Solvent dependent absorption and fluorescence of a ketocyanine dye in neat and binary mixed solvents

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Received 11 March 1994; revised and accepted 23 September 1994

The environmental effect on the ground and excited state properties of a ketocyanine dye has been studied by monitoring its absorption and fluorescence characteristics in various pure and binary mixed solvents. The spectroscopic transition leading to the longest wavelength absorption or fluorescence has been found to involve considerable intramolecular charge transfer as evidenced by semiempirical MO calculations at the AM1 level. Ground state complexation is indicated in protic solvents, aromatic hydrocarbons and cyclic ethers. The fluorescence maximum, \( E(F) \), shows a correlation with \( E_1(30) \) scale of solvent polarity. A multiple linear correlation of \( E(F) \) with Kamlet-Taft parameter representing solvent dipolarity (\( \pi^* \)) and hydrogen bonding ability (\( \alpha \) and \( \beta \)) suggests that apart from dipolar interactions specific solute-solvent interactions are important in determining fluorescence maxima. Study of \( E(F) \) in mixed binary solvents points to a preferential solvation of the solute in the \( S_1 \) state.

The polarity probes have found extensive applications during the last couple of years, especially for the evaluation of various microenvironmental properties. Although a large number of micropolarity reporters involving solvatochromic spectral transition are known, e.g., 4-methoxycarbonylpyrindium iodide, betaine, 4-cyanopyridinium iodide, etc., practically all of them are non-fluorescent. Fluorescent polarity probes are more advantageous compared to non-fluorescent probes because of their widespread applications in biological systems. Merocyanine dyes constitute an interesting system for solvatochromic studies. Some of these compounds show solvent-sensitive fluorescence. Recently, Kessler and Wolfbeis have reported the synthesis of a series of strongly fluorescent ketocyanine dyes having unique solvatochromic properties in both absorption and fluorescence. It has been observed that these compounds may act as good fluorescent probes for studying solvent polarity. Although fluorescence characteristics of the ketocyanine dyes have been studied in a few solvents, a systematic study of solvation characteristics is yet to be done. Besides this, a study of spectral characteristics in mixed binary solvents is of particular interest, for it may provide information regarding the preferential solvation characteristics of the absorbing/emitting species. The objective of the present paper is to study the solvation characteristics of a ketocyanine dye in pure and mixed binary solvents by monitoring its longest wavelength absorption and fluorescence band. The dye chosen for the present study is (1-1), (9-1)-di-1,9-di-(2,3-dihydroindolyl)-4,6-dimethylene- nona-1,3,6,8-tetraene-5-one (Fig. 1). Semiempirical calculations have been carried out to provide the optimised geometry, the charge distribution and the dipole moment in the ground state of the solute. It also gives information regarding the nature of the electronic transition associated with the longest wavelength absorption.

Materials and Methods

The dye (solute) was synthesised as described in literature. Indoline, 1,1,3,3-tetramethoxypropane and cyclopentanone were purchased from Sigma Chemicals (USA) and used as received. Purity of the prepared compound was checked by IR spectral data [IR bands obtained in KBr disc: 1620, 1580, 1485, 1400 cm\(^{-1}\)] and from absorption and fluorescence, spectral data [\( \lambda_{\text{max}} \) (abs) = 525 nm; \( \lambda_{\text{max}} \) (fl.) = 622 nm in ethanol]. All the solvents were purified and dried by standard procedures and distilled over CaH\(_2\) immediately before use to ensure the absence of peroxides and oxidising agents. Mixed solvents and corresponding solutions were prepared by carefully mixing the components so as to minimise contamination by moisture. Absorption spectra
were measured on a Shimadzu UV-160A spectrophotometer provided with a peak detection algorithm. Fluorescence spectra were recorded on a Hitachi F-3010 spectrofluorimeter equipped with a microprocessor and a chart recorder. Freshly prepared solutions were used for each measurement and the concentrations were chosen to give absorbances less than 0.1 to avoid distortion of the spectra due to reabsorption of the fluorescence light. The spectral studies were done using solutions having concentration of the dye in the range \(10^{-5}\) to \(10^{-6}\) mol dm\(^{-3}\). The observed absorption/fluorescence spectrum did not, however, depend on the concentration of the solute.

