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Lithium Ion−Ketocyanine Dye Interactions in the Ground and Excited States

Jayanta Kumar Basu, Mrinmoy Shannigrahi, and Sanjib Bagchi*

Department of Chemistry, The University of Burdwan, Burdwan 713104, India

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Electronic absorption and emission spectral characteristics of a ketocyanine dye have been studied in solution in the presence of lithium perchlorate. Absorption spectral studies indicate complex formation between lithium ion and the dye in the ground state. The value of the equilibrium constant along with the molar absorbance of the absorbing species has been determined for the dye−cation interaction. The energy of maximum fluorescence shifts toward the red with the addition of $LiClO_4$. Steady-state emission studies point to the existence of two emitting species, viz., the solvated and the complexed dye in equilibrium. The values of the equilibrium constant for the process have been determined in acetone and acetonitrile. Time-resolved studies in the picosecond domain in pure solvents reveal that the lifetime (τ) value increases as the solvation interaction increases. Time-resolved studies also indicate the presence of two emitting species in equilibrium.

Introduction

Interaction of electrolytes with a dipolar solute leading to modification of spectral parameters of the solute in solution has long been studied.[1] The effect is particularly prominent when the solute possesses charge separation in the ground or in the excited state. In analogy to the introduction of solvent polarity as provided by solvent effect on charge transfer (CT) transitions,[2−4] the polarity parameters involving the maximum energy of absorption have been proposed for electrolyte solutions.[4−6] Attempts have been made to explain the spectral changes as due to the electric field effect of the ion,[7] but in many instances it has been found that the observed spectral changes are due to a change in speciation, rather than due to the nonspecific electric field effect.[8] In most of the investigations the absorption spectral parameters of solutes have been utilized. Studies involving emission properties of solutes are rather scanty.[9,10] Besides providing information regarding the maximum energy of transition, the emission studies in the steady-state and time-resolved domain provide parameters that depend on the microenvironment of the solute molecule. Ketocyanine dyes form a class of compounds that are characterized by solvent dependent absorption and fluorescence properties.[11] The electronic spectral transition in these compounds depends significantly on the interaction of the dye molecule with the molecules in its micro-environment. As a result, they act as good probes for studying environmental effects. In our laboratory we have studied solvation interaction of these dyes in pure,[12] mixed binary[13] and ternary[14] solvents and also in various microheterogeneous media[15] by using the fluorescence parameters. In a recent communication we have reported a preliminary study on the effect of electrolytes on ground- and excited-state properties of a ketocyanine dye.[16] It has been observed that the Li^+ ion in aprotic solvents brings about a significant change in spectral properties. Further, a complex is formed between the cation and the dye molecule in the ground (S_0) and the excited (S_1) states. The objective of the present work is to investigate in detail the interaction of Li^+ with these dyes in solution. To this end we have studied the electronic absorption, steady-state and time-resolved fluorescence of the ketocyanine dye (as shown in Figure 1) in solutions containing different concentrations of lithium perchlorate. Solvents used are acetonitrile (ACN), acetone (AC) and ethanol (ETOH).

Experimental Section

Materials. The ketocyanine dye has been prepared by the method described in the literature.[11] Purity of the prepared compound was 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.[17,18] All the solvents were refluxed for several hours with calcium hydride and then distilled immediately prior to the experiment. Lithium perchlorate [Lancaster] was dried in an oven before use. Samples were prepared in a drybox so as to avoid contamination by air or moisture. the concentration of the dye was taken in the range $10^{-5}-10^{-6}$ M in all the spectral measurements. The concentration of lithium ion was on the order of $\sim 10^{-2}$ M.

Steady-State Spectral Measurements. Absorption (UV−vis) spectral measurements were performed on a Shimadzu UV 1601 PC spectrophotometer fitted with an electronic temperature controller unit (TCC-240 A). The steady-state fluorescence emission and excitation spectra were recorded on a Hitachi F-4500 spectrofluorometer equipped with a temperature controlled cell holder. The temperature was controlled within ±0.1 K by circulating water from a constant-temperature bath (Heto Holten, Denmerk).

Time-Resolved Fluorescence Measurement. Fluorescence decay was studied by time correlated single photon counting (TCSPC) using the Fluorocube lifetime system (IBH, s/n 04412). The detailed experimental setup is as follows. A nanoLED of 463 nm (IBH, UK, NanoLED-07 B, s/n 04224) was used as the excitation source with fwhm on the order of 1 ns and the pulse is passed through a 5000 M emission monochromator. The fluorescence signal was detected in magic angle polarization using cooled red-sensitive photocathode (TBX-04-A) detector with a response time of 180 ps. The decays were analyzed using IBH DAS-6 decay analysis software. Intensity decay curves were then fitted with single/biexponential decay equations. The

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* Corresponding author. E-mail: bsanjibb@yahoo.com.

