

# The Fluorosolvatochromism of Brooker's Merocyanine in Pure and in Mixed Solvents

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The fluorescence-based solvatochromism (fluorosolvatochromism) of 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (Brooker's merocyanine) was studied. The results revealed that the fluorescence emission band of the dye was dependent on the medium ( $\lambda_{\text{max}}^{\text{fl}} = 573$  nm in water and  $\lambda_{\text{max}}^{\text{fl}} = 622$  nm in DMF). The fluorescence quantum yields ( $\phi_f$ ) were calculated for the dye in the solvents investigated. Low  $\phi_f$  values ( $< 10\%$ ) were obtained for the dye and in order to better comprehend the radiative and nonradiative decay processes of this dye, its fluorescence lifetime in methanol was measured and was found to be very short (230 ps). The results suggest that the dye in the excited state decays rapidly through nonradiative processes. The behavior of the probe in binary mixtures including a hydrogen-bond accepting solvent (acetonitrile, *N,N*-dimethylformamide, and dimethylsulfoxide) and a hydroxylic solvent (water, methanol, ethanol, propan-2-ol, and butan-1-ol) was also investigated. All data were successfully fitted to a model based on solvent exchange equilibria, which allowed the separation of the different contributions of the solvent species in the solvation shell of the dye. The data obtained for the mixed solvents were explained based on solute-solvent and solvent-solvent interactions.

**KEYWORDS:** Fluorosolvatochromism; preferential solvation; solvatochromic dyes; binary mixtures; merocyanines.

## INTRODUCTION

Merocyanine dyes are heterocyclic compounds that have a large variety of applications [1] due to their properties as electrochromic [2], photochromic [3], and photoelectrochemical [4] agents. This class of dyes shows potential applications in photodynamic therapy [5], nonlinear optics [6], liquid crystals [7], solar energy conversion [8], and in the construction of molecular devices [9]. The spectral properties of these dyes have recently interested different research groups. These compounds

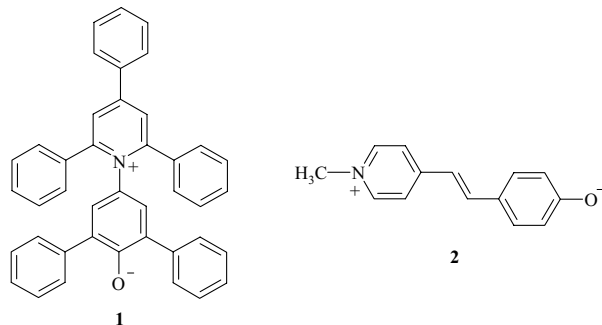
can exhibit solvent-dependent fluorescence in the red region of the spectrum, and their structures are therefore of interest for the design of new fluorescent probes with applications as tools in medical and biological diagnoses [10]. The structure of merocyanines can also be used as a chromophoric unit in the design of chromo- and fluoroionophores for cationic recognition [11], which along with anionic recognition [12], represents a field of current interest. Many merocyanines are solvatochromic, i.e. their UV-vis spectra change if the polarity is altered [13–15]. Reichardt's betaine, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**) [13,15], is a very well-known example of these dyes. The maximum absorption of **1** in different solvents represents the basis of the Reichardt polarity parameter  $E_T(30)$ , one of the most popular solvent polarity scales [13,15]. Another well-known solvatochromic dye is 4-[(1-methyl-4(1*H*)-pyridinylidene)

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-ethylidene]-2,5-cyclohexadien-1-one (**2**), better known as Brooker's merocyanine [16]. Merocyanines have been used in the study of salt solutions [11,17], mixed solvents [18–21], and solutions containing cyclodextrins [22]. Studies involving mixed solvents have become very important in the last few years because these systems are widely used in fields such as kinetics, spectroscopy, thermodynamics, analytical chemistry, and industrial processes.



Although the UV–vis bands of **1**, **2**, and other merocyanines [23] have been used to study the polarity of different media, relatively few fluorescent merocyanines have been employed as polarity probes [24]. These compounds exhibit fluorescence-based solvatochromism, which has also been called fluorosolvatochromism [25]. The fluorescence technique is a very important tool due to its high sensitivity. Therefore, the study of the potential of merocyanine dyes as fluorescent probes can lead to new applications for these dyes. In addition, a detailed understanding of the influence of the microenvironment of these probes on their spectral and physicochemical properties is important for the comprehension of their chemical and photochemical activity. Dye **1** is not fluorescent at room temperature due to the many possibilities to transform its electronic energy into thermal energy [26], but there are no reports in the literature concerning the fluorescence of dye **2**, although its UV–vis-based solvatochromism is well investigated [16,21]. In this paper, we describe the influence of the solvent on the absorption and fluorescence spectra of 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (Brooker's merocyanine, **2**). We also show here the behavior of dye **2** in binary mixtures comprising a hydrogen-bond accepting (HBA) solvent [acetonitrile, *N,N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO)] and a hydroxylic solvent (water, methanol, ethanol, propan-2-ol, and butan-1-ol). The data obtained for the binary mixtures are interpreted based on solute-solvent and solvent-solvent interactions.

