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Extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) Ions with Organophosphorous Compounds

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The pH-dependent extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions with organophosphorous extractants such as bis(2-ethylhexyl) phosphate (DEHPA), diphenyl phosphate (DPP) and diphenyl phosphinic acid (DPPA) in *n*-heptane, chloroform and *n*-amyl alcohol were investigated. All studied metal ions were extracted at highly acidic medium (pH 0.2–4.8) within 3 min at 96–99% yield using DEHPA, DPP and DPPA. The best solvent is chloroform for three studied extractants but *n*-heptane could be secondly usable solvent for only DEHPA. In the stripping studies, high recovery percentage was accomplished with 1 M NaOH and 0.1–1 M HCl for studied metal ions.

Key Words: **Organophosphorous compounds, Extraction, Y(III), La(III), Ce(III), Th(IV) and U(VI).**

INTRODUCTION

Rare-earth elements have been widely utilized in industrial products such as metallurgy, ceramics and electronics and their demands are getting larger[1]. The separations of the rare-earth elements from each other and from the actinides are often required especially in the treatment process of nuclear wastes. These separations, however, are very difficult due to the chemical similarity of the rare-earth elements[2].

Fractional precipitation, selective oxidation and ion-exchange methods can be used for separation of rare-earth elements. Besides, one of the most effective ways to separate these elements is the liquid-liquid extraction method using organophosphorous compounds such as phosphoric, phosphonic and phosphinic acids[3]. Phosphorous-based extractants of the general type $(X_1)(X_2)PO(OH)$ are monomeric in alcohols but exist as dimers in non-polar solvents such as benzene. The dimers are believed to be strongly hydrogen-bonded eight-membered rings[4]. Di-2-methylnonylphosphoric acid (DMNPA), bis(2-ethylhexyl)phosphoric acid (DEHPA), bis(2,4,4-trimethylpentyl)phosphinic acid (cyanex-272) and bis(2-ethylhexyl)phosphinic acid (PIA-8) are some of the extractants commonly used in liquid-liquid extraction of rare-earth elements[5–8].

In this work, appropriate conditions for performing pH-dependent extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) metals with bis(2-ethylhexyl) phosphate (DEHPA), diphenyl phosphate (DPP) and diphenyl phosphinic acid (DPPA) in *n*-heptane, chloroform and *n*-amyl alcohol were investigated and stripping studies were performed at 298 K. The effect of solvent and extractant on extraction was also studied.

EXPERIMENTAL

Bis(2-ethylhexyl) phosphate (DEHPA) (Fluka), diphenyl phosphate (DPP) (Aldrich) and diphenyl phosphinic acid (DPPA) (Fluka) were used as organophosphorous compounds and no further purification was done before use. *n*-Heptane (Riedel-deHäe*n*-5677), chloroform (Riedel-deHäe*n*) and *n*-amyl alcohol (Merck) of analytical reagent grade were used as organic solvents. Y(III), La(III), Ce(III) and Th(IV) stock solutions (1×10^{-2} M) were prepared by dissolving their nitrates and U(VI) was prepared by dissolving uranyl acetate in 1×10^{-4} M nitric acid. 1×10^{-2} M sodium tartarate (Riedel-deHäe*n*) and 0.1 M sodium nitrate (Merck) were used for preventing hydrolysis and adjusting ionic strength, respectively. Arsenazo-III (Aldrich) and all other reagents used were of analytical reagent grade.

An Inolab WTW model pH-meter and a Heildolp MR 3001 model magnetic shaker were used in the extraction experiments. Metal concentrations were determined by a Shimadzu 1601 model UV-Vis spectrophotometer.

