

Extraction Kinetics of Rare Earth Elements with *sec*-Octylphenoxy Acetic Acid

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The kinetics of RE (La, Gd, Er, Yb and Y) extraction with *sec*-octylphenoxy acetic acid was investigated using a constant interfacial area cell with laminar flow at 303 K. The natures of the extracted complexes have some effect on the extraction rate which is controlled by the reaction rate of M(III) and extractant molecules at two-phase interface for Er(III), Yb(III) and Y(III), by a mixed chemical reaction-diffusion for Gd(III) and a diffusion for La(III). The extractant molecules tend to adsorb at the interface. So an interfacial extraction reaction model was derived.

Keywords rare earth, extraction kinetics, *sec*-octylphenoxy acetic acid

Introduction

It is well known that yttrium can be used in many fields, such as metallurgy, ceramics, lasers and electronics, especially in fluorescent materials whose need for high purity yttrium oxide is increasing. In China, the resource of yttrium is rich, and the high pure yttrium is being obtained mainly with the process of naphthenic acid extraction¹⁻³ which has some problems. It has drawn more attention to develop a new process for separating high purity yttrium superior to the old one of naphthenic acid extraction.

Ye *et al.* synthesized a new carboxylic acid with very simple composition, *sec*-octylphenoxy acetic acid (HA). In the same extraction conditions, HA is better

than naphthenic acid.⁴ Li *et al.* studied the extraction of rare earth(III) with HA and put forward a HAB two-solvent extraction system with HA and HB (another acidic extractant).^{5,6} However, the kinetics of rare earth extraction with HA was unreported. In the present work, the extraction kinetics of Y(III), La(III), Gd(III), Er(III) and Yb(III) with HA was examined following a thermodynamic study.⁵

Experimental

Apparatus and procedure for kinetics study were described previously.⁷ Volumes of both aqueous and organic phases were $9.25 \times 10^{-5} \text{ m}^3$ and the interfacial area was $2.1 \times 10^{-3} \text{ m}^2$. pH in aqueous phase was adjusted by a NaAc-HAc solution with the total concentration of 0.2 mol/L and determined with a pH meter (Model 720, Orion Co., America).

The purity of HA (supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences) was more than 93%. After being dissolved in heptane, HA was washed in turn by sodium carbonate, hydrochloric acid and distilled water, and then was saponified with ammonia water to 57.3%. The stock solutions of rare earths were prepared by dissolving their oxides (>99.99%) in concentrated hydrochloric acid and by evaporating the excess HCl. The metal concentration in the

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aqueous phases was determined by EDTA titration with a deviation of < 1% which leads a deviation of ~ 7% in the reaction constant. The concentration of metal ions in the organic phase was determined by difference.

Interfacial tension measurements were performed as described in reference 8.

Data treatment

Experimental data were treated following Danesi.⁹ Assuming that the mass transfer process could be formally treated as a pseudo-first-order reversible reaction with respect to the metal cation:



The rate is given by the following equation:

$$-d[M]_{(o)}/dt = (Q/V)(k_{oa}[M]_{(o)} - k_{ao}[M]_{(a)}) \quad (2)$$

where a and o stand for the aqueous and organic phase, respectively, Q is the area of the interface in cm^2 , V the volume of the organic or aqueous phase, k_{ao} and k_{oa} are forward and backward pseudo-first-order rate constants respectively.

Integrating gives:

$$\ln(1 - [M]_{(o)}/[M]_{(o)}^e) = -(Q/V)(k_{oa} + k_{ao})t \quad (3)$$

where e refers to equilibrium.

At constant stirring speed, the pseudo-first-order rate constants, k_{ao} and k_{oa} , are functions of the concentration of HA in the organic phase and the concentration of the hydrogen ion in the aqueous phase (where f_1 and f_2 refer to the functions):

$$k_{ao} = f_1([HA]_{(o)}, [H^+]_{(a)}) \quad (4)$$

$$k_{oa} = f_2([HA]_{(o)}, [H^+]_{(a)}) \quad (5)$$

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

$$K_d = [M]_{(o)}^e/[M]_{(a)}^e = k_{ao}/k_{oa} \quad (6)$$

where K_d is the distribution ratio of metal cation.

