

Solvatochromism, Preferential Solvation of 2,3-Bis(Chloromethyl)-1,4-Anthraquinone in Binary Mixtures and the Molecular Recognition Towards *p*-Tert-Butyl-Calix[4]arene

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Abstract Optical absorption and fluorescence emission spectra of 2,3-bis(chloromethyl)-1,4-anthraquinone (DCMAQ) in single solvents namely, carbon tetrachloride, acetonitrile, chloroform, propan-2-ol and its binary mixtures [carbon tetrachloride/chloroform, chloroform/acetonitrile, chloroform/propan-2-ol] have been investigated. The preferential solvation of DCMAQ in above mixtures has been studied by monitoring the absorption and fluorescence spectra of DCMAQ. The spectral features indicate that DCMAQ is preferentially solvated by CHCl_3 in the above mixtures. This can be elucidated from the local mole fraction, non-linearity in transition energy plot, preferential solvation index (δ_{s2}) and (f_2/f_1) values. Molecular recognition properties of *p*-tert-butylcalix[4]arene (tBC) to DCMAQ via hydrogen bonding and π - π interaction were

sensed successfully on the basis of absorption and fluorescence emission spectroscopies, by which the stoichiometry ratio and the binding constant of the tBC–DCMAQ complex were determined.

Keywords 2,3-Bis(chloromethyl)-1,4-anthraquinone · Binary mixtures · Fluorescence emission · Optical absorption · Solute–solvent interaction · Solvent–solvent interaction · Preferential solvation

Introduction

Solvent mixtures are widely used in chemical and biochemical practice to modify molecular environments in order to modulate interesting phenomena such as chromatographic separation, organic synthesis, reaction kinetics and to improve the solubility [1]. The studies of solute–solvent and solvent–solvent interactions, and how they affect the intimate structure of the solute, have attracted much attention as they play a major role in all phenomena occurring in the liquid phase. There is currently considerable interest in the study of physicochemical phenomena in mixed solvent systems [2]. The term “preferential solvation” is usually employed to signify that the solute induces a change in its environment with respect to the situation in the bulk solvent, whether through nonspecific solute–solvent interactions referred to as “dielectric enrichment” or through specific solute–solvent association. The variation of these data with the composition of the bulk solvent deviates from ideality. The occurrence of deviations is taken as the evidence of preferential solvation [1, 3].

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Quinones, natural and synthetic, are organic compounds of major importance in biological systems and industrial applications as dye stuffs or pharmaceuticals [4]. Quinone compounds have been the subject of photochemical and photophysical investigations [5, 6]. Anthraquinones are extremely important taking into account of their properties and broad field of their application [7]. 1,4-Anthraquinone is an anticancer drug that blocks nucleoside transport, inhibits macromolecule synthesis, induces DNA fragmentation, and decreases the growth and viability of L1210 leukemic cells in the same nanomolar range as daunorubicin *in vitro*. Spectroscopic measurements are well suited for characterizing the local environment of a molecule. Solvatochromic shifts reflect the extent of stabilization that the molecular ground and excited states experience due to solvent-solute interactions [8]. Itoh et al. [9] have analysed emission and absorption spectra of 1,4-anthraquinone in CCl_4 solvent.

Molecular recognition, which is a specific interaction between molecules or different parts of a molecule, plays an important role in the selective reaction in the organism and in the folding of large biomolecules such as the folding of proteins. Calix[*n*]arenes are macrocyclic polyphenols with a cyclic framework linked by methylene bridges [10]. Functionalization of the upper rim, the lower rim or both and the conformation of the calixarene moiety determine the size and geometry of the host and, therefore, significantly change the selectivity of binding. So they are frequently selected as host molecules in sensor research or in separation sciences as well as catalysis [11]. *p*-Tert-butylcalix[4]arene composed of an hydroxyl groups in the lower rim which is used to stabilize the cone shape by intramolecular hydrogen bonding, intermolecular hydrogen bonding with guest molecule and an aromatic π chromophore (i.e. benzene ring) for π - π interaction act upon recognition of a guest molecule. Since both hydrogen bonding and π - π interactions act upon host and/or guest molecules, spectroscopic studies on such systems are worth exploring in detail. Several work has been reported on the interaction of metal ions with calix[4]arenes [12–17]. Very few investigations are available on the recognition of organic molecules [18–25]. Our group has recently investigated the single solvent effect on 2,3-bis (chloromethyl)-1,4-anthraquinone and the molecular recognition of 2,3-bis (chloromethyl)-1,4-anthraquinone in calix[8]arene [26]. As an extension of the above, in this paper we report on how we have investigated optical absorption and fluorescence emission of DCMAQ in neat solvents and binary mixtures as a function of composition to analyse solute-solvent and solvent-solvent interaction and host-guest complexation of DCMAQ by tBC.

Experimental

Preparation of guest and host molecule

DCMAQ was prepared from 1,4-anthraquinone according to Thomson's procedure [27]. A solution of 1,4-anthraquinone (2.6 g, 12.48 mM) in glacial acetic acid (50 ml) containing aqueous formaldehyde (20 ml, 37%) was cooled and dry hydrogen chloride was passed through it for 2 h. The mixture was allowed to stand at room temperature overnight and was poured into 200 ml of ice water. The product was collected by filtration, washed with water and dried over anhydrous magnesium sulfate. Purification by chromatography on silica gel eluting with dichloromethane gave DCMAQ in 61% yield. The tBC used in this study was synthesized by method previously described [28].

Other chemicals

Solvents such as CCl_4 , CH_3CN , CHCl_3 , and propan-2-ol from Sisco Research Laboratory with 99.9% purity were used without further purification.

