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ORIGINAL PAPER

Spectral Investigations of Solvatochromism and Preferential Solvation on 1,4-Dihydroxy-2,3-Dimethyl-9,10-Anthraquinone

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Abstract Solvatochromic and preferential solvation of 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone (DHDMAQ) have been investigated using optical absorption and fluorescence emission techniques. Optical absorption spectra of DHDMAQ in different solvents show the intra molecular charge transfer band in the region 400–550nm. The observed blue shift with solvent polarity indicates the delocalisation of the excited state, owing to reduction in quasiaromaticity of the chelate rings formed by intra molecular hydrogen bonds, due to electrostatic or hydrogen bonding interaction. This is also confirmed by the observed low oscillator strength and the transition dipole moment. The observed quantum yield of DHDMAQ in different solvents is due to the inter molecular hydrogen bond in the excited state in addition to the intra molecular hydrogen bond. It also reveals from the low oscillator strength, which indicates that the radiative decay is low. Excited state dipole moment of DHDMAQ is calculated by solvatochromic data and it shows a lower value than ground state dipole moment. The preferential solvation parameter shows that in dimethyl formamide (DMF) + ethanol mixture, the DHDMAQ is preferentially solvated by ethanol in DMF rich region and by DMF in ethanol rich region. In the case of DMF + dichloromethane mixture DHDMAQ is preferentially solvated by DMF.

Keywords 1,4-Dihydroxy-2,3-dimethyl-9,10-anthraquinone · Optical absorption · Fluorescence emission · Preferential solvation · Solvent effect · Binary mixture

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. Solute–solvent interactions can change the geometry, the electronic structure and the dipole moment of a solute. This could be due to both intra and inter molecular hydrogen bonding which shows a profound effect on the geometric, electronic, vibrational and photodynamic radiationless transition properties of aromatic molecules in their excited states [1, 2].

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 [3]. The interactions can be classified into: (1) non-specific solute–solvent interaction caused by polarity–polarizability effects and (2) specific solute–solvent interaction such as hydrogen bonding or electron

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donor acceptor interactions. In order to analyze the interactions, one of the most successful approaches is the solvatochromic comparison method of Kamlet et al. [4]. In this method empirical parameters are used to quantify specific interactions and to separate them from non-specific interactions. 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 [5]. 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 [6].

Widely used methods to study solute–solvent interactions are optical absorption and fluorescence emission spectral studies of solvatochromic dyes as solvent polarity indicators. The shifts of the absorption/fluorescence maxima are due to solute–solvent interactions [7]. It is also possible to study solvent–solvent interactions in the binary mixtures.

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. Hydroxy anthraquinone in certain medicinal plants such as *Rubia tinctorium* L. is a genotoxic and rodent colon carcinogen [8–10]. Hydroxy anthraquinone derivatives have been isolated from the roots of *Prismatomeris tetrandra* and *Rubia Cordiofolia* L.[11, 12]. Hydroxy anthraquinone glycosides are concentrated in leaves and flowers of *Cassia fistula* Linn [13]. It also found in leaves and bark of *Cassia podocarpa*. It enhances its commercialization as laxative due to its antimicrobial effect [14].

The biological importance of this molecule has prompted the study of its photo physical properties and the influence of solvents on this derivative. The electronic distribution of electronically excited molecules was also studied using the measurement of solvatochromic shifts of absorption and fluorescence emission.

Preferential salvation (PS) of some organic dyes in different binary solvent systems have been studied [15–17]. Recently our group has investigated the PS of 1,4-dimethylamino anthraquinone and 1,2-dihydroxy anthraquinone in different binary mixture [18, 19].

In the present study, optical absorption and fluorescence emission spectroscopic techniques have been employed to investigate solvatochromism and preferential solvation of 1,4-dihydroxy-2,3-dimethyl,9,10-anthraquinone (DHDMAQ).

Experimental

Spectral grade CCl_4, CH_2Cl_2, acetonitrile, ethanol, methanol, propan-2-ol and DMF were obtained from SISCO laboratory and were used without further purification.

1,4-Dihydroxy-2,3-dimethyl-9,10-anthraquinone was prepared using the following procedure. A mixture of anhydrous aluminium chloride (5.6g; 42.0mM) and sodium chloride (1g; 17.1mM) was melted in an Erlenmeyer flask at 160°C. The melt was allowed to cool to 140°C and an intimate mixture of phthalic anhydride (0.7g; 4.7mM) and 2,3-dimethylhydroquinone (0.6g; 4.4mM) was added. The reaction mixture was heated rapidly to 190°C and kept at that temperature for 2min. The resulting red melt was cooled, added to ice and hydrochloric acid (5ml, 37%), and heated on a steam bath for 2h. The resulting red precipitate was filtered, dried, and crystallized from acetic acid to afford 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone as red needles in 80% yield (1.07g) [20].

All the mass measurements were performed on an electronic balance (Shimadzu) accurate to four decimal places. Solvent effect on DHDMAQ has been performed for the above mentioned solvents using optical absorption and fluorescence measurements keeping the concentration of DHDMAQ as 0.02mM. Optical absorption spectra were measured for varying mole fraction of CH_2Cl_2, C_2H_5OH and DMF, keeping the total volume (10ml) of the mixture (CH_2Cl_2 + DMF and DMF+C_2H_5OH) and the concentration of the DHDMAQ (0.02mM) constant.

Parker's method was employed to determine the relative fluorescence quantum yield (ϕ_{rel}) [21] in which 2,3-dichloromethyl-1,4-anthraquinone in dichloromethane was used as fluorescence standard ($\phi = 4.87 \times 10^{-3}$) [18].

