Study of room-temperature phosphorescence of 1-bromonaphthalene in sodium dodecylbenzene sulfonate and β-cyclodextrin solution

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Abstract

Intense room-temperature phosphorescence (RTP) of 1-bromo-naphthalene (1-BrN) was studied in aerated aqueous solutions containing sodium dodecylbenzene sulfonate (SDBS) and β-cyclodextrin (β-CD). It has been found that considerably enhanced RTP arises from the formation of the 1:1:1/SDBS:1-BrN:β-CD ternary inclusion complex in premicellar solutions. The spectral and structural analyses of molecules indicate that the phenyl ring of SDBS is included in the apolar cavity of β-CD and the polar head group and a part of hydrocarbon chain located outside the cavity. Surface tension of the solutions demonstrates that the presence of micelles results in serious phosphorescence quenching. © 1997 Elsevier Science B.V.

Keywords: Room-temperature phosphorescence; Detergent; Cyclodextrin; 1-Bromonaphthalene; Inclusion complex

1. Introduction

Micelle-stabilized room-temperature phosphorescence (MS-RTP) [1–4] and cyclodextrin induced RTP (CD-RTP) [5–7] were proposed for analytical purposes in the 1980s. For MS-RTP, deoxygenation is required for the observation of RTP, which results in plentiful bubbles in micellar solution by nitrogen-purging technique. For CD-RTP, brominated alkanes or alcohols were required as external heavy-atom perturber, and

sometimes combined with deoxygenation by ultrapure nitrogen [8–11]. Although no bubbles appear, a phosphorescence attachment was generally needed for phosphorescence measurements because scattered light arises from seriously cloudy solutions.

Halogenated naphthalenes are a series of surprising compounds. In the presence of acetonitrile or alcohols, intense RTP has been observed from aerated aqueous CD solutions in a conventional spectrofluorimeter [12,13]. However, the microcrystals of inclusion complexes adsorb onto the inner walls of glassware and this is considered a

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main disadvantage of CD systems. For this reason, Turro appended a long chain detergent to bromonaphthalene which was included in CD [14]. The chain coiled over the top of the CD thereby preventing oxygen quenching and hence bright phosphorescence was observed. Nocera has reported a glucosyl modified β-CD which included 1-BrN and used hydrogen bonding substrates to form a lid to the CD cup to prevent oxygen quenching [15,16]. In this work, a detergent, SDBS, was employed as a second guest molecule which can induce bright phosphorescence of 1-BrN in the presence of β-CD and improve the solubility of the inclusion complex like a long chain detergent attached to bromonaphthalene and a glucosyl group attached to CD. The purpose is to investigate the effect of a detergent on phosphorescence and to mimic the effect of a substituent (especially with a long hydrocarbon chain) on the rim of CD cup on a luminophor included in CD. Surface tension of the solutions was also measured and used to account for the effect of SDBS and β-CD on RTP. A possible binding site of SDBS in the cavity is proposed on the basis of molecular size.

2. Experimental

2.1. Chemicals

1-BrN (Shanghai Reagent) was distilled under reduced pressure. β-CD (Suzhou Gourmet Factory) was dissolved in distilled water and recrystallized three times. SDBS (Guangzhou Reagent) was used as received. Solution of 1.0×10^{-3} mol dm^{-3} 1-BrN was prepared by dissolving it in SDBS solution of 0.04 mol dm^{-3} on ultrasonic bath. Twice demineralized water was distilled.

2.2. Apparatus

All steady-state luminescence spectra were measured on Hitachi 650-10S spectrofluorimeter equipped with a 150-W xenon lamp as excitation light source and a Shanghai Dahua XWT-10 chart recorder (2V maximum). Excitation and emission slits of 3 nm were employed. A Hitachi

F-4500 spectrofluorimeter was employed to measure phosphorescence lifetime. The quartz cell was washed with ethanol prior to analysis.

2.3. Procedures

An aliquot of 0.04 mol dm^{-3} SDBS solution containing 1-BrN was transferred into a 10 ml volumetric flask and an appropriate amount of β-CD was added. After dilution to the mark with water, the solutions were allowed to stand for 2 h and introduced into the cell with Teflon stopper for fluorescence and phosphorescence measurement on spectrofluorimeter. Finally, surface tension of the solutions was measured at $(25 \pm 1)°C$ by using maximum bubble pressure method as described in literature [17].

