

Studies of solvation in homogeneous media by a spectroscopic method: a ketocyanine dye in neat and mixed binary solvents

Debashis Banerjee, Ashis Kumar Laha, Sanjib Bagchi*

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

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Abstract

The solvation characteristics of the ground and excited states of a ketocyanine dye were studied by monitoring the solvatochromic absorption and fluorescence bands. Multiple linear regression analysis indicates that both non-specific dipolar interaction and specific hydrogen-bonding interaction play an important role in the positions of the absorption and fluorescence maxima in pure solvents. In mixed binary solvents, the solute is preferentially solvated. The preferential solvation characteristics of the excited state are determined predominantly by the hydrogen-bond donating nature of the two solvents, while the preferential solvation of the ground state is determined by both dipolar and hydrogen-bonding interactions. In mixed aqueous solvents, the solute acts as a 'probe' for studying the 'microheterogeneity' of the mixture.

Keywords: Ketocyanine dye; Mixed binary solvents

1. Introduction

The optical response of a solute in a solution reflects the solute–solvent interactions on a microscopic level and thus the spectral parameters, e.g. the transition energy, fluorescence quantum yield and other photo-physical properties, are dependent on the nature of the molecular environment around the solute [1]. Using the solvatochromic spectral behaviour of suitable indicator solutes, empirical polarity scales have been established which find widespread application in analytical chemistry [1–3].

A variety of dyes have been reported to be sensitive to solvent polarity [2]. The conventional 'probes' for solvatochromic studies, e.g. phenyl *N*-pyridinium betaines [1] and *N*-alkyl pyridinium iodides [2], suffer from the disadvantage that they are non-fluorescent. Fluorescent polarity probes are more advantageous especially for biological systems [4]. Merocyanine dyes [3] provide an interesting system for solvatochromic studies. Some of these compounds show solvent-sensitive fluorescence [5]. A striking example of a solvent-dependent fluorophore is the compound 1-phenyl-4-(4-cyano-1-naphthyl-methylene)piperidine [6], but it suffers from the limitation that the absorption band for

the compound is hardly affected by the solvent polarity. Recently, Kessler and Wolfbeis [7] have reported the synthesis of ketocyanine dyes, a special class of merocyanine dyes possessing polarity-sensitive absorption and fluorescence bands. These compounds are characterized by high molar absorptivities and very strong fluorescence at ordinary temperatures. Although the absorption and fluorescence maxima of these compounds have been studied in a small number of solvents, a more extensive study is required to obtain an insight into the nature of the solute–solvent interactions in the ground and excited states of the solute.

Another interesting point is the study in mixed binary solvents. An unambiguous measure of the solvent polarity by a spectroscopic method may not be possible for a solvent mixture because the local composition of the solvent near the solute may be different from the bulk composition. It has been reported that a non-linear solvatochromic shift of the electronic spectrum of the solute vs. the solvent composition provides information about the local solvent composition [8]. The phenomenon of preferential solvation, leading to a local excess or deficiency of a component solvent, depends on the nature of the solute–solvent and solvent–solvent interactions. For a given binary mixture, the nature and extent of preferential solvation may depend on the solute. Moreover, for the same solute, preferential

*Corresponding author.

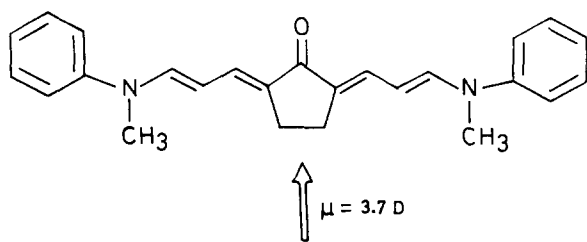


Fig. 1. The ketocyanine dye (KCD).

solvation characteristics may depend on whether the absorption ($S_0 \rightarrow S_1$) or fluorescence ($S_1 \rightarrow S_0$) bands are studied.

The purpose of this study is to investigate the solvation characteristics of an indicator solute in various homogeneous media (pure and mixed binary) by monitoring the absorption and fluorescence band maxima. We have monitored the absorption and emission characteristics of a typical ketocyanine dye (KCD) (Fig. 1) in 27 pure solvents and various binary mixed solvents. In this paper, we report our results in mixed aqueous solvents and mixed binary solvents containing dichloromethane.

