JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 420–427

Solute–solvent and solvent–solvent interactions in the preferential solvation of Brooker's merocyanine in binary solvent mixtures

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Received 19 December 2001; revised 13 March 2002; accepted 19 March 2002

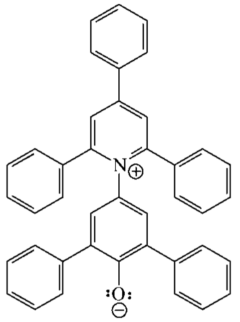
ABSTRACT: The E_T polarity values of 4-[(1-methyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one, better known as Brooker's merocyanine, were collected in binary mixtures comprising a non-protic [acetonitrile, dimethyl sulfoxide (DMSO) and acetone] and a protic (water, methanol, ethanol, propan-2-ol and butan-1-ol) solvent. Data referring to mixed systems involving water and alcohols (methanol, ethanol, propan-2-ol and 2-methylpropan-2-ol) were also collected. These data were used in the investigation of the preferential solvation of the dye. Each solvent system was analyzed in terms of both solute–solvent and solvent–solvent interactions. These latter interactions are responsible for the synergistic effects observed for the E_T parameter in many binary mixtures. 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. This model was then successfully applied to explain the kinetic behavior of the methylation of sodium 4-nitrophenoxide in acetone–water mixtures. This result suggests that this solvatochromic strategy can be successful in the analysis of many other solvent-dependent kinetic and thermodynamic processes occurring in mixed solvents. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: solvent effects; synergism; preferential solvation; binary solvents; solvent–solvent interactions; solute–solvent interactions; Brooker's merocyanine; kinetic synergistic behavior

INTRODUCTION

Interest in physicochemical properties involving solute–solvent interactions in mixed solvents has increased over the past decade in view of their greater complexity in comparison with pure solvents.[1–5] This puzzling behavior results from the combined effects of preferential solvation (PS) of the solute by one of the components in the binary mixture[6,7] and of solvent–solvent interactions.[8] Preferential solvation occurs when the polar solute has in its microenvironment more of one solvent than the other, in comparison with the bulk composition. The understanding of these phenomena may help in the elucidation of kinetic, spectroscopic and thermodynamic events that occur in solution.

In order to analyze different aspects of mixed solvents, the UV–vis band of solvatochromic compounds is generally studied. A very interesting example is Reichardt's betaine (**1**),[1,4] which is one of the most commonly employed solvatochromic dyes in studies involving binary mixtures.[9–13] Another well-known solvatochromic dye is 4-[(1-methyl-4(1*H*)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one (**2**), better known as Brooker's merocyanine.[3,14] It was recently suggested that **2** occurs as a resonance hybrid, which is weighted toward the dipolar form even in solvents presenting low dielectric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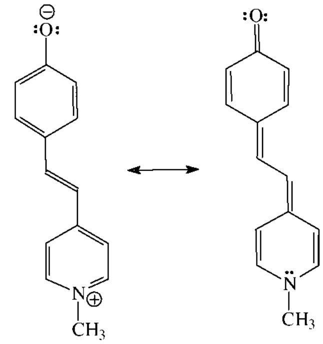
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Contract/grant sponsor: Conselho Nacional de Pesquisa Científica e Tecnológica (CNPq).
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Table 1. 'Polarity' parameters of pure solvents at 25 °C

Solvent	ε^a	π^{*b}	α^b	β^b	E_T^{Na}	$E_T(BM)^c$
Acetonitrile	35.94	0.75	0.19	0.31	0.460	50.9
Dimethyl sulfoxide	46.45	1.00	0.00	0.76	0.444	50.3
Acetone	20.56	0.71	0.08	0.48	0.355	48.6
Water	78.30	1.09	1.17	0.18	1.000	64.4
Methanol	32.66	0.60	0.93	0.62	0.762	59.0
Ethanol	24.55	0.54	0.83	0.77	0.654	55.6
Butan-1-ol	17.51	0.47	0.79	0.88	0.602	53.6
Propan-2-ol	19.92	0.48	0.76	0.95	0.546	52.4
2-Methylpropan-2-ol	12.47	0.41	0.68	1.01	0.389	49.6

[a] Ref. 1.
[b] Ref. 20.
[c] This work.

constants.[15] Despite the considerable number of experimental and theoretical studies on the solvatochromic behavior of **2**,[16] studies applying this dye to mixed solvents are very scarce.[17]

