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Effects of solvent polarity on the absorption and fluorescence spectra of 3-cyano-7-hydroxy-4-methylcoumarin: Determination of the dipole moments.

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Abstract
The Absorption and fluorescence emission spectra of 3-cyano-7-hydroxy-4-methylcoumarin (3C7H4M) were studied in solvents of different dielectric constant ε and refractive index n. Experimental ground and excited state dipole moments were established by means of solvatochromic shift method. Both the ground state and excited state dipole moments were established. Results revealed that the excited state dipole moments of 3C7H4M were higher than those of the ground state. Further it is evident from these results that, the changes in the dipole moments on electronic excitation are small.

Keywords*:* 3-cyano-7-hydroxy-4-, dipole moments, solvent polarity, spectral shifts

Introduction

Classical studies on photochemical properties of molecules require knowledge of spectral features.Fluorophoreshavedistinctive electronic and photonic properties such as, relatively shorter lifetime, high quantum yield and broad spectral band width which can be useful in a number of technological applications(Raikar et al., 2006).

Coumarin dyes are well known photosensitizing agents(Zhang, Zhang, & Xia, 2008). They can be used in photobiology because of their photodynamic actions. They are known to show interesting photochemical behavior, particularly dimerization in polar and non-polar solvents(Perez-Rodriguez, Aguilera, & Figueroa, 2003).

The widespread occurrence of coumarin derivatives in nature(Kirsch, Abdelwahab, & Chaimbault, 2016) and their variety of applications have made their study very interesting. Dipole moments of short-lived speciesare of significant interest as they provide bothelectronic and geometrical structure information of the dye(Sharma, Jain, & Rastogi, 2007).The information on dipole moments of electronically excited species is helpful in the designing non-linear optical materials and understanding their photochemical transformations(Patil, Melavanki, Kapatkar, Ayachit, & Saravanan, 2011). Fluorescence experimental data on excited states are handy in the parameterization of semi-empirical quantum chemical procedures for these states(Xie, Ho, Truelove, Corry, & Stewart, 2010).

Determination of the ground and excited state dipole moments of dye molecules is important, because the values so obtained provide information about the change in electronic distribution upon excitation(Biradar, Siddlingeshwar, & Hanagodimath, 2008)The most popular technique for the determination of excited state dipole moments is based on the Lippert–Mataga equationLippert(1955), Mataga, Kaifu& Koizumi, 1956), in which absorption and fluorescence shiftsdescribed by dielectric constant ε and refractive index n are followed using the solvent polarity.

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In this paper we report determination of dipole moments using different solvent parameters, refractive index, dielectric constant *ε*, spectral parameters like stokes shift. We have calculated the ground and excited state dipole moments of 3C7H4M dye by solvent perturbation method based on absorption and fluorescence shift in solvents with varied polarities.

Theoretical Bachground

From the quantum mechanical perturbation theory of absorption($\tilde{V}_a$) and fluorescence ($\tilde{V}_f$) band shifts in different solvent permittivity (ε) and refractive index (η), the following equations(Nagaraja, Patil, Kusanur, Patil, & Melavanki, 2012), were used to determine both ground state and excited state dipole moments of the sample dye;

$$\tilde{V}_a - \tilde{V}_f = m_1 f(\varepsilon, n) + constant \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and

$$\tilde{V}_a + \tilde{V}_f = m_2[f(\varepsilon, n) + 2g(n)] + constant \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

the solvent polarity parameter is given by;

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$g(n) = \frac{3}{2}\left[\frac{n^4-1}{(n^n+2)^2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

with

$$m_1 = \frac{2(\mu_e-\mu_g)}{hca^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and

$$m_2 = \frac{2(\mu_e^2-\mu_g^2)}{hca^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where *h* is thePlanck's constant, *c* is the velocity of light in vacuum.The parameters m1 and m2 occurring in eqns (1) and (2) are thelinear function of the solvent polarity parameters ($f(\varepsilon_r$, n), g(n)) andwere determined from the slopes of the straight line. Similarly, thesolvent polarity function resulting in the Lippert–Mataga equationcan be expressed using eqn(7).

$$f_{(\varepsilon_r, n)} = \frac{\varepsilon_r-1}{2\varepsilon_r+1} - \frac{n^2-1}{2n+1} \ldots\ldots\ldots\ldots\ldots (7)$$

