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Solvatochromic behavior of substituted 4-(nitrostyryl)phenolate

dyes in pure solvents and in binary solvent mixtures composed

of water and alcohols

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Abstract

Several 4-(nitrostyryl)phenolates have been used recently as solvatochromic dyes in the investigation of pure solvents. Changes in their molecular structures allow a comparison of their solvation patterns to be made in different binary solvent mixtures, in an effort to relate structural factors to the preferential solvation (PS) observed in these media. Firstly, the solvatochromism of four of these probes was studied and a reversal in their solvatochromism was verified, which was expected following a comparison with other similar systems previously studied. The solvatochromic behavior of a series of twelve 4-(nitrostyryl)phenolate dyes was then investigated in water-alcohol mixtures. A sigmoid behavior was verified for one of the dyes in ethane-1,2-diol-water mixtures, and the dye was preferentially solvated by water in the alcohol-rich region. For all other mixture compositions a strong synergy was observed, with the PS of the dye molecules occurring through the less polar moiety of the water-alcohol aggregates in the binary mixtures. In addition, synergy was observed for some dyes, with PS occurring through the less polar moiety of the alcohol-water aggregates. For all of the other water-alcohol mixtures, the probes were preferentially solvated by the alcohol cosolvent. In order to quantify these deviations, a PS (or non-ideality) index PSI was proposed. The PSI values obtained correlated well with the hydrogen-bond donating ability of the alcoholic co-solvent, and also with the basicity of the phenolate dyes, and the trends observed were confirmed with data from the literature for two other phenolate dyes.

Keywords: solvatochromism; synergism; preferential solvation; solvatochromic reversal; solute-solvent interactions; binary solvent mixtures.

1. Introduction

The influence of solvents on the rate and the course of many chemical processes is well known [1, 2], being usually attributed to changes in the medium polarity. Solvatochromic probes are commonly used in the physicochemical investigation of solvent properties [1-6]. Reichardt's pyridinium-*N*-phenolate betaine dye (1) [6-8] and Brooker's merocyanine (2) [9-11] are two solvatochromic dyes which have been used in recent decades (Scheme 1).

((Scheme 1 here))

In the investigations carried out with respect to solvent effects, a growing interest can be verified in the study of binary solvent mixtures [12-18]. A very large number of papers dealing with solute-solvent interactions in binary solvent mixtures have employed solvatochromic probes to make evident the phenomenon of preferential solvation (PS) in such media [3-5, 11, 19]. The assumption that the spectral response reflects the composition of the probe-solvating layer leads to the conclusion that the composition of this cybotactic region often departs considerably from that of the bulk mixture. This is readily visualized in plots of the variation of the transition energy (E_T) values of the solvatochromic probe with the binary mixture composition, often expressed as the mole percentage of one of the solvents [11, 20, 21]. These plots are unique for a particular probe in a certain binary solvent mixture, since they reflect specific interactions in this three-component system. Nevertheless, if a series of analogous probes is compared, analogous plots should be obtained, that may shed light on these specific interactions in solution.

We have reported in a number of papers the solvatochromic behavior of a family of probes comprised of a phenolate donor conjugated through an ethylene or an imino bridge with a polynitro-phenyl or heteroaryl group [22-25]. They all exhibit an inverted solvatochromic behavior, changing from a positive response in non-polar, non-hydrogen-bond donating (non-HBD) media, to a negative behavior in hydrogen-bond donating (HBD) solvents [22-25]. This reflects their hybrid nature, with a phenolate donor that dictates their negative solvatochromism in HBD solvents and a polynitroaryl acceptor, which is responsible for their positive solvatochromism in non-polar media [23].

In this paper we describe the solvatochromic behavior of a series of such "hybrid" stilbenes **3b-14b** in water-alcohol mixtures, generated by *in situ* deprotonation of the corresponding phenols **3a-14a** (**Scheme 2**). Variations in their molecular structures allowed a comparison of their solvation patterns to be made in different binary solvent mixtures, in an effort to relate structural factors to the PS verified in these media. The observed trends were also compared with results reported for previous studies, carried out in the same solvents, on other solvatochromic phenolate probes, such as Reichardt's betaine **1** and Brooker's merocyanine **2**. In addition, the solvatochromism of compounds **9b**, **10b**, **13b**, and **14b** was studied, since this had not been previously investigated for these dyes.

((Scheme 2 here))

2. Experimental

2.1 Materials and methods

All reagents and solvents were analytically pure and were purchased from commercial sources (Sigma-Aldrich, Merck, Vetec, and Synth), being employed without

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further purification. All solvents were HPLC grade and were purified following the methodology described in the literature [26, 27]. The deionized water used in the measurements was boiled and bubbled with nitrogen and then kept in a nitrogen atmosphere to avoid the presence of carbon dioxide.

NMR spectra were recorded using a 400-MHz AS 400 spectrometer. Chemical shifts were recorded in ppm with the solvent resonance as the internal standard and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double doublet, m = multiplet), and coupling constants (Hz). IR spectra were obtained on an FT Varian 3100 spectrometer, with KBr pellets. High-resolution mass spectra were obtained with an electrospray ionization-quadrupole time-of-flight mass spectrometer (HR ESI-QTOF-MS). UV-vis spectra were obtained on an HP 8452 spectrophotometer equipped with thermostatted cell compartments at ± 0.1 °C, using 1 cm square quartz cuvettes. Melting points were recorded with a Didática SP MQAPF-302 apparatus and were not corrected.