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

Results and discussion

Pure solvent effect

Optical absorption spectral studies

The polarity and hydrogen bonding properties of several solvents used in this study represented by the normalized Reichardt polarity scale E_T^N and Kamlet–Taft α, β, and π^* parameters, are summarized in Table 1. The solvents can be separated into two groups. The first group comprises non-protic dipolar solvents, which are very good hydrogen bond acceptors (high β values) and poor hydrogen bond donor (low α values). The other group embraces protic solvents,

Table 1 Properties of pure solvents [24]

Solvent	π^*	α	β	ε	n	E_T^N
Carbon tetrachloride	0.28	0	0.10	2.23	1.4601	0.324
Dichloromethane	0.82	0.13	0.10	9.08	1.4242	0.407
Acetonitrile	0.75	0.19	0.40	35.94	1.3442	0.456
N,*N*-dimethyl formamide	0.88	0	0.69	36.71	1.4270	0.438
Propan-2-ol	0.48	0.76	0.95	18.30	1.3775	0.546
Ethanol	0.54	0.86	0.75	24.30	1.3611	0.519
Methanol	0.60	0.98	0.66	32.63	1.3266	0.554

which display strong hydrogen bond donor and hydrogen bond acceptor capabilities.

Figure 1 shows the structural formula of DHDMAQ. The electronic absorption spectra of DHDMAQ in selected organic solvents are depicted in Fig. 2. The absorption spectrum consists of a two band system, an intense short wavelength band at ≈290nm (not shown in Fig. 2) and a relatively intense but structured band in the wavelength range of 400–550nm. An inspection of the spectra reveals that as the solvent polarity increases, it shows a blue shift.

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 [22]. In the present case DHDMAQ have their intra molecular charge transfer band between 400–550nm, which is due to the electron donating characters of the hydroxyl groups to the carbonyl groups.

The spectra show a progression of peaks in all the solvents. 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 481, 913 and 1,141cm^{-1} in CCl_4, 511, 871 and 1,139cm^{-1} in propan-2-ol and 531, 833 and 1,116cm^{-1} in ethanol. Skeletal deformation and CH bending modes of anthraquinone are responsible for the observed progression of peaks in the visible region [23].

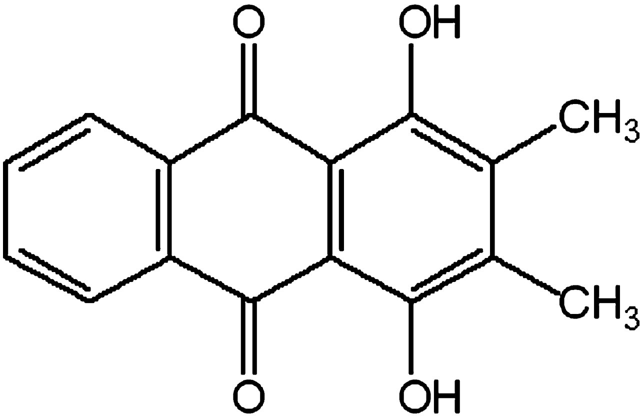

Fig. 1 Structural formula of 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone

Taft and Kamlet's solvatochromic comparison method [24] was used to analyze the solvatochromism of the DHDMAQ band around 485nm. This method rationalizes solvent effects in terms of a linear combination, which depends on three fundamental indexes: the scale π^* of solvent dipolarity/polarizability parameter which measures the ability of the medium to stabilize the charge on a dipole by virtue of its dielectric effects; the α scale of solvent hydrogen bond donor acidity, which describes the solvent's ability to donate a proton in a solvent to solute hydrogen bond and the β scale of hydrogen bond acceptor basicities which provides a measure of the solvent's ability to accept a hydrogen bond.

These solvatochromic parameters are used in linear solvation energy relationships of the general form in Eq. 1.

$$\mathrm{XYZ} = \mathrm{XYZ}_o + s\pi^* + a\alpha + b\beta \qquad (1)$$

where XYZ is the property to be correlated; *s*, *a* and *b* coefficients measure the relative sensitivity of XYZ to the

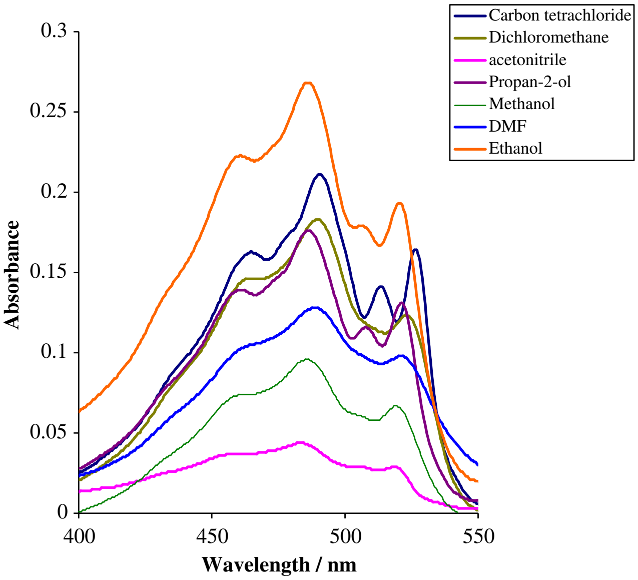

Fig. 2 Optical absorption spectra of DCMAQ in different solvents. [DHDMAQ]=0.02 mM

indicated solvent property scales. The parameters of organic solvents π^*, α, and β are reported in Table 1 [24].

The following regression equation is obtained

$$\overline{\nu}_{\mathrm{a}}(\mathrm{nm}) = 491.28 - 2.91\alpha - 1.44\beta - 3.73\pi^* \qquad (2)$$

which indicates that $\overline{\nu}_{\mathrm{a}}$ is determined mainly by π^* and α, and has a significant correlation with β also. The greater coefficient of π^* term indicate that dipolarity–polarizability interaction is more important. In addition Eq. 2 also indicates that the specific hydrogen bond donor interaction of the dye with the solvent is high since the increased electron density on the carbonyl oxygen in the S_1 state, which favours the hydrogen bond interaction, leads to extra stability.

Solvatochromic shifts in absorption spectra with increase in polarity of solvent give information only on the variation of solvation energy occurring immediately after the molecular excitation, thus not reflecting time averaged effects that would eventually result from a subsequent switching to the internal bond. The observed blue shift thus indicate a reduced strength of intermolecular hydrogen bonds in the excited molecules rather than an increased strength of internal bonds.

DHDMAQ chromophores have a negative charge excess and proton accepting ability due to the substituent. When this DHDMAQ 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 DHDMAQ is again directly confirmed by solvatochromic data that show a small but a noticeable blue shift with increasing solvent polarity [25].

