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Kinetics and Mechanism of Yb(III) Extraction and Separation from Y(III) with Mixtures of bis(2,4,4-trimethylpentyl)phosphinic acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester

Ying Xiong^a; Wei Li^a; Dongbei Wu^a; Deqian Li^a; Shulan Meng^a

^a Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of Chinese Academy of Sciences, Changchun, P.R. China

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**Kinetics and Mechanism of Yb(III)
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Ying Xiong, Wei Li, Dongbei Wu, Deqian Li, and Shulan Meng

Key Laboratory of Rare Earth Chemistry and Physics,
Changchun Institute of Applied Chemistry, Chinese Academy of
Sciences, Graduate School of Chinese Academy of Sciences, Changchun,
P.R. China

Abstract: The ytterbium(III) extraction kinetics and mechanism with mixtures of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) dissolved in heptane have been investigated by constant interfacial cell with laminar flow. The effects of the stirring rate, temperature, extractant concentration, and pH on the extraction with mixtures of Cyanex272 and P507 have been studied. The results are compared with those of the system with Cyanex272 or P507 alone. It is concluded that the Yb(III) extraction rate is enhanced with mixtures extractant of Cyanex272 and P507 according to their values of the extraction rate constant, which is due to decreasing the activation energy of the mixtures. At the same time, the mixtures exhibits no synergistic effects for Y(III), which provides better possibilities for Yb(III) and Y(III) separations at a proper conditions than anyone alone. Moreover, thermodynamic extraction separation Yb(III) and Y(III) by the mixtures has been discussed, which agrees with kinetics results. Extraction rate equations have also been obtained, and through the approximate

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Address correspondence to Deqian Li, Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of Chinese Academy of Sciences, Changchun 130022, P.R. China. Tel.: +86-431-5262036; Fax: +86-431-5698041; E-mail: ldq@ciac.jl.cn

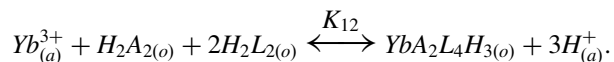
solutions of the flux equation, diffusion parameters and thickness of the diffusion film have been calculated.

Keywords: Extraction kinetics, ytterbium(III), Cyanex272, P507, separation

INTRODUCTION

Organophosphorus extractants have been widely studied in the past decades(1–5). At present the rare earth (RE) separation process using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) has been applied widely in China. This process provides industrial production of all the individual RE (except Pm) up to 4 N (N:9) or even more purity. However, the industrial practice indicates that there are some problems in P507 extraction process, (6) including higher aqueous acidity in extraction and stripping of heavy rare earth ions (especially for Tm, Yb, Lu), and lower separation factors of heavy rare earth ions. Thus, to explore some new extractants or extraction system superior to P507 has been interesting subject for many researchers.

Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex272) is a kind of organophosphorus extractants developed by Cytec Canada Inc. It is well-known that the pKa value (6.4) of Cyanex272 is bigger than that (4.5) of P507, and especially, steric hindrance effects of the former are superior to the latter.(7, 8) Thus, the average separation coefficients (β_z^{z+1}) of rare earth ions and selectivity using Cyanex272 as an extractant are higher and superior than those obtained using P507 under the same conditions, respectively. Furthermore, acidities of extraction of rare earth ions and other higher valence metal ions with Cyanex272 are lower, and stripping is easier than those with P507. However, due to the higher $\text{pH}_{1/2}$ value of Cyanex272 than P507, the extraction ability of rare earth ions with Cyanex272 is lower than that of latter. In our earlier work, (9) the extraction mixed solution of heavy Ln(III) with mixtures of P507 and Cyanex272 has been investigated, which indicates that the mixtures have better separation abilities for heavy lanthanide, and the synergistic equilibrium extraction reaction can be written as:



But to date, little research has been reported on the extraction kinetics of rare earth metals with the mixtures of Cyanex272 and P507 by constant interfacial cell with laminar flow (10–12). In the present work, the research of the kinetics of ytterbium(III) extraction with the mixtures of Cyanex272 and P507 (abbreviation as HDP) in heptane was reported. The effect of stirring speed, temperature, and species concentration on the extraction rate with Cyanex272, P507 and HDP were discussed.

