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## Solubilization behaviors of interfacial lutetium-extractant complex in a solvent extraction system<sup>☆</sup>

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### ABSTRACT

Knowledge of the solubilization behaviors of rare-earth-extractant complex is mandatory for full comprehension of interfacial phenomenon and intermediate state of rare earth (RE) ion transport from water to oil during solvent extraction. The lutetium with 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (P507) extraction system was explored as a case study for the solubilization behaviors in this paper. With a quantitative analysis of a white crud obtained in the practical process, the results demonstrate that the insoluble  $REL_3$  ( $L =$  the anion of P507) complex enriches at the oil/water interface and forms the network polymers. Besides, with the increase of RE loading ratios in the oil phase, the interfacial tension increases while the free ligand in the bulk phase decreases, which results in the flocculation of  $REL_3$  complex and the formation of polymers at the interface. Furthermore, the properties of the oil phase and the interface reveal that the free ligand can solubilize the  $REL_3$  complex along with the transfer of water from microemulsion to aqueous phase. In addition, the change of aqueous acidity can regulate the solubilization behaviors of the interfacial complex to improve RE extraction efficiency. These fundamental studies will hopefully provide new insights into the solubilization of metal-extractant complex and a technical guidance to the transfer of RE from water to oil.

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### 1. Introduction

Rare earth (RE) is considered as a critical resource in modern technologies from catalysis to clean energy.<sup>1</sup> Recently, lutetium-oxorthosilicate (LSO), which has the advantages of high light output and density, quick decay time, excellent energy resolution, is adopted to build electromagnetic calorimeters in particle physics and as a scintillator explored in clinical practice of PET.<sup>2,3</sup> As the demand of RE in modern technologies is much highly increasing, solvent extraction process has been extensively used and studied to separate RE. This process is based on the different partition of RE in two immiscible phases, usually aqueous and oil phase. Because of the poor solubility of RE ions in oil phase, the use of oil-soluble extractant is first to coordinate the target ions and second to

solubilize the metal-extractant complex in the oil phase.<sup>4,5</sup> These two main procedures could be described by taking the organo-phosphorus acid extractant for example, which are widely employed in RE extraction, as the following steps.<sup>6,7</sup>

(a) Coordinate reaction of the extractant HL and the RE ions  $M^{3+}$ :



(b) Solubilization of the  $ML_n$  complex in the oil phase:



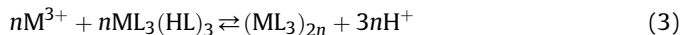
The solubilization of the interfacial complex is one of the most significant processes to selectively transport the target ions. However, some undesirable phenomena have taken place in the extraction process at high RE loading.<sup>8–11</sup> The grayish white crud suspended in the extraction system might be a polymer which was presumed to be composed of extractant and RE. The speculation of

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the polymers formation could be described by the reaction as follows.<sup>12</sup>



The polymers will affect the transfer of targeted metal species, which is a key issue of extraction mechanism. The consequences of this phenomenon will lead to some serious technological manufacture problems, such as the interruption of extraction process and the limit of high efficient RE utilization.<sup>9</sup> Although these studies<sup>11–14</sup> provided valuable speculations of the polymers in the RE extraction, there was a paucity of relevant data about the polymers in a practical extraction process. The definite chemical composition of the polymers and the cause of the polymers formation in the practical extraction process are still unclear. The lacks of experimental data in this area make it difficult to understand the underlying mechanisms of extraction-mediated process, where the interfacial RE complex transports from oil/water interface to oil. Furthermore, a deep understanding of the solubilization behaviors of interfacial complex could help to grasp the key factors that affect the transfer of RE.

Extractants are often used to adjust RE transport properties across oil/water interfaces. Although the hydrophilic polar moiety of extractant could provide solubilization environments of the RE complex to drive interfacial transfer,<sup>15</sup> it is seldom known how the extractant influences the solubilization process of interfacial complex. Besides, the solubilization of interfacial complex is more complicated in an actual production process. Taken as an example, the organophosphorus acid extractant should be saponified before RE extraction to form microemulsion, in which some water molecules solubilized in the oil phase.<sup>13</sup> The formation of microemulsion is an important behavior which could greatly improve RE extraction efficiency. The nano scale droplets of microemulsion lead to a significant increase in the specific interface area. Besides, the saponified extractant with strong interfacial activity extracts RE near the interfacial region of the microdroplets.<sup>16</sup> Then the microemulsion was destroyed when the complex dissolved in oil phase.<sup>17</sup> The change of microemulsion structure would also influence the solubilization of RE complex in oil phase.<sup>18</sup> However, it is rarely known how the solubilization of RE complex and the microemulsion structure affect each other, which is important to understand the interfacial phenomenon and the process of mass transfer.

