



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)

Full Length Article

# Study on the luminescence behavior of lanthanide ions with luminol by flow injection chemiluminescence analysis

Xiaoqing Liu<sup>a</sup>, Zhuming Wang<sup>b</sup>, Yajuan Li<sup>a</sup>, Yun Zhang<sup>c</sup>, Jie Guo<sup>a</sup>,  
Jingchan Zhao<sup>a</sup>, Zhenghua Song<sup>a,\*</sup><sup>a</sup> College of Chemistry and Material Science, Northwest University, 710069 Xi'an, China<sup>b</sup> College of Earth Sciences and Land Resources, Chang'an University, 710054 Xi'an, China<sup>c</sup> Department of pharmacy, Xi'an Medical University, 710021 Xi'an, China

## ARTICLE INFO

### Article history:

Received 4 April 2014

Received in revised form

30 January 2015

Accepted 1 February 2015

Available online 11 February 2015

### Keywords:

Lanthanide ions

Luminescence behavior

Luminol

Chemiluminescence

Flow injection

## ABSTRACT

This work first described the linear quenching of Ln<sup>III</sup> (including La<sup>III</sup>, Ce<sup>III</sup>, Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>, Tm<sup>III</sup>, Yb<sup>III</sup> and Lu<sup>III</sup>) on luminol–dissolved oxygen chemiluminescence system and possible quenching mechanism by flow injection analysis. The general equation of the decrement of CL intensity with Ln<sup>III</sup> concentration,  $\Delta I = A \ln C_{Ln} + B$ , was given and the interaction model of Ln<sup>III</sup> with luminol,  $\lg[(I_0 - I)/I] = r \lg[Ln] + \lg K$ , was established. The sensitive factor  $A$  was found to be linear with the physical parameters ( $Z$ ,  $\gamma_{\pm}$ ,  $E^{\circ}$  and  $\Delta H_{hyd}$ ). By plotting  $A$  against  $Z$ , it could be seen light lanthanides (LL) and heavy lanthanides (HL) presented a good symmetry. The results showed that the reaction of Ln<sup>III</sup> with luminol was a spontaneous process by the electrostatic force with the association constants  $K$  at  $10^6$ – $10^7$  level. The binding constants  $K_D$  (about  $10^4$ – $10^5$ ) and the number of binding sites  $n$  (about 1) of Ln<sup>III</sup> (La<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup> and Lu<sup>III</sup>) to bovine serum albumin were first given by FI–CL, and the binding ability of Ln<sup>III</sup> followed the pattern: La<sup>III</sup> < Eu<sup>III</sup> < Gd<sup>III</sup> < Tb<sup>III</sup> < Lu<sup>III</sup>.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Lanthanide ions (Ln<sup>III</sup>), possessing the special features of fluorescence, have been widely applied in different fields [1–3]. The lanthanide family was divided into light lanthanides (LL) from La to Eu and heavy lanthanides (HL) from Gd to Lu. Among these ions, Eu<sup>III</sup> and Tb<sup>III</sup> with the luminescence activities were commonly acted as probes [4–8] in the chemical and biomedical analyses [9], such as DNA hybridization assay [10], cell imaging [11,12], *in vivo* sensing [13], protease activities detecting [14], drug delivery monitoring [15] and so forth. Based on the intrinsic fluorescence, the photochemical, photo-physical and optical–magnetic properties of Ln<sup>III</sup> and current trends of lanthanide-based luminescent materials have arisen great attentions and were applied in telecommunications, LED devices and solar energy conversion were summarized by some important reviews [16–19] in recent years. The luminescence behavior of the lanthanide family with an extrinsic probe has rarely been reported.

Luminol (3-aminophthalhydrazide), as one of the most widely used luminescence probes, has stirred particular interest in view

of exciting applications in the fields of chemiluminescence (CL) and fluorescence [20,21]. Although chromatographic separation of Ln<sup>III</sup> with luminol–H<sub>2</sub>O<sub>2</sub> system CL detection has been reported [22,23], the subtle changes of the luminescence behavior for the lanthanide family have not been described and interaction parameters of Ln<sup>III</sup> with luminol have not been given by CL with flow injection (FI) analysis.

