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Liquid-Liquid Extraction Studies of Trivalent Yttrium from Phosphoric Acid Solutions Using TOPS 99 as an Extractant

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Liquid-liquid extraction studies of trivalent yttrium (Y) from phosphoric acid solutions have been carried out with commercial organophosphoric acid based extractant TOPS 99 (Talcher Organo phosphorus solvent, an equivalent of di-2-ethylhexyl phosphoric acid). The parameters studied include equilibration time, acid concentration, extractant concentration, diluent, metal concentration, temperature, stripping, and regeneration of the extractant. Increase of phosphoric acid concentration in the range from 0.01 to 0.5 M on the extraction of trivalent Y with 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent) decreases the percentage extraction, indicating the transfer of metal follows ion exchange type reaction. The plot of $\log D$ vs. equilibrium pH gave a straight line with a slope of 3.1 indicating the exchange of three moles of hydrogen ions for every mole of trivalent Y extracted into the organic phase. Stripping of metal from the loaded organic with mineral acids indicate sulphuric acid as the best stripping agent. The extraction behavior of associated elements clearly follows their ionic radii with a maximum separation factor of 414 for Lu-Tb.

Keywords associated metals; phosphoric acid; separation factors; TOPS 99 (talcher organo phosphorus solvent); trivalent yttrium

INTRODUCTION

During the past decades, the separation and purification of rare earth elements has gained considerable importance with the increasing demand for these elements and their compounds individually and collectively. The largest use of rare earths has been in fluorescent lighting phosphors, computer displays, and ceramics followed closely by automotive catalytic converters. The main sources of rare earth elements, especially for yttrium, are xenotime, fergusonite, and gadolinite. In addition to these, rock phosphates are a major source for production of fertilizer grade phosphoric acid and also contain minor quantities of rare earth (RE) elements. Phosphate rocks generally contain uranium about 30–100 mg/Kg and other rare earths less than 100 mg/Kg depending on the source of rock phosphate. The industrial wet process phosphoric acid (WPA) uses

sulphuric acid to leach the phosphate rock and the leach liquor obtained is a complex solution with organic and inorganic impurities (heavy metals). The removal of heavy metals from these effluents is environmentally important referring mainly to their toxicity (1). Efforts are being made to recover uranium from fertilizer grade wet phosphoric acid. There are no reports on the solvent extraction studies of yttrium from phosphoric acid solutions using commercial organophosphorus based reagents.

Separation processes of heavy metals from phosphoric acid by classical precipitation (2) and solvent extraction by organophosphorus and thio organophosphorus acid based reagents have been proposed to deal with the problem. Mellah and Benachour (3) reported solvent extraction studies of heavy metals from phosphoric acid. Literature search revealed that various kinds of organophosphorus based extractants such as di-(2-ethylhexyl)-phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC 88A), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) have been widely used from mineral acid solutions for the separation and purification of rare earth elements (4–10). Wu et al. (11) studied the extraction and separation of trivalent Ho, Y, and Er with the mixtures of Cyanex 302 and another extractant, such as P204, P507, P229, CA-100, Cyanex 925, TBP, P350, or N1923. They concluded that Cyanex 302 individually and combined with others show same extraction efficiency. Wang et al. (12) reported the quantitative extraction of Ytterbium by Cyanex 923 from sulfuric acid medium at equilibrium pH 3.0. The extracted species appears to be $\text{YbSO}_4(\text{HSO}_4) \cdot 2\text{Cyanex 923}$ following salvation mechanism. In another study, the separation of Y from the rare earths with sec-octylphenoxy acetic acid in chloride media was reported (13). Reddy et al. (14) reported the extraction of trivalent lanthanides and yttrium from nitrate solutions by TRPO as $\text{M}(\text{NO}_3)_3 \cdot 3\text{TRPO}$, where TRPO denotes Cyanex 923, whereas Gupta et al. (15) reported the species as $\text{M}(\text{NO}_3)_3 \cdot 2\text{TRPO}$ from nitric, hydrochloric, sulphuric, and phosphoric acid media and

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possible separation of trivalent lanthanides and yttrium. Desouky et al. (16) studied liquid-liquid extraction of yttrium using primene-JMT from acidic sulfate solutions.

Literature survey on solvent extraction and separation of rare earths reveals that a lot of work has been carried out from mineral acid media. However, there are few studies on the extraction behavior of heavy rare earths (HREs) from phosphoric acid (H_3PO_4) medium. Koopman et al. (17) examined the separation possibility of heavy metals and lanthanides from a fertilizer industry phosphoric acid by solvent extraction with D2EHPA, DDNSA (di dodecyl naphthalene sulphonic acid), Cyanex 301/302 and Aliquat 336 and Alanmine 336 and ion exchange using Dowex C-5000 and Amberlite IR-120. Cationic carriers showed selectivity for heavy metals and anionic carriers showed selectivity for mercury. D2EHPA showed affinity for the heavy lanthanide ions and increased with increasing atomic number, where as DDNSA showed affinity for all lanthanide ions and increased with decreasing atomic number. Krea and Khalaf (18) studied the solvent extraction of uranium and lanthanides from phosphoric acid. The present paper deals with the solvent extraction studies of Y (III) from phosphoric acid solutions with TOPS 99 (Talcher Organo phosphorus solvent) as extractant. The parameters studied include the effect of time, acid concentration, extractant concentration, diluent, metal concentration temperature, stripping of metal from loaded organic phase, and the extraction behavior of commonly associated rare earth ions and separation factors.

