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Phosphorescence study of 1-bromonaphthalene in aerated aqueous solution of surfactant and β-cyclodextrin

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Abstract

Surfactant (S) induced room-temperature phosphorescence (RTP) from 1-bromonaphthalene (1-BrN) in aerated aqueous solution of β-cyclodextrin (β-CD) has been investigated in detail. Benesi–Hildebrand analyses indicate that bright phosphorescence arises from a stable 1:1:1/S:1-BrN:β-CD ternary complex in aqueous solution. Of the surfactants employed, cetylpyridinium bromide (CPB) shows much lower phosphorescence enhancement than cetyltrimethylammonium bromide (CTAB) and polyethylene tert-octyl phenyl ether (OP), and sodium dodecylbenzene sulfonate (SDBS) shows higher phosphorescence enhancement than Tween-20 and sodium dodecyl sulfate (SDS), respectively since the intermolecular energy transfer occurs between 1-BrN in the cavity and an aromatic group of a surfactant in a ternary complex. Simultaneously, the external heavy-atom effect of 1-BrN results in the fluorescence quenching of OP and SDBS. In combination with equilibrium constants, surface tension of solutions and spectral structure, a comparison of molecular size shows that part of the hydrocarbon chain of surfactants is included in the cavity of β-CD and the hydrophobic part with the polar head group located outside the cavity coils at the mouth of β-CD cavity. As a result, the excited 1-BrN is shielded from the efficient phosphorescence quenching oxygen molecules dissolving in water and intense RTP is obtained.

Keywords: Phosphorescence; 1-Bromonaphthalene; Surfactant; β-cyclodextrin

1. Introduction

Cyclodextrin solutions and micellar solutions are extensively used as media for the attainment of phosphorescence [1,2]. A number of groups have presented their work on phosphorescence in two separate systems [3–10]. However, few literature works have dealt with phosphorescence in the mixed media of cyclodextrins and surfactants [11,12]. Turro et al. have studied the host–guest inclusion type association between β-CD and a series of [n-(4-bromonaphthoyl)alkyl] trimethylammonium bromides (n = 1,5,10) via the phosphorescence method, suggesting the two limiting situations where the bromonaphthyl group is buried deep in the cavity or close to surface of the cavity, whereas the alkyl with quaternary ammonium ion coils over the top of the cavity or is included in the cavity, respectively [11]. Femia and ClineLove investigated RTP from phenanthrene in a mixed system of 1,2-dibromoethane, Na/Tl dodecyl sulfate and β-CD [12]. It was postulated that the surfactant monomers aggregate at the open end of the β-CD torus and/or partial inclusion which serves to reduced phenanthrene–water contact. In this work, cationic, non-ionic and anionic surfactants with and without an aromatic group were employed as the second guests for the systematic investigation of the effect of surfactants on RTP of 1-BrN. The purpose is to mimic the inclusion of luminophores and cyclodextrin with a long hydrocarbon chain or cyclodextrins and luminophores with a long hydrocarbon chain and thus provide favorable information for the preparation of targeted cyclodextrins or luminophores. In the experiment, intermolecular energy transfer between 1-BrN and an aromatic group of a surfactant and the fluorescence quenching by 1-BrN of a surfactant was observed in a mixed system. In combination with equilibrium constants, surface tension of solutions and a comparison of molecular size, the inclusion of a surfactant, 1-BrN and β-CD was discussed.

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2. Experimental details

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. CTAB and CPB (Shanghai Reagent Co.) was recrystallized in ethanol. SDS (Sigma), SDBS (Guangzhou Reagents Co.), Tween-20 (Sigma) and OP (Shanghai Reagent Co.) were all used as received. A stock solution of 1.0×10^{-3} mol. dm^{-3} 1-BrN was prepared by dissolving it in appropriate surfactant solutions on ultrasonic bath. Through this work, a solution of 5.0×10^{-5} mol. dm^{-3} 1-BrN was 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 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. Surface tension of the solutions was measured by the maximum bubble pressure method at 25 ± 1°C.

