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Fluorometric study of solvation characteristics of ketocyanine dyes in mixed binary solvents

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Abstract

The fluorescence characteristics of two ketocyanine dyes have been studied in six mixed binary solvents. Several parameters such as the maximum energy $E_{12}(F)$ of fluorescence, the quantum yield Φ_{12} of fluorescence and the normalized intensity of the fluorescence have been investigated as functions of solvent composition. In protic + aprotic binary mixtures a dramatic change at the aprotic end has been observed. The results point to a preferential solvation of the solute by the protic component.

Keywords: Fluorescence; Solvation; Ketocyanine dyes

1. Introduction

Solvation of a solute depends on the interaction of the solute with solvent molecules and on how these interactions modify the interactions between the solvent molecules in the vicinity of the solute. Study of the solvation of a solute molecule in a binary liquid mixture is interesting because this provides a means of varying the solvent–solvent interaction. Again, in a mixed binary solvent the microenvironment near the solute may be different from the bulk environment owing to the difference between the natures and extents of interaction of the solute with component solvents. This phenomenon, known as preferential solvation (PS), has been studied exclusively in recent years [1]. The spectroscopic method provides a convenient experimental means for studying PS [2–5]. Here the spectral response (R_{12}) in a mixed binary solvent is given by a weighted local mole fraction average of the responses R_1 and R_2 of the solute in two pure solvents:

$$R_{12}=x_1^{\mathrm{L}}R_1+(1-x_1^{\mathrm{L}})R_2 \tag{1}$$

where x_1^{L} is the local mole fraction of the solvent component 1. Several spectral parameters are used for monitoring PS. These include shifts in the absorption and/or emission wavelength [2–4], quantum yield of fluorescence [6] and the intensities of fluorescence [5]. However, here the question is whether PS characteristics measured by monitoring different parameters for the same solute are the same or not [7]. In the present paper we have addressed the problem of solvation in mixed binary solvents by monitoring the fluorescence characteristics of a suitable fluorophore, namely ketocyanine dyes, a special class of merocyanine dyes [8], as the indicator solute. These compounds are characterized by strong solvent-sensitive fluorescence at ordinary temperatures [9]. The fluorescence behaviours of two typical compounds KD1 and KD2 of the class have been investigated as a function of solvent composition in acetonitrile + ethanol, dichloromethane + ethanol, acetone + ethanol, ethanol + water, acetonitrile + water and dichloromethane + benzene binary mixtures.

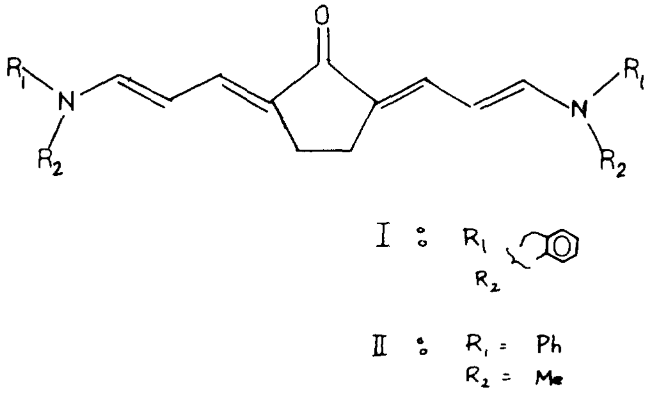

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Table 1
Fluorescence parameters for the two dyes in several mixed binary solvents at 298 K

