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Solute–solvent and solvent–solvent interactions in binary solvent mixtures. Part 8. The $E_T(30)$ polarity of binary mixtures of formamides with hydroxylic solvents

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ABSTRACT: Solvent effects on the binary mixtures of amides with alcohols and water were investigated by means of Reichardt's $E_T(30)$ solvatochromic indicator. E_T^N parameters of binary solvent mixtures of formamide, *N*-methylformamide and *N,N*-dimethylformamide with water, methanol, propan-2-ol, 2-methylpropan-2-ol, formamide, *N*-methylformamide and *N,N*-dimethylformamide were measured over the whole composition range of the mixtures. Application of a preferential solvation model to the solvatochromic data shows that the preferential solvation of the solvatochromic indicator by the amides decreases in the order *N*-methylformamide > formamide > *N,N*-dimethylformamide. Synergism is observed for the mixtures of the amides with alcohols of similar polarity (E_T^N value), i.e. methanol–formamide, methanol–*N*-methylformamide, propan-2-ol–*N,N*-dimethylformamide and 2-methylpropan-2-ol–*N,N*-dimethylformamide binary systems. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: solute–solvent interactions; solvent–solvent interactions; binary solvents; amide–water mixtures; amide–alcohol mixtures; amide–amide mixtures; solvatochromic indicators

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INTRODUCTION

Solvent polarity plays an important role in many chemical processes in solution.[1,2] There are different definitions of solvent polarity and several ways to measure it. According to Reichardt,[1,2] solvent polarity can be defined as the overall solvation capability of solvents, which depends on the action of all possible intermolecular interactions between solutes and solvent, excuding those interactions leading to definite chemical alterations of the solute (such as protonation and oxidation). One of the simplest ways to measure these interactions is by solvatochromic indicators. The most widely used solvatochromic indicator is 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate, commonly known as $E_T(30)$ dye or Reichardt's betaine dye since it was proposed by this author.[1,2] The ground and excited states of the $E_T(30)$ dye present a large difference in dipole moment and therefore the $\pi \rightarrow \pi^*$ transition energy of the dye is highly sensitive to solvent polarity. The $E_T(30)$ polarity parameter is defined as the excitation energy (kcal mol^{-1}) of the dye in a particular solvent, which can be calculated from the wavenumber ($\tilde{\nu}_{\max}$ in cm^{-1}) or wavelength ($\lambda_{\max}$ in nm) of the maximum of the absorption spectrum according to the equation

$$\begin{aligned} E_T(30)(\text{kcal mol}^{-1}) &= hc\tilde{\nu}_{\max}N_A \\ &= 2.8591 \times 10^{-3}\tilde{\nu}_{\max} \\ &= 28591/\lambda_{\max} \end{aligned} \quad (1)$$

A normalized parameter E_T^N with reference to tetramethylsilane (TMS) ($E_T^N = 0$) and water (H_2O) ($E_T^N = 1$) is now recommended instead of $E_T(30)$.[1,2] E_T^N can be calculated from $E_T(30)$ through

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} \quad (2)$$

The E_T^N parameter has been measured for over 360 pure solvents[1,2] and at least for 80 different binary solvent systems.[2–7] However, the interpretation of the E_T^N parameter in pure and in mixed solvents is different. E_T^N measures the polarity of the solvent surrounding the solvatochromic indicator.[2] In a pure solvent, the composition of the sphere of solvation of the indicator is the

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same as in the bulk solvent. However, in a mixed solvent, the solvatochromic indicator interacts to a different extent with the solvents of the mixture and the composition of the solvation sphere can be different from the composition of the bulk solvent. This phenomenon is called selective or preferential solvation.