## EXPERIMENTAL

### Apparatus

The UV–vis experiments were recorded on an HP 8452A spectrophotometer at 25°C. Fluorescence emission spectra were recorded on a Hitachi F-4500 spectrofluorimeter at 25°C. Fluorescence lifetime measurements were performed with the photon temporal correlation technique, using an Edinburgh spectrophotometer model CD-900. The decay register was achieved by excitation with a hydrogen lamp operating at a frequency of 40 kHz and the detection was made with a Hamamatsu R-928 photomultiplier. The time increment employed in the acquisition was 50 ps per channel and the lifetime was obtained by means of decay analysis with instrumental response, attained by pulse scattering.

### Reagents

All solvents were HPLC grade and were purified following methodology described in the literature [27]. The purity of the solvents was then checked with the fluorescence apparatus in the wavelength range of interest. Deionized water was used in all measurements. This solvent was boiled and bubbled with nitrogen and kept in a nitrogen atmosphere to avoid the presence of carbon dioxide. Dye **2** [28] was prepared as described in the literature.

### UV–vis Measurements

The following procedure was typical for all experiments performed. A  $5 \times 10^{-3}$  mol dm<sup>-3</sup> stock solution of the dye was prepared in anhydrous ethanol. Then, 10 mm<sup>3</sup> from this stock solution was diluted in 3 cm<sup>3</sup> of the solvent under investigation in a 1-cm quartz cuvette. In order to deprotonate the dye, 2 mm<sup>3</sup> of a 0.2 mol dm<sup>-3</sup> tetraethylammonium hydroxide aqueous solution were added to the cuvette. It was observed that this very small amount of added water did not interfere in the UV–vis band of the dye. The maxima on the UV–vis spectra were calculated from the first derivative of the absorption spectrum. The  $\lambda_{\max}$  values thus obtained were transformed into  $E_T$  values, according to the expression  $E_T(\text{kcal mol}^{-1}) = 28590/\lambda_{\max}(\text{nm})$  [13,15].

### Fluorescence Measurements

All solutions were prepared exactly as described above. Aerated solutions at 25°C were used for the collection of all corrected emission spectra, employing a 1-cm

square cuvette. Samples were excited at 485 nm, with excitation and emission slit width settings of 5.0 and 2.5 nm, respectively. The quantum yields ( $\phi_f$ ) were determined for the dye using rhodamine B in ethanol ( $\phi_{f,\text{ref}} = 0.70$ ) as an internal standard, with the use of the expression  $\phi_f = \phi_{f,\text{ref}}(A_{\text{ref}}/A)(\eta/\eta_{\text{ref}})(a/a_{\text{ref}})$ ,  $A$  being the absorbance of the sample,  $A_{\text{ref}}$  the absorbance of the internal standard,  $\eta$  and  $\eta_{\text{ref}}$  the refractive index of the solvent and the internal standard and  $a$  and  $a_{\text{ref}}$  the area under the fluorescence peak of the sample and the internal standard, respectively [29]. The fluorescence charge transfer energies ( $E_T^{\text{fl}}$ ) were calculated from the maxima of the fluorescence emission values ( $\lambda_{\text{max}}^{\text{fl}}$  with the expression  $E_T^{\text{fl}}(\text{kcal mol}^{-1}) = 28590/\lambda_{\text{max}}^{\text{fl}}(\text{nm})$ ).

### Fluorescence Studies in Mixed Solvents

Binary mixtures were prepared by weighing the solvents and the final values are expressed in terms of the hydroxylic co-solvent mole fraction ( $X_2$ ) in the mixtures. The following procedure was typical for all experiments performed. A  $5.3 \times 10^{-3} \text{ mol dm}^{-3}$  stock solution of **2** was prepared in anhydrous ethanol. From this stock solution  $34 \text{ mm}^3$  was then transferred to two  $10 \text{ cm}^3$  volumetric flasks. After the evaporation of the ethanol, the probe was solubilized in the pure solvents, resulting in solutions presenting final concentrations of  $1.8 \times 10^{-5} \text{ mol dm}^{-3}$ . Binary mixtures were prepared from these stock solutions by weighing the solvents in a quartz cuvette. In order to deprotonate the dye,  $2 \text{ mm}^3$  of a  $0.2 \text{ mol dm}^{-3}$  tetraethylammonium hydroxide aqueous solution were added to the cuvette. This very small amount of added water did not interfere in the UV-vis or fluorescence emission band of **2**. The maxima on the emission spectra were determined and the  $\lambda_{\text{max}}$  values thus obtained were transformed into  $E_T^{\text{fl}}$  values (see above).

