Separation of Ce(IV) from High Concentration Nitric Acid Medium by Cyanex-302 and Cyanex-921 Kinetic, Thermodynamic and Reaction Mechanism

N. El-Said, A. Mekhael and E. El-Shreif
Hot Laboratories Center, Atomic Energy Authority, P. No. 13759, Egypt.

ABSTRACT

The kinetic extraction of tetravalent cerium(IV) from high concentration nitric acid medium (9M HNO₃+2M Na₂BrO₃) by Cyanex 302 and Cyanex 921 in kerosene was investigated using Lewis cell. The effects of stirring speed, temperature and specific interfacial area on the extraction rate were studied. The results showed that the reaction is controlled by a chemical reaction in the interface rather than in the bulk phase for Cyanex-921. The results showed that the activation energies was found to be 29.4±0.5 kJ Mol⁻¹, the heat of activation is 28.2±0.25 kJ Mol⁻¹ while the entropy was – 103 kJ Mol⁻¹ for Cyanex-921. The Cyanex-302 showed unstability in 9M HNO₃ medium. The extraction process was expressed by a reaction mechanism in which the extracted species were investigated.

Key Words: Ce(IV) / Cyanex-302 / Cyanex-921 / Kinetic / Thermodynamic.

INTRODUCTION

Because of a very wide application of cerium for Pyrophoric alloys for cigarette lighters, aluminium alloys of steels and irons, opposing graphitisation and produces a malleable iron, the separation of cerium was very important. Cerium is mostly dangerous in the working environment, due to the fact that damp and gases can be inhaled with air. Cerium can be a threat to the liver when it accumulates in the human body. Some of the literature on the toxicological behavior of cerium has arisen because of the concern about exposure to radioactive cerium species produced in nuclear reactions. As cerium was found in radioactive waste in trivalent state and due to the presence in lanthanide group and its harmful effect as a radionuclide, the study of extraction is of great importance. Tri-n-octylphosphine oxide (TOPO) is one of the neutral organo-phosphorous solvating reagents, although having the highest extractive power, some problems can be found with solubility common hydrocarbon diluents especially at low temperatures. To overcome these problems Cyanamid had produced Cyanex-921 which is considered as a commercial product of TOPO (93%). The Purex process is a continuous solvent extraction process which has been developed and used very successfully for several years now for the separation of uranium, plutonium and fission product elements from irradiated natural and enriched uranium fuel. This method is based on the separation of uranium and plutonium from 3M nitric acid solution by 30% TBP in kerosene using mixer settlers, pulsed columns or centrifugal extractors. Dusek and Kutek separated cerium from a mixture of the phosphate concentrate of rare earths from HNO₃ solution in the form of Ce₆(PO₄)₄·4H₂O. Cerium could be separated from permanganate and dichromate as Ce₆(PO₄)₄. Also it was separated in the Dowex 50WX8 cation exchanger and the solvent mixture acetone / hydrochloric acid (3:1) with one intermediate washing using 2N HC/H₂SO₄. Ce(IV) could be separated from thorium from 0.1M 4-(5-nonyl) pyridine/xylene mixture. Cerium (III) has been separated from young fission products by extraction of uranium and fission products using tri-n-octylamine oxide and an anion exchange column for preconcentration followed by extraction of Ce(IV) with 0.2M xylene solution of 4-(5-nonyl) pyridine oxide from 0.1M HNO₃. Ce(IV) is then back extracted by reduction with HCl-H₂O₂ mixture. An aqueous solution containing Ce(III) and rare earths was oxidized in the anodic
compartment of an electrolytic cell. Ce(IV) was extracted by an organic solvent and the organic phase containing Ce(IV) was reduced in the cathodic compartment of the same electrolytic cell and Ce(IV) was extracted in nitric acid aqueous phase\textsuperscript{(13)}. During the solvent extraction of Ce(III) with benzoyl trifluoroacetone (Hbfa) into air saturated carbon tetrachloride. The rate of oxidation was not very dependent on the Hbfa concentration. The oxidation was suppressed by trioctylphosphine oxide. When carbon tetrachloride solution contained the Ce(IV) (bfa)\textsubscript{4} complex, the reduction to Ce(III) occurred by an addition of TOPO. The rate of reduction of Ce(IV)(bfa)\textsubscript{4} complex in organic solution was first order with respect to the TOPO but it was not dependent on the Hbfa concentration\textsuperscript{(14)}. The dependence of the distribution ratios of \textsuperscript{241}Am and lanthanides between purified Cyanex-301 (HBTMPDTP)-TBP- kerosene/nitrate solution on pH, lanthanide concentration in aqueous phase and degree of saponification of HBTMPDTP was investigated. Extraction of plutonium from acidic media using various phosphine oxides was investigated by M.S.Murali et al.\textsuperscript{(15)} extraction, loading and stripping studies of Pu(IV) have been carried out using three phosphine oxides namely Cyanex-923, Cyanex-925 and TOPO in dodecane from nitric acid medium.

