Effect of solvent polarity on the fluorescence properties of (Acriflavine) molecular

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Abstract:

The absorption and fluorescence spectra have been studied and measured for Acriflavine (AF) solution which dissolved in [*N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water*] solvents as a function of concentration and solvent at excitation wavelength (λ_{ex}= 414*nm*) . Have been calculated peaks the fluorescence spectra of Acriflavine (AF) solution dissolved in *N-N-dimethyl formamide (Dmf) and dimethyl sulphoxide (Dmso)* at concentration ($1x10^{-5}$M) , and found that it is equal to (λ_{max}= 497) ، (λ_{max}= 501) and (λ_{max}= 505), respectively. Also been calculated the value stokes shift of these peaks found to be equal to (1292.5) ، (1316.5) and (2469.7) , respectively. Where we note that (stokes shift) shifted peak of fluorescence spectra towards the longer wavelength (redshift) increases with increase solvent polarity . The increase of solvents polarity lead to decrease in the intensity of the fluorescence spectra . All measurement were at room temperature .

(1). Introduction:

Many studies have been reported for the Acriflavine molecule, such as M. Maeda in (1984) has been used the acriflavine as 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) study that has been shown the magnitude of the Stokes shift (frequency shifts in absorption and fluorescence spectra) is observed on changing the solvents and further has been used to calculate experimentally the dipole moments (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].

It is well known that the loss of energy of an excited molecule in a solution, both by radiative and non-radiative processes characteristically depend upon the molecular structure and the environment of the molecules. Therefore, not only the structure of solute molecules but the solvent also plays an important role in determining its radiative and non- radiative properties. A change for the type of a solvent when it produces alteration in both the excitation and fluorescence wavelength indicates that the solvent, in some way, is able to interact with the solute in the ground state. However, when solvent produces a shift in fluorescence wavelength only, it indicates an interaction between solvent and solute molecule, in excited state. Therefore , when a molecule is excited, its dipole moment gets changed and it remains no more in equilibrium with its immediate environment. As a molecule relaxes and is in equilibrium with its surroundings, some energy is dissipated in the form of heat energy and the fluorescence emission wavelength gets shifted according to Frank - Condon principle[5]. 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[6].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. 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[7]. The interactions responsible for general solvent effects are best understood by derivation of the Lippert equation. This equation can be written as follows:

$$hc\ \Delta\bar{\nu} = hc(\bar{\nu}_a - \bar{\nu}_f) = \frac{2\Delta f}{a^3}(\mu_E - \mu_G)^2 + constant \quad \ldots(1)$$

where ($\Delta\bar{\nu}$) 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)[8].

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

Where :(ϵ) is the dielectric constant, n is the refractive index.

(2). Experimental section:

(2-1) materials:

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

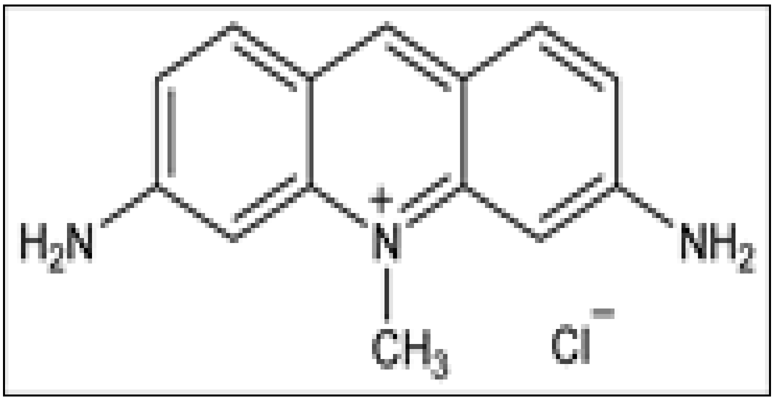

Fig.(1): Chemical formula of Acriflavine ($C_{14}H_{14}CLN_3$)[3]

(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. This optical geometry was chosen to eliminate the effect of scattered incident radiation and the self-absorption phenomena. 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. The exiting wavelength $\lambda_{ex=}$ (414 *nm*) is used in the measurements and all measurements were at room temperature performances.

