Ground and Excited State Complexation of Ketocyanine Dyes with Alkaline Earth Metal Ions

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Electronic absorption and emission spectral characteristics of two ketocyanine dyes have been studied in solution in the presence of alkaline earth metal ions. Absorption spectral studies indicate complex formation between the ions and the dyes in the ground state. Values of the equilibrium constant and the enthalpy change characterizing dye (S_0)−metal ion interaction have been determined from the absorption spectral data. In the presence of the metal ions the fluorescence spectrum of the dyes shows two bands pointing to the existence of two emitting species, viz., the solvated and the complexed dye in solution. Time-resolved studies of the dyes in solution containing the metal ions can be explained by a two-state model and indicate the presence of two emitting species in equilibrium. Values of the equilibrium constant for the interaction of metal ion and the dyes in the S_1 state have also been estimated.

1. Introduction

N-Substituted derivatives of 2,5-bis[propylene]cyclopentanone, commonly known as ketocyanine dyes, form a class of compounds which are characterized by solvent dependent absorption and fluorescence properties.[1,2] The presence of electron donor (amino) and electron acceptor (carbonyl) groups in the molecule leads to an increase in charge separation on electronic excitation, and as a result, the electronic spectral transition in these compounds depends significantly on the interaction of the dye molecule with the molecules in its microenvironment. Photophysical and spectroscopic properties of these dyes have been the subject of intensive investigation in recent years. Solvatochromism/fluorosolvatochromism exhibited by these dyes make them good probes for monitoring micropolarity, for hydrogen bonding interactions, and for investigation of microenvironmental characteristics of biochemical and biological systems.[3−10] Some of them are also used as laser dyes and have several industrial applications in photopolymer imaging systems.[11−13] The ultrafast reaction dynamics of a ketocyanine dye in different media has also been investigated by Palit and co-workers.[14] Doroshenko et al. have studied the interaction of bis-azacrown-substituted derivatives of ketocyanine dyes with Mg^{2+} and Ba^{2+} ions.[8] In recent communications we have reported studies on the effect of alkali metal ions on the ground and excited state properties of the dyes.[15−17] It has been observed that Li^+ ion in aprotic solvents brings about the most significant change in spectral properties. Further, lithium ion forms a complex with the dye molecule in the ground state (S_0) as well as in the first singlet excited state (S_1). The objective of the present work is to investigate in detail the interaction of ketocyanine dyes with alkaline earth metal ions. To this end we have studied the electronic absorption, steady state emission, and time-resolved fluorescence of a ketocyanine dye (dye 1 in Figure 1) in solutions containing the alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) as a function of concentration of metal ions and temperature. The solvents used were acetonitrile (ACN), acetone (AC), and ethanol (EtOH). Perchlorate salts of the metal ions have been used due to their higher solubilities in the solvents. Spectroscopic and thermodynamic parameters have been determined for dye−metal ion complexes. In order to study the effect of structure of the dye on these parameters, we have also carried out an investigation on the interaction of Mg^{2+} with a structurally similar ketocyanine dye (dye 2 in Figure 1) in AC and ACN.

2. Experimental Section

2.1. Materials. The ketocyanine dyes have been prepared by the method described in the literature.[1] The purities of the prepared compounds were checked by IR, absorption, and fluorescence spectral data and also by thin layer chromatography. Ethanol [Bengal Chemicals], acetone [E. Merck], and acetonitrile [E. Merck] were dried by standard procedures.[18,19] To remove traces of moisture and other oxidizing impurities, all the solvents were refluxed for several hours with calcium hydride and then distilled immediately prior to the experiment. Perchlorate salts were dried in an oven at reduced pressure before use. Samples were prepared in a drybox to avoid contamination by air or mixing. The concentration of the dye was taken in the range 10^{-5}−10^{-6} M in all the spectral measurements. The concentration of metal ions was in the range 10^{-2}−10^{-3} M.

2.2. Steady State Spectral Measurements. Absorption (UV−vis) and steady state emission spectral measurements were performed as described in earlier communications.[15−17] The emission anisotropy at a wavelength λ was calculated using the following equation.[20]

$$r_{em}(\lambda) = [I_{VV}(\lambda) - G(\lambda)\, I_{VH}(\lambda)]/[I_{VV}(\lambda) + 2G(\lambda)\, I_{VH}(\lambda)] \quad (1)$$

where $I(\lambda)$ denotes the fluorescence intensity at the wavelength λ and the first and second subscripts ("H" and "V") respectively refer to the setting of the excitation and emission polarizers. $G(\lambda)$ is an instrumental factor representing the polarization characteristics of the photometric system and is given by

$$G(\lambda) = I_{HV}(\lambda)/I_{HH}(\lambda) \quad (2)$$

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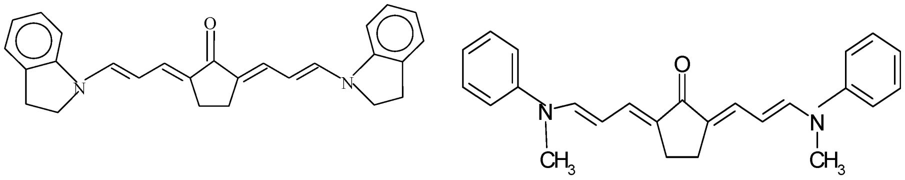

Dye 1 Dye 2

Figure 1. Ketocyanine dyes used in the present work.

The subscripts in the expression represent the same meaning as in eq 1. Excitation anisotropies (r_{em}) were calculated similarly. Anisotropy was measured in several replicate measurements, and the values were within ±0.005.

