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Studies on the use of octyl (phenyl) phosphinic acid (OPPA) for extraction of yttrium (III) from chloride medium

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ABSTRACT

Extraction behaviour of Y(III) from hydrochloric acid medium by octyl phenyl phosphinic acid (OPPA) has been investigated over a wide range of experimental conditions such as feed acidity, yttrium concentration, OPPA concentration, diluents, temperature, stripping reagents. The extraction mechanism of Y(III) with OPPA was established using distribution data obtained by slope analysis technique and it showed the formation of $Y(HA_2)_3$ type of neutral species in the organic phase. This was also confirmed by non-linear least square regression of the distribution data to the mathematical expression correlating percentage extraction and acidity. The extraction constant (log K_{ex}) of the two phase reaction has been evaluated to be 3.2. Distribution ratio (D) decreased with the increase in temperature with $\Delta H = -16$ kJ/mole. Amongst the reagents studied, 7 M H_2SO_4 was found to be better with 70% stripping of Y(III) in a single contact. Extraction of Y(III) in different diluents followed the order: dodecane > dichlorobenzene > xylene > chlorobenzene. A mathematical model $D = (183.69 \pm 7.24)/(0.5)^{0.59}*(H_i)^3$ was proposed to predict the concentration of yttrium in organic as well as in aqueous phases at any initial concentration of yttrium [C_i] and initial hygrogen ion concentration [H_i]. In addition, the extraction efficiency for other rare earths by OPPA was also investigated and followed the trend: La<Ce<Pr<Nd<Sm<Eu<Gd<Tb<Dy<Ho<Er<Tm<Yb<Lu, which raised with increasing atomic number of elements. Separation factors between adjacent rare earths were also evaluated for OPPA system.

Keywords: Solvent extraction; Rare earths; Yttrium; OPPA; Separation factors; Extraction constant (K_{ex})

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1. Introduction

Rare earth elements (REE) are widely used for industrial products such as phosphor materials, magnetic substances, alloys, catalyst, lasers, superconductors, LEDs, solid oxide fuel cells, nuclear application, among others and the demand for REE is increasing [1]. The REE occur together in nature in minerals like monazite, xenotime, bastnasite etc. The high value of these elements depends on their effective separation into high purity compounds. The separation into individual REE is very difficult to achieve, due to the very low separation factors involving the adjacent REE owing to the similar chemical properties. The separation of REE is usually carried out by solvent extraction or ion exchange, which is based on basicity, which decreases

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from La to Lu. There are several reports on the separation of REE in different media employing various types of extractants such as 2-ethylhexyl 2-ethyhexylphosphonic acid (EHEHPA), di-2-ethyl hexyl phosphoric acid (D2EHPA) bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302), bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) and *n*- tributyl phosphate (TBP) all of which have been widely used for the separation and purification of rare earths [2–6]. Nuclear grade dysproxium oxide was also obtained using EHEHPA by solvent extraction [7,8].

OPPA is an organo phosphorus based liquid cation exchanger. It is an aromatic analogue of CYANEX 272 (2,4,4-trimetylpentyl phosphinic acid). CYANEX 272 is a weak acid having pKa close to 6. However, replacing the branched alkyl groups of CYANEX 272 by phenyl and *n*-octyl group, the acidity of resulting compound (OPPA) increases substantially to 4.6, which is very close to that of PC88A (pKa=4.5). In rare earth industry, EHEHPA plays a vital role in separation and purification of individual rare earths. OPPA having acidity close to EHEHPA, should show similar extraction behavior of rare earths. There is little information available in literature regarding OPPA as extractant for REE. It is interesting to explore new organic solvents to achieve better separation factors among the adjacent rare earths. Therefore, an attempt has been made to investigate the feasibility of the use of OPPA in rare earth extraction processes. The present paper describes the extraction characteristics of yttrium(III) from chloride medium with OPPA dissolved in *n*-dodecane. The effect of hydrochloric acid concentration, extractant concentration, metal ion concentration, temperature and diluents on the distribution ratio (*D*) has been studied. The stoichiometry of the extracted species, equilibrium constant, mechanism of extraction of yttrium with OPPA have been evaluated and discussed. The stripping behaviour of yttrium from the loaded organic phase with various reagents has also been studied. Separation factors between two adjacent rare earths were also evaluated for OPPA solvent. A mathematical model correlating distribution ratio with metal concentration and the acidity has been developed to predict the extraction behaviour of Y(III) under experimental conditions.

