

## Solvent Extraction and Ion Exchange Studies on the Separation of Ce, Nd, Gd, Tm and Zr

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### ABSTRACT

The sorption behavior of ionic species of Ce, Nd, Gd, Tm and Zr elements has been studied from carbonate solutions on organic and some prepared inorganic ion exchangers. In addition, their extraction behavior, in the presence of each other, from aqueous solutions containing ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepenta acetic acid (DTPA) with the organic extractants: bis-2(ethylhexyl)phosphoric acid (HDEHP), tributyl phosphate (TBP), N-lauryltrialkylamine (Amberlite-LA-2) and tricaprylmethyl ammonium chloride (TCMA) in toluene, has also been studied. The influence of some factors affecting the extraction and the sorption of ionic species of the aforementioned elements has been studied. Good separation of the studied elements from each other has been achieved.

**Key Words:** Ion Exchange /Solvent Extraction /Lanthanides /Separation.

### INTRODUCTION

Separation of lanthanides (Ln) has acquired increasing importance in the present time owing to their modern applications in various modern fields. Lanthanides and Zr present in some cases together, e.g., in the monazite ore. According to Hecht <sup>(1)</sup> Ln<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> present in monazite ore with percentages ~59.2 and 1.75, respectively. According to Greenwood and Earenschaw <sup>(2)</sup> however, Ln<sub>2</sub>O<sub>3</sub> has a percentage of ~48% in monazite. Moreover, isotopes of Zr and some lanthanides present together in some solutions, as fission products. The fission yields of these isotopes ranging from ~0.001-6.77% and ~5.90-6.28% for lanthanides and Zr, respectively. These considerable proportions of the fission products, stimulated a great surge of interest. Solvent extraction and more especially, ion exchange techniques were developed for their separation.

Concerning solvent extraction, some new extractants have been used. Recently HPLC technique has been used for rapid lanthanide and actinide separation using 2,6-bis (5,6-dipropyl-1,2,4-triazin-3-yl) pyridine (n Pr-BTP) as a modifier and HNO<sub>3</sub>-α-hydroxyisobutyric acid as mobile phase <sup>(4,5)</sup>. Cerium and other light lanthanides have been separated from heavy lanthanides and Am applying partitioning process using octyl (phenyl)-N,N-diisobutylcarbamoyl-methyl phosphine oxide (CMPO) and DTPA <sup>(6)</sup>. An advanced extraction chromatographic process has been studied for separation of minor actinides and lanthanides from HLLW, using columns packed with (CMPO) and 2,6-bis-(5,6-dialkyl-1,2-triazine-3-yl) pyridine (R-BTP)<sup>(7)</sup>. Simultaneous separation of major radionuclides (Cs, Sr, Ln and Ac) from radioactive wastes has been developed using a synergistic mixture of chlorinated cobalt dicarbollide (CCD), polyethylene glycol (PEG) and diphenyl-, N,N-di-n butyl-carbamoyl ethyl phosphine oxide (Ph<sub>2</sub>CMPO)<sup>(8)</sup>. According to Alyapyshev *et al.*, the presence of the bulky hydrophobic anion (CCD) increase the extraction of Ln metals by neutral "soft" or "hard donors" ligands <sup>(9)</sup>. Synergistic mixtures of (CCD) and diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid has been used for separation of Ln/Ac as well as, individual lanthanides <sup>(10)</sup>. Addition of N,N'-dimethyl-N,N'-di-octyl-2-(2-hexyl-oxy-ethyl) malonamide (DMDOHEMA), as phase transfer was found to

enhance the extraction kinetics for the extraction of Ln(III), Am(III) and Cm(III) using 6,6'-bis(5, 5, 8, 8-tetramethyl-5, 6, 7, 8-tetra-hydro-benzo [1,2,4] triazene-3-yl)-[2,2'] bipyridine (CyMe<sub>4</sub>-BTBP)<sup>(11)</sup>. New separation of Ln/Ac using N,N,N',N', tetrakis(2-pyridyl-methyl) ethylenediamine (TPEN) has been developed<sup>(12)</sup>. The factors affecting the extraction of Ln using (TPEN) is greatly enhanced by dissolution in ionic liquids compared to chloroform<sup>(13)</sup>. New extractants for separation of Ac/Ln has been synthesized; bis(0-trifluoromethylphenyl)phosphinic acid and bis(0-trifluoro-methylphenyl) dithiophosphinic acid<sup>(14)</sup>.