EXPERIMENTAL

Reagents and Analysis

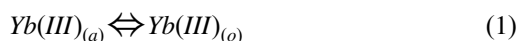
P507 and Cyanex272 were kindly supplied by Shanghai Organic Chemistry Institute and CYTEC Canada Inc., respectively, and they were used without purification. Ytterbium and yttrium stock solutions were prepared by dissolving their oxide with a purity >99.9% in hydrochloric acid. All other reagents were of analytical grade. The concentrations of Yb(III) and Y(III) in the aqueous phase were determined by EDTA titration using xylenol orange as an indicator. The concentration of metal ions in the organic phase was determined by difference.

Experimental Procedures and Apparatus

The extraction kinetics was investigated by using a constant interfacial area cell with laminar described previously (11). In the kinetics experiments, the concentrations of Cyanex272, P507 and mixtures of Cyanex272 and P507 (at a ratio of 1 to 1, which agrees with the thermodynamic result in this paper) were all $3.0 \times 10^{-2} \text{ mol l}^{-1}$, and varied when studying the effect of their concentration. The pH value of aqueous phase was kept at 2.08 (ionic strength 1.0 mol l^{-1}), and varied when the effect of pH was studied. The aqueous phases contained $3.1 \times 10^{-3} \text{ mol l}^{-1}$ ytterbium or yttrium ion. Kinetics experiments in a constant interfacial area cell with laminar flow were carried out at 250 rpm and 303 K, respectively. Both aqueous and organic phase volumes were $9.5 \times 10^{-5} \text{ m}^3$ (95 ml). The interfacial area was $1.94 \times 10^{-3} \text{ m}^2$ (19.4 cm^2).

Data Treatment

Assuming that the mass-transfer process could be formally treated as a pseudo-order reversible reaction with respect to the metal cation, one can write the following equation: (13)



The following equation of extraction can be obtained as described in Eq. 13:

$$R_F = -\frac{d[\text{Yb(III)}]_{(o)}}{dt} = k_F[\text{Yb(III)}]^b[\text{H}^+]^c[\text{H}_2\text{A}_2]^d \quad (2)$$

$$-\frac{d[\text{Yb(III)}]_{(o)}}{dt} = -\frac{Q}{V}(k_{oa}[\text{Yb(III)}]_{(o)} - k_{ao}[\text{Yb(III)}]_{(a)}) \quad (3)$$

$$\ln\left(1 - \frac{[Yb(III)]_{(o)}}{[Yb(III)]_{(o)}^e}\right) = -\frac{Q}{V}(1 + K_d)k_{oa}t \quad (4)$$

$$K_d = \frac{[Yb(III)]_{(o)}^e}{[Yb(III)]_{(a)}^e} = \frac{k_{ao}}{k_{oa}} \quad (5)$$

where “a” refers to the aqueous phase, “o” is the organic phase, “e” indicates the equilibrium of extraction, “ k_F ” represents the extraction rate constant; “ k_{ao} ” and “ k_{oa} ” are respectively the forward as well as backward pseudo-first-order rate constants of extraction or the interfacial mass-transfer coefficients, “ K_d ” represents the distribution extraction constants of ytterbium, “ Q ” stands for the interfacial area and “ V ” is the volume of the aqueous phase or the organic phase.

The slopes of the plots $\ln(1 - [Yb(III)]_{(o)}/[Yb(III)]_{(o)}^e)$ vs. t have been used to evaluate k_{ao} and k_{oa} . All plots are straight lines in the work, indicating that the mass transfer process could be treated as a pseudo-first-order reversible reaction is reasonable.

