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Investigation on the electrochemiluminescent behaviors of oxypurinol in alkaline $Ru(bpy)_3^{2+}$ solution using a flow injection analytical system

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Abstract

Electrochemiluminescent (ECL) behaviors of oxypurinol in alkaline tris(2,2-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) solution were studied in a flow injection electrochemiluminescent system (FI-ECL) in this paper. It was found that the ECL response of oxypurinol was significantly pH-dependent. It inhibited the ECL of $Ru(bpy)_3^{2+}$ at $\leqslant$pH 10.0, whereas exhibited enhanced ECL response at pH $\geqslant$ 11.0. Additionally, other experimental conditions such as the applied potential of working electrode, the flow rate of carrier solution, and the concentration of $Ru(bpy)_3^{2+}$ were all observed to affect the ECL response of oxypurinol. Under the optimum conditions, the logarithm of enhanced ECL intensity, ΔI, was found linearly proportional to the logarithm of oxypurinol concentration in the range of 1.0×10^{-7}–1.0×10^{-4} mol L^{-1}, and the detection limit ($S/N = 3$) was 3.0×10^{-9} mol L^{-1}. The mechanism of inhibited and enhanced $Ru(bpy)_3^{2+}$ ECL by oxypurinol was studied, and a new and sensitive flow injection analysis (FIA) method basing on the enhanced ECL was proposed for detection of oxypurinol.

Keywords: Electrochemiluminescence; Oxypurinol; Flow injection analysis; Tris(2,2′-bipyridine) ruthenium (II)

1. Introduction

As the oxidative product of allopurinol, oxypurinol is a well-known inhibitor of xanthine oxidase [1–3], and has the similar pharmacodynamic activity as allopurinol. Now, oxypurinol is more and more being used to replace allopurinol in the therapy of some diseases, such as testicular damage [4], gout [5], nonbacterial prostatitis [6], ischemic brain injury [7–10] and coronary artery disease [11], especially after some patients were found to have hypersensitivity syndrome to allopurinol [12,13].

The establishment of a sensitive method to determine oxypurinol at low level is of great significance for pharmacokinetic and clinical studies. The conventional methods for the determination of oxypurinol include ultraviolet (UV) spectrophotometry and electrochemical methods, usually combining with HPLC and capillary electrophoresis (CE) [14–19]. As far as we know, no attention has been paid to determination of oxypurinol by electrochemiluminescence (ECL), although ECL is a powerful analytical method with high sensitivity and wide linear response range [20–24]. Herein the ECL behaviors of oxypurinol in the presence of tris(2,2′-bipyridine) ruthenium (II) ($Ru(bpy)_3^{2+}$) were studied, and on this basis a rapid and sensitive flow injection electrochemiluminescent (FI-ECL) detection method for oxypurinol was established.

2. Experimental

2.1. Materials

Tris(2,2-bipyridine)ruthenium(II) chloride hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$) and oxypurinol were purchased from Sigma–Aldrich and used without further purification. A

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1×10^{-2} mol L^{-1} stock solution of $Ru(bpy)_3^{2+}$ was prepared with double-distilled water. A 1×10^{-2} mol L^{-1} stock solution of oxypurinol was prepared by adding 0.0136 g sample in 10 mL of 2×10^{-2} mol L^{-1} sodium hydroxide solution. All above stock solutions were stored in a refrigerator.

The phosphate buffer solutions (pH 2–13) were prepared by titrating 0.1 mol L^{-1} phosphoric acid solutions with a concentrated sodium hydroxide solution to the required pH value. Carrier solution was prepared by diluting $Ru(bpy)_3^{2+}$ with phosphate buffer solution. Sample solution was prepared by adding required volume of the oxypurinol stock solution into the carrier solution.