All experiments were performed at 298 K. Equal volumes of organic phase (1×10^{-2} M) and aqueous phase containing Y(III), La(III), Ce(III), Th(IV) and U(VI) ions were shaken on a magnetic shaker at 1000 rpm for 3 min. The initial pH of the aqueous phase was roughly adjusted with dilute HCl and NaOH. After shaking, both phases were separated by standing for 10 min and then the equilibrium pH value of aqueous phase was measured. The concentrations of the metal ions in the aqueous phase were determined spectrophotometrically at 654 nm for Y(III), La(III), Ce(III), U(VI) ions and at 668 nm for Th(IV) ion by using Arsenazo-III reagent[9, 10]. The amounts of metals extracted were obtained from the difference of the metal concentration before and after equilibration.

The extraction efficiency was calculated according to the following equation:

$$R\% = \frac{[M]_i - [M]_e}{[M]_i} \times 100 \tag{1}$$

where $[M]_i$ and $[M]_e$ denote initial and equilibrium concentrations of metal in aqueous phase, respectively.

Stripping experiments were also carried out at 298 K. The loaded organic phase containing high concentration of metal and different concentrations of HCl or NaOH was shaken for 3 min. The amount of metal stripped into the aqueous phase was determined spectrophotometrically as described above. Stripping efficiency was calculated according to the following equation:

$$R_{\text{stripping}}\,(\%) = \frac{V_{aq}[M]_{aq}}{V_{org}[M]_{org}} \tag{2}$$

In this equation, $[M]_{aq}$ and $[M]_{org}$ denote metal concentration (mg L^{-1}) in aqueous phase after stripping and metal concentration in organic phase before stripping and V_{aq}, V_{org} represent volumes of aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

The extraction of the metal ions (Y(III), La(III), Ce(III), Th(IV) and U(VI)) with the DEHPA, DPP and DPPA in *n*-heptane, chloroform and *n*-amyl alcohol depending upon the solubilities of the extractants were studied.

The extractant effects for Y(III) ion with DEHPA, DPP and DPPA in *n*-amyl alcohol are shown in Fig. 1. The extraction efficiency increases with DEHPA by the increase of pH but decreases with DPP and DPPA. The extraction yields were found as 94, 93 and 92% while the equilibrium pH values were 4.25, 0.45 and 0.50 respectively.

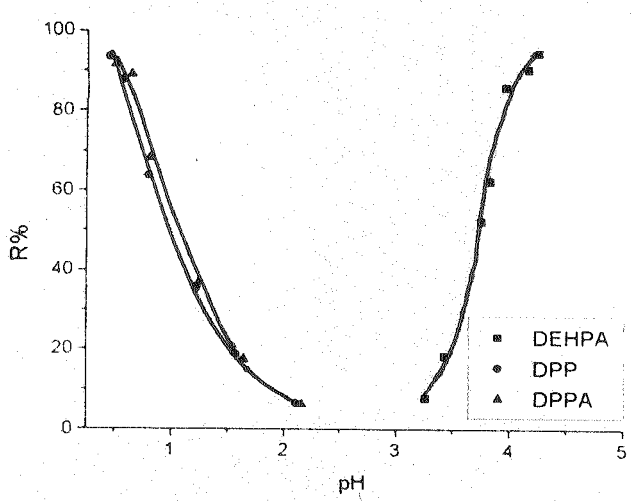

Fig. 1 Extraction of Y(III) ion with DEHPA, DPP and DPPA in *n*-amyl alcohol

Extraction of Y(III) with DPP and DPPA in chloroform proceeded at very low pH with high yield (96%). The extraction yield for Y(III) ion with DEHPA in chloroform was found in the range of 26–96% at 1.63–2.80 equilibrium pH range.

Extraction yields for La(III) ion with DEHPA and DPPA in chloroform increase similarly by the increase of pH but decrease with DPP. Extraction yields were found 97, 95 and 89% at equilibrium pH values 4.74, 0.50 and 3.37 (Fig. 2). Chloroform and *n*-amyl alcohol show similarities about pH-dependence of the extraction with DEHPA and DPP for La(III) ion. Extraction yields in *n*-amyl alcohol were found 77 and 88% at equilibrium pH 4.92 and 0.90, respectively but no graph was designed for DPPA because of low extraction yield (11%).

