Lanthanum, Neodymium and Samarium Extraction from Aqueous Nitrate Solutions by Solvent Extraction


(a) Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt
(b) Chemistry Department, Faculty of Science, Ain-Shams University, Egypt

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ABSTRACT

Solvent extraction of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ has been investigated with bis(2,4,4-trimethyl-pentyl) monothiophosphinic acid, commonly known as Cyanex 302, in kerosene from aqueous nitrate medium. Parameters affecting the extraction equilibrium of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ from aqueous nitrate medium were studied and the stoichiometry of the La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ extracted species was elucidated. The separation of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ depending on the difference in the extraction behavior of the extractant towards these metal ions is given and discussed.

1. INTRODUCTION

Owing to the growing uses and applications of rare earth elements and their compounds in many fields as electronics (semi/super medicine, conductors), ceramics and aerospace engineering sectors$^{(1-3)}$, they become of huge demand in recent days. They are being used as novel materials with specific functions in advanced technology development due to their unique spectroscopic and magnetic properties. These elements are also incorporated into components of hybrid or electric cars, wind turbines, thin film solar cells, LEDs, high performance batteries and cell phones. Modern warfare and security or emergency instruments also contain lanthanides as essential components for radar, missile guidance systems, navigation, and night vision goggles$^{(4)}$. In this regard, it may be of great concern that their expected wide applications in industrial sectors, may lead to the depletion of their ores. Therefore, it is necessary to develop methods for their recovery from secondary resources as NiMH batteries, LCD screens and etc.

As a result, various methods are used to purify and separate the rare earth elements, such as chemical precipitation, fractional crystallization, ion exchange and solvent extraction; through which the solvent extraction has the advantage that it is fast, continuous, and works on more concentrated solutions. Solvent extraction attracts great interest due to its high selectivity and significant capital and operating cost savings$^{(2)}$. Many researchers have studied and reported the extraction of La, Sm and Nd from different media using different extractants. Panda et al., studied the extraction of La and Nd from hydrochloric acid solution using Cyanex 272 in kerosene and reported that more than 99% La and 97% Nd were extracted from the model solution containing 0.57 g/L La and 0.48 g/L Nd at pH 3.3 and 2.7 respectively, at phase ratio (O/A) 1:1 using 10% Cyanex 272 diluted with kerosene in two stages$^{(5)}$. Panda and co-workers investigated the extraction of Nd from nitrate solution using Cyanex 921 in kerosene and found that the extraction of Nd increases very slowly with increasing in...
the concentration of HNO₃ in the range of 0.001–0.008 mol/L and then decreased when 0.01 mol/L HNO₃ was used⁶. Wu et al., investigated the extraction of Sc, Y, La, and Gd using Cyanex 302 in heptane from HCl solutions and observed that it is possible to separate them mutually by controlling the aqueous acidity⁷. Banda et al., developed a process to separate La from Pr and Nd using saponified Cyanex 272 and found that, the extraction percentage of La depressed to zero as the saponification degree of Cyanex 272 increased to 50%, and thus it was possible to separate La from the solution⁸. El-Nadi et al. investigated the extraction of lanthanum (III) and samarium (III) from nitrate solutions by some phosphine oxide compounds (Cyanex 921, Cyanex 923, and Cyanex 925) in kerosene. The extraction of these metals using the above extractants was compared and the sequence of extraction was found to be Cyanex 921 > Cyanex 923>> Cyanex 925⁹. Masry et al., investigated the extraction and separation of Pr (III), Sm (III) and Nd (III) from 1M nitric acid using Cyanex 923 in kerosene¹⁰. Swain and Otu investigated the competitive simultaneous extraction and separation of 14 lanthanide elements from perchloric acid aqueous solution using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) as an extractant and elucidated that the type of mechanism is an ion exchange type (¹¹). Kao et al., studied the extraction of La (III) and Nd (III) from nitrate solution using PC 88A in kerosene at 298 K by varying metal (2.5-35 mol/m³) and extractant (1.7-100 mol/m³) concentration¹².

Although information on separation and extraction mechanism for the lanthanide series is available, it is not completely understood in some cases. Selective separation of individual lanthanide element continues to be a challenge. The lack of selectivity is due to the high degree of chemical similarity of the elements. Developing an efficient, economic and environmentally-friendly technology to separate the Ln elements requires understanding the fundamental behavior and mechanism of the extraction process. The aim of this work is to investigate the extraction properties of Cyanex 302 towards La³⁺, Nd³⁺ and Sm³⁺ from nitrate medium, and to study the effect of different parameters on extraction and stripping processes.

