

Extraction of La (III) from nitric acid using Tri-octyl amine in kerosene

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Abstract: The extraction behaviour of La(III) with Tri-n-octylamine in Kerosene has been studied through a novel method solvent extraction. The mechanism of extraction and the species extracted have been identified. Quantitative extraction of La(III) with TOA was achieved in Kerosene by changing different parameters such as acid variation, diluent effect, metal concentration variation, extractant variation and effect of chloride ion concentration on extraction of La (III) were studied. The percentage of La (III) became 42.4% with 0.1M TOA from 1M nitric acid. Chloroform was found to be effective diluent for the extraction of La(III) with TOA.

Keywords: lanthanum; solvent extraction; nitric acid; tri-octyl amine; kerosene

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I. Introduction

La(III) is one of the most abundant rare earth element. Rare earth elements are extensively used in Metallurgy, Lasers, textiles, petroleum agriculture, magnets and batteries. A Swedish Chemist Carl Gustav Mosander was discovered La(III) in 1839, but in 1923, it was isolated in the pure form. Rare earths were originally used to designate the Lanthanides which includes oxides of Scandium (Sc, 21), Yttrium (Y, 39), Lanthanum (La, 57) and 14 elements following Lanthanum in the 3rd row of the periodic table i.e; from Cerium (Ce, 58) to Lutetium (Lu, 71). Rare earth elements are relatively abundant in earth's crusts. However they are rarely occurred in concentration form. In general, such rare earth elements and their compounds are rapidly expanding their range of applications in chemical catalytic electrical, magnetic and optical properties. Solvent extraction is the most prominent appropriate commercial technique to obtain small quantities of high purity rare earth metals as per requirement because of its simplicity, speed, ready adaptability to both tracer and macro amount of metal ions and playing an important role as a separation technique [1]. Rare earth elements containing large number of minerals including Monazite, Bastnasite, Gadolinite, Cerite and Allanite etc. Out of them Monazite and Bastnasite are most common mineral [2]. La(III) is a rich rare earth element which plays an important role in laser crystals, green phosphorus, hydrogen storage batteries and an important element of misch-metal and hydrogen absorbent [3]. The separation process in case of rare earth elements are too much difficult because they possess very similar and chemical properties. La(III) can be separated using saponified acidic extractant such as Di-2-ethylhexylphosphoric acid (P204) under certain conditions which can enhance the extraction capacity, but it results loss of Ammonium ion causes serious pollution [4,5]. Therefore it is need to develop a new model for extraction of La(III). A systematic investigation on the extraction behaviour of La(III) using Nitrogen containing compounds like Amides, Hydroxamic acid derivatives, quaternary Ammonium salts & Amines was reported by E.A Mowafy et al [6]. The diamide compound DMDPhPDA (N,N'-Dimethyl-N,N'-Diphenylpyridine-2,6-dicarboxamide) was used for the extraction of La(III) in acidic medium which is highly efficient extraction reported by Shimada et al. The mutual separation of La(III) using divalent quadridentate Schiff base through ion pair extraction system investigated by N. Hirayama [7]. The trace amount of Ce(IV) and La(III) using n-Phenyl-(1,2-Methanofullerene-C60)-61-formohydroxamic acid (PMFFA) [8] was investigated through liquid-liquid extraction process. Extraction of La, Ln, Pr, Nd and Gd from nitrate solution using Aliquat 336 in aromatic and aliphatic diluents were found, extraction of Lanthanides decrease with increase in atomic number and increases with increase in the concentration 4M-8M acid by adding Ammonium nitrate as a supportive electrolyte [9] and synergistic extraction of La(III) was investigated in combination with Thenoyltrifluoroacetone [10,11], 1-Phenyl-3-methyl-4-benzoylpyrazole-5-one [12] and 4-Benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one [13].

