Preferential Solvation of a Hydrophobic Probe in Binary Mixtures Comprised of a Nonprotic and a Hydroxylic Solvent: A View of Solute−Solvent and Solvent−Solvent Interactions

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The fluorescence of pyrene, a hydrophobic probe, was investigated in binary mixtures comprising a nonprotic [acetonitrile, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofurane (THF)] and a protic (water, methanol, ethanol, propan-2-ol, and butan-1-ol) solvent. The variation in I/III values, the intensity ratios between the first and third bands in vibronic fine structures of the emission spectra, along with the variation in the more polar component was studied for each binary mixture. A preferential solvation (PS) model was adapted from the literature and successfully applied to the experimental data. In the mixtures containing acetonitrile, pyrene is always preferentially solvated by the nonprotic component. However, the extent of PS by acetonitrile diminishes with a decrease in the polarity of the protic cosolvent. These results were explained by the fact that pyrene is a highly hydrophobic probe. Thus, a replacement of the more polar protic cosolvent for one which is more hydrophobic may lead to a comparatively stronger interaction of the probe with the cosolvent through hydrophobic interactions. Synergism was observed for binary mixtures comprising THF and the studied alcohols, for DMSO with water and methanol, and for DMF with water. Finally, D_2O−DMF and D_2O−DMSO mixtures were studied and compared with the corresponding H_2O mixtures. It was verified that the extent of PS in both cases is diminished if water is replaced by deuterium oxide. All data were interpreted in terms of solute−solvent and solvent−solvent interactions.

Introduction

It is well-known that the solvent can influence the physicochemical properties of a solute in a wide variety of chemical processes.[1,2] Effects of this nature are commonly interpreted as resulting from changes in the polarity, a general term that comprises the overall solvating capability of the medium.[3] Physicochemical investigations involving solvent properties are commonly performed by means of chemical probes.[1,2,4] In these studies, we can note a growing interest in mixed solvents.[1,2,4−13] This is due to the possibility of preferential solvation, which makes the solute−solvent and solvent−solvent interactions more complex in the case of mixed solvents than pure solvents. Preferential solvation (PS) occurs when the polar solute has in its microenvironment more molecules of one solvent than the other in comparison with the bulk composition. This concept is relevant because it allows us to explain spectroscopic,[4−13] equilibrium,[14−17] and kinetic data[14,18−21] for mixed solvents. Preferential solvation commonly results from specific (e.g., hydrogen-bonding)[11] and nonspecific (dielectric enrichment)[12] solute−solvent interactions. It can also be a result of solvent−solvent interactions.[13] In the latter case, one component of the binary mixture prefers a molecule of the same type in its neighborhood, leading to the formation of clusters. Although the solute cannot be proved to be responsible for the clustering, it can be solvated in these solvent aggregates. There is, therefore, interest in the search for probes able to detect these medium microheterogeneities.

To analyze different aspects of the binary mixtures, 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 utilized solvatochromic dyes in studies involving binary mixtures.[9,14,18−20] In contrast, a few fluorescent compounds have been used as polarity probes.[1,2,4,6] Among them, pyrene (**2**) has been extensively utilized as a fluorescence probe in the study of micelles and of lipophilic environments.[22−24] Its use as a probe is arised from the fact that the intensities of the various fluorescence vibronic bands depend strongly on the solvent microenvironment.[25,26] More specifically, an enhancement in the intensity of the first fluorescence band (I) is observed in the presence of polar solvents while only a slight effect is observed on the third band (III).[25,26] Therefore, the ratio of the intensities I/III has been applied in solvation studies and is the basis for the Py scale of solvent polarities.[27] An interesting aspect related to this probe is its inability to interact with the medium through hydrogen bonding,[27,28] contrary to pyridiniophenoxide, **1**, which shows major dependence on this specific solute−solvent interaction.[29] Thus, the use of **2** may provide interesting insights with respect to mixed solvents. Despite the widespread use of pyrene, very little work has been performed utilizing this compound to probe solvent binary mixtures.[10,30]

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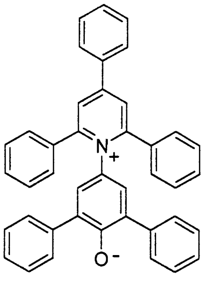
More recently, Kusumoto et al.[10] have utilized pyrene in the investigation of PS in water−alcohol mixtures. In this work, we describe the investigation of the PS of pyrene in binary mixtures comprising a nonprotic [acetonitrile, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofurane (THF)] and a protic (water, methanol, ethanol, propan-2-ol, and butan-1-ol) solvent. In addition, D_2O−DMF and D_2O−DMSO mixtures were studied and compared with the corresponding H_2O mixtures. The obtained data will be explained based on solute−solvent and, mainly, solvent−solvent interactions.