Extraction curves of Ce(III) ion with DEHPA, DPP and DPPA in chloroform and *n*-amyl alcohol are given in Figs. 4 and 5. Extraction yield percentages and equilibrium pH values of Ce(III) ion with DEHPA, DPP and DPPA in chloroform was similar to the extraction of La(III) ion in the same solvent. Extraction recovery with DPP and DPPA for Ce(III) in *n*-amyl alcohol was same. Extraction

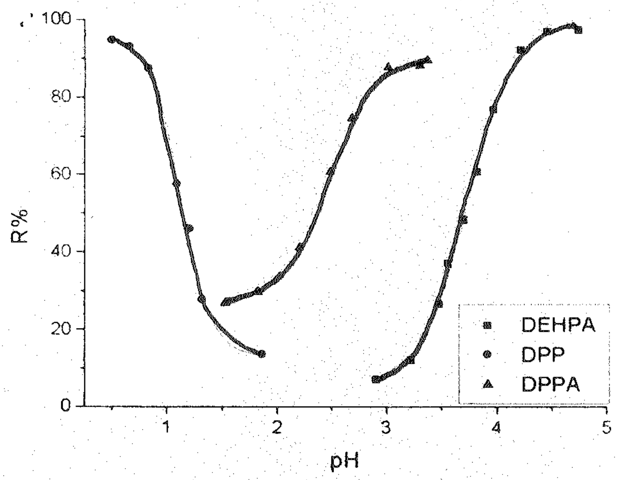

Fig. 2 Extraction of La(III) ion with DEHPA, DPP and DPPA in chloroform

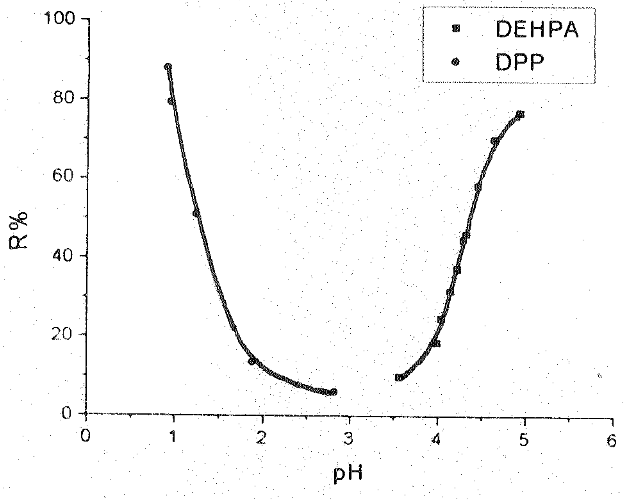

Fig. 3 Extraction of La(III) ion with DEHPA and DPP in *n*-amyl alcohol

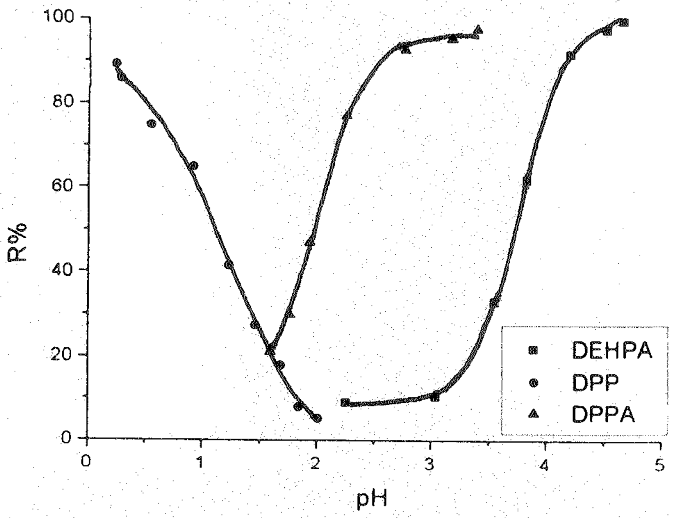

Fig. 4 Extraction of Ce(III) ion with DEHPA, DPP and DPPA in chloroform

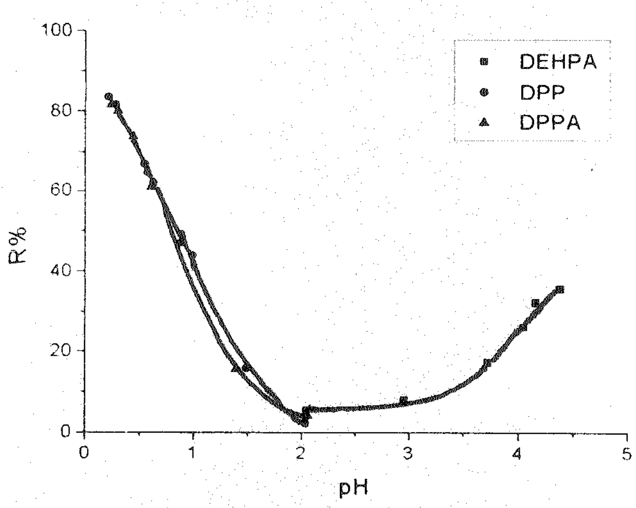

Fig. 5 Extraction of Ce(III) ion with DEHPA, DPP and DPPA in *n*-amyl alcohol

yields increase by decrease of equilibrium pH for these compounds, but inversely decreases for DEHPA. The extraction yields were found 99, 89, 98% at equilibrium pH values of 4.67, 0.24 and 