Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Liu, Jianjun , Wang, Yanliang and Li, Deqian(2008) 'Extraction Kinetics of Thorium(IV) with Primary Amine N1923 in Sulfate Media Using a Constant Interfacial Cell with Laminar Flow', Separation Science and Technology, 43: 2, 431 — 445

To link to this Article: DOI: 10.1080/01496390701784187

URL: http://dx.doi.org/10.1080/01496390701784187

Separation Science and Technology, 43: 431–445, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701784187

Extraction Kinetics of Thorium(IV) with Primary Amine N1923 in Sulfate Media Using a Constant Interfacial Cell with Laminar Flow

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Abstract: Extraction kinetics of thorium(IV) with primary amine N1923 in sulfate media has been investigated by a constant interfacial cell with laminar flow. Studies of interfacial tension and effects of the stirring rate, temperature, and specific interfacial area on mass transfer rate show that the most probable reaction zone takes place at the liquid-liquid interface. According to the experimental data correlated as a function of the concentration of the relevant species involved in the extraction reaction, the rate equation of extracting thorium has been obtained as follows:

$$-d[\mathrm{Th(IV)}]_{(o)}/dt = 10^{-3.10} \cdot [\mathrm{Th(IV)}]^{0.89} \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]^{0.74}.$$

The kinetic mechanism of the extraction process is proposed taking an interfacial chemical reaction as the rate-determining step of the overall reactions.

Keywords: Extraction kinetics, thorium, primary amine N1923, constant interfacial cell

INTRODUCTION

Resources and environments are the base of sustainable development for human society. A clean process is always a matter of great concern because

Received 21 March 2007, Accepted 30 September 2007
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environment pollution is created by many industries such as textile, cosmetic, paper, leather, pharmaceutical, and food industries (1–3). Baotou Beiyunoboite, mainly consisting of Bastnaesite and Monazite, is 90% of rare earth resources in China, which contains 0.2%–0.3% thorium in addition to the rare earths. The traditional process in hydrometallurgy of the rare earth in industry is to remove the thorium as an impurity element from sulfate leaching solutions by precipitation with the addition of magnesium salt. This process has many problems such as low recovery of rare earths, disposal of precipitate and pollution arising from the storage of radioactive precipitate. It is known that thorium is one of the most vital elements for nuclear energy programme (4). Its natural sources generally co-exist with lanthanides (Ln) in Bastnaesite or Monazite, which in their own right has diverse technological applications. Thus the methodology adopted for the separation of these metal ions from different ores has always attracted the attention of separation scientists (5, 6).

As known, the solvent extraction is the most widely used technique for the separation and recovery of metal ions (7). During the last few years, extraction kinetics also has been a subject of fundamental interest in the study of solvent extraction. The knowledge of the extraction kinetics not only provides information useful for reactor designs, but also it is helpful to clarify the mechanism of extraction.

Solvent extraction by primary amine N1923 (RNH_2) has received considerable attention because of its importance for the selective separation between metal ions (8, 9) including various metals such as rare earth, iron, (10, 11) etc. Studies indicate that this extractant has several advantages including low solubility in aqueous phase, low stripping acidity, and high separation factors between rare earth and thorium in contrast with 2-ethyhexyl phosphonic acid–mono-2-ethyhexyl ester. However, in most papers reported, researchers concentrated their attentions on the thermodynamics of the extraction. Only a few papers have ever been published on the subject of extraction kinetics. One is the extraction kinetics of palladium (12) with constant interfacial cell method, the other is that of lanthanum (13) adopted by single drop rising method. So far the extraction kinetic of thorium with primary amine N1923 has not been reported.

Based on the extraction thermodynamic studies of thorium(IV) with primary amine N1923 (10), a new clean process has been proposed by our lab (14) for the separation and the recovery of thorium and preventing the pollution by thorium as hazardous industrial wastes. Although a great deal of information is available on the thermodynamic of thorium extraction by primary amine N1923, very little information is available on the mass-transfer model of this system. Therefore, in order to try to elucidate the extraction mechanism of thorium complex species by primary amine N1923 sulfate and to localize the region where the rate determining processes are occurring (aqueous or organic bulk or interface), the rate of extraction of thorium(IV) from sulfate solutions by primary amine N1923 in n-heptane diluents has been studied. A constant interfacial cell with laminar flow, following a method previously reported in detail (15) has been used.

