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Solute–solvent and solvent–solvent interactions in the preferential solvation of 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide in 24 binary solvent mixtures

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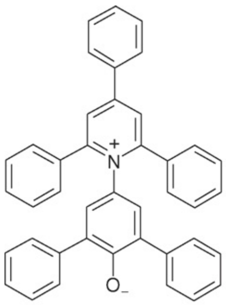
Abstract

The molar transition energy (E_T) polarity values for the dye 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide were collected in binary mixtures comprising a hydrogen-bond accepting (HBA) solvent (acetone, acetonitrile, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF)) and a hydrogen-bond donating (HBD) solvent (water, methanol, ethanol, propan-2-ol, and butan-1-ol). Data referring to mixtures of water with alcohols were also analyzed. These data were used in the study of the preferential solvation of the probe, in terms of both solute–solvent and solvent–solvent interactions. These latter interactions are of importance in explaining the synergistic behavior observed for many mixed solvent systems. All data were successfully fitted to a model based on solvent-exchange equilibria. The E_T values of the dye dissolved in the solvents show that the position of the solvatochromic absorption band of the dye is dependent on the medium polarity. The solvation of the dye in HBA solvents occurs with a very important contribution from ion–dipole interactions. In HBD solvents, the hydrogen bonding between the dimethylamino group in the dye and the OH group in the solvent plays an important role in the solvation of the dye. The interaction of the hydroxylic solvent with the other component in the mixture can lead to the formation of hydrogen-bonded complexes, which solvate the dye using a lower polar moiety, i.e. alkyl groups in the solvents. The dye has a hydrophobic nature and a dimethylamino group with a minor capability for hydrogen bonding with the medium in comparison with the phenolate group present in Reichardt's pyridiniophenolate. Thus, the probe is able to detect solvent–solvent interactions, which are implicit to the observed synergistic behavior.

Keywords: Preferential solvation; Binary mixtures; Merocyanines; Solvent effects; Solvent–solvent interactions; Solute–solvent interactions

1. Introduction

The rate and course of chemical processes can be influenced by the medium in which they are carried out [1,2]. These effects of the medium are commonly interpreted as resulting from changes in its polarity, a general term that is related to the overall solvating capability of the solvent [3]. The polarity of the medium provokes changes in the absorption and emission spectra of many organic dyes [1–4]. Merocyanines comprise a class of solvatochromic compounds that are commonly used in the investigation of solvent properties [3,4]. An important example is Reichardt's betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**), which is one of the most commonly employed solvatochromic dyes [1,2,4].



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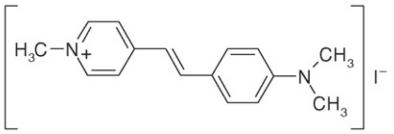

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In studies performed in order to better understand these solvent effects, considerable research has been carried out on the physical organic chemistry of mixed solvents [4–27], due to their

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important applications in many fields, such as chromatography, hydrometallurgy, organic synthesis, and the kinetics of chemical processes [5]. The analysis of the behavior of solutes in mixed solvent systems is more complex than in pure solvents due to the possibility for preferential solvation (PS), which occurs when the solute has in its microenvironment more of one solvent than the other, in comparison to the bulk composition. A comprehension of phenomena related to PS may help in the elucidation of kinetic, spectroscopic, and equilibrium data for mixed solvents.

An important aspect in the studies performed on mixed solvents is the role of solvent–solvent interactions in competition to the solvation of solutes [5,13,25–27]. In these interactions, one component of the binary mixture preferentially binds to a molecule of the same type in its neighborhood, forming clusters. Although the solute cannot be proved to be responsible for the clustering, it can be solvated in these solvent aggregates. In these molecular associations, hydrogen bonding can play an important role and has been widely investigated because it is present in a large variety of chemical, biochemical, and pharmacological events.

Although the literature shows many studies on mixed solvents using **1** as a dye [4,6–12,17–20], relatively few investigations of these solvent systems have been carried out using other classes of solvatochromic probes [13–15,21–24]. It is considered that structurally different probes should be able to detect different aspects of the physical chemistry of mixed solvents. Thus, in this paper we describe an investigation into the behavior of 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (**2**) in binary mixtures comprising a hydrogen-bond accepting (HBA) solvent [acetone, acetonitrile, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF)] and a hydrogen-bond donating (HBD) solvent (water, methanol, ethanol, propan-2-ol, and butan-1-ol) solvent. We also show data relating to mixed systems comprising water with alcohols (methanol, ethanol, propan-1-ol, and propan-2-ol). The obtained data are discussed in relation to solute–solvent and solvent–solvent interactions.