(3).Results and Discussions:

In this paper, the fluorescence spectra of (Acriflavine) solution dissolved in different polarity solvent like [*N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water*], are studied with concentration [$1x10^{-5}$]M and the effect of polarity on the fluorescence spectrum.

Fig. (2) and fig.(3) shows the absorption spectra and the fluorescence spectra of acriflavine solutions in different solvent polarity, respectively . From the fig. (3) the fluorescence spectra appears as structure-less with peak located at wavelength in (*N-N-dimethyl formamide (Dmf)* λ_{max}= 497 *nm*), (*dimethyl sulphoxide (Dmso)* λ_{max}= 501 *nm*) *and* (*water* λ_{max}= 505 *nm*).

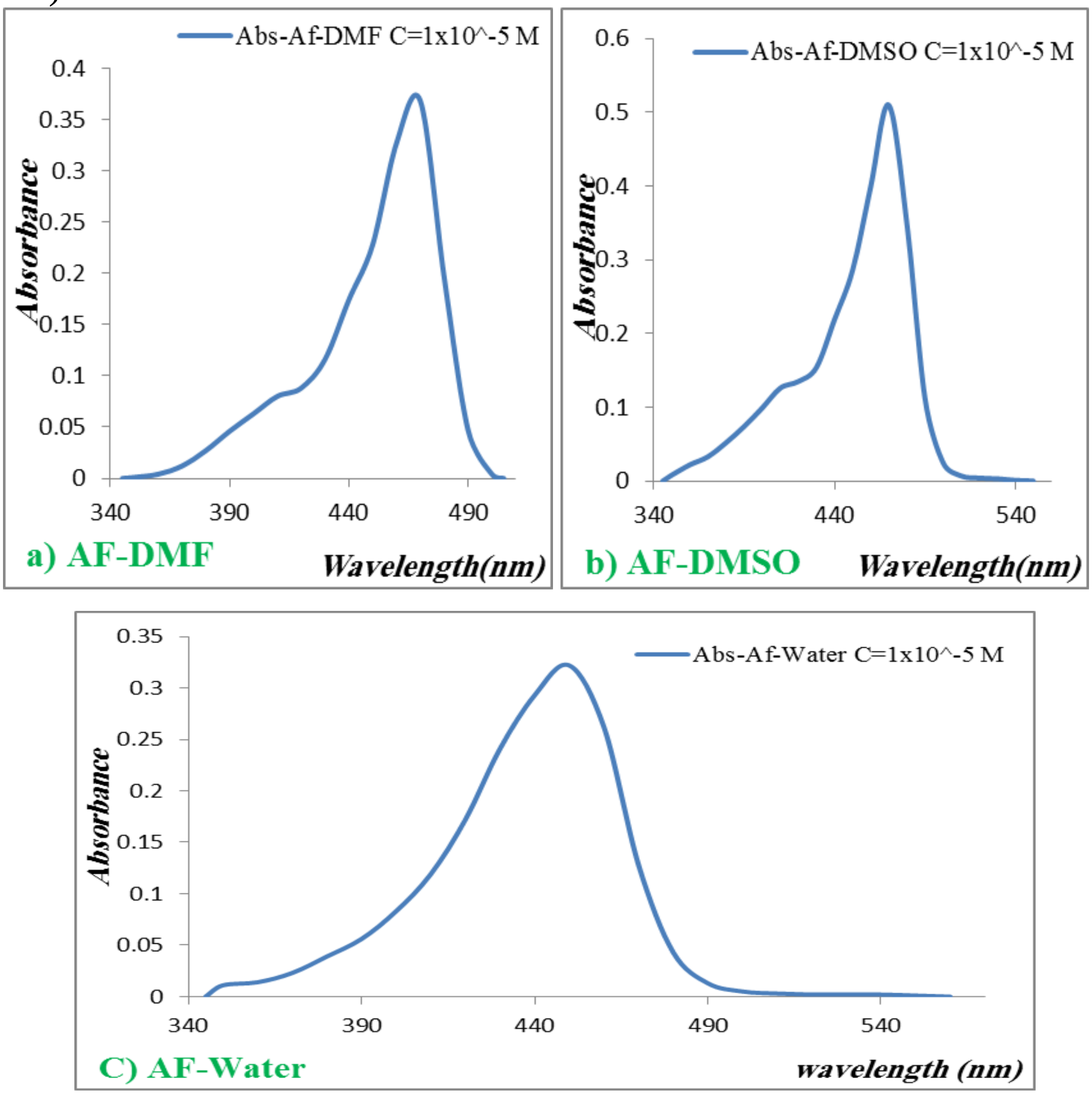

Fig.(2): Absorption spectra of Acriflavine in [a) N-N-dimethyl formamide (Dmf) , b)dimethyl sulphoxide (Dmso) and c)water] at concentration $1x10^{-5}$ M.

