Solvatochromic behavior of non-activated indolinobenzospiropyran 6-carboxylates in aqueous binary solvent mixtures. Part II[1]

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Abstract

The solvatochromic behavior of non-activated indolinobenzospiropyran 6-carboxylates **SP-1—2** in aqueous binary solvent mixtures was investigated.

Marked negative solvatochromism was exhibited by **SP-1—2** in the whole region of solvent polarity examined. Excellent linear relationships were observed between $\lambda_{\max}$ and the solvent polarity parameter, $E_T(BM)$, for the aqueous binary solvent mixtures. The sensitivity of the binary solvent system toward the transition energies of the MC form was highest in the water—methanol solvents in all SP molecules examined. As of other merocyanine dyes in neat solvents, the MC form of spiropyran 6-carboxylates in the aqueous binary solvents showed a negative solvatochromism. The aqueous solvent was found to affect the solvatochromic behavior of the merocyanine dyes by increasing the sensitivity of the chromophore to the effects of solvation via H-bonding.
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Keywords: Solvatochromic behavior; Non-activated thermo- and photochromic dyes; Solvent polarity parameter for binary solvent mixtures $E_T(BM)$; Solvation effects via H-bonding

1. Introduction

Thermo- and photochromic indolinobenzospiropyran dyes have recently become important on account of the rapid development of information recording systems, such as high-density optical data storage, optical switching, displays and non-linear optics [1—5].

Spiropyran dyes consist of two π systems linked by a tetrahedral spiro carbon. Upon heating or irradiation with UV light, they form a colored metastable state, while the reverse process can occur spontaneously or be induced by visible light or heat [1,2]. The metastable state is called *photomerocyanine*, because it resembles the structure of merocyanine dyes (MC). This process is shown in Scheme 1.

Because the rate of these reactions depends upon the polarity of the solvent due to the stabilization of the zwitterionic MC form in polar solvents, the effects of the solvent on the stability of the merocyanine chromophore have been an active area of research. Most studies [6—10] have focused on the spiropyran derivatives, which have an electron-withdrawing group such as a $-NO_2$ group substituted at the 6- or 8-position of the spiropyran, in order to utilize the photochemical ring opening reaction due to its stabilized merocyanine form.

Recently, attention has been paid to the so-called non-activated spiropyrans which lack a strong electron-withdrawing

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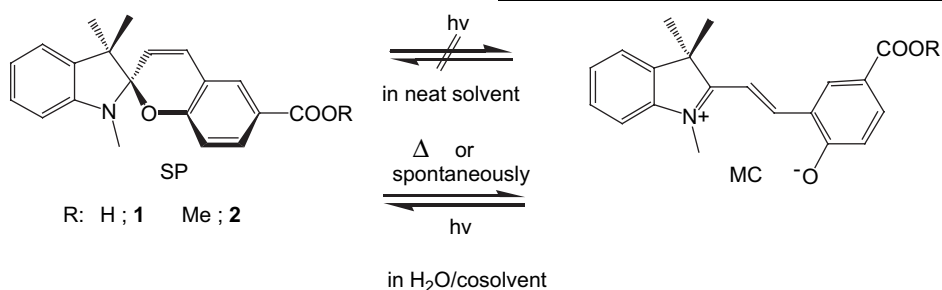* Corresponding author. Tel.: +82 41 860 1332; fax: +82 41 867 5369.
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[1] For Part 1, see Ref. [11].
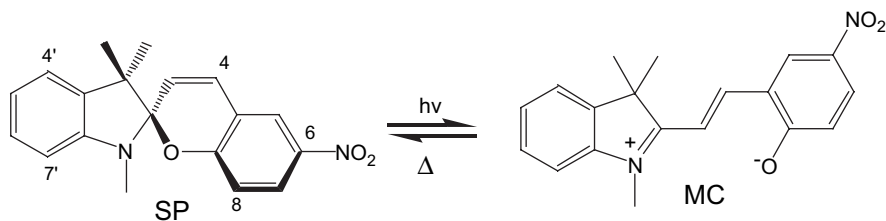
Scheme 1. Photochromism of 6-nitro SPs.

substituent. There are no reports of a solvatochromic study of non-activated spiropyrans due to its instability in neat organic solvents. Quite recently, we [11] observed the unusual stability of indolinobenzospiropyran 6-carboxylates in aqueous binary solvent mixtures, such as water/methanol, water/acetonitrile, and water/DMSO. The process is shown schematically in Scheme 2. We thus examined the solvatochromic behaviors of non-activated spiropyrans such as **SP-1—2** (Scheme 2) in aqueous solvent mixtures. Solvatochromism has made a large contribution to the understanding of the effects of solvation on various chemical phenomena. The UV—vis spectral data of solvatochromic MC substances in solvent mixtures can be used to analyze both the solvent—substance and solvent—solvent interactions [12,13].

was boiled, and bubbled with nitrogen and stored in a nitrogen atmosphere in order to avoid CO_2 contamination.