3. Results and discussion

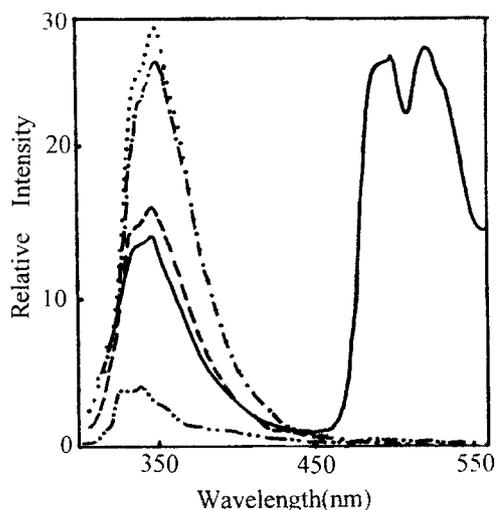### 3.1. Fluorescence and RTP spectra of a ternary complex

Fig. 1. Luminescence spectra of SDBS and corresponding complexes. SDBS ($\cdots$); 1-BrN + β-CD (– $\cdot$ $\cdot$ –); SDBS + β-CD (– $\cdot$ –); SDBS + 1-BrN (– – –) and SDBS + 1-BrN + β-CD (———). 1-BrN: 1.0×10^{-4} mol dm^{-3}; SDBS: 4.0×10^{-3} mol dm^{-3}; β-CD: 2.5×10^{-3} mol dm^{-3}.

Fig. 1 shows the fluorescence of SDBS and the phosphorescence spectra of corresponding complexes. SDBS exhibits strong fluorescence with the excitation wavelength of 283 nm and emission wavelength of 348 nm due to the internal phenyl ring. Upon addition of β-CD to the micellar solution of SDBS, the fluorescence intensity slightly decreases. In the presence of 1-BrN, appreciable fluorescence quenching of SDBS is observed. It suggests that 1-BrN is located close to the phenyl ring in SDBS micelles. In this case, 1-BrN can be regarded as an external heavy-atom perturber which induces the intersystem crossing from the excited singlet state to triplet state and results in the decreased fluorescence yield. This explanation also conforms to the suggestion shown by [^{1}H]NMR and [^{13}C]NMR spectroscopy that the polycyclic aromatic hydrocarbons are mainly dissolved near the C4 to C5 into the micelles and away from the hydrophilic charged micellar surface [18].

In aqueous solutions containing SDBS, 1-BrN and β-CD, the characteristic blue-green phosphorescence of 1-BrN is observed, accompanied by the appearance of slight microemulsion. It suggests that a ternary inclusion complex is formed in aqueous solutions since RTP is not observed from the solutions of 1-BrN and β-CD or 1-BrN and SDBS. The phosphorescence lifetime measurements provide direct evidence that the excited triplet state of 1-BrN in the cavity is effectively protected from the quencher in aqueous solutions (Fig. 2). Furthermore, the slightly more pronounced fluorescence quenching of SDBS also demonstrates that 1-BrN is situated close to the phenyl group of SDBS in the cavity and induces intersystem crossing from excited singlet state to triplet state like 1-BrN in SDBS micelles. As shown in Fig. 3, the higher concentration of 1-BrN results in more significant fluorescence quenching of SDBS and higher phosphorescence of 1-BrN. It further confirms that fluorescence quenching results from the external heavy-atom effect of 1-BrN.
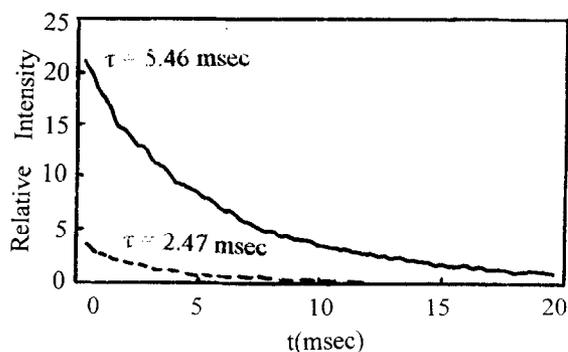

Fig. 2. Phosphorescence decay curves of 1-BrN in the absence (– – –) and presence (——) of SDBS. 1-BrN:1.0×10^{-4} mol dm^{-3}; SDBS: 4.0×10^{-3} mol dm^{-3}; β-CD: 2.5×10^{-3} mol dm^{-3}. In the absence of SDBS, 5.0×10^{-3} mol dm^{-3} β-CD was used and the solution was allowed to stand for 24 h prior to phosphorescence lifetime measurement.

