Photo physical properties of 8-hydroxy quinoline

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The steady state absorption, fluorescence excitation and emission spectra of 8-hydroxy quinoline (8-HQ) have been studied in a wide range of solvents of varying dipole moments. The dependence of fluorescence emission on concentration and excitation wavelength indicates the existence of two different emitting species in equilibrium. The fluorescence quantum yield exhibits a substantial solvent dependence. The high quantum yield observed in polar aprotic solvents such as dimethyl formamide and dimethyl sulphoxide might be due to severe overlapping of electronic transitions of various species/single species. The fluorescence and emission spectra of 8-HQ in various solvents exhibit dual fluorescence in the region 330-410 nm. The fluorescence emission of 8-HQ in pure dimethyl formamide, dimethyl sulphoxide and propanol solvents measured as a function of concentration in the range 10×10⁻⁶ to 5×10⁻⁴ mol dm⁻³ displays a clear iso-emissive point at 395 nm while in binary mixture of propanol and dimethyl formamide, iso-emissive point is obtained around 410 nm for excitation wavelength of 290 nm. This finding reveals the formation of two stoichiometric hydrogen-bonding complexes, namely, 1:1 and 1:2 complexes in the ground and excited state.

Keywords: Absorption, Fluorescence excitation, Emission spectra, H-bonding complexes, Monomers, Dimers

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1 Introduction

8-HQ is a bifunctional hydrogen-bonding molecule, which in aqueous or alcohol solution simultaneously acts as a H-donor at the OH site and an acceptor at the N-atom. Upon photoexcitation, the acid/base properties of this molecule change significantly at both the sites, rendering OH- group more acidic and the N-atom more basic. Excited state proton transfer [ESPT] from 6-HQ to the solvent has been reported to occur adiabatically in bulk water and other aprotic solvents. ESPT to bulk solvents at room temperature has been investigated for 7-HQ both by steady state and time-resolved measurements. However, such studies on 8-HQ have not appeared in literature. Various models have been put forth for solvent–assisted excited state proton transfer, mediated by several solvent molecules and the same kinetics scheme may be expected to be valid for 8-HQ with some difference depending mainly on the position of the -OH group. In 8-HQ, the acidic (H-bond donating) and basic (H-bond accepting) groups of the molecule are relatively close to each other and hence a single solvent can bind to both the sites simultaneously and monomer molecules can also arrange to form dimers via H-bonding. One might expect tautomerization in H-bond accepting solvents via intra-molecular hydrogen bonding and in all other solvent solutions, there may exist a competition between intra- and inter-molecular H-bonding. 8-HQ and its derivatives are capable of forming complexes with many metal ions. In recent years, metal chelates of 8-HQ have played an important role in organic electroluminescence (OEL), and were widely introduced in OEL cell as emission layer. 8-HQ and its derivatives are also used as insecticides, amoebicides, bactericides and fungicides. Another interesting feature is that some 8-HQ derivatives are expected to exhibit non-linear optical properties. For understanding inter- and intra-molecular hydrogen bonding and protonation and deprotonation processes coupled with electron transfer reactions, fluorescence quantum yield measurements for 8-HQ in various solvents are essential. From the viewpoint of photochemistry, ESPT is of particular interest, in which the reaction starts with photoexcitation and the new species formed after photoexcitation can be identified by their drastically modified electronic
spectra. Previous studies on 8-HQ have shown that 8-HQ and its derivatives are fluorescent in concentrated acid media but not in dilute acid, neutral and basic aqueous solutions. Some fluorescence information including quantum yields is available for this molecule in a few solvents in concentrated acidic media. The changes in absorption spectrum of 8-HQ in concentrated and dilute sulphuric acid were attributed ionic strength effect but not to the existence of ground state forms other than cation. The quenching of green fluorescence of 8-quinolinolium cations in solutions of low acidity has been attributed to the prototropic equilibrium in the $S_1$ state between 8-quinolinolium cations and the non-fluorescent zwitterions form of 8-HQ. The fluorescence of 8-HQ was studied in several media and concluded that the quenching of fluorescence is due to H-bonding by the hydroxylic solvents. In the present work, we have carefully examined the absorption and emission properties of 8-HQ under a wide range of solvents of varying polarities as a function of concentration and excitation energy. Interestingly, we found a number of striking differences between our results and previous ones, most significant of which is the observation of two emitting species that are in equilibrium and high fluorescence quantum yield of 8-HQ in aprotic solvents. The absorption spectra in some solvents reported by earlier researchers agree well with our results. But the significant changes in fluorescence behaviour are concentration and excitation energy dependence. The excitation spectrum monitored at two different emission maxima was found to be dependent on emission wavelength confirming the existence of different absorbing species.