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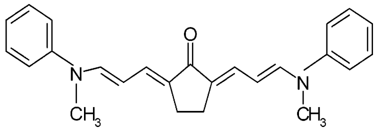

Figure 1. Dye used in the present work.

fluorescence decay was measured as a function of the concentration of $LiClO_4$. For a particular concentration the decay was studied at different emission wavelengths. 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

$$F(t) = a \exp(-t/\tau) \tag{1}$$

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

$$F(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \tag{2}$$

where *a*'s are the relative contributions to the lifetime componentsτ_1 and τ_2.

Analysis of Spectral Data. Equilibrium constant corresponding to dye−Li $^+$ interaction was determined as follows. A measured volume of the dye solution in a given solvent was taken in a stoppered quartz cuvette and 0.2 mL solution of $LiClO_4$ in that solvent was added to it. The absorption and fluorescence spectra were then determined. Addition of $LiClO_4$ solution was repeated several times and spectra were measured after each addition. The ineteraction of the dye (D) in the ground (S_0) state with Li $^+$ ion can be expressed by the following equilibrium.

$$n\mathrm{Li}^+ + \mathrm{D...S} = \mathrm{D...Li}_n{}^+ + \mathrm{S} \tag{3}$$

$$K = C_M/C_S(C_{Li^+})^n \tag{3a}$$

where *n* is the minimum order of participation of lithium ion in the equilibrium and C_S, C_M and C_{Li} represent the molar concentrations of the solvated dye, the metal-complexed dye and the lithium ion, respectively.

For a given solution where both the solvated dye (D...S) and the complexed dye (D...Li$_n{}^+$) are present, the absorbance for unit path length for a particular wavelength λ, $A(\lambda)$, is given by the Beer's law as follows

$$A(\lambda) = \epsilon_S(\lambda)C_S + \epsilon_M(\lambda)\mathrm{C_M} \tag{4}$$

In eq 4, ϵ (λ) represents the molar absorptivity at the wavelength λ and suffixes S and M denote the solvated and the metal-complexed dye, respectively. The ratio (C_M/C_S) can be obtained by measuring absorbance values at two wavelengths λ_1 and λ_2 and using[8]

$$(C_M/C_S) = [A(\lambda_1)\,\epsilon_S(\lambda_2) - A(\lambda_2)\,\epsilon_S(\lambda_1)]/[A(\lambda_2)\,\epsilon_M(\lambda_1) - A(\lambda_1)\,\epsilon_M(\lambda_2)] \tag{5}$$

Values of λ_1 and λ_2 were chosen as the wavelengths of maximum absorption of the solvated and the complexed dye, respectively. Values of ϵ_S and ϵ_M were determined from spectra of the dye in the given solvent and that saturated with $LiClO_4$, respectively. Equation 3a can be rearranged as

$$\log(C_M/C_S) = \log K + n \log C_{Li^+} \tag{6}$$

The equilibrium constant, *K*, and the minimum order of participation of the Li^+ ion, *n*, can be calculated by plotting log(C_M/C_S) versus log C_{Li^+} and using eq 6.

An alternative method can also be used to calculate *K* for *n* = 1. Using (3a) and (4), we can write

$$A(\lambda)/C_D = [\epsilon_S(\lambda) + \epsilon_M(\lambda)KC_{Li^+}]/[1 + KC_{Li^+}] \tag{7}$$

In eq 7 $C_D = C_S + C_M$ is the total concentration of the dye in solution. Values of *K*, $\epsilon_S(\lambda)$ and $\epsilon_M(\lambda)$ that give the best fit to eq 7 in the least-squares sense were determined, by a linear regression analysis. The equilibrium constant for the interaction between the dye in the excited state and the lithium ion was determined by a method described earlier.[16] The observed maximum fluorescence energy, *E*(F), can be considered as mole fraction average of E_S and E_M, the maximum fluorescence energy of the two species, viz., the solvated and complexed forms of the dye.[19−22] Thus, one gets

$$E(\mathrm{F}) = (C_S E_S + C_M E_M)/(C_S + C_M) \tag{8}$$

Equation 8 can be rearranged to give

$$E(\mathrm{F}) = E_S + E_M K_1 C_{Li} - K_1 E C_{Li} \tag{9}$$

where K_1 is the equilibrium constant for the following process.

$$S\mathrm{....D\ (S_1\ state)} + \mathrm{Li}^+ = \mathrm{Li....D\ (S_1\ state)} + \mathrm{S} \tag{10}$$

Values of E_S, E_M and K_1 that fit eq 10 can thus be obtained by a linear regression analysis.

