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# Ground and excited state preferential solvation behaviour of 1,4-dihydroxy-3-methylanthracene-9,10-dione in DMF + CCl$_4$ binary system

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## ARTICLE INFO

## ABSTRACT

Preferential solvation of 1,4-dihydroxy-3-methylanthracene-9,10-dione (DHMAD) has been investigated using optical absorption and fluorescence emission techniques. Optical absorption spectra of DHMAD in different solvents show the intra molecular charge transfer band in the region 400–550 nm. The preferential solvation parameter shows that in dimethyl formamide (DMF) + carbon tetrachloride (CCl$_4$) mixture, the DHMAD is preferentially solvated by DMF in the ground state and in the excited state DHMAD is preferentially solvated by CCl$_4$ in DMF rich region and by DMF in CCl$_4$ rich region.

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## 1. Introduction

Solvatochromic molecules are a class of molecules that exhibit absorption and/or emission spectral shifts that depend on the dielectric and dipolar properties of their local environment.

The solvatochromic shifts are indicative of interactions between the solvent and the solute in the immediate vicinity of the solute. This region being referred as the solute cybotactic region [1]. In order to analyze the interactions, one of the most successful approaches is the solvatochromic comparison method of Kamlet et al. [2]. Another methodology for the study of solute–solvent interactions is the use of binary mixtures of solvents. In solvent mixtures a preferential enrichment by one of the solvent components in the cybotactic region of a compound is observed. The fact that the solvent shell has a composition other than the macroscopic ratio is termed as selective or preferential solvation [3]. Studies involving mixed solvents have become very important in the last few years because these systems are widely used in fields such as kinetics, spectroscopy, thermodynamics, analytical chemistry and industrial processes [4].

The hydroxy anthraquinone chromophore is the biologically active site in several antitumor anthracyclines. The stacking interaction between the chromophore of the drug and the base pairs of DNA has been studied by means of several spectroscopic studies.

Suppan has reported the influence of the medium on the energy of electronic states on the basis of solvatochromic shifts [5]. The preferential salvation of p-nitroaniline in binary mixture has been reported [6]. The preferential salvation of pyridinium derivatives has been investigated using UV spectroscopic techniques [7]. The influence of hydrogen bond and preferential salvation of benzoate derivatives were studied [8]. Our group has investigated the PS of 1,4-dimethyl amino anthraquinone, 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone (DHDMAQ) and 1,2-dihydroxy anthraquinone in different binary mixtures [9–11].

In the present study, optical absorption and fluorescence emission spectroscopic techniques have been employed to investigate preferential solvation of 1,4-dihydroxy-3-methylanthracene-9,10-dione (DHMAD).

## 2. Experimental

Spectral grade CCl$_4$ and DMF were obtained from SISCO laboratory and were used without further purification.

All the mass measurements were performed on an electronic balance (Shimadzu) accurate to four decimal places. Preferential solvation effect on DHMAD has been performed in DMF + CCl$_4$ binary mixture using optical absorption and fluorescence measurements keeping the concentration of DHMAD as 0.0166 mM. Optical absorption spectra and fluorescence spectra were measured for varying mole fraction of CCl$_4$ and DMF, keeping the total volume (10 ml) of the mixture (CCl$_4$ + DMF) and the concentration of the DHMAD (0.0166 mM) constant.

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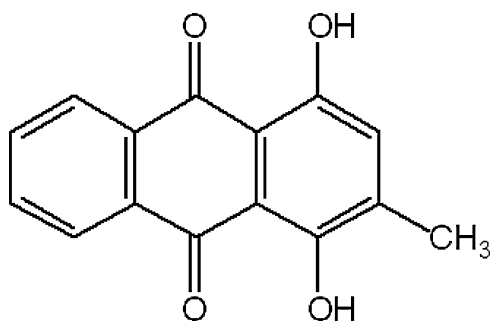 E-mail address: ums10@yahoo.com (M. Umadevi).