The extractant, N,N,N',N', tetra-octyl diglycol-amide (TODGA) has been evaluated for separation of Ac/Ln from high-active raffinate<sup>(15)</sup>. Mixtures of this extractants with TBP have been examined for extraction from aqueous solution containing oxalic acid, used for complexing Zr. In a similar study, a synergistic mixture of bis(chlorophenyl) dithiophosphinic acid and tris(2-ethylhexyl) phosphate dissolved in 20% isooctane and 80% tetrabutyl benzene has been used for selective separation of some Ac/ and Ln. from acidic solutions. For the same purpose, combination of new extractant, N,N,N',N', tetraoctyl-3,6-dioxatane diamide (DOODA) and a masking agent N,N,N',N', tetraethyldiglycolamide (TEDGA) has been used<sup>(17)</sup>.

With respect to ion exchange techniques, chelex-100 has been used in previous work<sup>(18)</sup> for sorption and separation of some elements of nuclear importance. Cyanex-923(trialkylphosphine oxide) coated magnetic particles (cross-linked polyacrylamide and acrylic acid entrapping charcoal and iron oxide 1:1:1) have been evaluated for Ln/Ac separation<sup>(19)</sup>. Anion exchange resin has been used for pre-irradiation and post-irradiation separations aiming at determining traces of lanthanides in some biological samples<sup>(20)</sup>. Also anion exchangers and mixed media of CH<sub>3</sub>COOH and some mineral acids have been used for sequential separation of lanthanides and some other elements in geological samples<sup>(21)</sup>. In a dynamic ion exchange chromatographic separation for rapid separation of individual lanthanides, as well as, U, Th, camphor-10-sulfonic acid (CSA) was used as ion-pairing and a-hydroxy isobutyric acid as complexing agent<sup>(22)</sup>.

The present work aims to separate Zr, Ce, Nd, Gd and Tm using ion exchange and solvent extraction techniques. The studied lanthanides are chosen to represent the light (Ce, Nd), the middle (Gd) and the heavy (Tm) lanthanides.

## EXPERIMENTAL

### Chemicals, Preparations and Instruments

All chemicals used were analytical grade quality.

HDEHP was a product of Fluka & Buchs; TBP was a product of B.D.H England, Amberlite-LA-2 was a product of Rhom & Haas, USA and TCMA was a product of Aldrich Chemical Company, USA.

Different solutions of these solvents were prepared by dilution with toluene, where the concentrations were given either in mole.L<sup>-1</sup> or in volume percent. All these extractants were used without further purifications. The concentrations of the extractants were: 0.1M (HDEHP), 20% TBP, 20% Amberlite-LA-2 and 0.1M TCMA, in toluene.

The metal oxides of Nd, Gd and Tm as well as CeCl<sub>3</sub>.7H<sub>2</sub>O, ZrOCl<sub>2</sub>.8H<sub>2</sub>O, EDTA and DTPA were products of Merck, Germany. Solutions of different concentrations, 10<sup>-5</sup> to 10<sup>-3</sup>M of EDTA and DTPA were prepared.

Chelex-100 was a product of Bio-rad Lab. GmbH, Germany. The used inorganic ion exchangers were ceric tungstate (CeW) and zirconium phosphate (ZrP). Details about the procedure used for the preparation of these ion exchangers, as well as the used materials were described in previous work<sup>(23,24)</sup>.

The radioactive isotopes <sup>141</sup>Ce, <sup>147</sup>Nd, <sup>153</sup>Gd and <sup>170</sup>Tm were used for tracing the corresponding elements and were assayed  $\gamma$ -radiometrically in the presence of each other at the corresponding characteristic  $\gamma$ -energies at 145, 91, 103 and 84 KeV, respectively, using a hyper pure Germanium detector connected to 8192 multichannel analyzer.

The radioactive isotopes were obtained by irradiating accurately weighed samples of the corresponding metal oxides M<sub>2</sub>O<sub>3</sub>, for 5 hrs in the Egyptian reactor ET-RR-2 at Inshas. The irradiated samples were then dissolved in solutions of 1N HCl of known volumes and were kept in polyethylene bottles till use.