Results and Discussion

Absorption Studies. Absorption band maximum of the dye in acetone or acetonitrile shifts to the red as $LiClO_4$ is added to the system. Only the cation of the electrolyte has been found to be effective in band shifts. The band maximum in aprotic dipolar solvents (AC and ACN) shows a moderate red shift for a lower concentration of the lithium ion. For a higher salt concentration a dramatic red shift is observed and a second band emerges that shows no substantial shift on further addition of the salt. Such a spectral variation agrees well with the observation made by Pocker et al.[23] and Rezende et al.[24] where a dye−cation complex formation takes place. For a fixed dye concentration an isosbestic point appears in the absorption spectrum in the solvents containing varying amount of the salt. Figure 2 shows representative absorption curves in solvents containing lithium perchlorate. This points clearly to the existence of an equilibrium between two forms, viz., the solvated and the Li^+ ion complexed dye. At a very high concentration of $LiClO_4$ the complexed form of the dye exists almost exclusively in the solution and the absorption band is due to this species only. Thus the complexed dye absorbs at 525 nm in AC and at 515 nm in ACN. This may be compared with the absorption maximum at 470 and 475 nm for the dye in pure AC and ACN, respectively. The position of the absorption maximum, however, does not change when salts containing bulky organic ions, e.g., tetramethylammonium (TMA) ions or tetrabutylammonium (TBA) ions, are added to AC/ACN solution of the dye. Significant spectral changes also do not take place when lithium percholorate is added to ethanolic solution of the dye.

In aprotic dipolar solvents such as AC or ACN a weak intermolecular interaction takes place between the solute and the surrounding solvent dipoles. With the addition of an electrolyte the positively charged cation competes with the solvent dipoles for the negative center in the dye molecule,

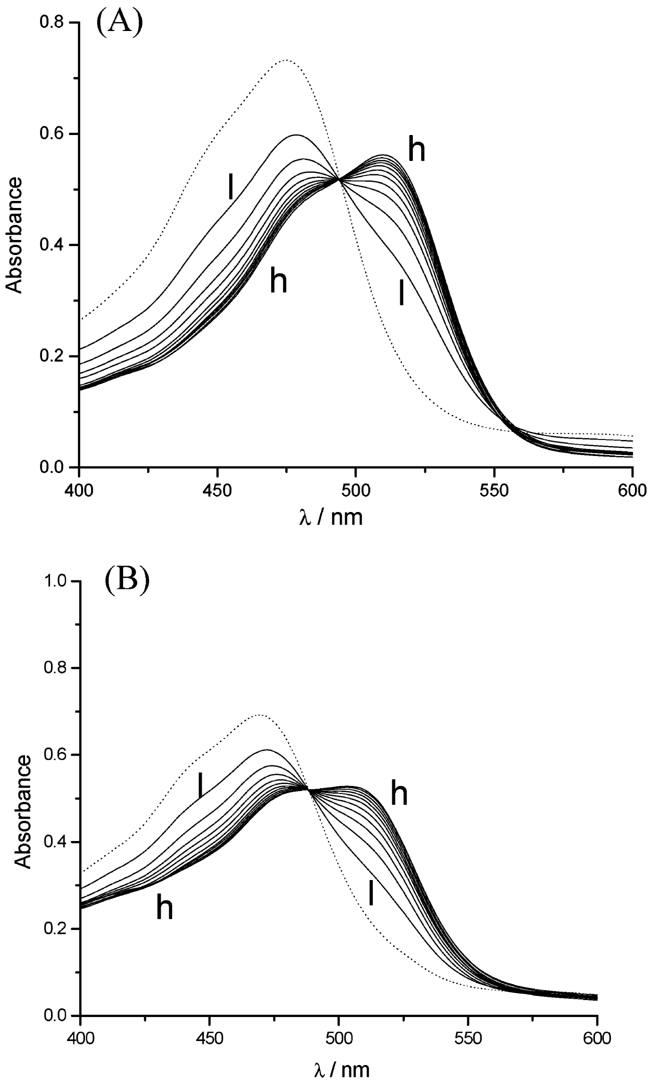

Figure 2. Absorption spectra of the dye in (A) ACN and (B) AC containing different concentrations of $LiClO_4$. The concentration increases in the order l → h. Dotted lines represent pure solvents.