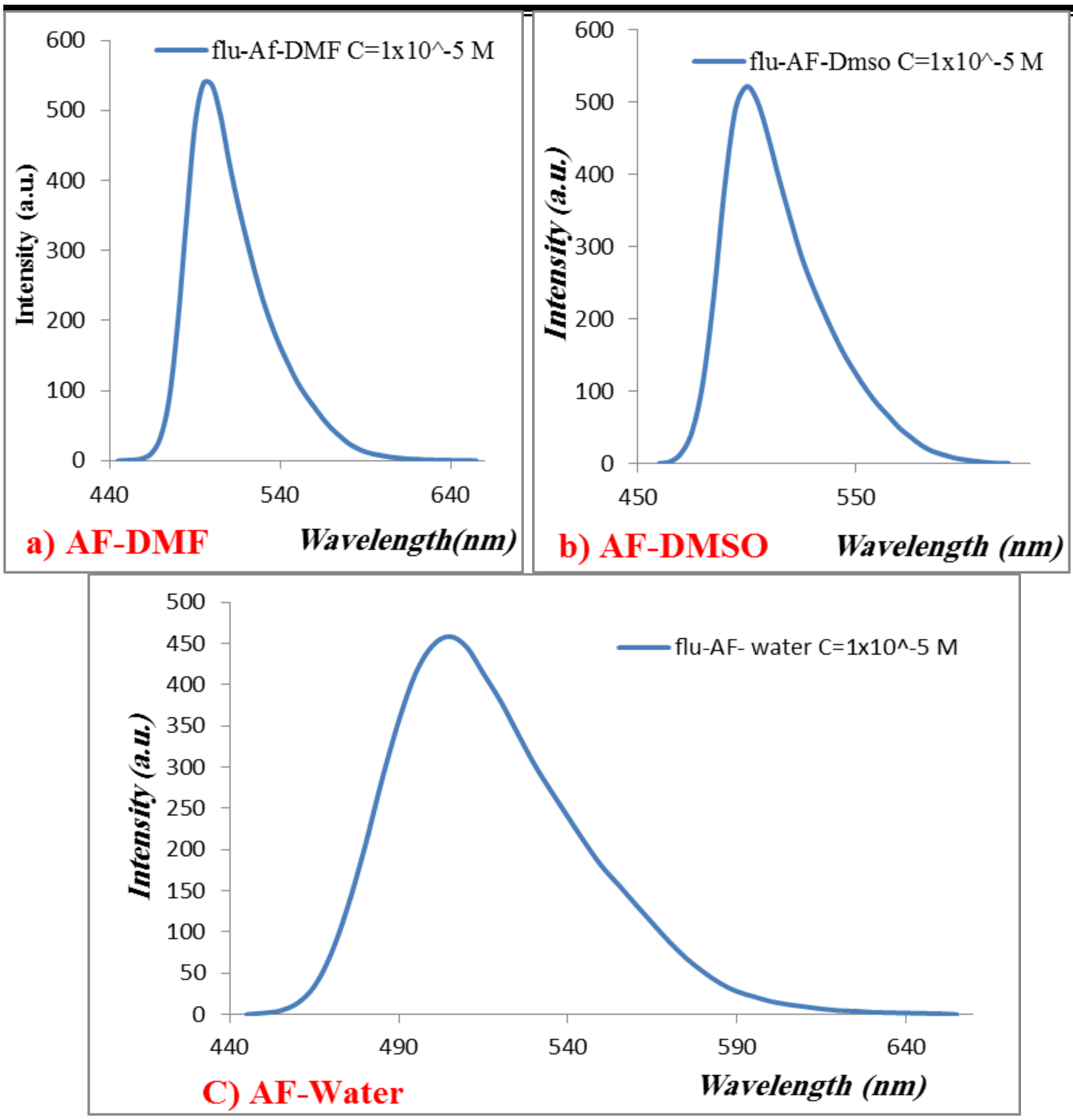

Fig.(3): Flurescence spectra of Acriflavine in [a) N-N-dimethyl formamide (Dmf) , b)dimethyl sulphoxide (Dmso) and c)water] at concentration $1x10^{-5}$ M.

From the fig.(4) can observe the effected of the solvent polarity on the fluorescence spectra, where the fluorescence intensity decreases, when polarity of solvent are increased because the molecule when absorbed the light and transitions to the excited electronic state, the molecule electronic configuration is changed and hence solute-solvent molecule interacts (dipole-dipole) [10].

From the figure (4), the acriflavine dye , It suggests that it is a locally excited intra molecular charge transfer (ICT) state. Amino group in the mero-phenyl ring is protonated to give high fluorescent and as a result, twisted ICT (TICT) states are not formed in case of acriflavine dye or interacting between solute with molecule solvent as dipole-dipole interacts.[11]