In previous studies,[3–9] we proposed and tested several preferential solvation models to relate the values of E_T^N and other solvatochromic parameters in binary solvents with the solvent composition. In the present study, we measured the E_T^N parameter of binary mixtures of formamide, *N*-methylformamide and *N,N*-dimethylformamide with water, methanol, propan-2-ol and 2-methylpropan-2-ol, and also formamide–*N*-methylformamide, formamide–*N,N*-dimethylformamide and *N*-methylformamide–*N,N*-dimethylformamide mixtures. The E_T^N data were analysed by means of one of the previously developed preferential solvation models, which had already been applied to binary solvent systems with a similar behaviour.[3,4]

PREFERENTIAL SOLVATION MODEL

The preferential solvation model is based on the two-step solvent exchange model first proposed by Skwierczynski and Connors:[10]

$$\mathrm{I(S1)_2 + 2S2 \rightleftharpoons I(S2)_2 + 2S1}$$
$$\mathrm{I(S1)_2 + S2 \rightleftharpoons I(S12)_2 + S1}$$

where S1 and S2 indicate the two pure solvents mixed and S12 represents a solvent formed by the interaction of solvents 1 and 2.[3] $\mathrm{I(S1)_2}$, $\mathrm{I(S2)_2}$, and $\mathrm{I(S12)_2}$ indicate the $\mathrm{E_T}$ indicator solvated by solvents S1, S2 and S12, respectively.

The two solvent-exchange processes can be defined by two preferential solvation parameters, $f_{2/1}$ and $f_{12/1}$, which measure the tendency of the indicator to be solvated by solvents S2 and S12 with reference to solvent S1 solvation:[3–9]

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

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \tag{4}$$

In Eqns 3 and 4, $x_1{}^s$, $x_2{}^s$ and $x_{12}{}^s$ are the mole fractions of solvents S1, S2 and S12, respectively, in the sphere of solvation of the indicator and $x_1{}^0$ and $x_2{}^0$ are the mole fractions of the two solvent in the bulk mixed solvent.

The E_T^N polarity of the mixed solvent is calculated as an average of the E_T^N values of solvents S1, S2, and S12 in the sphere of solvation of the indicator:

$$E_\mathrm{T}^\mathrm{N} = x_1^\mathrm{S} E_\mathrm{T1}^\mathrm{N} + x_2^\mathrm{S} E_\mathrm{T2}^\mathrm{N} + x_{12}^\mathrm{S} E_\mathrm{T12}^\mathrm{N} \tag{5}$$

Skwierczynski and Connors[10] assumed E_{T12}^N to be the simple average of E_{T1}^N and E_{T2}^N. However, this assumption did not hold for many solvent mixtures,[3,4] and it is not considered in our approach.

From Eqns 3–5, a general equation that relates the E_T^N polarity of a binary mixture to the E_T^N polarities of the two pure solvents, the preferential solvation parameters and the solvent composition can be derived according to

$$E_\mathrm{T}^\mathrm{N} = \frac{E_\mathrm{T1}^\mathrm{N}(1-x_2^0)^2 + E_\mathrm{T2}^\mathrm{N} f_{2/1}(x_2^0)^2 + E_\mathrm{T12}^\mathrm{N} f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \tag{6}$$

This general equation has been succesfully applied to many different binary solvent mixtures[3–7] and it was applied here to the systems studied.

EXPERIMENTAL

Apparatus. A Perkin-Elmer Lambda 2S UV/VIS spectrophotometer with 10 mm cells was used for recording the spectra.

Reagents. The organic solvents, of reagent grade, were purified by distillation in the presence of CaO (Na for methanol) and the appropriate fractions were collected: formamide (b.p. 74–75 °C, 1.1 Torr), *N*-methylformamide (b.p. 57–58.5 °C, 1.3 Torr), *N,N*-dimethylformamide (b.p. 53–56 °C), 2-methylpropan-2-ol (b.p. 81.8–81.9 °C), propan-2-ol (b.p. 82.0–82.1 °C) and methanol (b.p. 64.2–64.5 °C). The water content, measured by the Karl Fischer method, was 0.015, 0.02, 0.005, 0.02, 0.03 and 0.01% for formamide, *N*-methylformamide, *N,N*-dimethylformamide, 2-methylpropan-2-ol, propan-2-ol, and methanol, respectively. Doubly distilled water was used throughout. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate (Reichardt's dye) was obtained from Aldrich.

