

UV–visible spectroscopic study of the hydrophilic and solvatochromic 4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate betaine dye in eight binary solvent mixtures

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ABSTRACT: Solvent effects on the recently synthesized hydrophilic and negatively solvatochromic 4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate betaine dye [$E_T(8)$ dye] in binary solvent mixtures of dimethyl sulfoxide and acetonitrile with water, methanol, propan-2-ol and 2-methylpropan-2-ol were studied by UV–visible spectroscopy and compared with analogous measurements of the standard $E_T(30)$ betaine dye [2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate]. A preferential solvation model was applied to the data obtained. The applicability of the $E_T(8)$ betaine dye for the determination of $E_T(30)$ values for aqueous media is discussed. Copyright © 2003 John Wiley & Sons, Ltd.

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KEYWORDS: solvent effects; specific solvation; binary solvent mixtures; pyridinium *N*-phenolate betaine dyes; synergistic effects

INTRODUCTION

The large negative solvatochromism of the betaine dye **1** [2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate] (Scheme 1) has been used for a long time to measure empirically solvent polarities by means of $E_T(30)$ parameters.^{1,2}

The $E_T(30)$ parameter is defined as the molar electronic transition energy (in kcal mol⁻¹; 1 kcal = 4.184 kJ) of betaine dye **1** in a particular solvent according to the equation

$$E_T[\text{kcal mol}^{-1}] = hc\tilde{\nu}_{\text{max}}N_A = (2.8591 \times 10^{-3}) \times \tilde{\nu}_{\text{max}}[\text{cm}^{-1}] = 28591/\lambda_{\text{max}}[\text{nm}] \quad (1)$$

where h is Planck's constant, c is the speed of light, N_A is Avogadro's number and $\tilde{\nu}_{\text{max}}$ is the wavenumber and λ_{max} the wavelength of the solvent-dependent visible absorption maximum of the reference dye. The number 30 stems

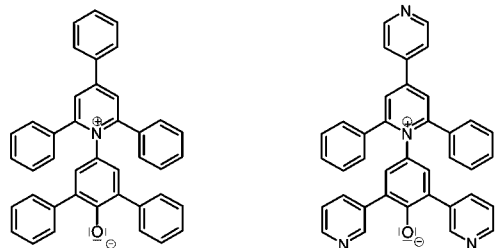
from the original publication,³ where dye **1** had by chance the reference number 30. $E_T(30)$ polarity values have been determined for more than 360 solvents,^{1,2} numerous binary^{1,4–13} and even some ternary^{11,14} solvent mixtures.

The very low solubility of the indicator dye **1** in water does not allow the direct determination of $E_T(30)$ parameters in water-rich regions of binary aqueous systems. Recently, Reichardt *et al.*^{2,15} proposed a new dye, i.e. 4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate (**2**), which is readily soluble in water and is thus suitable for the determination of the empirical solvatochromic polarity characteristics of aqueous media. The $E_T(8)$ parameter (using the notation from the original paper¹⁵) of the new betaine dye **2** is defined analogously to $E_T(30)$ by Eqn (1). $E_T(8)$ parameters of 26 pure solvents and one binary solvent mixture (water/1,4-dioxane) have been published.¹⁵

In the present study, $E_T(8)$ parameters of eight binary mixtures [acetonitrile (MeCN) and dimethyl sulfoxide (DMSO) with water, methanol (MeOH), propan-2-ol (iPrOH) and 2-methylpropan-2-ol (tBuOH)] were measured and compared with the $E_T(30)$ data from our earlier measurements^{4,5} and from the literature.^{6,7} All these E_T data were analyzed in terms of a two-step solvent-exchange model developed by Rosés *et al.*⁸

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**1** – standard $E_T(30)$ **2** – water-soluble

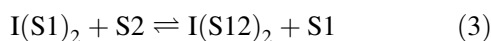
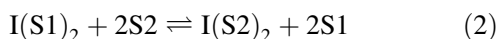
betaine dye

