Liquid-liquid Extraction of Lanthanide Ions with *bis*-2-Ethylhexylphosphinic Acid into Heptane

Wataru Ohmori*, Chunling Zheng*, and Yukio Nagaosa*

Bis-2-Ethylhexylphosphinic acid (BEHPA) has been studied as a useful extractant for some lanthanide ions (La(III), Ce(III), Pr (III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Y(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III)) from their aqueous solutions in the presence of sodium perchlorate. The extraction behavior of the metal ions were investigated and discussed in terms of pH dependency and extractability. The results indicated that the pH of the aqueous phase and BEHPA concentration of the organic solvent were the major parameters that affect the extraction efficiency of the metal ions. The half extraction pH ($pH_{1/2}$) was found to be 2.85~1.72 for La(III)~Nd(III), 1.75~0.61 for Sm(III)~Y(III) and 1.76~0.73 for Ho(III)~Lu(III) at different concentrations of BEHPA. The metal complexes extracted were proved to be all monomeric species using a slope analysis method. The curve fitting method was also applied to analyze the types of metal complexes extracted: MA_3HA (M means all the fifteen kind lanthanide metal ions). Furthermore, the extraction constants for the extracted metal complexes were estimated.

Key Words: *Bis*-2-ethylhexylphosphinic acid, Lanthanides, Extraction

1. Introduction

Liquid-liquid extraction is one of the most effective and versatile methods for the analytical separation and enrichment of target metal ions from aqueous medium. The multistage solvent extraction has given us an interesting field of inorganic chemistry and separation science because of the increased importance in industry [1]-[3]. Among many kinds of extractants that were used for the separation of metal ions, extensive attention has been paid to alkyl derivatives of organophosphorus acids such as dialkylphosphoric, -phosphonic and -phosphinic acids because of their selectivity and efficiency for some metal ions [4], [5]. In previous studies, we reported the extraction behavior of heavy and transition metal ions using di-2-methylnonylphosphoric acid (DMNPA) and *bis*-2-ethylhexylphosphinic (BEHPA) as extractants [6]. Similarly to the other dialkylphosphinic acids already reported, BEHPA greatly attracted our interest for the liquid-liquid extraction and separation of lanthanide ions,

due to its longer and hydrophobic alkyl chains [7]. It is expected that the P=O and P=OH groups in BEHPA can easily react with some metal ions in aqueous phase, considerably enhancing the selectivity in extraction. The extraction of transition metal ions using BEHPA as extractant has been also studied [8].

In the last decades the industrial demand of lanthanides has increased and the necessity for the high purity of these elements prompted us to develop the separation of the rare earths which is thus still of a great interest and importance. In the present work, the extraction behavior of some lanthanides with BEHPA in heptane was investigated and the extracted species and the extraction constants of these lanthanides were evaluated using both slope analysis and curve fitting methods.

2. Experimental

2.1 Reagents

BEHPA, above 96.6 wt.% in purity, was kindly supplied by Daihachi Chemical Industry Co. Ltd (Osaka, Japan) without further purification. Heptane of analytical

---

* Materials Science and Engineering Course, Graduate
  School of Engineering

reagent grade (Wako Pure Chemical Industry Co. Ltd, Tokyo, Japan) was used as the organic diluent. The standard nitrate solution (1000 ppm) of lanthanide ions of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Y(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III) were obtained from Wako Pure Chemical Industry Co. Ltd and diluted in a small excess of perchloric acid to make lower concentrations. Xylenol Orange (XO) and 2,7-bis (2-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonic acid (Arsenazo-III) from Dojion Industry Co. Ltd (Kumamoto, Japan) were used as the indicators in the titration and spectrophotometry. Ethyenediaminetetraacetic acid disodium salt (EDTA) from Dojion Industry Co. Ltd (Kumamoto, Japan) was used as the chelating reagent for the titration. All other chemicals were of analytical reagent grade and used without further purification.

