Effect of Solvent Polarity on the Quantum Yield of Acriflavine Molecule

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Abstract

The absorption and fluorescence spectra have been studied and measured for Acriflavine (AF) solution which dissolved in polar solvents as a function of concentration and solvent at excitation wavelength (λ_{ex}= 414nm) . The quantum yield (Φ_{fm}) , the Radiative fluorescence lifetime (τ_{FM}) , rate parameter of Radiative (K_{FM}) and non-Radiative processes (K_{IM}) are be calculated . Where the quantum yield be found equal to (Φ_{fm} =0.84) and (Φ_{fm} = 0.83) for Acriflavine (AF) solution dissolved in *N-N-dimethyl formamide (Dmf) and dimethyl sulphoxide (DMSO)at concentration* (1x10^{-5}M) , respectively. But the quantum yield of Acriflavine (AF) in water is equal to (Φ_{fm} = 0.81) 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) between the amine group and the aromatic ring , 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 longer wavelength (redshift) , 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 (λ_{ex}= 414nm) . The all furthermore measurements are be performed at room temperature .

Key word: Effect of Solvent Polarity on the Quantum Yield

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تأثير قطبية المذيب على الكفاءة الكمية لجزيئة الاكريفلافين

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الخلاصة

تم قياس ودراسة اطياف الامتصاص و الفلورة لمحلول جزيئة الاكريفلافين المذاب في بعض المذيبات القطبية كدالة للتركيز المولاري والمذيب ، بطول موجي مهيج (nm414 =λ_{ex}). لقد تم حساب الكفاءة الكمية Φ_{fm} ، زمن الفلورة الاشعاعي τ_{FM}ومعدل الإشعاعية K_{FM} واللاإشعاعية K_{IM} ، حيث وجد إن الكفاءة الكمية لمحلول الاكريفلافين المذاب في داي مثيل فورمامايد و داي مثيل سلفواوكسايد عند التركيز (M^{-5}10x1) تكون مساوية الى (0.84= Φ_{fm}) و (0.83 = Φ_{fm}) على التوالي . أما عند حساب الكفاءة الكمية لمحلول الاكريفلافين المذاب في الماء عند نفس التركيز فأنها تساوي (0.81 = Φ_{fm}) . ان هذا الاختلاف في قيم الكفاءة الكمية يشير الى تأثير القطبية وكذلك بسبب ظاهرة انتقال الشحنة بين مجموعة الامين وحلقة المركب العطري . حيث وجد عند زيادة قطبية المذيب تؤدي الى نقصان في شدة طيف الفلورة ، وكذلك إزاحة قمة طيف الفلورة تحدث بإتجاه الطول الموجي الطويل (إزاحة حمراء)، وهذا يؤدي الى نقصان في قيمة الكفاءة الكمية . لقد تم حساب الكفاءة الكمية نسبة الى مركب الرودامين بكفاءة مقدارها (0.97 = q_{FM}) كمركب قياسي عند نفس الطول الموجي المهيج (nm414 =λ_{ex}) . علاوة على ذلك فأن جميع القياسات انجزت بدرجة حرارة الغرفة .

الكلمات المفتاحية : تأثير قطبية المذيب ,على الكفاءة الكمية

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Introduction

Many studies reported for the Acriflavine molecule, such as M. Maeda in (1984) which used the acriflavine as an active medium for dye lasers[1]. Carlos M. Previtali in (1995) investigated the solvent effects on the rate constant and activation parameters of several intermolecular electron transfer reactions[2]. Vijay K. Sharma *et.al.* in (2003) introduction a study that which shows the magnitude of the Stokes shift (frequency shifts in absorption and fluorescence spectra) and observing this shift with types of solvent also they calculated dipole moments experimentally for ground state and excited state of acriflavine and acridine orange dye molecules[3]. M Lee lavathi et.al. in (2011) investigated the acriflavine lotion as topical antiseptic solution yellow or orange in colour, mainly used for minor wounds, burns, and infected skin. Although used in dilution (0.1%) for medical purposes, this agent has been documented to produce potential skin itchiness, irritation or burning sensation upon contact. Nevertheless, it is still widely used for wound dressing by health professionals and remains a popular topical antiseptic agent purchased over- the counter[4].

