

Solvatochromic Spectral Investigations of Acridine

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Abstract: Optical absorption and fluorescence emission spectral studies of acridine in different solvents namely, carbon tetrachloride, dichloromethane, propan-2-ol, ethanol, methanol, acetonitrile, and N,N- dimethyl formamide have been investigated. Oscillator strength and transition dipole moment of the acridine have been elucidated from the optical absorption measurement. The ratio of the excited state to the ground state dipole moment of acridine was determined by solvatochromatism method.

1. Introduction

The nature and extent of solute solvent interactions are able to affect various properties of some compounds in solution. The search for a better understanding of the effect that this factor has on properties variations has been an active area on research [1]. Solvents influence reaction rates, equilibria and mechanisms. The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of several investigations. It is therefore of interest to understand solute-solvent interactions and measure them quantitatively [2]. Usually many dyes have shifts in their absorption and emission spectra when the solvent is varied. The variation in the solvent may be; change from polar to non polar or the reverse, change in the dielectric constant of the solvent, and change in the polarizability of the solvent. Depending upon the nature and the extent of solute- solvent interactions, the spectral characteristics, viz, shape, maxima and intensity may change [3].

Fluorescence spectroscopy is a powerful method for studying the characterization of excited states such as exciplex formation, excited state intramolecular proton transfer reaction, solvent interaction, hydrogen bonding, fluorophore confirmation, binding sites, degree of flexibility, internal motions and many other physico-chemical parameters [4]. It is known that the spectral behavior of an organic molecule is strongly related to the structure in both ground and excited states. The knowledge of solvent effect on absorption and fluorescence spectra is of particular importance. A change in solvent is accompanied by a change in polarity, dielectric constant or polarization of the surrounding medium. Thus the change of the solvent affects on the ground and excited state is different depends on the polarity. A systematic analysis of the solvent effect is, therefore, informative and proves quite fruitful in studying the excited state behavior of the molecule. Dipole moments of short-lived species are of considerable interest, because they provide information about excited states. This is also useful in the parameterization of semi empirical quantum chemical methods employed for these systems. The excited state dipole moments of a molecule control the tunability range of their emission energy as a function of solvent polarity. It can be useful in optimizing the efficiency of the dye [5]. Dipole moment of short-lived species provides information about the electronic and geometrical structure. Absorption spectra reveal the solute solvent interaction, which can be predicted from the position, intensity and shape of the

absorption band [4]. The effect of solvent on UV absorption spectra of molecules can be used to determine the magnitude as well as direction of electric dipole moment of solute molecules in its first electronically excited state. The study of this parameter helps to understand electronic charge distribution, reactivity etc. of the solute molecule in its first electronically excited state [6]. UV and Fluorescence spectroscopy provides an important tool for the investigation of solvent effects on acridine through the changes in wavenumber, intensity and other spectral line parameters.

Acridine derivatives have antiseptic properties such as proflavine. They bind to RNA and DNA due to their abilities to intercalate. Acridine derivatives can act as a nucleic acid – selective meta chromatic stain and useful for cell cycle determination. Solvent effects and photophysical studies acridine(1,8)dione dyes [7,8] and excited state characteristics of acriflavine and acridine orange [9] were reported. Preferential solvation of acridine has been reported by our group [10]. In the present case, the optical absorption and emission spectral studies of acridine in different solvents have been investigated.

2. Experimental

For solvent effects on acridine, carbon tetrachloride, dichloromethane, methanol, propan-2-ol, ethanol, acetonitrile, and DMF from SISCO laboratory with 99% purity were used without further purification. The concentration of acridine in the above mentioned solvents was 0.04 mM. All optical absorption spectra were recorded with UV–VIS 1700 Shimadzu spectrophotometer. Fluorescence spectral measurements were recorded using ElicoIT spectrofluorimeter. All the measurements were performed using 380 nm as excitation wavelength and they were carried out at room temperature.

3. Results and Discussion

3.1 Optical absorption spectral studies

The absorption spectra of acridine are shown in Fig.1. The spectra show a single broad band in the region 340-400nm. The observed absorption maxima of acridine in different solvents are shown in Table 1.