Substituting equation (7) into equation (1), the Lippert–Mataga equation can be obtained. μ_g and μ_e are the dipole moments in the groundand exacted states respectively which are calculated as follows;

$$\mu_g = \frac{m_2-m_1}{2}\left[\frac{hca^3}{2m_1}\right]^{\frac{1}{2}} \ldots\ldots\ldots\ldots\ldots (8)$$

$$\mu_e = \frac{m_2+m_1}{2}\left[\frac{hca^3}{2m_1}\right]^{\frac{1}{2}} \ldots\ldots\ldots\ldots\ldots (9)$$

The Onsager radius "*a*" of the solute molecule can be evaluatedby using Edward's atomic increment methodassuming the molecules are spherical,(Kadolkar, Patil, Kariduraganavar, & Inamdar, 2019)as follows;

$$a = \left[\frac{3M}{4\pi\delta N_A}\right]^{1/3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where M is the relative molecular mass of the solute molecules,δ is density and N is Avogadro's number.

Change in dipole moment will be obtained from the slope of the graph of $\tilde{V}_a$-$\tilde{V}_f$versus the solvent polarity,

$$\Delta\mu = \mu_{\varepsilon} - \mu_{g} = \left(\frac{m\square ca^{3}}{2}\right)^{\frac{1}{2}}........................(11)$$

Experiment

3C7H4Mwas purchased from Aldrich Chemical Co. and was used without further purification. The molecular structure of 3C7H4M is as given in Fig. 1. All the solvents used viz., methanol, ethanol, ethyl acetate, THF, and *n*-hexane, were of spectroscopic grade. Electronic absorption spectra were recorded on a Merc UV-11 Model UV–Vis spectrophotometer. Fluorescence spectra were taken by using a Biobase-BKF93 Model F2000 fluorospectrometer at room temperature. Refractive index was measured using ATAGO model pocket refractometer PAL-1. Staining solutions of 3-cyano-7-hydroxy-4-methylcoumarin in water and methanol were prepared by dissolving 0.1 mg of the dye in 100 mL of distilled water (1 ppm). Iodine was prepared as per standard laboratory procedure. Each mixture was stirred for dye solubilization and filtered before use.

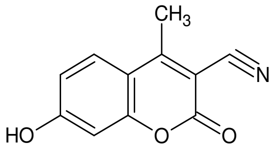

Fig.1. structure of 3-cyano-7-hydroxy-4-methylcoumarin

Results and discussion

Absorption and fluorescence emission spectra of 3-cyano-7-hydroxy-4-methylcoumarin (3C7H4M) and was recorded in solvents of different solvent parameters of dielectric constant ε and refractive index η. Figs. 2- and 3 show the absorption and fluorescence spectra of 3C7H4M respectively in solvents with various polarity indices as shown in table 1.