3.39 for the extraction of Ce(III) with DEHPA, DPP and DPPA in chloroform and 35, 84, 82% at equilibrium pH values of 4.38, 0.21 and 0.24 in *n*-amyl alcohol.

The extraction of Th(IV) ion with DPPA in chloroform was proceeded with high yield (85–93%) at high acidic pH range (1–3) and very low yield (4%) with DEHPA in *n*-amyl alcohol. For the extractions of Th(IV) ion with DEHPA and DPP in chloroform (Fig. 6) and also with DPP and DPPA in *n*-amyl alcohol (Fig. 7), their extraction efficiencies decrease by the increase at equilibrium pH in acidic range. Extraction yields were found 90 and 89% at the equilibrium pH 1.83 and 0.56 for the extraction with DEHPA and DPP in chloroform and 91 and 86% at pH 1.34 and 1.36 for extraction with DPP and DPPA in *n*-amyl alcohol.

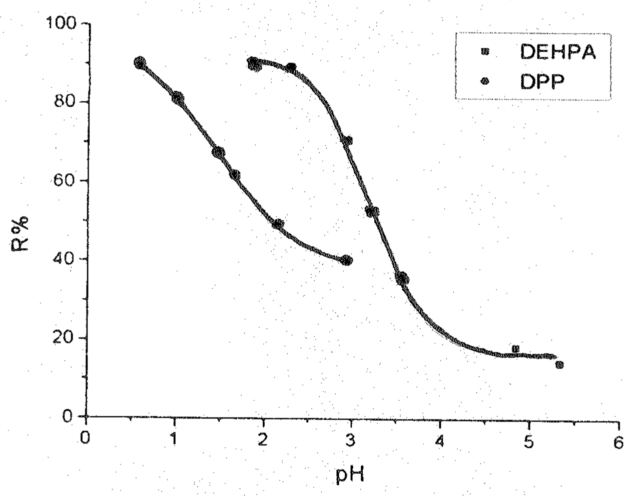

Fig. 6 Extraction of Th(IV) ion with DEHPA and DPP in chloroform

Extraction efficiencies for the extraction of U(VI) ion with DEHPA and DPP increase by the decrease of equilibrium pH in chloroform (Fig. 8). Extraction

