Properties and analytical application of room temperature phosphorescence of 1-bromonaphthalene induced by p-octylpolyethylene glycol phenylether in aqueous β-cyclodextrin solution

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Abstract

Intense room temperature phosphorescence of 1-bromonaphthalene (1-BrN) induced by p-octylpolyethylene glycol phenylether was studied in aqueous β-cyclodextrin solution. The mode of inclusion complex formation was approached. The optimal conditions were obtained. Interferences of foreign substances with phosphorescence were examined. The phosphorescence intensity is proportional to the concentration of 1-BrN in the range $0 \sim 5.18$ µg ml^{-1}. The recovery is 90–102% and the relative standard deviation is less than 4.5%. The proposed method is simple and convenient. © 1997 Elsevier Science B.V.

Keywords: 1-Bromonaphthalene; β-Cyclodextrin; p-Octylpolyethylene glycol phenylether; Phosphorescence

1. Introduction

Micelle-stabilized room temperature phosphorescence (MS-RTP) and cyclodextrin-induced room temperature phosphorescence (CD-RTP) have been proposed for analytical purposes in the eighties [1–5]. Good spectral selectivity was obtained because a majority of organic species do not show phosphorescence at room temperature and the substrates have little or lower background emission in the proximity of the phosphorescence wavelength. For MS-RTP, deoxygenation is needed for the attainment of RTP. However, oxygen removal from micellar solutions by the nitrogen-purging technique results in plentiful bubbles. It has an effect on the precision of analysis. For CD-RTP of polycyclic aromatic hydrocarbons (PAHs) without an internal heavy atom, a bromonated alkane or alcohol was required as an external heavy-atom perturber, sometimes combined with deoxygenation by nitrogen [6–9]. Although no bubbles appear, a phosphoroscope was required for phosphorescence measurements because serious emulsification of the solutions causes strong scattering lights.

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Bromonated naphthalenes are a series of interesting compounds which normally exhibit weaker fluorescence than their parent naphthalene due to their internal heavy atom effect [10,11]. In the presence of acetonitrile or an alcohol, the intense RTP of 1-bromonaphthalene (1-BrN) has been observed from aqueous cyclodextrin solutions without deoxygenation on a conventional spectrofluorimeter [12–15]. Since the microcrystals of the inclusion complex containing an alcohol absorb onto the inner walls of glassware, the phosphorescence intensity is usually unstable at a fixed concentration of phosphors. In this work, p-octylpolyethylene glycol phenylether (OP), a detergent, was employed for the attainment of stable phosphorescence. It can induce intense RTP of 1-BrN in aqueous β-cyclodextrin (β-CD) solution like an alcohol and enables the complex precipitate to disperse in solution due to the complex with the polar head group of OP. As a result, the accuracy and the precision were improved. Furthermore, the interaction of OP with β-CD and 1-BrN and the potential application were also discussed.

2. Experimental

2.1. Reagents

1-BrN, purchased from Shanghai Reagent Co., was distilled under reduced pressure. A solution of 200.7 μg ml^{-1} 1-BrN was prepared by dissolving it in 2.33×10^{-2} mol l^{-1} OP solution in an ultrasonic bath. β-CD, purchased from Suzhou Gourmet Factory, was dissolved in distilled water and recrystallized three times. OP was purchased from Shanghai Reagent Co. and was used as received. Twice demineralized water was distilled.

2.2. Apparatus

All steady-state luminescence spectra were performed on a Hitachi 650-10S fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation light source. Excitation and

emission slits of 3 nm were employed. The scan speed of the monochormators was maintained at 240 nm min^{-1}. The quartz cell was washed with ethanol to guarantee the thorough cleaning of organic species that absorb onto the inner walls of the glassware. It was carefully washed with distilled water prior to use.