### Calculation Methods

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

## RESULTS AND DISCUSSION

Table I displays the normalized Reichardt polarity scale  $E_T^{\text{N}}$  [15a] and Kamlet-Taft  $\alpha$  (solvent hydrogen-bond donor acidity),  $\beta$  (solvent hydrogen-bond acceptor basicity), and  $\pi^*$  (solvent dipolarity/polarizability) parameters [30], that are commonly used to describe solvent polarity

**Table I.** Polarity Parameters of Pure Solvents at 25°C

Solvent	$\pi^{*a}$	$\alpha^a$	$\beta^a$	$E_T^{\text{N}b}$
Water	1.09	1.17	0.47	1.000
Ethyleneglycol	0.92	0.90	0.52	0.790
Methanol	0.60	0.93	0.62	0.762
Ethanol	0.54	0.83	0.77	0.654
Propan-1-ol	0.52	0.78	0.90	0.617
Butan-1-ol	0.47	0.79	0.88	0.602
Propan-2-ol	0.48	0.76	0.95	0.546
Acetonitrile	0.75	0.19	0.31	0.460
Dimethyl sulfoxide	1.00	0.00	0.76	0.444
<i>N,N</i> -Dimethyl formamide	0.88	0.00	0.69	0.404

<sup>a</sup>Refs. [13, 14, 30].

<sup>b</sup>Ref. [15a].

and its hydrogen bonding properties. The solvents used in this work can be classified into two groups. The first group comprises the HBA solvents, which are recognized for their very strong hydrogen bond acceptor (high  $\beta$  values) and weak hydrogen bond donor (low  $\alpha$  values) properties. The other group includes the hydroxylic solvents, which display strong hydrogen bond donor capabilities, as well as appreciable hydrogen bond acceptor properties (appreciable  $\beta$  values).

Solutions of dye **2** in these solvents were analyzed with UV-vis spectroscopy. The data show that the solvatochromic band of the dye is extremely sensitive to changes in the polarity of the medium (Table II). A plot of the  $E_T$  values for dye **2** as a function of  $E_T(30)$  is shown in Fig. 1 and a very good linear relationship was obtained ( $r^2 > 0.99$ ). This probe, similarly to dye **1**, is able to interact specifically with hydrogen-bond donating (HBD) solvents through hydrogen bonding using its phenolate

**Table II.** Molar Transition Energy Values Based on the UV-vis Absorption Maxima, Molar Transition Energy Values Based on the Fluorescence Emission Maxima, and Fluorescence Quantum Yields of Dye **2** at 25°C

Solvent	$E_T(\text{BM})$ (kcal mol <sup>-1</sup> )	$E_T^{\text{fl}}(\text{BM})$ (kcal mol <sup>-1</sup> )	$\phi_f(\text{BM})$
Acetonitrile	50.2	46.4	$9.0 \times 10^{-5}$
DMF	49.0	46.0	$1.0 \times 10^{-4}$
DMSO	49.8	46.1	$2.9 \times 10^{-4}$
Water	64.4	49.9	$6.7 \times 10^{-3}$
Methanol	58.8	49.5	$9.8 \times 10^{-3}$
Ethanol	55.6	49.3	$1.4 \times 10^{-2}$
Propan-2-ol	52.4	48.0	$1.6 \times 10^{-2}$
Butan-1-ol	54.1	48.6	$5.2 \times 10^{-3}$
Propan-1-ol	54.6	48.8	$2.0 \times 10^{-2}$
Ethyleneglycol	60.1	49.2	$1.7 \times 10^{-2}$
Ethanol:water (4:1)	57.9	49.5	$3.4 \times 10^{-2}$

