



Selective separation of scandium (III) from rare earth metals by carboxyl-functionalized ionic liquids



Yuehua Chen, Huiyong Wang, Yuanchao Pei, Jianji Wang*

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, PR China

ARTICLE INFO

Article history:

Received 15 November 2016
Received in revised form 15 January 2017
Accepted 22 January 2017
Available online 24 January 2017

Keywords:

Solvent extraction
Selective separation
Carboxyl-functionalized ionic liquid
Sc (III)

ABSTRACT

It is always difficult to separate scandium from yttrium and lanthanides due to their similar physico-chemical properties. In this work, a selective separation strategy for Sc (III) from yttrium and lanthanides in aqueous solution was developed by using ionic liquids 1-alkylcarboxylic acid-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[(\text{CH}_2)_n\text{COOHmin}][\text{Tf}_2\text{N}]$) ($n = 3, 5, 7$) as extractants and 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$) ($n = 4, 6, 8, 10$) ionic liquids as diluents. The extraction parameters such as phase volume ratio, equilibrium time, pH value of the aqueous phase, alkyl chain length of the extractants and diluents, and system temperature were investigated systematically. It was shown that the extraction efficiency of Sc (III) increased with the increase of aqueous phase pH value, and was as high as 99.5% at pH 4.2. Sc (III) could be extracted selectively from yttrium and lanthanides by simple tuning of pH value of the aqueous phase, and the separation factor was 10^3 . After the extraction, stripping of Sc (III) from the ionic liquids was attempted by using dilute aqueous HNO_3 . In addition, an ion exchange mechanism of the proton of extractants and the cation of the diluents was proposed from a series of control experiments. Since both the proton of the extractants and cation of the diluents participated in the extraction process, amount of the ionic liquids transferred to water phase can be greatly reduced compared with the cation exchange based metal extraction using only ionic liquid extractants.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Rare earth elements are generally composed of 17 chemically similar metallic elements, including 15 lanthanides, scandium and yttrium [1]. As a crucial element, scandium and its compounds have been widely used in many fields of applications, such as catalysis, chemicals, laser glass, super conductor, hydrogen storage, carbon nanotube and metal treatment industries [2–4]. With increasing application of scandium in the world, it is believed that the demands of scandium would rapidly grow. Although the abundance of scandium in the earth's crust is relatively high, the yield of scandium is quite low, and its extraction and separation from yttrium and lanthanides are very difficult. This is the reason why scandium is so expensive. Therefore, it is significant to investigate the extraction and separation of scandium from yttrium and lanthanides. As a useful technique, liquid-liquid extraction is always found to be the most widely applied strategy in the separation of scandium from yttrium and lanthanum elements [5–8]. However,

in the conventional liquid-liquid extraction process, water-immiscible organic solvents such as toluene, n-dodecane, kerosene and chloroform were always used, which are usually flammable, volatile and toxic to environment. Therefore, the development of green and efficient technique is of great importance.

Ionic liquids (ILs) are tunable liquid organic salts composed of organic cations and inorganic or organic anions [9]. Due to their unique properties, such as extremely low volatility, no flammability, low melting point and high thermal stability, ILs have been used as alternative for conventional organic volatile solvents in the extraction of metal ions [10–13]. In the development of ILs based solvent extraction of scandium, Sun et al. [14,15] investigated the extraction of scandium from aqueous solution by alkylated phosphine oxides (Cyanex 925) which was dissolved in the IL 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$) or tricaprylmethylammonium nitrate [A336][NO_3]. Zhao et al. [16] studied the synergistic extraction of scandium from aqueous solution by the mixture of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) with 2-thenoyltrifluoroacetone (HTTA) and tri-n-octylphosphine oxide

* Corresponding author.

E-mail address: Jwang@htu.cn (J. Wang).

(TOPO). In these strategies, the ILs were used as organic phase to dilute the traditional specific extractant.

In recent years, some bifunctional ILs based on quaternary ammonium and quaternary phosphonium cations have been developed for the extraction of scandium and lanthanides [17–20]. Indeed, these ILs showed better extraction efficiency for scandium and lanthanides. For example, Shen et al. [21] investigated the extraction of scandium from aqueous HNO₃ or HCl using tricaprylmethylammonium di-(2-ethylhexyl)orthophosphinate ([A336][P507]). It was reported that at lower acidity other rare earth metal ions could not be extracted by this IL, suggesting that ([A336][P507]) was highly effective for the selective separation of Sc (III) from other rare earth metals. However, viscosity of these ILs is quite high, which is not beneficial to the mass transport of solutes in the extraction process. In order to reduce the viscosity of ILs and improve the kinetics of the liquid-liquid extraction, molecular diluents such as toluene and kerosene have to be used to dilute the ILs [17–21]. Since the diluents are always volatile organic solvents, the “green” nature of ILs was lost [22]. Recently, task-specific ILs with carboxyl-functional group have attracted great attention in the extraction of metal ions from aqueous phase [23–29]. In the case of Sc (III) extraction, Onghena and Binnemans [28] used betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf₂N] to extract scandium from aqueous solution. Depuydt et al. [26] reported the extraction of scandium by an aqueous biphasic system containing carboxyl-functionalized phosphonium IL ([P₄₄₄CH₂COOH]Cl) and a 16 wt% of aqueous NaCl solution. Although significant progress has been made in this field, the amount of dissolution loss of the ILs in water phase is quite high in direct liquid-liquid extraction, typically around 14 wt% for [Hbet][Tf₂N] in aqueous phase at room temperature, while the hydrophilic IL is not easy to recycle in the aqueous biphasic system extraction. Therefore, it is necessary to develop new strategies for the highly efficient separation of scandium from yttrium and lanthanides from aqueous solution.