Table 1: Optical absorption and Fluorescence emission maxima of acridine in different solvents

Solvents	Absorption maxima (nm)		Emission maxima (nm)	
	1	2	1	2
CCl ₄	353	379	544	574.6
CH ₂ Cl ₂	353	381	545.8	576
Propan-2-ol	353	384	545.8	585
Ethanol	353	380	541	571
Methanol	353	382	544	578
Acetonitrile	353	382	541	569
DMF	353	383	547	571

The first peak of optical absorption spectra is non sensitive to the solvent polarity where the second peak is sensitive. So the second peak is preferable to determine the characteristics of optical absorption spectra. An inspection of the spectra reveals that as the solvent polarity increases, second peak shows red shift in polar solvents dichloromethane, propan-2-ol, ethanol, methanol, acetonitrile, and DMF with respect to the apolar solvent. The observed bands in the region 340-400 nm is due to π - π^* transition [11]. The band due to π - π^* transition suffers the red shift in more polar solvents due to higher dipole moment of the excited state with respect to the ground state [12]. The wavelength of maximum intensity and full width at half maximum (FWHM) of a band are characteristic of the absorption spectrum. The FWHM value of the absorption band is 11.56 nm in Carbon tetrachloride, 12.74 nm in dichloromethane, 12.82 nm in propan-2-ol, 12.74 nm in ethanol, 13.08 nm in methanol, 11.42nm in acetonitrile, 12.44 nm in DMF. The observed FWHM value indicates that the strong association of the acridine via the intermolecular hydrogen bond between hydroxyl group of solvent (polar protic solvents) and acridine nitrogen. That implies in the case of protic polar solvents the acridine molecules are more stabilized in ground state. Eventhough intermolecular hydrogen bond is formed in propan-

2-ol, the steric effect due to the methyl groups in propan-2-ol is responsible for the observed FWHM in propan-2-ol. [13,14]. In acetonitrile FWHM value decreases with respect to carbon tetrachloride, which indicates that it is less stabilized in the ground state. Due to the self association nature, it acts as a non polar solvent.

The oscillator strength can be determined experimentally by integrating the molar absorptivity across the entire absorption band over the frequency ν (in cm^{-1}). The resulting relationship between the oscillator strength and integrated molar absorptivity is given by,

$$f_{lu} = (4.32 \times 10^{-9} \text{ mol.cm}^2 / L) F \int_{\nu_1}^{\nu_2} \epsilon_{\nu} d\nu \quad \text{----- (1)}$$

Where the molar absorptivity ϵ_{ν} has unit $\text{Lmol}^{-1} \text{ cm}^{-1}$ and the frequency ν is in wave number cm^{-1} . This integration extends from ν_1 to ν_2 which are the limits of the band associated with the electronic transition from state lower to upper. The term $F = \frac{9n}{(n^2 + 2)^2}$ in the above expression is a correction factor related to the

refractive index of the medium in which the absorbing molecule is dissolved. The intrinsic ability of a molecule to absorb light is often expressed in terms of the oscillator strength for the electronic transition. The oscillator strength f_{lu} is related to the transition dipole. The transition dipole moment was obtained using the expression

$$\mu_{ge} = \frac{f_{lu}}{4.7 \times 10^{29} \nu_{abs}} \quad \text{----- (2)}$$

Where f_{lu} is the oscillator strength and ν_{abs} is the frequency in cm^{-1} at the absorption maximum.

