Analysis of Solvent Effect in a Ketocyanine Dye Using Various Solvent Polarity Scales and Estimation of Dipole Moments

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Abstract
The solvatochromism of a ketocyanine dye 2,5-di[(E)-1-(4-dimethylaminophenyl) methylidene]-1-cyclopentanone (2,5-DMAPMC) is analyzed using Lippert-Mataga bulk polarity function, Reichardt’s microscopic solvent polarity parameter and Kamlet’s multiple linear regression approach. The spectral properties better follows Reichardt’s microscopic solvent polarity parameter than Lippert-Mataga bulk polarity function. This indicates that both general solute – solvent interactions and specific interactions are operative. Kamlet’s multiple linear regression approach indicates that polarizability/dipolarity solvent influences are more compare to HBD and HBA solvent influences. The solvatochromic correlations are used to estimate excited state dipole moment using theoretically determined ground state dipole moment. The excited state dipole moment of dye is found to be larger than its corresponding ground state dipole moment and, ground and excited state dipole moments are not parallel, but subtends an angle of 23°.

Introduction
The investigation on solvatochromism in organic fluorophores has been a subject of interesting investigation in recent years [1–6]. These investigations have considerable importance in the field of photophysics and photochemistry. Accordingly, photophysical properties like fluorescence quantum yield ($\Phi_f$), fluorescence life time ($\tau_f$), absorption and fluorescence spectral shift, etc., have been a subject of several investigations [7, 8]. The data from solvatochromism can be used to determine the electric dipole moment of molecules in the excited states. The knowledge of dipole moment of electronically excited molecules is useful in designing nonlinear optical materials [9], in elucidation of the nature of the excited states and also it reflects the charge distribution in the molecule.

Photophysical properties of ketocyanine dyes have been the subject of intensive investigations in previous years [10 – 25]. The pronounced solvent effects in both absorption and emission spectra of these dyes make them promising probes for monitoring micro-polarity, hydrogen-bond donating interaction, metal ion sensing, investigation of the cell membrane structures, evaluating the micro-environmental characteristics of biochemical and biological systems and many others [26–31]. Even though intensive investigations have been carried out on photophysics and photochemistry of a ketocyanine dye 2,5-di[(E)-1-(4-dimethylaminophenyl) methylidene]-1-cyclopentanone (2,5-DMAPMC), there is a lack of information on the analysis of spectral properties in terms of different solvent polarity parameters and, estimation of ground and excited state dipole moments to the best of present knowledge. This motivated to carry out the present work. The aim of the present work is to systematically analyse solvent effects on absorption transition energy, fluorescence transition energy and stoke’s shift using different solvent polarity scales and estimate ground and excited-state dipole moments of 2,5-DMAPMC. The molecular structure of 2,5-DMAPMC is given in Figure 1. The spectral properties are analyzed using Lippert and Mataga bulk solvent polarity parameter, Reichardt’s microscopic solvent polarity parameter and solvatochromic parameters proposed by Kamlet et al. The ground state dipole moment of the dye was determined by quantum chemical method using Gaussian 09 program. The excited state dipole moment was estimated using Bakhshiev’s, Kawasaki-Chamma-Viallet equations and Reichardt’s microscopic solvent polarity parameter $E_N^T$.

![Figure 1. Molecular structure of 2,5-DMAPMC](image)

2. Theoretical Background
The Lippert-Mataga bulk solvent polarity parameter ($F(\varepsilon, n)$) values of solvents used in the present study were calculated using equation (1) [32, 33],

$$F(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

(1)

where $\varepsilon$ and $n$ are respectively dielectric constant and refractive index of respective solvents.

