EFFECT OF SOLVENTS ON PHOTOPHYSICAL PROPERTIES OF BIOLOGICALLY ACTIVE IODINATED 4-ARYLOXYMETHYL COUMARIN 1IPBC

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Abstract :   The steady state absorption and fluorescence characteristics of newly synthesized biologically active iodinated coumarin derivative 1-(2-iodo phenoxymethyl)-benzo[f]chromen-3-one (1IPBC) is studied at room temperature in solvents of varying polarities. The effect of solvents on the photophysical properties are analyzed using Lippert–Mataga polarity function, Reichardt's microscopic solvent polarity parameter, Kamlet's and Catalan's multiple linear regression approaches. It has been found that non-specific solvent effects are predominant compared to specific solvent effects. The ground state dipole moment obtained using quantum chemical calculations is used to estimate excited state dipole moment. The bathochromic shift of the emission spectra and the increase in excited state dipole moment indicate the intramolecular charge transfer (ICT) character in the emitting singlet state.

Keywords: Coumarin, solvatochromic shift, dipole moment, intramolecular charge transfer.

I. INTRODUCTION

Coumarins belong to the family of benzopyrone compounds and are well known for their emission in blue-green region [1-5]. They exhibit various biological and medicinal properties like anticoagulant, antibacterial, anti-microbial, analgesic and anti-pyretic activity [6-10]. It is reported that 4-aryloxymethyl coumarins exhibit antimicrobial activity, long range coupling and centrosymmetric nature [11,12]. It is found from the literature that newly synthesized 4-aryloxymethyl coumarin 1-(2-iodo phenoxymethyl)-benzo[f]chromen-3-one (1IPBC) exhibited better anti-cancer and anti mycobacterial activities [13]. The photophysical properties like absorption. emission and spectral shift, fluorescence decay time, quantum yield, ground and excited state dipole moments of organic molecules in general and coumarins in particular have been a major area of discussion [14–20]. In the present work, photophysical properties of the dye 1IPBC have been investigated in solvents of varying polarity and the solvatochromic data of the dye is used to estimate excited state dipole moments of singlet state. The experimental results are snslysed using Lippert and Mataga bulk solvent polarity parameter [21,22], Reichardt's microscopic solvent polarity parameter [23], solvatochromic parameters proposed by Kamlet et al. [24–26] and Catalan and co-workers [27]. The ground state dipole moment of 1IPBC was obtained using quantum chemical method [28]. The excited state dipole moment was estimated using Bakshiev's [29], Bilot-Kawski [30–31] equations and equation based on Reichardt's microscopic solvent polarity parameter E_T^N [32]. Further, no reports are available in literature on the photophysical properties of 1IPBC. The promising biological activities and dearth of studies on photophysical properties of 1IPBC prompted us to take up this work.

II. MATERIALS AND METHODS

The coumarin dye 1IPBC was synthesized by our research group [13]. The molecular structure of 1IPBC is given in **Fig. 1**. The spectroscopic grade solvents used in the present investigation were procured from S.D. Fine Chemicals Ltd., India. The absorption and fluorescence spectra were recorded using UV-VIS spectrophotometer (Model: Shimadzu UV-1800) and fluorescence spectrophotometer (Model: Agilent Technologies Carry Eclipse-60) respectively at room temperature. The dye concentration was maintained at 10^{-5}M in all solvents in order to reduce the effect of self absorption and aggregation formation. Parker's method [33] was used to determine relative fluorescence quantum yield, in which quinine sulphate in 0.1 M H_2SO_4 was used as standard ($\Phi_f = 0.54$).

The bulk solvent polarity parameter ($\Delta f(\varepsilon, n)$ of solvents was determined using Eq. (1) [29, 30].

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

where the symbols ε and n represent dielectric constant and refractive index of solvents respectively. The values of ε and n of solvents were obtained from literature [34]. The E_T^N values of solvents were also taken from literature [23].
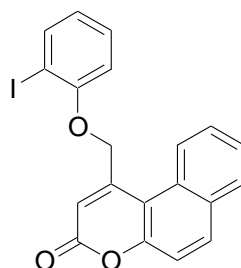

Figure. 1. Molecular structure of 1IPBC.

