SOLUTE–SOLVENT AND SOLVENT–SOLVENT INTERACTIONS IN BINARY SOLVENT MIXTURES. 2. EFFECT OF TEMPERATURE ON THE $E_T(30)$ POLARITY PARAMETER OF DIPOLAR HYDROGEN BOND ACCEPTOR–HYDROGEN BOND DONOR MIXTURES

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The effect of temperature on the Dimroth–Reichardt $E_T(30)$ parameter of binary mixtures of dimethyl sulfoxide, acetonitrile and nitromethane with alcohols and water was studied. The $E_T(30)$ polarity parameter of many of these binary mixtures exhibits a strong synergism. Dimethyl sulfoxide, acetonitrile and nitromethane form hydrogen-bonded complexes with the alcohols more polar than themselves. The $E_T(30)$ values of the mixtures were fitted according to an earlier model, based on solvent exchange equilibria, that allows calculation of the $E_T(30)$ values of the hydrogen-bonded complexes. The variation of the $E_T(30)$ values of the pure solvents and the hydrogen-bonded complexed solvents with temperature shows that the synergism decreases as the temperature increases.

INTRODUCTION

Solvatochromic indicators offer a simple and easy way to study solvent properties such as polarity, polarizability and hydrogen bonding ability. These properties are measured by means of solvatochromic parameters, which are calculated from the position of the maximum of the solvent-dependent absorption band of appropriate indicators, usually in the UV–visible or near-IR region.[1–3] The band position is sensitive to solvent properties because the transition energy of the indicator depends on intermolecular indicator–solvent interactions. Such solute–solvent interactions are much more complex in mixed than in pure single solvents. In binary solvents, solvent–solvent interactions must be considered together with solute–solvent interactions. Moreover, the solute can be preferentially solvated by any of the solvents present and, therefore, the composi-

tion of the microsphere of solvation of the indicator, the so-called cybotactic region, is different from the composition of the bulk solvent. However, since the position of the maximum of the absorption band depends on the properties in the cybotactic region, the measurement of this position provides information about the properties and composition of this region.

The most popular solvatochromic indicator is 2,6-diphenyl-4-(2,4,6-triphenyl-1 -pyridinio)-1-phenolate or $E_T(30)$ dye, proposed by Reichardt *et al.*[1–3] for measuring solvent polarity. The $E_T(30)$ parameter is defined as the excitation energy (kcal mol^{-1}) of the $E_T(30)$ dye in a particular solvent, which can be calculated from the wavenumber of the maximum of the long-wavelength absorption band ($\tilde{v}$), according to

$$E_T(30)/(\text{kcal mol}^{-1}) = hc\tilde{v}N_A = 2.859 \times 10^{-3} \, \tilde{v}/\text{cm}^{-1}$$

(1)

The $E_T(30)$ parameter has been widely used to measure empirically the polarity of many pure and

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mixed solvents,[1,3] and also to study preferential solvation in binary solvents. Dawber *et al.*[4] proposed the deviation from linearity [assuming additivity of the $E_T(30)$ values of the pure solvents according to their mole fractions] of experimental $E_T(30)$ values of binary solvents as a measure of preferential solvation and related the preferential solvation of the $E_T(30)$ dye with several thermodynamic and kinetic properties.[5] In previous studies,[6,7] we have proposed preferential solvation models to describe and interpret the $E_T(30)$ values of binary mixtures. Similar models have been also proposed by Skwierczynski and Connors.[8]

Among the different binary systems studied, mixtures of dipolar hydrogen-bond acceptors (HBA solvents, e.g. dimethyl sulfoxide, acetonitrile) with good hydrogen-bond donors (HBD solvents, e.g. alcohols) present a striking behavior. An earlier study[9] showed that binary mixtures of dimethyl sulfoxide or acetonitrile with alcohols show, in many instances, $E_T(30)$ values higher than those of the two pure solvent components, and the term 'synergetic' was proposed to describe this behavior. This synergism is produced by hydrogen bonding between the HBA and the HBD to give a hydrogen-bonded complex, which is often more polar than either of the two pure solvents. In a recent study,[7] a preferential solvation model that considers the solvation of the $E_T(30)$ indicator by the three solvents of the mixture (the two pure solvents and the hydrogen-bonded complex) was developed and successfully applied to synergetic and non-synergetic mixtures. This model allows the calculation of $E_T(30)$ polarity parameters of the hydrogen-bonded complexes.