2. Experimental

2.1. Materials

All solvents were HPLC grade and were purified following methodology described in the literature [28]. Deionized water was used in all measurements. This solvent was boiled and bubbled with nitrogen and kept under a nitrogen atmosphere to avoid the presence of carbon dioxide. Dye 2 was synthesized, following a reported procedure [29], refluxing 1-methyl-4-picolinium iodide with 4-(dimethylamino)benzaldehyde and piperidine in ethanol for 4 h in a water bath (80–90 °C). The reaction mixture was left to stand overnight, the red-purple crystals were filtered off and washed with ethanol. The crystals were washed with cold diethyl ether and were recrystallized twice from hot water and dried under vacuum. Yield: 45%; mp 254.5–255.5 °C (literature [29], 251–255 °C). ^{1}H NMR (200 MHz, DMSO-d_6): 3.02 (6H, s), 4.18 (3H, s), 6.79 (2H, d, $J = 8.8$ Hz), 7.17 (1H, d, $J = 16.1$ Hz), 7.60 (2H, d, $J = 8.8$ Hz), 7.92 (1H, d, $J = 16.1$ Hz), 8.05 (2H, d, $J = 6.8$ Hz), 8.69 (2H, d, $J = 6.7$ Hz).

2.2. UV–vis measurements

The following procedure was typical for all experiments performed. A 1.0×10^{-3} mol L^{-1} stock solution of **2** was prepared in dichloromethane. From this stock solution 100 μL aliquots were transferred to 10 mL volumetric flasks. After the evaporation of the dichloromethane, the probe was solubilized in the pure solvents, resulting in solutions with final concentrations of 1.0×10^{-5} mol L^{-1}. The UV–vis experiments were recorded on a Cary 1G spectrophotometer at 25 °C. The maxima on the UV–vis spectra were calculated from the first derivative of the absorption spectrum. The λ_{max} values thus obtained in nanometers were transformed into E_T values (kcal mol^{-1}), according to the expression $E_T(\text{dye}) = 28{,}590/\lambda_{max}$. Binary mixtures were prepared by weighing the solutions prepared as described above in a quartz cuvette closed with a rubber septum (the cosolvent solution was added with a 1 mL microsyringe) and the final values are expressed in terms of the hydroxylic cosolvent mole fraction (X_2) in the mixtures. The λ_{max} values thus obtained were transformed into E_T(dye) values (see above). All experiments with the mixed solvent systems were carried out in duplicate and the reproducibility of the curve features was confirmed.

2.3. Calculations

The parameters $E_T(\text{dye})_1$, $E_T(\text{dye})_2$, $E_T(\text{dye})_{12}$, $f_{2/1}$, and $f_{12/1}$ were calculated from non-linear regressions using the ORIGIN 5.0 program.

3. Results and discussion

Table 1 summarizes the polarity and hydrogen-bonding properties of the pure solvents used in this study, in the form of the Reichardt normalized E_N^T values [1] as well as α (solvent hydrogen-bond donor acidity), β (solvent hydrogen-bond acceptor basicity), and π^* (dipolarity/polarizability) Kamlet–Taft parameters [2,30]. On analysis of these parameters, the solvents can be separated into two classes. The first class is comprised

Table 1
Polarity parameters of pure solvents at 25 °C

Solvent	π^* [a]	α [a]	β [a]	E_N^T [b]	E_T(dye) [c]
Water	1.09	1.17	0.47	1.000	63.8
Methanol	0.60	0.93	0.62	0.762	60.1
Ethanol	0.54	0.83	0.77	0.654	59.7
Propan-1-ol	0.52	0.78	0.90	0.617	59.0
Butan-1-ol	0.47	0.79	0.88	0.586	58.8
Propan-2-ol	0.48	0.76	0.95	0.546	59.4
DMSO	1.00	0.00	0.76	0.444	60.7
DMF	0.88	0.00	0.69	0.386	60.9
Acetonitrile	0.75	0.19	0.31	0.460	60.8
Acetone	0.71	0.08	0.48	0.355	60.7

[a] References [2,30].
[b] Reference [4].
[c] This study, in kcal mol^{-1}.

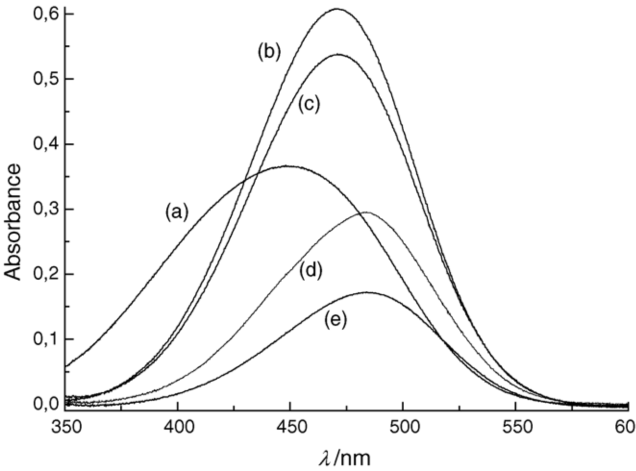


Fig. 1. UV–vis spectra of **2** in water (a), acetonitrile (b), DMSO (c), propan-2-ol (d), and propan-1-ol (e) at 25 °C.

by the HBD solvents, which show strong hydrogen-bond donor capabilities. The second class comprises the HBA solvents, for which high β values (except for acetonitrile) and low α values were obtained, indicating that these solvents are good hydrogen-bond acceptors and poor hydrogen-bond donors.