**Fig. 1.** Structural formula of 1,4-dihydroxy-3methylanthracene-9,10-dione.

Optical absorption spectra were recorded using a (Shimadzu UV-1700 pharmaspec) UV–visible spectrophotometer. Elico Spectrofluorimeter SL174 was used to record fluorescence spectra.

## 3. Results and discussion

### 3.1. Theory of preferential solvation

The extent of preferential solvation can be calculated in terms of two different methods. In the first case [12], the 'local' excess or deficiency of one solvent component over the bulk composition is used to describe preferential solvation

$$x_2^L = \frac{E_{12} - E_1}{E_2 - E_1}$$

where $E_1$ and $E_2$ are the values of the electronic transition energy in the solvents 1 and 2 respectively. This transition energy ($E_{12}$), defined as the excitation energy (kcal mol$^{-1}$) of any solvatochromic dye, can be calculated from the wavelength ($\lambda_{max}$) of the maximum of the long wavelength absorption band as in the case of Reichardt solvent polarity parameter [13], where $E_{12}$ (kcal mol$^{-1}$) = 28,591/$\lambda_{max}$ (nm). $x_1$ and $x_2$ are the bulk mole fraction of the solvents 1 and 2 while $x_1^L$ and $x_2^L$ are the mole fraction in the cybotactic region. The term $\delta_{s2} = x_2^L - x_2$ is an index of preferential solvation with respect to cosolvent.

The second method [14] incorporates a parameter ($f_2/f_1$), which is the proportionality coefficient of the ratio of the molecules of solvent 2 in reference to solvent 1 in the cybotactic region of the solvatochromic indicator. It is the ratio of molecules of the same solvent in reference to the other in the bulk of the solution, where $(f_2/f_1) = (x_1/x_2)((E_{12} - E_1)/(E_2 - E_{12}))$. This parameter is equivalent to the exchange constant $K_{ps}$ [15] for the description of $E_T(30)$ variation with composition in binary mixtures, where $K_{ps} = x_2^L x_1 / x_1^L x_2$.

### 3.2. Preferential salvation of DHMAD in the ground state

Studies of preferential solvation of DHMAD in binary solvent mixtures were carried out in CCl$_4$ + DMF system, where DMF being the cosolvent.

Fig. 1 shows the structural formula of DHMAD. The optical absorption spectra of DHMAD in CCl$_4$ + DMF binary system are depicted in Fig. 2. The absorption spectra show a structured band in the wavelength range of 400–550 nm. The observed spectra reveal that as the mole fraction of DMF increases, the wavelength of the long wavelength band (around 487.5 nm) decreases.

In the case of anthraquinone derivatives, when an electron donating substituent such as hydroxyl or amino group is introduced, a new absorption band appears in the visible region, which is assigned to an intra molecular charge transfer band between the substituent and the carbonyl groups [16]. In the present case DHMAD have their intra molecular charge transfer band between
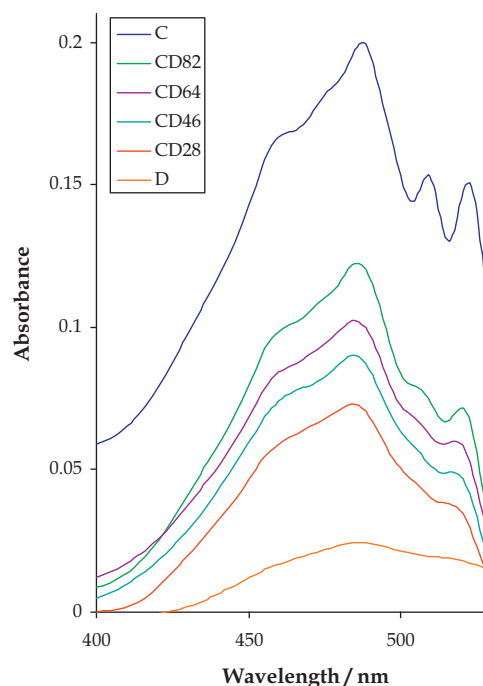


**Fig. 2.** Optical absorption spectra of DHMAD in CCl$_4$ + DMF mixture (C: CCl$_4$; D: DMF; CD28: volume of CCl$_4$ is 2 ml and DMF is 8 ml).

