

Solvatochromic effects on the fluorescence and triplet–triplet absorption of phenosafranine in protic and aprotic solvents

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Received 4 August 2005; received in revised form 13 September 2005; accepted 10 October 2005

Available online 15 November 2005

Abstract

Photophysical and spectroscopic properties of phenosafranine were investigated in 21 solvents, including pure aprotic solvents and pure and binary protic solvent mixtures. It was found that these properties are highly dependent of the nature of the medium in protic solvents. Characteristic parameters such as the Stokes' shift, the fluorescence quantum yield and lifetime and the T–T absorption maxima frequencies showed a very clean solvent dependence, with a strong incidence of the specific interactions of phenosafranine with solvent molecules, most likely through hydrogen bonding. On the other hand, in aprotic solvents these parameters are practically insensitive to changes in solvent properties. The experimental results in protic media suggest an increase of the dipole moment of the dye molecule as a consequence of the $S_0 \rightarrow S_1$ transition, while a decrease in the dipole moment come along with the $T_1 \rightarrow T_n$ transition. In selected protic solvents, the photophysical kinetic parameters were obtained from fluorescence quantum yield and lifetime determinations and intersystem-crossing quantum yields. Their solvent dependence is discussed.

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Keywords: Solvatochromic effects; Phenosafranine; Fluorescence; Triplet-state; Aprotic solvents; HBD solvents

1. Introduction

In recent years, the synthetic cationic dye phenosafranine, 3,7-diamino-5-phenylphenazinium chloride (PS) (Scheme 1) has received considerable attention in virtue of its use in diverse areas of research. It has been extensively employed as a sensitizer in energy and electron transfer reactions in homogeneous media [1–5], in semiconductors [6,7] and in polymeric media [8]. The dye was also employed as a probe in micellar systems [9,10], covalently bounded to macromolecules [11] and incorporated into polymer films [12,13] and its photostability in polymer-coated semiconductors was investigated [14].

In spite of the large amount of research about the uses of this dye, basic information on the excited-state properties that is required to understand its photochemical behavior is somehow incomplete. To the best of our knowledge, no detailed studies of the solvent effect on the photophysical properties of PS are reported in literature. Here, we present results concerning to the

influence of protic and aprotic solvents on the spectroscopic and kinetic properties of the singlet and triplet excited-states of this dye.

2. Experimental

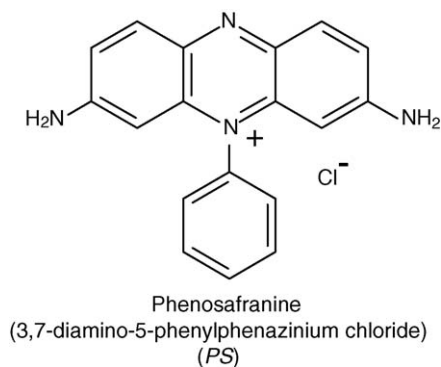
2.1. Materials

Phenosafranine (Aldrich) was used without further refinement. All the solvents employed were HPLC grade. EtOH was distilled before use. Water was purified through a Millipore Milli-Q system. The other solvents were used as such. As a purity criteria the absence of spurious emission was checked in all solvents. Solvent mixtures and the corresponding solutions were prepared by carefully mixing the components in a dry box so as to minimize contamination by moisture.

2.2. Methods

UV–vis absorption spectra were obtained using a Hewlett–Packard 8453 diode array spectrophotometer. The steady-state

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Scheme 1.

fluorescence measurements were made using a Fluoromax Spex Spectrofluorometer. Freshly prepared solutions were used for each measurement and the concentrations were chosen to give absorbances less than 0.1 to avoid distortion of the spectra due to reabsorption of the fluorescence light. No changes in the shape of the absorption and fluorescence spectrum were observed in the concentration range of 5×10^{-6} to 5×10^{-5} mol/l. Confirming that in this concentration range the dye do not present aggregation [15]. Fluorescence quantum yields were determined by integration of the corrected emission spectrum using cresyl violet in methanol as a standard with a quantum yield of 0.54 ± 0.03 [16].