2. EXPERIMENTAL

2.1 Materials and Chemicals

The commercial extractant Cyanex 302 was kindly supplied by Cytec Inc. and used as received without further purification. Kerosene (non-aromatic) was obtained from Misr Petroleum Ltd. Company, Egypt. All the other chemicals used were of analytical reagent grade. Lanthanum, neodymium and samarium nitrate were Aldrich products. Formic acid, ascorbic acid and Arsenazo III were products of Merck.

2.2 Analysis

Lanthanum, Neodymium and samarium concentrations were determined using a Shimadzu Uv-visible double beam recording spectrophotometer, Model 160-A Japan, using the Arsenazo III method (¹³). The Hydrogen ion concentration in the solutions was adjusted by using reagent grades nitric acid and sodium hydroxide and measured using a digital pH meter of Hanna instruments type at ambient laboratory temperature degree 25 ± 1°C.

2.3 Extraction Procedure

Batch experiments were carried out by contacting equal volumes of 0.075 M Cyanex 302 in kerosene with La³⁺, Nd³⁺, and Sm³⁺ (100 mg/L each) in aqueous solution of pH (4) for 30 min (sufficient to attain equilibrium) in stoppered glass vials using a thermostatic shaking water bath. After equilibration phase separation, metal ion concentrations in the aqueous phase before and after extraction were spectrophotometrically measured and the concentrations of the metals in the organic phase were obtained by mass balance.
The distribution ratio (D) was calculated as the ratio of concentration of the element in organic to aqueous phase according to the equation (1) and the extraction efficiency (E) is given in equation (2):

\[ D = \frac{[M]_t - [M]_a}{[M]_a} \frac{V_o}{V_a} \]  

\[ \% \ E = \frac{D}{D + (V_o/V_a)} \times 100 \]

Where, \([M]_i\) and \([M]_a\) represent the initial and final concentrations of metal ions in the aqueous phase, \(V_o\) and \(V_a\) are the volumes of the aqueous and organic phase, respectively.

3. RESULTS AND DISCUSSION

Different parameters affecting the extraction of \(\text{La}^{3+}\), \(\text{Nd}^{3+}\) and \(\text{Sm}^{3+}\) from aqueous nitrate medium using Cyanex 302 were investigated by the batch technique. These include the effect of shaking time, pH, metal ion concentrations, extractant concentrations, nitrate ions, phase ratio and temperature, closely followed by stripping investigations.

3.1 Effect of Shaking Time

The effect of shaking time on the extraction of \(\text{La}^{3+}\), \(\text{Nd}^{3+}\) and \(\text{Sm}^{3+}\) (100 mg/L each) by (0.075 M) Cyanex 302 in kerosene was performed by mechanical shaking of the two phases for various times, ranging from 1 to 30 min. at 25°C. The results, illustrated in Fig. (1), indicate that the system approaches equilibrium rapidly, and that two phases were equilibrated for 10 min. can ensure a complete equilibrium.

![Fig. (1): Effect of shaking time on the extraction of \(\text{La}^{3+}\), \(\text{Nd}^{3+}\) and \(\text{Sm}^{3+}\) by Cyanex 302. (Lm (100 mg/L each); [Cyanex 302] 0.075 M; pH= 4; Vo/Va=1:1; 25°C)](image_url)

3.2 Effect of pH

The extraction of \(\text{La}^{3+}\), \(\text{Nd}^{3+}\) and \(\text{Sm}^{3+}\) (100 mg/L each) by 0.075 M Cyanex 302 in kerosene from nitrate medium at various pH values in the range from 1 to 5 was investigated at 25°C. Fig. (2) shows that the extraction percentage increases by increasing the pH value to pH = 3. Beyond pH >3, the initial aqueous pH has no effect on the extraction percentage. Hence, other experiments were carried out at optimized value of initial aqueous pH that equals to 4. A decrease in pH (increase in hydrogen ion concentration) may result in the formation of non-extractable metal species as a result of complexation with the components of the aqueous phase.
3.3 Effect of Nitrate Ions Concentration

Different concentrations of NaNO₃ ranging from 0.01–0.30 M were used to know the involvement of nitrate ions in the extraction of La³⁺, Nd³⁺ and Sm³⁺ (100 mg/L each) by 0.075 M Cyanex 302 in kerosene. Fig. (3) shows that the extraction percentage slightly decreases for La³⁺ and Sm³⁺ and gradually declines for Nd³⁺ with increasing [NO₃⁻]. Hence, 0.01 M [NO₃⁻] was maintained throughout the study.

