Extraction studies of Lanthanum(III) from sodium salicylate medium using trialkyl phosphine oxide

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Keywords: Lanthanum(III), sodium salicylate, Extraction, Cyanex-923 & Stripping

ABSTRACT. Cyanex-923, a mixture of four trialkylphosphine oxide has been used for the extraction and separation of La(III) from sodium salicylate medium. Lanthanum(III) was found to be quantitatively extracted with Cyanex-923 in toluene at pH 6.0. The metal loaded organic phase is stripped with 2.0M HCl solution. Various parameters like effect of pH, Cyanex-923 concentration, sodium salicylate concentration, diluents, equilibration period and stripping agent on the extraction of La(III) has been studied. The stoichiometry of the extracted species of this metal ion was determined on the basis of the slope analysis method. The reaction proceed by solvation and the probable extracted species found were LaSal-HSal & Cyanex-923.

1. INTRODUCTION

Extraction of La(III) was systematically studied using N-n-octylaniline in salicylate medium (1). The solvent extraction of some trivalent rare earths metal ions like La(III), Eu(III) and Lu(III) was carried out from NaNO₃ solutions using two bis(4-acyl-5-hydroxypyrazoles), 1,12-bis(1-phenyl-3'-methyl-5'-hydroxy-4'-pyrazolyl)-dodecane, 1,12-dione and 1,6-bis(1'-phenyl-3'-methyl-5'-hydroxy)-4'-pyrazolyl)-hexane, 1,6-dione, in chloroform (2). The extraction of La(III) was studied from acidic nitrate-acetato medium by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and trioctylphosphine oxide (TOPO) in toluene (3). The solvent extractions of La(III), Eu(III), and Lu(III) in NaNO₃ solutions with 5,7-dichloro-8-quinolinol into chloroform were studied in the presence of tetrabutylammonium ions or trioctylphosphine oxide (4). The extraction and separation of cerium(III) was investigated from NaCl solutions with LIX 70 dissolved in kerosene or n-heptane (5). The extraction of lanthanum(III) and cerium(III) was also carried out with dialkylthiophosphonic acids from the aqueous solutions containing perchlorate, nitrate and chloride ions into different polar and nonpolar solvents (6). Solvent extraction of lanthanum(III), europium(III) and lutetium(III) was studied with fluorinated 1-phenyl-3-methyl-4-benzoyl-5-pyrazolones in chloroform (7). The distribution of La(III) between aqueous H₂SO₄ solutions and Primene JMT in the organic phase is described (8). Separation of La(III) from Fe(III), Mo(VI), V(V), Cr(VI), Ti(IV), Bi(III), Zr(IV), Sc(III), U(VI) and Be(II) is obtained by solvent extraction using mesityl oxide from sodium salicylate solution (9). Extraction of La(III) and Sm(III) was done from nitrate medium by some commercial organophosphorus extractant like Cyanex-921, Cyanex-923 and Cyanex-925 in kerosene (10). Extraction and Separation of La(III) from Ti(IV), Zr(IV), Hf(IV), Th(IV) and U(VI) was investigated using 1.5% triphenylphosphine oxide from sodium salicylate solution (11). The extraction and kinetic studies were carried out for Sc(III), Y(III), La(III) and Gd(III) using bis(2,4,4-trimethylpentyl)-mono thiophosphinic acid (Cyanex-302) in heptane from HCl solutions (12).
2. EXPERIMENTAL

Apparatus and Reagents
Trialkyl phosphine oxide extractant, Cyanex-923 used for the extraction of Lanthanum(III) was supplied by Cytec Industries Inc. Canada. It was used without further purification. A known amount of Lanthanum Oxide, La₂O₃, was dissolved in 5ml of hot 1:1 HCl solution and then diluted with double distilled water as per requirement. All other chemical used were of analytical grade. EQUIP-TRONIC model EQ-614 pH meter with combined electrode was used for pH measurements. ELICO UV-visible SL-27 spectrophotometer with 10 mm cortex quartz cuvettes was used for absorbance measurements.

Extraction Condition
An aliquot containing 40μg of La(III) was taken in 10ml beaker, its pH was adjusted to 6.0 with dilute HCl and NH₄OH. Sodium salicylate solution of required concentration was then added to the same solution. The solution was equilibrated with equal volume of Cyanex-923 diluted in toluene for the required shaking time of 10 minutes. After extraction, the two phases were allowed to separate, the organic phase containing the metal extracted species was stripped with 2.0M HCl. The amount of La(III) was determine spectrophotometrically by Arsenazo–I indicator (13). All the experiment was carried out at room temperature except the effect of temperature.