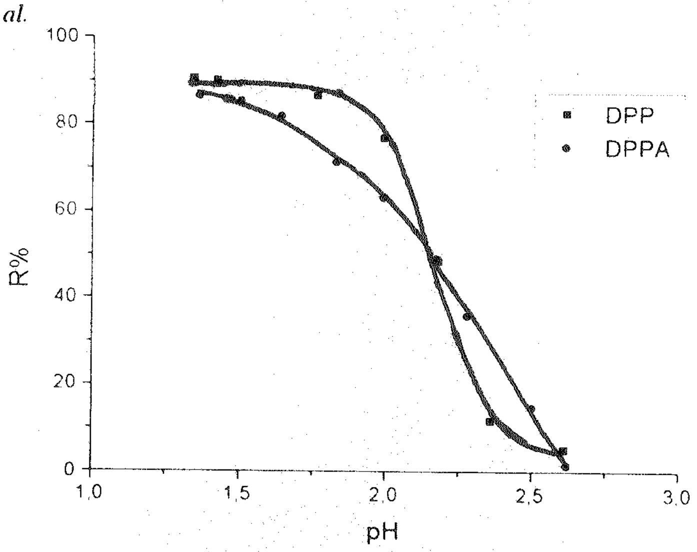

Fig. 7 Extraction of Th(IV) ion with DPP and DPPA in *n*-amyl alcohol

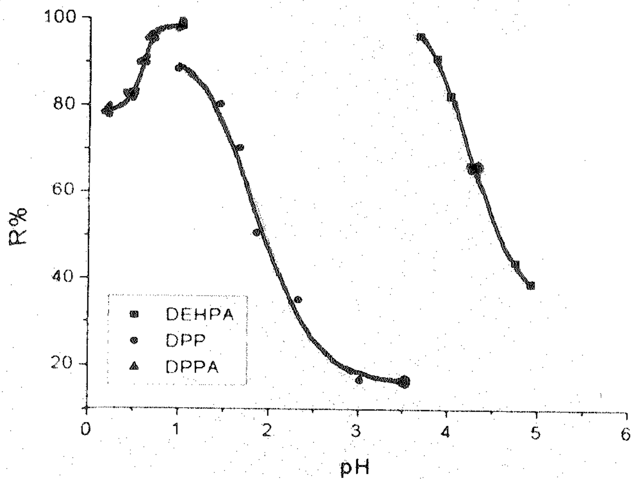

Fig. 8 Extraction of U(VI) with DEHPA, DPP and DPPA in chloroform

yields were found 96 and 88% for these compounds at 3.67 and 0.98 pH values. But, the extraction of U(VI) ion with DPPA in chloroform was succeeded at very low pH range (0–1) with a high yield (79–98%). In *n*-amyl alcohol, the high percentage of extraction of U(VI) was obtained after pH 2 for the studied all extractants (Fig. 9). Extraction yields were found 99, 97 and 99% at the pH values of 3.30, 2.31 and 2.51, respectively.

The effect of *n*-heptane on the extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions was only performed with DEHPA due to lack of solubilities of DPP and DPPA. The extraction behaviour of all investigated ions with DEHPA in *n*-heptane was mostly similar with the extraction in both of chloroform and *n*-amyl alcohol (Fig. 10). Differently, Y(III) ion was extracted at fairly narrow acidic pH range (0.98–1.19) with a high extraction yield (82–99%).

Extraction of U(VI) with DEHPA in *n*-amyl alcohol proceeded at a more acidic region than *n*-heptane and chloroform. Extraction efficiency of DEHPA increases by the increase of equilibrium pH as it was observed for Y(III), La(III) and Ce(III) in chloroform. The extraction of Y(III) in *n*-heptane was succeeded at higher pH