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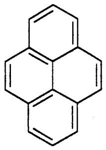

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Experimental Section

Materials. All solvents were HPLC grade and were purified following methodology described in the literature.[31] 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. Deuterium oxide (Aldrich) had a 99.9% deuterium content. Pyrene (Aldrich, >99%) was recrystallized three times from methanol and dried before use.

Fluorescence Measurements. To avoid the formation of pyrene microcrystals and extrinsic phenomena, the concentration of the probe was fixed at 4×10^{-7} mol dm^{-3}. The following procedure was valid for all experiments performed. A stock solution of **2** (1.25×10^{-4} mol dm^{-3}) was prepared in dichloromethane. With a microsyringe, 16 mm^3 of this solution was transferred to 5 cm^3 volumetric flasks. After the evaporation of the dichloromethane, the probe was solubilized in the mixed solvents. Binary mixtures were prepared weighing the aerated solvents with an analytical balance and the final values were expressed in terms of the protic cosolvent mole fraction (X_2).

The fluorescence experiments were recorded on a Hitachi F-4500 spectrofluorimeter. 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 315 nm, with excitation and emission slit width settings of 5.0 and 2.5 nm, respectively.

Calculation Methods. The parameters I/III$_1$, I/III$_2$, I/III$_{12}$, $f_{2/1}$, and $f_{12/1}$ (see below) were calculated from nonlinear regressions using the ORIGIN 5.0 program.

Results and Discussion

The polarity and hydrogen bonding properties of the solvents used in this work, represented by the normalized Reichardt polarity scale E_T^{N1} and Kamlet−Taft α, β, and π^* parameters,[32] are summarized in Table 1. These solvents can be separated into two groups. The first group comprises the nonprotic dipolar solvents, which are very good hydrogen bond acceptors (high β values) with the exception of acetonitrile, and poor hydrogen bond donors (low α values). The other group is composed of the protic solvents, which display strong hydrogen bond donor capabilities. Table 1 shows also I/III values for the solvents studied in this work. If plots of I/III vs Kamlet−Taft values for the solvents used here are made, we can verify a lack of linear relationship, a fact that agrees with the literature, since it has been verified that only I/III values for nonprotic, nonpolychlorinated, aliphatic solvents are linearly related to the Kamlet−Taft parameters.[28] The I/III values obtained in this work are very similar to those in the literature.[25,27] Experiments were performed in order to compare aerated samples with others treated through bubbling with a stream of argon. In both cases an alteration in the readings for pure solvents and for mixtures having $X_2 = 0.50$ was not verified.

TABLE 1: Polarity Parameters of Pure Solvents at 25°C

solvent	π^{*a}	α^a	β^a	$E_T^{N\,b}$	I/III^c
acetonitrile	0.75	0.19	0.31	0.460	1.63
N,*N*-dimethyl formamide	0.88	0.00	0.69	0.404	1.81
dimethyl sulfoxide	1.00	0.00	0.76	0.444	1.88
tetrahydrofuran	0.58	0.00	0.55	0.207	1.21
water	1.09	1.17	0.18	1.000	1.81
deuterium oxide				0.991	1.81
methanol	0.60	0.93	0.62	0.762	1.30
ethanol	0.54	0.83	0.77	0.654	1.18
propan-2-ol	0.48	0.76	0.95	0.546	1.09
butan-1-ol	0.47	0.79	0.88	0.602	1.07

[a] Reference 32. [b] Reference 1. [c] This work.

All data were arranged in the form of plots of I/III values of **2** as a function of X_2 (see below), the protic solvent mole fraction for mixtures of protic solvents and nonprotic solvents in the presence of **2**. These results were treated by considering the following two-step solvent exchange model:

$$\text{pyrene}(S_1)_2 + 2S_2 \rightleftarrows \text{pyrene}(S_2)_2 + 2S_1$$

$$\text{pyrene}(S_1)_2 + S_2 \rightleftarrows \text{pyrene}(S_{12})_2 + S_1$$

This model originates from a study by Skwierczynski and Connors,[33] and it has been successful in explaining the solvation of the pyridiniophenoxide **1** in many binary mixtures.[9] 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 with S_1, S_2, and S_{12} is represented by pyrene$(S_1)_2$, pyrene$(S_2)_2$, and pyrene$(S_{12})_2$, respectively.