2. Experimental details

The ketocyanine dye (I) was synthesized as described in the literature [7]. *N*-Methyl aniline, 1,1,3,3-tetra-methoxypropane and cyclopentanone were purchased from Sigma Chemicals (USA) and used as received. The purity of the prepared compound was checked by IR spectral data (IR peaks obtained in kBr disc: 1610, 1570, 1490 cm^{-1}) and absorption and fluorescence spectral data ($\lambda_{\text{abs.}}^{\text{max}} = 501 \text{ nm}$, $\lambda_{\text{fl.}}^{\text{max}} = 590 \text{ nm}$ in ethanol). All the solvents were purified and dried by standard procedures [9,10], and were distilled from calcium hydride immediately before use to ensure the absence of peroxides and oxidizing agents. Mixed solvents and corresponding solutions were prepared by carefully mixing the components so as to minimize contamination by moisture.

The absorption spectra were measured on a Shimadzu UV-160A spectrophotometer provided with a peak detection algorithm. The fluorescence spectra were taken on a Hitachi F-4010 spectrofluorometer equipped with a microprocessor and a chart recorder. Freshly prepared solutions were used for each measurement and the concentrations were chosen to give absorbances of less than 0.1 to avoid distortion of the spectra due to reabsorption of the fluorescence light. The observed absorption/fluorescence spectrum did not depend on the concentration of the solute in the concentration range 10^{-5} – $10^{-4} \text{ mol dm}^{-3}$.

3. Results

3.1. Pure solvents

The transition energies corresponding to the absorption maximum ($E(A)$) and the fluorescence maximum ($E(F)$) are listed in Table 1. Both $E(A)$ and $E(F)$ shift to lower energies as the polarity of the solvent increases. Fig. 2 shows a plot of $E(A)$ and $E(F)$ as a function of the Dimroth–Reichardt empirical solvent polarity parameter $E_T(30)$. While $E(A)$ is linearly correlated with $E_T(30)$, the available data points for $E(F)$ may be represented by two correlation lines. The data points for aprotic solvents fall on one line with a higher slope (about 0.5), while the protic solvents, forming a separate class, fall on another line with a lower slope (about 0.2). A similar trend has been observed by Kessler and Wolfbeis [7] using a smaller number of solvents. A correlation with $E_T(30)$ indicates that the nature of the transition in KCD is similar to that of the Dimroth–Reichardt dyes [1]. A double linear correlation in the case of fluorescence indicates that the nature of the emitting state is significantly different in the two classes of solvents [12].

In order to obtain an insight into the various modes of solvation (e.g. specific, non-specific) which determine the absorption and fluorescence energies, we have used the multiple linear regression analysis approach of

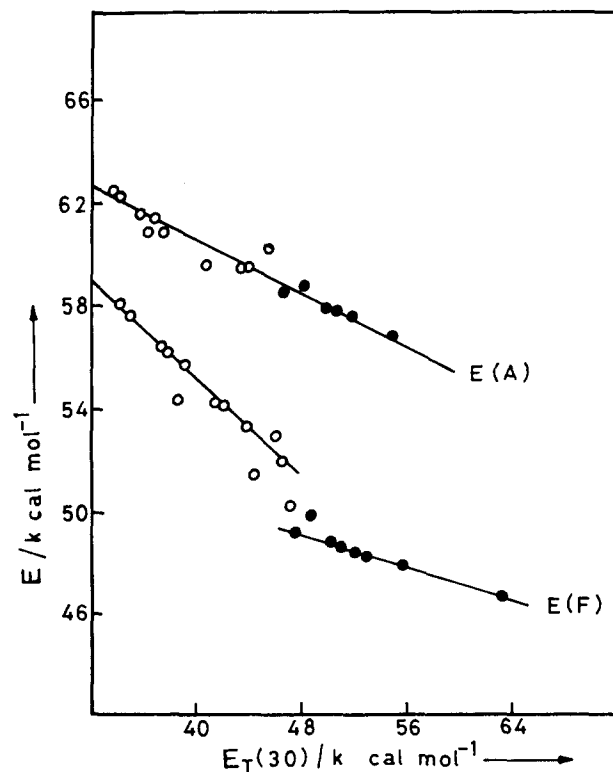


Fig. 2. Plot of $E(A)$ and $E(F)$ vs. $E_T(30)$ at 298 K. The filled circles indicate protic solvents.