The UV–vis absorption spectra of dye **2** were recorded in several HBD and HBA solvents. Fig. 1 shows the spectra of dye **2** in water, propan-1-ol, propan-2-ol, acetonitrile, and DMSO. Spectra were collected for the solvents with different dye concentrations and no changes in the shape and λ_{max} position were observed for the solvatochromic band, indicating that there is no formation of dye aggregates. The maxima in absorbance for all spectra were obtained with a precision of ±0.5 nm. The reproducibility of the λ_{max} values was verified by their determination from five spectra of the dye in each pure solvent. All data were transformed to molar transition energies for **2** (E_T(dye) values), given in kcal mol^{-1} with a precision of 0.1 kcal mol^{-1} and are shown in Table 1. The data show that the position of the solvatochromic band of the dye is dependent on the medium polarity, having a variation of $\Delta\lambda = 38$ nm for the solvents used.

Compound **2** is a salt, which can form, in principle, ion pairs in solution, especially in solvents with a low dielectric constant, such as acetone. The formation of ion pairs can influence the absorption spectra of **2** in these solvents. In order to verify this, UV–vis absorption spectra of the dye in acetone were collected in the presence of increasing concentrations of tetrabutylammonium iodide. It was verified that the addition of iodide up to 0.01 mol dm^{-3} did not change the position of the maximum on the UV–vis spectra of **2**. These data suggest that the dispersion of the positive charge on the nitrogen atom of the dye may prevent ion pairing. In other experiment, silver tetrafluoroborate was added to the solution of **2** in acetone, in order to give the precipitation of iodide as AgI. It was found that the UV–vis spectrum of **2** is exactly the same after the addition of $AgBF_4$. Similar experiments were performed in acetonitrile, DMSO, propan-1-ol, and water. The results showed that the solvatochromism observed is not influenced by the presence of iodide as a counteranion. In all cases, the solvatochromic absorption band was maintained without alteration. From these data the possibility of this dye being an ion-pair solvatochromic compound, such as the Kosower's 1-ethyl-4-(methoxycarbonyl)pyridinium iodide [31], can be discarded. In this respect, Al-Ansari [29] has demonstrated that the solvatochromic band of **2** disappears in acidified methanol, due to the protonation of the nitrogen lone-pair in the dye. This experiment helped to reveal the charge-transfer nature of the solvatochromic band of **2**. Another aspect to be considered regarding the solvatochromism of dye **2** is that, in a salt, the cation and the anion can be preferentially solvated by the components of the mixed system. In the solutions of **2**, only the PS of the cation of **2** can be investigated by means of solvatochromic measurements.

The elements discussed above suggest that different solute–solvent interactions are responsible for the solvation of the dye in HBD and HBA solvents. The solvation of **2** in HBA solvents occurs with a very important contribution from ion–dipole interactions. These interactions are responsible for the stabilization of the electronic ground state of the dye and, consequently, for the increase in its charge-transfer transition energy in solution with an increase in the polarity of the medium. In HBD media, simultaneously with ion–dipole interactions, hydrogen bonding between the dimethylamino hydrogen-bonding receptor group in the dye and the solvent can occur [29,32]. It has been reported that the pyridiniophenolate **1**, the basis for the E_N^T polarity scale, is able to interact through hydrogen bonding with proton donors by means of its phenolate group [33,34]. The formation of hydrogen bonds leads to a stabilization of the ground state of the dye, and a consequent increase in its charge-transfer transition energy. Thus, the greater the capability of the solvent to form hydrogen bonds with the dye the greater the increase in the E_T(dye) values.

