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Structural Investigations on Quinone Methides for Understanding Their Properties in Confined Media

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Abstract

Encapsulation of 4−[(4′-hydroxy−3′,5′-dimethylphenyl)(aryl)-methylene]−2,6−dimethyl-cyclohexa−2,5−dienones (when aryl = 4−hydroxyphenyl **1**, 4−methoxyphenyl **2**, 2,3,4-trimethoxy phenyl **3**) by β-cyclodextrin is studied. The compound **2** is selectively encapsulated by β-cyclodextrin. The result is rationalised by analysing the structural parameters from the crystal structure of **1**–**3**. The visible spectra of the compounds **2** and **3** at pH 9.0 show red shifts on the absorption maxima upon addition of cetyltrimethylammonium bromide (CTAB). For example, addition of a solution of CTAB to aqueous ethanolic solution of **2** at pH 9 causes shift of the absorption at 578–593 nm ($\Delta\lambda_{max} = 15$ nm). The advantage of this observation is taken to use **2** and **3** to determine the critical micelle concentration of CTAB in basic medium.

Introduction

Varieties of intermediates such as radical [1–3], cation [4–7] and anion [8] are easily generated from quinone methides. These intermediates have characteristic colour properties. Due to electron delocalisation in the quinone methides their chromogenic properties are sensitive to microenvironments [9–13]. Thus, there is further scope to study the colour properties of these intermediates in confined medium [9] and they may have application as sensors. Molecules whose spectroscopic properties are responsive to environment created by solvent or guest–host interaction needs thorough attention to elucidate their utility aspects. We had earlier observed that quinone methides have different colour at different pH ranging from pH 3 to 9 [14]. Pyrocatecohol violet has quinone methide part in its structure and it has sensing properties to detect tin and bismuth in supramolecular environment [15]. In this study we make a correlation on the basis of solid state structural parameters of quinone methides **1**–**3** with the dimension of cavity of different cyclodextrins for understanding selectivity in encapsulation of these quinone-methide by cyclodextrins. The quinone methides under investigation are **1**–**3** as shown in Figure 1. They are chosen for this purpose as these molecules have the distinction of having well separable visible absorptions of their cation, anion and of their own [14]. We also report here how these quinone methides changes thier colour properties in micellar solution. In the process we demonstrate a simple way to determine critical micelle concentration (CMC) of cetyltrimethylammonium bromide by using the chromogenic property of these quinone methides.

Materials and methods

The quinone methides **1**–**3** were synthesised by oxidation of the parent *bis*-phenols by ammonium persulphate as described earlier for analogous compounds [14]. The cyclodextrins and cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich Chemical Co. and were used without further purification. Deionised water from a Millipore Elix−6 was used in all the experiments reported here. The buffer solutions for different pH (4, 7 and 9) were obtained from Sigma and used as obtained. The solvents used in this study were of HPLC grade and used as obtained. In all the experiments, pH were measured by using combined glass electrodes and with a pH-meter calibrated by appropriate buffer solutions. When the comparison on the visible spectroscopic properties is done the substrate concentration and the identical solvent compositions were used. The nmr spectra were recorded on a

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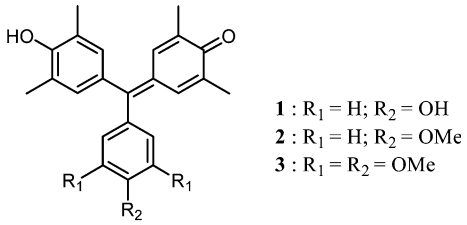

1-3

1 : $R_1 = H$; $R_2 = OH$
2 : $R_1 = H$; $R_2 = OMe$
3 : $R_1 = R_2 = OMe$

Figure 1.

Varian-Mercury 400 MHz nmr spectrometer using TMS as an internal standard.

X-ray crystallographic study

Compound **1** was crystallised from diethylether/hexane solution, **2** from acetonitrile/water solution, **3** from acetonitrile/dichloromethane solution. X-ray diffraction data were collected on Bruker 3-circle diffractometers with CCD area detectors ProteumM APEX (for **1**, **2**) or SMART 6000 (for **3**), using graphite-monochromated MoKα radiation (λ = 0.71073 Å) from a 60W microfocus Bede Microsource® with glass polycapillary optics (**1**, **2**) or a sealed tube (**3**). The low temperature of the crystals was maintained using Cryostream (Oxford Cryosystems) open-flow N_2 cryostats, thus the structures were determined at 120 K. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software [16]. All C and O atoms were refined in anisotropic approximation. All H atoms in **1**, the hydroxyl H atoms in **2** and all but disordered H atoms in **3** were refined in isotropic approximation, the rest were treated as 'riding' in idealised positions.

Encapsulation of quinone methide in cyclodextrin

Stock solutions of cyclodextrins (α, β and γ) of 2 mM concentration were prepared in deionised water (25 ml). Similarly, stock solutions of the quinone methides (10^{-5} mM) were prepared in ethanol (for **1** and **2**) and in 1:1 ethanol-water for **3**. During a typical experiment a calculated volume of such a solution was taken out with a graduated pipette and added to the cuvette (in case of UV–vis studies) and the volume was made up with water. To this solution the quinone methide was added from the corresponding stock solutions in aliquots (10 μl) and the visible absorption spectra were recorded. Triethylamine was used to generate the anion of the parent compounds when encapsulation of the anion was studied.