Spectroscopic measurements

The solution was prepared at the 0.1 mM solute concentration in pure solvents. Binary mixtures were prepared by mixing appropriate volumes of each homo solution in the ratio 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1. The solutions, host and guest, were mixed to a standard volume in varying molar ratios of the two components, keeping the sum of both concentrations equal to 0.08 mM to determine the stoichiometry ratio. To determine the association constant different concentration of tBC was added to a dilute solution of DCMAQ (0.06 mM). The optical absorption spectra were recorded using SPECORD S100

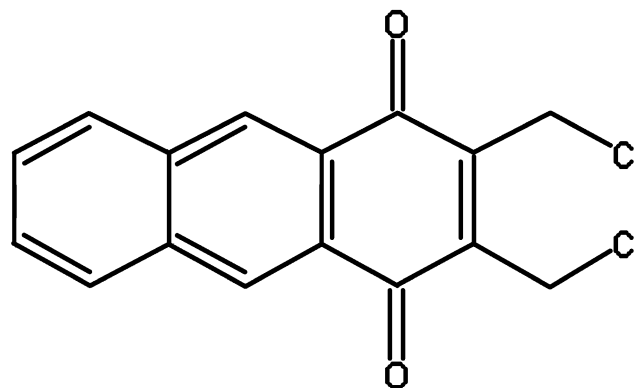
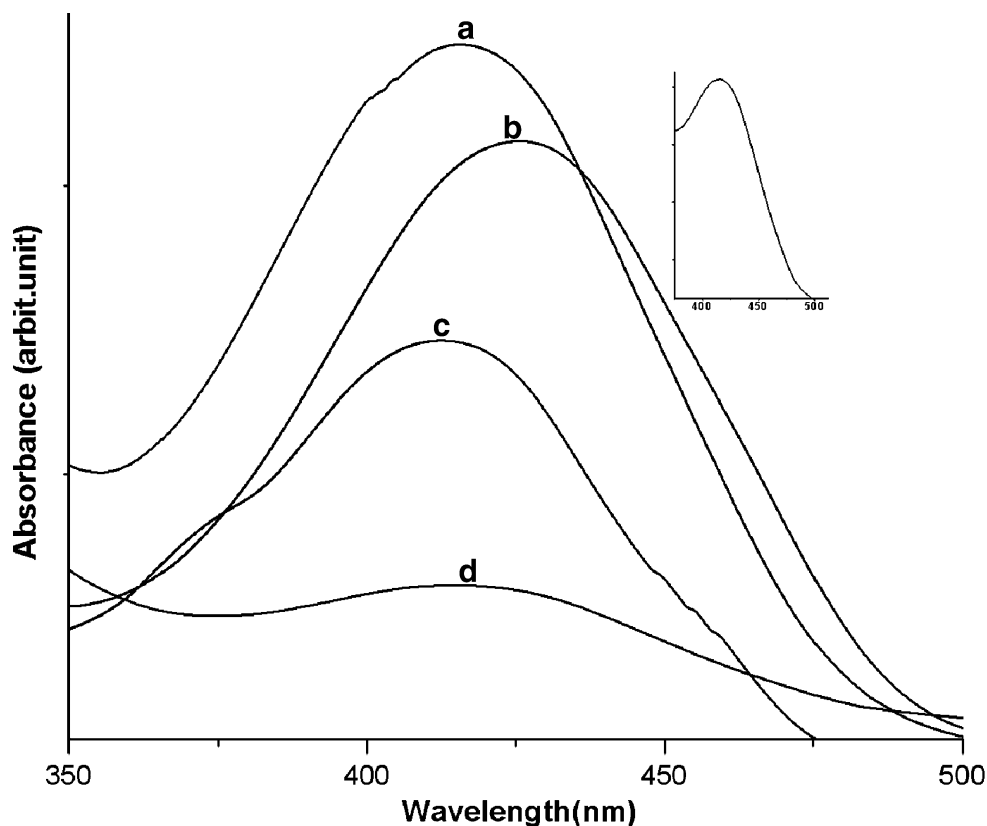


Fig. 1 Molecular structure of DCMAQ

Fig. 2 Optical absorption spectra of DCMAQ in different solvents. **a** CH₃CN, **b** CHCl₃, **c** CCl₄, **d** Propan-2-ol (inset: Propan-2-ol)



diode-array spectrophotometer. For fluorescence emission measurements the 457.9 nm line of Spectra Physics 2020-04S argon ion laser was used as the excitation wavelength at the laser power 30 mW. The emission was collected in 90° geometry and dispersed with the grating monochromator (SPEX-1250 M) and detected with the thermoelectrically cooled GaAs photomultiplier tube and photon counter (SR-400). A PC was interfaced through a data acquisition card to record the spectra. All measurements were performed at room temperature.

Results and discussion

The structural formula of DCMAQ is presented in Fig. 1. Optical absorption spectroscopic measurement (Fig. 2) of long wavelength maxima of probe solute in a solvent is known to provide valuable information on the intermolecular interactions between solute and solvent. Generally, the long wavelength absorption band in unsubstituted anthraquinone is due to $n \rightarrow \pi^*$ transition. This band, due to an $n \rightarrow \pi^*$ transition, suffers a blue shift in more polar solvents due to the lower dipole moment of the excited state with respect to the ground state. But in DCMAQ as the solvent polarity increases the peaks are red shifted with respect to

apolar solvent (CCl₄). This observed feature suggests that $\pi \rightarrow \pi^*$ state becomes the lowest excited state. The maximum of long wavelength emission (Fig. 3) is taken to analyse solute-solvent interactions in the excited state.

Solvatochromic shifts in single solvents

Transition energies (E_T) are calculated [29] from the wavelengths of the absorption, emission maxima according to Eq. 1

$$E_T (\text{kcal.mol}^{-1}) = \frac{28591}{\lambda_{\text{max}} (\text{nm})} \quad (1)$$

Figure 4 shows the plot between E_T and the solvents dielectric polarity $F(D) = \frac{2(\epsilon-1)}{(2\epsilon+1)}$ in the ground state and the excited state. The non-linear variation of the transition energy with the solvent dielectric polarity is observed (Fig. 4a). This suggests the existence of specific solute-solvent interactions. Further, an increase in the solvent polarity leads to a lower transition energy (positive solvatochromism). Though CH₃CN and Propan-2-ol are more polar than CHCl₃, they exhibit high E_T values. CH₃CN has the tendency to form its dimer through self-association which has nonpolar character. Propan-2-ol is a

