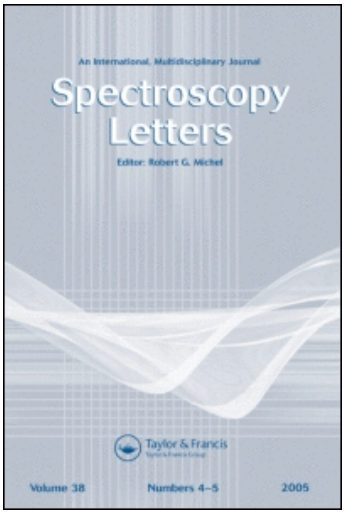

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Xinzhen Du[a]; Weihua Lu[a]; Xiangzhen Bai[a]; Yarong Wang[a]; Hualin Deng[a]; Jinguo Hou[a]
[a] Department of Chemistry, Northwest Normal University, Lanzhou, People's Republic of China

To cite this Article Du, Xinzhen , Lu, Weihua , Bai, Xiangzhen , Wang, Yarong , Deng, Hualin and Hou, Jinguo(2005) 'Spectral Properties of Cyclodextrin Inclusion Complexes with Nonionic Surfactants and 1-Bromonaphthalene', Spectroscopy Letters, 38: 4, 569 — 581
To link to this Article: DOI: 10.1081/SL-200062977
URL: http://dx.doi.org/10.1081/SL-200062977

Spectroscopy Letters, 38: 569–581, 2005

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1081/SL-200062977

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Spectral Properties of Cyclodextrin Inclusion Complexes with Nonionic Surfactants and 1-Bromonaphthalene

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Department of Chemistry, Northwest Normal University, Lanzhou, People's Republic of China

Abstract: Steady-state fluorescence and phosphorescence of inclusion complexes of cyclodextrins (CDs) with fluorescent nonionic surfactant and 1-bromonaphthalene (BN) are described in detail. The inclusion of the hydrophobic moiety of surfactants inside the cavity of CDs led to enhanced monomer-like fluorescence with a bathochromic shift of λ_{ex} and a hypsochromic shift of λ_{em}. ^{1}H-NMR provides additional evidence for deep inclusion of the hydrophobic moiety of surfactants. BN can squeeze into more hydrophobic cavity of β-CD that has accommodated the hydrophobic moiety of a surfactant and show its phosphorescence and remarkable quenching effect on the fluorescence of a surfactant in aerated aqueous solution. Stern–Volmer quenching depends on the inclusion of the phenyl rings of surfactants and BN into the cavity of CDs. Comparison of molecular sizes reveals that further inclusion of BN into the cavity of β-CD occupied by a surfactant may force the flexible octyl group of a surfactant to deform to a greater extent, and close-packing complexes were obtained. In the case of heptakis(2,6-di-*O*-methyl)-β-CD, BN only binds to its cavity opening due to the steric hindrance of methyl substituents at the rim of its cavity.

Keywords: Bromonaphthalene, cyclodextrins, fluorescence, phosphorescence, surfactants

Received 19 April 2003, Accepted 8 February 2005

Address correspondence to Xinzhen Du, Department of Chemistry, Northwest Normal University, Lanzhou 730070, People's Republic of China. E-mail: duxz@nwnu.edu.cn