3.1. Preferential solvation in mixed systems

Solutions of dye **2** in mixed solvents comprising aqueous alcohols and a HBA and a HBD component were studied in order to investigate the PS of the dye. All results were treated by considering the two-step solvent-exchange model shown below, taken from a study by Skwierczynski and Connors [17]:

$$\mathrm{dye(S_1)_2} + 2\mathrm{S_2} \leftrightarrows \mathrm{dye(S_2)_2} + 2\mathrm{S_1}$$

$$\mathrm{dye(S_1)_2} + \mathrm{S_2} \leftrightarrows \mathrm{dye(S_{12})_2} + \mathrm{S_1}$$

This model has been successfully employed to explain the solvation of the pyridiniophenolate **1** in many binary mixtures [18–20]. It has also been used to describe the solvation of pyrene [22] and Brooker's merocyanine [23,24] in mixtures comprising HBA and HBD solvents. In this model, S_1 and S_2 represent the two solvents in the mixture, with the subscript 2 relating to the most polar component. The interaction of these two solvents through hydrogen bonding yields a common structure S_{12}. The dye solvated by S_1, S_2, and S_{12} is represented by $\mathrm{dye(S_1)_2}$, $\mathrm{dye(S_2)_2}$, and $\mathrm{dye(S_{12})_2}$, respectively. The E_T(dye) value for a given mixture is considered equal to the average of the E_T(dye) values of solvents S_1, S_2, and S_{12} in the solvation shell of **2**. The mathematical development of this model results in Eq. (1), which

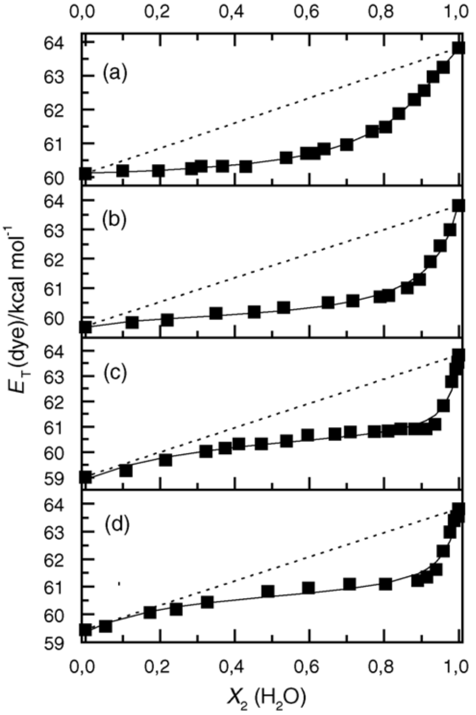


Fig. 2. Influence of water on the E_T values for **2** in aqueous mixtures of alcohols, the alcohol being methanol (a), ethanol (b), propan-1-ol (c), or propan-2-ol (d). (···) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.

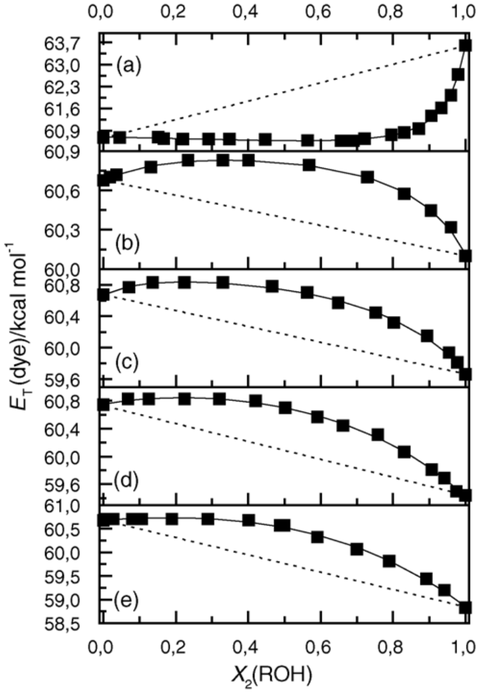


Fig. 3. Influence of the hydroxylic cosolvent on the E_T values for **2** in DMSO–ROH mixtures, the ROH component being water (a), methanol (b), ethanol (c), butan-1-ol (d), or propan-2-ol (e). (···) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.

relates the E_T(dye) value in a binary mixture to the E_T(dye) values of the two pure solvents [18–20,22–24].

$$E_T(\text{dye}) = \frac{E_T(\text{dye})_1(1-X_2)^2 + E_T(\text{dye})_2 f_{2/1} X_2^2 + E_T(\text{dye})_{12} f_{12/1}(1-X_2)X_2}{(1-X_2)^2 + f_{2/1}X_2^2 + f_{12/1}(1-X_2)X_2} \quad (1)$$

The PS parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of **2** to be solvated by the solvents S_2 and S_{12} with respect to solvent S_1.

The E_T(dye) values as a function of X_2 (Figs. 2–6) were plotted and the experimental data for each binary solvent mixture were fitted through a non-linear regression to Eq. (1). The results are displayed in Table 2 and show very good fits for all binary solvent mixtures studied (S.D. $< 5 \times 10^{-2}$). Table 2 shows also the PS parameter $f_{12/2}$, which is a measure of the tendency of **2** to be preferentially solvated by the solvent S_{12} in comparison with S_2. It was calculated for all mixtures studied using the expression $f_{12/2} = f_{12/1}/f_{2/1}$. In addition, the calculated E_T(dye) values in Table 2 for the pure solvents agree well with the experimental values given in Table 1.