Eq. (6) is substituted into Eq. (3), *i. e.*

$$\ln(1 - [M]_{(o)}/[M]_{(o)}^e) = -(Q/V)(1 + K_d)k_{oa}t \quad (7)$$

The function $\ln(1 - [M]_{(o)}/[M]_{(o)}^e)$ vs. time was plotted for each experiment. The slopes of the plots were used to evaluate k_{oa} and k_{ao} . All plots were straight lines, indicating that the mass transfer process could be treated as a pseudo-first-order reversible reaction with respect to the metal cation.

Results and discussion

Effect of stirring speed on k_{ao}

The apparatus used for the kinetic experiments is a constant interfacial area cell with laminar flow⁷ where the thickness of the stationary interfacial film is thicker at a lower stirring speed and the diffusion limits the rate. With increase of the stirring speed, the stationary diffusion film becomes thinner and the diffusion resistance smaller. At some stirring speed, the extraction rate may be limited by the chemical reaction only, or the extraction rate is independent of the stirring rate, *i. e.* "kinetics plateau". So this instrument leads to an easy discrimination of diffusion control or chemical reaction limitation.¹⁰ Fig. 1 shows the effect of the stirring speed on the extraction rate of yttrium(III) with *sec*-octylphenoxy acetic acid dissolved in heptane. When the stirring speed reached 200 r/min, it no longer influenced the extraction rate. The other kinetic experiments were processed at 250 r/min in order to maintain the same hydrodynamic conditions.

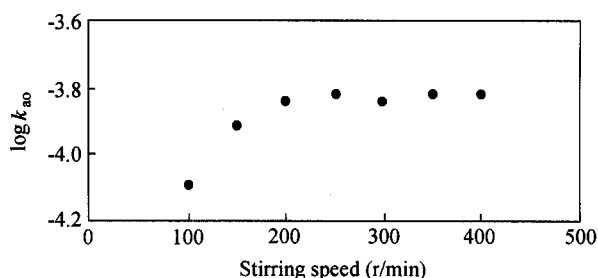


Fig. 1 Dependence of $\log k_{ao}$ vs. stirring speed, $[H_2A_2]_{(o)} = 1.0 \times 10^{-2} \text{ kmol/m}^3$, $\text{pH} = 4.05$, $[Y^{3+}] = 3.0 \times 10^{-3} \text{ kmol/m}^3$.

Dependence of $\log k_{ao}$ on pH

In pH values of ranging from 3.5 to 4.5, the effect of pH on the extraction rate was studied (Fig. 2). The orders of $[H^+]$ for La(III), Gd(III), Er(III), Yb(III)

and Y(III) are -0.32 , -0.46 , -1.1 , -0.73 and -0.79 , respectively. The thermodynamic study indicated that the extraction rates of La and Gd are higher than those of Er, Yb and Y, and their $\text{pH}_{1/2}$ values are lower than those of Er, Yb and Y. So the kinetic order of H^+ for the extraction of La or Gd is lower.

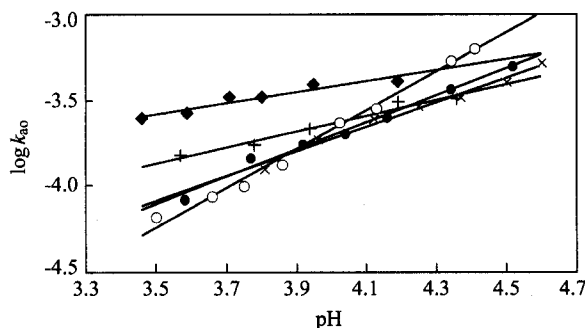


Fig. 2 Dependence of $\log k_{\text{ao}}$ vs. pH , $[\text{H}_2\text{A}_2]_{(\text{o})} = 1.0 \times 10^{-2} \text{ kmol/m}^3$, $[\text{RE}^{3+}] = 2.7 \times 10^{-3} \text{ kmol/m}^3$, \blacklozenge La, $+$ Gd, \circ Er, \times Yb, \bullet Y.

Dependence of $\log k_{\text{ao}}$ on the concentration of extractant

The effect of extractant concentration on the extraction rate is shown in Fig. 3. The results show that with increase of atomic number from La to Yb the extraction rate decreases. The orders of extractant for La(III), Gd(III), Er(III), Yb(III) and Y(III) extraction are 1.2, 1.0, 1.2, 1.2 and 1.2, respectively.

