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Solvation effects on spirooxazine to merocyanine thermal reversion kinetics in acetonitrile–water binary mixtures

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ABSTRACT: In solution, the photochromic molecule 5-methoxyspiro[indole-phenanthrolinoxazine] (**SPO**) is in equilibrium with its corresponding merocyanine open isomer. In pure acetonitrile, there is about 22.5% of the open form, whereas in acetonitrile–water binary solvents this proportion increases to more than 60% when the water molar fraction $\chi(H_2O)$ is around 0.80. Irradiation in the visible range leads to a photobleached steady state in which the proportion of the merocyanine open isomer decreases significantly. When irradiation is switched off, a slow thermal reversion of the closed spirooxazine to the open merocyanine takes place until the initial equilibrium position is reached. Kinetic analysis of a whole set of relaxation curves recorded at various water contents was used to establish a model involving multiple equilibria between three merocyanines in different solvation states (solvated by acetonitrile, solvated by an acetonitrile–water complex and hydrated). Their relative proportions, which are dependent on the binary mixture composition, were determined, in addition to their corresponding visible spectra. Copyright © 2004 John Wiley & Sons, Ltd.

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KEYWORDS: spirooxazine; merocyanine; thermal reversion; kinetics; solvation

INTRODUCTION

Spirooxazines[1] are among the best known photochromic molecules. According to Scheme 1, a spirocyclic isomer (or closed form, CF) can isomerize reversibly to an acyclic merocyanine (or open form, OF). The spirocyclic form absorbs in the UV region, whereas merocyanine absorbs in both the UV and visible regions. The photochromism of the spirooxazines is characterized by either a photochemical or a thermal isomerization between the closed and the open forms. For most spirooxazines, the thermal equilibrium is substantially shifted towards the spirocyclic isomer. However, in series of spirooxazines containing aromatic or heterocyclic fragments annelated to the oxazine nucleus, the equilibrium constant increases from naphthalene to phenanthrene and phenanthroline.[2] The insertion of an electron-donating group (*O*-Alk) at position 5 of the indoline fragment leads to an increase in concentration of the merocyanine at equilibrium.[3] The equilibrium position is sensitive to the changes in temperature (thermochromism[4]) and polar properties of the solvents (solvatochromism[5]).

The purpose of this work was to perform a detailed kinetic analysis of the photochromic and solvatochromic behaviour of 5-methoxyspiro[indole-phenanthrolinoxazine] (**SPO**) in water–acetonitrile binary mixtures. We investigated a wide range of water contents from pure CH_3CN to water molar fractions as high as 0.92. In this solvent system, the relative proportion of the two forms is very sensitive to the water content of the binary solvent. Under visible irradiation, almost complete bleaching was obtained (negative photochromism[6]). When visible irradiation was switched off, a slow thermal recoloration to the previous equilibrium position was recorded. Our study is based on the kinetic analysis of these relaxation curves at variable water contents. Moreover, analysis of the literature showed that there have not been many studies of photochromism in binary mixtures. Among the scarce data about solvent effects on photochromism,[7] most are related to spiropyrans[8] and very few to spirooxazines.[9]

RESULTS AND DISCUSSION

Effect of water content on spectral intensity

The NMR spectrum of **SPO** in pure CD_3CN at 25 °C indicates that at thermal equilibrium ∼22.5% of the compound is in the merocyanine OF. As can be seen in

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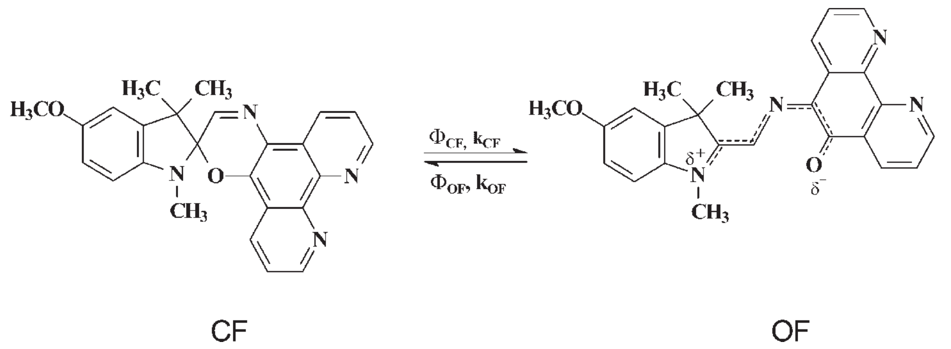

