Talanta 162 (2017) 423–427

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A simple method for the determination of benzoic acid based on room temperature phosphorescence of 1-bromopyrene/γ-cyclodextrin complex in water

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ARTICLE INFO

Keywords:
Room temperature phosphorescence
Benzoic acid
1-Bromopyrene

ABSTRACT

The addition of benzoic acid (BA) to an aqueous solution of 1-bromopyrene (1-BrPy) and γ-cyclodextrin (γ-CD) was found to form a ternary 1-BrPy/γ-CD/BA inclusion complex that exhibited strong and stable room temperature phosphorescence (RTP) without deoxygenation. The effects of several different factors on the RTP emission from the inclusion complex were subsequently investigated. A good linear relationship between the RTP intensity and the concentration of BA over the range of 0–0.70 mM was identified (R^2=0.9917), and the detection limit was determined to be 0.68 μm. Application of the new method was successfully proved for the detection of BA in various beverages with satisfactory results.

1. Introduction

Benzoic acid (BA) is naturally present in fruits, such as peaches, plums, strawberries and apples, as well as in cinnamon [1]. BA and its sodium salt are commonly used as preservatives to prevent the alteration and degradation of foods by microorganisms, since they both exhibit inhibitory activity against fungi, yeasts, molds, and bacteria [2,3]. However, BA is toxic when ingested in excessive quantities, and so BA detection is of great significance [4].

At present, there are numerous methods of identifying and quantifying BA, including high-performance liquid chromatography [5], gas chromatography [6], and capillary electrophoresis [7]. Although these chromatography techniques are highly accurate, they are unable to provide rapid determination. Moreover, when employing such methods, increasingly large numbers of samples inherently increase the quantity of solvent or carrier gas used, the preparation time required, and the costs incurred [8]. Several other methods, such as absorption spectrophotometer [9] and luminescence spectrometry [10], have also been applied to determine BA, which are fast, simple and convenient. However, UV spectrophotometer for quantification of BA might be interfered by other food additives [9]. Additionally, in the process of the lanthanide-sensitized luminescence to detect of BA, both of BA and saccharin could enhance the luminescence of the system. So that, it was required that the use of stopped-flow mixing technique to overcome the obstacle [10]. Thus it is necessary to establish a simple and high selective spectrophotometric method for the detection of BA.

Room temperature phosphorescence (RTP) is a sister technology to fluorescence spectroscopy [11], and is also a good choice for BA detection. RTP has many advantages, among which are a longer emission lifetime, good selectivity, a wide linear range, a low detection limit, a wider gap between the excitation and emission wavelengths, and minimal interference from short-lived auto-fluorescence and scattered light [12–14], and thus since RTP was established by Winefordner et al. [15], it has developed rapidly. In addition to solid substrate RTP [16], a variety of RTP methods in liquid solutions have been developed, such as micelle-stabilized RTP [17], cyclodextrin-induced RTP (CD-RTP) [18,19], sensitized/quenched RTP [20], colloidal/microcrystalline RTP [21], and non-protected RTP [22].

Comparing with the other RTP methods, CD-RTP has several advantages; it allows for fast, easy sample preparation, does not easy generate bubbles in the test solution, and exhibits high selectivity and sensitivity [23]. Acting as highly organized host media, CDs have been used to induce RTP under aerated conditions in conjunction with a third component as a space regulator [24]. The particular structure of CDs molecules is an important prerequisite for inducing RTP from the phosphorescent compounds because, in the absence of CD, the system does not produce a RTP signal [25]. CDs are cyclic oligosaccharides composed of 6, 7, and 8 glucopyranose units, which are referred to as α-, β-, and γ-CD, respectively, with hydrophobic cavities [26]. As a result of the confinement of phosphor in the cavity, the RTP was

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http://dx.doi.org/10.1016/j.talanta.2016.10.070
Received 20 July 2016; Received in revised form 7 October 2016; Accepted 17 October 2016
Available online 18 October 2016

enhanced, and the enhancement was found to be dependent on the relative sizes of phosphor and cavity [27]. Although many substances, such as menthol [28], quinine and quinidine [29], protein [30], camphorquinone [31], and bromate [32], have been detected using CD-RTP, to the best of our knowledge, there have been no reports regarding the detection of BA via this method.

In the present work, a system based on γ-CD in conjunction with 1-bromopyrene (1-BrPy) as a phosphor and without deoxygenation, was found to exhibit a strong, stable RTP signal upon the addition of BA. We investigated the formation of a ternary complex during the RTP process, and examined the effects of the concentration of each component on the resulting RTP intensity. Our goal was to optimize the experimental conditions and thus to establish a rapid, facile method for the detection of BA using CD-RTP that does not require any previous separation steps. The method was also meant to exhibit high sensitivity, to be easy to perform and low cost, as well as to be flexible with regard to readout options, and thus readily applied to the practical analysis of real-world samples.

2. Experimental section

2.1. Reagents and apparatus

All solvents were obtained from commercial suppliers (analytical grade) and used as received without further purification. The phosphor 1-BrPy was synthesized according to the literature [33]. γ-CD (Shanghai source leaf biological technology limited company, shanghai, China), was used as received.

RTP spectra were recorded on a Hitachi F-7000 spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan), using 1 cm quartz cells. Water was purified by using a Milli-Q (Billerica, MA, USA) purification system. All pH measurements were made with a Sartorius basic pH-meter PB-10 (Sartorius Instrument & System Engineering Co., Ltd, Göttingen, Germany).

