ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 171 (2003) 362–366

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/jssc

Mass-transfer kinetics of ytterbium extraction with sec-nonylphenoxy acetic acid

Y.G. Wang, Y.H. Zhu, and D.Q. Li*

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Received 22 April 2002; received in revised form 1 September 2002; accepted 12 September 2002

Abstract

The extraction kinetics of ytterbium with sec-nonylphenoxy acetic acid (CA-100) in heptane have been investigated using a constant interfacial area cell with laminar flow. The influence of stirring speed and temperature on the rate indicated that the extraction rate was controlled by the experiment conditions. The plot of interfacial area on the rate showed a linear relationship. This fact together with the low solubility in water and strong surface activity of CA-100 at heptane–water interfaces made the interface the most probable locale for the chemical reactions. The influences of extractant concentration and hydrogen ion concentration on the extraction rate were investigated, and the forward and reverse rate equations for the ytterbium extraction with CA-100 were also obtained. Based on the experimental data, the apparent forward extraction rate constant was calculated. Interfacial reaction models were proposed that agree well with the rate equations obtained from experimental data.

Keywords: Constant interfacial area cell; Ytterbium; Sec-nonylphenoxy acetic acid; Extraction; Kinetics; Extraction rate constant

1. Introduction

It is well known that kinetic separation is a possibility for the quantitative separation of metal ions which cannot be separated in the equilibrium state [1]. However, the still unresolved fundamental problems of the kinetics of the extraction of individual elements, related mainly to the identification for the rate determining stage and the location of the reaction, make it impossible for researchers to concentrate their attention on multicomponent extraction systems [2]. Thus, the kinetic studies of the extraction of individual elements are definitely necessary for the development of the experimental procedure and accumulation of data. Although the thermodynamics of the extraction are relatively well known, there is a lack of complete information on the kinetics of mass transfer in the biphasic liquid/liquid extraction system. Previous experimental work in this area was conducted with a variety of liquid contacting devices [3–6]. Among these devices, the constant interfacial area cell is the most recommended technique because it allows both a knowledge of the constant area between the two phases and at the same time a variance of the rate of stirring in a sufficiently broad range [7].

Sec-nonylphenoxy acetic acid (CA-100) is a novel organic carboxylic acid extractant. Studies indicate [8] that the extractant has several advantages including low solubility and stronger acidity in aqueous phase and high separation factors of scandium(III) or yttrium(III) with respect to lanthanide(III). Hence, it may be a promising extractant that will be superior to naphthenic acid. In previous work, we have explored the kinetics and mechanism of yttrium extraction with CA-100 [9], whereas no reports about the extraction kinetics of lanthanide by CA-100 have been seen to date. In the present work, the kinetics of ytterbium (Yb) extraction with CA-100 in heptane has been examined with constant interfacial area cell. The rate determining stage and the location of the reaction were determined and extraction reaction models were brought forward. The purpose is to understand the reaction kinetics of the system and provide fundamental information for dynamic separation of ytterbium from other rare-earth elements.

---

*Corresponding author. Fax: +86-431-5698041.
E-mail address: ldq@ciac.jl.cn (D.Q. Li).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(02)00213-X

2. Experimental

2.1. Reagents

CA-100 (>98% pure) was kindly supplied by Xiandai Chemical Plant of China. Before use, CA-100 was purified by washing with carbonate, hydrochloric acid and distilled water in turn and finally saponified with ammonia water. All other reagents were of analytical grade. Yb(III) stock solution was prepared by dissolving Yb_2O_3 (>99.9%) in hydrochloric acid and standardized by EDTA titration using xylenol orange as an indicator.

2.2. Procedures

The extraction kinetics were investigated using a constant interfacial area cell with laminar flow that was described previously [7]. The concentration of CA-100 in the organic phase and pH value in aqueous phase used in all kinetics experiments were 2.17×10^{-2} mol/L and 3.92, respectively, and these properties were varied to study their effects on rate. The aqueous phases contained 3.23×10^{-3} mol/L Yb(III) ion. Both aqueous and organic phase volumes were 92.5 cm^2. The two-phase interfacial area was 21 cm^2.