Using composite solid extractant based on polymer supported with trialkylamine [14] from Sodium Nitrate solution and trialkylmethyl ammonium nitrate [15] for the extraction of La(III). There are a very few reports using Amine extractant in the extraction of trivalent La(III) individually or synergists. The extraction of La(III) from nitric acid and HCl solutions using high molecular weight Amines [16,17]. The synergistic action of Tri-n-octylamine (TOA) [18] with Thenoyltrifluoroacetone (HTTA) was

studied in nitrate media for selective extraction of La(III). The present study represents the experimental data on extraction of La(III) from nitrate solution using TOA as an extractant in Kerosene. The various extraction effects on La(III) which give more information about the influence of various factors.

II. Experimental

2.1. Reagents

Stock solution of $\text{La}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ (Merck) (0.01M) was prepared by dissolving required amount in double distilled water. One ml of concentrated HNO_3 was added to the stock solution to avoid further hydrolysis. Distilled kerosene was used as organic phase diluent. The commercial extractant, Tri-octyl amine (TOA) (Merck) was used without further purification. All other reagents used were of analytical reagent grade.

2.2. Procedure

Equal aliquots (10 ml) of the aqueous phase containing $\text{La}(\text{NO}_3)_3$ solution (0.001M) in HNO_3 and the organic phase with TOA in kerosene were shaken in a separating funnel. Complete equilibrium was achieved in ten minutes. The phases were allowed to settle for five minutes and then they were disengaged. The lanthanum (III) concentration in the aqueous phase before and after the extraction was determined by Arsenazo (III) method using a Perkin Elmer UV-Visible spectrophotometer. The distribution coefficient (D) was calculated by taking the ratio of equilibrium concentration of lanthanum (III) in organic phase and that in the aqueous phase. The concentration of lanthanum in the organic phase was calculated by using the mass balance i.e., the difference of metal concentration in the aqueous phase before and after the extraction. From D value, the percentage of extraction was calculated ($\%E = 100(D/D+1)$).

The absorbance of metal was measured spectrophotometrically before and after extraction from which the distribution ratio was calculated as follows:

$$D = \frac{\text{Abs}_{\text{B.E.}} - \text{Abs}_{\text{A.E.}}}{\text{Abs}_{\text{A.E.}}}$$

The distribution ratio was obtained as the ratio of equilibrium concentration of metal in the organic phase to that in the aqueous phase

$$D = \frac{[\text{M}]_{\text{org}}}{[\text{M}]_{\text{aq}}}$$

Where $[\text{M}]_{\text{org}}$ and $[\text{M}]_{\text{aq}}$ are the metal concentration in the organic and aqueous phase after the extraction, respectively. From the D values, the percentage of extraction was calculated as

$$\%E = \frac{100 D}{D+1}$$

III. Results and Discussion

3.2.1. Effect of equilibration time

The effect of equilibration time on the extraction of La(III) from 1M HNO_3 with 0.1 M TOA in kerosene at 1:1 phase ratio has been studied. When shaking time was increased from three minutes to twenty minutes, the extraction percentage increased from 21.3 % in three minutes to 53.4 % in fifteen minutes and thereafter remained constant. The equilibrium was reached in 15 minutes as shown in fig. 3.1. Therefore, in all experiments fifteen minutes shaking time was maintained (Table 3.1).

Table 3.1.: Effect of equilibration time on extraction of 0.001 M La (III) from 1M HNO_3 using 0.1 M TOA in kerosene.

Time in minutes	D	% E
3	0.271	21.3
5	0.384	27.7
7	0.444	30.7
10	0.581	36.7
12	0.933	48.2
15	1.146	53.4
20	1.146	53.4

