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Phosphorescence-probed study on the association of surfactants with β -cyclodextrin

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Abstract

The formation of association complexes between surfactants (S) and β -cyclodextrin (β -CD) has been studied using 1-bromonaphthalene (1-BrN) as a phosphorescent probe. In combination with the spectral structure, phosphorescence lifetimes, surface tension of solutions and association constants of 1:1:1/S:1-BrN: β -CD complexes, a comparison of molecular size shows that the hydrocarbon chain of surfactants is partly included in the cavity of β -CD and the hydrophobic part with the polar head group is located outside the cavity coils at the mouth of the β -CD cavity.

1. Introduction

Cyclodextrin solutions and micellar solutions are widely used as media for studies of the photophysical and photochemical properties of aromatic compounds [1,2]. A mixture of surfactants (S) and cyclodextrins (CD) shows a synergetic effect and provides a favorable microenvironment surrounding luminophores [3–8]. A number of groups have presented their work on the association between surfactants and cyclodextrins [3–16]. However, while much attention has been paid to the stoichiometry and association constants of S:CD complexes [16–18], less information is available on the binding mode of surfactants with cyclodextrins in aqueous solutions [4,7,19]. Femia and Cline Love investigated the room temperature phosphorescence (RTP) from phenan-

threne in a mixed system of 1,2-dibromoethane, Na/Tl dodecyl sulfate and β -CD [4]. It was postulated that the surfactant monomers aggregate at the open ends of the β -CD torus and/or are partially included, which serves to reduce the phenanthrene–water contact.

Phosphorescent probes are convenient for microenvironmental analysis since when they are included into the CD cavity they show characteristic changes in their phosphorescence spectra and lifetimes. These changes can be employed to evaluate the properties of the microenvironment surrounding probes and consequently give insight into the association of surfactants with cyclodextrins. In this work, 1-bromonaphthalene (1-BrN) was employed as a phosphorescent probe to study the binding of ionic surfactants to β -CD. In combination with equilib-

rium constants, the surface tension of solutions and molecular size, the binding mode of a surfactant to β -CD was further explained.

2. Experimental

1-BrN (Shanghai Reagent Co.) was vacuum distilled prior to use. β -CD (Suzhou Gourmet Factory) was dissolved in boiling water and recrystallized three times. Cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPB, Shanghai Reagent Co.) were recrystallized in ethanol. Sodium dodecylsulfate (SDS, Sigma) and sodium dodecylbenzenesulfonate (SDBS, Guangzhou Reagent Co.) were used as received. Stock solutions of 1.0×10^{-3} mol/l 1-BrN were prepared in surfactant solutions. Through this work, solutions of 5.0×10^{-5} mol/l 1-BrN were utilized unless otherwise stated. The deionized water was triply distilled.

All steady-state luminescence spectra were performed on a Hitachi 650-10 S fluorescence spectrophotometer equipped with a 150 W xenon lamp as an excitation light source and a Shanghai Dahua XWT-104 chart recorder (2 V maximum). Excitation and emission slits of 3 nm were employed. Phosphorescence lifetimes were measured with a Hitachi F-4500 fluorescence spectrophotometer. The surface tension of the solutions was measured by the maximum bubble pressure method at $(25 \pm 1)^\circ\text{C}$.

3. Results and discussion

3.1. Phosphorescence spectra of S: 1-BrN: β -CD

1-BrN shows no RTP in aerated aqueous solutions of ionic surfactants or β -CD in spite of the presence of its inner heavy-atom effect. As shown in Figs. 1 and 2, however, phosphorescence was observed in the presence of both a surfactant and β -CD, accompanied by red-shifts in the excitation wavelength from 278 nm of the 1-BrN: β -CD system to 290 nm of the S: 1-BrN: β -CD system. This suggests that the presence of surfactants greatly changes the microenvironment surrounding 1-BrN and provides effective protection for the triplet since the phosphorescence is highly sensitive to its microenvironment. It is gener-

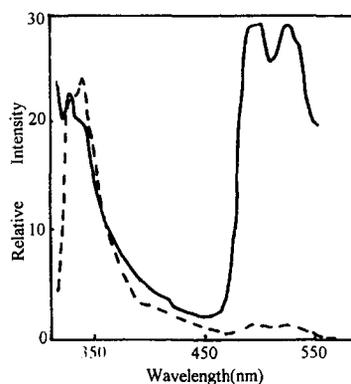


Fig. 1. Phosphorescence spectra ($\times 1$) of 1-BrN in the presence of CPB (---) and CTAB (—). CPB: 1.75×10^{-3} mol/l; CTAB: 1.0×10^{-3} mol/l; β -CD: 5.0×10^{-3} mol/l.