2.2 Synthesis of the compounds

Compounds 2a-7a, 10a, and 11a were prepared following previously reported procedures [24].

4-Nitrophenylacetic acid (**15**) was prepared according to the procedure described in the literature [28]. The melting point obtained was 148 °C (literature melting point of 150 °C) [28].

3,5-Difluoro-4-hydroxybenzaldehyde (**16**). This compound was prepared based on the methodology described by Lawrence et al. [29] with some modifications: 2,6difluorophenol (0.300 g, 2.3 mmol) and hexamethylenetetramine (0.323 g, 2.3 mmol) were refluxed in trifluoroacetic acid (3.5 mL, 45.7 mmol) for 15 h under argon atmosphere. The product was concentrated, combined with 15 mL of ice water and stirred for 30 min. The resultant mixture was basified with Na₂CO₃ and extracted with dichloromethane. The aqueous phase was acidified with HCl (1 mol L⁻¹) and then extracted four times with dichloromethane. The organic fractions were collected, dried with MgSO₄ and rotaryevaporated. The product is a cream solid (0.212 g, 58% yield) with a melting point of 116-118 °C.

(*E*)-2,6-Difluoro-4-(4-nitrostyryl)phenol (**8a**). 4-Nitrophenylacetic acid (0.145 g, 0.8 mmol), 3,5-difluoro-4-hydroxybenzaldehyde (0.093 g, 0.6 mmol) and piperidine (40 µL, 0.4 mmol) were refluxed (130-140 °C) for 50 min under argon atmosphere. The temperature was then lowered to 100-110 °C and 1.2 mL of an ethanol:water (3:1) mixture with 5 drops of acetic acid were added and reacted for 90 min. The reaction mixture was cooled to room temperature, the precipitate was filtered off, and washed with ice-cold ethanol. The purification was performed by column chromatography, eluting with ethyl acetate/*n*-hexane (7:3, v/v). A yellow solid was obtained (0.122 g, 75% yield) with a melting point of 182-184 °C; IR (KBr, \bar{v}_{max} /cm⁻¹): 3368 (O-H), 3106 (=C-H), 1591, 1537 and 1511 (C=C), 1347 (N=O); ¹H NMR (400 MHz, acetone-d₆) δ /ppm: 9.24 (1H, *s*), 8.23 (2H, *d*, *J* = 9.0 Hz,), 7.82 (2H, *d*, *J* = 9.0 Hz), 7.42 (1H, *d*, *J* = 16.4 Hz), 7.37-7.29 (3H, *m*); ¹³C NMR (100 MHz, acetone-d₆) δ /ppm: 155.3 (C, *d*, *J*_{CF} = 242.0 Hz), 155.2 (C, *d*, *J*_{CF} = 242.0 Hz), 148.3, 145.3,

135.6, 132.6, 128.5, 127.8, 125.3, 111.8 (C, *dd*, *J*_{CF} = 14.7 and 7.3 Hz). HRMS (ESI/TOF-Q) *m*/*z*: [M]⁻ calcd for C₁₄H₉F₂NO₃ 276.0467; found 276.0468.

(*E*)-2,6-Difluoro-4-(2,4-dinitrostyryl)phenol (**9a**). 2,4-Dinitrotoluene (0.170 g, 0.9 mmol), 3,5-difluoro-4-hydroxybenzaldehyde (0.150 g, 0.9 mmol) and pyrrolidine (62 μL, 0.8 mmol) were refluxed at 80-85 °C for 23 h. The purification was performed by column chromatography, eluting with ethyl acetate/*n*-hexane (1:1, v/v). A yellow solid was obtained (0.060 g, 20% yield) with a melting point of 198-200 °C; IR (KBr, \bar{v}_{max} /cm⁻¹): 3456 (O-H), 3096 (=C-H), 1698, 1533 and 1523 (C=C), 1354 (N=O); ¹H NMR (400 MHz, acetone-d₆) δ /ppm: 9.41 (1H, *s*), 8.77 (1H, *d*, *J* = 2.4 Hz), 8.52 (1H, *dd*, *J* = 2.4 and 9.0 Hz), 8.24 (1H, *d*, *J* = 9.0 Hz), 7.56 (1H, *d*, *J* = 16.1 Hz), 7.48 (1H, *d*, *J* = 16.1 Hz), 7.38 (2H, *dddd*, *J* = 3.4, *J* = 1.5 Hz, *J* = 1.7 and *J* = 3.4 Hz); ¹³C NMR (100 MHz, acetone-d₆) δ /ppm: 155.2 (C, *d*, *J*_{CF} = 242.0 Hz), 155.1 (C, *d*, *J*_{CF} = 242.0 Hz), 149.1, 147.9, 139.3, 136.8, 130.6, 128.4, 122.7, 121.6, 112.3 (C, *dd*, *J*_{CF} = 14.7 and 7.3 Hz); HRMS (ESI/TOF-Q) *m*/*z*: [M]⁻ calcd for C₁₂H₈F₂N₂O₅ 321.0318; found 321.0322.