Many examples in the recent literature illustrate the influence of PS in kinetic processes occurring in mixed solvents.[18,19] Since most transition states in chemical processes involve different charge separation in parts of the molecule in comparison with the reactant species, it is likely that PS of reactants or the transition state will result from the action of one of the components in the binary mixture and, as a result, this may influence the reaction rate. Dawber *et al.*[10] used this rationalization to study the relationship between the PS, using a solvatochromic pyridinium betaine, and some solvolytic processes in mixed solvents. For the processes analyzed, PS was suggested as an important factor in the solvent-dependent reaction rates.[10] More recently, Mancini and co-workers[12] interpreted successfully solvent effects in binary mixtures on the aromatic nucleophilic substitution reaction, by the comparison with the $E_T(30)$ parameter in the same solvent mixtures. However, these authors verified that the presence of a protic solvent in the mixture strongly determines the solvent effects on the reaction, making Reichardt's betaine not generally valid for interpreting the solvent effects under consideration.[12]

In this paper, we describe the investigation of the PS of dye **2** in binary mixtures comprising a non-protic [acetonitrile, dimethyl sulfoxide (DMSO) and acetone] and a protic (water, methanol, ethanol, propan-2-ol and butan-1-ol) solvent. We also present data concerning mixed systems involving water and alcohols (methanol, ethanol, propan-2-ol and 2-methylpropan-2-ol). The data obtained are explained based on solute–solvent and solvent–solvent interactions Finally, the solvatochromic strategy employed here was applied to suggest an explanation for the rates of methylation of sodium 4-nitrophenoxide in acetone–water mixtures.[19]

RESULTS AND DISCUSSION

The polarity and hydrogen bonding properties of several solvents used in this work, represented by the normalized Reichardt polarity scale E_T^{N1} and Kamlet–Taft α, β and π^* parameters,[20] are summarized in Table 1. The solvents can be separated into two groups. The first group comprises non-protic dipolar solvents, which are very good hydrogen bond acceptors (high β values) and poor hydrogen bond donors (low α values). The other group embraces protic solvents, which display strong hydrogen bond donor capabilities. Table 1 shows also calculated $E_T(BM)$ values for the solvents studied in this work. These E_T values agree very well with values found in the literature.[16e,17] A plot of the $E_T(BM)$ values as a function of E_T^N (not shown) is linear ($r > 0.99$), suggesting that probes **1** and **2** are sensitive to similar solute–solvent interactions in the media studied.

All data were arranged in the form of plots of the E_T values of **2** as a function of X_2 (see below), the protic solvent mole fraction for mixtures of protic solvents with non-protic solvents, or water in its mixtures with alcohols. These results were treated by considering the following two-step solvent exchange model:

$$BM(S_1)_2 + 2S_2 \rightleftharpoons BM(S_2)_2 + 2S_1$$

$$BM(S_1)_2 + S_2 \rightleftharpoons BM(S_{12})_2 + S_1$$

This model originated from a study by Skwierczynski and Connors,[21] and it has been successful in explaining the solvation of pyridiniophenoxide **1** in many binary mixtures.[13] S_1 and S_2 represent the aprotic and the protic solvent in the mixture, respectively. These two solvents interact in order to yield a common structure S_{12} with particular properties. The probe solvated by S_1, S_2 and S_{12} is represented by $BM(S_1)_2$, $BM(S_2)_2$ and $BM(S_{12})_2$, respectively.

The two solvent-exchange processes shown above are defined by PS parameters $f_{2/1}$ and $f_{12/1}$, which measure the