EXPERIMENTAL

Chemicals and Reagents

TOPS 99, Talcher Organo phosphorus solvent, an equivalent of di-2-ethylhexyl phosphoric acid from Heavy Water Plant, Talcher, India, was used as such without purification. Distilled kerosene (boiling point: 433–473 K) mostly aliphatic (96.2%) was used as diluent. The stock solution of trivalent yttrium was prepared by dissolving yttrium oxide (>99.9%) supplied by Treibacher Industry AG, Austria in concentrated hydrochloric acid. Analytical grade, H_3PO_4 (88%, specific gravity 1.75) was used. The concentrations of rare earth ions in stock solutions were estimated by EDTA titration using xylenol orange as an indicator (19). Working solutions were prepared by suitable dilution of these stock solutions. All other reagents used were of analytical grade.

Apparatus

A Digital pH meter (Digisun electronics, Model D707) was used for pH measurements. A temperature controlled shaking water bath (Jeio Tech, Model BS-06) was used for equilibrium studies. A Thermo Electron make inductively coupled plasma optical emission spectrometer (ICP-OES)

TABLE 1
Operating parameters of ICP-OES

RF Power	1150 W
Plasma gas flow rate	12 lpm
Auxiliary gas flow rate	1.0 lpm
Nebulizer gas flow rate	1.0 lpm
Wave lengths (nm)	
Yttrium	371.030
Terbium	350.917
Dysprosium	353.170
Holmium	345.600
Erbium	349.910
Ytterbium	328.937
Lutetium	261.542

(Model, IRIS Intrepid II XDL) was used to determine the rare earth ions in the aqueous solutions. The operating conditions of ICP-OES were given in Table 1.

Extraction Procedure

An aqueous feed solution containing 5.6×10^{-4} M trivalent yttrium was used for all the extraction experiments. Experiments were performed by shaking equal volumes (10 ml) of aqueous and organic phases for 15 min (sufficient to attain equilibrium) in reagent bottles using a thermostatic shaking water bath adjusted to 303 K. After equilibrium, the contents were allowed for phase disengagement. The two phases were separated using a separating funnel, the traces of organic impurities in the aqueous phase were removed with Whatman phase separation (1 PS) paper, and the equilibrium pH of aqueous phase was measured using pH meter. 2 ml of aqueous phase before and after extraction was taken for determination of metal ion concentration by ICP-OES after proper dilutions.

The distribution ratio (D) was calculated from the relation: $D = (C_o - C)/C$, where, C_o is the metal ion concentration in the aqueous phase before extraction and C is the metal ion concentration in the aqueous phase after extraction. Stripping experiments were carried out by shaking equal volumes of (5 ml) the organic phase loaded with the extracted metal for 15 min with a known volume of the aqueous acid solution under study. The concentration of the metal ion in the aqueous phase was determined and the stripping percent (%Strip) was calculated by the following relation: % Strip = $[C_s/(C_o - C)] \times 100$. Where, C_s is the stripped metal ion concentration in the aqueous phase after stripping.

RESULTS AND DISCUSSION

Effect of Equilibration Time

Figure 1 shows the time required to reach equilibrium, the percent extraction of trivalent Y was determined as a function of time 2–60 min at constant concentration of acid

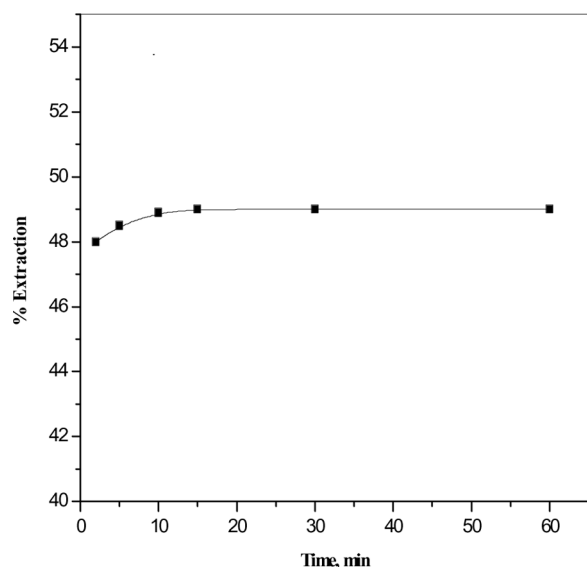


FIG. 1. Effect of equilibration time on percentage extraction of yttrium. Experimental conditions: $[\text{TOPS 99}] = 6 \times 10^{-3} \text{ M}$, $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$, $[\text{Y(III)}] = 5.6 \times 10^{-4} \text{ M}$, equilibration time = 2–60 min, temperature = 303 K.