2. Experimental

2.1. Reagent and apparatus

OPPA was synthesised indigenously in our laboratory. OPPA was dissolved in *n*-dodecane (guaranteed reagent grade) to prepare the organic solvent. Stock solutions of rare earth were prepared by dissolving their oxides (>99.9%) in concentrated hydrochloric acid and diluted with distilled water. Feed solutions were made by diluting the stock solution as when needed. All other chemicals used were of analytical reagent grade. ICP-AES (JY Ultima 2) of 5 picometer resolution was used for analysis of rare earths.

2.2. Preparation and properties of OPPA

OPPA was synthesised as per the procedure adopted by Mason et al. [9]. The synthesis was carried in toluene medium by addition reaction of 1-octene (1.1 mol) and phenyl phosphinic acid (1.0 mol) in the presence of benzoyl peroxide (0.1 mol) at a reflux temperature of 100°C. The cooled reaction mass was acidified with HCl (5%) and washed with water and evacuated at 70°C/0.01 mm Hg to obtain the product. The product was estimated by potentiometric titration in 75% ethanol and found to be 99% pure with almost no dibasic acid. Elemental analysis of OPPA was performed on a Thermofinnigan Flash EA TM 1112 elemental analyser. The results are as follows: C–66.67% (theoretical 66.12%), H–9.50% (9.12%) and P–11.58% (12.18%).

2.3. Procedure

The extraction experiments were carried out by equilibrating equal volumes (5 ml) of aqueous and organic phases for five minutes at 27 ± 1°C. This time was found to be sufficient for attaining equilibrium. The phases were allowed to settle and aqueous phase removed for assay. The concentration of Y(III) in the aqueous phase was determined by ICP-AES. The concentration of Y(III) in organic phase was calculated from the difference of the yttrium concentration in the aqueous phase before and after the extraction. The distribution ratio (*D*) represents the ratio of Y(III) in the organic phase to that in the aqueous phase. In all the experiments, each data point represents a mean value of three independent measurements. For separation factors evaluation study, binary pair of REE were taken in the aqueous solution of acidity 3 M HCl prior to their extraction with OPPA dissolved in *n*-dodecane.

In the present investigation the concentration of Cl^- was ~0.03 M and the stability constant value for Y^{3+} at ionic strength equal to zero at 25°C has been reported to be –0.1 and hence no correction for aqueous complexing with Cl^- has been applied [10].

3. Results and discussion

3.1. Extraction isotherm

The extraction of a metal ion (M^{n+}) with organophosphinic acid such as OPPA (H_2A_2, dimer form) in a non-polar diluent such as dodecane can be represented as:

$$M^{n+}{}_{(a)} + x[H_2A_2]_{(o)} \overset{K_{ex}}{=} [MA_{2x}H_{2x-n}]_{(o)} + n[H^+]_{(a)} \quad (1)$$

where H_2A_2 is the dimer form of extractant in non polar diluent, n is the valency of metal ion, x is the number of extractant dimer molecule attached with metal ion and K_{ex} is the extraction constant at equilibrium. Subscripts (a) and (o) denote the aqueous and organic phases respectively. K_{ex} is calculated as:

$$K_{ex} = [MA_{2x}H_{2x-n}]_{(o)} \times [H^+]^n{}_{(a)}/[M^{n+}] \times [H_2A_2]^x{}_{(o)} \quad (2)$$