The microscopic solvent polarity parameter ($E_N^T$) values of solvents were taken from literature [27].
The multiple linear regression method proposed by Kamlet and co-workers [34-36] has also been used to correlate absorption transition energy ($\bar{\nu}_a$), fluorescence transition energy ($\bar{\nu}_f$) and stoke’s shift ($\Delta\bar{\nu}$) with an index of the solvent’s ability to stabilize a charge or dipole through nonspecific dielectric interactions ($\pi^*$), and indices of the solvent’s hydrogen-bond donor (HBD) strength ($\alpha$) and hydrogen-bond acceptor (HBA) strength ($\beta$), according to the equation (2);

$$y = y_0 + a\alpha + b\beta + c\pi^*$$  \hspace{1cm} (2)

where $y$ is the spectroscopic property under consideration, $y_0$ is respective spectroscopic property in gas phase, $a$, $b$, and $c$ are respectively measures of solvents HBD, HBA and dipolarity/polarisability.

Theoretical ground state dipole moment ($\mu_g$) of the dye was obtained by quantum chemical calculations. The B3LYP model which is based on density functional theory was used. The 6-31G(d) basis set was employed in the calculation. All the computations were carried out using Gaussian 09 program [37] on a Pentium – 4 PC.

The solvatochromism exhibited by dye was used to estimate the excited-state dipole moment and is determined according to Bakshiev’s and Kawski-Chamma-Viallet’s [38-44] equations (3) and (4) as given below:

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\epsilon, n) + \text{constant}$$  \hspace{1cm} (3)

$$\frac{\bar{\nu}_a + \bar{\nu}_e}{2} = -m_2 F_2(\epsilon, n) + \text{constant}$$  \hspace{1cm} (4) where

$\bar{\nu}_a$ and $\bar{\nu}_f$ are the absorption and fluorescence maxima wavenumbers in cm$^{-1}$ respectively, and

$$F_1(\epsilon, n) = \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \frac{(2n^2 + 1)}{(n^2 + 2)}$$  \hspace{1cm} (5)

$$F_2(\epsilon, n) = \left[\frac{(2n^2 + 1)}{2(n^2 + 2)}\right] \left[\frac{\epsilon - 1}{\epsilon + 1} - \frac{n^2 - 1}{n^2 + 1}\right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2}$$  \hspace{1cm} (6)

From equations (3) & (4), the plots of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$ and $(\bar{\nu}_a + \bar{\nu}_f)/2$ versus $F_2(\epsilon, n)$ are linear with slopes $m_1$ and $m_2$ respectively and are given below:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hc\alpha^3}$$  \hspace{1cm} (7)

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hc\alpha^3}$$  \hspace{1cm} (8)

where $\mu_g$ and $\mu_e$ are ground and excited dipole moments of a molecule respectively, $\hbar$ is Planck’s constant, $c$ is the velocity of light and $\alpha$ is Onsager cavity radius of a molecule. The Onsager cavity radius of 2,5-DMAPMC was estimated using the method suggested by J. T. Edward [45].

If the ground and excited states are parallel, the following expressions can be obtained on the basis of above equations [46]

$$\mu_g = \frac{m_2 - m_1}{2} \left(\frac{hc\alpha^3}{2m_1}\right)^{1/2}$$  \hspace{1cm} (9)

$$\mu_e = \frac{m_1 + m_2}{2} \left(\frac{hc\alpha^3}{2m_1}\right)^{1/2}$$  \hspace{1cm} (10)

If dipole moments $\mu_g$ and $\mu_e$ are not parallel to each other but form an angle $\phi$, then $\phi$ can be calculated using equation (11).

$$\cos \phi = \frac{1}{2\mu_g\mu_e} \left[\left(\mu_g^2 + \mu_e^2\right) - \frac{m_1}{m_2}\left(\mu_g^2 - \mu_e^2\right)\right]$$  \hspace{1cm} (11)

We have also used a method based on empirical solvent polarity parameter $E_T^N$ to estimate excited state dipole moment. This method correlates the spectral shift better than the traditionally used bulk solvent polarity functions. In this method the problem associated with the estimation of Onsager cavity radius is minimized. Also, this polarity scale includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with $E_T^N$ is according to the equation (12) [47]

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_\theta}\right)^2 \left(\frac{a_\theta}{a}\right)^3\right] E_T^N + \text{const}$$  \hspace{1cm} (12)

where $\Delta\mu/\Delta\mu_\theta$ and $a_\theta/a$ are the change in dipole moment and Onsager cavity radius respectively of the Betaine dye, and $\Delta\mu$ and $a$ are the corresponding quantities of the molecule of interest. The change in dipole moment $\Delta\mu$
can be extracted from the slope of the plot \((\vec{v}_a - \vec{v}_f)\) versus \(E^N_T\) using the reported values of \(\Delta \mu_B = 9\)D and \(a_B = 6.2\)Å.

