Cloud Point Extraction and Fluorometric Analysis of Eu(III) with Thenoyltrifluoroacetone and the Nonionic Surfactant Triton X-114

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The extraction of the Eu(III) thenoyltrifluoroacetone (TTA) chelate was investigated by using the nonionic surfactant octylphenoxypolyethoxyethanol (Triton X-114, \( n = 8 \)). A cloud point extraction (CPE) method is proposed for the preconcentration of Eu(III) and subsequent determination was carried out by a fluorometric method using a microwell plate reader. Optimal experimental conditions were examined for fluorescence of the TTA chelate in the surfactant phase. Fluorescence was measured at \( \lambda_{em} = 616 \) nm after excitation at \( \lambda_{ex} = 355 \) nm. The extracted species is estimated to be Eu(TTA)\textsubscript{3}(Triton X-114)\textsubscript{1−2} and coordination is competitive between TTA and the oxygen atoms of Triton X-114 depending on each concentration. A content of Eu(III) was directly determined by a plate reader using 100 mm\textsuperscript{3} of surfactant phase without dilution. The fluorescence intensity, which was measured in a microwell, was a linear function of initial concentration from \( 1.0 \times 10^{-8} \) to \( 8.0 \times 10^{-6} \) mol dm\textsuperscript{-3} of Eu(III). The use of microwell plate system is convenient for handling small-volume samples.

1. Introduction

The extraction of trivalent lanthanide ions has been widely investigated with an acidic chelating agent and a neutral ligand of synergic agent [1-4]. The synergism is due to the formation of ternary complexes between the metal chelate and the neutral ligand in the organic phase and this enhances the extractability. The lanthanide elements are difficult to separate mutually due to their similar sizes and chemical properties. Some of the lanthanide ions, especially Eu(III), form highly fluorescent chelates with TTA in the presence of a synergic agent [5,6]. The formation and fluorescence properties of the Eu(III)-TTA-TOPO (trioctylphosphine oxide) ternary complex were investigated in a surfactant solution of Triton X-100 (\( n = 10 \)) [7]. The organic ligand TOPO is not soluble in water and it was necessary to use nonionic micelles to solubilize the ternary complex and to allow its extraction into the non-aqueous environment of the micelles. The fluorescence was derived from light absorption at a wavelength characteristic to the chelating agent, and the subsequent energy transfer from the coordinated TTA to the Eu(III) ion. This metal ion then emits a narrow-band line-type fluorescence at approximately 612 nm [8].

A cloud point extraction (CPE) method has been proposed for the preconcentration of lanthanide-TTA chelate with subsequent determination using ICP-OES in the surfactant solution of Triton X-114 [9]. Aqueous micellar solutions of nonionic surfactants became turbid over a narrow temperature range and this temperature is named the cloud point. Above the cloud point, the solution separates into two phases. One of the phases is a surfactant-rich phase (surfactant phase) and the other is a surfactant-depleted phase (aqueous
phase). It is important to identify the extracted species of TTA chelate in the surfactant phase. The purpose of this work was to elucidate the structure of the Eu(III) complex extracted into the nonionic surfactant phase and to apply fluorometric analysis of Eu(III)-TTA chelate. Although the CPE method is based on neutral micelle production and the subsequent separation of the surfactant phase, the volume of the surfactant phase generated in the literature was usually in the range from 50 to 250 µL [9]. Due to this low volume and the high viscosity of the surfactant phase, analysis is possible by using a specific sample introduction system. The microwell plate system [10-12] has been appropriate for the introduction of a small volume of sample for UV-Vis absorption and fluorescence measurements. The experimental conditions affecting the fluorescence reaction were investigated by the CPE method with TTA and Triton X-114. A fluorescence microplate reader was used to measure the emission intensity of Eu(III) complex extracted into the surfactant phase.

