

EFFECTS OF SOLVENTS ON ACRIDINE YELLOW G

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Abstract: The present paper reports about the study of Stokes shift for the Acridine Yellow G fluorescent laser dye molecule in different alcoholic and aqueous solvents. In all the solvents it is observed that the Fluorescence wavelength is greater than that of excitation wavelength (redshift, $\pi \rightarrow \pi^*$) The ground state dipole moment (μ_g) and the excited state dipole moment (μ_e) of Acridine Yellow G fluorescent laser dye are estimated in various alcoholic solvents by various Solvatochromic methods like Lippert, Bakhshiev, Kawski-Chamma-Viallet, McRae, Suppan, all these calculations are made by assuming that dipoles are oriented parallel in ground and excited state but in real molecule they are not in parallel; but oriented with some angle φ , and same estimated. The excited state dipole moments were also estimated by taking the variation of Stokes shift with microscopic solvent polarity parameter (E_T^N).

Introduction: A systematic analysis of the solvent effect on laser dye molecules is informative and proves fruitful in studying the excited state behaviour of the molecule. When a molecule is excited by interaction with radiation, its dipole moment gets changed and molecule remains no more in equilibrium with its immediate environment, and it relaxes with non-radiative emission further the shift in fluorescence wavelength occurs according to the Frank-Condon principle. In this paper we made systematic study on the photo-physical parameter i.e. dipole moment of ground and excited states of laser dye molecule Acridine yellow G by various solvatochromic methods and we also calculated the angle between the excited and ground state dipole moments and oscillating strength in various solvents, and estimated Einstein co-efficient which plays very important role in emission study. In the present paper we consider that solvent environment effect on acridine dye, It has biological importance as stain. Acridine yellow G is used as fluorescent probe for non invasive cytoplasmic PH changes in whole cell.

Theoretical Consideration: The change of dipole moment in excited with respect to ground state is determined by various solvatochromic methods which considers bulk solvent parameters such as dielectric constants and refractive index of media, while Ravi et-al theory correlates the microscopic polarity parameter (E_T^N). In this paper we studied both cases i.e bulk polarity functions and microscopic polarity functions. Here to determine the dipole moment in excited state with the solvatochromic method, several approaches were used viz., Lippert Bakhshiev, Kawski-Chamma-Viallet, McRae, Suppan.

Experimental: Chemicals: Laser dye from Sigma Aldrich, USA and was used directly.

Molecular structure given in Fig. 1. Product name: Acridine yellow G Brand: Aldrich Solvents used are Methanol, Ethanol, Propanol, Butanol and Decanol.

Instrumentation: Electronic UV/VIS absorption measurements are made using HITACHI 2000 double

beam spectrometer and fluorescence measurements done by F-7000 FL Spectrophotometer.

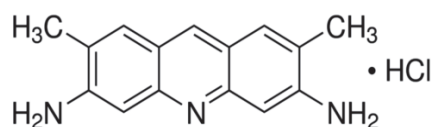
Molecular Structure

Fig 1. Molecular Structure of Acridine yellow G.

General Procedure: Determination of Dipole moment:

The independent equations are used for the determination of ground and excited state dipole moments are as follows

1) Lippert's Equation

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F(\epsilon, n) + \text{cons}$$

2) Bakshiev's polarity function

$$\bar{\nu}_a - \bar{\nu}_f = m_2 F_1(\epsilon, n) + \text{cons}$$

3) Kawski-Chamma-Viallet's polarity function

$$\frac{\bar{\nu}_a - \bar{\nu}_f}{2} = -m_3 F_2(\epsilon, n) + \text{cons}$$

4) McRae's equation

$$\bar{\nu}_a = m_4 F_3(\epsilon) + \text{cons}$$

5) Suppan's equation

$$\bar{\nu}_a = m_5 F_4(\epsilon) + \text{cons}$$

Where, ϵ -Dielectric constant of solvent, n -Refractive index of solvent, m_2 and m_3 are slopes from graph a-onsager cavity radius. The expression $F(\epsilon, n)$ [Lippert's polarity parameter], $F_1(\epsilon, n)$ [Bakhshiev's polarity parameter], $F_2(\epsilon, n)$ [Kawski-Chamma-Viallet's polarity parameter], $F_3(\epsilon, n)$ [McRae's polarity parameter] and $F_4(\epsilon, n)$ [Suppan's polarity parameter] are given as:

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

$$F_3(\epsilon) = \left[\frac{2(\epsilon - 1)}{\epsilon + 2} \right]$$

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

$$F_4(\epsilon) = \left[\frac{2(\epsilon - 1)}{2\epsilon + 2} \right]$$

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

Where ν_a and ν_f are absorption and fluorescence maxima are in wave numbers respectively and ϵ, n are dielectric constant and refractive index of the solvents respectively. Plotting the graphs of Equations 1-5 it follows that $(\nu_a - \nu_f)/\nu F(\epsilon, n)$,

$(\nu_a - \nu_f)/\nu F_1(\epsilon, n)$, $\frac{1}{2}(\nu_a + \nu_f) \nu/s F_2(\epsilon, n)$, $\nu_a \nu/s F_3(\epsilon)$, and $\nu_a \nu/s F_4(\epsilon)$ should give linear graphs with slopes m_1, m_2, m_3, m_4, m_5 respectively and these are given as:

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

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

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}$$

$$m_4 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3}$$

$$m_5 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3}$$

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2}$$

$$\mu_e = \frac{m_3 + m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2}$$

$$\mu_e = \left[\frac{m_3 + m_2}{m_3 - m_2} \right] \mu_g$$

Where μ_g and μ_e are the ground and excited state dipole moments of the solute molecule respectively, h and c are plank's constant and velocity of light in vacuum respectively and a is the onsager cavity radius.