0.1 M, metal $5.6 \times 10^{-4} \text{ M}$ and extractant $6 \times 10^{-3} \text{ M}$. It was observed that 15 min was sufficient to reach equilibrium for metal extraction. All the subsequent experiments were conducted by shaking the aqueous and organic phase together for 15 min.

Effect of Acid Concentration

Studies on the extraction of Y with $5.6 \times 10^{-4} \text{ M}$ were conducted using $6 \times 10^{-3} \text{ M}$ TOPS 99 (Talcher Organo phosphorus solvent) in kerosene as diluent in the acid range from 0.01 to 0.5 M. The corresponding change in the equilibrium pH of aqueous phase was 1.82–1.21. The percentage extraction of metal increased with decreasing acid concentration (Fig. 2) and increasing equilibrium pH, indicating the transfer of metal follows ion exchange mechanism. The percentage extraction increased from 9–87% in the equilibrium pH range from 1.2 to 1.82. Further, the plot of equilibrium pH vs. $\log D$ (Fig. 2) is linear with a slope of 3.1 ± 0.1 confirming the exchange of three moles of protons from the extractant for each mole of metal extracted.

Effect of Extractant Concentration

The effect of TOPS 99 (Talcher Organo phosphorus solvent) concentration on the percentage extraction of trivalent Y ($5.6 \times 10^{-4} \text{ M}$) in 0.1 M H_3PO_4 has been investigated by varying the extractant concentration in the range 3×10^{-3} – $1 \times 10^{-2} \text{ M}$. It was observed that the percentage extraction of yttrium increased from 19–88% (Fig. 3) with increase in the extractant concentration from 3×10^{-3} – $1 \times 10^{-2} \text{ M}$, respectively. The plot of the log extractant vs. $\log D$ (Fig. 3) shows that the plot gave a straight line with slope 2.9, indicating that three moles of

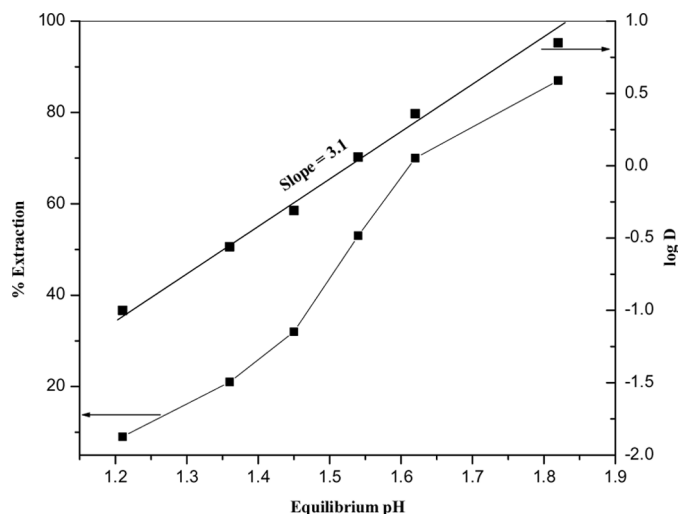


FIG. 2. Effect of equilibrium pH on extraction of yttrium with TOPS 99. Experimental conditions: $[\text{TOPS 99}] = 6 \times 10^{-3} \text{ M}$, $[\text{H}_3\text{PO}_4] = 0.01$ – 0.5 M , $[\text{Y(III)}] = 5.6 \times 10^{-4} \text{ M}$, equilibration time = 15 min, temperature = 303 K.

TOPS 99 (Talcher Organo phosphorus solvent) are involved with in the extracted complex.

Effect of Metal Concentration

Variation of metal concentration in the range 3×10^{-3} – $1 \times 10^{-2} \text{ M}$ on the extraction of trivalent yttrium was studied from 0.1 M H_3PO_4 with $6 \times 10^{-3} \text{ M}$ TOPS 99 (Talcher Organo phosphorus solvent). With an increase of metal concentration from $3 \times 10^{-3} \text{ M}$ to $8.9 \times 10^{-3} \text{ M}$, D values decreased systematically ($D = 0.22$ – 0.11) and remained constant thereafter ($D = 0.09$). The log-log plot (Fig. 4) of equilibrium organic phase metal concentration against

