

## Reaction stoichiometry and mechanism of tetravalent cerium liquid-liquid extraction in the Ce(IV)-H<sub>2</sub>SO<sub>4</sub>-Cyanex 302-kerosene system

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The single-stage extraction of cerium(IV) from sulfuric acid solutions with Cyanex 302 was scrutinized. The quantitative extraction of 0.002 mol L<sup>-1</sup> Ce(IV) at pH<sub>(eq)</sub> ~ 4.0 was achieved by 0.1 mol L<sup>-1</sup> Cyanex 302 diluted in kerosene. The stoichiometry of the extracted species and the mechanism of extraction were elucidated on the basis of conventional slope analysis method. The distribution data were utilized to cover the determination of the conditions of feed solution pH, extractant concentration, organic-to-aqueous volume ratios, and reaction temperature for maximum extraction of cerium(IV). The temperature variation studies indicate that the overall extraction reaction is an exothermic process, which is confirmed from the negative value of ΔH. The positive value of ΔG suggests that the extraction process is non-spontaneous and the positive value of ΔS indicates that extraction of Ce(IV) is more efficient at high temperatures.

**Keywords:** Cerium(IV); Liquid-liquid extraction; Cyanex 302; Mechanism; Stoichiometry.

### INTRODUCTION

Cerium compounds are widely used in magnets, polishing powders, phosphors, fluorescent powders, catalysts, and colorants [1-4]. This element is well found in minerals of monazite and bastnaesite groups. Generally, the easy oxidation of Ce(III) into Ce(IV) is used to separate Ce from other rare earth elements (REEs) [5]. Compared with REEs(III), Ce(IV) is more easily extracted [6, 7]. Liquid-liquid extraction is one of the common metal separation techniques from aqueous solutions [8-14]. This technique was utilized for the selective extraction of cerium from acidic leach liquors [8, 15-19]. The sulfuric acid leach liquors are among the cases from which Ce(IV) extraction is considered. 2-ethylhexyl phosphonic acid 2-ethylhexyl mono ester (EHEHPA, also known as PC88A, P-507 and Ionquest 801), di(2-ethylhexyl)phosphoric acid (D2EHPA or HDEHP also known as P204), Cyanex 923 as extractants for the Ce(IV) extraction have been scrutinized [16, 17, 20-25]. Cyanex 923 is considered as an effective extractant for Ce(IV). Wuping *et al.* [16, 24] investigated the extraction of Ce(IV) and F from simulated sulfuric acid liquor of bastnaesite with Cyanex 923. The latter can extract not only Ce(IV) as Ce(HSO<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>). 2(Cyanex 923) but also F as HF(Cyanex 923). The extraction mechanism of Ce(IV) together with F can be related to the formation of Ce(HF)(HSO<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>). 2(Cyanex 923).

However, the common organophosphorus esters, including di(1-methyl-heptyl) methyl phosphonate (P350), TBP, TOPO, Cyanex 925, and Cyanex 923 have their own downsides for the extraction of

Ce(IV). For instance, P350 cannot be utilized to extract Ce(IV) due to the difficulty of removing potential reducing impurities. For Cyanex 925 also the problem of reduction of Ce(IV) exists in sulfate medium [26]. TBP as an extractant for Ce(IV), requires high TBP concentrations and high acidities. Its ability to extract Ce(IV) is also low compared to other extractants. Cyanex 921 (TOPO) also has a high potential for the extraction of Ce(IV), but its solubility in aliphatic diluents is limited. A further disadvantage of TOPO is the slow kinetics of extraction. In the case of Cyanex 923, the impurities in Cyanex 923 reduce tetravalent cerium to the non-extractable trivalent state, and at high acidity, a third phase causing the decrease in extraction would appear. Cyanex 923 is more expensive than di(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP) and less utilized to Ce(IV) extraction [6, 23, 27]. D2EHPA requires higher acidity level in the stripping process which could affect the operational cost.

Despite the high extraction efficiency of D2EHPA for the REEs, the stripping difficulties in the loaded organic phase have limited its uses, especially for extraction of heavy REEs. Recently, particular attention has been paid to EHEHPA as an alternative extractant to D2EHPA for the separation of rare earth elements due to the high separation factors between any two adjacent rare earths [28]. In addition, REE-loaded extractants can be stripped at lower acidities in EHEHPA systems compared to D2EHPA systems [29-31], but the kinetics of

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extraction is slower and extraction efficiency is lower. Therefore, the development of new extraction systems for Ce(IV), especially in H<sub>2</sub>SO<sub>4</sub> media, is a topic of great importance. In the field of solvent extraction, a recent development is the use of organophosphinic acid derivatives and their sulfur analogues (Cyanex reagents). Cyanex 302 and Cyanex 301 are mono- and disulfide analogues of Cyanex 272. The sulfur substitution decreases the pK<sub>a</sub> values (6.4, 5.6 and 2.6 for Cyanex 272 [32], Cyanex 302 [33] and Cyanex 301 [34], respectively) allowing working at lower pH [35]. Cyanex reagents differ from other commercial organophosphorus reagents (e.g. D2EHPA, DDDPA, TBP, EHEHPA, etc.) in that the former reagents contain P-C bonding, whilst the latter contain P-O-C bonding. The presence of P-C bonding in Cyanex reagents makes them less susceptible to hydrolysis and less soluble in water [36]. Among organophosphorus extractants, dithio-substituted dialkylphosphinic acid, Cyanex 302, not yet used for cerium extraction, has received increasing regard due to its capability in the recovery of metal ions and for their separation from aqueous solutions [37-43]. Also there is no report on the extraction equilibrium and stoichiometry of Ce(IV) in the Ce(IV)-H<sub>2</sub>SO<sub>4</sub>-Cyanex 302-kerosene system.