3. Results And Discussion

3.1. Analysis of solvatochromism

Solvent polarity function values \(F(\epsilon, n), F_1(\epsilon, n), F_2(\epsilon, n)\) and \(E^N_T\) for various solvents used in the present study are collected in Table 1. The absorption and emission maxima, respective wave numbers, stokes shift and arithmetic mean of stokes shift values (in \(\text{cm}^{-1}\)) for 2,5-DMAPMC dye in different solvents are given in Table 2. Absorption and emission maxima were taken from Ref. [22]. From Table 2, it is observed that when solvent is changed from non-polar toluene to acetonitrile which is polar aprotic solvent, there is a spectral band shift of 6nm in the absorption spectrum, whereas it is 30nm for methanol which is polar protic solvent. Also, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile, there is a spectral band shift of 92nm in the fluorescence spectrum, whereas it is 139nm for polar protic solvent methanol. This implies that the ground state energy distribution is less influenced by change in polarity and hydrogen bonding property of solvent compared to excited state. The Stokes’ shift values increases with increase in solvent polarity. The Stokes’ shift of 4730\(\text{cm}^{-1}\) is observed in polar protic solvent methanol and 4480\(\text{cm}^{-1}\) in case of polar aprotic solvent acetonitrile. These observations indicate the good response of 2,5-DMAPMC to the polarity and hydrogen bonding characters of the solvents. The observed solvatochromic behavior could be due to the presence of two tautomeric forms of 2,5-DMAPMC (keto and charged enol forms, figure 2).

The degree of contribution of both tautomers in solution is governed by the nature and polarity of the used solvents. The less polar keto form contributes mainly in non- and less polar solvents. In contrast the highly polar enol form predominates in polar and strong hydrogen bonding donor solvents, thus, causing larger spectral shifts [1]. Further, both absorption and fluorescence band maxima undergoes pronounced red shifts with increase in solvent polarity. The observed solvent sensitivity is understandable in terms of \(\pi \rightarrow \pi^*\) with intramolecular charge transfer (ICT) from dimethyl amino group to the carbonyl oxygen.

<table>
<thead>
<tr>
<th>Solvents (^a)</th>
<th>(F(\epsilon, n))</th>
<th>(F_1(\epsilon, n))</th>
<th>(F_2(\epsilon, n))</th>
<th>(E^N_T) (^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.0131</td>
<td>0.0288</td>
<td>0.3498</td>
<td>0.0990</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.0205</td>
<td>0.0415</td>
<td>0.3074</td>
<td>0.1640</td>
</tr>
<tr>
<td>Butyl Acetate</td>
<td>0.1729</td>
<td>0.4156</td>
<td>0.4723</td>
<td>0.2410</td>
</tr>
<tr>
<td>DMF</td>
<td>0.2745</td>
<td>0.8357</td>
<td>0.7096</td>
<td>0.3860</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.3060</td>
<td>0.8627</td>
<td>0.6643</td>
<td>0.4600</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.2743</td>
<td>0.7701</td>
<td>0.6412</td>
<td>0.5460</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.2893</td>
<td>0.8138</td>
<td>0.6521</td>
<td>0.6540</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.3087</td>
<td>0.8545</td>
<td>0.6507</td>
<td>0.7620</td>
</tr>
</tbody>
</table>

\(^a\) Solvents are listed in the order of increasing \(E^N_T\).
\(^b\) Lipert-Mataga solvent polarity function
\(^c\) Bakshiev’s solvent polarity function
\(^d\) Kawasaki-Chamma-Viallet solvent polarity function
\(^e\) \(E^N_T\) values taken from Ref. [27]

