ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 101 (1996) 57–62

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Solution photophysics of ketocyanine dyes in neat and mixed binary solvents

Debashis Banerjee, Sanjib Bagchi *

Department of Chemistry, Burdwan University, Burdwan 713 104, India

Received 12 September 1995; accepted 18 June 1996

Abstract

The effect of the solvent on the excited state photophysics of two ketocyanine dyes was examined by studying the lifetime (τ) of the S_1 state in the picosecond domain. The overall luminescence decay constant ($1/\tau$) shows a linear correlation with the polarity parameter $E_T(30)$ in neat solvents. The radiative decay constant is practically independent of solvation, whereas the radiationless deactivation constant is sensitive to solvation; this has been attributed to hydrogen bond interaction of the solute carbonyl oxygen with the solvent. Preferential solvation by the protic component occurs in protic–aprotic binary mixed solvents. The influence of the solute–solvent interaction parameters and solvent non-ideality in determining the preferential solvation characteristics has been examined.

Keywords: Ketocyanine dyes; Neat and mixed binary solvents; Solution photophysics

1. Introduction

Ketocyanine dyes are suitable systems for studying the micropolarity of a medium [1,2]. These compounds are characterized by strong solvatochromic fluorescence and a large Stokes shift. The fluorescence is due to the $S_0 \leftarrow S_1$ transition involving a large change in the dipole moment. In recent studies [3–5], we have studied in detail the steady state fluorescence parameters in a variety of neat and mixed binary solvents. It was found that the emission characteristics are modified strongly by hydrogen bonding interaction in the excited state of the solute. In this paper, we investigate the excited state photophysics of ketocyanine dyes in various media. The excited state lifetimes of ketocyanine dyes in the picosecond domain in various neat and mixed binary solvents were investigated. The following neat solvents were used: water, ethanol (alcohol), acetonitrile (nitrile), dichloromethane (chlorohydrocarbon), dioxan (cyclic ether) and benzene (aromatic hydrocarbon). The mixed binary solvents used were water–dioxan, ethanol–acetonitrile, acetonitrile–benzene and ethanol–benzene.

2. Experimental details

The ketocyanine dyes **I** and **II** (Fig. 1) were synthesized as described in the literature [1]. Indoline, *N*-methylaniline, 1,1,3,3-tetramethoxypropane and cyclopentanone were purchased from Sigma Chemicals (USA) and were used as received. The purity of the prepared compounds was checked by IR, absorption and fluorescence spectral data and by thin layer chromatography. All the solvents were purified and dried by standard procedures [6,7], and distilled over calcium hydride immediately before use to ensure the absence of peroxides and oxidizing agents. Water was triply distilled. The mixed solvents and corresponding solutions were prepared by carefully mixing the components so as to minimize contamination by moisture. Freshly prepared solutions were used for each measurement and the concentration of the dyes varied in the range 10^{-5}–10^{-6} mol dm^{-3}.

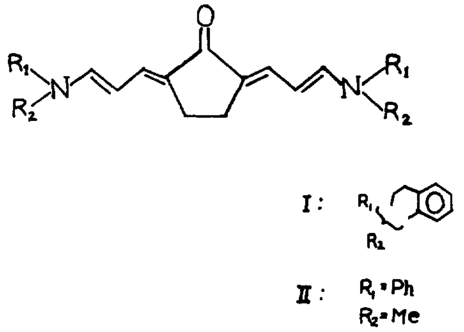

Fig. 1. Ketocyanine dyes **I** and **II**.

Details of the quantum yield measurements, corrected for the refractive index, have been described previously [5].

---

* Corresponding author.

1010-6030/96/$15.00 © 1996 Elsevier Science S.A. All rights reserved
PII S1010-6030(96)04441-3

For the lifetime measurements, a coherent, synchronously pumped, cavity-dumped dye laser (702-1) pumped by a coherent, continuous wave, mode-locked Nd:YAG laser (Antares 76 S) was used. The fundamental (1024 nm, 24 W, mode-locked) laser light was frequency doubled using an SHG crystal giving a 1.5–2 W mode-locked output in the green (532 nm). The pulse repetition rate was 76 MHz and the pulse width was 70 ps. The emission was detected using a Hamamatsu MCP photomultiplier tube (2809U). The response time of the set-up was 50–60 ps [8]. The fluorescence decays were deconvoluted using global lifetime analysis software [9].