Taking log of both sides of the Eq. (2), we get,

$$\log\ K_{ex} = \log D + n\log\,[H^+]_{(a)} - x\log\,[H_2A_2]_{(o)} \quad (3)$$

where

$$D = [MA_{2x}H_{2x-n}]_{(o)}/[M^{n+}]_{(a)} \quad (4)$$

The free $[H_2A_2]_{(o)}$ concentration was calculated using Eq. (5):

$$[H_2A_2]_{\text{free}} = \{[H_2A_2]_{\text{intial}} - nM_{\text{org}}\} \quad (5)$$

3.2. Slope analysis technique

For demonstrating the extraction mechanism of Y by OPPA, the conventional slope analysis method was adopted. On the basis of Eq. (3), a plot of log D vs log$[H^+]$ at constant OPPA concentration and a plot of log D vs log [OPPA] at constant $[H^+]$ should give straight lines with slopes of n and x respectively. The results for extraction of Y (III) from hydrochloric acid solutions by OPPA in n-dodecane are presented in Fig. 1. Experimental results shown in Figs. 1 and 2 confirm the above predictions and indicate the formation of monomeric neutral complex of the type Y $(HA_2)_3$ in the organic phase. The relation between D and $[H^+]$ obtained by least square regression method and corresponding co-relation coefficients are given in Table 1. The values of intercept in Table 1 is equal to log K_{ex}+ x log $[H_2A_2]$. Similarly, the relationship between log D and log $[H_2A_2]$ at O/A = 1 can be shown as:

$$\log D = (1.69) + 2.89\ \log[H_2A_2] \quad (6)$$

where intercept (1.69) includes the term log K_{ex}–3 log $[H^+]$. The correlation coefficient (r) for regression equations was found to be >0.997. Log K_{ex} values for the extraction reaction have been evaluated using Eq. (3) and are tabulated in Table 2. Log K_{ex} values were determined at different feed concentration and acidity. The fairly constant value (Table 2) and with that obtained from variation of extractant experiments, indicate the formation of similar type of species under experimental conditions.

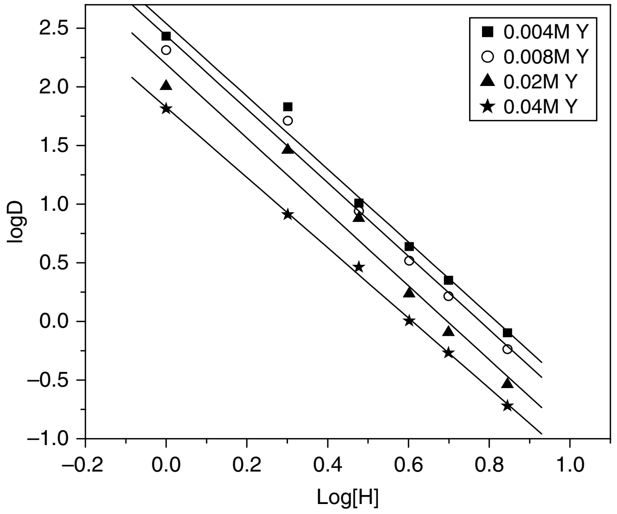

Fig. 1. Dependence of distribution ratio on acidity, 1 M OPPA/dodecane.