To get further insight on the solvatochromic behavior of 2,5-DMAPMC, spectroscopic properties are correlated with relevant solvent polarity scales. The spectroscopic properties \(\vec{v}_a, \vec{v}_f\) and \(\Delta \vec{v}\) are plotted as a function of Lipper-Mataga solvent polarity parameter \(F(\epsilon, n)\). The least square correlation analysis gave a better correlation in case of fluorescence \((r = 0.92)\) and stokes’ shift \((r = 0.92)\) as compared to absorption \((r = 0.74)\). The average correlation in case of absorption implies that Lipper-Mataga solvent polarity parameter is not a complete valid polarity scale to explain solvent effects in the present case. This could be due to the reason that this method not consider specific solute – solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation. The poor correlation of absorption transition energies with \(F(\epsilon, n)\) indicates the role of hydrogen bonding effect in the present case, as is evident.

Table 2. Solvatochromic data\(^a\) of 2,5-DMAPMC in different solvents

\(^a\) Absorption and fluorescence maxima were taken from Ref.[22]
from very large spectral shifts in polar protic solvents. Therefore, an attempt has been made to explain spectroscopic properties by solvent polarity parameter $E_{T}^{N}$.

The $\nu_{a}$, $\nu_{f}$ and $\Delta\nu$ are correlated with the microscopic solvent polarity parameter $E_{T}^{N}$. The least square correlation analysis gave a better correlation for all the three spectral properties $\nu_{a}$ ($r = 0.93$), $\nu_{f}$ ($r = 0.97$) and $\Delta\nu$ ($r = 0.88$). This implies that spectroscopic properties $\nu_{a}$, $\nu_{f}$ and $\Delta\nu$ of 2,5-DMAPMC have better dependence on $E_{T}^{N}$ compared to $F(e, n)$. The better correlation of $\Delta\nu$ with $E_{T}^{N}$ also confirms the presence of a general solute-solvent interactions as well as hydrogen bonding interactions.

In order to get information about the individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of the solvents on the spectroscopic properties, $\nu_{a}$, $\nu_{f}$ and $\Delta\nu$ are correlated with solvatochromic parameters $\alpha$, $\beta$ and $\pi^{*}$ using multiple regression. The multiple regression analysis data along with correlation coefficients is given in below equations.

$\nu_{a}$ (cm$^{-1}$) $= 23307 - 989\alpha - 75\beta - 1066\pi^{*}$

$r = 0.96$

$\nu_{f}$ (cm$^{-1}$) $= 23432 - 1407\alpha - 1023\beta - 2716\pi^{*}$

$r = 0.93$

$\Delta\nu$ (cm$^{-1}$) $= 1755 + 1823\alpha + 3806\beta + 4737\pi^{*}$

$r = 0.78$

From above equations it is clear that non-specific dielectric interaction ($\pi^{*}$) has the major solvent influence. However the contribution of HBD and HBA parameters cannot be neglected. It is clear from $\nu_{a}$ and $\nu_{f}$ multiple regression analyses with better correlation coefficients, HBD ($\alpha$) influence is more than HBA ($\beta$).

