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The fluorescence and resonance Rayleigh scattering spectral study and analytical application of cerium (IV) and cefoperazone system

Yusheng Yuan, Shenghui Fu, Qianying Xu, Jidong Yang, Xiaoli Hu, Shaopu Liu *

Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

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ABSTRACT

In weak acidic medium of pH 3.5–5.6, Ce(IV) can be reduced by cefoperazone (CPZ) to be Ce(III), which further combined with CPZ to form complex $Ce(OH)_3CPZ$. This complex not only has higher fluorescence than Ce(III), but also results in significant increase of resonance Rayleigh scattering (RRS), second order scattering (SOS) and frequency doubling scattering (FDS). The wavelengths of maximum fluorescence exciting and emission are located at 356 nm/349 nm, while the maximum wavelengths of RRS, SOS and FDS are at 312 nm, 550 nm and 390 nm, respectively. The intensity of fluorescence and scattering are all linear with the concentration of CPZ in certain conditions. The detection limit of most sensitive RRS method for CPZ is 2.1 ng mL^{-1}. The optimum conditions for detecting CPZ using RRS method are investigated. The effect of co-existing substances shows that the method has excellent selectivity, especially since other cephalosporins don't have similar reactions. Therefore, it can be achieved to determine CPZ in cephalosporins selectively. The paper also focuses on the reaction mechanism, the consistent and contracture of the resultant. The reasons for enhanced intensity are presumed in the meantime.

1. Introduction

Cefoperazone (CPZ) is a third-generation cephalosporin, stable for β-lactam enzyme, having a broad spectrum of antibacterial activity which includes Gram-negative *bacteria*, Proteus, *Escherichia coli*, Klebsiella and so on. Especially, unlike older cephalosporins, its antibacterial effect on *Pseudomonas aeruginosa* is several times stronger than the 2nd and 3rd penicillin drugs. Cefoperazone is a common therapy for respiratory infections, biliary tract infection and septicemia caused by the above bacteria, and exhibits excellent efficacy for treatment of *P. aeruginosa* infection. Therefore cefoperazone is one of the widely-used cephalosporins in clinical [1,2].

So far, a variety of methods such as UV–visible spectroscopy [3–6], fluorescence [7,8], chemiluminescence [9–11], HPLC [12–14], capillary electrophoresis [15,16], LC–MS [17], atomic absorption spectrometry [18] and thin layer chromatography [19] have been used to quantitate cefoperazone. However, most spectrophotometry methods have bad sensitivity and selectivity. They can't detect CPZ selectively because other cephalosporins have similar chromogenic reaction. The sensitivity of fluorescence, chemiluminescence and some electrochemical methods are high, but these methods are short of selective recognition for CPZ. Also other co-existing substances will influence the determination in some of these methods. HPLC and LC–MS improve the situation, but their sensitivities are not high enough and are relatively complicated (the detection limit of common RP-HPLC is 0.2–20 μg mL^{-1}, and LC–MS is 0.10 μg mL^{-1}). Furthermore, it made the simultaneous determination of multi-component and high separation efficiency come true, yet the equipment and analysis cost were expensive and high. As for capillary electrophoresis, it had higher efficiency, low waste production and fast separation. However, the repeatability was not very satisfactory. For this reason, it is still important to develop highly sensitive, selective, simple and rapid methods for determining CPZ.

Resonance Rayleigh scattering (RRS), a new simple and sensitive analytical technique developed in the 1990s [20,21], has been widely used to analyze biomacromolecule, pharmaceutics, organics and metal ions [22–24]. In recent years, the RRS increase system of Pd(II)–cephalosporins–dibromofluorescein, used for determining CPZ, has high sensitivity (the detection limit is 2.7 μg mL^{-1} [25]). However, ceftzideme, ceftrizxone, and cephalothin can cause the same phenomenon. So the selectivity is also poor. As we know, in alkaline medium, cefoperazone degrades by heating, and the degradation products can react with Ce(IV) in acidic medium to produce a new luminescent reaction. The addition of rhodamine 6G enhances the luminescence, and this reaction can be used for detecting CPZ. Although this method has high sensitivity (the detection limit is 40 ng mL^{-1}), it's too complicated, and other common cephalosporins can also react with it [9]. Herein, it is found that in weak acidic medium, the redox reaction between Ce(IV) and cefoperazone occurs at room temperature, at the same time, a Ce(III)–CPZ chelate with strong fluorescence formed, causing significant enhancement of resonance Rayleigh scattering (RRS), second-order scattering (SOS) and frequency

