

# Facile Evaluation of Thermodynamic Parameters for Reverse Thermochromism of Indolinobenzospiropyran-6-carboxylates in Aqueous Binary Solvents

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The position of the thermodynamic equilibrium for reverse thermochromic spiropyran 6-carboxylates (SP-COOHs) was easily determined in aqueous binary mixtures, such as water-methanol, water-acetonitrile and water-dimethyl sulfoxide. The existence of more than one type of interconvertible species of the ring-opened form of SP-COOH in aqueous binary solvents enables us to evaluate the molar extinction coefficients of the ring-opened species of SP-COOH and to obtain the thermodynamic parameters.

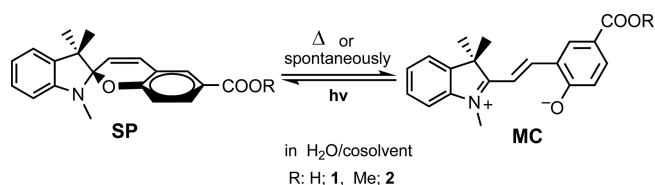
**Key Words :** Reverse thermochromism, Aqueous binary solvent mixtures, Prototropic equilibrium,  $E_{TE}(BM)$ ,  $E_T(BM)$ , Preferential solvation

## Introduction

Thermo- and photochromic indolinobenzospiropyran molecules have an important function in the rapid development of information recording systems, such as optical switching, displays and nonlinear optics.<sup>1-4</sup> These molecules equilibrate between the colorless spiropyran (SP) form and their metastable merocyanine colored form (MC). The absorption of ultraviolet light shifts the equilibrium towards the MC colored form. The reverse reaction to produce the colorless SP form is induced by visible light, heat or even occurs spontaneously. This behavior is designated as a normal photochromism.<sup>5-7</sup> The rate of these reactions depends on the reaction media (*i.e.*, solvent polarity by stabilization/destabilization of the zwitterionic MC form in polar/nonpolar solvents). Stabilization of the zwitterionic MC form in polar solvents leads to a larger activation energy and a slower MC→SP transition compared to non-polar solvents. The colored MC form is approximately 1-3 kcal/mol less stable than the SP form in polar solvents but approximately 5-8 kcal/mol less stable in nonpolar solvents.

The MC form is occasionally further stabilized under certain conditions, such as hydrogen bonding,<sup>8</sup> combination with crown ether or cyclodextrin<sup>9</sup> and complexation with metal.<sup>10,11</sup> Recently, the stability of the MC form of spiropyran 6-carboxylates was reported to be affected markedly in aqueous binary solvents.<sup>12,13</sup> In such media, the MC form becomes more stable than the SP form, and a reverse (negative) photochromic behavior is detected. Scheme 1 shows the reverse photochromic behavior of spiropyran 6-carboxylates in aqueous binary solvents. The initially colorless solutions of spiropyrans become deeply colored with spontaneous formation of the merocyanine species.

As a follow-up study of the unusual reverse photochromic behavior of spiropyran 6-carboxylates in aqueous binary solvents,<sup>12,13</sup> thermodynamic parameters, such as the equilibrium constants  $K_e$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ , for the equilibrium



**Scheme 1.** Reverse thermochromic behavior of spiropyran 6-carboxylates in aqueous binary solvents.

between the SP and MC species need to be evaluated.

Although thermodynamic data<sup>2</sup> related to the photochromic reaction of spiropyran derivatives has been reported for neat and/or binary organic solvents, little information has been reported on the SP molecules in aqueous binary solvents. The effect of the solvent on the kinetics of the thermodynamic parameters is of particular interest because this effect can yield important information on the nature of the solvated SP and MC molecules. Furthermore, because merocyanine dyes in solution normally exist in their dipolar ionic forms, their preferential solvation<sup>14,15</sup> in binary mixtures is expected to affect their photophysical behavior.

This study reports the examination of the effect of solvent mixtures on thermodynamic parameters, such as the equilibrium constants  $K_e$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ , for the reverse photochromic reaction of indolinobenzospiropyran 6-carboxylates.

