



Characterization of the interaction of rare earth elements with P507 in a microfluidic extraction system using spectroscopic analysis

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HIGHLIGHTS

- The role of lactic acid in the extraction process is analyzed.
- The characterization of extracted compound is studied by spectroscopic analysis.
- The structure of extracted complexes is confirmed.

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ABSTRACT

An attempt to characterize the interaction of rare earth elements with P507 in a microfluidic extraction system containing lactic acid as complexing agent is made using spectroscopic (FT-IR, UV-Vis, NMR and MS) analysis. The role of lactic acid in the extraction process is analyzed. The extraction mechanism confirmed that lactic acid does not involve in the extraction reaction. A comparative analysis of the composition of the extracts using FT-IR, UV-Vis, NMR and MS methods, indicates that the extracted complexes of rare earth ions located in the center is formed by the cation exchange process between P–O–H and RE³⁺, and coordination process between P=O and RE³⁺.

1. Introduction

Rare earth elements (REEs) are composed of lanthanide series elements in the periodic table, i.e. from lanthanum (La) to lutetium (Lu), together with yttrium (Y) and scandium (Sc) which possess unique physical and chemical characteristics [1,2]. Owing to REEs unique structures (4f orbitals) and distinctive physical/chemical properties, they find application in high-tech industries, such as superconductor [3,4], photonic device [5], permanent magnet material [6,7], agriculture area [8], etc. Currently, solvent extraction with mixer settler or extraction column is being widely employed as a reliable separation method of rare earth ions due to its simplicity, kinetics, and applicability [9]. The organophosphorous acids, di (2-ethylhexyl) phosphoric acid (D2EHPA, P204) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (HEHEHP, P507) are being utilized as the popular extractants for separating lanthanide commercially [10]. However, the

conventional acidic extractants always needs to be saponified by NH₃·H₂O, NaOH, or Ca(OH)₂ to facilitate the cation exchange of rare earths. This method results in a large amount of waste water containing NH₄⁺, Ca²⁺, and Na⁺, which cause discharge of ammonium nitrogen pollutants having high levels of total dissolved solids (TDS) [11–13]. Additionally the conventional separation unit operations such as mixer-settler, packed column, and centrifugal extractor, have many drawbacks, e.g., large equipment size, slow extraction rate, high energy consumption, and large solvent holdup, all leading to high separation cost [14].

In order to overcome the above problems, scientific community has been in search of alternative separation processes so as to improve the economics of commercial manufactures. It has been identified that one of the ways to improve the separation is to modify the aqueous phase by adding complexing agents [15]. In presence of the water-soluble complexing agent, part of the metals in aqueous phase combine with the

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complexing agent, thus hindering the extraction by masking effect. Within our group, the extraction and separation of rare earths were attempted utilizing complexing agent such as lactic acid or citric acid to avoid saponification of extractants, highlighting improved extraction capacity and separation selectivity [16–18]. Furthermore, the complexing agent is reserved in the raffinate after the extraction process, which could be extracted and recycled in a new extraction process, and this recycling is beneficial to reducing industrial pollution also caters the demand of “green chemistry”. Additionally the advantages of microstructured devices over macro scale reactors, are being highlighted due to high interface to volume ratio and short diffusion path, especially for microfluidic solvent extraction (μ SX) of rare earth elements. Nishihama et al. [19] have reported micro solvent extraction system to separate lanthanides in Pr/Nd and Pr/Sm binary solutions, wherein it was stated that both lanthanides are extracted together first, and then the lighter lanthanide extracted in the organic phase alternatively while the heavier one in the aqueous phase attaining extraction equilibrium. Kubota et al. [20] have studied the extraction of rare earths with PC-88A on a microreactor, and reported unhindered flow of two phases while keeping an aqueous-organic interface. Leblebici et al. [21] have reported successful recycling of rare earths from lamp phosphors using a milli-channel mixer. Chen et al. [22] have introduced gas into a simple one-step microfluidic device to enhance the extraction and enrichment of REEs with a low concentration (less than 100 ppm) from waste water at a high phase ratio (greater than 50:1). Hou et al. [23–25] have reported high efficiency of extraction of La, Ce and Pr with EHEHPA using membrane dispersion micro-extractor, with short residence time. Kolar et al. [26] have studied the microfluidic solvent extraction of rare earth elements from a mixed oxide concentrate using Cyanex 572 solvent, found good selectivity. Thus, compared with the batch solvent extraction, μ SX presents the advantages of precise control of contact time of two phases, leading to high speed and high performance separation without mechanical stirring, mixing or shaking. However, the application of microfluidic reactors to liquid–liquid extraction of rare earths in the presence of complexing agent (lactic acid), as well as extraction mechanism in microchannel has not been reported.

