



Applying basic research on a dialkylphosphoric acid based task-specific ionic liquid for the solvent extraction and membrane separation of yttrium

Li Chen^{a,b}, Ji Chen^{a,*}, Hailian Li^a, Maohua Yang^a, Dan Zou^a, Yuefeng Deng^a, Yu Liu^a

^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

ARTICLE INFO

Keywords:

Task specific ionic liquid
Solvent extraction
Membrane separation
Yttrium
Diethylhexyl phosphinic acid

ABSTRACT

Satisfactory extractant for the separation of yttrium (Y) from other heavy rare earth elements (HREEs) in dilute solutions has not been reported for the time being. In this article, diethylhexyl phosphinic acid (P227) with lower pK_a value, equilibrium and stripping acidity due to the absence of alkyl oxygen atoms, were incorporated into task-specific ionic liquids (TSILs) to realize the separation of Y. The synthesized [methyltrioctylammonium][di-(2-ethylhexyl) phosphinate] ([A336][P227]) were applied in both solvent extraction and membrane separation processes. Extraction and stripping of HREEs in both hydrochloric and nitric media were studied. A further understanding on the thermodynamics coordination mechanism with rare earths and acid was discussed. Separation factors implied it more suitable for the separation of Y in nitric medium. In addition, from the view of more sustainable and efficient application, polymer inclusion membrane (PIM) was fabricated. Membrane transport was demonstrated from the view of saving reagent and energy. Surface structure and composition analysis were characterized and transport experiments were conducted to verify the separation of Y. Stability and reusability of the PIM were proved well. All these provided the separation of Y from HREEs with a promising novel extractant and membrane separation technology.

1. Introduction

As is known to all, the ion-adsorption clays of rare earth deposits in China are unique because of the complete rare earth elements (REEs) from light REEs to heavy REEs, and comparably easy leaching essence [1–3]. But the mining processes for the ion-adsorption clays of rare earth deposits are still difficult on account of the low leaching grade, complex leachate composition and particularly dilute solution. In addition, the separation of heavy REEs with low partition, such as thulium (Tm), ytterbium (Yb) and lutetium (Lu), would be difficult if there is large amount of Y coexisted in the original leachate [4]. So it is important to explore efficient system for the separation of Y in dilute solution. Naphthenic acid [5–7] was a traditional extractant for Y since 1980s. However the disadvantages of naphthenic acid were obvious during its industrial application. It was a mixture of natural products with complex and unclear composition varied with different origins. The stability of extraction system was poor because of the changes in composition. What's more, the separation between La and Y was difficult by naphthenic acid [8]. Afterwards, researchers studied several systems like *sec*-octylphenoxy acetic acid (CA-12), mixtures of CA-12 with tributyl phosphate (TBP) or 2-ethylhexyl phosphonic acid mono-2-

ethylhexyl ester (P507) et al [6,9–12]. But no satisfactory efficient extractant for the separation of low content Y has been reported for the time being.

The past decade had witnessed the constant evolving of task specific ionic liquids (TSILs) for metal ions extraction and separation, such as rare earths [13–17]. Extractants traditionally employed in rare earth separation process, for example, 2-ethylhexyl phosphoric acid (P204), P507 and bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) had been synthesized as the anion parts of TSILs from the purpose of structure-activity relationship regulation [17–20]. Most studied TSILs were Aliquat336 series synthesized by researchers [21,22] and Cyphos IL [23,24] series produced by Cytec Canada Inc. As been proved by our previous study [25], dialkylphosphoric acid extractants had lower pK_a value, equilibrium and stripping acidity than P204 and P507, owing to the absence of electronegativity of alkyl oxygen atoms. Yuan et al had investigated the intrinsic relationship between pK_a values and the extraction performances, which could be ascribed from the changes in $-(P(=O)OH)-$ groups' alkyl oxygen atoms [26]. So incorporating this kind of acid phosphine extractant without the presence of alkyl oxygen atoms into TSILs would be a promising attempt in the separation of Y. Wang et al [17] had developed a sustainable Y separation process using

* Corresponding author.

E-mail address: jchen@ciac.ac.cn (J. Chen).

[N₁₈₈₈][CA12] ionic liquid and no acid or base was consumed during the extraction, scrubbing and stripping procedures. The same group had also published some other similar ionic liquid, such as [P_{6,6,6,14}][SOPAA] [27] for the separation of REEs.

According to the latest researches on the extraction behaviors and mechanisms of TSIL, the solvent extraction mechanism of REEs by TSILs may probably be one of cation exchange at elevated concentration, which would contain the conversion from zwitterions pairs to protonated phosphonic acid dimers and quaternary ammonium ions associated with chlorides [28]. So employing this kind of TSILs fixed in a solid/liquid process will be more efficient and sustainable from the view of much less TSILs consumption and stable separation performances. Being a highly integrated strategy in water treatment, membrane separation process [29,30] has been developed rapidly during recent years. It is a continuous and simultaneous process combining extraction and stripping into one. Less consumption of extractant, organic solvent and energy makes it being a promising alternative to solvent extraction process in rare earths separation [31]. We had previously applied one kind of TSIL containing the anion structure of P507 in the preconcentration and separation of Lu. The separation of Lu from Yb was proved promising, however the separation of Y from HREEs by the previous study was not satisfied, and the extraction mechanism of TSIL was not discussed in details.