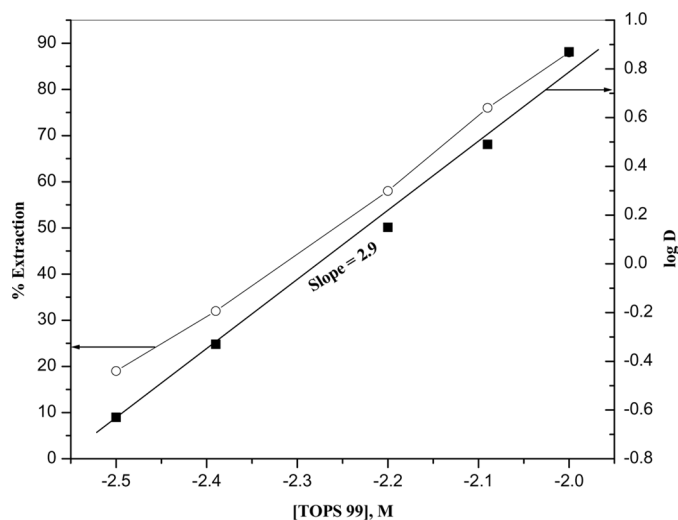


FIG. 3. Effect of extractant concentration on extraction of yttrium. Experimental conditions: $[\text{TOPS 99}] = 3 \times 10^{-3}$ – $1 \times 10^{-2} \text{ M}$, $[\text{H}_3\text{PO}_4] = 0.1 \text{ M}$, $[\text{Y(III)}] = 5.6 \times 10^{-4} \text{ M}$, equilibration time = 15 min, temperature = 303 K.

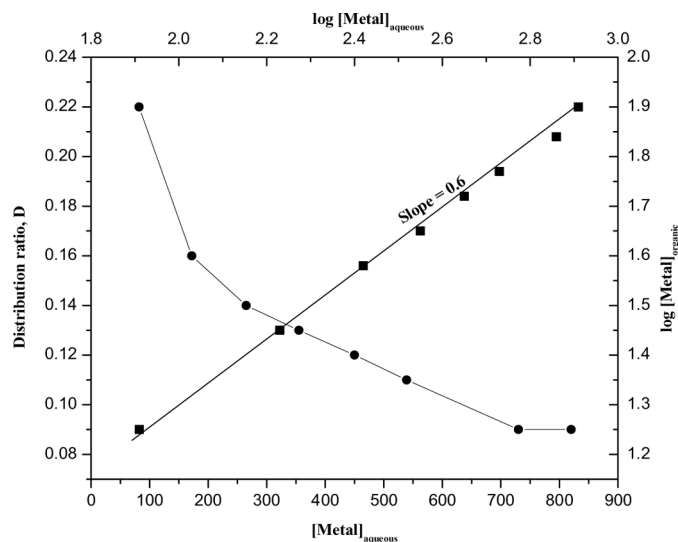
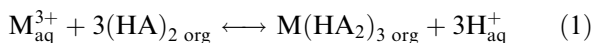


FIG. 4. Effect of metal concentration on distribution ratio of yttrium with TOPS 99. Experimental conditions: [TOPS 99] = 6×10^{-3} M, $[H_3PO_4] = 0.1$ M, $[Y(III)] = 3 \times 10^{-3} - 1 \times 10^{-2}$ M, equilibration time = 15 min, temperature = 303 K.

aqueous phase metal concentration is linear with the slope equal to 0.6 indicating the extraction of mononuclear species into the organic phase. Extraction mechanism and equilibrium

The extraction equilibrium of trivalent Y from phosphoric acid solutions with TOPS 99, Talcher Organic phosphorus solvent, can be presented as



Where, M represents the metal, and $(HA)_2$ represents the dimeric form of TOPS 99 (Talcher Organo phosphorus solvent) in kerosene (20).

The equilibrium constant, K_{ex} is defined as

$$K_{ex} = \frac{[M(HA_2)_3]_{org} [H^+]^3}{[M^{3+}] [(HA)_2]^3} \quad (2)$$

$$K_{ex} = \frac{D [H^+]^3}{[(HA)_2]^3} \quad (3)$$

$$\text{Where } D = \frac{[M(HA_2)_3]_{org}}{[M^{3+}]} \quad (4)$$

Taking logarithm of Eq. (3), and rearranging,

$$\log D = \log K_{ex} + 3 \log [(HA)_2] + 3 \text{ pH} \quad (5)$$

The number of moles of the extractant involved in the extraction equilibrium was estimated by analyzing the experimental data of D as a function of acid and extractant concentration at constant value of other parameters. From

the data effect of acid, metal, and extractant concentration variation, the species extracted appears to be $Y_3(HA_2)$. The equilibrium constant was calculated by considering complex constants of Y (III) and phosphate in aqueous phase as well as dissociation constant of H_3PO_4 (21). The calculated value of $\log K_{ex}$ is 0.99 ± 0.1 (Fig. 2 data).

Effect of Diluents and Temperature

The behavior of the diluent on the percentage extraction of trivalent Y with 5.6×10^{-4} M was studied from 0.1 M H_3PO_4 using 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent) dissolved in various diluents. The difference in extractive properties of an extractant in various diluents is usually reported to a varying extent of non-ideality of the solutes in diluent. A quantitative determination of these effects is at present hardly possible because of the lack of data on the physico-chemical properties of the systems. The results demonstrate that the percentage extraction of trivalent Y varies with the nature of diluent and increases in the order (% E): nitrobenzene (0) < toluene (5) < benzene (13) < kerosene (53) < cyclohexane (76) < n-hexane (91). The effect of temperature was studied from 303 to 363 K with the aqueous phase containing 5.6×10^{-4} M trivalent yttrium at 0.1 M H_3PO_4 using 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent). Variation of temperature in the range of 303–333 K showed no effect on the percent extraction of metal ($50\% \pm 1$), whereas a 20% increase of extraction was observed in the temperature range of 343–363 K.