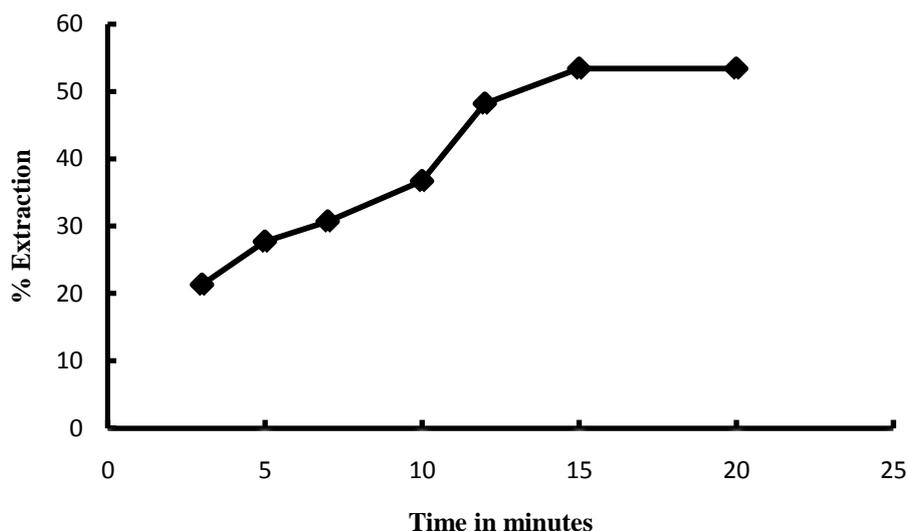


Fig.3.1. Plot of % Extraction versus equilibration time in the extraction of 0.001M La(III) from 1M HNO₃ using 0.1M TOA in kerosene.

3.2.2. Effect of acid concentration

The extraction of La (III) was studied with 0.1M TOA in kerosene by varying HNO₃ concentration from 0.1M to 1.5 M. Extraction was only 1.25 % with 0.1M HNO₃ and then increased up to 43.74% with 1.5M HNO₃. In the low acid concentration (<0.1M), turbidity appeared and phase separation was not possible. It was observed that extraction depends on aqueous phase acidity due to the formation of more amine salt which extracts the metal complex. The data are given in table 3.2 (Fig. 3.2). Biswas et al [19] studied that, extraction of Zr (IV) from hydrochloric acid solutions using 2.5% (v/v) TOA in carbon tetrachloride with increasing acid concentration from 2.4M to 9.6M the extraction increased from 1.76% to 17.83%.

Table 3.2.: Effect of HNO₃ concentration on extraction of 0.001M La (III) using 0.1 M TOA in kerosene.

[HNO ₃], M	D	% E
0.1	0.012	1.25
0.2	0.075	7.01
0.3	0.078	7.23
0.4	0.182	15.43
0.5	0.431	30.16
1	0.736	42.39
1.5	0.777	43.74

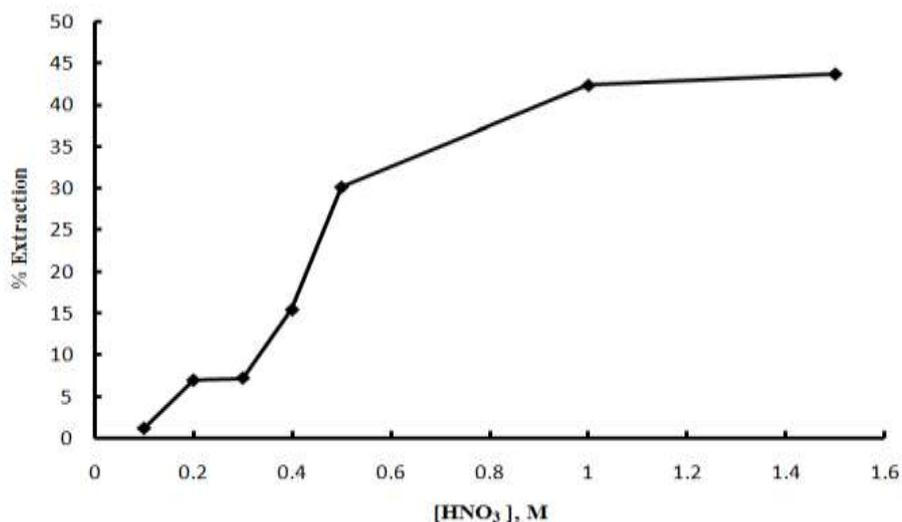


Fig.3.2. Effect of nitric acid concentration on the percentage of extraction of 0.001M La(III) using of 0.1M TOA

3.2.3. Effect of extractant concentration

The extraction of 0.001M La (III) with 0.03M to 0.3M TOA in kerosene was carried out from 1M HNO₃ solution. The percentage extraction of lanthanum was increased with the increase in amine concentration from 9.04 % to 60.18% (Table 3.3). The plot of log D versus log [TOA] yields a slope of 0.733 (Fig. 3.3), which revealed the incorporation of one molecule of amine extractant in the extracted lanthanum complex. Biswas et al [19] also represented that, the extraction of Zr (IV) increases regularly from 7.32% to 53.44% varying TOA concentration (1.25%-7%) in carbon tetrachloride diluents at fixed HCl concentration 9.6 M. Therefore with increase in amine concentration the extraction of La(III) increases.