## Experimental

**General.** Melting points were determined using a Fischer-Jones melting point apparatus and were uncorrected. The <sup>1</sup>H 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-visible spectrometer. Photoirradiation was performed using a mercury lamp (Ushio, 1 kW) as the excitation light source.

**Solvents and Materials.** All solvents were analytically pure and were pre-treated prior to use. Deionized water was used in all measurements. The deionized water was boiled and bubbled with nitrogen and kept in a nitrogen atmosphere to avoid carbon dioxide contamination. The additional organic solvents used in this study were of spectrophotometric grade (Aldrich, Sure-Seal) and used as supplied.

The spiropyran derivatives were obtained from a reaction of Fischer's base and substituted salicylaldehydes according to the reported method.<sup>16</sup> The necessary Fischer's base and substituted salicylaldehydes were purchased from Aldrich and used as received.

**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 of the solvent mixture could be calculated accurately. The solvent composition is always expressed in terms of the water mole fraction.

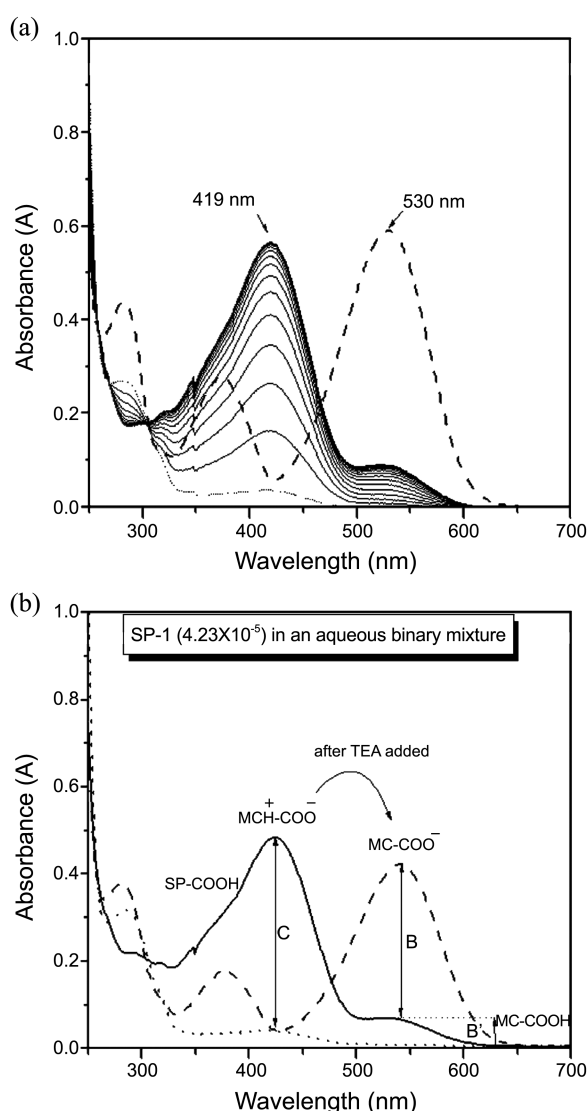
**Spectrophotometric Method.** Stock solutions of the SPs ( $1 \times 10^{-2}$  M) in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) were prepared in 5-mL volumetric flasks in an inert atmosphere. The flasks were then capped with a rubber septum, wrapped in aluminum foil and stored at 0 °C.

Reproducible results for the transformation of spiropyran to merocyanine were obtained by development of a protocol that maximized the formation of the colored form. Briefly, 3.00 mL of the selected aqueous binary solvent was injected into a 1.0-cm-path length quartz cuvette, which was then capped with a Teflon plug and placed into the thermostated (25 °C) cell compartment of the UV-Vis spectrophotometer. The maxima for the UV-Vis spectra were obtained from the final scan of the absorption spectra of the colored MC form of the SP molecules.