In this work, based on the linear quenching of Ln<sup>III</sup> (including La<sup>III</sup>, Ce<sup>III</sup>, Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>, Tm<sup>III</sup>, Yb<sup>III</sup> and Lu<sup>III</sup>) on luminol–dissolved oxygen CL reaction, the general equation of the decreased CL intensity with Ln<sup>III</sup> concentration,  $\Delta I = A \ln C_{Ln} + B$ , was given with the linear range of 0.3–700 nmol L<sup>-1</sup>, and the interaction model of Ln<sup>III</sup> with luminol,  $\lg[(I_0 - I)/I] = r \lg[Ln] + \lg K$ , was established. The relationships of the sensitive factor  $A$  with physical parameters (atomic number  $Z$ , ionic radius  $\gamma_{\pm}$ , standard redox potential  $E^{\circ}$ , and hydration enthalpy  $\Delta H_{hyd}$ ) were discussed, and the results indicated that the variation of  $A$  should originate in [Xe] 4f<sup>*n*</sup> configurations. The results revealed that the reaction of Ln<sup>III</sup> with luminol was a spontaneous process by the electrostatic force with the association constants  $K$  at  $10^6$ – $10^7$  level. The binding ability of Ln<sup>III</sup> (La<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup> and Lu<sup>III</sup>) to bovine serum albumin (BSA) was consistent with the expansion-inducing ability of Ln<sup>III</sup> by the obtained parameters. According to the general equation of the decreased CL intensity with Ln<sup>III</sup> concentration, the method for the

\* Corresponding author. Tel.: +86 29 88303798; fax: +86 29 88302604.

E-mail addresses: [songzhenghua@hotmail.com](mailto:songzhenghua@hotmail.com),  
[zhsong123@nwu.edu.cn](mailto:zhsong123@nwu.edu.cn) (Z. Song).

assay of  $\text{Ln}^{\text{III}}$  was developed and applied to the determination of  $\text{La}^{\text{III}}$  in samples.

## 2. Experimental

### 2.1. Apparatus

A peristaltic pump of the IFFM-E Luminescence Analyzer (Xi'an Remax Electronic Science-Tech. Co., Ltd., Xi'an, China) was applied to deliver all streams. Polytetrafluoroethylene (PTFE) tubing (1 mm i.d.) was used throughout the manifold for carrying the CL reagents. A six-way valve with loop of 100  $\mu\text{L}$  was used for sampling. The CL signal produced in flow cell was detected without wavelength discrimination, and the photomultiplier tube (PMT) output was recorded by PC with a IFFE-E client system. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Advantage, Thermo Scientific, America) was used as a reference technique for the comparison of the results among the samples. A water bath (HW.SY11-K6B/C, Leici, Shanghai, China) was used for controlling the temperature.

### 2.2. Reagents

All reagents were of analytical reagent grade and doubly deionized water was purified in a Milli-Q system (Millipore, Bedford, MA, USA) used in the whole procedure. Luminol (Fluka/Biochemika, Switzerland) of  $2.5 \times 10^{-2} \text{ mol L}^{-1}$  was prepared by dissolving 0.44 g luminol in 100 mL of  $0.1 \text{ mol L}^{-1}$  NaOH solution in a brown calibrated flask. The stock solution of BSA (Sigma-Aldrich) with the concentration of  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  was prepared with pure water.  $\text{Ln}_2\text{O}_3$  (99.99%) were purchased from Beijing Founde Star Science and Technology Co., Ltd. (Beijing, China). A series of  $\text{LnCl}_3$  stock solutions ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) were prepared by dissolving  $\text{Ln}_2\text{O}_3$  in  $12 \text{ mol L}^{-1}$  HCl with subsequent heating to deplete the excess HCl and dilute with water [24]. Samples with different  $\text{La}^{\text{III}}$  content were supplied by Dr. Zhao in College of Chemistry and Materials Science, Northwest University. The stock solutions were stored at  $4^\circ\text{C}$ , and working solutions were prepared daily from the above stock solutions by appropriate dilution as required.

Sample preparation: four samples were weighed exactly and placed in four crucibles, and then every sample (50.0 mg) was heated at  $700^\circ\text{C}$  for 4 h in muffle furnace. After that, each sample was dissolved in  $12 \text{ mol L}^{-1}$  HCl. Thereafter, the sample solutions were heated at  $80^\circ\text{C}$  to dry. After cooling to the room temperature, each sample was prepared with purified water in 25 mL calibrated flask. Suitable aliquots were taken and diluted with appropriate multiples for the determination of  $\text{La}^{\text{III}}$  by the proposed CL and ICP-AES methods.

### 2.3. General procedure

The configuration of the FI-CL system used in the luminol-dissolved oxygen system as shown in Fig. 1A, flow lines were inserted into luminol, carrier (pure water), NaOH and  $\text{Ln}^{\text{III}}$  solutions, respectively at a constant speed of  $2.0 \text{ mL min}^{-1}$ . The whole flow system was washed with purified water until a stable baseline was recorded. 100  $\mu\text{L}$  luminol was quantitatively injected into the carrier stream by the six-way valve and merged with  $\text{Ln}^{\text{III}}$  stream via a mixing tube, thereafter, mixed with the NaOH stream. The whole mixed solution was delivered into the CL cell, producing CL emission. The CL signals were detected by PMT at a high voltage of  $-700 \text{ V}$ . The signals were imported to the computer for data acquisition. The CL intensity was recorded as the peak height.