**Theoretical calculations**

Semiempirical MO calculations at the AM1\(^{12}\) (Austin model 1) level using the MOPAC program (QCPE 355) were carried out on a PC AT/386. A fully optimized geometry indicates a planarity of the molecule in the ground electronic state, except the aliphatic hydrogen atoms. The distribution of net charges over the atoms and the relevant bond distance is shown in Fig. 1. It appears that there is a significant alteration in the C–C bond length for C–C bonds occurring between the N-atom of the five-membered ring and the carbonyl oxygen atom. The dipole moment was found to be 4.02 D, directed exclusively in the direction of the carbonyl group. The molecule has a symmetry plane passing through the C=O bond and perpendicular to the molecular plane. The HOMO and LUMO have been found to be \(\pi\) molecular orbitals and the relevant coefficients of the \(p\)-atomic orbitals have been given in Table 1. While the HOMO is antisymmetric with respect to the symmetry plane, the LUMO shows a symmetrical behaviour. Moreover, HOMO→LUMO transition indicates a transfer of electron density from nitrogen to the oxygen atom. These findings indicate that in the ketocyanine dye (I) the shortest energy absorption band arises due to a \(\pi\text{-}\pi^*\) electronic transition involving an intramolecular charge transfer (ICT) from nitrogen donor to oxygen acceptor through the intervening conjugated system. The nature of electronic transition is thus similar to that in the merocyanine dyes\(^{2,6}\).

**Results**

**Absorption spectrum**

The results have been summarised in Table 2. Fig. 2A represents absorption spectra in some

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### Table 1 — Relevant coefficients of \(p\)-orbital appearing in LCAO for HOMO and LUMO

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Atom No.</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.29</td>
<td>9</td>
<td>-0.33</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>0.00</td>
<td>-0.30</td>
<td>18</td>
<td>0.33</td>
<td>0.16</td>
</tr>
<tr>
<td>3</td>
<td>0.29</td>
<td>-0.25</td>
<td>11</td>
<td>-0.18</td>
<td>-0.33</td>
</tr>
<tr>
<td>4</td>
<td>-0.29</td>
<td>-0.25</td>
<td>20</td>
<td>0.18</td>
<td>-0.33</td>
</tr>
<tr>
<td>7</td>
<td>0.15</td>
<td>0.33</td>
<td>13</td>
<td>0.34</td>
<td>0.08</td>
</tr>
<tr>
<td>16</td>
<td>-0.15</td>
<td>0.33</td>
<td>22</td>
<td>-0.34</td>
<td>0.08</td>
</tr>
</tbody>
</table>