2.2 Apparatus

An Iwaki Model V-S KM shaker was used to shake the aqueous and organic phases for the extraction experiments. A TOA-DKK Model IM-55G Ion Meter fitted with a Model GST-5721C glass electrode (TOA-DKK Electronics Co. Ltd, Tokyo, Japan) was used to measure the pH of aqueous phase after equilibration. An Apel PD-303 spectrophotometer (Apel Co., Ltd. Japan) was used for the spectrophotometry.

2.3 Procedures

Extraction experiments were carried out at 298 ± 0.4 K by shaking 10.0 cm^3 each of the aqueous and organic phases in a 50-cm^3 separation funnel using a mechanical shaker. The initial concentration of metal ion was varied from 1.0×10^{-4} to 5.0×10^{-3} M, and the ionic strength of the aqueous phase was kept at 0.10 with sodium perchlorate. The concentration of BEHPA in heptane was varied in the range from 0.16 to 0.64 M for La(III)~Y(III) and from 0.08 to 0.54 M for Ho(III)~Lu(III). After shaking for 30 minutes, the two phases were allowed to stand for 12 hours. The pH was then measured and the metal ion concentration of aqueous phase was determined after phase separation. The concentration of metal ion in the aqueous phase after extraction was finally determined by EDTA titration and spectrophotometry at 655 nm. The concentration of metal ion in the organic phase after extraction was estimated from the difference between the initial and equilibrium concentration of the metal ion in the aqueous phase.
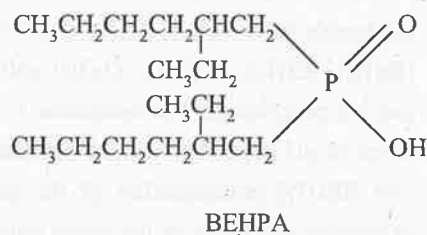
3. Results and discussion

3.1 Extractability of trivalent lanthanide ions using BEHPA in heptane
3.1.1 Effect of pH and BEHPA concentration on extraction

The molecular structure of BEHPA is illustrated as

CH$_3$CH$_2$CH$_2$CH$_2$CHCH$_2$ — CH$_3$CH$_2$ — CH$_3$CH$_2$ — CH$_3$CH$_2$CH$_2$CH$_2$CHCH$_2$ — P (=O) (OH)

BEHPA

Because of its comparatively longer alkyl chains, BEHPA is fairly soluble and usually exists as a dimer in non-polar organic solvents. Previous studies [9], [10] indicated that the solubility (S), the acidic dissociation constant (K_a), the dimerization constant (K_2) and the distribution constant (K_D) for BEHPA were 3.46×10^{-5} mol dm^{-3}, 3.31×10^{-5}, 1.78×10^2 and 2.04×10^5, respectively.

Fig.1 shows the extraction curves for trivalent lanthanide ions with BEHPA in heptane as the organic diluent. The extractability (E) for the lanthanides, which increased with increasing pH and in the order of atomic number except for Y(III).

For comparison, the extraction was carried out at different concentrations of BEHPA. Table 1 summarizes the half extraction pH ($pH_{1/2}$) values for the metal complexes with BEHPA in heptane. Obviously, the $pH_{1/2}$ values that obtained for the metal complexes with higher concentrations of BEHPA were lower than those with lower concentrations.

3.1.2 Effect of lanthanide ion concentration on extraction

The influence of lanthanide ion concentration was studied at different concentrations of BEHPA. Table 2 gives the $pH_{1/2}$ values for 1.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3} M La(III) at different concentrations of BEHPA. The results shown in Table 2 indicated that the $pH_{1/2}$ values were almost the same at different concentrations of metal ion when BEHPA concentration was fixed, and decreased