The effects of solvent polarity are one origin of the Stokes shift, which is one of the earliest observations in fluorescence. The emission of 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 Fig.(1) below. [5]. 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 fluorescences that are themselves polar display a large sensitivity to solvent polarity or large the value of (μ_E). Non polar molecules, such as unsubstituted aromatic hydrocarbons are much less sensitive to solvent polarity[6].
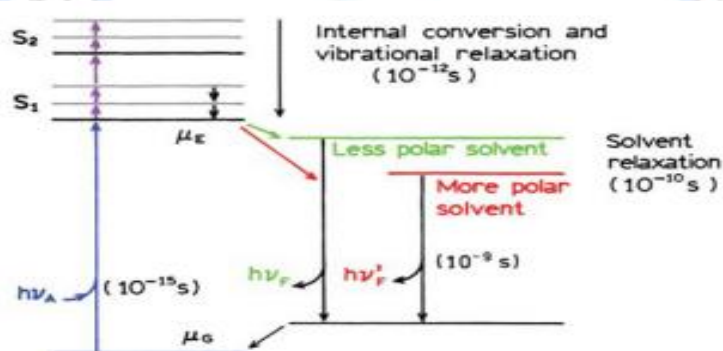

Fig (1):Jablonski diagram for fluorescence with solvent relaxation[5].

Most polarity probes undergo intermolecular charge transfer upon excitation so that $\mu_E > \mu_G$. 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 it lowers the energy of the relaxed state and increases the red-shift of the emission spectrum toward longer wavelength region[5].

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) [7].

The quantum yield can be calculated from this equation:[8]

$$\Phi_{Fx} = \Phi_{Fr} \left(\frac{A_r}{A_x} \right) \left(\frac{I(\lambda r)}{I(\lambda x)} \right) \left(\frac{n_x^2}{n_r^2} \right) \left(\frac{D_x}{D_r} \right) \quad \ldots\ldots\ldots (1)$$

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.

D_x, D_r: is the corrected area under the curve of fluorescence spectrum of unknown and stander compound, respectively.

Experimental section

2-1. materials:

The Acriflavine (AF) is derived from (acridine family) (AF) purchased from Uma Company imported from India , as be shown in figure (2). Its dissolved in different polarity solvent like [*N-N-dimethyl formamide (Dmf)* , *dimethyl sulphoxide (Dmso) and water*] as solutions. The acriflavine molecule solution are prepared at $1x10^{-5}M$ using different solvents

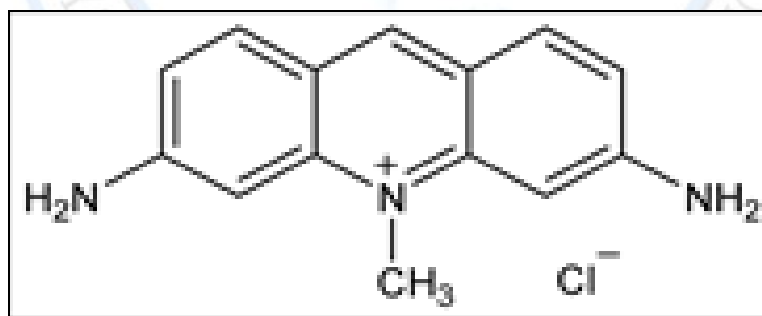**Fig.(2): Chemical structure of Acriflavine ($C_{14}H_{14}CLN_3$)**[3]

2-2. Absorption and Fluorescence measurements :

Absorption spectrum was measured by a (UV-V IS spectrophotometer CARY 100 Conc) and made by OPTIMA INC (January 2003). Fluorescence spectrum was record by using spectrofluorophotometer kind of (RF-5301 pc Shimadzu) sample were mounted cubic cell of quartz dimensions (1x1x5) *cm* at angle (90) with incident beam.

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This optical geometry was chosen to eliminate the effect of scattered incident radiation and minimizes the self-inner effect . The instrument computerized and operates in the wavelength range (220-900) *nm*. The fluorometer has dedicated computer which control instrumental operating (excitation and emission wavelength, scan, monochromator slit width, detector parameter) and the acquisition of spectral data. In this research, exciting wavelength (λ_{ex}= 414nm) is used in the measurements and slit width is used for excitation (S_{ex}=1.5 nm) and slit width of emission (S_{em}= 1.5 nm) were used. The measurements were made in the same sensitivity of photomultiplier. The (Rhodamine B) was used as a standard compound dissolved in ethanol with concentration 1×10^{-5}M and quantum efficiency equal to (q_{FM} = 0.97). all measurements performances at room temperature .

Results and Discussions

The solutions of (AF) are studied at small concentration 1×10^{-5}M this concentration is used to reduce the self-absorption phenomena and inner filter effect.