Table 2. Parameters of the binary mixtures at 25 °C

Binary mixture	$E_T(BM)_1$	$E_T(BM)_2$	$E_T(BM)_{12}$	$f_{2/1}$	$f_{12/1}$	SD
Methanol-water	58.9	64.4	64.2	0.01	0.34	0.002
Ethanol-water	55.6	64.4	57.4	1.23	5.62	0.005
Propan-2-ol–water	55.2	64.5	58.2	0.23	2.32	0.021
2-Methylpropan-2-ol–water	49.3	64.4	59.8	0.08	1.65	0.016
Acetonitrile–water	50.9	64.4	58.8	1.91	8.3	0.016
Acetonitrile–methanol	51.1	58.7	58.8	0.02	10.8	0.015
Acetonitrile–ethanol	51.1	55.6	56.1	0.52	17.6	0.004
Acetonitrile–propan-2-ol	50.9	52.4	54.2	4.37	20.4	0.004
Acetonitrile–butan-1-ol	51.0	54.0	55.1	3.79	21.9	0.008
DMSO–water	50.2	64.1	51.6	4.70	11.4	0.010
DMSO–methanol	50.2	59.0	53.5	6.01	7.69	0.003
DMSO–ethanol	50.4	55.8	54.6	2.26	3.28	0.003
DMSO–propan-2-ol	50.3	52.3	54.0	0.55	3.10	0.001
DMSO–butan-1-ol	50.2	53.6	54.3	0.97	4.86	0.003
Acetone–water[a]	48.5	64.6	58.8	3.01	9.54	0.063
Acetone–methanol[a]	48.6	59.1	59.3	0.44	2.80	0.007
Acetone–ethanol	48.6	55.8	53.6	9.62	9.58	0.002
Acetone–propan-2-ol	48.6	52.4	51.5	151.9	3.50	0.003
Acetone–butan-1-ol	48.6	53.7	47.2	3430	171	0.003

[a] These parameters were obtained by using the spectroscopic data from Ref. 17.

tendency of **2** to be solvated by solvents S_2 and S_{12} with respect to solvent S_1:

$$f_{2/1} = (X_2{}^L/X_1{}^L)/(X_2/X_1)^2 \tag{1}$$

$$f_{12/1} = (X_{12}{}^L/X_1{}^L)/(X_2/X_1) \tag{2}$$

where $X_1{}^L$, $X_2{}^L$ and $X_{12}{}^L$ are the mole fractions of components S_1, S_2 and S_{12} in the cybotactic region of **2**, respectively, and X_1 and X_2 are the mole fractions of the two solvents in the bulk binary mixture.

The E_T(BM) for a given mixture was considered equal to the average of the E_T(BM) values of solvents S_1, S_2 and S_{12} in the solvation shell of **2**:

$$\begin{aligned} E_T(BM) = X_1{}^L E_T(BM)_1 + X_2{}^L E_T(BM)_2 \\ + X_{12}{}^L E_T(BM)_{12} \end{aligned} \tag{3}$$

Substitution of Eqns (1) and (2) into Eqn. (3) resulted in Eqn. (4), which relates the E_T(BM) in a binary mixture to the E_T(BM) values of the two pure solvents:[13]

$$E_T(BM) = \frac{E_T(BM)_1(1-X_2)^2 + E_T(BM)_2 f_{2/1} X_2{}^2 + E_T(BM)_{12} f_{12/1}(1-X_2)X_2}{(1-X_2)^2 + f_{2/1}X_2{}^2 + f_{12/1}(1-X_2)X_2} \tag{4}$$

Thus, the experimental data for each binary mixture were fitted through a non-linear regression to Eqn. (4). The results are displayed in Table 2 and show very good fits for all binary mixtures studied. The E_T(BM) values in Table 2 for the pure solvents agree well with the experimental values given in Table 1.

Alcohol–water mixtures

Figure 1 depicts the variation in E_T(BM) values as a function of water mole fraction (X_2) for alcohol–water mixtures. Preferential solvation by the alcoholic component in these mixtures was always observed, but they change towards an ideal behavior in the alcohol-rich region if the alcoholic cosolvent is changed from methanol to propan-2-ol. This fact is reinforced by 2-methylpropan-2-ol–water mixtures [Fig. 1(d)], since a linear behavior in the alcohol-rich region up to $X_{water} \approx 0.5$ can be seen in these mixtures. It seems probable from the results that the dye is solvated by the alcoholic solvent in all mole fractions in water–methanol mixtures. This occurs because, in the water-rich region, water makes strong nets formed by hydrogen bonding, which the cosolvent added is unable to disrupt. Thus, water prefers interactions with itself and not with the dye. In addition, the alcohol in the methanol-rich region is present in great excess and can preferentially solvate the solute, since the alcohol makes weak hydrogen-bonded nets. If the alcoholic component in the mixtures is changed to ethanol or propan-2-ol, the same behavior is observed in the water-rich region. The approximation towards an ideal trend observed in the alcohol-rich region can be interpreted by the fact that the alcoholic cosolvent present in great amount is able to make a hydrogen-bonded complex with water and this S_{12} complex may be