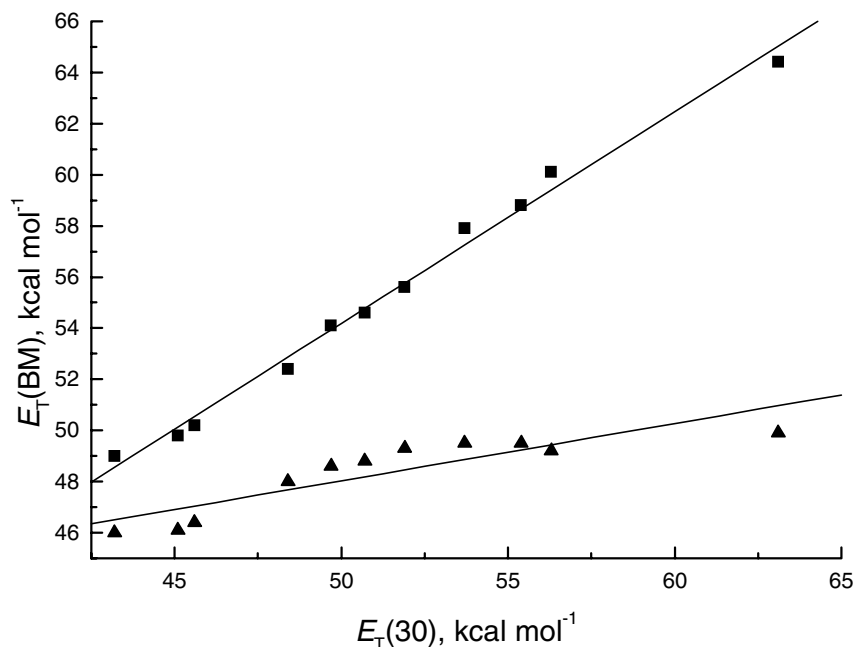


Fig. 1. Values of  $E_T$  (BM) (■) and  $E_T^{\text{fl}}$  (BM) (▲) for dye **2** as a function of  $E_T(30)$  values at 25°C.

donor moiety. Table II summarizes also the maxima in the emission spectra for dye **2** in the solvents used in this study, while Fig. 1 depicts the behavior of the  $E_T^{\text{fl}}$  values for the dye as a function of the parameter  $E_T(30)$ . Dye **2** showed a significant variation in the  $\lambda_{\text{max}}^{\text{fl}}$  values, exhibiting a strong negative fluorosolvatochromism ( $\lambda_{\text{max}}^{\text{fl}} = 573$  nm in water and  $\lambda_{\text{max}}^{\text{fl}} = 622$  nm in DMF).

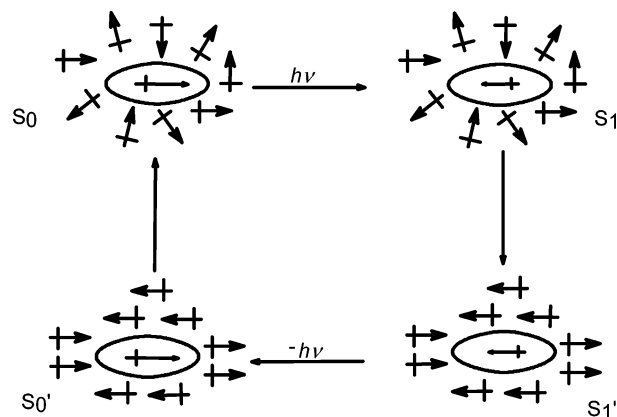
The fluorescence quantum yields were calculated for dye **2** in the solvents used in this study and are shown in Table II. Low  $\phi_f$  values (<10%) were obtained for the dye and in order to better comprehend the radiative and nonradiative decay processes of the dye, its fluorescence lifetime was measured. The lifetime measured in methanol was 230 ps, almost in the detection limit of the apparatus (ca. 300 ps) and this value can be considered very small. The results obtained suggest that molecules in the excited state decay rapidly to the ground state through nonradiative processes.

### Fluorescence Studies of Dye **2** in Mixed Solvents

The visible solvatochromic band of **2** was recently used in an investigation into preferential solvation (PS) in mixed solvents [21]. The phenomenon of PS occurs when the solute has in its microenvironment more of one solvent than the other, in comparison to the bulk composition. Thus, a study of some binary mixtures using **2** as the probe

was performed in this investigation in order to compare the ability of this dye to probe mixed solvents by means of UV-vis [21] and fluorescence techniques.

Scheme 1 shows a proposed model for the effect of the solvent on the emission spectrum of **2** [31]. After electronic excitation, the molecule enters into a Franck-Condon excited state ( $S_1$ ). The excitation is followed by the solvent relaxation, which reorients according to the new acquired electronic situation in  $S_1$  and the  $S'_1$  state is attained. The transition  $S'_1 \rightarrow S'_0$  represents the fluorescence emission. Finally, the solvent molecules revert to



Scheme 1.