The quasiaromatic rings formed by hydrogen bonding between the carbonyl and hydrogens of the substituents, where intra molecular hydrogen bond is possible, also contribute to the stabilization of the charge transfer band to a great extent. As the polarity of the solvent increases absorption maxima of the charge transfer band of DHDMAQ 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 DHDMAQ in polar solvents can also be explained only by assuming the delocalisation of the excited state, owing to reduction in quasiaromaticity of the chelate rings formed by intra molecular hydrogen bonds, due to association of the solvent via the quinonoid oxygens either by electrostatic or hydrogen bonding interaction [26].

In protic polar solvent, DHDMAQ are known to form hydrogen bonds in the ground states with solvent molecules i.e. the oxygen atoms of the carbonyl groups of DHDMAQ interact with the hydrogen atom of the protic solvent. In non-protic dipolar solvents, dipole–dipole interactions should play a dominant role in DHDMAQ solvation even though it has the tendency to form intermolecular hydrogen bond with DHDMAQ. Protic polar solvents provide an increasingly stronger solvation and stabilization of the ground state of DHDMAQ, thereby increasing their charge transfer transition energies in solution.

The observed blue shift indicates that the ground electronic state of the anthraquinone is stabilized by intermolecular hydrogen bond formation in protic polar solvents and by dipole–dipole interaction in non protic dipolar solvents.

This blue shift can be attributed to the increased energy required to transfer charge from the hydroxyl to the carbonyl group. The blue shifts in going from non-polar to polar solvents indicate that the dipole moment change and hence the change in geometry on electronic excitation is much smaller.

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 the integrated molar absorptivity is given by

$$f_{\mathrm{lu}} = \left(4.32 \times 10^{-9}\mathrm{mol.cm}^2/1\right) F \int_{\nu_1}^{\nu_2} \varepsilon_\nu \mathrm{d}\nu \qquad (3)$$

where the molar absorptivity, ε_ν, has units of $\mathrm{l\ mol}^{-1}\ \mathrm{cm}^{-1}$ and the frequency, ν_1 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 [27].

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 [28]. The transition dipole moment was obtained using the expression

$$\mu_{ge} = \frac{f_{lu}}{4.7 \times 10^{29} \nu_{abs}} \qquad (4)$$

where f_{lu} is the oscillator strength and ν_{abs} is the frequency in cm^{-1} at the absorption maximum. Generally oscillator strength describes the probability of an atom or molecule changing states depends on the nature of the initial and final state wave functions, how strongly light can interact with them, and on the intensity of any incident light. In the present case ethanol shows a strong transition when compared to all other solvents (Table 2). Carbon tetrachloride, Dichloromethane and propan-2-ol show the oscillator strength value (≈0.11) and DMF, methanol and acetonitrile show still lower value. Similar trend was observed in transition dipole moment also. The observed lower values of f_{lu} show that in the case of protic polar solvents the ground state of the DHDMAQ is stabilized by intermolecular hydrogen bond even though it has the tendency to form self association and in aprotic polar solvents the ground state of the DHDMAQ is stabilized by dipole–dipole interaction. Thus the stabilization of the ground state of DHDMAQ leads to the observed lower f_{lu} value and hence lower μ_{ge} value.

Fluorescence spectral studies

The fluorescence emission spectra of DHDMAQ in above mentioned solvents are depicted in Fig. 3. Figure 3 shows that the fluorescence emission of DHDMAQ is strongly solvent dependent. The emission maximum shift to longer wavelength in CH_2Cl_2, methanol, ethanol and DMF and shifts to shorter wavelength in propan-2-ol and acetonitrile with respect to non polar solvent. This red shift is an indicative of the charge transfer nature of the emitting state.

Table 2 Oscillator strength (f_{lu}), transition dipole moment (μ_{ge}) and fluorescence quantum yield (ϕ_{rel}) of DHDMAQ in different solvents

Solvent	Oscillator strength (f_{lu})	Transition dipole moment ($\mu_{\mathrm{ge}} \times 10^{-35}$)	Fluorescence quantum yield (ϕ_{rel})
Carbon tetrachloride	0.123	1.2836	0.0366
Dichloromethane	0.112	1.1665	0.0393
Acetonitrile	0.032	0.3289	0.0179
N,*N*-dimethyl formamide	0.090	0.9354	0.0259
Propan-2-ol	0.113	1.1685	0.0352
Ethanol	0.232	2.3989	0.0234
Methanol	0.057	0.5888	0.0283

Using Eq. 1, the multiple linear regression equation for the fluorescence maximum is

$$\bar{\nu}_{\mathrm{f}}(\mathrm{nm}) = 540.349 - 3.2779\alpha + 2.0392\beta + 7.2839\pi^{*} \qquad (5)$$

This equation indicates that $\bar{\nu}_{\mathrm{f}}$ is determined mainly by π^*, indicating that dipole-polarizability play a vital role in 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 DHDMAQ 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 an inter molecular hydrogen bonding interaction with an alcohol. 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. The steric effect due to methyl group and self association nature of acetonitrile leads to the observed blue shift in emission. The observed smaller magnitudes of Stoke's shifts again indicate that the geometry of the S_1 state is not significantly different from that of the S_0 state.

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

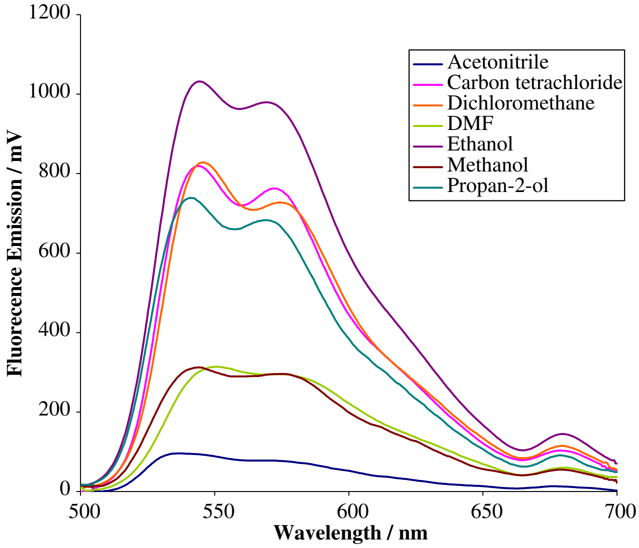

Fig. 3 Fluorescence emission spectra of DHDMAQ in different solvents (λ_{ext}=488nm); [DHDMAQ]=0.02 mM

