

Solvent extraction of La(III) and Nd(III) from nitrate solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester

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Abstract

Equilibrium and kinetic studies on solvent extraction of single and binary La(III) and Nd(III) from nitrate solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) in kerosene at 298 K were studied. Experiments were performed at different initial pH (2–6), metal concentrations (2.5–35 mol/m³), and dimeric extractant concentrations (1.7–100 mol/m³). The strip phase consisted of 500–1500 mol/m³ of HNO₃ (mostly, 500 mol/m³). The stoichiometry and equilibrium constant for the extraction reactions were determined. The extractant PC88A exhibited higher extractability for Nd(III) than La(III) under comparable conditions. Rate equations for the extraction and stripping of La(III) and Nd(III), as well as the related rate constants, were obtained at 298 K. It was shown that the extraction rates of La(III) and Nd(III) were comparable but the stripping rate of Nd(III) was near two order of magnitude larger than that of La(III). The present results had demonstrated extraction separation of Nd(III) over La(III) from nitrate solutions with PC88A to be kinetically and thermodynamically favorable.

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1. Introduction

Due to growing demand of high purity metals, concerns over environmental issues, and continuous depletion of high-grade ores, selective recovery of metal values from various raw or waste resources (e.g., ores, sludge, scrap, spent catalysts, etc.) becomes an important issue. One example is the recovery and separation of rare earth metals such as La(III) and Nd(III) from spent Ni-metal hydride (Ni-MH) secondary batteries [1,2]. The Ni-MH battery is a rechargeable cell with high energy density, which has many advantages like high performance of electrochemical properties, safe, and acceptable towards the environment over other batteries such as the Ni-Cd rechargeable batteries. Owing to such benefits, the Ni-MH batteries have been widely used in portable electronic applications including personal computer, video, camera, and telephone.

The rectangular and circular cylinder-shaped, commercially available Ni-MH batteries have been treated in the Energy and Resources Laboratories, ITRI (Hsinchu, Taiwan). The package of Ni-MH batteries is first dismantled, and the batteries are cut

in half crosswise to separate metallic cases from internal battery rolls that contain the cathode and anode plus a nylon separator. After washing with water to remove water-soluble components, they are heated in an oven at 600 °C for 0.5 h to remove organic constituents. They were then ground as fine powders and were sieved (<50 mesh). The powders were fully leached by 3000 mol/m³ HCl at a solid-liquid ratio of 1:7 under agitation for 1 h at 90 °C. The leaching liquor was treated by successively adding 6000 mol/m³ NaOH until all Al(OH)₃ and Fe(OH)₃ were precipitated. After separation by filtration, the solution (pH < 2) was extracted with 20 vol.% di(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene. The raffinate generally contained Ni(II), Co(II), and Mn(II), where the former two were recovered by electrodeposition [1]. The aqueous solution containing approximately 3.5 g/dm³ La(III) and 2.0 g/dm³ Nd(III) was obtained when the loaded organic phase was stripped by 1000 mol/m³ HNO₃.

Using different leaching procedures, Tzanetakis and Scott [1] have studied the recycling of Ni-MH batteries, and found that rare earth metals can be extracted and separated from Co(II) and Ni(II) at lower (pH < 3) with D2EHPA. The liquor with a composition of around, in g/dm³, 23.4 Ni, 1.7 Co, 3.4 Fe, 0.72 Zn, 0.46 Al, 1.2 Mn, 4.2 La, 0.26 Ce, and 2.6 Nd was obtained by Zhang et al. [2] when Ni-MH battery materials were leached

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Nomenclature

D_M	distribution ratio of metal ions defined in Eq. (2)
$(HX)_2$	PC88A dimer
K_2	dimerization constant of PC88A defined in Eq. (4) (m^3/mol)
K_{ex}	extraction equilibrium constant defined in Eq. (6) (-)
k_b	stripping rate constant defined in Eq. (12)
k_f	extraction rate constant defined in Eq. (12)
m	number of dimeric PC88A associated with one molecule of metal ion
R_b	backward stripping rate defined in Eq. (12) ($mol/(m^3 s)$)
R_f	forward extraction rate defined in Eq. (12) ($mol/(m^3 s)$)
t	time (s)
$[]$	concentration of species in the brackets (mol/m^3)

Greek letter

β	separation factor of Nd(III) over La(III) defined in Eq. (3)
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Subscript

[0]	initial (total)
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with 3000 mol/m^3 HCl at 95°C for 3 h. They also reported that rare earth metals can be recovered from the leaching liquor by a solvent extraction circuit with 25 vol.% D2EHPA in kerosene at pH 1.2. However, the separation of mixed rare earth metals themselves from aqueous media in these two studies was not done.