The present study aims to optimize the extraction reaction of cerium(IV) in the Ce(IV)-H<sub>2</sub>SO<sub>4</sub>-Cyanex 302-kerosene system. The stoichiometry of the extracted cerium(IV) complex and a plausible extraction mechanism were proposed by using slope analysis and graphical methods. The influence of aqueous pH, extractant concentration, and temperature on the extraction of Ce(IV) was studied. The extraction thermodynamics by Cyanex 302 from sulfuric acid solution was obtained under the experimental conditions and thermodynamic functions ΔH, ΔG and ΔS of the investigated system were determined.

## EXPERIMENTAL

### *Reagents and apparatus*

The stock solution of Ce(IV) was prepared by dissolving Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Merck) and diluting with distilled water. An amount of 1 mol L<sup>-1</sup> sodium hydroxide (Merck) was used for pH adjustment. The solution was standardized against 0.05 M EDTA solution [44] utilizing Eriochrome Black T as indicator. The commercial extractant, Cyanex 302 (bis-(2,4,4-trimethylpentyl) mono-thio-phosphinic acid) was supplied by Cytec Canada Inc. The organic phase was prepared by dissolving the extractant in kerosene (Sigma-Aldrich).

The concentration of Ce(IV) in the aqueous phase was measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Varian, Liberty 150AX Turbo, Australia). The aqueous pH adjustment was done using a digital pH meter (Metrohm 691 instrument). Also, extraction tests were conducted in a temperature-controlled circulating water bath 000-7126 (Haake A80).

### *Extraction procedure*

Solvent extraction experiments were conducted in stoppered glass tubes immersed in a thermostated water bath (25.0 ± 0.5 °C) using equal volumes (10 mL) of the aqueous solution (0.5 ≤ pH<sub>(ini)</sub> ≤ 6) containing 0.002 mol L<sup>-1</sup> Ce(IV) and organic phase containing the desired concentrations of extractant, Cyanex 302. Preliminary experiments demonstrated that equilibrium was achieved within 20 min. After phase disengagement, the aqueous phase was separated using a separating funnel, and the metal concentrations were determined by ICP-AES as mentioned above. The concentrations of the metal ions in the organic phase were calculated from the mass balance between the organic and aqueous solutions. The distribution coefficient (ratio), D, was calculated as the concentration of metal ion present in the organic to the aqueous solution at equilibrium. All the experiments were conducted at ambient temperature. The percentage extraction (%E) is defined as follows:

$$\%E = \frac{D}{D + \left(\frac{v_{aq}}{v_{org}}\right)} \times 100 \quad (1)$$

### *Stripping procedure*

The stripping procedure was similar to the extraction one, with the exception that the aqueous phase was a prepared aqueous stripping phase and the organic one consisted of the metal-loaded organic phase obtained in the extraction process. The fully loaded organic solution with the highest extracted metal concentration was chosen for the further stripping studies. Cerium(IV) in this solution was stripped by (0.1, 0.5 or 1.0) mol L<sup>-1</sup> mineral acid (H<sub>2</sub>SO<sub>4</sub>, HCl or HNO<sub>3</sub>) solution at 25±0.5 °C and at O:A of 1. The shaking time was 1 h. After equilibration and phase separation, the amount of the metal ions in the aqueous phase was measured by ICP-AES. The percentage stripping (%S) was calculated as follows:

$$\%S = \left( \frac{[Ce(IV)]_{(aq,eq)}}{[Ce(IV)]_{(o,ini)}} \right) \times 100 \quad (2)$$