TABLE 1: Best Fit Values of K, ϵ_M, and ϵ_S Calculated at Different λ along with the Fitting Statistics for the Two Solvents at 298 K

solvent	λ/nm	$10^{-5}\epsilon_M$[a]	$10^{-5}\epsilon_S$[a]	K[b]	av K	R^2	σ
AC	495	1.7 ± 0.1	2.4 ± 0.2	5.2 ± 0.2		0.998	0.0001
	500	1.7 ± 0.1	2.4 ± 0.2	5.8 ± 0.2		0.988	0.0001
	505	1.8 ± 0.2	2.3 ± 0.2	6.2 ± 0.2		0.999	0.0001
	510	1.8 ± 0.2	2.2 ± 0.2	6.6 ± 0.2	6.3 ± 0.2	0.999	0.0001
	515	1.6 ± 0.2	2.0 ± 0.2	6.8 ± 0.2		0.999	0.0001
	520	1.5 ± 0.1	1.7 ± 0.2	6.7 ± 0.2		0.999	0.0001
	525	1.2 ± 0.1	1.4 ± 0.1	6.6 ± 0.2		0.999	0.0001
	530	1.0 ± 0.1	1.0 ± 0.1	6.4 ± 0.2		0.999	0.0001
ACN	500	1.4 ± 0.2	1.5 ± 0.1	5.2 ± 0.1		0.978	0.0002
	505	1.4 ± 0.2	1.3 ± 0.1	7.1 ± 0.1		0.988	0.0002
	510	1.3 ± 0.2	1.0 ± 0.1	8.6 ± 0.2	7.0 ± 0.2	0.998	0.0002
	515	1.1 ± 0.2	0.6 ± 0.1	7.0 ± 0.2		0.999	0.0002

[a] In L mol^{-1} cm^{-1} unit. [b] The chosen concentration unit is mol L^{-1}.

namely, the carbonyl oxygen. At a low concentration of the electrolyte the cation cannot replace the solvent molecule in the vicinity of the carbonyl group. As a result, at low salt concentration the solvated dye molecule experiences relatively weak perturbation due to metal ion and the shift is less pronounced. At higher salt concentration, however, the cation replaces a solvent molecule and a weak bond between the metal ion and the carbonyl oxygen of the dye molecule is formed. Beyond this point there is no substantial perturbation on the dye−lithium ion complex and no significant change in spectral property is observed. Formation of a dye−cation complex is rationalizable in view of the small size and stronger Lewis acidity of the Li^+ ion. The absorption band is supposed to originate due to a $\pi \rightarrow \pi^*$ transition with a significant transfer of charge from the N-atom to the carbonyl oxygen in the molecule.[12] The dipole moment of the dye in the excited (S_1) state has been found to be greater than that in the ground state.[13] Thus, the greater the interaction of the dye with the surrounding molecules, the greater is the red shift of the absorption band. Our experimental results indicate that the dye−Li^+ ion interaction is greater than the dye−solvent interaction. In the case of TMA or TBA ions, the positive charge on the N atom is shielded by the bulky alkyl groups and as such they do not interact with the dye molecule and thus no spectral change takes place. A protic solvent, ethanol, forms a hydrogen bond with the carbonyl oxygen of the dye molecule in the ground state and a metal ion cannot dislodge the bond between the solvent and dye. Thus no dye−lithium ion complex is formed and the band shift is insignificant.

The equilibrium for dye−lithium ion interaction, as given by eq 3, has been studied from spectral data. The value of n, the number of Li^+ ion participating in equilibrium (3), has been determined by plotting $\log(C_M/C_S)$ versus $\log C_{Li}$, as discussed in the previous section. Linear plots with slope 1.1 ± 0.1 were obtained for both solvents, indicating 1:1 complex formation. Values of K as estimated from the plots were 10 and 12, respectively, for acetone and acetonitrile. Values of K, ϵ_S and ϵ_M have also been determined at different wavelengths assuming $n = 1$ by the alternative method described in the previous section (eq 7). Results have been summarized in Table 1. The agreement of K values obtained by the two methods differs slightly. Although the relative order of K values for the two solvents is the same. This is rationalizable in view of the weak nature of the complex formed in the ground state. Moreover, values of K for a particular solvent are almost independent of the wavelength of measurement. As expected, the values of ϵ_M and ϵ_S are dependent on the wavelength. Figure 3 shows ϵ_M and ϵ_S as a function of wavelength.