For the  $^1\text{H}$  NMR study, a series of solutions of SP-1 was prepared in 5-mm inside diameter NMR tubes with varying concentrations of solvent mixtures of DMSO- $d_6$ /D $_2$ O to analyze all species that existed in the thermochromic ring-opening reaction media. Proton NMR spectra were obtained 2-3 hours after sampling. For acquisition of the  $\text{MCH}^+\text{-COOH}$  spectrum, the SP-1 DMSO- $d_6$  solution was left in the dark for 3 hours after the addition of one drop of DCl to ensure that the ring-opening reaction had gone to completion and no SP-1 remained.

## Results and Discussion

**Spectroscopic Analysis.** Spiropyran 6-carboxylates (SP-1 and SP-2) were readily prepared as described previously.<sup>12</sup> In neat organic solvents, a solution of an activated spiropyran (e.g., 6-nitrospiropyran) was colorless or slightly colored. Upon UV irradiation, the solution displayed "normal" photochromism. However, nonactivated spiropyranes, such as SP-1 and SP-2, showed no chromotropism in neat organic solvents. Generally, nonactivated spiropyranes show no chromotropism in a range of neat solvents, such as methanol, ethanol, DMSO, acetone and DMF. However, non-activated spiropyran 6-carboxylates exhibited chromotro-

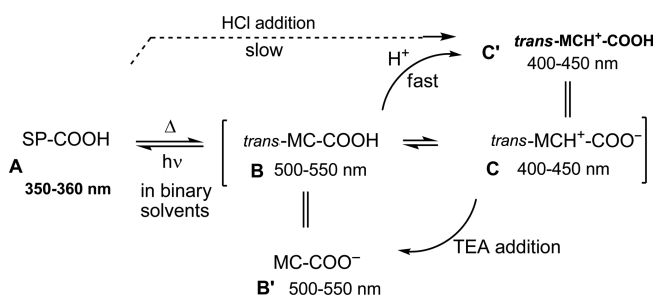


**Figure 1.** (a) Reverse thermochromic behavior of SP-1 (A) in 30% aqueous methanol at ambient temperatures. The dashed line refers to the final scan of SP-2 (B) in 30% aqueous methanol. That line is in accordance with the MC-COOH form of SP-1 formed when TEA was added to the reaction mixture after completion of the ring-opening reaction. The short-dashed lines correspond to the initial state of each SP. (b) Final scans from (a), showing the concentrations of various species (B, B' & C as indicated in Scheme 2).

pism in aqueous binary solvent mixtures, such as water/methanol, water/DMSO and water/acetonitrile.

The initially colorless solutions of these spiropyranes became deeply colored upon formation of merocyanine, which has a strong absorption at 500-550 nm with a high extinction coefficient in these aqueous binary solvents. The colored merocyanine solutions reverted to the colorless SP state upon exposure to the corresponding visible light, as shown in Figure 1.

The existence of more than one type of interconvertible species of the MC form of SP-1 in aqueous binary solvents enables us to evaluate the molar extinction coefficients of MC species of SP-2. After the reverse photochromic reac-