Both processes showed solvent-exchange characteristics as defined through the PS parameters $f_{2/1}$ and $f_{12/1}$, which measure the 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 the 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 I/III ratio for a given mixture was considered equal to an average of the I/III values of solvents S_1, S_2, and S_{12} in the solvation shell of **2** (eq 3).

$$\text{I/III} = X_1^{\,L}\,\text{I/III}_1 + X_2^{\,L}\,\text{I/III}_2 + X_{12}^{\,L}\,\text{I/III}_{12} \tag{3}$$

Application of eq 1 and 2 into eq 3 resulted in eq 4, which

TABLE 2: Calculated Parameters of the Binary Mixtures at 25°C [a]

binary mixture	I/III$_1$	I/III$_2$	I/III$_{12}$	$f_{2/1}$	$f_{12/1}$	standard deviation
acetonitrile−water	1.63	1.81	1.70	0.23	1.3	5×10^{-6}
acetonitrile−methanol	1.63	1.30	1.45	0.19	0.79	1×10^{-5}
acetonitrile−ethanol	1.63	1.18	1.39	0.11	1.3	2×10^{-5}
acetonitrile−propan-2-ol	1.62	1.09	1.20	0.18	0.69	5×10^{-5}
acetonitrile−butan-1-ol	1.63	1.07	1.24	0.20	1.7	5×10^{-5}
THF−water	1.21	1.80	1.31	0.21	5.2	3×10^{-4}
THF−methanol	1.21	1.32	1.34	6.5	32	1×10^{-5}
THF−ethanol	1.21	1.14	1.26	0.37	12	1×10^{-4}
THF−propan-2-ol	1.21	1.09	1.27	26	1.1×10^{2}	1×10^{-5}
THF−butan-1-ol	1.21	1.05	1.36	1.7	5.8	5×10^{-5}
DMSO−water	1.86	1.81	2.02	0.62	3.9	6×10^{-5}
DMSO−D_2O	1.87	1.82	1.89	0.99	33	1×10^{-5}
DMSO−methanol	1.86	1.31	1.92	4.6	20	4×10^{-5}
DMSO−ethanol	1.87	1.18	1.72	4.6	8.0	9×10^{-5}
DMSO−propan-2-ol	1.85	1.09	1.18	0.085	1.4	2×10^{-4}
DMSO−butan-1-ol	1.87	1.07	1.35	0.45	1.9	1×10^{-4}
DMF−water	1.80	1.81	1.73	0.33	8.3	4×10^{-6}
DMF−D_2O	1.81	1.81	1.64	0.26	0.35	7×10^{-7}
DMF−methanol	1.81	1.32	1.80	1.8	3.6	7×10^{-5}
DMF−ethanol	1.81	1.19	1.60	0.31	1.0	3×10^{-4}
DMF−propan-2-ol	1.82	1.13	1.50	0.47	2.2	4×10^{-4}
DMF−butan-1-ol	1.82	1.09	1.35	0.17	1.7	8×10^{-4}

[a] Obtained from the fitting of experimental data with eq 4.

relates the I/III ratio of pyrene in a binary mixture to the I/III ratios of the two pure solvents.

$$\mathrm{I/III} = \frac{\mathrm{I/III}_1(1 - X_2)^2 + \mathrm{I/III}_2\, f_{2/1}\, X_2^{\,2} + \mathrm{I/III}_{12}\, f_{12/1}(1 - X_2)X_2}{(1 - X_2)^2 + f_{2/1}\, X_2^{\,2} + f_{12/1}\,(1 - X_2)X_2} \quad (4)$$

Thus, the experimental data for each binary mixture were fitted with a nonlinear regression to eq 4. The results are showed in Table 2 and show very good fits for all binary mixtures studied (standard deviation $< 3.3 \times 10^{-4}$). The I/III values in Table 2 for the pure solvents agree well with the experimental values given in Table 1.

Acetonitrile mixtures. Figure 1 depicts the variation in the I/III ratio of **2** as a function of the hydroxylic component mole fraction (X_2). A strong PS of **2** by acetonitrile in aqueous mixtures was observed (Figure 1a). In view of the ability of molecules of water to self-associate in the water-rich region, yielding hydrogen-bonded nets, the isolated acetonitrile molecules can easily solvate the solute. On the other hand, in the acetonitrile-rich mixtures, acetonitrile is still the preferred solvent in the microenvironment of **2** because it is less polar than water. Matteoli and Lepori[35] and Marcus[36] have reported, with the use of Kirkwood−Buff integrals, that the self-clustering of the water takes place when the cosolvent has hydrophobic properties (i.e., when methyl or methylene groups are present). In such cases, the solutes used in studies of PS relating to the self-association do not represent a measure of the average shell solvation of the solutes.[37]