Various methods including chemical precipitation, adsorption, and ion exchange can be used to recover rare earth metals like La(III) and Nd(III) from aqueous solutions; however, these metals cannot be separated in a simple and economic way due to their similar physicochemical properties [3]. Adsorption and ion exchange techniques usually suffer from their poor selectivity [4]. In this regard, solvent extraction is of great interest due to its high selectivity and significant capital and operating cost savings [5]. A survey of literature has indicated that quaternary ammonium salts and organophosphorus acids are the commonly used extractants for the extraction and separation of rare earth metals from acidic aqueous media [6–12]. However, the former extractants might not be applicable for handling dilute mineral acid solutions ($<2000 \text{ mol/m}^3$) because in this situation no sufficient amounts of anionic ligands such as nitrate and chloride are provided to convert the rare earth metals to their anionic forms [6,7].

Solvent extraction has been operated in many types of the devices such as packed towers and mixer-settlers. Whatever equipments are applied, the good knowledge of extraction chemistry is essential to design a satisfactory contactor. In this work, the extraction equilibria and kinetics of single and binary La(III) and Nd(III) from nitrate solutions with organophos-

phorus acids were examined. Two acids D2EHPA and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) were selected, mainly due to their high chemical stability and operating versatility (reversibility by pH control, etc.) [13,14]. The separation ability of the two extractants for La(III) and Nd(III) was compared and screened. The aqueous (feed) phase contained nitrate salts of La(III) and/or Nd(III), and the strip phase consisted of HNO_3 . These fundamental data would also be useful for modeling continuous membrane-based processes such as liquid membranes and the so-called non-dispersive solvent extraction in hollow fiber modules [15,16]

2. Materials and methods

2.1. Reagents and solutions

The extractants D2EHPA (Merck Co., Germany, 98.5% purity) and PC88A (Daihachi Co., Japan, 95% purity) were used as received. Prior to use, the diluent kerosene (Union Chemical Co., Taiwan) was washed twice with 20 vol.% H_2SO_4 to remove aromatics and then with deionized water (Millipore Milli-Q) three times. The inorganic chemicals including $\text{La}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, HNO_3 , H_2SO_4 , and NaOH were all supplied by Merck Co. as analytical reagent grade.

The aqueous phase was prepared by dissolving $\text{La}(\text{NO}_3)_3$ and/or $\text{Nd}(\text{NO}_3)_3$ in deionized water. The initial concentration of metal ions ranged from 2.5 to 35 mol/m^3 and the pH was adjusted to be 2–6 by adding a small amount of 100 mol/m^3 of HNO_3 and NaOH. The organic phase was prepared by diluting D2EHPA or PC88A in kerosene. The initial extractant dimer concentration ranged from 1.7 to 100 mol/m^3 . In the stripping kinetic experiments, the metal-PC88A complex was pre-loaded into the organic phase (concentration range, 0.2– 8.4 mol/m^3) and the strip phase contained HNO_3 in the concentration range of 500– 1500 mol/m^3 .

2.2. Experimental procedures

The procedures for measuring extraction equilibrium data were as follows. Equal volumes of the organic and aqueous phases (25 cm^3 each) were placed in 125-cm^3 glass-stoppered flasks, and agitated with a magnetic stirrer at 300 rpm for 12 h. Preliminary experiments had shown that the extraction equilibria were attained within 4 h. The temperature was fixed at 298 K in water bath. After phase separation, the concentrations of La(III) and Nd(III) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin-Elmer, Optima 2000 DV). The organic-phase metal concentrations were calculated from a mass balance. The equilibrium pH was measured using a pH meter (Horiba Model F-23). Each experiment was at least duplicated under identical conditions. The reproducibility of the concentration measurements was within 3%.

A glass stirred cell with an I.D. of 50 mm and height of 105 mm was employed in the kinetic studies, as have described previously [17]. This cell had an ultrafiltration membrane in the bottom, just above which a plastic turbine type impeller (length 40 mm) connected to a magnetic stirrer was equipped. The tem-

perature was fixed at 298 K by circulating constant-temperature water into water jacket around the glass cell. A stirring speed of 300 rpm allowed homogeneous dispersion of the organic phase (100 cm³) in aqueous phase (100 cm³). Above this stirring speed, the extraction rate was no longer increased. This indicates that the thickness of aqueous-or organic-stagnant film is reduced to a minimum, and the effect of aqueous-and organic-film diffusion on the extraction process remains unchanged. The organic phase was poured into the cell first and then mixed with the aqueous phase in both (forward) extraction and (backward) stripping experiments. Timing was started upon addition of the aqueous phase. Aqueous samples (1 cm³) were taken at preset time intervals, which were directly separated from the organic phase through YM3 ultrafilter (MWCO 3000, regenerated cellulose, Millipore) at an applied pressure of 5 atm controlled by N₂ gas.

3. Results and discussion

3.1. Screening of extractants

The effect of equilibrium pH on the extraction of binary La(III) and Nd(III) from simulated acidic leaching solutions using D2EHPA and PC88A is shown in Fig. 1a. The extraction efficiency at an equal volume of organic and aqueous phases is

commonly defined by [5]

$$\text{Extraction}(\%) = 100 \times \frac{[\overline{M(III)}}{[M(III)]_0} = \frac{100D_M}{1 + D_M} \quad (1)$$

where the overbar refers to the organic phase, and D_M is the distribution ratio of metals defined as

$$D_M = \frac{[\overline{M(III)}}{[M(III)]} \quad (2)$$

As expected, the extraction increases with increasing aqueous pH, particularly for Nd³⁺. This reveals the much stronger affinity of Nd³⁺ than La³⁺ with both organophosphorus acids. Although PC88A exhibits lower extractability for La(III) and Nd(III) than D2EHPA, it is selected for further studies from the viewpoint of separation performance.