From the last figure, one can observe that, when the polarity was increased the fluorescence spectrum shiftted to a long wavelength (red shift) and decrease in the intensity of fluorescence. This shift value is dependent on the dielectric constant (**ε**) value of solvent and on the difference between dipole moment values of solvent[12], as shown in table (1).

Table (1): photo-physical parameters of acriflavine in different solvents at room temperature.

solvent	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
Dmf	**467**	**497**	**21413.2**	**20120.7**	**1292.5**	**20766.9**	**0.275**
Dmso	**470**	**501**	**21276.5**	**19960**	**1316.5**	**20618.25**	**0.263**
Water	**449**	**505**	**22271.7**	**19801.9**	**2469.7**	**21036.8**	**0.320**

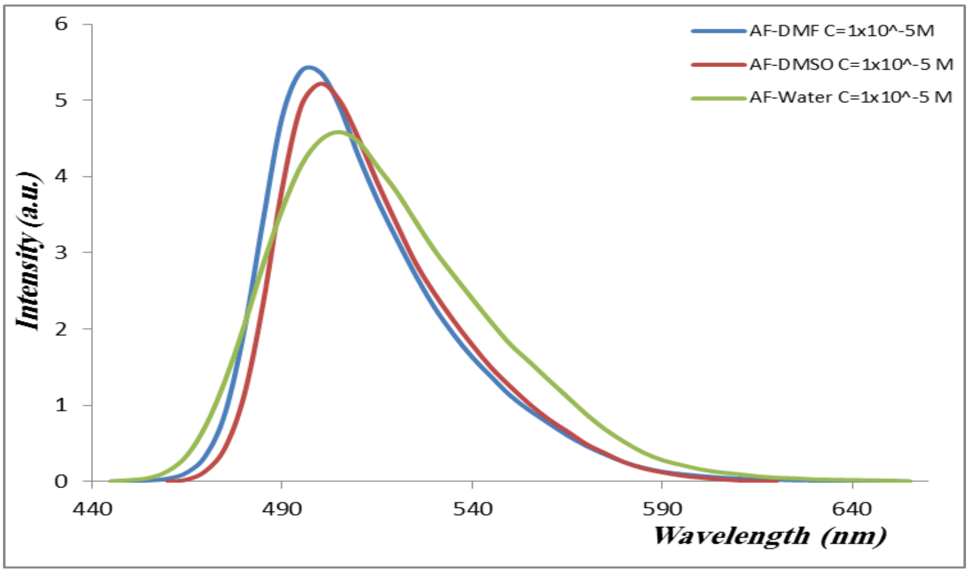

Fig.(4): fluorescence spectra of acriflavine solution in [N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water] at concentration 1x10^{-5} M.