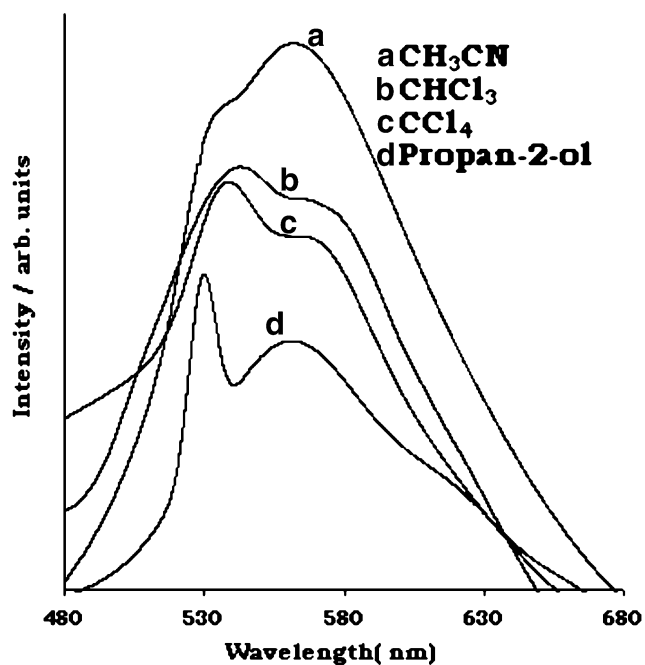


Fig. 3 Fluorescence emission spectra of DCMAQ in different solvents

bulky molecule with two methyl groups which may reduce the proton donating ability of propan-2-ol so as to form intermolecular hydrogen bonds [30, 31]. This makes the low polarity values for propan-2-ol molecules. Hence they exhibit high E_T values. From Fig. 4b our results for pure solvents in the excited state reflect the same features as in the ground state. This indicates that the strength of the intermolecular hydrogen bond remains same in the excited state due to the neutral substituents of DCMAQ.

Preferential solvation

The preferential solvation can be calculated in terms of two approaches. In the first approach the local excess or deficiency of one solvent over the bulk composition is used to describe preferential solvation. The mole fraction of the solvents in the cybotactic region (X_2^L) can be obtained using Eq. 2

$$X_2^L = \frac{(E_{12} - E_1)}{(E_2 - E_1)} \quad (2)$$

where E_1 , E_2 and E_{12} are the values of the electronic transition energy of DCMAQ in the solvent 1, solvent 2 and the mixture of solvents, respectively. Also the index of preferential solvation (δ_{s2}) with respect to the co-solvent can be calculated from Eq. 3

$$\delta_{s2} = X_2^L - X_2 \quad (3)$$

where X_2 is the bulk mole fraction of the co-solvent [32]. The second approach [33] incorporates a parameter (f_2/f_1)

which is the proportionality coefficient between the ratio of the molecules of solvent 2 in reference to solvent 1 in the cybotactic region of the DCMAQ and the ratio of molecules of same solvent in reference to the other in the bulk of the solution (Eq. 4), where

$$(f_2/f_1) = \frac{x_1}{x_2} \frac{(E_{12} - E_1)}{(E_2 - E_1)} \quad (4)$$

This parameter is equivalent to the exchange constant (K_{PS}) proposed by Skwierczynski et al. [34] for the description of E_T variation with composition in mixtures where

$$K_{PS} = \frac{x_2^L/x_2}{x_1^L/x_1} \quad (5)$$

The preferential solvation parameters of DCMAQ in binary mixtures are given in Table 1.

Binary mixtures containing $CCl_4/CHCl_3$

In this mixture, $CHCl_3$ is the co-solvent and hence the solvation of the solute in it is the important feature to be studied. Figure 5 depicts the plot of E_{12} versus the bulk

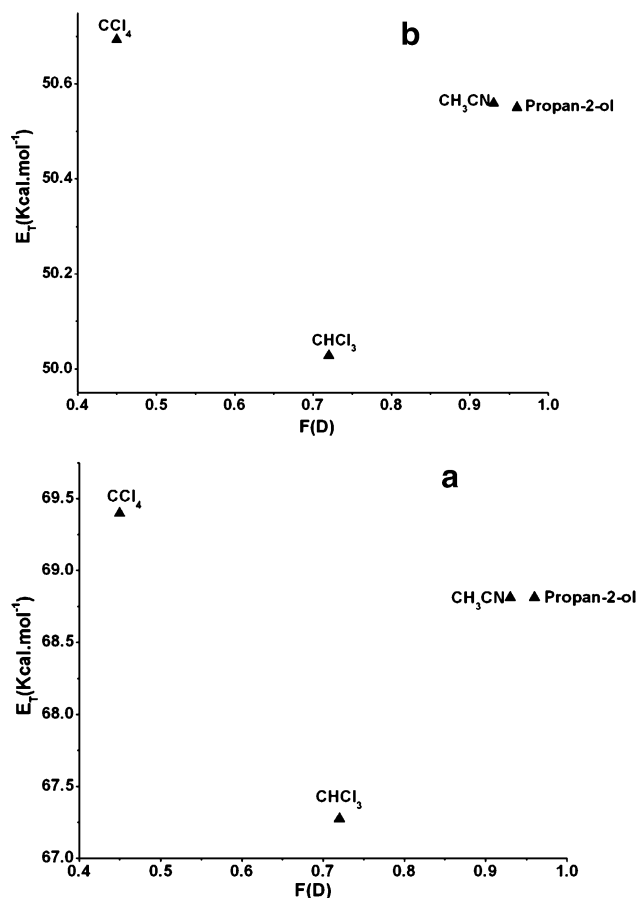


Fig. 4 Transition energies of DCMAQ (a), absorption (b). Emission versus solvents dielectric polarity $F(D)$ in single solvents

Table 1 Preferential solvation data of DCMAQ in binary mixtures

X_2	X_2^L	δ_{s2}	X_1^L	δ_{s1}	f_2/f_1
CCl ₄ :CHCl ₃					
0					
0.116	0.469	0.352	0.530	-0.352	6.691
0.227	0.546	0.319	0.453	-0.319	4.095
0.338	0.660	0.322	0.339	-0.322	3.805
0.445	0.698	0.253	0.301	-0.253	2.889
0.548	0.812	0.264	0.187	-0.264	3.567
0.646	0.850	0.204	0.149	-0.204	3.108
0.739	0.925	0.185	0.074	-0.185	4.358
0.828	0.962	0.133	0.037	-0.133	5.331
0.951	0.962	0.010	0.037	-0.010	1.306
1					
CHCl ₃ :CH ₃ CN					
0					
0.179	0.121	-0.057	0.878	0.057	0.633
0.318	0.186	-0.132	0.813	0.132	0.488
0.434	0.378	-0.055	0.621	0.055	0.793
0.559	0.464	-0.094	0.535	0.094	0.684
0.642	0.552	-0.090	0.447	0.090	0.686
0.721	0.596	-0.125	0.403	0.125	0.571
0.814	0.689	-0.124	0.310	0.124	0.507
0.877	0.814	-0.063	0.185	0.063	0.611
0.945	0.903	-0.041	0.096	0.041	0.543
1					
CHCl ₃ :Propan-2-ol					
0					
0.069	0.025	-0.169	0.267	0.044	0.342
0.188	0.025	-0.092	0.288	0.163	0.110
0.295	0.109	-0.251	0.549	0.186	0.292
0.394	0.193	-0.239	0.635	0.200	0.368
0.499	0.300	-0.199	0.699	0.199	0.429
0.604	0.364	-0.200	0.806	0.239	0.375
0.701	0.450	-0.186	0.890	0.251	0.347
0.803	0.711	-0.163	0.974	0.092	0.602
0.902	0.732	-0.044	0.974	0.169	0.296
1					

