

Preferential Solvation of 1,4-Dimethoxy-2,3-Dimethyl-9,10-Anthraquinone-A Spectrophotometric and Fluorometric Study

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Abstract Electronic absorption and fluorescence emission spectra of DMDMAQ (1,4-dimethoxy-2,3-dimethyl-9,10-anthraquinone) have been studied as a function of solvent composition in some binary mixtures and in different neat solvents. The binary mixtures consist CCl_4 (Carbon tetrachloride)-DMSO (Dimethylsulfoxide), EtOH (Ethanol)-DMSO, and CCl_4 -EtOH combination of single solvents. The wavelength maxima of the absorption band for DMDMAQ are quite solvent sensitive in aprotic solvents. But, in protic solvent, there is no marked shift in absorption and emission maximum which shows the absence of specific interaction. Excited state shows increasing shift with increasing solvent polarity compared to ground state. The ratio of dipole moment in the excited state to that in the ground state was calculated. Different criteria were considered to analyse preferential solvation characteristics in different binary mixtures, viz., local mole fraction (X_2^L), solvation index (δ_{S2}) and exchange constant (K_{12}).

Keywords 1,4-dimethoxy-2,3-dimethyl-9,10-anthraquinone · Solvatochromism · Preferential solvation · Optical absorption · Fluorescence emission · Specific interaction · Solute-solvent interaction · Solvent-solvent interaction

Introduction

9,10-anthraquinones are the largest group of naturally occurring quinones and industrially the most important. Beside they are frequently used as selective and sensitive reagents for the complex formation with a number of metal ions [1, 2]. Anthraquinones have a wide variety of industrial applications, especially in dyeing textiles [3–6]. In addition, some synthetic derivatives of anthraquinones as well as their naturally occurring derivatives have been recently used for medical purposes [7–12]. When electronic spectra are measured in solvents of different polarity and hydrogen bond donor/acceptor ability, it is found that the position, intensity and shape of absorptions bands are usually affected by the solvents. These changes are usually referred as solvatochromism [13]. It is due to the solute–solvent intermolecular forces. These forces can be non-specific electrostatic interactions [14–19] and/or specific interactions such as hydrogen bonding, electron donor–acceptor complexation [20–22]. The shift in spectral maxima depends mainly on the chromophore in the solvatochromic indicator probe molecule and the nature of the transition involved.

Solvent effects on quinone molecules are usually studied to obtain the photophysical properties, especially to understand the role of intra and intermolecular forces [23–27]. Another important approach is the study of solute–solvent interactions in binary mixtures. This approach is based on the fact that when one solvent component in binary mixture

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strongly interacts with a solute either by specific or non specific interaction compared to another component of the solvent in the mixture. This result, the solvation shell is enriched by the strongly interacting solvent component. So the enriched solvent composition is beyond the level of proportion as in the bulk composition [13, 28]. Preferential solvation of solute in binary mixture is important to elucidate nature of solute–solvent, solvent–solvent interaction as well as the molecular reasons that lead to the solute for the selective solvation of one component over another, hence altering the composition. Among different derivatives of anthraquinone, the hydroxy and amino substituents have been investigated [23, 29–31]. Photophysical properties of 1,4-diamino-9,10-anthraquinone and 1,4-dihydroxy-9,10-anthraquinone have been investigated in different solvents of varying polarities [23, 32–36]. The goal of this work was to monitor the effect of solute–solvent and solvent–solvent interactions on the preferential solvation characteristics. For this purpose, the optical absorption fluorescence emission spectral data of DMDMAQ in various single solvents and binary mixtures have been used as an indicator solute.

Experimental

Materials

Solvents such as CCl_4 , CH_2Cl_2 , ACN, DMF, EtOH and DMSO from Merck Research Laboratory with 99.9% purity were used without further purification. The 1,4-dimethoxy-2,3-dimethyl-9,10-anthraquinone was prepared in two steps from 2,3-dimethyl-1,4-hydroquinone and phthalic anhydride. According to Cava procedure [37], the first step was the condensation of phthalic anhydride and 2,3-dimethyl-1,4-hydroquinone in presence of aluminium chloride, which furnishes the 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone in 80% yield. The second step consists in a methylation of the latter compound with dimethylsulfate and potassium carbonate in dry acetone to form the 1,4-dimethoxy-2,3-dimethyl-9,10-anthraquinone in 86% yield [38].

