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UV–Vis 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 aqueous tetra-*n*-butylammonium bromide

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ABSTRACT: The solvent influence 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] dissolved in binary water–tetra-*n*-butylammonium bromide mixtures was studied by UV–Vis 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 $E_T(8)$ betaine dye can be applied for the determination of $E_T(30)$ values for aqueous media. However, the nonlinear nature of the relationship has to be taken into account if accurate results are desired. Copyright © 2005 John Wiley & Sons, Ltd.
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KEYWORDS: solvent effects; specific solvation; binary solvent mixtures; pyridinium *N*-phenolate betaine dyes; synergistic effects

INTRODUCTION

Studies of solvatochromism and solvatochromic dyes continue to attract attention both from the standpoint of fundamental interest[1,2] and because of a number of exciting possible applications. Solvatochromic dyes have been used for optochemical sensors for the detection of gases[3] and polar solvent vapors,[4] for sensing molecules in nanopores,[5] for adsorption studies,[6] etc. The best-known solvatochromic dye is dye **1** [2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, E_T (30)] (see Scheme 1). The large negative solvatochromism of this dye has been used for a long time to measure empirically the 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 Eqn (1)

$$E_T\left[\mathrm{kcal\,mol^{-1}}\right] = h\cdot c\cdot\tilde{\nu}_{\max}\cdot N_A = \left(2.8591\times10^{-3}\right)\cdot\tilde{\nu}_{\max}\left[\mathrm{cm^{-1}}\right] = 28591/\lambda_{\max}\ [\mathrm{nm}] \qquad (1)$$

where h is Planck's constant, c is the speed of light, N_A is Avogadro's number and $\tilde{\nu}_{\max}$ and $\lambda_{\max}$ are the wavenumber and wavelength of the solvent-dependent visible absorption maximum of the reference dye, respectively. The $E_T(30)$ polarity values have been determined for more than 360 solvents[1,2] (numerous binary[1,8–17] and even some ternary[15,18] solvent mixtures), making it the most extensive empirical solvent polarity scale available.

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. For that reason Reichardt *et al.*[2,19] have proposed a new dye—4-[2,6-diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate [dye **2**, $E_T(8)$]—that which is readily soluble in water and is thus suitable for determination of the empirical solvatochromic polarity characteristics of aqueous media. The $E_T(8)$ parameter (using the notation from the original paper[19]) of the new betaine dye **2** is defined in a similar way to $E_T(30)$ by Eqn (1). The $E_T(8)$ parameters of 26 pure solvents and 9 binary solvent mixtures (mixtures of dimethyl sulfoxide and acetonitrile with water, methanol, propan-2-ol and 2-methylpropan-2-ol[20] and a mixture of water with 1,4-dioxane[19]) have been published.

The properties of aqueous solutions of tetra-alkylammonium halides in general and tetra-*n*-butylammonium bromide (Bu_4NBr) in particular have received great attention because of their remarkable properties. In

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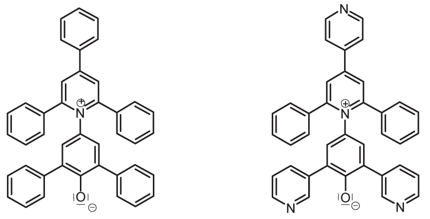

1–standard $E_T(30)$ betaine dye

2–water-soluble $E_T(8)$ betaine dye

Scheme 1

apolar anhydrous benzene the direct stoichiometric complex formation, evidently through dipole–dipole and/or dispersion interactions between the $E_T(30)$ betaine dye molecules and Bu_4NBr or Bu_4NClO_4 was detected spectrophotometrically. On the other hand, in media with high dielectric permittivity it has been found that the electrophilic solvation ability of water is dramatically decreased on addition of Bu_4NBr.[23] In particular, the $E_T(30)$ values were determined in an aqueous solution of Bu_4NBr up to a concentration of 3.2 M. It was found that the salt has a strong effect already at very low concentrations and at 3.2 M it reduces the E_T value to almost 46 kcal mol^{-1}, which is close to the E_T values of acetonitrile or dimethyl sulfoxide (DMSO). A significantly smaller polarity-reducing effect was found operating in the aqueous solution of Me_4NCl. Inorganic salts with 'small' ions (e.g. LiCl, $NaClO_4$, NaCl, KBr, etc.) caused the opposite (i.e. polarity-increasing) effect. At the same time the polarity-reducing effect of Bu_4NBr in DMSO solution was found to be very modest.[24]

The pK_a values of a number of neutral Brønsted acids have been determined in a 7.75 molal (2.34 M) aqueous solution of tetra-*n*-butylammonium bromide.[21] It was found that the pK_a values are systematically higher in the above-mentioned salt solution than in water. This is no doubt due to the reduction of electrophilic solvation of the anions of the acids by water molecules. The sensitivity of this reaction series was found to be intermediate between that of water and DMSO. The ^{1}H and ^{17}O (in water molecules) as well as ^{79}Br, ^{13}C and ^{14}N (in *n*-Bu_4NBr) NMR spectra of aqueous solutions of Bu_4NBr have been investigated.[22] These NMR spectra are expected to carry some valuable information about the physical nature of the interactions between the separate ions of the electrolyte and water in the studied systems. In particular, it was found that for *n*-Bu_4NBr the ^{79}Br and ^{17}O chemical shifts and the respective signal half-heights depend linearly on the $E_T(30)$ parameter of the system.