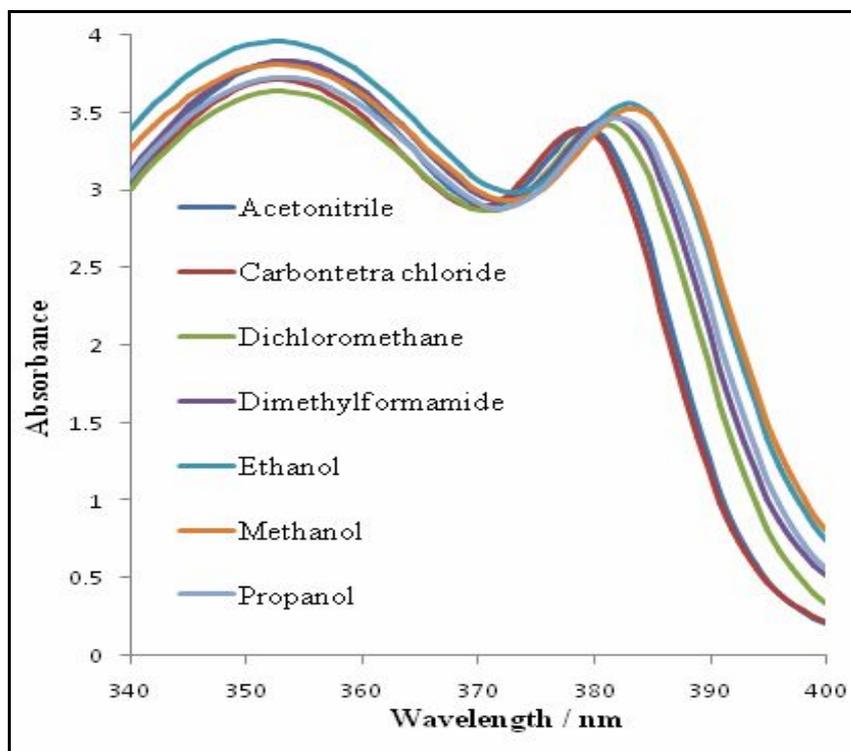


Fig 1: Absorption Spectra of Acridine in different solvents

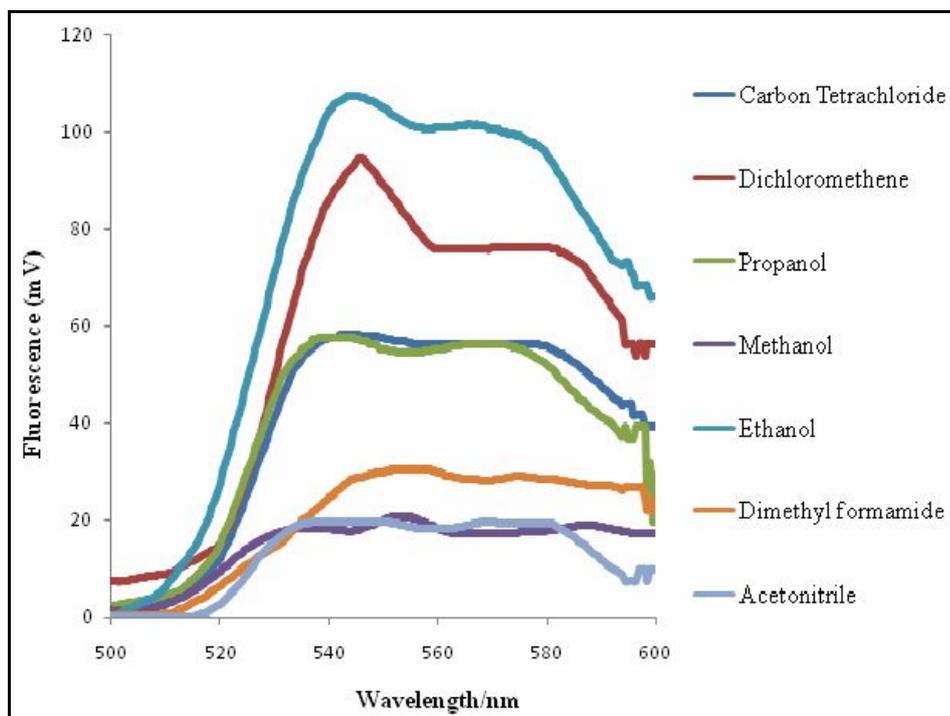
The observed f_{lu} and μ_{ge} values are shown in the table 2. These results indicate that the oscillator strength and dipole moment of the polar solvents are higher than the apolar solvent. Due to the movement of electron from ground state orbital to higher level orbital, there will be a increase of dipole moment with reference to the ground state dipole moment.

