

Study on Room-Temperature Phosphorescence of 1-Bromonaphthalene in Media of Surfactant and β -Cyclodextrin

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Abstract: Surfactants(S) induced room-temperature phosphorescence(RTP) from 1-bromonaphthalene(1-BrN) in aerated aqueous solutions of β -cyclodextrin(β -CD) has been investigated in detail. It has been found that the partial inclusion and coil of hydrocarbon chain of surfactants at the mouth of the β -CD cavity is responsible for bright RTP.

Cyclodextrin solutions and micellar solutions are extensively used as the media for the attainment of RTP. A number of groups have presented their work on RTP in the two separate systems^[1,2]. However, few literatures dealt with RTP in the mixed media of cyclodextrins and surfactants^[3]. In this work, a comprehensive study on the effect of surfactants on RTP was undertaken in aerated aqueous β -CD solutions. The purpose is to advance understanding of RTP and provide favorable information for application of RTP.

All surfactants trigger RTP from 1-BrN in aqueous β -CD solutions without deoxygenation. It suggests that the presence of surfactants greatly improves the microenvironment surrounding 1-BrN and provides effective protection for RTP. Since RTP is not observed from the solutions of 1-BrN and β -CD or surfactant, it is reasonable to attribute RTP to the formation of a ternary complex. As shown in Figure 1, however, it should be noted that CPB induces much weaker RTP of 1-BrN than CTAB although CPB with pyridinium group carries a long hydrocarbon chain ($\text{CH}_3(\text{CH}_2)_{15}$ -) like CTAB and should induce RTP from 1-BrN. On the contrary, SDBS with a phenyl group induces much higher RTP of 1-BrN than SDS. It implies that the intermolecular energy transfer occurs between 1-BrN and an aromatic group of CPB and SDBS. In addition, the external heavy-atom effect of 1-BrN also results in

the fluorescence quenching of SDBS(see Figure 1). Like the SDBS:1-BrN: β -CD system, similar result was obtained for the OP:1-BrN: β -CD system. It indicates that the phenyl groups next to the polar heads of OP and SDBS are close to 1-BrN molecule in a ternary complex.

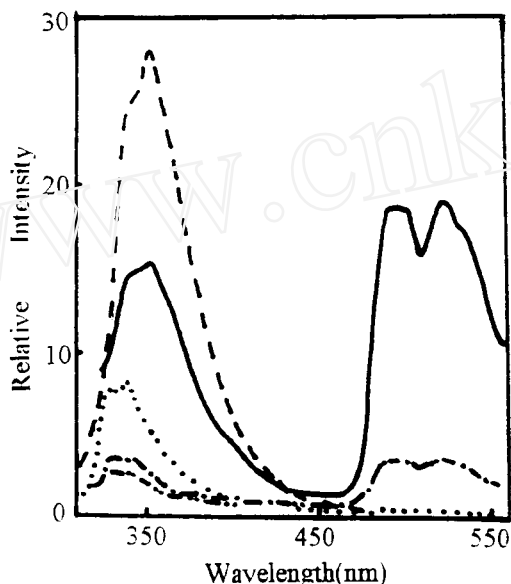


Fig.1 Luminescence spectra of the CPB:1-BrN: β -CD(...), CTAB:1-BrN: β -CD(----), SDS:1-BrN: β -CD(---) and SDBS:1-BrN: β -CD(—) systems and fluorescence spectrum of SDBS(---). For all systems, the spectra were recorded under optimum conditions.

RTP exhibits marked dependence on surfactant concentration. Below its critical micelle concentration(CMC), the intensity drastically increases and the highest phosphorescence is obtained. RTP disappears and the solutions become transparent at surfactant concentration above apparent CMC. 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 micellar solutions. 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.

The stoichiometry and apparent equilibrium constants(K) of the S:1-BrN: β -CD ternary complexes were evaluated by a Benesi-Hildebrand analysis. 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. The K

values are of the order of 10^5 and show no correlation with the type and structure of surfactants and RTP enhancement. These data demonstrate that the RTP enhancement depends on the structure of surfactants and the intermolecular energy transfer occurs between 1-BrN and an aromatic group of CPB, OP and SDBS. The phosphorescence lifetime measurements also strongly support this suggestion (Table 1).

Table 1. Phosphorescence lifetime(τ) of ternary inclusion complexes.

Ternary inclusion complexes	τ (ms)
SDBS:1-BrN: β -CD	4.83
SDS:1-BrN: β -CD	2.82
OP:1-BrN: β -CD	3.62
CTAB:1-BrN: β -CD	2.30
CPB:1-BrN: β -CD	1.09

β -CD is a cyclic oligosaccharide consisting of seven glucose units. The inner diameter, depth and total volume of its doughnut-like cavity are about 7.8Å, 7.9Å and 346Å³, respectively^[44]. 1-BrN molecule is small enough to be entirely buried in the cavity. The length(L) and volume(V) of the fully extended hydrocarbon chain C_nH_{2n-1} are estimated by L=1.5-1.265(n-1) and V=27.4+26.9(n-1)^[45]. However, only 6 methylene groups(L/7.8Å) 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. On the basis of the fluorescence quenching by 1-BrN of OP and SDBS, the aromatic groups of CPB, OP and SDBS are close to 1-BrN molecule in the cavity. This clearly suggests that the hydrophobic part located outside the cavity coils at the mouth of 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 in solutions and provides effective protection for 1-BrN phosphorescence, resulting in considerably enhanced RTP in aqueous solutions. Furthermore, the rate of intersystem crossing from singlet state to triplet state 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.

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