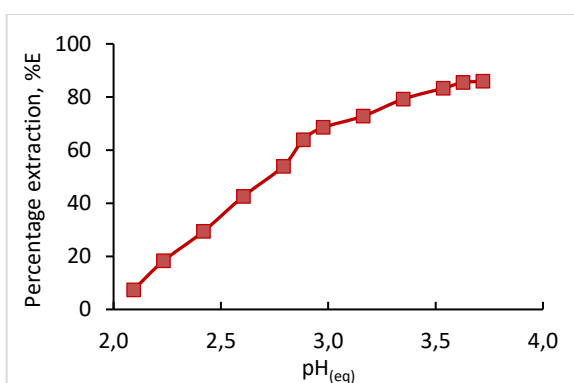
## RESULTS AND DISCUSSION

### Effect of aqueous feed pH

The pH dependence of the extraction of Ce(IV) with Cyanex 302 was determined in the initial pH range 2.25–4.5 with 0.08 mol L<sup>-1</sup> extractant as shown in Fig. 1. The percentage extraction of cerium(IV) is near to zero for solutions with pH lower than 2. This indicates that for highly acidic media, hydronium ions strongly compete with metal ions to be extracted by the Cyanex 302. Extraction of cerium (IV) was achieved at lower pH, suggesting that Cyanex 302 has more acidity, thus allows the extraction at a lower pH [45]. Similar results have been observed regarding the impact of pH<sub>(eq)</sub> on the extraction of various metal ions such as Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>2+</sup> with Cyanex 272 and 302 [46]. The extraction increased with pH to almost 88% at pH<sub>(ini)</sub> 4.0, pH<sub>(eq)</sub> const. = 3.72. Results suggest that the optimal pH value of the aqueous feed solution should be fixed at 4, in order to obtain efficient extraction.

### Effect of extractant concentration

The effect of the extractant concentration on the extraction of cerium(IV) was investigated by varying its concentration, as depicted in Fig. 2. Percentage extraction increased by augmenting the concentration of the extractant, due to the higher presence of extractant molecules. It was observed that the quantitative extraction of cerium(IV) was obtained by using 0.1 mol L<sup>-1</sup> Cyanex 302. Increased ion extraction with increasing Cyanex 302 concentrations has been reported in various studies [47-49].

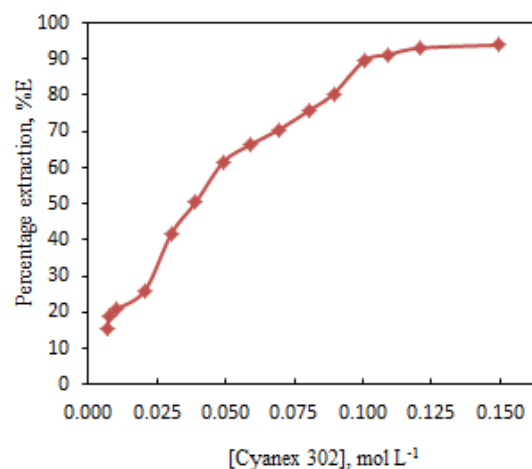


**Fig. 1.** Effect of pH<sub>(eq)</sub> on the percentage extraction of Ce(IV) under conditions of 0.002 mol L<sup>-1</sup> Ce(IV), 0.08 mol L<sup>-1</sup> Cyanex 302 ( $V_o/V_a = 1$ ),  $T = (25.0 \pm 0.5)^\circ\text{C}$ . Eq. time = 20 min.

### Stoichiometry of the extraction reaction

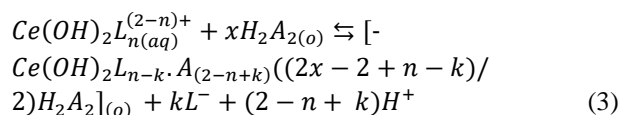
R<sub>2</sub>PSOH, the elemental constituent of Cyanex 302, is dimeric in non-polar diluents [46, 50]. In

aqueous solution, Ce(IV) virtually exists as Ce(OH)<sub>2</sub><sup>2+</sup> and Ce(OH)<sub>3</sub><sup>+</sup> [11, 51-53] which can form complexes with co-existing HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (L<sup>-</sup>).



**Fig. 2.** Effect of extractant concentration on percentage extraction of Ce(IV) under conditions of 0.002 mol L<sup>-1</sup> Ce (IV); pH<sub>(ini)</sub> = 4.0, pH<sub>(eq)</sub> const. = 3.72; ( $V_o/V_a$ ) = 1;  $T = (25.0 \pm 0.5)^\circ\text{C}$ , Eq. time = 20 min.

On considering the existence of  $Ce(OH)_2L_n^{(2-n)+}$  in the aqueous phase, the equilibrium for its extraction by HA can be represented as (“x”, “2 - n + k” and “n/k” are experimental extractant, pH and co-existing ligand dependences, respectively):



On defining “D” as

$$D = \frac{[Ce(OH)_2L_{n-k} \cdot A_{(2-n+k)}((2x-2+n-k)/2)H_2A_2]_{(o,eq)}}{Ce(OH)_2L_n^{(2-n)+}} \quad (4)$$

the  $K_{ex}$  of equation (3) can be expressed as:

$$\log D = \log K_{ex} + mpH + x \log [H_2A_2]_{(o)} - k \log [L^-] \quad (5)$$

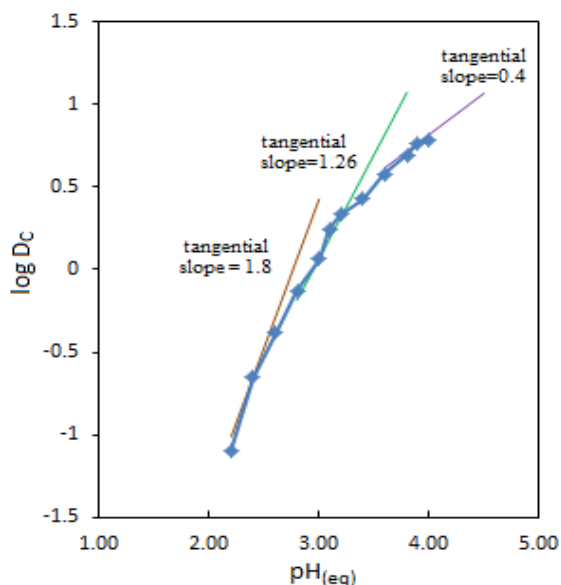
where “aq” and “o” represent the aqueous and organic phase, respectively; and  $m = (2 - n + k)$ .