SP-1 was obtained from the reaction between Fischer's base and the substituted salicylaldehydes, as described elsewhere [11].

2.3. Preparation of solvent mixtures

The binary mixtures were prepared by mixing volumes of each solvent at room temperature. In this way, the mole fraction of each component could be accurately determined. The solvent composition is expressed in terms of the water mole fraction.

Scheme 2. Reverse photochromism of SP:6-carboxylates.

2. Experimental

2.1. General

The melting points were determined using a Fischer—Jones melting point apparatus and were uncorrected. The ^1H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-300 spectrometer in deuterated chloroform. The UV—vis absorption spectra were recorded using a Varian Cary 1E UV—vis spectrometer. Photoirradiation was accomplished using a mercury lamp (Ushio, 1 kW) as the excitation light source.

2.2. Solvents and materials

All organic solvents were of spectrophotometric grade (Aldrich, Sure-Seal) and were used without further purification. Deionized water was used in all measurements. This solvent

2.4. Spectrophotometric method

Stock solutions of SPs (1×10^{-2} M) in DMF were made in 5-mL volumetric flasks in an inert atmosphere. The flasks were then capped with a rubber septum, wrapped in aluminum foil, and stored at 0 °C.

Reproducible results of the photochromic transformation of spiropyran to merocyanine were obtained using a protocol that maximized the formation of the colored form. Briefly, 3 mL of the selected aqueous binary solvent was injected into a 1-cm-path length quartz cuvette. The cuvette was then capped with a Teflon plug and placed in the thermostated (25 °C) cell compartment of a UV—vis spectrophotometer. The maxima on the UV—vis spectra were obtained from the final scan of the absorption spectra of the colored MC form of **SP-2**. The absorption maximum of the colored MC form of **SP-1** was determined by treating the final solution of the colored MC form of **SP-1** molecules with TEA to form the MC species.
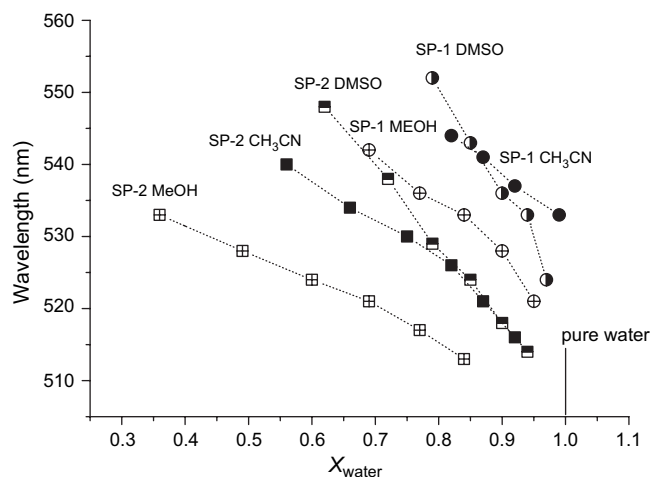
Fig. 1. Plots of λ_{max} of the MC form of **SP-1** (circled) and **SP-2** (squared) as a function of the X_{water} in the aqueous binary solvent mixtures (filled; CH$_3$CN, half filled; DMSO and x-marked; CH$_3$OH mixtures).

3. Results and discussion

3.1. Spectroscopic behavior of *SP-1−2* in various aqueous solvent mixtures

The spiropyran carboxylates **SP-1−2** showed no chromotropism in the neat solvents, unlikely to the activated spiropyran such as the 6-nitro derivative [1,2,6]. The electronic absorption spectra of the spiropyran carboxylates showed no absorbance in the visible region in the neat solvents, such as methanol, acetonitrile, DMSO, etc.

However, the spiropyran carboxylates showed chromotropism in aqueous binary solvent mixtures such as water/methanol, water/DMSO, water/acetonitrile, etc. The initially colorless solutions become deeply colored upon formation of the merocyanine, which has a strong absorption at 500−550 nm with a high extinction coefficient in aqueous binary solvents. Upon exposure to the corresponding visible light, the colored merocyanine solutions revert to the colorless spiropyran state. These systems showed the typical thermocoloration−photobleaching cycle, which is a reverse photochromic behavior [11,14]. The color reappears gradually when the illumination is stopped.