EXPERIMENTAL

Reagents

Primary amine N1923, collecting from Shanghai Organic Chemistry Institute (Chinese Academy of Sciences), was purified by distillation at 667 kPa and 175–205°C (12). The contents of nitrogen and primary amine in the purified mass were 4.99% and 99%, respectively. Iso-octyl alcohol (modifier) and n-heptane (diluent) used in this study were of analytical grade. In the experiments, iso-octyl alcohol was added into the organic phase to prohibit the third phase formation. The amount of iso-octyl alcohol in the organic phase was 0.7 vol. percent, otherwise stated. Primary amine N1923 sulfate, $(RNH_3)_2SO_4$, was prepared as reported in reference (16). A stock solution of thorium(IV) sulfate was prepared by dissolving thorium hydroxide (A.R.) in sulfuric acid solution with subsequent vaporization of the excess acid. The test solutions were kept constant at a constant ionic strength of 0.2 mol/l.

Analysis

The concentration of thorium(IV) in the aqueous phase was determined by spectrophotometric method (17). The thorium(IV) in the organic phase was stripped off with nitric acid and then analyzed. As thorium concentration analyzed in this way was found in keeping with that determined by the method of difference, the late method was used in this study.

Apparatus and Experimental Procedures

The apparatus used for kinetic measurements was that of Lewis cell (18) modified by Zheng and Li (15). Kinetics experiments were carried out by dipping the cell in a constant temperature water bath of 25 ± 0.2°C, otherwise stated. Aliquot of 95 ml aqueous phase followed by same aliquot of organic phase were added carefully to the cell chambers with the aid of a syringe and the stirring started. The speed of stirring for both phases in the majority of experiments was kept constant at 275 r.p.m., otherwise stated. Samples of the aqueous phase were collected at ten minutes intervals. The sampling volume was always 0.1 ml, therefore, no significant change in volume. In the experiments, the concentrations of primary amine

N1923 and thorium(IV) were 0.02 mol/l and 2.72 mmol/l, respectively, and varied when their concentration effects being investigated. The pH value of aqueous phase was kept at 1.9 and varied when the effect of pH was studied. The interfacial area was 19.22 cm^2 except for specific interfacial area experiments.

The interfacial tension experiments were performed on a Du Nouy tensiometer (Sigma 701, Finland) and a platinum/iridium ring of 9.545 mm diameter. Interfacial tension was measured by the Du Nouy ring method as described in the reference (19).

Data Treatment

Experimental data were treated as described by Danesi (20). Assuming that the mass-transfer process could be formally treated as a pseudo-first order reversible reaction with respect to the metal cation, one can write the following equation:

$$\mathrm{Th(IV)}_{(a)} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftharpoons}} \mathrm{Th(IV)}_{(o)} \tag{1}$$

The following equation can be obtained as (20):

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

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

$$\ln\left(1 - \frac{[\mathrm{Th\ (IV)}]_{(o)}}{[\mathrm{Th(IV)}]^e_{(o)}}\right) = -\frac{Q}{V}\cdot(k_{ao}+k_{oa})\cdot t \tag{4}$$

$$\ln\left(1 - \frac{[\mathrm{Th(IV)}]_{(o)}}{[\mathrm{Th(IV)}]^e_{(o)}}\right) = -\frac{Q}{V}\cdot(1+k_d)\cdot k_{oa}\cdot t \tag{5}$$

where, (a), (o), e, k_{ao}, (cm/s), k_{oa} (cm/s), k_d, V (ml) and Q (cm^2) represent aqueous phase, organic phase, equilibrium state, forward mass transfer coefficient (or pseudo-first order rate constant), backward mass transfer coefficient, the distribution constants for Th(IV), volume of each phase taken in the cell and the interfacial area, respectively.