Table 1
Absorption and emission energies of KCD in neat solvents with relevant solvent parameters

| Solvent | $E(A)$ (kcal mol ⁻¹) | $E(F)$ (kcal mol ⁻¹) | $E_T(30)$ (kcal mol ⁻¹) | α | β | π^* |
|-------------------|-------------------------------------|-------------------------------------|--|----------|---------|---------|
| Water | 52.3 | 46.9 | 63.1 | 1.17 | 0.47 | 1.09 |
| Methanol | 56.9 | 47.9 | 55.5 | 0.93 | 0.66 | 0.60 |
| Ethanol | 57.6 | 48.4 | 51.9 | 0.83 | 0.75 | 0.54 |
| 1-Propanol | 57.7 | 48.6 | 50.7 | 0.78 | 0.80 | 0.52 |
| 1-Butanol | 58.0 | 48.8 | 50.2 | 0.79 | 0.82 | 0.47 |
| 1-Pentanol | 58.2 | 49.3 | – | – | – | – |
| 1-Octanol | 58.6 | 50.3 | – | – | – | – |
| 2-Propanol | 58.9 | 50.1 | 48.6 | 0.76 | 0.84 | 0.48 |
| Isobutanol | 58.3 | 49.1 | 47.1 | – | – | – |
| 2-Methoxyethanol | 57.6 | 48.6 | 52.3 | – | – | – |
| 2-Ethoxyethanol | 57.6 | 48.6 | – | – | – | – |
| Cyclohexanol | 58.5 | 50.6 | 46.9 | – | – | – |
| Tertiarybutanol | 59.6 | 52.3 | 43.9 | 0.68 | 0.93 | 0.41 |
| Acetone | 60.9 | 54.3 | 42.2 | 0.08 | 0.48 | 0.71 |
| Cyclopentanone | 60.7 | 54.3 | – | 0.00 | 0.52 | 0.76 |
| Acetonitrile | 60.3 | 53.1 | 46.0 | 0.19 | 0.40 | 0.75 |
| Propionitrile | 60.4 | 53.1 | 43.7 | – | – | – |
| Dioxan | 61.6 | 56.8 | 36.0 | 0.00 | 0.37 | 0.55 |
| Tetrahydrofuran | 61.7 | 56.2 | 37.5 | 0.00 | 0.55 | 0.58 |
| Tetrahydropyran | 62.0 | 56.3 | – | 0.00 | 0.54 | 0.51 |
| Anisole | 60.8 | 55.8 | 37.2 | 0.00 | 0.22 | 0.73 |
| Benzene | 62.2 | 57.4 | 34.5 | 0.00 | 0.10 | 0.59 |
| Toluene | 62.6 | 58.0 | 33.9 | 0.00 | 0.11 | 0.54 |
| Dichloromethane | 59.6 | 53.7 | 41.1 | 0.13 | 0.10 | 0.82 |
| Ethylacetate | 60.9 | 55.0 | 38.1 | 0.00 | 0.45 | 0.55 |
| Nitromethane | 59.8 | 52.4 | 46.3 | 0.22 | 0.06 | 0.85 |
| Dimethylformamide | 59.6 | 53.1 | 43.9 | 0.00 | 0.69 | 0.88 |

Abraham et al. [12]. Correlations of $E(A)$ or $E(F)$ were sought with Taft's π^* value, an index of the solvent dipolarity/polarizability, and the α and β values, representing the hydrogen-bond donating (HBD) and accepting (HBA) ability respectively of the solvent [13]. The following regression equations were obtained

$$E(A) \text{ (kcal mol}^{-1}\text{)} = 65.59 - 6.22\pi^* - 5.13\alpha - 0.48\beta \quad (1)$$

($n = 22$, $r = 0.987$)

$$E(F) \text{ (kcal mol}^{-1}\text{)} = 57.83 - 2.46\pi^* - 7.28\alpha - 1.71\beta \quad (2)$$

($n = 22$, $r = 0.969$)

It appears that solvation is mainly determined by the dipolar interaction (π^*) and hydrogen-bond donation (α) with the solvent. The ratio of the regression coefficients of α and π^* indicates the relative importance of hydrogen-bond donation over dipolarity interaction. The ratio is almost equal to unity for $E(A)$, whereas it is about three for $E(F)$, meaning that hydrogen-bond donation plays a significantly greater role in the fluorescence spectrum. The result can be explained in terms of the tighter hydrogen bonding of the solvent hydrogen atom with the carbonyl oxygen atom in the excited state.