INTRODUCTION

The cavity of cyclodextrins (CDs) can provide a hydrophobic environment for guest molecules and may modify their photophysical properties in aqueous solution.[1,2] Many investigations have focused on the fluorescence of polyaromatic hydrocarbons included in CDs and related effect of alcohols.[3–7] Stern–Volmer analysis has shown that the influence of an alcohol on luminescence depends on its effectiveness in shielding photoexcited luminophore from a quencher in bulky phase. As compared with alcohols, the hydrophobic moiety of surfactants prefers to be incorporated into the hydrophobic cavity of CDs.[8] For this reason, surfactants may have a significant effect on the photophysical properties of an included molecule in the cavity of CDs.[7,9–13] Spectral investigations of included molecules and intermolecular interaction in the CD cavity are of great importance for potential applications of CDs in analytical chemistry[1] and industries.[2] Warner et al. studied the fluorescence lifetimes of pyrene and examined the interaction of β-CD and γ-CD with selected nonionic surfactants, concluding that CD and nonionic surfactant forms the 1:1 complexes and furthermore ternary inclusion complexes occur in the presence of pyrene.[9,10] Bhattacharyya et al. further pointed out that TX fails to insert into the α-CD cavity, and the preferential binding of TX over 2,6-*p*-toluidinonaphthalene sulfonate to β-CD causes its displacement from the CD cavity.[12] De la Pena et al. also performed equilibrium studies on formation of β-CD ternary complexes with 1-bromonaphthalene and surfactants.[7] However, few reports dealt with the comprehensive study of fluorescence, phosphorescence, and NMR of CDs complexes with a nonionic surfactant and a lumophore at the same time.[13] For this purpose, with resort to the artful selection of typically nonionic surfactants with phenyl rings, the fluorescent, phosphorescent, and NMR properties of CD inclusion complexes with luminophors and the intermolecular interactions involved in controlling spectral properties were discussed.

EXPERIMENTAL

Reagents

1-Bromonaphthalene (BN) was obtained from Beijing Zhonglian Fine Chemicals (Beijing, China) and distilled under reduced pressure. β-cyclodextrin (β-CD) was purchased from Sigma (St. Louis, MO, USA). Heptakis(2,6-di-*O*-methyl)-β-CD (DM-β-CD) was supplied by Beckman (Fullerton, CA, USA) and used without further purification. Polyethylene glycol (n = 9.5) *n*-octylphenyl ether (commercially OP) was purchased from Shanghai Reagent Company (Shanghai, China) and polyethylene glycol (n = 10) *tert*-octylphenyl ether (commercially Triton X-100:TX) was obtained from Merck (Darmstadt,

Germany) and used as received. 1-Butanol of analytical grade was obtained from Shanghai Reagent Company and distilled prior to use. Solutions of sodium sulfide and potassium iodide were newly prepared prior to use. BN of 5.0×10^{-5} M, β-CD of 5.0×10^{-3} M, and OP of 8.0×10^{-4} M for β-CD:OP:BN system as well as β-CD of 2.5×10^{-3} M and TX of 2.0×10^{-3} M for β-CD:TX:BN system were employed throughout the experiments, unless otherwise stated.

Apparatus

All steady-state fluorescence and phosphorescence spectra were performed on Shimadzhu RF-540 recording fluorescence spectrophotometer (Tokyo, Japan) equipped with a 150-W xenon lamp as an excitation light source and a thermostated cell holder (25°C). Excitation and emission bandpasses of 5 nm were employed. The absorption measurements were obtained with Hitachi U-3400 spectrophotometer (Tokyo, Japan). Barnstead|Thermolyne D8612-33 EASYpure UV/UF compact reagent water system (Dubuque, IA, USA) was used to purify distilled water with a resistivity of up to 18.3 megaohms-cm. ^{1}H-NMR studies were carried out in D_2O on a Varian INOVA-400 MHz spectrometer (Palo Alto, CA, USA).