Stripping Studies

In any commercial extraction process it becomes imperative to back extract the metal from the loaded organic (L.O) phase. The L.O phase for the stripping study was generated by contacting the organic phase 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent) and the aqueous phase (5.6×10^{-4} M Y) in a single stage at 0.01 M H_3PO_4 . L.O containing 0.042 g/l Y was stripped with various stripping agents such as H_2SO_4 , HCl and HNO_3 in the concentration range from 0.1–1.0 M and the results are presented in Table 2. Stripping of Y from L.O increases with increasing acid concentration and reaches quantitative stripping at >0.5 M acid concentrations. Comparison of stripping efficiency of acids at 0.1 M follows the order: H_2SO_4 (87%) > HCl (54%) > HNO_3 (45%).

Regeneration and Recycling Capacity of TOPS 99

Experiments on the recycling capacity of 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent) (Fig. 5) was conducted for the extraction of yttrium (5.6×10^{-4} M) with 0.01 M H_3PO_4 and stripping of metal from L.O with 0.5 M HCl. Single-stage extraction gave L.O containing 0.042 g/l trivalent Y corresponding to 87.0% yttrium

TABLE 2
Stripping of yttrium from loaded organic phase

[Acid] (M)	Stripping (%)		
	H ₂ SO ₄	HCl	HNO ₃
0.1	86.9	54.3	45.6
0.2	98.2	90.3	89.5
0.3	99.9	99.9	99.5
0.4	100	100	100
0.5	100	100	100
1.0	100	100	100

extraction efficiency. This L.O was further stripped with 1 M HCl that corresponds to 100% yttrium stripping efficiency. The stripped L.O was washed with distilled water. The regenerated organic phase was then used for second cycle extraction-stripping of metal and continued for six cycles. The recovery of each stage was calculated from the amount of Y extracted into the organic phase at each particular cycle. It was observed that there was no appreciable change in the percentage extraction/stripping of Y, which suggests the stability of reagent.

Comparison of the Extraction Behavior of Yttrium with Other Associated Metal Ions

The extraction behavior of commonly associated metals with yttrium such as trivalent terbium, Tb (3.1×10^{-4} M), dysprosium, Dy (3.0×10^{-4} M), holmium, Ho (3.0×10^{-4} M), erbium, Er (2.91×10^{-4} M), ytterbium,

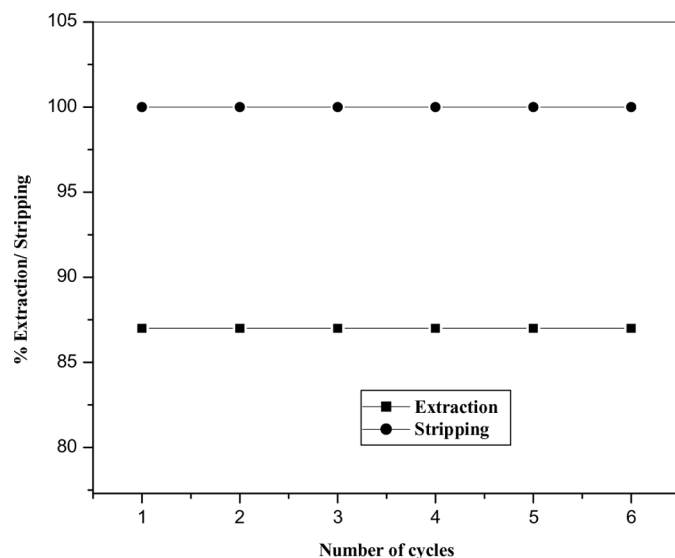


FIG. 5. Regeneration and recycling capacity of TOPS 99. Experimental conditions: [TOPS 99] = 6×10^{-3} M, [H₃PO₄] = 0.01 M, [Y(III)] = 5.6×10^{-4} M, equilibration time = 15 min, temperature = 303 K.