3.2. *Alcohol–water mixtures*

Fig. 2 shows a set of plots of E_T values for **2** as a function of the water mole fraction (X_2) for alcohol–water mixtures. The experimental data show the occurrence of strong PS by the alcoholic component in these mixtures, similarly to the results obtained by Ortega et al. [19] using dye **1** as an indicator. The plots in Fig. 2 also show that, with the lengthening of the alkyl chain of

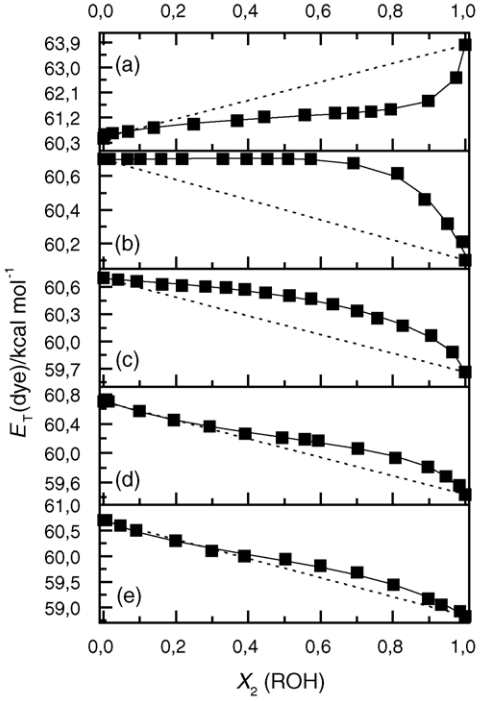


Fig. 4. Influence of the hydroxylic cosolvent on the E_T values for **2** in acetone–ROH mixtures, the ROH component being water (a), methanol (b), ethanol (c), butan-1-ol (d), or propan-2-ol (e). (···) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.

Table 2
Calculated parameters for dye **2** in binary solvent mixtures at 25 °C

Binary mixture	$E_T(\text{dye})_1$	$E_T(\text{dye})_2$	$E_T(\text{dye})_{12}$	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$[a]	S.D.
Water–methanol	60.1	63.8	62.2	0.027	0.16	5.9	2.0×10^{-3}
Water–ethanol	59.7	63.9	60.0	0.63	8.9	14	1.6×10^{-2}
Water–propan-2-ol	59.4	63.9	60.8	0.19	4.9	26	4.6×10^{-2}
Water–propan-1-ol	58.9	63.9	60.6	0.089	3.7	42	3.5×10^{-2}
DMSO–water	60.7	63.6	60.1	0.025	0.44	18	1.3×10^{-3}
DMSO–methanol	60.7	60.1	60.9	0.81	5.3	6.5	1.5×10^{-4}
DMSO–ethanol	60.7	59.7	61.0	1.7	6.9	4.1	6.5×10^{-4}
DMSO–propan-2-ol	60.8	59.4	61.1	0.87	2.5	2.9	7.2×10^{-4}
DMSO–butan-1-ol	60.7	58.9	61.1	0.54	1.4	2.6	1.2×10^{-3}
Acetone–water	60.5	63.8	61.3	0.12	4.1	34	1.3×10^{-3}
Acetone–methanol	60.7	60.1	60.8	0.040	0.24	6.0	3.5×10^{-4}
Acetone–ethanol	60.7	59.7	59.8	0.0015	0.27	180	2.4×10^{-4}
Acetone–propan-2-ol	60.7	59.5	60.1	0.35	3.2	9.1	3.2×10^{-4}
Acetone–butan-1-ol	60.7	58.8	60.0	1.4	5.1	3.6	1.5×10^{-3}
Acetonitrile–water	60.8	63.9	61.1	0.57	13	23	6.8×10^{-3}
Acetonitrile–methanol	60.8	60.1	60.4	0.0097	0.26	27	5.0×10^{-5}
Acetonitrile–ethanol	60.8	59.7	60.8	1.5	4.0	2.7	9.0×10^{-5}
Acetonitrile–propan-2-ol	60.8	59.0	60.0	0.46	3.0	6.5	3.0×10^{-4}
Acetonitrile–butan-1-ol	60.8	58.8	59.4	0.098	1.6	16	6.8×10^{-4}
DMF–water	61.0	63.8	60.5	0.014	0.67	48	1.9×10^{-3}
DMF–methanol	61.0	60.1	61.0	0.077	0.37	4.8	1.9×10^{-4}
DMF–ethanol	60.9	59.7	61.0	4.9	23	4.7	7.8×10^{-4}
DMF–propan-2-ol	60.9	59.5	60.7	0.11	0.75	6.8	3.1×10^{-4}
DMF–butan-1-ol	60.9	58.9	60.9	0.79	2.1	2.7	1.6×10^{-3}