3 Results and Discussion

3.1 Steady state absorption/excitation studies

The peak position of the absorption spectra of 8-HQ (1 × 10$^{-5}$ mol dm$^{-3}$) in various solvents at room temperature is given in Table 1. Absorption spectra are different in neutral, acidic and basic media, indicating the existence of the different absorbing species in the ground state. The absorption and fluorescence emission spectra are red-shifted with increasing polarity of the solvent, but shift of the absorption maxima is not significant for all solutions. Marked shift of fluorescence emission of this compound with increasing the solvent polarity indicates the nature of transition as of $\pi-\pi^*$ type. This feature leads to the conclusion that the dipole moment increases in the $S_0-S_1$ excitation, electronic charge being transferred from -OH group to the aromatic ring. The orientation of OH with respect to aromatic ring might change during the lifetime of $S_1-S_0$ state. Similar to 6-hydroxy quinoline, we do expect cis- and trans-form of 8-HQ, depending on the orientation of OH with respect to aromatic ring. The absorption spectrum in weak ethanolic acidic solutions seems to be resolved into two components with peak positions around 313 and 366 nm and similar observations have been reported by Bratzel et al. in weak acidic aqueous medium. The band at 366 nm has been attributed to the mechanism of charge transfer between the benzonoid ring and positively charged pyridinium ring. In order to understand the nature of this high wavelength band, the emission spectrum as a function of excitation wavelength/concentration/binary mixtures and also the excitation spectrum at different emission wavelengths have been measured.

The excitation spectra measured at different emission peaks for all solutions at concentration 1 × 10$^{-5}$ mol dm$^{-3}$ show that in dioxin, propanol, dimethyl sulfoxide (DMSO) and mixture of propanol and dimethyl formamide (DMF) solutions, excitation spectra show emission wavelength dependence. The results show that for all these solutions two distinct excitation spectra with their peak positions around 285 and 320 nm were obtained corresponding to emission band maxima at 340 and 410 nm, respectively, confirming that the bands correspond to distinct energy states of a single species or different species. It is seen that the excitation spectrum of the emission at 340 nm does not resemble the absorption, and the excitation spectrum for emission around 410 nm was...
nm is structureless and considerably red shifted relative to the first absorption band. The change in the excitation spectrum with two-emission wavelength would indicate the presence of two different emitting species formed in the excited state.

The excitation spectra (Fig. 1) of 8-HQ in mixed solvents in propanol and DMF, recorded as a function of composition of solvents show a clear isosbestic point, reflecting the equilibrium between the two emitting species. The intensity ratio \((I_2/I_1)\) of band II to band I as a function of composition of solvents represents a straight line yielding the slope equal to 2. The results are in favour of the formation of 1:1 and 1:2 H-bonded complexes in the excited state, because H-bonding being a particular case of specific association implies a fixed stoichiometry ratio (usually 1:1) of interacting molecules as well as a fixed geometry.