2.3. Time-Resolved Fluorescence Measurement. Fluorescence decay was studied by time-correlated single photon counting (TCSPC) using the Fluorocube lifetime system (IBH, Serial No. 04412) as described in previous communications.[15−17] Decay curves were analyzed using IBH DAS-6 decay analysis software. Intensity decay curves were fitted with single/biexponential decay equations. The decay parameters were recovered using a nonlinear-least-squares fitting procedure. Fitting with χ^2 values around 1 was taken as acceptable. The fluorescence decay of the dye was measured as a function of the concentration of the metal ions. For a particular concentration the decay was studied at different emission wavelengths in the emission band of the dye. In the present work, the fluorescence intensity for the dye in pure solvents as a function of time t, $F(t)$, could be fitted with a single-exponential equation:

$$F(t) = a \exp(-t/\tau) \tag{3}$$

For dye in salt solutions, however, a biexponential fit, as given by the following equation, was required.

$$F(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \tag{4}$$

where a_i's are the relative contributions to the lifetime components τ_1 and τ_2.

3. Results

3.1. Absorption Studies: Ground State Complexation. *3.1.1. Spectral Features.* Absorption band maximums of dye 1 in acetone and acetonitrile appear at 495 and 503 nm, respectively. On addition of $Mg(ClO_4)_2$ to the system, a new band at a longer wavelength appears and it becomes prominent as the concentration of the salt increases. Only the cation of the electrolyte has been found to be effective in spectral change. For a fixed dye concentration an isosbestic point appears in the absorption spectrum in the solvents containing varying amounts of the salt. Figure 2a shows representative absorption spectra in ACN containing magnesium perchlorate. Results point clearly to the existence of two species in equilibrium. While the lower wavelength band corresponds to the solvated dye, the longer wavelength band (580 nm in ACN and 570 nm in AC) is presumably due to the Mg^{2+}−dye complex. At a very high concentration of $Mg(ClO_4)_2$, the complexed form of the dye exists almost exclusively in the solution and only one absorption band characteristic of the complex is observed. Two bands also appear in the absorption spectra of the dyes in solution in aprotic solvents (AC, ACN) containing Ca^{2+}, Sr^{2+}, and Ba^{2+} ions, but the bands are not widely separated as in the case of Mg^{2+}. The absorption spectrum for a particular salt concentration, however, can be represented as a sum of two Gaussian functions. Figure 2b shows a representative spectrum and its resolution to two bands. In these cases also the band at lower wavelength corresponds to the solvated dye and that at longer wavelength is presumably due to the metal ion complexed dye. The existence of an isosbestic point in these cases points to the presence of two species in equilibrium in solution. Values of energy of maximum absorption, E_C, for the dye−metal ion complex in different solvents have been listed in Table 1. In the case of addition of Mg^{2+} to a solution of dyes in ethanol, the absorption band only slightly shifts to the red. For a fixed dye concentration an isosbestic point is observed (Figure 2c), indicating the existence of two absorbing species in solution. In this case, however, the band could not be separated into two bands characterizing the solvated dye and the complexed dye. The value of E(A) for the dye−Mg^{2+} complex has been determined by a procedure described later.

The absorption spectra of dye 2 in ACN and AC have been studied in the presence of $Mg(ClO_4)_2$. They show spectral features similar to those obtained for dye 1 (Figure 2d). Thus they show the existence of an isosbestic point when the concentration of the salt is varied at a fixed temperature or when temperature is varied at a fixed salt concentration. This indicates that dye 2 also interacts with Mg^{2+} in the solution and the solvated dye and the complexed dye exist in equilibrium in the S_0 state.

3.1.2. Equilibrium Constant. Spectral observations can be rationalized in terms of the existence of the following equilibrium in solution:

$$D\cdots S + nM^{2+} = D\cdots M^{2+} + S \qquad K = C_C/C_S(C_{M^{2-}})^n \tag{5}$$

here D⋯S and $D\cdots M_n{}^{2+}$ represent solvated dye and complexed dye, respectively, n is the minimum number of metal ion (M^{2+}) participation in the equilibrium, and C_S, C_C, and $C_{M^{2-}}$ represent the molar concentration of the solvated dye, the metal-complexed dye, and the metal ion, respectively. Spectral data can be used to determine the equilibrium constant for dye−M^{2+} interaction. A measured volume of the dye solution in a given solvent was taken in a stoppered quartz cuvette (1 cm path length), and a 0.01 mL solution of salt in that solvent was added to it. The absorption spectra were then determined. The addition of salt solution was repeated several times, and spectra were measured after each addition. In another experiment the dye solution in the solvent was saturated with the salt and the absorption spectrum was taken. In the event that the band maxima corresponding to the solvated dye and the metal-complexed species (λ_1 and λ_2, respectively) are widely different (as in the case of Mg^{2+}), one can assume that at wavelengths λ_1 and λ_2 the absorbing species are the solvated and the complexed dye respectively and eq 5 can be rearranged as

$$\log(A_2/A_1) = \log(A_S/A_0) + \log K + n \log C_{M^{2+}} \tag{6}$$

where A_2 and A_1 are absorbance values at λ_2 and λ_1 respectively for a salt concentration $C_{M^{2+}}$; A_0 and A_S respectively are the values of absorbance of solution containing dye in pure solvent