X_2 Mole fraction of more polar solvent.

mole fraction of CHCl₃ (X_2). E_{12} does not have a linear dependence on bulk mole fraction of CHCl₃. The deviation from linearity is an indicative of the preferential solvation of the solute by one of the component solvents. The transition energy gradually decreases with the increase of the mole fraction of CHCl₃ which also suggests that solute molecules are preferentially solvated by CHCl₃. This preferential solvation exists because of the interaction between CHCl₃ and DCMAQ. These interactions may be due to the formation of intermolecular hydrogen bonding of the type of C-H...O=C between the DCMAQ and CHCl₃ solvent and/or non-specific dipolar interactions [35, 36]. The local mole fraction of CHCl₃ in the solvation microsphere is higher than the bulk mole fraction (Table 1). This was also conformed by the positive δ_{s2} values (index of preferential solvation with respect to CHCl₃) and the

observed f_2/f_1 parameters are also greater than unity with respect to CHCl₃ (Table 1). Fluorescence emission studies in binary mixtures reflect the preferential solvation characteristics of the excited state. It is observed from the Fig. 5b, E_{12} decreases with respect to the mole fraction of CHCl₃ in the excited state also and solute prefers CHCl₃ over CCl₄.

Binary mixtures containing CHCl₃/CH₃CN

Figure 6 presents a plot of E_{12} versus the bulk mole fraction of CH₃CN (X_2). Figure 6a shows the value of E_{12} for absorption which increases with the mole fraction of CH₃CN. The value of transition energy of fluorescence also increases with the mole fraction of CH₃CN (Fig. 6b). The nonlinearity of the plots indicates that the solute

molecule is preferentially solvated by any one of the solvent molecules. The solvation data (Table 1) show that over the whole mole fraction range the DCMAQ is preferentially solvated by CHCl_3 . The preference of CHCl_3 near DCMAQ is not probably due to the higher dielectric constant owing to the fact that CH_3CN has a higher electrical permittivity than CHCl_3 . This means that less polar CHCl_3 solvent molecules concentrate around the DCMAQ. Also, the preferential solvation data shown in Table 1 confirm this conclusion by the negative δ_{s2} value, the lower mole fraction of the CH_3CN in the solvation microsphere (X_2^L) than in the bulk solvent as well as by the parameter f_2/f_1 values which are lower than unity. CH_3CN molecules being very small have an exceptionally large dipole moment in the non-associated free molecular case. These molecules can form a dimer through self-association owing to the strong dipole–dipole interaction between CH_3CN molecules. These dimers are non-polar in nature

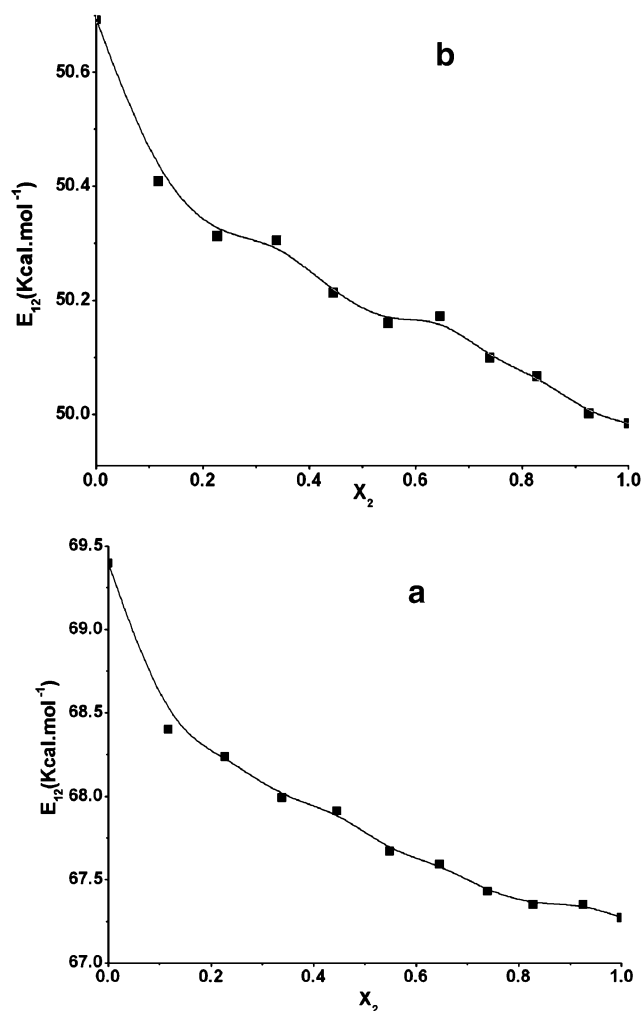


Fig. 5 Transition energies of DCMAQ (a), absorption (b). Emission versus X_2 (the bulk mole fraction of CHCl_3) in binary mixtures of $\text{CCl}_4/\text{CHCl}_3$