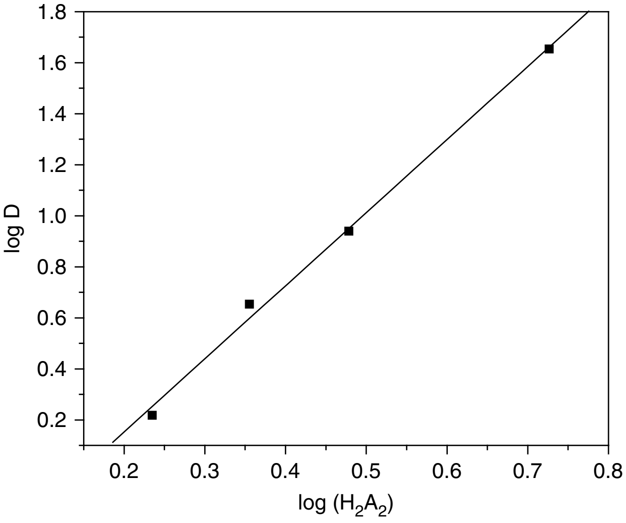

Fig. 2. Effect of extractant concentration on distribution ratio at 3 M HCl feed acidity.

3.3. Non linear least square regression

The percentage extraction (E) for a given phase ratio (A/O= 1) can be expressed as:

$$E = 100D/(D+1) \quad (7)$$

From which distribution ratio in terms of percentage extraction can be written as:

Table 1
Relation between log D and log $[H^+]$ for various concentrations of Y(III) extraction with OPPA

Y(III) concentration, M	Relation $[H^+]$	Correlation coefficient
0.004	Log $D = 2.54 - 3.10 \log [H^+]$	0.992
0.008	Log $D = 2.43 - 3.13 \log [H^+]$	0.992
0.02	Log $D = 2.24 - 3.15 \log [H^+]$	0.989
0.04	Log $D = 1.82 - 2.99 \log [H^+]$	0.999

Table 2
Values of log of extraction constant for various concentration of Y(III) at different initial acidity

Feed acidity, M	log K_{ex}			
	Y (0.004 M)	Y (0.008 M)	Y (0.02 M)	Y (0.04 M)
1	3.21	3.12	2.89	2.86
2	3.51	3.42	3.25	2.83
3	3.22	3.17	3.45	2.77
4	3.22	3.12	2.88	2.70
5	3.22	3.10	2.82	2.68
7	3.20	3.07	2.78	2.61

$$D = E/(100 - E) \tag{8}$$

Assuming that the activity coefficient and H_2A_2 concentration under the experimental conditions will remain constant and that $Y(A_2H)_3$ and Y^{3+} are the only species in the organic phases, respectively, Eq. (8) may be written as:

$$D = K/[H^+]^n \tag{9}$$

where K is a constant and is the product of (K_{ex}*$[H_2A_2]^3$) and n represents the number of the hydrogen ions liberated per yttrium ion extracted. Rearrangement of Eqs. (8) and (9) gives the non linear relationship between percentage extraction and aqueous acidity as:

$$E = 100K/(K + [H^+]^n) \tag{10}$$

The non-linear least square regression fitness of the E and H^+ in Eq. (10) will provide the values of K and n. Accordingly, in order to verify the results of slope analysis technique, the data of E and acidity of the extraction of yttrium metal ion at various concentration with 1 M OPPA in n-dodecane have been examined using Eq. (9). The non-linear plots obtained using Origin mathematical software is shown in Fig. 3 and the corresponding values of n and K with chi square are given in Table 3.

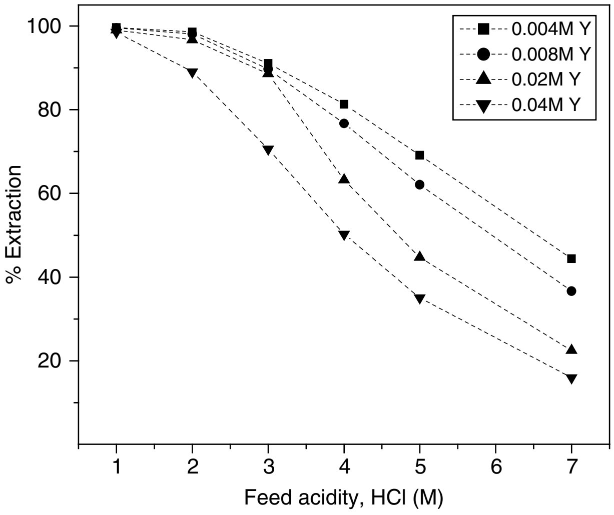

Fig. 3. Non linear least square regression plot for the extraction of various concentration of Y(III) with 1 M OPPA in dodecane at phase ratio (O/A) = 1.