The equation (5) illustrates the basic equation for a chelate-forming solvent extraction system by a dimeric acidic extractant. All concentrations and pH terms in equation (5) refer to the equilibrium values. Consequently, equation (5) represents that the value of log D should be independent of [Ce(IV)] at a set of constant equilibrium pH, [extractant] and [anion]. Corrected D-values (*i.e.* D<sub>c</sub>) at a set of constant equilibrium pH and [extractant] can be calculated by mass-balance (equation (6)):

$$\log D_c = \log K_{ex} + mpH + x \log [H_2A_2]_{(o)} - k \log [L^-]$$

$$\log D_C = \log D + m(\text{pH}_{(ini)} - \text{pH}_{(eq)}) + x \log [H_2A_2]_{(o,ini)} - \log \{ [H_2A_2]_{(o,ini)} - x [Ce(IV)]_{(o,eq)} \} \quad (6)$$

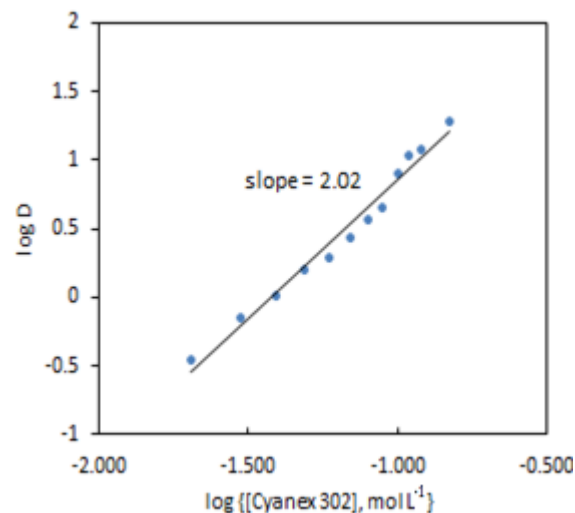
At a constant  $[H_2A_2]$ , the plot of  $\log D_C$  vs.  $\text{pH}_{(eq)}$  should be a straight line with a slope of “m” (the number of protons liberated during chelation reaction). Fig. 3 represents the  $\log D_C$  vs.  $\text{pH}_{(eq)}$  plot at constant  $[\text{extractant}]_{(o)}$  of  $0.10 \text{ mol L}^{-1}$ . Experimental points fall on a curve rather than on a straight line. Curve with limiting slope of almost 2 (1.8) is obtained at low pHs (l.pH) ( $\text{pH}_{(eq)} < 2.3$ ), while the tangential slope is almost unity (1.26) at  $\text{pH}_{(eq)} \sim 3.0$  and 0.40 at  $\text{pH}_{(eq)}$  3.7. It can be concluded from this result that the pH dependence is defined by the equilibrium pH range used: two hydrogen ions,  $2 \text{ H}^+$  are liberated per Ce(IV) being complexed and extracted by Cyanex 302 when  $\text{pH}_{(eq)}$  is kept below  $\sim 2.5$ . With increasing  $\text{pH}_{(eq)}$  value, the number of liberated  $\text{H}^+$  ions decrease from 2 to 1 at  $\text{pH}_{(eq)}$  of  $\sim 3.0$  and 0.4 at  $\text{pH}_{(eq)}$  of 3.7.



**Fig. 3.** Logarithmic plot of corrected distribution coefficient versus the equilibrium pH in batch extraction obtained under conditions of  $0.002 \text{ mol L}^{-1}$  Ce(IV),  $0.1 \text{ mol L}^{-1}$  Cyanex 302,  $V_o/V_a = 1$  ( $V_a = 10 \text{ mL}$ ),  $T = (25 \pm 0.5) \text{ }^\circ\text{C}$ . Eq. time = 20 min.

Based on equation (5), at a given constant pH, the  $\log D$  vs.  $\log [H_2A_2]_{(o)}$  plot should be a straight line with a slope indicating the mole ratio (x) of extractant/metal ion in the extracted species of Ce(IV) complex. The  $\log D$  vs.  $\log \{ [\text{Cyanex 302}]_{(o)} \}$  plot is depicted in Fig. 4. A straight line with a slope of  $\sim 2$  (2.02) is obtained which shows the relationship between 2 moles of the extractant and 1 mole of metal in the extracted metal species.