2.3. Data treatment

Assuming that the mass-transfer process can be formally treated as a pseudo-first-order reversible reaction with respect to the metal cation, one can write the following equilibrium:

$$M^{3+} \rightleftharpoons M(\mathrm{III})_{(\mathrm{o})}. \tag{1}$$

The following equations can be obtained as described in Ref. [10]:

$$-\frac{\mathrm{d}[M]_{(\mathrm{o})}}{\mathrm{d}t} = -\frac{Q}{V}(k_{\mathrm{oa}}[M]_{(\mathrm{o})} - k_{\mathrm{oa}}[M^{3+}]), \tag{2}$$

$$k_{\mathrm{d}} = \frac{[M]^{\mathrm{e}}_{(\mathrm{o})}}{[M^{3+}]^{\mathrm{e}}} = \frac{k_{\mathrm{ao}}}{k_{\mathrm{oa}}}, \tag{3}$$

$$\ln\left(1 - \frac{[M]_{(\mathrm{o})}}{[M^{3+}]^{\mathrm{e}}}\right) = -\frac{Q}{V}(1 + K_{\mathrm{d}})k_{\mathrm{oa}}t, \tag{4}$$

where species with no subscript and subscript o stand for aqueous phase and organic phase, respectively; "$[M]_{(\mathrm{o})}$" and "$[M]^{\mathrm{e}}_{(\mathrm{o})}$" refer to the organic concentration of Yb(III) at time t and at equilibrium, respectively; "k_{ao}" and "k_{oa}" are the forward and reverse pseudo-first-order rate constants or the interfacial mass-transfer coefficients, respectively; "K_{d}" represents the distribution constants of Yb(III); "Q" stands for the interfacial area; and "V" is the volume of the aqueous phase or the organic phase. At constant stirring speed, k_{ao} and k_{oa} are functions of the activities of the other two reactants presented in the system, i.e., the CA-100 in heptane and hydrogen ion in the aqueous phase.

The slopes of the plots $\ln(1 - [M]_{(\mathrm{o})}/[M]^{\mathrm{e}}_{(\mathrm{o})})$ vs. t have been used to evaluate k_{oa} and k_{ao}. All plots were straight lines in this work, indicating that the assumptions above were reasonable.

3. Results and discussion

3.1. Dependence of lg k_{ao} on stirring speed

In a constant interfacial area cell, the thickness of the stationary interfacial film is thicker at a lower stirring speed and the diffusion limits the rate because of a relatively fast chemical reaction. With the increase of the stirring speed, the stationary diffusion film becomes thinner and the diffusion resistance becomes smaller. At some value of the stirring speed, the extraction rate may be limited by the chemical reaction only, or the extraction rate may be independent of the stirring rate, which is called a "kinetics plateau". Hence, this kind of stirring cell allows an easy discrimination between limitation by diffusion or chemical reaction [11]. The influence of the stirring rate of the two phases on k_{ao} has been studied for Yb(III) at constant chemical composition, and the results are shown in Fig. 1. When the stirring speed is greater than 300 r/min, a plateau region is reached, which indicates that the extraction rate may be kinetically controlled in that zone. All other kinetic experiments are measured at 300 r/min in order to maintain the same hydrodynamic conditions.

3.2. Dependence of lg k_{ao} on temperature

The effect of temperature on the extraction rate has been studied in the temperature range from 293 to

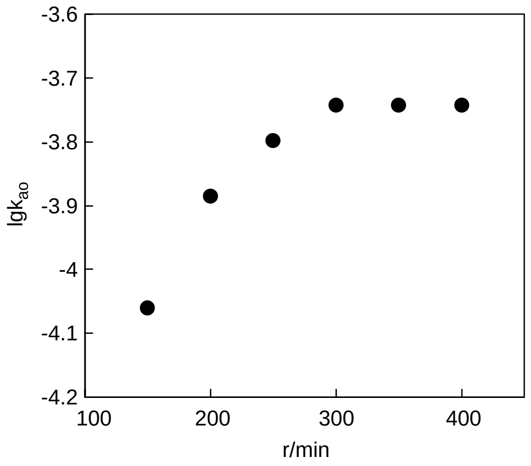

Fig. 1. The effect of the stirring speed on the extraction rate $T = 303 \pm 0.2$ K, $Q = 2.1$ cm^2, $V = 92.5$ mL, $[\mathrm{Yb}^{3+}] = 3.23 \times 10^{-3}$ mol/L, pH $= 3.92$, [CA-100] $= 2.17 \times 10^{-2}$ mol/L.