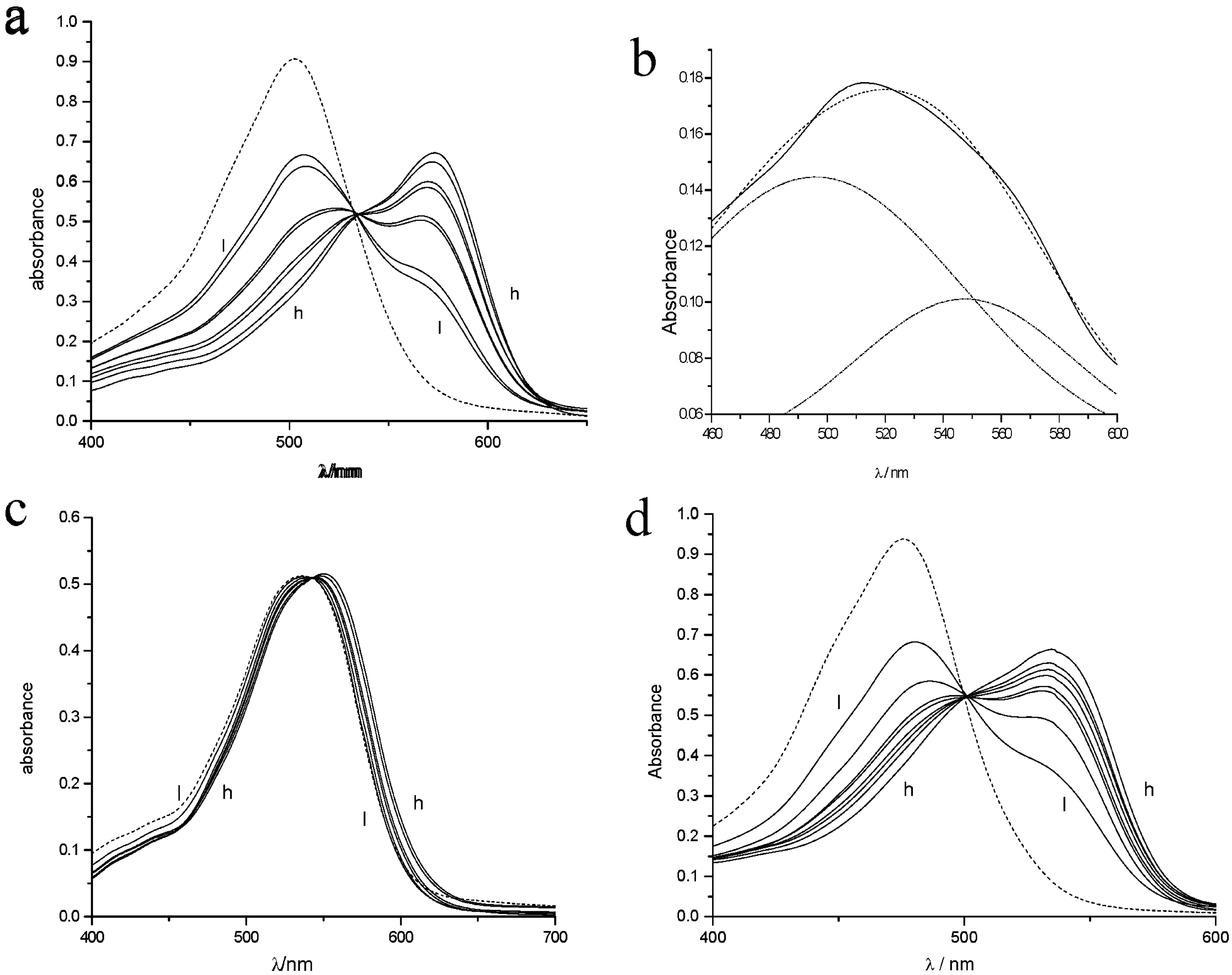

Figure 2. Absorption spectra of ketocyanine dyes in the presence of alkaline earth metal ions in different solvents: (a) Dye 1 in acetonitrile solution containing Mg^{2+} ion. The concentration of metal ion increases in the order l → h. Dotted line represents pure solvents. Effect of temperature at a fixed dye and metal ion concentration has been shown in the inset. (b) Decomposition of absorption band of dye 1 into two Gaussian curves in ACN solution containing $Sr(ClO_4)_2$. The experimental spectra (—), two Gaussian components (— ·· —), and their sum (···) have been shown. (c) Dye 1 in EtOH solution containing Mg^{2+} ion. (d) Dye 2 in ACN solution containing Mg^{2+} ion. "l" and "h" in (c) and (d) have the same significance as in (a).

TABLE 1: Spectroscopic and Thermodynamic Properties of Complexation of Ketocyanine Dye 1 (S_0 State) at 298 K for Various Metal Ions in Different Solvents

metal ion	solvent	E_C/kcal mol^{-1}	K	$\Delta H°$/kJ mol^{-1}
Mg^{2+}	ACN	49.3 ± 0.1	10 ± 1	3.34 ± 0.2
		(52.7 ± 0.1)[a]	(5.2 ± 0.6)[a]	(5.75 ± 0.2)[a]
	AC	50.2 ± 0.1	7.0 ± 0.7	1.25 ± 0.1
		(53.4 ± 0.1)[a]	(9.0 ± 1)[a]	(1.24 ± 0.2)[a]
	EtOH	49.3 ± 0.1	1.5 ± 0.2	
Ca^{2+}	ACN	50.2 ± 0.1	2.9 ± 0.3	2.34 ± 0.2
Sr^{2+}	ACN	51.1 ± 0.1	1.1 ± 0.1	−1.92 ± 0.1
Ba^{2+}	ACN	52.2 ± 0.1	1.5 ± 0.2	−1.22 ± 0.1

[a] Value for dye 2.