ally accepted that ternary complex formation is responsible for phosphorescence. However, it is worth noting in Fig. 1 that CPB shows a much lower phosphorescence enhancement of 1-BrN than CTAB although CPB with a pyridinium group carries a long hydrocarbon chain ($\text{CH}_3(\text{CH}_2)_{15}$) like CTAB and should induce a bright phosphorescence from 1-BrN. On the contrary, the phosphorescence enhancement of 1-BrN in the presence of SDBS with a phenyl group is much greater than that in the presence of SDS. In addition, as can be seen in Fig. 2, a continuous fluorescence quenching of SDBS was also observed when the phosphorescence intensity increased upon the addition of more 1-BrN to the mixed

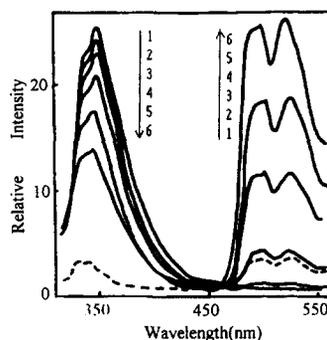


Fig. 2. Luminescence spectra ($\times 0.1$) of the SDS: 1-BrN: β -CD system (---) and the SDBS: 1-BrN: β -CD system at various concentrations of 1-BrN: (1) 0, (2) 5.0×10^{-6} mol/l, (3) 1.0×10^{-5} mol/l, (4) 2.5×10^{-5} mol/l, (5) 5.0×10^{-5} mol/l, (6) 1.0×10^{-4} mol/l. SDS: 2.0×10^{-3} mol/l (β -CD: 3.0×10^{-3} mol/l); SDBS: 4.0×10^{-3} mol/l (β -CD: 2.0×10^{-3} mol/l).

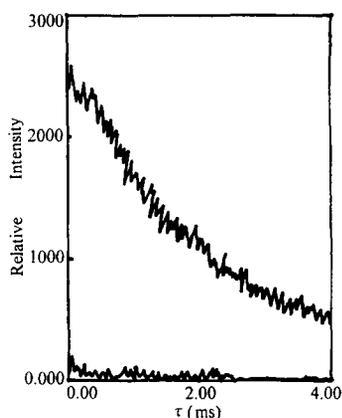


Fig. 3. Phosphorescence decay of 1-BrN in the presence of β -CD and CPB (lower) or CTAB (upper). The conditions are the same as in Fig. 1.

system of β -CD and SDBS. Evidently, the pyridinium group of CPB and the phenyl group of SDBS are located in the proximity of the 1-BrN molecule included into the β -CD cavity in the ternary complexes and the interaction between 1-BrN in the cavity and the pyridinium group or the phenyl group occurs.

Fig. 3 depicts the phosphorescence decay of 1-BrN in mixed systems of CPB or CTAB and β -CD. Clearly, the phosphorescence of 1-BrN is short-lived in the presence of CPB compared to that in the presence of CTAB. A structural comparison between CPB and CTAB also implies that the pyridinium group is responsible for the short phosphorescence lifetime. On the contrary, the phosphorescence lifetime of 1-BrN in the presence of SDBS with a phenyl group is much longer than that in the presence of SDS (Table 1). This suggests that the phenyl

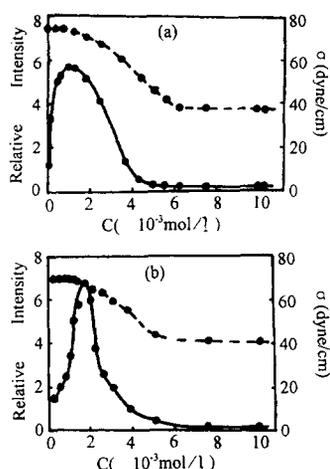


Fig. 4. Dependence of phosphorescence (—) and surface tension (---) on CPB (a) and CTAB (b). β -CD: 5.0×10^{-3} mol/l.

group connected with the polar head of SDBS contributes to an enhanced phosphorescence.

3.2. Effect of surfactants on phosphorescence

The phosphorescence exhibits a marked dependence on the surfactant concentration. As shown in Fig. 4, the phosphorescence of 1-BrN was observed upon the addition of surfactants to solutions of 1-BrN and β -CD. At a CTAB or CPB concentration below 2.0×10^{-3} mol/l, the phosphorescence intensity drastically increases and the highest phosphorescence is obtained, whereas the surface tension of the solutions slightly decreases. This reflects that the association of surfactants with β -CD reduces the number of available surfactant monomers for the formation of aggregates which are responsible for a decrease in the surface tension of solutions. Subsequently, the phosphorescence intensity greatly decreases while the surface tension of the solutions gradually decreases with an increasing concentration of CTAB or CPB. At a CTAB or CPB concentration above its apparent critical micelle concentration, the surface tension of the solutions begins to level off and the phosphorescence disappears when the solutions become transparent. Spectral analyses suggest that the ternary complexes have dissociated in aqueous solutions since the fluorescence spectra are simi-

