Effect Of Solvent Polarity On The Quantum Yield Of (C₁₇H₁₉N₃)

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Abstract—**The absorption and fluorescence spectra have been studied and measured for Acridine orange (Ac) (C₁₇H₁₉N₃) solution which dissolved in different polar solvents as a function of concentration and solvent at excitation wavelength (λₑₓ= 414nm). Where the quantum yield be calculated and found equal to (Φ_{fm} =0.39) and(Φ_{fm} = 0.42) for (Ac) solution dissolved in N-N-dimethyl formamide (Dmf) and Ethanol at concentration (1x10⁻⁵M), respectively. But the quantum yield of (Ac) in Chloroform is equal to (Φ_{fm} = 0.44) at same concentration . This different in the values of quantum yield refers to the effect of polarity and to the intermolecular charge transfer phenomena (ICT), since when the polarity of solvent increasing leads to decreasing in the intensity of the fluorescence spectra , also a shift of fluorescence spectrum occurs towards the shorter wavelength (blue shift), and this lead to decrease the quantum yield value. The quantum yield measurement was calculated relative to standard compound of Rhodamine B with quantum efficiency (q_{FM} = 0.97) at same excitation wavelength (λₑₓ=414nm). The all furthermore measurements are be performed at room temperature .**

Keywords—Acridine orange (Ac) molecular, Excitation wavelength, fluorescence, Spec-tra , Absorption,

1.Introduction

In previous studies for the solvent polarity such as in 1995, Carlos M. previtali [1], investigated the solvent effects on the rate constant and activation parameters of several intermolecular electron transfer reactions. In 2003, Vijay K. Sharma, *et.al.* [2] study the magnitude of the Stokes shift and calculate experimentally the dipole moments (ground state and excited state). In 2006, A. Cook and A.Le [3], study the solvent and pH effect on the stokes shift and the excitation energy of the fluorescein in various solutions. In 2007, Debabrata Seth, *et.al.*[4], study the solvent and rotational relaxation. In 2007, H.K. Park, *et.al.*[5], as well as in 2008, M.A. Haidekker, *et.al.* [6], study the effects of solvent polarity and solvent viscosity on the fluorescence properties of molecular rotors and related probes. In 2011, M. Homocianu, *et.al.*[7], study the solvent effects on the absorbance and fluorescence spectra.

The effects of solvent polarity are one origin of the Stokes shift, which is one of the earliest observations in fluorescence. Emission from fluorescence generally occurs at wavelengths that are longer than those at which absorption occurs. This loss of energy is due to a variety of dynamic processes that occur following light absorption as shown in figure 1 below [8].

Typically, the fluorescence has a larger dipole moment in the excited state μ_E than in the ground state μ_G. Following excitation, the solvent dipoles can reorient or relax around μ_E, which lower the energy of the excited state.

As the solvent polarity is increased, this effect becomes larger, lead to emission at lower energies or longer wavelengths. In general, only fluorescence that are themselves polar display a large sensitivity to solvent polarity. Non polar molecules, such as unsubstituted aromatic hydrocarbons are much less sensitive to solvent polarity [9] .
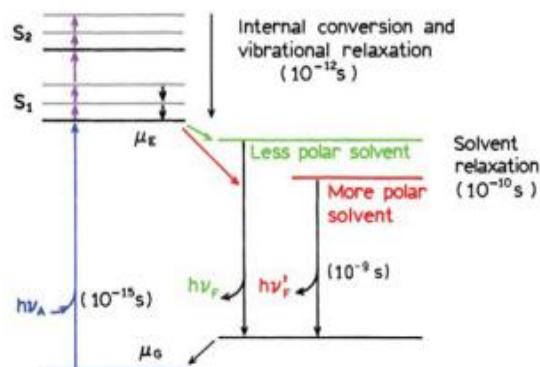

Fig 1:Jablonski diagram for fluorescence with solvent relaxation [8].

Most polarity probes undergo interm-olecular charge transfer upon excitation so that μ_E > μ_G . Therefore, following excitation, the solvent cage undergoes a relaxation, i.e. a reorganization, leading to a relaxed state of minimum free energy as illustrated previously in figure 1. The higher polarity of the solvent lowers the energy of the relaxed state and increases the red-shift of the emission spectrum [8] . The interactions responsible for general solvent effects are best understood by derivation of the Lippert equation. This equation can be written as follows:

$$hc\,\Delta\bar{v} = hc\left(\bar{v}_a - \bar{v}_f\right) = \frac{2\Delta f}{a^3}(\mu_E - \mu_G)^2 + constant\ldots(1)\text{Where}$$

$\Delta\overline{V}$ is the frequency shift (in cm⁻¹) between absorption and emission, *a* is the cavity radius, and **μ_E**

and μ_G are the excited and ground state dipole moments, respectively.