3.2. Separation performance

It is of considerable interest to quantitatively compare the separation ability. Under batch equilibrium conditions, the separation factor of Nd³⁺ over La³⁺, β , can be defined as [18,19]

$$\beta = \frac{([\overline{Nd(III)}]/[\overline{La(III)}])}{([Nd(III)]_0/[La(III)]_0)} = \frac{\text{Extraction of Nd}(\%)}{\text{Extraction of La}(\%)} \quad (3)$$

It is noticed that the value of β may change with the equilibrium pH.

Fig. 1b shows the effect of metal concentration ratio $[Nd(III)]_0/[La(III)]_0$, in binary systems on the extraction efficiencies at an initial pH of 5.0. The value of β with PC88A increases from around 4.0–8.0 when the concentration ratio increases from 0.1 to 9.0, which is larger than that with D2EHPA (nearly 1.0). The superior ability of PC88A, compared to D2EHPA, for extraction separation of Pr³⁺/La³⁺, Nd³⁺/Pr³⁺, Zn²⁺/Cd²⁺, and Co²⁺/Ni²⁺ has been previously reported under comparable conditions [6,11,18,19].

3.3. Extraction equilibria

It is known that acidic organophosphorus compounds such as PC88A (HX) tend to dimerize in non-polar or lowly polar solvents like kerosene [14,15]. The dimerization reaction of PC88A can be expressed by



The value of K_2 for PC88A in kerosene is unavailable in the literature, and that of 3.0 m³/mol in *n*-heptane is approximated here [20]. This indicates that around 96% of the initially 100 mol/m³ of monomeric PC88A, for example, exists as the dimers in kerosene.

Fig. 2 shows the effect of equilibrium pH on the distribution ratios of single metals at 298 K. According to these data, we want to determine the compositions of extracted complexes and their equilibrium relationships. The extraction of trivalent metals (M³⁺) from acidic aqueous media with acidic organophosphorus compounds such as PC88A has been widely studied [8–12].

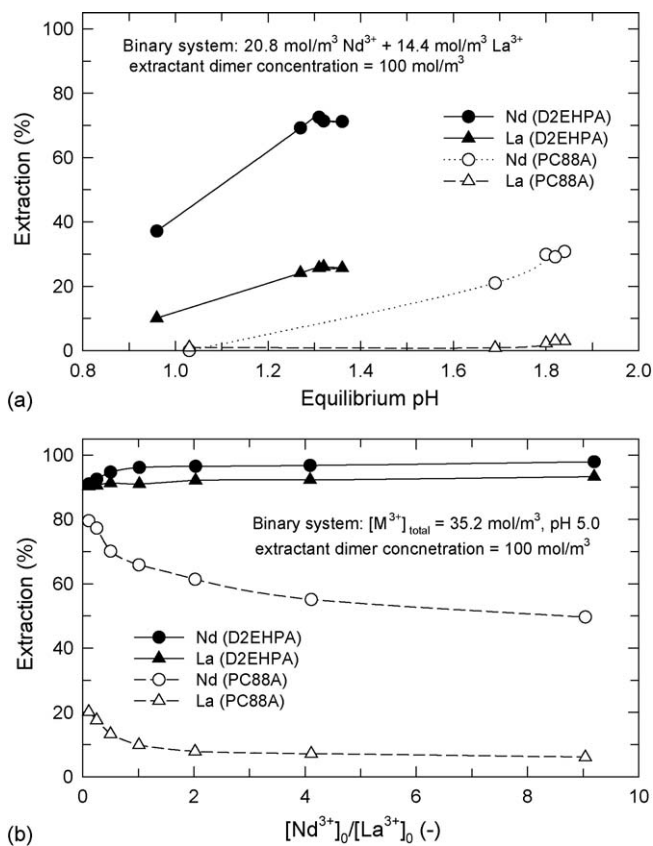


Fig. 1. Extraction efficiencies of La(III) and Nd(III) from simulated binary systems with D2EHPA and PC88A at different equilibrium pH and metal concentration ratios.