Procedure. For each binary system a *ca* 10^{-4} M solution of Reichardt's dye was prepared in one of the two pure solvents (solvent 1) and placed in the spectrophotometer cell. The cell was closed with PTFE cap and weighed (±0.05 mg). After recording the spectrum (450–700 nm), a drop of solvent 2 was added, the cell weighed and the spectrum of the new solution was recorded. The procedure was repeated after the addition of further drops of solvent 2. Subsequent sets of experiments were performed starting with a solution of solvent 2 and adding drops of solvent 1, or starting with selected solvent 1–solvent 2 mixtures and adding drops of one or the other solvent. The different sets of solvent mixtures were overlapped in composition in order to ensure concordance of the results. The measurement cell was externally thermostated with a water flow at 25.0 ± 0.1 °C.

Calculation methods. The $E_\mathrm{T}(30)$ and E_T^N values of each solvent mixture were calculated from the maximum of

Table 1. Properties of pure solvents at 25 °C[2,11,12]

Solvent	ε_r	μ (D)	n_D	π^*	β	α	E_T^N
Formamide	111.0	3.37	1.4468	0.97	0.48	0.71	0.775
N-Methylformamide	182.4	3.86	1.4300	0.90	0.80	0.62	0.722
N,*N*-Dimethylformamide	36.71	3.86	1.4282	0.88	0.69	0.00	0.386
Water	78.39	1.83	1.3325	1.09	0.47	1.17	1.000
Methanol	32.70	2.87	1.3265	0.60	0.66	0.98	0.762
Propan-2-ol	19.92	1.66	1.3752	0.48	0.84	0.76	0.546
2-Methylpropan-2-ol[a]	12.47	1.66	1.3851	0.41	0.93	0.42	0.389

[a] Parameters at 30 °C or as a supercooled liquid at 25 °C.

the long-wavelength charge - transfer absorption band through Eqns 1 and 2. The E_{T1}^N, E_{T2}^N, E_{T12}^N, $f_{2/1}$ and $f_{12/1}$ parameters that minimize the square residuals of E_T^N values of each binary solvent system studied were calculated by non-linear regression as described previously.[3]

RESULTS AND DISCUSSION

Some macroscopic and microscopic properties of the pure solvents used to prepare the mixtures are given in Table 1.[2,11,12] The macroscopic properties selected are the dielectric permitivity (ε_r), dipole moment (μ) and refractive index (n_D) and the microscopic parameters are E_T^N and the Kamlet–Taft parameters of dipolarity/polarizability (π^*), hydrogen-bond acceptor basicity (β) and hydrogen-bond donor acidity (α).[12–15] The microscopic parameters were determined from solvatochromic measurements and they reflect the properties in the solvation sphere of the solvatochromic indicator. However, the macroscopic parameters always measure the properties of the bulk solvent. Since pure solvents are not subject to preferential solvation, there is fairly good agreement between the macroscopic and microscopic properties in Table 1. Hence we can observe that amides are dipolar solvents (large μ and π^* values) with a considerable capability to accept hydrogen bonds (large β values). Formamide and *N*-methylformamide are also good hydrogen-bond donors (large α values), but *N*,*N*-dimethylformamide has a zero capacity to donate hydrogen bonds ($\alpha = 0$). Since Reichardt's dye is almost equally sensitive to solvent dipolarity and hydrogen-bond donor acidity, the E_T^N value of *N*,*N*-dimethylformamide is only about half those of the other two amides. Also, because *N*,*N*-dimethylformamide is not a hydrogen-bond donor, its dielectric permitivity is much lower than those of *N*-methylformamide and formamide. Water and alcohols are dipolar and hydrogen-bond acids and bases. The dipolarity (π^*) and hydrogen-bond donor acidity (α) decrease in the order water > methanol > propan-2-ol > 2-methylpropan-2-ol, and therefore E_T^N and the dielectric permitivity decrease in the same order. However, the hydrogen-bond acceptor basicity (β) increases in the same order. Amides are more polarizable than alcohols and water (larger n_D values).