* Corresponding author.
E-mail address: liusp@swu.edu.cn (S. Liu).

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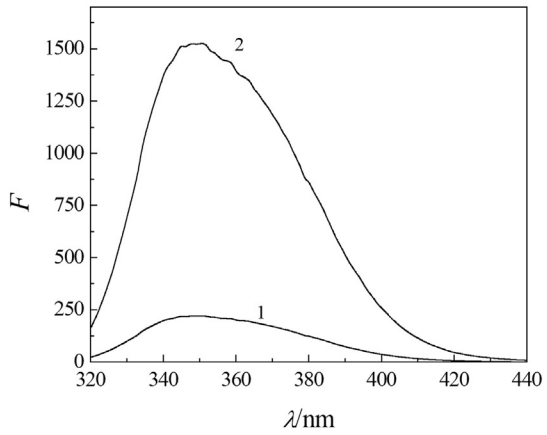

Fig. 1. Florescence spectra. 1: Ce(IV); 2: Ce(IV)–CPZ; $c_{Ce(IV)} = 3.0 \times 10^{-5}$ mol L^{-1}; $c_{(CPZ)} = 2.0$ μg mL^{-1}.

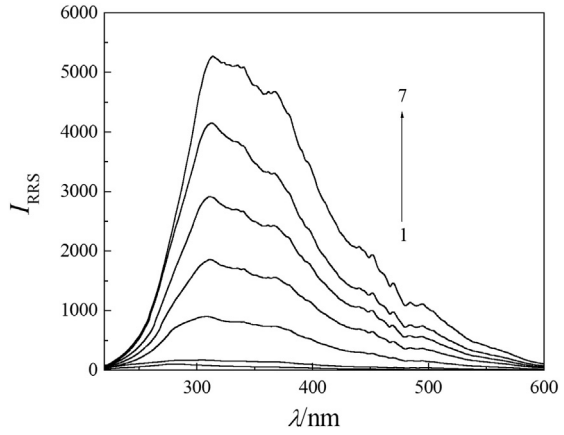

Fig. 2. RRS spectra. 1.: Ce (IV): 3.0×10^{-5} mol L^{-1}; 2.: CPZ: 2.5 μg mL^{-1}; 3.–7.: Ce(IV)–CPZ. $c_{Ce(IV)}$: 3.0×10^{-5} mol L^{-1}, $c_{(CPZ)}$: 0.5, 1.0, 1.5, 2.0, and 2.5 μg mL^{-1}.

doubling scattering (FDS). Therefore, fluorescence and scattering method can be used for detecting CPZ. They are simple and much more sensitive (the detection limit of fluorescence is 6.5 ng mL^{-1}, and RRS is only 2.1 ng mL^{-1}), and the more important is that some common cephalosporin drugs have no similar reaction, so the selectivity is better than the above methods.

In this paper the spectral characters of fluorescence, RRS, SOS, and FDS, the optimum reaction conditions and the influencing factors have been studied. The analytical chemical properties such as sensitivity and selectivity are investigated. The reaction mechanism, including the reasons for the increase of fluorescence and RRS and the composition of chelate is determined. Accordingly, a novel rapid, simple and sensitive RRS method for determination of cefoperazone is proposed using Ce(IV) as a probe.