**Table III.** Calculated Parameters for Dye **2** in Binary Mixtures at 25°C<sup>a</sup>

Binary mixture	$E_T(\text{BM})_1^{\text{fl}}$	$E_T(\text{BM})_2^{\text{fl}}$	$E_T(\text{BM})_{12}^{\text{fl}}$	$f_{2/1}$	$f_{12/1}$	$SD$
Acetonitrile–water	46.58	49.95	48.07	25.9	40.6	$4 \times 10^{-3}$
Acetonitrile–methanol	46.71	49.90	48.37	10.6	23.8	$2 \times 10^{-3}$
Acetonitrile–ethanol	46.53	49.05	47.99	132	65.2	$5 \times 10^{-3}$
Acetonitrile–butan-1-ol	46.49	48.57	47.14	$2.2 \times 10^3$	714	$1 \times 10^{-3}$
Acetonitrile–propan-2-ol	46.49	48.17	47.72	98.5	43.8	$1 \times 10^{-3}$
DMSO–water	46.17	50.45	47.04	13.0	31.2	$2 \times 10^{-2}$
DMSO–methanol	46.17	49.61	47.61	8.86	18.0	$2 \times 10^{-3}$
DMSO–ethanol	46.36	48.88	47.85	2.35	5.03	$1 \times 10^{-3}$
DMSO–butan-1-ol	46.17	48.54	48.30	0.450	3.85	$1 \times 10^{-3}$
DMSO–propan-2-ol	46.21	48.06	47.71	3.47	3.14	$1 \times 10^{-3}$
DMF–water	46.14	50.37	48.65	0.344	2.46	$4 \times 10^{-3}$
DMF–methanol	46.12	49.67	48.95	0.512	5.80	$7 \times 10^{-3}$
DMF–ethanol	46.11	48.90	47.90	9.05	14.4	$1 \times 10^{-3}$
DMF–butan-1-ol	45.93	48.53	48.16	1.29	5.60	$3 \times 10^{-3}$
DMF–propan-2-ol	46.13	47.97	48.05	0.463	3.94	$1 \times 10^{-3}$

<sup>a</sup>Obtained from the fitting of experimental data with Eq. (1).

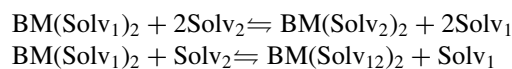
the electronic configuration  $S_0$ . The difference in the solvation of  $S_1$  and  $S'_1$  may be attributed the solvent influence on the fluorescence emission spectrum. The solute-solvent

values of solvents  $\text{Solv}_1$ ,  $\text{Solv}_2$ , and  $\text{Solv}_{12}$  in the solvation shell of **2**. The mathematical development of this model results in Eq. (1), which relates the  $E_T(\text{BM})^{\text{fl}}$  in a binary mixture to the  $E_T(\text{BM})^{\text{fl}}$  values of the two pure solvents [20,21,33].

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

interactions in the electronic state  $S'_1$  found in fluorescence are often reflected in the spectral location and in the shape of the emission bands, as well as in the lifetime of the solvent molecule rearrangement in the solvation sphere of the probe.

All results were treated by considering the two-step solvent exchange model shown below, taken from a study by Skwierczynski and Connors [19].



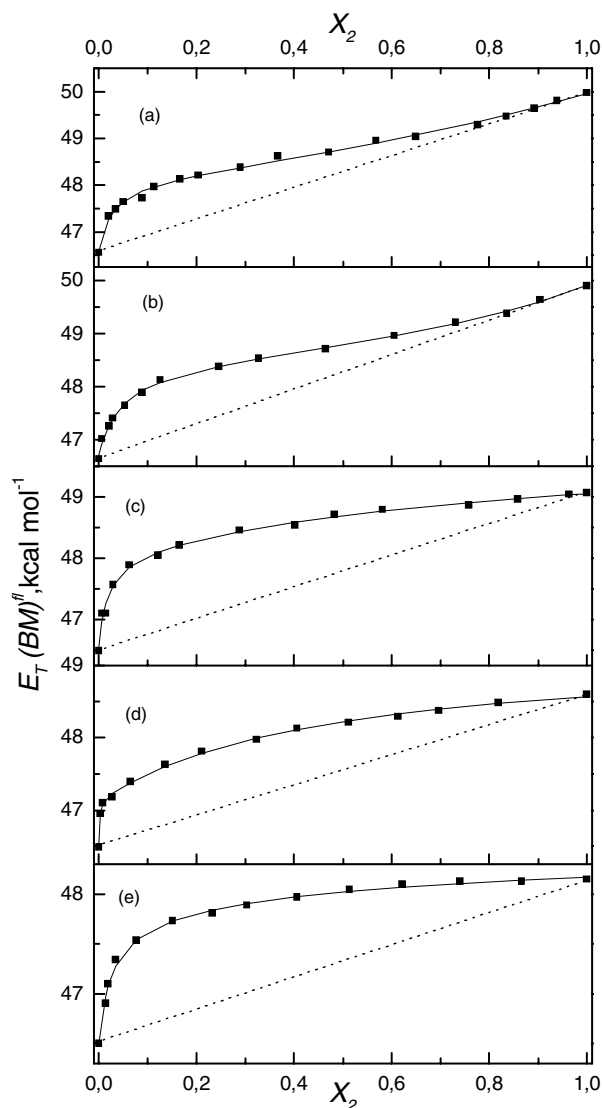
This model has been successful in explaining the solvation of the pyridiniophenolate **1** in many binary mixtures [20]. It has also been successful in describing the solvation of pyrene [32] and **2** [21] in mixtures comprising a HBA and a HBD solvent. In this model,  $\text{Solv}_1$  and  $\text{Solv}_2$  represent the HBA and the hydroxylic solvent in the mixture, respectively. The interaction through hydrogen bonding of these two solvents yields a common structure  $\text{Solv}_{12}$ . The dye solvated by  $\text{Solv}_1$ ,  $\text{Solv}_2$ , and  $\text{Solv}_{12}$  is represented by  $\text{BM}(\text{Solv}_1)_2$ ,  $\text{BM}(\text{Solv}_2)_2$ , and  $\text{BM}(\text{Solv}_{12})_2$ , respectively. The  $E_T(\text{BM})$  in a given mixture is considered equal to the average of the  $E_T(\text{BM})$

