

Effects of Solvents on photo physical properties of Acridine laser dye

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Abstract

In electronically excited molecules, the distribution of electrons can be described by the measurement of the permanent dipole moment (μ_e), which is obtained from the measurement of solvatochromic shifts of absorption and/or fluorescent spectra. Acridine orange has biological application as a popular stain for its use in fluorescence microscopy.

This paper reports the study of Stokes shift for the Acridine Orange hemi (zinc chloride) salt, a 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 (red shift, $\pi \rightarrow \pi^*$). The ground state dipole moment (μ_g) and the excited state dipole moment (μ_e) of Acridine Orange hemi (zinc chloride) salt 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 the dipoles are oriented parallel in the ground and excited state, but in real molecule they are not in parallel but oriented with some angle φ , which is estimated. The excited state dipole moments were also estimated by taking the variation of stokes shift with microscopic solvent polarity parameter (E_T^N). The oscillating strength of molecule and Einstein coefficients has been examined in different concentrations of the aqueous solvent by using the excitation wavelength of the molecule. Radiative life time and molar absorption co-efficient of the fluorophore is estimated.

1. Introduction

When a molecule is excited, its dipole moment gets changed and it 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. Knowledge of this state of the molecule is quite useful in designing non-linear optical material. An important property of this state is, the change in dipole moment, so the study of dipole moment gives us some information about the excited state.

The study of excited State of the molecule in the different solvent environment is very helpful to design medicine because that medicine does not behave in the same manner in all human body and in all situations. A number of experimental methods are available for this study among all these, we use solvetochromic method for our work. The Acridine orange hemi (zinc chloride) salt fluorescent laser dye is a very good media for efficient broadband laser dye in the green region fluorescence. Acridine orange is widely found its application in staining. Instead of all these, we made a systematic study of the photo-physical parameter i.e. dipole moment of ground and excited states are determined by various solvetochromic methods and are compared. We also calculated the angle between the excited and ground state dipole moments and oscillating strength in various solvents.

2. Experimental

2.1 Compound: The ACS grade Acridine Orange hemi (zinc chloride) salt fluorescent laser dye was obtained from Sigma Aldrich, USA and was used directly. The molecular structure of the Acridine Orange hemi (zinc chloride) salt fluorescent laser dye is given in

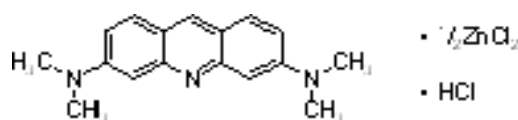


Figure 1

Product name: Acridine Orange hemi (zinc chloride) salt fluorescent laser dye

Solvents used: Methanol, Ethanol, Iso-propanol, Butanol, Nonanol, Deconal, DMSO and Water.

2.2 Instrumentation:

Electronic UV/VIS absorption measurements are made using HR4000 high resolution USB spectrometer [1] at room temperature.

2.3 General Procedure:

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

$$\text{Lippert's Equation [2]} \quad \bar{\nu}_a - \bar{\nu}_f = m_1 F(\epsilon, n) + \text{cons} \quad (1)$$

$$\text{Bakshiev's equation [3]} \quad \bar{\nu}_a - \bar{\nu}_f = m_2 F_1(\epsilon, n) + \text{cons} \quad (2)$$

$$\text{KawskiChammaViallet's equation [4]} \quad \frac{\bar{\nu}_a - \bar{\nu}_f}{2} = -m_3 F_2(\epsilon, n) + \text{cons} \quad (3)$$

$$\text{McRae's equation,} \quad \bar{\nu}_a = -m_4 F_3(\epsilon) + \text{cons} \quad (4)$$

$$\text{Suppan's equation [5]} \quad \bar{\nu}_a = -m_5 F_4(\epsilon) + \text{cons} \quad (5)$$

where $F(\epsilon, n)$, $F_1(\epsilon, n)$, $F_2(\epsilon, n)$, $F_3(\epsilon)$, & $F_4(\epsilon)$ are polarity parameters of Lippert's, Bakshiev's, KawskiChammaViallet, McRae, Suppanrespectively, Their expressions are given below

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

$$F_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \tag{7}$$

$$F_2(\epsilon, n) = \left[\frac{2n^2 + 1}{n^2 + 2} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3(n^4 - 1)}{2(n^2 - 1)^2} \right] \tag{8}$$

$$F_3(\epsilon) = \left[\frac{2(\epsilon - 1)}{\epsilon + 2} \right] \tag{9}$$

$$F_4(\epsilon) = \left[\frac{2(\epsilon - 1)}{2\epsilon + 2} \right] \tag{10}$$

By plotting graphs $\bar{\nu}_a - \bar{\nu}_f$ v/s $F(\epsilon, n)$, $\bar{\nu}_a - \bar{\nu}_f$ v/s $F_1(\epsilon, n)$, $\frac{1}{2}(\bar{\nu}_a + \bar{\nu}_f)$ v/s $F_2(\epsilon, n)$, $\bar{\nu}_a$ v/s $F_3(\epsilon)$, and $\bar{\nu}_a$ v/s $F_4(\epsilon)$, we obtain the m_1, m_2, m_3, m_4 & m_5 slopes respectively and are given as,