As part of an ongoing project to investigate the transfer mechanism of RE ions, the coordination equilibrium effect was put forward to explain the interfacial phenomenon in different extraction systems.<sup>19</sup> Subsequent experiments proved that the aqueous partition of extractant affected the aggregation of the interfacial complex.<sup>20</sup> Besides, the computer simulations have been utilized to understand the structure–performance relationship of the RE complex and the basis of efficient extraction of RE.<sup>21</sup> Along this line, to move toward a precise regulation of the solubilization behaviors

of the interfacial complex, experiment should be conducted to understand how RE extraction drives the changes of properties in extraction system and how they control the interfacial phenomenon.

The solvent extraction system chosen for investigation was the acidic organophosphorus extractant 2-ethylhexyl phosphoric acid mono (2-ethylhexyl) ester (P507) in n-heptane, which is not only current technology in relation to LSO production process but also mainly used to extract RE in the world.<sup>22–26</sup> This study includes the characterization of the polymers in the practical extraction process and the change of the system properties at different Lu<sup>3+</sup> loading ratios and aqueous acidity.

## 2. Experimental

### 2.1. Materials

2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (P507) (>95%) was purchased from Luoyang Aoda Chemical Co., Ltd. The extractant was diluted with n-heptane. Stock solutions of trivalent REs were prepared via dissolving their oxides (99.99%) in concentrated hydrochloric acid. The aqueous acidity was adjusted by hydrochloric acid. A stock solution of Rhodamine B was prepared by dissolving purified dye in deionized water. All the chemicals were of analytical reagent grade. All aqueous solutions were diluted with deionized water.

### 2.2. Methods

The extractant used in this work was saponified according to a published method.<sup>20</sup> The saponification percentage of P507 was kept at 36% ± 1%. The structure of P507 and saponified P507 is shown in Fig. 1. Extraction experiments were carried out by putting an equal volume of the aqueous and oil solutions into an equilibrium tube for 30 min with a constant temperature bath at 298 ± 1 K. The mixture was centrifuged for 10 min at 3500 r/min. The precipitation of polymers in the extraction system was washed by ethanol three times. The contents of carbon and hydrogen of the polymers were analyzed by an element analyzer (varioELcube, Elementar, Germany). The contents of phosphorus and lutetium in the polymers were analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES) with aThermo iCAP 6000 (Britain). The morphology and the scanning electron microscope X-ray energy dispersive analysis (SEM-EDX) of the polymers were observed via a field-emission SEM (S-4800, Hitachi, Japan). Thermal decomposition of the polymers was analyzed by a NETZSCH STA 449 F3 Jupiter® instrument thermogravimetric analyzer coupled to a NETZSCH QMS 403 Aëolos® quadrupole mass spectrometer. Fourier transform infrared spectroscopy (FT-IR) of the oil phase and the polymers was determined by a Bruker VERTEX 70 (Germany). The <sup>31</sup>P NMR spectra of the oil phase were obtained in Chloroform-d with a Bruker AV 600 NMR spectrometer (Germany).

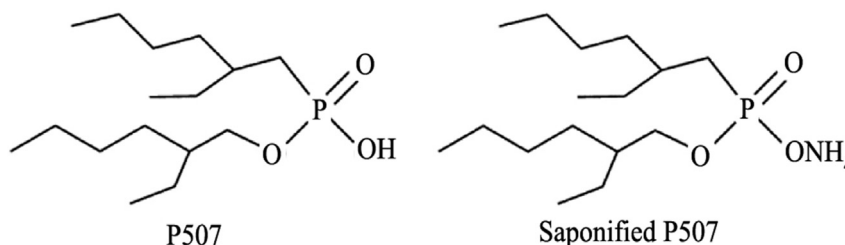


Fig. 1. Chemical structure of P507 and the saponified P507.

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