400 and 550 nm, which is due to the electron donating characters of the hydroxyl groups to the carbonyl groups.

It shows vibrational features in CCl$_4$ and less featured in DMF. The possible origin of the fine structures of the charge transfer bands is explained by the strong coupling between a vibrational mode or modes of the quinone moiety and the electronic charge transfer transition. In this case, it shows the vibrational spacing of 526, 845 and 1201 cm$^{-1}$ in CCl$_4$, 1390 and 1186 cm$^{-1}$ in DMF. In DMF ring stretching vibration modes of anthraquinone are responsible for the observed progression of peaks in the visible region. In CCl$_4$ in-plane C=O deformation and in-plane CH deformation modes are responsible for the observed progression of peaks in the visible region [17].

DHMAD chromophores have a negative charge excess and proton accepting ability due to the substituent. When this DHMAD is electronically excited some electron charge is displaced from the substituent to the anthraquinone core. This may lead to an increase of the acidity and proton donating properties of the substituent. In this case intra- and intermolecular hydrogen bonds are formed in competition and at equilibrium, both kinds of bonds will exist, each with a non vanishing probability. If in the ground state there is a balanced equilibrium between internal and external hydrogen bonds, electronic excitation is likely to shift it in favor of intramolecular hydrogen bonding because the carbonyl acquires some extra electronic charge. If the intramolecular hydrogen bond dominates both in the ground and excited states, there should be little variation of intermolecular interaction on excitation. In this case intramolecular hydrogen bond could be favored due to the electrostatic repulsion between the lone pairs of carbonyl and hydroxyl. The non vanishing variation of the intermolecular interaction strength in the excited state of DHMAD is again directly confirmed by solvatochromic data that show blue shift in DMF [18].

The quasiaromatic rings formed by hydrogen bonding between the carbonyl oxygen and hydroxyl hydrogen of the substituents, where intra molecular hydrogen bond is possible, also contribute to the stabilization of the charge transfer band to a great extent.
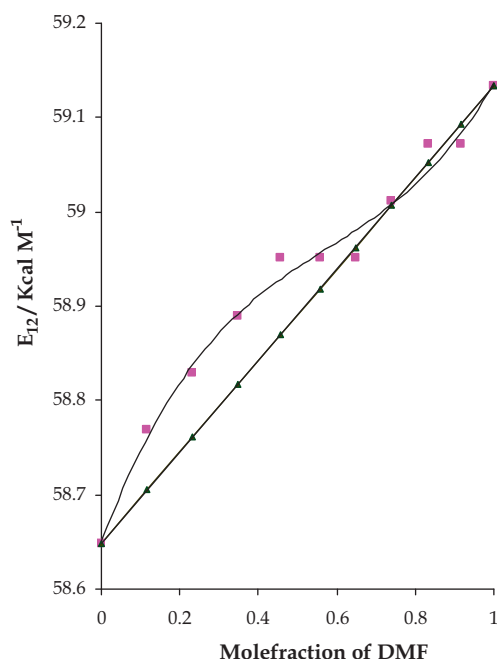
**Fig. 3.** Plot of $E_{12}$ of DHMAD in CCl$_4$ + DMF mixture as a function of mole fraction of DMF in the ground state.

As the polarity of the solvent increases (DMF) absorption maxima of the charge transfer band of DHMAD are blue shifted in spite of the fact that the band is due to a $\pi\pi^*$ transition. In this case intra molecular hydrogen bond and hence quasiaromatic ring formation is responsible for the observed blue shift. The blue shift of the absorption spectra of DHMAD in DMF can also be explained only by assuming the delocalization of the excited state, owing to reduction in quasiaromaticity of the chelate rings formed by intra molecular hydrogen bonds, due to association of the DMF via the quinonoid oxygen by hydrogen bonding interaction [19].