3.4 Effect of Extractant Concentration

The extraction of La³⁺, Nd³⁺ and Sm³⁺ (100 mg/L each) using various concentrations of Cyanex 302 in the range (0.015 – 0.202 M) in kerosene was studied. As shown in fig. (4), the extraction of these ions increased with increasing in concentration of Cyanex 302.

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Fig. (2): Effect of pH on the extraction of La³⁺, Nd³⁺ and Sm³⁺ by Cyanex 302. (Ln (100 mg/L each); [Cyanex 302] 0.075 M; Time= 10 min; Vo/Vₐ=1:1; 25°C)

Fig. (3): Effect of nitrate ions con. on the extraction of La³⁺, Nd³⁺ and Sm³⁺ by Cyanex 302. (Ln (100 mg/L each); [Cyanex 302] 0.075 M; Time= 10 min; Vo/Vₐ=1:1; 25°C, pH=4)

Fig. (4): Effect of Cyanex 302 con. on the extraction of La³⁺, Nd³⁺ and Sm³⁺. (Ln (100 mg/L each); pH=4; Time= 10 min; Vo/Vₐ=1:1; 25°C)
3.5 Effect of Phase Ratio

The volume ratio of the two phases plays an important role in the extraction process. The ratio of organic to aqueous phase \((V_o/V_a)\) changed from 1:4 to 3:1 as shown in Fig. (5), where it can be seen that the extraction efficiency increases with increasing (organic/aqueous) phase ratio.

![Graph showing the effect of phase ratio on the extraction of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) by Cyanex 302](image)

**Fig. (5):** Effect of phase ratio on the extraction of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) by Cyanex 302. (Ln (100 mg/L each); [Cyanex 302] 0.075 M; pH=4; Time= 10 min; 25°C)

3.6 Effect of Metal Ion Concentrations

The effect of the investigated metal ion concentrations on the extraction process from nitrate medium at (pH 4) was studied in the range (25 - 500 mg/L) using 0.075 M Cyanex 302 in kerosene.

The results represented in Fig. (6) show that the amount of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) in the organic phase increases with increasing their initial concentrates, to reach the maximum value then remains constant with further increase in the metal concentration.

![Graph showing the effect of metal ion conc. on the extraction of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) by Cyanex 302](image)

**Fig. (6):** Effect of metal ion conc. on the extraction of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) by Cyanex 302. ([Cyanex 302] 0.075 M; pH=4; Time= 10 min; Vo/Va=1:1; 25°C)

3.7 Loading Capacity

The loading capacity of 0.075 M Cyanex 302 in kerosene was studied by separately shaking with La\(^{3+}\), Nd\(^{3+}\), and Sm\(^{3+}\) (100 mg/L each) aqueous solution of pH 4 for 10 minutes at fixed organic to aqueous phase ratio of 1:1 and T = 25±1°C. The two phases were separated, the metals concentrations were determined and the same organic phase was shaken again with fresh aqueous metals solution. Fig. (7) shows that the maximum concentration of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) in the organic phase found to be 23, 88 and 95×10\(^{-4}\) mole per one mole of the extractant, respectively. Fig. (7) also shows that, only one stage is enough for La, two stages are sufficient for Nd and three stages are adequate for Sm.
Fig. (7): Loading Capacity of Cyanex 302 in kerosene in the extraction of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$.
(Ln = (100 mg/L each); [Cyanex 302] 0.075 M; pH=4; Time= 10 min; Vo/V$_a$=1:1; 25°C)

3.8 Equilibrium Studies

Equilibrium studies of the extraction of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ with Cyanex 302 were carried out on the separate effects of the initial concentrations of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$, Cyanex 302, H$^+$ and NO$_3^-$ in the respective concentration ranges of