In the present study, the $E_T(30)$ values of mixtures of dimethyl sulfoxide, acetonitrile and nitromethane with water, methanol, 2-propanol and *tert*-butanol were measured at several temperatures. The preferential solvation model was applied to these data and the variation of the $E_T(30)$ values of the solvents (including the hydrogen-bonded complexes) with temperature was assessed.

PREFERENTIAL SOLVATION MODELS

The proposed model[7] considers two solvent exchange equilibria between the solvatochromic indicator (I) solvated by solvent 1 (S1), solvent (S2), and the hydrogen-bonded complex between S1 and S2 (S12) according to

$$I(S1)_m + m\ S2 \rightleftharpoons I(S2)_m + m\ S1$$

$$I(S1)_m + \frac{m}{2}\ S2 \rightleftharpoons I(S12)_m + \frac{m}{2}\ S1$$
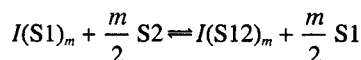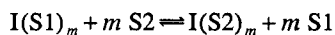
These equilibria can be described by two preferential solvation parameters ($f_{2/1}$ and $f_{12/1}$), which are equivalent to the constants of the equilibria:

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

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

where x_1^s, x_2^s and x_{12}^s are the mole fractions of solvents 1 and 2, and the hydrogen-bonded complex 12 in the solvation microsphere of the indicator respectively, and x_1^0 and x_2^0 are the mole fractions of the two pure solvents mixed. All these mole fractions satisfy the equation

$$x_1^0 + x_2^0 = x_1^s + x_2^s + x_{12}^s = 1 \tag{4}$$

The E_T value of the mixture, where E_T indicates any transition energy, is calculated from

$$E_T = x_1^s E_{T1} + x_2^s E_{T2} + x_{12}^s E_{T12} \tag{5}$$

where E_{T1}, E_{T2} and E_{T12} are the transition energies of the solvatochromic indicator completely solvated by solvents 1, 2 and 12, respectively.

If equations (2)–(4) are introduced into equation (5), the final equation (6) is obtained:

$$E_T = E_{T1} + \frac{a(x_2^0)^m + c\sqrt{[(1-x_2^0)x_2^0]^m}}{(1-x_2^0)^m + f_{2/1}(x_2^0)^m + f_{12/1}\sqrt{[(1-x_2^0)x_2^0]^m}} \tag{6}$$

where a and c are

$$a = f_{2/1}(E_{T2} - E_{T1}) \tag{7}$$

$$c = f_{12/1}(E_{T12} - E_{T1}) \tag{8}$$

Equation (6) has been used to fit the $E_T(30)$ values of many binary mixtures.[7] In this equation, m is the number of solvation of the solvatochromic indicator. For most of the studied mixtures m was found to be close to 2,[7] which is also the value used by Skwierczynski and Connors[8] within their model. With $m = 2$, equation (6) becomes

$$E_T = E_{T1} + \frac{a(x_2^0)^2 + c(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \tag{9}$$

Although this equation is based on only two solvent exchange processes that perhaps cannot account for the solvent sorting over the whole mole fraction range, it is approximate enough to describe the experimental $E_T(30)$ behavior of many binary mixtures,[7,8] and especially to explain the synergetic behavior of some HBD–HBA binary solvent mixtures.

EXPERIMENTAL

Apparatus. A Hitachi EPS-3T spectrophotometer with 10 mm cells was used for recording the spectra.

Reagents. The individual solvents used to prepare the mixtures were the same as used earlier.[9] 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate [$E_T(30)$ dye] was obtained from Aldrich.

Procedure. The studied mixtures were prepared by weight at 7–10 different mole. The spectrum of a 10^{-4} M solution of the $E_T(30)$ dye in each solvent mixture at each temperature was recorded in the range 450–700 nm. The measurement cell was externally thermostated with a water flow.