3. Results and discussion

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

Fig. 1 shows the phosphorescence spectra of 1-BrN in aerated aqueous solutions of ionic surfactants and β-CD. In the presence of CTAB, SDBS and SDS, bright phosphorescence was observed, accompanied by the emulsifying solutions and the red-shifts of excitation wavelength from 278 nm of the 1-BrN:β-CD system to 290 nm of the S:1-BrN:β-CD systems. For the OP or Tween-20:1-BrN:β-CD systems, OP and Tween-20 also trigger bright phosphorescence from 1-BrN in aqueous β-CD solutions without deoxygenation, and OP shows greater phosphorescence enhancement than Tween-20. These results suggest that the presence of surfactants greatly improves the microenvironment surrounding 1-BrN and provides effective protection for phosphorescence since the phosphorescence is highly sensitive to its microenvironment. Since the phosphorescence is not observed from the transparent solutions of 1-BrN and β-CD or 1-BrN and a surfactant under our experiment, it is reasonable to attribute such spectral changes to the formation of a ternary complex in aqueous solutions. However, it should be noted that CPB shows much lower phosphorescence enhancement of 1-BrN than CTAB although CPB with pyridinium group carries a long hydrocarbon chain ($CH_3(CH_2)_{15}$–) like CTAB and should induce RTP from 1-BrN. On the contrary, the phosphorescence enhancement of 1-BrN in the presence of OP and SDBS with the phenyl groups is greater than that in the presence of Tween-20 and SDS, respectively. It is probable that the intermolecular energy transfer occurs between 1-BrN and an aromatic group of CPB, OP and SDBS.

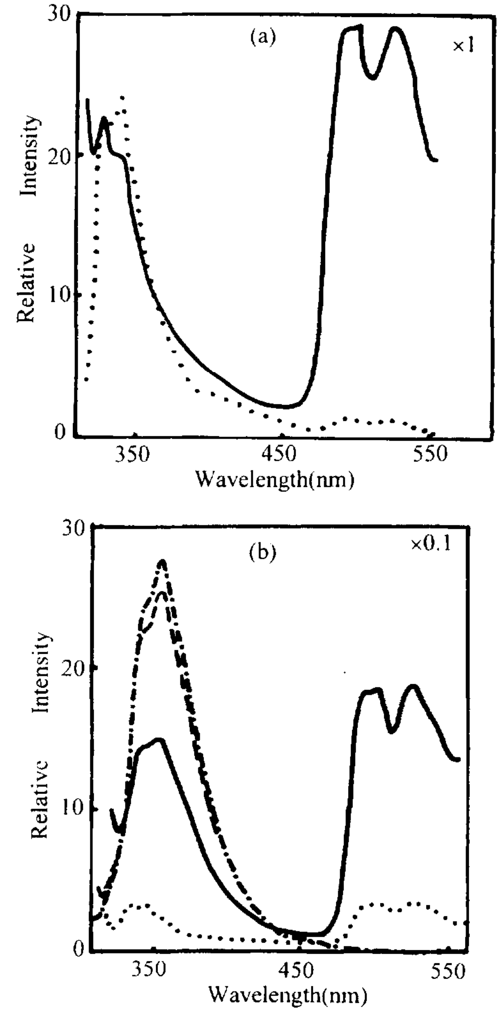

Fig. 1. Luminescence spectra of the S:1-BrN:β-CD systems. (a) CPB:1-BrN:β-CD (· · ·); CTAB:1-BrN:β-CD (———). (b) SDS:1-BrN:β-CD (· · ·); SDBS (- - -); SDBS:β-CD (—); SDBS:1-BrN:β-CD (———). For all systems, the spectra were recorded under the optimum conditions.

In addition, of the surfactants employed OP and SDBS display fluorescence in ultraviolet region for their internal phenyl groups. Fig. 2 shows the representative phosphorescence spectra of the SDBS:1-BrN:β-CD system at various 1-BrN concentration. The phosphorescence intensity was found to increase upon addition of more 1-BrN to the mixed system of β-CD and SDBS and, conversely, the fluorescence intensity gradually decreases. For the OP:1-BrN:β-CD system, a similar result was obtained. It directly indicates that the phenyl group next to the polar head locates in the proximity of the 1-BrN molecule in a ternary complex and the interaction between 1-BrN in the cavity and the phenyl group occurs. The external heavy-atom effect of 1-BrN molecule results in a decreased fluorescence quantum yield of the phenyl groups of OP and SDBS.