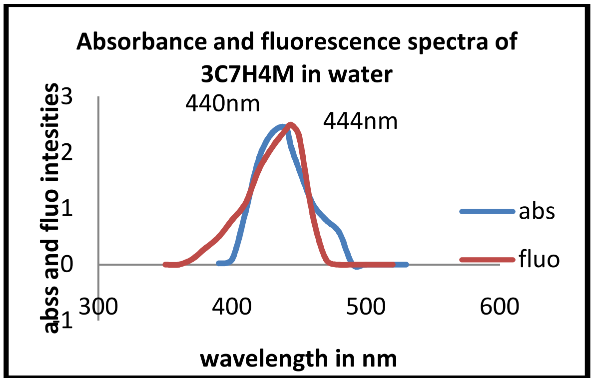

Fig. 2. Absorbance and fluorescence spectra of 3C7H4M in water

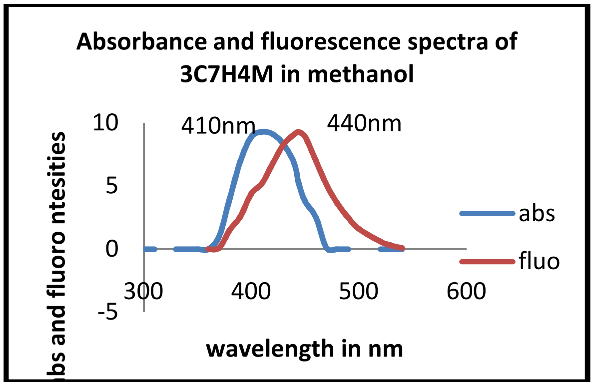

Fig. 3. Absorbance and fluorescence spectra of 3C7H4M in methanol

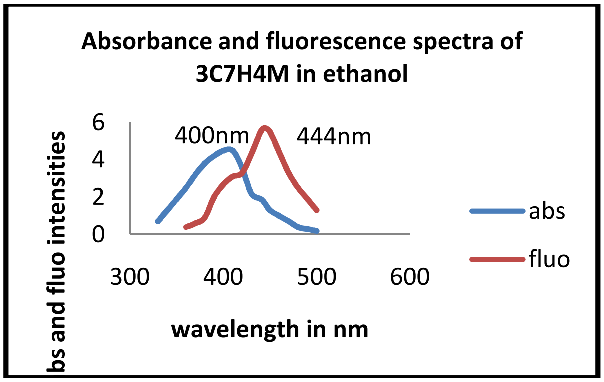

Fig.4. Absorbance and fluorescence spectra of 3C7H4M in ethanol

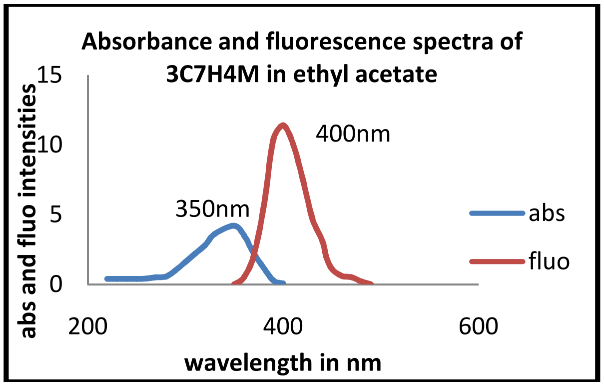

Fig.5. Absorbance and fluorescence spectra of 3C7H4M in ethyl acetate

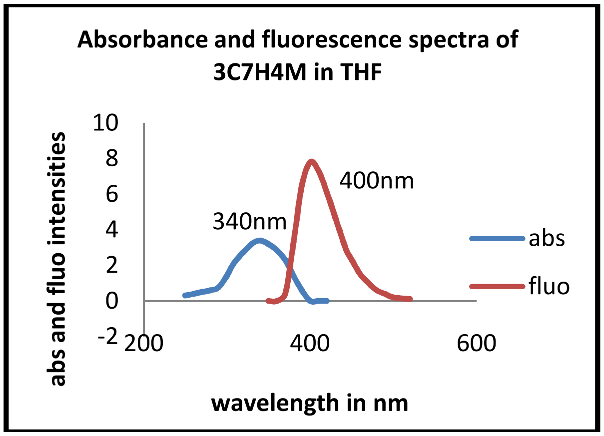

Fig.6. Absorbance and fluorescence spectra of 3C7H4M in THF

The absorption and emission spectra of 3C7H4M show maximum values around 340nm and 400nm respectively for THF, 350nm and 400nm respectively for ethyl acetate, 400nm and 444nm for ethanol respectively, 410nm and 440nm for methanol and 440nm and 444for water.

However, the hexane solution did not show any absorbance and emission. This resulted in stokes shift ranging from 04–60nm on changing the solvent from water to THF and the emission spectra. The absorption and emission maxima, dielectric constant and refractive index of 3C7H4M in different solvents are given in Table 1.

Table 1. The calculated values of the solvent polarity parameters

SOLVENT	polarity index	λ_{max} (Abs) nm	λ_{max} (Fluo) nm	ε	η	$\tilde{V}_a$-$\tilde{V}_f$ (cm^{-1})	$\tilde{V}_a$+$\tilde{V}_f$ (cm^{-1})	f(ε,η)	g(η)	f(ε, η)+2g(η)
THF	4	340	400	7.6	1.41	4411.76	54411.8	1.16	0.28	1.44
Ethyl Ac	4.4	349	400	6	1.37	3653.30	53653.3	1.26	0.25	1.51
Ethanol	5.2	400	444	24.3	1.34	2477.48	47522.5	1.01	0.23	1.24
Methanol	6.6	408	440	32.7	1.33	1782.53	47237.1	1.00	0.23	1.22
Water	10.2	440	444	78.4	1.33	204.75	45249.8	0.97	0.23	1.20

η =Refractive index of the solvent.
ε =Relative permittivity of the solvent.
$f(\varepsilon, \eta)$=Solvent polarity calculated using eqn (3).
$f(\varepsilon, \eta)+2g(\eta)$=Solvent polarity calculated using eqns (3) and (4).

The charge transfer band shows a shift of about 04–60 nm in the absorption spectra on changing the solvent from THF to water and the emission spectra show smaller shift as compared with the absorption spectra. Thehighly pronounced absorption shift between water and other solvents implies that the ground state energy distribution is affected to a greater extent possibly due to the polar nature of 3C7H4M.