The function ln (1-$[\mathrm{Th(IV)}]_{(o)}$/ $[\mathrm{Th(IV)}]^e_{(o)}$) was plotted against time (t) for each experiment. The slopes of the plots were used to evaluate k_{oa} and k_{ao}. All plots were straight lines in this work, indicating that the above assuming was reasonable.

RESULTS AND DISCUSSION

Reaction Regime

Dependence of the Mass Transfer Rate on the Stirring Speed

In extraction kinetics experiments, the criterion generally used to identify the extraction regime is the dependence of the extraction rate on the stirring speed (21). Figure 1 shows that the extraction rate constant increases sharply with the progressive increase of the stirring speed when the stirring speed is less than 275 r.p.m. This is attributed to the fact that the thickness of the stagnant interfacial films is thick at a lower stirring speed and the diffusion limits the rate because of relatively fast chemical reactions. The interfacial films will become thinner and the diffusion resistance smaller with an increase of the stirring speed larger than 275 r.p.m. This means that at this stirring value the diffusion processes in both the aqueous and the organic films have become so fast compared to the chemical reactions that they no longer influence the rate of extraction. Therefore, the presence of a “plateau region” in the plot of the extraction rate constant vs. the stirring speed is an indication that in the zone the extraction rate may be chemically controlled.

Dependence of Log k_{ao} on the Temperature

A further criterion that enables distinguishing between a diffusion-controlled and a kinetics regime is the experimental determination of the activation

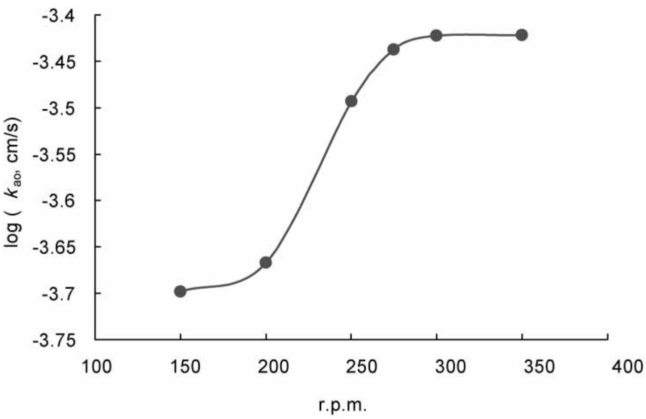

Figure 1. Effect of stirring speed on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, pH 1.5, $[SO4^{2-}]$ = 0.2 mol/l, Organic phase: [N1923] = 0.02 mol/l, Q = 19.22 cm^2.

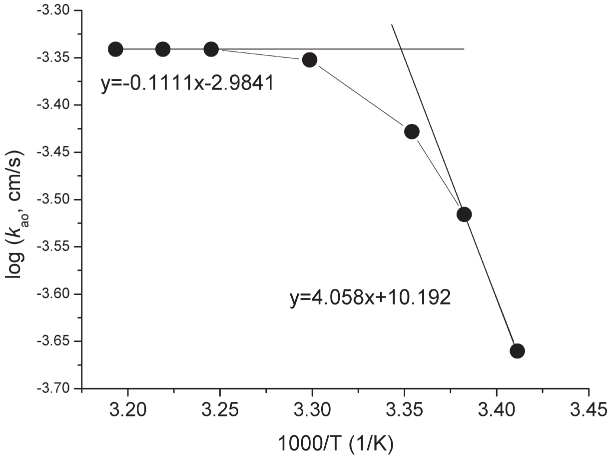

Figure 2. Effect of temperature on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, pH 1.5, [$SO4^{2-}$] = 0.2 mol/l, Organic phase: [N1923] = 0.02 mol/l, Q = 19.22 cm^2.

energy of the extraction process. Figure 2 shows that the extraction rate increases sharply with the temperature lower than 303 K and increases slightly at temperature higher than 303 K. The apparent activation energy (E_a) for the extraction was calculated from the slope of log k_{ao} vs. 1000/T according to the Arrhenius Equation.

$$T < 303\ K \quad E_a = 77.70\ kJ/mol$$
$$T > 303\ K \quad E_a = \ 2.12\ kJ/mol$$

According to the theory by Yu et al. (22, 23), the obtained value of E_a suggests a possible chemical reaction control regime in the temperature range of 293 K to 303 K and a diffusion controlled regime in the temperature range of 303–313 K, which indicates that the temperature conditions may alter the mechanism (24).