RESULTS AND DISCUSSION

Dependence of $\log k_{ao}$ on 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 in constant interfacial area cell. This theory has been reported in earlier work (14). The influence of the stirring rate on the extraction rate has been studied for Yb(III) with Cyanex272, P507 and HDP dissolved in heptane, respectively, and the results are shown in Fig. 1. When the stirring speed is greater than 250 rpm, a plateau region is reached, which indicates that the extraction rate with HDP may be chemically controlled in that zone, whereas the extraction rate with Cyanex272 and P507 is dependent of the stirring rate indicates that it is diffusion controlled in the range from 150 to 350 rpm. Nevertheless, a “plateau region” can also be generated by other phenomena, and it is still possible that in spite of the experimentally determined independence of extraction rate on the stirring speed, the rate of extraction is still diffusion controlled or, at least not fully kinetics controlled. Therefore, it is necessary with the help of other approach to identify the extraction regime. In addition, the data shown in Fig. 1 elucidate that the extraction rate is enhanced with HDP, a fact that has also been observed in the following experiments.

Effect of Temperature on the Extraction Rate

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

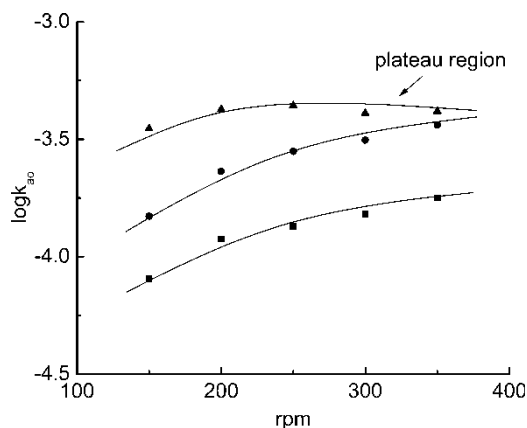


Figure 1. The effect of the stirring speed on the extraction rate. $[Yb(III)] = 3.1 \times 10^{-3} \text{ mol l}^{-1}$, $pH = 2.08$, $T = 303 \text{ K}$. (a) (■)— $[Cyanex272] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (b) (●)— $[P507] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (c) (▲)— $[HDP] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$.

energy of the extraction process. The effect of temperature on the extraction rate has been studied in the temperature range from 293 to 313 K and the results are given in Fig. 2 and Table 1. It is found that the rates increase sharply with temperature lower than 303 K and increase slightly at temperature higher than 303 K, which obeys Arrhenius equation. The apparent activation energy for Yb(III) with Cyanex272, P507 and HDP are 35.58, 35.56 and 19.90 kJ mol^{-1} from 293 to 303 K, and 8.76, 8.50, 7.12 kJ mol^{-1} from 303 to 313 K. That is, the admixture of Cyanex272 and P507

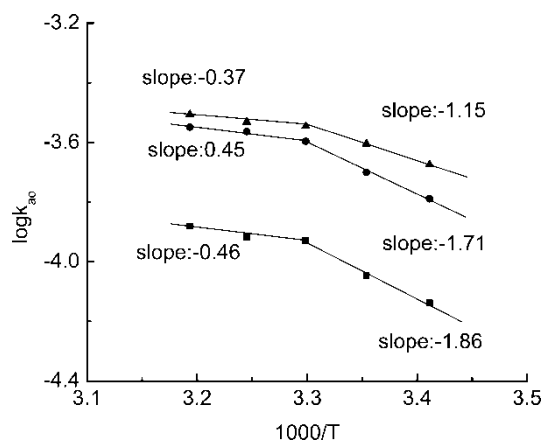


Figure 2. The effect of the temperature on the extraction rate. $[Yb(III)] = 3.1 \times 10^{-3} \text{ mol l}^{-1}$, $pH = 2.08$, $rpm = 250 \text{ rpm}$. (a) (■)— $[Cyanex272] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (b) (●)— $[P507] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (c) (▲)— $[HDP] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$.

Table 1. Thermodynamic parameters for the extraction of Yb(III)

Extractant	T	ΔEa	ΔH	ΔS	ΔG	Controlled
	K	kJ mol ^{−1}	kJ mol ^{−1}	J K ^{−1} mol ^{−1}	KJ mol ^{−1}	Regime
Cyanex272	293–303	35.58	29.65	−223.52	97.41	Mixed
	303–313	8.76	3.34	−310.35	97.42	Diffusion
P507	293–303	32.57	27.72	−201.11	88.68	Mixed
	303–313	8.50	4.20	−278.62	88.66	Diffusion
HDP	293–303	19.87	13.67	−233.33	84.40	Diffusion
	303–313	7.12	3.51	−266.90	84.42	

decreases the activation energy, which is the reason why it can accelerate the extraction rate of Yb(III) with HDP.