### 3.2 Fluorescence emission studies

The fluorescence emission spectra of 8-HQ were recorded in different solution over a wide range of concentration, e.g., from \(1 \times 10^{-5}\) to \(1 \times 10^{-3}\) mol dm\(^{-3}\) and the results show that in most of the solvents used here, there are less and high concentration regimes where fluorescence behaviour was different. Only in the high concentration regime, fluorescence emission (Fig. 2) was found to be dependent on excitation energy. The fluorescence emission of 8-HQ at \(1 \times 10^{-5}\) mol dm\(^{-3}\) in alcohols (EtOH, MeOH, Prop), dioxin, acetonitril, DMF, DMSO, water and binary solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption maxima ((\lambda, \text{nm}))</th>
<th>Extinction co-efficient (\varepsilon)</th>
<th>Excitation maxima at (\lambda_{em}, \text{nm})</th>
<th>Fluorescence maxima ((\lambda, \text{nm}))</th>
<th>Relative quantum yield (\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxane</td>
<td>319.0</td>
<td>1011</td>
<td>340</td>
<td>410 (I)</td>
<td>----</td>
</tr>
<tr>
<td>Ethanol</td>
<td>319.2</td>
<td>2420</td>
<td>----</td>
<td>315 (I)</td>
<td>----</td>
</tr>
<tr>
<td>EtOH+0.1N H(_2)SO(_4)</td>
<td>366.0</td>
<td>1820</td>
<td>----</td>
<td>274 (I)</td>
<td>----</td>
</tr>
<tr>
<td>EtOH+0.1N NaOH</td>
<td>335.6</td>
<td>21400</td>
<td>----</td>
<td>---- (I)</td>
<td>----</td>
</tr>
<tr>
<td>Methanol</td>
<td>314.0</td>
<td>2360</td>
<td>----</td>
<td>311 (I)</td>
<td>----</td>
</tr>
<tr>
<td>Propanol</td>
<td>319.2</td>
<td>3220</td>
<td>283</td>
<td>---- (I)</td>
<td>----</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>319.2</td>
<td>2660</td>
<td>281</td>
<td>343 (I)</td>
<td>----</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>312.4</td>
<td>2640</td>
<td>----</td>
<td>---- (I)</td>
<td>396</td>
</tr>
<tr>
<td>DMSO</td>
<td>322.4</td>
<td>3020</td>
<td>281</td>
<td>330 (I)</td>
<td>0.170</td>
</tr>
<tr>
<td>DMF</td>
<td>320.4</td>
<td>2900</td>
<td>----</td>
<td>285 (I)</td>
<td>0.340</td>
</tr>
<tr>
<td>Water</td>
<td>310.8</td>
<td>1920</td>
<td>291</td>
<td>---- (I)</td>
<td>0.002</td>
</tr>
</tbody>
</table>
of propanol and DMF at $1 \times 10^{-5}$ mol dm$^{-3}$, all at excitation wavelength 290 nm, consists of two broad bands, one ranging from 330 to 365 nm (I band) and another from 400 to 450 nm (II band). In low concentration regime ($1 \times 10^{-5}$ mol dm$^{-3}$), the emission spectrum of 8-HQ in ethylene glycol, DMSO, DMF and in mixed solvents of propanol and DMF, display two bands at 335 and 410 nm with an excitation wavelength of 290 nm. While in dioxin and propanol solutions, only one band at 340 nm is observed. Concentration dependence study of emission shows that as the concentration increases the intensity of the II band increases correspondingly. When the concentration reaches $1 \times 10^{-3}$ mol dm$^{-3}$, a band with a maximum around 420 nm alone is observed. This concentration dependence of the emission (Fig.2) behaviour evidently indicates the formation of dimers or associates and hence the band at 420 nm is attributed to dimers formed via hydrogen bonding and the low wavelength band at 340 nm to monomers. The fluorescence efficiency of the monomer decreases due to migration of electronic excitation from monomers to such associates. For small dye concentrations in DMSO, the spectrum consists of only one band at 340 nm (I band). As the concentration of 8-HQ in the solution increases, the emission spectrum displays an additional long wavelength band with maximum around 410 nm. Moreover, in the narrow range of concentration $[C] \approx (1.0-2.5) \times 10^{-4}$ mol dm$^{-3}$, the emission spectrum turns out to be a two-band system. With a further increase in the concentration, the intensity of the short wavelength band decreases while that of long wavelength band increases. When the concentration reaches a value of about $[C] \geq 5 \times 10^{-4}$ mol dm$^{-3}$ such a band at short wavelength is absent in the spectrum. The intensity of the fluorescence of the long wavelength band in the spectrum increases simultaneously with the decrease in the intensity of short wavelength band. A further increase in the concentration of 8-HQ to $[C] \approx 1.0 \times 10^{-3}$ mol dm$^{-3}$, the emission spectrum is accompanied by a decrease in the intensity of the long wavelength band. The dual band character of the spectrum is indicative of the participation of fluorescence components of 8-HQ. Such a spectral feature has already been reported for Rh-6G in aqueous solutions. We have recorded the excitation spectra of 8-HQ at low concentration solutions for two emission bands in order to avoid distortion at high concentration. The excitation spectra corresponding to these two emissions are entirely different. Therefore, the formation of dimers in the excited state and after excitation, these two species namely monomers and dimers emit independently and thus the process of fluorescence is the parallel one. Interestingly, at a concentration of $1 \times 10^{-3}$ mol dm$^{-3}$ in DMSO and ethylene glycol solutions another band at 365 nm develops as a shoulder. This band may be attributed to some form of dimer. We tentatively assign this band to $1L_b$ state of dimer. In this spectral region, the spectrum is the resultant spectrum corresponding to two overlapping electronic transitions ($1L_a \rightarrow 1A; 1L_b \rightarrow 1L_b$) of a single species. Another interesting feature is the excitation energy dependence of emission only in the high concentration region of the solution. This perhaps could be due to low yield of dimers formed in the low concentration region of the solution, with the exception of water solution for which the fluorescence intensity is low. All other solutions exhibit dual emission, which is dependent on excitation energy. We measured systematically the fluorescence spectrum as a function of excitation wavelength and the results show that as the excitation wavelength increases from 290 to 375 nm on the fluorescence spectra of 8-HQ, a new band at 500 nm (III band) is developed. A series of emission spectra taken as a function of excitation wavelength display a clear iso-emissive point reflecting the equilibrium between two distinct emitting species. A typical spectra corresponding to ethanol solution is shown in Fig. 3. The third long wavelength band is attributed to cationic form of the molecule based on the earlier report.
Alternatively, the third band at 510 nm may be attributed to the excited tautomer formed by intra-molecular proton transfer in the solution. It is seen that the relative strength of I and II emission changes with the excitation wavelength. In accordance with the previous reports, we feel that the band at 510 nm may be due to ionic or protonic excited character of 8-HQ. In a highly polar aprotic media, the fluorescence of 8-HQ exhibits an unusual high quantum yield of fluorescence and the spectrum shows broad and featureless band. The effect is attributed to overlapping bands corresponding to various forms of 8-HQ modulated by solvent behaviour. It is obvious that, it is not only polarity of the solvent that effects the fluorescence character but also the association between the solvent and the molecules (excited/ground state).