Table 3.3. Effect of extractant concentration on extraction of 0.001 M La(III) from 1 M HNO₃.

[TOA], M	D	% E
0.03	0.099	9.04
0.05	0.399	28.55
0.1	0.736	42.39
0.2	1.149	53.47
0.3	1.511	60.18

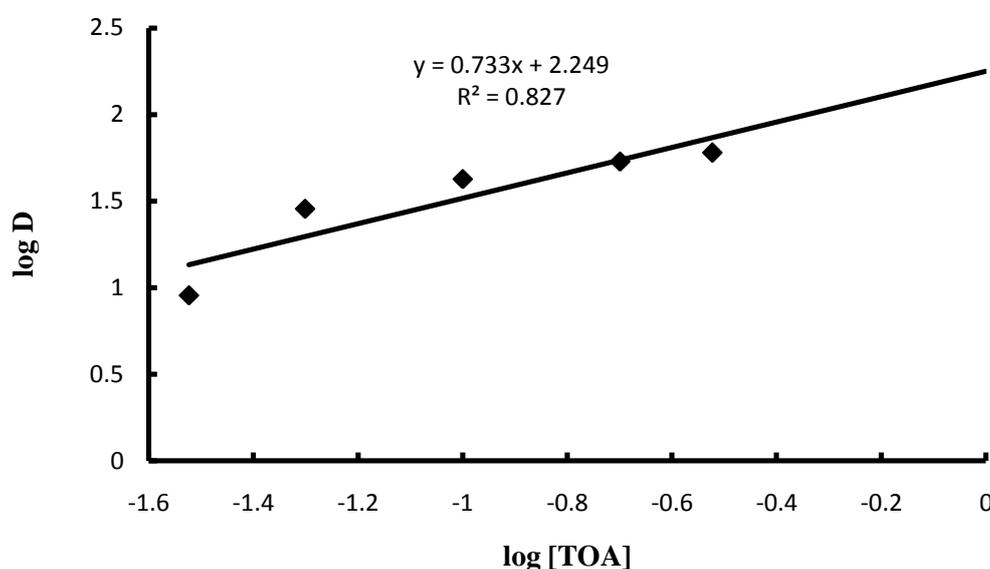
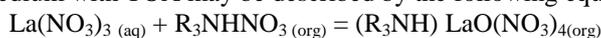


Fig.3.3. Plot of log D versus log [TOA] in the extraction of 0.001M La (III) from 1M HNO₃.

3.2.4. Extraction Equilibrium

The possible extraction mechanism of La(III) from HNO₃ medium with TOA in kerosene appears to proceed through the protonation of TOA (R₃N) forming R₃NHNO₃ followed by extraction of (R₃NH) LaO(NO₃)₄ species into the organic phase.

Under the studied experimental conditions and from the slope analysis results, the extraction of La (III) from acidic medium with TOA may be described by the following equation:



3.2.5. Effect of Chloride ion concentration

The effect of chloride ion concentration on the extraction of 0.001M La (III) from 1M HNO₃ using 0.1M TOA was studied. The percentage of extraction of La (III) increases from 2.53% to 41.24%, from 8.75% to 47.47% and 9.03% to 49.5% (Fig. 3.4) with increase in concentration of NH₄Cl, KCl and NaCl, respectively increasing chloride ion concentration from 0.001M to 0.08M (Table 3.4). The increase may be due to the extraction of the chlorocomplex of lanthanum with TOA.