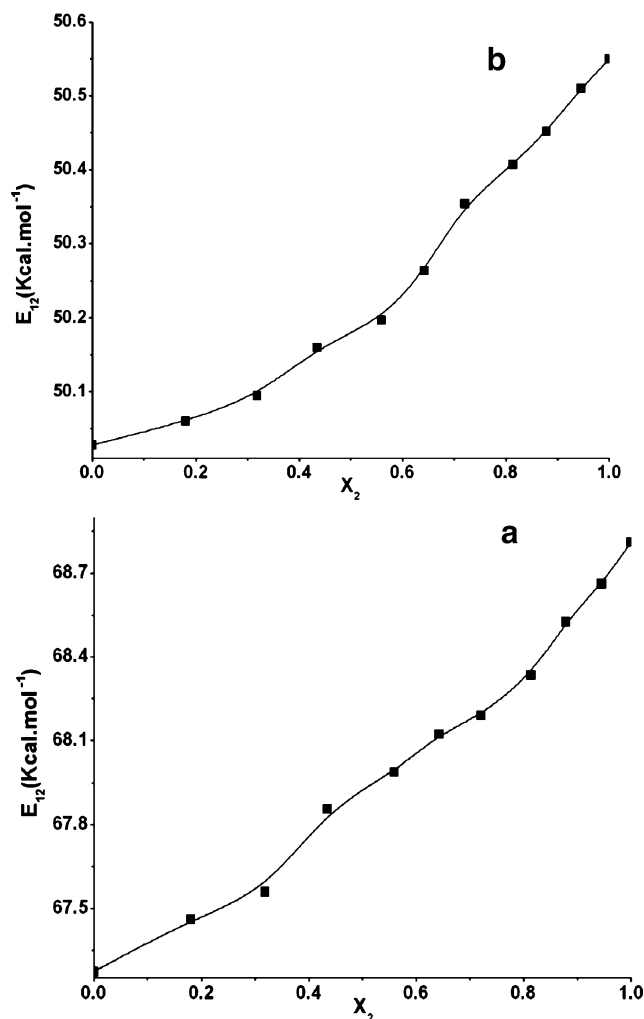


Fig. 6 Transition energies of DCMAQ (a), absorption (b). Emission versus X_2 (the bulk mole fraction of CH_3CN) in binary mixtures of $\text{CHCl}_3/\text{CH}_3\text{CN}$

and hence reduces the polarity of the solvent molecules in the associated CH_3CN [37]. This low polarity environment induces the DCMAQ molecule to have intermolecular hydrogen bonding with CHCl_3 . The dipole–dipole interaction between the CH_3CN molecules makes the CH_3CN molecule to be preferred by the other CH_3CN molecule rather than the solute molecule. This dipole–dipole interaction competes with the solute–solvent interaction. In fact it has to take more energy for CH_3CN molecule to enter into the solvation microsphere, because this can be achieved by breaking the solvent structure which requires energy.

Binary mixtures containing $\text{CHCl}_3/\text{Propan-2-ol}$

Figure 7 depicts the variation of E_{12} versus mole fraction of propan-2-ol. Figures 7a,b show that as the mole fraction of propan-2-ol increases the E_{12} value of ground and excited

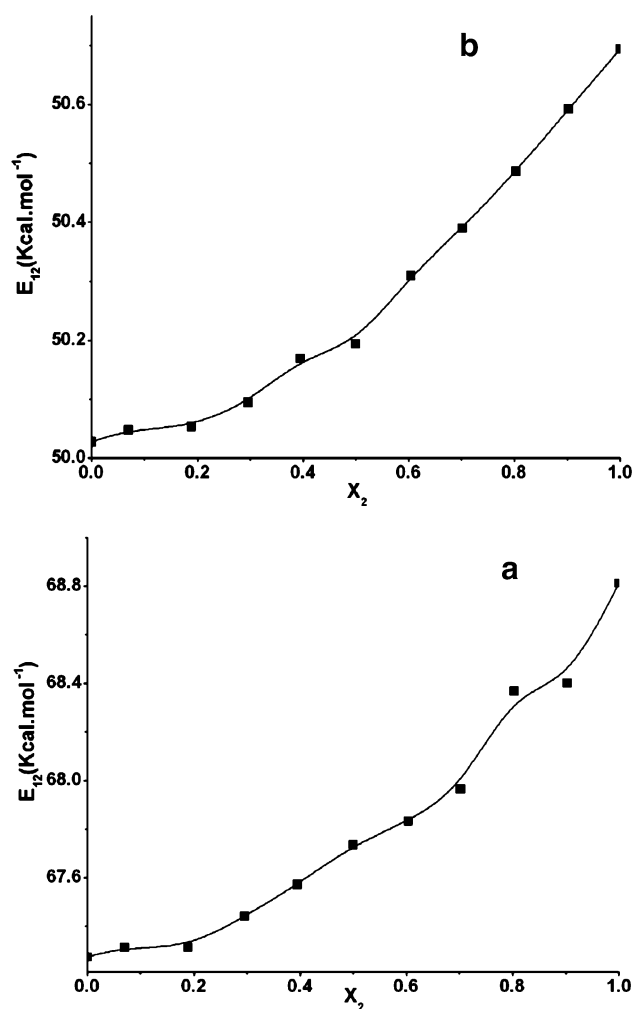


Fig. 7 Transition energies of DCMAQ (a), absorption (b). Emission versus X_2 (the bulk mole fraction of 2-Propanol) in binary mixtures of CHCl_3 /propan-2-ol

state of DCMAQ also increases. The non-linearity of plots show that there exhibits a preferential solvation of DCMAQ by anyone of the solvent (CHCl_3 or propan-2-ol). The observed negative δ_{s2} , the lower mole fraction in the solvation microsphere than the bulk mole fraction and the observed f_2/f_1 which are less than unity with respect to propan-2-ol conclude that DCMAQ is preferentially solvated by CHCl_3 . It may be due to the self-association behaviour of propan-2-ol, because it is a polar protic solvent and it can be associated through hydrogen bonding. Moreover a steric hindrance offered by branched alkyl groups attached to the OH group of propan-2-ol restricts the formation of hydrogen bonding between the solute and solvent. This leads to the situation that DCMAQ is preferentially solvated by CHCl_3 [30, 31].

In some cases, wavelength maximum used for solvation studies showed a higher value in the binary mixtures than for the pure solvents. This behaviour can be described in

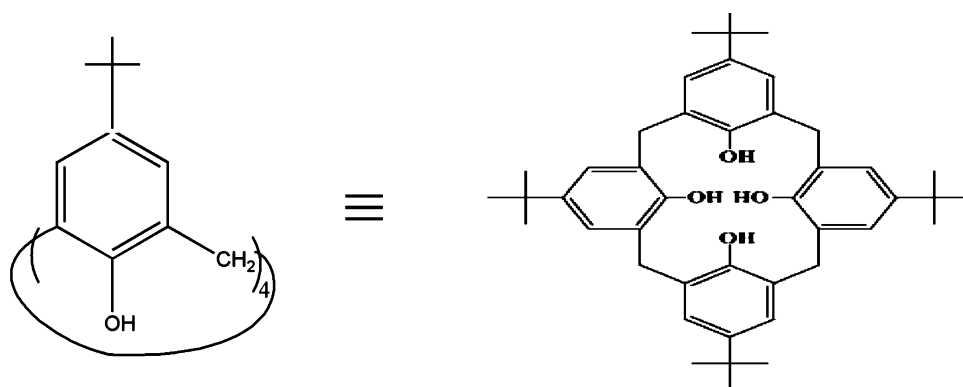
terms of synergistic in the sense that the joint action of the two solvents in the mixture achieves an effect nonexistent in the individual. This synergism is produced by hydrogen bonding between the hydrogen bond acceptor and the hydrogen bond donor to give a hydrogen bonded complex, which is often more polar than either of the two pure solvents [38]. The present case did not display synergistic behaviour. The low capability of this alcohol to form hydrogen bonded CHCl_3 /propan-2-ol aggregates may explain the fact that the curve is not synergistic. In addition, the lack of synergism in this mixture may be a result of the fact observed that the absorption maximum for the pure CHCl_3 differs greatly from the values for the pure propan-2-ol.