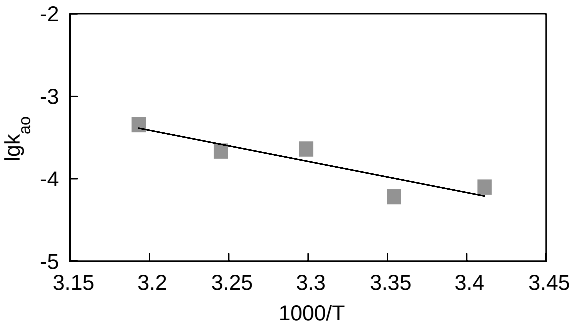

Fig. 2. The effect of the temperature on the extraction rate rpm = 300 r/min, $Q = 2.1\,cm^2$, $V = 92.5\,mL$, $[Yb^{3+}] = 3.23 \times 10^{-3}\,mol/L$, pH = 3.92, [CA-100] = 2.17×10^{-2} mol/L.

323 K. It is found that the extraction rate increases with increasing temperature and the experimental data obey the Arrhenius equation. The apparent activation energy for Yb(III) extraction is calculated to be 72 ± 19 kJ/mol from the slope of $\lg k_{ao}$ vs. $1/T$ shown in Fig. 2. In general [12], if the rate is controlled by a chemical reaction, E_a is more than 40 kJ/mol; if the rate is controlled by a diffusional process, E_a is less than 20 kJ/mol, and the E_a value between 40 and 20 kJ/mol is expected for a mixed controlled regime. The obtained value of E_a suggests a possible chemical reaction controlled regime in the temperature range of 293–323 K.

3.3. *Interfacial reaction*

An important criterion to determine whether the chemical reactions controlling the rate of extraction in a kinetic regime occur in the bulk phase or at the interface is the relationship between the extraction rate and the interfacial area [13]. If the slow chemical reactions occur in the bulk phases, the rate will be independent of interfacial area. If the extraction proceeds by the concurrent reaction of the ligand anion at the interface and in the bulk aqueous phase, the plot of rate vs. area will yield a line having an intercept. If the extraction proceeds solely by interfacial reaction of the ligand anion and the metal ion, there will be a direct proportionality between the rate and the interfacial area and the plot will pass the origin. Fig. 3 shows a linear relationship between the specific areas Q/V (interfacial area/phase volume) and the extraction rate. The plot, within experimental error, passes through the origin. This fact together with the low solubility of CA-100 ($s = 1.30 \times 10^{-4}\,mol/L$) in aqueous phase and strong surface activity of CA-100 at heptane–water interfaces ($\Gamma_m = 9.194 \times 10^{-10}\,mol/cm^2$, $A_i = 0.17\,nm^2$, $C_{min} = 1.96 \times 10^{-4}\,mol/L$) [9] makes the interface the most probable locale for the chemical reactions.

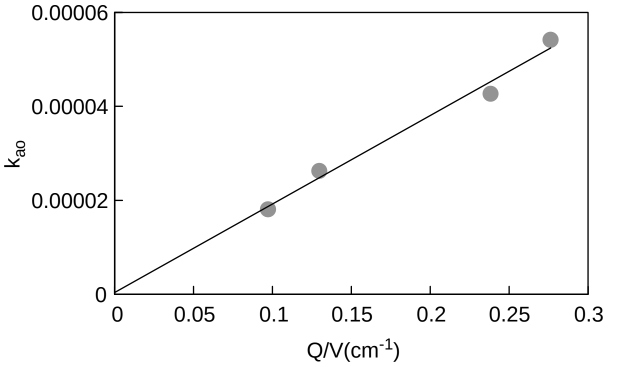

Fig. 3. The effect of the specific area on the extraction rate rpm = 300 r/min, $T = 303 \pm 0.2\,K$, $V = 92.5\,mL$, $[Yb^{3+}] = 3.23 \times 10^{-3}\,mol/L$, pH = 3.92, [CA-100] = 2.17×10^{-2} mol/L.

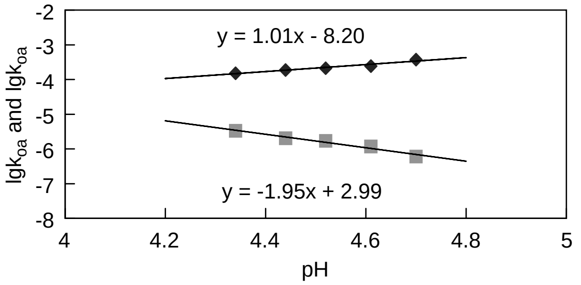

Fig. 4. The effect of pH on the extraction rate rpm = 300 r/min, $T = 303 \pm 0.2\,K$, $V = 92.5\,mL$, $Q = 2.1\,cm^2$, $[Yb^{3+}] = 3.23 \times 10^{-3}\,mol/L$, [CA-100] = 2.17×10^{-2} mol/L.