 $E_T(8)$ betaine dye

Scheme 1

Solvation model

The preferential solvation model is based on the two-step solvent-exchange model first proposed by Skwierczynski and Connors⁷ and further extended by Rosés *et al.*⁸ For the particular case of a solvatochromic indicator dye I in a mixture of two specifically solvating components, S1 and S2, equilibria (2) and (3) should be considered:



where S12 represents a solvent complex formed by specific interaction between solvent S1 and solvent S2.⁸ In our case, $I(S1)_2$, $I(S2)_2$ and $I(S12)_2$ represent the E_T indicator dye solvated by the pure solvents S1 and S2 and by the inter-solvent complexes S12, respectively. In more general cases, a more complex scheme has to be considered.^{8,11}

For the more specific solvation equilibria (2) and (3), which allow an arbitrary degree of self-association of components S1 and S2, two preferential solvation parameters, $f_{2/1}$ and $f_{12/1}$, are defined for these solvent-exchange processes:

$$f_{2/1} = \frac{x_2^S/x_1^S}{(x_2^0/x_1^0)^2} \quad (4)$$

$$f_{12/1} = \frac{x_{12}^S/x_1^S}{x_2^0/x_1^0} \quad (5)$$

where x_1^S , x_2^S , and x_{12}^S are the mole fractions of the individual solvents S1, S2 and their association complex S12, respectively, in the solvation sphere of the indicator dye, I, and x_1^0 and x_2^0 are the mole fractions of the two solvents in the bulk binary solvent mixture. The parameters $f_{2/1}$ and $f_{12/1}$ measure the preference of the indicator dye I to be solvated by solvents S2 and S12 with reference to solvation by solvent S1.

In the special case of E_T polarity parameters, the polarity of binary solvent mixtures is calculated as the weighted average of the E_T values of solvents S1, S2, and

S12 in the solvation sphere of the indicator dye, using the respective mole fractions x_1^S , x_2^S , and x_{12}^S as weights, according to Eqn (6):

$$E_T = x_1^S E_{T1} + x_2^S E_{T2} + x_{12}^S E_{T12} \quad (6)$$

$$x_1^0 + x_2^0 = x_1^S + x_2^S + x_{12}^S = 1 \quad (7)$$

From Eqns (4)–(7), Eqn (8) follows, which relates the E_T values of a binary solvent mixture to the E_T values of the two pure solvents, the preferential solvation parameters and the solvent composition:

$$E_T = \frac{E_{T1} (1 - x_2^0)^2 + E_{T2} f_{2/1} (x_2^0)^2 + E_{T12} f_{12/1} (1 - x_2^0) x_2^0}{(1 - x_2^0)^2 + f_{2/1} (x_2^0)^2 + f_{12/1} (1 - x_2^0) x_2^0} \quad (8)$$

This equation has been applied successfully to various binary solvent mixtures using different solvatochromic dyes^{5,7–11,16} and rate constants of some aromatic nucleophilic substitution reactions carried out in binary solvent mixtures.^{17,18}

An alternative, not yet formalized approach to this problem was described by Koppel and Koppel.⁴

EXPERIMENTAL

Apparatus

Absorption spectra were recorded in 10 mm quartz cells on a Perkin-Elmer Lambda 2S UV–visible spectrophotometer equipped with a thermostated ($25.0 \pm 0.1^\circ\text{C}$) cuvette holder. The wavelength accuracy of the spectrophotometer was checked with a didymium filter (Hitachi) having absorption maxima at $\lambda_{\text{max}} = 403.3, 529.5$ and 586.0 nm. The spectra were recorded and further treated on a computer.