In this work, three carboxyl-functionalized imidazolium ILs, namely 1-alkylcarboxylic acid-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [(CH₂)_nCOOHmim][Tf₂N] (n = 3, 5, 7), as shown in Fig. 1, were employed as extractants and four kinds of imidazolium-based ILs [C_nmim][Tf₂N] (n = 4, 6, 8, 10) were used as diluents to selectively separate Sc (III) from aqueous solutions. It was shown that the extraction efficiency of Sc (III) was as high as 99.5% under optimal conditions. Sc (III) could also be selectively extracted from yttrium and lanthanides by simple controlling of the pH value of the aqueous phase, and the separation factor was around 10³. After the extraction, Sc (III) in the ILs phase could be stripped by using dilute aqueous HNO₃ solution, and the ILs would be recycled for the separation process. In addition, the extraction mechanism was also investigated by a series of control experiments.

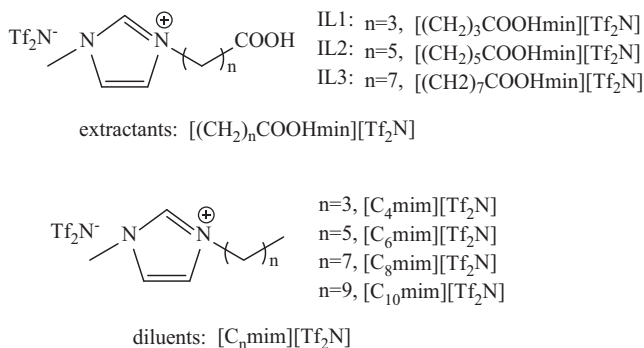


Fig. 1. Chemical structure of the ionic liquids extractants and diluents.

2. Experimental

2.1. Materials

N-methylimidazole (99%) was the product from Linhai Kaile Chem. Co. Ethyl-4-bromobutyrate (95%), 6-bromohexanoic acid (97%), hydrobromic acid (48%), Sc₂O₃ (>99.9%), Lu₂O₃ (>99.9%), Y(NO₃)₃·6H₂O (>99.9%), Sm(NO₃)₃·6H₂O (>99.9%), and La(NO₃)₃·6H₂O (>99.9%) were acquired from Aladdin Chem. Co. Ltd., and 8-bromooctanoic acid (97%) was purchased from Alfer Aser Co. Ltd. Analytical grade hydrogen nitrate (65%) and sodium hydroxide were obtained from Shanghai Chem. Co., respectively. All the chemicals were used as received except for N-methylimidazole which was distilled before use. The ILs were synthesized according to the procedures described in literature [27]. Their chemical structures were confirmed by ¹H and ¹³C NMR spectra.

Water used in the experiments was prepared by redistillation of deionized water. Stock solutions of Sc (III) and lutetium (III) were prepared by dissolving their oxides (99.9%) in the concentrated HNO₃, respectively. After evaporation of the residues, the stock solutions were diluted to 100 mL. The other stock solutions of the metal ions were prepared by dissolving their nitrate salts in aqueous solutions. The stock solutions of these metal ions were standardized by EDTA titration using xylenol orange as indicator. The dilute solutions were obtained by appropriate dilution of the stock solution.

2.2. Extraction experiments

The extraction experiments were performed in a jacket glass vessel, and the temperature of the system was controlled at 30.0 ± 0.1 °C by circulating water from a thermostat. Typically, 0.5 mL of [C_nmim][Tf₂N] containing a certain concentration of carboxyl-functionalized IL was mixed with 2 mL of aqueous solution containing a given concentration of metal ion, and the mixture was stirred for 40 min to attain extraction equilibrium. Then, the upper aqueous phase was well separated by centrifugation at 2800 rpm for 5 min followed by returning the system into the vessel again for 20 min. The concentrations of metal ion in aqueous phase were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer, ELAN DRC-e, USA). The concentration of metal ion in the IL phase was calculated by mass balance. Metal ion concentrations were determined in triplicate with the uncertainty less than 5%. The pH values of the aqueous phase were determined using a pH meter (pHSJ-4F, Leici, Shanghai, China), which was calibrated daily by the standard buffer solutions with pH 4.00 and 6.86.

For the stripping of Sc (III) from the ILs after extraction, the IL phase loaded with Sc (III) was separated from aqueous phase, and then was contacted with 1 mL of aqueous HNO₃ solution at different concentrations (from 0.003 mol/L to 0.03 mol/L). The stripping experiment was carried out at 30.0 ± 0.1 °C controlled by circulating water from a thermostat. The mixture was stirred with a magnetic stirrer for 60 min to reach equilibrium and then the aqueous phase was separated by centrifugation at 2800 rpm for 10 min. The subsequent procedures for the determination of metal ions concentrations in aqueous solution and in IL phase were the same as described above for metal ions extraction.

The distribution ratio (*D*), extraction efficiency (*E*), separation factor (*SF*) and stripping efficiency (*S*%) were defined by the following equations:

$$D = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{IL}} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/4990046>

Download Persian Version:

<https://daneshyari.com/article/4990046>

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