3. Results

The excited state decay profiles of dye **I** in ethanol and benzene are shown in Fig. 2. The full line is the calculated fit assuming an exponential decay convoluted with the instrument response function. The difference between the decay curves of dye **I** in benzene and ethanol clearly indicates that the excited state dynamics are affected by the polarity of the solvent. The excited state lifetimes (τ) of dye **I** in pure solvents are listed in Table 1. Some experiments were performed with the structurally similar dye **II**. These results are also included in Table 1. The fluorescence quantum yields (Φ_F) of the dyes in the solvents, and other relevant parameters representing the solvent polarity, are also given in Table 1. The polarity parameters include the solvatochromic polarity scale $E_T(30)$ [11] and the parameters π^*, representing the general, non-specific mode of the solute–solvent interaction, and α, representing the hydrogen bond donating ability of the solvent [10]. Generally, an increase in lifetime in the S_1 state in the picosecond domain is observed with increasing polarity of the solvent (in the $E_T(30)$ scale [11]). A plot of the luminescence decay constant k ($1/\tau$) against $E_T(30)$ shows a linear relationship (Fig. 3(a)). This figure clearly shows that the solvation effect for dye **I** which determines the decay of the excited state is not solely due to general dielectric factors, but is a coupled effect arising from both specific (hydrogen bonding) and non-specific interactions, as is the case for Reichardt's betaine [11], the indicator solute for the $E_T(30)$ scale. To study the effect of the viscosity of the medium on the dynamics of the decay of the S_1 state of the dye, the τ values of both the dye molecules were determined in an ethanol–glycerol (1 : 1) mixture; the τ value is practically the same as that in neat ethanol. Similarly, the τ values in neat benzene and benzene–triacetin (1 : 1) are practically the same. The insensitivity of the measured τ values towards a change in viscosity of the medium clearly indicates that the decay of the excited state does not involve any change in the conformation of the dye molecules, e.g. twisting of the C–N bond.

The sensitivity of the luminescence decay constant to the solvent polarity prompted us to undertake lifetime experiments in mixed binary solvents. The results for dye **I** are