This work aims to separate cerium(III) from fission products via oxidation to Ce(IV) and to obtain the optimum conditions. In this work there are two problems must be solved. (i) The presence of cerium in trivalent state with different lanthanides. (ii) The second problem for extraction of cerium due to the fact that Ce(III) can be oxidized to Ce(IV) and Ce(IV) can be reduced to Ce(III).

**EXPERIMENTAL**

All chemicals and reagents were of A.R grade. Nitric acid was a product of PROLABO, ceric ammonium nitrate was a product of May Beaker and sodium bromate was a product of Colnbrook Berks, England. Both Cyanex-921 and Cyanex-302 were supplied from Cyanamid, Canada. The UV-visible spectrum of the presolutions was determined using a Shimadzu UV-160A where Ce(IV) in 9M nitric acid was measured at 470 nm. Ce(IV) dissolved in 9M nitric acid and adding 2M sodium bromate was found to be stable for a long time (6 months). The thermodynamic investigations were carried out by carefully transferring equal volumes (20 ml) of the organic solution (0.01 M of Cyanex-921 or Cyanex-302 diluted with odorless kerosene) and the aqueous solution (9 M HNO\textsubscript{3} + 2 M Na\textsubscript{2}BrO\textsubscript{3}) into a double-jacket Lewis cell adjusted at 25±1°C. The reaction begun by starting the stirring motor at 315 rpm. At different time intervals equal volumes were withdrawn from the two phases and the concentration of Ce(IV) was determined spectrophotometrically. The concentration of Ce(IV) in the organic phase was consequently determined by the difference between the original concentration and the aqueous concentration at time, t, and denoted by A and a straight line through the origin at equilibrium it is denoted by A\textsubscript{eq}. The plots of ln(A\textsubscript{eq}−C) vs the time, t, yielded straight line relations. The first order reaction constant, k\textsubscript{obs}, was obtained from the slope of this line. The effect of interfacial surface area on the rate of extraction of Ce(IV) by both types of Cyanexes in kerosene was studied. The lanthanum, europium and gadolinium were determined by an ICP Spectrometer Plasmalab 8440, Labtum Ltd, Victoria Australia.

**RESULTS AND DISCUSSION**

**Extraction Behavior and Equilibrium Investigations**

The extraction of cerium, lanthanum, europium and gadolinium from a wide range of HNO\textsubscript{3} (0.1-9 M) by Cyanex-921 or Cyanex-302 in kerosene is given in Figs.(1, 2) and Table (1). From these figures, the extraction of Ce(IV) is almost quantitative (98%) after the concentration of 5 M HNO\textsubscript{3} in the entire range of Cyanex-921 molarities, while with Cyanex-302 molarities, it shows a very lower percent of extraction; Fig.(1). Cerium(IV) shows a maximum extraction at 0.1 M Cyanex-921, but it is negligible over the entire range of Cyanex-302. From Fig.(2) it is apparent that Ce(IV) can be
separated from different lanthanide cations at (9M HNO$_3$+2M Na$_2$BrO$_3$) by extracting it selectively in Cyanex-921 and leaving the lanthanide fraction in the aqueous phase. At the same time, from Fig.(2), it is clear that Ce(IV) can be separated from different lanthanide cations in the range (0.1-5M HNO$_3$) by extracting the lanthanide fraction from the aqueous phase by Cyanex-302 and leaving Ce(IV) in the aqueous phase. The effect of different parameters on the extraction of Ce(IV) was investigated at the entire range of Cyanex-302 and Cyanex-921.

Fig. (1): Effect of HNO$_3$ acid on the extraction of metal ions in a kerosene solution of Cyanex-302, conditions: [metal ion]= 0.003 M; [Cyanex]= 0.05 M.

Fig. (2): Effect of HNO$_3$ acid on the extraction of metal ions in a kerosene solution of Cyanex-921, conditions: [metal ion]= 0.003 M; [Cyanex]= 0.05 M.
Table (1): Extraction of some lanthanides in presence of Ce(IV) by Cyanex-302 and Cyanex-921 in kerosene from (9M HNO₃ +2M Na₂BrO₃).