The ability of solvents to stabilise a charge or dipole through non-specific dielectric interactions (π*), indices of hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength (β) has been measured by correlating the spectral properties of the dye with an index of solvent's dipolarity/polarizability using multiple linear regression method proposed by Kamlet and co-workers [24-26)] according to Eq. (2) [35].

$$y = y_0 + a\alpha + b\beta + c\pi* \tag{2}$$

where y is the spectroscopic property of interest, y_0 is the respective spectroscopic property in gas phase and a, b and c are the measures of solvents HBD ability, HBA ability and non-specific dielectric interactions respectively. This approach includes dipolarity and polarisability of solvent in single parameter π* [36], limiting understanding individual parameter contribution. In recent times, Catalan [27] proposed another method based on four empirical scales namely dipolarity (SdP, a new scale, polarizability (SP)), solvent acidity (SA) and basicity (SB) of the medium. This method is based on Eq. (3).

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \tag{3}$$

where y and y_0 have their usual meanings, a_{SA}, b_{SB}, c_{SP} and d_{SdP} are the measures of solvents SA, SB, SP and SdP respectively. Using this method, it is possible to break up the relative contributions of dipolarity, polarizability, acidity and basicity of the medium.

In order to obtain theoretical ground state dipole moment (μ_g) of dyes, quantum chemical computation carried out using Gaussian 09 program [28] on a Pentium – 4 PC with method B3LYP and built-in basis set 3-21G was used.

The excited state dipole moment of dye was estimated using Bakshiev's, Kawski-Chamma-Viallet equations and also by the equation based on E_T^N. According to Bakshiev [29] and Kawski-Chamma-Viallet [37-42] for a spherical molecule with the isotropic polarizability, the following Eqs. (4) and (5) hold good:

$$\bar{v}_a - \bar{v}_f = m_1 F_1(\varepsilon, n) + \text{constant} \tag{4}$$

$$\frac{\bar{v}_a + \bar{v}_f}{2} = -m_2 F_2(\varepsilon, n) + \text{constant} \tag{5}$$

where $\bar{v}_a$ and $\bar{v}_f$ are the absorption and fluorescence maxima wavenumbers in cm^{-1} respectively, and F_1 & F_2 are solvent polarity functions given by Eqs. (6) and (7) respectively.

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \tag{6}$$

$$F_2(\varepsilon, n) = \left[\frac{(2n^2 + 1)}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 1} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \tag{7}$$

where ε and n have their usual meanings. The plots of $(\bar{v}_a - \bar{v}_f)$ versus $F_1(\varepsilon, n)$, and $(\bar{v}_a + \bar{v}_b)/2$ versus $F_2(\varepsilon, n)$ for different solvents yield the slopes m_1 and m_2 respectively and are given below:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{8}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{9}$$

where h, c and a are Planck's constant, velocity of light and Onsager radius of a molecule respectively. μ_g and μ_e are the ground and excited state dipole moments respectively. The Onsager radius of the dye was estimated according to the method suggested by J T Edward [43].

If the ground and excited state dipole moments are parallel, and the symmetry of the investigated solute molecule remains unchanged upon electronic transition, the following equations are obtained [44] based on Eqs. (8) and (9).

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2}$$

(10)

$$\mu_e = \frac{m_1 + m_2}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2}$$

(11)

If the dipole moments μ_g and μ_e are not parallel to each other and form an angle ϕ, the Eqs. (10) and (11) can be written as

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

(12)

The excited state dipole moment of dye was also estimated using the Eq. (13) which is based on E_T^N [32].

$$\overline{\nu}_a - \overline{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + \text{constant}$$

(13)

where $\Delta\mu_B$ and a_B are the change in dipole moment and Onsager radius of betaine dye respectively, 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 of Stokes shift versus E_T^N using the reported values $\Delta\mu_B = 9D$ of the betaine dye and its Onsager radius $a_B = 6.2$Å.