Table 2: Oscillator Strength and transition dipole moment of acridine in different solvents

Solvents	$f_{lu} \times 10^{-5}$	$\mu_{ge} \times 10^{-39}$
Carbon tetrachloride	4.09	3.30079
Dichloromethane	4.35	3.52409
Propan- 2-ol	4.68	3.80752
Ethanol	5.05	4.11679
Methanol	5.06	4.13603
Acetonitrile	4.52	3.6558
DMF	4.56	3.70651

3.2 Fluorescence Spectral studies

The fluorescence spectra of acridine in different solvents are shown in Fig.2. The fluorescence emission spectra of acridine in different solvents show two peaks. It is observed with intensity maxima at 544 nm and 575 nm in carbon tetrachloride, 546 nm and 576 nm in dichloromethane, 541 nm and 569 nm in propan-2-ol, 546 nm and 571 nm in ethanol, 544 nm and 585 nm in for methanol and 541 nm and 571 nm in acetonitrile, and 554 nm and 581 nm for DMF. It also shows that, the emission maximum shift to longer wavelength in dichloromethane, methanol, DMF and propan-2-ol, whereas ethanol and acetonitrile shift to shorter wavelength with respect to apolar solvent carbon tetrachloride. It also shows that the shorter wavelength peak is more prominent than the long wavelength peak in all solvents. The observed more prominent short wavelength peak in propan-2-ol, methanol and ethanol are due to the methyl group in the solvent molecule. It is confirmed by measuring the wavelength difference between λ_{ext} and λ_{max} of propan- 2-ol, methanol, and ethanol. It is around 2900 cm^{-1} which is due to asymmetric stretching of methyl group[15].

**Fig 2: Fluorescence emission spectra of acridine in different solvents**

As solvent polarity increases, the short and long wavelength peaks are red shifted except propan-2-ol with respect to apolar solvent. Examination of spacing between vibrational structures reveals that a vibrational mode initiates the progression of peaks. The value is 991 cm^{-1} , 966 cm^{-1} , 747 cm^{-1} , 971 cm^{-1} , 1288 cm^{-1} , 971 cm^{-1} , 1070 cm^{-1} in carbon tetrachloride, dichloromethane, propan-2-ol, ethanol, methanol, acetonitrile and DMF respectively. This gives rise to CH out-of- plane bending progression of acridine in above mentioned solvents. In the case of polar protic solvents, the ground state is more stabilized by intermolecular hydrogen bond between the hydroxyl group of solvent and acridine nitrogen. The strength of this bond remains the same due to

the neutral substituent of acridine. In polar aprotic solvents, the observed red shift indicates the reorientation of the solvent molecule around the excited state dipole gives rise to minor effect.. Fluorescence quantum yield were obtained from the fluorescence spectra using equation (3).[16,17]

$$\phi_f = \left(\frac{A_s}{A_r}\right) \times \left(\frac{a_r}{a_s}\right) \times \left(\frac{n_s}{n_r}\right)^2 \times \phi_r \quad \text{----- (3)}$$

Where A_s and A_r are the area under the fluorescence spectrum. a_s and a_r are the absorbance at the wavelength of excitation 380nm, n_a and n_s are the refractive indices of the respective solvents for the sample and reference respectively. 2,3,Bis(chloromethyl)-1,4,-anthraquinone in dichloromethane was used as the reference ($\phi_r=4.87 \times 10^{-3}$) [14]. The relative fluorescence quantum yields of acridine in the above mentioned solvents were listed in table 3. Since the reorganization energy of acetonitrile and DMF get increased (i.e., the energy spent in the relaxation region is more), the relative quantum yield get reduced, and these solvents acetonitrile and DMF are red shifted with respect to carbon tetrachloride. In addition to the self association nature of alcohol molecules, in propanol, the OH group has the tendency to form an intermolecular hydrogen bonding with N group of Acridine, the intermolecular hydrogen bond OH...N-C acts as an acceptor mode which increases the nonradiative decay and gives rise to observed quantum yield. Dichloromethane shows a high quantum yield due to the reorientation of the solvent molecule around excited state dipole, which in turn gives the observed fluorescence quantum yield in polar aprotic solvents.