Table 3
Non-linear regression analysis data for the extraction of Y(III) with OPPA in n-dodecane

C_i, M	n	log K	χ^2
0.004	3.14	2.52	0.213
0.008	3.07	2.49	0.156
0.02	2.93	2.19	0.089
0.04	2.98	1.85	0.099

The low values of chi square in all cases indicate good fit of the data to theoretical line. The value of n for the system corresponds to ~3, which validate the results of slope analysis technique. Further, the values of log K_{ex} presented in Table 3, more or less match with the value obtained by linear fit equation, for various concentration ranges. The near constant values for K, obtained at different concentrations, shows that only $[Y(A_2H)_3]$ species was formed under the experimental conditions.

3.4. Development of mathematical model

The basic experimental data on the distribution of yttrium against initial aqueous acidity (D vs H_i) at varying initial yttrium concentration has been determined and utilized to develop mathematical model based on the extraction mechanism reaction of Y(III) with OPPA using Origin mathematical software. Earlier Thakur et al. has developed arbitrary mathematical models comprising exponential function for the rare earth ions and base metals with OPPA [11,12]. However, in the present investigation mathematical model has been developed based on the principle of solvent extraction representing the true behavior of the system. The data generated for D with variation of H_i and C_i, indicated that D decreases with increase in H_i at constant C_i and D also decreases with increase in C_i at constant H_i. These observations suggest that D, C_i and H_i are related to each other and can be quantified by the following equation:

$$D = K_i/[H_i]^3 \tag{11}$$

where K_i is a constant, whose values depend on C_i. With the help of Origin mathematical software, K_i values for different concentrations were determined (Table 4) from the graph of D vs H_i. The values of K_i decreased with increase in C_i and is related as:

$$K_i = K^* (C_i)^m \tag{12}$$

where K^* is known as curve parameter and is a constant, and m is another constant. K_i was plotted with C_i and the value of K^* was determined to be 183.69 ± 7.24. It was observed that the chi square values were minimum when m was 0.59. By putting the values of m and K^* in Eq. (11), K_i was expressed in terms of C_i which in turn, was substituted in Eq. (10). The final equation thus becomes:

$$D = (183.69 \pm 7.24) \,/\, (C_i)^{0.59} * (H_i)^3 \tag{13}$$

which is the general mathematical model, under the experimental conditions for the extraction of Y(III) from chloride medium with OPPA. The mathematical model is useful for predicting the concentration of yttrium ion in the organic and the aqueous phases at any initial concentration of yttrium and at any hydrogen ion concentration. The calculated values obtained by using Eq. (11) were found to be in good agreement with the experimentally obtained values (Fig. 4).

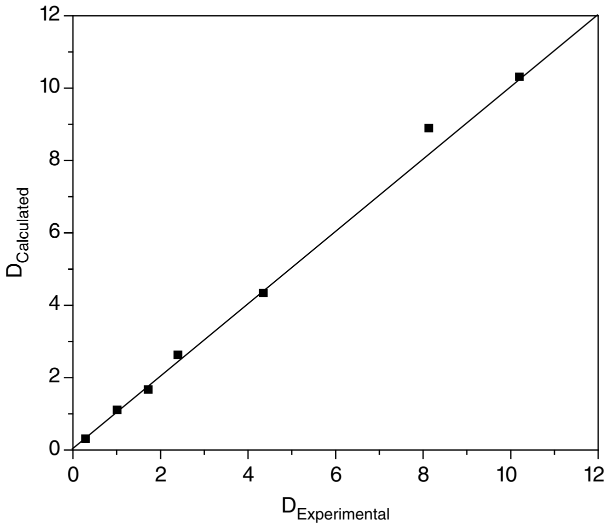

Fig. 4. Parity plot for distribution ratios of Y-OPPA system.