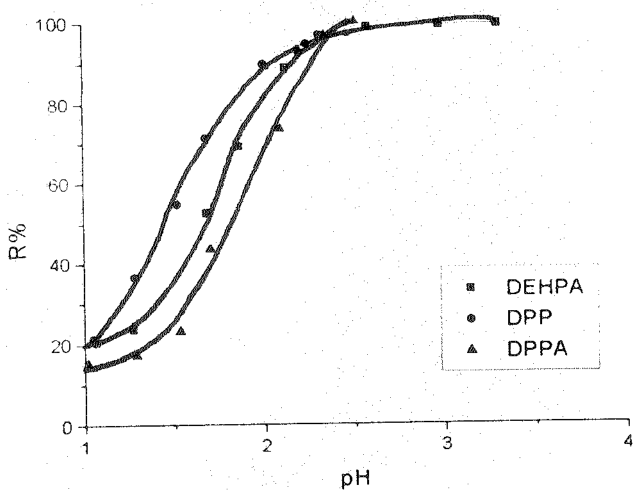

Fig. 9 Extraction of U(VI) ion with DEHPA, DPP and DPPA in *n*-amyl alcohol

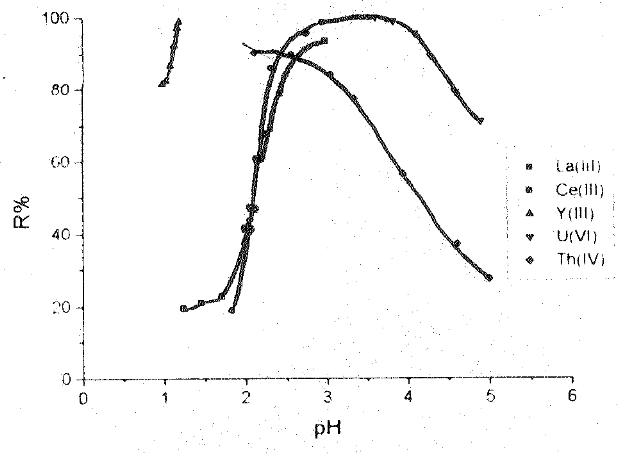

Fig. 10 Extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions with DEHPA in *n*-heptane

range than chloroform but pH ranges of La(III) and Ce(III) did not change too much in *n*-heptane and chloroform.

The extraction efficiencies for the extraction of Y(III), La(III), Ce(III) and U(VI) ions with DPP in *n*-amyl alcohol decrease by the increase in pH values. The extraction of Ce(III) ion with DPP did not change so much between chloroform and *n*-amyl alcohol but a wide pH range than chloroform for La(III) and a narrow pH range than chloroform for Th(IV) was observed.

The extraction recovery of La(III), Ce(III) and U(VI) ions with DPPA in chloroform increases similarly by the increase in equilibrium pH values but U(VI) ion was extracted at higher acidic region than La(III) and Ce(III) ions with a high extraction yield. The pH range for the extraction of U(VI) ion with DPPA in *n*-amyl alcohol rises to higher pH values than chloroform but the pH-dependence does not change and extraction efficiency increases by the increase in equilibrium pH. The extraction efficiency of Ce(III) ion with DPPA in *n*-amyl alcohol differs in chloroform and decreases by the increase at pH and the extraction proceeded at more acidic region. The extraction of Y(III) and Th(IV) ions with DPPA in *n*-amyl alcohol were also similar to the extraction of Ce(III) ions in this solvent.

All $pH_{0.5}$ values obtained from the extraction curves of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions with DEHPA, DPP and DPPA compounds in three different solvents is given in Table-1. The $pH_{0.5}$ values for La(III) and Ce(III) ions with DEHPA in chloroform and *n*-heptane were same. The pH values in the extraction of La(III) and Ce(III) ions were lower than for Th(IV) and U(VI) ions and higher than for Y(III) ion in these solvents. The $pH_{0.5}$ values for *n*-amyl alcohol were obtained at higher pH region for Y(III) and La(III) ions and at lower pH region for U(VI) ion.