Steady-State Emission Studies. The maximum wavelength of fluorescence of the dye shifts to the red as the concentration of Li^+ ion in the solution increases, as can be seen from Figure 4. However, the wavelength of maximum fluorescence reaches a limiting value (565 nm for ACN and 555 nm for AC) for higher Li^+ ion concentrations. Apart from a band shift, the shape of the band also changes. The band for a particular salt concentration can be represented of as a sum of two Gaussian functions. Table 2 shows some representative figures for acetone solution. The experimental results indicate that two emitting species with maximum fluorescence wavelength at ~520 nm and ~555 nm exist in acetone solution. Although the first value is very near to the wavelength of maximum fluorescence of the dye in pure acetone, the second value compares well with the value of maximum fluorescence wavelength for acetone solution of the dye saturated with $LiClO_4$. Thus the values of maximum wavelength correspond to the solvated and the complex form of the dye in the S_1 state. For ACN solvent the corresponding values are 540 and 570 nm, respectively. The emission spectra of solutions at various salt concentrations for a fixed total dye concentration indicate an isosbestic point, as can be seen from Figure 4. This also points to the existence of two emitting species in equilibrium in the solution. Note that TMA and TBA ions do not affect the fluorescence band maximum in ACN or AC solvent. No significant shift of

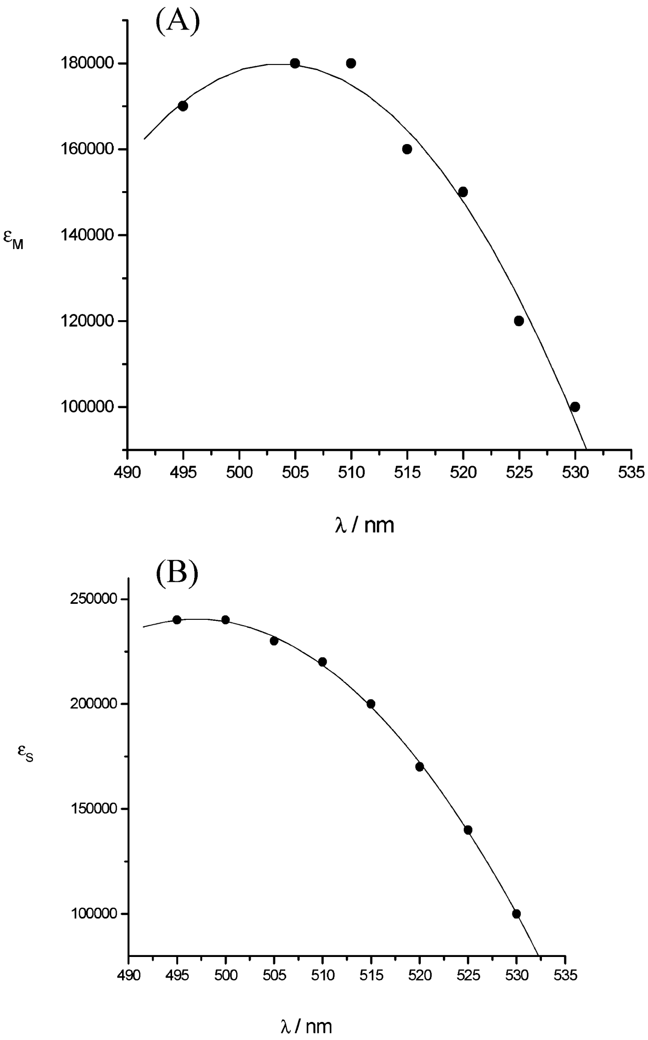

Figure 3. Plot of ϵ_M and ϵ_S in acetone as a function of wavelength.