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>(0.180 - 3.6) ×10$^{-3}$ M</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>(0.174 - 4.169) ×10$^{-3}$ M</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>(0.166 - 3.98) ×10$^{-3}$ M</td>
</tr>
<tr>
<td>Cyanex 302</td>
<td>(0.0150 - 0.213 M)</td>
</tr>
<tr>
<td>H$^+$</td>
<td>(0.001 - 0.03 M)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>(0.01 - 0.3 M)</td>
</tr>
</tbody>
</table>

As Cyanex 302 is generally found in a dimeric form, H$_2$A$_2$, in aliphatic diluents and the trivalent lanthanide cations are easily hydrolysed. As far as La$^{3+}$ is concerned, under condition of pH > 3, mono nuclear [La(OH)]$^{2+}$, [La(OH)$_2$]$^{1+}$ and [La(OH)$_3$]$, and polynuclear hydrolytic species [La$_2$(OH)]$^{5+}$ therefor, it is possible that hydroxyl ions take part in the extraction reaction.

Slope analysis of the experimental results for La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ is given in Fig. (8-10), respectively. The results indicate that two moles of Cyanex 302 participate in the extracted La$^{3+}$ species and one hydrogen ion is released in the aqueous medium, while no nitrate ions participate in the extracted complex.

La(OH)$_2$$^+$$2$ $H_2A_2$ $\leftrightarrow$ La(OH)$_2A(AHA)_3$ + $H^+$ $\quad (3)$

$$K_{ex} = \frac{[La(OH)A(AHA)_3][H^+]}{[La(OH)A^+]^2[H_2A_2]^2} \quad (4)$$

$$K_{ex} = \frac{D[H^+]}{[H_2A_2]^2} \quad (5)$$

Bars refer to organic phase. The mean value of extraction constant of La$^{3+}$, $K_{ex}$, was found to be (4.7 ± 0.2) ×10$^{-3}$ M$^{-1}$.

The results also indicate that, 2 moles of Cyanex 302 chelate separately with Nd$^{3+}$ and Sm$^{3+}$ with one $H^+$ releases and only one NO$_3^-$ participates in the extracted Nd$^{3+}$ and Sm$^{3+}$ complexes.

From these results, the extraction equilibrium of M(III)-Cyanex302/kerosene system is represented by:

M(OH)$_2$$^+$ + $2$ $H_2A_2$ + NO$_3^-$ $\leftrightarrow$ $\rightarrow$ M(OH)NO$_3A(AHA)_3$ + $H^+$ $\quad (6)$

$$K_{ex} = \frac{[M(OH)NO_3A(AHA)_3][H^+]}{[M(OH)_2][H_2A_2]^2[NO_3^-]} \quad (7)$$

Bars refer to organic phase.
\[ K_{ex} = \frac{D[H^+]}{[H_2A_2]^2[NO_3^-]} \] (8)

Where, \( M \) represents \( \text{Nd}^{3+} \) and \( \text{Sm}^{3+} \) with an extraction constant, \( K_{ex} \), given by equation (8). The mean value of extraction constant of \( \text{Nd}^{3+} \) and \( \text{Sm}^{3+} \), \( K_{ex} \), was found to be \((6.6 \pm 0.6) \times 10^{-3} \) M\(^2\) and \((5.6 \pm 0.3) \times 10^{-3} \) M\(^2\), respectively.

Fig. (8): Slope analysis of \([H^+], [\text{Cyanex302}], \text{and [NO}_3^-]\) on the extraction of \( \text{La}^{3+} \).

Fig. (9): Slope analysis of \([H^+], [\text{Cyanex302}], \text{and [NO}_3^-]\) on the extraction of \( \text{Nd}^{3+} \).

Fig. (10): Slope analysis of \([H^+], [\text{Cyanex302}], \text{and [NO}_3^-]\) on the extraction of \( \text{Sm}^{3+} \).
3.9 Effect of Temperature

The temperature effect on the extraction of the investigated La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) (100 mg/L each) from aqueous nitrate medium by Cyanex 302 in kerosene was studied in the range (25 - 50°C). The obtained results show that the extraction percentage of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) increases with increasing temperature, Fig. (11). The temperature effect on the complex extraction could be evaluated in terms of their thermodynamic values calculated from the following relations:

\[
\ln K_{ex} = -\frac{\Delta H}{RT} + C, \quad C: \text{constant} \quad (9)
\]

\[
\Delta H = -2.303R \frac{\partial \ln k_{ex}}{\partial (1/T)} \quad (10)
\]

\[
\Delta G = -RT \ln K_{ex} \quad (11)
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T} \quad (12)
\]