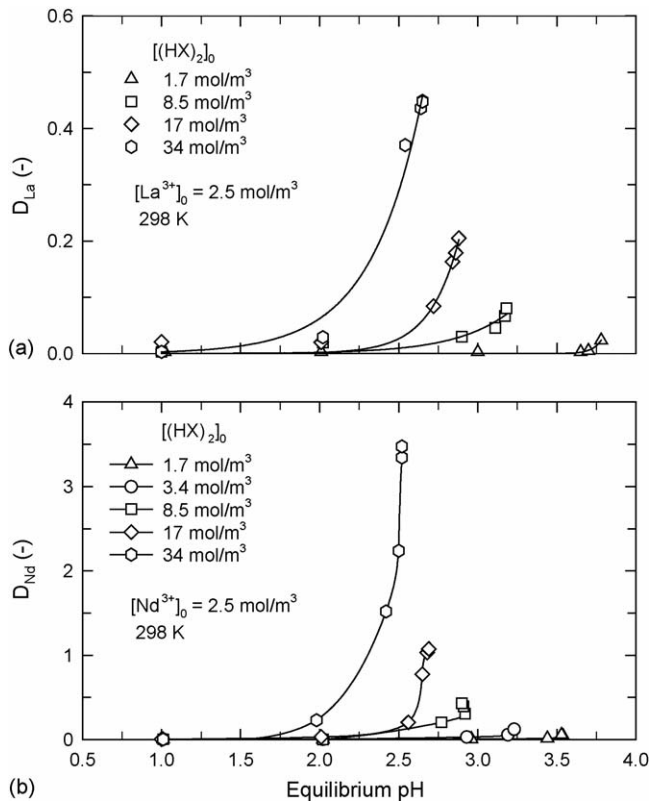
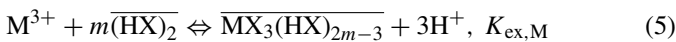


Fig. 2. Effect of equilibrium pH on distribution ratios of La(III) and Nd(III) from single systems with PC88A.

When the organic loading (i.e., the concentration ratio of metal-complexed extractant to the total extractant in the organic phase) is low enough, the reaction stoichiometry can be written as follows [4]:



The extraction equilibrium constant $K_{ex,M}$ is expressed by

$$K_{ex,M} = \frac{[\overline{MX_3(HX)_{2m-3}}][H^+]^3}{[M^{3+}][\overline{(HX)}_2]^m} \quad (6)$$

Substituting Eq. (2) into Eq. (6), we have

$$D_M[H^+]^3 = K_{ex,M}[\overline{(HX)}_2]^m \quad (7)$$

Evidently, m and $K_{ex,M}$ can be graphically determined from the slope and intercept of the log–log plot of $D_M[H^+]^3$ versus $[\overline{(HX)}_2]$, as shown in Fig. 3. Linear regression is good. The values of m and $K_{ex,M}$ are obtained to be 3.0 and 2.3×10^{-5} (–) for La(III), respectively, as well as 3.0 and 2.4×10^{-4} (–) for Nd(III) at 298 K.

The determined composition of M(III)-PC88A complex of $\overline{MX_3(HX)_3}$ is actually consistent with those of the PC88A and D2EHPA complexes reported previously [8,11–13]. In the extraction of La(III) from nitrate solutions with PC88A in *n*-dodecane, however, Abdeltawab et al. [9] have obtained the relationship $D_{La} = 3.8 \times 10^{-1}[\overline{HX}]^{3.2}[H^+]^{-2.5}$. If this relationship were correct, the complexes formed would possess different compositions while judging from Eq. (7).

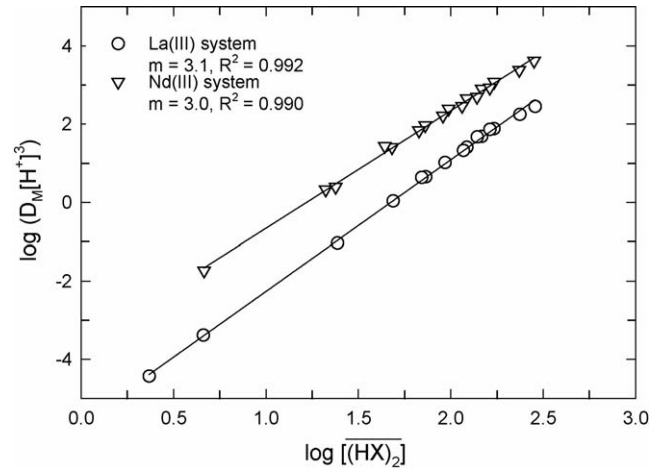


Fig. 3. Determination of reaction stoichiometries for the extraction of La(III) and Nd(III) from single systems with PC88A.

Fig. 4 compares the measured distribution ratios in binary metal systems with those predicted based on the equilibrium parameters obtained from single metal systems. It is inherently assumed that the extraction of both metals is independent and uncompetitive. Thus, we have

$$[La(III)]_0 = [La^{3+}] + [\overline{LaX_3}] = [La^{3+}] + K_{ex,La}[La^{3+}][\overline{(HX)}_2]^3[H^+]^{-3} \quad (8)$$

$$[Nd(III)]_0 = [Nd^{3+}] + [\overline{NdX_3}] = [Nd^{3+}] + K_{ex,Nd}[Nd^{3+}][\overline{(HX)}_2]^3[H^+]^{-3} \quad (9)$$

$$\begin{aligned} [\overline{(HX)}_2]_0 &= \left(\frac{1}{2}\right) [\overline{HX}] + [\overline{(HX)}_2] + 3[\overline{LaX_3}] + 3[\overline{NdX_3}] \\ &= \left(\frac{1}{2}\right) K_2^{1/2} [\overline{(HX)}_2]^{1/2} + [\overline{(HX)}_2] \end{aligned}$$