The values of the Stokes shifts are also indicative of the charge transfer transition. On changing the solvent from a low polar, like THF to high polar like ethyl acetate shows a difference in Stokes shift of about 9nm again indicative of a charge transfer transition. The large magnitude of the Stokes shift indicates that the excited state geometry could be different from that of the ground state. The general observation is that there is an increase in the Stokes shift values with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation.

Figs. 4 and 5 show the spectral shifts (in cm^{-1}) $\tilde{v}_a$- $\tilde{v}_f$ and $\tilde{v}_a + \tilde{v}_f$ of 3C7H4M in polarity functions $f(\varepsilon, n)$ and$f(\varepsilon, n) + 2g(n)$. A linear progression was done data was fit to a straight line. Theslopes m_1 and m_2 of the fitted lines shown in Figs. 4and 5.

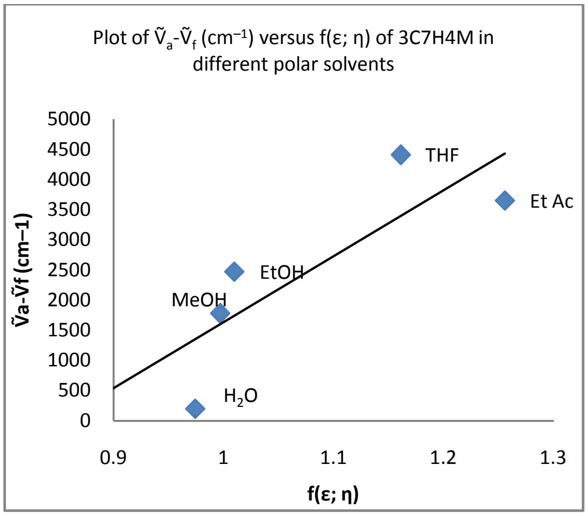

Fig.4. A Plot of $\tilde{V}_a$-$\tilde{V}_f$ (cm^{-1}) vs. $f(\varepsilon, n)$ of 3C7H4M in different solvents.

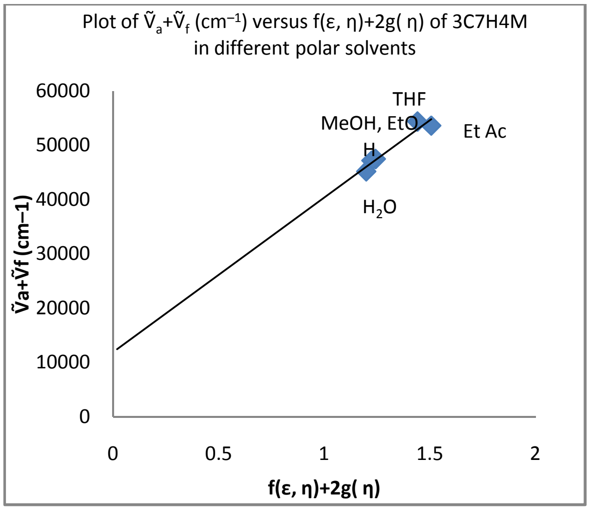

Fig.5. A Plot of $\tilde{V}_a$+ $\tilde{V}_f$ (cm^{-1}) vs. $f(\varepsilon, \eta)+2g(\eta)$of 3C7H4M in different solvents.

The slopes of Figs. 4 and 5 were found to bem_1 = 9308cm^{-1} and m_2 = 11945cm^{-1} and the Onsagerradius (a)of solute was calculated using the equation;

$$a = \sqrt[3]{\frac{3M}{4\pi\rho N}} \simeq 4.3A$$

Where M is the molecular weight of the dye; ρ is the density of the dye; N is the Avogadro's number. We have approximated the density of this compound to be1 g/mL.By using Eqns. (3)and (4), we get μg = 3.08 D and μe = 3.9 D and the changein the dipole moments ($\Delta\mu = \mu_g - \mu_e$)is 0.82 D. From Eqns. (8) and (9), the dipole moments μ_g and μ_e depends not only on m_1 and m_2 but also on radius of the solute. The linear dependence of spectralshifts on polarity function (Fig. 4 and 5) exhibits a good correlation. These experimental values were obtained in solution phase, where the solvent (matrix) is expected to introduce strong perturbation. Further it is evident from these results that, the changes in the dipole moments on electronic excitation are small.

Conclusion

Both excitation and emission wavelengths of 3C7H4M in different solvents varying in polarity index has been determined. The Onsager radius has been calculated and the surface area of the molecule has been established, assuming the molecule as spherical and density is 1 g/mL.The determinations of dipole moments of C7H4M in the ground and excited states have shown that C7H4M is more polar in the excited state than the ground state.

Conflict of interest statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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