Effect of Solvent on of 4- Phenyl-7-Hydroxy Coumarin - P – Chloro Anilide

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Abstract

The absorption and fluorescence emission spectra of 4- phenyl-7-hydroxy Coumarin - p-chloroanilide have been reported in various polar and non polar solvents. The increase in solvent polarity shows the increase in absorption and emission wave length i.e $\pi\rightarrow\pi^*$ transition. This indicates the value of excited state dipole moments can't be calculated using the solvatochromic data. The results are explained in terms of bathochromomic-shift, and possibility of hydrogen bonding.

1. Introduction

A large number of coumarin derivatives, with different substituent, occur as natural products and most of them are synthesize in laboratory[1]. The photo- physical property of coumarin depends on the nature and position of substituent in the parent molecule and also change, due to change in surrounding media. The solvatochromicanalysis using the Stoke's shift data is useful in calculating the excited state dipole moment (μ_e) of the molecule[2]. The knowledge of excited state dipole moment and excited state charge distribution[3] is important in understanding the photo – physical processes. A prior knowledge of the excited state is found helpful to assess the efficacies of quantum chemical derivation of wave function as well as electron correlation treatment. There has been a renewed interest in understanding excited state dipole moments, in connection with the design of organic molecules having large hyper – polarizabilities, to fabricate efficient nonlinear optical molecules[4]. A systematic study of solvent effect, in general, gives information about the first excited singlet sates behavior of a molecule. Structural stability of the molecule can be inferred from the study of their polarization values in different organic solvents and also from the temperature dependent studies of fluorescence emission[5-6]. In the present work, the authors have studied the Stoke's shift data for 4- phenyl-7-hydroxy Coumarin - p-chloroanilide & and calculated values of function $F_1(D,n)$ & $F_2(D,n)$ for different solvents.

2. Experimental Details

The flavanone and its derivatives were synthesized and investigated, by adopting standard method published elseware[7]. The absorption spectra were obtained with a Shimadzu-260, UV-VIS recording spectro-photometer and the fluorescence spectra using an Aminco-Bowman spectrophoto-fluorometer. The recorded fluorescence emission wavelengths are accurate with in ± 2 nm and the absorption wavelengths within ± 1 nm.

3. Results and discussion

The structure of the various flavanones studied (I) are given in Fig. 1. The observed values of $\overline{V}_a$ (longest absorption wavelength maxima) and $\overline{V}_f$ (fluorescence band maxima) in various polar and non polar organic solvents along with the calculated values of the solvents parameters $F_1(D,n)$ $F_2(D,n)$ are parented in Table 1.

Solvent effect excited state dipole moment

Solvatochromic analysis is generally used for estimating the excited state dipole moment of the fluorescence molecules[5-6,9]. The following relations obtained from the theoretical consideration for the solvents effect, are useful on obtaining the excited state dipole moments[2].

$$\left(\bar{\nu}_a - \bar{\nu}_f\right) = S_1 F_1(D,n) + K_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

And

$$\frac{1}{2}\left(\bar{\nu}_a - \dot{\nu}_f\right) = S_2 F_2(D,n) + K_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Here, $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima, n is the refractive index and D the dielectric constant of the solvent. The expression for S_1 and S_2 are :

$$S_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hCa^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

and

$$S_2 = \frac{-2\left(\mu_e^2 - \mu_g^2\right)^2}{hCa^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where μ_e and μ_g arec the excited and ground state dipole moment of the solute molecule, 'a' is the Onsagar cavity radius, h is the Planck's constant and C is the velocity of light. Further F_1 (D,n) and F_2(D,n) are given by the relation:

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

And

$$F_2(D,n) = \frac{1}{2} F_1(D,n) + \frac{3}{2}\left[\frac{\left(n^4-1\right)}{\left(n^2+2\right)^2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

If the included shifts are neglected in $\bar{\nu}_a$ and $\bar{\nu}_f$ due to complex formation, charge transfer and hydrogen bonding etc. and further assumed that, the angle between μ_e and μ_g is small and the cavity radius 'a' is same in both the ground and excited states, than from Eqs (1) and (2) the ratio of the dipole moments in the excited state and the ground state is given by:

$$\frac{\mu_e}{\mu_g} = \frac{\left|S_1 - S_2\right|}{\left|S_1 + S_2\right|} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Further the value of excited state dipole moment can be obtained if the Onsager cavity radius 'a' is known, using (3) and (4)

$$\mu_e = \frac{a}{2}\frac{\left(hCaS_1\right)^{1/2}}{} \left[1 - \frac{S_1}{S_2}\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Also knowing the value of μ_e the value of μ_g can be obtained. The value of Onsager cavity radius has been calculated using the method of Vander Waal increments[13] (Table2).

The plots of $\left(\bar{\nu}_a - \bar{\nu}_f\right)$ versus F_1(D,n) and $\frac{1}{2}\left(\bar{\nu}_a + \bar{\nu}_f\right)$ versus F_2(D,n) for compound (I) is drawn, Figs 1.1-1.2, using least square fit method. These plots are found not be linear, so excited state dipole moment can't be calculated.

