Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 173 (2017) 6–12

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Determination of dopamine hydrochloride by host-guest interaction based on water-soluble pillar[5]arene

Xue-Dong Xiao, Lin Shi, Li-Hui Guo, Jun-Wen Wang *, Xiang Zhang *

Department of Chemistry, Shanxi Normal University, Linfen 041004, China

ARTICLE INFO

Article history:
Received 3 June 2016
Received in revised form 23 August 2016
Accepted 25 August 2016
Available online 27 August 2016

Keywords:
Water-soluble pillar[5]arene
Dopamine hydrochloride
Spectrofluorometry
Supramolecular interaction

ABSTRACT

The supramolecular interaction between the water-soluble pillar[5]arene (WP[5]) as host and dopamine hydrochloride (DH) as guest was studied by spectrofluorometry. The fluorescence intensity of DH gradually decreased with increasing WP[5] concentration, and the possible interaction mechanism between WP[5] and DH was confirmed by ^{1}H NMR, 2D NOESY, and molecular modelling. Based on significant DH fluorescence, a highly sensitive and selective method for DH determination was developed for the first time. The fluorescence intensity was measured at 312 nm, with excitation at 285 nm. The effects of pH, temperature, and reaction time on the fluorescence spectra of the WP[5]-DH complex were investigated. A linear relationship between fluorescence intensity and DH concentration in the range of 0.07–6.2 μg mL^{-1} was obtained. The corresponding linear regression equation is $\Delta F = 25.76\ C + 13.56$ (where C denotes the concentration in μg mL^{-1}), with the limit of detection equal to 0.03 μg mL^{-1} and the correlation coefficient equal to 0.9996. This method can be used for the determination of dopamine in injection and urine samples. In addition, the WP[5]-DH complex has potential applications in fluorescent sensing and pharmacokinetics studies of DH.

1. Introduction

Pillar[*n*]arenes, first reported by Tomoki Ogoshi in 2008 [1], are a novel class of macrocyclic hosts following on from crown ethers, cyclodextrins, calixarenes and cucurbiturils. These compounds do not only show unique symmetrical pillar-shaped architecture but also possess other excellent properties of supramolecular macrocyclic host compounds [2–10]. Few years after their discovery, pillar[*n*]arenes have already been widely used in molecular recognition [11], self-assembly [12], preparation of liquid crystals [13], and other fields.

In recent years, research on efficient receptors work in water aroused great interest in the molecular recognition field, since most biological processes take place in aqueous media [14,15]. Therefore, to investigate the inclusion properties of pillar[5]arenes in water, various water-soluble pillararenes were obtained by introducing positively, and negatively charged or neutral groups onto the pillararene skeleton, as showed in Fig. 1. For example, an anionic pillar[5]arene with ten negatively charged carboxylate groups attached at both rims, capable of binding cationic viologen salts in water, was first reported by Tomoki Ogoshi [16] in 2010 (Fig. 1A). Huang [17] prepared a cationic pillar[5]arene in 2011, which forms a stable 1:1 host guest complex with sodium 1-octanesulfonate in water (Fig. 1B). In addition, the above groups reported pillar[5]arene-based imidazolium salts in 2012 [18], and the water-soluble pillar[5]arene (WP[5]) was used as a stabilizer to fabricate gold nanoparticles in water (Fig. 1C).

It is well known that dopamine is a naturally occurring messenger in the central nervous system, a neurotransmitter that controls many biological functions, e.g. emotion, cognition, endocrine regulation, motivation, etc. [19]. Furthermore, disordered levels of dopamine may lead to numerous neurological diseases, such as the Parkinson disease or schizophrenia [20], with the use of some type of drugs being linked to a dysregulation of dopaminergic transmission [21]. Therefore, much research is focused on developing methods for direct measurement of dopamine levels, which is particularly essential for the early diagnosis of certain diseases [22]. Dopamine has been studied and determined in biological samples and pharmaceutical formulations using electrochemical and HPLC methods [23]. However, the problem of electrochemical methods is the formation of a nonconductive dopamine quinoid polymer, which inactivates the electrode surface [19]. In addition, HPLC techniques are time-consuming and restricted to highly specialized laboratories.

Dopamine is easily oxidized to dopamine quinone in air. However, dopamine hydrochloride (DH) is relatively stable [24,25], since the dopamine molecules are protonated. In this report, we demonstrate that DH can be determined using a simple and sensitive spectrofluorometric method. Consequently, we investigated the inclusion interaction between WP[5] and DH using fluorescence spectrophotometry. We observed that the intensity of DH fluorescence gradually decreased as the concentration of WP[5] was increased. The effect of pH,

* Corresponding authors.
E-mail addresses: wangjunwen2013@126.com (J.-W. Wang), Xiangzh2000@hotmail.com (X. Zhang).

http://dx.doi.org/10.1016/j.saa.2016.08.050
1386-1425/

temperature, and reaction time were also investigated. A possible interaction mechanism between WP[5] and DH was confirmed by molecular modelling, ^{1}H NMR, and 2D NOESY.

2. Experimental

2.1. Instruments

Fluorescence spectra were measured on an F-380 fluorescence spectrofluorometer (Gang Dong, China). The slit widths of both excitation and emission monochromators were set to 5 nm. The fluorescence spectra scan rate was 240 nm min^{-1}. ^{1}H NMR and 2D NOESY spectra were recorded on a Bruker AVANCE III HD 600 MHz spectrometer in D_2O with TMS as an internal reference. All pH values were measured with a pHS-3TC digital precision pH meter (Jia Peng, China). Structural optimization was performed by a semiempirical quantum chemistry method (PM6) implemented in the Gaussian 09 software.