Fig. 1 shows a plot of the wavelengths (λ_{max} nm) as a function of the mole fraction of water X_{water} of **SP-2** in various aqueous binary solvents. The absorption maxima of **SP-2** showed a blue shift with increasing water content.

solvation [14−17] of the MC by the polar solvent, water, in the aqueous binary solvent systems.

3.2. Solvent polarity parameter $E_T(BM)$

The colored MC form shows solvatochromism in neat solvents. The stabilization of the MC form in polar solvents leads to a larger activation energy than in non-polar solvents. An excellent correlation was obtained between the $\pi−\pi^*$ transition energies of the MC form and the solvent polarity parameters such as Kosower's Z or Brownstein's S parameters, Dimroth and Rechardt's $E_T(30)$ values, etc. [13]. Various empirical solvent polarity parameters have been used to describe the influence of solvents on the different physicochemical solute properties.

In binary solvent mixtures, solvatochromism is further complicated by the so-called 'preferential solvation' of the substance by one component of the solvent mixture. This phenomenon includes specific substance−solvent interactions, e.g. H-bonding. The most significant aspects of preferential solvation are that the compositions of the solvation shells of most substances are different from those of the corresponding bulk solvents. Several attempts [15,16] have been made to correlate the solvation phenomena of empirical or experimental parameters of solvent polarity with the spectroscopic data in mixed binary solvents.

The following two-step exchange model was applied by DaSilva et al. [17] for the binary-solvent effects in the preferential dissolution of Brooker's merocyanine dyes in binary solvent mixtures:

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

$$BM(S_1)_2 + S_2 \rightleftharpoons BM(S_{12})_2 + S_1 \tag{1}$$
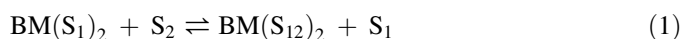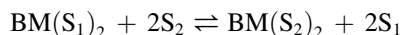
This model originated from a report of a pyridiniophenoxide dye in various solvent mixtures by Skwierczynski and Connors [15]. S_1 and S_2 represent solvent components 1 and 2 in the mixture, respectively. These two solvents interact to yield a common structure, S_{12}, with specific properties. The solute dye 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 the preferential (PS) parameters, $f_{2/1}$ and $f_{12/1}$, which measure the tendency of a solute dye to be dissolved by solvents, S_2 and S_{12}, with respect to solvent S_1. The $E_T(BM)$ values in a binary mixture were determined using Eq. (2):

$$E_T(BM) = \frac{E_T(BM)_1(1-x_2)^2 + E_T(BM)_2 f_{2/1} x_2^2 + E_T(BM)_{12} f_{12/1}(1-x_2)x_2}{(1-x_2)^2 + f_{2/1} x_2^2 + f_{12/1}(1-x_2)x_2} \tag{2}$$

The λ_{max} values are not a linear function of the solvent composition. This may be the result of preferential or selective

The $E_T(BM)$ values for the merocyanine of **SP-1−2** can be obtained by adopting parameters such as $E_T(BM)^1$, $E_T(BM)^2$,

Table 1
Solvent polarity parameters, E_T(BM), for the aqueous solvent mixtures

Water content (%)	Water/MeOH		Water/DMSO		Water/AcCN	
	X_2	E_T(BM)	X_2	E_T(BM)	X_2	E_T(BM)
90	0.95	63.7	0.97	63.2	0.99	64.1
80	0.90	63.1	0.94	62.4	0.92	62.8
70	0.84	62.5	0.90	61.4	0.87	62.1
60	0.77	61.9	0.85	60.3	0.82	61.5
50	0.69	61.3	0.79	59.1	0.75	60.9
40	0.60	60.7	0.72	57.9	0.66	60.1
30	0.49	60.23	0.62	56.43	0.56	59.4
20	0.36	59.76	0.49	54.84	0.43	58.6

$f_{2/1}$ and $f_{12/1}$ from Eq. (2) of Ref. [17]. The data are shown in Table 1.

3.3. Solvatochromism of MC-1–2

The correlation between the $\pi-\pi^*$ transition energies of the MC form and the solvent polarity parameter E_T(BM) in aqueous solvent mixtures was used in the absorption measurements of **SP-1–2**. Table 2 shows the absorption maxima of **MC-1–2** in equilibrium with **SP-1–2** in various aqueous organic solvent mixtures.

The table shows that the λ_{max} values of **MC-1–2** undergo a bathochromic shift with decreasing water content in these solvent mixtures. A linear relationship was obtained by plotting the absorption maxima (the transition energies) of the MC form of **SP-1–2** as a function of the E_T(BM) values of the solvents, as shown in Fig. 2.