x_1	KD1			KD2		
	$E_{12}(F)$	$\Phi_{12}(F)$	$I_{12}(F)$	$E_{12}(F)$	$\Phi_{12}(F)$	$I_{12}(F)$
Ethanol(1) + acetonitrile(2)						
0.00	50.4	0.45	0.42	52.9	0.30	0.26
0.03	48.5	0.52	0.42	51.2	0.36	0.40
0.09	47.2	0.58	0.81	50.2	0.40	0.66
0.19	46.9	0.62	0.90	49.6	0.43	0.82
0.28	46.6	0.64	0.93	49.3	0.45	0.90
0.42	46.3	0.65	0.95	49.0	0.47	0.94
0.53	46.1	0.67	0.97	48.8	0.48	0.97
0.65	46.0	0.66	0.95	48.6	0.48	0.98
0.80	46.0	0.66	0.99	48.5	0.47	0.99
1.00	46.0	0.66	1.00	48.5	0.48	1.00
Ethanol(1) + dichloromethane(2)						
0.00	50.8	0.40	0.50	53.5	0.24	0.32
0.02	48.8	0.46	0.71	52.0	0.31	0.50
0.06	47.6	0.54	0.89	50.4	0.36	0.66
0.14	47.0	0.60	0.94	49.8	0.41	0.88
0.28	46.8	0.63	0.96	49.3	0.44	0.93
0.42	46.5	0.65	0.98	49.0	0.46	0.95
0.55	46.3	0.66	0.97	48.8	0.47	0.97
0.80	46.1	0.65	0.99	48.6	0.48	0.99
1.00	46.0	0.66	1.00	48.5	0.48	1.00
Ethanol(1) + acetone(2)						
0.00	51.3	0.42	0.52	54.3	0.27	0.40
0.04	49.1	0.47	0.72	52.2	0.33	0.61
0.10	48.0	0.55	0.89	50.7	0.37	0.77
0.25	47.4	0.62	0.94	49.5	0.41	0.85
0.43	46.9	0.65	0.97	49.0	0.44	0.92
0.65	46.6	0.68	0.98	48.8	0.46	0.96
0.82	46.3	0.67	0.97	48.6	0.48	0.98
1.00	46.0	0.66	1.00	48.5	0.48	1.00
Dichloromethane(1) + benzene(2)						
0.00	54.2	0.29	–	57.3	0.12	–
0.09	52.6	0.29	–	55.2	0.13	–
0.18	51.9	0.30	–	55.0	0.13	–
0.26	51.5	0.30	–	54.7	0.14	–
0.41	51.2	0.31	–	54.3	0.15	–
0.58	51.0	0.32	–	54.0	0.16	–
0.74	50.9	0.34	–	53.8	0.17	–
0.90	50.8	0.36	–	53.6	0.19	–
1.00	50.8	0.40	–	53.5	0.24	–
Water(1) + ethanol(2)						
0.00	46.0	0.66	–	48.4	0.48	–
0.05	46.0	0.71	–	48.4	0.55	–
0.10	45.8	0.75	–	48.3	0.58	–
0.15	45.7	0.77	–	48.3	0.61	–
0.26	45.6	0.81	–	48.2	0.66	–
0.45	45.3	0.82	–	48.0	0.69	–
0.58	45.2	0.75	–	47.8	0.65	–
0.68	45.0	–	–	47.6	–	–
0.76	44.9	–	–	47.4	–	–
0.83	44.8	–	–	47.3	–	–
0.88	44.6	–	–	47.1	–	–
0.91	44.4	–	–	47.0	–	–
1.00	44.1	–	–	46.8	–	–
Water(1) + acetonitrile(2)						
0.00	50.4	0.45	–	52.9	0.30	–
0.04	48.0	0.55	–	51.0	0.43	–
0.07	47.5	0.61	–	50.7	0.51	–
0.15	46.8	0.68	–	49.7	0.55	–
0.25	46.2	0.72	–	49.0	0.59	–
0.30	46.0	0.76	–	48.8	0.64	–
0.43	45.7	0.74	–	48.6	0.61	–
0.60	45.2	0.69		48.2	0.56	–
0.72	45.1	–		47.9	–	–
0.80	44.9	–		47.6	–	–
1.00	44.1	–		46.8	–	–

2. Experimental details

The two compounds KD1 and KD2 were synthesized as described in the literature [9]. Indoline, *N*-methyl aniline, 1,1,3,3-tetramethoxy propane and cyclopentanone were purchased from Sigma Chemicals (USA) and used as received. Purities of the prepared compounds were checked by IR, absorption and fluorescence spectral data and by thin layer chromatography. All the solvents were purified and dried by standard procedures [10] and distilled from calcium hydride immediately before use to ensure the absence of peroxides and oxidizing agents. The water used was triply distilled. Mixed solvents and corresponding solutions were prepared by carefully mixing the components so as to minimize contamination by moisture. The absorbances of each solution for quantum yield measurements were measured on a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were taken on a Hitachi F-4010 spectrofluorometer equipped with a 150 W xenon lamp. Freshly prepared solutions were used for each measurement. The concentrations of the dye varied in the range 10^{-4}–10^{-5} mol dm^{-3}. The observed absorption–fluorescence spectrum did not depend, however, on the concentration of the solute in the concentration range studied. Quantum yields corrected for refractive index were based on the ratio of the areas under the emission curves to that of rhodamine B in ethanol; the quantum yield of the latter was taken as 0.71. The sample temperatures were controlled at 25.0 ± 0.5 °C. The $E_T(30)$ value [11,12] was measured, if necessary with pyridinium phenol betaine-30, through careful determination of the absorption maximum and conversion into units of kilocalories per mole.