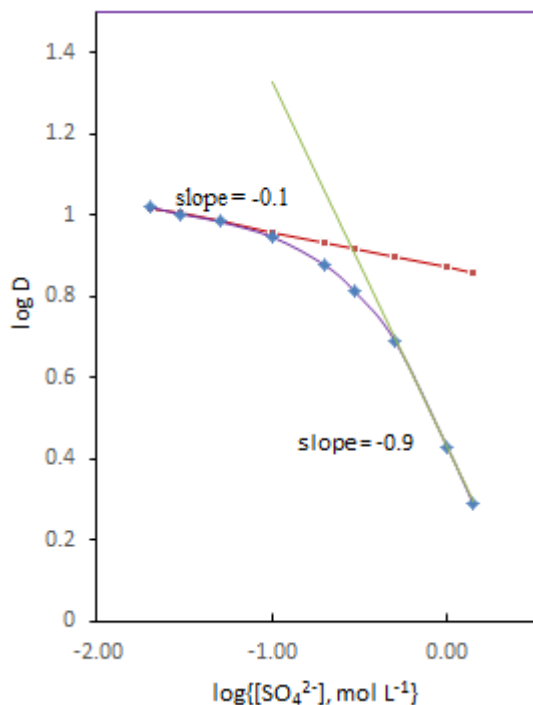
The anion co-existing with the metal ion in the aqueous phase usually influences the extraction characteristics of the metal ion by an extractant.



**Fig. 4.** Logarithmic plot of distribution coefficient vs the concentration of the extractant in batch extraction obtained under conditions of  $0.002 \text{ mol L}^{-1}$  Ce(IV),  $V_o/V_a = 1$  ( $V_a = 10 \text{ mL}$ ),  $\text{pH}_{(eq)} 3.54$ ,  $T = (25 \pm 0.5) \text{ }^\circ\text{C}$ . Eq. time = 20 min.

This phenomenon is most often observed when extraction occurs by ion-pair formation and solvation mechanisms. In chelate-forming extraction systems, the co-existing anion may be involved in chelate formation. Also, the chelate formation may be impeded by the prior formation of metal-coexisting anion complex. Since the extraction is performed in sulfuric acid medium, the impact of  $[\text{SO}_4^{2-}]/[\text{HSO}_4^-]$  on the extraction has to be studied. The 1st and 2nd ionization constants of  $\text{H}_2\text{SO}_4$  are  $10^3$  [46] and  $10^{-2}$  [50], respectively. These values suggest that  $\text{SO}_4^{2-}$  will be more available than  $[\text{HSO}_4^-]$  in the working pH region. So, L in equation (3) represents  $\text{SO}_4^{2-}$ . The related plot is displayed in Fig. 5. Experimental points fall on a curved line rather than on a straight line. At low concentrations (l.c.r) of  $\text{SO}_4^{2-}$ , D is scarcely changed, whereas at high concentrations (h.c.r) of  $\text{SO}_4^{2-}$ , it significantly decreases with increasing  $[\text{SO}_4^{2-}]$ . Tangential slope at l.c.r of sulfate ion is almost 0 (-0.1), whilst the respective slope at h.c.r of sulfate ion is almost -1 (-0.9).

It is obvious from these studies that the value of “x” is 2 whatever the experimental parameters but the value of “k” is 0 at low  $[\text{SO}_4^{2-}]$  and 1 at high  $[\text{SO}_4^{2-}]$ . The value of “m (= 2 - n + k)” is 2 at low pH (l.pH), 1 at middle pH (m.pH), and 0.4 at high pH (h.pH). At l.c.r of sulfate ion and at l.pH,  $m = 2$  suggests that  $n = 0$ ; but at intermediate pH,  $m = 1$  involves that  $n = 1$ , and finally at h.pH,  $m = 0.40$  implies that  $n = 1.60$ . On the other hand, at h.c.r of  $\text{SO}_4^{2-}$  and at l.pH,  $m = 2$  implies  $n = 1$ ; but at intermediate pH,  $m = 1$  suggests  $n = 2$  and at h.pH,  $m = 0.40$  insinuates  $n = 2.60$ .



**Fig. 5.** Logarithmic plot of distribution coefficient versus the initial concentration of co-existing  $\text{SO}_4^{2-}$  on batch extraction obtained under conditions of  $0.002 \text{ mol L}^{-1}$  Ce(IV),  $0.1 \text{ mol L}^{-1}$  Cyanex 302,  $V_o/V_a = 1$  ( $V_a = 10 \text{ mL}$ ),  $T = (25 \pm 0.5)^\circ\text{C}$ . Eq. time = 20 min.