Calculation methods. The $E_T(30)$ value of each mixture at each temperature was calculated from the maximum of the long-wavelength absorption band through equation (1). The $E_T(30)$ data were normalized (E_T^N) with respect to tetramethylsilane ($E_T^N = 0$) and water ($E_T^N = 1$) according to the equation[1]

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H_2O} - E_T(30)_{TMS}} = \frac{E_T(30) - 30.7}{32.4} \quad (10)$$

The E_{T1}^N, E_{T2}^N, E_{T12}^N, $f_{2/1}$ and $f_{12/1}$ parameters that minimize the square residuals of the E_T^N values of each binary solvent system studied were calculated by non-linear regression as described previously.[7]

RESULTS AND DISCUSSION

The properties (dielectric constant, E_T^N and Kamlet–Taft solvatochromic parameters) of the pure solvents used to prepare the binary mixtures in this work are given in Table 1. Acetonitrile, nitromethane, and dimethyl sulfoxide are dipolar (high π value), poor HBD (low α value) and fairly good HBA (high β value) solvents. The alcohols and water are also dipolar and good HBA solvents, but they are also good HBD solvents. Therefore, strong hydrogen bond interactions are expected in the binary mixtures of acetonitrile, nitromethane and dimethyl sulfoxide with water and alcohols.

The measured E_T^N values for the mixtures studied are given in Table 2. The E_T^N values of each mixture were measured at 25, 50 and 75 °C, except for methanol mixtures, which were measured at 15, 30 and 50 °C because of the low boiling point of methanol. The E_T^N

values of nitromethane–water mixtures were measured only up to a mole fraction of water of 0·4 because of the low solubility of the $E_T(30)$ dye in water-rich compositions. For the same reason, the E_T^N value of pure water at 25 °C was taken from Ref. 1.

The E_T^N values of the pure solvents at 25 °C are in good agreement ($\pm 0·01$) with those reported in the literature.[1-3] The E_T^N values of acetonitrile, dimethyl sulfoxide, 2-propanol and methanol at 50 and 75 °C differ by less than 0·005 from those reported by Laurence *et al.*[10] However, our E_T^N values for pure tert-butanol are about 0·04 E_T^N units higher than those reported by Laurence *et al.* Haak and Engberts[11] studied mixtures of water with acetonitrile and dimethyl sulfoxide at several temperatures and fitted the $E_T(30)$ values to empirical equations. Our results differ by less than 0·01 from the calculated values from these equations for pure acetonitrile and dimethyl sulfoxide. Although the compositions of the binary mixtures studied by Haak and Engberts are not the same as ours, the agreement between the two data sets can be approximately checked for close solvent compositions. For solvent compositions that differ by less than 0·02 mole fraction units, our values and those calculated from the equations of Haak and Engberts differ by less than 0·02 E_T^N units.

The data in Table 2 were fitted according to equation (9) and the results are presented in Table 3 for dimethyl sulfoxide mixtures, Table 4 for acetonitrile mixtures and Table 5 for nitromethane mixtures. Figures 1–4 show the plots obtained at 50 °C for the mixtures of the three dipolar hydrogen-bond acceptors with the alcohols and water. Plots of similar shape were obtained for the other temperatures but displaced towards lower (75 °C) or higher (30, 25 and 15 °C) E_T^N values.

The figures show that the behavior of acetonitrile and nitromethane binary systems is very similar, whereas the behavior of dimethyl sulfoxide mixtures is different. The similarity of the acetonitrile and nitromethane systems is not surprising because their polarity and hydrogen bond properties are very similar (Table 1). In fact, the behavior of the acetonitrile–nitromethane mixtures has recently been observed to be close to ideal.[12]

The main differences between dimethyl sulfoxide at the one hand and acetonitrile and nitromethane on the other are observed in the dipolar HBA-rich region. In this region, when the content in alcohol or water increases, the increase in E_T^N polarity, because of the formation of hydrogen-bonded complexes, is steeper for the nitromethane and acetonitrile systems than for the dimethyl sulfoxide system. This is reflected in the $f_{12/1}$ values in Tables 3–5. The $f_{12/1}$ values of the acetonitrile and nitromethane systems are much higher than those of the dimethyl sulfoxide systems. That is, the E_T indicator is much more preferentially solvated by the acetonitrile–co-solvent and nitromethane–co-solvent

Table 1. Properties of pure solvents at 25 °C[1,3,6,7]

Solvent	E_T^N	π^*	α	β	ε
Acetonitrile	0·460	0·75	0·19	0·40	36·05
Nitromethane	0·481	0·85	0·22	0·37	36·48
Dimethyl sulfoxide	0·444	1·00	0·00	0·76	46·45
tert-Butanol	0·389	0·41	0·68	1·01	12·47
2-Propanol	0·546	0·48	0·84	0·84	19·92
Methanol	0·762	0·60	0·98	0·66	32·66
Water	1·000	1·09	1·17	0·47	78·30

hydrogen-bonded complexes than by the dimethyl sulfoxide–co-solvent complexes. For this reason, maximum synergism is observed at lower alcohol concentrations for acetonitrile and nitromethane than for dimethyl sulfoxide mixtures.