---

Fig. 1 — The ketocyanine dye (I) [Numbering of atoms is shown in (a), the net charges over the atoms and the bond distances are shown in (b)]
representative pure solvents. The absorption 
spectra in all the aprotic solvents show similar 
structures which lose their prominence as the po-
larity of the solvent is increased. For aprotic 
solvents the shift of the absorption maximum \(E(A)\) 
is not very sensitive towards a change in the sol-
vent polarity as measured by \(E_T(30)\) parameter. 
Considering the ICT nature of the transition, one 
would expect the more polar solvent to yield the 
smaller transition energy. But the \(E(A)\) values for 
benzene, toluene, 1,4-dioxane and tetrahydrofur-
an are lower although these solvents are charac-
terised by lower polarity in the \(E_T(30)\) scale. 
Rather, the \(E(A)\) values in these solvents run par-
allel to the acceptor numbers of Gutmann. This 
points to an enhanced solute-solvent interaction 
in the ground state possibly through complex for-
mation in these solvents. This conclusion is also 
in accordance with the large solubility of the 
solute in these solvents. The solute is insoluble in \(n\)-hexane but it may be made soluble by addition of 
excess naphthalene; the solution gives similar 
spectrum as obtained with benzene. This also sug-
gests the solute-naphthalene interaction, possibly 
through the \(\pi\)-electron density of naphthalene. 
When \(n\)-hexane was added to a benzene solution 
of the dye a continuous blue shift was obtained 
and no isosbestic point could be detected. The 
structure and the shape of the band remained 
practically unaltered. A plot of \(E(A)\) against the 
mole fraction of \(n\)-hexane shows a deviation from 
linearity indicating that the solute is solvated pref-
rentially by benzene. The preference for benzene 
over \(n\)-hexane is intelligible in terms of enhanced 
benzene-solute interaction through complexation. 
A red shift (\(-3\) kcal mol\(^{-1}\)) is observed as we go 
from an aprotic solvent to a protic solvent. Simi-
larly of absorption in various alcohol solvents (as 
distinctly different from the other polar aprotic 
solvents) is suggestive of complex formation be-
tween an alcohol and the solute in the ground 
state. In a mixed solvent of ethanol with ethyl

![Figure 2](image-url)

**Fig. 2**—(A) Absorption spectra of (I) in neat solvents [1-propanol (1), benzene (2), ethyl acetate (3) & acetonitrile (4). (B) Absorption spectrum of (I) in ethanol + benzene binary mixture. Volume per cent of ethanol in the mixture: 0.2(1), 0.8(2), 2.0(3) 20.0(4) and 40.0(5)].