Reagents

The indicator dye 4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate (**2**) was synthesized by the procedure described recently.¹⁵ DMSO and MeCN of the highest available purity from Aldrich were used without further purification. Deionized water prepared with a Purite Analyst HP 5 analytical water system was used. The alcohols (chemically pure, Reakhim) were further purified and dried according to the methods used earlier.⁴

Procedure

For each binary solvent system, a ca 10^{-4} M solution of Reichardt's indicator dye **1** or **2** was prepared in one of

the two pure solvents (solvent 1) and placed in the spectrophotometer cell. The cell was closed with a Teflon cap and weighed (± 0.05 mg). After recording the spectrum (range 450–700 nm), a drop of solvent 2 was added to the cell via the Teflon tube, the solution was stirred with a magnetic stirrer, then the cell was again weighed and the visible spectrum of the new solution was recorded. The procedure was repeated after the addition of new drops of solvent 2. Subsequent sets of experiments were performed starting with a solution of betaine dyes **1** and **2** in 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 assure concordance of the results.

Calculation methods

The E_T values for both dyes in each solvent mixture were calculated from the maximum of the $\pi \rightarrow \pi^*$ charge-transfer (CT) absorption band through Eqn (1). The wavelength of the CT absorption band maximum was calculated by fitting the spectra to a Gauss function using Mathcad 2000 software (MathSoft). The goodness of fit was checked using residuals plot according to

$$y = ae^{-[b(x-c)]^2} \quad (9)$$

where y is the absorbance at wavelength x and a , b , and c are regression coefficients. Parameter c was used as the absorption band maximum.

The E_{T1} , E_{T2} , E_{T12} , $f_{2/1}$ and $f_{12/1}$ parameters of Eqn (8) were calculated by non-linear regression using Mathcad 2000 software, minimizing the sum of squared residuals of the E_T values.

RESULTS

Pure solvents

A comparison of measured $E_T(8)$ values of pure solvents with literature¹⁵ values along with the $E_T(30)$ parameters

and some physical properties of the pure solvents are presented in Table 1. Very good agreement between the experimental and literature values was found.

Reichardt *et al.*¹⁵ found a good linear relationship between $E_T(30)$ and $E_T(8)$ values for hydrogen-bond donor (HBD) and non-HBD (altogether $n = 26$) solvents with a correlation coefficient $r = 0.987$ and a standard deviation $\sigma[E_T(8)] = 1.172$ kcal mol⁻¹ according to

$$E_T(8) = 0.948E_T(30) + 2.799 \quad (10)$$

However, the linear correlation was found to be much better when HBD and non-HBD solvents were analyzed separately. For 12 HBD solvents, Eqn (11) was found with $r = 0.998$ and $\sigma[E_T(8)] = 0.238$, valid for $E_T(30)$ values ranging from 47.7 for decan-1-ol to 63.1 kcal mol⁻¹ for water:

$$E_T(8)(\text{HBD}) = 0.704E_T(30) + 16.236 \quad (11)$$

For 14 non-HBD solvents, Eqn (12) was found with $r = 0.997$ and $\sigma[E_T(8)] = 0.428$, valid for $E_T(30)$ values ranging from 34.3 for benzene to 55.8 kcal mol⁻¹ for formamide:

$$E_T(8)(\text{non-HBD}) = 0.914E_T(30) + 3.610 \quad (12)$$

Inclusion of tBuOH in the regression data set of 12 HBD solvents makes the correlation slightly worse ($n = 13$, $r = 0.994$, $\sigma[E_T(8)] = 0.444$), but extends the applicability of Eqn (11) by almost 4 kcal mol⁻¹ on the $E_T(30)$ scale (down to 43.8 kcal mol⁻¹), according to

$$E_T(8)(\text{HBD}) = 0.735E_T(30) + 14.508 \quad (13)$$

Binary solvent mixtures

Binary mixtures of dipolar aprotic solvents such as DMSO and MeCN with the HBD co-solvents water, MeOH, iPrOH, and tBuOH were investigated. The $E_T(8)$ values obtained were compared with the $E_T(30)$ data taken from our previous experiments^{4,5} and the literature.^{6,7}

Table 1. Properties of eight pure solvents at 25 °C (ϵ_r = dielectric permittivity, μ = dipole moment, n_D = refractive index)

Solvent	$E_T(8)^a$	$E_T(8)^b$	$E_T(30)^c$	ϵ_r^d	$\mu \times 10^{30}(\text{C m})^d$	n_D^d
DMSO	45.2	45.2	45.0	46.45	13.5	1.4793
MeCN	45.6	45.5	45.7	35.94	13.0	1.3441
Water	60.3	60.4	63.1	78.36	6.2	1.3330
MeOH	55.6	55.6	55.4	32.66	9.6	1.3284
iPrOH	50.3	50.2	48.3	19.92	5.5	1.3772
tBuOH	45.6	—	43.7	12.47	5.5	1.3877

^a This work.