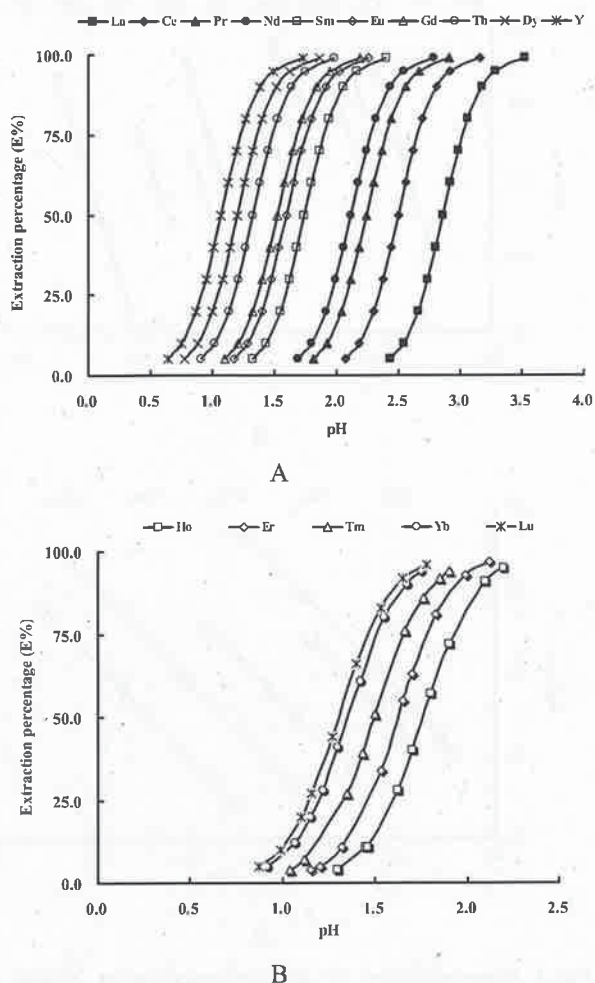with increasing concentrations of BEHPA.


A

B

Fig.1 Effect of pH on the extraction of lanthanides by BEHPA in heptane.
Organic phase: 0.16 M BEHPA in heptane for La(III)~Y(III) (A) and 0.08 M for Ho(III)~Lu(III) (B); aqueous phase: 1.0×10^{-3} M lanthanide ion in 0.10 M sodium perchlorate solution.

3.2 Extraction equilibrium of trivalent lanthanide complexes with BEHPA

If a j-merized trivalent metal complex with BEHPA, $M_jA_{3j}(HA)_{a,org}$, is extracted in heptane, the extraction equilibrium between the metal ion (M^{3+}) and extractant (HA) can be expressed as

$$jM^{3+} + \frac{3j+a}{2}(HA)_{2,\,org} \xrightarrow{K_{ex(j,a)}} M_jA_{3j}(HA)_{a,org} + 3jH^+$$

$$\tag{1}$$
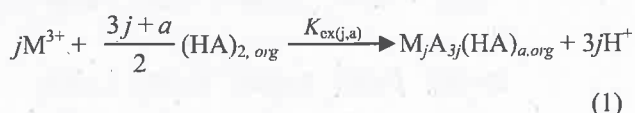
The extraction constant ($K_{ex(j,a)}$) is then

$$K_{ex(j,a)} = \frac{[M_jA_{3j}(HA)_{a,org}][H^+]^{3j}}{[M^{3+}]^j[(HA)_2]_{org}^{(3j+a)/2}} \tag{2}$$