Zr solutions were prepared by dissolving certain quantities of ZrOCl<sub>2</sub>.8H<sub>2</sub>O in known volume of 6N HCL and were kept in polyethylene bottles. Zr was assayed spectrophotometrically using arzenazo-III as cited elsewhere<sup>(25)</sup>. A spectrophoto-meter Shimadzu UV-120-20 was used for this purpose.

## **Procedure**

For studying the extraction behavior of these chosen elements from aqueous solutions of EDTA and DTPA, equal volumes (5 ml) of both aqueous and organic phases, were mechanically shaken for 30 minutes at room temperature (20±1°C). Preliminary experiments have shown that 30 min. were sufficient to reach equilibrium. After phase separation, aliquots were withdrawn from each phase for concentration determination. The distribution ratio was then determined as the ratio of the radioactivity of the individual radioisotopes of lanthanides (or Zr-concentration), in the organic phase to that in the aqueous phase.

For studying the distribution of the aforementioned elements between the organic ion exchanger Chelex-100, as well as the prepared ion exchangers (CeW) and (ZrP), and aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, 5 ml of the aqueous phase containing the studied elements at the desired (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> concentration were contacted with 0.05 g of the ion exchangers, individually, for 24 h at room temperature (20±1°C). The distribution coefficients were determined using the following equation:

$$k_d = \frac{(A_o - A)}{A} \cdot \frac{V}{m} \left[ \frac{ml}{g} \right]$$

where, A<sub>o</sub> and A are the activities of the individual isotopes of the studied lanthanides (or concentration of Zr), before and after contacting the ion exchangers, respectively, V is the volume of the aqueous phase (ml) and m is the weight of the ion exchanger in (g).

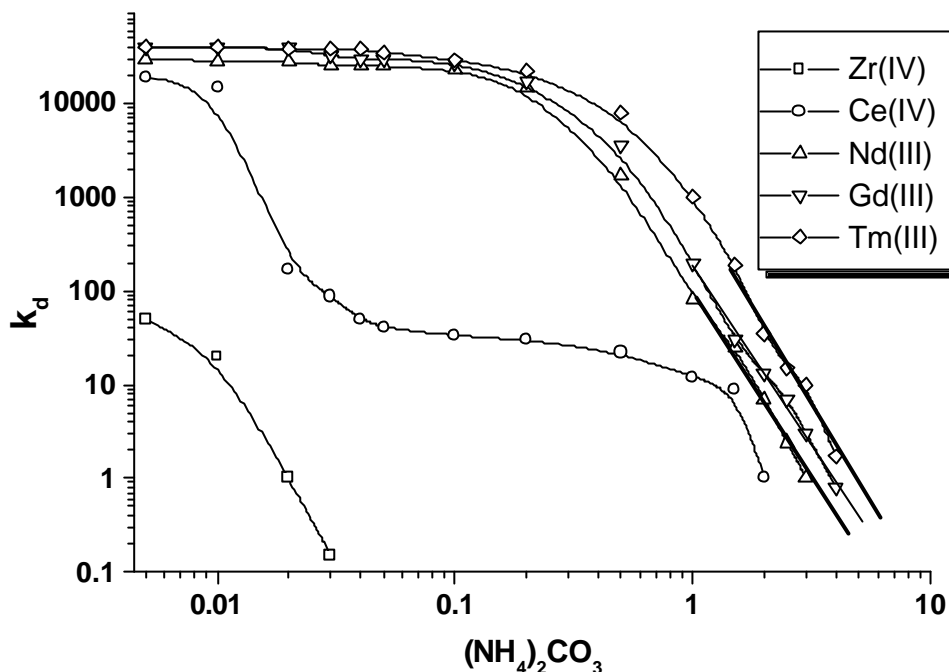
## **RESULTS AND DISCUSSION**

### **Ion Exchange**

#### **a) On Chelex-100**

Figure (1) represents the effect of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> concentration on the distribution of Zr(IV), Ce(IV), Nd(III), Gd(III) and Tm(III) between the chelating ion exchanger Chelex-100 and aqueous solutions of ammonium carbonate of concentration varies from 5.0x10<sup>-3</sup> to 4.0M. As can be seen from

this figure, the distribution ratios of all studied metal ions, generally decrease with increasing  $(\text{NH}_4)_2\text{CO}_3$  concentration. Moreover, very high distribution ratios of the trivalent lanthanides Nd(III), Gd(III) and Tm(III) are observed from dilute  $(\text{NH}_4)_2\text{CO}_3$  solutions up to 0.5M.