The dipole moment of the solute may be determined by the solvatochromic comparison method [14]. In this method ($E(A) + E(F)$) and ($E(A) - E(F)$) are plotted against appropriate dielectric functions and the ratio of the dipole moment in the S_1 state (μ_1) to that in the S_0 state (μ_0) is obtained from the ratio of the slopes. The advantage of this method is that it does not require the value of the cavity radius. In the present case (μ_1/μ_0) is 1.4 using the non-associating solvents. Semiempirical molecular orbital calculations at the Austin model 1 (AM1) level [15] using the MOPAC program (QCPE 355) (involving complete geometry optimization of the ground state of the title compound (**I**)) gives the ground state dipole moment (μ_0) as 3.7 D. Thus μ_1 is 5.2 D.

3.2. Mixed solvents

The position of the band maximum (absorption/fluorescence) gradually shifts to the red as the percentage of dichloromethane (DCM) or water is increased. The continuous shift and the absence of an isosbestic point rule out the possibility of complexation with the solvents. Moreover, the shifts are independent of the concentration of the solute in the concentration

range studied. This indicates the absence of solute–solute interactions.

3.2.1. Binary solvent mixtures containing DCM

The cosolvents used were ethanol (ETOH), tetrahydrofuran (THF) and benzene (BZ). Plots of $E(A)$ vs. x_1 , the bulk mole fraction of DCM, are given in Fig. 3. It appears from the figure that $E(A)$ is a linear function of x_1 only for the DCM–THF mixture. A deviation from linearity of $E(A)$ vs. x_1 may be explained in terms of the preferential solvation of the solute by one of the component solvents [16]. In the present case, the curvature for the DCM–BZ system points to a preferential solvation of the indicator solute by DCM, while for the DCM–ETOH system the solute appears to be solvated preferentially by ETOH. Moreover, $E(A)$ changes rapidly as ETOH is added to pure DCM, but at $x_1 < 0.8$, there is very little change in $E(A)$.

Fig. 3 also shows plots of $E(F)$ vs. x_1 . The steady state emission studies in mixed binary solvents reflect the preferential solvation characteristics of the S_1 state [17]. It appears that, like the S_0 state, the S_1 state prefers ETOH over DCM and DCM over BZ in the respective binary mixtures. However, unlike the S_0 state, the S_1 state shows a preference for DCM over THF. Our results for pure solvents indicate that the fluorescence maximum is largely determined by HBD interactions, while the influence of HBD and dipolar interactions is almost equal for the absorption maximum. Thus the preferential solvation characteristics of the S_1 state are probably determined by the α values of the solvents, and a preference for the more protic component of the solvents is expected. The α values for ETOH and DCM are 0.83 and 0.13 respectively, while THF and BZ are characterized by $\alpha=0$. This explains the preferential solvation in the S_1 state. On the other hand, preferential solvation characteristics in the S_0 state are determined by the difference between the dipolarity interaction (dielectric enrichment [16]) and the HBD interaction. Thus THF interacts with the

solute through dipolarity interaction to a greater extent than BZ, and the observed linearity over the entire range for the THF–DCM system in the absorption studies may be due to similar solute–DCM and solute–THF interactions.