3.2. Dependence of RTP on β-CD

RTP exhibits marked dependence on β-CD concentration. As shown in Fig. 1, 1-BrN shows no RTP in SDBS micellar solution in the absence of β-CD. Upon addition of β-CD to the micellar solutions, the phosphorescence is observed but the surface tension of solutions is unchanged at β-CD
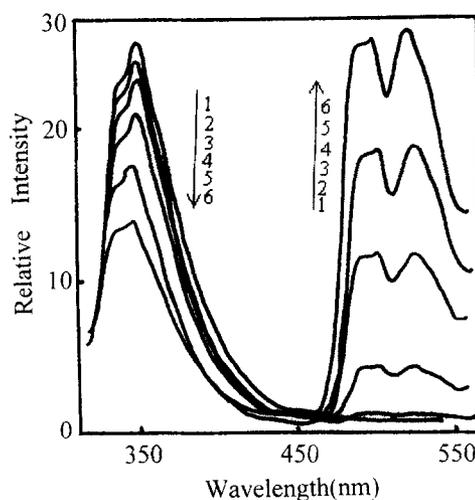

Fig. 3. Luminescence spectra of a SDBS:1-BrN:β-CD system at various concentration of 1-BrN. (1) 0, (2) 5.0×10^{-6} mol dm^{-3}, (3) 1.0×10^{-5} mol dm^{-3}, (4) 2.5×10^{-5} mol dm^{-3}, (5) 5.0×10^{-5} mol dm^{-3}, (6) 1.0×10^{-4} mol dm^{-3}. SDBS: 4.0×10^{-3} mol dm^{-3}; β-CD: 2.5×10^{-3} mol dm^{-3}.
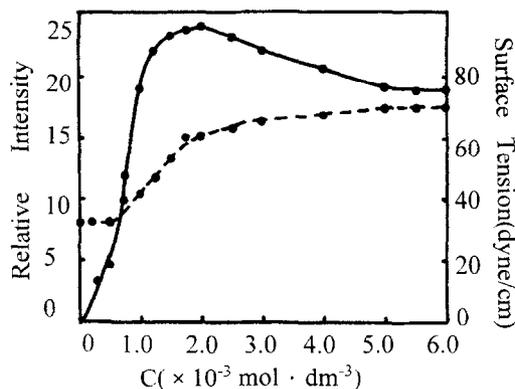
Fig. 4. Dependence of surface tension (– – –) of solutions and RTP (——) on β-CD. 1-BrN: 1.0×10^{-4} mol dm^{-3}; SDBS: 4.0×10^{-3} mol dm^{-3}.

Fig. 5. Surface tension of the solutions in the absence (●) and presence (△) of β-CD. Top: SDBS; bottom: SDBS + β-CD. β-CD: 5.0×10^{-3} mol dm^{-3}.

concentration below 5.0×10^{-4} mol dm^{-3} (see Fig. 4). Subsequently, the phosphorescence intensity drastically increases and the surface tension of the solutions also begins to increase gradually with the increasing concentration of β-CD. It reflects the micelles are gradually dissociating in solutions. At about 2.0×10^{-3} mol dm^{-3} β-CD, the highest phosphorescence is observed and the micelles break down since the surface tension of solutions approaches to that of the solutions containing 1-BrN and β-CD in the absence of SDBS. A continuous increase in β-CD concentration results in a decrease in phosphorescence intensity and a slight increase in surface tension of the solutions. When the β-CD concentration is greater than 4.0×10^{-3} mol dm^{-3}, both phosphorescence intensity and surface tension begin to level off.

3.3. Dependence of RTP on SDBS

Fig. 5 shows the surface tension of solutions as a function of SDBS concentration. In the absence of β-CD, the critical micelle concentration (CMC) of SDBS is about 2.4×10^{-3} mol dm^{-3}. In the presence of 5.0×10^{-3} mol dm^{-3} β-CD, however, the surface tension of the solutions remains constant at SDBS concentration below 5.0×10^{-3} mol dm^{-3}, very different from that in the absence of β-CD. It indicates that the hydrophobic part is included in β-CD cavity since the assembly of
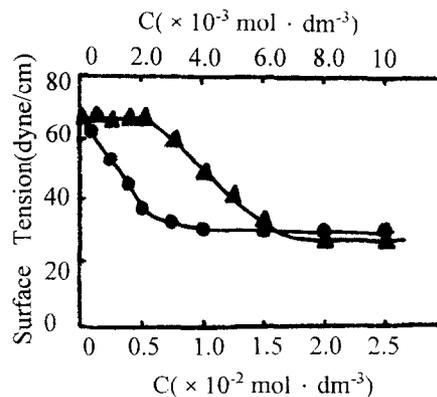
hydrocarbon chain at the surface of solutions is responsible for the decreased surface tension of the micellar solutions. When the SDBS concentration is greater than 5.0×10^{-3} mol dm^{-3}, the surface tension of solutions begins to decrease. These data imply that the 1:1/SDBS:β-CD complex is formed in aqueous solutions. For this reason, the higher SDBS concentration is needed for the micelle formation in the presence of β-CD, for instance, the apparent CMC of SDBS is 1.62×10^{-2} mol dm^{-3} in the presence of 5.0×10^{-3} mol dm^{-3} β-CD.