2.2. Apparatus

A homemade FIA-ECL system (see Fig. 1) was used for the ECL measurements. The FIA-ECL system was similar with those reported previously [23–25], except for a different ECL flow cell was used. The ECL flow cell consisted of two pieces of Perspex blocks (0.5 cm and 1.0 cm thick respectively) and a piece of Teflon membrane (50 μm thick). The 0.5 cm thick Perspex block was used as an optical window, and the 1.0 cm thick Perspex block was utilized for mounting a Pt disk working electrode (22.1 mm^2), a Ag/AgCl reference electrode, a counter electrode (a piece of stainless steel pipe at the outlet) and solution channels. The Teflon membrane with a rectangle hole in the center was sandwiched between the two Perspex blocks to keep ca. 2.5 μL of thin layer solution.

A CHI660C electrochemical workstation (CH Instruments, USA) with a three-electrode system was used for cyclic voltammetric experiments. The three electrode system included a Pt disk working electrode (1.6 mm, BAS), a Ag/AgCl reference and a Pt wire counter electrode.

2.3. ECL measurement

Before experiments, the working electrode was carefully polished with superfine aluminum powder and cleaned by double distilled water in an ultrasonic bath. The FIA-ECL manifold is shown in Fig. 1. The ECL measurement was carried out in two steps. *Step 1*: the sample solution was pumped into the sampling valve to fill the loop (100 μL) for 10 s by pump A. Simultaneously, the carrier solution was pumped into the ECL detector by pump B. *Step 2*: Pump A was stopped, and the sampling valve was turned to injection position; the carrier solution was pumped to the loop by pump B to take the sample solution to the ECL flow cell, where the ECL of sample was generated and measured. The flow rate of solution was adjusted by changing turning rate of pumps.

3. Results and discussion

3.1. ECL response of oxypurinol in the presence of $Ru(bpy)_3^{2+}$

The ECL activity of oxypurinol has been examined primarily in a wide pH range (pH 2–13) and the results showed that no light emission could be observed, but it could enhance the ECL emission of $Ru(bpy)_3^{2+}$ under a strongly alkaline condition over pH 11, giving rising to sensitive FI-ECL responses (see Fig. 2). The fact that the enhanced portion of ECL intensity (ΔI), i.e. FI-ECL peak height, which was increased with increasing of the concentration of oxypurinol indicates that oxypurinol acts as an enhancer to $Ru(bpy)_3^{2+}$ ECL. In order to reveal the enhanced ECL mechanism, effects of experimental conditions such as the mode of applied voltage signal, the potential of working electrode, pH value, the flow rate of carrier solution, and the concentration of $Ru(bpy)_3^{2+}$ and oxypurinol were investigated and discussed.

3.1.1. Effect of applied potential

Different modes of potential, such as the constant potential (DC), double step potential (rectangular wave) and linear sweep potential (triangular wave) have been tried to examine the ECL response of oxypurinol in the presence of $Ru(bpy)_3^{2+}$. It was found that oxypurinol had the most

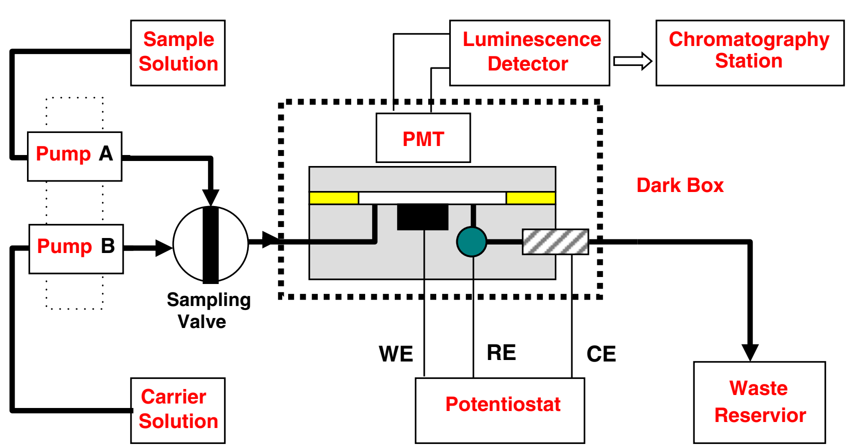

Fig. 1. Schematic diagram of the flow injection electrochemiluminescent (FI–ECL) system used for ECL measurements.