(*E*)-2,6-Dimethoxy-4-(4-nitrostyryl)phenol (**12a**). This compound was synthesized according to the literature [30]. The product is an orange solid (0.130 g, 72% yield) with a melting point of 178-180 °C (literature melting point [30] of 186-187 °C).

(*E*)-2,6-Dimethoxy-4-(2,4-dinitrostyryl)phenol (**13a**). This compound was synthesized according to the literature [30], but the purification was performed using chromatographic column with ethyl acetate/*n*-hexane (1:1, v/v) as the eluent. The product is an orange solid (0.290 g, 30% yield) with a melting point of 250-252 °C (dec).

2.3 UV-vis measurements

The following procedure was typical for all measurements performed. A stock solution of each compound $(5.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol } \text{L}^{-1})$ was prepared in acetone. From this stock solution, 4-8 µL was transferred to thirty-one 5-mL volumetric flasks. After evaporation of the acetone the probe was dissolved in the pure solvent, resulting in a solution presenting a final dye concentration of $2.0 \times 10^{-5} - 5.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$. In order to generate the deprotonated probes, 20-40 µL of a methanolic $0.1 \text{ mol } \text{L}^{-1}$ tetra-*n*-butylammonium hydroxide (TBAOH) solution was added to each flask. The addition of this very small amount of methanol did not change the position of the UV-vis band of the dye. The bulky tetra-*n*-butylammonium ion has no influence on the UV-vis spectrum of the anionic dye. The UV-vis spectra were recorded at 25.0 °C. The maxima of the UV-vis spectra were calculated from the first derivative of the absorption spectrum, with a precision of $\pm 0.5 \text{ nm}$, and the reproducibility of the λ_{max} values was verified through the determination of two spectra for each dye in each pure solvent.

2.4 Solvent mixtures

Binary solvent mixtures were prepared and the final values are expressed in terms of the water co-solvent mole fraction (X_2) in the water-alcohol mixtures. The following procedure was typical for all experiments performed. A stock solution of each dye (5.0×10^{-3} - 1.0×10^{-2} mol L⁻¹) was prepared in acetone. From this stock solution 8-32 µL was transferred to two 5-mL volumetric flasks. After the evaporation of the acetone, the probe was dissolved in the pure solvents, resulting in solutions presenting final concentrations of 2.0×10^{-5} - 4.0×10^{-5} mol L⁻¹. Binary mixtures were prepared from these stock solutions by weighing one of the

solvents in a quartz cuvette and adding small amounts of the cosolvent with a microsyringe. The maxima on the UV-vis spectra were determined and used to provide the corresponding $E_{T}(dye)$ values (see above). All experiments with the mixed solvent systems were carried out in duplicate and the reproducibility of the curve features was confirmed.

2.5 Calculation methods

The parameters $E_T(dye)_1$, $E_T(dye)_2$, $E_T(dye)_{12}$, $f_{2/1}$, and $f_{12/1}$ were calculated from nonlinear regressions using the ORIGIN 8.5 software.

3. Results and Discussion

The preparation of the novel 4-hydroxy-4'-nitrostilbenes **9a** and **13a** followed the same procedure described previously for the synthesis of analogs **3a**, **5a**, **7a**, and **11a**, which involved the base-catalyzed condensation of 4-nitrophenylacetic acid with the corresponding 4-hydroxybenzaldehyde (**Scheme 3**) [23]. The 4-hydroxy-2',4'-dinitrostilbenes **10a** and **14a** were prepared by basic condensation of 2,4-dinitrotoluene with the corresponding 4-hydroxybenzaldehyde, following the same procedure employed for the preparation of analogous **4a**, **6a**, **8a**, and **12a** [23].

((Scheme 3 here))

The treatment of all hydroxystilbenes with TBAOH generated *in situ* the corresponding solvatochromic phenolates **3b-14b** in all investigated solvent mixtures. The solvatochromic behavior of the new phenolates **9b**, **10b**, **13b**, and **14b**, illustrated in **Fig. 1**,

was recorded in 27-29 solvents. The λ_{max} values obtained from the UV-vis spectra were transformed into $E_T(dye)$ values, according to the expression $E_T(dye) = 28590/\lambda_{max}$ [1, 6], given in kcal mol⁻¹ with a precision of ±0.1 kcal mol⁻¹ (**Table 1**).

((Fig 1. here))

Table 1

 $E_{\rm T}$ (dye) values for compounds **9b**, **10b**, **13b**, and **14b** in solvents of various polarities and the $E_{\rm T}$ (30) values in kcal mol⁻¹.

