Determination of Heavy Metal Ions Based on Quenching of the Rare Earth Luminescence

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The determination of heavy metal ions based on quenching of the rare earth luminescence was investigated. A few heavy metal ions efficiently quenched the luminescence of Ce^{3+} in polymerized cellulose films which were obtained by Na-CMC (sodium carboxymethyl cellulose) solution and CeCl_3 solution or the mixed solution of CeCl_3 and a heavy metal chloride. Also, the decay time of Ce^{3+} ions(τ) in Ce^{3+} - Cu^+ , Ce^{3+} - Cu^{2+} , Ce^{3+} - Zn^{2+} and Ce^{3+} - Pb^{2+} system was shorter than that of only Ce^{3+} system(τ_0). The linear relationship between the concentration of Cu^{2+} , Zn^{2+} or Pb^{2+} ions and τ_0/τ reflected the dynamic quenching, as predicted by the Stern-Volmer equation.

Key Words : Heavy Metal Ions, Rare Earth, Luminescence, Decay Time

1 Introduction

Many rare earth complexes attract the interest as fluorescent probes in detection applications. The structural optimization of the rare earth complexes enhanced the availability in the molecular recognition and chirality sensing of biological substances.^{1, 2)} It was reported that terbium chelate was used as a label in fluorescent immunoassays.³⁾ The polymers including the rare earth complex were synthesized, and the fluorescence was examined with the aim of the application to laser materials, etc..⁴⁾ The hydrolysis product of the nerve agent Soman in water could be measured by the luminescence of Eu^{3+} -polymer complexes containing methyl-3, 5-dimethylbenzoate ligand.⁵⁾ We reported that the copper ions (Cu^+ or Cu^{2+}) could be detected using the fluorescence property of rare earth element (Eu^{3+}) in polymerized cellulose films, which was prepared from sodium carboxymethyl cellulose (Na-CMC) solution and the mixed solution of heavy metal chloride and europium chloride.⁶⁾ In this paper, we demonstrated the ability to detect heavy metal ions (Pb^{2+} or Zn^{2+}) using the luminescence of polymerized cellulose films by assisting of rare earth ions (Ce^{3+}).

2 Experimental

The cellulose film was prepared by the use of the 30 ml glass bottle container of which two parts was separated by a 100 mesh nylon cloth. The rare earth chloride (CeCl_3) solution (10 mM-100 mM) or the mixed solution of heavy metal chloride and rare earth chloride was put on the bottom of container. There was the viscous Na-CMC solution (4 mM) on a nylon cloth. Then the container was turned up side down and the solution contacted with each other through nylon cloth, followed by the formation of cellulose film containing of Ce^{3+} ions or Ce^{3+} ions and heavy metal ions. The nylon mesh cloth (20 mm ϕ $\times$ 0.3 mm) attaching cellulose thin film was re-

moved from the container, washed and dried in a desiccator. The emission and excitation spectra were recorded by a Hitachi recording absolute spectrofluorophotometer (F-4500) at room temperature. The life times were measured with Nd-YAG laser (266 nm) having pulses of less than 5 ns.

3 Results and Discussion

3.1 The luminescence of Ce^{3+} in the cellulose film

The luminescence of Ce^{3+} ions($5d \rightarrow 4f$ transition) was strong and simple. Also the photo-excitation energy of Ce^{3+} is larger than that of Eu^{3+} . In this paper, europium ion changed to cerium ion as fluorescent probes. Photoluminescence spectra of Ce^{3+} for a Ce^{3+} -cellulose film and some Ce^{3+} - M^{n+} (M :heavy metal) cellulose films under the excitation of 255 nm are shown in Fig. 1. The optimum excitation wavelength was same in every cases. The emission band centered at 350 nm which is well explained in terms of the dipole allowed $5d \rightarrow 4f$ transition,

Fig. 1 The emission spectra of cellulose films containing Ce^{3+} ions. The film was prepared by the use of (a) CeCl_3 (100 mM) solution, (b) the mixed solution of CeCl_3 (100 mM) and PbCl_2 (50 mM), (c) the mixed solution of CeCl_3 (100 mM) and ZnCl_2 (50 mM).

Fig. 2 The emission intensity and the content of Ce^{3+} ions in a polymerized Cellulose film vs the concentration of CeCl_3 solution.