Figures 1–3 show that the maximum synergism (as measured by the difference between the E_{T12}^N value and the highest E_{T1}^N or E_{T2}^N value) is observed for those binary systems with the closest E_{T1}^N and E_{T2}^N values, viz.

dimethyl sulfoxide–*tert*-butanol, acetonitrile–*tert*-butanol, acetonitrile–2-propanol, nitromethane–*tert*-butanol and nitromethane–2-propanol. This synergism is caused by the formation of a hydrogen-bonded complex more polar than the pure solvent components, provided that these solvents do not differ too much in their own polarities.[7] Table 1 shows that the E_T^N polarity of dimethyl sulfoxide is close to that of *tert*-butanol, and the polarities of acetonitrile and nitromethane lie

Table 2. E_T^N values of binary mixtures of dipolar hydrogen-bond acceptors with water and alcohols at several temperatures

Dimethyl sulfoxide mixtures				Acetonitrile mixtures				Nitromethane mixtures			
$x_{t\text{-BuOH}}$	25 °C	50 °C	75 °C	$x_{t\text{-BuOH}}$	25 °C	50 °C	75 °C	$x_{t\text{-BuOH}}$	25 °C	50 °C	75 °C
0·0000	0·442	0·427	0·414	0·0000	0·460	0·449	0·431	0·0000	0·480	0·455	0·436
0·0984	0·453	0·438	0·421	0·0997	0·513	0·480	0·464	0·0858	0·521	0·487	0·462
0·1969	0·462	0·446	0·429	0·3619	0·513	0·485	0·462	0·1943	0·528	0·494	0·467
0·4336	0·478	0·460	0·438	0·3751	0·506	0·483	0·453	0·4027	0·518	0·480	0·458
0·5906	0·478	0·455	0·433	0·4562	0·506	0·478	0·451	0·5894	0·501	0·471	0·442
0·7912	0·458	0·431	0·410	0·7027	0·483	0·453	0·431	0·7827	0·478	0·444	0·412
0·8808	0·444	0·418	0·398	1·0000	0·418	0·389	0·366	0·8760	0·458	0·425	0·398
1·0000	0·418	0·389	0·366					1·0000	0·418	0·389	0·366
$x_{i\text{-PrOH}}$	25 °C	50 °C	75 °C	$x_{i\text{-PrOH}}$	25 °C	50 °C	75 °C	$x_{i\text{-PrOH}}$	25 °C	50 °C	75 °C
0·0000	0·442	0·427	0·414	0·0000	0·460	0·449	0·431	0·0000	0·480	0·455	0·436
0·0987	0·473	0·453	0·436	0·1029	0·558	0·528	0·499	0·0847	0·574	0·538	0·494
0·1979	0·497	0·473	0·453	0·2317	0·579	0·553	0·506	0·2050	0·592	0·553	0·511
0·3974	0·528	0·499	0·478	0·3972	0·592	0·558	0·536	0·3047	0·598	0·556	0·521
0·4686	0·536	0·509	0·487	0·5043	0·601	0·558	0·528	0·5007	0·598	0·553	0·523
0·6150	0·548	0·518	0·492	0·5844	0·587	0·553	0·518	0·6444	0·595	0·558	0·517
0·7816	0·558	0·528	0·497	0·6154	0·592	0·566	0·523	0·7977	0·584	0·546	0·511
0·8908	0·558	0·528	0·492	0·7215	0·592	0·556	0·504	0·8953	0·574	0·541	0·499
0·9429	0·556	0·523	0·494	1·0000	0·536	0·511	0·492	1·0000	0·536	0·511	0·492
1·0000	0·536	0·511	0·492								
x_{MeOH}	15 °C	30 °C	50 °C	x_{MeOH}	15 °C	30 °C	50 °C	x_{MeOH}	15 °C	30 °C	50 °C
0·0000	0·449	0·440	0·427	0·0000	0·480	0·457	0·449	0·0000	0·493	0·477	0·455
0·0873	0·501	0·485	0·467	0·0617	0·657	0·628	0·590	0·1152	0·721	0·696	0·657
0·1751	0·553	0·531	0·511	0·0913	0·681	0·657	0·617	0·2209	0·749	0·724	0·696
0·3365	0·614	0·595	0·569	0·1844	0·724	0·699	0·666	0·4016	0·763	0·743	0·717
0·4860	0·669	0·648	0·623	0·4031	0·759	0·740	0·711	0·5976	0·773	0·753	0·730
0·6429	0·711	0·696	0·669	0·6172	0·769	0·756	0·730	0·8007	0·773	0·756	0·736
0·7946	0·743	0·727	0·705	0·7979	0·776	0·759	0·736	0·9031	0·773	0·756	0·736
0·9088	0·759	0·743	0·724	1·0000	0·766	0·749	0·733	1·0000	0·766	0·749	0·733
1·0000	0·766	0·749	0·733								
$x_{\text{H}_2\text{O}}$	25 °C	50 °C	75 °C	$x_{\text{H}_2\text{O}}$	25 °C	50 °C	75 °C	$x_{\text{H}_2\text{O}}$	25 °C	50 °C	75 °C
0·0000	0·442	0·427	0·414	0·0000	0·460	0·449	0·431	0·0000	0·480	0·455	0·436
0·3743	0·553	0·546	0·528	0·2952	0·717	0·693	0·660	0·0421	0·634	0·601	0·543
0·5569	0·654	0·651	0·617	0·4991	0·766	0·730	0·714	0·0969	0·684	0·657	0·603
0·6984	0·687	0·678	0·631	0·5700	0·773	0·756	0·717	0·1400	0·681	0·675	0·634
0·8129	0·786	0·763	0·740	0·7520	0·796	0·783	0·763	0·1888	0·687	0·669	0·654
0·8895	0·846	0·839	0·796	0·8450	0·832	0·824	0·803	0·2989	0·746	0·733	0·654
0·9451	0·899	0·883	0·839	0·9146	0·879	0·861	0·832	0·3933	0·733	0·699	0·678
1·0000	1·000[a]			1·0000	1·000[a]			1·0000	1·000[a]		