Solvent	$E_{\rm T}(30)^{\rm a}$	9b	10b	13b	14b
Water	63.1	68.9	64.2	62.3	56.5
Ethane-1,2-diol	56.3	66.8	61.4	59.2	51.7
Methanol	55.4	67.7	61.9	59.7	51.7
Ethanol	51.9	65.0	57.9	56.7	47.8
Propan-1-ol	50.7	64.2	57.3	56.3	47.0
Benzyl alcohol	50.4	63.1	56.2	56.8	46.6
Butan-1-ol	49.7	63.7	56.3	55.6	46.3
Pentan-1-ol	49.1	63.7	55.9	55.6	46.4
Propan-2-ol	48.4	62.0	53.7	53.6	44.0
Octan-1-ol	48.1	63.4	55.2	55.5	46.2
Decan-1-ol	47.7	63.5	55.6	55.5	46.3
Butan-2-ol	47.1	61.1	52.9	52.8	43.3
Acetonitrile	45.6	59.1	51.4	50.5	41.5
DMSO	45.1	53.0	46.3	43.6	38.5
2-Methylpropan-2-ol	43.7	59.6	51.4	51.5	42.3
DMF	43.2	54.2	46.3	44.9	39.2
DMA	42.9	52.9	44.8	44.9	39.2
Acetone	42.2	58.5	49.5	49.0	39.9
1,2-Dichloroethane	41.3	61.2	52.2	52.6	42.9
Dichloromethane	40.7	61.9	52.0	52.6	42.7
Acetophenone	40.6	58.1	47.6	47.9	39.2
Trichloromethane	39.1	61.9	50.2	53.2	48.2
1,2-Dimethoxyethane	38.2	58.3	52.3	50.3	41.5
Ethyl acetate	38.1	58.8	50.5	51.6	42.6
THF	37.4	57.5	49.3	49.5	40.9
Diethyl ether	34.5	61.2	51.8	53.4	44.2
Toluene	33.9	63.4	52.0	55.4	46.6
<i>n</i> -Hexane	31.0	65.7	56.7	58.8	b
Cyclohexane	30.9	65.1	56.5	57.6	b

^a Values obtained from the literature [1, 6].

^b Insoluble.

The dyes all showed the same inverted pattern obtained for other analogous "hybrid" probes, as illustrated in **Fig. 2** [22-25].

((Fig. 2 here))

As discussed in a previous publication [23], the high dispersion verified in the plots of **Fig. 2** reflects the different nature of the dyes **3b-14b**, with a neutral polynitro acceptor group, from that of Reichardt's reference probe **1**, with a charged pyridinium acceptor moiety. This hinders a direct comparison of the analogous members of this family from such plots. A better alternative is to use the unsubstituted probe **3b** as a reference [23]. Plots of the transition energies $E_{\rm T}$ of a particular dye against the $E_{\rm T}$ (**3b**) values yielded in all cases straight lines with good correlations, as illustrated in **Fig. 3**, and a linear dependence expressed by **Eq. (1)**,

$$F_{\rm m}({\rm dve}) = m + n F_{\rm m}(3)$$

(1)

where the slope n measures the sensitivity of the dye to the solvent, compared to the reference **3b**.

((Fig 3. here))

The values of m and n for dyes **4b-14b** are listed in **Table 2**. In general, dyes bearing two nitro substituents on the acceptor ring are more sensitive than their analogs with one nitro group. Also, electron-releasing substituents on the phenolate ring tend to increase the dye sensitivity, compared with electron-withdrawing substituents [23].

Table 2

Dye	\mathbb{R}^1	\mathbb{R}^2	m	n	r^2
4b ^a	NO_2	Н	-4.9±2.4	0.95 ± 0.04	0.95 (28)
5b ^a	Н	Br	20.9±1.6	0.67 ± 0.03	0.96 (28)
6b ^a	NO_2	Br	11.6 ± 2.5	0.70 ± 0.04	0.91 (28)
7b ^a	Н	Cl	18.6±1.7	0.71 ± 0.03	0.96 (28)
8b ^a	NO_2	Cl	7.8±2.5	0.77 ± 0.04	0.93 (28)
9b	Н	F	13.5±2.5	0.81 ± 0.04	0.93 (29)
10b	NO_2	F	-1.2±3.5	0.93 ± 0.06	0.90 (29)
11b ^a	Н	Me	3.4±2.5	0.87 ± 0.04	0.94 (28)
12b ^a	NO_2	Me	-4.5 ± 3.1	0.86 ± 0.05	0.91 (28)
13b	Н	OCH ₃	-1.5 ± 3.0	0.93 ± 0.05	0.92 (29)
14b	NO_2	OCH ₃	-4.7 ± 4.0	0.84 ± 0.07	0.85 (27)

Values of m and n for compounds **4b-14b**, according to **Eq. (1)**.

^a Values obtained from the literature [23].

The dispersion verified in the plots of $E_T(dye)$ as a function of $E_T(30)$ values can be explained through a comparison of the coefficients of Catalán multiparametric regression equation [**Eq. (2**)] for dyes **9b**, **10b**, **13b**, and **14b**. Table 3 shows the results of the multiple square correlation analysis for the dyes, obtained employing Catalán's parameters for solvent acidity (SA), basicity (SB), polarizability (SP), and dipolarity (SdP) [31], in 29 solvents for dyes **9b**, **10b**, and **13b**, and 27 solvents for **14b**. The inclusion in Catalán approach of log *P*, which is a parameter associated with the lipophilicity of the medium [32,33], generally led

to an improvement in the correlations (see Supporting Information). As verified previously for dyes **3b-8b**, **11b**, and **12b** [23-25], data show that the solvent acidity contributed to hypsochromic shifts in the solvatochromic band of dyes **9b**, **10b**, **13b**, and **14b**, with positive values for coefficient a. On the other hand, the medium basicity, polarizability, and dipolarity, all of them exhibiting negative values for the coefficients b, c, and d, were responsible for bathochromic shifts in the solvatochromic band of the probes.

$$E_{\mathrm{T}}(\mathrm{dye}) = E_{\mathrm{T}}(\mathrm{dye})_0 + aSA + bSB + cSP + dSdP + p(\log P)$$

Table 3

Correlation coefficients a, b, s, d and p obtained from Catalán multiparametric analysis, correlation coefficient (*r*) and standard deviation (S.D.) by the treatment of $E_{\rm T}$ (dye) values for compounds **9b**, **10b**, and **13b** in 29 solvents and **14b** in 27 solvents.