(in the absence of salt) and that for solution saturated with salt. The equilibrium constant, K, and the minimum order of participation of M^{2+} ion, n, can be calculated from the linear plot of $\log(A_2/A_1)$ versus $\log C_{M^{2+}}$ as suggested by eq 6. The value of $n = 0.8 \pm 0.2$ is obtained for the interaction for both dyes in AC and ACN with Mg^{2+}. This points to the formation of a 1:1 complex. Formation of a 1:1 complex has also been established for the interaction of dye 2 with lithium ion.[16] The value of K can also be determined by choosing a wavelength (600 nm in the present experiment) where only one species (e.g., the complexed dye) absorbs. Assuming $n = 1$, we have the following equation:

$$A/(C_D C_{M^{2+}}) = K\epsilon_2 - KA/C_D \qquad (7)$$

where A is the absorbance of solution at 600 nm and C_D is the concentration of the dye in solution. ϵ_2 is the molar absorbance for the absorbing species at the wavelength of measurement. A linear plot of $A/(C_D C_{M^{2+}})$ vs A/C_D gives K. Values of K as determined by the two procedures for the dye−Mg^{2+} ion interaction come within 5%. For M^{2+} ion−dye interaction (M = Ca^{2+}, Sr^{2+}, and Ba^{2+}) the absorption bands due to the two species overlap appreciably, and we have used eq 7 for the determination of K. Values of K for different systems have been listed in Table 1.

For the interaction of dye with Mg^{2+} ion in ethanol, where the band shifts due to complexation with the metal only to a small extent, the value of K has been found out by assuming that the observed maximum energy of a spectroscopic transition, E, is a mole fraction average of those for the two species, viz.,

TABLE 2: Spectroscopic and Thermodynamic Parameters for Ground State Complexation of the Ketocyanine Dye 1 with Various Metal Ions in ACN at 298 K

metal ion	ionic potential	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1}
Mg^{2+}	3.08	-3.46 ± 0.2	3.34 ± 0.2	23 ± 1
Ca^{2+}	2.02	-2.65 ± 0.2	2.34 ± 0.2	17 ± 1
Sr^{2+}	1.82	-0.24 ± 0.05	-1.92 ± 0.1	-6 ± 1
Ba^{2+}	1.55	-1.01 ± 0.1	-1.22 ± 0.1	-0.7 ± 0.1

the solvated and complexed forms of the dye.[15,16] Thus, one gets

$$E(\mathrm{A}) = (C_S E_S + C_C E_C)/(C_S + C_C) \tag{8}$$

where E(A) is the maximum energy of absorption for a salt concentration $C_{Mg^{2+}}$; E_S and E_C are those for the solvated dye and the complexed dye, respectively. Equation 8 can be rearranged to give

$$E(\mathrm{A}) = E_S + E_C K C_{Mg^{2+}} - K E(\mathrm{A}) C_{Mg^{2+}} \tag{9}$$

Values of E_S, E_C, and K that fit eq 9 can thus be obtained by a linear regression analysis. Values of E_C and K are listed in Table 1. The value of E_S, as obtained from the linear regression analysis, is 54 kcal mol^{-1} for dye 1. This compares well with the value of the energy of maximum absorption of the dye in ethanol (54.4 kcal mol^{-1}).

Absorption spectra for fixed salt and dye concentrations, studied in aprotic solvents at different temperatures, shows the existence of an isosbestic point as shown in a representative plot in Figure 2a (inset). Values of $\Delta H°$ for the dye−metal ion complexation, as determined from such studies, are given in Table 1.

Thermodynamic parameters, e.g., $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the alkaline earth metal ion complex of dye 1 in acetonitrile have been listed in Table 2. A systematic trend is observed as one goes from Mg^{2+} to Ba^{2+}. Note that a good linearity is observed when $\Delta H°$ is plotted against $\Delta S°$ [$\Delta S° = 4.93 + 5.34\Delta H°$; $R^2 = 0.9987$].

3.2. Fluorescence Studies: Complexation of the S_1 State. *3.2.1. Steady State Emission Studies.* Positions of maximum fluorescence of dye 1 in acetone and acetonitrile appear at 557 and 565 nm, respectively. On addition of alkaline earth metal perchlorates, a second band appears at a longer wavelength in addition to the band for the pure solvents. Positions of the band maxima are independent of the excitation wavelength. The second band becomes prominent as the concentration of the metal ion in solution increases. For fixed dye and metal ion