Figure (3) shows the fluorescence spectrum for standard compound of Rhodamine B solution in ethanol with concentration 1×10^{-5}M at exciting wavelength (λ_{ex}= 414nm), where it's clear the shape of spectrum consists of one peak located at wavelength (572 nm).
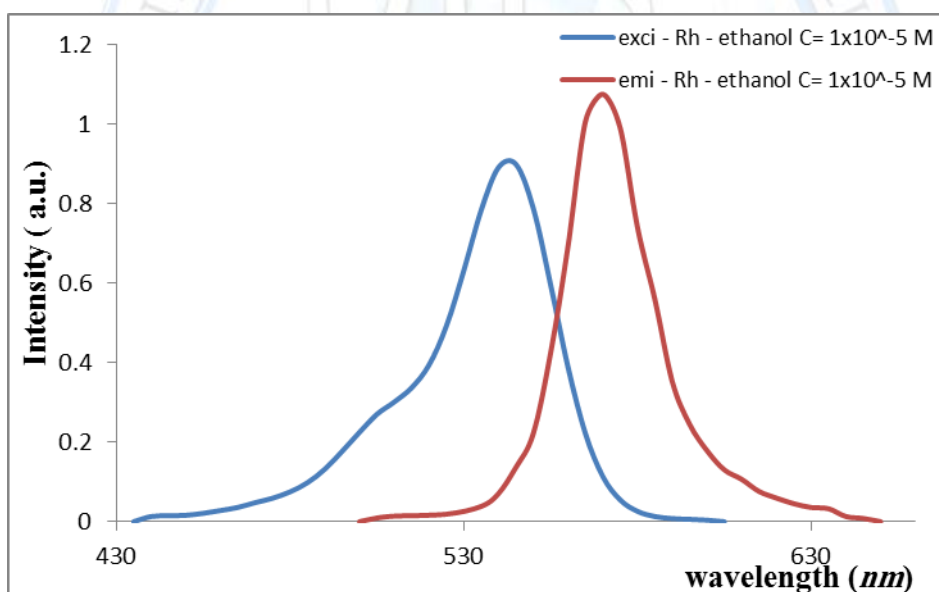
Fig.(3): the fluorescence and excitation spectra to

Rhodamine B dissolved in ethanol [1×10^{-5} M].

Fig. (4) and fig.(5) shows the absorption and the fluorescence spectra of acriflavine solutions in different solvents, respectively .

Figure (5) shows the fluorescence spectrum of acriflavine solutions in [*N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water*].at concentrations [1×10^{-5}M] its observed that structure-less of the emission spectrum and consist of one peak located at