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 $\text{ROH}(\%) = \frac{(\lambda_{0.5} - \lambda_{0.0})}{(\lambda_{1.0} - \lambda_{0.0})} \times 100$ where $\text{ROH}(\%)$ is the estimated mol% 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 [39]. In CHCl_3 /propan-2-ol mixtures, only 29 and 32% of the propan-2-ol molecules are available in mixture containing 50% of each one of the mixed bulk components in ground state and excited state, respectively. This indicates that only 29 and 32% propan-2-ol molecules compete with the CHCl_3 molecules to enter into the cybotactic region. This leads to DCMAQ is being solvated by CHCl_3 .

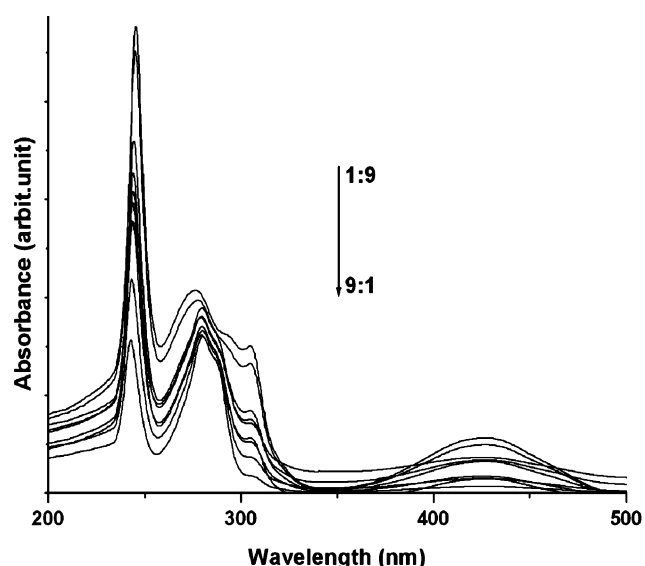
Molecular recognition of DCMAQ by tBC

Study of the UV-Vis spectrum

The molecular structure of tBC is given in Fig. 8. Absorption spectral responses of DCMAQ in CHCl_3 upon addition of tBC in varying molar ratios of two compounds keeping the sum of both concentration equal to 0.08 mM is shown in Fig. 9. Absorption pattern show a major sharp peak at 245 nm and broad peaks at 275 and 420 nm with a shoulder at 305 nm. The peaks at 245 and 275 nm show blue shift and red shift in tBC rich region, respectively, in addition to the increase in intensity in DCMAQ rich region. The absence of isobestic point in the absorption spectra suggests that multiple-site binding and dye aggregation may occur within the used range of concentration [11]. The UV visible spectrum of tBC-DCMAQ complex did not show any new absorption band. This observation has ruled out the possibility of formation of charge transfer complexes between tBC and DCMAQ [19].

Fig. 8 Molecular structure of tBC

The observed peaks around 245 and 275 nm are assigned to π - π^* transition. The observed band at 420 nm does not show appreciable change in wavelength maximum of absorption. So we have taken 275 nm band to analyse host-guest interaction. The change in wavelength maxima and absorbance (at wavelength maxima) at 275 nm with addition of tBC reveals the quinone-calixarene interaction. And also it suggests that the main contribution to the varying of host-guest interaction must come from polar interaction and hydrogen bonding of the guest with host molecules. Job's method [11] is widely used in the spectroscopic determination of complex stability constants also in calixarene chemistry. To determine the stoichiometry of the complex formation 0.08 mM stock solution of tBC and DCMAQ were mixed in nine different $[H]/([G]+[H])$ ratios by step wise (n) ml of host to $(10-n)$ ml of guest solutions ($n=1-9$) keeping 0.08 mM total concentration ($[G]+[H]$). The change in absorbance obtained in the peak at 275 nm under the effect of guest-host interaction (δA)

**Fig. 9** Optical absorption spectra of tBC:DCMAQ in different molar ratio

was plotted (Fig. 10) against the mole fraction of tBC (Job method of continuous variation). Job's curve shows a minimum value at 0.39 in the mole fraction of tBC indicating the formation of 1:2 complexes. The low absorbance value in the complex when compared to free guest is due to the intermolecular hydrogen bond formation between C=O group of guest and phenolic hydroxyl group of host.

Study of fluorescence emission spectrum

The fluorescence emission spectra of DCMAQ in the presence of tBC is presented in Fig. 11. It shows the emission maximum at 540 nm. The emission spectrum of DCMAQ is altered in the presence of tBC. Generally, the iso-emissive point in the emission spectra is an indication of two species are in equilibrium (i.e. the formation of 1:1 complexes) [40]. In our case, the lack of iso-emissive point suggests that there is a possibility of interaction between more than one molecule of DCMAQ with one molecule of tBC or vice versa. The fluorescence intensity decreases with an increase in the concentration of tBC. Moreover, the enhancement in the fluorescence emission intensity is also observed in the presence of tBC at the stoichiometry ratio