[a] $f_{12/2} = f_{12/1}/f_{2/1}$.

the alcohol, the extent of the PS of the dye cation increases in the water-rich region and, simultaneously, PS by the alcoholic component in the alcohol-rich region changes towards an ideal behavior. These results show that the dye cation is preferentially solvated by the alcoholic component in all mole fractions in aqueous mixtures with methanol and ethanol. It has been previously discussed that water makes strong hydrogen-bonded nets in the water-rich region, which are not easily disrupted

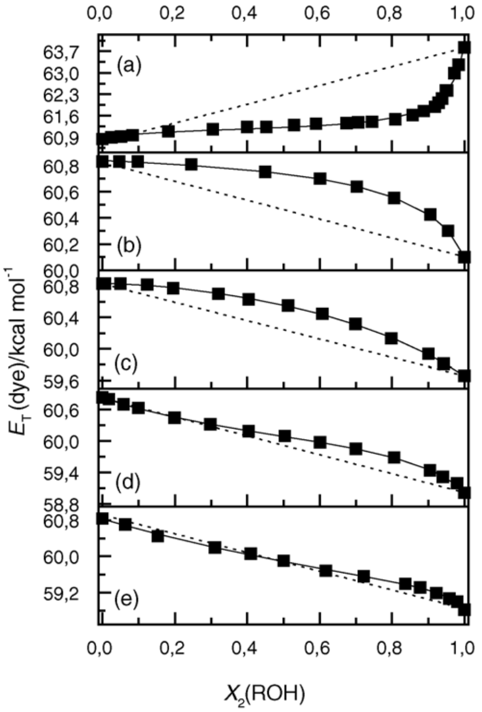


Fig. 5. Influence of the hydroxylic cosolvent on the E_T values for **2** in acetonitrile–ROH mixtures, the ROH component being water (a), methanol (b), ethanol (c), butan-1-ol (d), or propan-2-ol (e). (···) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.

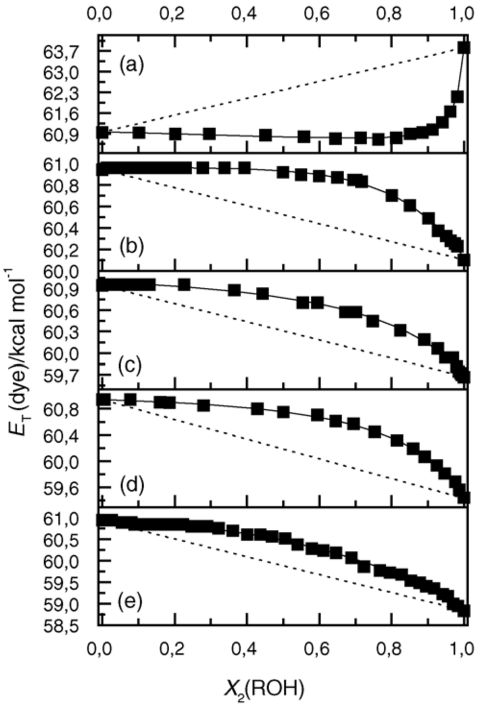
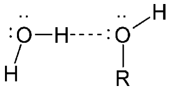


Fig. 6. Influence of the hydroxylic cosolvent on the E_T values for **2** in DMF–ROH mixtures, the ROH component being water (a), methanol (b), ethanol (c), butan-1-ol (d), or propan-2-ol (e). (···) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.



Scheme 1.

by the cosolvent [23,24]. This can explain the strong PS by the alcoholic component in this region since water preferentially interacts with itself rather than with the dye. Thus, it is expected that the interaction of the alcoholic component with the dye through both hydrogen bonding and a hydrophobic effect increases with the lengthening of the alkyl chain of the alcohol. The ability of the alcoholic cosolvent to solvate the dye cation in the water-rich region increases in the following order: methanol < ethanol < propan-2-ol ≈ propan-1-ol. This is also the increasing order of the β values, suggesting that the increase in the basicity of the alcohol makes it able to compete efficiently with the dye for the water, hindering the interaction between the water and the dye.

In the alcohol-rich region, the alcohol molecules are freer to interact with the water and with the dye, since their nets formed by hydrogen bonds are weaker than in water. In this situation, the alcohol molecules can, to a greater or lesser extent, interact with water through hydrogen bonding. The plots in Fig. 2 show that the extent of PS by the alcoholic component in the alcohol-rich region decreases in the order methanol > ethanol > propan-1-ol > propan-2-ol. This is also the decreasing order of the solvent's hydrogen-bond donation capability (see α values in Table 1), suggesting that the increase in the facility of the alcohol for hydrogen-bond donation makes its interaction with the dimethylamino group in the dye cation stronger and, consequently, the PS by the alcohol in the alcohol-rich region increases. This order is also the increasing order of the solvent's hydrogen-bond acceptance (see β values in Table 1), indicating that the change in the alcoholic component in the mixture from methanol to propan-2-ol increases the capacity of the alcohol to form hydrogen-bonded complexes with water (Scheme 1), and these complexes can be responsible for the solvation of the dye cation in the alcohol-rich region [23,24], reflected in the ideal behavior observed, e.g., in propan-2-ol mixtures. In addition, it can be seen that the parameter $f_{12/2}$ in Table 2 points to the fact that **2** is preferentially solvated by S_{12} in the following order for the alcohols: methanol < ethanol < propan-2-ol < propan-1-ol.