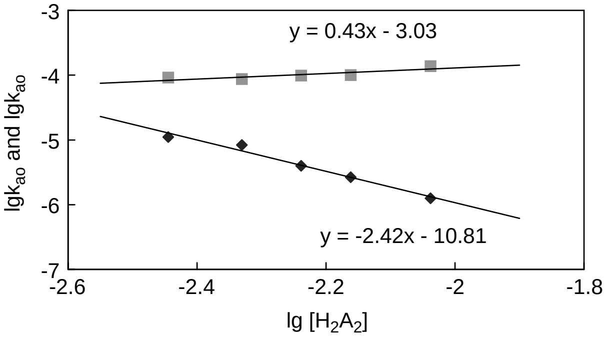

Fig. 5. The effect of the extractant concentration on the extraction rate rpm = 250 r/min, $T = 303 \pm 0.2\,K$, $V = 92.5\,ml$, $Q = 2.1\,cm^2$, $[Yb^{3+}] = 3.23 \times 10^{-3}\,mol/L$, pH = 3.92.

3.4. *Mechanism and kinetic model*

The dependence of extraction rate on the concentration of extractant and hydrogen ion is shown in Figs. 4 and 5, respectively. The relationship between extraction rate and species concentration remains linear with the increase of species concentration. In Fig. 4, the slopes of lg k_{ao} and lg k_{oa} vs. pH at a constant concentration of CA-100 in the organic phase are 1.01 and –1.95, respectively. In Fig. 5 the slopes of lg k_{ao} and lg k_{oa} vs. extractant concentration at a constant concentration of hydrogen ion in the aqueous phase are 0.43 and –2.42, respectively.

According to the above results, the kinetic equation for extraction of Yb(III) with CA-100 can be written as

$$\frac{-\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{Yb}^{3+}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.43}[\mathrm{H}^+]^{-1.01}, \tag{5}$$

$$\frac{\mathrm{d}[\mathrm{Yb(III)}_{(\mathrm{o})}]}{\mathrm{d}t} = k_\mathrm{r}[\mathrm{Yb(III)}_{(\mathrm{o})}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{-2.42}[\mathrm{H}^+]^{1.95}, \tag{6}$$

where H_2A_2 represents the dimer of CA-100; k_f and k_r refer to apparent forward and reverse extraction rate constants, respectively.

The reverse extraction rate and the variation of concentration can be ignored when there is a high concentration of extractant in the organic phase and a low metal concentration in the aqueous phase. Based on Eqs. (2) and (5), one can write the following equation:

$$(Q/V)k_{ao} = k_\mathrm{f} + ([\mathrm{H}^+]^{-1.01}[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.43}). \tag{7}$$

The plot of lg $(Q/V)k_{ao}$ vs. lg $([\mathrm{H}^+]^{-1.01}[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.43})$ gives straight line (Fig. 6) and the apparent forward extraction rate constant, k_f, can be calculated to be $2.10\times10^{-7}\pm0.77\times10^{-7}\,\mathrm{s}^{-1}$ via the intercept.

These results show that the chemical reaction for the extraction of Yb(III) with CA-100 occurs at the liquid–liquid interface. Referring to the interfacial reaction model proposed by Danesi et al. [11] the following reactions will be considered:

$$\mathrm{H}_2A_{2(\mathrm{o})} \overset{K_{e1}}{\rightleftharpoons} 2\mathrm{H}A_{(\mathrm{o})}, \tag{8}$$

$$\mathrm{H}A_{(\mathrm{ad})} \overset{K_{e2}}{\rightleftharpoons} \mathrm{H}^+ + A^-_{(\mathrm{ad})}, \tag{9}$$

$$\mathrm{Yb}^{3+} + A^-_{(\mathrm{ad})} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Yb}A^{2+}_{(\mathrm{ad})} \text{ slow}, \tag{10}$$