wavelength (λ_{max}=497 nm) in *N-N-dimethyl formamide (Dmf)*, (λ_{max}=501 nm) in *dimethyl sulphoxide (Dmso)* and (λ_{max}= 505 nm) in water.
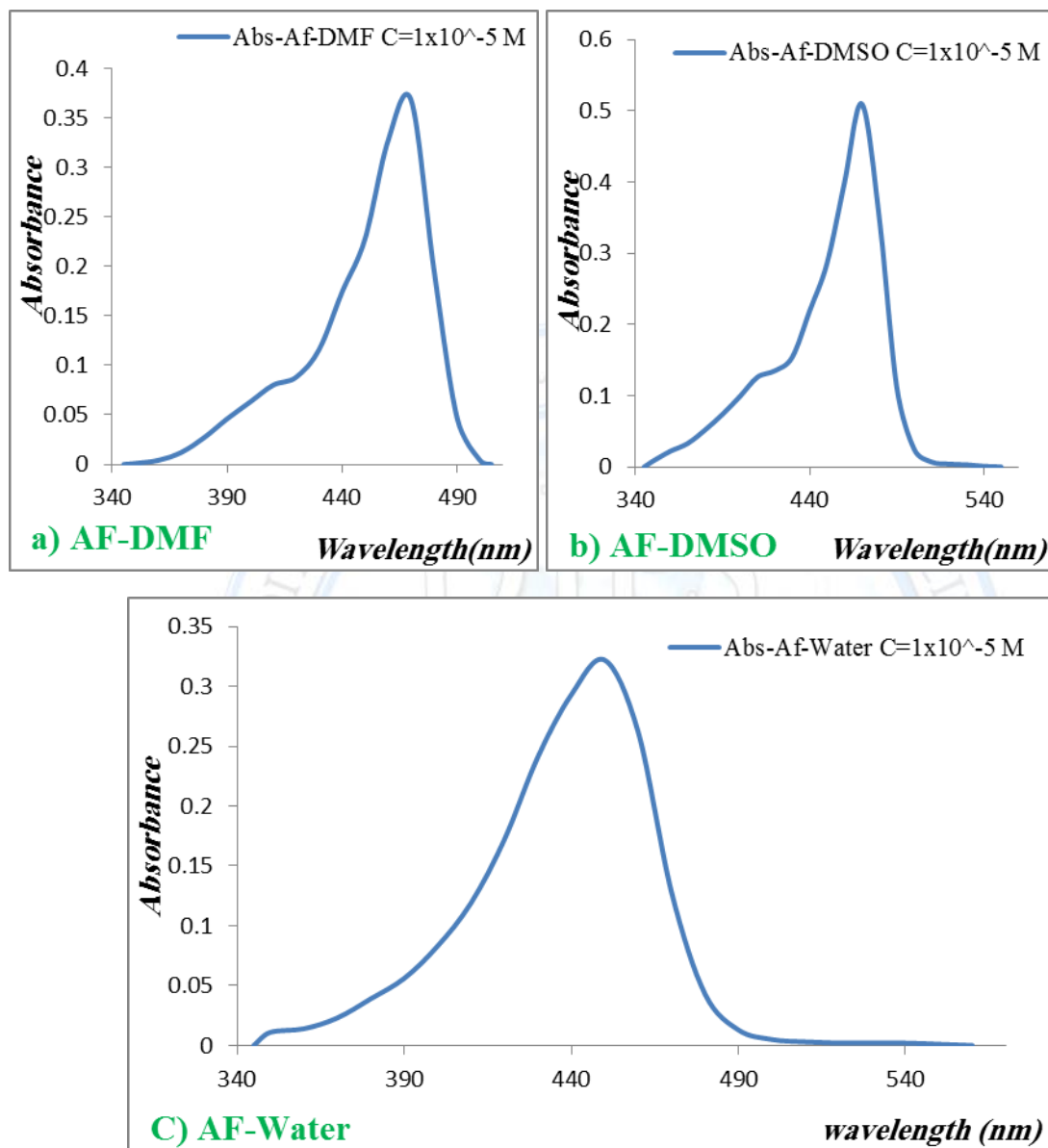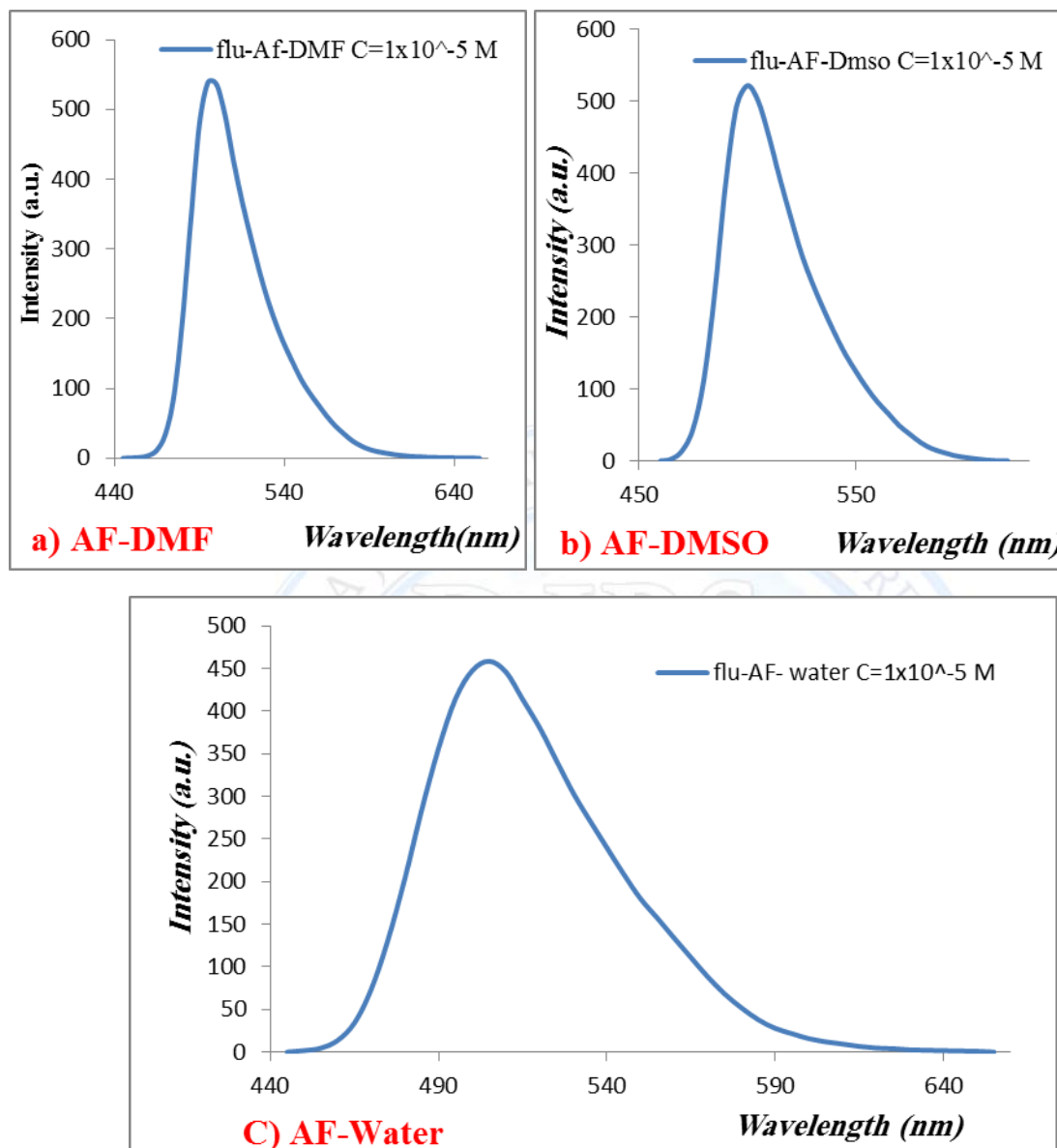