Fig. 3 Dependence of emission intensity of Ce^{3+} for Ce^{3+} - Zn^{2+} , Ce^{3+} - Pb^{2+} , and Ce^{3+} - Cu^{2+} cellulose films on the content of cations. The cellulose films prepared using aqueous solution which changed the concentration of the heavy metal chloride by fixing the concentration of CeCl_3 (100 mM).

are observed. The effect of varying Ce^{3+} ion concentration of cellulose films on the emission band is presented in Fig. 2. The abscissa indicates the concentration of CeCl_3 when a cellulose film was prepared. At first, the intensity of emission band increased logarithmically with the concentration of Ce^{3+} ions in cellulose film up to ca. 0.25 mM/g (This point was corresponded to the concentration of solution for preparing a film), and then became almost constant. If the Ce^{3+} -containing cellulose film was prepared together with PbCl_2 , ZnCl_2 or CuCl_2 , the intensity of emission band of Ce^{3+} ions decreased as shown in Fig. 1. Moreover, the intensity of the emission band decreased with the concentration of these heavy metal chlorides as shown in Fig. 3. The concentration of Pb^{2+} , Zn^{2+} , and Cu^{2+} in the cellulose film became almost constant over 50 mM for the concentration of metal chloride solutions under experimental conditions. When the concentration of heavy metal ions and Ce^{3+} ions in a Ce^{3+} - M^{2+} cellulose film was measured by X-ray fluorescence analysis, the cerium ion concentration was almost constant about 0.25 mM/g for every cases. On the other hand, there was the increase of the M^{2+} concentration in the cellulose film during the increase of M^{2+} ions of solution and then the M^{2+} ion concentration reaches almost constant value (ca. 0.20 mM/g) at 50 mM solution, after which the concentration slightly increased up to ca. 0.24 mM/g at 100 mM solution. There was not large difference of M^{2+} concentration in a Ce^{3+} - M^{2+} cellulose film between three heavy metal ions. The quenching effect was

Table 1 The relative intensity (I_0/I) of 350 nm emission band and the relative decay time (τ_0/τ) of Ce^{3+} ions for Ce^{3+} - M^{n+} system.

M^{n+}	$I_0/I^a)$	$\tau_0/\tau^b)$
Cu^{2+}	2.5	3.1
Co^{2+}	1.0	1.0
Mn^{2+}	1.0	1.0
Cr^{3+}	1.0	1.1
Fe^{3+}	5.0	2.3
Zn^{2+}	1.7	1.7
Pb^{2+}	1.7	1.7

^{a)} These values were compared at 0.25 mM/g of Ce^{3+} and 0.2 mM/g of M^{n+} . ^{b)} τ_0 was 3.4×10 ns. These values were compared at 0.25 mM/g of Ce^{3+} and 0.2 mM/g of M^{n+} , except for Ce^{3+} - Cr^{3+} (0.1 mM/g) and Ce^{3+} - Fe^{3+} (0.1 mM).

Fig. 4 Luminescence decay curves of an Ce^{3+} cellulose film and an Ce^{3+} - Cu^{2+} cellulose film.

stronger in the lower concentration range of these heavy metal ions. The effect on the intensity of luminescence under coexistence of heavy metal ions were summarized in Table 1, together with the results of decay time as described later. When Cu^{2+} , Fe^{3+} , Pb^{2+} , Zn^{2+} coexisted in the cellulose film, the luminescence was extremely decreased. In general, the luminescence of rare earth ion was strongly affected by Fe^{3+} ions as large absorption by Fe^{3+} ions exists from near 450 nm. Therefore, in this paper the Ce^{3+} - Fe^{3+} system was not discussed. It is well known that the intensity of luminescence for the cerium complexes is affected by the ligand.⁷⁾ On the other hand, heavy metals are known to be strong quenchers of luminescence.⁸⁾ The quenching of perdeuterated naphthalene by paramagnetic ions (Co^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+}) was explained as the exchange-type interaction between the triple state molecules and the paramagnetic ions. But, the decrease in the luminescence of Ce^{3+} - Co^{2+} and Ce^{3+} - Cr^{3+} was hardly observed, although Co^{2+} and Cr^{3+} is paramagnetic. Since Zn^{2+} or Pb^{2+} is not paramagnetic, it could not induce quenching by interaction from the viewpoint of Hoijtink's mechanism,⁹⁾ but it may cause quenching by spin-orbit interaction due to its large atomic number. In our measurements with Zn^{2+} or Pb^{2+} , the decrease of fluorescence intensity of Ce^{3+} was observed.