[a] Value from Ref. 1.

Table 3. Parameters of binary mixtures of dimethyl sulfoxide with three alcohols and water at various temperatures

Solvent 2	$t(°C)$	E_{T1}^{N}	E_{T2}^{N}	E_{T12}^{N}	$f_{2/1}$	$f_{12/1}$	S.d.	n
tert-Butanol	25	0·442	0·419	0·553	0·58	0·98	0·001	8
	50	0·427	0·390	0·523	0·66	1·2	0·002	8
	75	0·413	0·366	0·483	0·53	1·3	0·002	8
2-Propanol	25	0·442	0·536	0·572	0·13	2·9	0·001	10
	50	0·427	0·511	0·542	0·20	2·6	0·001	10
	75	0·414	0·492	0·517	2·0	2·2	0·002	10
Methanol	15	0·449	0·766	0·768	0·24	2·1	0·003	9
	30	0·440	0·749	0·743	0·52	1·8	0·002	9
	50	0·427	0·733	0·724	0·35	1·7	0·002	9
Water	25	0·442	1·000	0·829	0·046	0·69	0·017	8
	50	0·426	0·966	0·667	0·25	1·4	0·023	7
	75	0·414	0·911	0·521	1·1	3·8	0·027	7

Table 4. Parameters of binary mixtures of acetonitrile with three alcohols and water at various temperatures