2.3. General procedures

An aliquot of 2.33×10^{-2} mol l^{-1} OP 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 samples were allowed to stand for at least 45 min. The samples were introduced into the cell, which was later capped with a Teflon stopper. The RTP signal was monitored at 492 nm when the samples were excited at 290 nm.

3. Results and discussion

3.1. RTP spectra of a ternary inclusion complex

In aqueous solution, 1-BrN exhibits weak fluorescence with an excitation wavelength of 277 nm and emission wavelength of 337 nm. Upon addition of β-CD to the solution, the fluorescence intensity slightly increases due to the formation of the β-CD:1-BrN inclusion complex but no RTP appears. In the presence of both β-CD and OP, 1-BrN gives rise to intense phosphorescence emission at 492 nm and 525 nm at room temperature in aerated aqueous solution, accompanied by the emulsification of the solution. The excitation wavelength redshifts to 290 nm (see Fig. 1). These phenomena suggest that OP has a significant effect on the microenvironment surrounding 1-BrN because phosphorescence is highly sensitive to the properties of environment. A favorable microenvironment is provided in the apolar cavity of β-CD upon addition of OP. It is reasonable to attribute the appearance of RTP to the formation of a ternary complex among β-CD, 1-BrN and OP.
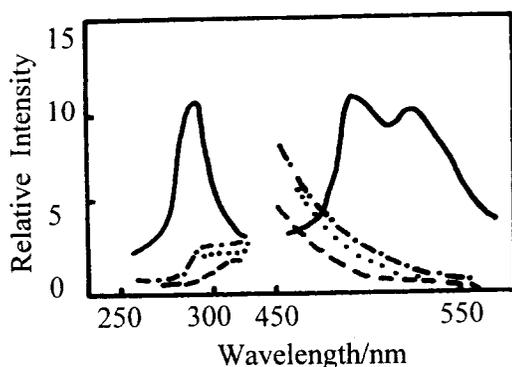
Fig. 1. RTP spectra of inclusion complexes. OP (•-•), β-CD + OP(•••), 1-BrN + OP(- - -) and β-CD + 1-BrN + OP(——). 1-BrN: 20.70 μg ml^{-1}; β-CD: 8.0 × 10^{-3} mol l^{-1}; OP: 2.33 × 10^{-3} mol^{-1} l^{-1}. Photomultiplier, gain: 1.0. Slit width: 3 × 3 mμ.

3.2. Effect of β-CD on RTP

The influence of β-CD on the RTP of 1-BrN was examined at a fixed concentration of 1-BrN and OP. As shown in Fig. 2, the phosphorescence is too weak to be observed at a β-CD concentration below 1.0×10^{-3} mol l^{-1} in the presence of 2.33×10^{-3} mol l^{-1} OP. Subsequently, the phosphorescence intensity rapidly increases with the increasing concentration of β-CD. Although the higher β-CD concentration results in more intense RTP, β-CD of 8.0×10^{-3} mol l^{-1} was used in the experiment due to the limit of its solubility in water.
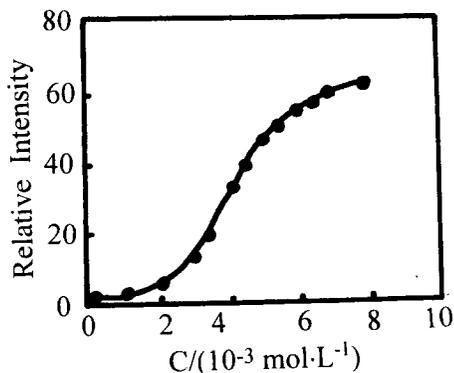

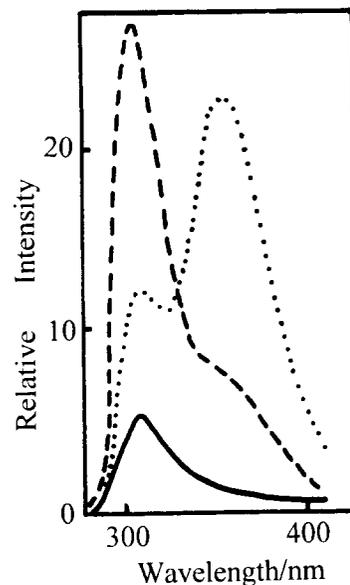Fig. 2. Dependence of RTP on β-CD concentration. 1-BrN: 20.70 μg ml^{-1}; OP: 2.33 × 10^{-3} mol l^{-1}.