The E_T^N values of binary mixtures of water, methanol, propan-2-ol and 2-methylpropan-2-ol with the three studied amides, and the three binary systems of the amides, over the whole range of solvent compositions (from 20 to 70 different mixtures for each system) were measured. Because of the insolubility of Reichardt's $E_T(30)$ indicator in water-rich mixtures, E_T^N could not be measured in pure water and in some water–formamide mixtures (for mole fractions of formamide lower than 0.33). The literature value[1,2,12] $E_T^N = 1.000$ for pure water was used for all calculations involving aqueous mixtures. In fact, this value is taken as one of the two reference points of the E_T^N scale [see Eqn 2].

As far as we know, only E_T^N or $E_T(30)$ values for some water–*N*,*N*-dimethylformamide[10,16] and methanol–*N*,*N*-dimethylformamide[17] mixtures have been published previously. Our E_T^N data agree very well (±0.01) with the data published for these mixtures.

Equation 6 was applied to the E_T^N data for the mixtures studied, and the results are presented in Table 2 and Figs 1–6. Very good fits ($SD < 0.005$) are obtained for all binary systems. The E_T^N values in Table 2 that correspond to pure solvents (E_{T1}^N and E_{T2}^N) agree very well with the literature values reported in Table 1. Only the value obtained here for 2-methylpropan-2-ol (*ca* 0.405) is slightly larger than that in Table 1 (0.389). This small discrepancy can be attributed to the difficulties in the measurement of the E_T^N for this solvent, because it freezes at 25.8 °C.[11] The E_T^N value in Table 1 was measured at 30 °C, but here as a supercooled liquid at 25 °C.

The E_{T12}^N values should be a measure of the polarity of the mixed structure formed by interaction of solvent 1 (water or alcohol, in general) with solvent 2 (amide). In previous studies,[3,4,18] we demonstrated that when a good hydrogen-bond donor (such as an alcohol) is mixed with a good hydrogen-bond acceptor (e.g. acetonitrile, acetone or dimethyl sulphoxide) of similar polarity (similar E_T^N value), synergetic mixtures with E_{T12}^N parameters higher than E_{T1}^N and E_{T12}^N can be easily obtained. This is attributed to the formation of a solvent hydrogen-bond

Table 2. Parameters of the binary mixtures studied

Solvent 1	Solvent 2	E_{T1}^N	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	SD	*n*
Water	Formamide	1.000	0.775	0.794	0.31	3.0	0.004	23
Water	*N*-Methylformamide	1.000	0.721	0.882	31	19	0.002	56
Water	*N*,*N*-Dimethylformamide	0.997	0.396	0.702	6.1	7.9	0.003	37
Methanol	Formamide	0.762	0.774	0.806	1.8	5.6	0.001	38
Methanol	*N*-Methylformamide	0.764	0.720	0.798	3.7	4.8	0.001	25
Methanol	*N*,*N*-Dimethylformamide	0.765	0.388	0.465	0.012	0.40	0.003	51
Propan-2-ol	Formamide	0.543	0.775	0.671	3.9	6.9	0.001	67
Propan-2-ol	*N*-Methylformamide	0.543	0.722	0.575	351	69	0.001	44
Propan-2-ol	*N*,*N*-Dimethylformamide	0.541	0.390	0.586	5.6	21	0.003	42
2-Methylpropan-2-ol	Formamide	0.411	0.771	0.550	24	21	0.004	54
2-Methylpropan-2-ol	*N*-Methylformamide	0.405	0.720	0.502	749	196	0.001	61
2-Methylpropan-2-ol	*N*,*N*-Dimethylformamide	0.403	0.392	0.496	0.81	3.4	0.002	45
N-Methylformamide	Formamide	0.721	0.776	0.767	0.13	1.1	0.001	44
N,*N*-Dimethylformamide	Formamide	0.395	0.775	0.607	5.9	8.9	0.002	30
N,*N*-Dimethylformamide	*N*-Methylformamide	0.394	0.719	0.571	125	40	0.001	39