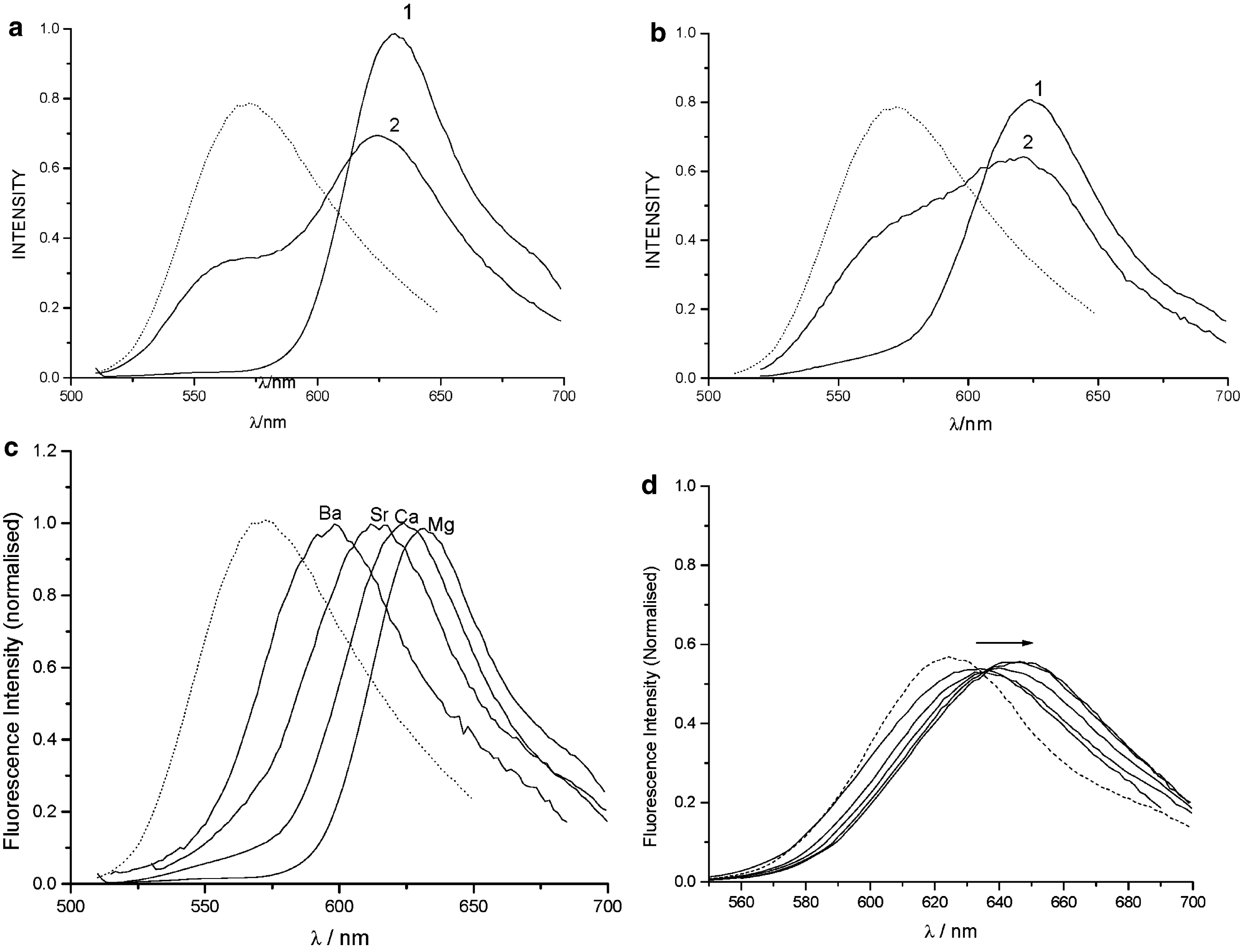

Figure 3. Fluorescence spectra of ketocyanine dyes in the presence of alkaline earth metal ions in different solvents. Mg^{2+} (a) and Ca^{2+} (b) ion in ACN solution of dye 1. Symbols “1” and “2” refer respectively to solution saturated with salt and that containing salt at an intermediate concentration. (c) Fluorescence spectra of dye 1 in ACN solution saturated with alkaline earth metal perchlorates. (d) Fluorescence spectra of dye 1 in EtOH solution containing Mg^{2+} ion. The arrow indicates the direction of increasing salt concentration. The dotted lines in (a)−(d) represent the fluorescence spectra in pure solvents.

TABLE 3: Spectroscopic and Thermodynamic Properties of Complexation of Ketocyanine Dye 1 (S_1 State) at 298 K for Various Metal Ions in Different Solvents

metal ion	solvent	E(F)/kcal mol^{-1}	Δ_S/cm^{-1}	K_1	$\tau_2{}^b$/ns	$\tau_1{}^c$/ns
Mg^{2+}	ACN	45.3 ± 0.1	1400 ± 50	330 ± 30	1.8	0.8
		(48.1 ± 0.1)[a]	(1600 ± 50)[a]	(340 ± 30)[a]	(1.4)[a]	(0.6)[a]
	AC	46.1 ± 0.1	1410 ± 50	160 ± 16	1.7	0.6
		(48.8 ± 0.1)[a]	(1620 ± 50)[a]	(180 ± 18)[a]	(1.4)[a]	(0.4)[a]
	EtOH	43.3 ± 0.1	2090 ± 50	5.2 ± 0.5	1.5	1.5
Ca^{2+}	ACN	45.6 ± 0.1	1600 ± 50	90 ± 9	1.7	0.8
Sr^{2+}	ACN	46.3 ± 0.1	1670 ± 50	70 ± 7	1.6	0.8
Ba^{2+}	ACN	46.7 ± 0.1	1990 ± 50	60 ± 6	1.5	0.8

[a] Value for dye 2. [b] Value for dye−metal ion complex. [c] Value for dye in pure solvent.

concentrations, fluorescence spectra at different temperatures exhibit an isosbestic point. Only the longer wavelength band appears in a solution saturated with salt. Figure 3 shows a few representative fluorescence spectra. Results thus point to the existence of two emitting species in equilibrium in the solution. The red-shifted band is due to the dye−metal ion complex. Values of energy of maximum fluorescence, E(F), for the complexed dyes as calculated by the formula E(F)/kcal mol^{-1} = 28590/(λ/nm), have been listed in Table 3. For a particular solvent the E(F) value of the complexed dye follows the order $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, as can be seen from Figure 3c. It has been explained earlier that the greater the interaction of a metal ion with the S_1 state of the dye, the less will be the E(F) values.[15−17] Thus strength of interaction between the dye (S_1 state) and the metal ion follows the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The Stoke's shift ($\Delta_S$) of the complexed dye is less than that for the dye in a pure solvent. This has been rationalized by other workers in terms of increased rigidity of the dye on complexation.[8] A similar observation has been made by us for the dye−Li^+ ion complex.[17,18] The increased rigidity of the dye−metal ion complex also finds support from fluorescence anisotropy studies. For example, the value of fluorescence anisotropy of dye 1 in pure ACN is 0.05, while the value increases to 0.19 in a solution saturated with $Mg(ClO_4)_2$. Only a small red shift of the fluorescence band is observed when $Mg(ClO_4)_2$ is added to an ethanol solution of the dye as shown in Figure 3d. It is known that the dye interacts with ethanol through hydrogen bond formation. Thus a small shift in the position of the band maximum can be rationalized in view of the comparable strength of the dye−Mg^{2+} and dye−ethanol interactions. The energy of maximum fluorescence of the complexed dye and the equilibrium constant for the complexation process in this case have been determined by a method described earlier.[16,17] The observed fluorescence energy, E(F), can be considered as a mole fraction average of the solvated and the complexed species, E_{S1} and E_{C1}, respectively. Thus one gets