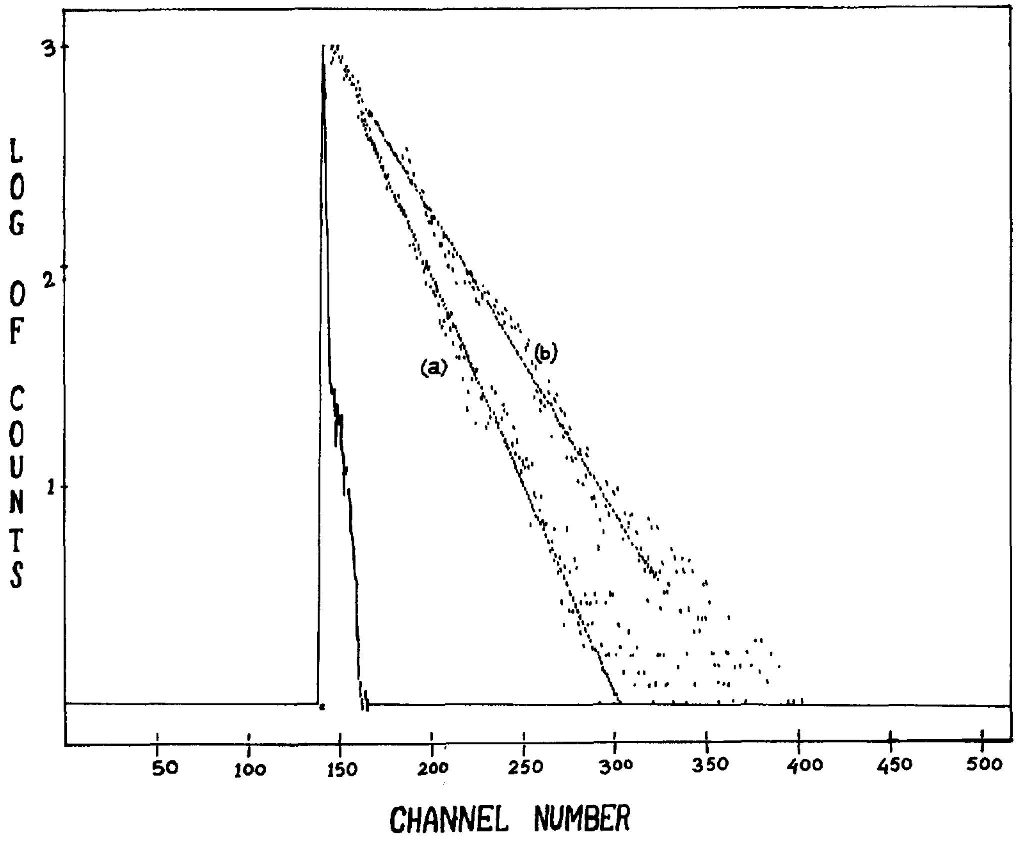

Fig. 2. Fluorescence decay curves for dye I in benzene (a) and ethanol (b) (1 channel = 28 ps).

Table 1
Photophysical parameters in neat solvents. Values in parentheses are for dye **II**

Solvent	$E_T(30)$ (kcal mol^{-1})	α^a	π^{*a}	Φ_F	τ (ps)	k_r ($\times 10^{-8}$)	k_{nr} ($\times 10^{-8}$)
1 Benzene	34.5	0.00	0.59	0.29	766	3.86	0.45
2 Dioxan	36.0	0.00	0.55	0.32	820	3.90	8.29
3 Dichloromethane	41.1	0.13	0.82	0.40	980	4.08	6.12
4 Acetonitrile	46.0	0.19	0.75	0.45	1020	4.40	5.38
5 Ethanol	51.9	0.83	0.54	0.66	1680	3.89	2.00
				(0.48)	(1515)	(3.17)	(3.43)
6 Methanol	55.5	0.93	0.60	0.69	1750	3.93	1.76
				(0.50)	(1562)	(3.20)	(3.20)

[a] α and π^* are polarity parameters representing hydrogen bond donation ability and the general solvating ability due to the dielectric effect respectively [10].

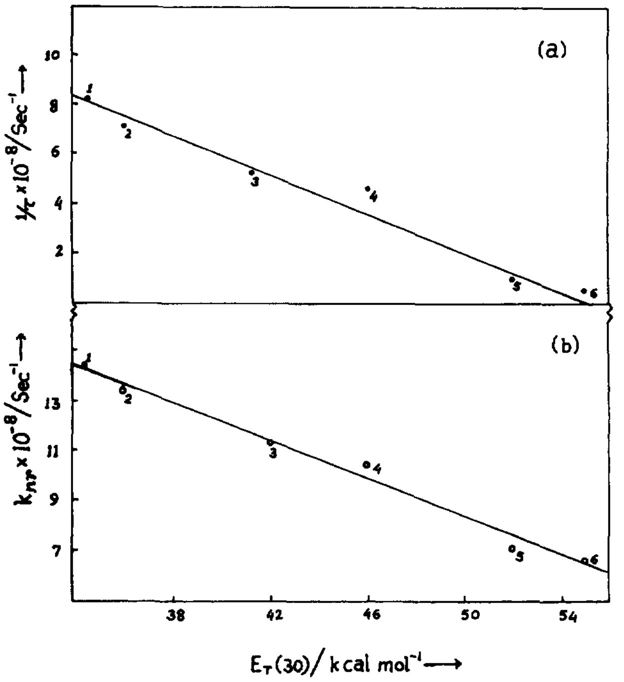

Fig. 3. Plot of $1/\tau$ (a) and k_{nr} (b) vs. $E_T(30)$ for dye **I**. The numbers of the solvents are given in Table 1.

given in Table 2. A plot of the luminescence decay constant k for dye **I** as a function of x_1, the mole fraction of the more polar component, is shown in Fig. 4. Although the k values are not very sensitive to the solvent composition for aprotic–aprotic mixed binary solvents, for protic–aprotic mixtures, k changes dramatically in the aprotic range up to a mole fraction of approximately 0.1 of the protic component. Beyond this region, the k values are not very sensitive to a change in the solvent composition. Because of the insolubility of the dye in water, we could not obtain data points beyond $x_{water} = 0.6$ in dioxan–water mixtures.