Fig.(4): Absorption spectra of Acriflavine in [a) N-N-dimethyl formamide (Dmf) , b)dimethyl sulphoxide (Dmso) and c)water] at concentration 1x10^{-5} M.

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Fig.(5): Flurescence spectra of Acriflavine in [a) N-N-dimethyl formamide (Dmf) , b)dimethyl sulphoxide (Dmso) and c)water] at concentration $1x10^{-5}$ M.

From the above figure (5) when its observed there is a shift has been happened in the fluorescence spectra toward longer wavelength (redshift) 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 , the moleculear electronic configuration is changed and hence the re-change in the dipole moment of solute molecule[9]. For Acriflavine 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 shiftted to a long wavelength as shown in figure (6). This shift value is dependent on the dielectric constant (ε) value of solvent and on the difference between dipole moment values of solvent [10].

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 (S_o and S_1) states the rate parameters of non-radiative processes is be increased .
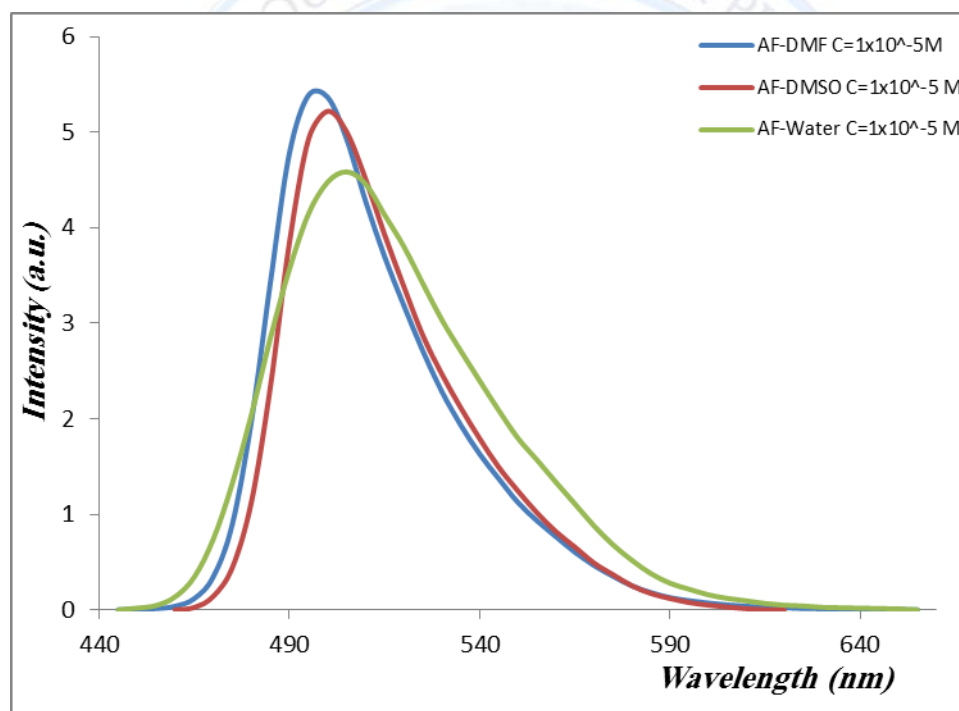
Fig.(6): fluorescence spectra of acriflavine solution in [N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water] at concentration 1x10^{-5} M.