RESULTS AND DISCUSSION

Fluorescence of CD:Surfactant Complexes

OP and TX exhibit intrinsic fluorescence due to their built-in phenyl rings. Figure 1 shows fluorescence from OP in the absence and presence of β-CD. OP gives rise to fluorescence at 305 nm with excitation wavelength maximum of 276 nm at 5.0×10^{-5} M. However, it displays a new broad featureless fluorescence at 350 nm with excitation wavelength maximum of 286 nm around 1.0×10^{-4} M very close to its critical micelle concentration (CMC).[14] Because OP molecules homogeneously disperse in aqueous solution below 5.0×10^{-5} M, one can predict that the fluorescence at 305 nm arises from OP monomers. The fluorescence at 350 nm should be assigned to aggregates of OP. In the presence of β-CD, OP shows enhanced fluorescence accompanied by the bathochromic shift of excitation wavelength maximum and the hypsochromic shift of emission wavelength maximum below CMC. The spectral behavior was similar to that of phenolic derivatives in water and dioxane, respectively.[15] This result reveals that the phenyl ring between the *n*-octyl and polyethylene glycol was located in less polar CD cavity compare to water phase, and thereby the hydrophobic *n*-octyl group appended with the phenyl ring was entrapped into the cavity to form inclusion complex. Especially the fluorescence of OP aggregates at 350 nm almost disappears and that of OP

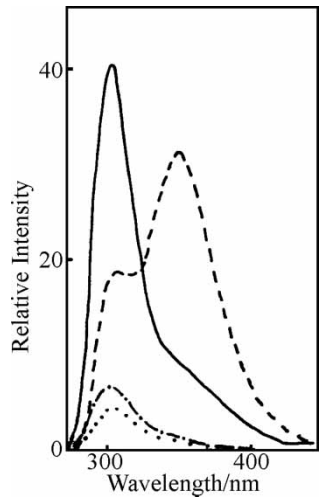

Figure 1. Fluorescence of OP in the presence of β-CD: 5.0×10^{-5} M OP (dotted), 5.0×10^{-5} M OP and 5.0×10^{-3} M β-CD (dashed and dotted), 8.0×10^{-4} M OP (dashed), 8.0×10^{-4} M OP and 5.0×10^{-3} M β-CD (solid).

monomers at about 305 nm greatly increases in the presence of excess β-CD. This experimental phenomenon further demonstrates that the channeled cavity of β-CD includes the hydrophobic tail of OP responsible for the aggregation of OP, and the aggregates are absent in this case. As a result, OP included by β-CD loses its unique amphiphilicity. It is also in a good agreement with the general conclusion that the hydrophobic moiety of surfactant is encapsulated into the CD cavity obtained by conductance and surface tension.[16] In the case of DM-β-CD, the same results were obtained. TX also shows similarly enhanced fluorescence.

The stoichiometry of binary inclusion complexes was determined by the difference in fluorescence in the presence and absence of excess CD. For 1:1 inclusion complexes, all plots are linear according to a Benesi–Hildebrand expression $1/\Delta I_F = 1/a + 1/a \cdot K \cdot [\mathrm{CD}]$ (where ΔI_F is the difference in fluorescence intensity of a surfactant in the presence and absence of CD, K the apparent stability constant, a the instrumental constant combined, and [CD] the equilibrium concentration of CD).[17] Figure 2 shows the double reciprocal plot of $1/\Delta I_F$ versus $1/[\beta\text{-CD}]$ for the representative β-CD:OP complex. Apparent stability constants obtained by the ratio of intercept to slope are summarized in Table 1. The K values are much larger than those of CD with alcohols.[18] Moreover, the larger K values of β-CD and DM-β-CD complexes with TX indicate that the *tert*-octyl chain of TX is better fit for the rigid channel of β-CD cavity than the *n*-octyl chain of OP. In addition, the inclusion complexation of 1:1 was further confirmed by the fluorescence titration curve of β-CD to OP in Fig. 3 based on its fluorescence at 350 nm.

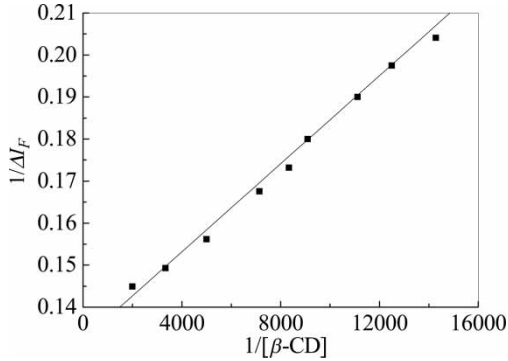

Figure 2. A Benesi–Hildebrand plot of $1/\Delta I_F$ versus $1/[\beta\text{-CD}]$ for β-CD:OP complex (5.0×10^{-5} M OP).