The PS parameters  $f_{2/1}$  and  $f_{12/1}$  measure the tendency of **2** to be solvated by solvents  $\text{Solv}_2$  and  $\text{Solv}_{12}$  with respect to solvent  $\text{Solv}_1$ .

The  $E_T$  values of **2** were plotted as a function of  $X_2$  (Figs. 2–4) and the experimental data for each binary mixture were fitted through a non-linear regression according to Eq. (1). The results are displayed in Table III and show very good fits for all binary mixtures studied ( $SD < 2 \times 10^{-2}$ ). In addition, the  $E_T(\text{BM})^{\text{fl}}$  values in Table III for the pure solvents agree well with the experimental values given in Table II.

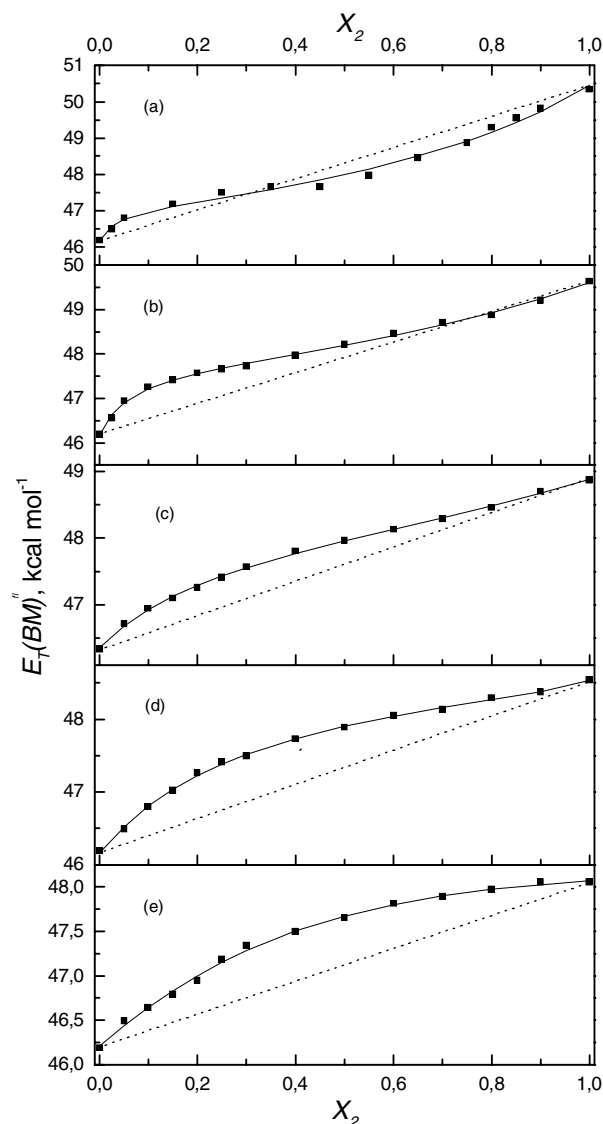
Figure 2 depicts the behavior of dye **2** in mixtures of acetonitrile with a hydroxylated component. Preferential solvation of the dye by the HBD cosolvent was verified in all mixtures.

The behavior of compound **2** in DMSO and DMF mixtures with hydroxylated solvents is shown in Figs. 3 and 4, respectively. It may be firstly remarked that the DMSO-water plot exhibits a sigmoidal shape (Fig. 3a). This behavior, commonly found in the literature [20,21,23d], shows PS of the dye by water in the DMSO-rich region and by the HBA solvent in the water-rich region. This phenomenon is due to the fact that the hydroxylic solvent forms, in the water-rich region, a strong



**Fig. 2.** Influence of the HBD cosolvent on the  $E_T(\text{BM})^{\text{II}}$  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.

net of hydrogen-bonded water molecules. The resulting hydrophobic effect is responsible for bringing together the DMSO molecules and the solute. In the dilute aqueous solutions, water molecules are relatively free to interact with the donor group of the dye through hydrogen bonding. It seems that the same sigmoidal feature occurs in DMF–water mixtures (Fig. 4a), although with a very small PS by water in the DMF-rich region. Preferential solvation of **2** by the alcoholic component occurred in all DMF–alcohol and DMSO–alcohol mixtures.



**Fig. 3.** Influence of the HBD cosolvent on the  $E_T(\text{BM})^{\text{II}}$  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.