*Extraction mechanism*

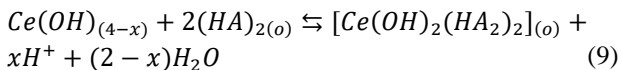
The afore-mentioned experimental results lead to the following expression relating the equilibrium constant with the distribution coefficient in the extraction of Ce(IV) in the Ce(IV)- $\text{H}_2\text{SO}_4$ -Cyanex 302-kerosene system:

$$K_{ex} = \frac{D[L]^{-k}[H^+]^x}{[(HA)_2]^2} \quad (7)$$

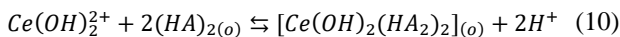
At l.c.r of  $\text{SO}_4^{2-}$ ,  $k = 0$ , so that equation (7) becomes:

$$K_{ex} = \frac{D[H^+]^x}{[(HA)_2]^2} \quad (8)$$

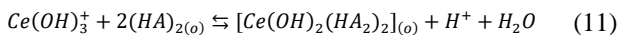
Equation (8) propounds the following general chemical reaction as the extraction equilibrium reaction:



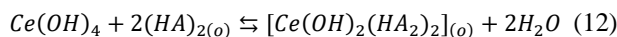
When  $x = 2$ , i.e. at  $\text{pH} \leq 2.4$ , equation (9) becomes:



and when  $x = 1$ , i.e. at  $\text{pH} \approx 3.0$ , equation (9) becomes:



and when  $x = 0$ , i.e. at  $\text{pH} \geq 3.9$ , equation (9) becomes:



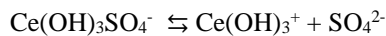
At h.c.r of  $\text{SO}_4^{2-}$ , equation (7) becomes:

$$K_{ex} = \frac{D[SO_4^{2-}][H^+]^x}{[(HA)_2]^2} \quad (13)$$

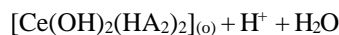
Equation (13) implies the liberation of sulfate ion during the extraction reaction. But at a certain pH, the values of  $K_{ex}$  at l.c.r and h.c.r of sulfate are identical. It is inferred that at h.c.r of  $\text{SO}_4^{2-}$ , the general equation (9) also represents the extraction equilibrium reaction. But in this case, as the sulfate concentration increases, the free non-sulfated/bisulfated Ce(IV)-species concentration decreases during the extraction of the metal ion. This gradual depletion is probably compensated through dissociation of sulfated/bisulfated Ce(IV)- species. Moore and Anderson [54] made a spectrophotometric study of cerium perchlorate in perchloric acid sodium perchlorate-sodium sulfate solution. Up to  $0.01 \text{ M}$  sulfate,  $Ce(SO_4)^{2+}$  and  $Ce(OH)(SO_4)^+$  ( $\text{pH} \ 0.72\text{-}0.76$ ) were reported to predominate and evidence for higher complexes was obtained [54, 55]. It appears therefore that the equilibrium shift occurs between sulfated and non-sulfated species as suggested below:



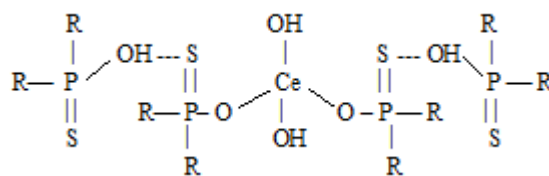
Equation (10)  $\uparrow + 2(HA)_2$



Equation (11)  $\uparrow + 2(HA)_2$



The proposed structure of the oligomeric cerium complex with the  $R_2\text{PSO}^-$  ligand is shown in Fig. 6.



**Fig. 6.** Postulated structure of the oligomeric cerium complex with Cyanex 302.

*Thermodynamic investigation of the extraction*

Distribution coefficients were determined by shaking equal volumes of the aqueous feed solution and  $0.1 \text{ mol L}^{-1}$  Cyanex 302 solution in kerosene.

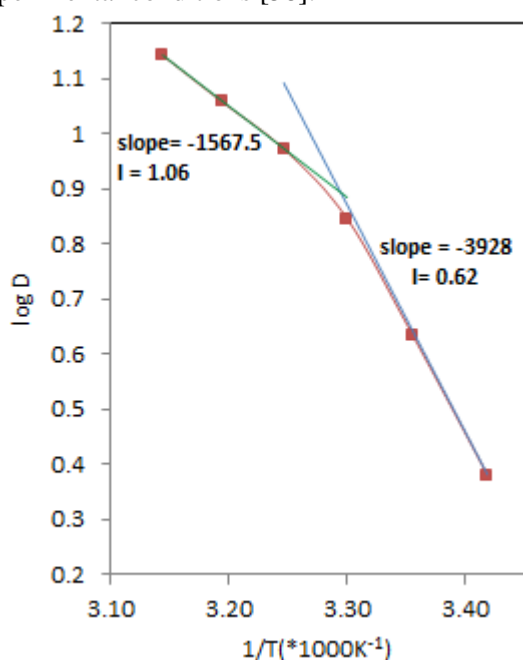
The experiments were performed at Cyanex 302 concentrations lower than the optimum concentration to better see the effect of temperature. Other parameters were as in Fig. 2. The Van't Hoff plots for the studied system are shown in Fig. 7. It is deemed that the extraction ratio increases with raising temperature but the straight line relationship does not hold over the entire temperature range.