2. Experiment

2.1. Apparatus and reagents

A Hitachi F-2500 spectrofluorophotometer (Tokyo, Japan) was used for recording fluorescence and scattering spectra and measuring intensities at a given wavelength using a 1 cm path length. A UV-2450 spectrophotometer (Shimadzu, Japan) was used for acquiring absorption spectra and measuring absorbance. A pHS-3D pH meter (Shanghai Scientific Instruments Company, China) was used to measure the pH values.

A stock solution of cefoperazone (200 μg mL^{-1}, Zhonghua Pharmaceutical Co. Ltd.) was prepared and kept at 4 °C. A stock solutions of Ce(IV) (1.0×10^{-2} mol L^{-1}, Shanghai Chemical reagent procurement and supply station) was prepared. Working solutions were freshly prepared by diluting the corresponding stock solutions. HAc–NaAc buffer solution was used to control the acidity. All other reagents were analytical reagent grade and used without further purification. Doubly distilled water was used throughout.

2.2. General procedure

Into a 10.0 mL calibrated flask, 0.8 mL of pH 4.4 HAc–NaAc buffer, 0.3 mL of Ce(IV) solution and appropriate amount of CPZ solution were added. Then it was diluted to the mark and thoroughly mixed. After 5 min, the fluorescence spectra of the system were recorded and the RRS spectra were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ ($\Delta\lambda = 0$ nm) and the SOS and FDS spectra were measured at $\lambda_{ex} = 1/2\lambda_{em}$ and $\lambda_{ex} = 2\lambda_{em}$, respectively. According to the spectra, the intensities were measured at their maximum wavelengths. The enhanced intensity was denoted as $\Delta F = F^0 - F$, $\Delta I = I - I^0$ (I and I^0 were scattering intensities of system and reagent blank, F and F^0 were fluorescence intensities of system and reagent blank, respectively).

3. Results and discussion

3.1. Spectral characters

3.1.1. Florescence spectra

Ce(IV) could be deoxidized by CPZ to reduce the same amount of Ce(III), which has fluorescence itself. When Ce(III) further combined with CPZ to form a new complex, the florescence enhanced greatly, and the λ_{ex} and λ_{em} were located at 256 nm and 349 nm. The enhanced florescence intensities were linear with the concentration of CPZ (Fig. 1), so the reaction could be used for detecting CPZ by florescence method.

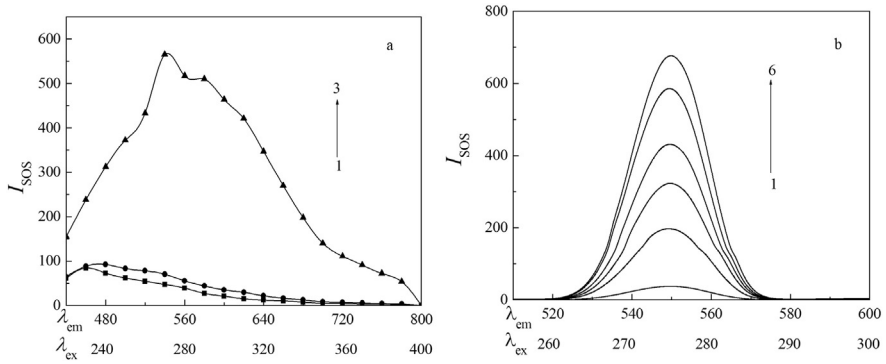

Fig. 3. SOS spectra. (a) SOS spectra of Ce(IV)–CPZ system: 1. Ce(IV); 2. CPZ; 3. Ce(IV)–CPZ. $c_{Ce(IV)}$: 3.0×10^{-5} mol L^{-1}. $c_{(CPZ)}$: 2.0 μg mL^{-1}. (b) The relationship between SOS intensity and the concentration of CPZ of the system. $c_{Ce(IV)}$: 3.0×10^{-5} mol L^{-1}. $c_{(CPZ)}$ (1–6): 0, 0.5, 1.0, 1.5, 2.0, and 2.5 μg mL^{-1}.