Fluorescence Quenching of CD:Surfactant Complexes

In homogeneous solution, dynamic fluorescence quenching is described by the following Stern–Volmer equation:

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 and I are the fluorescence intensity in the absence and presence of quencher, respectively, K_{SV} the quenching constant, and [Q] the concentration of a quencher. A summary of the K_{SV} extracted from the slope of Stern–Volmer plots is listed in Table 2. β-CD shows much better protection for fluorescence of β-CD:TX complex than that of β-CD:OP complex. For the case of TX, the values of K_{SV} are also very different in the presence of β-CD and DM-β-CD, respectively. These data provide direct evidence that the phenyl rings of OP and TX were also included into the cavity of β-CD together with their octyl groups and demonstrate that dynamic fluorescence quenching effect depends on nature of surfactants and CDs.

Fluorescence and Phosphorescence of Ternary Inclusion Complexes

BN shows weaker fluorescence than its native naphthalene due to internal heavy-atom effect. Generally, it forms 1:1 inclusion complex with β-CD.[4]

Table 1. Apparent stability constants for binary inclusion complexes

Complexes	K/M^{-1}
β-CD:OP	$(2.62 \pm 0.17) \times 10^4$
β-CD:TX	$(3.04 \pm 0.22) \times 10^4$
DM-β-CD:OP	$(1.52 \pm 0.10) \times 10^4$
DM-β-CD:TX	$(5.99 \pm 0.88) \times 10^4$

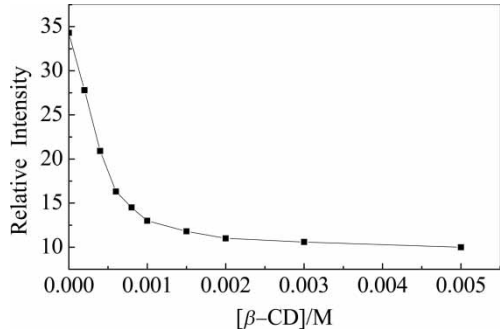

Figure 3. Fluorescence titration curve of β-CD to OP (1.0×10^{-3} M OP).

Because the absorption and fluorescence of aqueous solution of BN were slightly influenced by the addition of β-CD, the fluorescence of nonionic surfactants and the phosphorescence of BN were examined instead. Phosphorescence from BN was observed when BN was added into aqueous solution of β-CD:TX complex.[7] Figure 4 shows excitation and typical phosphorescence of BN for β-CD:TX:BN system. Intense phosphorescence from BN implies that the excited BN locates in very favorable microenvironment shielding from dissolved oxygen. Great bathochromic shift of excitation wavelength maximum further reflects that BN is situated in a significantly less polar environment. Furthermore, as shown in Fig. 5, appearance of phosphorescence was accompanied by the significant fluorescence quenching of TX at the same time. It also indicates that the phenyl ring of TX locates in the proximity of BN because fluorescence quenching by BN is an intermolecular process and dependent on the distance between the phenyl ring and BN. Thus both the *tert*-octylphenyl group of TX and BN are included into the cavity of β-CD. With respect to β-CD:OP:BN ternary complex, intense phosphorescence

Table 2. Stern–Volmer quenching constants for binary inclusion complexes

Complexes	K_{SV}/M^{-1}	$[Q]_{1/2}/M^a$
Free OP	12.937 ± 0.583	0.077 ± 0.009
β-CD:OP	3.916 ± 0.400	0.257 ± 0.064
DM-β-CD:OP	3.925 ± 0.123	0.248 ± 0.047
Free TX	11.474 ± 0.105	0.087 ± 0.001
β-CD:TX	0.765 ± 0.113	0.878 ± 0.491
DM-β-CD:TX	4.021 ± 0.212	0.249 ± 0.033

[a]The concentration of quencher when the fluorescence intensity decreases by 50%.

