

Kinetics of cerium(IV) and fluoride extraction from sulfuric solutions using bifunctional ionic liquid extractant (Bif-ILE) [A336][P204]



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Abstract: The extraction kinetics of Ce(IV) and Ce(IV)–F[−] mixture systems from sulfuric solutions to *n*-heptane solution containing Bif-ILE [A336][P204] ([trialkylmethylammonium][di-2-ethylhexanxylphosphinate]) with a constant interfacial area cell with laminar flow were studied, just to elucidate the extraction mechanism and the mass transfer models. The data were analyzed in terms of pseudo-first-order constants. The effects of stirring speed, specific interfacial area and temperature on the extraction rate in both systems were discussed, suggesting that the extractions were mixed bulk phases-interfacial control process. Supported by the experimental data, the corresponding rate equations for Ce(IV) extraction system and Ce(IV)–F[−] mixture extraction system were obtained. The experimental results indicated the rate-controlling step. The kinetics model was deduced from the rate-controlling step and consistent with the rate equation.

Key words: Ce(IV)–F[−] system; Bif-ILE; kinetics model; extraction kinetics; constant interfacial area cell with laminar flow

1 Introduction

Solvent extraction processes represent a significant technique in rare earths extraction and separation, as well as in industrial scale separation process [1,2]. As solvent or extractant in solvent extraction process [3–8], the quaternary ammonium ILs have recently attracted wide attention [5] due to their lower cost and toxicity, compared with other categories of ILs, i.e., imidazolium-type, pyrrolidinium-type, and phosphonium-type [9]. The pure bifunctional ionic liquid extractants (Bif-ILEs) by combining the cation of A336 (aliquat336/trialkylmethylammonium chloride) with phosphonic acid group or carboxylic acid group as anions, can be prepared by acid/base neutralization method. And the physical and chemical properties have been extensively researched [10]. Based on its potential advantages, such as low cost, good physico-chemical properties, low aqueous solubility, good resistance to

hydrolysis and low extraction acidity, it has been systematically studied in the extraction of metal ions [11,12], especially for rare earths [13–15]. To access the extraction behavior of Bif-ILEs, our group also investigated the extraction and recovery of cerium(IV) (Ce(IV)) and fluoride (F[−]) from sulfuric solutions using Bif-ILE [A336][P204](tricaprylmethylammonium di-2-ethylhexylphosphinate) [14]. During the extraction process, if using neutral Bif-ILE instead of the traditional acidic extractants, the extraction acidity will be much lower and this will help to reduce the extraction cost [16]. Moreover, the Bif-ILEs are easy to be synthesized and have good purity. The Bif-ILEs may highlight considerable opportunities in such fields [17].

The extraction thermodynamics of rare earths with Bif-ILEs have been reported in our previous work [13,14]. However, there is no report on the extraction kinetics with Bif-ILEs. It is generally known that extraction kinetics research can provide useful information for optimizing processes, and is helpful in

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clarifying the mechanism of extraction. Hence, it is necessary to investigate the extraction kinetics of rare earths with Bif-ILEs and elucidate the extraction mechanism and mass transfer models. Table 1 shows the extraction kinetics study of Ce(IV) or Ce(IV) and F^- from sulfuric acid or nitric acid solution. The extraction system of Ce(IV) or Ce(IV)– F^- from bastnaesite has been concerned widely [24,25]. The theoretical research on the extraction thermodynamics and kinetics can provide reference for industry application. Therefore, as part of continuing work, the extraction kinetics of Ce(IV) and Ce(IV)– F^- mixture system from sulfuric solutions using Bif-ILEs [A336][P204] was investigated following the thermodynamic investigation. Among the experimental equipments and techniques used in traditional extraction system, such as the single-drop technique, the constant interfacial area stirred cell and the rotating membrane cell, the constant interfacial area cell with laminar flow developed by ZHENG et al [26] has been used widely [18–22], owing to the stability and reproducibility of data.