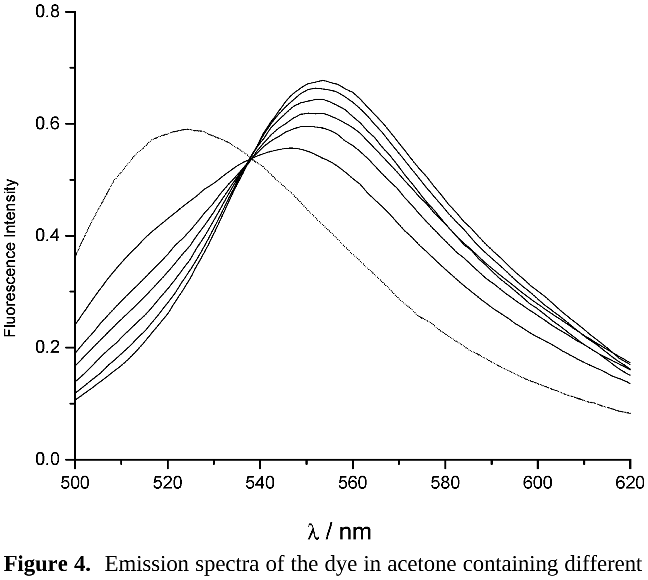

Figure 4. Emission spectra of the dye in acetone containing different concentrations of $LiClO_4$.The dotted line represents pure solvent.

fluorescence band could be detected when lithium perchlorate is added to ETOH solution of the dye. As stated earlier, in ethanol the dye molecule exists as H-bonded species and the metal ion cannot break the H-bond in theground state. In the S_1 state the dye molecule has greater charge density on the carbonyl oxygen and as such the H-bond becomes tighter.

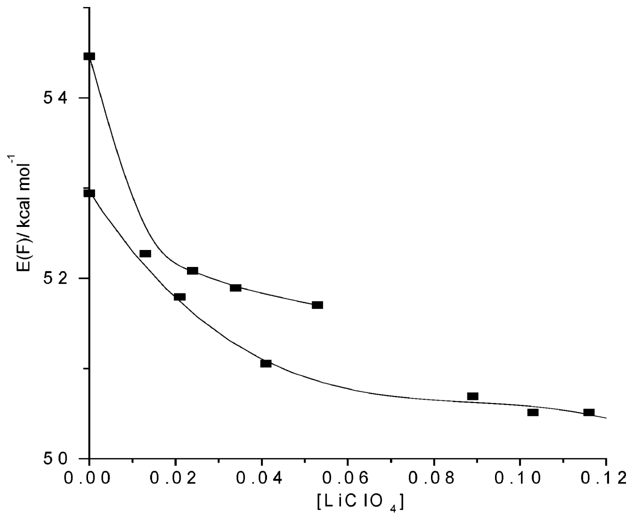

Figure 5. Plot of E(F) as a function of the concentration of $LiClO_4$ for acetone (top curve) and acetonitrile (bottom curve).

TABLE 2: Parameters Showing the Decomposition of Emission Band into Two Gaussian Curves

	centers			
concn of $LiClO_4$ in AC/M	λ_1/nm	λ_2/nm	A_1/A_2	R^2
0.013	518	552	0.1286	0.983
0.024	515	553	0.0127	0.978

TABLE 3: Best Fit Values of E_S, E_M, and K_1 as a Function of Solvent at 298 K

solvent	$E_S{}^a$	$E_M{}^a$	K^b
acetone	53.8 ± 0.1	51.3 ± 0.1	91 ± 9
acetonitrile	52.9 ± 0.1	50.0 ± 0.1	31 ± 3

[a] In kcal mol^{-1}. [b] The chosen concentration unit is mol L^{-1}.

Figure 5 shows plots of E(F) values, the energy of maximum fluorescence, calculated by using the relation: $E(F)/kcal\ mol^{-1} = 28\,590/(\lambda/nm)$, as a function of lithium ion concentration, C_{Li}. For a particular solvent the slope of E(F) versus C_{Li} plot is large for small values of C_{Li} and the slope decreases with salt concentration and finally E(F) tends toward a limiting value. The equilibrium constant, K_1, representing the dye (S_1 state)$-Li^+$ ion interaction (eq 10), along with the values of E_S and E_M have been calculated from the observed E(F) values using eq 9. The calculated values for AC and ACN have been listed in Table 3. Note that value of E_S is greater than that of E_M for both solvents. Moreover, these values agree well with the values of wavelength of maximum fluorescence of the corresponding species as obtained by a Gaussian analysis of spectral band. The value of K_1 depends on the nature of the solvent and in the present case it follows the order AC > ACN. The relative order of K_1 values in two solvents reverses to that obtained from absorption study. This indicates a stronger complexation in the excited state as compared to the ground state of the dye. It is interesting to compare the effect of addition of $LiClO_4$ to solutions of the dye in acetonitrile and acetone. It has also been shown that[13] the dye−solvent interaction is determined by the dipolarity−dipolarizability, hydrogen bond donation and acceptor ability of a solvent as represented respectively by the solvatochromic parameters π^*, α and β.[25] Values of α, β and π^* for acetonitrile are 0.19, 0.40 and 0.75, whereas those for acetone are 0.08, 0.48 and 0.71, respectively.[25] Thus the dye−solvent interaction would be higher in acetonitrile than in acetone. This is also reflected in the values of the fluorescence maximum of the dye in acetone (55.0 kcal mol^{-1}) and