In the present study, $E_T(8)$ parameters of the water/Bu_4NBr binary mixture have been measured, the data have been compared with the results of earlier measurements in the same mixture with the $E_T(30)$ dye and a rationale for this dramatic decrease of E_T value is proposed. The data are interpreted in terms of the two-step solvent exchange model developed by Rosés *et al.*[12]

SOLVATION MODEL

The preferential solvation model is based on the two-step solvent-exchange model first proposed by Skwierczynski and Connors[11] and further extended by Rosés *et al.*[12] For the particular case of solvatochromic indicator dye **2** (Scheme 1) in a mixture of two specifically solvating components S1 and S2, the formal equilibria (2) and (3) should be considered

$$\mathrm{I(S1)_2} + 2\cdot \mathrm{S2} \rightleftarrows \mathrm{I(S2)_2} + 2\cdot \mathrm{S1} \qquad (2)$$

$$\mathrm{I(S1)_2} + \mathrm{S2} \rightleftarrows \mathrm{I(S12)_2} + \mathrm{S1} \qquad (3)$$

where S12 represents a complex formed by specific interaction between the components S1 and S2 of the binary mixture.[12] 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, as well as by the inter-solvent complexes S12, respectively. In more general cases, a more complex scheme has to be considered.[12,15] 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 as follows

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

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

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)

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

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

From Eqns (4)–(7) Eqn (8) is derived, 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[9,11–15,20,25] and rate constants of some aromatic nucleophilic substitution reactions carried out in binary solvent mixtures.[26,27]

This is a formal approach, especially in our case of an aqueous solution of Bu_4NBr. First of all Bu_4NBr is not a neutral solvent molecule and in water, which is a high-permittivity solvent, it is dissociated extensively into two ions of opposite charges (and thus very different properties). Also, it has been suggested that the first solvation sphere of Bu_4NBr includes 14 molecules of water (see Ref. 24 and references therein). An alternative, not yet formalized, approach to this problem is described by Koppel and Koppel.[8] This approach takes into account the simultaneous influence of the specific and nonspecific solvent–solute interactions.

EXPERIMENTAL

Apparatus

Absorption spectra were recorded in 10-mm quartz cells on a Perkin-Elmer Lambda 2S UV–Vis spectrophotometer equipped with a thermostated (25.0 ± 0.1 °C) cell-holder. This is a fixed slit-width (2 nm) spectrophotometer. The scan speed was 120 nm min^{-1}, the data interval was 0.2 nm and a default smooth factor (2 nm) was used. The wavelength accuracy of the spectrophotometer was checked with a didymium filter (Hitachi) having absorption maxima at $\lambda_{max} = 403.3$, 529.5, and 586.0 nm. The spectra were recorded and further treated on a computer.

Reagents

The indicator dye **2** was synthesized by the procedure recently described in Ref. 19. Tetra-*n*-butylammonium bromide from Fluka ($\geqslant 99\%$) was used without further purification.

Procedure

For each binary system a $\sim 10^{-4}$ M solution of Reichardt's indicator dyes **1** or **2** was prepared in a 2.95 M solution of Bu_4NBr in water in the spectrophotometer cell. The cell was closed with a Teflon cap and weighed (± 0.05 mg). A small quantity (a drop) of water was added to the cell and the solution was stirred with a magnetic stirrer; then the cell was weighed again and the visible spectrum of the solution was recorded. The procedure was repeated after the addition of new drops of water. The different sets of mixtures were overlapped in composition in order to assure concordance of results.

Calculation methods

The E_T values of each mixture were calculated from the maximum of the $\pi \rightarrow \pi^*$ charge-transfer absorption band through Eqn (1). The wavelength of the charge-transfer absorption band maximum was calculated by fitting the spectra to a Gaussian function using the Mathcad 2000 software (MathSoft, Inc.). The goodness of fit was checked using a residuals plot according to Eqn (9)

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

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 the Mathcad 2000 software, minimizing the sum of squared residuals of the E_T values.