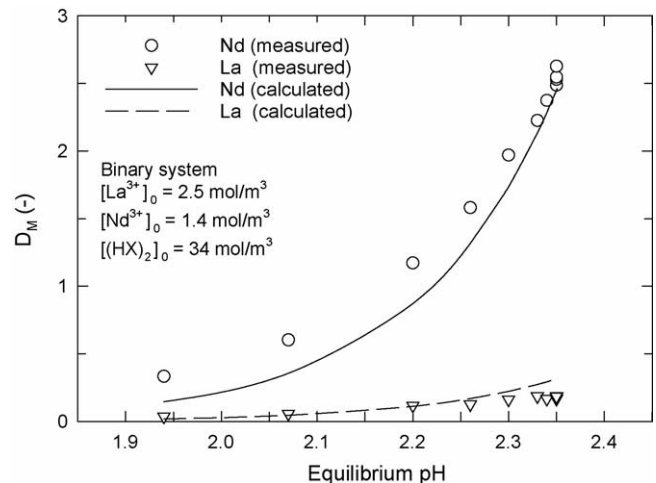


Fig. 4. Comparison of the measured and calculated distribution ratios of La(III) and Nd(III) from binary systems with PC88A at different equilibrium pH values.

$$\begin{aligned}
 &+ K_{\text{ex,L a}}[\text{La}^{3+}][\overline{(\text{HX})}_2]^3[\text{H}^+]^{-3} \\
 &+ K_{\text{ex,N d}}[\text{Nd}^{3+}][\overline{(\text{HX})}_2]^3[\text{H}^+]^{-3} \quad (10)
 \end{aligned}$$

where MX_3 denotes an abbreviated form of $\text{MX}_3(\text{HX})_3$. Although the distribution ratio of Nd(III) is slightly underestimated under the conditions studied (Fig. 4), the distribution of both metals is not significantly affected due to the presence of the second metals. This is likely a result of low organic loadings (less than 12% with PC88A) and relatively large difference of $\text{pH}_{1/2}$ values (the pH of 50% extraction). In this regard, the “theoretical” separation factor of Nd(III) over La(III) can be expressed as Eq. (11) by combining Eqs. (1), (3), and (7):

$$\beta = \frac{K_{\text{ex,N d}}/K_{\text{ex,L a}}}{(1 + K_{\text{ex,N d}}[\overline{(\text{HX})}_2]^3[\text{H}^+]^{-3}) / (1 + K_{\text{ex,L a}}[\overline{(\text{HX})}_2]^3[\text{H}^+]^{-3})} \quad (11)$$

This equation indicates that the separation is more effective at lower extractant concentrations and lower pH values, but in this case the extractability is lowered as well.

3.4. Extraction kinetics

Due to the surface-active properties of acidic organophosphorus compounds, the reactions likely occurring at the interface between two immiscible phases are very complicated [13]. Geist et al. [8] have studied the kinetics of rare earth extraction from nitric acid into D2EHPA/kerosene in a constant interfacial-area stirred cell. They indicated that the forward extraction rate is limited by diffusion under the conditions of pH 2.1, 10 g/m³ M(III), and 50 mol/m³ dimeric D2EHPA. This is not wholly the case because the stirring intensity is much higher in the present work. Moreover, the extraction tends to be diffusion controlled by aqueous stagnant layer at extremely low metal concentration [15]. Therefore, we still assume that the mass transfer resistance is minimized and negligible because the solution was vigorously stirred (300 rpm) here.

In this regard, the rate equation of the overall extraction has the following power-law form:

$$\begin{aligned}
 -\frac{d[\text{M}^{3+}]}{dt} &= R_f - R_b = k_f[\text{M}^{3+}]^a[\overline{(\text{HX})}_2]^b[\text{H}^+]^c \\
 &- k_b[\overline{\text{MX}_3}]^d[\overline{(\text{HX})}_2]^e[\text{H}^+]^f \quad (12)
 \end{aligned}$$

where R_f and R_b are the (forward) extraction rate and (backward) stripping rate in mol/(m³ s), respectively, and k_f and k_b are the corresponding rate constants. Applying the initial-rate technique for the forward extraction, Eq. (12) can be simplified as

$$\left(-\frac{d[\text{M}^{3+}]}{dt} \right)_{t=0} = R_f = k_f[\text{M}^{3+}]^a[\overline{(\text{HX})}_2]^b[\text{H}^+]^c \quad (13)$$

Figs. 5 and 6 are the log–log plots of the reaction rates against the concentrations of metal, extractant, and H⁺ for the La(III) and Nd(III) systems, respectively. The slopes of these lines and the corresponding correlation coefficients (R^2) are also shown. Based on the results, the forward extraction rates of La(III) and