Table 1
Association constants and phosphorescence lifetimes

Complexes	K (l^2/mol^2)	t (ms)
1-BrN: β -CD	$(7.02 \pm 0.29) \times 10^2$	—
CPB: 1-BrN: β -CD	$(1.48 \pm 0.18) \times 10^5$	1.09
CTAB: 1-BrN: β -CD	$(4.03 \pm 0.40) \times 10^5$	2.30
SDBS: 1-BrN: β -CD	$(3.38 \pm 0.50) \times 10^5$	4.83
SDS: 1-BrN: β -CD	$(2.40 \pm 0.30) \times 10^5$	2.82

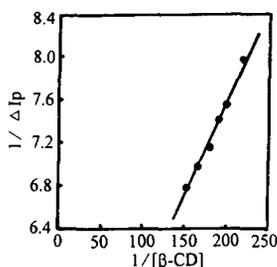


Fig. 5. Benesi–Hildebrand plot for the CPB:1-BrN:β-CD system. CPB: 1.75×10^{-3} mol/l.

lar to those of 1-BrN in micellar solutions of CTAB or CPB. The same trends were also observed for anionic surfactants. It directly indicates that the phosphorescence quenching correlates well with the surfactant aggregation which is responsible for a decrease in the surface tension of the solutions.

β-CD is capable of accommodating a 1-BrN molecule to form a 1:1 complex and a 1:1:1 ternary complex in the presence of a second appropriate guest [20,21]. For S:β-CD complexes, a 1:1 stoichiometry has usually been assumed [16]. With respect to the S:1-BrN:β-CD systems, a Benesi–Hildebrand analysis was conducted based upon the modified Benesi–Hildebrand equation described by Hamai [22], $1/\Delta I_p = 1/a \cdot K \cdot [S] \cdot [\beta\text{-CD}] + 1/a$ (where ΔI_p is the difference in the phosphorescence intensity of 1-BrN in the presence and absence of β-CD, and K is an apparent equilibrium constant). Fig. 5 shows a representative double-reciprocal plot of $1/\Delta I_p$ vs. $1/[\beta\text{-CD}]$ for the CPB:1-BrN:β-CD system. For all systems, a linear relationship was observed with correlation coefficients of 0.99, suggesting that the 1:1:1/S:1-BrN:β-CD ternary complexes are formed in aqueous solutions. Table 1 lists the apparent equilibrium constants of the ternary complexes estimated by the ratio of the intercept to slope. The K values show no correlation with the type and structure of the surfactants and the phosphorescence enhancement. For instance, the K values of the association complexes are of the same magnitude but the phosphorescence is much lower in the presence of CPB than that in the presence of CTAB. Conversely, SDBS with a phenyl group shows a much greater phosphorescence enhancement than SDS. These data provide additional evidence for the interaction between 1-BrN in the cavity and the

aromatic groups of CPB and SDBS in the ternary complexes.

3.3. Association of surfactants with β-CD

β-CD consists of seven glucose residues and has a lipophilic cavity with inner diameter, depth and volume of ~ 7.8 Å, ~ 7.8 Å and ~ 346 Å³ [23], respectively. One 1-BrN molecule (length ~ 7.2 Å and volume ~ 131.35 Å³ [24]) is small enough to be entirely buried in the cavity. In terms of the length (L) and volume (V) of the fully extended hydrocarbon chain C_nH_{2n+1} estimated by $L = 1.5 + 1.265(n - 1)$ and $V = 27.4 + 26.9(n - 1)$ [25], however, the hydrophobic moiety is not entirely enclosed in the β-CD cavity that has accommodated one 1-BrN molecule since the total volume of the 1-BrN molecule and the hydrophobic part is larger than that of the β-CD cavity. On the other hand, a comparison between the length of the hydrophobic tail and the depth of the β-CD cavity suggests that only six methylene groups ($L \sim 7.8$ Å) of a fully extended hydrocarbon chain of a surfactant are included in the cavity. Thus, both the polar head group and a part of the hydrophobic moiety protrude from the β-CD cavity. Since the 1-BrN phosphorescence quenching by the pyridinium group of CPB and the SDBS fluorescence quenching by the external heavy-atom effect of 1-BrN do not occur at an interval of 6–8 methylene groups of a fully extended hydrocarbon chain in aerated aqueous solutions, the pyridinium group and the phenyl group connected with the respective polar head of CPB and SDBS must be close to the 1-BrN molecule in the cavity. This suggests that the hydrophobic part is located outside the cavity coils at the mouth of the β-CD cavity through the hydrophobic interaction and an interaction between 1-BrN in the cavity and the pyridinium group or the phenyl group occurs. As a result, the coiled hydrophobic part shields the excited 1-BrN from the efficient phosphorescence quenching oxygen molecules dissolving in water and provide an effective protection for the 1-BrN phosphorescence, resulting in a considerably enhanced RTP in aqueous solutions. Furthermore, the rate of intersystem crossing from the singlet state to the triplet state of a phenyl group increases due to the external heavy-

atom effect of 1-BrN, which is responsible for the fluorescence quenching of the phenyl group of SDBS. For the CPB:1-BrN: β -CD system, charge transfer from the excited 1-BrN to the pyridinium ion may occur because the positively charged pyridinium ion is a strong electron-accepting group [5].

Acknowledgements

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