The main species formed in 8-HQ solution consist of neutral (N), cationic (C) and anion (A), the relative contributions being dependent on the degree of acidic and basic character of the medium. It is established that the zwitterions form though predominant in the excited state is known to be non-fluorescent in most of the solvents. In all the pure solvents, H-bonded complexes have been reported to be the main emitting species and the low quantum yield of their fluorescence has been attributed to either to hydrogen bonding or to the prototropic equilibrium between excited states of two ionic species. In agreement with the previous researchers, the fluorescence intensity is very weak in aqueous solution. Though the intensity of fluorescence has been reported to be enhanced in high acidic concentration, we did not make any attempt to study the fluorescence at high acidic concentration simply because of the fact that the previous researchers have already attributed the observed changes in the absorption spectra to environmental effect. In acidic media at high concentration of 8-HQ, the emission spectrum consists of only broad and featureless band in the range 360-500 nm with a emission peak around 427 nm; this shows that the green fluorescence due to cationic species is quenched for two alternative explanations. In basic media (0.1N NaOH), the spectrum consists of weak emission band around 503 nm and the band maxima is red shifted to 520 nm when the excitation wavelength is changed from 290 to 375 nm. This high wavelength band is assigned to ionic form of 8-HQ. In all other neutral solution at high concentration of 8-HQ (1×10⁻³ mol dm⁻³), the spectrum consists of two bands with maxima around 410 and 487-510 nm and the relative intensity of the two emission bands considerably changes with excitation wavelength. As shown in Fig. 3, a clear cut iso-emissive point is obtained in a series of spectra recorded at various excitation wavelengths, reflecting the existence of two emitting species in equilibrium mainly with dimeric and cationic species in the S₁ state. Looking to the data on spectral regions, it appears that in pure solvents the fluorescence band corresponding to cationic and ionic species overlaps.

