	21
2-Methylpropan-2-ol–dimethyl sulfoxide	8	0.400	0.444	0.548	1.4	2.3	1.6	3.9	11	21

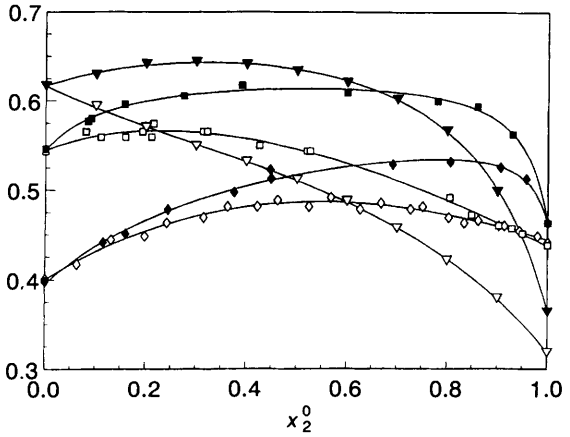

Fig. 7 Binary solvent mixtures of propanol (S1) and butanols (S1): ▼, propanol–acetone; ▽, propanol–chloroform; ■, propan-2-ol–acetonitrile; □, propan-2-ol–dimethyl sulfoxide; ◆, 2-methylpropan-2-ol–acetonitrile; ◇, 2-methylpropan-2-ol–dimethyl sulfoxide. Lines computed by eqn. (8) from the parameters of Table 6.

2-Methoxyethanol mixtures

The 2-methoxyethanol mixtures studied can be well fitted to the one-step model [eqn. (10)].[24] The results obtained are given in Table 5 and in Figs. 3, 4 and 6. 2-Methoxyethanol–ethane-1,2-diol and 2-methoxyethanol–ethanol are ideal binary systems. The mixtures with ethanol are particularly interesting because 2-methoxyethanol and ethanol have practically the same $E_T(30)$ value, and therefore the same E^N_T value (0.660 ± 0.001) is obtained for any solvent composition.[24]

In the mixtures with methanol, preferential solvation for 2-methoxyethanol is observed ($f_{2/1} < 1$ and $f_{12/1} < 2$).

Propanol and butanol mixtures

The results for these hydroxylic systems are given in Table 6. The E^N_T *vs.* x^0_2 plots can be found in Figs. 3, 6 and 7. The alcohols form synergetic mixtures with the dipolar hydrogen bonds acceptors, acetone, acetonitrile and dimethyl sulfoxide, already explained.[10,11] Of course, these data sets must be fitted to the general two-step model [eqn. (8)] and the simplification of eqn. (9) does not apply to them.

The two-step model must also be applied to the mixtures with water. For these mixtures, the $E_T(30)$ indicator is preferentially solvated by the alcohol and the hydrogen bond complex. The E^N_{T12} value is close to the E^N_T value of the alcohol.

The mixtures of 2-methylpropan-2-ol with ethanol can be fitted to the one-step model [eqn. (10)].

Table 7 Parameters of non-hydroxylic binary mixtures

Solvent (S1)–solvent (S2)	Eqn.	E^N_{T1}	E^N_{T2}	E^N_{T12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	SD/10^{-3}	N	Refs.
Tetrachloromethane–chloroform	8	0.056	0.277	0.159	23	22	0.95	2.0	9	28
Benzene–nitrobenzene	10	0.123	0.329	0.298	5.7	6.7	1.2	3.5	6	29
Benzene–pyridine	10	0.120	0.304	0.241	1.9	2.9	1.5	3.7	14	25
1,2-Dibromoethane–1,2-dibromopropane	10	0.236	0.260	0.248	1	2	2	0.38	11	27
Tributyl phosphate–trimethyl phosphate	10	0.274	0.399	0.336	1	2	2	1.4	11	28

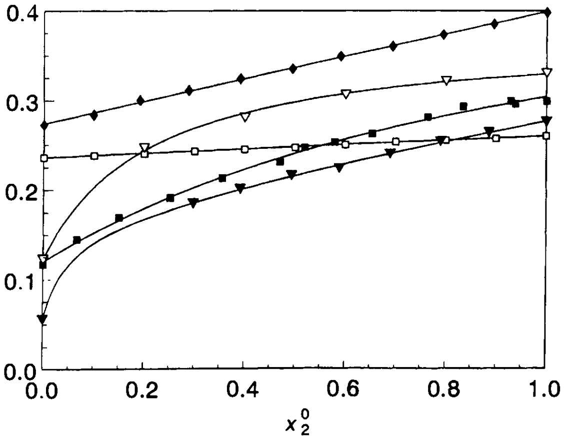

Fig. 8 Binary solvent mixtures of non-hydroxylic binary solvents: ▼, tetrachloromethane–chloroform; ▽, benzene–nitrobenzene; ■, benzene–pyridine; □, 1,2-dibromoethane–1,2-dibromopropane; ◆, tributyl phosphate–trimethyl phosphate. Lines computed by eqn. (8) from the parameters of Table 7.