Determination of the CMC:

Stock solution of CTAB in deionised water (10 mM) was prepared and calculated amounts of the solution (in aliquots) were taken for each experiment from this stock solution. In typical experiment, the quinone methide solution was prepared in the cuvette by adding 50 μl of the respective stock solution (2 mM) in buffer solution of pH 9 prepared in deionised water and making up the volume to 2.5 ml. The visible spectrum of this of the solution was recorded. The same solution was taken out of the spectrometer and the surfactant solution was added in small aliquots (10 μl) from the CTAB stock solution (10 mM). The visible absorption spectra of solution after each addition were recorded. This process continued so that sufficient number of absorptions is obtained for plotting the concentration of CTAB *versus* absorbance. Independent titration experiments with CTAB at different concentrations of quinone methides were carried out to study the concentration dependence of micelle formation. Volume corrections were done in each case.

Results and discussion

The chromogenic properties of quinone methides **1**–**3** in confined medium was studied by monitoring the changes in the visible spectra of the compounds in solution by externally adding cyclodextrin solutions. The compound **2** in aqueous ethanol (20% v/v) has visible absorption at 446 nm. The same compound under identical condition but with cyclodextrin has visible absorption at 456nm. This suggests the presence of β-cyclodextrin in solution has an effect on the electronic spectra of **2**. On the other hand the visible spectra of the compound **2** with β-cyclodextrin in aqueous solution containing ethanol (5% v/v) with excess triethylamine has absorption at 595 nm. Whereas the compound **2** under identical condition but without β-cyclodextrin has absorbance at 581 nm. This absorption peak is due to the anion of 2. These show that the compound **2** in neutral form as well as its anion interacts with β-cyclodextrin. Such interaction may arise from an ecapsulation process of **2** into the cavity of β-cyclodextrin as shown in Figure 2. Since in the neutral and basic medium cyclodextrin can cause shift of the absorption maximum of the compound **2** it can be concluded that the interaction between **2** and cyclodextrin is not effected by a basic medium. The compound **2** has poor solubility of in water, so the visible spectroscopic studies were performed in aqueous ethanol. But due to non-availabilty of ethanol-d^6 with us we have studied the interaction in DMSO-d^6 by mixing **2** with cyclodextrin and recording the proton nmr. On comparison of the spectra with parent compound significant effect on the chemical shift of methyl-groups at *o*-postions of the aromatic rings rings is observed. The parent compound has only a broad unresolved signal at 2.05 ppm from these methyl groups but the signals are splited into three singlets to appear at 1.87, 2.04, 2.14 ppm in the presence of β-cyclodextrin. The methoxy peak of the parent compound appears at 3.78 ppm whereas it appears at 3.81 ppm on interaction with β-cyclodextrin (Figure 3). There is also a significant shift

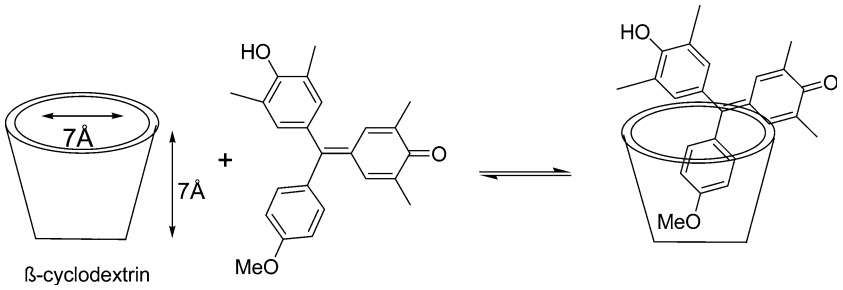

Figure 2. Encapsulation of **2** in β- cyclodextrin.

in the quinonic protons of the parent compounds; on interaction with β-cyclodextrin it shifts from 6.8 to 6.9 ppm. The observation of multiple number of signals from methyl-groups of **2** on interaction with β-cyclodextrin suggests that there is restricted rotation of the phenolic aromatic ring. It is also interesting to note that the compound **2** shows only a broad siglet for the aromatic methyl protons. This happens due to delocalisation of π–electrons over the two rings making them close to equivalent, thus, the encapsulation of the compound possibly decreases the delocalisation and allowing the two rings to be distinguisable.

It is also interesting to note that the compounds **1**–**3** do not show any changes in the visible absorbance in the presence of either of α and γ-cyclodextrins. This shows that they do not interact with α and γ-cyclodextrins. The visible absorption of the compound **2** occurs at 446 nm which has high extinction co-efficient (5.1×10^5 mol^{-1} cm^{-1}), thus we could not ascertain the composition of the adduct of β-cyclodextrin with **2** as in such dilute solution it remains in equilibrium and we could not carry out low temperature experiments because of precipitation of the compound due to poor solubility. However, we took advantage of pH measurement as an indirect tool to study the composition of the encapsulated form. For this purpose we carried out an indirect method by measuring the pH of an aqueous ethanolic solution of **2** in the presence of excess cyclodextrin by adding aqueous triethylamine. The result obtained from this titration is compared with the pH plot of the parent compound obtained from titrating the parent compound with triethylamine in the absence of β-cyclodextrin. From this comparison we have observed that there are two inflection of pH in the titration plot when carried