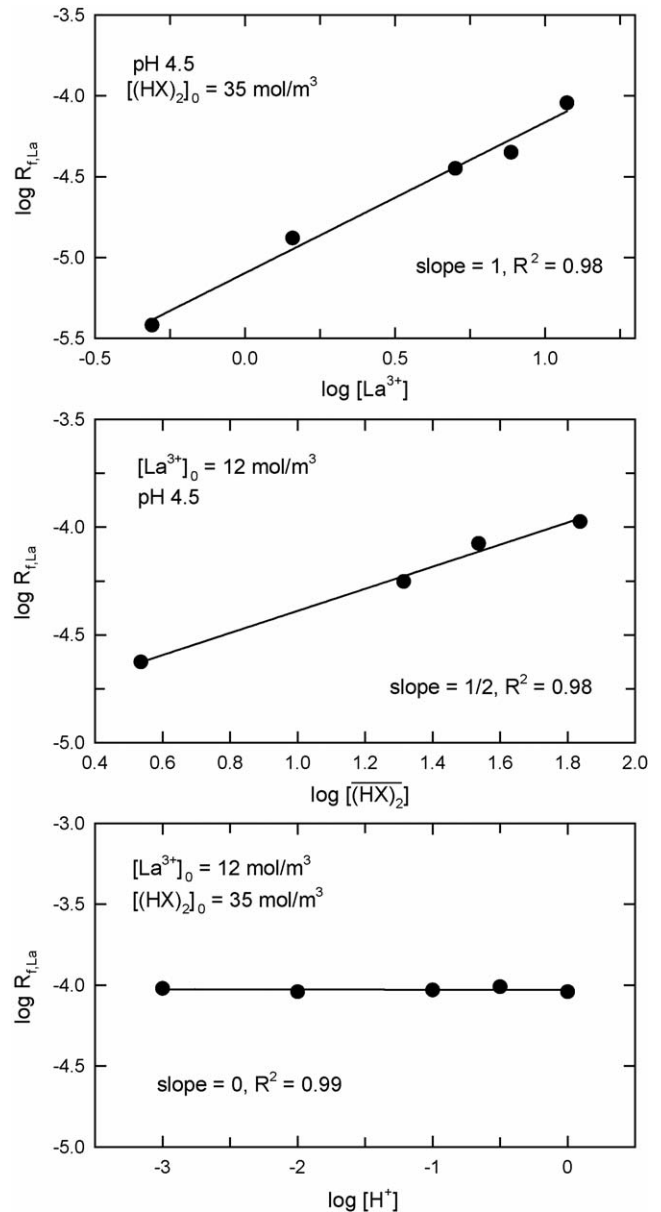


Fig. 5. Effect of various system variables on the initial (forward) extraction rate of La(III).

Nd(III) with PC88A can be written as

$$R_{f,\text{La}} = k_{f,\text{La}}[\text{La}^{3+}][\overline{(\text{HX})}_2]^{1/2} \quad (14)$$

$$R_{f,\text{Nd}} = k_{f,\text{Nd}}[\text{Nd}^{3+}][\overline{(\text{HX})}_2] \quad (15)$$

The extraction rate constants k_f are obtained to be $(2.4 \pm 0.7) \times 10^{-5} \text{ m}^{3/2}/(\text{mol}^{1/2} \text{ s})$ and $(6.5 \pm 0.8) \times 10^{-6} \text{ m}^3/(\text{mol s})$ for La(III) and Nd(III), respectively, at 298 K.

Applying the initial-rate concept for the backward stripping, we have

$$\left(\frac{d[\text{M}^{3+}]}{dt} \right)_{t=0} = R_b = k_b[\overline{\text{MX}_3}]^d[\overline{(\text{HX})}_2]^e[\text{H}^+]^f \quad (16)$$

The effects of concentrations of the metal-PC88A complex, PC88A, and H⁺ on the stripping rate for the La(III) and Nd(III)