Reaction Zone

Dependence of Initial Mass Transfer Rate on Specific Interfacial Area

The chemical reactions which control the rate of extraction in a kinetic regime can occur either in the bulk phases or at the interface. The distinction between the two types of reactions can be performed by studying how the extraction rate varies with the specific interfacial area. In fact (21), if interfacial chemical reactions are the rate determining process of the mass transfer, the rate has to be proportional to the specific interfacial area, Q/V,

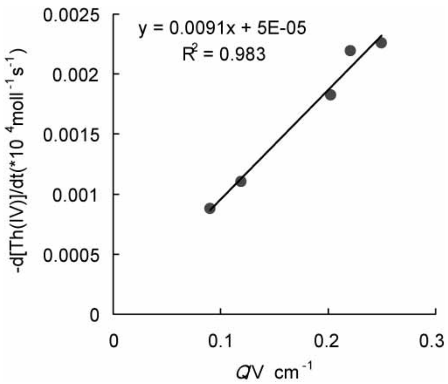

Figure 3. Effect of specific interfacial area on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, pH 1.9, [SO4^{2-}] = 0.2 mol/l, Organic phase: [N1923] = 0.02 mol/l, V = 95 ml.

i.e. the ratio between the interfacial area, Q, and volume, V, of the phase. The result shown in Fig. 3 indicates that a linear relationship is found between the mass transfer rate ($-$d[Th(IV))$_{(o)}$/dt] and specific interfacial area, which is the characteristic of an interfacial reaction for Th(IV) extraction with primary amine N1923. Consequently we can reasonably assume that the mass transfer rates at 275 r.p.m. and 298 K are mainly controlled by chemical reactions taking place at the interface on the basis of the results from Figs. 1, 2, and 3.

Interfacial Activity of Primary Amine N1923

Further support to the hypothesis that the reactions are taking place at the interface can be obtained by studying the interfacial tension of the biphasic system. Interfacial tension studies are particularly important since they can provide useful information about the interfacial concentration of the extractant. The measurements were carried out at 298 K $\pm$ 0.2 K by using pre-saturated phases as described in reference (24). Fig. 4 shows the results investigated under the form γ (mN/m) vs. log C (analytical concentration of the primary amine N1923 in the n-heptanes) curves on the basis of the Szyszkowski isotherm equations (25). That is:

$$\gamma = \gamma_0\left[1 - B_{SZ}\ln\left(\frac{\mathrm{C}}{A_{SZ}} + 1\right)\right] \tag{6}$$

where, A_{SZ} (mol/l) and B_{SZ} are the adsorption coefficients; γ and γ_0 is the interfacial tension for a given extractant concentration C (mol/l) and $C = 0$,