4. Discussion

Steady state spectroscopic results [3–5] indicate that the observed fluorescence of the ketocyanine dye involves an $S_0 \leftarrow S_1$ state transition which has intramolecular charge transfer (ICT) character, the S_1 state being more polar than the S_0 state. The dipole moments in the S_0 and S_1 states are 4.02 D and 7.6 D for dye **I** and 3.7 D and 5.2 D for dye **II** respectively. In the S_1 state, the carbonyl oxygen forms a tighter hydrogen bond with protic solvents and this influences the observed fluorescence parameters, e.g. the band maximum and the quantum yield. To investigate the effect of solvation on the dynamics of the excited state, the radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated using the following two expressions

$$k_r = \Phi_F/\tau \qquad (1)$$

$$k_{nr} = \tau^{-1} - k_r \qquad (2)$$

In the above equations, Φ_F is the fluorescence quantum yield and τ is the experimentally observed fluorescence lifetime. Table 1 shows the observed radiative and non-radiative rate constants for both dyes in pure solvents. It appears that the radiative decay constants are practically insensitive to a change in solvation. The difference between the radiative rate constants for the two dyes in a particular solvent (e.g. an alcohol) may be interpreted in terms of the Strickler–Berg (SB) relation [12]

$$k_r(\mathrm{SB}) = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}^{-3} \rangle_{av}^{-1} \int \epsilon \, \mathrm{d} \ln \bar{\nu} \qquad (3)$$

where $\langle \bar{\nu}^{-3} \rangle_{av}^{-1}$ refers to the average over the emission spectrum and the integral extends over the absorption band to the transition of interest. In order to obtain an approximate measure of the relative radiative rates from this relationship, the absorption bands are assumed to be gaussian and the value of $\langle \bar{\nu}^{-3} \rangle^{-1}$ is assumed to be proportional to the cube of the energy of the fluorescence maximum $\bar{\nu}_f$. Within these approximations, the radiative rate constant should be proportional to $\epsilon_{max} \bar{\nu}_f^3$, where ϵ_{max} is the value of ϵ at the absorption maximum. The ϵ_{max} values for dye **I** and dye **II** in ethanol are 6×10^5 and 4.5×10^5 respectively. Combining these values with those of $\bar{\nu}_f$ for the two dyes in ethanol (16 077 cm^{-1} and 16 978 cm^{-1} for dye **I** and dye **II** respectively), the radiative rate constant ratio is calculated to be

$$k_r(\mathrm{SB})(\text{dye } \mathbf{I}) / k_r(\mathrm{SB})(\text{dye } \mathbf{II}) = 1.13 \qquad (4)$$

This value compares favourably with the experimental ratio of 1.2 for ethanol. Unlike the radiative rate constant, the non-radiative rate constant (k_{nr}) for the dye exhibits extreme

Table 2
Lifetime and decay constant for dye **I** in various mixed binary solvents at 298 K (top). Photophysical parameters for dye **I** in ethanol–aetonitrile mixed solvent at 298 K (bottom)

x_1	τ (ps)	$(1/\tau)\times10^{-8}$	x_1	τ (ps)	$(1/\tau)\times10^{-8}$
Ethanol–benzene			Ethanol–acetonitrile		
0.00	766	13.0	0.00	1020	9.8
0.01	968	10.3	0.01	1150	8.7
0.04	1110	9.0	0.04	1280	7.8
0.10	1300	7.7	0.10	1400	7.1
0.20	1410	7.1	0.20	1490	6.7
0.35	1480	6.7	0.32	1536	6.5
0.50	1540	6.5	0.40	1575	6.3
0.70	1615	6.2	0.60	1615	6.2
1.00	1680	5.9	1.00	1680	5.9
Water–dioxan			Acetonitrile–benzene		
0.00	820	12.2	0.00	766	13.0
0.04	1100	9.1	0.08	826	12.1
0.14	1300	7.7	0.20	877	11.4
0.25	1390	7.2	0.40	910	10.9
0.40	1450	6.9	0.60	948	10.5
0.60	1515	6.6	0.80	1020	9.8
0.70	1590	6.3	1.00	1020	9.8

x_1	τ (ps)	$(1/\tau)\times10^{-8}$	Φ_F	$k_r\times10^{-8}$	$k_{nr}\times10^{-8}$	x_1^{La}
0.00	1020	9.8	0.45	4.4	5.1	0.00
0.01	1150	8.7	0.48	4.2	4.5	0.18
0.04	1280	7.8	0.52	4.0	3.7	0.44
0.10	1400	7.1	0.58	4.1	3.0	0.69
0.20	1490	6.7	0.62	4.2	2.5	0.83
0.32	1536	6.5	0.64	4.1	2.3	0.90
0.40	1575	6.3	0.65	4.1	2.2	0.94
0.60	1615	6.2	0.66	4.1	2.1	0.98
1.00	1680	5.9	0.66	3.9	2.0	1.00

[a] Calculated using Eq. (6).