^b From Ref. 15.

^c From Ref. 4.

^d From Refs 2 and 19.

Table 2. Parameters of the preferential solvation model for the eight binary solvent mixtures studied (SD = standard deviation of the fit, df = degrees of freedom)

Solvent 1	Solvent 2	$f_{2/1}$	$f_{12/1}$	E_{T12}	E_{T1}	E_{T2}	SD	df
$E_T(30)$								
DMSO	Water	0.01	0.43	61.4	44.9	63.2	0.411	28
DMSO	MeOH	0.14	1.96	55.2	45.2	55.4	0.161	15
DMSO	iPrOH	0.41	1.87	50.0	45.0	48.3	0.160	21
DMSO	tBuOH	0.61	1.39	48.5	45.1	43.8	0.147	24
MeCN	Water	1.2	13	55.0	45.7	62.7	0.325	27
MeCN	MeOH	0.21	20	55.7	45.7	55.4	0.203	8
MeCN	iPrOH	1.8	24	50.5	45.6	48.3	0.328	13
MeCN	tBuOH	12	36	48.3	45.6	43.8	0.354	13
$E_T(8)$								
DMSO	Water	0.26	1.1	52.4	45.2	60.2	0.087	40
DMSO	MeOH	0.19	1.6	55.5	45.3	55.6	0.051	43
DMSO	iPrOH	0.17	2.0	50.6	45.2	50.2	0.015	24
DMSO	tBuOH	0.42	1.6	48.8	45.2	45.6	0.008	28
MeCN	Water	1.1	10	54.8	45.6	60.5	0.081	39
MeCN	MeOH	630	77	49.0	45.6	55.7	0.039	39
MeCN	iPrOH	1.5	18	51.1	45.7	50.2	0.036	32
MeCN	tBuOH	3.6	23	48.6	45.5	45.6	0.030	54

The $E_T(30)$ and $E_T(8)$ parameters of the binary mixtures were investigated by means of the preferential solvation model according to Eqn (8). The results are presented in Table 2. From Table 2, and also from Figs 1 and 2, one can see that mixtures of DMSO and MeCN with iPrOH and tBuOH are synergistic (i.e. at some composition of the mixture the E_T value is higher than that for the corresponding pure solvents). The presence of a rather shallow, not well-expressed maximum for $E_T(30)$ values of the mixture MeCN–MeOH has also been reported earlier by two other groups.^{4,11}

The synergistic maxima are less pronounced for $E_T(8)$ than for $E_T(30)$ versus mole fraction plots. The $E_T(8)$ indicator dye can form three additional hydrogen bonds with HBD solvents via its three pyridyl rings, which results in an additional stabilization of its electronic ground state. This, in turn, makes the $E_T(8)$ dye less sensitive to changes in its solvation sphere,¹⁵ thus lowering the synergistic maximum as compared with that of $E_T(30)$. At the same time, the maxima of the $E_T(8)$ curves are shifted towards higher concentrations of alcohol by about 0.16 units as compared with the $E_T(30)$ maxima. This effect can be explained in terms of the parameters of the preferential solvation model in Table 2. In the mixtures of DMSO with alcohols, the indicator dye is preferentially solvated by DMSO as compared with the hydroxylic component and hydrogen-bonded complex ($f_{2/1} < 1$ and $f_{12/1}$ is relatively small). Smaller values of $f_{2/1}$ for $E_T(8)$ as compared with $f_{2/1}$ for $E_T(30)$ explain the shift of the synergistic maximum. The situation is rather different for the mixtures of MeCN. According to the $f_{12/1}$ values, the indicator dye is preferentially solvated by solvent–solvent hydrogen-bonded complexes, which determines the position of the maximum.