TABLE-1

$PH_{0.5}$ VALUES FOR DEHPA, DPP AND DPPA COMPOUNDS

		Y(III)	La(III)	Ce(III)	Th(IV)	U(VI)
$pH_{0.5}$ (DEHPA)	*n*-Heptane	*	2.10	2.11	4.14	*
	loroform	2.28	3.72	3.72	3.26	4.56
	n-Amyl alcohol	3.73	4.35	†	—	1.67
$pH_{0.5}$ (DPP)	Chloroform	*	1.15	1.11	2.09	1.96
	n-Amyl alcohol	1.01	1.23	0.85	2.16	1.47
$pH_{0.5}$ (DPPA)	Chloroform	*	2.34	1.96	*	*
	n-Amyl alcohol	1.07	—	0.80	2.13	1.83

*High extraction efficiency (> 70%); †Low extraction efficiency (< 40%); — No extraction.

The half extraction of all metals with DPP in chloroform and *n*-amyl alcohol proceeded at low pH values. The $pH_{0.5}$ for La(III) and Ce(III) was around 1 and for Th(IV) and U(VI) was around 2. The $pH_{0.5}$ values for the extraction of Y(III), Ce(III), Th(IV) and U(VI) ions with DPPA in *n*-amyl alcohol were low as with DPP and the extraction of Ce(III) ion with DPP and DPPA in both solvents was achieved at the lowest pH 0.80.

When the $pH_{0.5}$ values for the extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions with DEHPA, DPP and DPPA in chloroform increases in the order of DPP < DPPA < DEHPA except Y(III) but in *n*-amyl alcohol this order could be given as DPP ≅ DPPA < DEHPA.

It was concluded that the liquid-liquid extraction yields of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions could be based on the chemical structure of organophosphorous extractants because of the differences in the $pH_{0.5}$ values of these studied extractants for each ion in the same extraction solvent.

Stripping behaviour of Y, La, Ce, Th and U metal complexes with DEHPA, DPP and DPPA in *n*-heptane, chloroform and *n*-amyl alcohol by using HCl and NaOH were investigated. The results shown in Figs. 11 and 12 indicate that it could be possible to strip Y(III), La(III) and Ce(III) ions into hydrochloric acid from DEHPA in *n*-heptane and chloroform. The stripping order of extracted metals was distinctly opposite to the extraction order of the studied metals. For the other solvent and the extractants no stripping curves could be designed but Table-2 shows the results of stripping studies for all metals with 1 M NaOH.

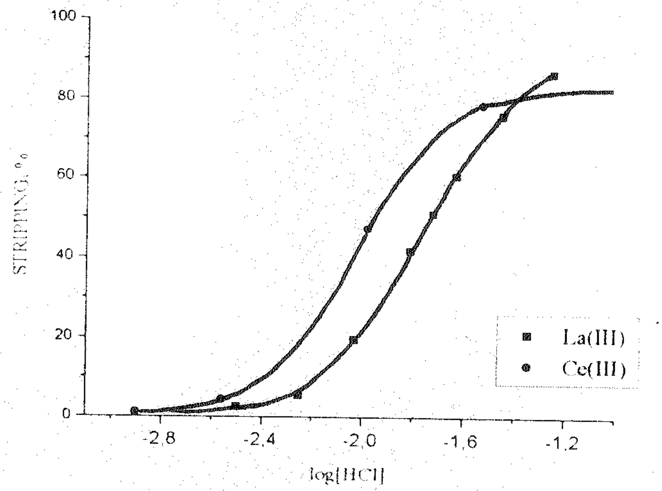

Fig. 11 Stripping curves of La (III) and Ce(III) ions into HCl from DEHPA in *n*-heptane

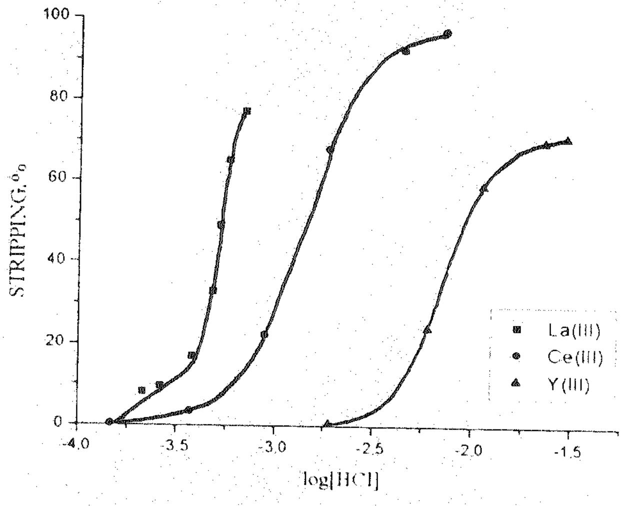

Fig. 12 Stripping curves of Y(III), La(III) and Ce(III) ions into HCl from DEHPA in chloroform.