**Fig.(1): Effect of  $(\text{NH}_4)_2\text{CO}_3$  concentration on the sorption of Zr(IV), Ce(IV), Nd(III), Gd(III) and Tm(III) on Chelex-100.  $V/m=100$ , Temp.  $20\pm 1^\circ\text{C}$  and contact time 24h.**

With respect to cerium, high  $k_d$  values are found from  $(\text{NH}_4)_2\text{CO}_3$  solutions at concentrations =0.01M. At higher concentrations, a sharp decrease in  $k_d$ -values is observed. In  $(\text{NH}_4)_2\text{CO}_3$  solutions cerium forms stable carbonate complexes, with a spontaneous oxidation of Ce(III) to Ce(IV) <sup>(26)</sup>. This was also observed from  $\text{Na}_2\text{CO}_3$  solutions <sup>(27)</sup>. According to Doležal and Novák <sup>(28)</sup>, these complexes may have the compositions:  $[\text{Ce}(\text{CO}_3)_4]^{4-}$  or  $[\text{Ce}(\text{CO}_3)_5]^{6-}$ .

With respect to Zr(IV) the distribution ratios, are, relatively low, even at lower  $\text{CO}_3^{2-}$  concentrations and decrease very sharply with  $\text{CO}_3^{2-}$  concentration to reach negligible values at  $\text{CO}_3^{2-}$  concentrations > 0.01M. This may also be attributed to the formation of very stable negatively charged Zr-carbonate complexes. According to Busev *et al.*,<sup>(29)</sup> the carbonate complexes of Zr(IV) is readily soluble in excess ammonium carbonate. Besides, the non-absorbability of Zr-carbonate complexes on some cation exchangers has been utilized for its separation from some metal ions <sup>(30)</sup>.

These highly stable soluble carbonate complexes of Ce(IV) and Zr(IV) remain in the aqueous solutions, where the other trivalent lanthanide ions are highly adsorbed on the chelating ion exchanger Chelex-100 from carbonate solutions at concentration up to ~0.5 – 1.0M. This enables the separation of Ce which represents the main constituent among the lanthanides either in their ores <sup>(1,2)</sup> or in the fission products <sup>(3)</sup>. According to philippini <sup>(31)</sup>, the lightest lanthanides La to Nd(except Ce) form complexes of the form:  $[\text{Ln}(\text{CO}_3)_4]^{5-}$ , where as the heaviest one (Eu – Dy) form complexes of the form  $[\text{Ln}(\text{CO}_3)_3]^{3-}$ .

The high distribution ratios of the lanthanide ions Nd(III), Gd(III) and Tm(III) on Chelex-100, may be attributed to the higher stability of their complexes formed with the functional groups on the resin i.e., the iminodiacetate compared to those formed with carbonate in solution. This leads to the dissociation of the carbonate complexes in the presence of the chelating resin, and consequently results in these high  $k_d$  values. With further increase of carbonate concentration (>1M), the adsorption of all studied lanthanide ions decreases, which is attributed to the competition between the increased carbonate ions in the aqueous phase and the functional groups on the resin, for complexing the trivalent lanthanide ions.

Table (1) represents the separation factors, ( $a = k_{d1}/k_{d2}$ ) of Nd(III), Gd(III) and Tm(III), on one side from Ce(IV) and Zr(IV), as well as, from each other at certain carbonate concentrations under static conditions.

As can be observed from this table, the separation factors of Ce from Zr ranging from  $1.7 \times 10^2$  to values higher than  $3.3 \times 10^3$  depending on the  $(\text{NH}_4)_2\text{CO}_3$  concentration. With respect to the other studied lanthanides, the separation factors have very high values ranging from  $6.0 \times 10^2$  to values higher than  $2.6 \times 10^6$  as the  $(\text{NH}_4)_2\text{CO}_3$  concentration increases from  $5.0 \times 10^{-3}$  to 0.5M. In addition, very good separation of Nd, Gd and Tm from Ce can be achieved from  $(\text{NH}_4)_2\text{CO}_3$  solutions at concentration ranging from  $2.0 \times 10^{-2}$  to 0.5M, as can be deduced from the separation factors cited in Table (1). With respect to the separation of Nd, Gd and Tm from each other, low separation factors are achieved from dilute  $(\text{NH}_4)_2\text{CO}_3$  solutions, however from solutions at concentration 0.5 – 1.0M  $(\text{NH}_4)_2\text{CO}_3$ , appreciable increase of separation factors is observed. The high separation factors of cerium and zirconium from each other, as well as from the other studied lanthanide ions indicate that the use of Chelex-100, as a chelating resin, is more preferable for separation of these metal ions than on other ion exchangers. No actual separations of lanthanides from one another were achieved, as reported neither on anion exchangers nor on cation exchangers, from carbonate solutions.