TABLE 4: Values of τ and k_{nr} for Different Pure Solvents

solvent	τ/ps	10^8k_{nr}/s^{-1}	a	π^b
methanol	1560	3.2	0.93	0.6
ethanol	1210	5.1	0.83	0.6
2-butanol	850	8.5		
acetonitrile	620	12.9	0.19	0.75
butyronitrile	400	21.8	0.00	0.7
acetone	400	21.8	0.08	0.7
triacetin	690	11.3		
ethyl acetate	300	30.2	0.00	0.55

acetonitrile (52.9 kcal mol^{-1}). Thus, on addition of $LiClO_4$ a pronounced change will be observed for acetone than for acetonitrile. Note that the E(F) values change more sharply when $LiClO_4$ is added to acetone (Figure 5). The S_1 state of the dye, being more polar, is expected to interact with the solvent to a greater extent. The value of K_1 which indicates the differential interaction between dye−solvent and dye−metal ion, also points to this.

Time-Resolved Studies. The decay of the excited singlet state of the dye has been measured in some representative solvents and also in electrolyte solutions. For pure solvents the decay has been found to be represented by a single exponential (eq 1). Values of lifetime (τ) for a various solvents have been listed in Table 4. It appears that the τ value increases with the polarity of solvents. A solvent characterized by greater solvation interaction with the dye shows higher τ value. Values of k_r and k_{nr}, the decay constant via radiative and nonradiative pathways, have been determined from a knowledge of quantum yield of the dye in pure solvents.[26] It has been reported earlier that the value of k_r for the ketocyanine dyes is independent of the nature of the solvents.[27] Values of k_{nr} can be calculated using the following equation

$$\tau^{-1} = k_r + k_{nr} \qquad (11)$$

We have calculated k_{nr} using $k_r = 3.2 \times 10^8$ s^{-1}.[27] Values of k_{nr} in different pure solvents have been listed in Table 4. Note that the k_{nr} values depend significantly on the polarity of solvents. To investigate the dependence of k_{nr} on different modes of solvation interaction, a multiple linear regression analysis of log k_{nr} with the Kamelet−Taft parameters[25] α, β and π* has been sought. It appears that the correlation is best represented by the following equation.

$$\log k_{nr} = 9.97 - 0.9626\alpha - 0.869\pi^*$$

$$n = 6,\ R^2 = 0.989,\ \sigma = 0.54 \qquad (12)$$

Thus apart from the polarity−polarizability parameter π*, log k_{nr} depends on the hydrogen bond donation (HBD) ability of the solvents represented by the parameter α. This is rationalizable in view of electron pair donation by the carbonyl oxygen in the excited state to HBD solvents.

In solutions containing lithium perchlorate, however, a biexponential decay, as given by eq 2, has been observed. A single-exponential decay, characterized by a τ value of 1100 ps, has been observed only in a solution saturated with the electrolyte, and the value is practically independent of the aprotic solvent (AC and ACN) used. The biexponential decay characteristics have been studied at different concentrations of salt. For a fixed salt concentration the decay characteristics have been studied by collecting emission at various wavelengths (λ) in the emission band of the dye. Results have been summarized in Table 5. For all the solutions the decay is characterized by a shorter (τ_1) and a longer (τ_2) lifetime. Our studies with pure solvent indicate that the species characterized by a faster decay rate (τ_1) corresponds to the form of the dye with smaller interaction and vice versa. Again results in the steady-state fluorescence indicate that the dye−lithium ion interaction is greater than the dye−solvent interaction and hence the species with greater τ value can be identified as the cation-complexed dye. This is also consistent with the observed τ value of 1100 ps, in saturated electrolyte solutions. For a fixed salt concentration the ratio of a_1 and a_2, the relative contributions of lifetime values τ_1 and τ_2, respectively, have been found to be dependent on the choice of λ, as can be seen from Table 5. The fluorescence intensity for a given λ is given by

