

Thermodynamics and mechanism of liquid–liquid extraction of cerium (IV) from sulfuric acid solutions with di-(2-ethylhexyl) phosphoric acid (D2EHPA)

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This paper reports studies on Ce (IV) extraction from sulfuric acid solutions using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as extractant with a view to elucidate the Ce (IV) extraction mechanism. The effects of pH, extractant concentration, metal-ion concentration in aqueous solution, temperature, and contact time between the two phases were observed in detail. The experimental results indicated that Ce (IV) could be effectively extracted from sulfuric acid medium; Ce (IV) was extracted into the organic phase in the form of $Ce(SO_4)_{0.5}A_2$. A cation exchange mechanism was proposed for the extraction of Ce (IV) in the H_2SO_4 / D2EHPA system and thermodynamic functions such as ΔG , ΔH , and ΔS were determined. The results of this research showed that the D2EHPA organic phase in kerosene can successfully be used to separate Ce (IV) from other RE (III) in binary initial solutions.

Keywords: Ce (IV); Liquid–liquid extraction; D2EHPA; Extraction mechanism; Thermodynamic functions.

INTRODUCTION

Cerium (IV) has received much attention in various fields, including the production of aluminum, aluminum alloys, certain steels, permanent magnets, catalysts, polishing powder, glass, in cinema and ceramic technology [1, 2]. Cerium is utilized in low-energy light bulbs, flat-screen TVs, and floodlights [3]. The pharmacological properties of the cerium compounds have also been shown [4, 5].

Metals are recovered from aqueous solutions by different techniques such as solvent extraction [6-12], liquid membrane [13-20], ion exchange (IX) [21-23], polymer inclusion membrane [24-26], electrodialysis [27-30], sorption [31-35], precipitation [36-38], and ultrafiltration [39-41]. In the industry, solvent extraction is one of the most effective techniques for purification of cerium [42]. Much research has been done on the extraction of Ce (IV) using various extractants including high-molecular weight amines [43, 44], organophosphorus acids [45, 46], and organophosphorus esters [47, 48].

The use of organophosphorus esters as extractants has attracted much attention [49]. Extraction of Ce (IV) from nitric acid (HNO_3) solutions by TBP has been reported in the first study by Warf [50]. Afterward, Korpusov *et al.* [51] and Healy and McKay [52] attributed Ce (IV) extraction

from nitric acid solutions to the formation of $Ce(NO_3)_4(TBP)_2$ and $H_2Ce(NO_3)_6(TBP)_2$, respectively. As a neutral extractant, Cyanex 923 is considered to effectively extract Ce (IV). Lu *et al.* [53] reported the formation of $Ce(SO_4)_2 \cdot 2Cyanex923$ species in the extraction of Ce (IV) from sulfate solutions. Cerium extraction with Cyanex 302 [46] and Cyanex 301 [45] extractants has been reported. However, the cost of Cyanex extractants is high [54].

Moreover, these well-established organophosphorus esters, essentially di (1-methylheptyl) methyl phosphonate (P350), TBP, TOPO, Cyanex 925 and Cyanex 923 have their own disadvantages for the extraction of cerium (IV). In between them, P350 cannot be used for the extraction of Ce (IV) because of the problem of removing possible reducing impurities. For Cyanex 925, Ce (IV) reduction is observed in the sulfate system [49]. Higher acidities are needed when using TBP as the extractant for Ce (IV), in addition, the extractability is lower compared with others. TOPO is a good extractant for Ce (IV), but its solubility in aliphatic diluents limits the maximum loading. In the case of Cyanex 923, the commercial outlook is not attractive due to the high cost compared with di-(2-ethylhexyl) phosphoric acid (D2EHPA). Therefore, the development of new extraction systems for the extraction of Ce (IV), especially in sulfuric acid solutions, is an issue of great importance.

D2EHPA is a well-known extractant of the

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organophosphorus acids group and therefore extracts metal ions by the cation exchange mechanism [55, 56]. D2EHPA, owing to its lower cost, good physicochemical properties, complete miscibility with all common hydrocarbon diluents even at low ambient temperatures, low aqueous solubility, good resistance to hydrolysis, and high purity (99%) has potential advantages. D2EHPA is a very strong acid extractant, commonly used in sulfuric acid solutions for the extraction of many metal ions such as uranium, vanadium, zinc, copper, iron, rare earths and other precious metals.