**Table (1): Separation factors of Zr(IV), Ce(IV), Nd(III), Gd(III) and Tm(III) in the system  $(\text{NH}_4)_2\text{CO}_3$  –Chelex-100 under static conditions, V/m = 100 [ml/g], Temp.  $20 \pm 1^\circ\text{C}$ , contact time 24 h.**

$\text{CO}_3^{2-}$ conc.	Ce/Zr	Nd/Zr	Gd/Zr	Tm/Zr	Nd/Ce	Gd/Ce	Tm/Ce	Gd/Nd	Tm/Nd	Tm/Gd
$5 \times 10^{-3}$	$3.8 \times 10^2$	$6.0 \times 10^2$	$7.8 \times 10^2$	$8.0 \times 10^2$	1.6	2.1	2.1	1.3	1.3	-
$1 \times 10^{-2}$	$7.5 \times 10^2$	$1.4 \times 10^3$	$2.0 \times 10^3$	$2.0 \times 10^3$	1.9	2.6	2.7	1.4	1.4	-
$2 \times 10^{-2}$	$1.7 \times 10^2$	$2.8 \times 10^4$	$3.9 \times 10^4$	$3.9 \times 10^4$	$1.6 \times 10^2$	$2.3 \times 10^2$	$2.2 \times 10^2$	1.4	1.4	-
$3 \times 10^{-2}$	$5.8 \times 10^5$	$1.7 \times 10^5$	$2.1 \times 10^5$	$2.5 \times 10^5$	$2.9 \times 10^2$	$3.7 \times 10^2$	$4.4 \times 10^2$	1.3	1.5	-
$4 \times 10^{-2}$	$>1.0$ $\times 10^3$	$>5.0$ $\times 10^5$	$>6.0$ $\times 10^5$	$>7.6$ $\times 10^5$	$5.0 \times 10^2$	$6.0 \times 10^2$	$7.6 \times 10^2$	1.2	1.5	1.3
$5 \times 10^{-2}$	$>2.0$ $\times 10^3$	$>1.3$ $\times 10^6$	$>1.5$ $\times 10^6$	$>1.7$ $\times 10^6$	$6.3 \times 10^2$	$7.5 \times 10^2$	$9.0 \times 10^2$	1.2	1.4	1.2
$1 \times 10^{-1}$	$>3.3$ $\times 10^3$	$>2.3$ $\times 10^6$	$>2.7$ $\times 10^6$	$>2.9$ $\times 10^6$	$7.0 \times 10^2$	$8.2 \times 10^2$	$8.8 \times 10^2$	1.2	1.3	1.1
$2 \times 10^{-1}$	-	V.high	V.high	V.high	$5.0 \times 10^2$	$5.6 \times 10^2$	$7.3 \times 10^2$	1.1	1.5	1.3
$5 \times 10^{-1}$	-	V.high	V.high	V.high	77.3	$1.6 \times 10^2$	$3.6 \times 10^2$	2.0	4.7	2.3

**b) On ZrP and CeW:**

The sorption behavior of the studied metal ions from  $(\text{NH}_4)_2\text{CO}_3$  solutions on (ZrP) and (CeW), is represented in Table (2) as a relation between  $k_d$  and  $\text{CO}_3^{2-}$  concentration. As can be seen from this table the distribution ratios of the studied metal ions are lower than that on Chelex-100, especially on CeW. However, a similar trend in the adsorption behavior is observed. Table (3) represents the

separation factors of the studied metal ions from each others in this case. Since the  $k_d$  values for the three trivalent ions have, nearly similar values on the two ion exchangers, the separation factors of Gd, as representative of the three studied lanthanides ions from Ce(IV) and Zr(IV) are represented in Table(3).