where the subscript *org* refers to the organic phase and a

Table 1 $pH_{1/2}$ values of lanthanide ions extraction using BEHPA in heptane

BEHPA Ions	0.16 M	0.32 M	0.48 M	0.64 M
La(III)	2.86	2.65	2.51	2.42
Ce(III)	2.50	2.28	2.17	2.08
Pr(III)	2.24	2.03	1.90	1.84
Nd(III)	2.11	1.92	1.79	1.72
Sm(III)	1.75	1.56	1.41	1.33
Eu(III)	1.59	1.41	1.28	1.18
Gd(III)	1.53	1.33	1.21	1.11
Tb(III)	1.33	1.12	1.00	0.91
Dy(III)	1.20	0.99	0.86	0.76
Y(III)	1.07	0.87	0.74	0.61
	0.08 M	0.30 M	0.46 M	0.54 M
Ho(III)	1.76	1.37	1.24	1.19
Er(III)	1.62	1.23	1.10	1.05
Tm(III)	1.50	1.10	0.98	0.93
Yb(III)	1.35	0.96	0.83	0.78
Lu(III)	1.30	0.91	0.78	0.73

Table 2 $pH_{1/2}$ values of La(III) extraction using BEHPA in heptane

BEHPA La (M)	0.16 M	0.32 M	0.48 M	0.64 M
5.0×10^{-3}	2.82	2.61	2.49	2.40
1.0×10^{-3}	2.86	2.65	2.51	2.42
1.0×10^{-4}	2.83	2.62	2.51	2.41

denotes the number of BEHPA involved in the dimeric species $[(HA)_2]_{org}$.

The total concentration of trivalent lanthanides in the organic phase, $C_{M,org}$, is written as follows:

$$C_{M,org} = \sum_j \sum_a jK_{ex(j,a)}[M^{3+}]^j[(HA)_2]_{org}^{(3j+a)/2}[H^+]^{3j}$$

$$\tag{3}$$

$$\log C_{M,org} = j(\log[M^{3+}] - 3\log[H^+]) + \frac{3j+a}{2}\log[(HA)_2]_{org}$$
$$+ \log j + \log K_{ex(j,a)} \tag{4}$$

According to formula(4), the degree of polymerization of the extracted species (j) can be found from the plot of $\log C_{M,org}$ against $(\log[M^{3+}] + 3pH)$ at constant $[(HA)_2]_{org}$.

If only a monomeric species $MA_3(HA)_a$ or a dimeric species $M_3A_6(HA)_b$ was extracted, the plot must be a straight line with a slope of 1 or 2, respectively. If both are extracted, the plot should be a curve. By using slope analysis, the degree of polymerization of the extracted species can be checked.

It was found that all the slopes were about 1 at four different concentrations of BEHPA. These results suggest that only monomeric species exist for the lanthanide ions. It is generally accepted that the reaction coefficient (α) of a metal ion with the chelate anion of extractant in aqueous phase is unity ($[M^{n+}] = C_{M,w}$) when an extractant having a considerably large distribution coefficient, $D_{HA} = C_{HA,org}/C_{HA,w}$, is used. Since the distribution coefficient of BEHPA is 2.04×10^5 and the total concentration of BEHPA is in large excess over the concentration of lanthanide ions under the present experimental conditions, the effect of the reaction coefficient of lanthanide metal ions with BEHPA anion in the aqueous phase can be neglected (Fig.2).

As monomeric species are responsible for the extraction of all the ten kinds of lanthanide metal ions and since $[M^{3+}] = C_{M,w}$, the following expression can be derived from formula(3) for the lanthanide ions in the region where the monomeric species prevails:

$$\log C_{M,org} = \log[M^{3+}] - 3\log[H^+]$$
$$+ \log \sum_a K_{ex(1,a)}[(HA)_2]_{org}^{(3+a)/2} \quad (5)$$