Fluorescence lifetime measurements were performed with an Edinburgh Instruments OB 900 time-correlated single-photon counting fluorometer. The excitation and emission wavelengths were selected near maximums of absorption and fluorescence bands in each solvent. In all cases, the fluorescence decay time could be fitted with a mono-exponential function, optimizing chi-square, residuals and standard deviation parameters. The lifetime values were independent of excitation and emission wavelengths.

Transient absorption measurements were made using laser-flash photolysis equipment. A Spectron SL400 Nd:YAG laser generating 532 nm laser pulses (~ 18 ns pulse width) was used for sample excitation. The laser beam was defocused in order to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The experiments were performed with rectangular cells with right-angle geometry. The detection system comprises a PTI monochromator coupled to a Hamamatsu R666 PM tube. The signals were initially captured by a HP54504 digitizing oscilloscope where they were averaged and then transferred to a computer for storage and analysis. Measurements were performed in samples subjected to continuous argon bubbling. All measurements were performed at 25 ± 0.5 °C.

Semi-empirical molecular orbital calculations (AM1) were carried out using CS Chem3D Pro software from Cambridge Soft Corporation.

Values of relative permittivities (ϵ_r), refraction index (n_D) and empirical parameter $E_T(30)$ of pure solvents and solvent mixtures were obtained from literature [17–20].

3. Results and discussion

3.1. Ground-state UV–vis absorption and fluorescence parameters

Absorption and fluorescence spectrum of PS are highly dependent on the polarity of the solvent in protic solvents. In Fig. 1, these spectra, measured in water and 2-propanol, are shown as an example. A blue shift in the ground-state absorption and a red shift in the emission band are clearly distinguished as the solvent polarity increases. However, a polarity trend is not observed for absorption and fluorescence spectrum in aprotic solvents.

The absorption and fluorescence data for PS are collected in Table 1. In protic solvents, the augment of the Stokes' shift ($\Delta\bar{\nu} = \bar{\nu}_A - \bar{\nu}_F$), where $\bar{\nu}_A$ and $\bar{\nu}_F$ are the frequencies of the absorption and fluorescence maxima, respectively, with the solvent polarity is an understandable signal of a more polar excited-state.

In order to determine the change in dipole moment for the $S_0 \rightarrow S_1$ transition in the PS molecule, evaluation of the data was attempted using the solvatochromic method (Eq. (1)) proposed by Ravi et al. [21] based on the normalized empirical microscopic solvent polarity parameter E_T^N . This parameter also considers interactions of specific character in addition to the non-specific solvent effects [22]. E_T^N is defined by extreme reference solvents water and tetramethyl silane (TMS) as follows: $E_T^N = (E_T(30)_S - E_T(30)_{TMS})(E_T(30)_W - E_T(30)_{TMS})^{-1}$, where $E_T(30)$ is an empirical solvent polarity parameter based on the spectral shifts of *N*-phenolbetaine dye [23] and $E_T(30)_S$, $E_T(30)_W$ and $E_T(30)_{TMS}$ are the values of this parameter for the sample, water and TMS, respectively:

$$\bar{\nu}_A - \bar{\nu}_F = 11307.6 \left[\left(\frac{(\mu_E - \mu_G)_{PS}}{(\mu_E - \mu_G)_B} \right)^2 \left(\frac{a_B}{a_{PS}} \right)^3 \right] E_T^N + C \quad (1)$$

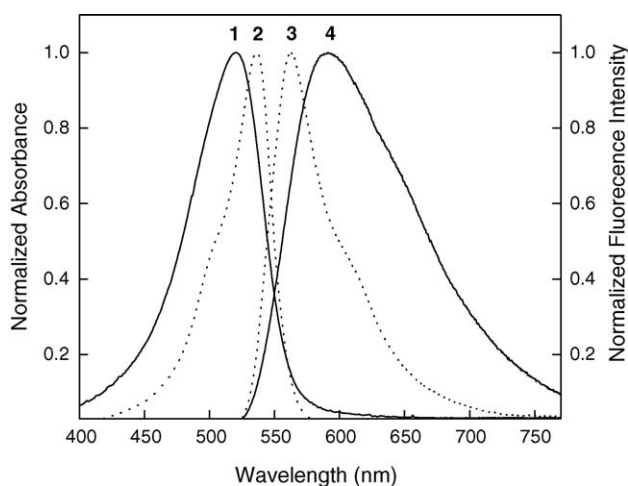


Fig. 1. Fluorescence and ground-state absorption spectra of PS in water and 2-propanol: (1) absorption in water, (2) absorption in 2-propanol, (3) emission in 2-propanol and (4) emission in water.