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{11}$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{12}$$

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{13}$$

$$m_4 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3} \tag{14}$$

$$\text{and } m_5 = \frac{\mu_g(\mu_e - \mu_g)}{hca^3} \tag{15}$$

Using these slopes Ground state and excited state dipole moments are determined as below

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

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

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

In reality, the dipole moments are not in collinear and parallel to each other but they oriented with some angle[6] that can be calculated as follows.

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

Solvent polarity parameter (E_T^N) calculated by using the formula[7,8]

$$E_T^N = \left\{ \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} \right\}$$

2.4 Determination of Einstein co-efficient:

Albert Einstein introduced co-efficients [9] to describe the spontaneous emission (A) and induced absorption (B). They are given by

$$A = \frac{2\pi e^2}{\epsilon_0 m c \lambda^2} f \text{ and } B = \frac{\lambda^2}{8\pi h} A$$

Where m=mass of the electron, c=velocity of light, ϵ_0 =permittivity of space, f=oscillating strength, λ =Absorption wavelength, h=Planks constant.

Oscillating strength can be calculated

$$f = \frac{2.303 m c^2}{\pi N e^2} \int \epsilon(\bar{u}) d\bar{u}$$

Where

N=Avogadro number, m=mass of the electron, c=velocity of light, e=charge of the $1.06 \times \epsilon \times \text{FWHM}$ electron. The integral gives the area of transition band under consideration, the approximation value is

2.5 Determination of Radiative life time:

The time period in which the fluorophore remains in its excited state is called radiative life time [9] and is given by reciprocal of spontaneous Einstein coefficient.

$$\text{i.e. } \tau = \frac{1}{A} \text{ nS}$$

2.6 Determination of Molar absorption co-efficient:

Molar absorption co-efficient is a measurement of how strongly light get absorbed by chemical species at given wavelength

$$\epsilon = \frac{A}{bc} \text{ (Theoretical)}$$

$$\epsilon = \frac{M}{b} \text{ (Practical)}$$

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

Results and Discussions:

Table1. Wave numbers (cm^{-1}) for the absorption and fluorescence emission maxima of Acridine Orange hemi (zinc chloride) salt molecule in different solvents and Stokes shift.

Solvents	Absorption Max (nm)	Fluorescence Max (nm)	$\bar{\nu}_a$	$\bar{\nu}_f$	$\bar{\nu}_a - \bar{\nu}_f$	$\frac{1}{2}(\bar{\nu}_a + \bar{\nu}_f)$	E_T^N
Methanol	488.55	543.14	20468.7	18411.4	2057.3	19440.0	0.858
Ethanol	487.84	535.76	20498.5	18655.0	1833.5	19581.7	0.861
Isopropanol	487.84	541.63	20468.7	18462.7	2006.0	19465.7	0.858
Butanol	489.30	538.69	20437.3	18563.5	1873.8	19500.4	0.855
Nanonol	489.30	543.14	20437.3	18411.4	2025.9	19424.3	0.855
Decnol	490.06	541.63	20405.6	18462.7	1942.9	19434.1	0.853
DMSO	488.55	565.28	20468.7	17690.3	2778.4	19079.5	0.858

Table 2. Onsager cavity radius, Ground state and excited state dipole moment (in Debye, D), excited state dipole moment from microscopic solvent polarity methods & angle of orientation of dipoles results of Acridine Orange hemi (zinc chloride) salt by various methods.

Onsagar cavity radius 'a' (\AA^0)	Bakshiev & Chamma μ_g, μ_e		Lippert μ_e	Mc'Rae μ_e	Suppan μ_e	$\frac{\mu_e}{\mu_g}$	$\cos \phi$
3.34	0.83	2.47	5.51	1.95	4.37	2.9	0.99

Table3.Einstein coefficients for various aqueous solvents

Concentrations $\times 10^{-4}$	Oscillating strength 'f'	Einstein coefficient 'A' $\times(10^8)$	Einstein coefficient 'B' $\times(10^{20})$	Molar extension co- efficient ϵ (mol^{-1} cm^{-2}) $\times 10^4$	Radiative life time $\tau_x(10^{-8})$ S
1	0.071	0.205	0.029	351	4.87
2	0.063	0.185	0.026	286	5.40
4	0.040	0.118	0.016	200	8.46
6	0.031	0.090	0.012	167	11.11
8	0.029	0.080	0.010	156	11.70
10	0.027	0.070	0.010	134	12.80