Where, \(\Delta G\) is the free energy change, \(\Delta H\) is the enthalpy change and \(\Delta S\) is the entropy change. \(R\) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \(T\) is the absolute temperature (K). From equation (9) and the slopes obtained from Fig. (11), the respective enthalpy variations (\(\Delta H\)) are elucidated. The free energy variations (\(\Delta G\)) are obtained by applying equation (11) at standard state, 298 K. Also, the entropy variations, (\(\Delta S\)) were given by applying equation (12). From the thermodynamic parameters shown in table (1), the positive value for the enthalpy change (\(\Delta H\)) indicates that the extraction of La\(^{3+}\), Nd\(^{3+}\), and Sm\(^{3+}\) by Cyanex 302 is endothermic. The positive value of the entropy (\(\Delta S\)) indicates that the reaction is accompanied with an increase in the random nature of the species involved. The negative value of (\(\Delta G\)) indicates that the reaction is spontaneous in nature for Nd\(^{3+}\) and Sm\(^{3+}\) except for La\(^{3+}\) where the reaction is non-spontaneous in nature.

![Graph](image)

**Fig. (11):** Effect of temperature on the extraction constant of La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) by Cyanex 302 (Ln = (100 mg/L each); [Cyanex 302] 0.075 M; pH=4; Time= 10 min; Vo/V\(_a\)=1:1)

**Table (1):** Thermodynamic parameters for La\(^{3+}\), Nd\(^{3+}\) and Sm\(^{3+}\) extraction by Cyanex 302 (Ln = (100 mg/L each); [Cyanex 302] 0.075 M; pH=4; Time= 10 min; Vo/V\(_a\)=1:1)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>La(^{3+})</th>
<th>Nd(^{3+})</th>
<th>Sm(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H), kJ mol(^{-1})</td>
<td>27.18</td>
<td>19.32</td>
<td>29.79</td>
</tr>
<tr>
<td>(\Delta G), kJ mol(^{-1})</td>
<td>12.87</td>
<td>-4.37</td>
<td>-4.18</td>
</tr>
<tr>
<td>(\Delta S), J mol(^{-1})K(^{-1})</td>
<td>48.00</td>
<td>79.5</td>
<td>114.00</td>
</tr>
</tbody>
</table>
3.10 Stripping of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ from the Loaded Cyanex 302 in Kerosene

The stripping investigations were carried out to choose an appropriate strippant that can successfully strip lanthanum, neodymium and samarium from the loaded Cyanex 302 in kerosene solution.

3.10.1 Acidic Stripping Reagents

Different acidic stripping reagents namely HCl, HNO$_3$, H$_2$SO$_4$ of the same concentration (1M) were used at fixed A/O phase ratio of 1:1, equilibration time of 30 minutes and at room temperature. It is clear from the obtained result that HNO$_3$ is the best reagent for stripping of lanthanum, neodymium and samarium as shown in Table (2).

Table (2): Effect of HCl, HNO$_3$ and H$_2$SO$_4$ (1M) concentrations on the stripping percentage of 25, 77, 75 mg/L La$^{3+}$, Nd$^{3+}$, and Sm$^{3+}$ from the loaded Cyanex 302 in kerosene solution, respectively

<table>
<thead>
<tr>
<th>Stripping reagent</th>
<th>% La stripping</th>
<th>% Nd stripping</th>
<th>% Sm stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl, 1M</td>
<td>36</td>
<td>81</td>
<td>86</td>
</tr>
<tr>
<td>HNO$_3$, 1M</td>
<td>49</td>
<td>82</td>
<td>91</td>
</tr>
<tr>
<td>H$_2$SO$_4$, 1M</td>
<td>35</td>
<td>75</td>
<td>85</td>
</tr>
</tbody>
</table>

3.10.2 Effect of Different Nitric Acid Concentrations

A series of stripping experiments were carried out using NHO$_3$ solutions of concentrations ranging from 0.1 to 2 M. The obtained results for La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ are shown in Fig. (12). It is clear from the obtained results that, stripping by HNO$_3$ decreases after 1 M HNO$_3$. The best La, Nd and Sm re-extraction percentage was given by 0.5 M for La and 1 M HNO$_3$ for both Nd and Sm within 30 minutes, phase ratio (1:1) (v$_o$/v$_a$) and T = 25°C.