3. 2 The decay time of Ce^{3+} in the cellulose film

The decay times and amplitudes of cerium lumines-

Fig. 5 Calibration graph for Cu^{2+} , Pb^{2+} and Zn^{2+} in the linearized form of a Stern-Volmer plot.

cence for a Ce^{3+} - Cu^{2+} and Ce^{3+} system are shown in Fig. 4. In the presence of Cu^{2+} ions, the decay time τ (slope) was smaller than that of only Ce^{3+} system (τ_0). At the same time, the decrease of the amplitude was almost consistent with that of the luminescence intensity estimating by I_0/I . The same phenomena were observed in the Ce^{3+} - Pb^{2+} and Ce^{3+} - Zn^{2+} system. In comparison of Ce^{3+} - Pb^{2+} with Ce^{3+} - Zn^{2+} system, the difference was hardly appeared in the decay time. The changes in decay time and amplitude indicate the co-existence of static and dynamic quenching. The correlation between the concentration of these ions and τ_0/τ are shown in Fig. 5. That is, the linear relationship in the range of lower concentration reflects the dynamic process, as predicted by the Stern-Volmer equation,⁹⁾ whereas the decreasing of amplitude (or luminescence intensity) is mainly a result of static quenching. The relative decay times (τ_0/τ) for other heavy metal ions are summarized in Table 1. According to the Stern-Volmer equation, the extent of quenching is proportional to the decay time of the cerium luminescence. The absorption spectrum of Fe^{3+} , which was a dynamic quencher, has a higher overlap with the emission spectrum of the cerium ion. On the other hand, it was expected that in the Ce^{3+} - Pb^{2+} and Ce^{3+} - Zn^{2+} system the dynamic quenching and the decrease of the decay time were not observed, because none of the completely colorless ions showed dynamic quenching. In the Eu^{3+} - Pb^{2+} and Eu^{3+} - Zn^{2+} system, quenching and the decrease of decay time were not clearly observed as reported in elsewhere.⁶⁾ Although the mechanism of quenching for Ce^{3+} - M^{2+} system could not be clarified, the clear quenching of Ce^{3+} - Pb^{2+} and Ce^{3+} - Zn^{2+} system may be due to

the larger photo-excitation energy; the photo-excitation energy of Ce^{3+} - M^{2+} system ($\text{Ex} = 255 \text{ nm}$) was larger than that of Eu^{3+} - M^{2+} system ($\text{Ex} = 395 \text{ nm}$). In Pb^{2+} or Zn^{2+} ions which the d orbital has satisfied, one of 3d or 4d electron would be excited in 4s or 5s orbital when Pb^{2+} or Zn^{2+} ions was excited by 255 nm light. In the Ce^{3+} - Pb^{2+} and Ce^{3+} - Zn^{2+} system the early energy transfer process going through excitation state of Pb^{2+} or Zn^{2+} ions would predominantly occur.

The operation of the method presented is simple. These results suggest that the present method has the ability of the detection of transition metal ions in environmental waters, including river water and industrial wastewater.

4 Conclusions

The luminescence and the decay time of Ce^{3+} ions in cellulose polymer film which was prepared by Na-CMC solution and CeCl_3 solution or the mixed solution of CeCl_3 and a heavy metal chloride, was studied. The quenching of cerium luminescence depended on the kind of the heavy metal ion. In the Ce^{3+} - Cu^{2+} , Ce^{3+} - Pb^{2+} and Ce^{3+} - Zn^{2+} system, the relative decay time linearly varied with the concentration of these heavy metal ions in the range of lower concentrations. This method based on quenching of cerium luminescence may be useful for the determination of the heavy metal.

References

- 1) E. P. Diamandis and T. K. Christopoulos, *Anal. Chem.*, **62**, 1149A (1990).
- 2) T. Yamada, S. Shinoda, J. Uenishi, and H. Tsukube, *Tetrahedron Lett.*, **42**, 9031 (2001).
- 3) M. P. Baily, B. F. Rocks, and C. Riley, *Analyst*, **109**, 1449 (1984).
- 4) Y. Ueba, E. Banks, and Y. Okamoto, *J. Appl. Poly. Sci.*, **25**, 2007 (1980).
- 5) A. L. Jenkins, O. M. Uy, and G. M. Murray, *Anal. Chem.*, **71**, 373 (1999).
- 6) T. Arakawa and M. Akamine, 9th International Meeting on Chemical Sensors, Abstr., p.184 (2002).
- 7) C. O. Hill and S. H. Lin, *J. Chem. Phys.*, **53**, 608 (1970).
- 8) G. J. Hoijtink, *Mol. Phys.*, **3**, 67 (1960).
- 9) O. S. Wolfbeis, *Molecular Luminescence Spectroscopy* (Ed. Schulman), Wiley, New York, 202 (1988).