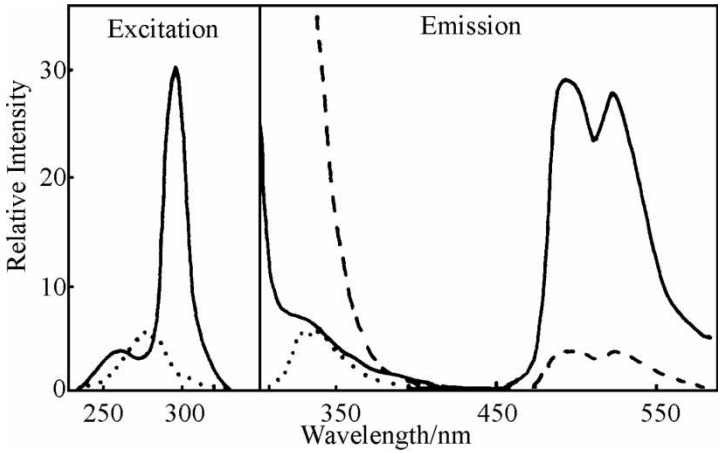

Figure 4. Fluorescence and phosphorescence from inclusion complexes. β-CD:BN (dotted) and β-CD:TX:BN (solid for $\lambda_{ex} = 298$ nm and dashed for $\lambda_{ex} = 264$ nm).

from BN was also obtained. The double reciprocal plots of a Benesi–Hildebrand equation follow 1:1:1 ternary inclusion complexation. Apparent stability constants of β-CD:OP:BN and β-CD:TX:BN complexes were estimated to be $(3.23 \pm 0.77) \times 10^6\,M^{-2}$ and $(1.70 \pm 0.39) \times 10^7\,M^{-2}$, respectively. In the case of DM-β-CD, the similar fluorescence quenching effect was observed but no phosphorescence was detected.

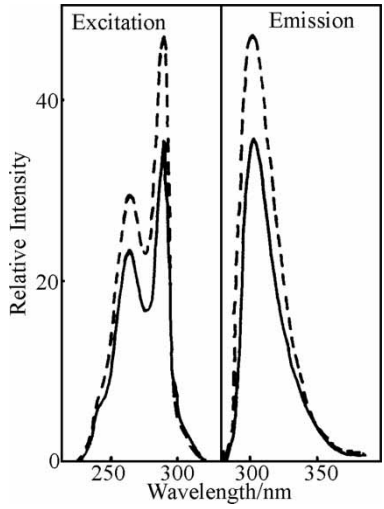

Figure 5. Fluorescence of TX in the presence of β-CD and BN: β-CD:TX (dashed) and β-CD:TX:BN (solid).

In addition, it is noteworthy from Fig. 4 that the sharp 298 nm excitation band is accompanied by the shoulder band at 264 nm that corresponds to the shorter excitation wavelength of TX in Fig. 5. When TX was irradiated at 264 nm, excitation energy is transferred from the phenyl ring of TX to BN, which is responsible for the observed phosphorescence of BN. Energy transfer clearly shows that the close distance needed for efficient energy transfer is imposed by the spatial constraints of the inclusion complexation because the rate constant for energy transfer exhibits a $1/r^6$ (Forster) distance dependence.[19]