3.5. The effect of temperature

The effect of temperature was determined by carrying out experiments by varying temperature from 27 to 60°C at O/A =1. The change in enthalpy ΔH for the reaction was calculated from the slope of the log D versus $1/T$ using the Van't Hoff`s equation as follows:

$$\log D = -\Delta H/2.303RT + C \tag{14}$$

where R is the gas constant and C is a constant. From the plot (Fig. 5) it is evident that the extraction of Y(III) decreased with increase in temperature, indicating the exothermic nature of the two phase reaction and ΔH was found to be –16 kJ/mole.

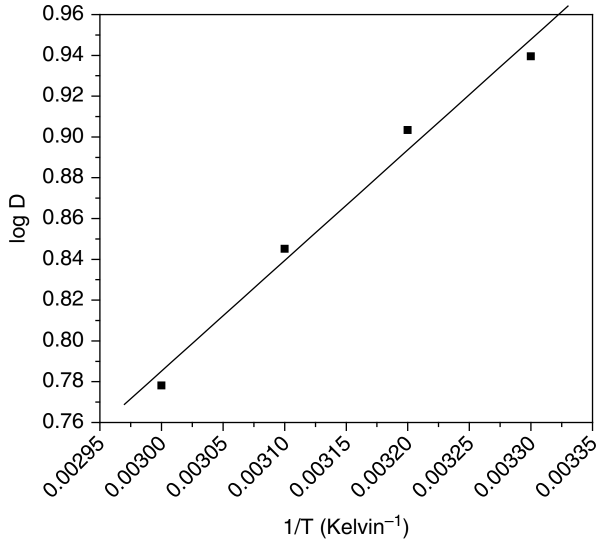

Fig. 5. Temperature dependence of distribution ratio for extraction of Y(III) by OPPA.

Table 4
Values of curve fitting parameter for various initial Y(III) concentration (C_i) with chi square (χ^2)

C_i, M	K_i	χ^2
0.004	271.85	0.697
0.008	198.73	0.123
0.02	99.83	0.042
0.04	65.06	0.031

3.6. Effect of diluents

The role of diluents is very important in solvent extraction process. The diluents decrease the tendency of emulsification of the extractants and improve their dispersion and coalescence properties. Diluents are used to reduce the viscosity of the extractants. Diluents should have the ability to retain in solution both complexed and uncomplexed extractant, should have low solubility in aqueous phase, high flash point, low volatility, low surface tension and should be stable. In this context, diluents such as petrofin, dodecane, toluene, xylene, chlorobenzene, dichlorobenzene were tested. In general, the diluents having low dielectric constant exhibit minimum interaction between diluents and extractant and thus lead to high extraction of metal by the solvent. The effect of different diluents was evaluated and it was found to follow the order as shown in Fig. 6: dodecane > petrofin > xylene > toluene > chlorobenzene > dichlorobenzene.

3.7. Effect of Y concentration

Additional experiments were carried out at fixed extractant concentration (1 M OPPA), feed acidity (3 M HCl) and O/A = 1 to investigate the effect of Y(III) concentration in aqueous phase. The results indicated that the D values decreased with increase in Y(III) concentration in the range of 1 to 6.0 g/l Y_2O_3. Further, it was observed that when the extraction was performed with a feed containing 7.0 g/l Y_2O_3 having a acidity 0.5 M HCl, there was a gel formation in the organic phase, This is in contrast with D2EHPA and EHEHPA where loading is quite high for rare earths (25–30 g/l T. REO) and no gel formation is observed.

3.8. Stripping behaviour

The stripping of Y(III) from loaded OPPA consisting of 1 M OPPA+0.008M Y(III) were tested with various types of reagents with O/A = 1 at room temperature(28°C). The results are summarized in Fig. 7. Stripping reagents studied include 7 M H_2SO_4, 5.4 M H_2SO_4, 5.4 M H_2SO_4 + 0.8 M Na_2SO_4, 4.7 M HNO_3, HCl.