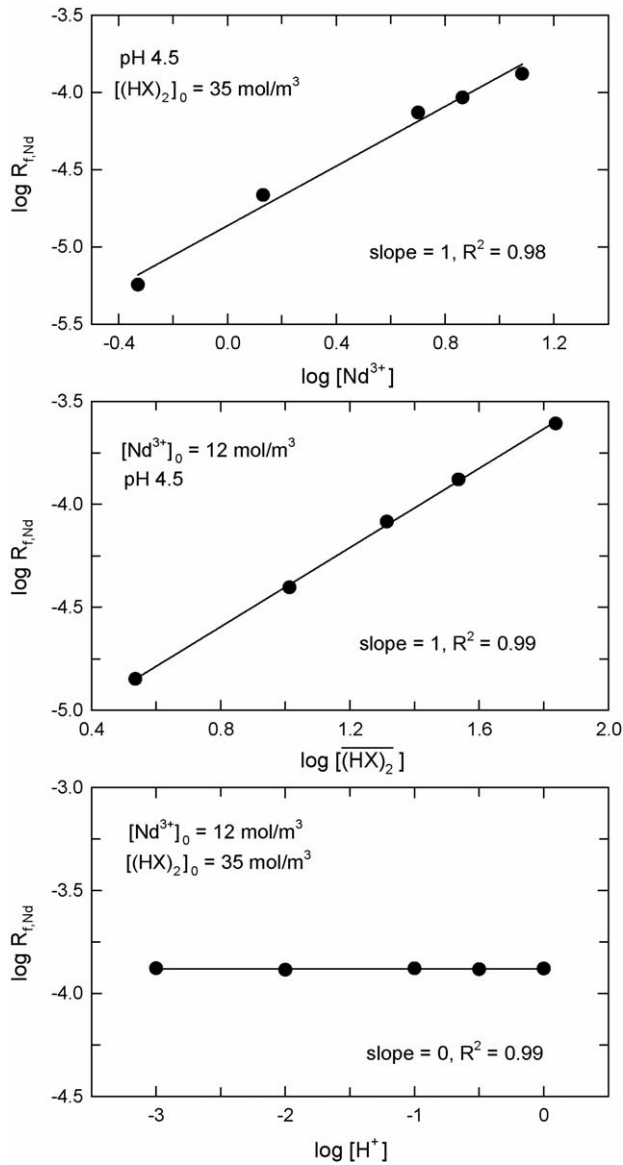


Fig. 6. Effect of various system variables on the initial (forward) extraction rate of Nd(III).

systems are shown in Figs. 7 and 8, respectively. Similarly, the slopes of the lines and the corresponding correlation coefficients (R^2) are shown. According to these results, the backward stripping rates of the metal-PC88A complexes are expressed as

$$R_{b,La} = k_{b,La} [\overline{LaX_3}] [H^+]^{-1/2} \quad (17)$$

$$R_{b,Nd} = k_{b,Nd} [\overline{NdX_3}] [H^+]^{-1} \quad (18)$$

The stripping rate constants k are obtained to be $(1.5 \pm 0.2) \times 10^{-3} \text{ mol}^{1/2}/(\text{m}^3/2 \text{ s})$ and $(5.3 \pm 1.2) \times 10^{-3} \text{ mol}/(\text{m}^3 \text{ s})$ for La(III) and Nd(III), respectively, at 298 K.

Comparisons of the present kinetic data with previous results are not made here because, to our best knowledge, few literature results are available. Under comparable conditions, it is found that the extraction rates of La(III) and Nd(III) are equivalent but the stripping rate of Nd(III) is near two orders of magnitude larger than that of La(III). The present results reveal that extrac-

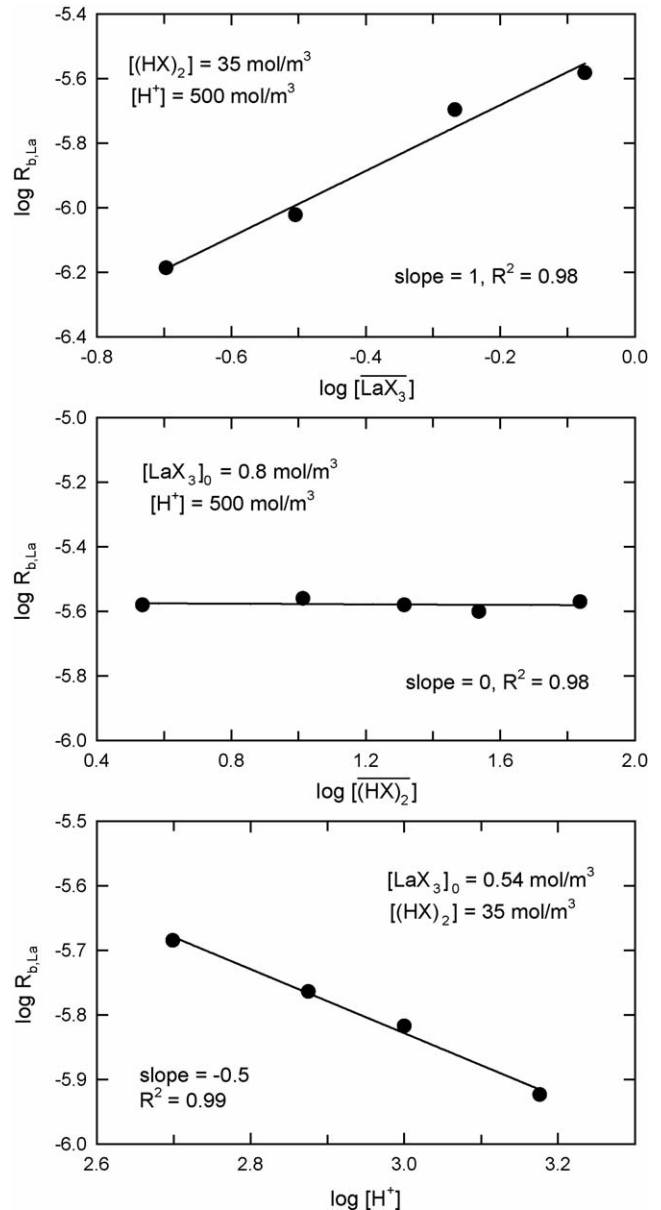


Fig. 7. Effect of various system variables on the initial (backward) stripping rate of La(III).

tion separation of Nd(III) over La(III) from nitrate media with PC88A is kinetically favorable, mainly via selective stripping.