Procedure

The concentration of DMDMAQ in single solvents was 0.1 mM. Binary mixtures were prepared by mixing appropriate volumes of each homo solution in the ratio 1:5, 2:4, 3:3, 4:2 and 5:1.

Measurements

Absorbance measurements and emission measurements were carried out with a UV-VIS JASCO spectrophotometer

and JASCO spectrofluorimeter respectively. All measurements were performed at room temperature.

Results and discussion

Optical absorption and fluorescence spectral studies in single solvents

The absorption spectrum of unsubstituted anthraquinone shows absorption maxima at 252, 272 and 326 nm. The anthraquinone can be considered as a carbonyl substitution in 9,10 position of anthracene. So, one can compare absorption spectrum of anthraquinone with anthracene. The observed peak at 252 nm was assigned to benzenoid $\pi-\pi^*$ transition and other two peaks were assigned to quinonoid $\pi-\pi^*$ transitions [32]. The absorption bands of substituted anthraquinone when compared with the unsubstituted anthraquinone, distinctly shift to shorter or longer wavelengths according to the substituting group. When electron donating group (OH, NH_2 , etc) is substituted in anthraquinone, there will be an absorption band longer than 350 nm. Moreover the increase of electron donating ability of the substituents leads the shift to bathochromic region. Yoshida et al. investigated the solvent effect on the longest wavelength absorption band of $\pi-\pi^*$ in various electron donating substituted anthraquinones [39]. Molecular structure of DMDMAQ is shown in Fig. 1. Optical absorption spectra of DMDMAQ show absorption peak at 360 nm. The representative example spectrum in single solvents is given in Fig. 2. It confirms the presence of electron donating groups into anthraquinone moiety. Moreover this observed longer wavelength maxima is less than that of

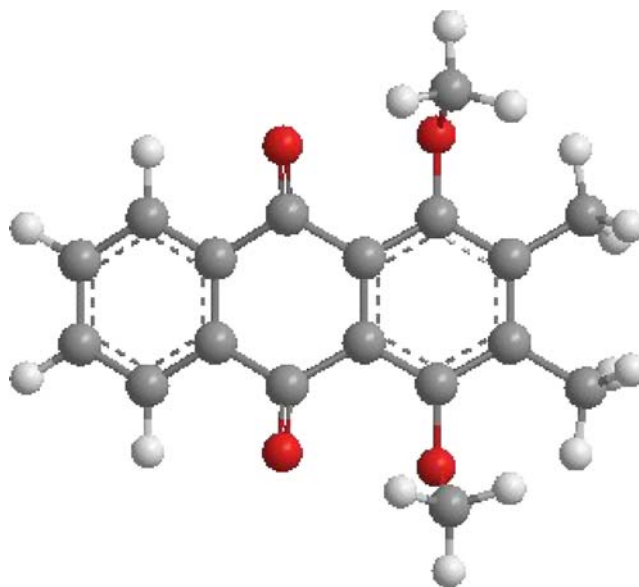


Fig. 1 Molecular structure of DMDMAQ

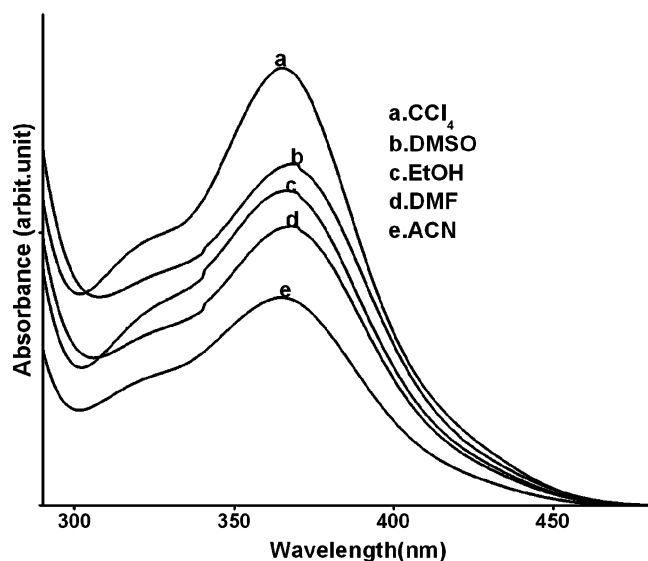


Fig. 2 Optical absorption spectra of DMDMAQ in single solvents

recently investigated 1,4-dihydroxy-2,3-dimethyl anthraquinone [40]. Because the electron donating ability of substituted methoxy group in the present molecule is less than that of hydroxyl group. The absorption maximum shifts to bathochromic region while solute environment is changing from non polar to polar solvents. Hydrogen bonding is an interaction with potentially strong effect on the behaviour of many systems. The introduction of methoxy groups cannot form intramolecular hydrogen bonding with neighbouring oxygen atom in the quinone ring [41]. The proton accepting ability of methoxy group is already reported [23, 42, 43]. Even though the polar protic solvent has hydrogen bond donor and acceptor nature, there is no influence by this solvent in the present investigation.