Scheme 1. Photochemical and thermal reversibility between the closed (CF) and open (OF) forms of 5-methoxyspiro[indole-phenanthrolinoxazine]

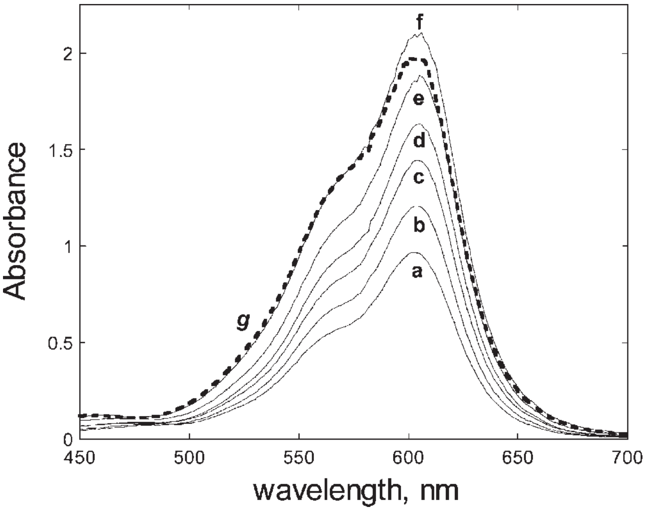

Figure 1. Variation of the visible spectra of **SPO** solution ($[\mathbf{SPO}]_0 = 8.5 \times 10^{-5}$ mol dm^{-3}) in water–acetonitrile binary mixtures with various water molar fractions $\chi(H_2O)$: (a) 0; (b) 0.13; (c) 0.24; (d) 0.42; (e) 0.66; (f) 0.87; (g) (dotted line) 0.92

Fig. 1, on increasing the water content of the solution, the percentage of merocyanine OF increases until it reaches a maximum for a water molar fraction $\chi(H_2O) = 0.87$ and then decreases for $\chi(H_2O) = 0.92$. This decrease is significant and fully reproducible. At water contents $\chi(H_2O) > 0.92$, **SPO** is no longer soluble and slow precipitation occurs. Although no noticeable spectral shift of the λ_{max} (604 nm) was detected, the absorbance–absorbance plot of Abs(570 nm) vs Abs(604 nm) was not rigorously linear, indicating a slight deformation of the whole spectral shape.

Although it is well known[10] that at low temperature (−45 °C) open merocyanines of the spirooxazine exist in two isomeric forms (CTC and TTC), we have assumed that under our conditions (25 °C), the merocyanine OF is likely to be under the most stable TTC structure. The observed absorbance variations effects are mainly related to the displacement of a unique CF $\rightleftharpoons$ OF equilibrium under the influence of specific solvent–solute interactions.

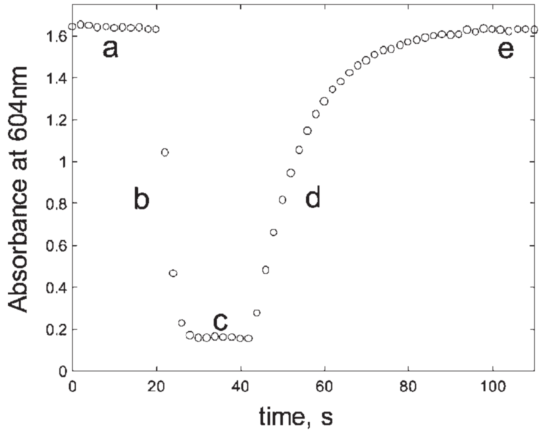

Figure 2. Negative photochromism of an **SPO** solution in water–acetonitrile at $\chi(H_2O) = 0.42$ at 25 °C. $[\mathbf{SPO}]_0 = 8.5 \times 10^{-5}$ mol dm^{-3}. (a), (e) Thermal equilibrium; (b) photobleaching; (c) photosteady state under visible light irradiation; (d) thermal relaxation