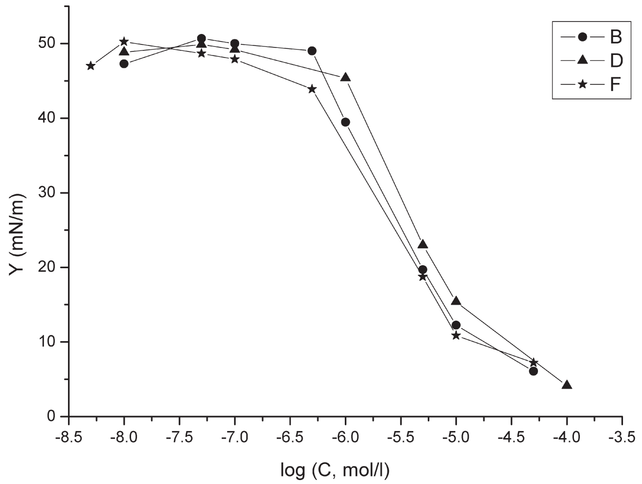

Figure 4. Effect of iso-octyl alcohol on the interfacial tension of primary amine N1923. Aqueous phase: $[\text{Th(IV)}] = 2.72\,\text{mmol/l}$, pH 1.5, $[\text{SO4}^{2-}] = 0.2\,\text{mol/l}$, volume percent of iso-octyl alcohol in the organic phase are B, 0; D, 0.7 and F, 1.4. equilibration time is 15 minutes.

respectively. By using Eq. (6) and introducing the term $d\gamma/dC$ into the Gibbs isotherm, Eq. (7) is obtained for the surface excess:

$$\Gamma_{SZ} = \frac{\gamma_0 \cdot C \cdot B_{SZ}}{\mathrm{R} \cdot \mathrm{T} \cdot (C + A_{SZ})} \tag{7}$$

where, $\Gamma(\text{mol/m}^2)$, R $(\text{J} \cdot \text{mol/K})$ and T (K) represent surface excess concentration, the gas constant and absolute temperature, respectively. According to the literature (25), A_{SZ} and B_{SZ} in the Szyszkowski isotherm have their own physico-chemical meanings and can be used to determine maximum surface excess ($\Gamma_{\max}$, mol/m^2) at saturation, minimum interfacial area occupied by a statistical molecule in the absorbed layer (A_I, nm^2). The values of the

Table 1. Effect of iso-octyl alcohol on the interfacial activity of primary amine N1923 aqueous phase: 0.2 mol/l SO_4^{2-}, pH 2.0, $\text{T} = 298 \pm 0.2$ K

Amount of iso-octyl alcohol in the organic phase, % (v/v)	$-\log C_{\min}$ (mol/l)	$\Gamma_{\max} \cdot 10^6$ (mol/m^2)		$A_{\min}$ (nm^2)		A_{SZ} (mol/l)	B_{SZ}
		$\Gamma_{\max}^{G}$	$\Gamma_{\max}^{SZ}$	A_G	A_{SZ}		
0	5.87	4.98	4.48	0.33	0.37	6.97E-7	0.219
0.7	5.62	4.52	4.13	0.37	0.40	8.68E-7	0.208
1.4	5.42	3.59	2.80	0.46	0.59	1.98E-7	0.153

interfacial parameters are obtained from Fig. 4 and listed in Table 1. A_I, the apparent molecular interfacial area, was calculated from the constant slope portion of these curves through the relationship (26):

$$A_I = -\frac{2.303\, k \cdot T \cdot 10^{16}}{\Delta\gamma/\Delta(\log\, C)} \tag{8}$$

where, *k* is the Boltzman constant, The data in Table 1 show that The iso-octyl alcohol has little influence upon the interfacial activity when the amount is 0.7% (v/v). With the increasing amount of iso-octyl alcohol, the effectiveness of adsorption decreases in terms of values of T_{max}. Both primary amine N1923 and its sulfate have surface active behavior for C_{min} (the minimum bulk concentration of the extractant necessary to saturate the interface) lower than 10^{-5} mol/l. A result of this strong interfacial activity is that the interfacial concentration can be larger than that of the reagent in the organic bulk, and this fact can strongly favor the occurrence of interfacial reactions (21).

Extraction Rate Equation

Effect of Thorium Concentration on Initial Extraction Rate

Figure 5 presents the variation of mass transfer coefficient k_{ao} with thorium(IV) concentration. The slope of the straight line is 0.89. It is therefore conducted that the reaction order with respect to Th(IV) concentration is 0.89.

Effect of the Extractant Concentration on Extraction Rate

Figure 6 represents the variation of k_{ao} with the variation of primary amine N1923 concentration in the organic phase. The slope of the plot is 0.74. It indicates that the overall reaction order with respect to primary amine N1923 concentration is 0.74.