III. RESULTS AND DISCUSSION

(A) EFFECT OF PURE SOLVENTS ON ABSORPTION AND FLUORESCENCE SPECTRA

The absorption and fluorescence spectra of 1IPBC in different solvents were recorded and typical spectra in toluene, acetonitrile and methanol are given in **Fig. 2.** The energies of absorption ($\overline{\nu}_a$) and emission transitions ($\overline{\nu}_f$), Stokes' shift ($\Delta\overline{\nu}$) and arithmetic mean of wavenumbers ($\overline{\nu}_a + \overline{\nu}_f$)/2 (in cm^{-1}) for different solvents are given in Table 1.

It is observed from Table 1 that, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile and a polar protic solvent methanol, there is no appreciable spectral band shift in absorption spectra 1IPBC. But, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile and a polar protic solvent methanol, there is a spectral band shift of 3 nm in acetonitrile and 9 nm in methanol in the emission spectra. This implies that the ground state energy distribution of the dye is not much affected by change in polarity and hydrogen bonding characteristics of solvents [15, 16]. However, the excited state of the dye is influenced by change in polarity of solvents. Also, the comparison of emission maxima of the dye in acetonitrile and methanol suggests that the emission characteristics of the dye are also influenced by hydrogen bond characteristics of solvents. The Stokes' shift of 4499 cm^{-1}, 4838 cm^{-1} and 5178 cm^{-1} were observed in non polar solvent toluene, polar aprotic solvent acetonitrile and polar protic solvent methanol respectively indicating the increase in Stokes' shift with solvent polarity. Further, the fluorescence band maxima of 1IPBC undergo red shift with increase in solvent polarity. The red shift with increase in solvent polarity indicates the involvement of $\pi \rightarrow \pi^*$ transition [15, 16]. The red shift with increase in solvent polarity could be due to the marked difference between the solute's excited state and ground state charge distribution, resulting in a stronger intermolecular interaction with polar solvents in the excited state [15, 16].

To get further insight on the solvatochromic behavior of the dye, spectroscopic properties are correlated with relevant solvent polarity scales. The spectroscopic properties $\bar{\nu}_f$ and $\Delta\bar{\nu}$ are plotted as a function of $\Delta f(\varepsilon, n)$. The variation of $\bar{\nu}_a$ was not discussed further because of the reasons mentioned earlier. The least square correlation analysis gave a moderate correlation in case of $\bar{\nu}_f$ (r = 0.48) and $\Delta\bar{\nu}$ (r = 0.47). The moderate correlation of spectral properties with $\Delta f(\varepsilon, n)$ implies that this is not a sufficiently valid polarity scale to explain solvent effect in 1IPBC. This could be due to the reason that the polarity scale $\Delta f(\varepsilon,n)$ does not consider specific solute–solvent interactions such as hydrogen bonding effect, charge transfer interactions, complex formation and ignores molecular aspects of solvation. Therefore, an attempt has been made to explain spectroscopic properties by solvent polarity parameter E_T^N. The values of $\bar{\nu}_f$ and $\Delta\bar{\nu}$ are correlated with E_T^N. The least square analysis gave once again a moderate correlation of r = 0.59 and r = 0.56 for $\bar{\nu}_f$ and $\Delta\bar{\nu}$ graphs respectively.
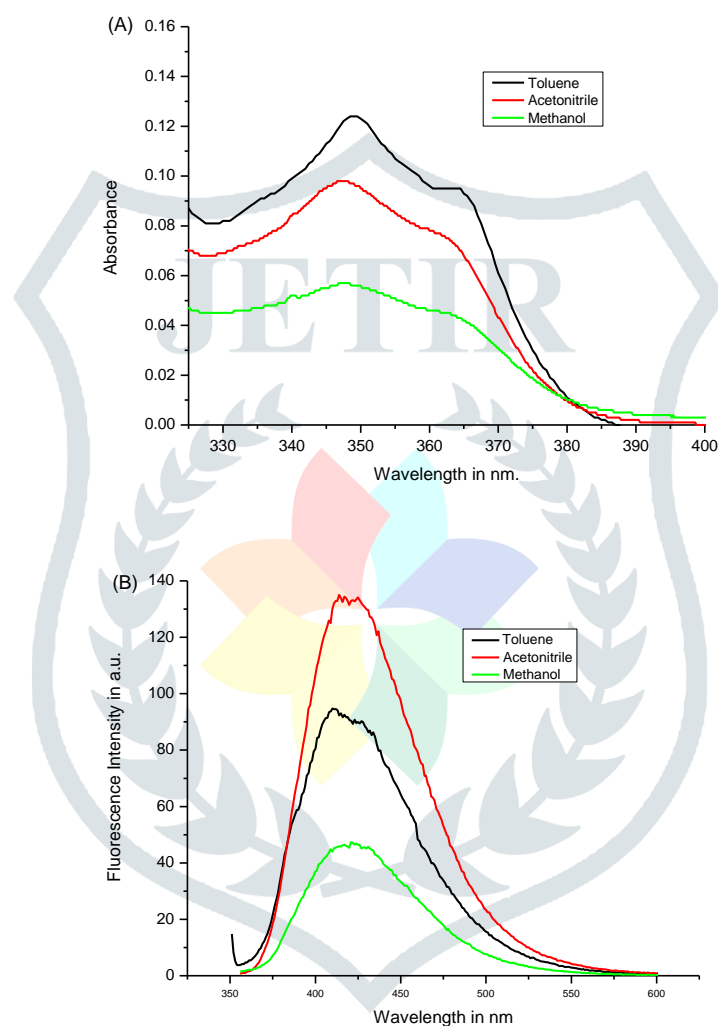