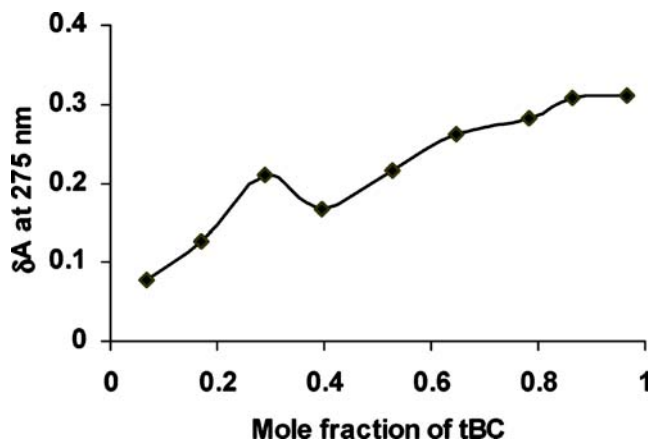
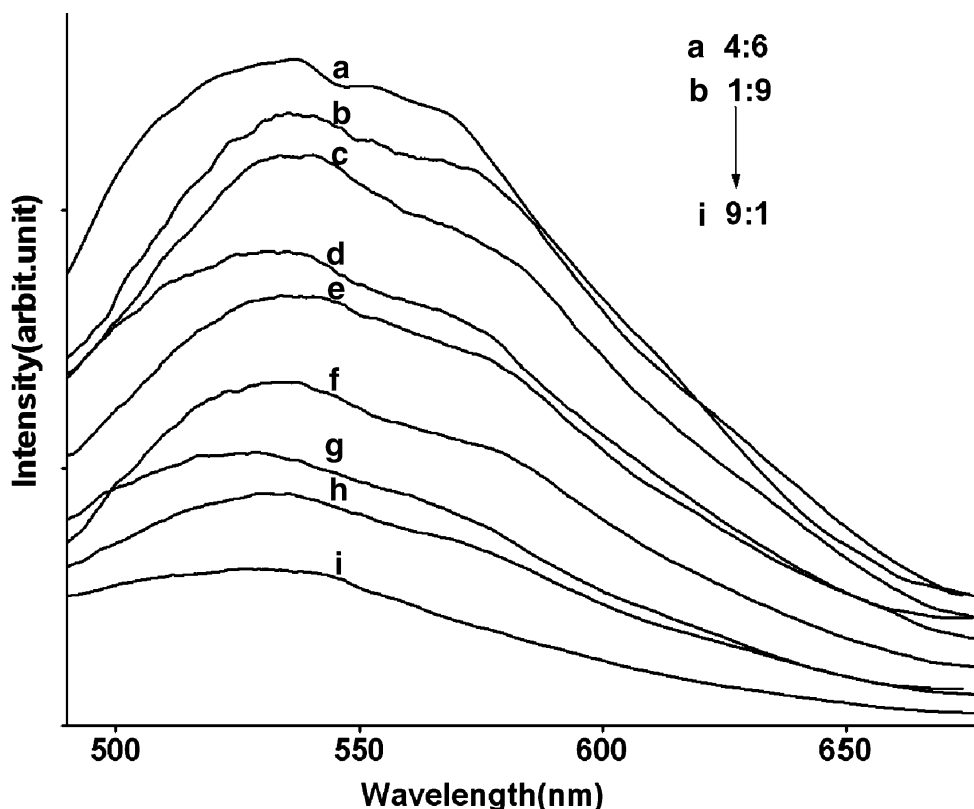
**Fig. 10** Variation of δA at 275 nm with mole fraction of tBC

Fig. 11 Fluorescence emission spectra of tBC:DCMAQ complexes in CHCl_3



1:2 compared to other host/guest ratios. Integrated area under the emission spectra of DCMAQ in the absence of tBC (Fig. 3) as well as for DCMAQ in the presence of tBC (Fig. 11) was obtained in order to calculate the fluorescence quantum yield. The calculated quantum yields using Parker's method [41] (by comparison of the integrated area under the emission spectra) are tabulated in Table 2. 1,5-Diaminoanthraquinone is taken as a fluorescence standard ($\phi_r=2.46 \times 10^{-4}$) [42]. From this Table 2 it is noted that there is a fluorescence quenching of host–guest complexes in addition of tBC with respect to DCMAQ itself and there is an enhancement of fluorescence quantum yield at 1:2

stoichiometry ratio (i.e. volume ratio 4:6) when compared to other ratios. Moreover, the plot of F/F_0 versus mole fraction tBC (Fig. 12) gives the further support for the enhancement of quantum yield. Because this figure reflects that there is an increase in the value of F/F_0 at the stoichiometry ratio of 1:2 host–guest complexes. Here F and F_0 are the fluorescence intensities in the presence and in the absence of tBC, respectively.

It should be noted that the spectra in Fig. 11, a blue shift of the spectrum was observed with a fluorescence maximum of 526 nm in the tBC rich region with respect to 540 nm in DCMAQ itself (Fig. 3). Generally, the shift in

Table 2 Fluorescence quantum yield (ϕ) of tBC:DCMAQ complexes

tBC:DCMAQ (volume ratio)	$\phi \times 10^{-4}$
DCMAQ	0.42
1:9	0.37
2:8	0.34
3:7	0.30
4:6	0.41
5:5	0.29
6:4	0.23
7:3	0.19
8:2	0.16
9:1	0.10

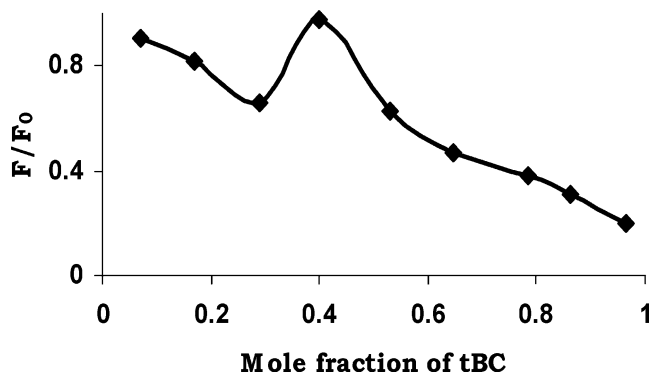
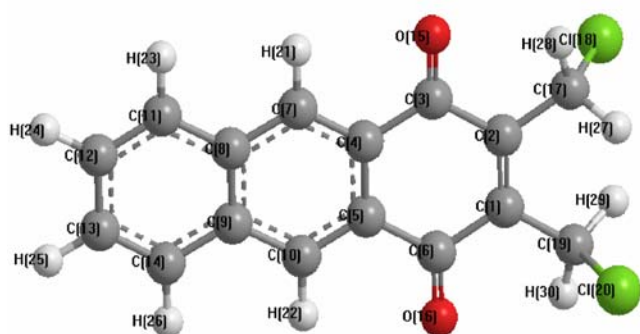