$$E(\mathrm{F}) = (C_S E_{S1} + C_C E_{C1})/(C_S + C_C) \qquad (10)$$

Assuming equilibrium between the two species in solution, one gets

$$E(\mathrm{F}) = E_{S1} + E_{C1} K_1 C_{Mg^{2+}} - K_1 E(\mathrm{F}) C_{Mg^{2+}} \qquad (11)$$

where K_1 is the equilibrium constant for the following process:

$$M^{2+} + S\cdots D(S_1\ \text{state}) = M^{2+}\cdots D(S_1\ \text{state}) + S \quad (12)$$

Values of E_{S1}, E_{C1}, and K_1 that fit eq 11 can thus be determined by a linear regression analysis. In the present case for M = Mg we get E_{S1} = 45.5 kcal mol^{-1}, E_{C1} = 43.3 kcal mol^{-1}, and K_1 = 5.2 (R^2 = 0.984, σ = 0.08) The value of E_{S1} compares well with the experimentally observed value for the dye in pure ethanol (45.8 kcal mol^{-1}).

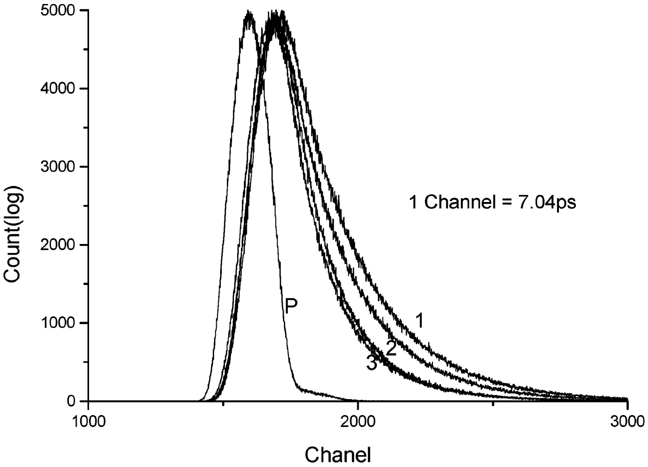

Figure 4. Decay profile of the prompt (P) and dye 1 in ACN saturated with alkaline earth metal perchlorates: (1) Mg^{2+}, (2) Ca^{2+}, and (3) Sr^{2+} and Ba^{2+}. One channel = 7.04 ps.

3.2.2. Time-Resolved Fluorescence. The decay of the excited states of the dyes has been studied in the pure solvents and also in electrolyte solutions. Figure 4 shows some representative decay curves. It has been found that for pure solvents the decay is best fitted with a single-exponential equation as given by eq 3. In solutions containing metal ions in aprotic dipolar solvents, however, the decay curve is best represented by a biexponential fit, as given by eq 4. Only in solutions saturated with metal perchlorates does a single-exponential fit apply. The biexponential decay characteristics have been studied at different concentrations of the salts. For fixed salt concentration the decay characteristics have been studied by collecting emission at various wavelengths (λ) in the emission band of the dyes. Table 4 gives some representative results. For all cases the decay is characterized by shorter (τ_1) and longer (τ_2) lifetimes. Values of τ_1 and τ_2 are almost independent of λ and the concentration of metal ion. For a fixed salt concentration, however, the ratio of a_1 and a_2 has been found to be dependent on the choice of λ. While the shorter lifetime (faster decay) corresponds to that for the dye in the pure solvent, the longer lifetime (slower decay) is presumably due to the dye complexed with alkaline earth metal ions. Moreover, the τ_2-value is close to the lifetime of the dye in solutions saturated with salt. Thus the species with greater τ-value can be identified as the cation-complexed dye. In our earlier studies it has been established that the dyes complexed by lithium ion are characterized by a longer lifetime.[16,17] In a fixed solvent like ACN, the τ-values corresponding to the metal ion complexed dye follows the order $Mg^{2+} \approx Ca^{2+} > Sr^{2+} = Ba^{2+}$.