Dye	constant	a	b	с	d	р	r	S.D.
9b	71.20±3.72	13.73 ± 1.30	-3.21±1.24	-14.02 ± 6.06	-2.80 ± 2.34	1.22 ± 0.22	0.93	1.63
10b	61.79±3.67	17.23±1.29	-1.62±1.23	-11.12±5.97	-5.62±2.31	0.78±0.22	0.95	1.60
13b	63.74±4.31	15.82±1.51	-3.28±1.44	-14.19±7.00	-4.36±2.71	1.31±0.25	0.93	1.88
14b	55.62±2.68	15.83±0.89	-4.93±0.86	-7.23±3.41	-8.89±1.73	0.58±0.23	0.94	1.11

Preferential solvation in aqueous alcohols

The solvatochromic behavior of dyes **3b-14b** in binary mixtures of water and an alcohol was investigated in the next part of this study, in an attempt to relate the PS of the dye in these mixtures to the solute structure and the alcoholic co-solvent.

(2)

Following a common practice, the experimental data were fitted to **Eq. (3)**, which relates the transition energy $E_{\rm T}$ of a dye in a binary mixture of solvents 1 and 2 to the mole fraction of solvent 2.

$$E_T = \frac{E_{T_1}(1-X_2)^2 + E_{T_2}f_{2/1}X_2^2 + E_{T_12}f_{\frac{12}{1}}(1-X_2)X_2}{(1-X_2)^2 + f_{2/1}X_2^2 + f_{12/1}(1-X_2)X_2}$$

(3)

Eq. (3) was derived from a model based on an equilibrium between the dye, solvated by solvent 1, with the value E_{T1} , and by solvent 2, with the value E_{T2} . In addition, a third solvated species is introduced, giving rise to a transition energy value E_{T12} , which corresponds to the dye solvated by a 1:1 complex of the two solvents. The PS by solvent 2 is expressed by factors $f_{2/1}$ and $f_{12/1}$, which are ratios between the mole fractions of solvent 2 and of complex 12 in the bulk mixture and in the cybotactic region of the dye [34, 35].

Plots of the $E_{\rm T}$ values in binary mixtures have been traditionally fitted to Eq. (3) (or related equations [36, 37], with considerable success [11, 21, 34-50]. This was also the case of our study, as shown by the very good correlation ($r^2 > 0.98$) obtained between the experimental and the calculated data. Values for the fitting parameters $E_{\rm T1}$, $E_{\rm T2}$, $E_{\rm T12}$, $f_{2/1}$, and $f_{12/1}$ are listed in **Table 4**.

Table 4

Calculated parameters for dyes 3b-14b in binary mixtures of water with an alcoholic co-solvent.

Dye	Co-solvent	$E_{\rm T}({\rm dye})_1$	$E_{\rm T}({\rm dye})_2$	$E_{\mathrm{T}}(\mathrm{dye})_{12}$	$f_{2/1}$	$f_{12/1}$	r^2	SD
3b	Methanol	66.84	66.78	62.39	0.61	0.76	0.9916	4.24×10 ⁻²
3b	Ethanol	62.52	66.62	67.76	0.01	0.06	0.9993	3.46×10 ⁻²
3b	Propan-1-ol	61.71	67.03	62.83	0.12	2.91	0.9806	1.54×10 ⁻¹
3b	Propan-2-ol	58.87	67.04	62.35	0.23	4.11	0.9898	1.69×10 ⁻¹
4 b	Ethane-1,2-diol	58.04	61.70	62.10	0.01	0.10	0.9978	5.34×10 ⁻²
5b	Ethane-1,2-diol	65.35	67.67	66.42	0.04	0.23	0.9969	3.95×10 ⁻²
6b	Ethane-1,2-diol	59.50	62.82	59.53	1.22	2.87	0.9972	5.35×10 ⁻²
7b	Ethane-1,2-diol	65.48	67.86	67.08	0.06	0.21	0.9983	2.92×10 ⁻²
8b	Ethane-1,2-diol	60.14	63.28	62.53	0.03	0.43	0.9955	5.83×10 ⁻²
9b	Ethane-1,2-diol	66.79	68.80	66.65	9.82	58.0	0.9958	3.75×10 ⁻²
9b	Methanol	67.65	68.81	66.23	0.21	0.54	0.9939	3.61×10 ⁻²
10b	Ethane-1,2-diol	61.45	64.19	61.80	0.43	2.00	0.9977	3.67×10 ⁻²
11b	Ethane-1,2-diol	61.33	63.15	60.79	0.53	2.05	0.9960	4.23×10 ⁻²
12b	Ethane-1,2-diol	53.33	57.44	54.02	0.15	0.41	0.9977	6.14×10 ⁻²
13b	Ethane-1,2-diol	59.36	62.30	62.20	0.01	0.19	0.9967	5.08×10 ⁻²
14b	Ethane-1,2-diol	51.59	56.36	53.71	0.09	0.21	0.9984	6.00×10 ⁻²

The good quality of the fitting curves to the experimental data can be seen in Figs. 4-6.