Table 1
Absorption and fluorescence spectral properties and fluorescence lifetimes of PS in protic and aprotic solvents

Solvent	$E_T(30)$ (kcal mol ⁻¹)	$\bar{\nu}_A$ (cm ⁻¹)	$\bar{\nu}_F$ (cm ⁻¹)	$\bar{\nu}_A - \bar{\nu}_F$ (cm ⁻¹)	τ_F (ns) ^a
1,4-Dioxane	36.0	18939	17794	1145	2.14
THF	37.4	18762	17528	1234	2.22
Ethyl acetate	38.1	18904	17483	1421	1.70
Dichloromethane	40.7	19493	18536	957	2.36
1,2-Dichloroethane	41.3	19399	18198	1201	2.22
Acetone	42.2	19084	17953	1131	3.11
Butyronitrile	42.5	19231	18083	1148	3.27
Propionitrile	43.6	19286	18018	1268	3.27
<i>N,N</i> -Dimethylformamide	43.8	18762	17746	1016	2.73
DMSO	45.1	18587	17652	935	2.36
Acetonitrile	45.6	19342	17905	1437	3.56
2-Propanol	49.2	18657	17781	876	2.89
1-Butanol	50.2	18587	17624	963	2.78
1-Propanol	50.7	18657	17640	1017	2.75
Ethanol (EtOH)	51.6	18797	17753	1044	2.60
EtOH/water (60.14%, w/w)	54.3	18833	17605	1228	2.01
Methanol	55.4	18975	17637	1338	2.10
EtOH/water (19.5%, w/w)	58.9	18904	17244	1660	1.29
EtOH/water (12.0%, w/w)	61.2	19084	17115	1969	1.07
EtOH/water (9.64%, w/w)	61.8	19011	17085	1926	0.99
Water	63.1	19194	16921	2274	0.87

^a Estimated error $\pm 2\%$ or ± 0.02 ns, whichever the greater.

In Eq. (1), μ_E and μ_G are the dipole moments of the excited singlet- and ground-state, respectively, a denotes the radius of the cavity in which the fluorophore resides, meanwhile the subscripts PS and B correspond to the phenosafranine and pyridinium *N*-phenolate betaine dyes, respectively.

Fig. 2 shows a representation of $\Delta\bar{\nu}$ versus the solvent parameter E_T^N for the hydroxylic solvents. Also in Fig. 2, a representation of $\Delta\bar{\nu}$ versus the Bakhshiev's solvent parameter, $f(\epsilon_r, n)$ (Eq. (2)) [24] is presented. Eq. (2) is based on a dielectric continuum description of the solvent:

$$f(\epsilon_r, n) = \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{2n^2 + 1}{n^2 + 2} \quad (2)$$

where ϵ_r and n are the relative permittivity and the refractive index of the solvent, respectively.

A good linear dependence of $\Delta\bar{\nu}$ versus E_T^N was obtained in the entire series of protic solvents, in contrast to the one observed by a $\Delta\bar{\nu}$ versus $f(\epsilon_r, n)$ representation. These results are a clear evidence of the existence of specific solute/solvent interactions, in particular the good linear correlation obtained with the solvent parameter $E_T(30)$ implies that hydrogen bonding might have a considerable responsibility in the stabilization of the PS cation by solvation with protic solvents.

From the slope in Fig. 2(A), the excited singlet-state dipole moment (μ_E) of PS can be estimated in the following way: semi-empirical molecular modeling AM1 was employed in structure geometry optimization and calculations, giving values of $a_{PS} = 5.7 \text{ \AA}$ and $\mu_G = 1.28 \text{ D}$ for the solute ground-state cavity radius and dipole moment, respectively. The corresponding parameters for the reference betaine ($a_B = 6.2 \text{ \AA}$ and $\Delta\mu = 9.0 \text{ D}$) were obtained from the literature [21]. In this way, a value of 5.47 D for μ_E of PS was determined.