So in this article we firstly synthesized a dialkylphosphoric acid based TSIL [A336][P227], which incorporated P227 with lower pK_a value, equilibrium and stripping acidity. In virtue of the absence of electronegativity of alkyl oxygen atoms, [A336][P227] showed better selectivity and lower equilibrium and stripping acidity. The extraction thermodynamics mechanisms were researched and deduced. The extraction and stripping properties in both hydrochloric and nitric media were demonstrated. A further understanding of these TSILs thermodynamics coordination mechanism with rare earths and acid was discussed in details. In addition, from the view of more sustainable and efficient application, PVDF inclusion membrane was employed for the purpose of high-efficient separation of Y in dilute solution. Membrane transport process was demonstrated as a more efficient and green technology to verify its separation performance of Y. Surface structure and composition analysis were characterized and the transport of HREEs was conducted. Stability and reusability of the membrane were proved well. All these provided the separation of Y from HREEs in dilute solutions with a promising novel TSIL extractant and membrane separation strategy.

2. Experimental

2.1. Materials and reagents

P227 (> 90%) was synthesized and kindly offered by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Aliquat336 was purchased from the Cytec Canada Inc. Solef® PVDF-1008 was purchased from Solvay online. According to published method [6], the task-specific ionic liquid [A336][P227] was synthesized. Stock solutions of RECl₃ and RE(NO₃)₃ were prepared via dissolving their oxides (> 99.99%) in hydrochloric acid or nitric acid, then diluted to required concentrations. Other reagents applied in this research were all of analytical grade.

2.2. Solvent extraction and data treatment

Equal volumes of aqueous and organic phases (3 mL each) were mixed in equilibrium tube, and shaken for 30 min at 298 ± 1 K via a desktop constant temperature oscillator (TH2-318, Shanghai Jinghong Equipment Co. Ltd.). The stripping process was conducted with equal volumes of acid and loaded organic phases (3 mL each) under the same condition as extraction. After phase separation, rare earth ions in aqueous phase were determined by a UVmini-1240 UV-visible

spectrophotometer (Shimadzu, Kyoto, Japan) using 3 mL ClCH₂COOH-NaOH as buffer solution (pH 2.8) and 2 mL 0.05% Arsenazo III as color developing agent. The concentration of rare earth ions in organic phase was calculated by mass balance. The equilibrium acidity was determined by a Mettler Toledo (FE20) pH meter.

The extraction efficiency *E*, distribution ratios *D*, separation factor *β* and stripping efficiency *S* are defined as follows:

$$E = \frac{[M](e, o)}{[M](i)} \times 100\% \quad (1)$$

$$D = \frac{[M](e, o)}{[M](e, a)} \quad (2)$$

$$\beta = \frac{D_z + 1}{D_z} \quad (3)$$

$$S = \frac{[M](e, a)}{[M](i, o)} \times 100\% \quad (4)$$

where subscripts *e*, *o*, *i* and *a* represent the equilibrium concentration, organic phase concentration, initial concentration and aqueous phase concentration, respectively. The subscript *z* refers to the atomic number of rare earth ion.

2.3. Membrane preparation and characterization

The preparation of PIM was prepared via phase inversion process. Briefly, 0.5 g PVDF powders were dissolved in 5.0 mL N,N-dimethylacetamide (DMAc) at 353 K, then [A336][P227] with needed amount was added. After being stirred for 6 h at 313 K to be homogeneously mixed, it would be added dropwise on a glass plate (diameter 5.5 cm) by a spin coater at room temperature to casting membranes. Afterwards, the nascent membrane was placed into deionized water bath for 12 h, during which the water bath was changed with fresh deionized water several times in order to remove the solvent DMAc. In order to reduce the size loss from thermal expansion and shrinkage, the glass plate and water bath were both preheated to 303 K. After being dried for 24 h, it would be cut into a suitable size (diameter 3 cm) for the following transport experiment.

A field-emission SEM (Hitachi S-4800) was applied to observe the porous structure after the membrane sample being sprayed with gold. The surface morphology of the PIM was characterized by a AFM (Bruker Dimension ICON) under tapping mode at room temperature. A Bruker VERTEX 70 (Germany) was applied to get the attenuated total reflection infrared spectroscopy of the PIMs. The thickness was measured by a micrometer caliper after each transport experiment.

2.4. Transport experiment and data treatment

A two-compartment membrane cell with the volume of 100 mL each was applied to demonstrate the transport experiment at 298 ± 0.2 K, and the membrane was sandwiched between the two compartments. The effective membrane contact area was a circular window with the diameter of 3 cm. Feed and stripping solutions were respectively poured in each compartment, and both compartments were stirred at 450 rpm by stirrers.

The permeability coefficient (*P*, μm s⁻¹) of RE(NO₃)₃ transported through the membrane was obtained by the following equation:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (5)$$

where *c* (mol L⁻¹) and *c_i* (mol L⁻¹) are RE(NO₃)₃ concentrations in the feed phase at the selected time and the initial time, respectively. *k* represents the rate constant (s⁻¹), and *t* represented the selected time during the transport (s).

The plots of ln(*c/c_i*) versus *t*, were deduced to calculate the value of *k*. The linear relationship of ln(*c/c_i*) versus *t* was confirmed by the high

Download English Version:

<https://daneshyari.com/en/article/7043530>

Download Persian Version:

<https://daneshyari.com/article/7043530>

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