RESULTS

The dependence of the $E_T(8)$ and $E_T(30)$ values (from Ref. 23) on the composition of the mixture is presented in Fig. 1. The $E_T(8)$ and $E_T(30)$ parameters of the binary mixtures were investigated by means of the preferential solvation model according to Eqn (8) and the results are presented in Table 1. From Table 1 and Fig. 1 one can see that the E_T values decrease sharply with the addition of Bu_4NBr. For both dyes there is a significant preferential solvation by Bu_4NBr with respect to water. Alternatively, Fig. 1 could be interpreted in terms of Bu_4NBr strongly changing the properties—e.g. nonspecific (dielectric constant) and specific solvation (first of all the hydrogen-bond donor abilities)—and structure of the water in the vicinity of the betaine dye. In absolute terms the effect of addition of Bu_4NBr on the $E_T(8)$ value of water is somewhat less pronounced: the decrease is less steep and the overall predicted decrease is 18 kcal mol^{-1} vs 23 kcal mol^{-1} for the $E_T(30)$ value (see Table 1).

The values of $f_{2/1}$ and $f_{12/1}$ (122 and 49, respectively) also formally indicate that the dye is preferentially solvated by the salt with respect to water. The value of $E_{T12}(8)$, which is the $E_T(8)$ value of the hypothetical solvent composed of 1:1 complexes of water and

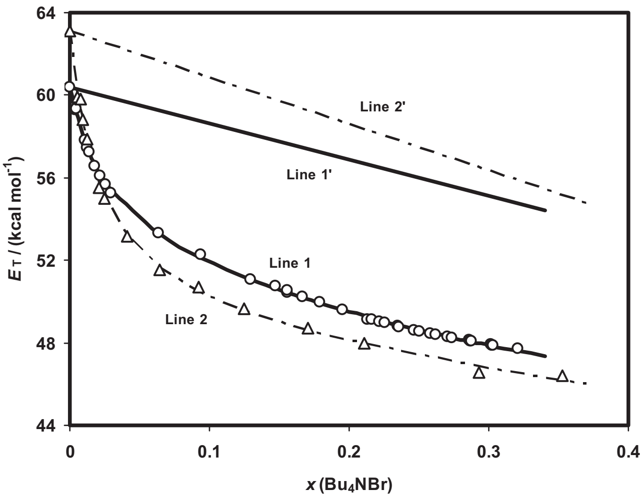

Figure 1. The $E_T(8)$ (circles and line 1) and $E_T(30)$ (triangles and line 2) values of the binary mixture of water–tetra-*n*-butylammonium bromide. Lines 1′ and 2′ correspond to the hypothetical additive relationships between the salt molar fraction and the $E_T(8)$ and $E_T(30)$ values, respectively

n-Bu$_4$NBr, is 52.9 kcal mol^{-1}. This is half-way between the (experimental) $E_T(8)$ of water and the (model-based) $E_T(8)$ of Bu$_4$NBr. A similar situation holds for the $E_T(30)$ dye, with the exception of the $f_{2/1}$ value: its value is 51, which is very similar to the respective $f_{12/1}$ value of 48.

It is well known that addition of electrolytes to water decreases its dielectric constant. In Ref. 23 it has been estimated that in a 3.0 M solution of Bu$_4$NBr the dielectric constant is 9.1 [$x(\mathrm{Bu_4NBr}) = 0.35$, $E_T(30) = 46.4$]. Nevertheless, if one refers to the definition equation of the solvent electrophilicity parameter E (Ref. 28)

$$E = E_T - 25.10 - 14.84\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - 9.59\frac{n^2 - 1}{n^2 + 2} \qquad (10)$$

one easily discovers that, despite the significant changes in ε_r and n, the significant decrease of the E_T parameters (in this case: decrease of $E_T(30)$ from 63.1 to 46.3, i.e. by 16.8 kcal mol^{-1}) is primarily accounted for by the substantial decrease of the electrophilicity of water.[23] The change in E_T due to the decrease of ε_r from 78 to 9 is about -3.5 kcal mol^{-1}. The change due to the increase of n from 1.333 to 1.486 is about $+1.2$ kcal mol^{-1}. The difference resulting from the changes in ε_r and n is thus -2.3 kcal mol^{-1}. The remaining difference of 14.5 kcal mol^{-1} results from the decrease of the electrophilicity. The deviations of $E_T(8)$ and $E_T(30)$ from their mole fractional additivity, ΔE_T, as calculated by Eqn (11), could be visualized as vertical deviations between straight lines 1′ and 2′ corresponding to the mole fractional additivity of $E_T(8)$ and $E_T(30)$ and the respective experimental curves 1 and 2 as a function of the solvent composition in Fig. 1.

$$\Delta E_T = E_T - x_1 E_T^1 - x_2 E_T^2 \qquad (11)$$

where x_1 and x_2 are the mole fractions and E_T^1 and E_T^2 are the E_T parameters of components 1 and 2, respectively. For both indicator dyes large negative deviations are found: up to -7.4 kcal mol^{-1} for $E_T(8)$ and up to -10.8 kcal mol^{-1} for $E_T(30)$. These deviations are significantly larger than observed previously in the case of mixtures of DMSO and MeCN with alcohols.[20] The highest deviation (positive) for those mixtures is observed in the binary mixture MeCN—MeOH for $E_T(30)$ with ca. 6.4 kcal mol^{-1} [$\Delta E_T(8) \approx 5.8$]. It can be seen that $E_T(30)$ shows a more pronounced deviation from linearity than $E_T(8)$.