The results show the marked solvatochromism by the merocyanines derived from spiropyrans **1** and **2**. A hypsochromic shift was observed as the solvent polarity is increased. Fig. 2 shows that there is a fairly good relationship between the λ_{max} and the solvent polarity parameter, E_T(BM). The linear relationships are generally represented as in Eq. (3).

$$\text{Spiropyrans}: \lambda_{max} = A \times E_T(\text{BM})$$
$$+ B(n, r \text{ in water/co-solvent}) \qquad (3)$$

The slope parameters, A and B, are summarised in Table 3. Among the three solvent mixtures examined in this work, the sensitivity of the binary solvent system toward the transition
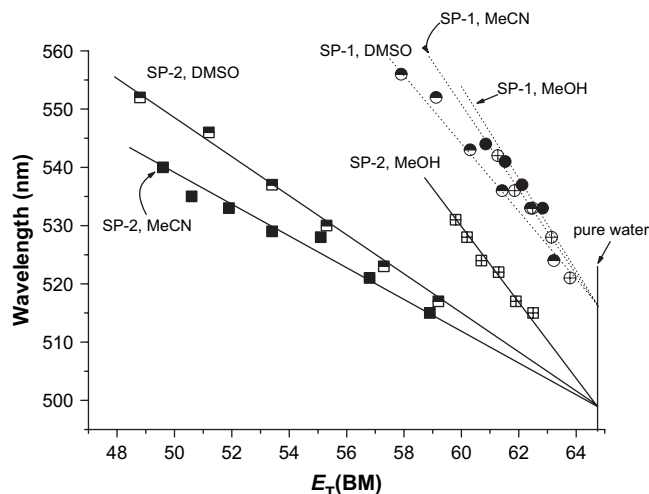

Fig. 2. Plots of λ_{max} of the MC form of **SP-1** (circled) and **SP-2** (squared) versus the solvent polarity parameters, E_T(BM), in the aqueous binary solvent mixtures (filled; CH$_3$CN, half filled; DMSO and x-marked; CH$_3$OH mixtures).

energies of the MC form was highest in the water/methanol solvents.

The excellent correlation between the $\pi-\pi^*$ transition energies (λ_{max}) of the MC form and the E_T(BM) suggests that the contributions of the different solute–solvent interaction forces, as measured by the Brooker's styrylpyridinium betain dye are almost the same as for the $\pi-\pi^*$ absorptions of **MC-1–2**.

In conclusion, an aqueous solvent affects the solvatochromic behavior of merocyanine dyes by increasing the sensitivity of the chromophore to the effects of solvation via H-bonding. Like the merocyanines in neat solvents, the MC form of the spiropyran 6-carboxylates (**SP-1–2**) in aqueous binary solvents is a negative solvatochromic dye, i.e. the absorption maxima of MC decreased with increasing solvent polarity.

An excellent linear relationship was obtained by plotting the absorption maxima (the transition energies) of the MC form of the non-activated **SP-1–2** as a function of the E_T(BM) values of the solvents.

The excited state of hydrated MC was also less dipolar than the ground state. Therefore, the hydrated MC showed negative solvatochromism, as of the MC in neat solvents [18,19]. The

Table 2
Values of λ_{max} of the MC form of **SP-1–2** in the aqueous binary solvent mixtures at 25 °C

Water content	MeOH			CH$_3$CN			DMSO		
	X_{water}	1[a]	2	X_{water}	1[a]	2	X_{water}	1[a]	2
80	0.90	528 (418)	510	0.92	533 (420)	515	0.94	533 (417)	513
70	0.84	533 (422)	515	0.87	537 (419)	521	0.90	536 (418)	517
60	0.77	536 (422)	517	0.82	541 (423)	528	0.85	543 (421)	523
50	0.69	542 (425)	522	0.75	544 (425)	529	0.79	552 (422)	530
40	0.60	547 (430)	524	0.66	–	533	0.72	556 (423)	537
30	0.49	–	528	0.56	–	535	0.62	–	546
20	0.36	–	531	0.43	–	540	0.49	–	556

[a] Data in parentheses are absorption maxima before TEA addition.

Table 3
Parameters[a] for the linear relationship between λ_{max} and the solvent polarity parameter $E_T(BM)$

Molecules	Co-solvents	A	B	N-values	R-values
SP-1	MeOH	7.90	1027	5	0.992
	CH$_3$CN	7.73	1015	4	0.997
	DMSO	6.04	906	6	0.990
SP-2	MeOH	5.97	887	6	0.992
	CH$_3$CN	2.59	668	7	0.987
	DMSO	3.29	713	6	0.998

[a] A and B parameters denote slope and intercepts from Fig. 2.

transition energy of the MC form can be used to determine the micropolarity of various solvent mixtures at the molecular level.

Acknowledgements

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