between vibrational levels. The spacing between the spectral lines is 890cm^{-1} in carbontetrachloride, 920cm^{-1} in CH_2Cl_2, 905cm^{-1} in propan-2-ol, 1,018cm^{-1} in methanol, 788cm^{-1} in ethanol, 680cm^{-1} in DMF and 1,105cm^{-1} in acetonitrile. Skeletal deformation and CH bending mode of anthraquinone ring is responsible for the observed vibrational feature in fluorescence spectra [23]. These vibrational modes are responsible for the absence of mirror image relationship even though it does not show any excited state proton transfer reactions.

The relative fluorescence quantum yields of DHDMAQ are listed in Table 2. In addition to intramolecular hydrogen bonding, intermolecular hydrogen bonding with the hydroxyl group of alcohol was revealed to be a dominant mode of radiationless deactivation to the ground state and the electronic excited energy was supposed to dissipate through the hydrogen bond as vibrational energy. The steric factor predominates over the electronic one in the fluorescence quenching, while the intermolecular hydrogen bonding requires an orientation of the hydroxyl hydrogen toward the carbonyl oxygen atom of anthraquinone. Intermolecular interaction involving charge transfer has been proved to be another mechanism for efficient radiationless deactivation of the excited state [29].

The radiative decay rate depends on the refractive index, the strength of the pertinent electronic transition and its energy. The observed lower quantum yield shows that in all the solvents the radiative decay rate is very low. It is also confirmed by the observed low value of oscillator strength in all the solvents.

Dipole moment determination

The effect of solvent on absorption spectra of molecules can be used to determine the magnitude as well as direction of electric dipole moment of 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 [30, 31].

It is well established from [32–34] that the bulk dielectric constant (ε) and refractive index (n) of solvent play major roles in effecting dipole moments of solute molecules. An interaction with environment e.g. solvent, temperature etc. affects differently in various electronic states. The universal interaction between solute and solvent molecules is due to solvent acting as a dielectric medium. It also depends upon dielectric constant, refractive index of the solvent and dipole moment of the solute molecules.

According to Bakshiev [35], Chamma and Viallet [36]

$$\overline{\nu}_a - \overline{\nu}_f = m_1 F_1(\varepsilon, n) + C_1 \tag{6}$$

$$\overline{\nu}_a - \overline{\nu}_f = -m_2 F_2(\varepsilon, n) + C_{12} \tag{7}$$

where $\overline{\nu_a}$ and $\overline{\nu_f}$are absorption maximum and fluorescence maximum and $F(\varepsilon,n)$ is the solvent polarity parameter.

$$F_1(\varepsilon, n) = \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right)\left(\frac{2n^2 + 1}{n^2 + 2}\right) \tag{8}$$

$$F_2(\varepsilon, n) = F_1(\varepsilon, n) + 2G(n) \tag{9}$$

$$G(n) = \frac{3}{2}\frac{(n^4 - 1)}{(n^2 + 2)^2} \tag{10}$$

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

$$m_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3} \tag{11}$$

$$m_2 = \frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca^3} \tag{12}$$

where μ_e and μ_g are excited state and ground state dipole moment of solute molecules respectively, h is the Planck's constant, c is the velocity of light and a is Onsager cavity radius.

From Eqs. 11 and 12, the ratio of dipole moments in excited and ground state is given by

$$\frac{\mu_e}{\mu_g} = \left|\frac{m_1 + m_2}{m_2 - m_1}\right| \tag{13}$$

The photophysical parameters deduced from the observed absorption and emission spectra of DHDMAQ in different solvents are tabulated in Table 3. Fig. 4 shows correlation between $\overline{\nu}_a - \overline{\nu}_f$ and $F_1(\varepsilon, n)$ and Fig. 5 shows correlation between $\overline{\nu}_a + \overline{\nu}_f$ and $F_2(\varepsilon, n)$ (by eliminating the dichloromethane and DMF data which show much deviation, linear plot has been drawn). It can be seen that, the dichloromethane and DMF solvents show much deviation from linear plot. This deviation from linearity may be due to specific solute–solvent interaction [37]. The ratio of dipole moments in excited state to the ground state for the present case is found to be 0.10. This also confirmed by the observed blue shift in absorption spectra.

The following conclusion has been drawn from the dipole moment determination using solvent polarity parameter

1. The polarity of a molecule depends on electron density. With supply of additional energy there will be transition of electron from ground state to excited state which leads to the delocalisation of the excited state,

Table 3 Photo physical parameters of DHDMAQ deduced from optical absorption and fluorescence measurements

Solvent	λ_a (nm)	λ_f (nm)	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a + \bar{\nu}_f$ (cm^{-1})	$F_1(\varepsilon, n)$	$F_2(\varepsilon, n)$
Carbon tetrachloride	490.5	543.5	1,988.10	38,786.62	0.0210	0.6440
Dichloromethane	489.5	546.0	2,113.99	38,744.03	0.5950	1.1708
Acetonitrile	483.0	542.5	2,270.75	39,137.11	0.8592	1.3281
N,*N*-dimethyl formamide	488.5	550.5	2,305.53	38,636.13	0.8367	1.4161
Propan-2-ol	486.0	541	2,091.84	39,060.42	0.7652	1.2787
Ethanol	486.0	544.5	2,210.66	38,941.60	0.8117	1.3033
Methanol	485.5	544.0	2,214.97	38,979.68	0.8550	1.3001

owing to reduction in quasiaromaticity of the chelate rings formed by intra molecular hydrogen bonds, due to association of the solvent via the quinonoid oxygens either by electrostatic or hydrogen bonding interaction.

2. The observed blue shift (absorption maximum) in polar solvent provides the evidence for the observed dipole moment of the excited state, which is less than dipole moment of the ground state.
3. In addition the observed blue shifted absorption spectra with solvent implies that the excited state energy distribution is not affected to a greater extent, possibly due to the less polar nature of the DHDMAQ in the excited state rather than the ground state.