Table 3: Quantum yield of acridine in different solvents

Solvents	$\phi_{rel} \times 10^{-4}$
Carbon tetra chloride	1.190
Dichloromethane	1.540
Propanol	0.997
Ethanol	1.740
Methanol	0.375
Acetonitrile	0.317
Dimethyl formamide	0.537

3.3 Dipole moment of the Excited state

The dipole moment of an electronically excited state of a molecule is an important property that provides information on the electronic and geometrical structure of the molecule in the short lived state. Knowledge of the excited state dipole moment of the electronically excited molecule is quite useful in designing non linear molecules [18].

Table 4 shows the photo physical parameters deduced from the observed absorption and emission spectra of acridine in different solvents. The effect of solvent on absorption spectra of molecules can be used to determine the magnitude as well as the direction of electric dipole moment of the solute molecule in its first electronically excited state. The study of this parameter helps to understand electronic charge distribution, reactivity etc. of the solute molecule in its first electronically excited state [19,20] Measurements of dipole moments in the excited state are useful to extract parameters like molecular polarizability [21], and to access the electron density distribution in the excited singlet and triplet states. A number of experiment methods like microwave conductivity [22], electric dichroism [23], electric polarization of fluorescence [24] and stark splitting [25] are available to determine the dipole moment more precisely but applications have been limited to instrument intensive and restricted to small organic molecules. But solvatochromic molecules offer a simplest method to determine the dipole moment.

Among the existing methods, for the determination of the change in dipole moments associated with electronically excitation of a molecule, the most popular ones are based on a linear correlation between the wave numbers absorption and fluorescence maxima $\bar{\nu}_a - \bar{\nu}_f$ and the solvent polarity function which usually involves both the dielectric constant (ϵ) and refractive index (n) of the medium

According to Bakshiev [26], Chamme and viallet [27]

$$\bar{\gamma}_a - \bar{\gamma}_f = m_1 F_1(\epsilon, n) + C_1 \quad \text{----- (4)}$$

$$\bar{\gamma}_a + \bar{\gamma}_f = -m_2 F_2(\epsilon, n) + C_2 \quad \text{-----}$$

where $\bar{\gamma}_a$ and $\bar{\gamma}_f$ are absorption maximum and fluorescenc maximum and $F(\epsilon, n)$ is the solvent polarity parameter

$$F_1(\epsilon, n) = \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{2n^2 + 1}{n^2 + 2} \right) \quad \text{----- (6)}$$

$$F_2(\epsilon, n) = F_1(\epsilon, n) + 2G(n) \quad \text{----- (7)}$$

Where

$$G(n) = \frac{3(n^4 - 1)}{2(n^2 + 2)^2}$$

Where ϵ is dielectric constant and n is refractive index of the solvent.

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad \text{----- (8)}$$

$$m_2 = \frac{2(\mu_e - \mu_g)}{hca^3} \quad \text{----- (9)}$$

where μ_e and μ_g excited state and ground state dipole moment of the solute molecule respectively, h is the Planks constant, c is the velocity of light, and a is Onsager cavity radius.

From eqns (8) and (9) the ratio of dipole moment in excited and ground state is given by,

$$\frac{\mu_e}{\mu_g} = \left| \frac{m_1 + m_2}{m_2 - m_1} \right| \quad \text{----- (10)}$$

Fig .3. Shows correlation between $\bar{\gamma}_a - \bar{\gamma}_f$ and $F_1(\epsilon, n)$ by eliminating DMF which shows much deviation and Fig.4. Shows correlation between $\bar{\gamma}_a + \bar{\gamma}_f$ and $F_2(\epsilon, n)$ (by eliminating acetonitrile) linear plot has been drawn. This deviation from linearity may be due to specific solute- solvent interaction [28].