Non-hydroxylic mixtures

To check the general validity of the equations and models we have also applied them to the available data on non-hydroxylic mixtures. In Part 1 of this series,[10] the equations were successfully applied to mixtures with dipolar hydrogen bond acceptors and also to some mixtures containing tetrachloromethane. There are only a few other available mixtures, whose results are presented in Table 7 and Fig. 8.

1,2-Dibromoethane–1,2-dibromopropane and tributyl phosphate–trimethyl phosphate are ideal systems, as expected from the similarity of the two solvents mixed.

Benzene–pyridine and benzene–nitrobenzene can be fitted to the one-step model [eqn. (10)], but tetrachloromethane–chloroform must be fitted to the general two-step model [eqn. (8)]. In these three systems, the preferential solvation of the $E_T(30)$ indicator is by the most polar solvents pyridine, nitrobenzene and chloroform.

Conclusions

Among the different preferential solvation models studied, the so-called two-step solvent exchange model of Skwierczynski and Connors seems to be the most consistent with the $E_T(30)$ behaviour of binary solvent mixtures. However, the simplification of taking the $E_T(30)$ value of the mixed solvent S12 as a simple average of the $E_T(30)$ values of the two solvents mixed does not hold for the majority of systems. Without this restriction, the model fits well with all the binary systems studied, including the synergetic systems,[10,11] and explains the different behaviours observed. The division between one-step and two-step class binary systems is artificial because the one-step systems are particular cases of the two-step model. Nevertheless, the fit to the one-step model, when feasible, is useful to avoid overparameterization of the equation and obtain good estimates of the parameters. Ideal binary systems are also particular cases of the one-step and two-step models, and they can be consistently explained from the two-step solvent exchange model.

Acknowledgements

Financial support from Spanish (project PB94-0833) and Catalan (project GRQ-93-1028) Governments is gratefully acknowledged.

References

1 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 2nd edn., 1988.
2 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
3 J. G. Dawber, J. Ward and R. A. Williams, *J. Chem. Soc., Faraday Trans.*, 1988, **84**, 713.
4 J. G. Dawber, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 287.
5 P. Chatterjee and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1785.
6 P. Chatterjee and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 587.
7 A. K. Covington and K. E. Newman, *Pure Appl. Chem.*, 1979, **51**, 2041.
8 E. Bosch and M. Rosés, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 3541.
9 R. D. Skwierczynski and K. A. Connors, *J. Chem. Soc., Perkin Trans. 2*, 1994, 467.
10 M. Rosés, C. Ràfols, J. Ortega and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1607.
11 E. Bosch, M. Rosés, K. Herodes, I. Koppel, I. Leito, I. Koppel and V. Taal, *J. Phys. Org. Chem.*, in the press.
12 K. Dimroth and C. Reichardt, *Z. Anal. Chem.*, 1966, **215**, 344.
13 Y. Marcus, *Ion Solvation*, Wiley, New York, 1985.
14 T. M. Krygowski, P. K. Wrona, U. Zielkowska and C. Reichardt, *Tetrahedron*, 1985, **41**, 4519.
15 J. J. Michels and J. G. Dorsey, *J. Chromatogr.*, 1988, **457**, 85.
16 E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Ottolenghi and N. Orbach, *J. Am. Chem. Soc.*, 1975, **97**, 2167.
17 Y. Migron and Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1339.
18 E. Casassas, G. Fonrodona and A. de Juan, *J. Solution Chem.*, 1992, **21**, 147.
19 J. R. Haak and J. B. F. N. Engberts, *Rec. Trav. Chim. Pays-Bas.*, 1986, **105**, 307.
20 J. Jouanne, D. A. Palmer and H. Kelm, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 463.
21 I. A. Koppel and J. B. Koppel, *Organic Reactivity (Tartu)*, 1983, **20**, 523.
22 Y. Marcus and Y. Migron, *J. Phys. Chem.*, 1991, **95**, 400.
23 S. Balakrishnan and A. J. Easteal, *Aust. J. Chem.*, 1981, **34**, 943.
24 M. Rosés, J. Ortega and E. Bosch, *J. Solution Chem.*, 1995, **24**, 51.
25 I. A. Koppel and J. B. Koppel, *Organic Reactivity (Tartu)*, 1983, **20**, 547.
26 H. Elias, G. Gumbel, S. Neitzel and H. Volz, *Z. Anal. Chem.*, 1981, **306**, 240.
27 S. Balakrishnan and A. J. Easteal, *Aust. J. Chem.*, 1981, **34**, 933.
28 Z. B. Maksimovic, C. Reichardt and A. Spirić, *Z. Anal. Chem.*, 1974, **270**, 100.
29 K. Tamura, Y. Ogo and T. Imoto, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2988.

Paper 5/07375H
Received 9*th November* 1995
Accepted 22*nd February* 1996