Preferential solvation of DHDMAQ

Theory

The extent of preferential solvation can be calculated in terms of two different methods. In the first case [38], the 'local' excess or deficiency of one solvent component over the bulk composition is used to describe preferential solvation

$$x_2^L = \frac{E_{12} - E_1}{E_2 - E_1} \qquad (14)$$

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 (λ_{max}) of the maximum of the long wavelength absorption band as in the case of Reichardt solvent polarity parameter [39], where E_{12} $(kcal\,.mol^{-1}) = 28591/\lambda_{max}$ (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 [40] 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 $\frac{f_2}{f_1} = \frac{x_1}{x_2}\frac{(E_{12}-E_1)}{(E_2-E_{12})}$. This parameter is equivalent to the exchange constant K_{ps} [41] for the description of $E_T(30)$ variation with composition in binary mixtures, where $K_{ps} = \frac{x_2^L x_1}{x_1^L x_2}$.

Optical absorption spectral studies

Studies of preferential solvation of DHDMAQ in binary solvent mixtures were carried out in ethanol–DMF and CH_2Cl_2–DMF systems, where DMF being the cosolvent.

DMF–Ethanol mixture Figure 6 shows the long wavelength optical absorption spectra of DHDMAQ in mixed solvents over different compositions. The observed spectra reveal that as the mole fraction of DMF increases, the wavelength of the long wavelength band (around 486nm) increases.

The variation of the transition energy (E_{12}) of the long wavelength absorption band versus the bulk mole fraction

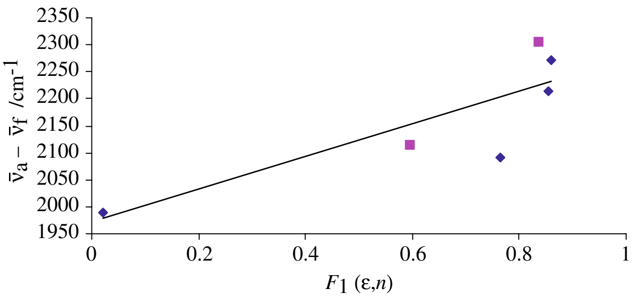

Fig. 4 Plot of $\bar{\nu}_a - \bar{\nu}_f$ against polarity function $F_1(\varepsilon, n)$

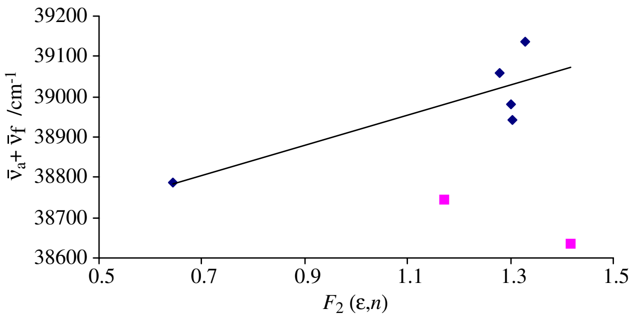

Fig. 5 Plots of $\bar{\nu}_a + \bar{\nu}_f$against polarity function $F_2(\varepsilon, n)$

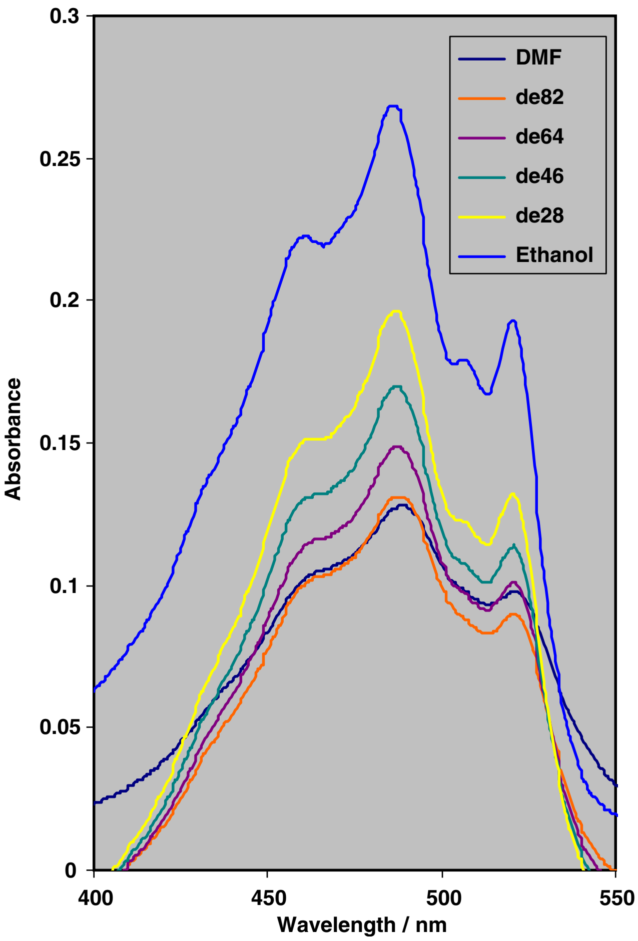

Fig. 6 Optical absorption spectra of DHDMAQ in DMF + Ethanol binary mixture (*d* DMF, *e* ethanol, *de82* volume of DMF is 8 ml and ethanol is 2 ml)

of (x_2) are depicted in Fig. 7. Figure 7 shows that, the value of E_{12} of the DHDMAQ decreases slowly as DMF is added to ethanol. The slight deviation from the ideal curve shows that DHDMAQ 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 DHDMAQ by one of the component solvents, packing effects vary in molecular properties of the DHDMAQ [42]. In fact the plot of E_{12} is diphasic indicating that the DHDMAQ is preferentially solvated by ethanol in DMF rich region while at lower mole fraction of DMF, DHDMAQ is preferentially solvated by DMF.