((Fig. 4 here)) ((Fig. 5 here)) ((Fig. 6 here))

Fig. 4 (a) shows a sigmoid behavior for dye **3b** in ethane-1,2-diol-water mixtures, the dye being preferentially solvated by water in the alcohol-rich region (X_2 between 0-0.2). A strong synergy occurs for all other mixture compositions (X_2 between 0.2-1.0), with PS of the dye molecules occurring via the less polar moiety of the water-alcohol aggregates in these binary mixtures. **Fig. 4 (b)** shows a strong downward synergy for dye **3b** in methanol-water

mixtures. A weak synergy was verified for dyes **4b**, **9b**, and **11b**, with PS occurring via the less polar moiety of the alcohol-water aggregates. For all other water-alcohol mixtures (**Figs. 4**-**6**), the polynitrophenolates **3b-14b** were preferentially solvated by the alcohol.

In spite of these good fits, the values of $f_{2/1}$ and $f_{12/1}$ did not follow any trend when the solvent mixtures were varied in a systematic way, from the most polar and strongest HBD alcohol (ethane-1,2-diol) to the least polar and weakest HBD alcohol in the series (propan-2-ol). The same erratic behavior was verified when mononitrated dyes **3b**, **5b**, **7b**, **9b**, **11b**, and **13b** were compared with their dinitrated analogs (**4b**, **6b**, **8b**, **10b**, **12b**, and **14b**). This rather disappointing observation cast doubt on the meaning of these parameters and on the existence of the postulated solvent complexes, as depicting real physical-chemical entities, or being ultimately mathematical artifacts.

This led us to look for another tool to analyze our data on the PS of phenolate dyes in aqueous alcohols. We started from the usual plots of the variation in the transition energy of the dye ($\Delta E_{\rm T} = E_{\rm T}^{\rm B} - E_{\rm T}^{\rm A}$) as a function of the mole fraction of co-solvent B, $X({\rm B})$, where the superscripts refer to the $E_{\rm T}$ values in pure solvents A or B. **Fig. 7** illustrates five model situations for deviations from an ideal behavior. Plot (**a**) corresponds to a negative deviation from ideality, corresponding to PS by solvent A, while plot (**b**) shows a positive deviation corresponding to PS by solvent B. Plot (**c**) corresponds to a negative deviation where a synergistic effect is verified, due to an HBA/HBD interaction between the two solvents, leading to $E_{\rm T}$ values smaller than $E_{\rm T}^{\rm A}$. Plot (**d**) corresponds to a positive deviation with a synergistic effect of both solvents, with $E_{\rm T}$ values larger than $E_{\rm T}^{\rm B}$. The occurrence of positive and negative deviations for the same system, as the binary composition is varied, produces the situation represented in plot (**e**) [38, 42, 43].

((Fig. 7 here))

In order to quantify these deviations, a PS (or non-ideality) index (PSI) can be devised, based on the ratio between the areas S_1 and S_2 of the model graphs in Fig. 7 (a) and 7 (b). S_1 is the area between points A and B, limited by the ideal straight line and the real experimental curve, and S₂ is the area of the triangle ABC. The PSI value is then defined as the ratio S_1/S_2 . In an arbitrary way, the PSI values receive a positive signal in the case of graphs with positive deviations and negative signal when negative deviations occur. Absolute PSI values vary between 0 and 1, where 0 characterizes an ideal behavior and 1 corresponds to maximum non-ideality. Exceptionally, absolute values of PSI greater than 1 may be obtained from plots such as that of Fig. 4 (b), denoting an extreme non-ideal behavior. For such extreme cases, the PS index is no longer useful, and a quantification of the system nonideality employing this parameter has little meaning. The same limitation holds for graphs with a sigmoid shape, as in Fig. 7 (e). In this case, two PSI values could be calculated independently, S_1/S_2 and S_1/S_2 , corresponding, respectively, to the positive and negative portions of the graph. However, for comparison purposes with graphs 7a and 7b, a sum of these obtained PSI values has again little meaning.

Thus, the above treatment should be applied to PS graphs such as those of **Figs. 7a** and **7b**, losing its meaning with extreme situations such as those of **Fig. 4B**, or with sigmoidal plots like graph **7e**. This limitation should not deter us from employing this index as a quantitative measure of non-ideality in related systems, allowing a systematic comparison to be made for related probes and analogous solvent mixtures, as was the case for most of the PS curves of **Figs. 4-6**. In fact, as shown below, PSI values for a series of related mixtures

can reveal trends that shed light on the solute-solvent interactions in solution, contrary to the fitting parameters $f_{2/1}$ and $f_{12/1}$ of **Table 4**.