Figure. 2(A) Absorption spectra of 1IPBC in toluene, acetonitrile and methanol
(B) Fluorescence spectra of 1IPBC in toluene, acetonitrile and methanol

Table 1: Photophysical parameters of 1IPBC in different solvents

Solvents[a]	E_T^N	λ_a (nm)	λ_f (nm)	$\Delta\bar{\nu}$ (cm^{-1})	$(\bar{\nu}_a + \bar{\nu}_f)/2$ (cm^{-1})	Φ_f
Cyclohexane	0.006	347	413	4605	26516	0.0175
Toluene	0.099	349	414	4499	26404	0.0394
Diethyl ether	0.117	347	415	4722	26457	0.0436
1,4 Dioxane	0.164	347	418	4895	26371	0.0470
THF	0.207	348	409	4286	26593	0.0169
EAC	0.228	347	416	4780	26428	0.0384
Chloroform	0.259	348	418	4812	26330	0.0368
Acetone	0.355	347	420	5009	26314	0.0648

DMF	0.386	349	421	4900	26203	0.0889
DMSO	0.444	349	425	5124	26091	0.0730
Acetonitrile	0.460	347	417	4838	26400	0.0585
Butanal	0.586	348	415	4639	26416	0.0794
Propanol	0.617	348	418	4812	26330	0.0813
Ethanol	0.654	348	420	4926	26273	0.0543
Methanol	0.762	347	423	5178	26230	0.0350

[a]Abbreviations of the solvents: THF, Tetrahydrofuran; EAC, Ethylacetate; DMF, Dimethyl formamide; DMSO, Dimethyl sulfoxide