**Table (2): Effect of  $(NH_4)_2CO_3$  concentration on the sorption of Zr(IV), Ce(IV), Nd(III), Gd(III) and Tm(III) on CeW and ZrP. V/m=100, Temp.  $20\pm 1^\circ C$ , contact time 24 h.**

$(NH_4)_2CO_3$ Conc.	Zr(IV)		Ce(IV)		Nd(III)		Gd(III)		Tm(III)	
	CeW	ZrP	CeW	ZrP	CeW	ZrP	CeW	ZrP	CeW	ZrP
0.01	40.0	45.0	90.0	$1.7 \times 10^2$	$4.2 \times 10^2$	$1.5 \times 10^3$	$4.5 \times 10^2$	$1.7 \times 10^3$	$4.7 \times 10^2$	$1.9 \times 10^3$
0.02	30.0	40.0	90.0	$1.5 \times 10^2$	$4.2 \times 10^2$	$1.5 \times 10^3$	$4.5 \times 10^2$	$1.7 \times 10^3$	$4.6 \times 10^2$	$1.8 \times 10^3$
0.04	12.0	30.0	90.0	$1.4 \times 10^2$	$4.2 \times 10^2$	$1.3 \times 10^3$	$4.5 \times 10^2$	$1.5 \times 10^3$	$4.6 \times 10^2$	$1.6 \times 10^3$
0.08	10.0	22.0	70.0	$1.3 \times 10^2$	$4.2 \times 10^2$	$1.1 \times 10^3$	$4.3 \times 10^2$	$1.3 \times 10^3$	$4.5 \times 10^2$	$1.4 \times 10^3$
0.1	3.0	18.0	60.0	$1.2 \times 10^2$	$4.1 \times 10^2$	$1.0 \times 10^3$	$4.2 \times 10^2$	$1.2 \times 10^3$	$4.4 \times 10^2$	$1.3 \times 10^3$

**Table (3): Separation factors of Zr(IV), Ce(IV) and Gd(III) in the system  $(NH_4)_2CO_3$  – CeW and ZrP.**

$(NH_4)_2CO_3$ Conc.	CeW			ZrP		
	Ce/Zr	Gd/Zr	Gd/Ce	Ce/Zr	Gd/Zr	Gd/Ce
0.01	2.25	11.25	5.0	3.8	38.0	10.0
0.02	3.0	15.0	5.0	3.75	42.5	11.0
0.04	7.5	35.0	5.0	4.7	50.0	10.0
0.08	7.6	43.0	6.1	5.9	54.5	10.0
0.1	20.0	140.0	7.0	6.7	67.0	10.0

### Solvent Extraction

The second part of this study comprises solvent extraction of the trivalent lanthanide Nd(III), Gd(III) and Tm(III) from EDTA and DTPA solutions at different concentrations, with the studied extractants, i.e., TBP, Amb. LA-1 TCMA and HDEHP in toluene.

#### a) Extraction with TBP, Amb. LA-1 and TCMA

Table (4) shows the relation between the distribution ratios of the studied trivalent lanthanides and concentration of EDTA, as well as DTPA with TBP, Amb. LA-1 and TCMA. As can be observed from this table, Nd(III) is either not extracted or very poorly extracted under all the studied conditions. Only Tm(III) is extracted to some extent. Consequently Tm(III) may be separated from the other two ions under some of the studied conditions. Trivalent lanthanides form complexes with EDTA and DTPA, of fairly high stability at high concentration (0.1M) of these complexing agents<sup>(32)</sup>. The non extractability of these complexes may be attributed either to steric hinderance or to competition of EDTA and DTPA anions for the extraction.

The mechanisms of the extraction using these studied extractants have been discussed in details in previous work<sup>(33,34)</sup>.

Table (4): Relation between distribution ratios and EDTA & DTPA concentration for the extraction of Nd(III), Gd(III) and Tm(III) with TBP, Amb.LA-1 and TCMA.