3. Results

The fluorescence parameters in various mixed solvents have been listed in Table 1. The position of the band maxi-

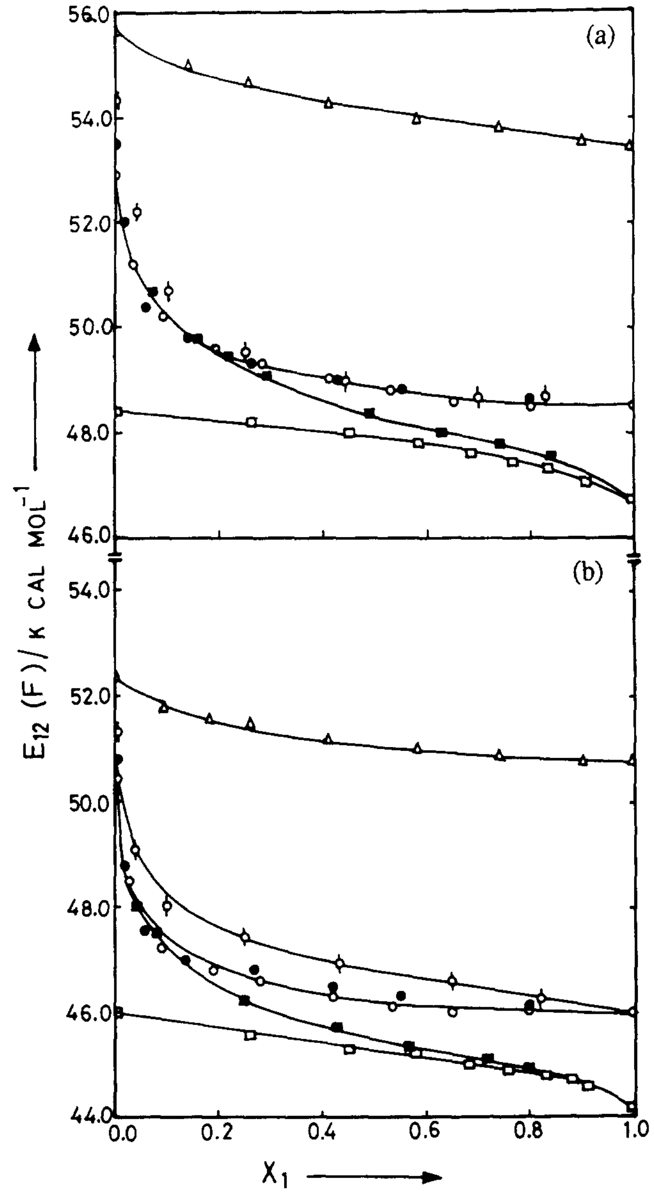

Fig. 1. E_{12}(F) as a function of mole fraction in various mixed binary solvents where x_1 is the mole fraction of the more polar component: for (a) dye I and (b) dye II, ○, acetonitrile + ethanol; ●, dichloromethane + ethanol; ϕ, acetone + ethanol; △, dichloromethane + benzene; □, ethanol + water; ■, acetonitrile + water.

mum gradually shifts to the red as the percentage of the more polar component (e.g. on the $E_T(30)$ scale) increases. The shifts are independent of the concentration of the solute in the concentration range studied and this indicates the absence of solute–solute interaction. A plot of the transition energy E_{12}(F) corresponding to the fluorescence maximum for both the dyes as a function of the mole fraction x_1 of the more polar component is given in Fig. 1. While the E_{12}(F) values are not very sensitive to solvent composition for aprotic + aprotic mixed binary solvent, it appears that, for a protic + aprotic mixture, E_{12}(F) changes dramatically in the aprotic range, up to a mole fraction of about 0.1 of the protic component and then the E_{12}(F) values are not very sensitive towards a change in the solvent composition. For ethanol + aprotic cosolvents the nature of the variation in E_{12}(F) vs. x_{ethanol} is almost independent of the nature of the aprotic component. For mixed aqueous solvents, however, the E_{12}(F) vs. x_1 shows a different behaviour at the aqueous end and this may be due to the existence of a self-associated structure of liquid water [13]. For the water + ethanol system there is almost a linear variation in E_{12}(F) vs. x_{water} in the concentration range studied. In this context, mention may be made of the fact that the two dyes are insoluble in water and data points for $x_{\text{water}} > 0.9$ could not be taken.