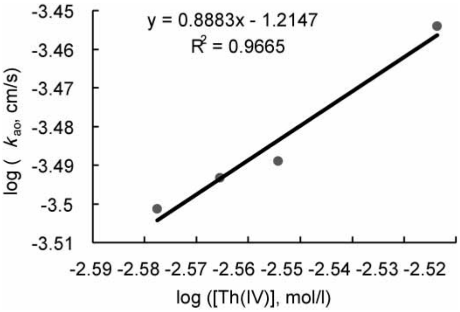

Figure 5. Effect of thorium concentration on the mass transfer rate. Aqueous phase: pH 1.9, $[SO4^{2-}] = 0.2$ mol/l, Organic phase: [N1923] = 0.02 mol/l, Q = 19.22 cm^2.

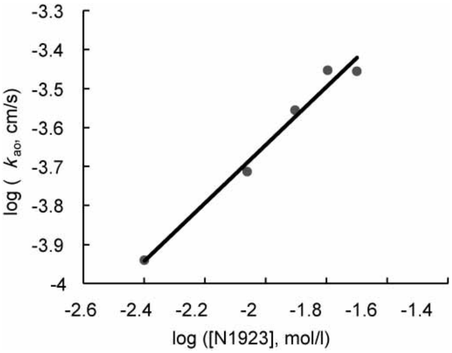

Figure 6. Effect of primary amine N1923 concentration on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, pH 1.9, $[SO4^{2-}] = 0.2$ mol/l, $Q = 19.22\ cm^2$.

Effect of Sulfate and Bisulfate Concentration on Extraction Rate

The effects of sulfate and bisulfate concentration on the extraction rate have been investigated and the results are shown in Fig. 7. Within experimental error, the zero sloped lines indicate that the extraction rate is independent on the sulfate and bisulfate concentrations. This fact together with the report on the Th(IV) extraction equilibrium (27) indicate that the stable Th(IV) species in the sulfate medium is $Th(SO_4)_2$.

Effect of pH on Extraction Rate

The influence of pH on the extraction rate has been measured and the result shown in Fig. 8 demonstrates that the extraction rate is independent on the pH in the investigated region.

According to the experimental results, the rate equation can be written as follows:

$$-\frac{\mathrm{d}[\mathrm{Th(IV)}]_{(\mathrm{o})}}{\mathrm{d}t} = k_f \cdot [\mathrm{Th(IV)}]^{0.89} \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]^{0.74} \tag{9}$$

where, k_f is apparent forward extraction rate constant. The reverse extraction rate can be ignored where there is a high concentration of extractant in the organic phase and a low metal concentration in the aqueous phase. Based on Eq. (2) and (9), one can write the following equation:

$$\frac{Q}{V} \cdot k_{\mathrm{ao}} \cdot [\mathrm{Th(IV)}]^{0.11} = k_f \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{o})}^{0.74} \tag{10}$$

The plot of log $(Q \cdot k_{\mathrm{ao}} \cdot [\mathrm{Th(IV)}]^{0.11}/\mathrm{V})$ vs. log $([(\mathrm{RNH_3})_2\mathrm{SO_4})]_{(\mathrm{o})}^{0.74})$ gives straight line (Fig. 9) and the apparent forward extraction rate constant, k_f, can be calculated to be $10^{-3.10}$ via the intercept.