The deviation of E_T from its mole fractional additivity, ΔE_T , is calculated by the equation

$$\Delta E_T = E_T - x_1 E_T^1 - x_2 E_T^2 \quad (14)$$

where x_1 and x_2 are the mole fractions and E_T^1 and E_T^2 are the E_T parameters of solvents 1 and 2, respectively,

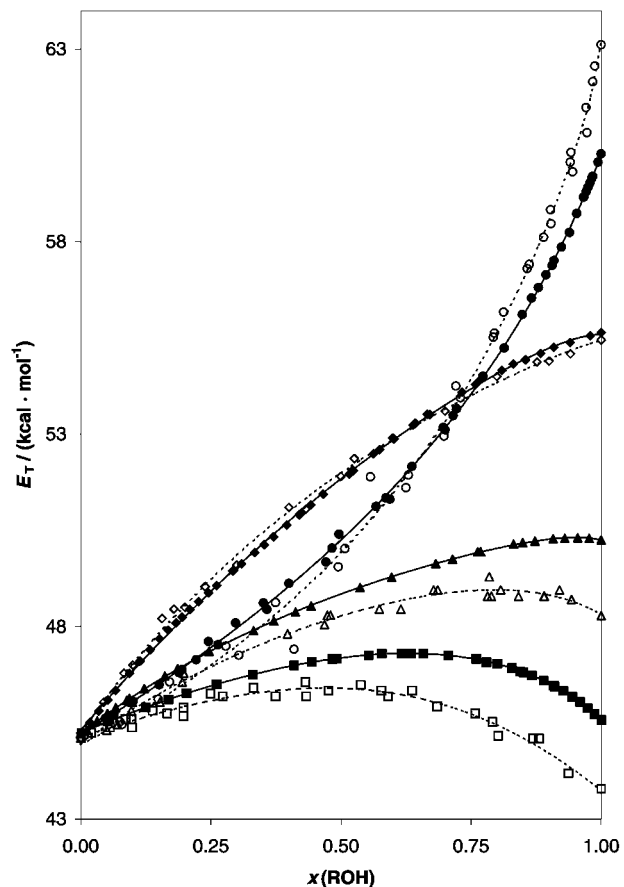


Figure 1. $E_T(8)$ (closed symbols and full lines) and $E_T(30)$ (open symbols and dashed lines) of the binary mixtures of DMSO with HBD solvents: \circ , water; \diamond , MeOH; \triangle , iPrOH; \square , tBuOH. $x(\text{ROH})$ = mole fraction of water or alcohol