Fig. 3. Fluorescence spectra of OP. OP(•••); β-CD + OP(- - -) and β-CD + 1-BrN + OP(——). 1-BrN: 20.70 μg ml^{-1}; β-CD: 8.0 × 10^{-3} mol l^{-1}; OP: 2.33 × 10^{-3} mol l^{-1}.

3.3. Effect of OP on RTP

OP is a nonionic detergent with a tert-octyl group as its hydrophobic part and a polyethylene glycol group as its hydrophilic one. It contains ether groups, a phenyl group and a hydroxyl group. Surface tension measurements suggest that the micelles are not present in aqueous solution containing excess β-CD since the β-CD molecule includes an OP molecule. Fig. 3 shows the fluorescence spectra from a micellar solution of OP in the absence and presence of excess β-CD. The fluorescence at 307 nm ($\lambda_{ex} = 287$ nm) and 360 nm ($\lambda_{ex} = 297$ nm) can be attributed to the OP monomer and OP aggregates, respectively.

Upon addition of OP to the solution containing 1-BrN and 8×10^{-3} mol l^{-1} β-CD, RTP can be observed at 1.54×10^{-4} mol l^{-1} OP. This is accompanied by the slight emulsification of the solution, in which the micelles are not present in aqueous solution due to the inclusion of β-CD with OP. As shown in Fig. 4, the addition of more OP to the solution leads to more intense RTP. In the presence of 2.33×10^{-3} mol l^{-1} OP, the phosphorescence maximum is obtained. Since OP
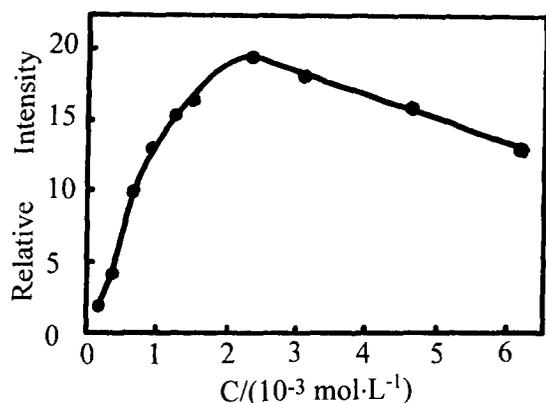
Fig. 4. Dependence of RTP on OP concentration. 1-BrN: 20.70 µg ml^{-1}; β-CD: 8.0×10^{-3} mol l^{-1}.

is an amphiphilic molecule, the complex precipitate homogeneously disperses in aqueous solution. Consequently, the phosphorescence intensity appears stable and good precision was achieved. After the highest phosphorescence intensity, a further increase in OP concentration results in a decrease in the phosphorescence intensity. RTP completely disappears and the solutions become transparent in the presence of more than 1.24×10^{-2} mol l^{-1} OP (more than 8.0×10^{-3} mol l^{-1}). The spectral changes indicate that the complex has completely dissociated. In terms of the surface tension of the solutions, the micelles occurs in the presence of excess OP. Since the spec-

tral properties of 1-BrN in the solutions are similar to those of 1-BrN in the micellar solution of OP, it is possible that the 1-BrN molecule transfers from the β-CD cavity to the micellar core.