Fluorescence emission spectrum of DMDMAQ in single solvents is given in Fig. 3. It appears that the position of band maxima undergoes a bathochromic shift with increasing solvent polarity. The emission spectrum is structured in all solvents. This suggests that the splitting of the electronic states caused by dimethoxy substitution to quinone moiety is equally coupled to the vibrational modes contributing to the vibrational structure [44]. The magnitudes of Stokes shifts ($\nu_a - \nu_f$ (cm^{-1})) for DMDMAQ (Table 1) indicate that the geometry of excited state is not significantly different from that of ground state.

Solvatochromism

When a solute is dissolved in a solvent, the solvent exerts a definite influence on the solute, depending on nature of the solvent, that is the dielectric constant and refractive index, which is reflected in as a shift in absorption and fluorescence bands [13, 45]. The approach is based on the assumption that the solvent is a homogenous continuum

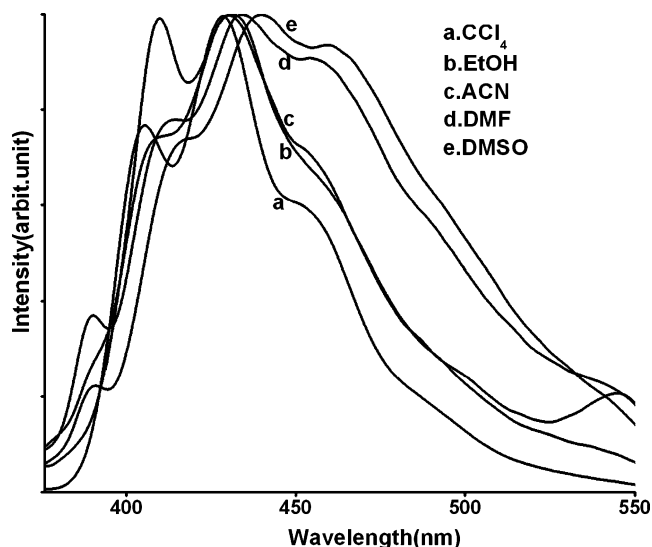


Fig. 3 Fluorescence emission spectra of DMDMAQ in single solvents

and that the solute resides with a permanent dipole in its own reaction field. The loss of energy between absorption and reemission of light in solvent, or Stokes shift is a simple approach of the result of general and specific solvent effects. Fluorescence band maxima are largely red shifted compared to absorption band under same condition. This indicating an increase in dipole moment of excited state compared to ground state. The change in the dipole moment ratio can be estimated using the analysis of absorption and fluorescence spectra from the following equations.

$$\nu_a - \nu_f = m_1 f(\epsilon, n) + const \quad (1)$$

$$\nu_a + \nu_f = -m_2 [f(\epsilon, n) + 2g(n)] + const \quad (2)$$

where

$$f(\epsilon, n) = \left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right] \left[\frac{2n^2+1}{n^2+2} \right] \quad (3)$$

Table 1 Solvent parameters and solvatochromic parameters of DMDMAQ deduced from optical absorption and emission spectral data

Solvents	$f(\epsilon, n)$	$f(\epsilon, n) + 2g(n)$	$(\nu_a - \nu_f)$ cm^{-1}	$(\nu_a + \nu_f)$ cm^{-1}
CCl_4	0.019	0.650	4,032	50,761
CH_2Cl_2	0.595	1.171	3,920	50,649
ACN	0.860	1.330	4,066	50,578
DMF	0.840	1.423	4,132	50,215
DMSO	0.842	1.488	4,109	49,864
EtOH	0.812	1.301	4,136	50,433