A simple way to analyze the results of PS in mixed solvents is by supposing that the mixtures are composed exclusively of the two species  $\text{Solv}_1$  and  $\text{Solv}_2$ . This assumption can be made only because synergistic effects are absent in these curves [20,21,32]. Thus, the molar percentage of the hydroxylic component (ROH) for a 1:1 bulk mole fraction in a given mixture can be weighed through Eq. (2), where ROH (%) is the estimated molar

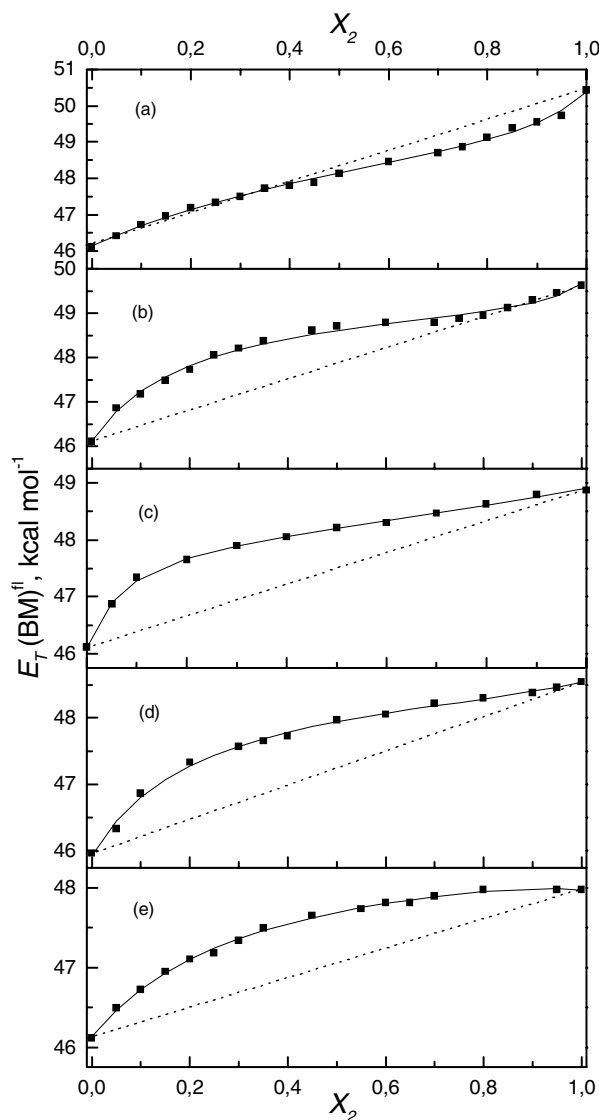


Fig. 4. Influence of the HBD cosolvent on the  $E_T(\text{BM})^{\text{fl}}$  values for **2** in DMF-ROH mixtures, the ROH component being water (a), methanol (b), ethanol (c), butan-1-ol (d), or propan-2-ol (e). (.....) Theoretical linear dependence for no PS; (—) curve fitted with Eq. (1); (■) experimental data.

percentage of the hydroxylic component in the mixture.

$$\text{ROH}(\%) = \frac{(E_T(\text{BM})_{0.5}^{\text{fl}} - E_T(\text{BM})_{0.0}^{\text{fl}})}{(E_T(\text{BM})_{1.0}^{\text{fl}} - E_T(\text{BM})_{0.0}^{\text{fl}})} \times 100 \quad (2)$$

$E_T(\text{BM})_{0.0}^{\text{fl}}$ ,  $E_T(\text{BM})_{0.5}^{\text{fl}}$ , and  $E_T(\text{BM})_{1.0}^{\text{fl}}$  are the  $E_T$  values for the HBD solvent mole fractions of 0.0, 0.5, and 1.0, respectively. Values for  $E_T(\text{BM})_{0.5}^{\text{fl}}$  were calculated with the use of Eq. (1) and the parameters given in Table III for each mixed system. Estimated molar percentages of hy-

Table IV. Estimated Molar Percentage of the Hydroxylic Component in the Microenvironment of Dye **2** for a Binary Mixture Containing 1:1 Bulk Mole Fraction<sup>a</sup>

Hydroxylic component	% ROH		
	Acetonitrile	DMF	DMSO
Water	65	47	43
Methanol	65	70	59
Ethanol	86	75	64
Butan-1-ol	83	77	74
Propan-2-ol	91	85	79

<sup>a</sup>Calculated from Eq. (2) (see text).