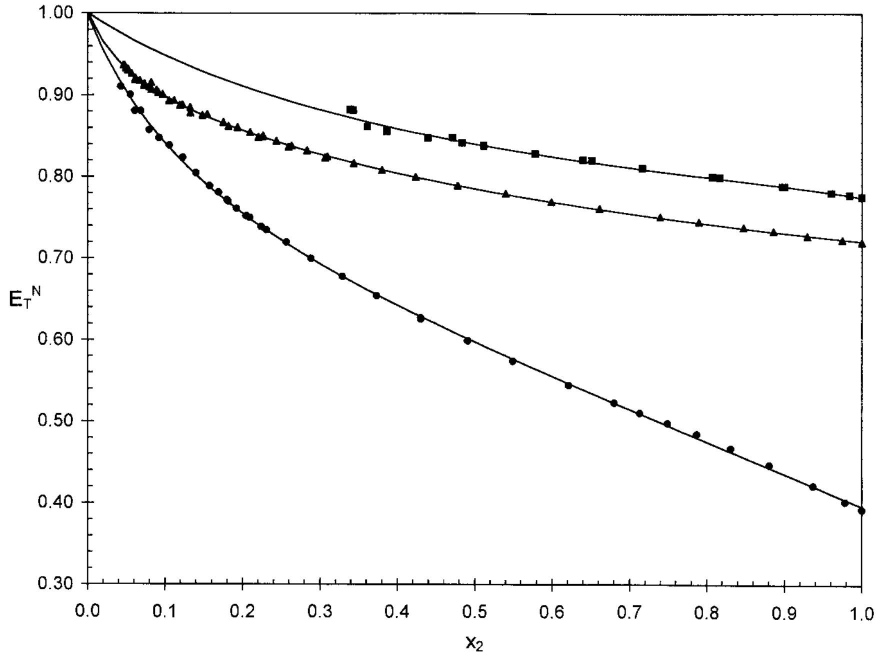

Figure 1. E_T^N of binary mixtures of water with amides: (■) formamide; (▲) *N*-methylformamide; (●) *N*,*N*-dimethylformamide. x_2 is the mole fraction of amide

complex more polar than either of the two pure solvents mixed. Since amides are good hydrogen-bond acceptors, the synergism is also observed here for some of the binary systems. Formamide and *N*-methylformamide have E_T^N values close to that of methanol (Tables 1 and 2), and therefore synergistic mixtures are obtained for these two binary systems. However, the E_T^N value of *N*,*N*-dimethylformamide is much lower than that of methanol and the E_{T12}^N value of this system is not larger than the E_{T1}^N and E_{T12}^N values. Conversely, the E_T^N value of *N*,*N*-dimethylformamide is close to the E_T^N values of propan-2-ol and 2-methylpropan-2-ol, and synergism is observed in these two binary systems, but not in the mixtures of propan-2-ol or 2-methylpropan-2-ol with formamide or *N*-methylformamide (which have larger E_T^N values). The synergistic behaviour of the methanol–formamide, methanol–*N*-methylformamide, propan-2-ol–*N*,*N*-dimethylformamide and 2-methylpropan-2-ol–*N*,*N*-dimethylformamide mixtures can be also observed in Figs 2–4. Some of the binary mixtures of these systems show E_T^N values larger than those of the two pure solvents mixed, and this produces a maximum in the E_T^N vs solvent composition plots. No synergism is observed in the mixtures with water (large E_T^N value) or in the mixtures between two amides.