The Δf **is** called orientation polarizability, one can find this parameter as in the following equation 2 [10] .

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad …………..(2)$$

Where ϵ is the dielectric constant, n is the refractive index. There are many processes bimolecular which commonly compete with fluorescence emission (and internal quenching) in solutions, and thereby modify the fluorescence characteristics. This processes are collision impurity quenching, concentration quenching ,energy transfer quenching and self-absorption quenching [11].

The self-absorption quenching is in principle, an increase in the concentration of the fluorescence solute in a given material should be accompanied by an increase in the emitted light intensity.

This is due to the corresponding increase in the absorption efficiency. This is due to the corresponding increase in the absorption efficiency. However, such behavior only occurs up to a certain critical concentration of the fluorescence solute. Above this concentration, the fluorescence intensity starts to decrease. This process is known as concentration quenching of fluorescence [8].

The quantum yield can be defined as the ratio of the number of fluorescence photons emitted by a system of molecules in dilute solution to the number of molecules in excited state (the number of absorbed photons) [12].

The quantum yield can be calculated from this equation [11] :

$$\Phi_{Fx} = \Phi_{Fr} \left(\frac{A_r}{A_x} \right) \left(\frac{I(\lambda r)}{I(\lambda x)} \right) \left(\frac{n_x^2}{n_r^2} \right) \left(\frac{D_x}{D_r} \right) \quad …. (3)$$

where n_r ,n_x is the refractive index for standard and unknown compound respectively, Φ_{Fx}, Φ_{Fr} is the quantum yield of unknown and stander compound, respectively, A_r, A_x is the absorbance of standerd and unknown compound, respectively, $I(\lambda_x)$,$I(\lambda_r)$ is the excitation wavelength of unknown and stander compound, respectively and D_x, D_r is the corrected area under the curve of fluorescence spectrum of unknown and stander compound, respectively.

2.Experimental

The Acridine orange (Ac) purchased from Uma Company imported from India , as be shown in figure (2). Its dissolved in different polarity solvent like [*Chloroform* , *Ethanol* and *N-N-dimethyl formamide* (Dmf)] as solutions. The solution of acridine orange (Ac) in solvents are prepared at concentration [1x10$^-$^{5}]M.
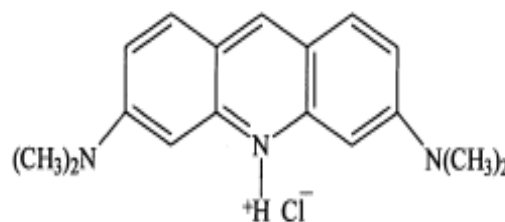

Fig. 2: Chemical formula of Acridine orange ($C_{17}H_{19}N_3$) [11] .

The absorption spectrum was measured by a (UV-V IS spectrophotometer CARY 100 Conc) and made by OPTIMA INC (January 2003). The fluorescence emission was measured from the samples at using spectrofluorophotometer kind of (RF-5301pc Shimadzu). Sample was mounted cubic cell of quartz dimensions (1x1x5) *cm* at angle (90°) with incident beam. This optical geometry was chosen to eliminate the effect of scattered incident radiation. The instrument computerized and operates in the wavelength range (220-900) nm. The (Rhodamine B) was used as a standard compound dissolved in ethanol with concentration [1x10^{-5}]M and quantum efficiency equal to (q_{FM} = 0.97). all measurements performances at room temperature .

3.Results and Discussion

The solutions of ($C_{17}H_{19}N_3$) are studied at small concentration [1x10^{-5}]M (this concentration is used to reduce the self-absorption phenomena) . Figure 3 and figure 4 shows the absorption and the fluorescence spectra of ($C_{17}H_{19}N_3$) solutions in different solvents, respectively .