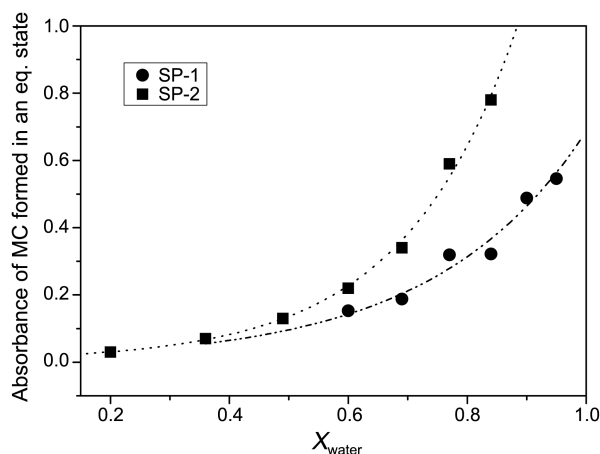


**Scheme 2.** Prototropic equilibrium of SP-1 in aqueous binary solvents.

tion was completed, SP-1 showed strong absorption at 500-550 nm in addition to an extra absorption band in the 400-450 nm region. The extra absorption band was attributed to the protonated MC ( $\text{MCH}^+\text{-COO}^-$ ). The proton might migrate from the substituent 6-COOH to the oxygen atom of the phenoxide anion in aqueous solvents because the COOH group is more acidic than the OH group of the benzopyran ring. Separate UV-Vis spectral studies of spiropyran in HCl/aqueous methanol<sup>17</sup> confirmed this observation. In acidic, neutral and basic solutions, SP-1 shows competitive behavior with the acidity of the phenol and the carboxylic group of the ring-opened MC species. This behavior explains why the spectral change from carboxylic acid to carboxylate would have such a drastic influence on the absorption maxima. The prototropic equilibrium of SP-1 in aq. solvents is shown in Scheme 2.

The reverse photochromic reaction of SP-2 showed a strong absorption band at 500-550 nm without showing any prototropic behavior. The dashed line in (a) of Figure 1 refers to the final scan of SP-2 (b) in 30% aqueous methanol.

The spectroscopic behavior of the conversion of SP to MC in the dark highlights the strong effect of the medium. The formation of the colored MC form of SP-1 and SP-2 in thermal equilibrium varied according to the water content of the aqueous methanol solvents. The stability of the corresponding MC forms increased with the increasing mole fraction of water, as shown in Figure 2.



**Figure 2.** Plots of the mole fraction of water versus the stability of the corresponding MC forms of SP-1 (●) and SP-2 (■).

The MC form was stabilized further as the water content in the binary solvent was increased. Structural studies of the MC form of the spiropyran based on X-ray diffraction<sup>18</sup> showed that the zwitterionic MC form of a spiropyran can be stabilized by a water molecule located between the N and O atoms. This phenomenon is consistent with the work reported by Nishimura *et al.*,<sup>19</sup> who reported that the MC opened form of SP-8-COOH is dramatically stabilized by H-bonding between the phenolic and carboxylic oxygen atoms and shows reverse photochromism in neat solvents.

**Determination of the Equilibrium Constants  $K_e$  between SP and MC.** The equilibrium between SP and MC is a typical intramolecular Lewis acid-base equilibrium.<sup>20</sup> Scheme 2 presents the thermochromic reaction of spiropyrans between a Lewis acidic  ${}^+\text{N}=\text{C}$  center and a Lewis basic center  $\text{O}^-$  via tight ion pairs to provide a covalent N-C-O bond intramolecularly. The position of this equilibrium depends on the electrophilicity and nucleophilicity of the  $\text{C}=\text{N}^+$  of the indolinium unit and the  $\text{O}^-$  of the phenolate unit, respectively, as well as the solvation ability of the surrounding medium. The solvent can affect the ionization and dissociation steps. The position of the Lewis acid/base equilibrium will depend mainly on the differential solvation of the covalent and ionic species, SP and MC.

Solutions of SPs were prepared at concentrations producing measurable absorption intensities in the visible region to determine the equilibrium constants,  $K_e$ , between SP and MC in various solvent mixtures. The solutions were kept at room temperature in the dark for 2-3 hours until the reaction was complete. To determine the concentration of the colored MC form, species C ( $\text{MCH}^+\text{-COO}^-$ ) was treated with tetraethylamine (TEA) to form species B' ( $\text{MC-COO}^-$ ). C was assumed to transform completely to its conjugate base B'. The molar extinction coefficient of C was obtained from the protonation of SP to form species C' ( $\text{MCH}^+\text{-COOH}$ ), assuming that A had been protonated completely. The molar extinction coefficients of species B and C were assumed to be equivalent to the molar extinction coefficients of species B' and C', respectively. The total concentration of the MC form is the sum of the concentrations of B' and B, as shown in Figure 1(b). The equilibrium constant,  $K_e$ , between SP and MC can be determined using Eq. (1).

$$K_e = \frac{[\text{MC}]}{[\text{SP}]} = \frac{[\text{B}' + \text{B}]}{[\text{A}]} = \frac{[\text{B}' + \text{B}]}{C_{\text{total}} - [\text{B}' + \text{B}]} \quad (1)$$

The equilibrium constants  $K_e$  for SP-1 and SP-2 obtained using Eq. (2) are listed in Table 1.

