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Kinetics of thorium extraction with di-(2-ethylhexyl) 2-ethylhexyl phosphonate from nitric acid medium

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ABSTRACT

The extraction kinetics of thorium (IV) by di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP) in n-heptane from nitric acid medium was investigated by using a constant interfacial cell with laminar flow. Parameters affecting the mass transfer mechanism such as stirring rate, temperature, specific interfacial area, Th (IV) concentration, DEHEHP concentration, and interfacial tension were studied. The rate equation of extracting thorium determined by slope analysis was as follows: $-\mathrm{d}[\mathrm{Th}]/\mathrm{d}t = k_0 \cdot [\mathrm{Th}^{4+}]^{0.72} \cdot B^{0.80} \cdot [\mathrm{NO}_3^-]^{0.82}$. The extraction regime was deduced to be mixed controlled by investigating the influence of stirring rate on extraction rate and by considering the activation energy (E_a; 27.46 kJ/mol). The extraction rate was independent of the specific interfacial area, which indicated that the bulk phase was the reaction zone. Furthermore, thorium extraction increased the specific gravity (d) of the organic phase and interfacial tension (γ).

1. Introduction

With the launch of nuclear program that consists of the thorium molten salt reactor (TMSR) and the accelerator driven system (ADS) by the Chinese Academy of Sciences (CAS), research of thorium resource utilization in China becomes a promising field (Jiang et al., 2012). China dominates 97% of the world's rare earth production over the past 30 years and disposes radioactive thorium into tailings which can contaminate water and lands (Xu et al., 2005). But now thorium resource associated with rare earth ore are suggested to be recovered as thorium enrichment and then purified to nuclear grade. Fortunately, thorium in monazite and bastnasite was recovered with 99% yield and 99% purity successfully in industry by prime amine N1923 extraction (Li et al., 1998, 2002; Wang et al., 2013).

Di−(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP, B), an intermediate product of 2-ethylhexyl phosphonic acid 2-ethylhexyl ester (P507), has several advantages such as easy preparation, and low cost (Xu et al., 1987). The extraction equilibrium of Ce(IV) from rare earth containing thorium was systematically studied (Zhao et al., 2004). The results revealed that DEHEHP can be used for selective extraction and separation of Ce(IV) in nitrate medium from other RE(III) and Th(IV). Further research (Wang et al., 2013) showed that DEHEHP is suitable for thorium purification compared with other neutral organophosphate extractants, e.g. tri-butyl phosphate (TBP). Organic and aqueous phases are rapidly separated in an extraction reactor after being mixed and without adding any phase modifier. In order to further elucidate extraction mechanisms, uncover mass transfer models and optimize the extraction process, extraction kinetics of thorium with DEHEHP were suggested.

Many techniques have been developed to study the kinetics of metal extraction, e.g., highly stirred tanks (Danesi and Chiarizia, 1980), moving drops (Baumgaertner and Finsterwalder, 1970), and constant interfacial area stirred cell (Lewis cell) (Hurst, 1986; Lewis, 1954). A Lewis cell provides direct liquid–liquid contact with a well-defined interfacial area. However, the cell design does not permit efficient stirring of the fluid near the interface, so large diffusion films are present in the cell (Hanna and Noble, 1985). Some important developments in Lewis cells have been made in the late 1980s (Chen and Zhu, 1994; Danesi et al., 1982). A revised Lewis cell called a constant interfacial cell with laminar flow was developed (Zheng et al., 1998). Investigation of the extraction kinetics of this apparatus has proven that this instrument can keep the interface stable and maintain good reproducibility during experiments (Lu et al., 1998; Wu et al., 2006; Xiong et al., 2006).

In the present research, a constant interfacial cell with laminar flow was used to study the kinetic of extraction of Th (IV) by DEHEHP in n-heptane from nitric acid medium. The reaction regime (chemical reaction or diffusion) and extraction zone were determined by studying the effect of stirring rate, temperature, and interfacial area on extraction.

2. Experimental

2.1. Reagents

DEHEHP (>98% purity) supplied by Tianjin Beicheng Chemical Plant (China) was purified as previously described (Zhao et al., 2006).

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DEHEHP was dissolved in n-heptane to prepare the organic solvent. A stock solution of thorium was prepared by dissolving a fixed amount of $Th(NO_3)_4 \cdot 4H_2O$ in double-distilled water. All the other reagents used were analytical reagent grade.

2.2. Apparatus and experimental procedures

The thorium concentration in the aqueous phase was determined with a spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.) using arsenazo III as the chromomeric agent (Baotou, 1972). Interfacial tension was measured by the Du Nouy ring method (accuracy of interfacial tension measurement, ±0.01 mN/m) with a Sigma 701 tensiometer (KSV Instrument Ltd., Finland). The specific gravities of both organic and aqueous phases were measured by the buoyancy method according to Archimedes' Law.

Extraction kinetics was examined using a constant interfacial area cell with laminar flow. This cell is cubic (Fig. 1) and made with organic glass whose phase was independently agitated with a stirring paddle. Temperature was controlled with a circulating water bath at constant temperature (298 K), except for temperature experiments. Interfacial plates with areas of 8.55, 11.76, 15.47, 19.22, and 24.50 cm^2 were used.

Equal volumes (94 mL each) of aqueous and organic phases were individually added to the cell chamber using a syringe. After stirring was started, 0.18 mL of sample was collected at 10 min intervals from the aqueous phase. The experiments were carried out at a constant stirring rate of 300 rpm, except for stirring rate experiments.