According to formula(5), the number of BEHPA molecules involved in the monomeric species can be determined from the slope of the plots of ($\log C_{M,org} - \log C_{M,w} - 3pH$) against $\log[(HA)_2]_{org}$. As illustrated in Fig.3, all slopes of the straight lines obtained for the ten lanthanide metal ions were found to be about 2 and therefore $a = 1$, indicating that the monomeric species were LaA_3HA, CeA_3HA, PrA_3HA, NdA_3HA, SmA_3HA, EuA_3HA, GdA_3HA, TbA_3HA, DyA_3HA, YA_3HA, HoA_3HA, ErA_3HA, TmA_3HA, YbA_3HA, LuA_3HA. The respective extraction constants were obtained using the curve fitting method, as listed in Table 3. The extraction equilibrium for the ten lanthanide metal ions can be expressed as

$$M^{3+} + 2(HA)_{2,\,org} \xrightarrow{K_{ex(1,1)}} MA_3HA + 3H^+$$
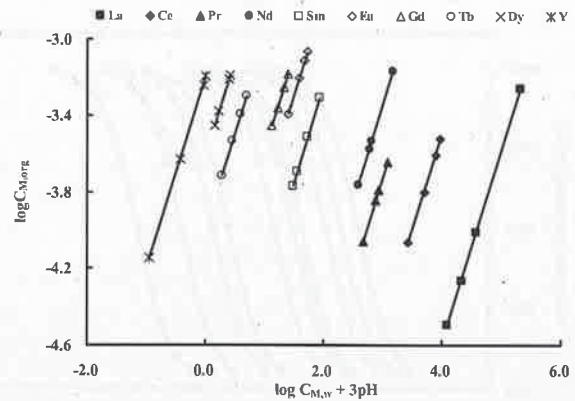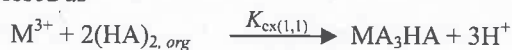
A
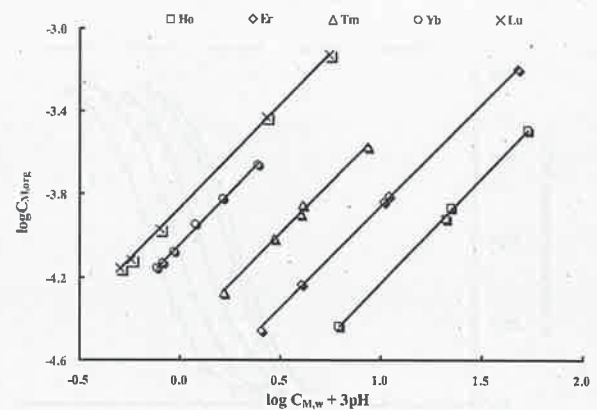
B

Fig.2 Determination of the polymerization degree of lanthanide species extracted with BEHPA in heptane. Organic phase: 0.16 M BEHPA in heptane for La(III)~Y(III) (A) and 0.08 M for Ho(III)~Lu(III) (B); aqueous phase: 1.0×10^{-3} M lanthanide ion in 0.1 M sodium perchlorate solution.