A schematic profile of the equipment in luminol-BSA system was described in Fig. 1B, and flow lines were inserted into luminol/NaOH, carrier, BSA and  $\text{Ln}^{\text{III}}$  solutions at a constant speed

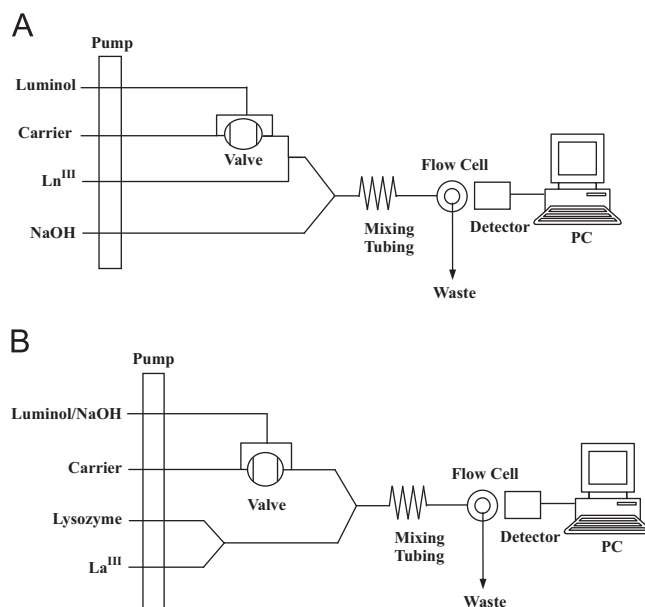


Fig. 1. Schematic diagram of the present FI-CL system. (A) Luminol-dissolved oxygen system; (B) luminol-BSA system; Luminol:  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ ; NaOH:  $0.025 \text{ mol L}^{-1}$ ; BSA:  $5.0 \times 10^{-8} \text{ mol L}^{-1}$ ; flow rate:  $2.0 \text{ mL min}^{-1}$ ; high voltage:  $-700 \text{ V}$ .

of  $2.0 \text{ mL min}^{-1}$ . The luminol standard solution (100  $\mu\text{L}$ ) was injected into the carrier stream by the injection valve and merged with a mixture flow of BSA and  $\text{Ln}^{\text{III}}$ . The mixed solution was delivered into the CL cell, producing CL emission. The experimental parameters and concentration of  $\text{Ln}^{\text{III}}$  were measured by the decrement of CL intensity,  $\Delta I = I_0 - I_s$ , where  $I_0$  and  $I_s$  were CL signals in the absence and in the presence of  $\text{Ln}^{\text{III}}$ , respectively. The temperature of working solutions was controlled by a water bath, which was kept in a certain range ( $T \pm 0.1^\circ\text{C}$ ) throughout the experiment. Since the speed of detection was rapid, the time of the solution flowing in the tube was short, and the temperature of solutions maintain to constant, so during detection, the error of temperature was negligible.

## 3. Results and discussion

### 3.1. Optimization of experimental conditions

The flow rate was an important instrumental factor which could affect the  $\Delta I$  of the CL system. So, the effect of flow rate was tested in the range of  $0.5\text{--}5.0 \text{ mL min}^{-1}$ . Flow rate of  $2.0 \text{ mL min}^{-1}$  offering the highest S/N ratio was then chosen as suitable condition considering analytical precision. The length of the mixing tube on the  $\Delta I$  signals was investigated between 5.0 and 20.0 cm and for the purpose of obtaining the maximum CL signal in the flow cell the optimal length of mixing tube selected for further experimentation was 10.0 cm.

The effect of luminol concentration on the CL intensity was also tested from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ , and the optimum concentration was  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ . NaOH was added into the luminol solution to increase the sensitivity of the system, due to the nature of the luminol reaction. A series of NaOH solutions with different concentration ranging from  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-1} \text{ mol L}^{-1}$  were tested, and  $2.5 \times 10^{-2} \text{ mol L}^{-1}$  was the optimum concentration and used in subsequent experiments.

The pH effect of  $\text{Ln}^{\text{III}}$  solutions on luminol-dissolved oxygen CL intensity was tested ranging from 4.0 to 9.0, which were adjusted by HCl or NaOH solutions. It was found that the pH effect for  $\text{Ln}^{\text{III}}$  solutions was the same, and Fig. 2 shows ( $\text{La}^{\text{III}}$  as an example) that

Download English Version:

<https://daneshyari.com/en/article/5398879>

Download Persian Version:

<https://daneshyari.com/article/5398879>

[Daneshyari.com](https://daneshyari.com)