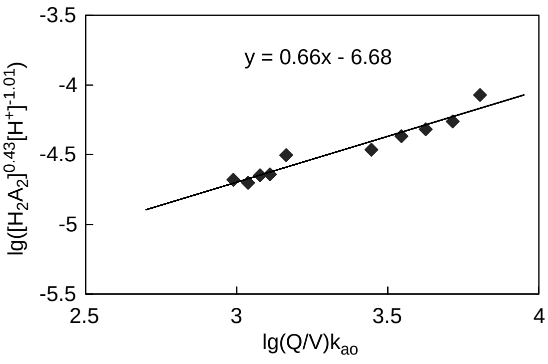

Fig. 6. The plot of lg $(Q/V)k_{ao}$ vs. lg $([\mathrm{H}^+]^{-1.01}[\mathrm{H}_2\mathrm{A}_{2(\mathrm{o})}]^{0.43})$.

$$\mathrm{Yb}A^{2+}_{(\mathrm{ad})} + \mathrm{H}A_{(\mathrm{ad})} \overset{K_{e3}}{\rightleftharpoons} \mathrm{Yb}A^+_{2(\mathrm{ad})} + \mathrm{H}^+, \tag{11}$$

$$\mathrm{Yb}A^+_{2(\mathrm{ad})} + \mathrm{H}A_{(\mathrm{ad})} \overset{K_{e4}}{\rightleftharpoons} \mathrm{Yb}A_{3(\mathrm{ad})} + \mathrm{H}^+, \tag{12}$$

$$\mathrm{Yb}A_{3(\mathrm{ad})} + 3\mathrm{H}A_{(\mathrm{o})} \overset{K_{e5}}{\rightleftharpoons} \mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3(\mathrm{o})}. \tag{13}$$

Considering equilibrium (10) as the rate-controlling step, we have the following equations, where ad and o stand for interface and organic phase; k_1 and k_{-1} are the forward- and the reverse reaction rate constants for step (10), respectively; and $K_{e1}, K_{e2}, K_{e3}, K_{e4}$ and K_{e5} represent the equilibrium constants, respectively.

$$K_{e1} = \frac{[\mathrm{H}A_{(\mathrm{o})}]^2}{[\mathrm{H}_2A_{2(\mathrm{o})}]}, \tag{14}$$

$$K_{e2} = \frac{[\mathrm{H}^+]\,[A^-_{(\mathrm{ad})}]}{[\mathrm{H}A_{(\mathrm{ad})}]}, \tag{15}$$

$$K_{e3} = \frac{[\mathrm{Yb}A^+_{2(\mathrm{ad})}]\,[\mathrm{H}^+]}{[\mathrm{Yb}A^{2+}_{(\mathrm{ad})}]\,[\mathrm{H}A_{(\mathrm{ad})}]}, \tag{16}$$

$$K_{e4} = \frac{[\mathrm{Yb}A_{3(\mathrm{ad})}]\,[\mathrm{H}^+]}{[\mathrm{Yb}A^+_{2(\mathrm{ad})}]\,[\mathrm{H}A_{(\mathrm{ad})}]}, \tag{17}$$

$$K_{e5} = \frac{[\mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3(\mathrm{o})}]}{[\mathrm{Yb}A_{3(\mathrm{ad})}]\,[\mathrm{H}A_{(\mathrm{o})}]^3}. \tag{18}$$

Based on Eqs. (14) and (15), we obtain then for the forward initial rate of extraction:

$$\frac{-\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = k_1[\mathrm{Yb}^{3+}]\,[A^-_{(\mathrm{ad})}], \tag{19}$$

$$\frac{-\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = k_1 a K_{e2} K_{e1}^{0.5}[\mathrm{Yb}^{3+}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.5}[\mathrm{H}^+]^{-1}, \tag{20}$$

where a is adsorption constant of extractant. Based on Eqs. (16)–(18), one can write the following equation:

$$K_{e3}K_{e4}K_{e5} = \frac{[\mathrm{H}^+]^2[\mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3(\mathrm{o})}]}{[\mathrm{Yb}A^{2+}_{(\mathrm{ad})}]\,[\mathrm{H}A_{(\mathrm{o})}]^3[\mathrm{H}A_{(\mathrm{ad})}]^2}. \tag{21}$$