The validity of these equations is based on certain assumptions:

1. μ_g and μ_e dipole moments are collinear.
2. In ground and excited state Onsager cavity radius remains same
3. Polarizability of the molecule and Hydrogen bonding effects are ignored.

All these calculations are calculated by assuming the μ_g and μ_e are parallel with each other, but in real they are not parallel the angle between them is calculated by

$$\cos \phi = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{m_2}{m_3} (\mu_e^2 - \mu_g^2) \right]$$

These calculations are also compared by correlation as the spectral shift with E_N^T parameter proposed by Reichardt et.al and improved by Ravi et.al

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a}\right)^3 \times 11307.6}}$$

Where m is slope of stoke shift versus E_N^T

Determination of Einstein coefficients and oscillating strength

To describe spontaneous emission, induced absorption and emission Albert Einstein introduced coefficients (A&B),

These are defined by equations

$$A = \frac{2me^2}{\epsilon_0 mc \lambda^2} f \quad \& \quad B = \frac{\lambda^2}{8\pi h} A$$

Where m =mass of electron, c =velocity of light

ϵ_0 =permittivity of space, f =oscillating strength, λ =Absorption wavelength, h =Planks constant The oscillating strength (f) can be calculated using

$$\text{equation } f = \frac{2.303mc^2}{\pi N e^2} \int \epsilon(\nu) d\nu$$

Where N =Avogadro number, ν =frequency in wave numbers, m =mass of electron, c =velocity of light, e =charge of the electron The integral $\int \epsilon(\nu) d\nu$

Gives the area of the transition band under consideration, The approximate value is given by $\int \epsilon(\nu) d\nu = 1.06 * \epsilon * \text{bandwidth} * \text{half maximum}$

Determination of radiative life time: The radiative life time is given by reciprocal of spontaneous Einstein coefficient i.e $\tau = \frac{1}{A}$ nano sec

Molar extinction coefficient calculation: $\epsilon = \frac{A}{bc}$

(Theoretical) $\epsilon = \frac{M}{b}$ (Graphically)

Where A=absorption, C=concentration, b=path graph length, M=slope of absorption v/s concentration

Table 1

Sl No	Dye	Solvent	u_a	u_f	$(u_a - u_f)$	$(u_a + u_f)/2$	E_N^T
1	Acridine Yellow G	Ethanol	463.5	509.4	39.6	483.55	0.65
2		Propanol	458	500.7	42.5	479.25	0.54
3		Butanol	458.25	497.9	39.3	477.9	0.58
4		Decanol	462.5	503.6	41.15	483.07	0.525

Table 2.

Compound	Dipole moment μ_g	Bakshew & Chemmavillatte μ_e	Lippert μ_e	Mac rae μ_e	Suppan μ_e	$\Delta\mu$ Expt	$\Delta\mu$ Ravi et.al	Angle between dipole moment
Acridine Yellow	2.12	2.48	2.61	2.30	2.67	0.36	0.12	$\cos \phi = 1.00$

Table 3:

Acridine Yellow G in Ethanol solvent

Con (M)	F	A	B
1×10^{-5}	0.00348	1.09×10^6	1.39×10^{25}
2×10^{-6}	0.01112	3.5×10^6	4.46×10^{25}
3×10^{-6}	0.01038	3.3×10^6	4.16×10^{25}
4×10^{-6}	0.07246	2.1×10^6	2.91×10^{26}

Acridine Yellow G in Propanol solvent

Con (M)	f	A	B
1×10^{-5}	0.01317	4.2×10^6	5.29×10^{25}
2×10^{-6}	0.00267	8.5×10^5	1.07×10^{25}
3×10^{-6}	0.00247	7.8×10^5	9.91×10^{25}
4×10^{-6}	0.00144	4.5×10^5	5.78×10^{25}

Acridine Yellow G in Butanol solvent

Con (M)	F	A	B
1×10^{-5}	0.00823	2.6×10^6	3.3×10^{25}
2×10^{-6}	0.00411	1.3×10^6	1.65×10^{25}
3×10^{-6}	0.00065	2.09×10^5	2.64×10^{24}
4×10^{-6}	0.00173	5.5×10^5	6.94×10^{24}

Acridine Yellow G in Decanol solvent

Con (M)	F	A	B
1×10^{-5}	0.00033	1.02×10^5	1.3×10^{24}
2×10^{-6}	0.00082	2.5×10^5	3.3×10^{24}
3×10^{-6}	0.00123	3.8×10^5	4.9×10^{24}
4×10^{-6}	0.00100	3.14×10^5	4.0×10^{24}