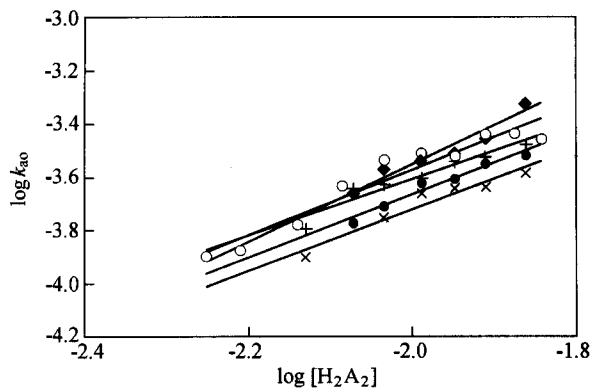


Fig. 3 Dependence of $\log k_{\text{ao}}$ vs. $\log [\text{H}_2\text{A}_2]$, $[\text{RE}^{3+}] = 3.0 \times 10^{-3} \text{ kmol/m}^3$, \blacklozenge La, $+$ Gd, \circ Er, \times Yb, \bullet Y.

Dependence of $\log k_{\text{ao}}$ on temperatures

It was found that the extraction rate increased with

temperature and the experimental data obeyed Arrhenius equation. The apparent activation energies for La(III), Gd(III), Er(III), Yb(III) and Y(III) extraction were calculated with the slope of $\log k_{\text{ao}}$ versus $1/T$ shown in Fig. 4 to be 18.4, 30.0, 46.2, 55.2 and 49.9 kJ/mol, respectively. Generally,¹² when an extraction activation energy (E_a) is more than 42 kJ/mol, the extraction process is controlled by chemical reaction. When E_a is lower than 20 kJ/mol, species diffusion is rate-determining step. When E_a is in ranging from 20 kJ/mol to 42 kJ/mol, the extraction rate is controlled by a mixed chemical reaction-diffusion. Thus, the extraction rate is controlled by chemical reaction for Er(III), Yb(III) and Y(III), by a mixed chemical reaction-diffusion for Gd(III), and by a diffusion for La(III).

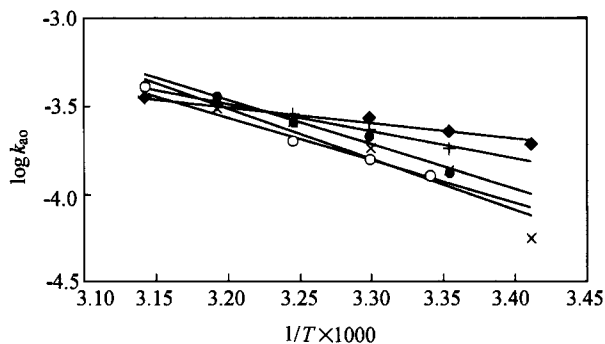


Fig. 4 Dependence of $\log k_{\text{ao}}$ vs. $1/T$. $[\text{H}_2\text{A}_2]_{(\text{o})} = 1.0 \times 10^{-2} \text{ kmol/m}^3$, $[\text{RE}^{3+}] = 3.0 \times 10^{-3} \text{ kmol/m}^3$, \blacklozenge La, $+$ Gd, \circ Er, \times Yb, \bullet Y.

According to the experimental results, the following rate equations were obtained:

$$-\frac{d[\text{La}^{3+}]_{(\text{a})}}{dt} = k[\text{La}^{3+}]_{(\text{a})}[\text{H}_2\text{A}_2]_{(\text{o})}^{1.2}[\text{H}^+]_{(\text{a})}^{-0.32} \quad (8)$$

$$-\frac{d[\text{Gd}^{3+}]_{(\text{a})}}{dt} = k[\text{Gd}^{3+}]_{(\text{a})}[\text{H}_2\text{A}_2]_{(\text{o})}^0[\text{H}^+]_{(\text{a})}^{-0.45} \quad (9)$$

$$-\frac{d[\text{Er}^{3+}]_{(\text{a})}}{dt} = k[\text{Er}^{3+}]_{(\text{a})}[\text{H}_2\text{A}_2]_{(\text{o})}^2[\text{H}^+]_{(\text{a})}^{-1.1} \quad (10)$$

$$-\frac{d[\text{Yb}^{3+}]_{(\text{a})}}{dt} = k[\text{Yb}^{3+}]_{(\text{a})}[\text{H}_2\text{A}_2]_{(\text{o})}^2[\text{H}^+]_{(\text{a})}^{-0.73} \quad (11)$$

$$-d[Y^{3+}]_{(a)}/dt = k[Y^{3+}]_{(a)}[H_2A_2]_{(o)}^{\frac{1}{2}}[H^+]_{(a)}^{0.79} \quad (12)$$

Interfacial tension measurements of HA

In order to estimate the extraction mechanism of RE, the interfacial property of the extractant HA was studied. The interfacial excess of HA at the *n*-heptane-water interface was determined from the plot of the interfacial tension (γ , mN/m) vs. $\log c$, c being the concentration of HA. The plot is shown in Fig. 5.