2. Experiments

2.1 Reagents and apparatus

All reagents used were guaranteed reagent grade and solutions were prepared in ultrapure water using a MiliQ system (Merck Millipore, Germany). A 1.00 × 10^{-2} mol dm^{-3} stock solution of Eu(III) was prepared by dissolving 1.76 g of europium oxide (Kanto Chemical, Co. Japan) in 100 cm^3 of 1.0 mol dm^{-3} HCl and diluting to 1000 cm^3 with water. A 20% (w/v) Triton X-114 (Fujifilm Wako Pure Chemical Co. Japan) stock solution was prepared by weighing 20 g of the reagent which was then made up to 100 cm^3 with water. A 0.10 mol dm^{-3} TTA stock solution (Fujifilm Wako Pure Chemical Co. Japan), used for the fluorescence measurements, was prepared by dissolving 0.444 g of the reagent in 20 cm^3 of ethanol. The same concentration of TTA stock solution was prepared for the CPE method by dissolved TTA in 10% (w/v) Triton X-114. An acetate buffer solution was prepared by mixing 0.10 mol dm^{-3} of acetic acid and 0.10 mol dm^{-3} of sodium acetate solution and the pH adjusted to 5.6 for the CPE method with 0.010 mol dm^{-3} of buffer. To investigate the extractability of the complexes, the metal concentration in the aqueous phase was determined using an Agilent 5110 inductively coupled plasma atomic emission spectrometer (ICP-OES). All pH measurements were performed using a Horiba F-51 pH meter with a glass electrode. A Kubota 2800 centrifuge was used for phase separation. Thermal gravimetric analysis data was collected using a Rigaku TG-DTA8122 thermal analyzer. The fluorescence spectra measurements were generated on a Jasco FP-8200 fluorescence spectrophotometer with a four-window 1 cm quartz cell (1 cm cell). After CPE, the emission intensity of the surfactant phase was measured using a Berthold Twinkle LB970 plate reader equipped with a 96-microwell plate.

2.2 Procedure

Solutions which contained a proper quantity of Eu(III), 5.0 x10^{-4} mol dm^{-3} of TTA, 1.0% (w/v) Triton X-114 and 0.010 mol dm^{-3} of buffer solution, were transferred to a 10 cm^3 centrifuge tube. The solution was gently shaken and warmed to 40°C in a water bath for 5 minutes. The cloud point of Triton X-114 is 23°C in water. The solution was centrifuged at 4000 rpm at 40°C for 5 min, and the aqueous and surfactant phases were separated. The aqueous phase was transferred to another tube and its metal concentration was determined by ICP-OES in order to obtain the percent extraction of the metals.

For the fluorescence measurements, the experimental conditions were investigated with respect to the
spectra of excitation and emission, and effect of pH and reagent concentrations. The separated surfactant phases were approximately 0.50 cm³ after CPE. The fluorescence of these solutions were diluted with ethanol and measured by the fluorescence spectrophotometer using a 1.0 cm cell. The excitation and emission wavelengths were 355 nm and 616 nm, respectively. In order to obtain the linear concentration range of Eu(III), the 100 mm³ of surfactant phase was taken into the microwell using a calibrated capillary with graduation lines of 50 mm³ each without ethanol dilution. The fluorescence intensities were measured by the microwell plate reader.

3. Results and Discussion

3.1 The structure of the Eu(III) complex in the Triton X-114 phase

In the presence of synergic agents such as TOPO, various compositions of Eu(III) complexes can form depending on the relative concentrations of TTA and synergic agents and, for these two specific reagents, the stoichiometric composition of the predominant complex has been postulated to be Eu(TTA)₃(TOPO)₂ [7]. TOPO is the neutral monodentate ligand and, for the bidentate ligand of N-donor such as bipyridine (bpy), Eu(TTA)₃(bpy) was extracted into the solvent of chloroform [3]. Three TTA molecules occupy only six in the eight or nine available coordination sites of the Eu(III) ion; therefore, the metal ion is sensitive to quenching by remaining water molecules [13]. Completing the coordination sphere can be achieved by using synergic agents, such as TOPO. Complexation with synergic agents contributes to expulsion of the remaining water molecules from the coordination sphere and resulted in enhanced fluorescence.

We found that the Eu(III)-TTA chelate in the surfactant phase exhibited a characteristic emission spectrum without synergic agents such as TOPO and bpy. A brilliant red color was observed in the fluorescence emission study of extracted Eu(III)-TTA chelate in Triton X-114 phases. Figure 1 shows the excitation and emission spectra of the Triton X-114 phase. Excitation at λ = 355 nm is due to an absorption of TTA [7] and the hypersensitive ⁵D₀ → ⁷F₂ transition has a high intensity and is a characteristic emission of the Eu(III) ion [14]. It reflects the TTA complex formation and the elimination of water molecules from the

![Figure 1. Fluorescence spectra of Eu(III) – TTA chelate for (a) excitation and (b) emission.](image)

![Figure 2. Predicted structure of the Eu(III)-TTA chelate in the surfactant phase of Triton X-114.](image)
coordination sphere (Figure 2). The oxygen atoms in the hydrophilic chains of the surfactant can coordinate to the neutral Eu(TTA)₃ chelate, in a similar manner to synergic agents, and expel the water molecules.