Solvent Ln(III)	TBP			Amb.LA-1			TCMA		
	Nd(III)	Gd(III)	Tm(III)	Nd(III)	Gd(III)	Tm(III)	Nd(III)	Gd(III)	Tm(III)
[EDTA] M									
$10^{-5}$	$<10^{-4}$	$<10^{-4}$	0.2	-	$<10^{-3}$	0.16	$<10^{-4}$	$<10^{-3}$	0.08
$10^{-4}$	$<10^{-4}$	$<10^{-3}$	0.22	$<10^{-3}$	$<10^{-3}$	0.17	$<10^{-4}$	0.06	0.60
$10^{-3}$	0.02	0.07	0.25	$<10^{-3}$	$<10^{-3}$	0.18	$<10^{-4}$	0.60	0.60
$10^{-2}$	0.06	0.09	0.26	$<10^{-3}$	$<10^{-3}$	0.19	6.02	0.40	0.70
$10^{-1}$	0.14	0.18	0.30	0.13	0.19	0.21	0.02	0.43	0.75
[DTPA] M									
$10^{-5}$	$<10^{-4}$	$<10^{-3}$	0.12	$<10^{-3}$	0.03	0.16	$<10^{-4}$	$<10^{-4}$	0.40
$10^{-4}$	$<10^{-4}$	$<10^{-3}$	0.19	$<10^{-3}$	0.03	0.16	$<10^{-4}$	$<10^{-4}$	0.43
$10^{-3}$	$<10^{-4}$	0.06	0.22	$<10^{-3}$	0.07	0.17	$<10^{-4}$	$<10^{-4}$	0.45
$10^{-2}$	0.06	0.15	0.23	$<10^{-3}$	0.07	0.18	$<10^{-4}$	0.04	0.50
$10^{-1}$	0.14	0.18	0.24	0.16	0.19	0.20	$<10^{-4}$	0.04	0.50

**b) Extraction with HDEHP**

Figure (2) represents the relation between D-values and EDTA, as well as DTPA concentrations. Nd(III) is not extracted from solutions of EDTA or DTPA at the studied concentrations. With respect to Gd(III) and Tm(III), the D-values, generally decrease with the EDTA and DTPA concentration. The D-values of Tm(III) are 100 folds higher than that of Gd(III). This enables very good separation of the three lanthanide ions from each other.

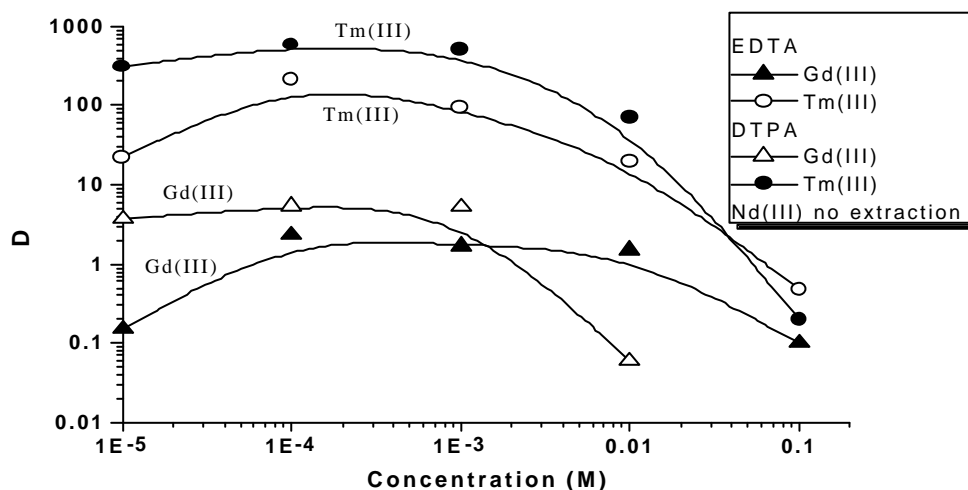
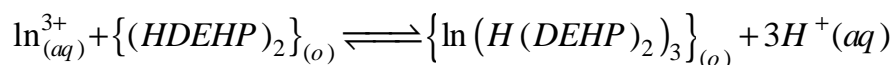


Fig.(2): Effect of EDTA and DTPA concentration on the distribution ratios of Gd(III) and Tm(III) for the extraction with 0.1M HDEHP in toluene .