3.2. Estimation of ground and excited state dipole moments

The ground state dipole moment of 2,5-DMAPMC was obtained using quantum chemical calculation following geometry optimisation and is found to be 5.23 D. The optimized molecular geometry with the direction of dipole moment is shown in Figure 3.
Figure 4 shows the plots of \((\overline{\nu}_a - \overline{\nu}_f)\) versus \(F_1(\varepsilon, n)\) (figure 4(a)) and \((\overline{\nu}_a + \overline{\nu}_f)/2\) versus \(F_2(\varepsilon, n)\) (figure 4(b)). The linear progression was done and the data was fit to a straight line. The corresponding values of slopes, intercepts and correlation coefficients are collected in Table 3. In both the cases the correlation coefficients are more than 0.90 with selected number of data points. The excited state dipole moment \((\mu_e)\) is calculated from the slopes of respective plots and are given in Table 4. From Table 4, it is clear that calculated excited state dipole moments from Bakshiev’s \((\mu_e^b)\) and Kawski-Chamma-Viallet’s \((\mu_e^c)\) equations are fairly in good agreement with each other. The excited state dipole moment is also calculated using polarity parameter \(E_{TN}^N\) according to equation (12) and figure 4(c). The value of excited state dipole moment calculated from this method is represented as \(\mu_e^d\) and is also collected in Table 4. This value is slightly smaller than one calculated from Bakshiev’s and Kawski-Chamma-Viallet’s equations. This could be due to the fact that, methods based on Bakshiev’s and Kawski-Chamma-Viallet’s equations not consider specific solute – solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation, whereas these aspects are incorporated in the method based on \(E_{TN}^N\) [27].

The ground and excited state dipole moments of 2,5-DMAPM were also estimated assuming that they are parallel using equations (9) and (10). The estimated values are \(\mu_g = 3.54D\) and \(\mu_e = 8.18D\). The difference in values of \(\mu_g\) and \(\mu_e\) compared to respective values from other methods (Table 4) suggest that \(\mu_g\) and \(\mu_e\) are not parallel. This prompted to estimate the angle between \(\mu_g\) and \(\mu_e\) according to equation (11) and the value is found to be 23°. It means that \(\mu_g\) and \(\mu_e\) are not parallel.

### Table 3. The slope (m), Intercept (C), Correlation coefficient (r) and number of data points (n) corresponding to statistical treatment of spectral shifts with \(F_1\), \(F_2\) and \(E_{TN}^N\) parameters

<table>
<thead>
<tr>
<th>Function</th>
<th>m</th>
<th>C</th>
<th>r</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_1)</td>
<td>2655</td>
<td>2204</td>
<td>0.91</td>
<td>8</td>
</tr>
<tr>
<td>(F_2)</td>
<td>6701</td>
<td>1454</td>
<td>0.92</td>
<td>6</td>
</tr>
<tr>
<td>(E_{TN}^N)</td>
<td>2672</td>
<td>2828</td>
<td>0.93</td>
<td>7</td>
</tr>
</tbody>
</table>

### Table 4. The Onsager cavity radius and, Ground-state and singlet excited state dipole moments (in Debye, D)

<table>
<thead>
<tr>
<th>Radius (Å)</th>
<th>(\mu_g^a)</th>
<th>(\mu_e^b)</th>
<th>(\mu_e^c)</th>
<th>(\mu_e^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.02</td>
<td>5.23</td>
<td>9.87</td>
<td>9.04</td>
<td>7.79</td>
</tr>
</tbody>
</table>

\(^a\)Ground state dipole moments estimated by Gaussian software.
Excited – state dipole moments calculated from Bakhshiev’s equation.

Excited – state dipole moments calculated from Kawski-Chamma-Viallet’s equation.

Excited – state dipole moments calculated from $\bar{N}\bar{N}$.

From Table (4) it is clear that the dipole moment of 2,5-D MAPPMC is higher in the first excited-state as compared to the ground-state. The dipole moment increases almost two times on excitation. This indicates the existence of a more relaxed excited state, due to ICT favoured by the cooperative effects of the dimethyl aniline moieties as donors and the carbonyl group as an acceptor, and suggests that the present dye can serve as good candidate component of non-linear optical materials [1].

Conclusion

The solvatochromism of 2,5-D MAPPMC has been analysed using different polarity parameters. The spectral properties of this dye are influenced more by dipolarity/polarizability of solvents. However, the contributions from solvents HBD and HBA cannot be ignored. HBD influences are more than HBA. The dye has higher dipole moment in the excited state than in the ground state. This clearly indicates that dye has more relaxed excited state due to ICT and suggests that it can serve as good candidate component of nonlinear optical materials. To the present day knowledge this is the first report on detailed analysis of effect of solvents and estimation of dipole moments of 2,5-D MAPPMC, and would be of great help in many fields as mentioned in the introduction.

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References