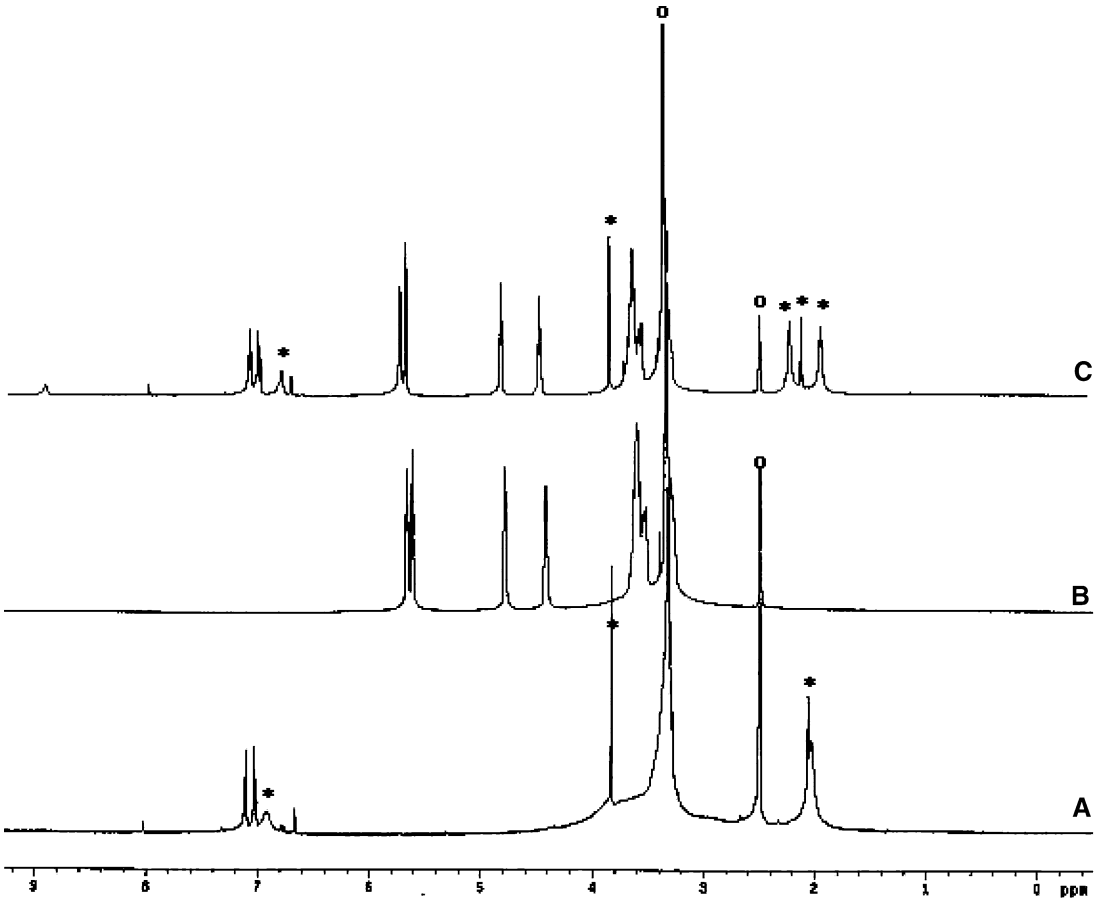

Figure 3. ^{1}H-nmr spectra (400 MHz, DMSO-d^6) of (a) **2**, (b) β-cyclodextrin (c) mixture of β-cyclodextrin and **2.**

out in the presence of β-cyclodextrin (Figure 4b) whereas there is only one such inflection of pH in the case of the parent compound alone (Figure 4a). Although this experiment does not allow us to make conclusion on the nature of the adduct but it clearly depicts that at room temperature approximately 50% of the molecule **2** gets encapsulated into the cyclodextrin.

The compound **3** has absorption maximum at 440 nm and the corresponding anion of **3** has at 581 nm. Shift in the visible spectra of **3** and its anion were not observed in the presence of β-cyclodextrin. Same is true for the visible spectra of compound **1** also. This implies that compound **2** can selectively interact with β-cyclodextrin. To reason out the selective interaction of **2** with β-cyclodextrin we looked at the structural features of **1**–**3** and compared with the cavity size of cyclodextrins. It is well known fact that depending on the type of cyclodextrins, the cavity sizes are different [17]. Encapsulation depends on the size of the molecule and its hydrophobicity hence it is very selective to different forms of cyclodextrins. Among the cyclodextrins, the β-cyclodextrin has inner cavity diameter 7 Å with a depth of 7 Å (Figure 2). Compounds **1**–**3** have structures such that three rings are disposed in three different directions of a central carbon atom. In order to see which of the segment of these molecules would be encapsulated into the cyclodextrin we have analysed the dimensions of different segments of these three molecules **1**–**3** from their crystallographic data. For this purpose the crystal structure of molecules **1**–**3** were determined. The structure of molecules **1** and **2** have revealed that they do not have crystallographic symmetry (Figure 5) and are found to be conformationally similar to 2,6-dimethyl−4-(diphenylmethylene)-cyclohexa−2,5-dienone in its three polymorphs already reported in the literature [18, 19]. In these molecules (**1** and **2**), the central C(7) atom has