Again, from the specific reaction rate theory (15), one gets:

$$\log \frac{R_F h}{kT} = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} + \log f(R)$$

(6)

where “k” represents the Boltzman. “h” represents Planck’s constant. f(R) is the function of reactant and is equal to [Yb(III)]^b[H⁺]^c[H₂A₂]^d.

From Eq. 6, the values of ΔS and ΔH can be easily calculated, shown in Table 1 and Fig. 3. The negative value of ΔS in 293 to 303 K indicates that more order than that of Cyanex272 or P507 is introduced in HDP system upon metal extraction, that is, the disorder caused by metal ion dissociation

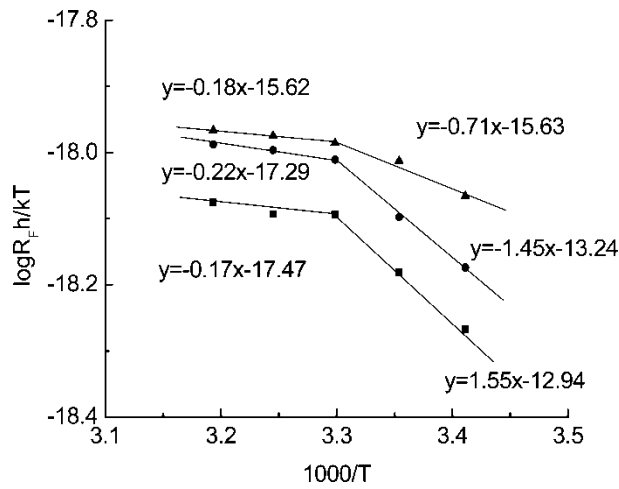


Figure 3. Plot of logR_{F(B)}h/kt vs (1/T) × 10³: [Yb(III)] = 3.1 × 10^{−3} mol l^{−1}, pH = 2.08, rpm = 250 rpm. (a) (■)—[Cyanex272] = 3.0 × 10^{−2} mol l^{−1}, (b) (●)—[P507] = 3.0 × 10^{−2} mol l^{−1}, (c) (▲)—[HDP] = 3.0 × 10^{−2} mol l^{−1}.

is more than compensated for by the reduction of the number of particles brought about by the formation of the synergistic complex, which is quite the reverse with ΔS of in 303 to 313 K. The larger values of ΔH extracting by Cyanex272 or P507 in the 293 to 303 K suggests that the heat effects involved in the dissociation of the metal cation from its complex are the more predominant enthalpy factor. The small values of ΔH in the temperature range of 303 to 313 K in all these systems indicate that the dissociation of the metal ion and the formation of the complex are almost equal.

In general (16), if the rate is controlled by a chemical reaction, E_a is more than 40 kJ mol^{-1} ; if the rate is controlled by a diffusion process, E_a is less than 20 kJ mol^{-1} ; and the E_a value between 40 kJ mol^{-1} and 20 kJ mol^{-1} is expected for a mixed controlled regime. Thus, whether there is P507 as an extractant or Cyanex272, the obtained value of E_a of extraction suggests a possible mixed controlled regime in the temperature range of 293 to 303 K and a diffusion controlled regime in the temperature range of 303 to 313 K, while for HDP, diffusion controlled regime from 293 to 313 K (given in Table 1). All other kinetics experiments are measured at 250 rpm and 303 K in order to maintain the same hydrodynamic conditions.

Extraction Rate Equation

Figure 4 presents the rate constant k_{ao} as a function of the concentration of Cyanex272, P507 and HDP in the organic phase. The slopes of the plots for Cyanex272 and P507 are 0.46 and 1.04, respectively. However, in the HDP system, the slopes are 0.20 for Cyanex272 and 0.58 for P507.