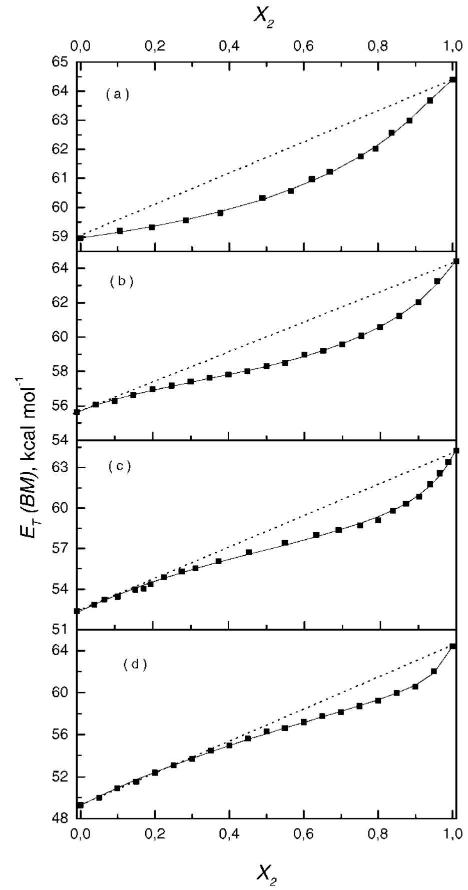


Figure 1. Influence of water on E_T(BM) values of **2** in aqueous mixtures of alcohols, the alcohols being (a) methanol, (b) ethanol, (c) propan-2-ol and (d) 2-methylpropan-2-ol. Dotted lines, theoretical linear dependence for no PS; solid lines, curves fitted with Eqn. (4); (■) experimental data

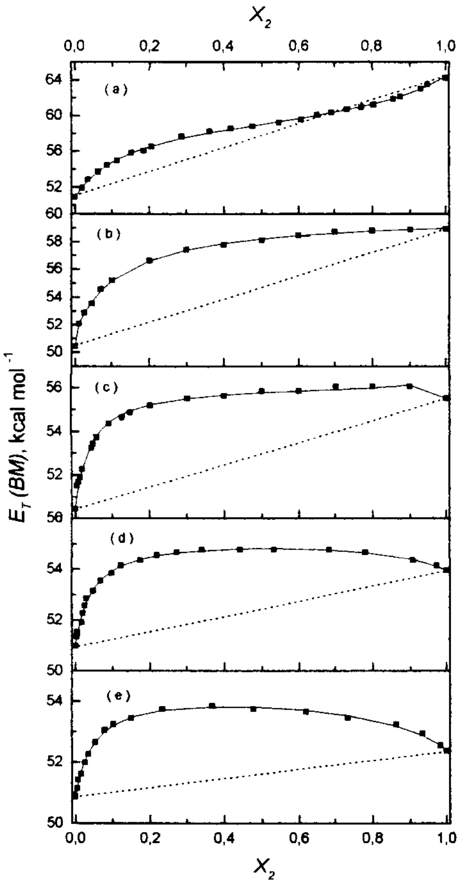


Figure 2. Influence of the protic cosolvent on E_T(BM) values of **2** in acetonitrile–ROH mixtures. ROH = (a) water, (b) methanol, (c) ethanol, (d) butan-1-ol and (e) propan-2-ol. Dotted lines, theoretical linear dependence for no PS; solid lines, curves fitted with Eqn. (4); (■) experimental data

responsible for the solvation of the dye. Since methanol is a very good hydrogen bond donor, this solvent is very able to solvate specifically the merocyanine on its phenoxide hydrogen acceptor group. However, the capability of the alcoholic component to perform this kind of solvation diminishes in the order methanol < ethanol < propan-2-ol < 2-methylpropan-2-ol, which is exactly the decreasing order of solvent hydrogen bonding donation (see the α values in Table 1). Simultaneously, this order corresponds to the increasing order of solvent hydrogen bonding acceptance. In other words, if the ability of the alcohol as a hydrogen bond donor decreases, it becomes unable to solvate the dye specifically, but its capability to form a hydrogen-bonded complex with water increases. This complex, S_{12}, can then efficiently solvate the solute.