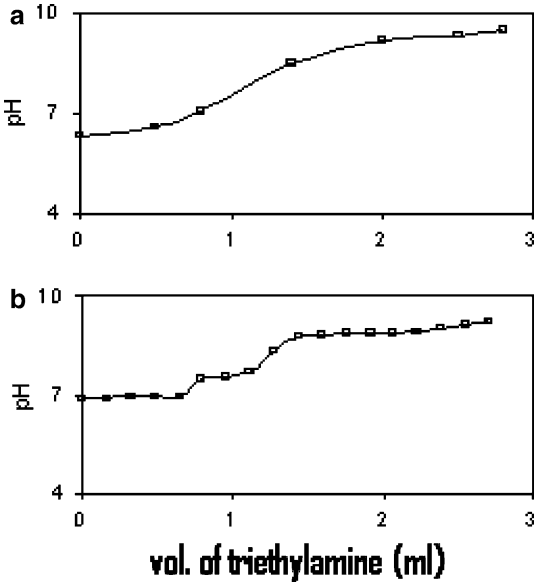

Figure 4. Titration plots of **2** (10^{-5} mM) with triethylamine (0.1 M in H_2O) in (a) aqueous EtOH (20% v/v) (b) β-cyclodextrin (2 mM) aqueous EtOH (20% v/v) at 25 °C (pH values are not absolute as non-aqueous medium was used).

planar-trigonal bond geometry, with the two planar benzene rings and one nearly-planar quinonic ring (Q) inclined to its plane in a propeller-like fashion. The torsion angles around the C(7)–C(4) and C(7)–C(14) single bonds are 39.5° and 36.5° in **1**, 42.4° and 34.4° in **2**, respectively.

More remarkable is the substantial twist around the double bond C(7) = C(24), amounting to 18.0° in **1** and 20.1° in **2**. This occurs obviously due to steric repulsion between peri-H atoms. Such conformation of the molecules precludes any effective stacking of the rings. Molecule **3** (Figure 6) is located on a crystallographic twofold axis, which passes through the atoms C(1), C(4) and C(7). The existence of a twofold axis relating a quinonic and a phenolic moiety is not a real one but it originates from the disordered nature of the molecule. The methoxy group $O(1)C(5)H_3$ is disordered between two positions related by this axis. The high displacement parameters of the $O(3)C(6)H_3$ group also indicate a disorder, probably of a continuous character, which could not be represented satisfactorily by discrete atomic positions. Since the aromatic rings are crystallographically equivalent, distinction between the aromatic ring and quinonic ring is not possible in this case.

We observe a superposition of a –O(2)–H···O(2″) = and a =O(2)···H–O(2″)– hydrogen bonds (O(2)–H 0.97, H···O(2″) 1.73 Å, O–H···O 169°), linking the molecules into an infinite chain parallel to the [1 0 1] crystallographic direction. As in **1** and **2**, the C(7) atom in **3** has a planar-trigonal geometry, with a propeller-like orientation of the three benzene/quinone rings around it. The torsion angles around the C(4)–C(7) and C(7)–C(14) bonds are 29.7° and 33.3°, respectively.

In order to have an insight into the extent of delocalisation present in the molecules, the multiple bond character around the C7 carbon is analysed. The bond distances and bond angles involving C4, C7, C14 and C24 (C14′ in case of **3**) for the quinone methides are given in Table 1. The bond distances suggests that in the case of **1**and **2**, the quinonic and aryl rings could be easily distinguised in the solid state. However, in the case of **3** the disorder in the system precludes an effective understanding of the extent of quinonic component in the ring. Crystal parameters of compound **1**–**3** are listed in Table 2.

The distances of the segments that may get encapsulated to cyclodextrin are demarcated in Figure 7. The distances that would play crucial role in the formation of inclusion compound are listed in Table 3. Table 3 suggests that all the independent aromatic rings except one ring of **3** has appropriate size to be accommodated into the cavity of β-cyclodextrin. The cavity of α-cyclodextrin is too small to accommodate any of the aromatic rings of these molecules, whereas the diameter of γ-cyclodextrin being 9.5 Å would allow easy de-encapsulation due to weaker interactions relative to β-cyclodextrin. It is well known fact that the cavity of cyclodextrin in either of the forms facilitates encapsu-