<table>
<thead>
<tr>
<th>Extracted species</th>
<th>Ce(IV)</th>
<th>La(III)</th>
<th>Eu(III)</th>
<th>Gd(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex-302</td>
<td>19.5 ± 0.1</td>
<td>12.0 ± 1.0</td>
<td>4.5 ± 0.9</td>
<td>5.0 ± 0.8</td>
</tr>
<tr>
<td>Cyanex-921</td>
<td>97 ± 0.7</td>
<td>3 ± 0.05</td>
<td>4 ± 0.06</td>
<td>6 ± 0.7</td>
</tr>
</tbody>
</table>

Effect of HNO₃ Acid Concentration

The effect of concentration of nitric acid on the extraction of Ce(IV) and Ce(III) by Cyanex-921 & Cyanex-302 was investigated in Figs.(3, 4). Figure (3) shows that Cyanex-302 has a negligible effect for separation over 5M HNO₃ concentration which may be attributed to the instability of Cyanex-302 at 5M HNO₃. Figure (4) also shows that percent of extraction of Ce(III) and Ce(IV) by the percent of Cyanex-921 has a wide range of HNO₃ concentration. It is obvious that Cyanex–921 has a strong effect on the percent of extraction of Ce(IV) and unremarkable effect on Ce(III) which present in a dimer form.

![Graph showing effect of HNO₃ acid concentration on the extraction of Ce metal ions in a kerosene solution of Cyanex-302](image)

Fig.(3): Effect of HNO₃ acid concentration on the extraction of Ce metal ions in a kerosene solution of Cyanex-302, conditions: [metal ion] = 0.003 M; [Cyanex]= 0.05 M.
Fig. (4): Effect of HNO$_3$ acid concentration on the extraction of Ce metal ions in a kerosene solution of Cyanex-921, conditions: [metal ion]= 0.003 M;[Cyanex]= 0.05 M.

From Fig. (4) it is obvious that extraction of Ce(IV) by Cyanex-921 in the range 5-9M HNO$_3$ is high while Cyanex–302 which present in dimer shown unstability in this range. From the above discussion it can be concluded that Ce(III) can be separated from trivalent lanthanides via oxidation to Ce(IV) at 9M HNO$_3$ by Cyanex–921 in kerosene. The distribution ratio increases with increasing concentration of the extractants. A slope of around two for the two types of Cyanex suggest the involvement of two molecules of Cyanex in the formation of the reacting species which may be proposed as Ce(NO$_3$)$_4$.2R (R=Cyanex-921 or the dimer form Cyanex-302); Fig. (4). The extraction equilibria can be written as when [NO$_3^-$]$_{aq}$ remains in excess and constant

$$K = \frac{[M(NO_3)_n^+ nR]}{[M{}^{n+}]_{aq} [R]^n [NO_3]_{aq}^n}$$

where n is the charge of the cation and m is the solvation number of the extracting species. The values of conditional extraction constant, K, for Cyanex-921 and Cyanex-302 with cerium (IV) are 4.3x10$^6$ and 2.1x10$^3$, respectively. The effect of nitric acid concentration was studied in range 0.1-9M and the slope analysis was found to be around 3.8, Fig. (5).

$$\log K = \log D - m \log [R]$$

$$D = \frac{[M(NO_3)_n^+ nR]}{[M{}^{n+}]_{aq}}$$
Fig.(5): Effect of Cyanex in kerosene concentration on the extraction of Ce(IV) from nitrate medium condition [Ce(IV)] = 0.003 M.

Effect of Concentration of Metal Ion
The effect of Ce(III) concentration on the extraction using 0.05M of Cyanex-921 is shown in Fig.(6). A straight line in the concentration range of 10$^{-6}$M to 10$^{-2}$M for Ce(IV) for Cyanex-921 indicates the distribution ratio increases by increasing the metal ion concentration in the studied range.

Effect of cerium concentration, M, ion Ce(III) by Cyanex-921 in kerosene from 9M nitric acid.
Effect of Stirring Rate

The effect of stirring rate on the extraction of Ce(IV) by Cyanex-921 and Cyanex-302 in kerosene from (9M nitric acid +2M Na$_2$BrO$_3$) was studied by changing stirring speed of the solutions from 100 to 500 rpm. The plot of $k_{obs}$ vs. stirring rate was shown in Fig.(7). It is obvious that the increase in the stirring rate from 100 to 300 rpm increased the distribution ratio. The distribution ratio of Ce(IV) increased with Cyanex-921 is more than with Cyanex-302.