3.3. DMSO–ROH mixtures

Fig. 3 shows the E_T(dye) values plotted as a function of the hydroxylic component in DMSO–ROH mixtures. All mixtures display a strong synergistic behavior, their E_T values being lower than those for the two pure solvents in the aqueous mixtures and greater than those for the two pure solvents in the alcoholic mixtures. In addition, in all mixtures dye **2** is preferentially solvated by the less polar component of the binary mixture. It is interesting to observe that dye **1** is preferentially solvated by the more polar components in all DMSO–alcohol mixtures, while PS by DMSO or S_{12} species is verified in its aqueous mixtures [19].

The term 'synergism' was first proposed by Reichardt and coworkers in a study involving solutions of the pyridiniophenolate **1** in binary mixtures of dialkyl ketones, trialkyl phosphates, or DMSO with chloroform [7]. Synergistic effects are due to the formation of 1:1 complexes through hydrogen bonding between the HBD and the non-HBD components of the mixture, yielding the S_{12} species [7,18–20,22–24]. These species can be differentiated by structurally different probes: compound **1** and Brooker's merocyanine, for instance, recognize S_{12} species as more polar because their more polar moiety solvates the dyes [18–20,23,24]. On the other hand, pyrene recognizes the S_{12} species as less polar because this non-polar solute is solvated by the less polar groups in these species [22]. It was noted by Marcus that highly polar, mutually miscible solvents, such as DMF or DMSO, interact so strongly with water that the mole fraction of the hydrogen-bonded DMSO–water associate is greater than the free water mole fraction and the self-associated water mole fraction [35]. Since DMSO shows a high β value, it can form strongly associated complexes through hydrogen bonding with the hydroxylic solvents and these S_{12} species may be responsible for the solvation of the dye. Thus, the microenvironment of **2** in these mixtures is crowded by these DMSO–ROH partners, which orient their hydrophobic methyl groups towards the probe. This can be the origin of the hydrophobic microenvironment reported for **2**. The behavior of this dye in these mixtures is similar to that described for pyrene, a hydrophobic probe, which is also preferentially solvated by S_{12} species in a similar manner [22]. The values of $f_{12/2}$ in Table 2 show that **2** is preferentially solvated by S_{12} in the following order for the HBD solvents: butan-1-ol < propan-2-ol < ethanol < methanol < water. This is the same increasing order of solvent hydrogen bonding donation (see α values in Table 1), which shows that the change of butan-1-ol to water strengthens the interaction with DMSO by hydrogen bonding and these S_{12} complexes formed are mainly responsible for the solvation of **2**.

3.4. Acetone–ROH mixtures

Fig. 4 depicts the variation in E_T values for the longest-wavelength band of **2** as a function of the HBD component mole fraction in acetone–ROH mixtures. For all mixtures, acetone, or the less polar moiety of the S_{12} species (with the methyl groups of acetone oriented towards the dye), is always responsible for the PS of **2**. However, as the hydroxylic component becomes less polar, the intensity of the PS diminishes and approaches a nearly ideal behavior in butan-1-ol mixtures, with the solvent composition in the microenvironment of **2** and that in the bulk mixture being almost equal in all mixtures. These results can be explained by the fact that **2** is a hydrophobic probe. Thus, the exchange of the more polar HBD cosolvent for one which is more hydrophobic may lead to a comparatively stronger interaction of the probe with the cosolvent through hydrophobic interactions. The synergism observed for the acetone–methanol curve (Fig. 4(b)) suggests that S_{12} species play an important role in the PS of the dye. In this situation, the methyl groups of acetone are responsible for the solvation of the dye.

A comparison between our data and those obtained by Ortega et al. [19] shows that dyes **1** and **2** have a completely different behavior: the acetone–water plot for **1** exhibits a sigmoidal shape while, in acetone–alcohol mixtures, **1** is preferentially solvated by the more polar component of the mixtures. The analysis of the preferential solvation parameters in Table 2 seems more complex because these did not indicate a relationship with the Kamlet–Taft parameters in Table 1. Data in Table 2 show that for methanol and ethanol mixtures the $E_T(\text{dye})_{12}$ values are very close to that for acetone in its methanolic mixtures and to that for ethanol in acetone–ethanol mixtures. This point is important because it introduces, according to a study by Ortega et al. [19], an expressive error in the calculation of $f_{12/1}$ and $f_{12/2}$ values. If these uncertainties are considered, the same general trends observed for DMSO mixtures can be visualized for the acetone mixtures.