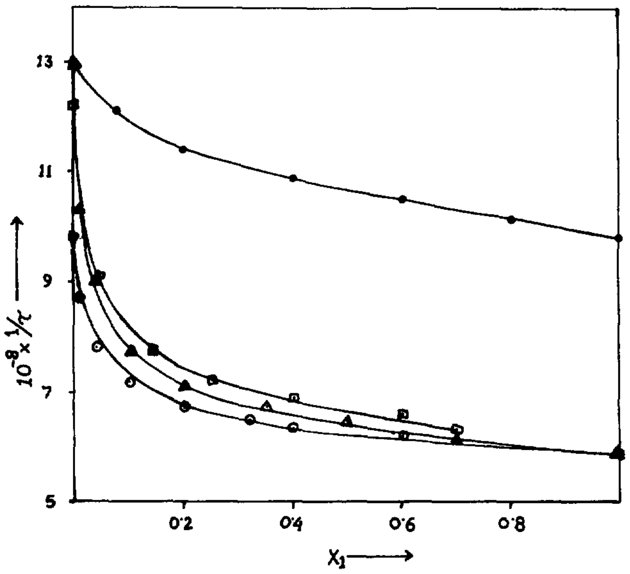

Fig. 4. Plot of $1/\tau$ for dye **I** in mixed binary solvents vs. the mole fraction of the more polar cosolvent (x_1): ●, benzene–acetonitrile; square, dioxan–water; triangle, acetonitrile–ethanol; ⊙, benzene–ethanol.

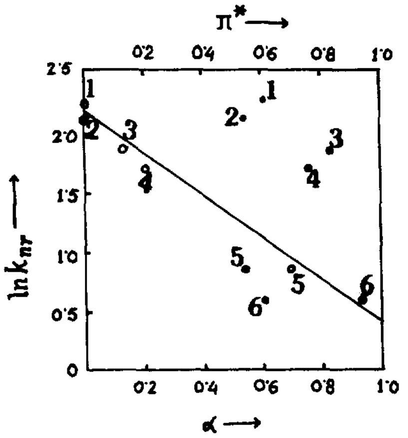

Fig. 5. Plots of ln k_{nr} vs. α (○) and π^* (●). The numbers of the solvents are given in Table 1.

solvent sensitivity. The rate constant decreases as the polarity of the solvent increases. A plot of k_{nr} against $E_T(30)$ (Fig. 3(b)) shows a linear relationship with practically the same slope as that observed for a plot of k against $E_T(30)$.

To investigate the role of non-specific and specific solute–solvent interactions on the decay constant k_{nr}, we plotted ln k_{nr} vs. the parameters π^* and α [10], representing non-specific and specific hydrogen bonding solute–solvent interactions respectively (Fig. 5). While ln k_{nr} is linearly correlated with α, there is no such correlation with π^*. Thus we conclude that specific hydrogen bonding interactions occurring between the dye in the S_1 state and protic solvent molecules lead to a decrease in the non-radiative relaxation rates from S_1 to S_0. The importance of hydrogen bonding interactions in influencing the steady state fluorescence parameters of these dyes has previously been demonstrated [3–5]. The influence of hydrogen bonding interactions in determining the excited state dynamics of other solutes has also been observed by other workers [13].

The non-linearity of plots of k vs. x_1 in mixed binary solvents may be explained in terms of the preferential solvation of the solute by one of the component solvents [14,15]. In the present case, the curvature of the plot indicates that the solute is preferentially solvated by the more polar component. This effect is more pronounced when the more polar component is the protic component. Thus, for the acetonitrile–benzene system, the extent of preferential solvation of the solute is small compared with the protic–aprotic binary mixtures studied. Furthermore, we have partitioned the net luminescence decay constant in ethanol–acetonitrile into radiative and non-radiative rate constants using the quantum yield data in this mixture. The results are given in Table 2. It has been found that it is the non-radiative rate constant which varies with the solvent composition. The general observation of a dramatic change in k (or k_{nr}) values when a small quantity of protic component is added to the aprotic solvent indicates that the protic solvent molecules, when added to a solution of the dye in aprotic solvent, replace preferentially the aprotic solvent molecules in the solvation shell of the dye. When the replacement is complete, there is only a small change in the k (or k_{nr}) values due to general solvation effects. Under the assumption that the observed property is a weighted average of the properties in pure solvents with respect to the local composition [16], the observed k_{nr} value may be written as