![Fig.(7): Effect of stirring rate on the reaction rate of 0.003M Ce(IV) by Cyanex-921 and Cyanex-302 in kerosene from 9M nitric acid.](image)

Kinetic Investigations

The controlling effect in Lewis cell technique is determined by stirring speed and the temperature. When the extraction rate is controlled by diffusion, the extraction increases by increasing the stirring speed while there is no effect on the extraction rate governed the chemical reaction. The effect of stirring speed on the rate of extraction of Ce(IV) by Cyanex in kerosene from nitrate medium was investigated and different rate constants $k_{obs}$ at different speeds were calculated and plotted as semi-log relation in Fig.(7). A plateau was observed in the region 300-400 rpm indicate that the control of chemical reaction in the reacting of Ce(IV) carried out in this region. The rate of extraction of Ce(IV) can be written as:

$$\frac{-d[\text{Ce(IV)}]}{dt} = k_{obs}[\text{Ce(IV)}]$$  \hfill (5)

$$\log \frac{[\text{Ce(IV)}]}{[\text{Ce(IV)}]} = (k_{obs}/2.303)t$$  \hfill (6)

where $k_{obs}$ is the observed rate constant
Since the oxidation of Ce(III) to Ce(IV) is achieved under certain specified conditions (9M HNO₃) where NO₃⁻ is present in excess. Therefore

\[ k_{\text{obs}} = k \overline{[\text{Cyanex}]} \]  

(7)

where \( k_{\text{obs}} \) is the conditional rate constant.

When the extracted species Ce(III) is oxidized and the Ce(IV) species should be formed. However, such as a reduction in the aqueous phase was found to be negligible under the condition of present study (9M HNO₃+2M Na₂BrO₃). Since the reduction of Ce(IV) to Ce(III) is negligible, the conditional constant should be larger as the oxidation proceeds and the extraction equilibrium can be written as

\[ \text{Ce(NO}_3\text{)}_4 + 2[\text{Cyanex}] \rightarrow \text{Ce(NO}_3\text{)}_4(\text{Cyanex})_2 \]  

(8)

The above equation (8) indicates that the extracted species were four with respect to nitrate and two with respect to Cyanex-921. In addition equation (7) represents a straight line passing by the origin. The plot of the different metal ion Ce(III) molarities in the organic phase versus the corresponding values of \( k_{\text{obs}} \) in Fig.(6) yields a straight line passing by the origin which verifies eq.(7) and supports the proposed mechanism.

Thermodynamic Investigations

The effect of temperature on the rate of extraction of Ce(IV) by Cyanex-302 and Cyanex-921 was studied in the range of 5-35°C as shown in Fig.(8). The plot of the respective \( k_{\text{obs}} \) vs 1000/T gave a straight line in Fig.(9). The activation energy were calculated from the slope of the straight line. This value of activation energy and the rate of stirring speed at 350 justify that the chemical process is the rate determining factor for the process and the calculated values were found to obey Arrhenius equation:

\[ k_{\text{obs}} = A e^{E/RT} \]  

(9)

![Fig.(8): Kinetic reaction plots for log(Aq.-C) against time for extraction of 0.003M Ce(IV) by Cyanex-921 in kerosene from 9M nitric acid at different temperatures.](image-url)
where $R$ is the gas constant, $T$ is the absolute temperature, Fig.(9) and given in Table (2). From the thermodynamic functions, it is noted that the effect of Cyanex-302 is similar to Cyanex-921 while Cyanex-921 has a higher extractive power. Two moles of Cyanex and two moles of nitrate are present in the final extracted species. The rate constant of Ce(IV) with Cyanex-921 is higher than that with Cyanex-302. The higher entropy in case of Cyanex-921 ($\Delta S^*$ less negative) is due to the presence of bulky group case (citric effect) in Cyanex-921 which leads to more disordering system.

Table (2): The thermodynamic functions for the extraction of Ce(IV) by Cyanex-302 and Cyanex-921 in kerosene from (9M HNO$_3$ +2M Na$_2$BrO$_3$).