The results presented in Table 2 also give information about the solvation of the solvatochromic indicator. We

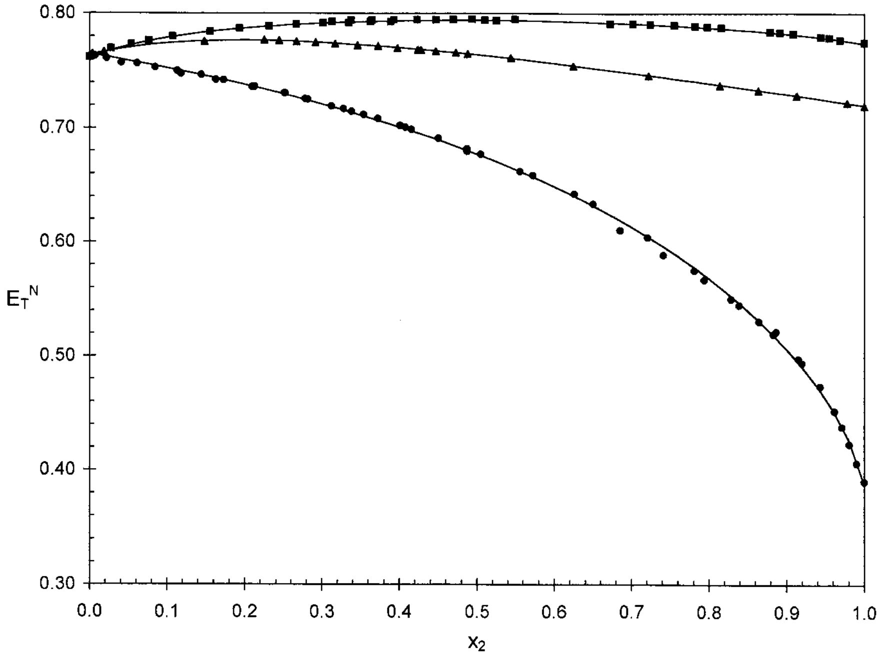

Figure 2. E_T^N of binary mixtures of methanol with amides. Symbols as in Fig. 1

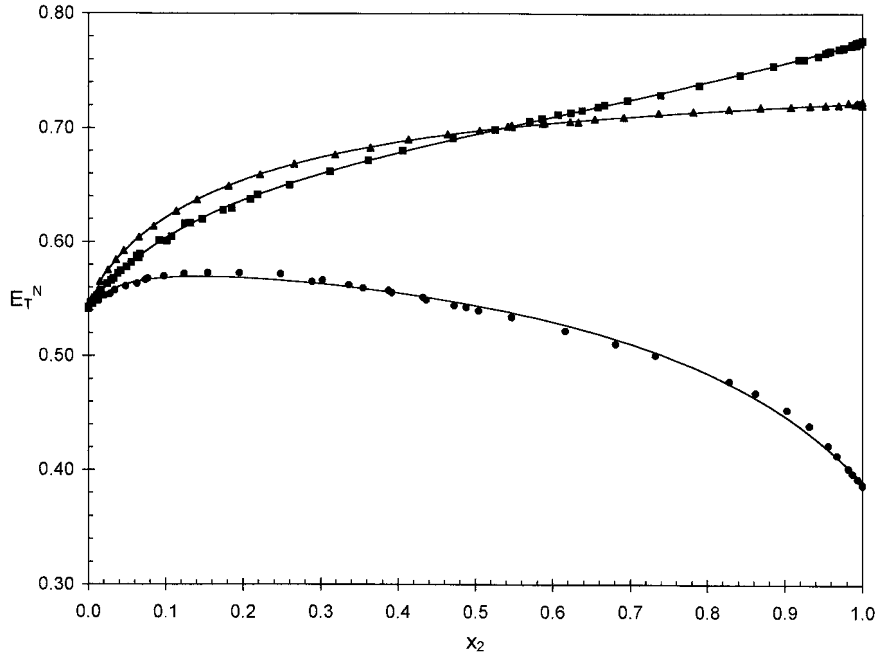

Figure 3. E_T^N of binary mixtures of propan-2-ol with amides. Symbols as in Fig. 1