Table 5 lists the PSI values for all systems whose plots were fitted by Eq. (3), employing the parameters listed in **Table 4**, with the exception of dye **3b** in aqueous 1,2ethanediol (entry 10) or methanol (entry 11), for which, as discussed above, the PSI had little meaning. For all water-alcohol mixtures, negative PSI values were obtained, indicating a PS by the alcohol. Unlike the fitting parameters $f_{2/1}$ and $f_{12/1}$ of **Table 4**, whose values do not seem to follow any trend, there is a clear correlation between the PSI values of Table 5 and the nature of the alcohol, expressed by its normalized $E_{\rm T}^{\rm N}$ polarity value [1, 6, 7]. For dye **3b**, the PSI values increase with the polarity of the alcoholic co-solvent. Non-ideality, expressed by the PSI value, is greatest in mixtures where the water ($E_T^N = 1$) and the alcohol have similar polarities, decreasing as the alcohol becomes less polar than water (entries 10-14). This trend is also verified for phenolate dyes 1 and 2, for which data are available in the literature [34, 42]. Plots of the variations of their transition energies ($\Delta E_{\rm T}$) as a function of the mole percentage of water in the alcoholic mixtures $[X(H_2O)]$ (graphs in the Supplementary Material) yielded the PSI values shown in Table 5, that exhibited the same trend observed for the phenolate 3b (see entries 1-5 for compound 1, and 6-9 for compound 2).

A second trend is found in **Table 5**, on comparing the mononitrated derivatives **3b**, **5b**, **7b**, **9b**, **11b**, and **13b** with their dinitrated analogs **4b**, **6b**, **8b**, **10b**, **12b**, and **14b**. In general, for each pair, the absolute PSI value for the dinitrated compound is smaller, compared with its mononitrated analog.

Table 5

Entry	Probe	Alcoholic	$E_{\rm T}^{\rm N}$ value of	PSI
		co-solvent	the alcohol ^a	
1	1 ^b	Ethane-1,2-diol	0.790	-0.400
2	1 ^b	Methanol	0.762	-0.349
3	1 ^b	Ethanol	0.654	-0.140
4	1 ^b	Propan-1-ol	0.617	-0.184
5	1 ^b	Propan-2-ol	0.546	-0.135
6	2 ^c	Methanol	0.762	-0.342
7	2 ^c	Ethanol	0.654	-0.285
8	2 ^c	Propan-2-ol	0.546	-0.216
9	2 ^c	2-Methylpropan-2-ol	0.389	-0.114
10	3b	Ethane-1,2-diol	0.790	-
11	3b	Methanol	0.762	-
12	3b	Ethanol	0.654	-0.621
13	3b	Propan-1-ol	0.617	-0.570
14	3b	Propan-2-ol	0.546	-0.231
15	4b	Ethane-1,2-diol	0.790	-0.575
16	5b	Ethane-1,2-diol	0.790	-0.530
17	6b	Ethane-1,2-diol	0.790	-0.354
18	7b	Ethane-1,2-diol	0.790	-0.542
19	8b	Ethane-1,2-diol	0.790	-0.363
20	9b	Ethane-1,2-diol	0.790	-0.558
21	10b	Ethane-1,2-diol	0.790	-0.426
22	11b	Ethane-1,2-diol	0.790	-0.611
23	12b	Ethane-1,2-diol	0.790	-0.454
24	13b	Ethane-1,2-diol	0.790	-0.465
25	14b	Ethane-1,2-diol	0.790	-0.459

Values for the preferential solvation index (PSI) for compounds 1, 2, and 3b-14b in various binary mixtures of water with alcohols.

^aData from the literature [1, 6].

^bData from the literature [34].

^c Data from the literature [42].

These trends can be explained by an analysis of the equilibrium depicted in **Eq. (4)**, corresponding to the replacement of one molecule of alcohol by one of water in the solvation layer of the dye.

As more water is added to the alcoholic solution of the dye, this gradual replacement is responsible for the change observed in the $E_{\rm T}$ value for the solution. This replacement is dependent on two factors: the intrinsic discrimination of the dye between the two hydroxylic solvents, and the concentration of hydroxylic solvents and, in particular, of free water molecules, close to the cybotactic region of the dye.

The former factor is responsible for the greater ideality (lower PSI values) of the plots of the dinitrated phenolates **4b**, **6b**, **8b**, **10b**, **12b**, and **14b** when compared with their mononitrated and more strongly basic analogs **3b**, **5b**, **7b**, **9b**, **11b**, and **13b**. The more strongly basic mononitrated phenolates should be less selective toward hydroxylic solvents with different hydrogen-bonding strength. For them, therefore, it is the second factor, the relative concentrations of the two hydroxylic solvents close to the cybotactic region, which becomes the major factor to determine the equilibrium (**Eq. 4**).

The concentration of free water molecules close to the solvation layer of the phenolate dye is dependent on their affinity for the bulk alcoholic molecules. Greater affinity, through stronger hydrogen-bonding with a hydroxylic solvent of similar polarity, reduces the concentration of free water molecules close to the dye. A more polar alcohol, like ethane-1,2-diol, is a more effective scavenger of water molecules from the cybotactic region of the dye than a less polar and less acidic solvent like propan-2-ol. As a result, the addition of water to an alcoholic solution of the dye leads to a less effective replacement of the solvating alcohol molecules, according to Eq. (4), in the case of a polar solvent like ethane-1,2-diol,

compared with the less polar propan-2-ol. This results in a less ideal behavior in the plots of $E_{\rm T}$ as a function of $X({\rm H_2O})$ for the more acidic alcohols.