figure 4 shows the fluorescence spectrum of ($C_{17}H_{19}N_3$) solutions.Its observed that structure-less of the fluorescence spectrum and consist of one peak located at wavelength (λ_{max}= 516 nm) in N-N-dimethyl formamide (Dmf), (λ_{max}=519 nm) in ethanol and (λ_{max} = 524 nm) in Chloroform. From figure 4 above of when its observed there is a shift has been happened in the fluorescence spectra toward short wavelength (blue shift) with the increasing of solvents polarity furthermore. This changes of fluorescence spectra in the intensity and the location of peak, can be interpret as follow when the solvent polarity increases. The fluorescence intensity was decreases because molecule absorbed the light and transitions to the excited electronic state .
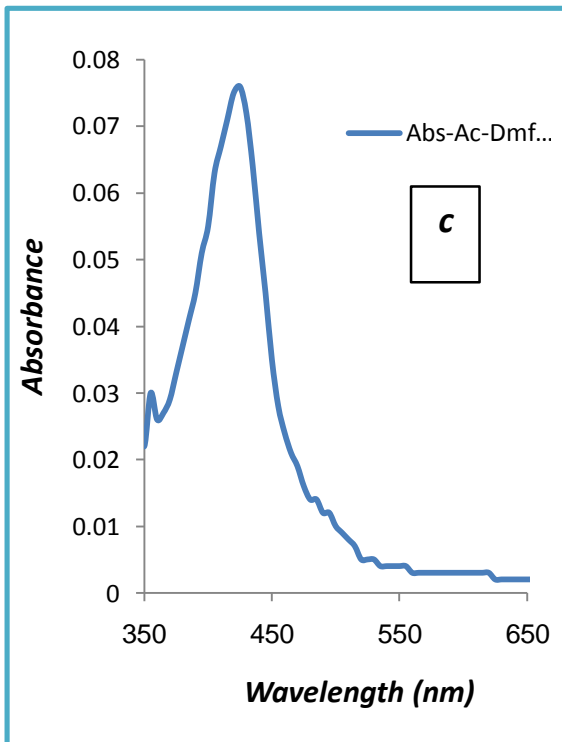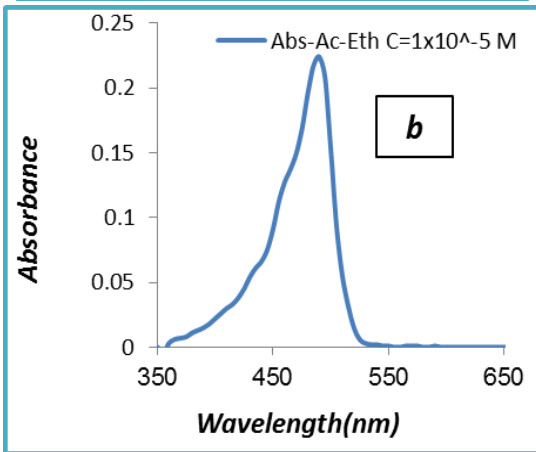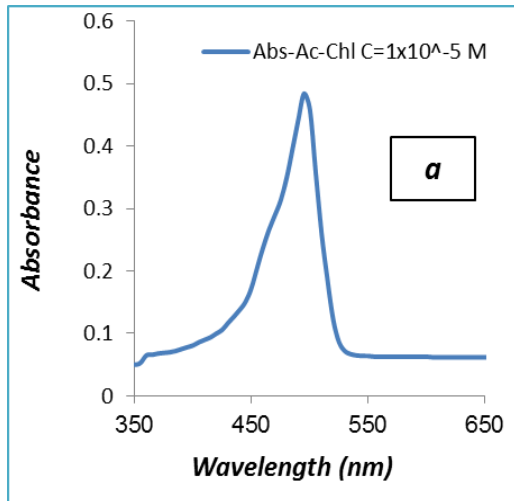
Fig. 3: Absorption spectra of $(C_{17}H_{19}N_3)$ in [a] Chloroform , b) ethanol , and c) N-N-dimethyl formamide (Dmf)] at concentration[$1x10^{-5}$] M.
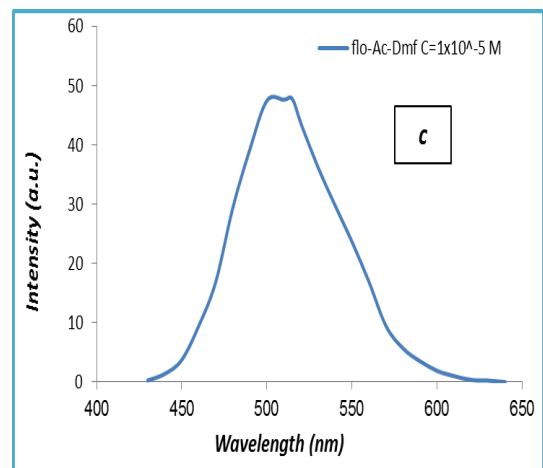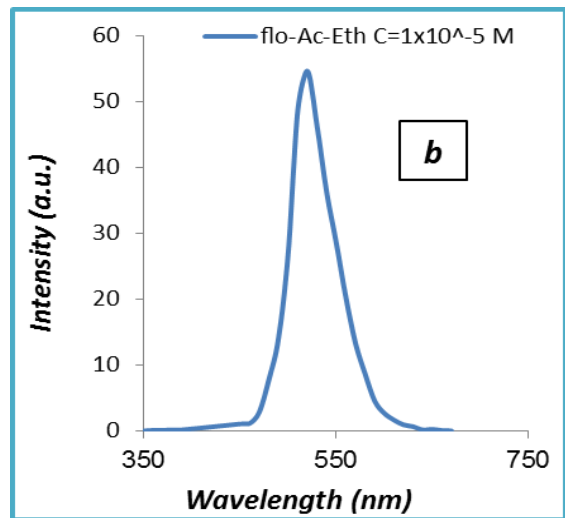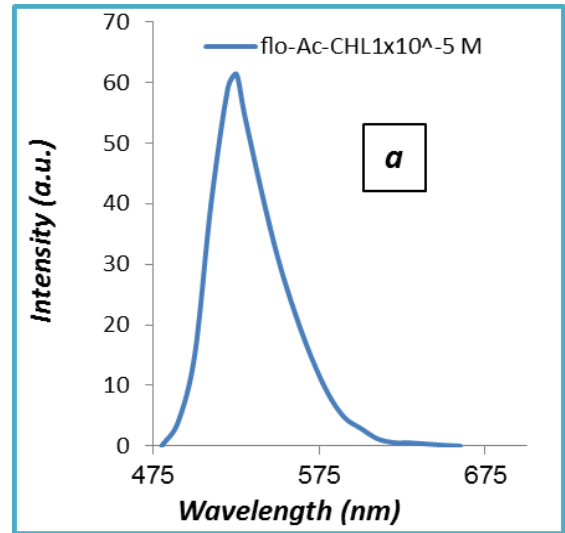