Phosphorescence Quenching of Ternary Inclusion Complexes

Phosphorescence quenching interactions were also employed to provide further information about inclusion phenomena because of the extremely high sensitivity of triplet state to oxygen and iodide ions dissolved in aqueous solution. Figure 6 depicts phosphorescence quenching by iodide ions for the β-CD:TX:BN system. The data in the plots exhibit normal Stern–Volmer quenching behavior in aqueous solution. The K_{SV} values were estimated by linear regression of experimental data to be $(0.694 \pm 0.094)\ M^{-1}$ for phosphorescence with excitation wavelength maximum of 298 nm and $(13.477 \pm 0.491)\ M^{-1}$ for that of 264 nm, respectively. These data clearly show that β-CD–included BN can be greatly shielded from dissolved oxygen and iodide ions in the presence of TX, whereas the phenyl ring of TX exposes to the bulk phase to some extent. In the case of β-CD:OP:BN complex, the K_{SV} value was $(10.220 \pm 0.524)\ M^{-1}$, much larger than that of corresponding β-CD:TX:BN complex. In addition, chemical deoxygenation using sodium sulfite as an oxygen scavenger results in greatly enhanced phosphorescence (3.3-fold) from the β-CD:OP:BN complex. Under the same conditions, however, the phosphorescence intensity only increases by 10% in the case of β-CD:TX:BN complex. It reveals that the excited BN was shielded in the β-CD:OP:BN complex to less extent than its counterpart in the β-CD:TX:BN complex.

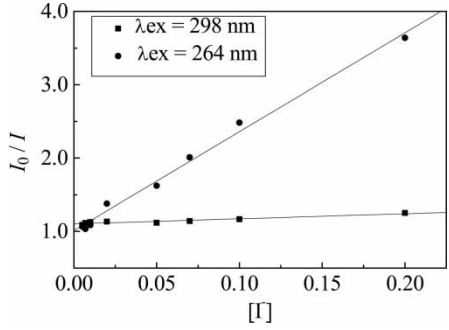

Figure 6. Stern–Volmer plots of I_0/I versus $[I^-]$ for β-CD:TX:BN complex.

Effect of 1-Butanol on Fluorescence and Phosphorescence of Ternary Inclusion Complexes

Aliphatic alcohols can induce bright phosphorescence from BN in aerated aqueous solution of β-CD at room temperature.[4] Figure 7 shows the effect of 1-butanol on the fluorescence of OP and phosphorescence of BN from the β-CD:OP:BN complex. The phosphorescence of BN disappears and greatly enhanced fluorescence of OP appears at the same time when 1-butanol of 0.40% (v/v) is added to the solution of β-CD:OP:BN complex. It suggests that BN retreats from the cavity and fails to exert its external heavy-atom effect on the fluorescence of phenyl ring of OP included inside the cavity. The result also provides strong support for the conclusion that both *n*-octylphenyl group and BN are simultaneously buried inside the limited cavity of β-CD. However, the β-CD:OP inclusion complex still exists in aqueous solution because OP shows its enhanced monomer-like fluorescence from the β-CD/OP complex. With respect to the more stable β-CD:TX:BN complex, the phosphorescence intensity only decreases by 10%.

^{1}H-NMR of CD:Surfactant Complexes

NMR of β-CD, surfactants, and their inclusion complexes was also studied. Figure 8 shows representative ^{1}H-NMR of β-CD, TX, and their binary system of β-CD and TX in D_2O. Proton shifts of β-CD and TX follow their

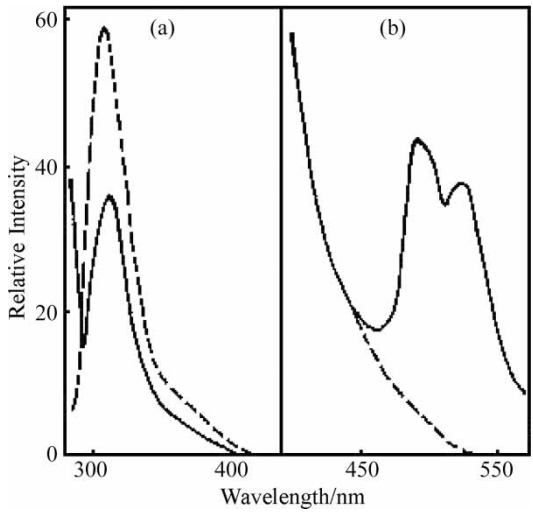

Figure 7. Fluorescence of OP (a) and phosphorescence of BN (b) in the absence (solid) and presence of 0.40% (v/v) 1-butanol (dashed) (9.0×10^{-3} M β-CD).