A good correlation between the $E_T(8)$ and $E_T(30)$ values in different solvents and solvent mixtures has been found. Reichardt *et al.*[19] 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 of $r = 0.987$ and a standard deviation of $\sigma[E_T(8)] = 1.172$ kcal mol^{-1}. The correlation significantly improves when HBD and non-HBD solvents were analyzed separately. For 12 HBD solvents, a correlation was found with a correlation coefficient of $r = 0.998$ and a standard deviation of $\sigma[E_T(8)] = 0.238$, valid for $E_T(30)$ values ranging from 47.7 for 1-decanol to 63.1 kcal mol^{-1} for water. For 14 non-HBD solvents, a correlation 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.

The correlation between the $E_T(8)$ and $E_T(30)$ values in binary mixtures of water and Bu$_4$NBr is presented in Fig. 2. The linear correlation obeys the equation

$$E_T(8) = 12.1 + 0.783 \cdot E_T(30) \qquad (12)$$

with $r = 0.989$ and $\sigma[E_T(8)] = 0.66$ kcal mol^{-1}. For more accurate predictions of the $E_T(30)$ or $E_T(8)$ values the slight nonlinearity of the correlation could be taken into account using the non-linear fit of the data

$$E_T(8) = -60.1 + 3.48 \cdot E_T(30) - 0.0249 \cdot E_T^2(30) \qquad (13)$$

Table 1. Parameters of the preferential solvation model according to Eqn (8) (water is solvent 1) for the solvent mixture of water–tetra-*n*-butylammonium bromide

Indicator	$f_{2/1}$	$f_{12/1}$	E_{T12}	E_{T1}	E_{T2}	Standard deviation	Degrees of freedom
$E_T(30)$	51	48	49.0	63.2	40.4	0.26	10
$E_T(8)$	122	49	52.9	60.6	42.6	0.09	33

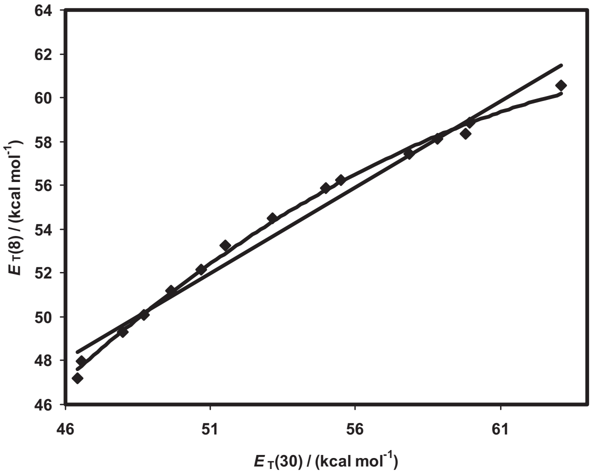

Figure 2. Plot of $E_T(8)$ vs. $E_T(30)$ for the binary mixture of water–tetra-*n*-butylammonium bromide. The data points have been interpolated using Eqn (8) with parameters from Table 1. The regression lines correspond to Eqns (12) and (13)

with $r = 0.998$ and $\sigma[E_T(8)] = 0.26\,\text{kcal mol}^{-1}$. The correlation lines corresponding to Eqns (12) and (13) are presented in Fig. 2.

CONCLUSIONS

The solvent influence 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 [the $E_T(8)$ dye] dissolved in binary water–tetra-*n*-butylammonium bromide mixtures was studied by UV–Vis spectroscopicy 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 significant decrease of the $E_T(8)$ polarity of water on addition of even small amounts of the Bu_4NBr salt parallels the same effect on the classical $E_T(30)$ polarity but is somewhat less sharp: the decrease is less steep and the overall predicted decrease is $18\,\text{kcal mol}^{-1}$ vs. $23\,\text{kcal mol}^{-1}$ for the $E_T(30)$ value. The $E_T(8)$ betaine dye can be applied for the determination of $E_T(30)$ values for aqueous media and media where the $E_T(30)$ betaine is not soluble. However, the somewhat nonlinear nature of the relationship has to be taken into account if accurate results are desired.

Supplementary material

A table with mixture compositions and $E_T(8)$ and $E_T(30)$ values of the binary mixtures studied is available in *Wiley Interscience*.

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