The fluorescence quantum yields Φ(F) for pure and mixed binary solvents are sensitive towards solvent polarity. A plot of Φ(F) vs. $E_T(30)$ for pure and mixed binary solvents as given in Fig. 2 shows linearity, Φ(F) being higher in solvents of higher polarity on the $E_T(30)$ scale. Plots of the quantum yield Φ_{12}(F) of fluorescence in mixed solvents vs. x_1 for the two dyes in all the solvent mixtures have been given in Fig. 3. The general nature of variation in Φ_{12}(F) for all the binary mixtures except the mixed aqueous systems is similar to the variation in E_{12}(F) vs. x_1 as discussed earlier, i.e. an abrupt change at the aprotic end in protic + aprotic binary mixture and very little change over the rest of the region. For mixed aqueous solvents the fluorescence quantum yield value at first increases steeply on the addition of water, passes through a maximum and then decreases. Here we could not take data points beyond $x_{\text{water}} = 0.6$ owing to insolubility of the dyes in water.

We have also measured the normalized fluorescence intensity I_{12}(F) as a function of solvent composition in binary mixed solvents containing ethanol, taking the value 1.0 for the neat polar cosolvents. It appears that the variation in I_{12}(F) values with solvent composition shows similar trends as with the other two parameters.

4. Discussion

4.1. $E_{12}(F)$ vs. x_1 plots

The non-linearity of the plots may be explained in terms of PS of the solute by one of the component solvents [2–4]. In the present case the curvature of plots indicates that the solute is preferentially solvated by the more polar component. The effect is more pronounced when the more polar component is the protic solvent. Thus for the dichloromethane + benzene system there is only little preferential solvation of the solute compared with protic + aprotic binary mixtures. It has been shown in our recent communication [14] that the transition energy maximum for fluorescence is very much dependent on the hydrogen-bond-donating ability of the solvent. Thus the observed PS of the solute by the more protic component is rationalizable in terms of the hydrogen bond donation interaction of the protic solvent. The steep decrease in E_{12}(F) with the mole fraction at the aprotic end indicates a large extent of PS of the protic component in this

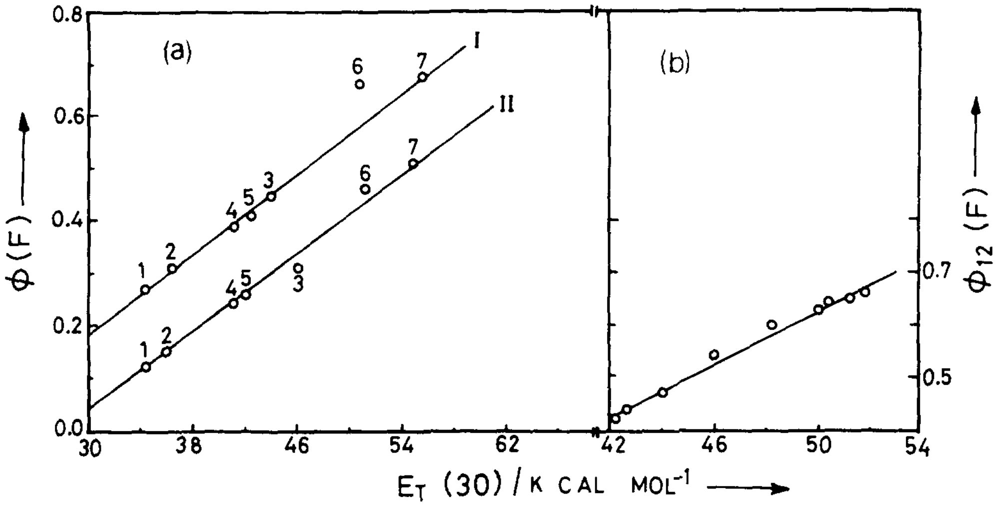

Fig. 2. (a) Plot of Φ(F) vs. $E_T(30)$ for pure solvents with dye I and dye II; 1, benzene; 2, dioxane; 3, acetonitrile; 4, dichloromethane; 5, acetone; 6, ethanol; 7, methanol. (b) Plot of Φ_{12}(F) vs. $E_T(30)$ for acetone + ethanol binary mixture for dye I.