3.2. Effect of surfactants on phosphorescence

1-BrN shows no RTP in aqueous β-CD solutions without deoxygenation. Upon addition of surfactants to the solutions of 1-BrN and β-CD, intense RTP from 1-BrN was observed.

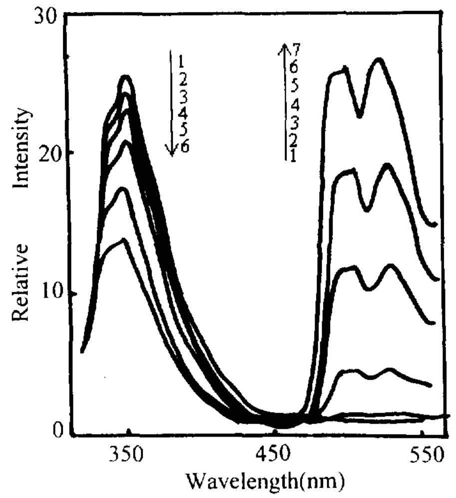

Fig. 2. Luminescence spectra of the SDBS:1-BrN:β-CD system at various concentration of 1-BrN. (1) 0, (2) 5.0×10^{-6} mol dm^{-3}, (3) 1.0×10^{-5} mol dm^{-3}, (4) 2.5×10^{-5} mol dm^{-3}, (5) 5.0×10^{-5} mol dm^{-3}, (6) 1.0×10^{-4} mol dm^{-3}. β-CD, 2.0×10^{-3} mol dm^{-3}.

Fig. 3 shows the phosphorescence intensity and the surface tension of solutions as a function of CTAB and CPB concentration. At CTAB or CPB concentration below 1.5×10^{-3} mol. dm^{-3}, the phosphorescence intensity drastically increases and the highest phosphorescence is obtained, whereas the surface tension of solutions remains constant. Subsequently, the phosphorescence intensity greatly decreases when the surface tension of solutions gradually decreases with the increasing concentration of CTAB or CPB. At CTAB or CPB concentration above its apparent critical micelle concentration, the surface tension of solutions remains constant and the phosphorescence disappears when the solutions become transparent. The spectral analyses suggest that the ternary complexes have dissociated in aqueous solutions since the fluorescence spectra are very similar to those of 1-BrN in CTAB or CPB micellar solutions. The same trends were also observed for non-ionic and anionic surfactants. Clearly, it indicates that the phosphorescence enhancement correlates well with the surfactant aggregation which is responsible for a decrease in the surface tension of solutions.

Until now it has been found that 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 [4,5]. For the S:1-BrN:β-CD system, the formation of a complex can be expressed by the following equilibrium:

$$\mathrm{S}+1-\mathrm{BrN}+\beta-\mathrm{CD}\overset{K}{\rightleftarrows}\mathrm{S}:1-\mathrm{BrN}:\beta-\mathrm{CD}$$

Based on the modified Benesi–Hildebrand equation described by Hamai [13], the following expression can be given:

$$1/\Delta I_p=1/a\cdot K\cdot[\mathrm{S}]\cdot[\beta-\mathrm{CD}]+1/a$$

where ΔI_p is the difference in the phosphorescence intensity of 1-BrN in the presence and absence of β-CD, a is a combined instrumental constant, K is an apparent equilibrium constant and [S] is the equilibrium concentration of a surfactant. When the initial concentration of β-CD, $C_{\beta\text{-CD}}$, is much greater than that of the complex, [β-CD] can be replaced by $C_{\beta\text{-CD}}$. Fig. 4 shows a representative double-reciprocal plot of $1/\Delta I_p$ vs. $1/[\beta\text{-CD}]$ for the OP:1-BrN:β-CD system. For all systems, a linear relationship was observed with correlation coefficients ≥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 a Benesi–Hildebrand analysis. Although they are much greater than the equilibrium constant of the 1-BrN:β-CD complex, the K values show no clear correlation with the type and structure of surfactants and the phosphorescence enhancement. For