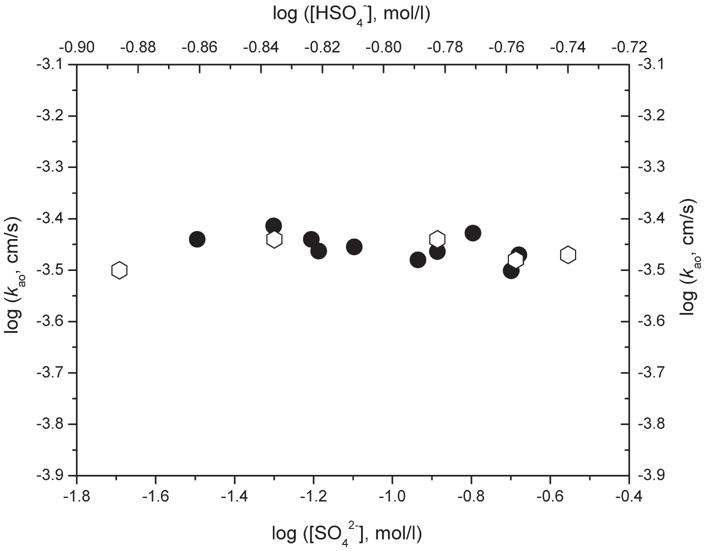

Figure 7. Effects of sulfate concentration and bisulfate concentration on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, pH 1.5, Organic phase: [N1923] = 0.02 mol/l, Q = 19.22 cm^2.

Mechanism and Kinetic Model

The composition of extractive Th(IV) complex is $(RNH_3)_4Th(SO_4)_4$ according to the thermodynamic of thorium(IV) extraction by primary amine N1923 (10). From this fact together with the above discussion, the

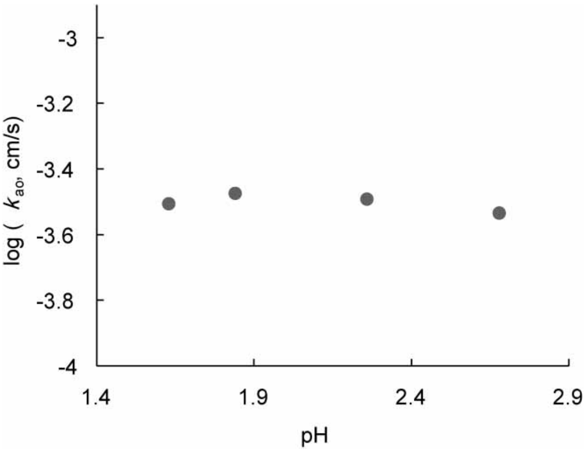

Figure 8. Effect of pH on mass transfer rate. Aqueous phase: [Th(IV)] = 2.72 mmol/l, [SO4^{2-}] = 0.2 mol/l, Organic phase: [N1923] = 0.02 mol/l, Q = 19.22 cm^2.

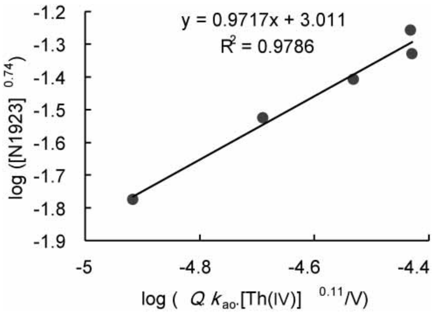

Figure 9. The plot of log $(Q/V \cdot k_{ao} \cdot [\mathrm{Th(IV)}]^{0.11})$ vs. log $(k_f \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(o)}^{0.74})$. Aqueous phase: $[\mathrm{Th(IV)}] = 2.72$ mmol/l, pH 1.5, $[\mathrm{SO4}^{2-}] = 0.2$ mol/l, Organic phase: primary amine N1923-n-heptane.

extraction process can be considered by the following equations according to the interfacial reaction model proposed by Danesi and Chiarizia (21),

$$\mathrm{Th(SO_4)_2} + (\mathrm{RNH_3})_2\mathrm{SO}_{4(i)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{RNH_3})_2\mathrm{SO_4Th(SO_4)}_{2(i)} \tag{11}$$

$$(\mathrm{RNH_3})_2\mathrm{SO_4Th(SO_4)}_{2(i)} + (\mathrm{RNH_3})_2\mathrm{SO}_{4(o)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{RNH_3})_4\mathrm{Th(SO_4)}_{4(i)} \tag{12}$$

$$(\mathrm{RNH_3})_4\mathrm{Th(SO_4)}_{4_{(i)}} + (\mathrm{RNH_3})_2\mathrm{SO}_{4(o)} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\mathrm{RNH_3})_4\mathrm{Th(SO_4)}_{4(o)} + (\mathrm{RNH_3})_2\mathrm{SO}_{4(i)} \tag{13}$$