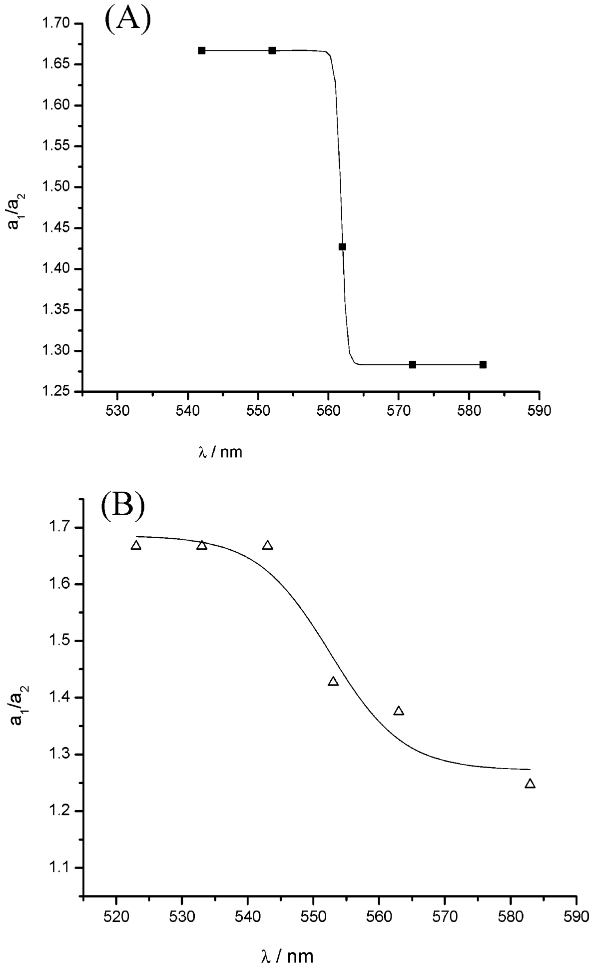

Figure 6. Plot of a_1/a_2 as a function of wavelength for fixed salt concentration: 0.041 M in ACN (A) and 0.045 M in AC (B).

TABLE 5: Analysis of Decay Curve for a Fixed Concentration of $LiClO_4$ as a Function of λ at 298 K

solvent	λ/nm	τ_1/ps	τ_2/ps	a_1	a_2	a_1/a_2
acetone	523	260	840	0.625	0.375	1.667
$C_{Li^+} = 0.045$ M	533	260	840	0.625	0.375	1.667
	543	260	840	0.625	0.375	1.667
	553	260	840	0.588	0.412	1.427
	563	260	860	0.579	0.421	1.375
	573	250	850	0.526	0.474	1.109
	583	270	850	0.555	0.445	1.247
acetonitrile	522	200	760	0.769	0.231	1.667
$C_{Li^+} = 0.014$ M	532	300	910	0.588	0.412	1.427
	542	260	820	0.625	0.375	1.667
	552	310	880	0.625	0.375	1.667
	562	300	910	0.588	0.412	1.427
	572	330	950	0.562	0.438	1.283
	582	320	960	0.562	0.438	1.283

$$F_\lambda = \int_0^\infty F_\lambda(t)\,\mathrm{d}t \tag{13}$$

Using eq 2, one can write

$$F_\lambda = a_1\tau_1 + a_2\tau_2 \tag{14}$$

Thus $a_1\tau_1$ and $a_2\tau_2$ represent the contribution of steady-state fluorescence intensity due to the two species decaying with decay constants $\tau_1$and τ_2, respectively. The ratio of the amount of two species in solution is given by $(a_1\tau_1/\Phi_1)/(a_2\tau_2/\Phi_2)$, where Φ_1 and Φ_2 are the quantum yields of the two emitting species. In the event that quantum yield is proportional to τ values (i.e., constantly of k_r), a_1/a_2 gives the ratio of the concentration of the two decaying species. Our experimental findings show that a sigmoid curve is obtained when a_1/a_2 is plotted against λ. Figure 6 shows a representative plot. The result indicates that in the solution two decaying species exists in equilibrium.

Conclusions

(1) The energy of maximum absorption and the steady-state fluorescence of the ketocyanine dye depend significantly on the presence of Li^+ ion.

(2) Absorption spectral studies point to the formation of a cation−dye complex in the ground (S_0) state.

(3) Steady-state and time-resolved studies in the picosecond domain indicate that the ketocyanine dye forms a complex with Li^+ the S_1 state.

(4) The lifetime of the excited state of the dye complexed by Li^+ ion is greater than that of an uncomplexed dye.

(5) Value of log k_{nr} shows a linear correlation with the dipolarity−polarizability (π^*) and hydrogen bond donation ability (α) of solvents.

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