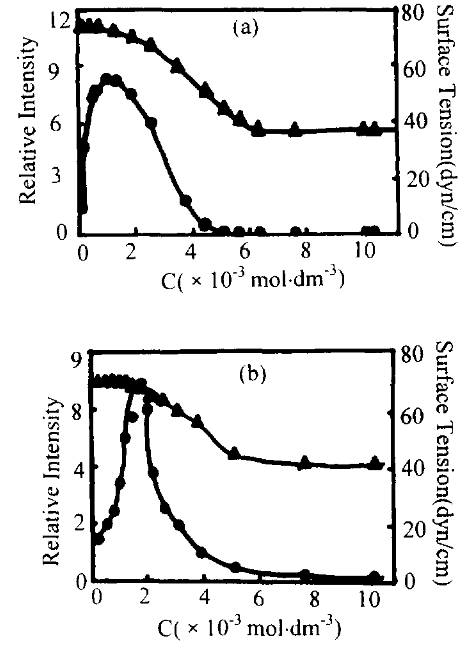

Fig. 3. Dependence of phosphorescence (———) and surface tension (—) of solutions on CTAB and CPB. (a) CTAB (b) CPB. β-CD, 5.0×10^{-3} mol dm^{-3}.

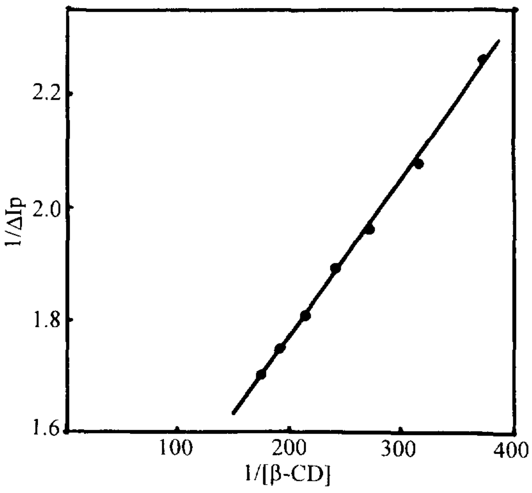

Fig. 4. Benesi–Hildebrand plot for the OP:1-BrN:β-CD system. OP, 2.3×10^{-3} mol dm^{-3}.

Table 1
Equilibrium constants for the S:1-BrN:β-CD ternary complexes

Surfactants	K ($mol^{-2}\,dm^{-6}$)	ι (ms)
NO	$(7.02 \pm 0.29) \times 10^5$	
CTAB	$(5.75 \pm 0.40) \times 10^5$	2.30
CPB	$(1.48 \pm 0.18) \times 10^5$	1.09
OP	$(1.80 \pm 0.20) \times 10^5$	3.62
Tween-20	$(1.90 \pm 0.20) \times 10^4$	3.42
SDS	$(2.40 \pm 0.15) \times 10^5$	2.82
SDBS	$(3.38 \pm 0.50) \times 10^5$	4.83

instance, the K values of the CTAB:1-BrN:β-CD and CPB:1-BrN:β-CD complexes are in the order of 10^5 but CPB with the pyridinium group shows much lower phosphorescence enhancement than CTAB. On the contrary, OP and SDBS with phenyl groups show much greater phosphorescence enhancement than that of Tween-20 and SDS, respectively. These data provide additional evidence for the intermolecular energy transfer between 1-BrN and an aromatic group in a ternary complex. The phosphorescence lifetime measurements also strongly support this suggestion (Table 1).