Negative photochromism of water–acetonitrile SPO solutions

The ring-opening quantum yield (Φ_{CF}) is negligible. Moderate-intensity 365 nm irradiation of has no effect on the already deep blue **SPO** solutions (filtered 250 W Hg high-pressure lamp: $\lambda_{irr} = 365$ nm; $I_0 = 6 \times 10^{-6}$ mol dm^{-3} s^{-1}). In contrast, the quantum yield of ring closure (Φ_{OF}) is more significant. The solution is almost completely bleached by visible light irradiation from a non-filtered 150 W quartz–halogen lamp. After switching off the visible light, the system underwent a slow relaxation towards its initial equilibrium position (Fig. 2).

Kinetics of thermal relaxation

Analysis of the thermal relaxations recorded after photobleaching at various water contents showed monoexponential behaviour (Fig. 3). When the water content of the binary mixture increased, the absorbance at equilibrium (Abs_{eq}) increased whereas the observed rate constant (k_{obs}) decreased significantly.

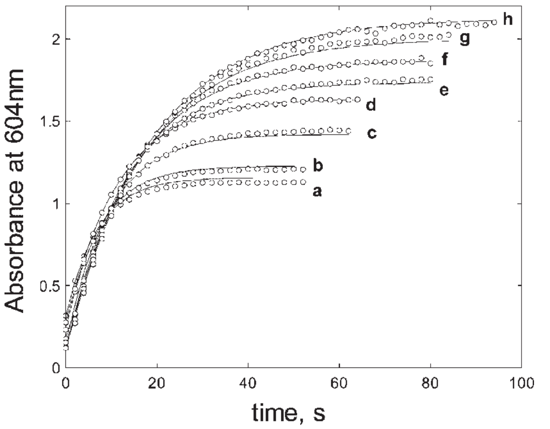

Figure 3. Kinetic analysis at 604 nm of the thermal relaxations after photobleaching at various water contents $\chi(H_2O)$: (a) 0.07; (b) 0.13; (c) 0.24; (d) 0.42; (e) 0.56; (f) 0.66; (g) 0.81; (h) 0.87. Dots are experimental points and solid lines are fits

Single equilibrium qualitative modelling

For a preliminary analysis of these relaxations, we shall consider first only a single thermal equilibrium between CF and OF ($CF \rightleftharpoons OF$). The forward (k_{CF}) and reverse (k_{OF}) rate constants can be determined from the following relationship:

$$k_{CF} + k_{OF} = k_{obs} \tag{1}$$

where k_{obs} is the apparent first-order thermal relaxation rate constant.

At equilibrium

$$K_{eq} = [OF]_{eq}/[CF]_{eq} = k_{CF}/k_{OF} \tag{2}$$

and the mass balance equation gives

$$[CF] + [OF] = [SPO]_0 \tag{3}$$

where $[SPO]_0$ is the initial concentration of the photochromic molecule. At a wavelength where the closed form does not absorb, Beer's law gives:

$$Abs_{eq} = \varepsilon_{OF}[OF]l \tag{4}$$

where ε_{OF} is the molar absorption coefficient of the open form OF and l the optical path.

From Eqns (1)–(4), it can be deduced that

$$k_{CF} = (k_{obs}Abs_{eq})/(\varepsilon_{OF}[SPO]_0 l) \tag{5}$$

and

$$k_{OF} = k_{obs}\left[1 - Abs_{eq}/(\varepsilon_{OF}[SPO]_0 l)\right] \tag{6}$$

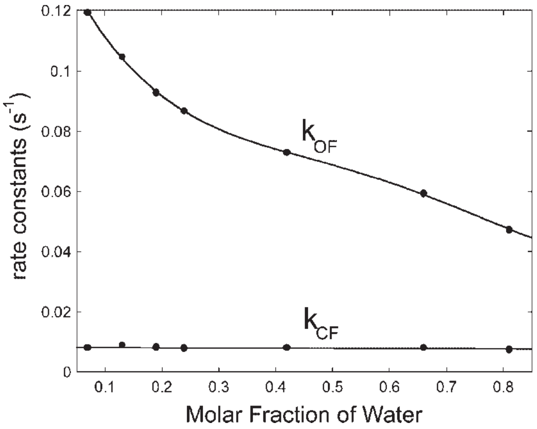

Figure 4. Variation of the forward and reverse rate constants with molar fraction of water in the 0.05–0.85 range