3.2.2. Mixed aqueous solvents

The cosolvents used were ETOH, acetonitrile (ACN), acetone (AC) and THF. Fig. 4 shows plots of $E(A)$ vs. x_w , the bulk mole fraction of water. For all aqueous binary mixtures in the absorption studies, a straight line is obtained in the range $0.0 < x_w < 0.8$; beyond this region, i.e. in the water-rich region, the points fall on another straight line with a steeper slope. In all cases, the results indicate a local deficiency of water, i.e. preference of the solute for the organic component. Information on solvation of the ground state may also be obtained from other physicochemical properties. e.g. solubility data. It should be noted that the preference of the indicator solute observed in the present case runs parallel with the solubility of the dye in the respective solvents: the dye is appreciably soluble in organic solvents and practically insoluble in water. The change in slope of the $E(A)$ vs. x_w plot in the water-rich region may be due to the self-associated structure of liquid water. The linear plots in the water-rich region for all the aqueous binary mixtures converge to a point at $x_w = 1$. The transition energy corresponding to this point may be taken as the value in pure water, which is otherwise inaccessible. In contrast, the fluorescence studies show that water is always preferred by the solute (Fig. 4). The $E(F)$ vs. x_w curves show three distinct regions. In the region rich in organic cosolvent ($0.0 \leq x_w < 0.15$), a steep decrease in $E(F)$ vs. x_w is observed. The $E(F)$ values in the region $0.2 < x_w < 0.8$ change only slightly, and beyond this region, the values change again although at a slower rate than in the first region. It is interesting to note at this point that the experimentally determined α parameters (representing the HBD interaction) of water–ACN [18] and

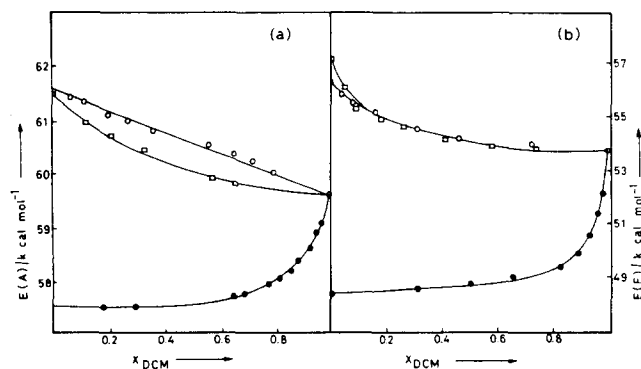


Fig. 3. Plot of $E(A)$ (a) and $E(F)$ (b) vs. the mole fraction of dichloromethane: \circ , tetrahydrofuran; \square , benzene; \bullet , ethanol.

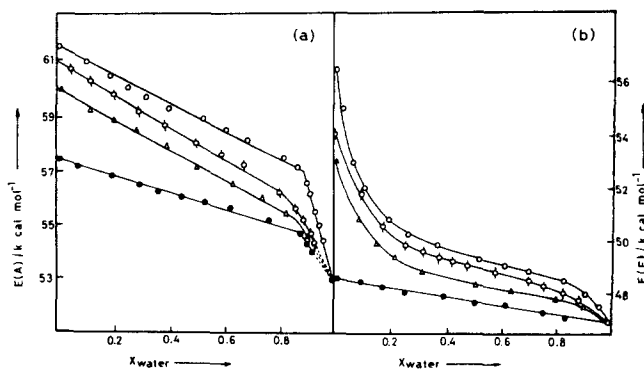


Fig. 4. Plot of $E(A)$ (a) and $E(F)$ (b) vs. the mole fraction of water: \circ , tetrahydrofuran; \diamond , acetone; \triangle , acetonitrile; \bullet , ethanol.

water–THF [19] binary mixtures also show similar trends, indicating a three-region model for the mixtures. Thus the above observation is in line with the fact that the fluorescence maximum $E(F)$ is determined predominantly by the HBD interaction in protic media. For the water–ETOH binary mixture, no preference for either solvent is observed, which is probably due to the similar HBD interactions in the composition range studied.

4. Discussion

The spectroscopic transition involves an initial equilibrium state and a final non-equilibrium Franck–Condon state. We can partition the Franck–Condon energies $E(A)$ and $E(F)$ using the procedure of Marcus [20,21]. Thus

$$E(A) = \Delta G(\text{solv.}) + E_{\text{RO}}^* \quad (3)$$

$$E(F) = \Delta G(\text{solv.}) - E_{\text{RO}} \quad (4)$$

where $\Delta G(\text{solv.})$ denotes the difference between the free energies of the solvated ground and solvated relaxed excited states, E_{RO} represents the solvent reorganization energy and the asterisk indicates the excited state (Fig. 5). Under the condition that the reorganization energies are equal [21], we obtain