Table 1 Shows that Stokes shift varies accordingly refractive index (n) and dielectric constant (ϵ) of various solvents. The absorption spectra show maximum around 490nm and the emission spectra are recorded by the exciting the sample at its largest absorption maxima. For the prediction of excited state dipole moment E_T^N is tabulated. From the Table2 it is clear that excited state Dipole moment is greater than the ground state and the angle between these dipoles is calculated. Einstein coefficient, molar absorption coefficient and a radiative life time of a fluorophore in an aqueous solvent are estimated and tabulated in Table 3

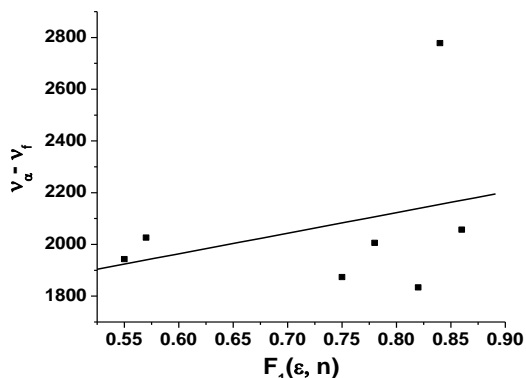


Fig.2 Plot of $(v_a - v_f) v/s F_1(\epsilon, n)$ Slope M_2

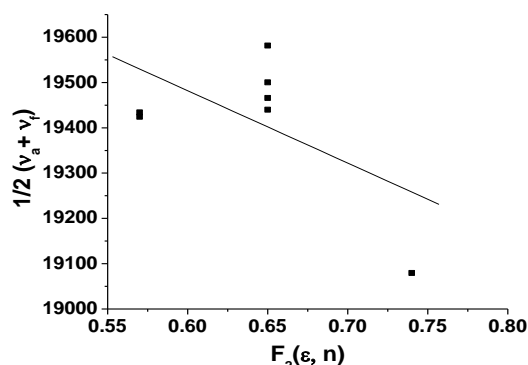


Fig.3 Plot of $1/2 (v_a + v_f) v/s F_2(\epsilon, n)$ slope M_3

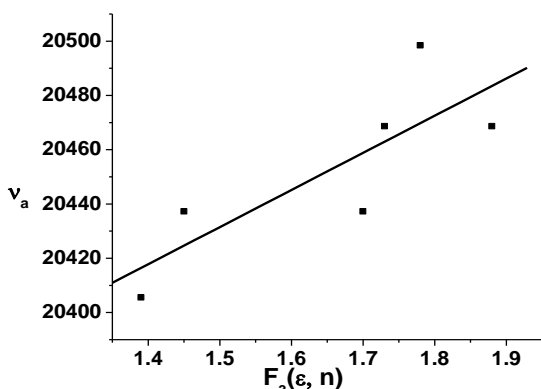


Fig.4 plot of $F_3(\epsilon, n) v/s v_a$ Slope M_4

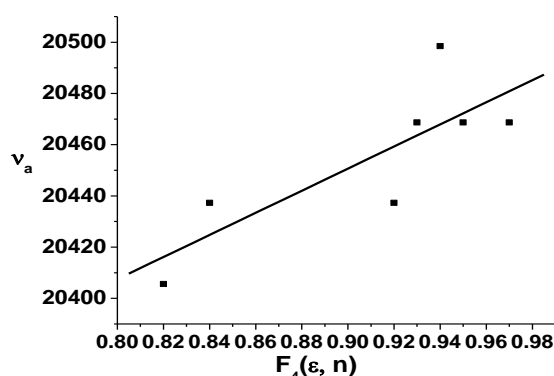


Fig.5 Plot $v_a v/s F_4(\epsilon, n) M_5$

Conclusion:

From the above results, we made the inference that the magnitude of the stoke shift varies between 1942 cm^{-1} to 2006 cm^{-1} (Table 1), which is indicating intra-molecular charge be different from that of the ground state.

Due to $\pi \rightarrow \pi^*$ transition, there is an increase in the dipole moment from the ground state to the excited state, which is due to the fact that the organic molecules become considerably more polar, when electronically excited. The electronic charge distribution of $\pi \rightarrow \pi^*$ transition in the excited state is more extended than that of the ground state making the excited state more polarizable. This suggests that it is a locally excited intra- molecular charge transfer (ICT) state. The amino group in the mero-phenyl ring is protonated to give high fluorescent and as a result, twisted ICT (TICT) states are formed. Further, the absorption band of the acridine orange is pH sensitive because the central nitrogen atom acts as a base.

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