However, when $\bar{\nu}_f$ and $\Delta\bar{\nu}$ were correlated with E_T^N separately for alcoholic and non-alcoholic solvents, the correlation is found to be good. The least square correlation coefficient in case of $\bar{\nu}_f$ for both non-alcoholic and alcoholic solvents is r = 0.93. The least square correlation in case of $\Delta\bar{\nu}$ for non-alcoholic solvents is r = 0.83 and alcoholic solvents is r = 0.98. The double linear fits are shown in **Fig. 3** and **Fig 4**. The double linear correlation indicates that, solvent stabilization of excited states is due to a variety of solute-solvent interactions such as hydrogen bonding and dipole-dipole interactions [45]. In protic solvents, increasing polarity stabilizes the molecule through hydrogen bonding. On the other hand in aprotic solvents, dipole-dipole and dipole induced dipole forces are assumed to be the predominant interactions [46].
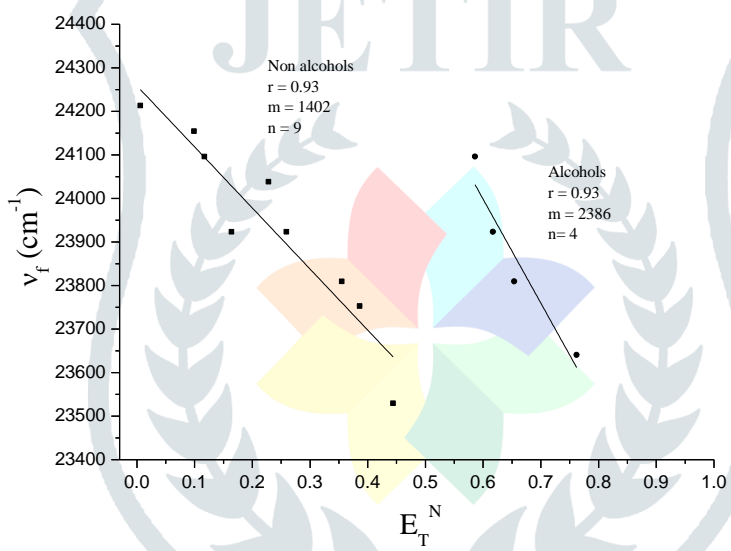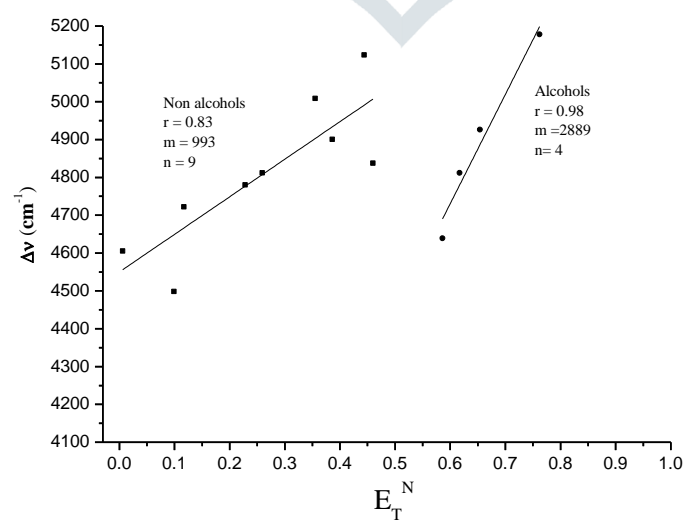

Figure. 3. Plot of $\bar{\nu}_f$ versus E_T^N

Figure. 4. Plot of Stokes' shift ($\Delta\bar{\nu}$) versus E_T^N

In order to get information about the individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of solvents on spectroscopic properties of the dye 1IPBC, $\bar{V}_f$ and $\Delta\bar{V}$ were correlated with solvatochromic parameters α, β and π* using multiple regression. The multiple regression analysis data along with correlation coefficients is given below in Eqs. (14) and (15).

$$\bar{V}_f \text{ (cm}^{-1}) = 24495 - 167\,\alpha + 69\,\beta - 428\,\pi^* \qquad r = 0.80 \tag{14}$$

$$\Delta\bar{V} \text{ (cm}^{-1}) = 4636 + 473\,\alpha + 148\,\beta + 836\,\pi^* \qquad r = 0.81 \tag{15}$$

From above equations, it is clear that non-specific dielectric interaction (π*) has a major solvent influence. However, the contributions of HBD and HBA parameters cannot be neglected.