It is known that the quantities $A_1 = a_1\tau_1/(a_1\tau_1 + a_2\tau_2)$ and $A_2 = a_2\tau_2/(a_1\tau_1 + a_2\tau_2)$ represent the fraction of contribution

TABLE 4: Decay Parameters for Fixed Metal Ion (M^{2+}) Concentration as a Function of Wavelength at 298 K

solvent	λ/nm	τ_1/ns	τ_2/ns	A_1	A_2
	$M^{2+} = Mg^{2+}$ Ion				
acetone (dye 1)					
$C_{M^{2+}} = 1.59 \times 10^{-3}$	590	0.52	1.25	0.73	0.27
	600	0.52	1.43	0.66	0.34
	620	0.58	1.5	0.63	0.37
acetonitrile (dye 1)					
$C_{M^{2+}} = 1.99 \times 10^{-3}$	590	0.42	1.05	0.22	0.78
	600	0.63	1.29	0.43	0.57
	610	0.66	1.44	0.40	0.60
	620	0.71	1.6	0.39	0.61
$C_{M^{2+}} = 7.84 \times 10^{-3}$	590	0.69	1.45	0.47	0.53
	600	0.57	1.56	0.3	0.70
	610	0.53	1.63	0.16	0.84
	630	0.71	1.68	0.15	0.85
acetonitrile (dye 2)					
$C_{M^{2+}} = 7.8 \times 10^{-3}$	570	0.3	1.34	0.17	0.83
	580	0.26	1.35	0.14	0.86
	590	0.26	1.29	0.14	0.86
acetone (dye 2)					
$C_{M^{2+}} = 1.6 \times 10^{-3}$	556	0.31	1.13	0.71	0.29
	566	0.3	1.24	0.61	0.39
	576	0.31	1.27	0.48	0.52
	$M^{2+} = Ca^{2+}$ Ion				
acetonitrile (dye 1)					
$C_{M^{2+}} = 1.97 \times 10^{-2}$	595	0.73	1.30	0.52	0.48
	615	0.72	1.55	0.34	0.66
	625	0.67	1.56	0.26	0.74
	626	0.7	1.6	0.20	0.80
	$M^{2+} = Sr^{2+}$ Ion				
acetonitrile (dye 1)					
$C_{M^{2+}} = 1.62 \times 10^{-2}$	600	0.71	1.3	0.36	0.64
	620	0.60	1.18	0.33	0.67
	630	0.60	1.18	0.32	0.68
	640	0.72	1.3	0.31	0.69
$C_{M^{2+}} = 1.94 \times 10^{-2}$	600	0.62	1.37	0.37	0.63
	605	0.65	1.43	0.38	0.62
	615	0.66	1.48	0.34	0.66
	625	0.67	1.51	0.33	0.67
	$M^{2+} = Ba^{2+}$ Ion				
acetonitrile (dye 1)					
$C_{M^{2+}} = 5.47 \times 10^{-2}$	590	0.66	1.48	0.40	0.60
	600	0.59	1.52	0.26	0.74
	605	0.60	1.54	0.23	0.77
	615	0.63	1.59	0.21	0.79
	625	0.70	1.58	0.13	0.87

of steady state fluorescence intensity due to the two species decaying with decay constants τ_1 and τ_2, respectively. Values of A_1 and A_2 for different systems are given in Table 4. Our experimental findings indicate that the value of A_2/A_1 increases as the wavelength of collection of emission increases. This can be rationalized in view of increased percentage of steady state emission due to dye−metal ion complex at higher wavelength. The value of A_1/A_2 for a particular salt concentration, however, reaches a limiting value at higher wavelength. The result indicates that in the solution two decaying species exist in equilibrium. Thus both steady state and time-resolved studies indicate complexation of a ketocyanine dye (S_1 state) with alkali metal ions. The value of K_1, characterizing the equilibrium (12), can be estimated from the time-resolved fluorescence data as follows. The ratio of the amount of two decaying species in solution is given by $(A_2/A_1)_l(\Phi_1/\Phi_2)$, where $(A_2/A_1)_l$ represents the limiting value of (A_2/A_1) and Φ_1 and Φ_2 are the values of the quantum yields of the two emitting species. When the radiative decay constant (k_r) is constant, quantum yield is proportional to τ-values, and the ratio of the concentration of the two decaying species is given by $(A_2/A_1)_l(\tau_1/\tau_2)$. The value of the equilibrium constant can thus be estimated from the limiting value of (A_2/A_1) at higher wavelength, the values of the lifetimes for the complexed and solvated dyes, and the corresponding salt concentration. The values of K_1 have been listed in Table 3. Note that for a particular solvent and a particular metal ion the value of the equilibrium constant for complexation involving the S_1 state of the dye is greater than that for the complexation involving the dye in the S_0 state. This indicates formation of a stronger complex with the S_1 state of the ketocyanine dye. The decay curve for ethanol solution of the dye containing metal ions can be best fitted by a single-exponential fit. The decay constant as given in Table 3 is close to that of the dye in ethanol (Table 3), indicating that the nature of dye−metal ion interaction is similar to that of dye−ethanol interaction.

4. Discussion

In a protic dipolar solvent a ketocyanine dye exists as charge-separated form (Figure 5) and a weak intermolecular interaction takes place between the solute and the solvent dipoles. The absorption band is supposed to originate due to a $\pi \rightarrow \pi^*$ transition with a significant intramolecular charge transfer (ICT) from the N-atom to the carbonyl oxygen in the molecule.[2a] The dipole moment of the dye in the S_1 state has been found to be greater than that in the ground state.[2a,b] Due to the ICT following excitation, the structure of the dye in the excited state can be presumably be represented by a resonance hybrid having contributions from the "keto" form and to a small extent the charged transferred "enol" form (Figure 5).[14] The relative weights of the two resonating forms have been found to depend on solvent polarity.[21] Thus the interaction of the dye molecule with the surrounding solvents molecules is greater in the S_1 state and a red shift of the absorption band on increasing the polarity of solvent occurs. In a protic solvent such as ethanol the enol form is likely to contribute to the ground state structure due to strong hydrogen bond interaction with the solvent.[1,3,5] The contribution of the enol form increases on excitation. Thus, following excitation the system changes from mostly two isolated diene-like structure to an almost fully conjugated structure involving nine carbon atoms. The extensive conjugation results in a dramatic decrease in the value of the energy of the $S_1(\pi\pi^*)$ state which leads to the pronounced red shift of the absorption/fluorescence band of the dye in protic solvents. Alkaline earth metal ions, when present in solution in aprotic solvents, interact with the carbonyl group of the dye, and the relative weight of the enol form in the ground state as well as in the excited state increases. The situation is similar in the case of the dye in protic solvents. This is also reflected in the closeness of the values of E(A) and E(F) of the dye in ethanol