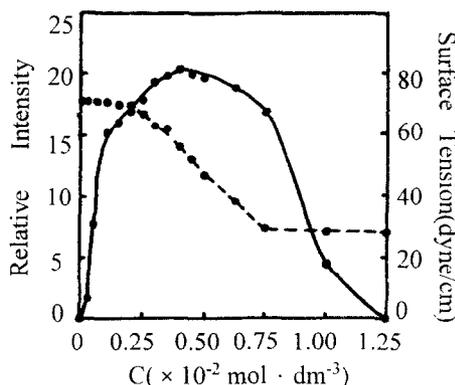Fig. 6 shows the dependence of RTP on SDBS. In the absence of SDBS, 1-BrN shows no phos-

Fig. 6. Dependence of the surface tension (– · –) of solutions and RTP (——) on SDBS. 1-BrN: 1.0×10^{-4} mol dm^{-3}; β-CD: 2.0×10^{-3} mol dm^{-3}.
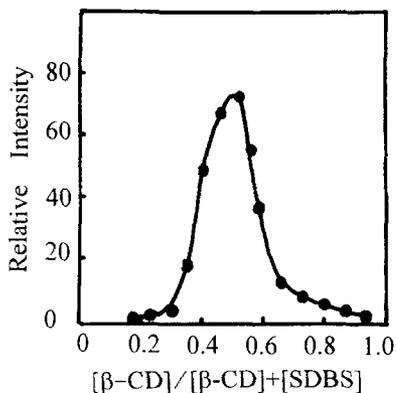
Fig. 7. A Job plot for the SDBS:1-BrN:β-CD system. 1-BrN: 5.0×10^{-5} mol dm^{-3}; [β-CD] + [SDBS] = 4.0×10^{-3} mol dm^{-3}.

phorescence at room temperature in the presence of 2.0×10^{-3} mol dm^{-3} β-CD despite the presence of the heavy-atom on the naphthalene. At SDBS concentration lower than that of β-CD, the surface tension of the solutions is unchangeable but the phosphorescence intensity drastically increases. Subsequently, the surface tension of the solutions begins to decrease and the emission intensity continuously increases with increasing SDBS concentration. As a second guest of the ternary complex herein, SDBS plays the similar role to an alcohol. In this case, SDBS is also a microenvironment regulator in the apolar cavity of β-CD, which restricts the rotation of 1-BrN molecule in the cavity and promotes the rigidity of the inclusion complex. After the highest phosphorescence, the emission intensity begins to decrease due to the micelle formation in solutions and quickly decreases at SDBS concentration above 7.5×10^{-3} mol dm^{-3} which corresponds to the apparent CMC in the presence of β-CD. When RTP disappears, the solutions become transparent. The spectral analysis indicates that the ternary complex has dissociated.

3.4. Inclusion of SDBS, 1-BrN and β-CD

1-BrN can form 1:1 inclusion complex with β-CD in aqueous solution [12]. For the SDBS:1-BrN:β-CD system, the ratio of β-CD to SDBS was determined by the continuous variation

method [19]. As shown in Fig. 7, the observed phosphorescence intensity goes through a maximum value at β-CD molar fraction of 0.52 under the conditions of [β-CD] + [SDBS] = 4.0×10^{-3} mol dm^{-3} when the 1-BrN concentration was held constant. This result strongly supports a 1:1 stoichiometry between β-CD and SDBS, suggesting the formation of of a 1:1:1 ternary complex.