Further, spectroscopic properties of 1IPBC $\bar{V}_f$ and $\Delta\bar{V}$ were also correlated with solvatochromic parameters SA, SB, SP and SdP proposed by Catalan. The linear correlation analysis along with correlation coefficients is shown in Eqs. (16) and (17) respectively.

$$\bar{V}_f \text{ (cm}^{-1}) = 25721 - 241\,SA + 157\,SB - 604\,SP - 503\,SdP \qquad r = 0.81 \tag{16}$$

$$\Delta\bar{V} \text{ (cm}^{-1}) = 4970 + 490\,SA + 230\,SB + 1245\,SP + 721\,SdP \qquad r = 0.86 \tag{17}$$

From above equations, it is observed that influence of polarizability (SP) and dipolarity (SdP) parameters is more. However, the contributions of solvent influences due to acidity and basicity cannot be neglected. The solvent acidity (SA) influences more than solvent basicity (SB). This is in good agreement with the results obtained by Kamlet analysis.

The relative quantum yield of 1IPBC was estimated in different solvents and is given in Table 1. The relative quantum yield varies from 0.0169 to 0.0889 depending on the nature of solvents. The general observation is that, the relative quantum yield value is more in polar solvents compared to non-polar solvents.

(B) ESTIMATION OF GROUND AND EXCITED STATE DIPOLE MOMENTS

The ground state dipole moment of 1IPBC was obtained using quantum chemical calculation following geometry optimisation and is given in **Table 2** ($\mu_g{}^a$). The optimized molecular geometry of 1IPBC is shown in **Fig. 5**. This kind of calculation assumes that molecules involved are in gas phase and does not include solvent interactions. The ground state dipole moment was also calculated using equation (10) and is also given in Table 2 ($\mu_g{}^b$). From **Table 2**, it is clear that ground state dipole moment obtained using quantum chemical calculations ($\mu_g{}^a$) is more than the ground state dipole moment ($\mu_g{}^b$) obtained using equation (10). The ground state dipole moment obtained using quantum chemical calculations is used for further calculations, as equation (10) assumes dipole moment are parallel in ground and excited states.

Fig. 6 shows the plots $\Delta\bar{V}$ versus $F_1(\varepsilon, n)$ and $(\bar{V}_a + \bar{V}_b)/2$ versus $F_2(\varepsilon, n)$. The linear progression was done and the data was fit to a straight line. The corresponding values of the slopes (m), correlation coefficients (r) and number of data points (n) are mentioned on respective plots. In both the plots good linearity was obtained for selected number of data points. The excited state dipole moments (μ_e) were calculated from the slopes of the respective plots and are given in Table 2 ($\mu_e{}^c$ and $\mu_e{}^d$).
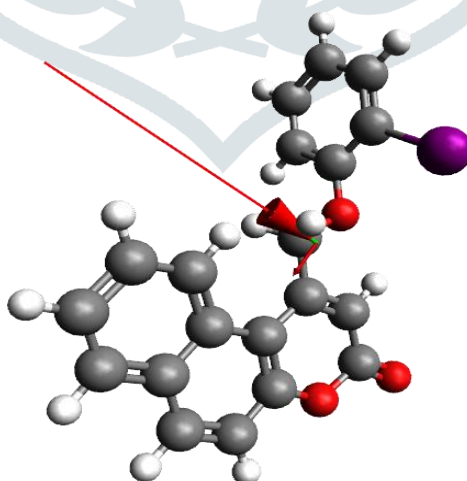

Figure. 5. Ground state optimized molecular geometry of 1IPBC.

Table 2: Onsager radius, ground-state and excited-state dipole moments in Debye (D).