Slopes of the lines in the high temperature region (h.t.r) and in the l.t.r are  $-1567.5$  and  $-3928$ , respectively. From the slope and intercept obtained from Fig. 7 and applying the Van't Hoff equations [56, 57], the thermodynamic parameters are calculated as:

$$\log D = -\frac{\Delta H}{2.303RT} + C \quad (14)$$

where R, T, and C are the universal gas constant, absolute temperature, and conditional constant, respectively. Activity coefficients for other components are considered to be constant under the experimental conditions [58].



**Fig. 7.** Relationship between distribution coefficient (D) and reaction temperature under conditions of  $0.002 \text{ mol L}^{-1}$  Ce(IV),  $0.08 \text{ mol L}^{-1}$  Cyanex 302,  $V_o/V_a = 1$  ( $V_a = 10 \text{ mL}$ ), initial solution pH(eq) 3.54. Eq. time = 20 min.

The slopes equal  $-\Delta H/2.303R$ . On the basis of Eq. (14) and Fig. 7, the values of  $\Delta H$  are calculated to be  $30.00$  at h.t.r and  $75.21 \text{ kJ mol}^{-1}$  at l.t.r, indicating that the extraction reaction is endothermic. Therefore, the extraction efficiency increased by temperature raise. Also, the values of the change in the Gibbs free energy ( $\Delta G$ ) and the entropy ( $\Delta S$ ) were calculated from the following equations for extraction reaction at  $298 \text{ K}$ :

$$\Delta G = -2.303RT \log D \quad (15)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (16)$$

The values of  $\Delta G$  and  $\Delta S$  were calculated equal to  $23.96 \text{ kJ mol}^{-1}$  and  $20.26 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $71.76 \text{ kJ mol}^{-1}$  and  $11.87 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The positive  $\Delta G$  specified that the extraction reaction by Cyanex 302 proceeded not spontaneously. The positive values of  $\Delta S$  indicated that the extraction of Ce(IV) is more efficient at high temperatures.

In a similar research, the thermodynamic study of copper(II) extraction from sulfate, nitrate and chloride media using Cyanex 302 in kerosene has shown that the extraction reaction is endothermic and non-spontaneous [47].

#### Effect of diluent type

In order to ascertain the impact of diluent type on Ce(IV) distribution, %E-values were evaluated when  $0.002 \text{ mol L}^{-1}$  Ce(IV) was extracted separately from the same aqueous feed solution by  $0.10 \text{ mol L}^{-1}$  extractant in various diluents while keeping constant all other conditions ( $\text{pH}_{\text{ini}} = 3.6$  and  $[\text{SO}_4^{2-}] = 0.0002 \text{ mol L}^{-1}$ ) (Table 1). It was observed that the percent extraction increases in the following order with the variation of diluent used to prepare the organic solution:  $\text{CHCl}_3$  ( $D = 1.02$ ) <  $\text{CCl}_4$  ( $D = 4.73$ ) = cyclo- $\text{C}_6\text{H}_{12}$  ( $D = 4.73$ ) < kerosene ( $D = 5.80$ ) < 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$  ( $D = 7.36$ ) =  $\text{C}_6\text{H}_4$ -( $\text{CH}_3$ )<sub>2</sub> (xylene) ( $D = 9.85$ ) <  $\text{C}_6\text{H}_6$  ( $D = 14.44$ ) =  $\text{C}_6\text{H}_5$ - $\text{CH}_3$  (toluene) ( $D = 14.44$ ). The study allows concluding on the effect of diluent on the rate of extraction of cerium and on the best ones of the diluents for the cases studied.  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_5$ - $\text{CH}_3$  are very good diluents followed by  $\text{C}_6\text{H}_4$ -( $\text{CH}_3$ )<sub>2</sub> for the extraction of Ce(IV) by Cyanex 302. Kerosene is a better diluent over  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and cyclo- $\text{C}_6\text{H}_{12}$ .

#### Stripping of Ce(IV)-loaded organic phase

The maximum Ce(IV) loaded organic phase, after the extraction step, was submitted to a stripping step using various mineral acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  solutions at  $25 \text{ }^\circ\text{C}$  and  $V_o:V_a = 1$ . The stripping results are presented in Table 2. It deemed that stripping percentage is roughly acceptable in all three mineral acids used alone. In all cases, the percentage stripping increased by raising concentration of acid. Sulfuric acid (1 M) is sufficient to quantitatively strip off Ce(IV).  $\text{HNO}_3$  and  $\text{HCl}$  can also be utilized in stripping if two-stage stripping is implemented.