Solvent 2	$t(°C)$	E_{T1}^{N}	E_{T2}^{N}	E_{T12}^{N}	$f_{2/1}$	$f_{12/1}$	S.d.	n
tert-Butanol	25	0·460	0·418	0·528	12	41	0·003	7
	50	0·449	0·390	0·510	4·2	11	0·001	7
	75	0·431	0·366	0·472	17	63	0·004	7
2-Propanol	25	0·460	0·536	0·606	1·5	18	0·005	9
	50	0·449	0·511	0·573	2·0	16	0·005	9
	75	0·432	0·490	0·565	6·2	7·6	0·010	9
Methanol	15	0·481	0·766	0·778	0·029	21	0·003	8
	30	0·457	0·749	0·763	0·0050	19	0·004	8
	50	0·449	0·733	0·741	0·0076	14	0·003	8
Water	25	0·460	1·001	0·766	0·94	11	0·007	8
	50	0·449	0·967	0·739	1·1	9·7	0·008	7
	75	0·431	0·901	0·703	1·7	9·1	0·007	7

Table 5. Parameters of binary mixtures of nitromethane with three alcohols and water at various temperatures

| Solvent 2	$t(°C)$	E_{T1}^{N}	E_{T2}^{N}	E_{T12}^{N}	$f_{2/1}$	$f_{12/1}$	S.d.	n
tert-Butanol	25	0·480	0·419	0·542	7·9	25	0·002	8
	50	0·455	0·389	0·506	7·6	24	0·003	8
	75	0·436	0·366	0·486	5·7	14	0·002	8
2-Propanol	25	0·480	0·536	0·609	3·3	29	0·001	9
	50	0·455	0·511	0·564	3·6	36	0·003	9
	75	0·436	0·491	0·540	5·1	13	0·003	9
Methanol	15	0·493	0·766	0·778	2·1	30	0·002	8
	30	0·477	0·749	0·758	0·057	27	0·001	8
	50	0·455	0·733	0·739	0·089	19	0·001	8
Water	25	0·480	0·801	0·660	198	87	0·021	7
	50	0·465	0·733	0·615	417	48	0·026	7
	75	0·436	0·683	0·630	148	17	0·010	7
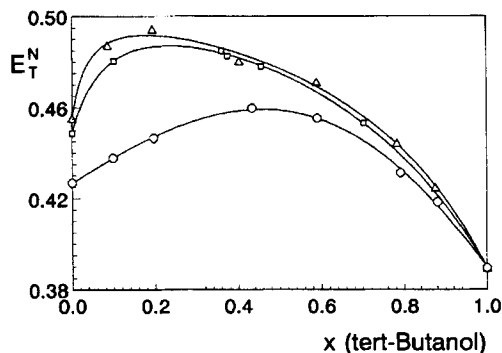
Figure 1. Binary mixtures of dipolar hydrogen-bond acceptors with *tert*-butanol at 50 °C. Co-solvent: (o) dimethyl sulfoxide; (□) acetonitrile; (△) nitromethane
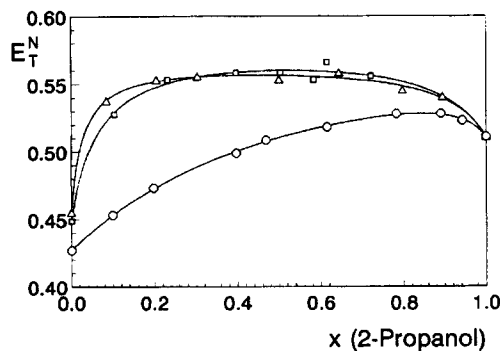

Figure 2. Binary mixtures of 2-propanol with dipolar hydrogen-bond acceptors at 50 °C. Symbols as in Figure 1
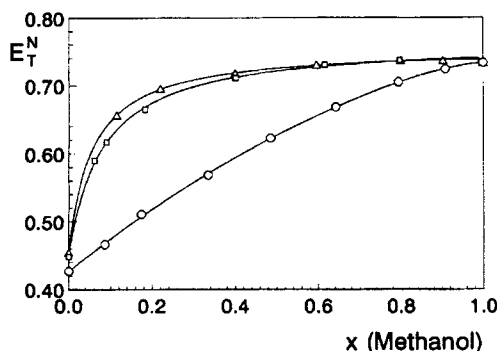

Figure 3. Binary mixtures of methanol with dipolar hydrogen-bond acceptors at 50 °C. Symbols as in Figure 1
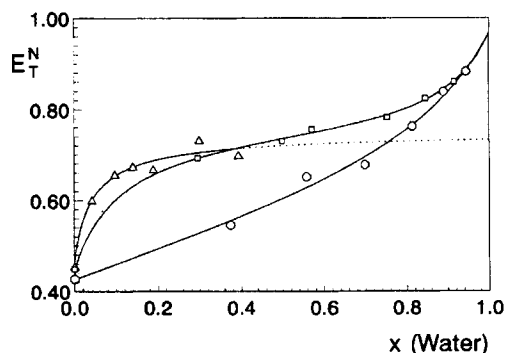