The following reverse initial rate of extraction is then derived:

$$\frac{\mathrm{d}[\mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3(\mathrm{o})}]}{\mathrm{d}t} = k_{-1}[\mathrm{Yb}A^{2+}_{(\mathrm{ad})}], \tag{22}$$

$$\frac{\mathrm{d}[\mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3(\mathrm{o})}]}{\mathrm{d}t} = \frac{a^{-2}k_{-1}}{K_{e1}^{2.5}K_{e3}K_{e4}K_{e5}} \times [\mathrm{H}^+]^2[\mathrm{Yb}A_3\cdot(\mathrm{H}A)_{3_{(\mathrm{o})}}]\,[\mathrm{H}_2A_{2_{(\mathrm{o})}}]^{-2.5}. \tag{23}$$

Eqs. (20) and (23) can be simplified as follows:

$$\frac{-\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{Yb}^{3+}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.5}[\mathrm{H}^+]^{-1}, \tag{24}$$

$$\frac{\mathrm{d}[\mathrm{Yb(III)}_{(\mathrm{o})}]}{\mathrm{d}t} = k_{\mathrm{r}}[(\mathrm{Yb(III)})_{\mathrm{o}}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{-2.5}[\mathrm{H}^+]^2, \qquad (25)$$

where $k_{\mathrm{f}} = k_1 \mathrm{a} K_{\mathrm{e}2} K_{\mathrm{e}1}^{0.5}$, $k_{\mathrm{r}} = a^{-2}k_{-1}/(K_{\mathrm{e}1}^{2.5}K_{\mathrm{e}3}K_{\mathrm{e}4}K_{\mathrm{e}5})$.

The mechanism above is consistent with the rate equations (5) and (6) obtained from experimental results.

4. Conclusion

The extraction of Yb(III) with CA-100 is a complex kinetic process with an interfacial reaction. The extraction is controlled kinetically and the most probable chemical reaction zone is at the liquid–liquid interfacial area. The dependence of extraction rate on species concentration has been studied and the rate equations of Yb(III) extraction with CA-100 in heptane are deduced as follows:

$$\frac{-\mathrm{d}[\mathrm{Yb}^{3+}]}{\mathrm{d}t} = k_{\mathrm{f}}[\mathrm{Yb}^{3+}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{0.43}[\mathrm{H}^+]^{-1.01},$$

$$\frac{\mathrm{d}[\mathrm{Yb(III)}_{(\mathrm{o})}]}{\mathrm{d}t} = k_{\mathrm{r}}[\mathrm{Yb(III)}_{(\mathrm{o})}]\,[\mathrm{H}_2A_{2(\mathrm{o})}]^{-2.42}[\mathrm{H}^+]^{1.95}$$

which are in good agreement with the interfacial extraction reaction models proposed.

Acknowledgments

This project was supported by the National Program entitled "Basic Research of Rare Earths" (G1998061301) and National Natural Science Foundation of China (29771028, 29801004).

References

[1] H. Irabashi, Y. Takazawa, N. Niibe, H. Kawamoto, Anal. Sci. 13 (1997) 921–924.
[2] N.F. Kizim, Russ. Chem. Rev. 61 (1992) 830–850.
[3] A. Geist, P. Plucinski, W. Nitsch, Solvent Extr. Ion Exch. 18 (2000) 493–515.
[4] F. Kneißl, A. Geist, W. Nitsch, Solvent Extr. Ion Exch. 17 (1999) 475–493.
[5] H. Alkiko, M. Jilska, F.G. Perera, W.S. Geoffrey, Solvent Extr. Ion Exch. 16 (1998) 619–636.
[6] Z. Lazarova, Solvent Extr. Ion Exch. 13 (1995) 525–540.
[7] Z. Zheng, J. Lu, D.Q. Li, G.X. Ma, Chem. Eng. Sci. 53 (1998) 2327–2333.
[8] Y.G. Wang, S.T. Yue, D.L. Qian, M.J. Jin, C.Z. Li, Solvent Extr. Ion Exch. 20 (2002) 345–358.
[9] Y.G. Wang, S.T. Yue, D.L. Qian, M.J. Jin, C.Z. Li, Solvent Extr. Ion Exch. 20 (2002) 701–716.
[10] P.R. Danesi, G.F. Vandergrift, J. Phys. Chem. 85 (1981) 3646–3651.
[11] P.R. Danesi, R. Chiarizia, CRC Crit. Rev. Anal. Chem. 10 (1980) 1–126.
[12] J.F. Yu, C. Ji, Chem. J. Chin. Univ. 13 (1992) 224–226.
[13] M.L. Dietz, H. Freiser, Langmuir 7 (1991) 284–288.