Dye	Radius(Å)	$\mu_g{}^a$ (D)	$\mu_g{}^b$ (D)	$\mu_e{}^c$(D)	$\mu_e{}^d$(D)	$\mu_e{}^e$(D)	$\mu_e{}^h$(D)
1IPBC	4.08	7.01	0.21	8.66	7.15	8.44 [f]	1.44
						9.62 [g]	

[a] The ground state dipole moment from quantum chemical calculations
[b] The ground state dipole moment calculated using Eq. (10).
[c] The excited state dipole moment calculated from Bakshiev's equation.
[d] The excited state dipole moment calculated from Kawski-Chamma-Viallet's equation.
[e] The excited state dipole moment calculated from microscopic solvent polarity parameter function.
[f] The excited state dipole moment calculated from microscopic solvent polarity parameter function for non alcohols.
[g] The excited state dipole moment calculated from microscopic solvent polarity parameter function for alcohols.
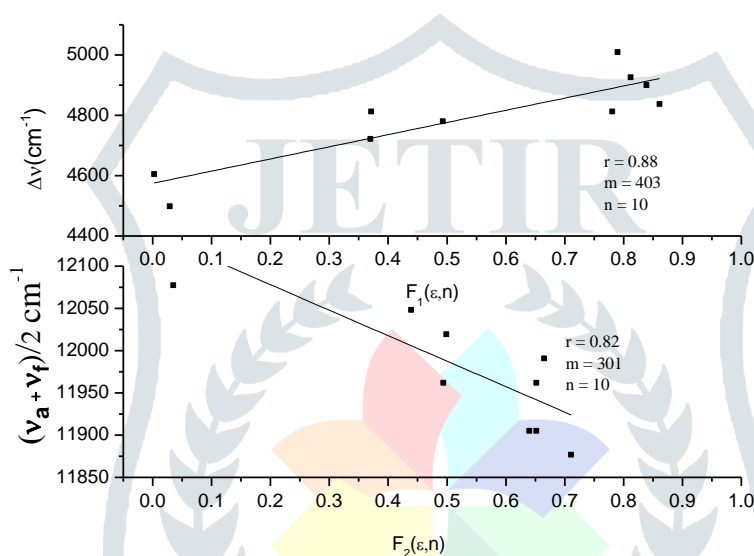[h] The excited state dipole moment calculated using Eq. (11).

Figure. 6. (A) Plot $\Delta \overline{v}$ versus $F_1(\varepsilon, n)$ and (B) Plot of $(\overline{v}_a + \overline{v}_f)/2$ versus $F_2(\varepsilon, n)$.

The double linear correlation of Stokes' shift with E_T^N prompted us to calculate excited dipole moments separately for non- alcoholic and alcoholic solvents according to **Fig. 3** and **Fig 4**. These values are also collected in Table 2 ($\mu_e{}^e$). The values of excited state dipole moments determined from different methods are slightly different. This could be due to difference in type of solute – solvent interactions considered.

The excited state dipole moment of 1IPBC was also estimated assuming that they are parallel using Eqs. (11). The estimated value is also given in **Table 2**   ($\mu_e{}^h$). The major difference in value μ_e with this assumption compared to respective values from other methods (Table 2) suggests that μ_g and μ_e are not parallel. This prompted us to estimate the angle between μ_g and μ_e according to Eq. (12). The estimated value is found to be 13.19^0. From **Table 2**, it is clear that the dipole moment of 1IPBC   is higher in the first excited-state compared to ground-state. This indicates the existence of a more relaxed excited state, due to intramolecular charge transfer (ICT).

IV. CONCLUSION

The effect of pure solvents on absorption and fluorescence characteristics of biologically active iodinated coumarin dye 1IPBC was studied with different solvent polarity parameters. A bathochromic shift with increase in polarity of solvent for the dye indicates the involvement of $\pi \rightarrow \pi^*$ transition. The double linear correlation of spectral properties with E_T^N indicates the role of solute-solvent interactions such as hydrogen bonding and dipole-dipole interactions. The contribution of general solute-solvent and hydrogen bonding interactions were quantified using Kamlet's and Catalan's multiple linear regression approach. The dipole moment of the dye is more in the first excited singlet state than in the ground state indicating the existence of a more relaxed excited state, due to ICT. As per our knowledge, this is the first report on extensive study of photophysical properties of the dye 1IPBC. This investigation would help in understanding the usage of the dye in various bio-medical applications.

V. ACKNOWLEDGMENT

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