Omori et al [20] reported that, the distribution co-efficients of Zr (IV) with tribenzyl amine in hydrochloric acid-lithium chloride mixed solutions are lower than those in a hydrochloric acid solution. Poriel et al [21] using Aliquat 336 from hydrochloric acid solution investigated that the extraction of Zr and Hf increased with an increase in chloride ion concentration. The observed trend is in agreement with Poriel's investigation.

Table 3.5. Effect of chloride ion concentration on extraction of 0.001M La (III) from 1M HNO₃ using 0.1M TOA in kerosene.

[Cl ⁻], M	% E		
	NH ₄ Cl	KCl	NaCl
0.001	2.53	8.75	9.03
0.005	9.08	15.89	17.85
0.01	12.73	23.83	24.51
0.04	20	27.32	29.31
0.08	41.24	47.47	49.5

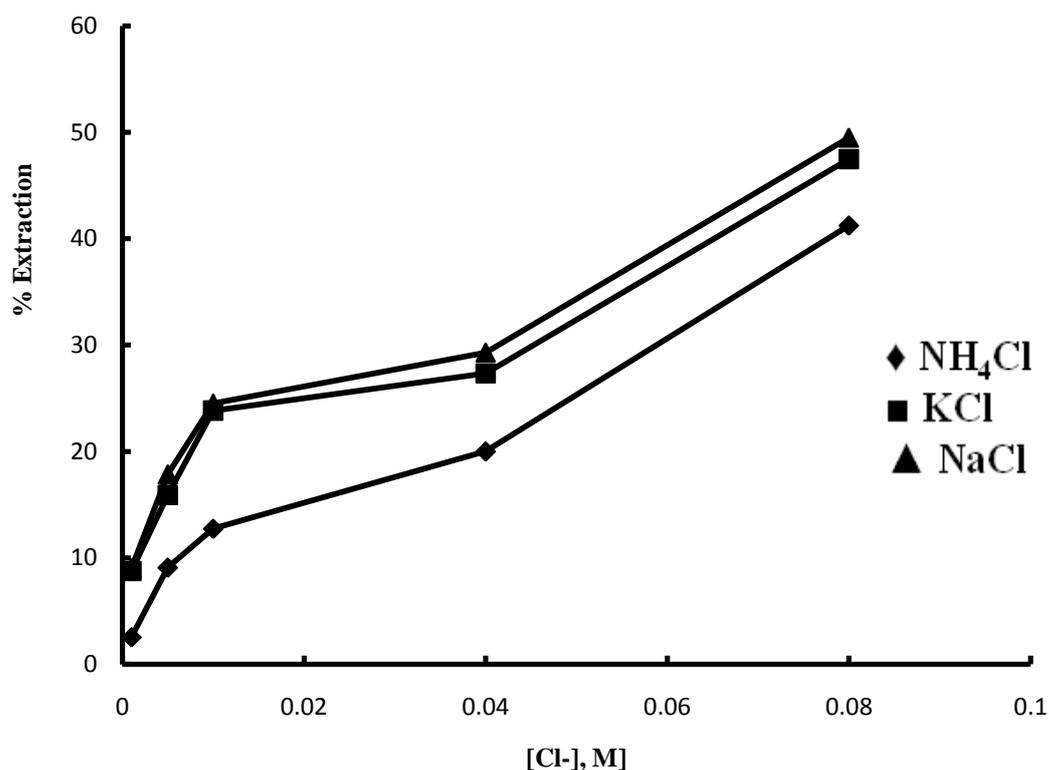


Fig.3.5. Effect of chloride ion concentration on the extraction of 0.001M La (III) from 1M HNO₃ using 0.1M TOA in kerosene.

3.2.6. Effect of metal ion concentration

The extraction of La(III) from 1M HNO₃ using 0.1M TOA has been studied by increasing the concentration of the lanthanum(III) from 0.0001M to 0.002M. The percentage of extraction was increased from 2.43% to 53.66% with the increase in metal ion concentration upto 0.001M and thereafter remains constant. The detail data showed in table 3.6 and fig. 3.6.

Table 3.6.: Effect of metal ion concentration on extraction of 0.001M La (III) from 1M HNO₃ using 0.1 M TOA in kerosene.