Fig. 12 Variation of F/F_0 with the mole fraction of tBC

emission band maximum of guest in the presence of host molecule conforms that guest molecule goes in to the cavity of host molecule [43]. But it is not applicable in the present case. It may be explained by the molecular dimension of guest and host molecule. The obtained molecular dimension of DCMAQ by MOPAC/AM1 is shown in the Fig. 13. The molecular dimension of tBC is $3 \times 2 \text{ \AA}$ [19]. It suggests that on approaching the upper rim of tBC, DCMAQ hits the upper rim edge before it interacts with benzene π system. That is the cavity of tBC is too small to include two DCMAQ molecules. This observation ruled out the possibility of DCMAQ to be included by tBC. But the change in emission wavelength maximum and the intensity variation proves that there is a possibility of interaction between these two guest–host complexes. The observed blue shift is minimum in DCMAQ rich region and it is maximum at tBC rich region. The minimum blue shift is due to a strong interaction between host–guest molecule through intermolecular hydrogen bonding between hydroxyl group in the lower rim of tBC and the carbonyl group of the guest molecule. And the observed maximum shift in the tBC rich region is a result of either by decreasing the strength of hydrogen bonding interaction or guest molecule goes to a polar region [26]. Further, quenching of fluorescence in DCMAQ on addition of tBC and enhancement of the fluorescence at 1:2 stoichiometry ratio suggest that there may be an electrostatic interaction called π – π interaction between the aromatic π electron systems of tBC phenolic units and that of the aromatic DCMAQ molecule and coexistence of intermolecular hydrogen bond between the OH group of tBC and C=O group DCMAQ [25, 40, 44].



H25 - C120	-	10.444 Å
H24 - C118	-	10.397 Å
H23 - H26	-	5.009 Å
O15 - O16	-	5.403 Å
C118 - C120	-	4.539 Å
H28 - H30	-	5.101 Å

Fig. 13 Optimized structure of DCMAQ

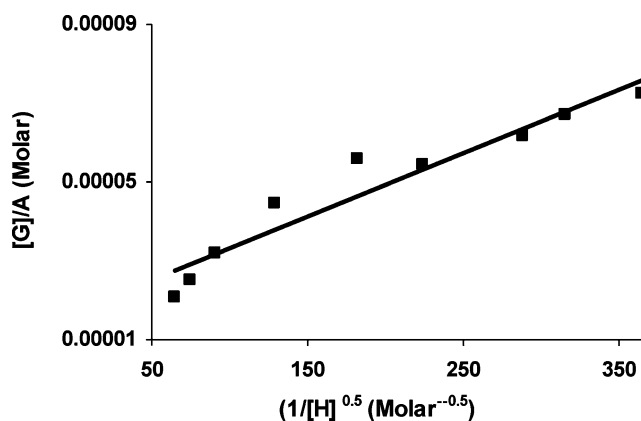
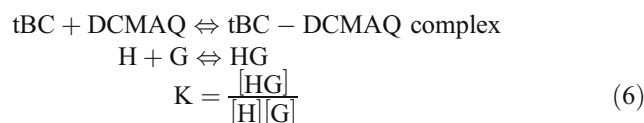


Fig. 14 Variation of $[G]/A$ at 275 nm with $1/[H]^{0.5}$

Determination of association constant

The calixarene–quinone interaction was further investigated by determination of association constant (K) between calixarene and quinone as per the Eq. 6.



To obtain association constant absorptivity measurements were made on dilute solutions containing tBC and DCMAQ in various molar ratios, where the ratio of tBC is changed from $0.75 \times 10^{-5} \text{ M}$ to $0.24 \times 10^{-3} \text{ M}$ and the data were analysed by the double reciprocal plot (Fig. 14) of the data (the Hildebrand–Benesi expression) [45] as per Eq. 7.

$$\frac{[G]}{A} = \frac{1}{K\alpha[H]^n} + \frac{1}{\alpha} \quad (7)$$

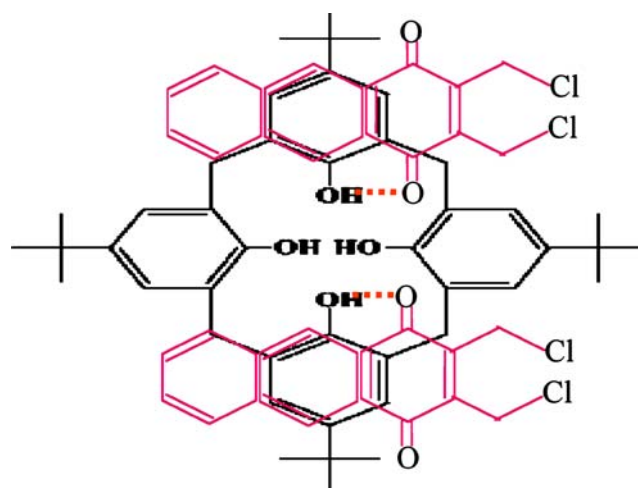


Fig. 15 Optimized structure of tBC-DCMAQ complexes

where $[H]$ is the concentration of tBC, $[G]$ concentration of DCMAQ and A is the absorptivity at 275 nm. α is the constant and K is the association constant for the reaction. By plotting the $[G]/A$ versus $1/[H]^n$ graph with different n values, the n that results a straight line can be taken as the number of host molecules, consequently, the complexes ratio can be taken as 1: n . From the intercept and the slope of the straight line the association constant can be obtained. From Fig. 14, the evaluated association constant value is equal to 100 M^{-1} and $n=0.5$ which also conforms that the composition ratio of the host–guest complex is 1:2 for tBC:DCMAQ. The possible structure of tBC:DCMAQ stabilized complexes is shown in the Fig. 15.

It is interesting to compare our results with previously reported data for DCMAQ in Calix[8]arene [26], which has a larger cavity size ($3 \times 11.7 \text{ \AA}$). 1:4 stoichiometry complexes of DCMAQ by Calix[8]arene was reported with a higher value for association constant (529 M^{-1}). It is proposed that the probe experiences strong interaction with Calix[8]arene compared to *p*-tert-butylcalix[4]arene.

Conclusions

Optical absorption and fluorescence emission techniques have been used to study solvent effect, preferential solvation and solute–solvent interaction, interaction of DCMAQ in [carbon tetrachloride/chloroform, chloroform/ acetonitrile, chloroform/ propan-2-ol] solvent mixtures. The optical absorption and fluorescence emission spectral studies indicate that DCMAQ is preferentially solvated by CHCl_3 in the above binary mixtures. This can be conformed from the observed local mole fraction, non-linearity of the E_T plot, preferential solvation index (δ_2) and (f_2/f_1) values. Recognition of the DCMAQ by tBC was elucidated on the basis of absorption and fluorescence spectroscopic studies. Fluorescence quenching of DCMAQ by tBC has been observed in solution due to the formation of a host–guest complexes. The proposed structure of the 1:2 complex is accompanied by the enhancement of the fluorescence at the stabilization conclude that hydrogen bonding and π – π interaction between tBC and DCMAQ in the ground state took place cooperatively, and this gave rise to enhancement of the fluorescence quantum yield.

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