<table>
<thead>
<tr>
<th>Extracted species</th>
<th>$E$ kJ mol$^{-1}$</th>
<th>$\Delta H^*$ kJ mol$^{-1}$</th>
<th>$\Delta S^*$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NO$_3$)$_2$(Cyanex-921)$_2$</td>
<td>13±0.21</td>
<td>11±0.24</td>
<td>-65±0.6</td>
</tr>
</tbody>
</table>

**Effect of Interfacial Area**

The rate of extraction increases by increasing the specific interfacial area ($a$) (where $a = Q/V$ volume of the phase). The effect of varying the specific interfacial area from Fig.(10) on the rate of extraction was investigated using different Lewis cells with constant volume (25 cm$^3$) and different specific interfacial areas. The obtained results of Fig.(11) show that the reaction rates for Cyanex-921 depend on specific interfacial area indicating that the controlling reactions take place at the interface. The use of stirring speed 350 rpm which lies in the plateau region where the stirring speed has no effect on the rate of extraction with the obtained value of activation energy (kJ mol$^{-1}$) indicate that the extraction of Ce(IV) in the investigated system is controlled by a chemical reaction which take place either in the bulk or at the interface. It is important to know the role of high concentration nitric acid (9M) for stabilization of Ce(IV) in aqueous and organic phase. The determination of nitrate in the species
extracted in the organic phase shows that four moles are attached to one mole of cerium. Also it is confirmed by stability of Ce(IV) in the organic phase in presence of nitrate and Cyanex together in the extracted species while the stability of Ce(IV) was suppressed by the presence of TOPO only in the species extracted in the organic phase\(^{(13)}\). Based on the above kinetic and thermodynamic results taking into account the extracting properties and experimental conditions, the extraction of Ce(IV) by Cyanex-302 or Cyanex-921 can be expected to proceed the following steps.

\[
\text{Cyanex} \, \text{f} \, \text{Cyanex} \quad K_D = \frac{\text{Cyanex}}{\text{Cyanex}} \quad (10)
\]

\[
\text{HNO}_3 \quad \rightarrow \quad \text{H}^+ + \text{NO}_3^- \quad K_a = \frac{[\text{H}^+][\text{NO}_3^-]}{[\text{HNO}_3]} \quad (11)
\]

The reaction between Ce(IV) and nitrate species in the aqueous

\[
\text{Ce}^{4+} + 4 \text{NO}_3^- \rightarrow \text{Ce(NO}_3)_4 \quad (12)
\]

The reaction between CeA\(_4\) with a mole of Cyanex, which is expected to be the slow step.

\[
\frac{\text{Ce(NO}_3)_4}{\text{slow}} + \text{Cyanex} \rightarrow \frac{\text{Ce(NO}_3)_4(\text{Cyanex})}{\text{interface}} \quad (13)
\]

\[
\frac{\text{Ce(NO}_3)_4(\text{Cyanex})}{\text{fast}} + \text{Cyanex} \rightarrow \text{Ce(NO}_3)_4(\text{Cyanex})_2 \quad (14)
\]

**Fig.(10):** Effect of interfacial area on the reaction rate constant of 0.003M Ce(IV) using 0.05M Cyanex-921 in kerosene from 9M HNO\(_3\)+2M Na\(_2\)BrO\(_3\).
The studied system indicates that, the higher extractive power of Cyanex-921 than Cyanex-302, at the same time is due to the unstability of Cyanex-302 at the concentrations more than 5M HNO₃.

Separation and Regeneration of the Extractant

The stability of Cyanex towards nitric acid was determined by the extractant in contact with 9M HNO₃ solution and checking percent of Ce(IV) for two days. No significant decrease in the extraction of Ce(IV) is observed even after 3 days. The recycling of the extractant after regeneration (washing the organic phase with water, till the washing was neutral) where no significant change was observed in the presence of the extractant of Ce(IV); Table (3).

Table (3): The stability and regenering* capacity of Cyanex-921 in kerosene.

<table>
<thead>
<tr>
<th>% uptake of Ce(IV) after</th>
<th>1 day</th>
<th>2 days</th>
<th>3 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96±1.0</td>
<td>97±0.1</td>
<td>95.5±1.0</td>
</tr>
</tbody>
</table>

*The regeneration after each time interval from 1 to 3 days

CONCLUSION

Cerium (III) can be separated completely from a multi component system containing lanthanum, europium and gadolinium in (9M HNO₃ +2M Na₂BrO₃) via oxidation to Ce(IV) and extracted by Cyanex-921 which shows a very high extracting power than Cyanex-302. The extraction process goes through a chemical reaction controlled at the interface. This work can be useful in PUREX process for separation of cerium from fission products in the second cycle.

Fig.(11): Kinetic reaction plots for log(A_aq-C) against time for effect of interfacial area on extraction of Ce(IV) by Cyanex-302 in kerosene from nitrate.
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