The corresponding  $K_e$  value increases with increasing solvent polarity, which suggests that the polarity of the SP form is lower than the polarity of the MC form. With increasing solvent polarity, the decrease in the Gibbs energy of the MC form by solvation is larger than the decrease in the Gibbs energy of the SP-form.

The change in the equilibrium constant  $K_e$  is in the direction anticipated with more ionization occurring as the solvent becomes more polar. The change in Gibbs free energy

**Table 1.** Equilibrium constants  $K_e$ ,  $E_T$ (BM), and  $\Delta G^\circ$  for reverse photochromism of SP-1 and SP-2 in aqueous binary solvents

Compds	media	H <sub>2</sub> O (%)	$X_{\text{water}}$	A <sup>a</sup> [SP] ( $1 \times 10^{-5}$ )	B <sup>a</sup> [MC-COOH] ( $1 \times 10^{-5}$ )	C <sup>a</sup> [MCH <sup>+</sup> -COO <sup>-</sup> ] ( $1 \times 10^{-5}$ )	$A_e$	$K_e$	$-\Delta G^\circ$ (kJ/mol)	$E_T$ (BM) <sup>b</sup> (kcal/mol)	Note <sup>c</sup>
SP-1	aq. MeOH	60	0.77	1.36	0.51	2.36	0.35	2.12	1.86	61.8	rev
		70	0.84	1.09	0.64	2.51	0.38	2.91	2.65	62.5	
		80	0.90	0.57	0.45	3.21	0.48	6.49	4.63	63.1	
		90	0.95	0.37	0.35	3.51	0.53	10.5	5.83	63.8	
	aq. MeCN	60	0.82	2.89	0.60	0.74	0.11	0.46	-1.90	61.5	rev
		70	0.87	2.38	0.54	1.31	0.19	0.78	-0.62	62.1	
		80	0.92	0.99	0.56	2.68	0.38	3.26	2.93	62.8	
		90	0.99	0.59	0.40	3.25	0.51	13.0	6.35	64.2	
	aq. DMSO	50	0.79	1.89	0.53	1.81	0.26	0.57	0.52	59.1	rev
		60	0.85	1.38	0.38	2.47	0.36	2.07	1.80	60.3	
		70	0.90	0.96	0.41	2.86	0.41	3.40	3.03	61.4	
		80	0.94	0.71	0.46	3.06	0.44	4.97	3.97	62.4	
		90	0.97	0.52	0.47	3.25	0.47	7.14	4.87	63.2	
SP-2	aq. MeOH	40	0.60	-	-	-	0.22	58.5	5.45	60.7	rev
		50	0.69	-	-	-	0.34	77.9	2.51	61.3	
		60	0.77	-	-	-	0.59	177	-5.90	61.9	
		70	0.84	-	-	-	0.78	439	-15.5	62.5	

<sup>a</sup>Symbols A-C are the same as in Scheme 2. <sup>b</sup>Solvent polarity parameters for the binary solvents are from ref. 13. <sup>c</sup>rev and nor denote reverse and normal photochromism, respectively.

decreases linearly with increasing solvent polarity. Polar solvents tend to be more structured and stabilized than less polar solvents. Proportionally fewer negative free energy changes are observed in more polar solvents, such as a higher water percentage in aqueous methanol solvents. For the SP-6-carboxylates examined, the colored MC form was 1-2 kJ/mol more stable than the SP form in polar solvents but 3-6 kJ/mol more stable in the aqueous methanol solvents

containing a higher water percentage.