The phosphorescence enhancement upon addition of OP indicates that OP is also a micorenvironment regulator in the apolar cavity of β-CD like an alcohol. The hydrocarbon part of OP is incorporated into the apolar cavity of β-CD through the hydrophobic interaction. This result is analogous to those reported by Park and Song [16] and Li and Purdy [17]. By the Benesi–Hildebrand method [18], the stoichiometry of the 1:1:1/ β-CD:1-BrN:OP complex was obtained with phosphorescence measurements. The apparent inclusion constant was estimated as 1.80×10^{-5} mol^{-2} l^2, which is much greater than the value of 720 mol^{-1} l of the β-CD:1-BrN complex. On the other hand, it is seen from Fig. 3 that the ternary complex formation results in a greatly decreased fluorescence of OP at 307 nm. One plausible explanation is that 1-BrN and the phenyl ring of OP locate close to each other in the cavity and 1-BrN seriously quenches the fluorescence of OP due to its external heavy-atom effect. For this reason, most of water molecules in the cavity are replaced by the 1-BrN molecule and the hydrocarbon part of the OP molecule. The rotation of the 1-BrN molecule in the cavity is restricted and the

Table 1
Analytical results of the synthetic samples

Components (µg ml^{-1})	Added (µg ml^{-1})	Found (µg ml^{-1})	Recovery (%)	RSD (%)
1-BrN	1.24	1.26	102	1.4
1-BrN	1.66	1.68	101	1.8
1-BrN	3.31	3.35	101	4.1
naphthalene: 5.13; anthracene: 7.13; biphenyl: 6.16	4.14	3.76	91	4.2
naphthalene: 1.28; acenaphene: 1.54; biphenyl: 1.54; 1-naphthol: 1.44	4.14	3.89	93	1.9
naphthalene: 1.28; anthacene: 1.78; phenanthrene: 1.78; acenaphthenel: 1.54; fluorene: 1.66; biphenyl1: 1.54; 1-Naphthol: 1.44; chrysene: 2.28	4.14	3.86	93	1.9
naphthalene: 2.56; anthacene: 3.56; Phenanthrene: 3.56; acenaphthene: 3.08; fluorene: 3.32; biphenyl: 3.08; 1-naphthol: 2.88; chrysene: 4.56	4.14	3.71	90	1.6

RSD relative standard deviation.

rigidity of the 1-BrN molecule is promoted. Furthermore, the longer phosphorescence lifetime of 1-BrN (3.62 ms) also indicates that the excited triplet state of the 1-BrN molecule in the β-CD cavity is shielded from efficient triplet state quencher oxygen molecules in the solution to some extent. As a result, the probability of a radiationless transition greatly decreases and the phosphorescence intensity dramatically increases.

3.4. Interferences of foreign species

Interferences of other PAHs with the RTP of 1-BrN were studied. Under our experimental conditions, the PAHs examined do not phosphoresce but show strong fluorescence at room temperature. For the determination of 4.14 μg ml^{-1} 1-BrN, 9-fold amounts of anthracene and an equivalent amount of chrysene do not interfere, and 3.7-fold amounts of biphenyl and an equivalent amount of fluorene result in a decrease by 10% in the phosphorescence intensity. Equivalent amounts of phenanthrene and acenaphthene reduce the phosphorescence intensity by 15%. Three-fold amounts of naphthalene and an equivalent amount of 1-naphthol reduce the phosphorescence intensity by 25%.

3.5. Analysis of synthetic samples

A linear relationship between the phosphorescence intensity and 1-BrN concentration was examined. In the range $0 \sim 5.18$ μg ml^{-1}, the phosphorescence intensity is proportional to the concentration of 1-BrN. The straight line has a regression equation of $I_p = 3.355C + 5.703$ and a regression coefficient of 0.9994. Based on a signal-to-noise ratio of three, the limit of detection was estimated as 4.04 ng ml^{-1}. The analytical results of synthetic samples are listed in Table 1. The recovery is 90–102% and the precision is good ($n = 11$). It is suitable for the determination of 1-BrN in a mixture of PAHs.

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