Figure 4. Binary mixtures of water with dipolar hydrogen-bond acceptors at 50 °C. Symbols as in Figure 1

between those of *tert*-butanol and 2-propanol. The difference in E_T^N polarity between methanol and the HBA solvents is fairly large ($0.27-0.31$ E_T^N units) and this results in an E_{T12}^N value close to that of methanol. Consequently, methanol mixtures are only slightly synergetic or even show no synergism as for dimethyl sulfoxide, which has the lowest polarity.

Water has an E_T^N value much higher than those of the HBA solvents and therefore its mixtures are not synergetic at all.[7] Figure 4 presents the results obtained for these mixtures. The E_T^N values of dimethyl sulfoxide–water mixtures increase smoothly with the water content, as explained earlier. However, the high $f_{12/1}$ and the close to unity $f_{2/1}$ values of acetonitrile–water together with the E_{T12}^N value close to the average of E_{T1}^N and E_{T2}^N determines the reversed S shape of its plot.[7] Nitromethane–water is expected to show similar behavior. It is found that the nitromethane-rich region follows this trend, but the exact trend of the water-rich region cannot be exactly determined because of the lack of data. However, the shape of the plot must be similar to that for acetonitrile–water to reach the E_T^N value expected for pure water (about 0.97 for 50 °C). Although the E_T^N value of pure water has not been measured because of the insolubility of the $E_T(30)$ dye, the extrapolations of the dimethyl sulfoxide–water and acetonitrile–water plots lead to concordant values (0.966 ± 0.001 and 0.906 ± 0.005 for 50 and 75 °C, respectively). These values are not far from those calculated from the equations of Haak and Engberts[11] (0.957 and 0.925, respectively).

The E_T^N values of the mixtures not only vary with the solvent composition (solvatochromism) but also with the temperature of the medium (thermochromism). The $E_T(30)$ indicator exhibits a negative thermo-solvato-chromism, caused by the increased differential stabilization of the dipolar betaine ground state, relative to its less dipolar excited state, with decrease in temperature.[13] At low temperatures, the solute–solvent
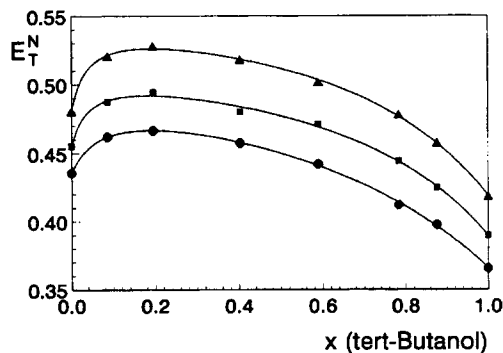
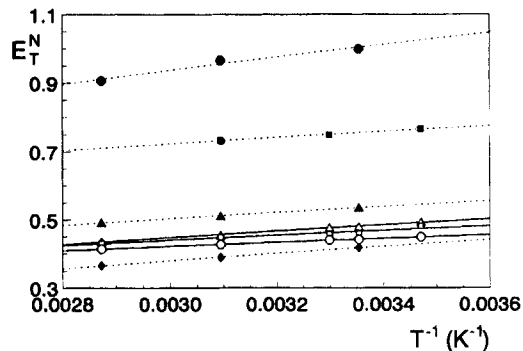Figure 5. Binary mixtures of nitromethane and *tert*-butanol at different temperatures: (▲) 25 °C; (■) 50 °C; (●) 75 °C

Figure 6. Variation of the E_T^N values of pure solvents with the reciprocal of absolute temperature: (○) dimethyl sulfoxide; (□) acetonitrile; (△) nitromethane; (◆) *tert*-butanol; (▲) 2-propanol; (■) methanol; (●) water

interactions between the $E_T(30)$ indicator and the solvent molecules are strengthened, and the transition energy and thus the E_T^N value increase. This can be observed in Figure 5 for the nitromethane–*tert*-butanol mixtures. In general, it is found that the synergism increases with decreasing temperature. For example, the plot for nitromethane–*tert*-butanol at 25 °C is more convex than the same plot for 50 or 75 °C. This is related to the different variation of the E_T^N values of the pure solvents and hydrogen-bonded complexes with temperature.