Knowing the equilibrium constant at various temperatures, the thermodynamic quantities  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  can be evaluated using the following equation:

$$\ln K_e = -\Delta H^\circ/R(T^{-1}) + \Delta S^\circ/R \quad (2)$$

By plotting  $\ln K_e$  versus  $1/T$ , the thermodynamic quantities  $\Delta H^\circ = -R \cdot m$  and  $\Delta S^\circ = -R \cdot b$  ( $R = 8.3145 \times 10^{-3}$  kJ/mol·K)

**Table 2.** Thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  for the reverse photochromism of SP-1 in aqueous binary solvents

SP derivatives	Solvents (50/50 V %)	Temp (°C)	$K_e^a$	$-\ln K_e$	$-\Delta G^\circ$ (kJ/mol)	$-\Delta H^\circ$ (kJ/mol)	$-T\Delta S^\circ$ (kJ/mol)	Note
SP-6-COOH	aq. MeOH	20	2.64	0.971	6.25			this work
		25	2.21	0.793	1.97			
		30	1.73	0.548	1.38			
		35	1.46	0.377	0.96			
	aq. MeCN	20	2.04	0.713	3.54			this work
		25	1.48	0.392	0.97			
		30	1.00	0.000	0.00	53.6	52.8	
		35	0.74	-0.298	0.76			
	aq. DMSO	20	3.57	1.273	3.10			this work
		25	2.86	1.051	2.60			
		30	2.10	0.742	1.87	39.8	37.3	
		35	1.42	0.527	1.35			
SP-6-NO <sub>2</sub>	EtOH	25	8.43E-3	4.78	-11.8	-8.79	2.99	normal <sup>b</sup>
	CHCl <sub>3</sub>	25	9.76E-5	9.23	-18.4	-25.1	-6.73	
	Acetone	25	1.34E-3	6.62	-16.3	-7.53	8.85	normal <sup>b</sup>
SP-6-N=N-Ph	BzOH	25	1.00E-2	4.60	-11.0	1.00	11.9	reverse <sup>c</sup>
SP-6-N=N-( <i>p</i> -nitro-Ph)	BzOH	25	3.00E-2	3.51	-9.0	1.50	10.4	reverse <sup>c</sup>

<sup>a</sup>The  $K_e$  values are the ratios of [MC]/[SP] of SP-1 at the thermal equilibrium state in various binary solvent media. <sup>b</sup>Normal photochromism, data obtained from ref. 21. <sup>c</sup>Reverse photochromism, data obtained from ref. 22.

can be obtained from the *slope* and *intercept*, respectively. Table 2 lists the thermodynamic equilibrium constants. The high  $\Delta H^\circ$  values and negative  $\Delta S^\circ$  values are characteristic of the solvation of the reverse photochromic reaction as the solvent mixture becomes increasingly polar. The negative entropy changes in most cases may represent the ordering of the solvent molecules around the product. More polar solvents are normally more ordered than less polar solvents.

Although the thermodynamic quantities  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  cannot provide insight into the mechanisms of the reverse reaction, these thermodynamic quantities are characteristic of the reactants and products. These data indicate the feasibility of the reaction.

The  $^1\text{H}$  NMR study of SP-1 confirmed further the position of the equilibrium in the solvent mixtures of DMSO- $d_6$  and  $\text{D}_2\text{O}$ . The solutions of SP-1 in various solvent mixtures were left at the NMR bench for 3 hours to ensure that the ring-opening reaction established an equilibrium. To produce intense signals for the ring-opened species, relatively high concentrations of SP-1 and high percentages of water were required. However, the solubility tends to decrease drastically upon increasing the water content of the solvent mixtures. The use of solvent mixtures was very limited for this NMR study, unlike the UV-Vis spectroscopic study.