The coordination of the surfactant molecule to the metal ion was confirmed by studying the influence of Triton X-114 concentration on the extractability of Eu(III) with and without TTA. Figure 3 shows the effect of Triton X-114 concentration on the percent extraction of Eu(III) for the different concentration of TTA. As shown by curve(a), when excess TTA was added to the solution and the concentration of Triton X-114 was more than 1.0% (w/v), Eu(III) was completely extracted into the surfactant phase. At low Triton X-114 concentrations, extractability of Eu(III) increased with increasing TTA concentration. The TTA concentration of curve (a) is five times higher than that of curve (b). In the absence of TTA, as shown by curve (c), Eu(III) was increasingly extracted with increasing surfactant concentrations.

These results support the hypothesis that there is competition between Triton X-114 and TTA for coordination sites on the metal ion. The extracted species changes with changing concentrations of both TTA and Triton X-114. In the absence of TTA, a charged complex of [Eu(Triton X-114)ₓ]³⁺ is produced and its extraction percent is 80–90%. This charged species was extracted to a lesser extent compared to the neutral Eu(TTA)₃(TritonX-114)₁⁻, which was completely extracted into the surfactant phase. The remaining two sites of Eu(TTA)₃ chelate are coordinated by not only two molecules but also one molecule of Triton X-114, because a hydrophilic portion of this surfactant has plural oxygen atoms. The separated surfactant phase should be electrically neutral and acetate anions, which were added as a buffer, reportedly serve as counterions to the cationic complex [13]. The surfactant phase of Triton X-114 is a mixture of the surfactant molecule and water. A water content was about 60% which was obtained by thermal gravimetric analysis; therefore, a substantial quantity of organic ions can dissolve in the surfactant phase. Constant and adequate extractability was obtained when mole ratio of TTA/Eu(III) was more than 50.

3.2 Fluorometric Analysis of Eu(III)

Optimal experimental conditions were examined for the CPE method and fluorescence studies. After phase separation of CPE, the dependence of pH and Eu(III) concentrations in the aqueous phase was measured. The separated surfactant phase was diluted with ethanol and fluorescence was measured by the fluorescence spectrophotometer. Figure 4 shows the effect of pH on the extraction percent of Eu(III). The extraction of Eu(III) began at pH 4 and was complete above pH 5.5. Complexation between TTA and lanthanide ions did not occur if the pH of the solution was less than 3.0 and it has also been suggested that
the fluorescence properties of the TTA chelate are dominated by its initial reagent concentration in the solution rather than by its complex composition [13]. The fluorescence gave maximum intensities around pH 5.6 and rapidly decreased with increasing pH.

Solutions of the surfactant phase were prepared by the CPE method under conditions of $5.0 \times 10^{-4}$ mol dm$^{-3}$ TTA, 1.0% (w/v) Triton X-114 and at pH 5.6. Samples of these solutions were placed in the microwell. The fluorescence intensity of the solutions was then measured by the plate reader. Figure 5 is a photograph showing microwells on the plate into which 100 mm$^3$ aliquots of surfactant phase were pipetted. The intensity was a linear function of Eu(III) concentration over three orders, extending from $1.0 \times 10^{-8}$ to $8.0 \times 10^{-6}$ mol dm$^{-3}$ ($R^2 = 0.993$). Eu(III) was quantitatively extracted into the surfactant phase in the presence of other lanthanide ions. The percentage extractabilities of these lanthanides are given in Table I. However, the apparent fluorescence intensities (arbitrary units) were 12000, 30, 23, 11, and 11 for Eu(III), La(III), Sm(III), Tb(III), and Yb(III), respectively, which were measured using a microwell plate reader, after CPE, and with a metal ion concentration of $1.0 \times 10^{-5}$ mol dm$^{-3}$. The influence of these diverse lanthanide ions on the fluorometric analysis was not significant, because most of these ions exhibit little to no fluorescence.

![Figure 5. Solutions of surfactant phase irradiated by UV light in microwell.](image)

| Diverse ion | Ln(III) Extrability / % | Eu(III) Extrability / % |
|-------------|-------------------------|-------------------------|
| La(III)     | 91.6                    | 99.9                    |
| Sm(III)     | 97.7                    | 98.9                    |
| Tb(III)     | 99.7                    | 96.4                    |
| Yb(III)     | 98.8                    | 99.5                    |

4. Conclusion

The experimental conditions for Eu(III) extraction were investigated by the CPE method with TTA and Triton X-114 affecting the fluorescence reaction. The coordination of oxygen atoms of the surfactant molecules to the Eu(III) ions eliminated quenching by water at the remaining coordination sites and enhanced the fluorescence intensity. This method was found to be suitable for fluorometric analysis of small sample
volumes of Eu(III) solutions by microwell plate readers.

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