The influence of the solvent on the fluorescence lifetime (τ_F) was investigated in protic and aprotic solvents (see Table 1). Also, here a clear distinction between the two solvent groups can be observed. In hydroxylic media, a noticeable decrease

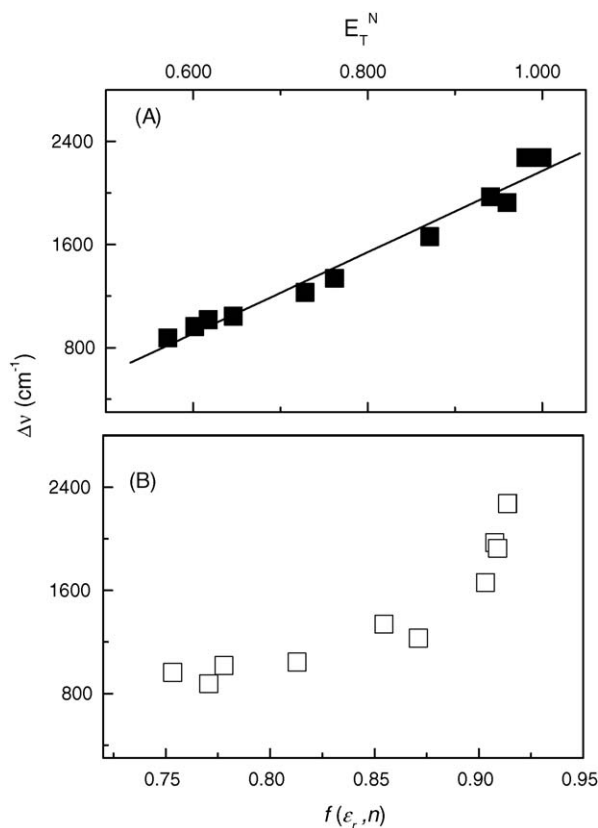


Fig. 2. Plot of the Stokes' shift vs. (A) the normalized solvent polarity parameter, E_T^N , (■) and (B) the Bakhshiev's solvent parameter, $f(\epsilon_r, n)$, (□).

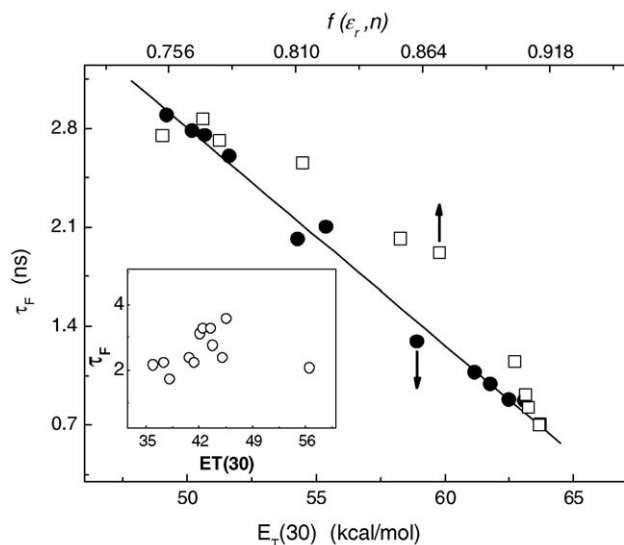


Fig. 3. Fluorescence lifetime vs. the Bakhshiev's solvent parameter, $f(\epsilon_r, n)$, (□) and $E_T(30)$ solvent polarity parameter (●) in protic solvents. Inset: Fluorescence lifetime vs. $E_T(30)$ solvent polarity parameter in aprotic solvents.

of τ_F with an increase of the $f(\epsilon_r, n)$ is observed (Fig. 3). In this figure is also shown a very good linear dependence of the fluorescence lifetime with the $E_T(30)$ parameter. On the other hand, the values in aprotic solvents do not follow any tendency (inset, Fig. 3). These results represent an additional proof of the significance of the hydrogen bond specific interactions on photophysical behavior of PS.

3.2. Triplet-state properties

Contrasting with the excited singlet-state only comparatively few systematic studies of solvent effects on the triplet–triplet absorption process on organic molecules have been reported [25–30].