where, (i), (o), (k_1, k_2, k_3) and (k_{-1}, k_{-2}, k_{-3}) represent the interface, organic phase, forward reaction rate constants of Eqs. (11–13) and the backward reaction rate constants of Eqs. (11–13), respectively. Considering equilibrium (12) as the rate-controlling step, the forward initial rate of this extraction process can be expressed as follows:

$$-\mathrm{d[Th(IV)]/dt} = k_2 \cdot [(\mathrm{RNH_3})_4\mathrm{Th(SO_4)_3}]_{(i)} \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(o)} \tag{14}$$

$$\frac{\mathrm{d}[(\mathrm{RNH_3})_3\mathrm{Th(SO_4)_3}]_{(i)}}{\mathrm{dt}} = k_1 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(i)}[\mathrm{Th(SO_4)_2}] - k_{-1} \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4Th(SO_4)_2}]_{(i)} - k_2 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4Th(SO_4)_2}]_{(i)}[(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(o)} \tag{15}$$

According to the steady state approximation (21), Eq. (15) = 0, then:

$$[(\mathrm{RNH_3})_2\mathrm{SO_4Th(SO_4)_2}]_{(i)} = \frac{k_1 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(i)}[\mathrm{Th(SO_4)_2}]}{(k_{-1} + k_2 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(o)})} \tag{16}$$

When Eq. (16) is substituted into Eq. (14), then:

$$-\mathrm{d}[\mathrm{Th(IV)}]/\mathrm{dt} = \frac{k_1 \cdot k_2 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{i})} \cdot [\mathrm{Th(SO_4)_2}] \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{o})}}{(k_{-1} + k_2 \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{o})})} \tag{17}$$

In the experimental conditions, the rate of Th(IV) transfer from the aqueous to the organic phase is faster than the reverse rate, i.e. $k_{-1} \gg k_2 \cdot (\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{o})}$; $[(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{i})}$ was a constant (13). Considering $[\mathrm{Th(SO_4)_2}] \approx [\mathrm{Th(IV)}]$, the extraction rate equation can be written as:

$$-\mathrm{d}[\mathrm{Th(IV)}]/\mathrm{dt} = K' \cdot [\mathrm{Th(IV)}] \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{O})} \tag{18}$$

where,

$$K' = \frac{k_1 k_2 [(\mathrm{RNH_3})_2\mathrm{SO_4}]_{(\mathrm{i})}}{k_{-1}}$$

The rate Eq. (18) derived for chemical reaction (12) is identical to Eq. (9). The non-integral values of reaction orders are due to the non-ideality of the phases.

CONCLUSIONS

The extraction of thorium with primary amine N1923 in n-heptane using a constant interfacial cell with laminar flow is a chemical controlled kinetics process with an interfacial reaction. Based on the experimental data correlated as functions of the concentration of the relevant species involved in the extraction reaction, the rate equation is deduced as follows:

$$-\mathrm{d}[\mathrm{Th(IV)}]_{(\mathrm{o})}/\mathrm{dt} = 10^{-3.10} \cdot [\mathrm{Th(IV)}]^{0.89} \cdot [(\mathrm{RNH_3})_2\mathrm{SO_4}]^{0.74}$$

Interfacial tension of primary amine N1923 has been investigated by the Du Nouy ring methods. The interfacial adsorption isotherms are processed by matching both the Gibbs and the Szyszkowski adsorption equations. The results demonstrate that primary amine N1923 has strong interfacial activity and it is enriched at the interface in terms of surface excess concentration ($\Gamma_{\max}$). The presence of iso-octyl alcohol in the organic phase exerts a rather slight effect on the interfacial activity of N1923 when its amount is 0.7 volume percent. It can also be concluded that the reaction of thorium(IV) extraction by primary amine N1923 occurs at the interface.

ACKNOWLEDGMENTS

This project is supported by the National Program entitled "basic research on high efficiency utilization of rare earth elements in the field of environmental protection" (2004CB719506), Natural Science Foundation of China (20371046; 50574080).

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