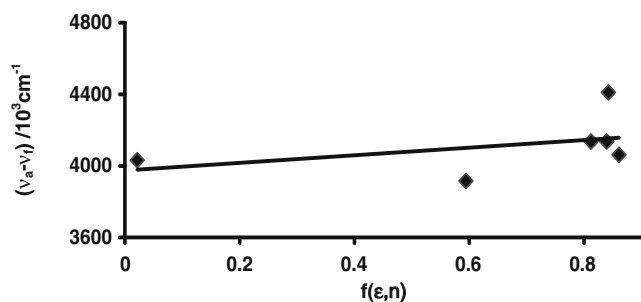


Fig. 4 Plot of $(\nu_a - \nu_f)$ versus the solvent polarity function $f(\epsilon, n)$

$$g(n) = \frac{3}{2} \left[\frac{(n^4 - 1)}{(n^2 + 2)^2} \right] \quad (4)$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (5)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (6)$$

In the above equations $f(\epsilon, n)$ indicates the polarity parameter of the solvent and orientation polarizability. n and ϵ are the refractive index and dielectric constant of the solvents chosen. μ_e and μ_g represent the dipole moments of DMDMAQ in excited and ground states respectively. h is the Planck's constant, c is the velocity of light, and a is the Onsager cavity radius. The slope m_1 , between $f(\epsilon, n)$ and $\nu_a - \nu_f(\text{cm}^{-1})$ and the slope m_2 between $f(\epsilon, n) + 2g(n)$ and $\nu_a + \nu_f(\text{cm}^{-1})$ are obtained from Figs. 4 and 5. The above photo physical parameters are gathered in Table 1. From the slope values m_1 and m_2 , the ratio of excited state to ground state dipole moment of solute molecule was calculated using the following eqn.

$$\frac{\mu_e}{\mu_g} = \left| \frac{m_1 + m_2}{m_2 - m_1} \right| \quad (7)$$

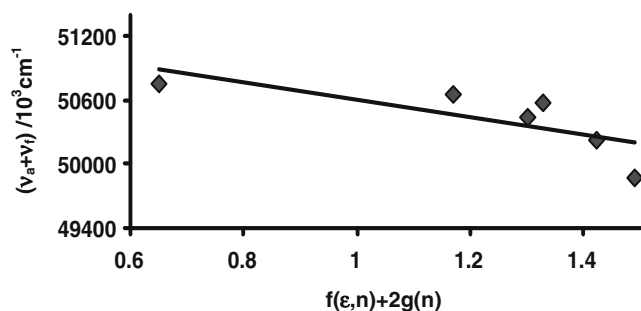


Fig. 5 Plot of $(\nu_a + \nu_f)$ versus the solvent polarity function $f(\epsilon, n) + 2g(n)$

The ratio of the dipole moment in excited state to that in ground state for the present case is found to be 1.70 [46, 47].

Studies in binary solvent mixtures

The shifts in the ν_{12} maximum values of the solvatochromic indicator observed in binary mixtures. The non-linearity of the ν_{12} versus mole fractions plots in binary mixtures arises due to preferential solvation of the solute, which is common, and because it modifies the neighborhood of the solute. In order to quantify the preferential solvation characteristic of the solute, different preferential solvation parameters, local mole fraction (X_2^L), excess function ($\delta_{s,2}$), preferential solvation constant (K_{12}) were calculated.

The binary solvent mixtures are considered to be an ideal dielectric and then the preferential solvation is