3. RESULTS AND DISCUSSION

Effect of pH
The extraction of La(III) was carried out at various pH ranging from 1.0 to 7.0. The extraction of Lanthanum(III) increases with increase in pH and it became quantitative in the pH range 5.0-7.0. After pH 7.0, the extraction decreases, hence all the extraction of La(III) with Cyanex-923 and sodium salicylate was carried out at a fixed pH of 6.0 (Fig-1).

![Fig:1 Effect of pH on percentage extraction of La(III) with Cyanex-923 in toluene.](image-url)
Effect of Reagent Concentration

The concentration of Cyanex-923 diluted in toluene was varied from 1.0 x 10^{-3} M to 1x10^{-1} M. It was found that the extraction of Lanthanum(III) increased with increase in the Cyanex-923 concentration. Quantitative extraction of La(III) was found in the range 1.0 x 10^{-2} M to 1x10^{-1} Cyanex-923 in toluene. Therefore 1.0 x 10^{-2} M of Cyanex-923 was used for all the further experiments.

Effect of Sodium Salicylate Concentration

The effect of Sodium Salicylate concentration on the percentage extraction of La(III) with 1.0x10^{-2} M Cyanex-923 in toluene at fix pH of 6.0 was studied in the sodium salicylate range from 1.0 x 10^{-4} M - 1.0 x 10^{-3} M. As the sodium salicylate concentration increases the extraction goes on increasing and becomes quantitative in the range 7.5 x 10^{-4} M - 1.0 x 10^{-3} M with Cyanex-923 in toluene. Hence all the extractions were carried out at 7.5 x 10^{-4} M sodium salicylate with Cyanex-923 in toluene.

Effect of stripping agents

After extraction of Lanthanum(III) in the organic phase of Cyanex-923 diluted in toluene, it was stripped back to the aqueous phase with different strengths of acids like HCl, HNO_{3} and H_{2}SO_{4}. It was found that 2.0 M HCl was sufficient to strip the lanthanum ions into the aqueous phase. The amount of La(III) was then determined spectrophotometrically using Arsenazo-1 method. However incomplete recovery of metal ion was observed with other acids (Table-1).

### Table 1: Effect of Stripping agents on the percentage recovery of La(III) from metal loaded organic phase of Cyanex-923 in toluene.

| Acids (M)  | 1.0  | 2.0  | 3.0  | 4.0  |
|-----------|------|------|------|------|
| HCl       | 47.4 | 99.9 | 85.4 | 60.0 |
| HNO_{3}   | 30.2 | 16.6 | 10.2 | 9.4  |
| H_{2}SO_{4}| 24.3 | 81.9 | 85.0 | 90.1 |

Influence of diluents and equilibration period

In order to determine the effect of nature of diluents on the extraction of La(III) various diluents like toluene, cyclohexane, xylene, chloroform, n-hexane and carbon tetrachloride are used. It was found that all the above diluents showed quantitative extraction except xylene (86.4%) and carbon tetrachloride (74.5%). Toluene was preferred as the best diluents for the extraction of La(III) since it provided better phase separation.

Extraction equilibrium was studied for different periods of shaking ranging from 1-30 mins. It was observed that 1 minute of shaking period was sufficient for quantitative extraction of La(III) with 1.0x10^{-2} M Cyanex-923 in toluene and 7.5 x 10^{-4} M sodium salicylate. However there was no change in extraction by increasing the extraction period up to 30 mins.

Stoichiometry of the extracted Species:

The nature of the extracted species was established using log-log plots (Fig.2,3). A plot of log D versus log Cyanex-923 concentration at fixed pH and sodium salicylate concentration and a plot of log D versus log of sodium salicylate concentration at fixed pH and Cyanex-923 concentration gave a slope of 2.15 and 2.37 respectively, indicating a molar ratio of 1:2 of Lanthanum with respect to both extractant, Cyanex-923 and sodium salicylate. The extracted species must be a neutral complex with the composition LaSal-HSal. 2Cyanex-923, where Sal is...
Salicylate which is similar to the early reported with Triphenylphosphine oxide (11). The probable mechanism of extraction can be written as,

\[
\begin{align*}
La^{3+}_{\text{(aq)}} + Sal^{2-}_{\text{(aq)}} & \rightleftharpoons LaSal^{+}_{\text{(aq)}} \\
LaSal^{+}_{\text{(aq)}} + HSal^{-}_{\text{(aq)}} & \rightleftharpoons LaSal-HSal^{-}_{\text{(aq)}} \\
LaSal-HSal^{-}_{\text{(aq)}} + 2\text{Cyanex-923}_{\text{(org)}} & \rightleftharpoons LaSal-HSal \cdot 2\text{Cyanex-923}_{\text{(org)}}
\end{align*}
\]

Cyanex-923, being more basic, replaces water molecules and renders Lanthanum(III) salicylate more hydrophobic.