Table 4: The photo physical parameters deduced from the observed absorption and emission spectra of acridine in different solvents

Solvents	Absorption maxima (nm)	Emission maxima (nm)	$\bar{\gamma}_a - \bar{\gamma}_f$ (cm ⁻¹)	$\bar{\gamma}_a + \bar{\gamma}_f$ (cm ⁻¹)	F ₁ (ϵ, n)	F ₂ (ϵ, n)
CCl ₄	379	544	8002.871	44767.58	0.021025	0.64395
CH ₂ Cl ₂	381	545.8	7931.701	44561.74	0.594957	1.170678
Propan-2-ol	384	545.8	7693.722	44662.3	0.765158	1.27874
Ethanol	380	541	7794.642	44424.68	0.811712	1.303295
Methanol	382	544	7659.314	44424.02	0.855018	1.300061
Acetonitrile	382	541	7831.501	44800.08	0.859236	1.328104
DMF	383	547	8127.469	44228.55	0.836682	1.416103

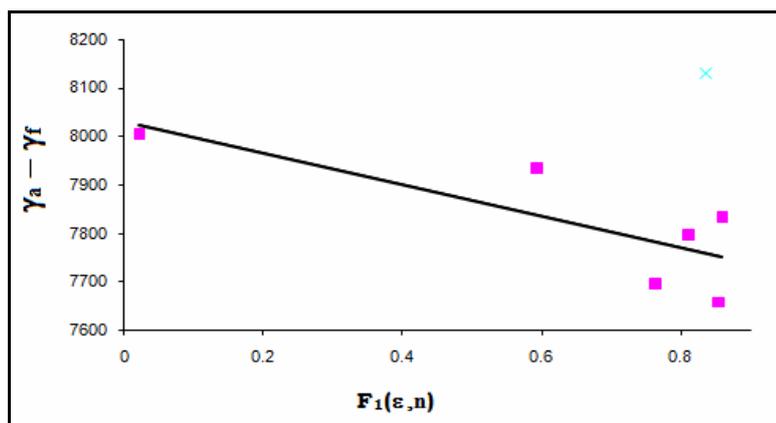


Fig 3: Plots of $\bar{\gamma}_a - \bar{\gamma}_f$ against polarity function $F_1(\epsilon, n)$

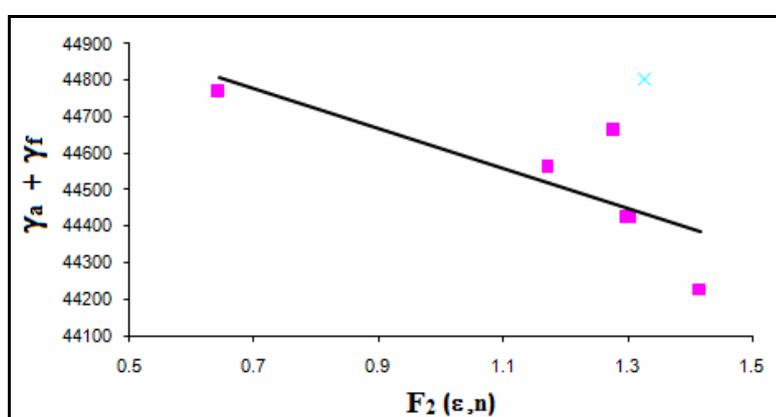


Fig 4: Plots of $\bar{\gamma}_a + \bar{\gamma}_f$ against polarity function $F_2(\epsilon, n)$

The following conclusion has been drawn from the dipole moment determination using the solvent polarity parameter. The polarity of a molecule depends on electron density. With supply of additional energy there will be transition from ground state to excited state. Due to the movement of electron from ground state orbital to higher level orbital, there will be an increase of dipole moment with reference to the ground state dipole moment. Therefore in general the values of the excited state dipole moments are higher than the ground state dipole moments. The observed redshift (absorption maximum) in polar solvents provides the evidence for the observed dipole moment of the excited state which is greater than the dipole moment of the ground state.

4. Conclusion

Optical absorption and emission studies on acridine were carried out to study the solvent effects on acridine. Oscillator strength and transition dipole moment are elucidated from the observed features of optical absorption spectra. Fluorescence quantum yield are calculated from the observed features of fluorescence spectra. Excited state dipole moment of acridine was higher than that of ground state dipole moment determined by solvatochromism method.

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