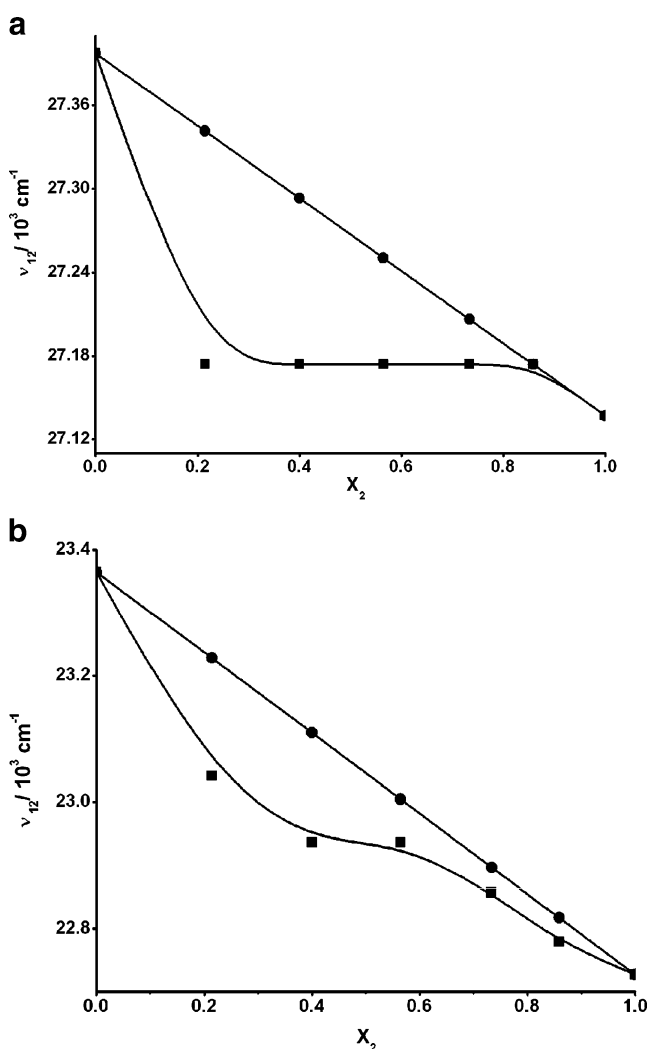


Fig. 6 Plot of ν_{12} vs. X_2 (mole fraction of DMSO) for **a** ground state, **b** excited state of DMDMAQ in CCl_4 -DMSO mixture (—●— ideal mixture), (—■— Experimental data)

correlated with spectral measurements using the following equation

$$P_{\text{mix}} = P_1 \cdot X_1 + P_2 \cdot X_2 \tag{8}$$

in which P_1 and P_2 are spectral properties such as peak position, peak intensity, and kinetic rate constant of solute in neat solvents 1 and 2 while P is the same property in binary mixtures of the solute measured. X_1 and X_2 is the mole fraction of the solvents [33, 48, 49]. The mole fraction of the component solvents in the cybotatic region can be calculated using the equation (9) based on the assumption that the solvents in the non-ideal binary mixtures distributed into two phases, the bulk solvent and the solvation shell of the solute [19].

$$X_2^L = \frac{(\nu_{12} - \nu_1)}{(\nu_2 - \nu_1)} = 1 - X_1^L \tag{9}$$

where ν_1 , ν_2 and ν_{12} are the values of maximum absorption or emission wavenumber (in cm^{-1}) of DMDMAQ in the solvent 1, solvent 2 and the mixture of solvents respectively.

The excess function (index of preferential solvation (δ_{s2})) may be taken as a measure of preferential solvation with respect to the co-solvent and can be defined as the difference between X_2^L and X_2 .

$$\delta_{s2} = X_2^L - X_2 \tag{10}$$

A more quantitative way to explain the preferential solvation of the compound in binary mixtures can be made by employing the preferential solvation constant K_{12} (ex-

change constant) using the model of Frankel et al. [50] according to the equation (11)

$$K_{12} = \frac{(X_1^L/X_2^L)}{(X_1/X_2)} \tag{11}$$

where, X_1^L and X_2^L represent mole fraction of solvents 1 and 2 in the cybotatic region. $K_{12} < 1$ indicates a preference for solvent 1 over solvent 2, in contrast $K_{12} > 1$ signifies the opposite trend [51].

CCl₄-DMSO mixture

The wavenumbers for DMDMAQ in this mixture are plotted as a function of X_2 , the bulk mole fraction of the DMSO (Fig. 6). As can be observed, the experimental curve deviate from linearity, which represent the situation where the local and bulk mole fractions are different. It is further indication of the more interaction of solute with component of CCl_4 -DMSO mixture. The curvature of the plot indicates that the solute is preferentially solvated by DMSO. Table 2 shows calculated values of preferential solvation parameters for the DMDMAQ in binary mixtures. Positive values of excess function in ground and excited states give further evidence. Moreover $K_{12} > 1$ indicates a preference of DMSO over CCl_4 . This is due to the solute prefer more polar component to solve.