In the acetonitrile−alcohol mixtures (Figure 1b−e), the nonprotic solvent always preferentially solvates the solute. However, it can be observed that as the alcohol becomes less polar, the extent of PS by acetonitrile diminishes. The binary mixtures approach an almost ideal behavior in acetonitrile−butan-1-ol. A simple manner to analyze these results is by supposing that the mixtures are composed exclusively of the two species S_1 and S_2. This assumption can be made only because synergistic effects are absent in these curves (see below). Thus, the molar percentage of the hydroxylic component for a 1:1 bulk mole fraction in a given mixture can be estimated through the following equation,

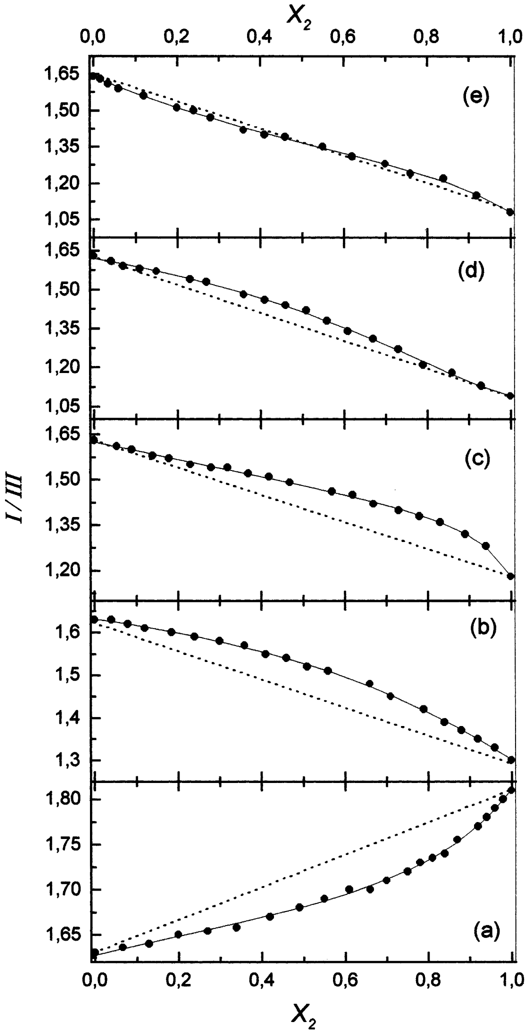


Figure 1. Influence of the protic cosolvent on the I/III ratio for the emission bands of **2** in acetonitrile−ROH mixtures, the ROH components being water (a), methanol (b), ethanol (c), propan-2-ol (d), and butan-1-ol (e). (· ·) Theoretical linear dependence for no PS, (—) curve fitted with eq 4, (●) experimental data.

$$\mathrm{ROH}(\%) = (\mathrm{I/III}_{0.5} - \mathrm{I/III}_{0.0})/(\mathrm{I/III}_{1.0} - \mathrm{I/III}_{0.0})100 \quad (5)$$

where ROH(%) is the estimated molar percentage of the hydroxylic component in the mixture. I/III$_{0.0}$, I/III$_{0.5}$, and I/III$_{1.0}$ are the values of I/III for the protic solvent mole fractions equal to 0.0, 0.5, and 1.0, respectively. In acetonitrile−water mixtures, only 29% of the water molecules are in the cybotactic region of the solute in a mixture containing 50% of each one of the mixed bulk components. The alcoholic cosolvent of the solvation shell of **2** in methanol, ethanol, and propan-2-ol mixtures under the same conditions is equal to 31, 33, and 40%, respectively. In contrast, the solvation by the alcohol is equal to 48% in acetonitrile−butan-1-ol mixtures. In other words, the solvation of **2** by the hydroxylic cosolvent in these mixtures increases in the order: water < methanol < ethanol < propan-2-ol < butan-1-ol. Although these data should be analyzed cautiously, they give data compatible with the visual analysis of Figure 1. These results can be explained by the fact that pyrene is a very hydrophobic probe. Thus, replacing the more polar protic cosolvent for one which is more hydrophobic may lead to a comparatively stronger interaction of the probe with the cosolvent through hydrophobic interactions.