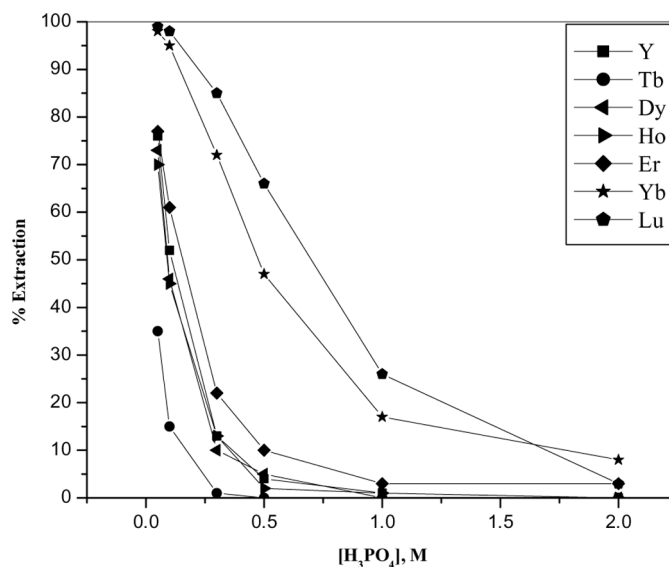


FIG. 6. Extraction of associated metals as a function of acid concentration. Experimental conditions: [TOPS 99] = 6×10^{-3} M, [H₃PO₄] = 0.05–2 M, [Y(III)] = 5.6×10^{-4} M, [Tb(III)] = 3.1×10^{-4} M, [Dy(III)] = 3.0×10^{-4} M, [Ho(III)] = 3.0×10^{-4} M, [Er(III)] = 2.91×10^{-4} M, [Yb(III)] = 2.8×10^{-4} M, [Lu(III)] = 2.8×10^{-4} M, equilibration time = 15 min, temperature = 303 K.

Yb (2.8×10^{-4} M) and lutetium, Lu (2.8×10^{-4} M) have been studied as a function of phosphoric acid concentration in the range from 0.05 to 2 M using 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent) (Fig. 6). It was observed that the percent extraction of all the metals decreases with increasing acid concentration. Further, the results suggest possible separation of Lu/Yb from Tb selectively or separation of Lu and Yb from other metals around 0.3–0.5 M acidity. Separation factors (β) for Lu and Yb from others at 0.1 M and 0.3 M H₃PO₄ concentration were calculated (Table 3). The observed decrease in β values (entries 1–5) for Lu and (entries 6–10) for Yb clearly follows the decrease in ionic radii of Dy (99 pm), Y (97.4 pm), Ho (97 pm), and Er (96 pm). Similar results were also observed at 0.1 M acid (entries 11–20). The separation factors for trivalent yttrium from other metals at 0.3 M acid were calculated and a comparison of these β values with already reported values (13,22) were given in Table 4. Equilibrium constant, $\log K_{\text{ex}}$ were determined for all the metals without considering metal phosphate formation constants and dissociation constant of H₃PO₄ in aqueous solutions at 0.1 M and 0.3 M (Table 5). The results suggest $\log K_{\text{ex}}$ values are inversely proportional to ionic radii of metals with the exception of Ho, Y, and Dy, the $\log K_{\text{ex}}$ remains same. The higher the $\log K_{\text{ex}}$ value of a particular metal ion indicates high extraction efficiency the better possible separation over the others. With an increase in acid

concentration, a decrease in $\log K_{\text{ex}}$ values observed for all the metals.

Determination of Separation Factors for Binary and Ternary Metal Ion Systems

Based on the β values for single metal ions as shown in Fig. 6, Table 3, the separation factors for the ternary mixtures containing Tb (1.0×10^{-4} M), Y (1.7×10^{-4} M), Yb (9.2×10^{-5} M) and Lu (9.1×10^{-5} M) were determined from 0.1 M H_3PO_4 with 6×10^{-3} M TOPS 99 (Talcher Organo phosphorus solvent). The percentage extraction of Y and Tb was nil, whereas Yb and Lu were 95% extracted. A combination of the ternary mixture (Y, Tb, and Lu) and binary mixtures (Lu-Tb and Tb-Yb) the separation factors were determined. The β values obtained for Lu with Y and Tb in ternary (Lu-Y and Lu-Tb pairs) and binary (Lu-Tb and Tb-Yb) systems (Table 6) were comparable with those obtained for Lu with Y, Tb, studied individually (Table 3), supporting the high separation possibility of Lu from Tb.

TABLE 3
Determination of separation factors ($\beta = D_a/D_b$) of associated metal ions

Entry	[H_3PO_4], M	Distribution Ratio		Separation factor
		a	b	
1	0.3	Lu 5.8	Tb 0.01	414
2	0.3	Lu 5.8	Dy 0.10	58
3	0.3	Lu 5.8	Ho 0.14	41
4	0.3	Lu 5.8	Y 0.15	38
5	0.3	Lu 5.8	Er 0.28	21
6	0.3	Yb 2.5	Tb 0.01	180
7	0.3	Yb 2.5	Dy 0.10	25
8	0.3	Yb 2.5	Ho 0.14	18
9	0.3	Yb 2.5	Y 0.15	17
10	0.3	Yb 2.5	Er 0.28	9
11	0.1	Lu 59.1	Tb 0.17	347
12	0.1	Lu 59.1	Dy 0.81	72
13	0.1	Lu 59.1	Ho 0.84	70
14	0.1	Lu 59.1	Y 1.06	55
15	0.1	Lu 59.1	Er 1.57	37
16	0.1	Yb 20.3	Tb 0.17	119
17	0.1	Yb 20.3	Dy 0.81	25
18	0.1	Yb 20.3	Ho 0.84	24
19	0.1	Yb 20.3	Y 1.06	19
20	0.1	Yb 20.3	Er 1.57	13

Experimental conditions: [TOPS 99] = 6×10^{-3} M, [H_3PO_4] = 0.05–2 M, [Y(III)] = 5.6×10^{-4} M, [Tb(III)] = 3.1×10^{-4} M, [Dy(III)] = 3.0×10^{-4} M, [Ho(III)] = 3.0×10^{-4} M, [Er(III)] = 2.91×10^{-4} M, [Yb(III)] = 2.8×10^{-4} M and [Lu(III)] = 2.8×10^{-4} M, equilibration time = 15 min, temperature = 303 K.