The emission spectrum of 8-HQ in DMSO and DMF with λₐₓ = 375 nm seems to be an admixture of the profiles of dimer and protonated species. However, contribution to the emission from the excited tautomer formed by intra-molecular proton transfer in the solution cannot be neglected. The excited tautomer formation is quite possible in non-hydrogen bonding solvents. In view of the relatively close distance between acidic (H-bond donating) and basic (H-bond accepting) group of the molecule, in the presence of hydrogen bonding solvents such as ethanol and water, a single solvent molecule can bind both the groups and this effect is obviously expected to compete with the intra-molecular hydrogen bonding process. It is well known that the principal influence of intra-molecular H-bonding in 8-HQ is that it increases the efficiency of S₁→S₀ (IC). In acetonitrile, which is a weakly associated solvent, the fluorescence quantum yield of 8-HQ is very low. Regarding ethylene glycol [C₂H₄(OH)₂], this solvent has two hydroxyl groups which can hydrogen bond with other ethylene glycol molecule of the liquid to form polymeric structure which perhaps is responsible for the higher viscosity of the liquid, relative to the linear alcohols which have only one hydroxyl group for H-bonding.

Fig. 3 — Fluorescence emission spectra of 8-HQ in ethanol at concentration 1×10⁻³ mol dm⁻³ as a function of excitation wavelength 280, 345, 350, 355, 360, 365 and 375 nm.
The fluorescence spectrum of 8-HQ in ethylene glycol and DMSO shows two overlapping bands at 365 and 410 nm whereas in all other solvents a single band around 410 nm is observed, all at excitation wavelength of 290 nm and the band at 410 nm is assigned to mono cation, formed by the protonation of the N-atom. In order to understand the origin of the second band at longer wavelength, the effect of concentration and/or excitation energy on the fluorescence spectra was investigated and the resulting spectra are depicted in Fig. 3. As shown in Fig. 2, with an increase in concentration from $1 \times 10^{-5}$ to $10 \times 10^{-4}$ mol dm$^{-3}$, we find a regular drop in the intensity of the fluorescence band at shorter wavelength, and increase in intensity of the higher wavelength band in all these solvents. The emission spectra of 8-HQ in propanol, DMSO and in the binary mixture of propanol and DMF (v/v at $5 \times 10^{-5}$ mol dm$^{-3}$) measured as a function of concentration ranging from $1 \times 10^{-5}$ to $10 \times 10^{-4}$ mol dm$^{-3}$, displays a clear iso-emissive point at 390 and 410 nm respectively for excitation wavelength 290 nm, reflecting the equilibrium between two distinct emitting species. At higher concentration for almost all solvents, a fluorescence spectrum exhibits excitation wavelength dependence. The trend is such that at high concentration around $1 \times 10^{-3}$ mol dm$^{-3}$, fluorescence emission spectra (Fig. 3) of 8-HQ in ethanol as a function of excitation wavelength ranging from 280 to 375, displays a clear iso-emissive point at 470 nm, reflecting the equilibrium between two distinct emitting species. The intensity ratio $I_2/I_1$ of band II to band I as a function of concentration/composition of solvents/excitation wavelength represents a straight line yielding slope equal to 2. Thus, the fluorescence spectrum shows not only the emission band of the cationic form (maximum at 410 nm) and the tautomer form (maximum at 520 nm) but also equilibrium between these two emitting states. The possible resonance structures of 8-HQ are shown in Fig. 4.

The relative fluorescence quantum yields of 8-HQ were measured using Rh-6G as the reference for low concentrations and the values are collected in Table 2. According to previous researchers, the fluorescence quantum yield is relatively higher in aqueous concentrated media compared to those in all other solvents. In contrast, the present study reveals that the fluorescence quantum yield is higher in most of the polar aprotic solvents and also in ethylene glycol relative to all other solvents. This feature perhaps could be due to the fact that the emission spectrum in the range 300-560 nm is broad and featureless and the entire spectrum is a combination of individual fluorescence spectrum of different species present. Alternatively, the enhanced fluorescence intensity in DMSO and DMF is probably related to the significant charge transfer from solvent to the chromophore. Electron donation on the aromatic ring generally increases the fluorescence efficiency as it increases the $\pi$-electron density on the ring and hence the increase in the oscillator strength. Thus, relatively high quantum yield of 8-HQ in polar aprotic solvents is the manifestation of the electron donating effect of the solvent. In the present work, we could not measure the lifetimes of species, as the signal was too weak. However, efforts are being made to improve the
intensity level of the signal by the proper choice of the media and the experimental conditions.

References