3.3. Inclusion of surfactants, 1-BrN and β-CD

β-CD is a cyclic oligosaccharide consisting of seven glucose units. The internal diameter, the depth and the total volume of its doughnut-like cavity are about ~7.8 Å, ~7.9 Å and ~346 $Å^3$ [14]. In view of phosphorescence enhancement of 1-BrN, it is likely that 1-BrN ($L \sim 7.2$ Å and $V \sim 131.35$ $Å^3$ [15]) is entirely buried in the cavity. In terms of the length, L (Å), and the volume, V ($Å^3$), of the fully extended hydrocarbon chain C_nH_{2n+1} estimated by $L = 1.5 + 1.265(n-1)$ and $V = 27.4 + 26.9(n-1)$ [16], however, the hydrophobic moiety is not entirely enclosed in the β-CD cavity that has accommodated one 1-BrN molecule since their total volume is larger than that of the β-CD cavity (Table 2). On the other hand, a comparison between the length of the hydrophobic tail and the depth of 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 length of the hydrophobic parts of surfactants employed is longer than the depth of β-CD cavity. On the basis of the fluorescence quenching of OP and SDBS due to the external heavy-atom effect of 1-BrN and the intermolecular energy transfer between 1-BrN and an aromatic group in a ternary complex, the aromatic groups of CPB, OP and SDBS are close to the 1-BrN molecule in the cavity. This clearly suggests that the hydrophobic part located outside the cavity coils at the mouth of the β-CD cavity through the hydrophobic interaction. As a result, the coiled hydrophobic part shields the excited 1-BrN from the efficient phosphorescence quenchers oxygen molecules dissolving in water and provide effective protection for 1-BrN phosphorescence, resulting in considerably enhanced RTP in aqueous solutions. In addition, the rate of intersystem crossing of a phenyl group increases and the intermolecular energy transfer from a phenyl group to 1-BrN occurs due to the external heavy-atom effect of 1-BrN. For the CPB:1-BrN:β-CD system, the energy transfer from 1-BrN to pyridinium ion is present because the positively charged pyridinium ion is a strong electron-accepting group. If not, the fluorescence quenching of the phenyl groups by 1-BrN and the intermolecular energy transfer do not occur at an interval of 6~8 methylene groups of a fully extended hydrocarbon chain.

Table 2
Length (L) and volume (V) of hydrocarbon chains in a surfactant molecule

CnH_{2n+1}	L (Å)	V ($Å^3$)
$CH_3(CH_2)_{15}$–(CTAB)	20.48	430.9
$CH_3(CH_2)_{15}$–(CPB)	20.48	430.9
$CH_3(CH_2)_{11}$–(SDS)	15.42	323.3
$CH_3(CH_2)_{11}$–(SDBS)	15.42	323.3
$(CH_3)_3C(CH_2)_4$–(OP)	7.83	215.7
$CH_3(CH_2)_{11}CO_2$–(Tween-20)	~16.68	~350.2

4. Conclusions

Cationic, non-ionic and anionic surfactants all trigger the phosphorescence from 1-BrN in aerated aqueous solutions of β-CD. A Benesi–Hildebrand analysis and surface tension measurements demonstrate that the phosphorescence arises from the stable 1:1:1/S:1-BrN:β-CD ternary complexes in the premicellar solutions. The phosphorescence enhancement of 1-BrN is strongly dependent upon the structure of surfactants. However, the equilibrium constants shows no clear correlation with the type and structure of surfactants and the phosphorescence enhancement of 1-BrN. CPB with pyridinium group induces much lower phosphorescence than CTAB and conversely, OP and SDBS with a phenyl group induce much higher phosphorescence than respective Tween-20 and SDS for the intermolecular energy transfer between 1-BrN in the cavity and an aromatic group of CPB, OP and SDBS located outside the cavity, which is consistent with the phosphorescence lifetime measurements. Meanwhile, the fluorescence quenching by 1-BrN of OP and SDBS was also observed. A comparison of molecular size suggests that a part of the hydrocarbon chain of surfactants is included in the cavity of β-CD and the hydrophobic part with a polar head group located outside the cavity sits at the open end of the cavity in a folded form. This is responsible for the bright phosphorescence of 1-BrN and results in the intermolecular energy transfer between 1-BrN and an aromatic group of CPB, OP and SDBS and the fluorescence quenching by 1-BrN of OP and SDBS due to their close position.

Acknowledgements

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