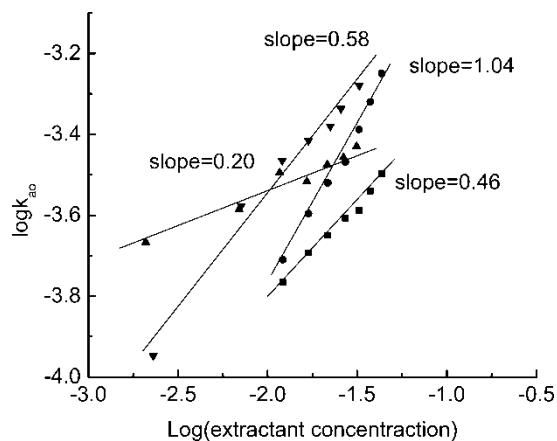


Figure 4. The effect of the extractant concentration on the extraction rate. $[\text{Yb(III)}] = 3.1 \times 10^{-3} \text{ mol l}^{-1}$, $\text{pH} = 2.08$, $T = 303 \text{ K}$, $\text{rpm} = 250 \text{ rpm}$. (a) (■)—Cyanex272, (b) (●)—P507 (c) (▲)—HDP, $[\text{P507}]$ constant, (d) (▼)—HDP, $[\text{Cyanex272}]$ constant.

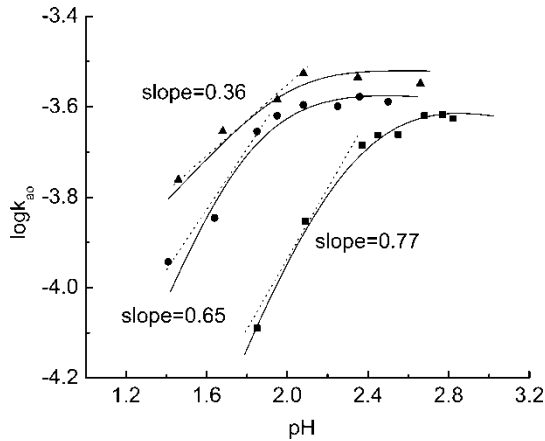


Figure 5. The effect of pH on the extraction rate. $[Yb(III)] = 3.1 \times 10^{-3} \text{ mol l}^{-1}$, $T = 303 \text{ K}$, $\text{rpm} = 250 \text{ rpm}$. (a) (■)— $[Cyanex272] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (b) (•)— $[P507] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$, (c) (▲)— $[HDP] = 3.0 \times 10^{-2} \text{ mol l}^{-1}$.

The influence of pH on the extraction rate has been measured and the results are shown in Fig. 5. It is interesting to find that the relationship between extraction rate and pH does not remain linear when the interfacial pH is changed almost instantly whatever the bulk aqueous pH is. The reason is that the rate is proportional to the hydrogen ion concentration at the interface rather than its bulk concentration (10). Thus, the result given at higher pH is invalid and the plot of $\log k_{ao}$ vs. pH gives a straight line at lower pH. From the slopes of the plots one can calculate that the orders of hydrogen ion concentration for Cyanex272, P507 and HDP are -0.77 , -0.65 , and -0.36 , respectively.

Using the data in Figs. 4–5, the extraction rate constants (k_F) are evaluated. It is represented in Table 2. The estimated $\log k_F$ for Yb(III) with Cyanex272 and P507 are 4.00, 3.20 and 1.78, respectively. The k_F value of HDP is much larger than these of Cyanex272 and P507, which shows that the admixtures of Cyanex272 and P507 accelerates the extraction rate of Yb(III).

Table 2. The values of extraction rate constant (k_F) and separation factor (β) for the extraction of Yb(III) and Y(III)

Extractant	Cyanex272	P507	HDP
$k_{F(Yb)}$	$10^{-4.00} \pm 0.04$	$10^{-3.20} \pm 0.06$	$10^{-1.78} \pm 0.03$
$k_{F(Y)}$	$10^{-4.41} \pm 0.03$	$10^{-3.60} \pm 0.02$	$10^{-3.72} \pm 0.03$
$\Delta k_F = k_{F(Yb)}/k_{F(Y)}$	2.57	2.51	87.1
$\beta(D_{Yb}/D_Y)$	7.66	2.24	11.19

According to the experimental results, the following rate equations extracting Yb(III) by Cyanex272 (HA), P507 (HB) and HDP in heptane are obtained.