The preferential solvation parameter of DHDMAQ in binary mixture containing DMF and ethanol are given in Table 4. 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) at x_2 is greater than 0.4. For all other values of x_2, the mole fraction of ethanol in the solvation microsphere (x_1^L) is greater than in the bulk solvent (x_1). The variation of δ_{s2} (an index of preferential solvation with

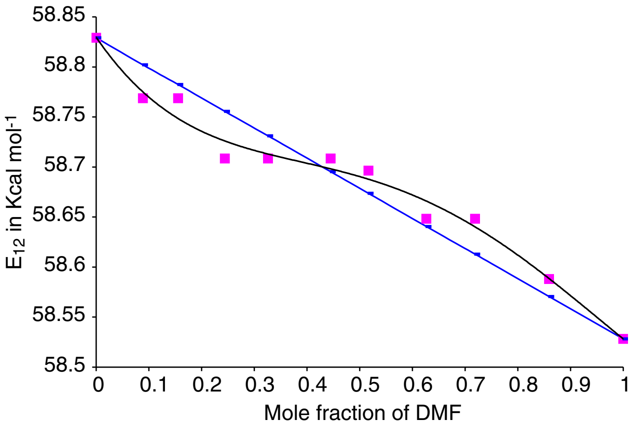

Fig. 7 Solvatochromic plot of E_{12} of DHDMAQ in DMF + Ethanol binary solvent system as a function of mole fraction of DMF

respect to DMF) against the solvent composition shows that δ_{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 ethanol. Furthermore at the DMF rich side, δ_{s2} values are negative. It also shows that the DHDMAQ is preferentially solvated by ethanol in DMF rich region (negative δ_{s2}) and by DMF in ethanol rich region (positive δ_{s2}). This can be explained by strong interactions between the solvent and DHDMAQ. These

Table 4 Preferential solvation data for DHDMAQ in binary solvent systems

x_2	x_2^L	δ_{s2}	f_2/f_1 (K_{ps})
CH_2Cl_2 + Ethanol mixture			
0	0	0	0
0.0887	0.2008	0.1121	2.5827
0.1553	0.2008	0.0455	1.3668
0.2443	0.4012	0.1570	2.0732
0.3260	0.4012	0.0752	1.3852
0.4448	0.4012	−0.0436	0.8364
0.5166	0.4413	−0.0753	0.7390
0.6266	0.6012	−0.0253	0.8986
0.7188	0.6012	−0.1176	0.5897
0.8591	0.8008	−0.0583	0.6592
1	1	0	0
CH_2Cl_2 + DMF mixture			
0	0	0	0
0.0908	0.6663	0.5755	19.9958
0.1818	0.6663	0.4844	8.9826
0.2748	1.1113	0.8365	−26.3534
0.3813	0.4440	0.0628	1.2958
0.4813	1.1113	0.6300	−10.7601
0.5703	0.6663	0.0960	1.5042
0.7284	1.5571	0.8287	−1.0422
0.8104	1.4456	0.6352	−0.7591
0.9014	1.1113	0.2099	−1.0924
1	1	0	0

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. Solute–solvent interactions dominate at low concentrations of alcohol and solvent–solvent interactions dominate at high concentration of ethanol.

The preference of ethanol near DHDMAQ and its competition to DMF in the solvation shell around DHDMAQ in the DMF rich region is not probably due to dielectric enrichment, owing to the fact that DMF has a higher electric permitivity than ethanol. This means that the less polar ethanol concentrates around the DHDMAQ molecules by intermolecular hydrogen bonding. This can be explained by self-association nature of ethanol. A dynamic equilibrium in pure liquid alcohol is assumed to exist as hydrogen bonds are broken and formed at a high rate. If a DMF is added, the dynamic equilibrium continues until the limit of dilute solution is reached, in this point, the concentration of the hydrogen bonded species becomes very low. Therefore addition of DMF gradually breaks the self-association of ethanol and the resulting free ethanol molecules then forms an intermolecular hydrogen bond with DHDMAQ.

The preference of DMF in the solvation shell of DHDMAQ in the ethanol rich region can be explained by dielectric enrichment. In this case dielectric enrichment precedes hydrogen bond formation because the overall energetic hydrogen bonding is generally unfavorable due to the energy spent in breaking solvent–solvent associations. This is probably due to the strong association of ethanol molecules so that the energy necessary to break these associations is very large in comparison to the energy necessary to form hydrogen bonds. This leads to the formation of dielectric enrichment before the formation of the hydrogen bond between the DHDMAQ and the ethanol.

The present case did not show synergistic behavior. Generally synergism is produced by hydrogen bonding between the hydrogen bond acceptor and the hydrogen bond donor to give a hydrogen bonded complex, which is often more polar than either of the two pure solvents. Even though the hydrogen bond donor ability (α = 0.86) of ethanol and hydrogen bond acceptor ability of DMF (β = 0.69) are high, the formation of hydrogen bonded complex between DMF and ethanol is less due to the higher probability of intermolecular hydrogen bond between solvent (DMF and ethanol) and DHDMAQ. This leads to the absence of synergistic behavior in this solvent mixture.

The molar percentage of the hydroxylic component for a 1:1 bulk mole fraction in a given mixture can be estimated through the following equation ROH (%)$=\frac{\lambda_{0.5}-\lambda_{0.0}}{\lambda_{1.0}-\lambda_{0.0}}\times 100$ where ROH(%) is the estimated molar % of the hydroxylic component in the mixture. $\lambda_{0.0}$, $\lambda_{0.5}$ and $\lambda_{1.0}$ are the maximum absorption wavelength for the protic solvent mole fractions equal to 0.0, 0.5 and 1 respectively. This assumption can be made only for mixtures in which the synergistic behaviour is absent [43]. In C_2H_5OH + DMF mixtures, only 60% of the ethanol molecules are available in mixture containing 50% of each one of the mixed bulk components. This indicates that only 60% ethanol molecules compete with the DMF molecules to enter the cybotactic region (the rest being involved in self associated hydrogen bond formation). This leads to DHDMAQ being solvated by ethanol in DMF rich region.