region. Each molecule of the protic component in this mole fraction range presumably goes in the solvation shell of the dye, leading to an increased interaction. Beyond this range the E_{12}(F) values are less sensitive towards bulk environment changes and plot may be approximated by a straight line. Note the similarity of the values of slope in this mole fraction range for protic + aprotic and dichloromethane + benzene systems. Thus probably general dielectric effects are operative in determining the solvent effect in this region. The model may be illustrated by Fig. 4. Up to a small mole fraction range ($0<x<0.1$) the alcohol molecule replaces the aprotic solvent molecule and the solvated complex may be considered as being immersed in a background environment comprising mainly the aprotic cosolvents. After the complete replacement of all the aprotic solvent molecules in the microenvironment the solvated species "sees" an average environment comprising both the cosolvent and "feels" an average dielectric effect.

4.2. Fluorescence yield vs. x_l plots

Here also the same general observation as discussed above follows for mixed ethanol + aprotic solvents and dichloromethane + benzene. The Φ_{12}(F) values, however, increase as the polarity of the medium increases. A linear variation in Φ_F with $E_T(30)$ indicates that a similar solute solvent interaction is operative in determining the solvent effect in both the parameters. In the case of $E_T(30)$ it is known that the solute–solvent hydrogen bonding interaction plays a predominant role [12,15]. Thus Φ_F values in the present case are mostly determined by the hydrogen-bonding ability of the medium in which the fluorophore is placed. Φ_{12}(F) gives the same information about the solvation of the solute as obtained from the E_{12}(F) values for these systems. It may be mentioned that the variation in I_{12}(F) with solvent composition is similar to the variations in E_{12}(F) and Φ_{12}(F). Fig. 5 shows the variation in the three parameters for a particular dye in one figure.

The observed results for these binary mixtures thus fit the model of solvation as discussed earlier. In the cases of mixed aqueous solvents, however, the results are different. For aqueous acetonitrile the initial rapid increase in Φ_{12}(F) is explained as due to increased hydrogen-bonded interaction as more and more water molecules replace the acetonitrile molecules in the microenvironment. However, at a higher mole fraction of water owing to the strong self-association of water molecules the background consists mainly of associated water clusters and these interact with the water molecules in the solvation shell, decreasing the hydrogen-bonding ability of bare water molecules. Thus the observed value of Φ_{12}(F) tends to decrease. Hence the decreasing trend in Φ_{12}(F) vs. x_1 plot for a higher mole fraction of water is presumably due to a modification of water–dye hydrogen-bonding interaction by the three-dimensional hydrogen-bonded network present in liquid water. A similar explanation was invoked to explain the variation in the Stokes shift for the ketocyanine dyes in mixed aqueous solvents [16]. Such an anomalous hydrogen bonding behaviour for water + aprotic solvents has also been observed for other solutes [13,17].

4.3. The microenvironment and the index of preferential solvation

The local mole fraction of a solvent component may be calculated from Eq. (1) as

$$x_1^L = \frac{R_{12}-R_2}{R_1-R_2} \qquad (2)$$

At this point it is important to make some comments on the use of Eq. (2). Although extensively used by many workers [2–4,6], a rigorous derivation of the equation using spectroscopic principle is not possible. Some workers have attempted