$$(k_{nr})_{12}=x_1^{\mathrm{L}}(k_{nr})_1+(1-x_1^{\mathrm{L}})(k_{nr})_2 \tag{5}$$

where the subscripts 1, 2 and 12 represent pure ethanol, pure acetonitrile and their binary mixture respectively and x_1^{L} represents the local mole fraction of ethanol. x_1^{L} may thus be obtained from Eq. (5) as

$$x_1^{\mathrm{L}}=[(k_{nr})_{12}-(k_{nr})_2]/[(k_{nr})_1-(k_{nr})_2] \tag{6}$$

Table 2 shows the calculated x_1^{L} values of ethanol–acetonitrile. Fig. 6 shows the calculated x_1^{L} values as a function of the bulk values of x_1 for the same mixture. It appears from this figure that the x_1^{L} value is always greater than the bulk value (i.e. preferential solvation by ethanol) and the difference is more prominent at the acetonitrile end. The x_1^{L} values are related to the parameter K_{PS}, representing the index of preferential solvation [17,18], as

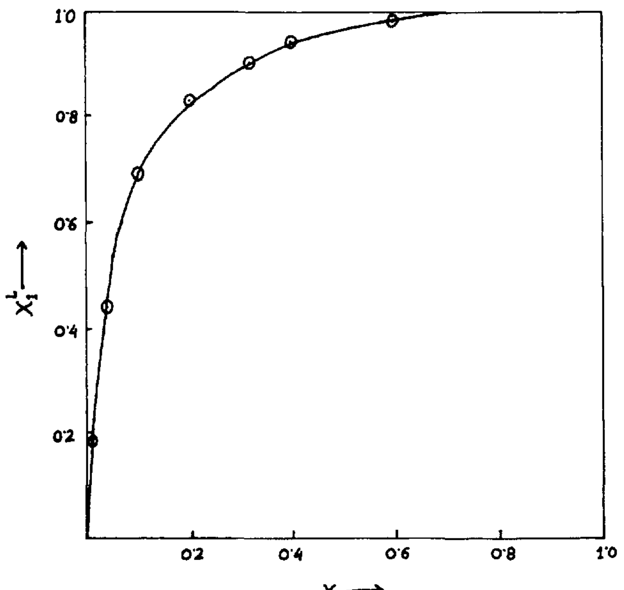

Fig. 6. Plot of x_1^{L} vs. x_1 in ethanol–acetonitrile binary mixture using dye **I**. Circles represent experimental points and the full line represents the theoretical curve obtained from Eqs. (9) and (10) using $K=24.0$, $n=6$ and $h=-0.08$.

$$K_{\mathrm{PS}}=(x_1^{\mathrm{L}})(1-x_1)/[(1-x_1^{\mathrm{L}})x_1] \tag{7}$$

The parameter K_{PS} is associated with the following solvent exchange equilibrium

$$\text{Solv. }1+\text{Solv. }2(\text{bound})\rightleftharpoons\text{Solv. }2+\text{Solv. }1(\text{bound}) \tag{8}$$

According to the existing models of preferential solvation, the parameter K_{PS} is given by the following equation [18]

$$K_{\mathrm{PS}}=\frac{x_1^{\mathrm{L}}x_2}{x_1x_2^{\mathrm{L}}}=K^{1/n}\mathrm{f}(Y) \tag{9}$$

$$\mathrm{f}(Y)=\frac{\displaystyle\sum_{i=1}^{n}\frac{(n-1)!}{(n-i)!(i-1)!}(K^{1/n}Y)^{i-1}\exp\left(-\frac{i(n-i)h}{RT}\right)}{\displaystyle\sum_{i=1}^{n}\frac{(n-1)!}{(n-i)!(i-1)!}(K^{1/n}Y)^{n-i}\exp\left(-\frac{i(n-i)h}{RT}\right)}$$