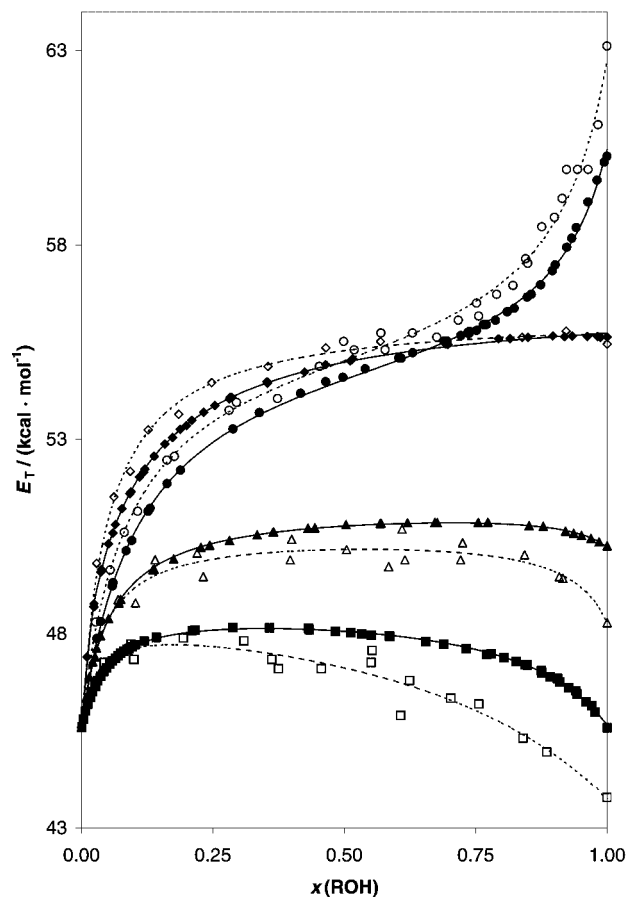


Figure 2. $E_T(8)$ (closed symbols and full lines) and $E_T(30)$ (open symbols and dashed lines) of the binary mixtures of MeCN with HBD solvents (symbols as in Fig. 1)

and the results are presented as function of the solvent composition in Figs 3 and 4 [the lines are computed from model Eqn (8), and from Eqn (14), using parameters from Table 2; experimental points are omitted for clarity]. It can be seen that in all cases $E_T(30)$ shows more pronounced deviations from linearity than $E_T(8)$. For example, the highest positive deviation from additivity in the case of DMSO mixtures is observed for $\Delta E_T(30)$ of the mixture DMSO–tBuOH with ca 2 kcal mol^{-1} [$\Delta E_T(8) \approx 1.8 \text{ kcal mol}^{-1}$]. In the binary mixtures of MeCN, the maximum $\Delta E_T(30)$ is observed for MeCN–MeOH with ca $6.4 \text{ kcal mol}^{-1}$ [$\Delta E_T(8) \approx 5.8 \text{ kcal mol}^{-1}$].

The binary mixtures of MeCN and DMSO with water exhibit negative deviations from linearity (Figs 1 and 3). The DMSO–water mixture shows a minimum at an approximate water mole fraction of $x(\text{H}_2\text{O}) = 0.65$ [$\Delta E_T(30)$ and $\Delta E_T(8)$ have minima at the same concentration]. The appearance of an extremum at that concentration has been explained as being due to the maximum concentration of associates such as $\text{DMSO} \cdot 2\text{H}_2\text{O}$ in the mixture.^{20,21}

The plot of ΔE_T for MeCN–water versus mole fraction of water has two extrema (Fig. 4). At first it reaches a maximum at a water mole fraction of $x(\text{H}_2\text{O}) \approx 0.15$ and a minimum at $x(\text{H}_2\text{O}) = 0.88$. In the range $0.2 \leq$

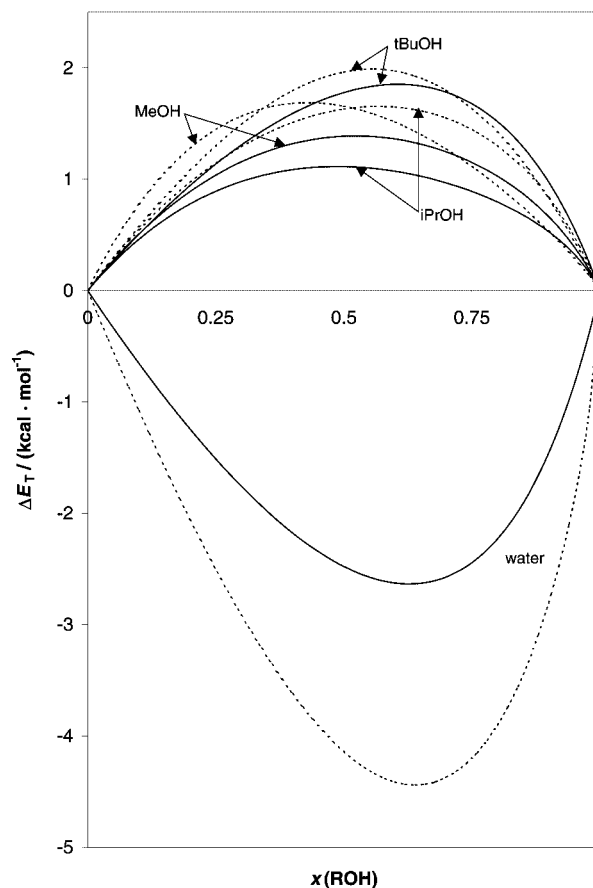


Figure 3. Deviation of $E_T(8)$ (full lines) and $E_T(30)$ (dashed lines) of the binary mixtures of DMSO with HBD solvents from the mole fractional additivity