TABLE 4
Comparison of β values of Y(III) with reported literature

Metal pair	HCl* (CA-12)	$\text{HNO}_3^\#$ (Cyanex 925)	0.3 M H_3PO_4 (TOPS 99)
Y-Tb	4.1	0.95	15
Y-Dy	2.8	0.79	1.5
Y-Ho	2.5	0.81	1.0
Y-Er	2.0	0.81	1.8
Y-Yb	2.1	0.61	17
Y-Lu	1.6	0.65	38

*Ref (13).

$^\#$ Ref (22).

TABLE 5
Evaluation of log equilibrium constant, $\log K_{\text{ex}}$ for the extraction of rare earths by TOPS 99

RE	Ionic radii (pm)	Acid, 0.1 M		$\log K_{\text{ex}}$	Acid, 0.3 M		$\log K_{\text{ex}}$
		D	% E		D	% E	
Lu	93	59.1	98	3.87	5.81	85	3.58
Yb	94	20.3	95	3.37	2.53	72	3.04
Er	96	1.57	61	2.35	0.28	22	2.16
Ho	97	0.81	45	2.02	0.15	13	1.87
Y	97.4	1.15	52	2.1	0.27	21	2.02
Dy	99	0.84	46	2.06	0.1	9	2.08
Tb	100	0.17	15	1.58	0.01	1	1.15

Experimental conditions: [TOPS 99] = 6×10^{-3} M, [H_3PO_4] = 0.05–2 M, [Y(III)] = 5.6×10^{-4} M, [Tb(III)] = 3.1×10^{-4} M, [Dy(III)] = 3.0×10^{-4} M, [Ho(III)] = 3.0×10^{-4} M, [Er(III)] = 2.91×10^{-4} M, [Yb(III)] = 2.8×10^{-4} M and [Lu(III)] = 2.8×10^{-4} M, equilibration time = 15 min, temperature = 303 K.

TABLE 6
Determination of separation factors for binary and ternary mixture of metal ions

System	Metal pair	D	β
Binary*	Lu-Tb	55.8–0.15	372
Binary*	Yb-Tb	27.2–0.11	247
Ternary $^\#$	Lu-Tb	22.7–0.07	324
Ternary $^\#$	Lu-Y	22.7–0.55	41

Experimental conditions: [TOPS 99] = 6×10^{-3} M, [H_3PO_4] = 0.1 M.

*[Lu(III)] = 1.4×10^{-4} M, [Yb(III)] = 1.4×10^{-4} M, [Tb(III)] = 1.5×10^{-4} M.

$^\#$ [Lu(III)] = 1.1×10^{-4} M, [Y(III)] = 2.2×10^{-4} M, [Tb(III)] = 1.2×10^{-4} M.

CONCLUSIONS

In this paper, we report the extraction behavior of Y from phosphoric acid medium using the commercially available organophosphoric acid based extractant TOPS 99 (Talcher Organo phosphorus solvent). Solvent extraction studies of trivalent yttrium from phosphoric acid medium with TOPS 99 (Talcher Organo phosphorus solvent) diluted in kerosene confirmed the transfer of metal follows cation exchange mechanism. Extraction of Y depends on time, diluent, acid, extractant, and metal concentration of the aqueous phase. The species extracted appears to be $M(HA_2)_3$ (M: trivalent RE ion). Stripping of metal with HCl from L.O and its recycling for the extraction of Y for six cycles indicated the greater stability of TOPS 99 (Talcher Organo phosphorus solvent). Extraction of metals such as Tb, Dy, Ho, Er, Yb, and Lu which are generally associated with Y showed that there is a possibility for separation of Lu and Yb from Tb and other associated metals. β values obtained for ternary mixtures and binary mixtures were comparable with individual metal β values. The results of the present study will be applied to rare earths extraction from WPA solutions for their practical importance.