In this work, the extraction mechanism of rare earths from chloride solution in the presence of complexing agent lactic acid in micro-channel, with P507/sulfonated kerosene has been assessed, and the extracted complex has been characterized using spectroscopic techniques including FT-IR, UV–Vis, NMR and MS spectroscopies, to understand the extraction performance of μ SX.

2. Materials and methods

2.1. Materials

The organic phase is prepared by dissolving 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester (HEH/EHP, P507; Luoyang Zhongda Chemical Industry Co., Ltd.) in sulfonated kerosene. The aqueous phase is prepared by dissolving rare earth oxide (99.95%, Guosheng Rare Earth Co., Ltd., Jiangsu) in hydrochloric acid and lactic acid solutions. All chemicals are of reagent grade received from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Microfluidic setup and extraction

The schematic of microfluidic extraction of rare earth ions is shown in Fig. 1. The microchannel has an extraction length (L) of 12.5 cm, a width (W) of 300 μ m and a depth (D) of 100 μ m with the rectangular section (made of polydimethylsiloxane (PDMS) by pouring and composed of three stages: inlet, channel and outlet plates). The aqueous and organic phases are introduced using two syringes connected to the microfluidic device with PEEK capillary tubing on a double syringe pump (LSP02-1B, Baoding Longer Precision Pump Co., Ltd.), fed into a Y-junction microreactor at equal flow rate (5.6×10^{-10} to

$4.5 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$). The slug flows are generated at this site which flow within the reaction tube, monitored by a high-speed camera, connected to a computer for data storage.

The rare earth ions concentration in the aqueous phase is determined by a Prodigy high dispersion inductively coupled plasma spectrometer (Leeman, America), and that in organic phase is measured by mass balance. Distribution ratio (D) is defined as the ratio of concentrations of metal ion in the organic and aqueous phases. The loaded organic phase containing REEs is used to analyze the molecular structure by spectrums.

$$D = \frac{C_{in} - C_{out}}{C_{out}} \quad (1)$$

where C_{in} and C_{out} are the aqueous phase concentrations at the inlet and outlet, respectively.

2.3. Characterization of extracted complexes

FT-IR analysis: Fourier transform infrared (FT-IR) spectrum of the extracted complexes is recorded at room temperature in the range of 4000–400 cm^{-1} with an infrared spectrometer (Nicolet-740, USA) using KBr pellet technique, is used to understand the molecular structure.

UV–Vis analysis: The extracted complexes are placed into quartz cell to measure the absorption peaks with the sulfonated kerosene as the reference solution in a UV–Vis spectrophotometer (Optizen 2120UV, Meacsys. Co., Ltd), and UV–Vis spectra are recorded within the wavelength range from 280 nm to 800 nm with a scan speed of 300 nm/min.

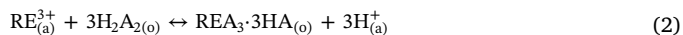
NMR analysis: NMR experiments are performed in CDCl_3 on a Bruker AV-600 spectrometer equipped with a TXI cryoprobe (Bruker, Fällanden, Switzerland). The chemical shifts of ^1H NMR and ^{31}P NMR spectra are referenced to the internal standard 10% tetramethylsilane (TMS) and external standard 85% phosphoric acid.

MS analysis: Firstly, 0.5 mL sample is dissolved in acetonitrile, and uniformly mixed by ultrasonic oscillation. Secondly, the ionization mode such as electrospray ionization (ESI) is chosen. MALDI-HRMS are analyzed with an Axima Performance Maldi-TOF mass spectrometer (Shimadzu Biotech, Japan).

3. Results and discussions

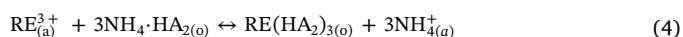
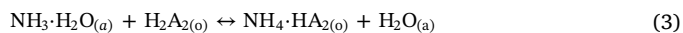
3.1. Extraction process

In principle, the ion exchange mechanism is responsible for the extraction of rare earths using P507 (abbreviated as H_2A_2) at lower acidic range; usually the transfer of a rare earth ion is accompanied by release of three hydrogen ions from the organic phase under these conditions, as shown in Eq. (2).



The hydrogen ions affect negatively the rare earth ions extraction due to the increase of acidity in aqueous phase. So it is important to control the pH to keep the equilibrium, and two different methods are commonly used for this propose. As for the first method, the pH in the aqueous phase is adjusted (e.g. by buffering or continuously adding NaOH or $\text{NH}_3 \cdot \text{H}_2\text{O}$) which proceeds based on the Eq. (2).

In the second method, using saponification procedure by neutralizing acidic extractant with aqueous ammonia, the acidic extractant can be converted to ammonium salt (Eq. 3), accordingly, the hydrogen bonds in dimers are broken. Although saponification can enhance the extraction capacities of acidic extractants, the release of ammonium ion to aqueous phase causes serious pollution (Eq. 4).



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