The transient absorption spectrum of PS has been previously reported [1,4,31], showing absorptions from the UV to near IR in the 250–900 nm range. The difference spectrum obtained by laser flash photolysis can be divided in three spectral regions, two with positive bands at each side of the negative band corresponding to the bleaching in the region around the maximum of the ground-state absorption (near 500 nm). The region corresponding to the more energetic transitions (250–450 nm) can be

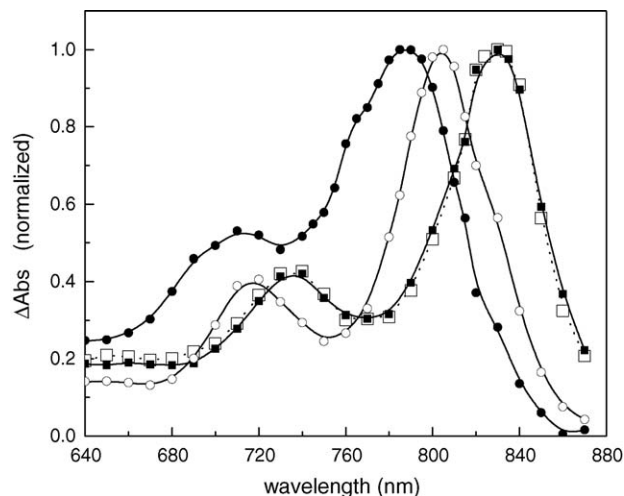


Fig. 4. Triplet–triplet absorption spectra of PS in water (●), 2-propanol (○), acetonitrile (□) and acetone (■).

assigned to the combined absorption of triplet-state and the semi-oxidized and semi-reduced forms of the dye, and on the other side (600–900 nm) the absorption bands are assigned exclusively to the triplet–triplet absorption ($T_1 \rightarrow T_n$) [5]. These latter bands present notable changes with the solvent nature in protic media, while they are almost identical in the aprotic solvents employed (acetonitrile, dimethylformamide, acetone and THF).

In Fig. 4 are presented, as examples, the $T_1 \rightarrow T_n$ absorption spectra of PS in four solvents (two protics and two aprotics). A clear bathochromic shift is observed when the solvent polarity increase in the protic solvents. The T–T absorption frequency ($\bar{\nu}_T$) for the main band of PS in protic solvents are collected in Table 2. It can also be seen in Fig. 4 that the T–T transition is at lower energies in aprotic media.

The solvent dependence of $\bar{\nu}_T$ in protic media cannot be reasonably fitted by a polarity parameter based only on a dielectric continuum model. However, a good linear correlation is obtained with the $E_T(30)$ parameter (see Fig. 5). These results also imply that the $T_1 \rightarrow T_n$ transitions of PS are strongly influenced by specific solute–solvent interactions.

However, at the contrary of the conclusion for the $S_0 \rightarrow S_1$ transition, the blue shift of the $T_1 \rightarrow T_n$ band with increasing polarity observed in protic solvents can be rationalized by a decrease in the dipole moment of the triplet-state upon excitation [25,26,30].

Table 2
Spectral and kinetic properties of PS in protic solvents

Solvent	$E_T(30)$ (kcal mol ⁻¹)	ϵ_G (l mol ⁻¹ cm ⁻¹)	$\bar{\nu}_T$ (cm ⁻¹)	ϵ_T (l mol ⁻¹ cm ⁻¹)	Φ_T	Φ_F	τ_F (ns)	k_F (10 ⁻⁸ s ⁻¹)	k_{isc} (10 ⁻⁸ s ⁻¹)	k_d (10 ⁻⁸ s ⁻¹)
2-Propanol	49.2	38600	12420	19300	0.42	0.40	2.89	1.38	1.46	0.61
Ethanol	51.6	45000	12460	24400	0.29	0.28	2.60	1.08	1.10	1.17
Methanol	55.4	48000	12500	21000	0.28	0.20	2.10	0.95	1.33	2.48
EtOH/water (19.5%, w/w)	58.9	34800	12579	20900	0.12	0.085	1.29	0.66	0.89	6.21
Water	63.1	30000	12700	15800	0.19	0.04	0.87	0.46	2.17	8.86