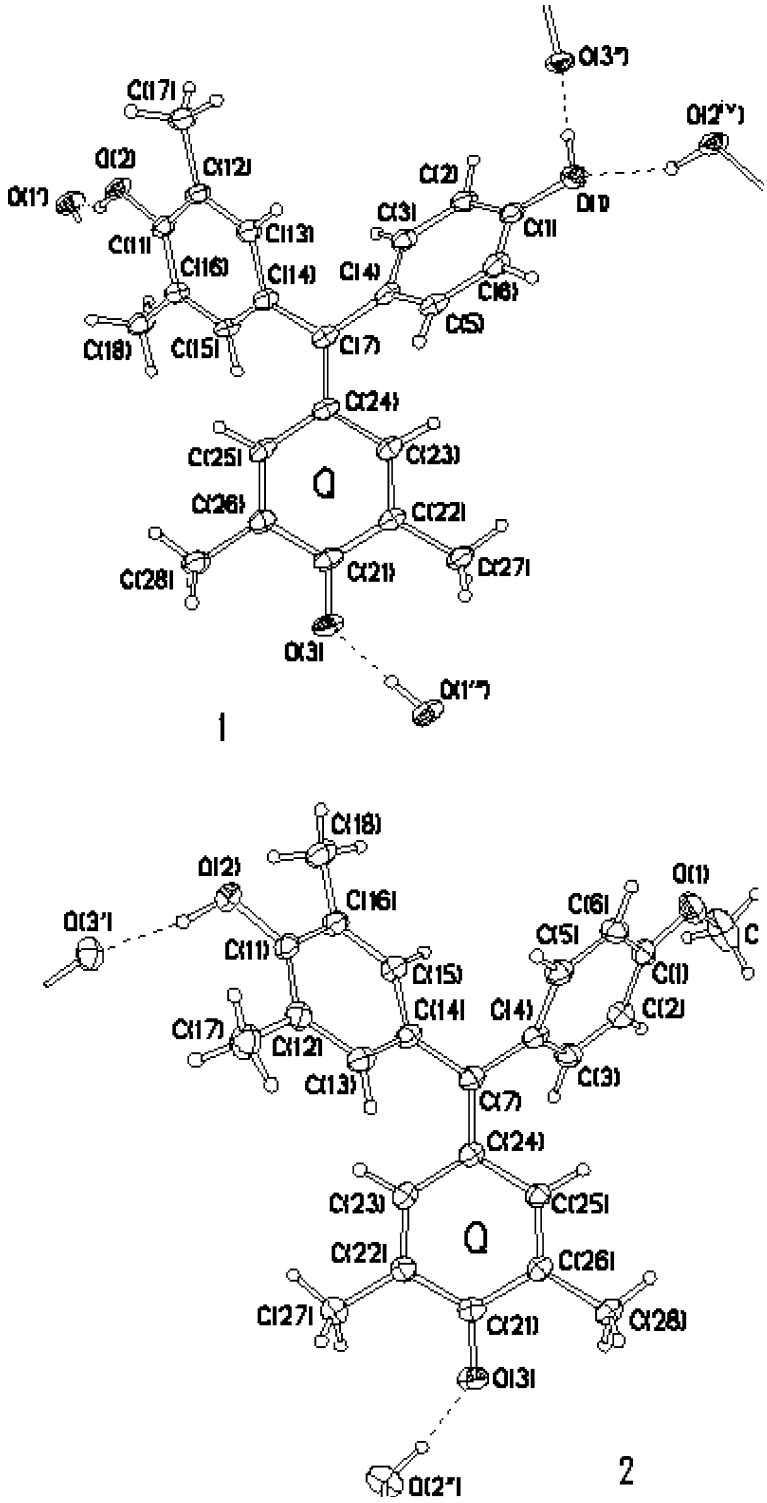

Figure 5. Molecules of **1** and **2** in crystal, with intermolecular hydrogen bonds. Symmetry transformations for **1**: (i) $x+\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$, (ii) $x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$, (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$, (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2}$; for **2**: (i) $1-x, y+\frac{1}{2}, 3/2-z$, (ii) $1-x, y-\frac{1}{2}, 3\backslash 2-z$. Thermal ellipsoids are drawn at the 50% probability level.

lation of the hydrophobic part into their cavity, thus the aromatic ring containing –OH group would be less likely to get encapsulated into the cyclodextrin. Logically it can be predicted that the rings having correct size and more hydrophobicity will get encapsulated preferentially into the cavity of β-cyclodextrin. The molecules under consideration have both quinonic ring and a phenolic group separated by a methine group. Thus, these molecules have conjugation between the two rings making them equivalent and they are unlikely to get encapsulated to cyclodextrin due to their hydrophilic nature. The compound **1** has hydrophilic end on two aromatic rings and the quinone part can delocalise over these rings; accordingly, the molecule should not get encapsulated to any of the cyclodextrin even if it satisfies the size requirement for encapsulation. In fact, this is true

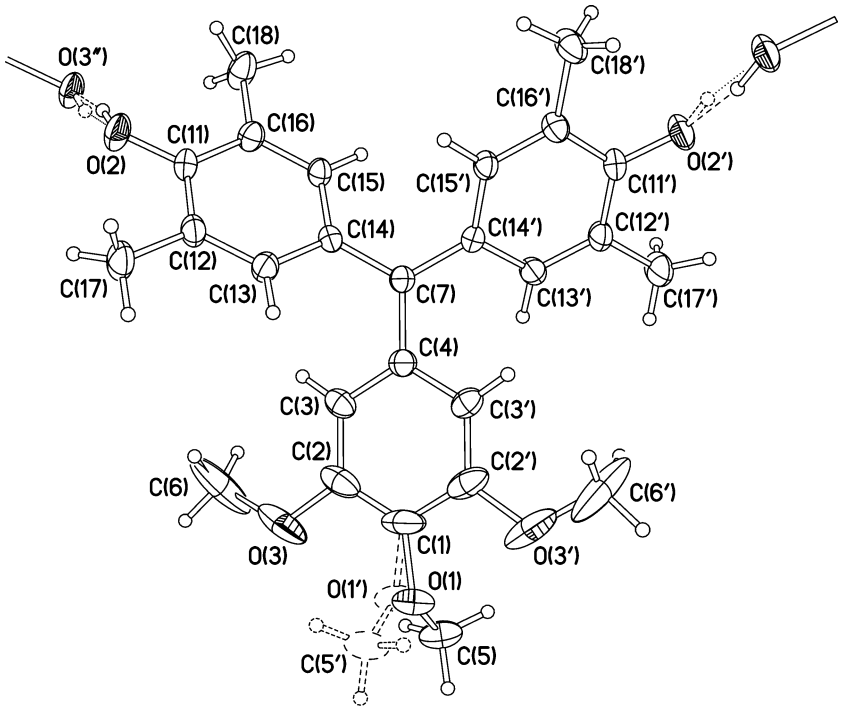

Figure 6. Structure of **3** (atoms generated by the twofold axis are primed; those generated by the inversion centre are double-primed).