$$E(A) + E(F) = 2\Delta G(\text{solv.}) \quad (5)$$

$$E(A) - E(F) = 2E_{\text{RO}} \quad (6)$$

Using Onsager's reaction field model, Eq. (6) may be written as

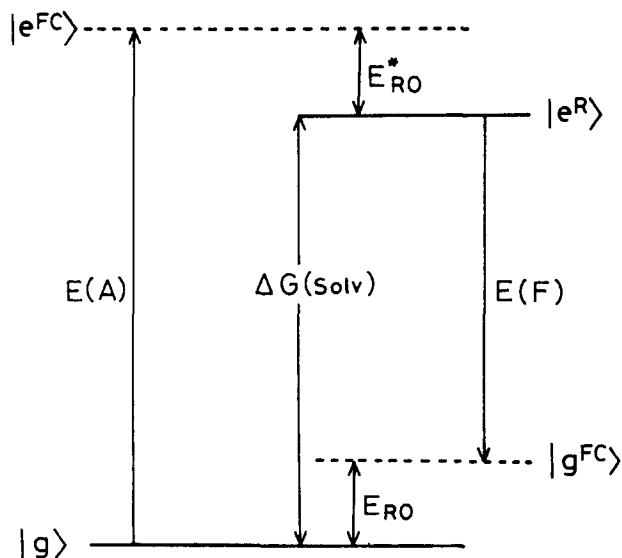


Fig. 5. Schematic energy level diagram: $|g\rangle$ = ground state; $|g^{\text{FC}}\rangle$ = Franck–Condon (FC) ground state; $|e^{\text{FC}}\rangle$ = FC excited state; $|e^{\text{R}}\rangle$ = relaxed excited state.

$$E(A) - E(F) = (\mu_e - \mu_g)^2 / a^3 \times [2(\epsilon - 1)/(2\epsilon + 1) - 2(n^2 - 1)/(2n^2 + 1)] \quad (7)$$

which is the Lippert–Mataga equation [22].

A plot of the Stokes shift in neat solvents vs. the dielectric function in Eq. (7) ($F(\epsilon, n^2)$) is given in Fig. 6. It follows that the protic solvents, capable of strong HBD interactions, form a separate class characterized by a higher reorganization energy. Thus the solvent reorganization energy possibly depends on the extent of HBD interaction with the solute. We have plotted the Stokes shift in a mixed binary solvent as a function of the solvent composition (Fig. 7). Although the solvent reorganization is practically insensitive to the solvent composition for aprotic–aprotic mixed binary solvents, there is a significant variation when one of the component solvents is protic. The general trend that emerges is a rapid increase in the solvent reorganization as a small amount of the protic component is added to the protic–aprotic mixture (e.g. water–THF, water–AC, water–ACN, ETOH–DCM). This may be explained by the preferential solvation of the protic component. Each molecule of the protic component presumably enters

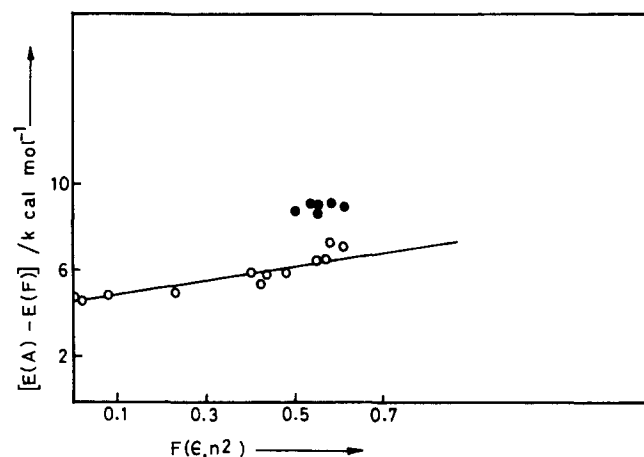


Fig. 6. Plot of the Stokes shift vs. $F(\epsilon, n^2)$ for pure solvents. The filled circles represent protic solvents.