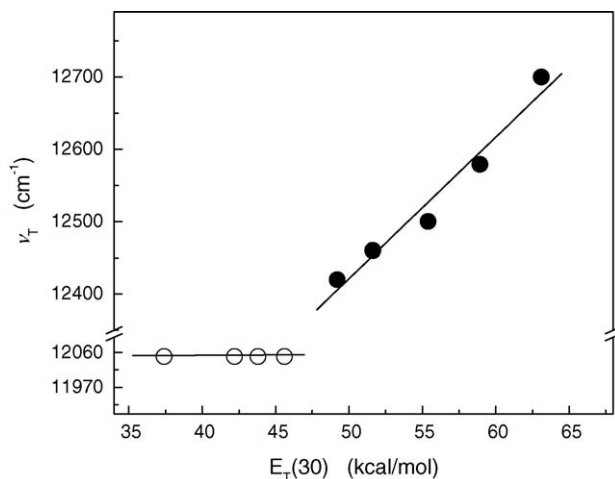


Fig. 5. Dependence of the triplet-triplet absorption maximum frequency with the $E_T(30)$ solvent polarity parameter in aprotic (○) and protic (●) solvents.

3.3. Deactivation rate constants

With the aim to elucidate the solvent influence on the singlet excited-state decay pathways of PS, the fluorescence (Φ_F) and intersystem-crossing (Φ_T) quantum yields were measured in various protic solvents.

The experimental fluorescence quantum yields showed a well-defined diminishing tendency with the augment of solvent polarity (Table 2).

In order to obtain the triplet quantum yields Φ_T , the relative actinometry method [32] was employed. In this method, the product of the triplet quantum yield and its absorption coefficient at a working analysis wavelength, $\Phi_T \varepsilon_T$, was determined. The triplet yield of zinc tetraphenyl porphyrin (ZnTPP) in benzene was used as reference.

The product $\Phi_T \varepsilon_T$ for the dye was obtained from Eq. (3):

$$(\Phi_T \varepsilon_T)_D = \frac{\text{slope}_D}{\text{slope}_{\text{ZnTPP}}} (\Phi_T \varepsilon_T)_{\text{ZnTPP}} \quad (3)$$

where slope_D and $\text{slope}_{\text{ZnTPP}}$ are the initial slopes of the plots of T–T absorption versus laser energy for the dye and the reference, respectively. Values of $7.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.83 were used for ε_T and Φ_T of ZnTPP, respectively. The initial absorbance change extrapolated at zero laser pulse energy was measured at 470 nm for ZnTPP triplet and at the wavelengths of maximum absorbance for the PS triplet with solutions of matched absorbance at 532 nm.

In order to determine Φ_T by means of Eq. (3) the absorption coefficients of the triplet dye in all solvents are necessary. They were determined by the ground-state depletion (GSD) method [32]. The transient negative difference absorbance at the maximum wavelength of the ground absorption, ΔA_G , was compared with the absorption at the maximum of the T–T spectrum of the dye, ΔA_T , both extrapolated to $t=0$, with the aid of Eq. (4):

$$\varepsilon_T = \left(\frac{\Delta A_T}{\Delta A_G} \right) \varepsilon_G \quad (4)$$

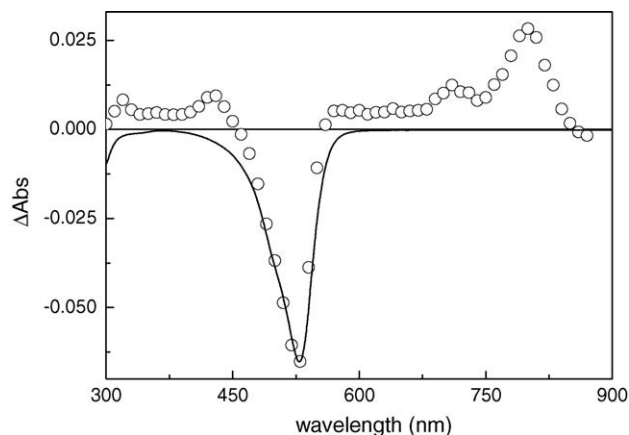


Fig. 6. Transient absorption spectrum extrapolated at zero time (○) and normalized ground-state absorption spectrum (—) of PS in methanol.

In Eq. (4), ε_T and ε_G are the molar absorption coefficients of the triplet- and ground-state, respectively, at the wavelengths of maximum absorbance.