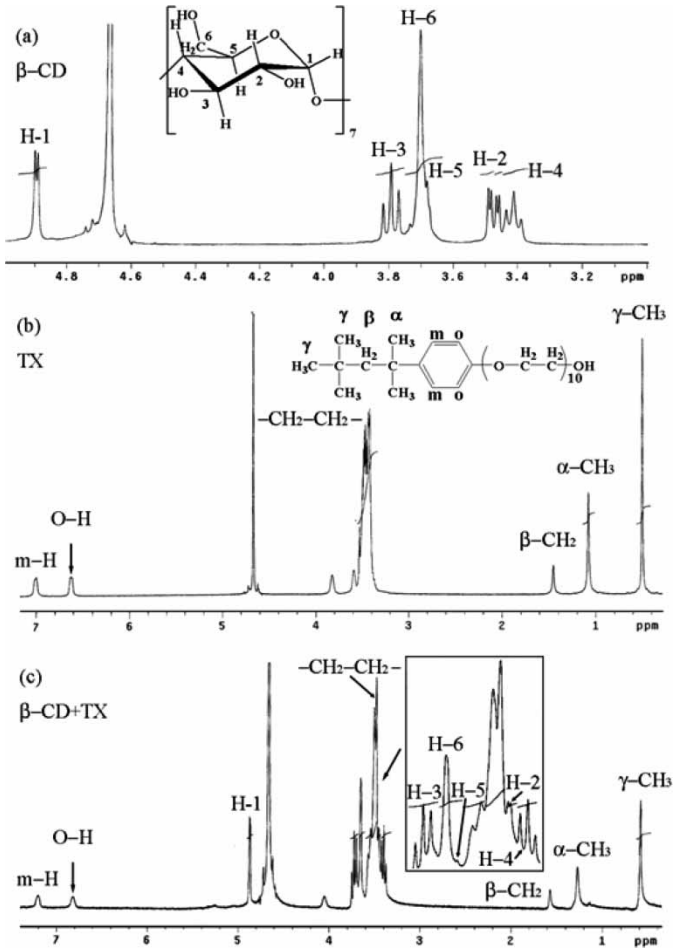

Figure 8. ^{1}H-NMR of β-CD (a), TX (b), and β-CD:TX complex (c).

individual regular patterns.[20] The available ^{1}H-NMR shifts shows significant ^{1}H downfield shifts from δ0.501 to δ0.593 for γ-CH_3, from δ1.079 to δ1.272 for α-CH_3, and from δ1.451 to δ1.569 for β-CH_2- of *tert*-octyl chain in the presence of β-CD. Especially *m*-H and *o*-H of phenyl ring give ^{1}H downfield shifts from δ6.617 to δ6.821 and from δ6.998 to δ7.205, respectively. Furthermore, slight splitting occurs. Inversely, TX leads to remarkable ^{1}H upfield shifts from δ3.794 to δ3.729 for H-3 signals (triplet) and from δ3.683 to δ3.660 for H-5 signals (singlet) of β-CD at the same time. Such chemical shifts are generally believed to indicate the inclusion of guest in the cavity of β-CD.[10,21] However TX almost has no effect on H-1 (doublet), H-2 (two doublet), H-4 (triplet), and H-6 (singlet) signals of β-CD even though H-3 and H-5 protons involved in inclusion are more shielded than

those of free β-CD. These data provide additional evidence for deep inclusion of *tert*-octyl chain and phenyl ring of TX. Corresponding proton shifts of β-CD and OP are smaller in the case of β-CD:OP inclusion complex.