Table 4. Molar extinction coefficients (ϵ) of Acridine Yellow G

Solvents	$\epsilon \times 10^5$
Ethanol	0.78
Propanol	0.16
Butanol	0.22
Decanol	0.06

Result and discussion: To estimation of ground state and excited state dipole moment experimentally we considered the absorption and emission spectral data in different solvents and that is recorded in Table 1. The shift in emission is more than absorption this indicates that dipole moment in excited state is more than ground state. In table 2 we estimated the dipole moment for the dye and recorded angle between dipole moment in ground and excited states for the molecule. We calculated the oscillating strength, Einstein co-efficient and radiative life time and finally molar absorption co-efficient for the dye Table 3 and 4.

There is no much difference in theoretical and experimental values of dipole moments because assumptions what we made in theory are almost valid in practical

The assumptions are a) dipole moments are collinear in ground and excited state

b) Solute molecules are spherical in solvent

There is small discrepancy may be attributed to Cl^- ions and protonated N present in acridine skeleton. It has been observed that this theory may deviate for dyes containing halogen atom.

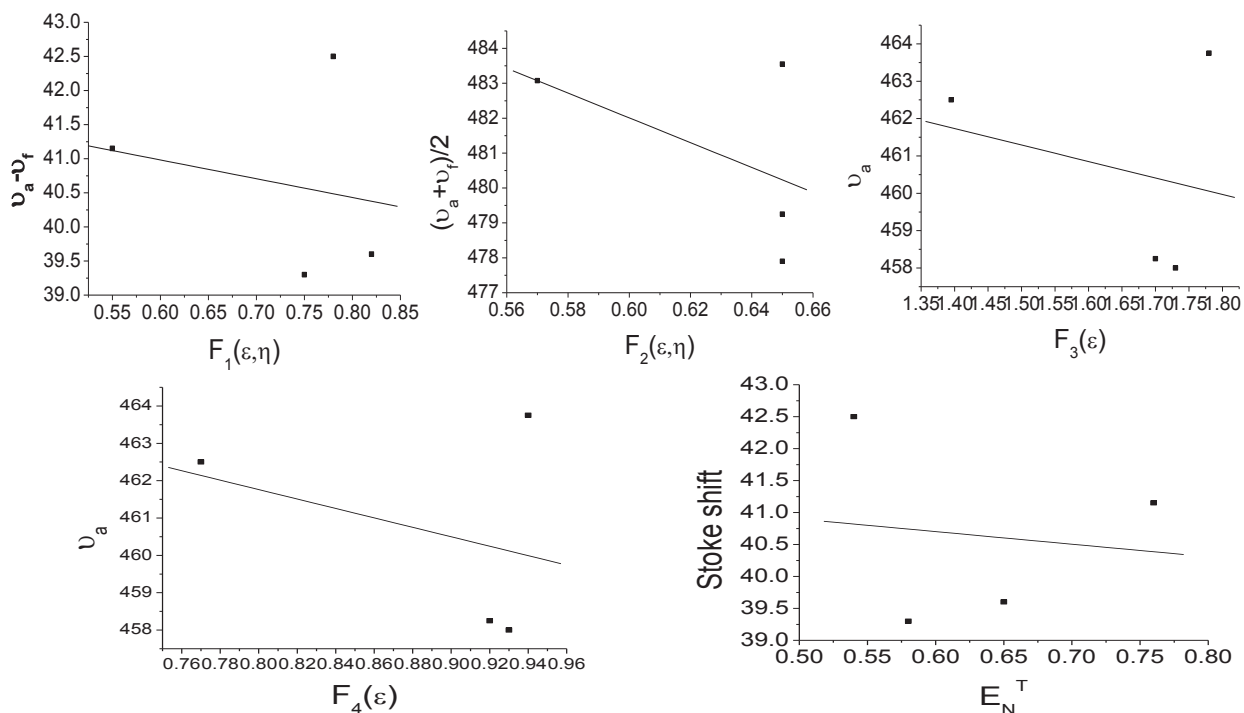
The theory in the Ravi et.al paper is a good agreement with experimental values this indicates that both microscopic polarity functions and bulk polarity functions are plays important role in present case. On comparison with all solvatochromic methods Bakhshive's and chemmavillet is more good agreement with Ravi et.al theory.

The N atom in amino group is protonated to give high fluorescent property. The basic nature of central nitrogen in molecules is PH sensitive therefore the dye may lose their energy in non-radiative form into media which lead to the efficiency loss, comparatively other acridine dyes like acriflavine dye.

Conclusion: This paper reports the following results,

- Dipole moment in excited state is more than in ground state.
- The absorption and emission in both dyes results $\pi-\pi^*$ transition.
- The angle between the ground and excited state of acridine yellow G is also calculated which makes us clear that dipoles are collinear in ground and excited state.
- Einstein co-efficient, oscillating strength are estimated and recorded.

Graphs for acridine Yellow G



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