Acetonitrile–ROH mixtures

Plots showing the variation in E_T values for dye **2** as a function of X_2 values are depicted in Fig. 2. It may first be noted that the acetonitrile–water plot shows a sigmoidal shape [Fig. 2(a)]. This behavior is commonly found in the literature,[4d,6d,13] meaning that **2** is preferentially solvated by water in the acetonitrile-rich region and, although to a minor extent, by acetonitrile in the water-rich region. This occurs because in the water-rich region, the hydroxylic solvent forms a strong net of hydrogen-bonded water molecules, and the resulting hydrophobic effect is responsible for closing together the molecules of acetonitrile and the solute. On the other hand, in dilute aqueous solutions, water molecules are relatively free to interact with the phenoxide group of **2** through hydrogen bonding.

For all other mixtures [Fig. 2(b)–(e)], PS by the protic component of the mixture was also observed, but with an interesting particularity: with the exception of methanol–acetonitrile, all other mixtures display a synergistic behavior, since the E_T values for the mixed solvents are greater than for the pure components. The term 'synergism' was first proposed by Koppel and Koppel in studies involving solutions of pyridiniophenoxide **1** in binary

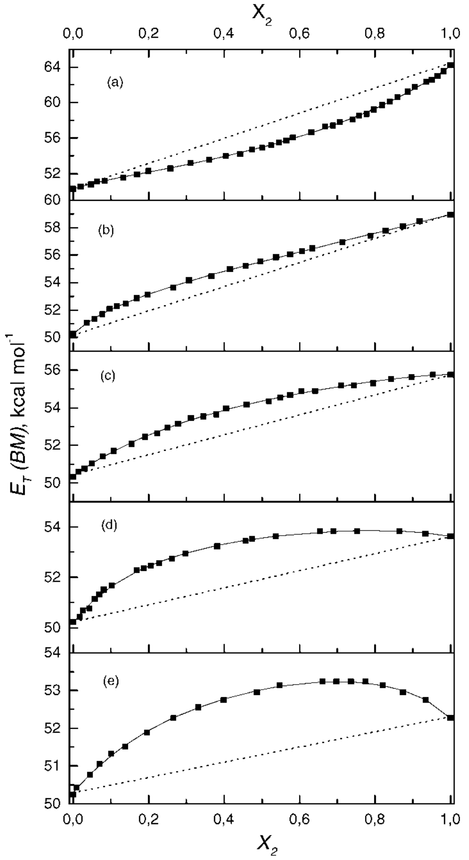


Figure 3. Influence of the protic cosolvent on E_T(BM) values of **2** in DMSO–ROH mixtures. ROH = (a) water, (b) methanol, (c) ethanol, (d) butan-1-ol and (e) propan-2-ol. Dotted lines, theoretical linear dependence for no PS; solid lines, curves fitted with Eqn. (4); (■) experimental data

mixtures in which the $E_T(30)$ values are higher than those for the pure solvents present in the mixtures.[22] The synergistic behavior observed here may result from an interaction through hydrogen bonding between the protic and the non-protic components of the mixture, yielding S_{12} species. These species are more polar than the individual solvents, being responsible for the observed trends. It is apparent from the plots in Fig. 2(c)–(e) that synergism increases with a change from ethanol to butan-1-ol. These observations can be interpreted through the fact that the synergistic pattern is accentuated if the polarities of the pure solvents are more similar. In addition, the results suggest that the interaction that yields S_{12} species is achieved by more than hydrogen bonding, since the order of the increase in synergism is the opposite to that for the hydrogen donor ability of the alcohols. Thus, the two solvents interact also by solvophobic interactions, which are expected to increase with an increase in the length of the alkyl group of the alcohol. These interactions, in addition to hydrogen bonding, seem to be very important in the solvation of the dye, which despite being dipolar also presents a hydrophobic nature.