Table 3 Extraction constants of lanthanides by BEHPA

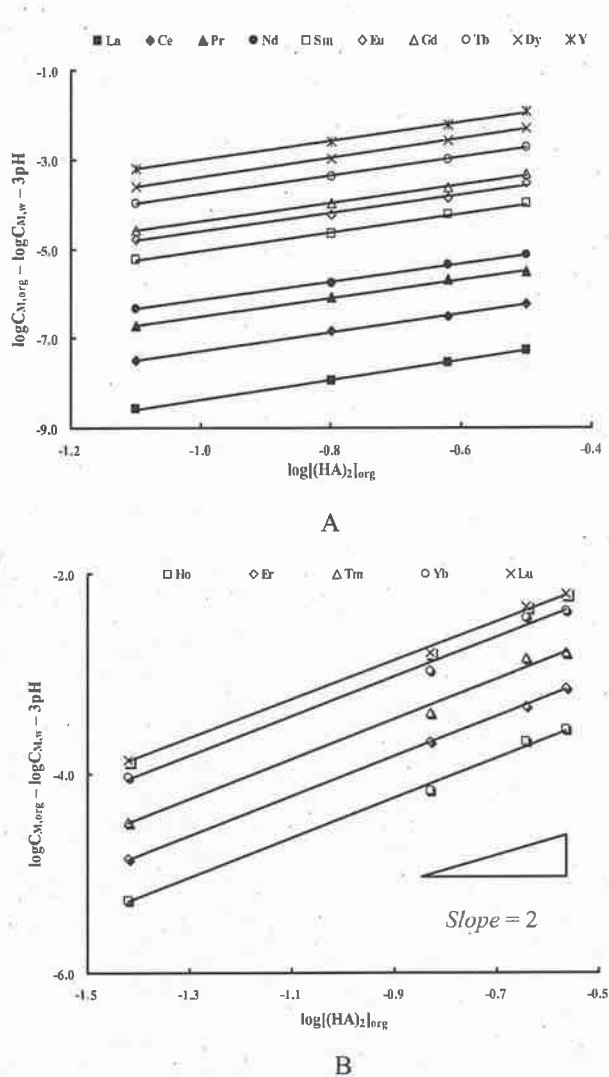| Ions	La(III)	Ce(III)	Pr(III)	Nd(III)	Sm(III)
$\log K_{ex(1,1)}$	-6.20	-5.20	-4.47	-4.14	-2.95
	Eu(III)	Gd(III)	Tb(III)	Dy(III)	Y(III)
	-2.55	-2.34	-1.70	-1.23	-0.90
	Ho(III)	Er(III)	Tm(III)	Yb(III)	Lu(III)
	-2.44	-2.03	-1.65	-1.22	1.07

A

B

Fig.3 Determination of the number of BEHPA molecules involved in monomeric lanthanide complexes. Organic phase: 0.16 M BEHPA in heptane for La(III)~Y(III) (A) and 0.08 M for Ho(III)~Lu(III) (B); aqueous phase: 1.0×10^{-3} M lanthanide ion in 0.10 M sodium perchlorate solution.

4. Conclusions

The research in this work revealed that BEHPA was a very effective organic extractant for the extraction of fifteen kinds of lanthanide ions from perchlorate media. The extracted species for lanthanides investigated are monometric species $M_j A_{3j}(HA)_a$ in heptane, with the j and a values of extracted species determined by slope analysis and curve fitting methods: $j = 1$ and $a = 1$. The extractability of the lanthanide ions by BEHPA decreased in the order Y(III)>Dy(III)>Tb(III)>Gd(III)>Eu(III)>Sm(III)>Nd(III)

>Pr(III)>Ce(III)>La(III) and Lu(III)>Yb(III)>Tm(III)> Er(III)>Ho(III). Based on above results, it seems that high performance centrifugal partition chromatography enables the mutual separation of all lanthanide ions.

References

[1] G. W. Mason, S. Lewey, D. F. Peppard: *J. Inorg. Nucl. Chem.*, 26, 2271 (1964).

[2] H. Sakka, H. Nakamura, M. Takagi, K. Ueno: *Bunseki Kagaku*, 32, 335 (1983).

[3] S. Motomizu, H. Freiser: *Solvent Extr. Ion Exch.*, 3, 637 (1985).

[4] J .L. Solka, A. H. Reis, G. W. Mason, S. M. Lewey, D. F. Peppard: *J. Inorg. Nucl. Chem.*, 40, 663 (1978).

[5] W. A. Rickelton, R. J. Boyle: *Sep. Sci. Technol.*, 23, 1227 (1988).

[6] B. H. Yao, Y. Nagaosa, M. Satake, K. Horita, A. Nomura: *Solvent Extr. Ion Exch.*, 14, 849 (1996).

[7] X. L. Wang, W. Li, S. L. Meng, D. Q. Li: *J. Chem. Technol. Biotechnol.*, 81, 761 (2006).

[8] Y. Nagaosa, B. H. Yao: *Talanta*, 44, 327 (1997).

[9] I. L. Jenkins, H. A. C. Mckay: *Tran. Faraday Soc.*, 50, 107 (1954).

[10] G. M. Kosolapoff: *Organophosphorus compounds*, Wiley & Sons, Inc., New York, 1950.