Inclusion of Surfactants and 1-Bromonaphthalene by CDs

A comparison of molecular dimensions allows a rough evaluation of spectral properties dependent on structure of inclusion complexes. With respect to the *n*-octyl group of OP, the cross section of the fully extended alkyl chain corresponds to the axial diameter of 4.85 Å.[22] As compared with the cavity diameter (D) of β-CD (D/6.5 Å), the cavity of β-CD is wide enough to include the *n*-octyl group of OP. In the case of TX, the diametrical size of the *tert*-octyl group approximately corresponds to 6.87 Å, and the good fit of *tert*-octyl group to the cavity of β-CD was obtained. In terms of the length (L/Å) and volume (V/Å^3) of the fully extended alkyl chain[23] and the depth (D/Å) and the approximate volume of β-CD cavity (D/7.9 Å and V/262 Å^3), the shorter *tert*-octyl group (L/5.3 Å and V/215.7 Å^3) of TX may be encapsulated into the hydrophobic cavity, whereas the longer *n*-octyl group (L/10.4 Å and V/215.7 Å^3) of OP may occupy the cavity in a coiled manner by hydrophobic interaction. Thereby, the phenyl ring appended with octyl group of OP and TX was entrapped into the cavity. For this reason, the fluorescence quenching of OP and TX by iodide ions was greatly attenuated, and the groups/protons of β-CD and surfactants experience different chemical environments in inclusion complexes. Especially the β-CD:TX complex shows more effective protection for fluorescence of TX, higher stability, and larger proton shifts for good fit of *tert*-octyl chain with phenyl ring to the cavity of β-CD. As a consequence, the inclusion complexation induces the release of water molecules from the CD cavity, and strong hydrophobic interaction drives BN to penetrate into the cavity of β-CD to form ternary inclusion complexes with the stoichiometry of 1:1:1. According to overall molecular size of BN and the octyl moiety with phenyl ring of OP or TX, rigid BN may squeeze into the hydrophobic cavity occupied by OP or TX and force the flexible octyl group to deform to some extent. The crowded packing of BN and the hydrophobic moiety of OP or TX in the constrained cavity of β-CD leads to the bright phosphorescence of BN in aerated aqueous solutions due to better rigidity and shield from dissolved oxygen and the significant quenching effect of BN on the fluorescence of neighboring phenyl ring of OP or TX due to the heavy-atom effect. Particularly, BN was deeply included because of stronger binding strength of BN to the β-CD cavity occupied by the hydrophobic moiety of TX. The more favorable microenvironment protects the excited BN from external quenchers. Phosphorescence quenching of BN was slight and intermolecular energy transfer from the phenyl ring of TX to BN was observed for tightly compact β-CD:TX:BN complex.

In the case of DM-β-CD, the methyl substituents at 2- and 6-position of β-CD direct toward the cavity and result in self-inclusion.[24] It may cut down the diameter and the volume of the cavity for steric considerations. As a result, the phenyl ring of OP and TX included by DM-β-CD exposes to bulk phase to a greater extent compare to that included by β-CD and exhibits a greater fluorescence quenching by iodide ions. Accordingly, DM-β-CD cavity fails to further accommodate BN into the cavity occupied by OP or TX due to the steric hindrance of methyl groups at the rim of its cavity. Yet BN can reside in the region of the annular hydroxyl groups of β-CD with the help of hydrophobic interaction. For this reason, BN exposes to the bulk water and shows no phosphorescence but still induces marked fluorescence quenching of its neighboring phenyl ring of OP or TX situating at the opening of the cavity.

ACKNOWLEDGMENTS

We acknowledge and thank the Natural Science Foundation of Gansu Province (ZS011-A25-011-Z) and Innovation Foundation of Science and Technology (NWNU-KJCXGC-02-09) for financial aid.

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