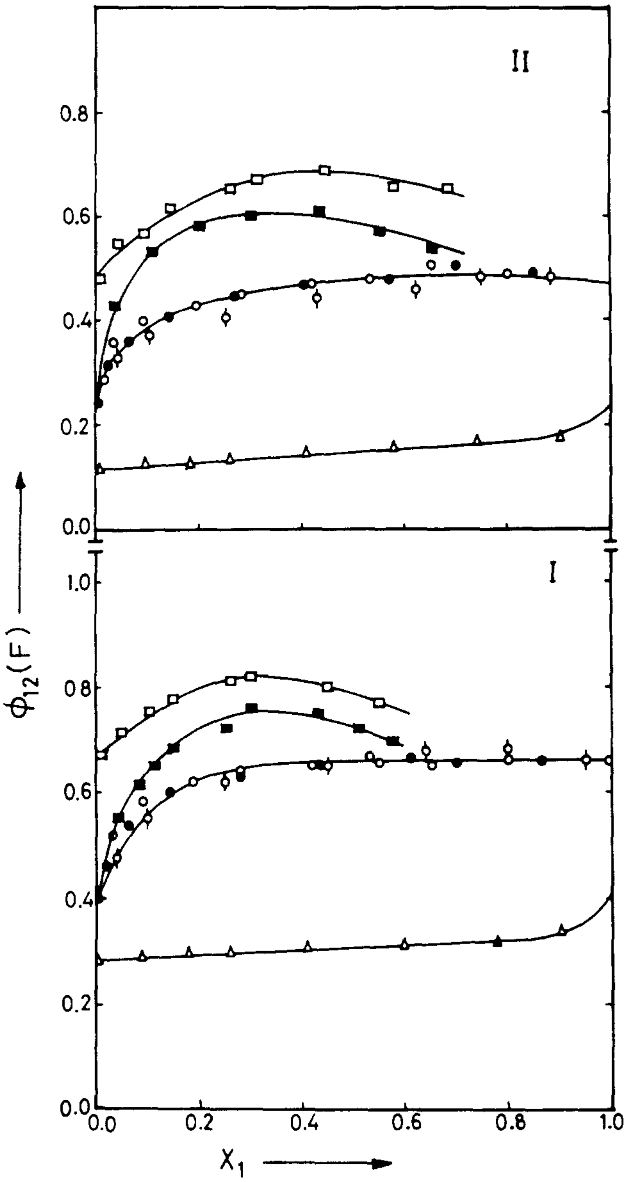

Fig. 3. Plot of $\Phi_{12}(F)$ vs. x_1 for dye I and dye II. The symbols have the same meanings as in Fig. 1.

to obtain the equation under certain special conditions [6,18]. The equation serves only as an operational definition of the local composition [7]. Again, there is no unambiguous definition of the "local" region around the solute. Thus the value of the local composition for a particular solute–solvent system at a particular bulk concentration may come out to be different if one uses different parameters for the estimation of x_1^L. It is therefore instructive to compare the x_1^L values calculated by using different spectroscopic parameters. Fig. 6 shows a plot of x_1^L vs. x_1 for mixed solvents containing ethanol. For a mixed aqueous system, x_1^L could not be obtained because of the lack of information about the property for pure water as the dyes are insoluble in water. It appears that within experimental inaccuracy all the data points (using three different parameters) may be represented by the same curve. The nature of the variation in x_1^L vs. x_1 indicates a preferential solvation of the solute by the protic component, the effect being prominent at the aprotic end.

The x_1^L values calculated in the above manner are supposed to contain information regarding the solvation of the solute, i.e. the solute–solvent and solvent–solvent interactions. In the various models of PS these are expressed in terms of several parameters. Thus the Covington–Newman [19] model expresses the PS in terms of $K^{1/n}$, an index of solute–solvent interaction, depending on the difference between the free energies of solvation of the solute and the component solvent; the solvation number n and a parameter h represent solvent non-ideality according to the following equations [21]:

$$K_{PS}=\frac{x_1^L x_2}{x_1 x_2^L}=K^{1/n}f(Y) \tag{3}$$

$$f(Y)=\sum_{i=1}^{n}\frac{(n-1)!}{(n-i)!(i-1)!}(K^{1/n}Y)^{i-1}\exp\left(-\frac{(n-i)ih}{RT}\right)\Bigg/ \sum_{i=1}^{n}\frac{(n-1)!}{(n-i)!(i-1)!}K^{1/n}Y)^{n-i}\exp\left(-\frac{(n-i)ih}{RT}\right) \tag{4}$$

It appears that the x_1^L vs. x_1 curve in ethanol + cosolvents in the present case is well represented by the Covington-Newman parameters $K^{1/n}=24.5$, $n=6$ and $h/2RT=-0.085$ (see Fig. 6). The high value of $K^{1/n}$ indicates strong solute-alcohol interactions.