The phosphorescence excitation wavelength was 345 nm. The excitation and emission slit-widths were set both at 20 nm, and the scanning speed were 240 nm/min. All measurements were made at room temperature.

2.2. The samples preparation procedures

A stock solution of 0.10 mM 1-BrPy was prepared in dichloromethane, and stood in the dark for one night. The stock solutions of 0.010 M γ-CD and 0.10 M BA were prepared and kept in volumetric flask. The pH was adjusted either with analytical grade HCl or NaOH aqueous solution.

Typically, appropriate amount of stock solutions of 1-BrPy was transferred into a 5.0 mL volumetric flask (the dichloromethane was evaporated gently) and then proper volumes of γ-CD and BA solutions were added. The mixed solution was diluted to the final 5 mL with Ultra-pure water and Ultrasonic vibration. The working solutions were left to equilibrate at room temperature and then were transferred into a 1 cm standard quartz cell to measure the phosphorescence spectra.

3. Results and discussion

3.1. RTP spectra of 1-BrPy/γ-CD/BA system

The cavity of γ-CD is hydrophobic, while the exterior portion of the molecule is hydrophilic. Because of this particular molecular structure, the phosphor tends to enter the cavity to form an inclusion complex in which it is protected, reducing various quenching processes that might otherwise occur and the third component played an important role to obtain strong RTP [34]. So we thought the addition of BA to the aqueous solution of 1-BrPy and γ-CD could form a 1-BrPy/γ-CD/BA ternary inclusion complex and generated a strong RTP signal. In order to verify the idea, the RTP spectra of 1-BrPy/γ-CD/BA system were researched. The excitation and emission spectra obtained from this complex were shown in Fig. S1, from which it was evident that the excitation wavelength and emission wavelength were 345 nm and 612 nm, respectively.

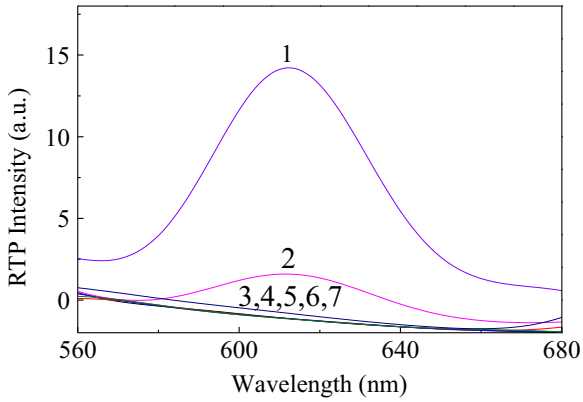

Fig. 1. RTP spectra of different solutions. 1: 1-BrPy/γ-CD/BA; 2: 1-BrPy/γ-CD; 3: 1-BrPy/BA; 4: γ-CD/BA; 5: 1-BrPy; 6: γ-CD; 7: BA. ([1-BrPy]=0.10 μm, [γ-CD]=3.0 mM, [BA]=1.0 mM, λ_{ex}=345 nm).

As shown in Fig. 1, no RTP signals were obtained from the solutions containing 1-BrPy, BA, γ-CD, 1-BrPy/BA or γ-CD/BA, although a mixture of 1-BrPy and γ-CD shown very weak phosphorescence (I_{P0}=1.43, $\lambda_{max(em)}$=612 nm), presumably resulting from the inclusion of 1-BrPy into the γ-CD cavity in the presence of oxygen. However, a powerful synergetic effect resulted from mixing both γ-CD and BA with 1-BrPy, such that the RTP emission of the 1-BrPy was significantly enhanced (I_P/I_{P0}=9.96, $\lambda_{max(em)}$=612 nm). Thus, it could be inferred that a γ-CD/1-BrPy/BA complex was indeed generated.

To optimize the experimental conditions, the effects of γ-CD concentrations and pH on the RTP emission intensities of 1-BrPy/γ-CD/BA solutions were tested. The data in Fig. 2 show that the RTP intensities increased with increasing addition of γ-CD during the initial stage. Then the RTP intensities reached a maximum, and a plateau was obtained in the concentration range of γ-CD from 2.5 mM to 3.5 mM, indicating that the complex formation was complete. Therefore the γ-CD concentration of 3.0 mM was used in all subsequent experiments.

In order to eliminate the disturbance by the effect of pH on the RTP, the effects of pH on the RTP intensities of 1-BrPy/γ-CD and 1-BrPy/γ-CD/BA solutions were studied. As shown in Fig. 3, the plots of the emission intensities as functions of pH both without and with BA, it could be found that the pH value had little effect on the RTP intensities in both cases.

3.2. RTP response towards BA

The effects of adding BA and other food additives for drinks, as well as common acids (all at 1.0 mM) on the RTP spectra and intensities of the 1-BrPy/γ-CD complex were also investigated. As shown in Fig. 4, the RTP intensity of the 1-BrPy/γ-CD complex increased significantly upon the addition of BA, while the intensities of the 1-BrPy/γ-CD complex in the presence of other food additives for drinks and common acids did not influence relative to the intensity obtained with blank.

The results provided evidence that the RTP intensities of the 1-BrPy/γ-CD complex shown specific selectivity towards BA, which was result from multiple factors, such as hydrophobic forces, π-π interactions, molecular size and shape [35,36]. Among the food additives for drinks and common acids, BA, saccharin and phenylalanine are the organic molecules consisting of a phenyl ring, which is a hydrophobic group and probably form π-π stacking with 1-BrPy in the cavity of γ-CD. However, only did BA obviously enhance the RTP of the system. It may be caused by the differences of molecular shape and charge