3.5. *Acetonitrile–ROH mixtures*

The variation in E_T(dye) values as a function of the HBD component mole fraction in acetonitrile–ROH mixtures is shown in Fig. 5. A simple comparison of these plots with those in Fig. 4 shows that their behavior is very similar: for acetonitrile–ROH mixtures acetonitrile (or the less polar moiety of the S_{12} species) preferentially solvates **2**. Again, as the hydroxylic component becomes less polar, PS diminishes in magnitude and comes close to an ideal behavior in butan-1-ol mixtures. The only difference observed in the comparison of acetone and acetonitrile mixtures is that while acetone–methanol mixtures are synergistic (Fig. 4(b)) the same was not observed for acetonitrile–methanol mixtures (Fig. 5(b)). The behavior of pyridiniophenolate **1** in acetonitrile with HBD solvents is also similar to the mixtures of acetone with the same cosolvents [19].

The explanation for the behavior of **2** in these mixtures is the same as that given for acetone mixtures and the similar effects observed for acetone and acetonitrile mixtures can be explained through a comparison of the polarity parameters of these two solvents (see Table 1). The π^* value for the two solvents is very similar and the α values are very low. The difference observed in the β values can explain the differences observed in the methanolic mixtures, since acetone is more able than acetonitrile to interact through hydrogen bonding with the alcohol due to the higher basicity of acetone. In addition, the same explanation for the apparent discontinuities in the calculated $f_{12/2}$ values for acetone mixtures can explain the data with acetonitrile mixtures.

3.6. *DMF–ROH mixtures*

Fig. 6 depicts the variation in E_T(dye) values as a function of the hydroxylic component mole fraction for DMF–ROH mixtures. DMF is an amide that is unable to form hydrogen bonds with **2** but is capable of interacting with the HBD cosolvent through hydrogen bonding due to its high β value ($\beta = 0.69$), yielding the S_{12} species. The plots show that in all cases the dye cation is preferentially solvated by the less polar component (DMF or DMF-like S_{12} species) of the mixture. In addition, a strong synergistic behavior for DMF–water mixtures can be observed (Fig. 6(a)), which diminishes if the HBD solvent is changed from water to butan-1-ol. A comparison with the data presented for DMSO–ROH mixtures (Fig. 3) shows that **2** displays similar trends with both HBA solvents. This results from the fact that DMSO and DMF present similar Kamlet–Taft parameters. A view of $f_{12/2}$ values in Table 2 shows that **2** is preferentially solvated by S_{12} in an order similar to that observed for the DMSO mixtures. Again, the discontinuities in the calculated $f_{12/2}$ values can be explained as shown above for the acetone mixtures. Thus, the explanation for the data for DMF mixtures is the same as that offered for DMSO mixtures (see above), and the differences in synergistic behavior can be explained by the fact that it increases when the E_T values for the pure solvents participating in the mixtures are more similar [18–20,22–24]. Herodes et al. [20] studied the behavior of **1** in binary mixtures of DMF with hydroxylic solvents and also observed a similarity with the DMSO mixtures [19]: in its aqueous mixtures it is preferentially solvated by DMF or S_{12} species while in the DMF–alcohol mixtures the PS of **1** occurs via the alcoholic component or by the most polar moiety of the S_{12} species.

4. Conclusion

The spectroscopic studies involving dye **2** dissolved in binary solvent mixtures show that the behavior of the dye is dictated by solute–solvent and solvent–solvent interactions. The two-step solvent-exchange model of Skwierczynski and Connors [17] was successfully fitted to all mixed systems studied here. The combination in the mixtures of a solvent with a high β value and hydroxylic solvents, which display large α values, allows the formation of complexes formed through hydrogen bonding. The cation of compound **2** is solvated by the less polar moiety of these complexes, i.e. by the alkyl groups of the solvents, since the dye cation is of hydrophobic nature and has a dimethylamino group with a minor capability to form hydrogen bonds with the medium in comparison with the phenolate group present in other dyes, such as dye **1** [18–20] and Brooker's merocyanine [23,24]. In this aspect, in mixtures comprised of a HBA solvent and a HBD solvent, the cation of dye **2** behaves in a similar way to pyrene [22], a highly hydrophobic probe that interacts with the medium exclusively through dipole–dipole and dispersion interactions. Thus, these probes are able to detect solvent–solvent interactions, which are implicit to the observed synergistic behavior. This is very important in the comprehension of phenomena related to the solvation of chemical species and to the importance of hydrophobicity in biological events [36].

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