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Recovery of Ru(III) from hydrochloric acid by cloud point extraction with 2-Mercaptobenzothiazole-functionalized ionic liquid

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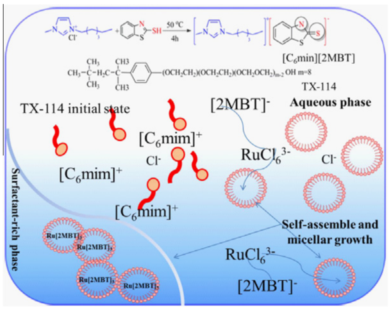
HIGHLIGHTS

- Ru(III) was firstly recovered by 2-Mercaptobenzothiazolate-functionalized ionic liquid based CPE system.
- Influence factors in CPE system was studied in detail.
- Superior extractability of Ru(III) was achieved under optimum conditions.
- Mechanism on Ru(III) extraction during CPE process was investigated by UV–vis and FT-IR.

GRAPHICAL ABSTRACT



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ABSTRACT

An arisen and environment-friendly method of cloud point extraction (CPE) which involved Octylphenoxypolyethoxyethanol (TX-114) as surfactant and 2-Mercaptobenzothiazole-functionalized ionic liquid as extractant was carried out to separate Ru(III) from aqueous phase to bottom surfactant phase for the first time. A host of variable (*e.g.*, the extractant concentration, hydrochloric acid concentration, nitric acid concentration, TX-114 mass fraction, TX-114 volume and sodium chloride concentration) were evaluated and optimized to investigate the extraction behavior. At optimized experimental conditions, the extraction percentage of Ru(III) was found to be 82%, together with the enrichment factor of 40. A special complexation extraction mechanism of Ru(III) in CPE process was studied systemically and confirmed *via* job method, UV–vis spectrum and FT-IR spectrum in detail. Taking together, the rational-designed functional ionic liquid as a novel extractant exhibited superior extractability for Ru (III) in CPE system.

1. Introduction

A great diversity of preconcentration and separation methods (*e.g.*, liquid–liquid extraction [1], cloud point extraction (CPE) [2], electrolytic deposition [3] and solid–liquid extraction [4]) have been proposed for metal extraction. Among these universal technologies, CPE has attracted tremendous attention as a promising environmentally benign separation approach for their inherent characteristics such as: (i) high efficiency and satisfactory enrichment factor can be obtained during CPE process, and the enrichment factor can be modified freely by varying the surfactant amount [5]; (ii) the solubility of hydrophobic complexes and affinity of metal-complexes to the surfactant-rich phase have been greatly improved [6]; (iii) in comparison with the conventional extraction involves hazardous organic solvent, minimal amount of surfactant is employed in the CPE system, which is consistent

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with environmental friendly, safe and economical concept [7]. On top of the above-mentioned advantages, this method has been extensively exploited as an ideal alternative to the traditional liquid–liquid extraction for metal separation and holds great promise in various analytical fields. For example, Mehrorang Ghaedi et al. introduced CPE technology for the preconcentration of Cd(II), Pb (II), Pd(II), Ag(I), Cu(II), Ni(II) and Co(II) ions in diverse samples with high efficiency [8,9]. Although many advances of CPE to separate metals have been achieved, there are still a great deal of restrictions need to be solved, especially, the mechanism for extracting metals.

To cater for the ever-increasing demands of high-performance electronic devices and/or automobiles, intensive exploration have been made to utilize Ru(III)-based materials. However, the scarce availability of Ru(III) could not meet the continually expanding demand, and the spent Ru(III) containing materials also pose potential environmental risk [10]. In this context, recovery and separation of Ru(III) from spent catalysts or waste liquor using high-efficiency extractant is urgently required [11]. Recently, huge research efforts have been devoted to recover and separate Ru(III) with conventional extractants (*e.g.*, TBP [12], N,N′-Dimethy-N,N′-Dicyclohexylmalonamide [13], tertiary, quaternary [14], n-paraffin hydrocarbon [15], Cyanex 923 [16], o-methoxyphenyl thiourea [17], *etc.*). However, these conventional extractants have been restricted by their limited extractability. For this reason, searching for an efficient extractant for Ru(III) separation becomes of paramount importance.

Among various extracting systems, functional ionic liquids (FILs) related separation methods have received recent attention for applications as solvent/extractant alternatives to extract desired metal ions with high selectivity [18]. Koichiro group have exploited a novel technique for Ru(III) extraction using Betainium-based FILs ([Hbet][Tf_2N]) with excellent extractability [19], but the deficiency stems at least in part from the lack of plausible mechanism for Ru(III) separation. FILs are ionic liquids (ILs) with functional groups incorporated in their cations and/or anions which could improve the properties of ILs such as complexing and solubility. This means that FILs can act as promising important extractant/solvent by virtue of their remarkable properties such as low flammability, low toxicity and hydrophobic property [20]. 2-Mercaptobenzothiazole-functionalized ionic liquids (MFILs) exhibit excellent solubility and strong coordinating ability by altering the nature of 2-Mercaptobenzothiazole as conventional extractant. Of particular interest, the preferable performance of selected MFILs for selective Pd(II) extraction has been systemically investigated in our previous work [21]. However, that system requires the massive use of expensive hydrophobic ionic liquids as organic phase. In this condition, the combination of eco-friendly CPE technique and high-efficiency MFILs for Ru(III) extraction needs to be revealed, then push its forward further development. In particular, the fundamental extraction mechanism for Ru(III) extraction in CPE process should be studied in detail.