As an example, the transient absorption spectrum and the normalized ground-state absorption spectrum of PS in methanol are shown in Fig. 6. It can be seen that the bleaching in the region around the maximum matches the ground-state absorption, such as is required for the appropriated usage of the GSD method. The triplet parameters are collected in Table 2.

The error of T–T absorption coefficient obtained by this procedure is difficult to assert, however, considering the assumptions involved and the experimental errors of the measured quantities the uncertainty in the values would be at least of 10%.

From the experimental Φ_F , τ_F and Φ_T values, the kinetic constants of the pathways involved in the deactivation of the singlet excited-state of the dye were calculated using Eqs. (5)–(7):

$$k_F = \frac{\Phi_F}{\tau_F} \quad (5)$$

$$k_{isc} = \frac{\Phi_T}{\tau_F} \quad (6)$$

$$k_d = \tau_F^{-1} - k_F - k_{isc} \quad (7)$$

where k_F , k_{isc} and k_d denote the fluorescence, intersystem-crossing ($S_1 \rightarrow T_1$) and non-radiative decay ($S_1 \rightarrow S_0$) rate constants, respectively. The calculated values for the kinetic constants are also given in Table 2. Fig. 7 shows a plot of the rate constants versus the solvent polarity parameter $E_T(30)$ (lines were added for visual guide).

It is clear from the results illustrated in Fig. 7 that the non-radiative decay rate constant controls the solvent dependence of the fluorescence lifetime; showing a significant augment (one order of magnitude) with the solvent polarity increase. In comparison, the others kinetic constants involved in the deactivation of the singlet excited-state present only minor changes with the solvent properties.

Table 3
Statistical treatment of the Kamlet–Abboud–Taft correlations

Solvatochromic property	<i>s</i>	<i>a</i>	<i>b</i>	Correlation coefficient	<i>a/s</i>	<i>a/b</i>
Stokes' shift ($\Delta\bar{\nu}$)	931	2078	443	0.960	2.23	4.69
T–T absorption maxima frequency ($\bar{\nu}_T$)	257	275	63	0.951	1.07	4.37

The *s*, *a* and *b* values of pure solvents were obtained from ref. [19]. The corresponding values by binary hydro-alcoholic mixtures were obtained from ref. [34].

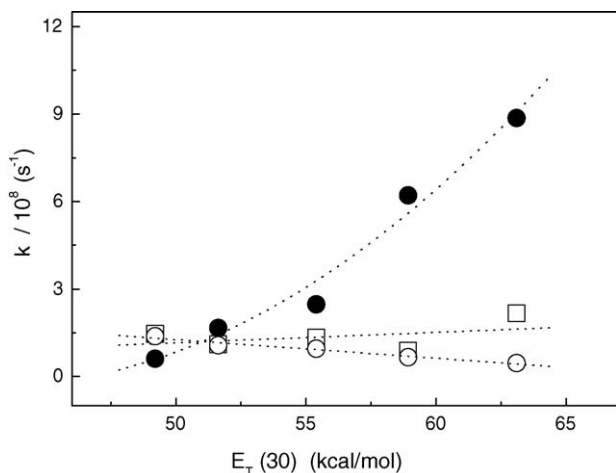


Fig. 7. Radiative and non-radiative rate constants vs. the $E_T(30)$ solvent polarity parameter in protic solvents. k_F (○), k_{isc} (□) and k_d (●). The lines in the figure are drawn as an illustrative aid for the tendency shown and do not represent the result of any model calculation.

3.4. Multiparametric analysis

In accordance with the results described above, the hydrogen bond interactions perform an unquestionable role in the photo-physics of PS. In order to estimate the individual contributions of the solvent polarity/polarizability, hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) abilities on the photophysical properties of PS, we applied the Kamlet–Abboud–Taft solvation relationship [33] (Eq. (8)) to the $\Delta\bar{\nu}$ and the $\bar{\nu}_T$ obtained in protic solvents:

$$(XYZ) = (XYZ)_0 + s\pi^* + a\alpha + b\beta \quad (8)$$

where (XYZ) is the solvatochromic property, π^* the solvent polarity–polarizability parameter, α and β the solvent HBD and HBA abilities, while *s*, *a* and *b* are the corresponding regression coefficients.