The 1:1:1 stoichiometry of the SDBS:1-BrN:β-CD system was also confirmed by the Benesi–Hildebrand equation, $1/\Delta I_p = 1/aK[\text{SDBS}][\beta\text{-CD}] + 1/a$ (where K is the apparent equilibrium constant and a is an instrumental constant combined, [β-CD] and [SDBS] are the equilibrium concentration of β-CD and SDBS, respectively) [20]. Fig. 8 shows a double-reciprocal plot of $1/\Delta I_p$ vs. $1/[\beta\text{-CD}]$ for the SDBS:1-BrN:β-CD system. A linear relationship with correlation coefficient of 0.9920 is obtained, providing additional evidence for the 1:1:1 stoichiometry of a ternary complex. The evaluated K from the ratio of the intercept to slope is $(3.38 \pm 0.50) \times 10^5$ mol^{-3} dm^6 which is much greater than 720 mol^{-1} dm^3 for the 1-BrN:β-CD complex. It reflects that the ternary complex is much more stable than the binary complex. This is also supported by the fact that 1-BrN still shows relatively intense RTP at 60°C (Fig. 9).

On the basis of molecular structure, β-CD is a macrocyclic sugar molecule composed of 6 glucopyranose units arranged in a torus with an
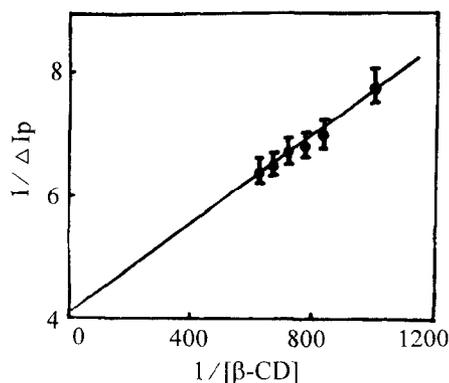

Fig. 8. A Benesi-Hildebrand plot for a SDBS:1-BrN:β-CD system. 1-BrN: 5.0×10^{-5} mol dm^{-3}; SDBS: 4.0×10^{-3} mol dm^{-3}.
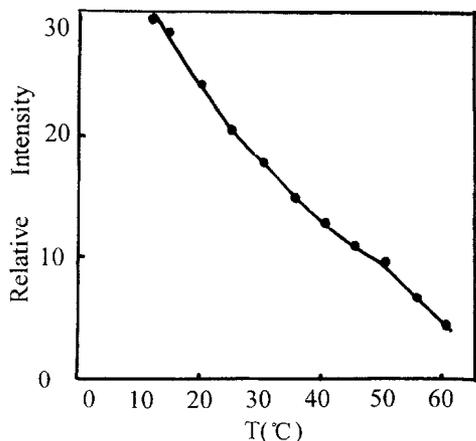
Fig. 9. Dependence of RTP on temperature. 1-BrN: 1.0×10^{-4} mol dm^{-3}; SDBS: 4.0×10^{-3} mol dm^{-3}; β-CD: 2.0×10^{-3} mol dm^{-3}.

internal diameter, a depth and a volume of ~ 7.8, ~ 7.8 Å and ~ 346 Å^3, respectively. Its hydrophobic cavity is able to accommodate 11 water molecules ($V/ \sim 220$ Å^3 [21]) [22]. Nocera and co-workers suggested that one 1-BrN molecule could be entirely buried in the apolar cavity through hydrophobic interaction with respect to the size of 1-BrN molecule (length $(L)/ \sim 7.2$ Å and $V/ \sim 131$ Å^3 [23]) [16]. However, the hydrocarbon chain ($L/ \sim 15.4$ Å and $V/ \sim 324$ Å^3 [24]) of SDBS is not entirely enclosed in the cavity since the β-CD cavity accommodates at most six methylene groups ($L/ \sim 7.8$ Å and $V/ \sim 161$ Å^3) of a fully extended hydrocarbon chain C_nH_{2n+1}. On the other hand, the SDBS fluorescence quenching by 1-BrN also suggests that the phenyl ring of SDBS is close to the 1-BrN molecule in the ternary complex and the external heavy-atom effect of 1-BrN results in the decreased fluorescence yield of SDBS. For this reason, we inferred that the phenyl ring of SDBS was embedded in the apolar cavity and a part of the hydrophobic hydrocarbon tail and the polar head group of SDBS located outside the cavity. So 1-BrN molecule and the part included of SDBS will occupy the greater space in the cavity and most of water molecules will be excluded from the cavity. The excited 1-BrN in the cavity of β-CD is shielded from efficient triplet state quenchers oxygen molecules

dissolved in aqueous solution to a large extent. As a result, the radiationless energy transfer greatly decreases, which is responsible for the pronounced phosphorescence enchancement. Since it carries a polar head group, the ternary complex is homogeneously dispersed in the aqueous solutions which are stable and emits considerably enhanced RTP. It has been found that the emission intensity is proportional to 1-BrN concentration in the range $0 \sim 5.0 \times 10^{-5}$ mol dm^{-3}. The limit of detection is 8.0×10^{-8} mol dm^{-3}.

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