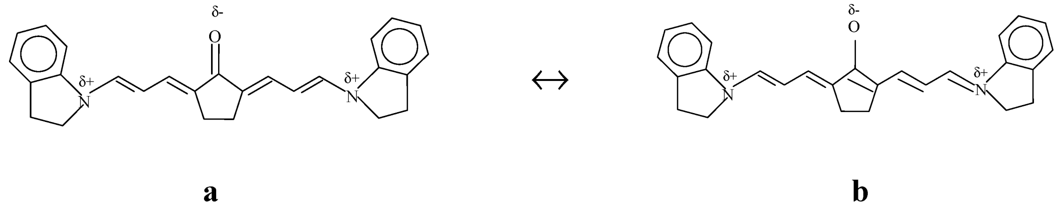

Figure 5. Resonating structures of a ketocyanine dye: the charge-separated keto form (a) and enol form (b).

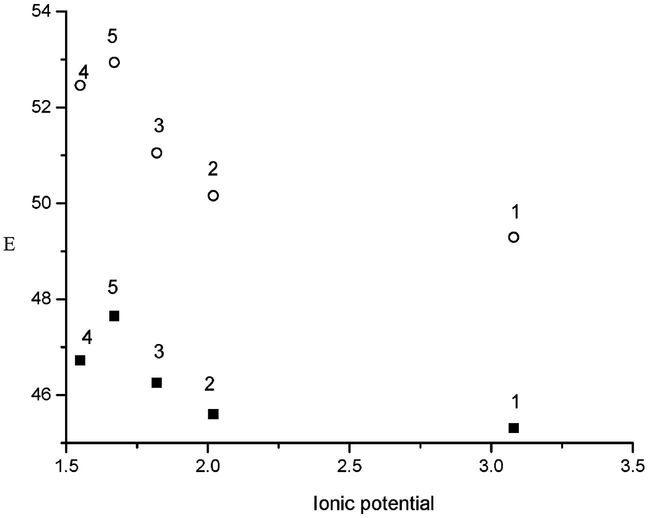

Figure 6. Plot of energy of maximum absorbance, *E*(A) (○), and energy of maximum fluorescence, *E*(F) (■), of dye 1−metal ion complexes as a function of ionic potential. (1) = Mg^{2+}, (2) = Ca^{2+}, (3) = Sr^{2+}, (4) = Ba^{2+}, and (5) = Li^{+}.

(52.0 and 46.1 kcal mol^{-1}) and those of the dye−metal ion complex (Tables 1 and 2). The value of the equilibrium constant for ground state complexation is also similar to that for the dye−ethanol interaction reported in the literature.[2a] This also indicates the similarity of the strength of dye−M^{2+} and dye−ethanol interactions. The strength of the interaction of metal ions with the dye (S_0 state), as reflected from the values of E_C, the energy of maximum absorption, follows the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The observed order of thermodynamic parameters also supports this. Similarly, the variation of spectroscopic and thermodynamic parameters involving the dye in the S_1 state also follows the same order.

The interaction of M^{2+} with the S_1 state of the dye is expected to be stronger in view of the greater relative weight of the enol-like structure. This is also reflected in significantly higher values of the equilibrium constant for the complexation involving the S_1 state of dye compared to that involving the S_0 state. The nature of the interaction in the weak molecular complex formed between the dye and the metal ion is predominantly electrostatic as is reflected from the plots of *E*(A) and *E*(F) versus the ionic potential of the ions (Figure 6). However, a small electron donor−acceptor interaction as suggested by Doroshenko et al.[8] cannot be ruled out. The lower value of *K* for ground state complexation in ethanol as compared to that in aprotic solvent is also rationalizable in terms of the comparable strengths of dye−Mg^{2+} and dye−ethanol interactions.

The longer lifetime of the dye−metal ion complex as compared to that of the dye in aprotic solvent can be explained as follows. The presence of the carbonyl group in molecules of dyes introduces the singlet and triplet ($n\pi^*$) terms in addition to singlet and triplet ($\pi\pi^*$) terrms in the system of energy levels. It has been observed by others[5] that the relative positions of the energy levels change with a change of solvents. Normally in aprotic solvents the lowest excited singlet, $S_1(\pi\pi^*)$, lies above the $T(n\pi^*)$ state. However, in protic solvent the $S_1(\pi\pi^*)$ state gets stabilized and becomes lower in energy relative to the $T(n\pi^*)$ state. A similar situation can arise when the dye interacts with a metal ion. This makes the nonradiative decay path through ISC [$S_1(\pi\pi^*) \rightarrow T(n\pi^*)$] unfavorable, decreasing the overall value of k_{nr}. Thus the lifetime increases. A similar mechanism is also believed to operate for making the lifetimes of these dyes in protic solvents longer.[5,4]

5. Conclusion

Alkaline earth metal ions form complexes with ketocyanine dyes in the S_0 and S_1 states. Spectroscopic and thermodynamic parameters for the interactions in solution can be studied by absorption, steady state, and time resolved fluorescence spectroscopic methods. The extent of interaction for a particular dye in an aprotic solvent follows the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. For a particular ion the extent of interaction as reflected by spectroscopic and thermodynamic parameters depends on the nature of the solvent. Stronger interactions are exhibited in aprotic dipolar solvent.

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