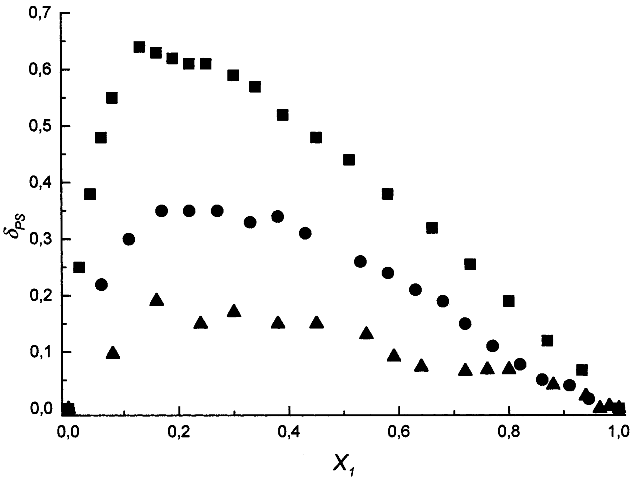


Figure 2. Plots of δPS of **2** as a function of the bulk mole fraction of acetonitrile for mixtures of acetonitrile with water (■), ethanol (●), and butan-1-ol (▲).

Another way to compare the degree of PS among the different mixtures is through the determination of the extent of PS (δPS), defined as $\delta\mathrm{PS}=X_1{}^{\mathrm{L}} - X_1$, where δPS is the extent of PS, $X_1{}^{\mathrm{L}}$ is the local mole fraction of the aprotic solvent, and X_1 is the bulk mole fraction of the aprotic solvent. Values of $X_1{}^{\mathrm{L}}$ can be determined through the procedure of Acree and co-workers,[30] with the use of eq 6,

$$\mathrm{I/III} = [X_1{}^{\mathrm{L}}\mathrm{I}_1 + (1 - X_1{}^{\mathrm{L}})\mathrm{I}_2]/[X_1{}^{\mathrm{L}}\mathrm{III}_1 + (1 - X_1{}^{\mathrm{L}})\mathrm{III}_2] \quad (6)$$

where I/III is the value for the pyrene ratio in a determined binary mixture, I_2 and I_1, and III_2 and III_1 represent the values for I and III intensities of the pyrene in pure protic and pure aprotic solvent, respectively. It may be observed that this interpretation of PS is also made exclusively in terms of the contributions of S_1 and S_2, with no participation of the S_{12} species, this only being valid in the absence of synergistic effects. Plots of δPS as a function of the bulk mole fraction of acetonitrile for mixtures of acetonitrile with water, ethanol, and butan-1-ol are shown in Figure 2. It can be visualized that the more hydrophobic the protic cosolvent, the lesser the extent of PS by acetonitrile, a result that agrees with the results given in the preceding paragraph.

Tetrahydrofuran Mixtures. Variations in the I/III ratio of **2** as a function of the hydroxylic component mole fraction (X_2) are shown in Figure 3. A strong PS of **2** by THF in its aqueous mixtures was observed (Figure 3a). This result can be explained by the fact that in the water-rich region a strong self-association of water occurs through solvent−solvent hydrogen bonding. The "free" THF molecules present in the mixture are therefore responsible for the PS of the solute. Although this self-associated structure is gradually broken down with the addition of THF, **2** is still preferentially solvated by the less polar solvent due to its greater affinity with the hydrophobic solute (see discussion for acetonitrile−water mixtures).

All other mixtures involving THF showed an interesting particularity: they showed higher I/III values for the mixtures than for the pure solvents (Figure 3b−e]. We describe this behavior here as synergistic in the sense that the joint action of the two solvents in the mixture achieves an effect nonexistent in the individual components. Synergistic behavior in mixed solvents is well-established in the literature for the PS of the pyridiniophenoxide **1** in mixed solvents.[9,20,38] It is apparent from the results shown here that the synergistic behavior is observed only in cases where the I/III ratio for the pure protic solvent is close to that of the pure nonprotic component in the mixture under investigation. This observation is in conformity with data from the literature.[9] Synergistic effects for dye **1** in mixed solvents are interpreted as being a result of the solvation of the dye by a more polar species S_{12}.[9] This is observed here for THF−methanol mixtures since the intermediate I/III values, although higher than both I/III ratios for pure solvents, are close to those for the more polar solvent (methanol). However, for the other synergistic THF mixtures, it was observed that their I/III values were close to the I/III value for pure THF, the more hydrophobic cosolvent. In other words, in these THF mixtures, the probe seems to be solvated by a less polar species S_{12}. It may be considered that these species result from solvent−solvent interactions between THF and the alcohols through both hydrogen and hydrophobic bonding. The hydrophobic interaction is unimportant for THF−methanol species, but reaches increasing importance with the increase in the alkylic chain length of the alcohol. As a result, S_{12} species lead to a more polar microenvironment in the solvation shell of **2** for THF−methanol mixtures, while the similar species in the other THF−ROH mixtures form a gradually less polar microenvironment able to interact through hydrophobic bonding with the apolar probe.