TABLE-2

STRIPPING RESULTS OF Y(III), La(III), Ce(III), Th(IV) AND U(VI) IONS FROM DEHPA, DPP AND DPPA INTO 1M NaOH (Rs%)

		Y(III)	La(III)	Ce(III)	Th(IV)	U(VI)
DEHPA	*n*-Heptane	96.7	94.1	91.1	97.0	98.5
	loroform	77.6	93.5	97.0	89.4	80.3
	n-Amyl alcohol	79.2	91.2	98.0	---	94.9
DPP	Chloroform	75.5	92.0	96.8	94.0	99.7
	n-Amyl alcohol	87.6	98.6	94.2	96.2	98.2
DPPA	Chloroform	74.5	89.1	78.6	93.9	98.1
	n-Amyl alcohol	89.1	---	98.2	99.9	96.2

High stripping yield has been obtained with 1 M NaOH for all metal ions and with different concentrations of HCl for some studied metal ions. Stripping yields for La(III) and U(VI) ions with 1 M HCl from DEHPA in *n*-amyl alcohol were 66 and 51%, U(VI) ion from DPP in *n*-amyl alcohol was 51% and Th(IV) ion from DPPA in chloroform was 84%. Besides these, it was found that the stripping yield for Th(IV) ion from DEHPA in chloroform with 0.5 M HCl was 89% and U(VI) ion from DPP in chloroform with 0.1 M HCl was 76%.

The results obtained in this study could be summarized thus: DEHPA, DPP and DPPA compounds are suitable for the extraction of Y(III), La(III), Ce(III), Th(IV) and U(VI) ions. It was observed that chloroform and *n*-heptane were more suitable solvents than *n*-amyl alcohol for DEHPA, whereas chloroform was more suitable for DPPA and DPP. All studied metal ions were extracted in a short period of time with the high extraction yield at the different equilibrium pH values with the studied organophosphorous compounds. High stripping yield has also been obtained with 1 M NaOH for all studied metal ions and with different concentrations of HCl for La(III), Th(IV) and U(VI) ions.

REFERENCES

1. Y. Jiang, A. Shibayama, K. Liu and T. Fujita, *Hydrometallurgy*, **76**, 1 (2005).
2. C. Grüttner, V. Böhmer, A. Casnati, J.F. Dozol, D.N. Reinhoudt and M.M.R. Garcia, *J. Magnetism and Magnetic Materials*, **293**, 559 (2005).
3. Y. Nagaosa and Y. Binghua, *Fresenius J. Anal. Chem.*, **357**, 635 (1997).
4. J.L. Solka, A.H. Reis, G.W. Mason, S.M. Lewey and D.F. Peppard, *J. Inorg. Nucl. Chem.*, **40**, 663 (1978).
5. T. Wang and Y. Nagaosa, *J Chem. Tech. Biotech.*, **77**, 1316 (2002).
6. L. Soko, L. Chimuka, E. Cukrowska and S. Pole, *Anal. Chim. Acta*, 485, 25 (2003).
7. A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A.S. and M.B. Mansur, *J. Power Sources*, **115**, 367 (2003).
8. Y. Nagaosa and Y. Binghua, *Talanta*, **44**, 327 (1997).
9. P.G. Jeffery, Chemical Methods of Rock Analysis, Pergamon Press, Oxford (1970).
10. M. Yurdakoc and H. Hosgoren, *Turk J. Chem.*, **22**, 373 (1998).

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