$x(\text{H}_2\text{O}) \leq 0.8$, the E_T parameters vary linearly with the composition (Figs 2 and 4). Such a behavior can be explained^{13,22} in terms of the Naberukhin–Rogov²³ structural model. According to this model, the structure of water is enhanced by addition of MeCN up to a mole fraction of $0.15 \leq x(\text{MeCN}) \leq 0.2$. In the MeCN concentration range $0.3 \leq x(\text{MeCN}) \leq 0.7$, two microphases exist in the system: highly structured globules of water and a disordered microphase consisting predominantly of MeCN. Within this range, the composition of the microphases remains constant in addition to the size of the globules; only the number of globules and their distances apart can change.²³ At MeCN concentrations higher than $x(\text{MeCN}) = 0.8$, the globules of water ‘dissolve’ and the E_T value rapidly decreases to the value of pure MeCN. In terms of the solvation model parameters, the sigmoid shape of E_T for the MeCN–water mixture is due to the preferential solvation of the indicator dye by the hydrogen-bonded MeCN–water complex (high $f_{12/1}$) and the equal solvating power of the components of the binary solvent mixture ($f_{2/1}$ about unity).

Figure 5 shows $E_T(8)$ versus $E_T(30)$ for the binary mixtures of DMSO (mixtures of MeCN are omitted for the sake of clarity because the same trends hold for the mixtures of MeCN). The straight lines are calculated

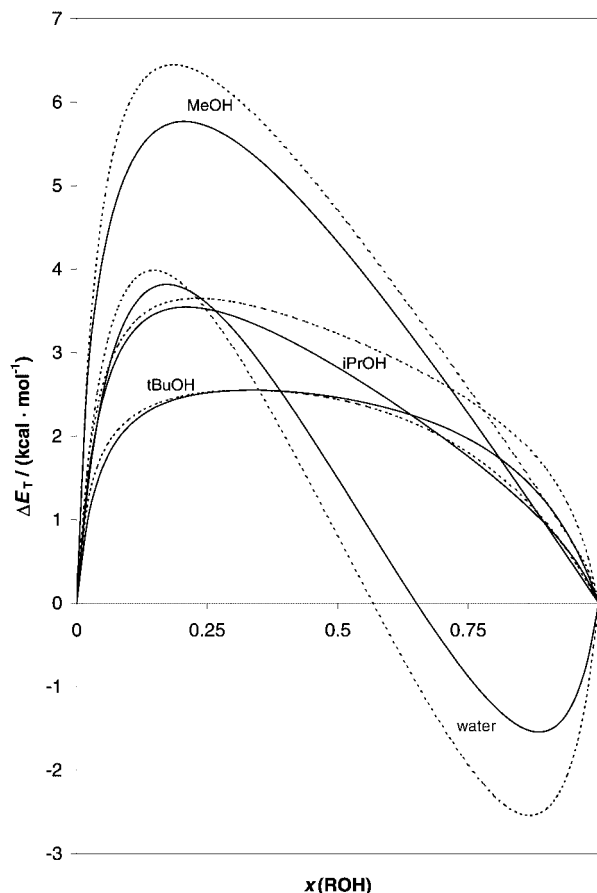


Figure 4. Deviation of $E_T(8)$ (full lines) and $E_T(30)$ (dashed lines) of the binary mixtures of MeCN with HBD solvents from the mole fractional additivity