The half-order dependence of R_f on $[(HX)_2]$ in the La(III) system (Eq. (14)) likely implies the occurrence of the dissociation of PC88A dimers to its monomers [13]. On the other hand, the half-order dependence of R_b on $[H^+]$ in the Nd(III) system (Eq. (17)) probably indicates that the acid dissociation reaction of dimeric or monomeric PC88A occurs. This can be supported from the acid dissociation constant of PC88A monomers (pK_a) of 4.3 [14].

It is found that the ratio of R_f/R_b for La(III) system (Eqs. (14) and (15)) and for Nd(III) system (Eqs. (17) and (18)) cannot lead to the corresponding equilibrium relationship (Eq. (6)). In general, the ratio of rate constants in the forward and reverse directions is equal to the equilibrium constant only if a reaction

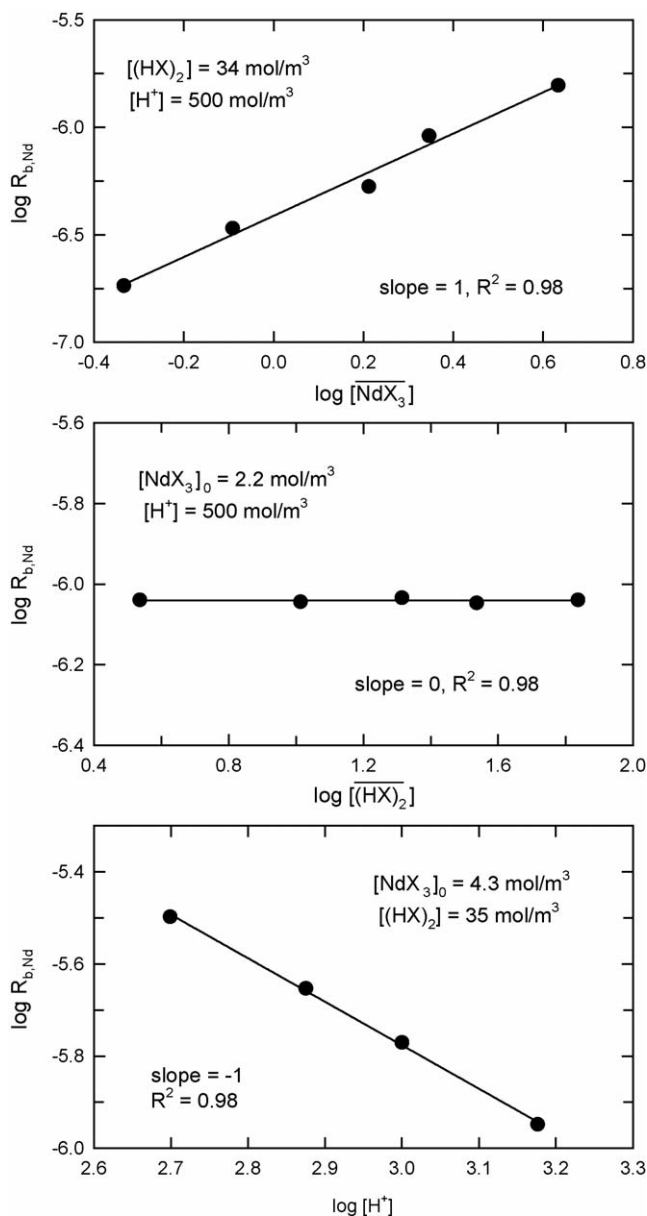


Fig. 8. Effect of various system variables on the initial (backward) stripping rate of Nd(III).

is elementary [21]. For a reaction that occurs by a composite mechanism, the ratio of these two constants is not necessarily the equilibrium constant for the overall reaction. The reason for this is that rate equations for composite reactions change with experimental conditions, such as reactant concentrations, and the rate constants also change [21].

4. Conclusions

Under comparable conditions, PC88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) exhibited superior separation performance for binary Nd(III) and La(III) from nitrate solutions by solvent extraction than D2EHPA (di(2-ethylhexyl)phosphoric acid). The separation factor of Nd(III) over La(III) increased with increasing the initial concentration

ratio of Nd(III) and La(III). Also, the separation was improved by lowering pH and/or extractant concentration. Separation of Nd(III) with PC88A by extraction was not only thermodynamically but also kinetically favorable.

The reaction stoichiometry for the extraction of La(III) and Nd(III) with PC88A (HX) could be written as Eq. (5), which suggested the formation of the complex $MX_3(HX)_3$. The equilibrium constant K_{ex} was 2.3×10^{-5} (-) and 2.4×10^{-4} (-) for La(III) and Nd(III), respectively, at 298 K. Under the conditions studied, the rate equations of forward extraction (R_f) and backward stripping (R_b) were shown in Eqs. (14), (15), (17) and (18). The corresponding rate constants were also evaluated at 298 K. These fundamental data would be essential for modeling and designing a good extraction device in practical applications.

Acknowledgement

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