$$R_F = 10^{-4.00} [Yb(III)]_{(a)} [H_2A_2]_{(o)}^{0.46} [H^+]_{(a)}^{-0.77} \text{ kmol} \cdot \text{m}^{-2} \text{s}^{-1} \quad (7)$$

$$R_F = 10^{-3.20} [Yb(III)]_{(a)} [H_2B_2]_{(o)}^{1.04} [H^+]_{(a)}^{-0.65} \text{ kmol} \cdot \text{m}^{-2} \text{s}^{-1} \quad (8)$$

$$R_F = 10^{-1.78} [Yb(III)]_{(a)} [H_2A_2]_{(o)}^{0.20} [H_2B_2]_{(o)}^{0.58} [H^+]_{(a)}^{-0.36} \text{ kmol} \cdot \text{m}^{-2} \text{s}^{-1} \quad (9)$$

Comparing Eq. 9 with Eqs. 7 and 8, we can conclude that admixtures of Cyanex272 and P507 not only accelerates Yb(III) extraction but also modifies the rate equation.

Mass-transfer Rate Controlled by Interfacial Film Diffusion

The strong surface activity of HDP at heptane-water interfaces ($\Gamma_m = 1.72 \times 10^{-10} \text{ mol/cm}^2$, $A_i = 96.5 \text{ \AA}^2$, $C_{\min} = 3.65 \times 10^{-5} \text{ mol/L}$) makes the interface the most probable locale for the chemical reactions or species diffusion. This fact together with temperature criterion mentioned above, the mass-transfer rate of Yb(III) extraction with HDP is controlled by interfacial film diffusion. The rate-determining processes would be diffusion of each species to and from the interface through stagnant organic and aqueous diffusion zones of thickness δ_o and δ_w , (17), then:

$$J = k_f([Yb(III)]_{(a)} - J\Delta)([H_2A_2]_{(o)} - J\Delta)([H_2B_2]_{(o)}^2 - \frac{1}{2}J\Delta) - k_r([Yb(III)]_{(o)} + J\Delta)([H^+]_{(a)}^3 + \frac{1}{3}J\Delta) \quad (10)$$

where $\Delta_o = \Delta_w = \delta_o/D_o = \delta_w/D_w$ are the diffusional parameter, that is the ratios between the thickness of the diffusion films and the diffusion coefficients D , assumed to depend only on the nature of the liquid phase. In this case the rate-determining step in the extraction is considered to be diffusional instead of chemical, and local chemical equilibrium at the interface is assumed, i.e.

$$K_e = \frac{[Yb(III)]_{(o,i)} [H^+]_{(a,i)}^3}{[Yb(III)]_{(a,i)} [H_2A_2]_{(o,i)} [H_2B_2]_{(o,i)}^2} \quad (11)$$

$$K_e = \frac{([Yb(III)]_o + J\Delta)([H^+]_a + \frac{1}{3}J\Delta)^3}{([Yb(III)]_a - J\Delta)([H_2A_2]_o - J\Delta)([H_2B_2]_o^2 - \frac{1}{2}J\Delta)^2} \quad (12)$$

An approximate and explicit form of J can be easily obtained from Eq (11), and Eq (12), by neglecting the terms containing J^2 , $J[Yb(III)]_{(a)}$, $J[Yb(III)]_{(o)}$ because of the low fluxes ($10^{-6} \text{ kmol m}^{-2} \text{s}^{-1}$) and the metal

concentrations ($10^{-3} \text{ mol l}^{-1}$) used in our experiments.

$$\Delta = \frac{1}{k_F} \cdot \frac{[H_2A_2]_{(o)}[H_2B_2]_{(o)}^2}{[H_2A_2]_{(o)}[H_2B_2]_{(o)}^2 + Ke^{-1}[H^+]_{(a)}^3} \tag{13}$$

Using Equation (13), we can obtain the following values for the diffusional parameter $\Delta = 0.94 \text{ cm s}^{-1}$. If one assumes a diffusion coefficient $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (10), the thickness of the diffusion film δ is calculated to be $4.73 \times 10^{-6} \text{ cm}$ at 250 rpm.