This self-association of ethanol was also confirmed from the value of equilibrium constant. Hydrogen bonding is presumably the strongest available interaction, but it can only take place when two molecules both possess suitable donor–acceptor capabilities and approach each other in specific interactions. The tendency toward an hydrogen bond dimerization can be quantitatively expresses by means of empirical scales, such as those developed by Abraham [44] in terms of two parameters α_2^H and β_2^H describing respectively the hydrogen bond acidity and hydrogen bond basicity of a given species [24]. These parameters can be employed to estimate the equilibrium constants for hydrogen bond dimerization of specific donor–acceptor pairs in a solvent.

$$\begin{aligned} &\mathrm{A-H+B}\rightleftarrows\mathrm{A-H\cdots B}\\ &\log\mathrm{K}=7.354\alpha_2^H(\mathrm{A})\beta_2^{\mathrm{H}}(\mathrm{B})-1.094 \end{aligned} \tag{15}$$

The resulting equilibrium constants clearly show that a log*K* value for C_2H_5OH + C_2H_5OH (3.6493) is larger than that of C_2H_5OH + DMF (3.2699) and DMF + DMF (−1.094). Thus ethanol forms hydrogen bonds with ethanol molecules more favorably than with DMF which is responsible for ethanol association. In addition log*K* value for DMF and ethanol is high, but this association is less probable due to the intra molecular charge transfer nature of DHDMAQ. These two solvents involved in solute–solvent interaction through an intermolecular hydrogen bond with DHDMAQ rather than solvent–solvent interactions through hydrogen bonding between solvents. This also confirmed by the observed absence of synergistic behavior.

Ethanol and DMF molecules specifically interacts with DHDMAQ through intermolecular hydrogen bonding and this interaction seems to be the key factor for the preferentially solvation of DHDMAQ by these solvents. It is probable that the hydrogen bonded acceptor solvent molecules aggregate near the hydroxyl group of the DHDMAQ since this group plays an important role in the electronic transition responsible for the long wavelength absorption and the solvatochromic behavior of DHDMAQ.

The observed f_2/f_1 values (Table 4) are also confirmed that the DHDMAQ is preferentially solvated by ethanol in DMF rich region and by DMF by ethanol rich region.

DMF–CH_2Cl_2 mixture Figure 8 shows the long wavelength absorption spectra of DHDMAQ in mixed solvents over different compositions. The plot of the transition energy (E_{12}) of the long wavelength absorptions band versus the bulk mole fraction of the cosolvent (x_2) is shown in Fig. 9. This plot shows that the value of E_{12} of the DHDMAQ increases slowly as DMF is added to pure CH_2Cl_2. The non-linearity of the plot indicates that the DHDMAQ is preferentially solvated by DMF. The preferentially solvation parameter of DHDMAQ in binary mixture containing CH_2Cl_2 and DMF are given in Table 4. The solvation data shows that over the whole range of composition range, there is a higher mole fraction of the DMF in the solvation microsphere (x_2^L) than in the bulk solvent (x_2). The δ_{s2} values are positive over the entire range of composition. The f_2/f_1 parameters are greater than one over the entire range of composition.

The preference of DMF near DHDMAQ and its competition to CH_2Cl_2 in the solvation shell around DHDMAQ in binary mixture of DMF–CH_2Cl_2 is probably due to dielectric enrichment, owing to the fact that DMF has a higher electric permittivity than CH_2Cl_2.

In pure CH_2Cl_2, due to the hydrogen bond donor ability of CH_2Cl_2 is a weak intermolecular hydrogen bond is formed between the carbonyl group of DHDMAQ and hydrogen atom of the CH_2Cl_2 molecule. When DMF is added into the solution of DHDMAQ in CH_2Cl_2, intermolecular hydrogen bond is immediately formed between the hydroxyl group of DHDMAQ and carbonyl group of DMF, since DMF is a very good hydrogen bond acceptor. This leads to the preference of DHDMAQ by DMF than CH_2Cl_2.

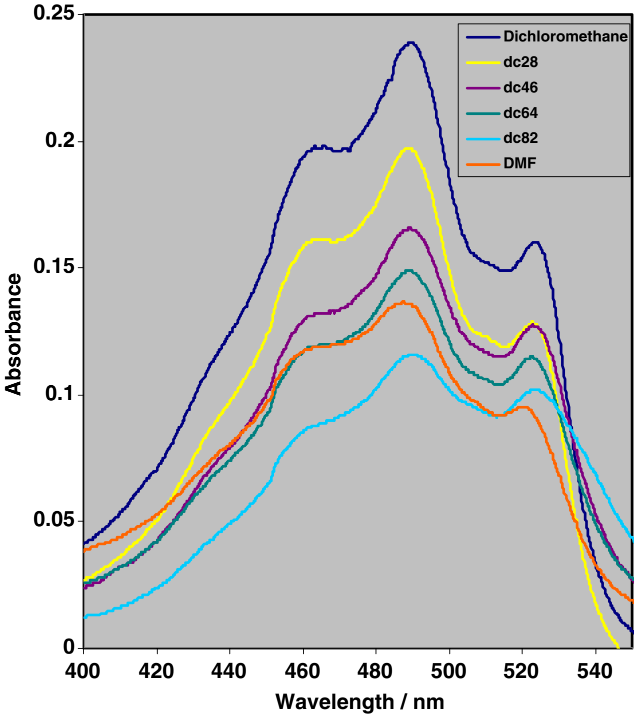

Fig. 8 Optical absorption spectra of DHDMAQ in DMF + dichloromethane binary mixture (*d* DMF, *c* dichloromethane, *dc82* volume of DMF is 8 ml and dichloromethane is 2 ml)

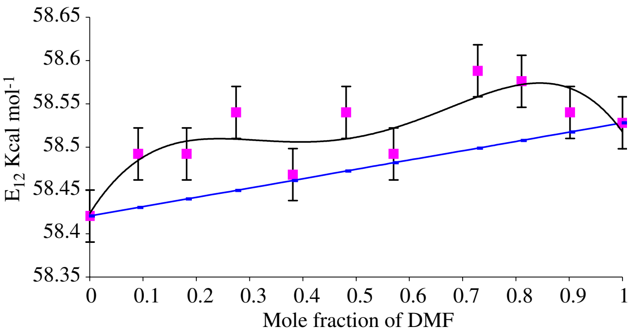

Fig. 9 Solvatochromic plot of E_{12} of DHDMAQ in CH_2Cl_2 + DMF binary solvent system as a function of mole fraction of DMF

In this case, E_{12} used for solvation studies showed a higher value in the binary mixtures than the pure solvents i. e. the present case shows synergistic behavior. Synergistic effects are generally due to the formation of 1:1 complexes through the hydrogen bonds between the two solvents in the mixture. Eq. 15 shows that log$K$ value for DMF + CH_2Cl_2 is less (−0.4343) which indicates that there is no complex formation between DMF and CH_2Cl_2 through hydrogen bonding. Even though CH_2Cl_2 and DMF forms intermolecular hydrogen bond with DHDMAQ, the higher polarizability of CH_2Cl_2 and DMF increases the dipole–dipole interaction between DHDMAQ and solvents. Therefore the observed synergistic effect is due to dipole–dipole interaction between DMF and CH_2Cl_2.