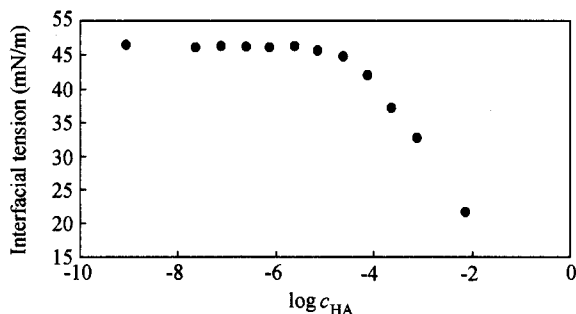


Fig. 5 Interfacial tension of HA vs. $\log c$.

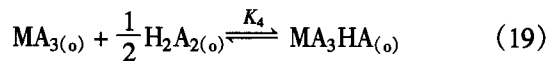
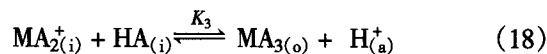
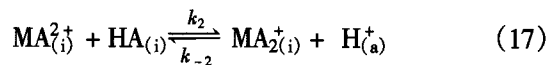
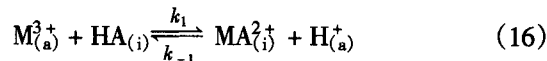
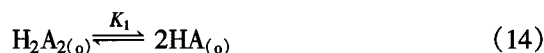
According to the Gibbs equation

$$\Gamma = -\frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log c} \right)_T \quad (13)$$

the interfacial excess Γ derived from the linear part of the plot is 3.54×10^{-6} mol/L². Here, γ is the interfacial tension (in mN/m), c the bulk concentration (in mol/L), T the absolute temperature and $R = 8.314$ J·K⁻¹·mol⁻¹. It is evident that HA has high interfacial activity and tends to adsorb at the interface.

Because rare earth ions in aqueous solution can not easily enter the organic phase directly, it is more likely that the extraction reaction occurs at the two-phase interface. The previous thermodynamic study showed that the complexes extracted into the organic phase were MA₃·HA for La(III), Gd(III), Er(III) and Yb(III), and YA₃ for Y.³

Based on the results of kinetics and thermodynamics, the following extraction reaction mechanism for Er(III), Yb(III) and Y is given [Eq. (19) is invalid to the extraction of Y(III)]:



where *i* refers for interface, K_1 , K_2 , K_3 and K_4 stand for equilibrium constants, k_1 and k_2 are the forward reaction rate constants while k_{-1} and k_{-2} are the backward ones.

From Eqs. (14) and (15), Eq. (20) can be obtained:

$$[HA]_{(i)} = K_1^{1/2} K_2 [H_2A_2]_{(o)}^{1/2} \quad (20)$$

Assuming an instantaneous state and ignoring the k_{-2} rate constant, the concentration of $[MA^{2+}]_{(i)}$ can be easily calculated.

$$[MA^{2+}]_{(i)} = k_1 [M^{3+}]_{(a)} [HA]_{(i)} / (k_{-1} [H^+]_{(a)} + k_2 [HA]_{(i)}) \quad (21)$$

Assuming that Eq. (17) is the controlling-rate-step, the following rate law can be written:

$$R_f = k_2 [MA^{2+}]_{(i)} [HA]_{(i)} \quad (22)$$

Both Eqs. (20) and (21) are substituted into Eq. (22), then:

$$R_f = k_1 k_2 K_1 K_2^2 [M^{3+}]_{(a)} [H_2A_2]_{(o)} / (k_{-1} [H^+]_{(a)} + k_2 K_2 K_1^{1/2} [H_2A_2]_{(o)}^{1/2}) \quad (23)$$

When $k_{-1} [H^+]_{(a)} \gg k_2 K_2 K_1^{1/2} [H_2A_2]_{(o)}^{1/2}$, Eq. (23) can be simplified as:

$$R_f = k [M^{3+}]_{(a)} [H_2A_2]_{(o)} [H^+]_{(a)}^{-1} \quad (24)$$

where $k = k_1 k_2 k_{-1}^{-1} K_1 K_2^2$.

This mechanism is consistent with the experimental

results.

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