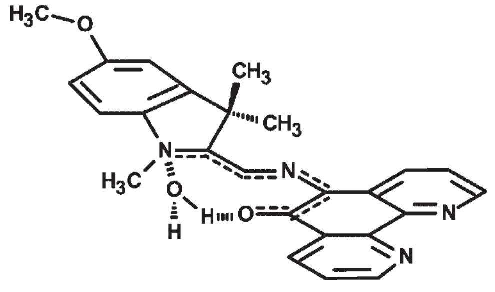

Figure 5. Schematic representation of the hydrated open form OF_h

Applying Eqns (5) and (6) to our results showed that for water molar fractions ranging from 0.05 to 0.87, the observed variations on Abs_{eq} and k_{obs} could be interpreted by a decrease in k_{OF} while k_{CF} remained constant (Fig. 4).

Such a variation is an indication that stabilization of the OF occurs when the water content increases within the binary solvent. This hypothesis is justified by recent structural studies based on x-ray diffraction,[11] showing that the OF of a zwitterionic spiropyran can be stabilized by a water molecule located within the $N^{\delta+}$—$O^{\delta-}$ interval. In our case, such interaction could be represented as in Fig. 5, resulting in inhibition of the ring closure.

Multiple equilibria quantitative modelling

It is likely that water inhibition is not sufficient to interpret accurately the whole group of relaxation kinetic curves. In particular, to describe the significant decrease in equilibrium absorbance at $\chi(H_2O) > 0.87$, the non-ideality of the acetonitrile–water binary mixtures must be taken into account. It is well known (see Supplementary material) that acetonitrile–water complexes are formed. Although the stoichiometries and sizes of such complexes are known to be probe dependent, it appears that π^*-dyes such as *N*-methyl-2-nitroaniline (NM2A) are able to detect the presence of an acetonitrile–water complex[12,13] exhibiting a maximum around a water molar fraction of $\chi(H_2O) \approx 0.7$. Such a value is remarkable because it is very close to the maximum of the excess molar volume[14] in pure acetonitrile–water binary mixtures [$\chi(H_2O) \approx 0.7$]. It can then be assumed that π^*-dyes (like **SPO**) do not cause a strong disturbance of the binary mixture equilibria. Under these conditions, it was possible to describe the non-ideality of the acetonitrile–water binary solvent by the formation of a unique reversible complex with appropriate stoichiometric factors and equilibrium constant:

$$p\mathrm{CH_3CN} + q\mathrm{H_2O} \rightleftharpoons \mathrm{CPX}$$

To interpret the observed slight spectral deformation, such an acetonitrile–water complex (CPX) has been assumed to be able to associate with the **SPO** OF. This solvation can be described by another equilibrium giving rise to the complex-solvated open form (OF_c):

$$\mathrm{OF} + \mathrm{CPX} \rightleftharpoons \mathrm{OF_c}$$

Establishment of a quantitative model

In order to describe the solvatochromic effects of **SPO** in the acetonitrile–water binary system, the reversible processes in Table 1 were considered.

The first process simply corresponds to the spontaneous isomerization occurring between the closed spiro form (CF) and the open merocyanine form (OF) in neat acetonitrile. In this process, the OF is assumed to be acetonitrile solvated. Hydration of the open form is the second process. The third process is intended to be a rough description of the non-ideality of the pure acetonitrile–water binary mixture. Process 4 corresponds to the solvation of the open form by the acetonitrile–water complex.

From this model, it was possible to fit all the thermal relaxation kinetic curves recorded at various water molar fractions (see Fig. 3) and to reproduce the equilibrium absorbances recorded at 570 and 604 nm (see Fig. 6).