Conclusion

Optical absorption and fluorescence emission techniques have been employed to study the solvatochromic and preferential solvation of DHDMAQ. The delocalisation of the excited states due to electrostatic or hydrogen bonding interaction has been interpreted from the observed blue shift in absorption spectra. Intermolecular hydrogen bond in the excited state act as a acceptor mode, which provides less quantum yield. It is also confirmed by low oscillator strength and the transition dipole moment. Excited state dipole moment of DHDMAQ is lower than the ground state. In DMF + ethanol binary mixture, DHDMAQ is preferentially solvated by ethanol in DMF rich region and DMF by ethanol rich region and in the case of DMF+dichloromethane binary mixture DHDMAQ is preferentially solvated by DMF.

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References

1. Reichardt C (1994) Chem Rev 94:2319
2. Inamdar SR, Nadaf YF, Mulimani BG (2003) J Mol Struct (Theochem) 624:47
3. O'Neil ML, Kruus P, Burk RC (1993) Can J Chem 71:1984
4. Kamlet KJ, Abbound JKM, Abraham MH, Taft RW (1983) J Org Chem 48:2877
5. Toselli NM, Silber JJ, Anunziata JD (1988) Spectrochim Acta 44A:829
6. Linert W, Strauss B, Herlinger E, Reichardt C (1992) J Phys Org Chem 5:275
7. Catalan J (1995) J Org Chem 60:8315
8. Tanaka T, Kohno H, Murakami M, Shimada R, Kagami S (2000) Oncol Rep 7:501
9. Eriksson M, Norden B, Eriksson S (1988) Biochemistry 27:8144
10. Nonaka Y, Tsuboi M, Nakamoto KJ (1990) J Raman Spectrosc 21:133
11. Feng ZM, Jiang JS Wang YH, Zhang PC (2005) Chem Pharm Bull (Tokyo) 53:1330
12. Wang SX, Hua HM, Wu LJ, Li X, Zhu TR (1992) Yao Xue Xue Bao 27:743
13. Abo KA, Adeyemi AA, Sobowale AO (2001) Afr J Med Med Sci 30:9
14. Abo KA, Adeyemi AA (2002) Afr J Med Med Sci 31:171
15. Laus G, Schottenberger H, Wurst K, Schutz J, Ongania KH, Horvath UEI, Schwarzler A (2003) Org Biomol Chem 1:1409
16. Bevilaqua T, da Silva DC, Machado VG (2004) Spectrochim Acta 60A:951
17. Blanco SE, Gasull EI, Ferretti FH (2003) Spectrochim Acta 59A:2985
18. Umadevi M, Suvitha A, Latha K, Rajkumar BJM, Ramakrishnan V (2007) Spectrochimica Acta 67A:910
19. Sasireka V, Umadevi M, Ramakrishnan V (2008) Spectrochimica Acta A 69A:148
20. Kerdesky FAJ, Ardecky RJ, Lakshmikantham MV, Cava MP (1981) J Am Chem Soc. 103:1992
21. Parker CA, Rees WT (1960) Analyst 85:587
22. Yoshida Z, Takabayash F (1967) Tetrahedron 24:933
23. Marzocchi MP, Mantini AR, Casu M, Smulevich G (1998) J Chem Phys 108:534
24. Marcus Y (1993) Chem Soc Rev 22:409
25. Marrucci L, Paparo D, Vetrano MR, Colicchio M, Santamato E, Viscardi G (2002) J Chem Phys 108:10361
26. Palit DK, Pal H, Mukherjee T, Mittal JP (1990) J Chem Soc Faraday Trans 86:3861
27. Calvert JG, Pitts Jr J (1966) N Photochemistry. Wiley, New York
28. Srividya N, Sinha A, Rao TAP (2000) J Solution Chem 29:847
29. Inoue H, Hida M, Nakashlma N, Yoshlhara K (1982) J Phys Chem 86:3184
30. Medhi RN, Barman R, Medhi KC, Jois SS (1998) Spectrochim Acta 54A:623
31. Kumar S, Rao VC, Rastogi RC (2001) Spectrochim Acta 57A:41
32. Prabhmirachi LS, Kutty DKN, Bhide AS (1983) Spectrochimica Acta 39A:663
33. Suppan P (1983) Chem Phys Lett 94:272
34. Bakshiev NG (1962) Opt Spectrosc 13:507
35. Bakshiev NG (1964) Opt Spectrosc. 16:821
36. Chamma A, Viallet P, Hebdo CR (1970) Seances Acad Sci Ser France 270:1901
37. Nadaf YF, Mulimani BG, Gopal M, Inamdar SR (2004) J Mol Struct (Theochem) 678:177
38. Chatterjee P, Laha AK, Bagchi S, Chem J (1992) Soc Faraday Trans I 88:1675
39. Dimroth K, Reichardt C, Sieomann T, Bohlmann F (1963) Ann Chem 661:1
40. Roses M, Ortega J, Bosch E (1995) J Solution Chem 24:1
41. Skwierczynski RD, Connors KA (1994) J Chem Soc Perkin Trans 2:467
42. Roses M, Rafols C, Ortega J, Bosch E (1995) J Chem Soc Perkin Trans 2:1607
43. Silva MAR, de Silva DC, Machado VG, Longhinotti E, Frescura VLA (2002) J Phys Chem 106A:8820
44. Abraham MH (1993) Chem Soc Rev 22:73