The observed blue shift indicates that the ground electronic state of the anthraquinone is stabilized by dipole–dipole interaction in DMF. It may also be due to the change of solute–solvent intermolecular repulsion, in the first solvate shell, at excited state.

The variation of the transition energy ($E_{12}$) of the long wavelength absorption band (around 487 nm) versus the bulk mole fraction of ($x_2$) DMF is depicted in Fig. 3 shows that, the value of $E_{12}$ of the DHMAD increases slowly as DMF is added to CCl$_4$. The slight deviation from the ideal curve shows that DHMAD exhibits a preferential solvation in all the composition of binary mixture. The non-linearity of the plot indicates that together with preferential solvation of the DHMAD by one of the component solvents, packing effects vary in molecular properties of the DHMAD [20]. In fact the plot of $E_{12}$ is diphasic indicating that the DHMAD is preferentially solvated by DMF in the entire region except at $X_{DMF}$ = 0.65 and 0.92 where it is preferentially solvated by CCl$_4$.

The preferential solvation parameters of DHMAD in binary mixture containing DMF and CCl$_4$ are given in Table 1. The solvation data shows that the mole fraction of DMF in the solvation microsphere ($x_2^L$) is greater than in the bulk solvent ($x_2$) except at $X_{DMF}$ = 0.65 and 0.92. The variation of $\delta_{s2}$ (an index of preferential solvation with respect to DMF) against the solvent composition shows that $\delta_{s2}$ tends to zero in the limit $x_1$ or $x_2$ equals zero, and passes through a maximum which corresponds to a solvent composition rich in the CCl$_4$. Furthermore $\delta_{s2}$ values are negative at $X_{DMF}$ = 0.65 and 0.92. It also shows that the DHMAD is

**Table 1**
Preferential solvation data for DHMAD in binary solvent system CCl$_4$ + DMF mixture in the ground state.

| $x_2$ | $x_2^L$ | $\delta_{s2}$ | $f_2/f_1$ ($K_{ps}$) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.12 | 0.25 | 0.13 | 2.48 |
| 0.23 | 0.37 | 0.14 | 1.95 |
| 0.35 | 0.50 | 0.15 | 1.86 |
| 0.46 | 0.62 | 0.16 | 1.98 |
| 0.56 | 0.62 | 0.06 | 1.32 |
| 0.65 | 0.62 | −0.03 | 0.89 |
| 0.74 | 0.75 | 0.01 | 1.04 |
| 0.83 | 0.87 | 0.04 | 1.41 |
| 0.92 | 0.87 | −0.05 | 0.63 |
| 1 | 1 | 0 | 0 |

preferentially solvated by DMF in the entire region except at $X_{DMF}$ = 0.65 and 0.92 where it is preferentially solvated by CCl$_4$.

This can be explained by strong interactions between the solvent and DHMAD. These interactions may be hydrogen bonding and/or non-specific dipolar interactions. This may be due to the competition between solute–solvent and solvent–solvent interactions.

The preference of DMF near DHMAD and its competition to CCl$_4$ in the solvation shell around DHMAD is probably due to dielectric enrichment, owing to the fact that DMF has a higher electric permittivity than CCl$_4$.

In pure CCl$_4$, there is dipole-induced dipole interaction exists between DHMAD and CCl$_4$. When DMF is added into the solution of DHMAD in CCl$_4$, intermolecular hydrogen bond is immediately formed between the hydroxyl group of DHMAD and carbonyl group of DMF, since DMF is a very good hydrogen bond acceptor. This leads to the preference of DHMAD by DMF than CCl$_4$.