The calculated visible spectra of the three solvated open forms are shown in Fig. 7. The hydrated open form (OF_h) gives rise to the least intense spectrum. This result is consistent with the presence of a water molecule in the $C^{\delta+}$—$O^{\delta-}$ interatomic interval hindering the full conjugation of the two aromatic moieties and giving rise to a less intense absorption band. Such an effect also occurs (but to a lesser extent) when the merocyanine is surrounded by the acetonitrile–water complex. Under these conditions, the spectrum (OF_c) exhibits an intensity which is intermediate between those of the hydrated (OF_h) and the acetonitrile-solvated (OF) open forms.

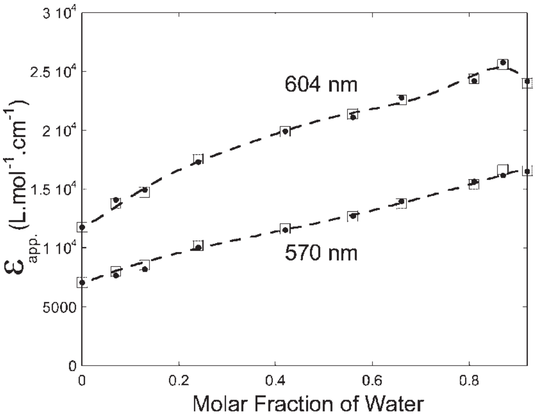

Figure 6. Apparent molar extinction coefficient of **SPO** (Abs_{eq}/[**SPO**]$_0$) in acetonitrile–water binary mixtures. □, Experimental data; ●, calculated; smoothed curves serve as a visual guide)

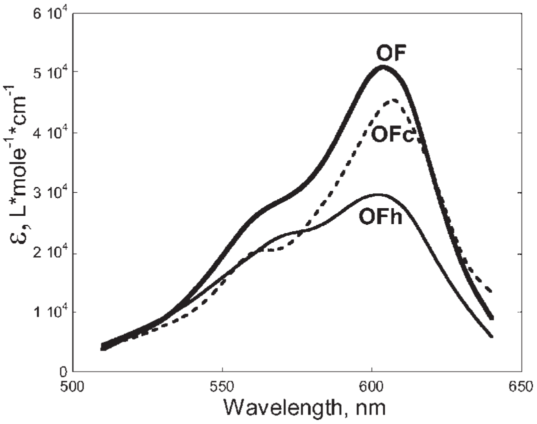

Figure 7. Calculated visible spectra of the open merocyanine in the various solvation environments: OF, surrounded by neat acetonitrile; OF_c, surrounded by the acetonitrile–water complex; OF_h, hydrated

From our modelling approach, it has been possible to reach the preferential solvation states of the SPO merocyanine OF as a function of the water content in acetonitrile–water binary mixtures.

The proportion of the acetonitrile-solvated open form (OF) decreases regularly as the acetonitrile content decreases (Fig. 8). However, owing to the hydrophobicity of

Table 1. Equilibria used to describe the solvatochromism of **SPO** in acetonitrile–water binary solvent at 25 °C

No.	Process	Parameters	Parameter determination technique
1	$\mathrm{CF} \rightleftharpoons \mathrm{OF}$	$k_{CF} = 0.04\,\mathrm{s^{-1}}$; $k_{OF} = 0.14\,\mathrm{s^{-1}}$	^{1}H NMR; first-order analysis of the thermal relaxation after photobleaching in pure CH_3CN
2	$\mathrm{OF} + \mathrm{H_2O} \rightleftharpoons \mathrm{OF_h}$	$K_h = 0.17\,\mathrm{mol\,dm^{-3}}$	Fitting on our kinetic data
3	$p\mathrm{CH_3CN} + q\mathrm{H_2O} \rightleftharpoons \mathrm{CPX}$	$p = 0.38$; $q = 0.64$; $K_{CPX} = 1.73\,\mathrm{mol}^{1-p-q}\,\mathrm{dm}^{-3(1+p+q)}$	Fitting on literature data from Nigam *et al.*[12b] (see Supplementary material)
4	$\mathrm{OF} + \mathrm{CPX} \rightleftharpoons \mathrm{OF_c}$	$K_c = 0.15\,\mathrm{mol\,dm^{-3}}$	Fitting on our kinetic data