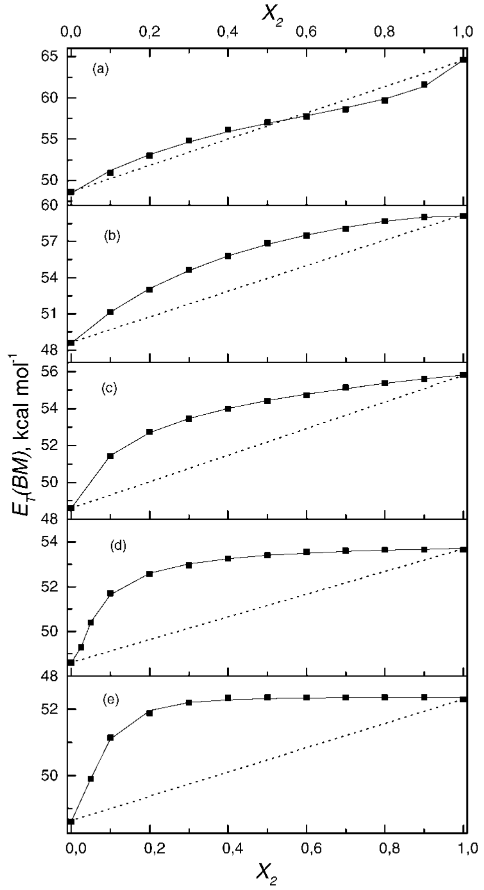


Figure 4. Influence of the protic cosolvent on E_T(BM) values of **2** in acetone–ROH mixtures. ROH = (a) water, (b) methanol, (c) ethanol, (d) butan-1-ol and (e) propan-2-ol. Dotted lines, theoretical linear dependence for no PS; solid lines, curves fitted with Eqn. (4); (■) experimental data. Experimental data for curves (a) and (b) were obtained from Ref. 17

DMSO–ROH mixtures

Figure 3 shows the influence of the protic cosolvent on E_T values in their mixtures with DMSO. Preferential solvation by DMSO in its aqueous mixtures was observed, and this reflects the fact that water, a highly structured solvent, allows the 'free' molecules of DMSO to solvate the dye. In methanol and ethanol mixtures [Fig. 3(b) and (c)], PS by the alcoholic cosolvent was observed, because these protic solvents are less structured than water and they are able to solvate **2** through hydrogen bonding. A synergistic behavior was observed in propan-2-ol and butan-1-ol mixtures [Fig. 3(d) and (e)], evidencing the presence of more polar S_{12} aggregates in the solvation shell of the dye.

Acetone–ROH mixtures

The solvatochromic behavior of **2** in acetone mixtures is

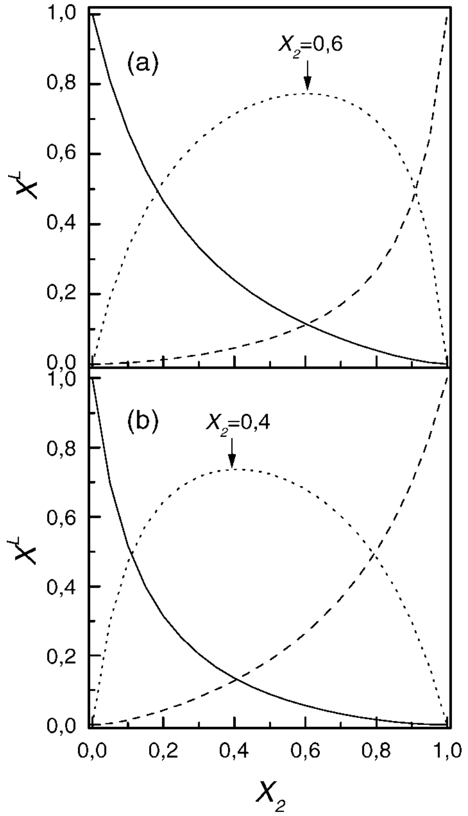
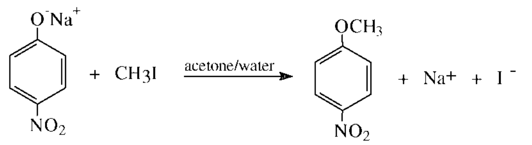


Figure 5. Species distribution diagram for acetone–water mixtures using dyes (a) **1** and (b) **2**. The curves represent (solid line) X_1^L, (dashed line) X_2^L and (dotted line) X_{12}^L in the cybotactic region of dye **2** (see text)

shown in Fig. 4. The data for the water and methanol mixtures were obtained from the literature.[17] Preferential solvation by water was observed in the acetone-rich region and by acetone in the water-rich region in acetone–water mixtures (see the explanation above). For all other acetone mixtures studied, PS by the protic cosolvent was observed. Since the alcohols do not form hydrogen bonding nets as strong as those observed in water, the non-protic cosolvent can easily break them. Hence the alcohols solvate the dye better even in the protic component rich region. The ability of the alcoholic component to solvate the dye increases in the order methanol < ethanol < propan-2-ol < methylpropan-2-ol, which is the decreasing order of solvent acidity (see the α values in Table 1). With the diminution of the ability of the alcohol to interact with other alcoholic molecules, because the hydrogen bonding is weakened, these molecules can interact more strongly with acetone molecules and also with the dye. In addition, if the alcoholic component is more hydrophobic, such as in the case of 2-methylpropan-2-ol, it is more able to interact with the hydrophobic merocyanine through hydrophobic interactions.