EtOH-DMSO mixture

The variation of ν_{12} in the case of hydrogen bond donor and hydrogen bond acceptor mixture as a function of

Table 2 Preferential solvation data of DMDMAQ in binary mixtures

	X_2	X_2^L		δ_{s2}		f_2/f_1 (or) K_{12}	
		a	b	a	b	a	b
CCl₄-DMSO(X_2)							
	0						
	0.214	0.858	0.506	0.643	0.292	22.189	3.766
	0.400	0.858	0.672	0.458	0.272	9.075	3.080
	0.564	0.858	0.672	0.293	0.108	4.669	1.585
	0.734	0.858	0.796	0.124	0.061	2.192	1.414
	0.858	0.858	0.918	0	0.060	0.998	1.863
	1						
EtOH-DMSO(X_2)							
	0						
	0.143	0.501	0.715	0.358	0.572	6.013	15.061
	0.295	0.751	0.504	0.455	0.208	7.175	2.419
	0.452	0.501	0.253	0.048	-0.199	1.214	0.409
	0.621	0.251	0.303	-0.370	-0.317	0.204	0.265
	0.797	0.751	0.126	-0.046	-0.670	0.768	0.037
	1						

a: Preferential solvation parameters obtained from absorbance data.

b: Preferential solvation parameters obtained from fluorescence data.

X_2 : Bulk mole fraction

DMSO mole fraction is shown in Fig. 7. It is interesting to observe the dual behaviour of this mixture. The addition of DMSO ($X_2 < 0.5$) with EtOH causes decrease in ν_{12} . This positive deviation suggests that in this region probe molecules prefer to solve in DMSO. Further increase in concentration of DMSO the negative deviation is observed. So, one can conclude that the EtOH is preferred by the solute to solve. The present case either in the ground state or in the excited state specific association is not dominated by the hydrogen bonding between the solute and hydrogen donating solvent. This means that the protic solvent does not replace preferentially the aprotic solvent molecules in the solvation shell of the dye. So the observed negative deviation indicates decrease in mole fraction of DMSO in the solvation shell. But in this region there is a possibility of more DMSO molecules compared to EtOH ($X_2 > 0.5$). It

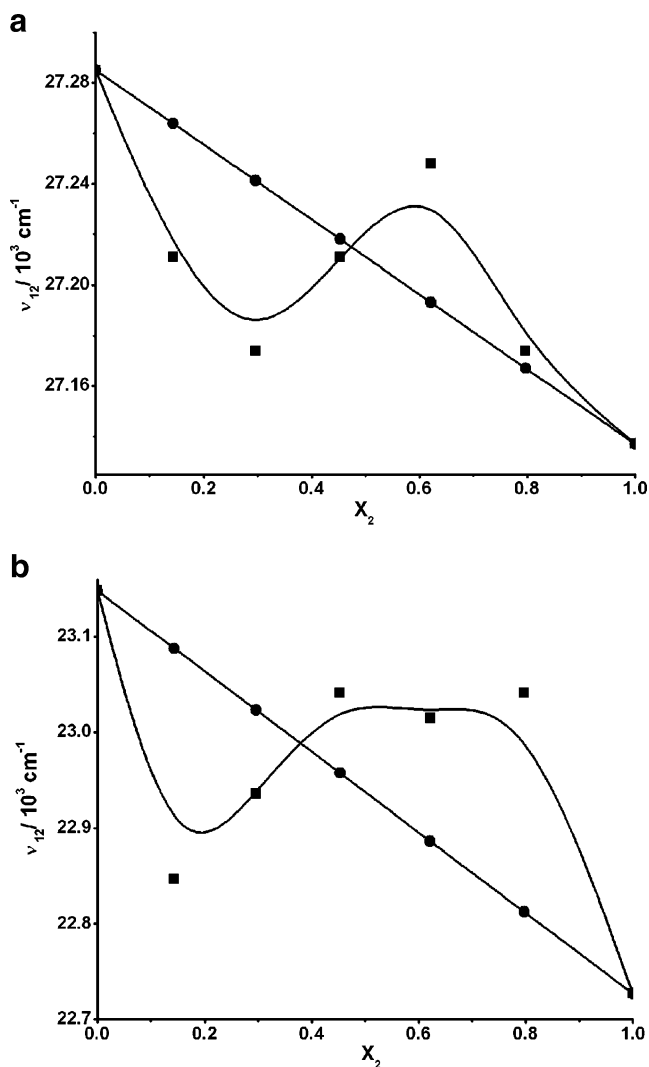


Fig. 7 Plot of ν_{12} vs. X_2 (mole fraction of DMSO) for **a** ground state, **b** excited state of DMDMAQ in EtOH-DMSO mixture (—●— ideal mixture), (—■— Experimental data)