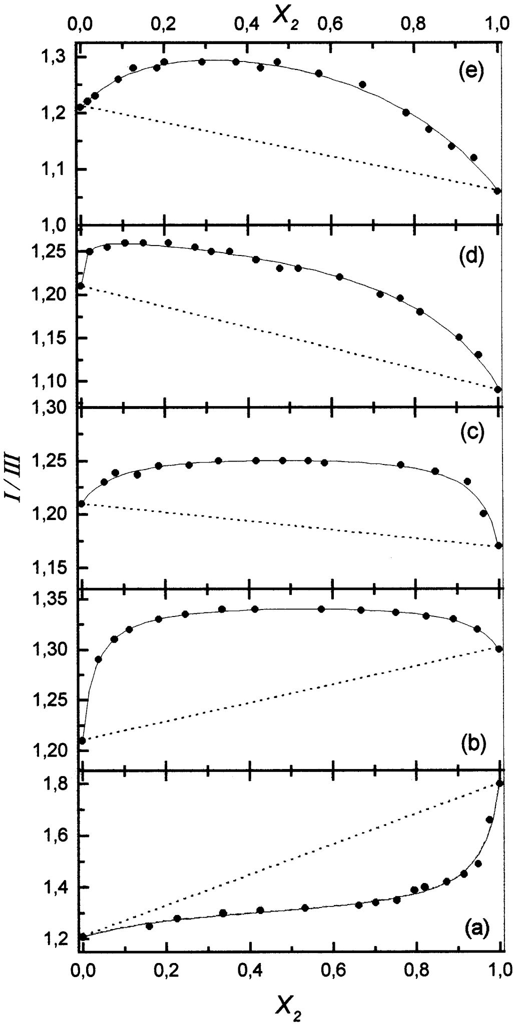


Figure 3. Influence of the protic cosolvent on the I/III ratio for the emission bands of **2** in THF−ROH mixtures, the ROH components being water (a), methanol (b), ethanol (c), propan-2-ol (d), and butan-1-ol (e). (• •) Theoretical linear dependence for no PS; (—) curve fitted with eq 4; (●) experimental data.

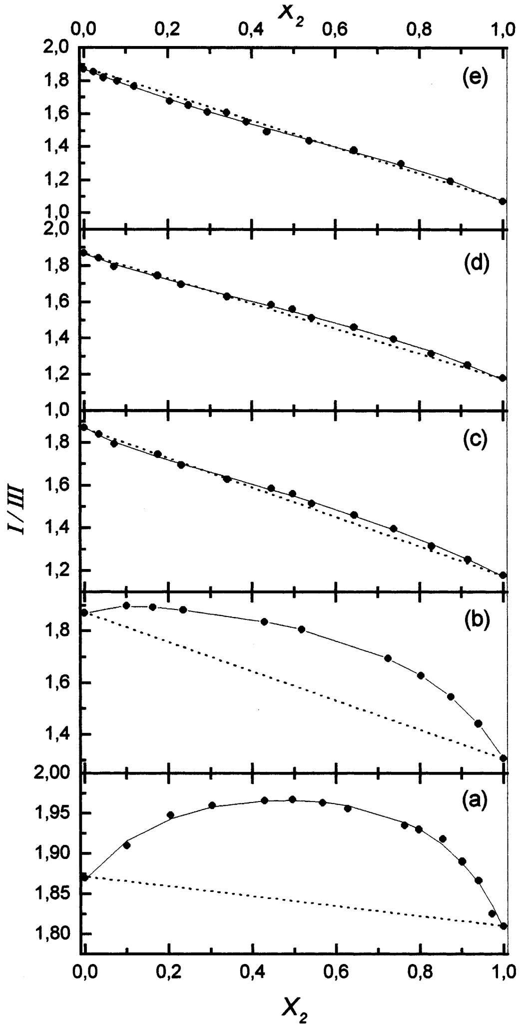


Figure 4. Influence of the protic cosolvent on the I/III ratio for the emission bands of **2** in DMSO−ROH mixtures, the ROH components being water (a), methanol (b), ethanol (c), propan-2-ol (d), and butan-1-ol (e). (• •) Theoretical linear dependence for no PS; (—) curve fitted with eq 4; (●) experimental data.