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REFERENCES

- Schrodter, K.; Bettermann, G.; Stiffed, T.; Klein, T.; Hofmann, T. (1998) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th Ed.; Wiley-VCH: Weinheim, Germany.
- Ennaassia, Et.; El Kacemi, K.; Kossir, A.; Cote, G. (2002) Study of the removal of Cd (II) from phosphoric acid solutions by precipitation of CdS with Na_2S . *Hydrometallurgy*, 64 (2): 101–109.
- Mellah, A.; Benachour, D. (2006) Solvent extraction of heavy metals containing phosphoric acid solutions by 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline in kerosene diluent. *Hydrometallurgy*, 81 (2): 100–103.
- El-Nadi, Y.A.; El-Hefny, N.E.; Daoud, J.A. (2007) Extraction of lanthanum and samarium from nitrate medium by some commercial organophosphorus extractants. *Solvent Extr. Ion Exch.*, 25 (2): 225–240.
- Ohto, K.; Yoshida, S.; Yoshizuka, K.; Inoue, K.; Ohtsuka, M.; Goto, M.; Nkashio, F. (1995) Solvent extraction equilibria of rare earth metals by acidic organophosphorus extractants with bulky substituents. *Anal. Sci.*, 11 (4): 637–641.
- Rabie, K.A. (2007) A group separation and purification of Sm, Eu and Gd from egyptian beach monazite mineral using solvent extraction. *Hydrometallurgy*, 85 (2–4): 81–86.
- Morais, C.A.; Ciminelli, V.S.T. (2007) Selection of solvent extraction reagent for the separation of europium(III) and gadolinium(III). *Miner. Eng.*, 20 (8): 747–752.
- Wu, D.; Niu, C.; Li, D.Q.; Yan, B. (2004) Solvent extraction of scandium(III), yttrium(III), lanthanum(III) and gadolinium(III) using Cyanex 302 in heptane from hydrochloric acid solutions. *J. Alloys Comp.*, 374 (1–2): 442–446.
- Reddy, M.L.P.; Bharathi, J.R.B.; Smitha, P.; Ramamohan, T.R. (1999) Synergistic extraction of rare earths with bis(2,4,4-trimethylpentyl) dithiophosphinic acid and trialkyl phosphine oxide. *Talanta*, 50 (1): 79–85.
- Wang, X.; Li, W.; Meng, S.; Li, D.Q. (2006) The extraction of rare earths using mixtures of acidic phosphorus-based reagents or other thio-analogues. *J. Chem. Technol. Biotechnol.*, 81 (5): 761–766.
- Wu, D.B.; Li, W.; Li, D.Q. (2009) The extraction and separation of Ho, Y, and Er(III) with the mixtures of Cyanex 302 and another organic extractant. *Sep. Sci. Technol.*, 42 (4): 847–864.
- Wang, W.; Wang, X.; Meng, S.; Li, H.; Li, D.Q. (2006) Extraction and stripping of Ytterbium(III) from H_2SO_4 medium by Cyanex 923. *J. Rare Earths*, 24 (6): 685–689.
- Li, W.; Wang, X.; Meng, S.; Li, D.Q.; Xiong, Y. (2007) Extraction and separation of yttrium from the rare earths with sec-octylphenoxycetic acid in chloride media. *Sep. Purif. Technol.*, 54 (2): 164–169.
- Reddy, M.L.P.; Varma, R.L.; Ramamohan, T.R.; Sahu, S.K.; Chakravorty, V. (1998) Cyanex 923 as an extractant for trivalent lanthanides and yttrium. *Solvent Extr. Ion Exch.*, 16 (3): 795–812.
- Gupta, B.; Malik, P.; Deep, A. (2003) Solvent extraction and separation of tervalent lanthanides and yttrium using Cyanex 923. *Solvent Extr. Ion Exch.*, 21 (2): 239–258.
- Desouky, O.A.; Daher, A.M.; Monem, Y.K.A.; Galhoum, A.A. (2009) Liquid-liquid extraction of yttrium using primene-JMT from acidic sulfate solutions. *Hydrometallurgy*, 96 (4): 313–317.
- Koopman, C.; Witkamp, G.J.; Van Rosmalen, G.M. (1999) Removal of heavy metals and lanthanides from industrial phosphoric acid process liquors. *Sep. Sci. Technol.*, 34 (15): 2997–3008.
- Krea, M.; Khalaf, H. (2000) Liquid-liquid extraction of uranium and lanthanides from phosphoric acid using a synergistic DOPPA-TOPO mixture. *Hydrometallurgy*, 58 (3): 215–225.
- Vogel, A.I. (1961). *A TextBook of Quantitative Analysis Including Elementary Instrumental Analysis*, 3rd Ed.; ELBS and Longmans, Green and Co Ltd.
- Biswas, R.K.; Habib, M.A.; Islam, M.L. (2000) Some physico-chemical properties of (D2EHPA). 1. Distribution, dimerization, and acid dissociation constants of D2EHPA in a kerosene/0.10 K mol m (Na,H)Cl system and the extraction of Mn(II). *Ind. Eng. Chem. Res.*, 39 (1): 155–160.
- Smith, R.M.; Martell, A.E. (1976). *Critical Stability Constants, Vol.4; Inorganic Complexes*, Plenum Press: New York.
- Li, W.; Wang, X.; Hui, Z.; Meng, S.; Li, D.Q. (2007) Solvent extraction of lanthanides and yttrium from nitrate medium with Cyanex 925 in heptane. *J. Chem. Technol. Biotechnol.*, 82 (4): 376–381.