This NMR work was performed only in the ~60% DMSO- $d_6$  and ~40%  $\text{D}_2\text{O}$  solvent mixture. After the ring-opening reaction is completed in the solvent mixture, three detectable species (SP, *trans*-MC-COOH and *trans*-MCH $^+$ -COO $^-$ ) are equilibrated. The *cis*-MC-COOH is not detected because it is a transient species.<sup>23,24</sup>

Some of the resonance frequencies were very characteristic of the chemical structures of the species formed in this reverse thermochromic reaction. The SP molecules have been known to exhibit the characteristic peaks of diastereotopic *gem*-dimethyl, N-CH $_3$  and vinylic hydrogen H3' peaks, whereas the ring-opened MC species has enantiotropic *gem*-dimethyl and N $^+$ -Me. N-Methyl peaks sometimes overlap with the DMSO- $d_6$ / $\text{D}_2\text{O}$  solvent peaks. The *gem*-dimethyl was therefore chosen to be monitored for this work.

The chemical shifts of H3' and H4' were also studied to confirm the presence of the open-form MC species of SP-1 in the solvent mixtures.  $^1\text{H}$  NMR data for SP-1 in DMSO- $d_6$  solution containing a drop of DCl indicated the presence of the ring-opened MCH $^+$ -COOH species, which has the vinylic hydrogen H3' and H4' resonances at 7.83 and 8.46 ppm, respectively, in addition to enantiotropic *gem*-dimethyl and N $^+$ -Me from the *trans*-MC-COOH and *trans*-MCH $^+$ -COO $^-$  species. Selected  $^1\text{H}$  resonances ( $\delta$ , in ppm) and coupling constants (Hz) of SP-1 for the ring-opened MC species in the 60/40 volume % DMSO- $d_6$ / $\text{D}_2\text{O}$  solvent mixture, in addition to the resonances of MCH $^+$ -COOH for comparison, are collected in Table 3.

Monitoring the resonance frequency of the *gem*-dimethyl could differentiate between the closed SP and the opened MC forms and eventually allow the evaluation of the equilibrium constant  $K_e$ . The  $K_e$  values that have been determined are collected in Table 4.

**Table 3.**  $^1\text{H}$  NMR data for some selected resonance peaks of SP-1 and its ring-opened MC species in the 60/40 volume % ratio of DMSO- $d_6$ / $\text{D}_2\text{O}$  solvent mixture.

Species	Characteristic proton resonance peaks $\delta$ (ppm)		
	<i>gem</i> -dimethyl	N-Me	vinylic H3' & H4'
SP-COOH <sup>a</sup>	1.20 & 1.10	2.65	5.85 & 6.75
SP-COOH	1.13 & 1.03	2.58	5.80 & 6.99
MC-COOH/MCH $^+$ -COO $^-$	1.68	3.96	-
MCH $^+$ -COOH <sup>b</sup>	1.76	4.11	7.83 & 8.46

<sup>a</sup>in DMSO- $d_6$ . <sup>b</sup>in DMSO- $d_6$  containing one drop of DCl

**Table 4.** Intensity ratios between *gem*-dimethyl peaks of  $^1\text{H}$  NMR spectroscopy of SP-1 in the thermal equilibrium state in various percent ratios of DMSO- $d_6$ / $\text{D}_2\text{O}$  solvent mixtures.

% of DMSO- $d_6$	Relative intensities of the <i>gem</i> -dimethyl peaks		Rel. ratios ( $K_e$ )
	SP-COOH	MC-COOH and MCH $^+$ -COO $^-$	
50	7.89	4.34	0.55 <sup>a</sup>
55	6.89	2.62	0.38
60	5.56	1.00	0.18
65	5.29	0.74	0.14

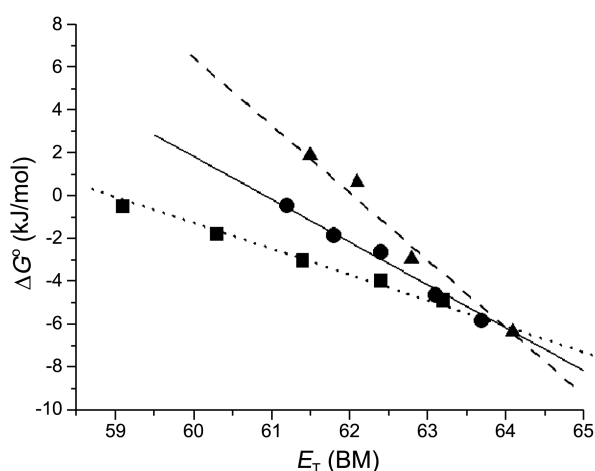
<sup>a</sup>Comparable to the value 0.57 obtained from the UV-Vis study in Table 1.