![Fig. (12): Effect of nitric acid concentration on the stripping of 25, 77, 75 mg/L La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ from the loaded Cyanex 302 in kerosene solution, respectively](attachment:fig12.png)

3.10.3 Effect of Contact Time on the Stripping Process

The effect of contact time on the attaining of an equilibrium state has been studied at the time intervals 1 - 60 minutes, while the other factors were kept at 0.5 M HNO$_3$ for La, 1 M HNO$_3$ for both Nd and Sm, and (v$_o$/v$_a$) 1:1. The experiments were carried out at room temperature. The results obtained are shown in Fig. (13). It is obvious that contact time of 30, 45, and 30 minutes are sufficient for high stripping efficiency of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ from the loaded solvent, respectively.
3.10.4 Effect of Aqueous/Organic Phase Ratio on the Stripping Process

This effect on the stripping of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ was studied by changing the aqueous/organic phase ratio ($v_a/v_o$) from 1:1 to 1:3, while the other factors were kept at 0.5 M HNO$_3$ for La, 1 M HNO$_3$ for both Nd and Sm, and 30, 45, and 30 minutes for La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$, respectively. The experiments were carried out at room temperature. The results obtained are given in Table (3). It is clear from the obtained results that aqueous/organic phase ratio 1:1, 1:2 and 1:3 is the best ratio as it gives the best stripping efficiency of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$, respectively.

Table (3): Effect of aqueous/organic phase ratio on the stripping percentage of La$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$

<table>
<thead>
<tr>
<th>Phase ratio $v_a/v_o$</th>
<th>% La stripping</th>
<th>% Nd stripping</th>
<th>% Sm stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>53</td>
<td>85</td>
<td>91</td>
</tr>
<tr>
<td>1:2</td>
<td>40</td>
<td>98</td>
<td>92</td>
</tr>
<tr>
<td>1:3</td>
<td>43</td>
<td>85</td>
<td>96</td>
</tr>
</tbody>
</table>

3.11 Separation Feasibility

Separation of two components is possible when the distribution ratio of one component, $D_i$, differs from that of the other components, $D_j$. Thus, separation is possible when $D_i / D_j \neq 1$. The ratio of the distribution ratios is a measure of the ease or difficulty of a separation and is known as the separation factor (SF). This relation is applied if $D_i$ and $D_j$ are determined under similar conditions.

The effects of temperature, concentration of nitrate ion and pH on the separation factor for Cyanex 302 system under similar experimental conditions are shown in Table (4).

While the results showed that the SF of Nd/La more than doubled from 4.45 to 10.04 when the pH only increases by just a unit from 2 to 3, it decreases by increasing nitrate ion concentration. Hence, an effective separation (SF=10.04) could be reached at 0.01[N\O$_3$]. The highest SF could be obtained at 30°C where it is 10.60.

On the other hand, the SF of Sm/La reached the highest at 0.1M nitrate ions where it is 14.33. Moving further, SF of Sm/La almost tripled (3.32 to 9.00) by increasing the pH from 2 to 3. It was also noticed that the lowest categorized temperature, 30°C, corresponds to an observable separation between Sm and La where the SF is 13.20.
### Table (4): Separation factors between Nd/La and Sm/La at different values of pH, Temp., and nitrate ions concentrations

<table>
<thead>
<tr>
<th>SF</th>
<th>[NO₃⁻], M</th>
<th>pH</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Nd/La</td>
<td>10.04</td>
<td>8.77</td>
<td>6.14</td>
</tr>
<tr>
<td>Sm/La</td>
<td>9.00</td>
<td>10.17</td>
<td>14.33</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION

The extraction of La³⁺, Nd³⁺ and Sm³⁺ by Cyanex 302 in kerosene from aqueous nitrate medium was found to increase with the extractant concentration. The increase in hydrogen ion and nitrate ion concentrations in the medium were found to decrease the extraction process. The slope analysis of the equilibrium results obtained indicates that, La³⁺, Nd³⁺ and Sm³⁺ is extracted as La(OH)₂A(HA)₃ and M(OH)NO₃A(HA)₃, where M represents Nd (III) and Sm (III). The extraction reaction was found to be endothermic and the thermodynamic parameters were evaluated. Striping of metals from the loaded organic phase can be easily carried out with lower nitric acid concentrations. The extractant may be of practical importance for the separation of Nd or Sm from La.

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