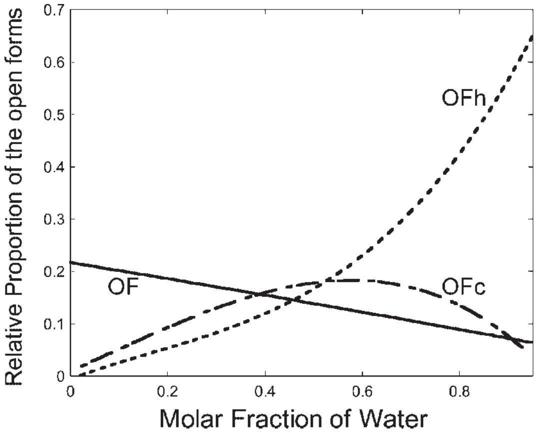

Figure 8. Calculated relative proportions of the solvated open forms of the SPO merocyanines in acetonitrile–water binary solvent

the open form, it still exists at high water contents. As expected, the complex solvated open form (OF_c) exhibits a maximum at intermediate molar fractions. The last curve corresponds to the hydrated species (OF_h); there is a more than 50% accumulation at high water molar fractions. The observed decrease in k_{obs} when the water molar fraction increases can then be interpreted by the accumulation of water- or complex-stabilized open forms (OF_h and OF_c).

CONCLUSION

The negative photochromism properties of 5-methoxy-spiro[indole-phenanthrolinoxazine] (**SPO**) were used to provide information on the solvent effects on the spirooxazine to merocyanine thermal reversion. Kinetic analysis of the various relaxation curves recorded after photobleaching showed that the solvation of this photochromic molecule in acetonitrile–water binary mixture can be described by four coupled equilibria. The relative proportion of the solvent species (pure acetonitrile, acetonitrile–water complex and pure water) in the solvation sphere of **SPO** varies with the composition of the binary mixture. The visible spectra associated with these three solvation states of the merocyanine were determined. The results are interesting because the details of the microscopic environment of a solute in a binary mixture are still a controversial despite recent investigations.[15] The question is of importance because mixed solvents are common in analytical and preparative chemistry.

EXPERIMENTAL

Compounds

5-Methoxy-1,3,3-trimethylspiro[indoline-2,2′-[2*H*]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] (**SPO**) was prepared by coupling 6-hydroxy-5-nitroso-1,10-phenanthroline with 5-methoxy-1,2,3,3-tetramethyl-3*H*-indolium iodide according to a previously described method.[16] Yield, 54%; m.p., 203 °C (lit.[2b] m.p. 204 °C). Solvents were of the highest available spectroscopic grade (Acros Organics).

^{1}H NMR analysis

Spectra were recorded on a Bruker 250 MHz instrument. Solvent, CD_3CN; T, 25 °C. NCH_3, δ_H (ppm) 2.71 and 3.88, ratio 0.299; OCH_3, δ_H (ppm) 3.80 and 3.79, ratio 0.289); $H^{3'}$, δ_H (ppm) 7.94 and 10.21, ratio 0.283. $[OF]/[CF] = K_{eq} = 0.29 \pm 0.01$.

UV–visible spectroscopy

Absorption spectra and photokinetic data [absorbance versus time (Abs vs t)] matrices were recorded on an Ocean Optics fibre-optic diode-array thermostated spectrophotometer.

Irradiation technique

A 150 W, IR-filtered halogen lamp with glass-fibre optics was used for visible irradiation of the samples ($400 < \lambda < 800$ nm). The fibre is fitted to the thermostated cell in order to place the irradiation beam perpendicular to the monitoring beam.

Calculations

Laboratory-written software was used to process the Abs vs t matrices. Experimental photokinetic curves (Abs_{exp} vs t) at various water contents were fitted by the model (Abs_{calc} vs t). The calculated curves were obtained from numerical integration of the differential kinetic equations using a Runge–Kutta semi-implicit procedure for the concentrations and Beer's law for the absorbances. The residual error function $RE = \Sigma_p \Sigma_j [Abs_{calc}(j) - Abs_{exp}(j)]^2/pj$ (where p is the number of plots fitted simultaneously and j is the number of points in each plot) is computed and the parameters optimized until a minimum in RE is reached. The set of optimised parameters was proved to be unique. See Supplementary Material for details.

Acknowledgements

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