### Table 2—Relevant solvent parameters and the absorption and fluorescence energies of the ketocyanine dye in pure solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption (E(A)) max/kcal mol(^{-1})</th>
<th>Fluorescence (F(\epsilon)) max/kcal mol(^{-1})</th>
<th>(F(\epsilon))</th>
<th>(E_T(30))/kcal/mol (\pi^*)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\pi^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Methanol</td>
<td>54.5</td>
<td>45.0</td>
<td>0.616</td>
<td>0.95</td>
<td>56.3</td>
<td>0.93</td>
<td>0.66</td>
</tr>
<tr>
<td>(2) Ethanol</td>
<td>54.5</td>
<td>45.8</td>
<td>0.578</td>
<td>0.94</td>
<td>51.9</td>
<td>0.83</td>
<td>0.75</td>
</tr>
<tr>
<td>(3) 1-Propanol</td>
<td>54.8</td>
<td>46.1</td>
<td>0.548</td>
<td>0.93</td>
<td>50.7</td>
<td>0.78</td>
<td>0.80</td>
</tr>
<tr>
<td>(4) 1-Butanol</td>
<td>54.8</td>
<td>46.2</td>
<td>0.526</td>
<td>0.91</td>
<td>50.2</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>(5) 1-Pentanol</td>
<td>54.7</td>
<td>46.2</td>
<td>0.498</td>
<td>0.89</td>
<td>50.0</td>
<td>0.70</td>
<td>0.92</td>
</tr>
<tr>
<td>(6) 1-Octanol</td>
<td>55.0</td>
<td>47.6</td>
<td>0.453</td>
<td>0.86</td>
<td>48.5</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>(7) 2-Methoxyethanol</td>
<td>54.1</td>
<td>45.9</td>
<td>0.516</td>
<td>0.91</td>
<td>52.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8) 2-Ethoxyethanol</td>
<td>54.1</td>
<td>45.9</td>
<td>0.554</td>
<td>0.94</td>
<td>50.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9) 2-Propanol</td>
<td>53.9</td>
<td>47.7</td>
<td>0.546</td>
<td>0.92</td>
<td>48.6</td>
<td>0.76</td>
<td>0.84</td>
</tr>
<tr>
<td>(10) Cyclohexanol</td>
<td>54.7</td>
<td>47.6</td>
<td>0.470</td>
<td>0.90</td>
<td>46.9</td>
<td></td>
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<tr>
<td>(11) Water</td>
<td>50.3</td>
<td>44.0</td>
<td>0.640</td>
<td>0.98</td>
<td>63.1</td>
<td>1.17</td>
<td>0.47</td>
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<td>(12) Acetone</td>
<td>57.8</td>
<td>51.3</td>
<td>0.568</td>
<td>0.93</td>
<td>42.2</td>
<td>0.08</td>
<td>0.48</td>
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<tr>
<td>(13) 3-Pentanone</td>
<td>57.9</td>
<td>52.6</td>
<td>0.528</td>
<td>0.91</td>
<td>39.3</td>
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<td>0.45</td>
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<tr>
<td>(14) 2-Heptanone</td>
<td>57.9</td>
<td>52.8</td>
<td>0.492</td>
<td>0.88</td>
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<tr>
<td>(15) Dichloromethane</td>
<td>56.3</td>
<td>50.9</td>
<td>0.434</td>
<td>0.84</td>
<td>41.1</td>
<td>0.30</td>
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<tr>
<td>(16) Dibromomethane</td>
<td>56.5</td>
<td>51.6</td>
<td>0.312</td>
<td>0.79</td>
<td></td>
<td></td>
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<tr>
<td>(17) Acetonitrile</td>
<td>56.8</td>
<td>50.8</td>
<td>0.610</td>
<td>0.96</td>
<td>46.0</td>
<td>0.19</td>
<td>0.40</td>
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<td>(18) Ethylacetate</td>
<td>58.8</td>
<td>53.1</td>
<td>0.398</td>
<td>0.77</td>
<td>38.1</td>
<td>0.00</td>
<td>0.45</td>
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<tr>
<td>(19) Benzene</td>
<td>57.8</td>
<td>54.6</td>
<td>0.005</td>
<td>0.46</td>
<td>34.5</td>
<td>0.00</td>
<td>0.10</td>
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<tr>
<td>(20) Toluene</td>
<td>57.8</td>
<td>55.3</td>
<td>0.026</td>
<td>0.54</td>
<td>33.9</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>(21) 1,4-Dioxan</td>
<td>57.8</td>
<td>54.1</td>
<td>0.042</td>
<td>0.45</td>
<td>36.0</td>
<td>0.00</td>
<td>0.37</td>
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<tr>
<td>(22) Tetrahydrofuran</td>
<td>57.8</td>
<td>55.3</td>
<td>0.418</td>
<td>0.81</td>
<td>37.4</td>
<td>0.00</td>
<td>0.55</td>
</tr>
<tr>
<td>(23) Dimethylformamide</td>
<td>56.1</td>
<td>50.6</td>
<td>0.548</td>
<td>0.96</td>
<td>43.8</td>
<td>0.00</td>
<td>0.69</td>
</tr>
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</table>
acetate and benzene an isosbestic point is clearly indicated (Fig. 2B). The equilibrium constant for complexation with ethanol comes out to be 3.2 and 4.3 when benzene and ethyl acetate respectively are used as cosolvents.

The spectrum of the solvents in an alcoholic solvent also reflects the overlap of band from H-bonded and bare forms of the solute. Absorption measurements in ethanol at various temperatures also indicate the existence of isosbestic point. An increase in temperature indicates an increase in the intensity of the higher energy band. These facts point to the exothermic formation of a hydrogen-bonded complex in ethanol. For mixed aqueous solvents no such isosbestic point could be detected. The band shows a gradual bathochromic shift as the mole fraction of water is increased. A plot of the transition energy in mixed aqueous solvents is shown in Fig. 3. Owing to the extreme insolubility of the solute in water the data could be recorded only up to a mole fraction of 0.8 with respect to water. It may be seen from the figure that in all the cases linear plots are obtained and they converge to a value of 51 kcal mol$^{-1}$ for pure water. Throughout the whole range of $X_{\text{cosolvent}}$, Fig. 3 indicates almost similar transition energy for acetone and 1,4-dioxane, although the solvent polarity is greater in the former case. This behaviour is in keeping with the 1,4-dioxane-solute complexation as discussed earlier.