Data in Table 4 obtained from  $^1\text{H}$  NMR spectroscopy confirmed the position of the equilibrium of SP-1 in solvent mixtures. The ratio ( $K_e$ ) obtained from this NMR work was 0.55, which was comparable to the value (0.57) obtained from the UV-Vis study.

Overall, the NMR studies described above are fully consistent with the prototropic schemes that we have proposed for the reverse thermochromism of SP-1 and SP-2 in the aqueous solvent mixtures.

**Solvent Effects on Thermodynamic Equilibrium.** This section examines what factors are responsible for the drastic difference between the neat solvents and the aqueous mixed solvents. Hydrogen bonding by water certainly plays an important role in the stabilization of the MC form of SP-carboxylates in aqueous solvent mixtures. The solvation of the zwitterionic MC form by water molecules through hydrogen bonding is presumably responsible for stabilizing the MC species.

Solvent effects on the equilibrium constant  $K_e$  are shown in the relationship between the equilibrium constant and  $E_T$ <sup>25</sup> in various solvents. In binary solvent mixtures, the stability of the MC form is complicated further by the so-called 'preferential solvation' of the substance by one component of the solvent mixture. This phenomenon includes specific substance-solvent interactions, such as H-bonding. The most significant aspect of preferential solvation is that the composition of the solvation shells of most substances is different from the composition of the solvation shells of the corresponding bulk solvents. For this matter, new solvent polarity parameter  $E_T$  (BM) in aqueous binary solvents has been developed by us.<sup>13</sup>



**Figure 3.** Plots of  $\Delta G^\circ$  versus  $E_T$ (BM) for the reverse thermochromism of SP-1 in aqueous binary solvents ( $\blacktriangle$ : water/CH<sub>3</sub>CN,  $\bullet$ : water/MeOH,  $\blacksquare$ : water/DMSO).

An excellent linear relationship (right) was obtained by plotting the equilibrium constant  $K_e$  between SP and MC as a function of the  $E_T$ (BM) values of the solvents, as in Eq. (3) adapting the spectroscopic Hammett equation.<sup>25</sup>

$$\ln K_e = m E_T(\text{BM}) + C \quad (3)$$

The plots are shown in Figure 3. The slopes for CH<sub>3</sub>CN, MeOH and DMSO were 1.66, 1.07 and 0.67, respectively. In particular, solvent effects on the equilibrium constant  $K_e$  via preferential solvation were the largest in aqueous CH<sub>3</sub>CN.

### Conclusions

The existence of more than one type of interconvertible species of the MC form of SP-6-COOH in aqueous binary solvents permits an evaluation of the molar extinction coefficients of the MC species of SP-6-COOH.

The concentration of the MC species in the thermal equilibrium state increases with increasing water content in the binary solvent mixtures. The stability of the MC form also increases with increasing water content in the binary solvent mixtures, suggesting that the MC form has lower polarity in the excited states than in the ground state and that the same effects contribute to the solvation of these SP molecules.

The excellent linear relationship obtained by plotting the equilibrium constant  $K_e$  between SP and MC as a function of the  $E_T$ (BM) values of the solvents indicates that solvent effects on the intramolecular Lewis acid-base equilibrium between SP and MC are closely related to the preferential solvation observed in the aqueous solvent mixtures. Overall, hydrogen bonding by water plays an important role in these effects on the equilibrium between the SP form and the MC form of SP-6-COOH in aqueous solvent mixtures.

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