The treatment of experimental data by the use of Eqn. (4) allows the separation of the contributions of solvents S_1, S_2 and S_{12} in the solvation shell of the probe. As an example, a species distribution diagram is shown in Fig. 5 for the solvation of **2** in acetone–water mixtures by the use of the parameters in Table 2 and with the help of Eqns (1) and (2). Figure 5 also depicts the species distribution for Reichardt's dye (**1**) in acetone–water mixtures. E_T values for this dye in relation to different X_2 values were collected from the literature[13a] and were fitted to Eqn. (4).[22] These diagrams illustrate well the importance of the local mole fractions of the S_{12} species in the solvation of the probes. The greatest contribution of X_{12}^L in these mixtures is verified as $X_2 = 0.55$ for dye **1**, and for dye **2** this value was 0.40.



Scheme 1

Application of the PS model

Chemical probes may provide a very important tool in the study of kinetic processes occurring in mixed solvents. If there is a structural similarity with a reactant in a given process, it may be expected that the 'reportage' performed by the probes in their microenvironment corresponds to the solvation of the reactant in the process under consideration. Recently, the rate constants of the S_N2 reaction of sodium 4-nitrophenoxide and iodomethane were determined in acetone–water mixtures (Scheme 1). The rate–X_2 (mole fraction of water) profile shows that the reaction strongly depends on the medium (Fig. 6).[19]

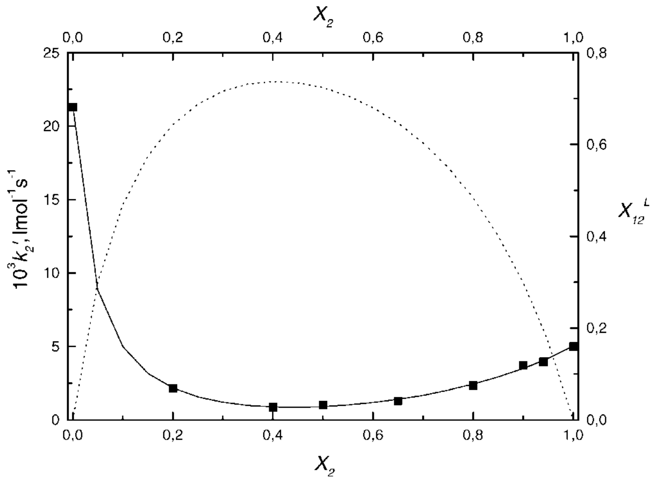


Figure 6. Influence of the medium in the methylation of sodium *p*-nitrophenoxide in acetone–water mixtures. Solid line, curve fitted with kinetic data from Ref. 19; dotted line, X_{12}^L in the cybotactic region of dye **2**

The highest rate constant was recorded in pure acetone and a minimum occurred at $X_2 = 0.4$, whereas the observed second-order rate constants increase again in the water-rich region. The kinetic synergistic feature of this profile was interpreted as resulting from specific and non-specific solute–solvent interactions.[19] These data find parallelism with the work of Mancini *et al.*,[23] which involved kinetic studies on aromatic nucleophilic substitution reactions, more specifically the reaction of 1-fluoro-2,4-dinitrobenzene with morpholine or piperidine as the nucleophile. A kinetic synergism in mixtures of ethyl acetate with chloroform or dichloromethane has been observed.[23]