[Metal], M	D	%E
0.0001	0.025	2.43
0.0002	0.099	9
0.0003	0.148	12.89
0.0004	0.176	14.96
0.0005	0.264	20.88
0.001	1.158	53.66
0.002	1.179	53.78

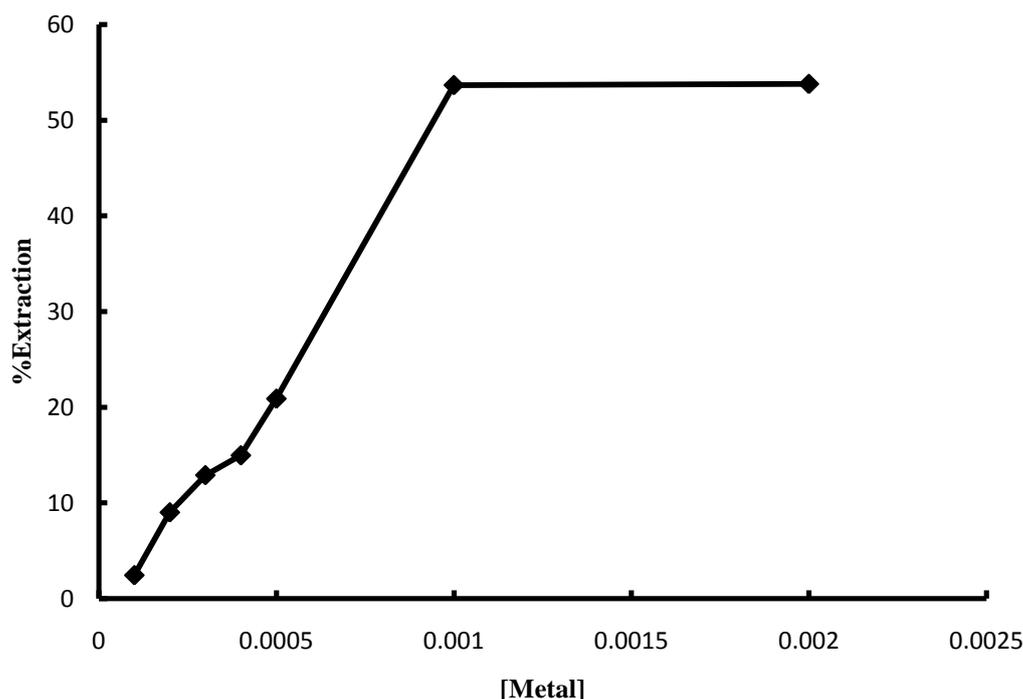


Fig. 3.6. Effect of metal ion concentration for extraction of La(III) from 1M HNO₃ using 0.1M TOA.

3.2.7. Effect of diluents

The selection of extractants and diluent are two important aspects of a successful solvent extraction system. The influence of diluent on distribution of metal is correlated with the physic-chemical properties of organic solvent such as solubility parameter, dipole moment, dielectric constant, etc. [22]. The extraction of La (III) from 1M HNO₃ using 0.1M TOA has been studied in different organic diluents namely kerosene, benzene, aniline, xylene and chloroform. The percentage of extraction was maximum when chloroform was used as diluent as shown in table 3.7. Kerosene was chosen as the diluent for the study due to low toxicity, low cost and easy availability. It is evident that extractability of La(III) can be correlated to some extent with ionization potential of diluents used decreasing order: straight chain aliphatic hydrocarbon > cycloparaffins > aromatics [23].

Table 3.7.: Effect of diluents on the extraction of La (III) from 1M HNO₃ using 0.1M TOA.

Diluents	1M HNO ₃	
	D	% E
Kerosene	0.736	42.39
Benzene	0.49	32.88
Chloroform	0.917	47.83
Aniline	0.209	17.28
Xylene	0.44	30.55

IV. Conclusions

- The extraction of La (III) increases with increase in acid concentration, extractant concentration and concentration of metal ion.
- The extraction of La(III) from 1M HNO₃ increases with increase in chloride ion concentration due to the extraction of chlorocomplex of lanthanum with TOA.
- It has been observed that percentage of extraction of La(III) from 1M HNO₃ was maximum in Chloroform.

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