### 3.3. Preferential salvation of DHMAD in the excited state

The fluorescence emission spectra of DHMAD in CCl$_4$ + DMF binary system are depicted in Fig. 4. The fluorescence emission spectra show a structured band in the wavelength range of 490–690 nm. The observed spectra reveal that as the mole fraction of DMF increases the wavelength of the band around 540 nm increases, i.e. the emission maximum shifts to longer wavelength
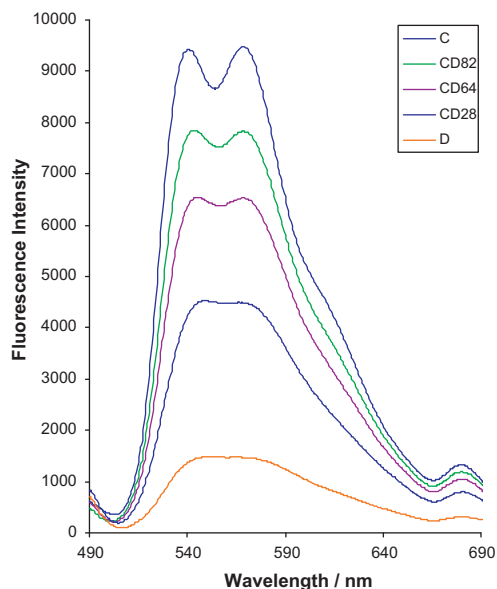


**Fig. 4.** Fluorescence emission spectra of DHMAD in CCl$_4$ + DMF mixture (C: CCl$_4$; D: DMF; CD28: volume of CCl$_4$ is 2 ml and DMF is 8 ml).
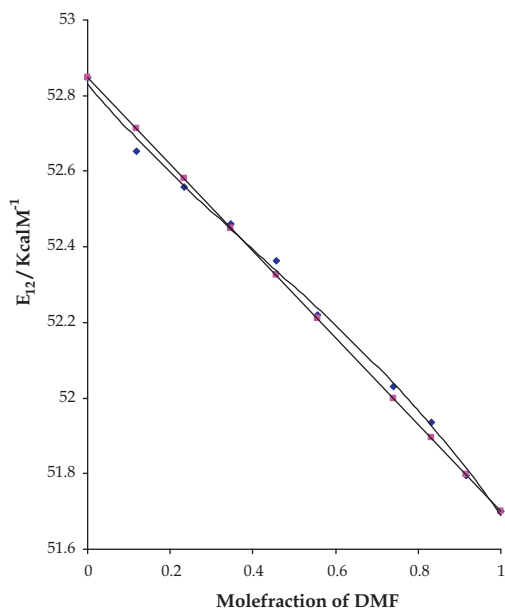
**Fig. 5.** Plot of $E_{12}$ of DHMAD in CCl$_4$ + DMF mixture as a function of mole fraction of DMF in the excited state.

**Table 2**
Preferential solvation data for DHMAD in binary solvent system CCl$_4$ + DMF mixture in the excited state.

| $x_2$ | $x_2^L$ | $\delta_{s2}$ | $f_2/f_1$ ($K_{ps}$) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.12 | 0.17 | 0.05 | 1.54 |
| 0.23 | 0.30 | 0.07 | 1.38 |
| 0.35 | 0.38 | 0.03 | 1.15 |
| 0.46 | 0.42 | −0.04 | 0.87 |
| 0.56 | 0.51 | −0.05 | 0.82 |
| 0.65 | 0.63 | −0.12 | 0.93 |
| 0.74 | 0.63 | −0.11 | 0.60 |
| 0.83 | 0.8 | −0.03 | 0.79 |
| 0.92 | 0.84 | −0.08 | 0.47 |
| 1 | 1 | 0 | 0 |

in DMF with respect to CCl$_4$. This red shift is an indicative of the charge transfer nature of the excited state.

The emission shifts can be explained by the increased stabilization of the quasiaromatic rings in the excited state. For this quinone, like the ground state, the lowest excited states also have the charge transfer character and the negative charge is mostly localized on the quinonoid oxygens. Hence DHMAD may exhibit strong intermolecular hydrogen bonding interaction in the excited state, since the excited states have a strong intramolecular charge transfer nature. The large electron density on the carbonyl oxygen of anthraquinone in the excited state strongly promotes inter molecular hydrogen bonding interaction with a polar solvents. This might have a distinctive influence on the photo physical behaviour of the quinone.