**Fig. 2** Effect of reagent concentration on Distribution ratio of La(III).
Influence of temperature

Extraction of Lanthanum(III) with 1.0x10^{-2} M Cyanex-923 in toluene at pH 2.0 having Salicylate concentration of 7.5x10^{-4} M, were carried out at different temperature (upto 343°K). The distribution ratio decreased with increase in temperature. The Van’t Hoff equation is, log $D_{La} = - \frac{\Delta H}{2.303RT} + C$, where $D_{La}$ represent the distribution ratio, $\Delta H$ is the enthalpy change for the reaction and $C$ is the constant. The slope obtained from plot of log $D_{La}$ Vs 1000/T is 1.505 (Fig.4). The $\Delta H$ values obtained is $-28.82$ kJ/mol indicating that the reaction is exothermic in nature.

![Graph showing logarithm of distribution ratio vs logarithm of salicylate concentration](image)

**Fig:3** Effect of Sodium Salicylate concentration on distribution ratio of La(III).

**Influence of temperature**

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La(III) was separated from various other metal ions, by exploiting the differences in their respective extracting and stripping conditions. A solution containing La(III) and Th(IV) is extracted with $1.0 \times 10^{-2}$ M Cyanex-923 in toluene at pH 6.0 and $7.5 \times 10^{-4}$ M sodium salicylate whereby La(III) and Th(IV) both get extracted simultaneously in the organic phase. From the organic phase, La(III) was first stripped with 2.0 M HCl and then Th(IV) is stripped with 2.0 M HClO$_4$. Similarly La(III) is separated from the other metal ions like Be(II), U(VI), Ni(II), Ti(IV) and Ce(IV) (Table 2).

**Table 2:** Separation of La(III) from multicomponent mixtures with Cyanex-923 in toluene.

| Sr. No. | Metal ions | Amount taken (μg) | pH  | Sodium Salicylate (M) | Cyanex – 923 (M) | Stripping Agents | Percentage Recovery (%) |
|---------|------------|-------------------|-----|-----------------------|------------------|-------------------|------------------------|
| 1.      | La(III)    | 40                | 6.0 | $7.5 \times 10^{-4}$  | $1.0 \times 10^{-2}$ | 2.0 M HCl         | 99.7                   |
| 2.      | Th(IV)     | 40                |     |                       |                  | 2.0 M HClO$_4$    | 99.4                   |
| 3.      | La(III)    | 40                | 6.0 | $7.5 \times 10^{-4}$  | $1.0 \times 10^{-2}$ | 2.0 M HCl         | 99.6                   |
| 4.      | Be(II)     | 50                |     |                       |                  | Unextracted       | 99.3                   |
| 5.      | U(VI)      | 40                | 6.0 | $7.5 \times 10^{-4}$  | $1.0 \times 10^{-2}$ | 2.0 M HCl         | 99.4                   |
| 6.      | Ni(II)     | 40                |     |                       |                  | 4.0 M H$_2$SO$_4$ | 99.5                   |
|         | La(III)    | 40                | 6.0 | $7.5 \times 10^{-4}$  | $1.0 \times 10^{-2}$ | 2.0 M HCl         | 99.5                   |
| 7.      | Ti(IV)     | 40                |     |                       |                  | Unextracted       | 99.3                   |
| 8.      | La(III)    | 40                | 6.0 | $7.5 \times 10^{-4}$  | $1.0 \times 10^{-2}$ | 2.0 M HCl         | 99.4                   |
| 9.      | Th(IV)     | 40                |     |                       |                  | 2.0 M HClO$_4$    | 99.3                   |
| 10.     | Ce(IV)     | 50                |     |                       |                  | Unextracted       | 99.1                   |
4. CONCLUSION

1. The results obtained show that commercially available trialkyl phosphine oxide, Cyanex-923 diluted in toluene can be used effectively for quantitative extraction of La(III) from sodium Salicylate media in the pH range 5-7. The minimum Cyanex-923 concentration required for the complete extraction of La(III) was 1.0 x10^{-2} M Cyanex-923 in toluene.

2. The thermodynamic study of the extraction reaction of Th(IV) with Cyanex-923 in toluene was also performed. It revealed that the extraction reaction is exothermic in nature with an enthalpy change (ΔH) value -28.82 kJ/mol.

ACKNOWLEDGEMENT

The authors are thankful to Cytec Industries Inc. Canada for supplying Cyanex-923 as a gift sample.

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