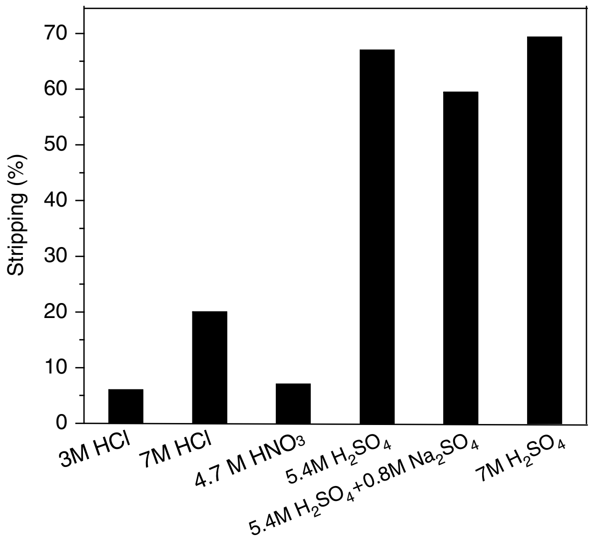

Fig. 7. Stripping of Y(III) from OPPA loaded with yttrium.

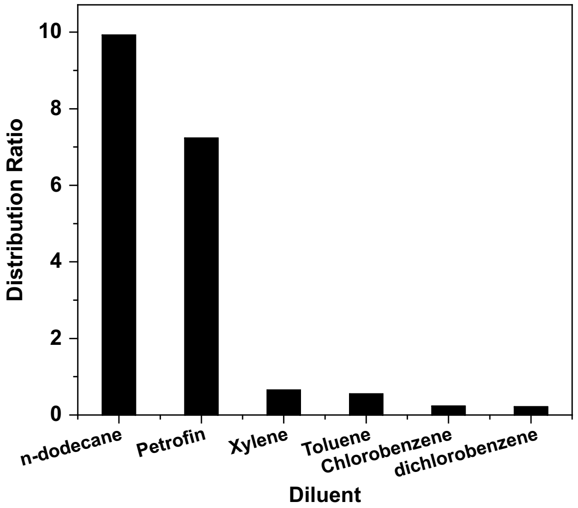

Fig. 6. Effect of diluents on distribution ratio.

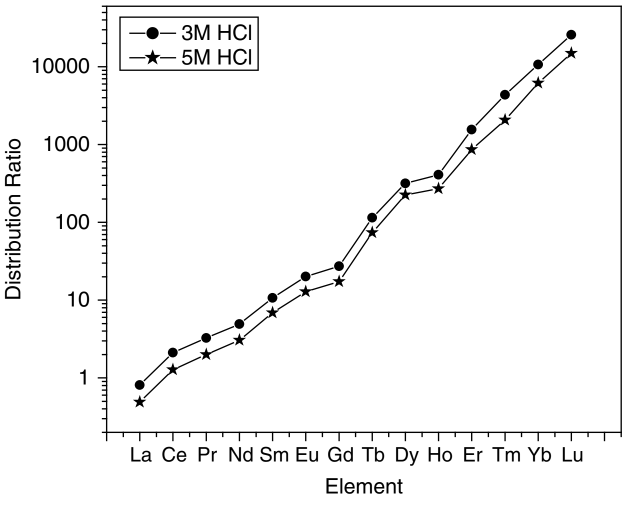

Fig. 8. Dependence of distribution ratio on rare earth elements arranged in order of their atomic numbers.