2.3. Data treatment

Following deduced theoretical formulas (Danesi and Vandegrift, 1981), the mass transfer process was treated as a pseudo-first-order reversible reaction:

$$[\mathrm{Th}]_{(a)} \underset{K_{oa}}{\overset{K_{ao}}{\rightleftharpoons}} [\mathrm{Th}]_{(o)} \tag{1}$$

where (a), (o), k_{ao} (cm/s), and k_{oa} (cm/s) represent the aqueous phase, organic, forward rate coefficient, and backward rate coefficient, respectively.

The rate of extraction is given by the following equation (Vandegrift and Horwitz, 1977):

$$-\frac{\mathrm{d}[\mathrm{Th}]_{(o)}}{\mathrm{d}t} = -\frac{\mathrm{d}n_o}{V\mathrm{d}t} = \frac{A}{V}\cdot\left(k_{oa}[\mathrm{Th}]_{(o)} - k_{ao}\cdot[\mathrm{Th}]_{(a)}\right) \tag{2}$$

where n_o is the number of moles of thorium in the organic phase, V (mL) is the volume of either aqueous or organic phase, and A (cm^2) is the interfacial area.

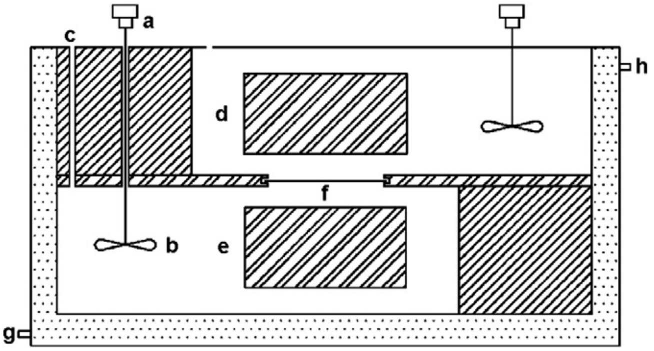

Fig. 1. Schematic diagram of the constant interfacial cell with laminar flow. a = Variable speed motor. b = Stirrer. c = Sampling hole. d = Organic phase. e = Aqueous phase. f = Interface of two phases. g = Water inlet. h = Water outlet.

At equilibrium, Eq. (2) is equal to zero; thus,

$$k_\mathrm{d} = \frac{[\mathrm{Th}]^e_{(o)}}{[\mathrm{Th}]^e_{(a)}} = \frac{k_{ao}}{k_{oa}} \tag{3}$$

where k_d refers to the distribution ratio, and e is the concentration at equilibrium. From the mass balance, the following equations are obtained:

$$[\mathrm{Th}]^{ini}_{(a)} = [\mathrm{Th}]_{(a)} + [\mathrm{Th}]_{(o)} \tag{4}$$

$$[\mathrm{Th}]^{ini}_{(a)} = [\mathrm{Th}]^e_{(a)} + [\mathrm{Th}]^e_{(o)} \tag{5}$$

Eq. (2) can thus be rewritten as

$$-\frac{\mathrm{d}[\mathrm{Th}]_{(o)}}{\mathrm{d}t} = -\frac{A}{V}\cdot k_{oa}\cdot\left(\frac{[\mathrm{Th}]^{ini}_{(a)}}{[\mathrm{Th}]^e_{(a)}}\cdot\left([\mathrm{Th}]_{(o)} - [\mathrm{Th}]^e_{(o)}\right)\right) \tag{6}$$

or

$$-\frac{\mathrm{d}[\mathrm{Th}]_{(o)}}{\mathrm{d}t} = -\frac{A}{V}\cdot k_{oa}(1+k_d)\left([\mathrm{Th}]_{(o)} - [\mathrm{Th}]^e_{(o)}\right) \tag{7}$$

Integrating Eq. (7) yields

$$\ln\left(1-\frac{[\mathrm{Th}]_{(o)}}{[\mathrm{Th}]^e_{(o)}}\right) = -\frac{A}{V}\cdot(1+k_\mathrm{d})\cdot k_{oa}\cdot t \tag{8}$$

k_d was determined by collecting samples from the aqueous phase at equilibrium.

The slopes of plots of $\ln(1–[\mathrm{Th(V)}]_{(o)}/[\mathrm{Th(IV)}]^e_{(o)})$ versus time (t) were used to evaluate k_{oa} and k_{ao} per experiment. By investigating the influences of various paramaters (i.e., concentrations of Th (IV), DEHEHP, and NO_3^-) on the extraction rate, the overall reaction orders can be deduced. Moreover, the extraction regimes and reaction zone can be determined.

3. Results and discussion

3.1. Identification of reaction regime

Extraction regimes in an oil/water extraction system have two representative types, i.e., diffusion-controlled and chemical reaction-controlled regimes (Hanna and Noble, 1985). One common criterion used to identify a reaction regime is the dependence of the extraction rate on the stirring rate of phases in a constant interfacial area cell. With increased stirring rate, the stationary diffusion film becomes thinner and the diffusion resistance becomes smaller (Chen and Zhu, 1994). Beyond a distinct stirring rate, the diffusion resistance may be ignored and only the chemical reaction needs to be considered.

The dependence of the mass transfer rate of extraction on the stirring rate is shown in Fig. 2. The extraction rate sharply increased with increased stirring rate when the stirring rate ranged from 150 rpm to 250 rpm. The extraction rate exhibited a “plateau region” when the stirring rate exceeded 300 rpm. The presence of a “plateau region” in the plot of the extraction rate constant vs. stirring rate can be taken as evidence that the extraction kinetics are chemical reaction controlled beyond 300 rpm. Therefore, all other kinetic experiments were measured at 300 rpm to maintain the same hydrodynamic conditions.

A further criterion for determining the type of extraction regime is the determination of the activation energy of extraction. The effect of temperature on extraction rate was studied from 293 K to 318 K (Fig. 3). The extraction rates were found to increase with increased