Table 1 Methods of extraction of Ce(IV) or Ce(IV) and F^- from sulfuric acid or nitric acid solution

System	Method	Ref.
Ce(IV)– H_2SO_4 /cyanex923– <i>n</i> -heptane	Constant interfacial area cell with laminar flow	[18]
Ce(IV)– F^- – H_2SO_4 /cyanex923– <i>n</i> -heptane	Constant interfacial area cell with laminar flow	[19]
Ce(IV), RE(III)– H_2SO_4 /N1923– <i>n</i> -heptane	Hollow fiber membrane	[20]
Ce(IV)– H_2SO_4 /N1923– <i>n</i> -heptane	Constant interfacial area cell with laminar flow	[21]
Ce(IV)– F^- – HNO_3 /DEHEHP– <i>n</i> -heptane	Constant interfacial area cell with laminar flow	[22]
Ce(IV)– HNO_3 /TBP– <i>n</i> -hexane	Single drop method	[23]

Following the thermodynamic investigation, in this study, the extraction kinetics of Ce(IV) and Ce(IV)– F^- mixture system from sulfuric acid solution using Bif-ILE [A336][P204] was investigated with a constant interfacial cell and laminar flow. Although this dynamic device still has its own drawbacks, this is the most effective method for the extraction systems to provide some reference data at present. The extraction mechanism and mass transfer models in extraction processes are proposed, providing more useful information for the application of the systems, especially for the advanced high-efficient clean processes. The reaction regimes deduced from the experimental results and the kinetics models were obtained from the rate-controlling step.

2 Experimental

2.1 Materials and reagents

Di-(2-ethyl hexyl) phosphate (95% purity, P204) was supplied by Tianjin Beicheng Chemical Plant (China) and used without further purification. Aliquat 336 (>99%) was purchased from Aldrich. The Bif-ILE [A336][P204] was synthesized in our lab according to published method [10]. The extractant was diluted with *n*-heptane. Stock solutions of Ce(IV) and F^- were prepared by dissolving $Ce(SO_4)_2 \cdot 4H_2O$ (>99.9%) into sulfuric acid and sodium fluoride into deionized water, respectively. Initial concentrations of F^- and Ce(IV) were maintained at 0.02 mol/L and 0.01 mol/L for all the studies, respectively. Ce(IV) concentration before extraction was determined by titration with standard $(NH_4)_2Fe(SO_4)_2$ using *o*-phenanthroline as indicator. The concentration of Ce(IV) in aqueous phase after extraction was determined spectrophotometrically using a Shimadzu (Kyoto, Japan) UVmini-1240 UV-visible spectrophotometer, and the concentration in organic phase was obtained by mass balance. The concentration of F^- was monitored by ion chromatography (Dionex ICS-1500, America) while the experiments on the effect of solution acidity were studied. The sulfuric acid concentration in aqueous phase was obtained by titrating with standard NaOH solution using phenolphthalein as indicator. The slope analysis was used to determine the extraction equations.

2.2 Apparatus and measurements

Kinetic experiments were carried out using a constant interfacial area cell modified with laminar flow by ZHENG et al [26] by immersing in a constant temperature water bath (DKB-501A, Senxin Co., Ltd., Shanghai). The schematic of the constant interfacial area cell with laminar flow is shown in Fig. 1.

Equal volume of the aqueous phase followed by organic phase was added carefully to the cell through injection hole for aqueous phase and organic phase using syringe, respectively, and stirring started at once. Both aqueous and organic phase volumes were 90.0 cm³. The organic phase was injected into the cell carefully in order to minimize the disturbance of the interface. The motors, digital overhead stirrers (IKA® RW 20 digital), were employed for stirring. The rotation speed was adjusted with the rotary knob on the front plate and displayed on the LED display. Compared with the motors used in previous researches, the operating is more convenient (speed display: LED-Display) and the data obtained are more accurate and reliable in stability and reproducibility (the measurement fault: max. ±0.5%). As we know, it is important that the equipment has good stability, reproducibility and convenience for the kinetic research.

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