**Table 1.** Effect of diluent type on extraction of Ce(IV). [Ce(IV)]<sub>(ini)</sub> = 0.002 mol L<sup>-1</sup>, pH<sub>(ini)</sub> = 3.6, [Cyanex 302] = 0.1 mol L<sup>-1</sup>, [SO<sub>4</sub><sup>2-</sup>] = 0.0002 mol L<sup>-1</sup>, T = (25 ± 0.5) °C. Eq. time = 1 h, V<sub>o</sub>/V<sub>a</sub> = 1, V<sub>a</sub> = 10 mL

Diluent	Ce(IV)] <sub>aq</sub> eq, mol L <sup>-1</sup>	Ce(IV)] <sub>o</sub> eq, mol L <sup>-1</sup>	%E	D
Carbon tetrachloride	0.00035	0.0017	82.54	4.73
Benzene	0.00013	0.0019	93.52	14.44
Toluene	0.00013	0.0019	93.52	14.44
Cyclohexane	0.00035	0.0017	82.54	4.73
1,2-Dichloroethane	0.00024	0.0018	88.03	7.36
Xylene	0.00018	0.0018	90.78	9.85
Chloroform	0.00099	0.0010	50.51	1.02
Kerosene	0.00029	0.0017	85.29	5.80

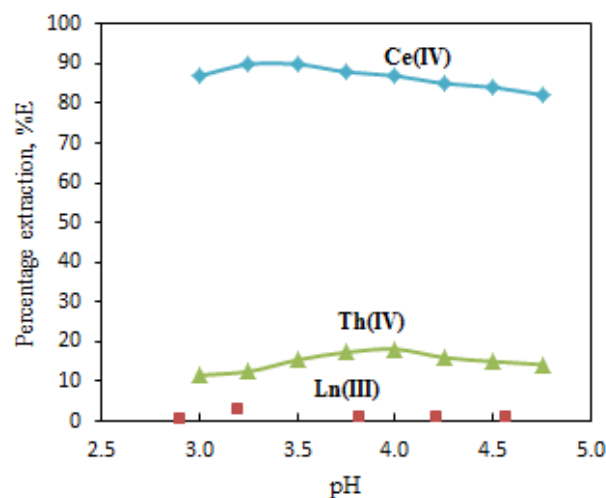
**Table 2.** Stripping of Ce(IV)-loaded organic phase using different mineral acid solutions. [Ce(IV)]<sub>o</sub> ≈ 0.0018 mol L<sup>-1</sup>, [Cyanex 301] = 0.10 mol L<sup>-1</sup>, Eq. time = 1 h, T = (25 ± 0.5) °C, V<sub>o</sub>/V<sub>a</sub> = 1 (V<sub>a</sub> = 10 mL).

Stripping agent	Concentration, mol L	Percentage stripping, %S
	0.1	70.43
H <sub>2</sub> SO <sub>4</sub>	0.5	94.50
	1.0	98.80
	0.1	85.12
HNO <sub>3</sub>	0.5	94.05
	1.0	98.50
	0.1	44.33
HCl	0.5	84.15
	1.0	92.59

#### Selectivity studies

The selective extraction of Ce(IV) considering the presence of many associated metal ions and impurities such as Th(IV), and REE(III) (REE = La<sup>3+</sup>, Ce<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Yb<sup>3+</sup>) using a solution containing 0.3 g L<sup>-1</sup> of the different metal ions in sulfuric acid solution (with pH<sub>(ini)</sub> range of approximately 3.0 – 4.5) with 0.1 M Cyanex 302 in kerosene at V<sub>o</sub>:V<sub>a</sub> = 1 and (25 ± 0.5) °C were investigated. The percent extraction data of the different metal ions shown in Fig. 8 indicate that a selective cerium separation can be done efficiently from H<sub>2</sub>SO<sub>4</sub> solution in the pH range of 3-4 as rare earth ions (III) are almost not extracted under these experimental conditions. The

extraction of Th(IV) is low. Therefore, by selecting the appropriate acidity, cerium can be separated from REEs(III) and Th(IV).



**Fig. 8.** Selectivity of Cyanex 302 for Ce(IV), Th(IV), and RE(III) under conditions of aqueous feed solution: 0.3 g L<sup>-1</sup> of the different metal ions in H<sub>2</sub>SO<sub>4</sub> solution (pH<sub>(ini)</sub> of approximately 3.0 to 4.5); organic phase: 0.1 M Cyanex 302 in kerosene; V<sub>o</sub>/V<sub>a</sub> = 1 (V<sub>a</sub> = 10 mL); T = (25 ± 0.5) °C.

#### CONCLUSIONS

Cyanex 302 extracts Ce(IV) from sulfuric acid medium at pH above 3.0. The equilibration time is 20 min. The recovery of Ce(IV) can be regulated by controlling the extractant and pH of aqueous feed solutions. Cyanex 302 is a forward-looking extractant for the Ce(IV) extraction. At various concentration levels of the experimental parameters, extraction equilibrium reactions were proposed. It is seen that at all conditions, [Ce(OH)<sub>2</sub>(HA<sub>2</sub>)<sub>2</sub>] is the extractable species though reacting Ce(IV) species in the aqueous phase may vary with its concentration and pH levels. Aromatic diluents appear as better diluents over other categories; kerosene is a better

diluent than  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and cyclo- $\text{C}_6\text{H}_{12}$ . The temperature-sensitive extraction process of this metal in the studied system is endothermic ( $\Delta H < 0$ ). The positive value of  $\Delta G$  reveals that the extraction reaction proceeds not spontaneously, and the positive value of  $\Delta S$  indicates that extraction of Ce (IV) is more desirable at high temperatures.

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