Table 1. Selected bond distances (Å) and bond angles of **1**–**3**

	C4–C7	C7–C14	C7–C24	C24–C7–C4	C14–C7–C4	C14–C7–C24
1	1.476(2)	1.474(2)	1.394(2)	121.8(2)	116.2(2)	121.8(2)
2	1.474(1)	1.466(1)	1.396(1)	121.4(1)	116.5(1)	122.1(1)
3*	1.470(3)	1.436(2)	1.436(2)	119.5(1)	119.5(1)	121.0(2)

* In case of **3**, C24 is denoted as C14′.

and on addition of β-cyclodextrin to a solution of **1** the visible spectral characteristic shown by its cation, anion as well as the neutral molecule remains unchanged.

Table 2. Crystal data and experimental parameters[a]

Compound	**1**	**2**	**3**
Formula	$C_{23}H_{22}O_3$	$C_{24}H_{24}O_3$	$C_{26}H_{28}O_5$
Formula weight	346.41	360.43	420.48
T (K)	120	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (#15)	$P2_1/c$ (#14)	$C2/c$ (#15)
a (Å)	13.361(1)	10.047(1)	21.246(5)
b (Å)	16.021(2)	13.904(2)	11.937(3)
c (Å)	16.631(2)	14.571(2)	8.705(2)
γ (°)	95.69(1)	105.10(1)	95.50(1)
V (Å^3)	3542.4(6)	1965.2(4)	2197.5(9)
Z	8	4	4
μ (mm^{-1})	0.09	0.08	0.09
Total reflections	17182	23571	12098
Unique refls.	4070	5736	2522
R_{int}	0.066	0.037	0.081
Refls. $I > 2\sigma(I)$	2577	4438	1823
R [F, $I > 2\sigma(I)$]	0.048	0.045	0.054
wR (F^2, all data)	0.115	0.131	0.152

[a]Far CIF files of the compounds 1–3. The CCDC Nos. are 253495, 253496 and 253497.

It is reported in the literature that the micelles of CTAB with different amounts of 1,3,5-trimethylbenzene can be modified by silica to obtain materials having different pore sizes [20–21]. This is interesting, as it suggests that an electron rich aromatic compound can be a component of such micelle. Thus, an aromatic compound having a chromophore whose colour property is sensitive to solvent or micro-environment would be of interest to evaluate the CMC. With this background and the initial observation on change that occurred in visible spectra of quinone methide on encapsulation, we studied the visible spectra of quinone methides in the presence of CTAB as surfactant. It is found that the absorption maximum of the anion of **1** at 572 nm in aqueous ethanol (2% v/v) shifts to 562 nm upon addition of excess amount of an aqueous solution of CTAB. It is to be noted that this shift is dependent on the concentration of CTAB both in terms of intensity as well as position of absorption maximum. However, we could not get a regular pattern to come to a definite conclusion with compound **1**. But, there is a bathochromic shift in the absorption band of the anion of **2** upon addition of CTAB where the effects could be identified by a distinct colour change (from purple to blue). Thus, addition of an aqueous solution of CTAB to an aqueous ethanolic solution (2% v/v) of 2 at pH 9

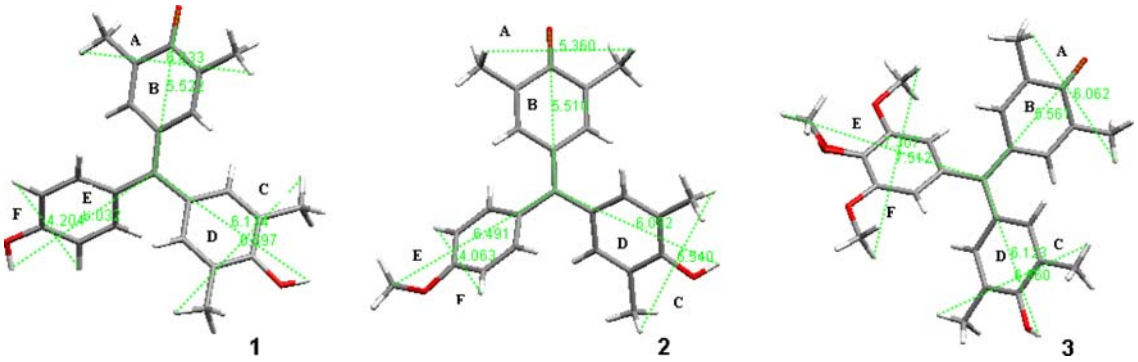

Figure 7. The breadth and length along different direction of **1**–**3** (refer Table 3 for details).