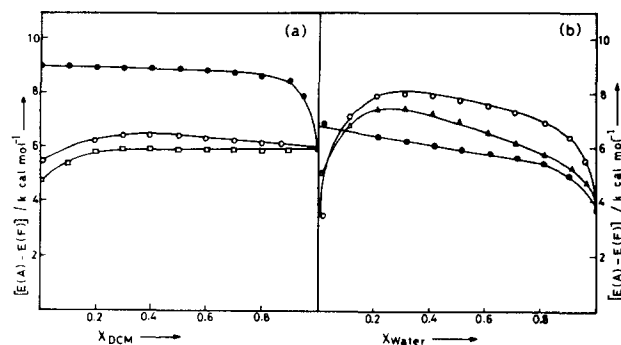


Fig. 7. Plot of the Stokes shift vs. solvent composition in mixed binary solvents containing dichloromethane (a) and water (b): \circ , tetrahydrofuran; \square , benzene; \bullet , ethanol; Δ , acetonitrile.

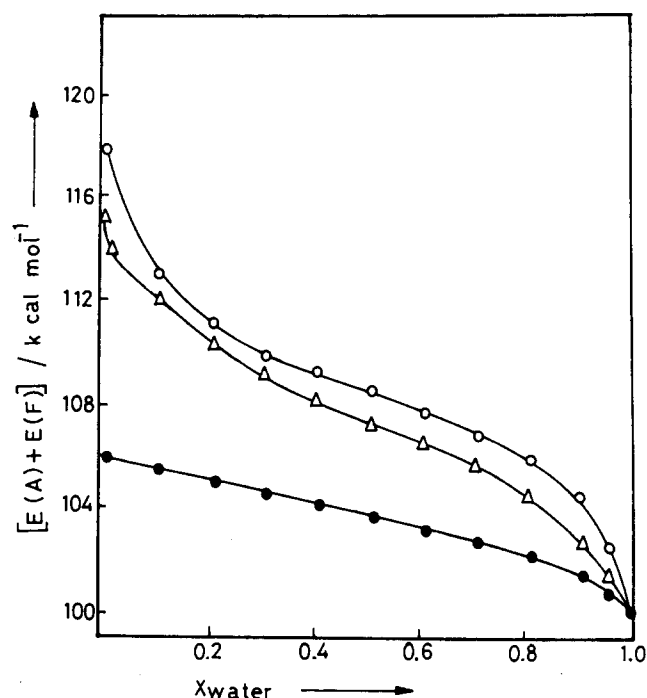


Fig. 8. Plot of $E(A)+E(F)$ vs. the solvent composition in mixed binary solvents containing water (symbols as in Fig. 4).

the solvation shell of the solute leading to increased HBD interaction. For the ETOH–DCM system, the solvent reorganization remains practically constant beyond the initial steep rise. However, for water–aprotic solvent mixtures, the curves show a slight decreasing trend in the region $0.2 < x_w < 0.9$, and beyond this region, there is a sharp decrease. Thus the Stokes shift vs. mole fraction curves also point to a three-region model for these mixtures. The decrease in the Stokes shift in the water-rich region in all the aqueous mixtures can be rationalized by the strong water–water association, which lowers the overall hydrogen-bonding ability of the solvent [17a, 23], thus reducing the solvent reorganization.

It appears from Eq. (5) that $(E(A)+E(F))$ is dependent on the equilibrium solvation of the ground (S_0) and excited (S_1) states. Plots of $(E(A)+E(F))$ against the solvent composition for a few representative binary mixtures containing water are shown in Fig. 8. Three distinct regions for water–aprotic solvent mixtures are observed. In Ref. 24, three distinct regions have been reported in water–ACN binary mixtures indicating microheterogeneity. Our observations also demonstrate the existence of microheterogeneity in water–aprotic cosolvent binary mixtures.

5. Conclusions

It can be concluded that the spectroscopic characteristics of a ketocyanine dye are determined by both

non-specific dipolar and specific hydrogen-bonding solute–solvent interactions, the latter being predominant in the excited state. In mixed binary solvents, the solute shows preferential solvation and the extent of this depends largely on the specific solute–solvent interactions. The Stokes shift in protic solvents is determined by the hydrogen bonding of the solute carbonyl group with the solvent; this property makes this class of dye a suitable ‘probe’ for studying hydrogen-bonding characteristics in mixed binary (protic–aprotic) solvents. In addition to solute–solvent interactions, solvent–solvent interactions in mixed binary solvents appear to modify the spectral characteristics of the solute. This is in agreement with the observations of other workers using other dyes [25].

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