Table 5
Separation factor of rare earth elements in the extraction system Ln(III)-HCl-OPPA

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La		1.14	4.07	6.18	13.6	25.6	34.5	55.2	159	198	692	1804	4913	11840
Ce			1.56	2.37	5.22	9.78	13.2	21.1	61	75.9	265	691	1880	4531
Pr				1.52	3.35	6.28	8.48	13.6	39.2	48.8	170	443	1208	2910
Nd					2.21	4.13	5.58	8.93	25.8	32.1	112	292	794	1914
Sm						1.87	2.53	4.05	11.7	14.5	50.7	132	360	868
Eu							1.35	2.16	6.23	7.76	27.1	70.6	192	463
Gd								1.6	4.62	5.75	20.1	52.2	142	343
Tb									2.89	8.59	12.5	32.7	88.9	214
Dy										1.25	4.34	11.3	30.8	74.2
Ho											3.49	9.09	24.7	59.6
Er												2.61	7.09	17.1
Tm													2.72	6.56
Yb														2.41
Lu														

Sulphuric acid of 5.4 and 7 M were found to give comparable results. The percentage stripping of Y(III) was 70, 67, 59 and 7 for 7 M H_2SO_4, 5.4 M H_2SO_4, 5.4 M H_2SO_4 + 0.8 M Na_2SO_4, 4.7 M HNO_3 (Fig. 7). Surprisingly, hydrochloric acid did not give the expected results as in the case of EHEHPA. The percentage stripping of Y(III) increased from 1% to 25% with increase in concentration of HCl (1 to 5 M). The lower stripping of Y(III) may be due to stronger complex with OPPA owing to the presence of phenyl group adjacent to phosphoryl group.

3.9. Separation factors

In a solvent extraction process the effect of separation of two metals from each other is based on the selectivity of these metals for the organic and aqueous phases. The selectivity is defined by separation factor, which is the ratio of the extraction equilibrium constants of the metal ions by the extractant. When the two metals are in the same feed solution then the separation factor is defined as the ratio of distribution coefficients of the two metal ions. The separation of individual rare earths from a mixture of rare earths is a difficult task. The separation factors between any two adjacent rare earths for extractants (D2EHPA, EHEHPA) have been reported to be very low as these are mainly related to the change in basicity of the rare earths which decreases very slowly along the rare earth series. The extraction efficiency for REE by OPPA followed the trend: La<Ce<Pr<Nd<Sm<Eu<Gd<Tb<Dy<Ho<Er<Tm<Yb<Lu, and are depicted in Fig. 8. Extraction was carried out at two different feed acidities namely 3 M and 5 M HCl with 1 M OPPA. From the distribution data obtained, the separation factors of rare earths by OPPA are evaluated and are illustrated in Table 5. From these it is inferred that separation factors between two heavy rare earths are high in comparison to EHEHPA and D2EHPA [3]. And also OPPA may be useful in separation of heavy rare earths from lighter rare earths because of very high separation factors.

4. Conclusions

The feasibility of using OPPA as an extractant for Y(III) from chloride medium has been explored. The slope analysis method indicated the formation of $Y(HA_2)_3$ type of the complex in the organic phase. This was also confirmed by non-linear least square regression of the distribution data to the mathematical expression correlating percentage extraction and acidity. A mathematical model $D = (183.69 \pm 7.24)/(C_i)^{0.59}*(H_i)^3$ was found to be useful to predict the extraction behaviour of Y(III) with OPPA under experimental conditions. The extraction reaction of Y(III) with OPPA was found to be exothermic in nature and ΔH was found to be –16 kJ/mole. Increase in Y(III) beyond 7.0 g/l in the aqueous phase resulted in gel formation. Extraction of Y(III) in different diluents followed the order: dodecane > petrofin > xylene > toluene > chlorobenzene > dichlorobenzene. Stripping of Y(III) from OPPA was difficult, however, about 70% stripping was observed with 40% H_2SO_4 in a single contact. Separation factors between adjacent rare earths were also evaluated for OPPA system and it was observed that OPPA may be useful for separation of heavy rare earths from lighter rare earths.

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