Table 3 Distances between different segments[#] in **1**–**3**

Distances (Å)	**1**	**2**	**3**
A	6.533	5.360	6.026
B	5.523	5.510	5.561
C	6.174	6.540	6.560
D	6.597	6.123	6.092
E	6.032	6.492	7.307
F	4.204	4.063	7.542

#As designated in Figure 7.

causes shift of the original absorption band at 578–593 nm. This effect is attributed to the change in environment around the anion of **2**. The cationic surfactant, CTAB contains polar head groups and non-polar alkyl groups; the molecules can organise in aqueous solution to form micelles beyond the CMC so that the hydrophobic alkyl groups avoid contact with water while the polar groups can interact with water. Thus, it should be possible to get the optimum condition for a micelle formation of CTAB in an aqueous ethanolic solution. The absorbance spectrum of **2** in the presence of different amounts of CTAB at pH 9 is shown in Figure 8. The upward arrow is suggesting the growth of new absorption at 593 nm on addition of CTAB, whereas the downward arrow shows the decrease in absorbance at 578 nm on addition of CTAB. Such process occurs till the micelle is formed. The plot of the changes in absorptions of at 578 and 593 nm *versus* the concentration of CTAB shows that there is a decrease in absorption at 578 nm with increase in concentration of CTAB. However, when the critical concentration for micelle formation is reached the absorption again starts increasing at 578 nm. The same kind of trend is observed in the absorption maximum at 593 nm also. The variation can be explained in terms of observing the changes that occurs due to closely spaced absorption maximum, which has overlapping effect. In a normal case when these two peaks are at well-separated wavelengths it would have been anticipated that the absorption should exponentially decay in case of absorption at 578 nm and increase exponentially at 593 nm. The intersection of these two plots should give the CMC. In fact this is true and the value of CMC can be obtained from analysis of the two spectra by constructing separate matrix for each components of absorption taking each absorption peak to have normal

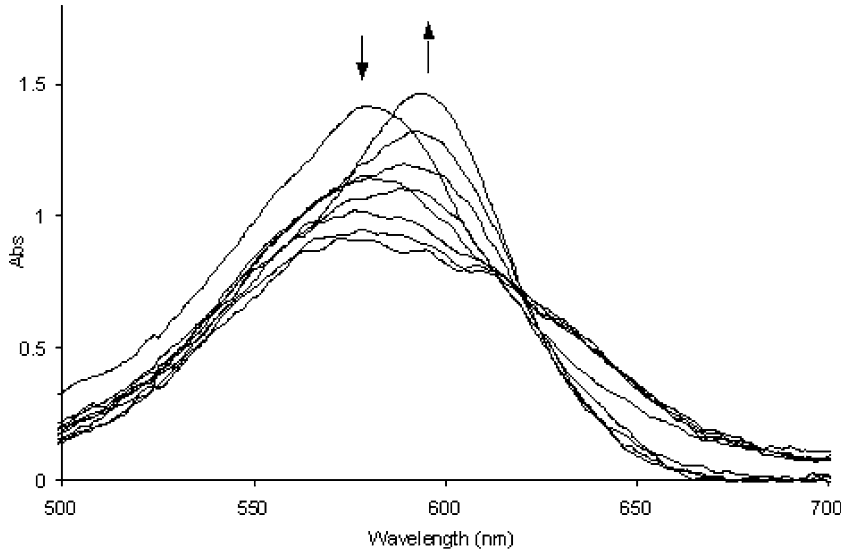

Figure 8. Change in absorbance of **2** (10^{-5} mM) at pH 9 upon addition of CTAB.

Gaussian shape. The apparent and real changes in absorption at two different wavelengths are shown in Figure 9.

Thus, the point at which the minimum absorption occurs corresponds to the CMC and it is found to be 0.62 mM when determined in aqueous ethanol by using **2**. Literature suggests that the CMC value for CTAB in water [20, 21] is 0.8 mM, so the observed CMC is about 22% lower than that is reported from measurements made in water. This deviation may be attributed to the difference in the solvent used in determining the CMC. Due to solubility problem, we had to take an aqueous ethanol (2%, v/v) solution of **2**, which was added to the aqueous surfactant solution. This led to the deviation of the CMC from pure water as the mixed solvent system modifies the structure of the Stern layer in two ways (a) by decreasing water molecules in the Stern layer and (b) by increasing electrostatic repulsion between the ionic head-groups. By these two ways the methylene groups of the alkyl chain of the surfactant can avoid contact with water. Consequently a lesser value of the CMC is observed. In order to prove this fact it was necessary to find out the CMC with an analogous compound in aqueous medium. The compound **3** is more soluble in water then the compound **2**. It is found that the aqueous solution of the anion of **3** has absorption at 581 nm, whereas in the presence of CTAB this anion has absorption at 596 nm. Thus, the absorptions at different concentrations of CTAB were recorded and a plot of concentration of CTAB *versus* the absorption of the anion of **3** at 581 nm as well as at 596 nm plotted. The apparent changes in absorbance with variation of CTAB are shown in Figure 10. It has also shown a similar trend as that observed for **2** but with a CMC at 0.8 mM for CTAB. This value exactly corresponds to the reported value of CMC [20, 21] for CTAB in water. Thus, in this study we could get a method to determine the CMC with a mixed solvent system which could be achieved in alkaline medium. The alkaline medium [22] has definite role in micelle-templated mesoporous silicates synthesis.

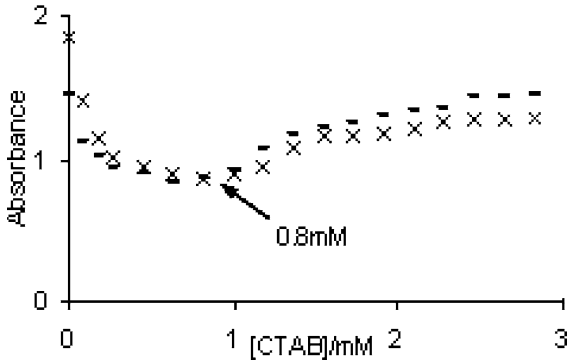

Figure 10. Apparent changes in the absorbance of anion of **3** (10^{-5} mM) at 581 nm (×) and 596 nm (−) in at different concentrations of CTAB.