In the light of the PS model applied here, three possibilities can be proposed for the solvation of 4-nitrophenoxide (or the dyes): phenoxide–S_1, phenoxide–S_2 and phenoxide–S_{12}. It could be considered that the hydrogen bonding donor ability of S_{12} would be in principle greater than in pure water, since the β value for acetone (0.48) is greater than that for water (0.18), which would make the complex $(CH_3)_2C{=}O\cdots HOH$ more acidic than pure water. However, this is not apparent from the collected E_T parameters, because of the order obtained for the two dyes studied: $E_T(\text{dye})_1 < E_T(\text{dye})_{12} < E_T(\text{dye})_2$ demonstrates that complex S_{12} is in principle less polar than the protic solvent. On the other hand, a minor reactivity for the phenoxide solvated by S_{12} can be expected, since a steric effect caused by the methyl groups in the acetone moiety in S_{12} may occur, and this makes the reaction of the phenoxide as nucleophile difficult. Since the greater contribution of $X_{12}{}^{L}$ in these mixtures for the more hydrophilic dye **2** is observed when the X_2 value is close to 0.4, these data can explain the minimum in the kinetic profile being exactly in this region (Fig. 6) and the synergism observed. It may be also observed that the maximum $X_{12}{}^{L}$ value for the more hydrophobic dye **1** does not fit the kinetic profile. This may be due to the lack of structural similarity when dye **1** is compared with the hydrophilic nucleophile 4-nitrophenoxide.[19]

CONCLUSIONS

The preferential solvation of dye **2** in mixed binary solvents is determined by solute–solvent and solvent–solvent interactions. Solvents such as acetonitrile, DMSO and acetone are able to form strong hydrogen bonds with protic solvents. These hydrogen-bonded complexes are responsible for the observed synergistic effects in many of the studied curves. The two-step solvent exchange model of Skwierczynski and Connors,[21] which was employed by Rosés and co-workers to describe the PS of pyridiniophenoxide **1** in many solvent mixtures,[13] was successfully fitted to all binary systems studied here.

Finally, in the same manner that a mixed solvent S_{12} in the microenvironment of **2** may be responsible for the synergy observed in many of the mixtures studied here, it might also exert an influence on kinetic and thermodynamic processes. Thus, we used the model employed here in order to separate the different contributions of S_1, S_2 and S_{12} in the solvation of the dye, and this solvatochromic strategy was successful in analyzing the influence of the medium on a determined kinetic process. This analysis, of course, has some limitations mainly because in a kinetic process the solvent interacts with reactants and transition state, instead of only the dye. Despite these restrictions, however, the rationalization presented here may be also important in the elucidation of a large number of other physical-chemical processes occurring in mixed solvents.

EXPERIMENTAL

Materials. All solvents were of HPLC grade and were purified following methodology described in the literature.[24] 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** was synthesized according to the method described in the literature,[25] recrystallized three times from hot water and dried under vacuum: yield, 89.6% (lit.[25] 86.3%); m.p. 220 °C (lit.[25] 220 °C). ^{1}H NMR (200 MHz, DMSO-d_6): δ (ppm) 3.90 (3H, s), 6.08 (2H, d, $J = 8.7$ Hz), 6.45 (1H, d, $J = 15.1$ Hz), 7.29 (2H, d, $J = 8.7$ Hz), 7.49 (2H, d, $J = 6.7$ Hz), 7.65 (1H, d, $J = 15.1$ Hz), 8.11 (2H, d, $J = 6.9$ Hz).

UV-vis measurements. Binary mixtures were prepared by weighing the solvents and final values were expressed in terms of the protic cosolvent mole fraction (X_2). The following procedure is typical for all experiments performed. A 5.3×10^{-3} mol l^{-1} stock solution of **2** was prepared in anhydrous ethanol, then 34 μl of this stock solution were transferred into two 10 ml volumetric flasks. After evaporation of the ethanol, the probe was solubilized in the pure solvents, resulting in a final concentration of 1.8×10^{-5} mol l^{-1}.

Binary mixtures were prepared from these stock solutions by weighing the solvents in a quartz cuvette. In order to deprotonate the dye, 2 μl of a 0.2 mol l^{-1} 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 **2**. The UV–vis experiments were recorded on a HP 8453 spectrophotometer at 25 °C, using a 1 cm square cuvette. The maxima on the UV–vis spectra were calculated from the first derivative of the absorption spectrum. The λ_{max} values thus obtained were transformed into $E_T(\text{BM})$ values, according to the expression $E_T(\text{BM}) = 28590/\lambda_{max}$.

Calculation methods. The parameters $E_T(\text{BM})_1$,

$E_T(BM)_2$, $E_T(BM)_{12}$, $f_{2/1}$ and $f_{12/1}$ (see above) were calculated from non-linear regressions using the ORIGIN 5.0 program.

Acknowledgements

The financial support of the Brazilian Conselho Nacional de Pesquisa Científica e Tecnológica (CNPq), CAPES, PRONEX, UFSC and UNISUL is gratefully acknowledged. We also thank Professor Faruk Nome for laboratory facilities.

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