Fig. 4: Fluorescence spectra of (C17H19N3) in [a) Chloroform , b) ethanol , and c) N-N-dimethyl formamide (Dmf)] at concentration[1x10-5] M.

The molecular electronic configuration is changed and hence the re-change in the dipole moment of solute molecule.

For $(C_{17}H_{19}N_3)$ (Ac) molecule it has big value for the dipole moment in the excited state , hence there is a strong interaction will occurs between

(solvent-solute) molecules a specially when the polar solvents are be used , thus the molecule of solvent are reorient and relaxed around the solute molecule .The Franck-Condon (Fc) excited state, this leads to makes the energy of the electronic excited more be lower than the original case. The consequently quantum yield is calculated is decreased when the polarity was increased and the fluorescence spectrum was shifted to a short wavelength as shown in figure 5.
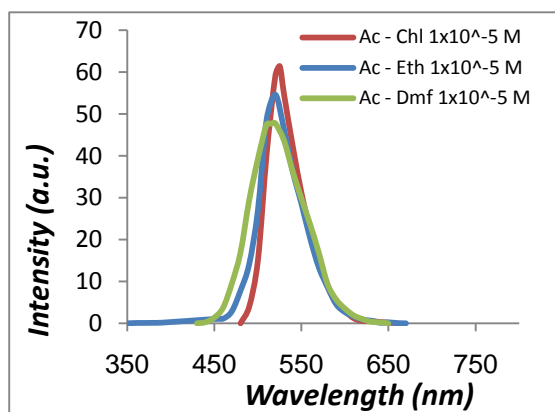

Fig.5: fluorescence spectra of $(C_{17}H_{19}N_3)$ in [Chloroform , ethanol , and N-N-dimethyl for mamide (Dmf)] at concentration $[1\times10^{-5}]$M.

This shift value is dependent on the dielectric constant ε value of olvent and on the difference between dipole moment values of solvent [13].
A change in the energy level (location) leads to the change in the life time of the electronic excited state then decrease in the rate parameters for radiative fluorescence because the small of the energy gap value of between (So and S1) states the rate parameters of non-radiative processes is be increased .

From Table 1 shows the change of the photo-physical parameters and quantum yield value with the more increasing of solvent polarity.

Table 1: the photo-physical parameters and quantum yield of $(C_{17}H_{19}N_3)$ in different solvents at room temperature.

solvent	Φ_{flm}	λ_a (nm)	λ_f (nm)	$\bar{\upsilon}_a$ (cm^{-1})	$\bar{\upsilon}_f$ (cm^{-1})	$\bar{\upsilon}_a - \bar{\upsilon}_f$ (cm^{-1})	$\frac{\bar{\upsilon}_a + \bar{\upsilon}_f}{2}$ (cm^{-1})	Δf
Chloroform	0.44	495	524	20202.02	19083.96	1118.06	19642.99	0.1484
Ethanol	0.42	490	519	20408.16	19267.82	1140.34	19837.99	0.289
Dmf	0.39	425	516	23529.41	19379.84	4149.57	21454.62	0.275

4.Conclusions

From this study following conclusions are reached to:
1- The fluorescence intensity decreases with the increasing of solvent polarity because of the formation of exciplexes complex or intra molecular charge-transfer (ICT) phenomenon.
2- . Decreasing the quantum yield with the increasing of polarity solvents .

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