can observe that the $f_{2/1}$ value for *N*-methylformamide–formamide is <1, which means that the indicator is preferentially solvated by *N*-methylformamide with reference to formamide. The $f_{2/1}$ values for *N*,*N*-dimethylformamide–formamide and for *N*,*N*-dimethylformamide–*N*-methylformamide are >1 (very much larger for the last system) and this shows that *N*,*N*-dimethylformamide is the least preferred solvent for solvation of the solvatochromic indicator. Therefore, the order of preferential solvation for amides is *N*-methylformamide > formamide > *N*,*N*-dimethylformamide. The preferential solvation of the indicator by *N*-methylformamide is confirmed by the mixtures with water and alcohols. The $f_{2/1}$ values for the *N*-methylformamide (S2) mixtures are >1 and larger than the $f_{2/1}$ values for the corresponding mixtures of the same

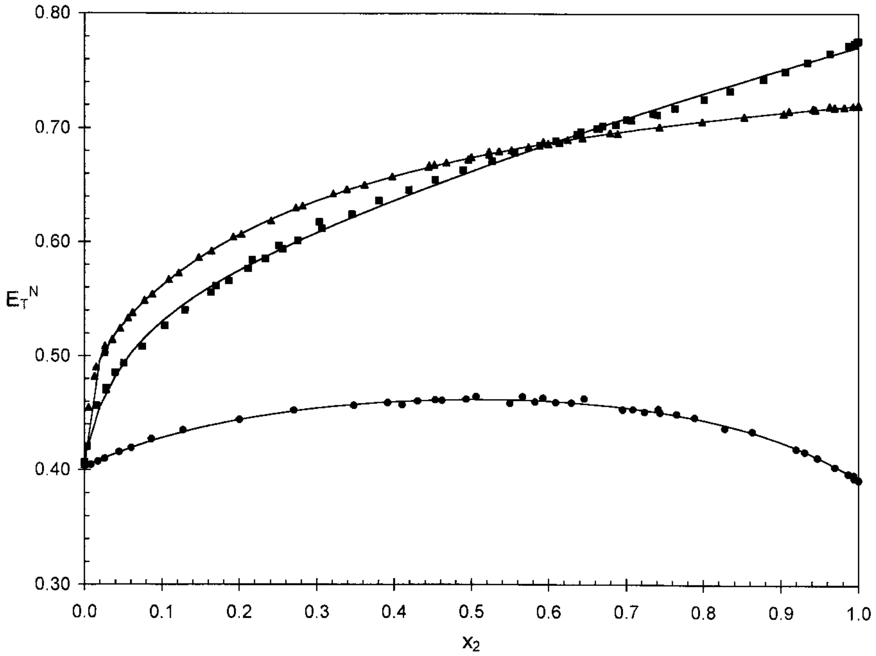

Figure 4. E_T^N of binary mixtures of 2-methylpropan-2-ol with amides. Symbols as in Fig. 1