The plots according to Eq. (8) are shown in Figs. 8 and 9. They present a suitable linearity with correlation coefficients larger than 0.95, even considering the reduced number of solvents in the $\bar{\nu}_T$ analysis. The results of the correlations are summarized in Table 3.

From the ratios of regression coefficients it can be seen that in $\Delta\bar{\nu}$ the major solvent influence is produced by its HBD ability, duplicating the non-specific dielectric interactions; while in $\bar{\nu}_T$ both, the polarity–polarizability and HBD parameters, have similar relevance. On the other hand, the HBA strength reveals only a small influence in the analyses in both cases.

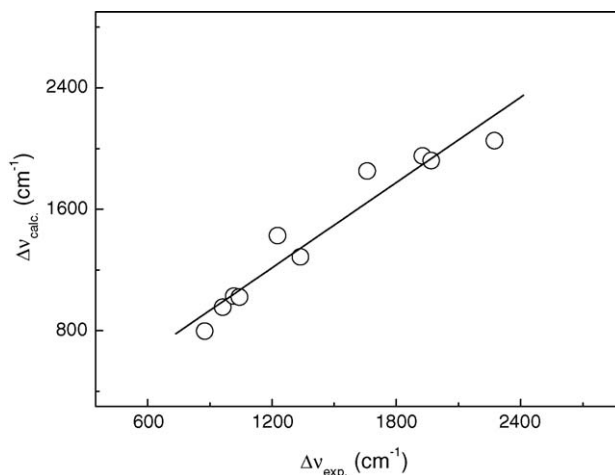


Fig. 8. Kamlet–Abboud–Taft's multiparameter solvation energy relationship for the Stokes' shift in protic solvents.

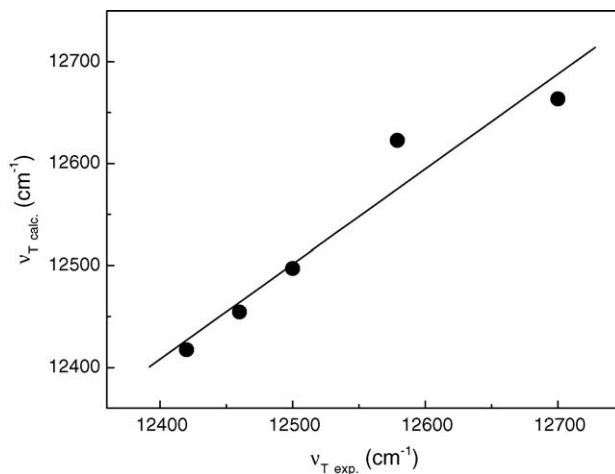


Fig. 9. Kamlet–Abboud–Taft's multiparameter solvation energy relationship for the triplet–triplet absorption maxima frequency in protic solvents.

4. Conclusions

The photophysical properties of phenosafranin are clearly dependent of the solvent nature in protic solvents. Characteristic photophysical parameters such as the Stokes' shifts, the fluorescence lifetime and the T–T absorption maxima frequency show a very marked solvent dependence, with a strong incidence of the specific interactions of the dye with solvent molecules, most likely hydrogen bonds. The dipole moment increases in the course of the $S_0 \rightarrow S_1$ transition, while a decrease in the dipole moment when the $T_1 \rightarrow T_n$ transition takes place. In these solvents, the non-radiative decay rate constant controls the solvent dependence of the fluorescence lifetime; showing a significant

augment with the solvent polarity increase. In comparison, the other kinetic constants involved in the deactivation of the singlet excited-state shown only a little changes with the solvent properties.

From all the experimental evidence, it can be concluded that hydrogen bonding must have an important contribution for the stabilization of the PS cation in hydroxylic media. According to the molecular structure of PS, the two amino groups and one of the two phenazine nitrogen atoms can be form hydrogen bonds with HBD solvents.

On the other hand, in aprotic solvents not clear tendencies of photophysical properties of PS are observed. This may be due to the minor stabilization of the dye molecule by non-specific solvent interactions.

Acknowledgements

Thanks are given to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET-PIP 3093-PEI 6261), Agencia Nacional de Promoción Científica (ANPCYT-PICT 06-9830) and Secretaría de Ciencia y Técnica de la Universidad Nacional de Río Cuarto-PPI 308, Argentina, for financial support of this work.

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