The CMCs were also determined at different concentration of the quinone methides and it is found to be invariant of the concentration of quinone methides. It shows that the CMC of the surfactant CTAB is independent of the quinone methides but depends on the nature of the solvents. However, this method could not be used to find out CMC at neutral pH. It is due to the fact on addition of aqeous to neutral aqueous ethanolic solution of **2** results in precepitation of **2**.

In conclusion, we have demonstrated selective encapsulation of **2** in β-cyclodextrin and the result is rationalised on the basis of comparison of the structural parameters of the quinone methide with the cavity size. A simple method for determination of CMC is also demonstrated.

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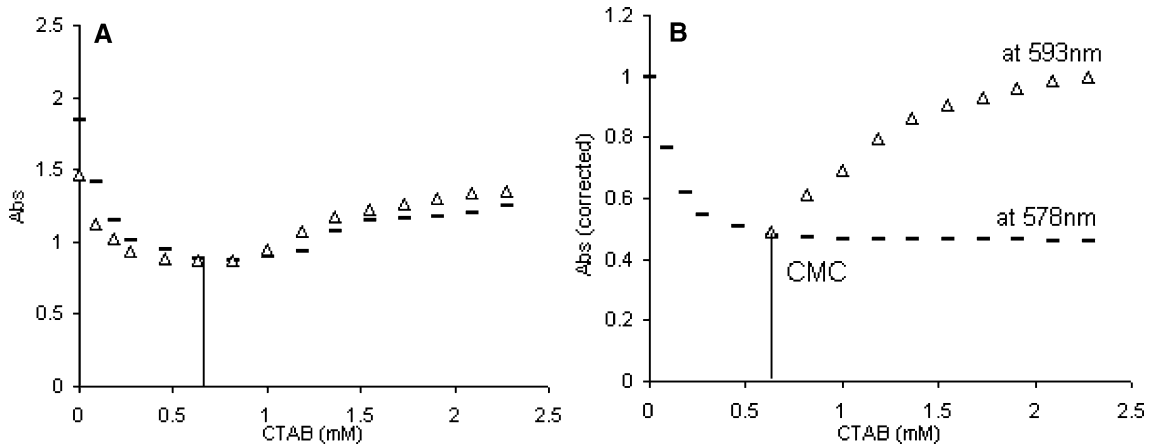

Figure 9. (a) Apparent and (b) corrected absorbance change for **2** (10^{-5} mM) at pH 9 with change in concentration of CTAB.

References

1. A. Rajca, S. Utamapanya, and J. Xu: *J. Am. Chem. Soc.* **113**, 9235 (1991).
2. S. Utamapanya and A. Rajca: *J. Am. Chem. Soc.* **113**, 9242 (1991).
3. D.A. Dougherty: *Acc. Chem. Res.* **24**, 88 (1991).
4. C.-H. Yang, W-F. Chen, B.-J. Jong, J.-C. Chang, M.J. Waring, L. Ma, and L. Sheh: *J. Am. Chem. Soc.* **16**, 8104 (2004).
5. A. Corma: *Chem. Rev.* **95**, 559 (1995).
6. G.A. Olah: *J. Org. Chem.* **66**, 5943 (2001).
7. M. Irie: *J. Am. Chem. Soc.* **105**, 2078 (1983).
8. S. Naya, K. Yoda, and M. Nitta: *Tetrahedron* **60**, 4953 (2004).
9. S.L. Wiskur, H. Ait-Haddou, J.J. Lavigne, and E.V. Anslyn: *Acc. Chem. Res.* **34**, 963 (2001).
10. M. Ballester, I. Pascual, and J. Torres: *J. Org. Chem.* **55**, 3035 (1990).
11. E. Barni, P. Savarino, and G. Viscardi: *Acc. Chem. Res.* **24**, 98 (1991).
12. M. Adachi and M. Murata: *J. Phys. Chem. A* **102**, 841 (1998).
13. K.S. Burnham and G.B. Schuster: *J. Am. Chem. Soc.* **120**, 12619 (1998).
14. R.J. Sarma and J.B. Baruah: *Dyes Pigment* **61**, 39 (2004).
15. D.E. Hughes and M.J. Cardone: *Anal. Chem.* **52**, 940 (1980).
16. SHELXTL: *ver. 6.12, Bruker AXS*, Madison, Wisconsin, U.S.A (2001).
17. Principles and Methods in Supramolecular Chemistry by Schneider H-J., Yatsimirsky A., 2000 Wiley, Chichester.
18. T.W. Lewis, I.C. Paul, and D.Y. Curtin: *Acta Crystallogr.* **B36**, 70 (1980).
19. E.N. Duesler, T.W. Lewis, D.Y. Curtin, and I.C. Paul: *Acta Crystallogr.* **B36**, 166 (1980).
20. A. Moscatelli, A. Galarneau, F. Di Renzo, and M.F. Ottaviani: *J. Phys. Chem. B* **108**, 18580 (2004).
21. M.F. Ottaviani, A. Moscatelli, D. Desplantier-Giscard, F. Di Renzo, P.J. Kooyman, B. Alonso, and A. Galarneau: *J. Phys. Chem. B* **108**, 12123 (2004).
22. F. Di Renzo, F. Testa, J.D. Chen, H. Cambon, A. Galarneau, D. Plee, and F. Fajula: *Micropor. Mesopor. Mater.* **28**, 437 (1999).