4. Conclusions

The present investigation thus shows that:

1. The increase in solvent polarity causes abathochromic shift for the longest absorption band maxima as well as for the fluorescence peak for 4- phenyl-7-hydroxy Coumarin - p-chloroanilide. This shows $\pi \rightarrow \pi^*$ transition.
2. The value of excited state dipole moment (μ_e) of 4- phenyl-7-hydroxy Coumarin - p-chloroanilide can't calculate, due to possibility of hydrogen bonding.
3. Structure of 4- phenyl-7-hydroxy Coumarin - p-chloroanilide also shows the possibility of formation of hydrogen bonding or molecular complexes.

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Table 1

Sr.No	Solvents	λ_a (nm)	λ_f (nm)	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$F_1(D,n)$	$F_2(D,n)$	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ (cm^{-1})
1	Benzene	279	305	35842	32786	0.005	0.34	3052	34314
2	Dioxane	288	328	34722	30487	0.04	0.31	4235	32604
3	Methenol	290	330	34482	30303	0.85	0.65	4179	32392
4	Isobutanol	393	342	34129	29239	0.75	0.65	4890	31684
5	Ethanol	292	343	34246	29154	0.81	0.65	5092	31700
6	n -butanol	292	342	34246	29239	0.77	0.65	5007	31742
7	Aceton	300	*360 to 365	33333	27586	0.79	0.64	5747	30459
8	Water	304	*360 to 370	32894	27397	0.91	0.68	5497	30145
9	Formamide	310	*360 to 370	32258	27397	0.89	0.75	4861	29827

*Broad band, mean value taken.

Stoke's shift data for 4- phenyl-7-hydroxy Coumarin - p-chloroanilide & and calculated values of function $F_1(D,n)$ & $F_2(D,n)$ for different solvents.

Graph

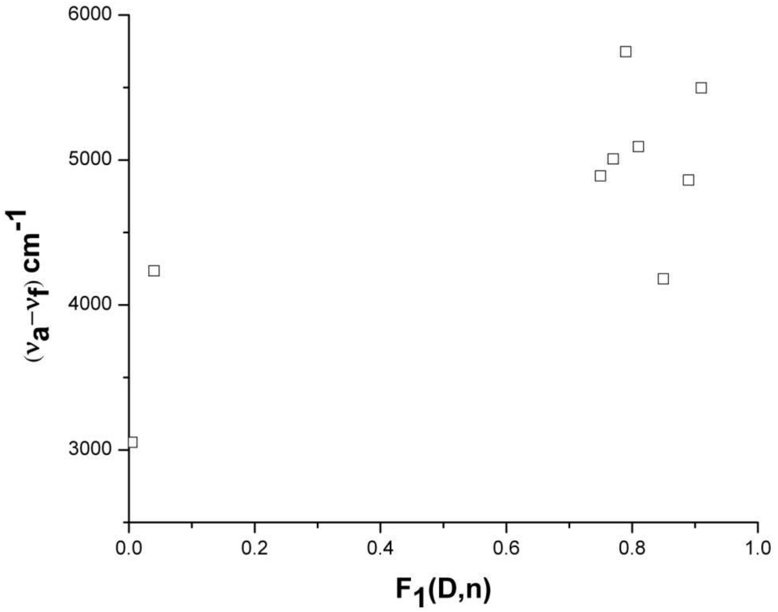

Figure 1.1 : Plot of F_1(D,n) versus Stoke's shifts according to Bakshiev's relation for 4- phenyl-7- hydroxy Coumarin - p-chloroanilide.

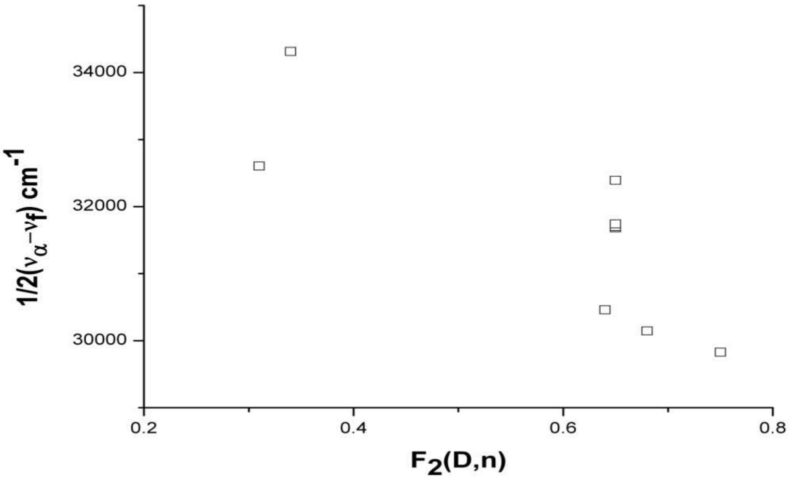

Figure 1.2 : Plot of F_2(D,n) versus Stoke's shifts according to Chamma and Viallet's relation for 4- phenyl-7- hydroxy Coumarin - p-chloroanilide.