droxylic components for all mixed systems studied here are shown in Table IV. It can be seen, for instance, that in the acetonitrile–water system, the cybotactic region of the dye in a mixture containing 50% of each of the bulk mixed components comprises 65% water molecules. In the DMSO–water mixture with the same bulk composition, only 43% of water molecules are present in the solvation sphere of the dye. Two aspects may be noted upon analysis of Table IV. Firstly, the capability of ROH to solvate the dye increases with the lengthening of the alkyl chain. For all three HBA solvent systems, in particular for the DMF and DMSO mixed systems, ROH solvation follows this increasing order: water < methanol < ethanol < butan-1-ol < propan-2-ol. This is exactly the opposite to the order of acidity of these solvents (see  $\alpha$  values in Table I) and is the same as their increasing order of hydrophobicity. The other aspect to be observed is that, for each ROH set of mixtures, the ability of the HBA solvents to solvate the dye increases in the order: acetonitrile < DMF < DMSO, which is the same as the increasing order of both basicity and polarity of these solvents ( $\beta$  and  $\pi^*$  values in Table I). It is well known that in mixed solvents containing a HBD component and a HBA solvent the presence of  $\text{Solv}_{12}$  species formed by hydrogen bonding can occur [18,20,21,32, 33]. This interaction is strong since the hydrogen bonding acceptor solvent has high  $\beta$  value and the hydrogen bonding donor partner has high  $\alpha$  value. The results shown here suggest that the formation of these species is related to the solvation of the dye. It is also important to observe that dye **2**, although dipolar, is a hydrophobic molecule. Thus, the hydrophobic effect of the solvents plays an important role in the solvation of the dye, and this interaction increases with the lengthening of the alkyl chain of the hydroxylic component. In each ROH set of mixtures, the increase in the  $\beta$  value of the HBA solvent makes the interaction with the HBD cosolvent stronger. It renders the ROH molecules less available to solvate the microenvironment of the dye. In addition,

the order of solvation by ROH in each HBA system can be explained by the fact that with the lowering of the medium acidity, the hydrogen bonds in the complexes are weaker and the HBD solvent is able to solvate specifically the dye.

The analysis of the results shows that the sensitivity of **2** to the medium differs when UV–vis data [21] are compared with fluorescence data, but the same general trends can be observed through these two techniques. Probe **2** possesses a ground state dipole moment [ $\mu(S_0)$ ] longer than that of the excited state [ $\mu(S_1)$ ] [34]. The effect of the medium on the emission spectrum is influenced by the lifetime of the excited state ( $\tau_e$ ) and if the  $\tau_e$  value is sufficiently high (ca.  $10^{-8}$  s), the rearrangement of the solvent in the solvation sphere of the probe is possible. It was reported above that  $\tau_e = 2.30 \times 10^{-10}$  s for dye **2** in methanol. If the contribution of the quinoidal form in the excited state was greater than the dipolar form, this state would probably have lower polarity. This would facilitate solvent rearrangement, with the less polar solvent in the mixture predominating in the cybotactic region of the dye, leading to a positive fluorosolvatochromism. However, following the studies carried out with the mixed solvents, this possibility was disregarded. Therefore, the similarity of the medium effects on the fluorescence and UV–vis spectra suggests that the  $\mu(S_1)$  value is still high and  $\tau_e$  is not sufficient for the rearrangement of the solvent according to the electronic distribution of  $S_1$ . The microenvironment of **2** in the excited state prior to fluorescence is therefore probably similar to that in  $S_1$  (the Franck-Condon state).

## CONCLUSIONS

The fluorosolvatochromism of Brooker's merocyanine (dye **2**), known for their UV–vis solvatochromic behavior, was investigated. This dye displayed fluorescence, suggesting that the structural factors responsible for UV–vis solvatochromism also lead to its emission in the visible region: i.e., the presence of electronic donor and acceptor groups linked by means of a single or conjugated bridge. Dye **2** was sensitive to changes in the medium with respect to the fluorescence technique, with  $\lambda_{\max}^{\text{fl}}$  values varying from 622 nm in DMF to 573 nm in water. This wide hypsochromic shift denotes that Brooker's merocyanine can be employed as a fluorescent probe for medium polarity. The small fluorescence quantum yields for **2** in the solvents used and its short lifetime measured in methanol (230 ps) suggest that the dye in the excited state decays rapidly through nonradiative processes.

The study of dye **2** in mixed solvents demonstrated that its fluorosolvatochromism is similar, although to a

minor extent, to its UV–vis solvatochromism. This suggests that the dipole moment for **2** in the excited state is still relatively high in comparison with its dipole moment in the ground state. The microenvironment of this dye in the excited state is very similar to its Franck–Condon excited state. Since the ground state of the dye is mainly stabilized by the polar solvent, the lifetime of the excited state is very short and is insufficient for the rearrangement of the solvent in the solvation sphere of the compound.

These results illustrate the versatility of merocyanine **2** as fluorescence-based solvatochromic probe in the study of pure and mixed solvents. Furthermore, the design of new merocyanine dyes displaying synthetic modifications in relation to the structure studied here may allow access to new classes of more efficient fluorescent dyes, with potential applications in many fields of knowledge.

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