Therefore following excitation, the solvent cage undergoes a relaxation, i.e. reorganization, leading to a relaxed state of minimum free energy. The higher the polarity of the solvent, the lower the energy of the relaxed state and the larger the red shift of the emission spectrum.

Even though it shows lower dipole moment and hence geometrical arrangement in the excited state, the loss of mirror image relationship might be due to the coupling between vibrational levels. The spacing between the spectral lines is 890 cm$^{-1}$ in CCl$_4$, and the spacing decreases as the mole fraction of DMF increases. Out-of-plane deformation mode of anthraquinone ring is responsible for the observed vibrational feature in fluorescence spectra [17]. This vibrational mode is responsible for the absence of mirror image relationship even though it does not show any excited state proton transfer reactions.

The variation of the transition energy ($E_{12}$) of the first emission band (around 540 nm) versus the bulk mole fraction of ($x_2$) DMF is depicted in Fig. 5 shows that, the value of $E_{12}$ of the DHMAD decreases slowly as DMF is added to CCl$_4$. The slight deviation from the ideal curve shows that DHMAD exhibits a preferential solvation in all the composition of binary mixture. The non-linearity of the plot indicates that together with preferential solvation of the DHMAD by one of the component solvents, packing effects vary in molecular properties of the DHMAD [20]. In fact the plot of $E_{12}$ is diphasic indicating that the DHMAD is preferentially solvated by

DMF in CCl$_4$ rich region ($X_{DMF} < 0.46$) and is preferentially solvated by CCl$_4$ in DMF rich region ($X_{DMF} > 0.46$).

The preferential solvation parameters of DHMAD in binary mixture containing DMF and CCl$_4$ are given in Table 2. The solvation data shows that the mole fraction of DMF in the solvation microsphere ($x_2^L$) is greater than in the bulk solvent ($x_2$) in the region $X_{DMF} < 0.46$ and is less than bulk solvent in the region $X_{DMF} > 0.46$. $\delta_{s2}$ values are positive in the region $X_{DMF} < 0.46$ and is negative in the region $X_{DMF} > 0.46$. It also shows that the DHMAD is preferentially solvated by DMF in CCl$_4$ rich region ($X_{DMF} < 0.46$) and is preferentially solvated by CCl$_4$ in DMF rich region ($X_{DMF} > 0.46$).

The preference of DMF near DHMAD and its competition to CCl$_4$ in the solvation shell around DHMAD is probably due to dielectric enrichment, owing to the fact that DMF has a higher electric permittivity than CCl$_4$. In pure CCl$_4$, there is dipole-induced dipole interaction exists between DHMAD and CCl$_4$. When DMF is added into the solution of DHMAD in CCl$_4$, intermolecular hydrogen bond is immediately formed between the hydroxyl group of DHMAD and carbonyl group of DMF, since DMF is a very good hydrogen bond acceptor. This leads to the preference of DHMAD by DMF than CCl$_4$ in CCl$_4$ rich region.

## 4. Conclusion

Optical absorption and fluorescence emission techniques have been employed to study the preferential solvation of DHMAD. The solvation data shows that the mole fraction of DMF in the solvation microsphere ($x_2^L$) is greater than in the bulk solvent ($x_2$) in CCl$_4$ + DMF binary mixture which shows that, DHMAD is preferentially solvated DMF in the ground state. In the excited state $\delta_{s2}$ values are positive in the region $X_{DMF} < 0.46$ and is negative in the region $X_{DMF} > 0.46$. This observation indicating that in the excited state the DHMAD is preferentially solvated by DMF in CCl$_4$ rich region ($X_{DMF} < 0.46$) and is preferentially solvated by CCl$_4$ in DMF rich region ($X_{DMF} > 0.46$).

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