The decrease in the distribution ratios with the EDTA and DTPA concentration reflects the increase of the stability of the formed EDTA and DTPA complexes with the increase of concentration. However, at low concentration of EDTA and DTPA these complexes of trivalent lanthanide ions

dissociate in the presence of the extractant owing to formation of complexes with the extractant in the organic phase, according to the following equation:

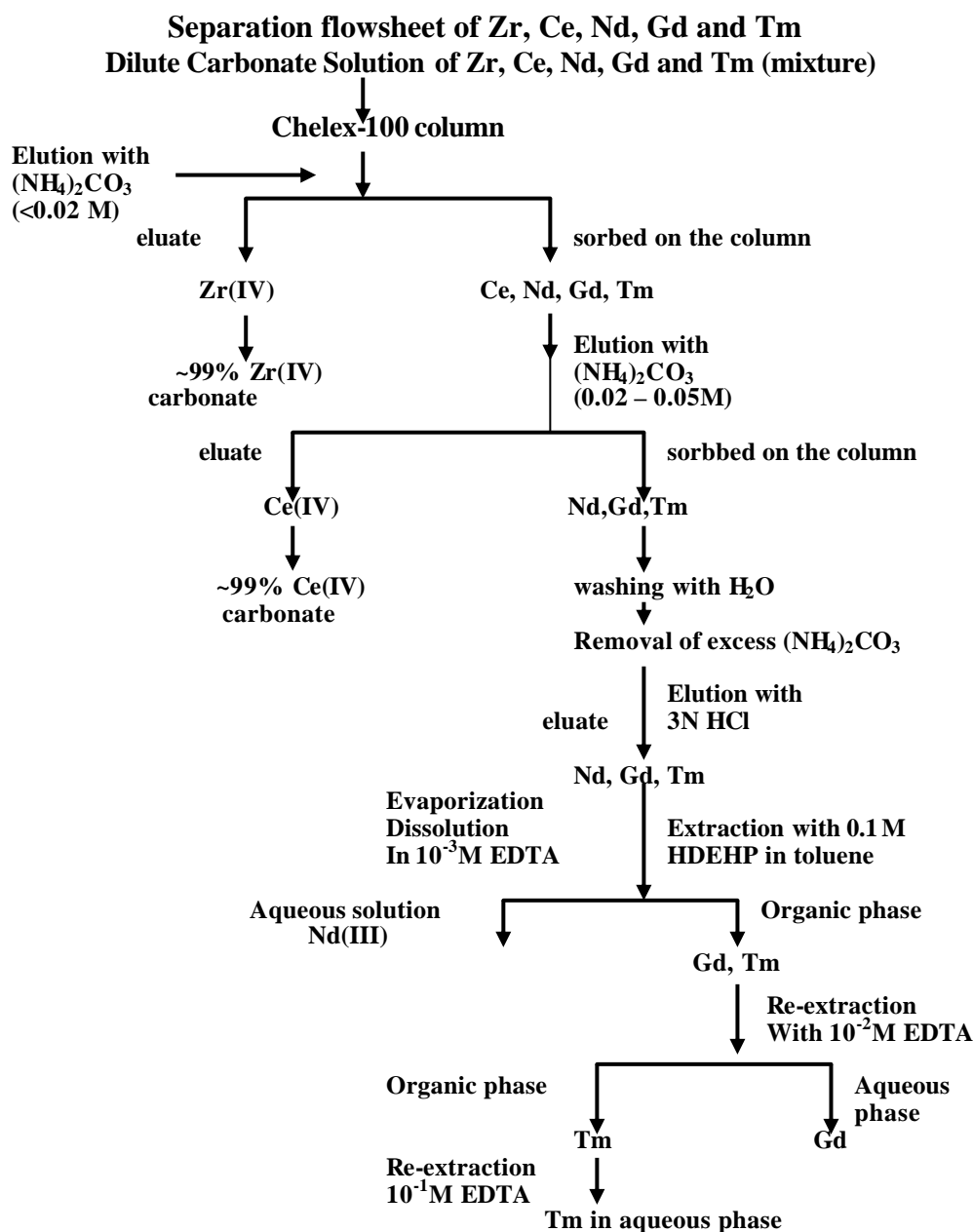


where  $\text{Ln}^{3+}$  is a trivalent lanthanide ion (aq) and (o) refers to aqueous and organic phases, respectively.

The sum of the effects of the two complexing agents in the aqueous and organic phases results in a good separation of the studied lanthanide ions.

### Proposed Separation Processes

A proposed separation steps are illustrated on the following flowsheet:





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