Haak and Engberts[11] related the $E_T(30)$ values of pure and mixed solvents with absolute temperature (T) empirically through a linear relationship. However, we observed that the fit is better with a linear relationship between E_T^N and $1/T$, according to the equation

$$E_T^N = a + b/T \qquad (11)$$

The plots obtained for these correlations are presented in Figure 6 for pure solvents and in Figure 7 for the hydrogen-bonded complexes. The numerical results are given in Table 6. The order of the susceptibility to the change in temperature (b coefficient) is dipolar HBA solvents < alcohols < hydrogen-bonded complexes. These results agree with those of Laurence *et al.*,[10] who related the change in E_T values with temperature to the main solute–solvent interactions expected. A small change is expected for alkane solvents because the interactions by dispersion and induction do not depend on temperature. A major change is expected for dipolar solvents because the energy of orientation depends on $1/T$, and this explains the better fit with $1/T$ than with T. A major change is expected even for the HBD–HBA solvents (e.g. alcohols and water), because the change
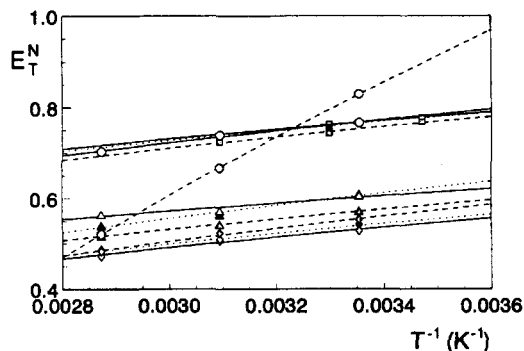
Table 6. Parameters for correlation of E_T^N with temperature according to equation (11)

Solvent	a	$b(K)$	S.d.	r
Dimethyl sulfoxide	0·245	58·8	0·001	0·9994
Acetonitrile	0·222	72·4	0·006	0·96
Nitromethane	0·161	95·5	0·001	0·9986
tert-Butanol	0·055	108·1	0·001	0·9998
2-Propanol	0·229	91·5	0·001	0·9994
Methanol	0·462	87·5	0·002	0·998
Water	0·357	193·4	0·014	0·98
Dimethyl sulfoxide–*tert*-butanol	0·071	144·5	0·006	0·992
Dimethyl sulfoxide–2-propanol	0·189	114·2	0·0003	0·99997
Dimethyl sulfoxide–methanol	0·363	116·3	0·004	0·992
Dimethyl sulfoxide–water	−1·313	639·0	0·003	0·99989
Acetonitrile–*tert*-butanol	0·146	115·0	0·010	0·97
Acetonitrile–2-propanol	0·313	86·2	0·009	0·96
Acetonitrile–methanol	0·436	98·7	0·002	0·998
Acetonitrile–water	0·332	130·0	0·006	0·992
Nitromethane–*tert*-butanol	0·148	116·9	0·005	0·993
Nitromethane–2-propanol	0·123	144·1	0·006	0·992
Nitromethane–methanol	0·418	103·4	0·002	0·998

Figure 7. Variation of the E_T^N values of hydrogen-bonded complexes with temperature: (◇) acetonitrile–tert-butanol; (△) acetonitrile–2-propanol; (□) acetonitrile–methanol; (○) acetonitrile–water; (◆) nitromethane–tert-butanol; (▲) nitromethane–2-propanol; (■) nitromethane–methanol; (◆) dimethyl sulfoxide–tert-butanol; (▲) dimethyl sulfoxide–2-propanol; (■) dimethyl sulfoxide–methanol; (●) dimethyl sulfoxide–water

in temperature has a large effect on the equilibrium constant for hydrogen-bond formation. Because of the nature of hydrogen-bonded complexes, the influence of temperature on their E_T values must be similar to or higher than that on the E_T values of alcohols. The most striking case is that of dimethyl sulfoxide–water which has a susceptibility about five times larger than those of the other hydrogen-bonded complexes and three times larger than that of water.

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