2.2. Reagents and chemicals

DH was purchased from Aladdin Company. WP[5] was prepared and characterized according to a procedure reported in literature [18]. All samples were prepared using double-distilled water and degassed by bubbling highly pure nitrogen for 15 min before preparation. All other reagents were of analytical grade. The Britton–Robinson buffer solution (pH 2.00–11.00) was prepared using 0.04 mol L^{-1} boric acid, followed by adjustment to the desired values by addition of 0.2 mol L^{-1} sodium hydroxide.

2.3. Experimental procedure

The 0.1 mM DH standard working solution (1.0 mL) was placed in a 10 mL colorimetric cylinder, and a certain volume of the 0.1 mM WP[5] standard working solution was then added. The mixture was diluted to 10 mL with fresh double-distilled water and shaken for 10 min at room temperature. The fluorescence intensity values of both WP[5]-DH and DH (blank solutions) were measured using an excitation wavelength of 285 nm.

3. Results and discussion

3.1. Optimization of experimental conditions

3.1.1. Quenching of DH Fluorescence in Presence of WP[5]

DH aqueous solutions exhibited strong fluorescence in absence of WP[5]. However, we observed significant quenching of DH fluorescence intensity after the addition of WP[5]. The result of fluorescence spectra between DH and WP[5] was confirmed. The DH fluorescence spectra are shown in Fig. 2. The DH fluorescence intensity decreased with increasing WP[5] concentration, and a red shift was observed, indicating the formation of an inclusion complex between DH and WP[5].

3.1.2. Influence of pH

In order to obtain maximum fluorescence decrease values (ΔF), the effect of pH in the range from 2 to 12 was investigated (Fig. 3a). The results show that ΔF was maximized in acidic environment, subject to slight changes. However, ΔF significantly decreased in alkaline environment (pH > 8). Hence, the pH was adjusted to 6.0 using hydrochloric acid, which was the desired value for subsequent experiments.

3.1.3. Influence of temperature and reaction time

The effect of temperature on ΔF was examined within 10–60 °C (Fig. 3b). ΔF tends to be a steady value below 35 °C. Above this temperature, ΔF decreased due to the dissociation of inclusion complex. Hence, all subsequent measurements were performed at room temperature.

In addition, ΔF reached a maximum within 10 min after addition of WP[5] to aqueous DH solutions and remained constant for several hours (Fig. 3c). Hence, fluorescence spectra were recorded after 10 min when WP[5] and DH were mixed in aqueous solution at room temperature.

3.2. Stoichiometry and apparent association constant

The stoichiometry and association constant of the inclusion complex were studied under the established conditions by the following method.

Assuming a 1:1 complex composition, the equilibrium can be depicted as follows:

$$WP[5] + DH \Longleftrightarrow WP[5]-DH \quad (1)$$

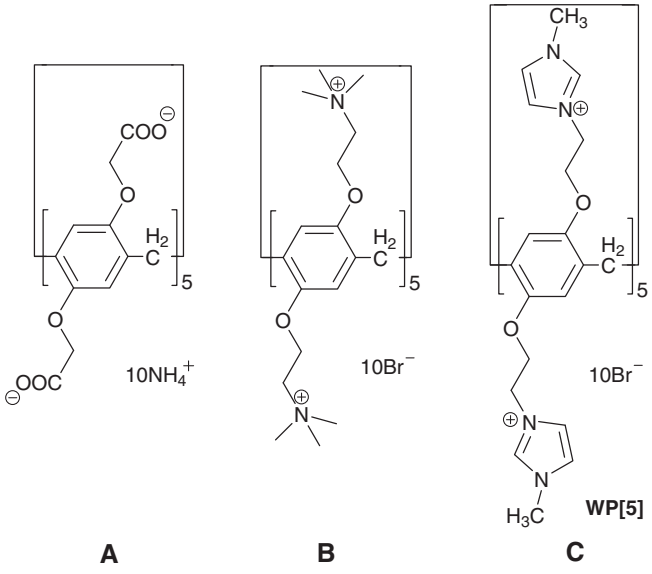

Fig. 1. Structures of partial water-soluble pillar[5]arenes.

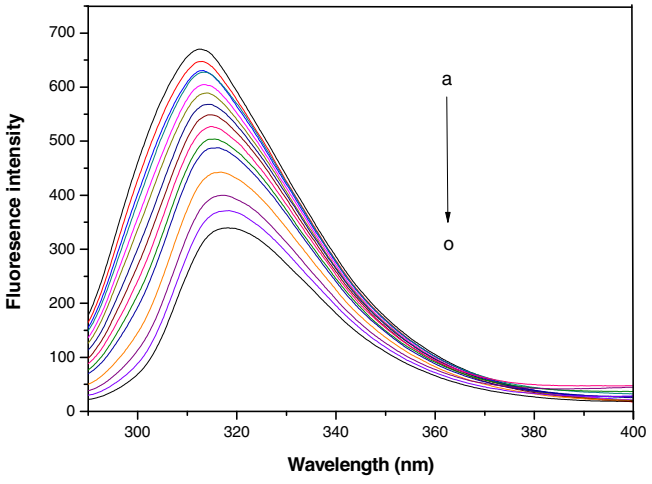

Fig. 2. Fluorescence spectra of the DH in different concentrations of WP[5] aqueous solution with $\lambda_{ex} = 285$ nm. The concentrations of WP[5] (10^{-5} mol L^{-1}): (a) 0; (b) 0.2; (c) 0.4; (d) 0.6; (e) 0.8; (f) 1.0; (g) 1.4; (h) 1.6; (i) 1.8; (g) 2.0; (k) 3.0; (l) 4.0; (m) 5.0; (n) 6.0; (o) 7.0. $C_{DH} = 1.0 \times 10^{-5}$ mol L^{-1}.