Thus K_{PS} depends on three factors: (1) K, which is determined by the difference between the solute–solvent interaction energies for the two solvents; (2) the solvent non-ideality h; (3) the coordination number [19]. x_1^{L} may be calculated from the K_{PS} values using the relation

$$x_1^{\mathrm{L}}=x_1K_{\mathrm{PS}}/[1+(K_{\mathrm{PS}}-1)x_1] \tag{10}$$

The experimental data (x_1^{L} vs. x_1 curve) in the present case are well represented by $K=24.0$, $h=-0.08$ and $n=6$ as shown in Fig. 6. The high value of K indicates that the interaction energy of the dye with ethanol is very large, and the negative value of h indicates that the solvent components repel each other [18,20]. Similar values of the above parameters have been obtained for dye **I** in the same binary mixture using steady state fluorescence parameters [5]. Thus a study of different properties of the solute provides the same information regarding the local environment around the solute.

5. Conclusions

The non-radiative decay constant for the ketocyanine dyes depends mainly on the hydrogen bonding interaction of the dye in the excited state with the solvent, but the radiative decay constant is practically insensitive to solvation. Preferential solvation of the solute by the protic component has been found to occur in protic–aprotic binary mixtures. Indices for solute–solvent interaction calculated from lifetime studies are similar to those obtained from steady state fluorescence parameters.

Acknowledgements

The authors wish to thank Dr. Kankan Bhattacharaya (IACS, Calcutta) for provision of the laboratory facilities for the measurement of the lifetimes in the picosecond domain (under SERC project no. SP/S2-L30/89 of the DST, Government of India and National Laser Programme). The authors gratefully acknowledge discussions with Professor M. Chowdhury (IACS, Calcutta). A grant from CSIR, India and financial assistance from UGC (India) under a SAP scheme are also acknowledged.

References

[1] M.A. Kessler and O.S. Wolfbeis, *Spectrochim. Acta, Part A, 47* (1991) 187.
[2] Ch. Reichardt, *Chem. Rev., 94* (1994) 2319.
[3] D. Banerjee, A.K. Laha and S. Bagchi, *Indian J. Chem. A, 34* (1995) 94.
[4] D. Banerjee, A.K. Laha and S. Bagchi, *J. Photochem. Photobiol. A: Chem., 85* (1995) 153.
[5] D. Banerjee, S. Mondal, S. Ghosh and S. Bagchi, *J. Photochem. Photobiol. A: Chem., 90* (1995) 171.
[6] A. Weissberger, *Techniques of Organic Chemistry*, Vol. 7, Interscience, New York, 1955.
[7] K. Medda, Studies of solute–solvent interaction, *Ph.D. Thesis*, University of Burdwan, 1991.
[8] N. Sarkar, K. Das, D. Nath and K. Bhattacharaya, *Chem. Phys. Lett., 218* (1994) 492.
[9] J.R. Knutson, J.M. Beecham and L. Brand, *Chem. Phys. Lett., 102* (1983) 501.
[10] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham and R.W. Taft, *J. Org. Chem., 48* (1983) 2877.
[11] Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinhiem, New York, 1988.
[12] S.J. Strickler and R.A. Berg, *J. Chem. Phys., 37* (1962) 814.
[13] R.S. Moog, M.A. Burozski, M.M. Desal, W.R. Good, C.D. Silvers, P.A. Thompson and J.D. Simon, *J. Phys. Chem., 95* (1991) 8466.
[14] P. Suppan, *J. Chem. Soc., Faraday Trans., 83* (1987) 495. C. Lerf and P. Suppan, *J. Chem. Soc., Faraday Trans., 88* (1992) 963. P. Chatterjee and S. Bagchi, *J. Chem. Soc., Faraday Trans., 87* (1991) 587; *86* (1990) 1785.
[15] F. Tanaka, Y. Kawaski and S. Yamashita, *J. Chem. Soc., Faraday Trans. I, 84* (1988) 1083.
[16] A. Ben-Naim, *Cell Biophys., 12* (1988) 255; *Pure Appl. Chem., 62* (1990) 25.
[17] P. Chatterjee and S. Bagchi, *J. Phys. Chem., 95* (1991) 3311.
[18] D. Banerjee, A.K. Laha and S. Bagchi, *J. Chem. Soc., Faraday Trans., 91* (1995) 631.
[19] A.K. Covington and M. Dunn, *J. Chem. Soc., Faraday Trans. I, 85* (1989) 2827.
[20] Y. Marcus, *J. Chem. Soc., Faraday Trans. I, 84* (1988) 1465.