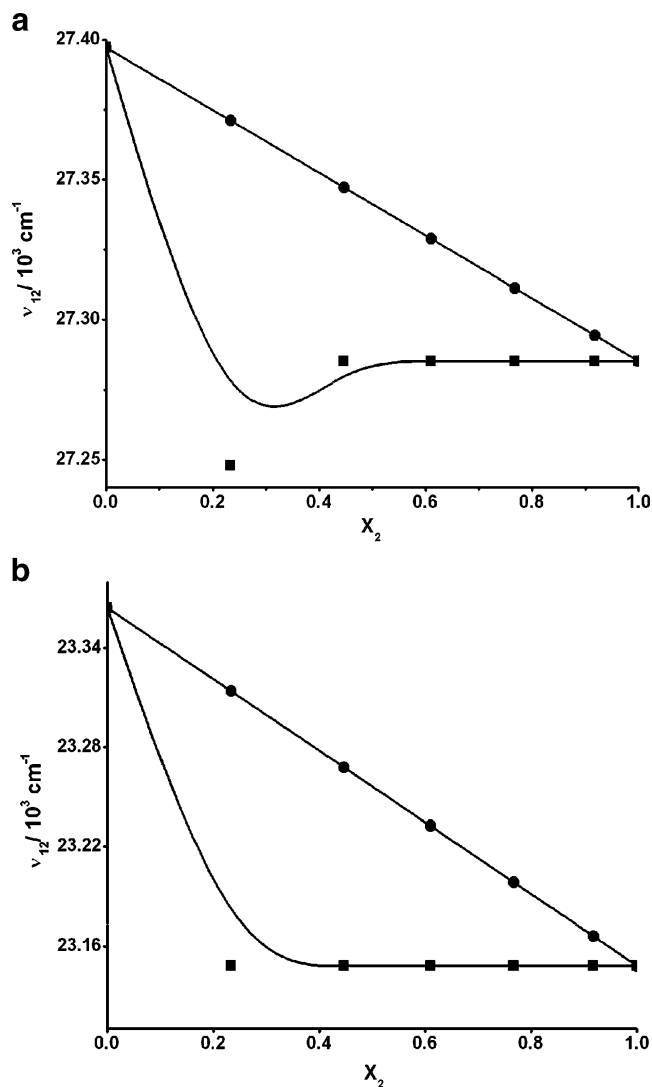


Fig. 8 Plot of ν_{12} vs. X_2 (mole fraction of EtOH) for **a** ground state, **b** excited state of DMDMAQ in CCl_4 -EtOH mixture (—●— ideal mixture), (—■— Experimental data)

confirms that there may be an association between DMSO-EtOH mixture. This solvent-solvent type interaction may possible by specific interaction. Because EtOH, DMSO has an ability to donate and accept a hydrogen respectively to form O-H...O type hydrogen bonding interaction[52].

CCl_4 -EtOH mixture

Figure 8 shows the plots obtained for ν_{12} of DMDMAQ as a function of EtOH concentration. In order to obtain more insight about the interaction between quinone and alcohol, the spectral behaviour was studied in CCl_4 -EtOH mixture. CCl_4 is considered quite an inert solvent. However in this solvent mixture self association between alcohol molecules usually occur [19]. In dynamic equilibrium of pure liquid alcohols, the breaking and formation of hydrogen

bonds are occurring at higher rate. It is important to point out that even pure EtOH has a free OH (that is free from intermolecular hydrogen bonding among themselves-dimer) to form intermolecular hydrogen bond with other component of the solvent or solute. So both solute–solvent and solvent–solvent interactions play important roles in determining the preferential solvation characteristics [53–55]. The deviation from the ideal curve is obtained. The addition of EtOH with CCl₄ at CCl₄ rich region leads to a sharp decrease in ν_{12} value in both ground and excited states. Further addition of EtOH does not alter the value of ν_{12} . This saturation in the curve confirms the absence of specific solute–solvent interaction and prevents any calculation of the preferential solvation parameters for DMDMAQ [30].

Conclusion

In this paper the spectral properties of DMDMAQ have been investigated in different solvent and solvent mixtures. The excited state is more influenced by the solvent polarity compared to the ground state. There is no specific solute–solvent interaction influence of shift in band maxima in the case of protic solvents. Ultimately, the dielectric enrichment is the driving force for the non-linearity effects in binary mixtures. Dipole moment ratio was deduced from the solvatochromic shift. It was found that the probe molecules have a greater dipole moment in excited state compared to ground state. Preferential solvation parameters are calculated from the experimental data and the preferential solvation characteristics were studied.

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