**Fluorescence spectra**

The emission may be characterised as the $S_1 \rightarrow S_0$ transition. Fig. 4 shows fluorescence spectra in some representative pure solvents. The fluorescence spectrum at 298 K is structureless except in aromatic hydrocarbon and cyclic ether solvents where two emission bands are clearly observed. For example, in benzene the observed fluorescence spectrum indicates two bands with the maximum at 525 and 548 nm respectively (Fig. 4). The 548 nm band appears to be similar to the fluorescence band in the more polar solvent ethyl acetate. This indicates complex formation with benzene. An interesting correlation between the fluorescence maxima is observed with Dimroth-Reichardt polarity parameter $E_T(30)$ as may be seen from Fig. 5 and this indicates that the nature of transition is similar in the two cases. It may be noted that the available data in neat solvents may be best represented by two correlation lines. The data points for aprotic solvents fall on one line while the protic solvents form a separate class.
The double linear dependence of the fluorescence energy on $E_T$ indicates that the nature of the emitting state is different in the two classes of solvents. For the aromatic hydrocarbons and cyclic ethers, the higher energy maximum is in line with the behaviour of other aprotic solvents, while the lower energy maximum falls below the line. Thus the lower energy band in these solvents arises due to a species in which the nature of solute-solvent interaction is different from that in the case of Reichardt's betaine, the indicator dye for $E_T$ values. Thus, the higher energy band is probably due to bare solute modified by dipolar solvation while the lower energy band is possibly due to complex formation in the excited state.

The sensitivity of the bands with solvent polarity prompted us to undertake the studies in mixed solvents. The following mixed binary solvents have been used: protic + aprotic (ethanol + benzene; ethanol + acetone; ethanol + ethyl acetate; water + acetone; and water + dioxane) and aprotic + aprotic (acetone + ethyl acetate and benzene + acetonitrile). Fig. 6 shows the fluorescence spectra in a representative mixed binary solvent as a function of solvent composition. The fluorescence maximum changes continuously to the red as increasing amounts of a cosolvent with a higher polarity [e.g. in the $E_T$ scale] are added to it. The intensity of the band increases with the addition of the polar cosolvent and then decreases. In benzene and dioxane, where the fluorescence spectrum is structured, the addition of a polar cosolvent leads to a very rapid decrease in the relative intensity of the band around 525 nm. The 548 nm band on the other hand shows a rapid red shift. The variation of $E_{12}(F)$, the maximum energy of fluorescence in mixed binary solvents, as a function of the mole fraction has been shown in Fig. 7. It may be seen that for all the protic + aprotic binary mixtures the fluorescence maximum changes rapidly when the mole fraction of the protic cosolvent is very small. But at higher mole fractions the position of the band maximum becomes less sensitive to the solvent composition. For aprotic + aprotic mixture the nature of variation depends on the component solvents. Thus a linear variation of $E_{12}(F)$ with the solvent composition is obtained in the case of acetone + ethyl acetate while for benzene + acetonitrile the variation is non-linear.

Discussion

Pure solvents

A spectroscopic transition, in general, involves
an equilibrium initial state and a non-equilibrium final state. Using the formalism developed by Marcus for treating polar media under equilibrium and non-equilibrium conditions, one can partition the Franck-Condon energies $E(A)$ and $E(F)$ as

\[
E(A) = E + (\delta F_c^{eq} - \delta F_c^{eq} - E_{RO}(0)) \quad \cdots (1)
\]
\[
E(F) = E + (\delta F_c^{eq} - \delta F_c^{eq}) - E_{RO}(1) \quad \cdots (2)
\]

where $E(A)$ and $E(F)$ denote the energies corresponding to maximum absorption and emission respectively. $E$ denotes the difference in the free energies of the ground and the equilibrium excited states. $\delta F_c^{eq}$ and $\delta F_c^{eq}$ denote the equilibrium solute-solvent interaction free energy in the $S_0$ and $S_1$ states respectively. The third term in equations (1) and (2) represents solvent reorganization energy in the $S_0$ and $S_1$ states. If the reorganization energies are equal, we obtain

\[
E(A) + E(F) = 2E + 2(\delta F_c^{eq} - \delta F_c^{eq}) \quad \cdots (3)
\]
\[
E(A) - E(F) = 2E_{RO} \quad \cdots (4)
\]