Since so that decrease in the rate parameters of radiative emission leads to decrease the quantum yield value with the more increasing of solvent polarity, as shown in table (1) and figure (7) show the graphical relation between quantum yield (Φ_{fm}) and dielectric constant value (ε) .The arameter (τ_{FM} , K_{FM} , τ_M and K_{IM}) have been calculated according to the following relationships,respectively.

$$\frac{1}{\tau_{FM}} = 2.88 \times 10^{-9}\, \acute{n}^2 \; < \bar{v}_f^{-3} >_{ave}^{-1} \int \frac{\varepsilon\, d\bar{v}}{\bar{v}} \qquad \ldots\ldots\ldots (\,2\,)$$

$$\tau_{FM} = \frac{1}{K_{FM}} \qquad \ldots\ldots\ldots\ldots(\,3\,)$$

$$q_{FM} = \frac{K_{FM}}{K_{FM} + K_{IM}} = \frac{\tau_M}{\tau_{FM}} \qquad \ldots\ldots\ldots(\,4\,)$$

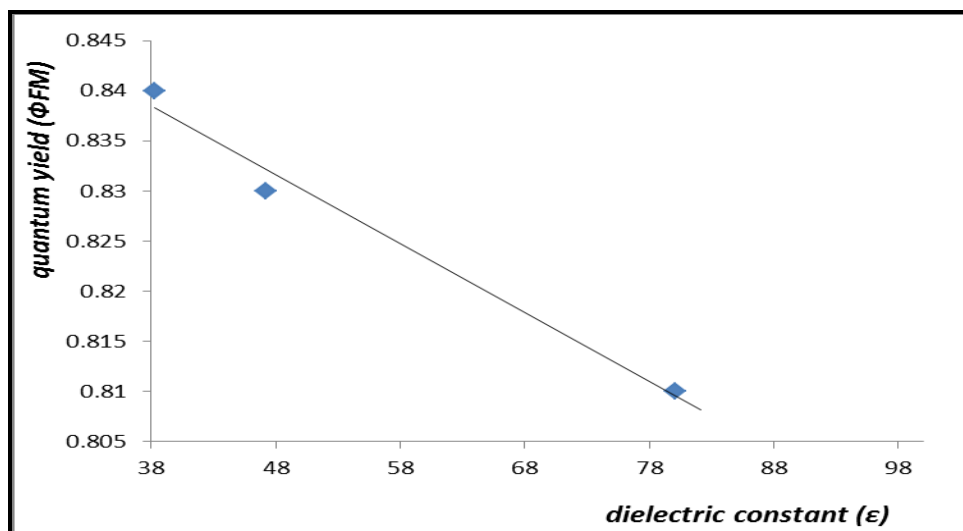$$\tau_M = \frac{1}{K_M} = \frac{1}{K_{FM} + K_{IM}} \qquad \ldots\ldots (\,5\,)$$

Fig.(7):Show the relation between quantum yield value and dielectric constant to acriflavine molecule dissolved in many different solutions at concentration

[1x10^{-5} M].

Table (1): the quantum yield Φ_{fm} , dielectric constant(ε)and rate parameter of radiative and non-radiative processes

solvent	Φ_{fm}	$K_{FM}\times10^9$ Sec^{-1}	$K_{IM}\times10^6$ Sec^{-1}	τ_{FM} $nSec$	τ_M $nSec$	dielectric constant(ε)
Dmf	0.84	0.264	0.05	3.775	20	38.25
Dmso	0.83	0.25	0.051	3.994	19.6	47.24
water	0.81	0.1698	0.039	5.89	25.64	80.1

4. Conclusion:

The study of acriflavine (AF) dye dissolved in [*N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water*] with a concentration $1x10^{-5}$M the following conclusions are reached to :

1. The redshift increasing with increasing of dielectric constant value (ε).
2. Decreasing the relative intensity and quantum yield with the increasing of polarity solvents
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