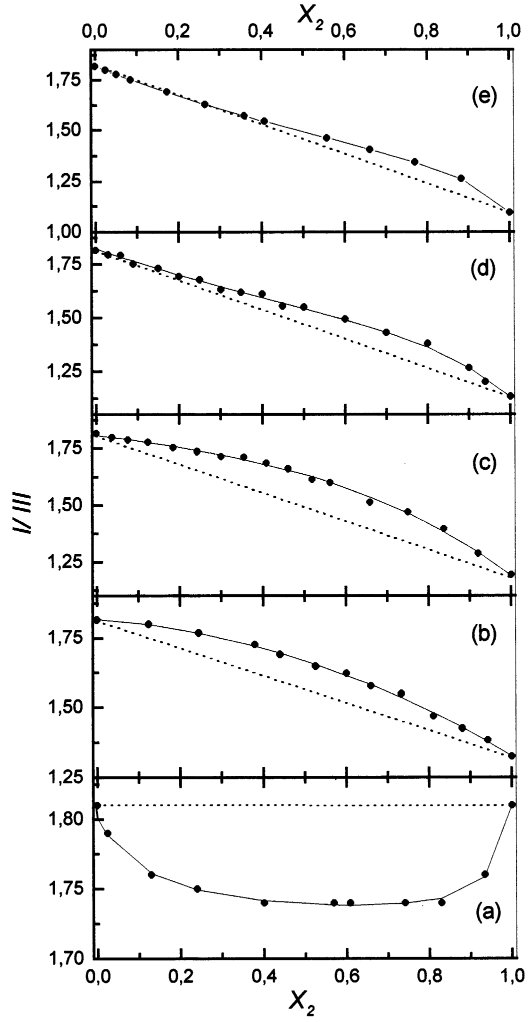


Figure 5. Influence of the protic cosolvent on the I/III ratio for the emission bands of **2** in DMF−ROH mixtures, the ROH components being water (a), methanol (b), ethanol (c), propan-2-ol (d), and butan-1-ol (e). (• •) Theoretical linear dependence for no PS; (—) curve fitted with eq 4; (●) experimental data.

Dimethyl Sulfoxide Mixtures. Figure 4 depicts the variations in the I/III ratio of **2** as a function of X_2 for DMSO−ROH mixtures. Synergism was observed for DMSO−water and DMSO−methanol mixtures (Figure 4a,b). It was noted by Marcus that highly polar 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.[37] This observation can explain not only the synergistic behavior in mixtures of water with DMSO but also in methanol−DMSO mixtures. The neighborhood of **2** in these mixtures is crowded by these DMSO−ROH partners, which orient their hydrophobic methyl groups toward the probe. This may be the origin of the hydrophobic microenvironment reported for **2**.

The other alcoholic mixtures containing DMSO did not display synergistic behavior (Figure 4c−e): the curves of I/III vs X_2 exhibited similar, almost ideal, behavior. The similarly low capability of these alcohols to form hydrogen-bonded DMSO−ROH aggregates, in comparison with DMSO−water or DMSO−methanol mixtures, may explain the fact that these curves are not synergistic. In addition, the lack of synergism in these mixtures may be a result of the fact observed above that the I/III ratio for the pure DMSO differs greatly from the ratios for the pure alcohols ethanol, propan-2-ol and butan-1-ol, whereas the I/III value for the nonprotic solvent (1.87) is close to that for pure water (1.81). Since methanol is an intermediate solvent among the protic solvents as regards I/III values, a synergism is observed in its mixtures with DMSO.

***N,N*-Dimethyl Formamide Mixtures.** Variations in the I/III ratio of **2** as a function of X_2 are shown in Figure 5 for DMF−ROH mixtures. First, it can be noted that DMF−water mixtures are synergistic (Figure 5a). In these mixtures, S_{12} species are responsible for a less polar microenvironment in the solvation shell of **2**. Contrary to the behavior observed for DMSO−methanol, the DMF−methanol mixtures are not synergistic, although DMSO and DMF have the same α and almost the same I/III values. These observed differences perhaps reflect the difference in β values for these solvents, which indicates that methanol is able to form stronger hydrogen bonds with DMSO than with DMF. For other alcoholic mixtures synergism was not observed, although the probe is preferentially solvated to a small extent by the less polar components of the mixtures. The PS extent diminishes with the increase of the alkylic chain due to the fact that the more hydrophobic the alcoholic cosolvents, the more solvated the hydrophobic dye. As a result, DMF−butan-1-ol mixtures (Figure 5e) showed an almost ideal behavior.