The two observed trends may thus be rationalized by the same argument. The ability of the bulk alcoholic medium to scavenge added water molecules from the cybotactic region of the dye increases with the alcohol acidity. As a result, the dye solvation layer requires relatively higher concentrations of added water to change its composition when the dye is less selective, or the alcohol is more acidic. Such a lag between the compositions of the cybotactic region and of the bulk solution is therefore responsible for the larger absolute PSI values (and greater non-ideality) observed for aqueous mixtures with more acidic alcohols, or with more basic dyes.

4. Conclusions

The PS of a series of solvatochromic 4-oxy-4'-nitro- and 4-oxy-2',4'-dinitrostilbenes **3b-14b** was studied in aqueous alcoholic solutions. Plots of the solvatochromic transition energy of the dyes (E_T) as a function of the mole percentage of water in the mixtures [X(H₂O)] yielded curves that were fitted to **Eq. 3**. This widely employed equation [21, 34-50] has been derived from the assumption of a differential solvation of the dye by the pure solvents (1 and 2) and by a 1:1 binary solvent complex (12), employing fitting factors $f_{1/2}$ and $f_{12/1}$ to express differences between the composition of the bulk solution and that of the cybotactic region of the dye [34, 35]. In spite of the good quality of the fittings, the obtained $f_{1/2}$ and $f_{12/1}$ parameters yielded values that did not correlate with any solvent property, such as the alcohol polarity or its HBD strength.

In the search of a more meaningful index to compare the curves obtained and different binary mixtures, a PS index (PSI) was proposed, as a measure of the ideality of the plots of $\Delta E_{\rm T}$ as a function of $X({\rm H_2O})$. The PSI value normally varies between 0 (ideal behavior) and 1 and can be used to compare the behavior of different analogous binary mixtures and/or dyes. The PSI value obtained correlated well with the polarity (HBD strength) of the alcoholic co-solvent and also with the basicity of the phenolate dyes. The trends observed were confirmed with data from the literature for two other phenolate dyes, Reichardt's betaine 1 and Brooker's merocyanine 2, in aqueous alcoholic mixtures. The good correlations suggest that the PSI index is potentially a useful tool for analyzing and comparing the PS of other solutes in binary solvent mixtures, without resorting to models based on entities with arguable physical reality.

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Scheme 1. Molecular structures of solvatochromic dyes 1 and 2.





	3a, b	4a, b	5a, b	6a, b	7a, b	8a, b	9a, b	10a, b	11a, b	12a, b	13a, b	14a, b
R^1	н	NO ₂	Н	NO ₂	Н	NO ₂						
R ²	н	н	Br	Br	CI	Cl	F	F	CH_3	CH_3	OCH ₃	OCH ₃

Scheme 2. Molecular structures of solvatochromic dyes 3b-14b.



Scheme 3. Synthetic route for the preparation of the compounds.

Figure Captions

Fig. 1. (A) Solutions and (B) respective UV-vis spectra for dye 10b in water (a), propan-1ol (b), acetonitrile (c), and *N*,*N*-dimethylformamide (d).

Fig. 2. E_T (14b) values for 27 solvents as a function of Reichardt's E_T (30) parameter.

Fig. 3. Linear plot of $E_{\rm T}(13b)$ as a function of $E_{\rm T}(3b)$.

Fig. 4. Influence of water on the E_T value for **3b** in aqueous mixtures with ethane-1,2-diol (**A**), methanol (**B**), ethanol (**C**), propan-1-ol (**D**), and propan-2-ol (**E**). (—) Theoretical linear dependence for no PS; (—) curve fitted with **Eq. 2**.

Fig. 5. Influence of water on the $E_T(dye)$ value for 3b (A), 5b (B), 7b (C), 9b (D), 11b (E), and 13b (F) in ethane-1,2-diol/water mixtures. (—) Theoretical linear dependence for no PS; (—) curve fitted with Eq. 2.

Fig. 6. Influence of water on the $E_T(dye)$ value for 4b (A), 6b (B), 8b (C), 10b (D), 12b (E), and 14b (F) in ethane-1,2-diol/water mixtures. (—) Theoretical linear dependence for no PS; (—) curve fitted with Eq. 2.

Fig. 7. Model graphs illustrating deviations from an ideal behavior due to PS of the dye by solvent A (a) or by solvent B (b). Graph (c) shows a synergistic effect of the binary mixture, with a negative deviation from ideality, with $E_T < E_T^A$. Graph (d) shows a positive deviation with a synergistic effect of both solvents, with $E_T > E_T^B$. Graph (e) shows positive and negative deviations for the same system, as the binary composition is varied.

(A) **(B)** 1.8 (a) 1.6 (a) (b) (c) (d) 1.4 (d) 1.2 (c) absorbance (b) 1.0 0.8 0.6 0.4 0.2 0.0 600 700 400 500 λ/nm Fig. 1



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Fig. 4



Fig. 5



Fig. 6



Fig. 7

Highlights

The solvatochromism of four 4-(nitrostyryl)phenolate dyes in 27-29 pure solvents.

A reversal in their solvatochromism.

The solvatochromic behavior of twelve 4-(nitrostyryl)phenolate dyes in wateralcohol mixtures.

A non-ideality preferential solvation (PS) index (PSI) to quantify the PS verified in the mixtures.

PSI values correlate well with the hydrogen-bond donating ability of the alcohol and also with the basicity of the dye.

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