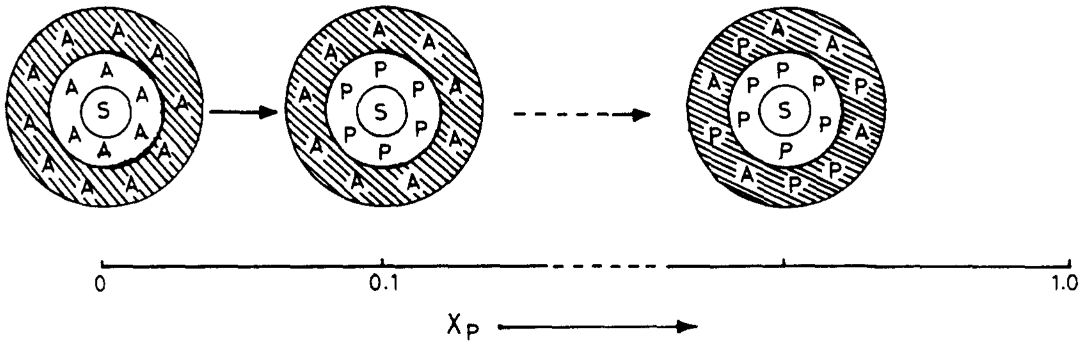

Fig. 4. The proposed model of the solvation of the dye in protic + aprotic binary mixture.

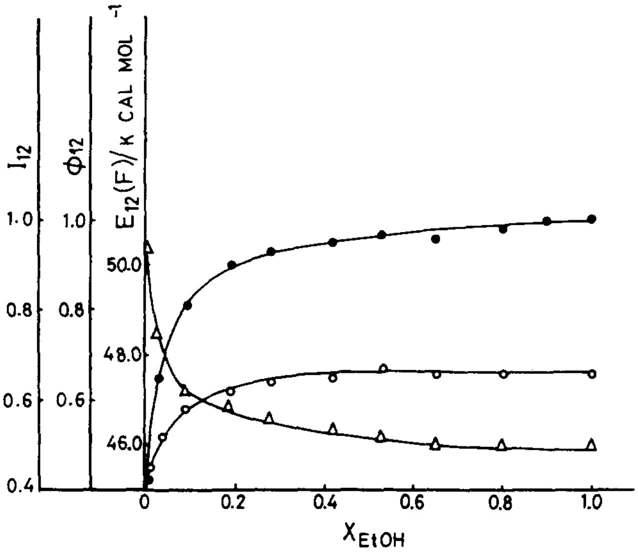

Fig. 5. Fluorescence parameters I_{12} (●), Φ_{12} (○) and E_{12} (△) of dye I in ethanol + acetonitrile binary mixtures as a function of the mole fraction of ethanol.

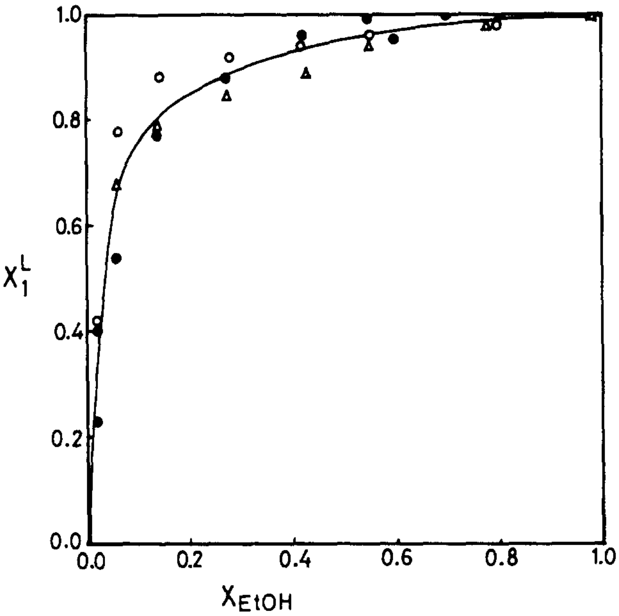

Fig. 6. PS of dye I in an acetonitrile + ethanol binary mixture using different fluorescence parameters: ●, I_{12}; ○, Φ_{12}; △, E_{12}; —, obtained with the values calculated using Eqs. (3) and (4) with $K^{1/n}$, h and n equal to 24.5, −0.085 and 6 respectively.

5. Conclusion

The ketocyanine dyes show a strong tendency towards a hydrogen-bonding interaction with protic solvents and this is reflected in the preferential solvation characteristics of the solute in protic + aprotic mixture. In mixed aqueous solvents, some peculiarities arise in the aqueous-rich region and this may be explained in terms of a strong self-association interaction in liquid water.

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