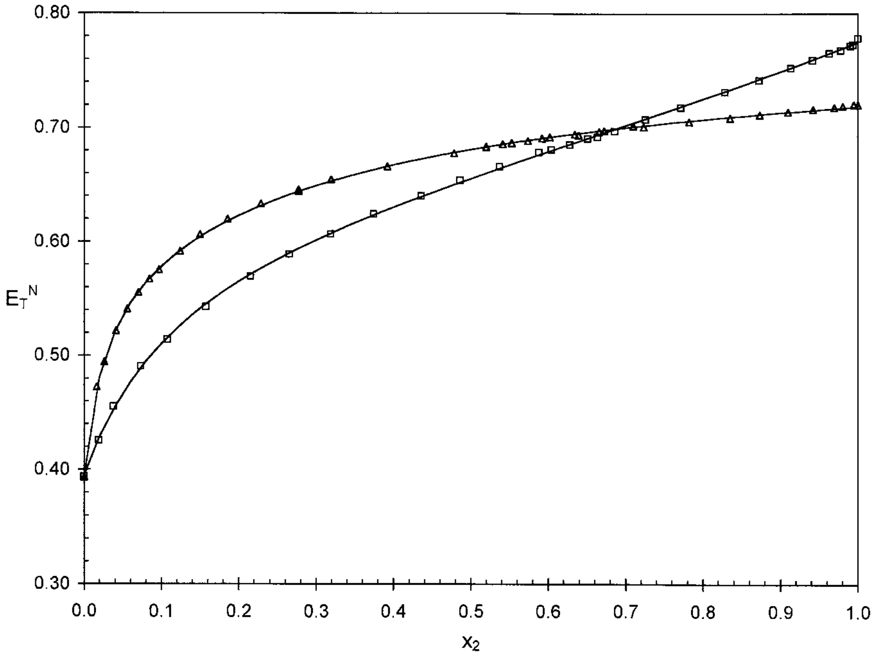

Figure 5. E_T^N of binary mixtures of *N,N*-dimethylformamide with (□) formamide and (△) *N*-methylformamide. x_2 is the mole fraction of formamide or *N*-methylformamide

cosolvents with formamide or *N,N*-dimethylformamide. In general, the $f_{2/1}$ values for the mixtures of amides with alcohols increase in the order methanol < propan-2-ol < 2-methylpropan-2-ol, which means that the preferential solvation of the indicator for these cosolvents is methanol > propan-2-ol > 2-methylpropan-2-ol. A similar behaviour has already been observed for mixtures of alcohols with dimethyl sulphoxide, acetonitrile and nitromethane,[3–5] which also form some synergistic mixtures. Almost all $f_{12/1}$ values are >1, which means

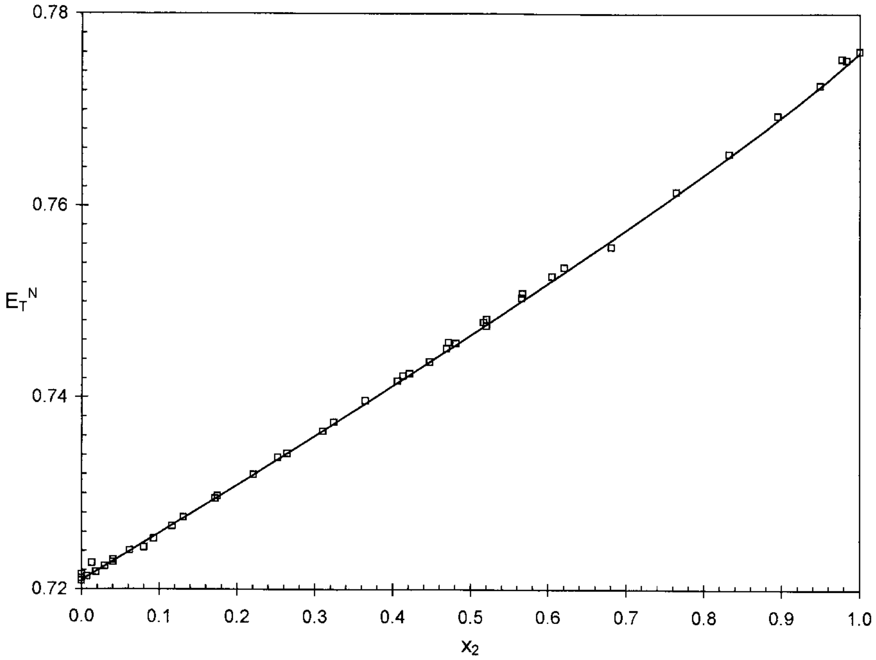

Figure 6. E_T^N of binary mixtures of formamide with *N*-methylformamide. x_2 is the mole fraction of formamide

that the solvatochromic indicator is largely solvated by the hydrogen-bond complex solvent formed by the interaction of the amide with the hydroxylic cosolvent.

Supplementary Material

A table with solvent compositions, wavelengths of absorption maxima and $E_T(30)$ and E_T^N values of the studied binary solvent mixtures is available as supplementary material on the epoc website at http://www.wiley.com/epoc.

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