Thus, the Stoke's shift is a measure of the non-equilibrium $E_{RO}$ term while $E(A) + E(F)$ terms have only the equilibrium contribution. Plots of $[E(A) - E(F)]$ and $[E(A) + E(F)]$ versus the appropriate dielectric functions according to Onsager reaction field model have been shown in Fig. 8. It appears from both the plots that the alkanols form a separate class and this suggests that specific solute-solvent interaction is important in protic solvents. For $[E(A) + E(F)]$ versus $[2(\varepsilon - 1)/(\varepsilon + 1)]$ plots the difference between the lines for a particular value of the dielectric function comes out to be around 10.5 kcal mol$^{-1}$, which is roughly of the order of hydrogen bond energy. Similar results are obtained when other dielectric functions are used to represent the reaction field, or the molecule is assumed to be placed in an ellipsoidal cavity. The ratio of the dipole moments in the $S_1$ and $S_0$ states may be obtained from the ratio of the slopes of the straight lines for the case where no complexation occurs and this does not require the value of $\alpha$, the cavity radius. Thus, for the solute value of $\mu_1/\mu_0$ comes out as 1.9. Using theoretically calculated value of $\mu_0 = 4.02D$, we estimate the dipole moment of the excited state ($\mu_1$) as about 7.60. This is consistent with the ICT nature of the transition as suggested by theoretical calculations. A correlation of $E(F)$ with $E_T(30)$ parameter also points to the ICT nature of the transition.

The enhanced sensitivity of $E(F)$ compared to $E(A)$ towards a change in solvent polarity is intelligible in terms of increased solute-solvent interaction in the excited state (due to an increase in the dipole moment upon excitation) which, for protic solvents, increases with the dipolarity of the solvent. For protic solvents, apart from the dipolar interaction, tighter hydrogen bonding is expected in the excited state solvate due to an increased electron density on the carbonyl oxygen. Moreover, as pointed out by Kessler and Wolfbeis, an increase in the electron density on the carbonyl oxygen leads to an extension of conjugation modifying the energy levels. This effect would be more prominent as the hydrogen bond donating (HBD) ability of the solvent increases. Thus, in protic solvents the emitting state differs significantly from that in the aprotic solvents. This is in accordance with the double linear correlation of $E(F)$ and $E_T(30)$ obtained in the present case. A schematic energy level diagram is given in Fig. 9. The large spectral shift (~9 kcal mol$^{-1}$) of the emission band in going from an alcohol to a nonpolar solvent, e.g., benzene is thus rationalisable in terms of an increased reorganisation energy $(S_1^{FC} - S_0^{FC})$ in alcohols due to HBD interaction. This is also reflected in the higher value of Stoke's shift for alcohols compared to that for aprotic solvents (Fig. 8).

In order to have an idea about the solvation effects on the fluorescence maximum due to non-specific solvent dipolarity and specific hydrogen bonding ability we turned to the multiple linear
regression approach of Kamlet, Abboud and Taft. The following regression equation has been obtained with a correlation coefficient of 0.98 using fifteen solvents in the present case for which all the three parameters are known.

$$E(F)/\text{kcal mol}^{-1} = 57.23 - 7.310 \alpha - 3.606 \beta - 4.036 \pi^*$$  \hspace{1cm} (5)

Here $\pi^*$, $\beta$ and $\alpha$ represent the dipolarity, hydrogen bond accepting (HBA) and hydrogen bond donating (HBD) ability of the solvent. The negative sign of the regression coefficient indicates greater stabilization of the excited state relative to the ground state. Moreover, the ratio of the regression coefficients of $\alpha$ and $\pi^*$ (viz. 7.31/4.04) indicates that the specific HBD interaction term is more important compared to the non-specific interaction term.