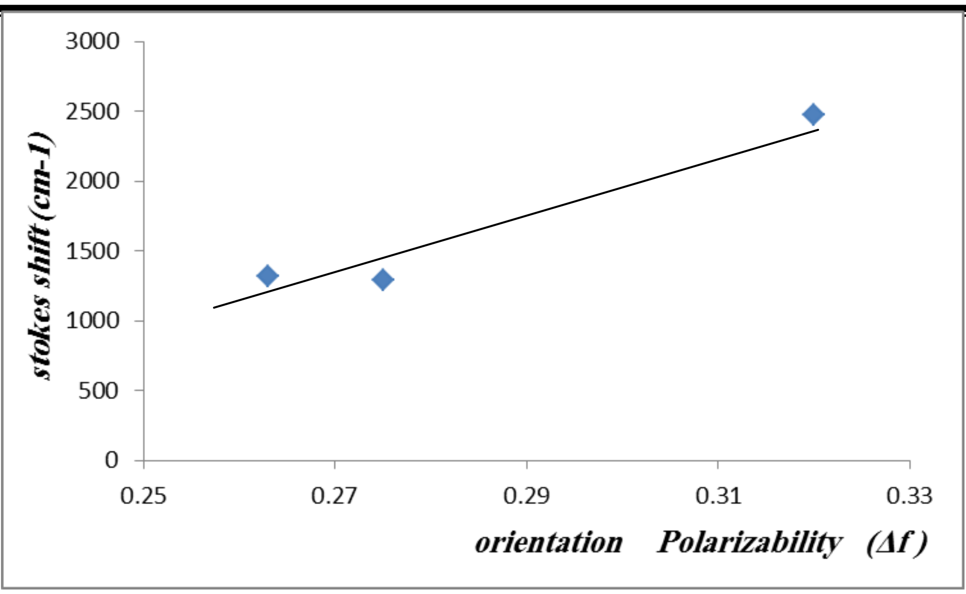

Fig.(5): the relation between the stokes shift value and orientation polarizablity (Δf) acriflavine molecule dissolved in [N-N-dimethyl formamide (Dmf) , dimethyl sulphoxide (Dmso) and water] at concentration [1x10^{-5} M].

(4). Conclusion:

Throughout 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 fluorescence intensity decreases with the increase of solvent polarity because of the formation of exciplexes complex or intra molecular charge-transfer (ICT) phenomenon.

2- The red shift of fluorescence was increased with the increasing of solvent polarity.

(5). References:

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تأثير قطبية المذيب على خصائص الفلورة لجزيئة (الاكريفلافين)

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الكلمات المفتاحية:
اطياف الامتصاص والفلورة, جزيئة الاكريفلافين, المذيب القطبي, الطول الموجي, داي مثيل فورمامايد, داي مثيل سلفوكسايد, التركيز المولاري, ازاحة ستوكس والازاحة الحمراء.

الخلاصة:
تم قياس ودراسة اطياف الامتصاص و الفلورة لمحلول الاكريفلافين المذاب في المذيبات (داي مثيل فورمامايد ، داي مثيل سلفوكسايد و الماء) كدالة للتركيز المولاري والمذيب القطبي ، بطول موجي مهيج (λ_{ex}= 414*nm*). لقد تم حساب قمم طيف الفلورة لمحلول الاكريفلافين المذاب في داي مثيل فورمامايد و داي مثيل سلفوكسايد عند التركيز ($1x10^{-5}$M) ووجد انها تساوي (λ_{max}= 497) ، (λ_{max}= 501) و (λ_{max}= 505) على التوالي . كذلك تم حساب قيمة ازاحة ستوكس لهذه القمم وجد انها تساوي (1292.5) ،(1316.5) و (2469.7) على التوالي . حيث نلاحظ ان (ازاحة ستوكس) إزاحة قمة طيف الفلورة بإتجاه الطول الموجي الطويل (إزاحة حمراء) تزداد مع زيادة قطبية المذيب ، ان الزيادة في قطبية المذيب تؤدي الى نقصان في شدة طيف الفلورة . إن جميع القياسات تمت بدرجة حرارة الغرفة .