Herein, we report Ru(III) extraction based on CPE system fabricated with the 2-Mercaptobenzothiazole-functionalized ionic liquid, [C_6mim][2MBT] and TX-114. The extracting parameters (*e.g.*, the extractant concentration, hydrochloric acid concentration, nitric acid concentration, TX-114 mass fraction, TX-114 volume and sodium chloride concentration) were investigated to determine the optimum extraction conditions. More importantly, the mechanism of CPE process in conjunction with FILs for Ru(III) extraction was proposed. Furthermore, back-stripping of Ru(III) from loaded surfactant-rich phase was studied and Ru simple substance was obtained. This contribution represents a promising direction for application merits of as-proposed Ru(III) extraction method.

2. Experiment

2.1. Regents and materials

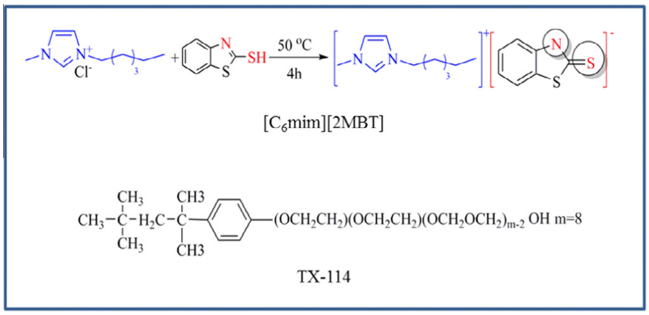
All the chemicals and reagents used in the study were of analytical grade. 1-hexyl-3-methylimidazolium chloride, [C_6mim]Cl, (99%) was purchased from Lanzhou Greenchem ILS, LICP, CAS, China. The stock solution of Ru(III) was purchased from Guangfu Institute of Fine Chemical (Tianjin, China). The non-ionic surfactant, TX-114, was obtained from Aladdin China Ltd. All the other reagents (hydrochloric acid, nitric acid, sodium chloride, ethanol, acetonitrile, methylene dichloride, acetone, chloroform, *etc.*) were used without additional purification. Distilled water was used to prepare the aqueous solutions in all experiments.

2.2. Analysis instrument

Before and after Ru(III) extraction, the Ru(III) concentration in the aqueous phase was determined by an atomic absorption spectrophotometer (AAS) (3150, Precision & Scientific Instrument Shanghai Co., Ltd., Shanghai, China). ^{1}H NMR was performed on a Bruker AV300 spectrometer with DMSO as solvent. UV–vis spectrum was recorded by UV spectrophotometry (UV-9000, Shanghai Metash, Instruments Co., Ltd. Shanghai, China). FT-IR characterization was performed on a Fourier transform infrared spectrophotometry (Tensor27, Bruker corporation, Karlsruhe, Germany) with the scanning wave number ranged from 4000 to 400 cm^{-1}. TEM observations were carried out on a JEM 100-CXII with an accelerating voltage of 80 kV.

2.3. Synthesis of 2-Mercaptobenzothiazole-functionalized ionic liquid, [C_6mim][2MBT]

The 2-Mercaptobenzothiazole-functionalized ionic liquid, [C_6mim][2MBT] was prepared by anion exchange processes, the details of which were described elsewhere [22]. As was shown in Scheme 1, typically, 30 mL ethyl alcohol solution containing a certain amount of sodium hydroxide was stirred in a round-bottom flask at 50 °C for 30 min. Subsequently, 2-Mercaptobenzothiazole and 1-hexyl-3-methylimidazolium chloride were added into the mixture under magnetic stirring at 50 °C, 4 h. Finally, after filtering off the inorganic solids, the obtained product was extracted with anhydrous acetone and dried under vacuum for 24 h. The as-prepared sample was brown viscous liquid. ^{1}H NMR (300 M, DMSO-d_6): δ ppm 0.86 (t, 3H), 1.24 (m, 6H), 1.75 (t, 2H), 3.85 (s, 3H), 4.15 (t, 2H), 6.89 (t, H), 7.05 (t, 1H), 7.22 aa (t, 1H), 7.38 (t, 1H), 7.70 (s, 1H), 7.78 (s, 1H), 9.19 (s, 1H).



Scheme 1. Synthesis of 2-Mercaptobenzothiazole-functionalized ionic liquid, [C_6mim][2MBT] and the structure of TX-114.