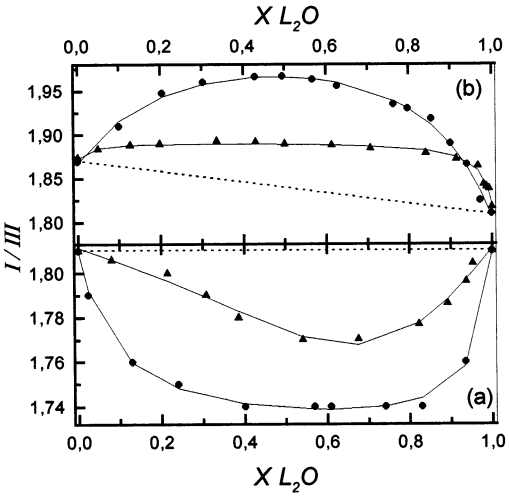
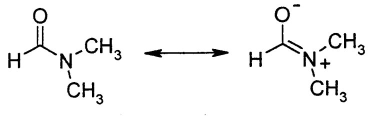


Figure 6. Influence of the protic cosolvent on the I/III ratio for the emission bands of **2** in DMF−L_2O (a) and DMSO−L_2O (b) mixtures, L_2O being H_2O (●) and D_2O (▲). (• •) Theoretical linear dependence for no PS; (—) curve fitted with eq 4.

Influence of D_2O on the Extent of PS in DMF and DMSO Mixtures. Although I/III values for **2** in H_2O and in D_2O show exactly the same values (Table 1), their mixtures with solvents such as DMF and DMSO display a different behavior. Figure 6a depicts a comparative study between the solvation of **2** in DMF−H_2O and DMF−D_2O mixtures. The differences between the solvation of **2** in DMSO−H_2O and DMSO−D_2O mixtures are shown in Figure 6b. It is interesting to observe that the extent of the PS in both cases is diminished if water is replaced by deuterium oxide. We have considered that the synergism observed in these mixtures is due to the solvation of **2** by the less polar S_{12} species assembled by specific and nonspecific interactions. Therefore, it is logical to assume from the data obtained here that the replacement of H_2O by D_2O makes these S_{12} species more polar and consequently provokes the diminution in the PS extent.

The observation that pyrene "sees" more polar S_{12} species in the studied D_2O mixtures, in comparison with H_2O mixtures, perhaps results from the fact that the deuterium bonding in these species is more effective than for S_{12} species in water. The greater strength of the deuterium bonding in comparison with the hydrogen bonding has been demonstrated in some studies. As an example, the donor ability of an −O−D group was compared with that of an −O−H group and it was observed that, compared with phenol, phenol-*d* interacts more exothermically, ca. 0.3 kcal mol^{-1}, with benzene, ethyl acetate, THF, and di-*n*-butyl ether.[39] A solvent such as DMF is a resonance hybrid of the two structures **A** and **B**. Recently, it was demonstrated by means of computational studies that the hydrogen bonding of formamide with water has an appreciable covalent character, and that the solvation of formamide by water increases the contribution of the dipolar structure (similar to structure **B**) for the resonance hybrid.[40] Therefore, if consider that the same is happening in DMF, we would expect structure **B** to be more favored in D_2O than in H_2O since the deuterium bonding is stronger. The positively charged nitrogen atom in **B** makes the methyl groups that are responsible for the solvation of **2** more polar and this could be the reason for the data obtained. The same argumentation can be employed in order to explain the observed behavior in the DMSO mixtures. However, this hypothesis presented here needs further investigation.



A **B**

Conclusions

The model of PS presented here for the solvation of pyrene in different mixed solvents, which uses eq 4, was very successful to fit all curves of I/III values of pyrene as a function of the bulk mole fraction. It is interesting to observe here that aggregates such as S_{12} in mixed solvents can show a different behavior depending on the probe used in the investigation. Thus, a dipolar dye such as **1** recognizes these species as more polar[9] while pyrene, a hydrophobic probe, "sees" S_{12} as a less polar species. This occurs because this mixed solvent is able to solvate differently these structurally different probes.

Although the interaction involving **2** and the medium may occur exclusively through dipole−induced dipole forces, since it would not be expected to occur through specific interactions (mainly hydrogen bonding), this probe is capable of detecting solvent−solvent interactions, which are implicit to the observed synergistic behavior. Thus, it was demonstrated here that hydrophobic probes such as **2** and other polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen molecules[30] can considerably enrich the knowledge to be attained in the field of solvation of chemical species and in the role of the solvent in biological phenomena related to hydrophobicity.[41]

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