Separation of Y(III) and Yb(III) with HDP

The extraction kinetics of yttrium(III) with Cyanex272, P507 and HDP has been studied under the same experimental conditions of ytterbium(III) extraction. The values of extraction rate constant for the extraction of Yb(III) or Y(III) are summarized in Table 2. The data indicate that the combining Cyanex272 with P507 accelerates the extraction rate of ytterbium. Contrary to the case of ytterbium, it neutralizes the effect of Cyanex272 with P507 when using extracting Y(III). Thus, we can assume that the separation of Yb(III) from Y(III) at a proper extraction time, pH and concentration of extractant could be easier with mixtures of Cyanex272 and P507 than anyone alone. It is confirmed by analyzing the value of Δk_F (defined as $\Delta k_F = k_{F(Yb)}/k_{F(Y)}$), which increases from about 2.5 to 87.1.

In thermodynamic extraction experiment, we have obtained the similar result from the values of separation and factor (β) and synergistic enhancement factor (R) (18) shown in Table 2 and Fig. 6. It is the synergistic effect

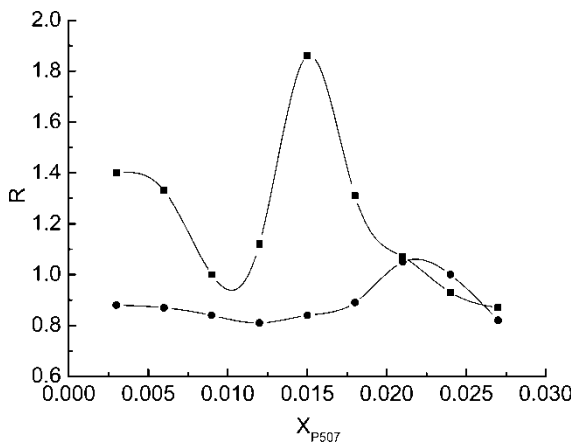


Figure 6. Synergistic enhancement factors of Yb(III) and Y(III) with mixtures of Cyanex272 and P507. $[Yb(III)] = [Y(III)] = 3 \times 10^{-3} \text{ mol l}^{-1}$, $[HDP] = 0.030 \text{ mol l}^{-1}$, $\text{pH} = 2.06$, $T = 298 \text{ K}$. (a) (■)—Yb, (b) (●)—Y.

($R > 1$) observed for the extraction of Yb(III) while no synergistic effect ($R < 1$) for Y(III), and the maximal synergistic enhancement could be obtained at a ratio of Cyanex272 to P507 of 1 to 1. That is, thermodynamic extraction and kinetics results agree with each other in HDP system.

CONCLUSIONS

The extraction of Yb(III) with HDP in heptane using a constant interfacial area cell with laminar flow is a diffusion controlled kinetics process with an interfacial reaction. The data have been analyzed in terms of pseudo-first order constant. It is concluded that the Yb(III) extraction rate is enhanced with mixtures extractant of Cyanex272 and P507 according to their values of the extraction rate constant. The reason is that the admixture of Cyanex272 and P507 decreases the activation energy from 35.58, 32.57 to 19.87 kJ mol⁻¹. The dependence of extraction rate on species concentration has been studied and the rate equations of ytterbium extraction by HDP in heptane are deduced as follows:

$$R_F = 10^{-1.78} [Yb(III)]_{(a)} [H_2A_2]_{(o)}^{0.20} [H_2B_2]_{(o)}^{0.58} [H^+]_{(a)}^{-0.36} \text{ kmol} \cdot \text{m}^{-2} \text{s}^{-1}$$

Through the approximate solutions of the flux equation, diffusion parameters and thickness of the diffusion film is calculated to be 0.94 cm s⁻¹ and 4.73 × 10⁻⁶ cm, respectively.

Contrary to the case of ytterbium, the mixtures of Cyanex272 and P507 exhibits no synergistic effects for Y(III), which provide better possibilities for Yb(III) and Y(III) separations at a proper conditions than anyone alone. Furthermore, thermodynamic extraction separation effect of Yb(III) and Y(III) has an agreement with the result of kinetics.

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