Mixed solvents

A considerable shift in the fluorescence maximum due to the addition of a very small quantity of a protic component to an aprotic one is often taken as evidence for the formation of excited state complex. In the present case an enhanced complexation of the $S_1$ state of the solute with a protic solvent is expected in view of increased negative charge on the carbonyl oxygen atom upon excitation. In general, a non-linearity of solvatochromic shift of the solute's UV-VIS absorption/emission spectra versus the mole fraction is explained as due to a preferential solvation of the solute. The nature of deviation of $E_{12}(F)$ versus mole fraction curve from linearity in the present case may thus be interpreted in terms of preferential solvation of the solute in the $S_1$ state.

As is evident from Fig. 7 a preference for the protic cosolvent has been observed in all the protic + aprotic solvent mixtures. The preference for one solvent component over the other in the local environment of the solute may be explained in terms of a difference in solute-solvent interactions for the component solvents. Apart from the nonspecific dipolar interaction, a protic solvent interacts with the $S_1$ state of the solute through specific H-bonding interaction. Thus, in addition to the general phenomenon of dielectric enrichment due to a difference in the nonspecific interaction, H-bonding plays a key role in determining the preferential solvation characteristics in protic + aprotic mixture.

It may be noted that while acetone and ethyl acetate cosolvents fall on the same line (Fig. 7A), the $E_{12}(F)$ values of benzene cosolvent are always lower than those in the former case throughout the whole range of $X_{EtOH}$. This can be explained in terms of complex formation of the solute with benzene. When the mole fraction of the protic component is very small probably each protic molecule goes to solvate solute molecules and this explains the initial steep decrease in $E_{12}(F)$ values (Figs 7A & B). In the region rich in the protic component, the $E_{12}(F)$ versus mole fraction curve for mixed aqueous solvent is different in nature from that in the mixed binary solvents containing ethanol. In the latter case, the addition of a small quantity of an aprotic cosolvent modifies the solute-water H-bonding characteristics to a considerable extent. This type of behaviour has been observed in other cases also and has been explained in terms of strong self-associated structure of water due to water-water hydrogen bonding. The preference for acetonitrile over benzene in their binary mixture may be explained on similar lines. Acetonitrile has a feeble H-bonding ability (as evidenced by Kamlet-Taft parameter value of 0.19 compared to 0.83 for ethanol and 1.17 for water) in addition to a stronger dipolarity. In the case of ethyl acetate + acetone the observed data indicate no preference of the solute for a particular solvent. This can be rationalised in terms of almost similar solute-solvent dipolar interaction of the two solvents.

Results for mixed aqueous solvents need special mention. The absorption maximum in these solvents varies linearly with the mole fraction (Fig. 3) indicating a lack of preference for acetone or dioxide over water by the solute in the ground state. On the other hand, water is preferred by the $S_1$ state of the solute (Fig. 7). Thus, the state of solvation in the $S_1$ state of the solute is different from that in the $S_0$ state. An interesting observation may be made from a plot of the Stoke's

\[ S_1^{FC}, S_0^{FC}, S_1^R, S_0^R \]

Fig. 9—Schematic energy level diagram of the solute 'S' in aprotic (A) and protic (B) environments. Subscripts 0 and 1 indicate ground and first singlet excited state. Superscripts 'FC' and 'R' denote Franck-Condon and relaxed states respectively.
IACS, Calcutta for helpful discussions. The authors thank Prof. Mihir Chowdhury of IACS, Calcutta for his assistance in MO calculations. The financial support from CSIR, New Delhi is also acknowledged.

References
3 Kosower E M, J Am chem Soc, 80 (1958) 3253.
14 Marcus R A (a) J chem Phys, 38 (1963) 1858; (b) 43 (1965) 1261.