from Eqns (10)–(12). It can be observed that the binary mixtures with a low content of the hydroxylic component follow the general correlation Eqn (10); only the DMSO–MeOH mixture seems to deviate from this general trend. At higher concentrations of the hydroxylic components, the linearity is lost and the synergistic mixtures (mixtures with tBuOH and iPrOH) even turn back downwards. The binary mixtures with a higher water content are best described by Eqn (11) for HBD solvents. Owing to the low solubility of the $E_T(30)$ betaine dye in water and mixtures rich in water, the $E_T(8)$ betaine dye has been suggested as a reference probe for the calculation of $E_T(30)$ values through Eqn (10).¹⁵ Considering Fig. 5, the use of Eqn (11) is justified at least in the case of some aqueous binary mixtures for which $E_T(8)$ values higher than about 56 kcal mol^{-1} are observed. The use of linear correlations of the type of Eqns (10), (11), and (12) for non-aqueous binary solvent mixtures can lead to unacceptably large errors.

CONCLUSIONS

The solvatochromic effects of 4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate

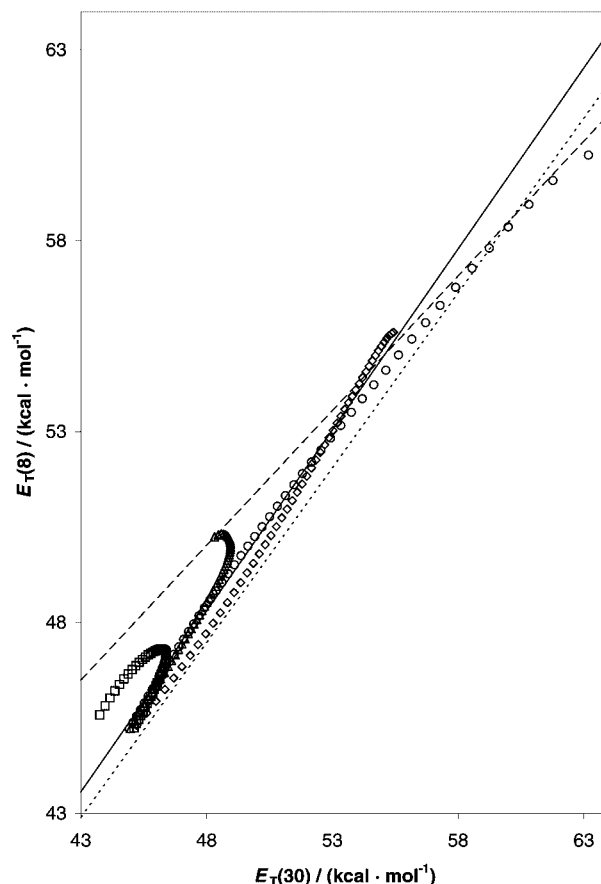


Figure 5. $E_T(8)$ versus $E_T(30)$ for binary mixtures of DMSO with HBD solvents: \circ , water; \diamond , MeOH; \triangle , iPrOH; \square , tBuOH. $x(\text{ROH})$ = mole fraction of water or alcohol. Linear regression lines: dashed line, HBD solvents [Eqn (11)]; dotted line, non-HBD solvents [Eqn (12)]; full line, all solvents [Eqn (10)]. The data points are calculated from Eqn (8) with parameters from Table 2

(2) by means of its $E_T(8)$ parameters were measured in binary mixtures of dipolar aprotic solvents (DMSO, MeCN) with protic solvents (water, MeOH, iPrOH and tBuOH) over the complete composition range. Comparison of the results to the $E_T(30)$ data revealed (see Figs 3 and 4) that the $E_T(30)$ betaine dye is slightly more sensitive towards the changes in the composition of the mixture, the differences being larger at compositions with a higher water or alcohol content. All the data can be fitted to the preferential solvation model.

It was shown that the $E_T(8)$ betaine dye can be used for the estimation of $E_T(30)$ parameters of binary aqueous mixtures with high water content by means of Eqn (11). In addition, the $E_T(8)$ betaine dye by itself can serve as a useful additional indicator dye for the empirical determination of solvent polarities.

Supplementary material

A table with solvent compositions, wavelengths of absorption maxima and $E_T(8)$ values of the binary mixtures

studied is available as supplementary material at the epoc website at <http://www.wiley.com/epoc>.

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