The present study aimed at the investigation of Ce (IV) extraction by D2EHPA, thermodynamics and mechanism of extraction from sulfuric acid solutions. The extracted species were determined from slope analysis and by graphic method, and thermodynamic functions ΔH , ΔG and ΔS of the investigated systems were calculated.

EXPERIMENTAL

Materials

Di-(2-ethylhexyl) phosphoric acid (D2EHPA), kerosene, n-hexane, and benzene were purchased from Fluka. Sulfuric acid and cerium oxide were products of Merck. The stock solution of Ce (IV) was obtained by dissolving a suitable amount of cerium oxide in deionized water. All of the used chemicals were of analytical grade and used without purification.

General procedure

All experiments, except experiments for temperature effect, were performed at 25 ± 1 °C. Equal volumes (5 mL) of organic and aqueous phases were placed in laboratory tubes and mechanically stirred for 10 min. Then the two phases were separated and the ion concentration in the aqueous phase was measured with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian, Liberty150ax Turbo, Australia).

Concentrations of the metal ion in the organic phase were calculated by mass balance. Then, the distribution coefficient was calculated. The distribution coefficient is the most desirable index for determining the response of the solvent extraction process and is defined as the ratio of the equilibrium concentration of metal ion in the organic phase to its equilibrium concentration in the aqueous phase:

$$D = \frac{C_0 - C}{C} \quad (1)$$

where C_0 and C are the initial and the equilibrium concentration of the metal ion in the aqueous phase,

respectively. The extraction percentage of extracted metal ion, E %, was calculated from the relation,

$$E(\%) = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \quad (2)$$

where D is the distribution ratio, V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

Effect of pH

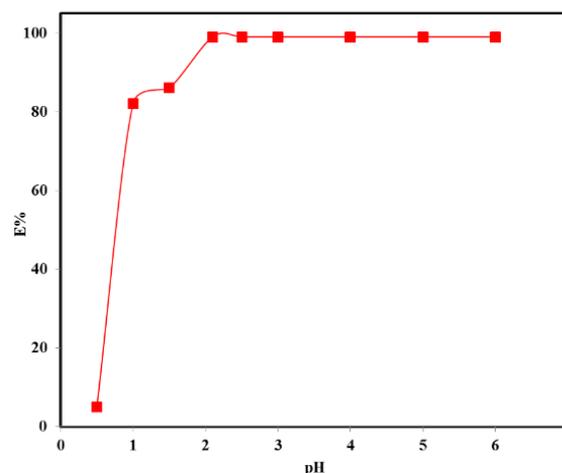
For cationic extractants, the pH (acidity) of the solution has a great influence on the extraction process because the H^+ ions participate in the extraction (Eq. 3). D2EHPA is an acidic extractant, offering both hydrogen bond donor and acceptor. Extraction of metal ions by D2EHPA can be described by the equation [54]:



where A represents the anion of D2EHPA.

The variation of aqueous phase pH within the range of 0.5-6 showed that the increase in pH of the aqueous solution from 0.5 to 2 noticeably increases the extraction percentage of Ce (IV), which reaches its maximum value at pH 2.1 and remains practically constant in the range 2.1-6, Fig. 1. From Equation (3) it can be seen that by increasing the pH (i.e., by decreasing acidity), the equilibrium will shift (according to Le Chatelier's principle) to the right to extract more Ce (IV). This indicates the importance of low acidity of the medium in Ce (IV) extraction.

Fig. 1. Effect of pH of the aqueous solution on the



extraction percentage of Ce (IV) by 0.4 M extractant/kerosene solutions.

Effect of extractant concentration

The effect of extractant concentration on the extraction of 0.006 mol L^{-1} Ce (IV) was studied by

varying the concentration of the considered extractants/kerosene solutions in the range 0.06-1.0 mol L⁻¹.

The results represented in Fig. 2 show that D2EHPA is an appropriate extractant for Ce (IV) extraction and the extraction percentage of Ce (IV) with D2EHPA increases with the increase in its concentration and reaches its maximum (>98 %) at extractant concentration of 0.7 mol L⁻¹ or higher. The use of high extractant concentrations may be economically unjustified despite the higher extraction percentage. Extraction percentage of about 90% is usually considered to be the best option because it permits to extract the desired element in approximately one or two stages in a counter-current method.

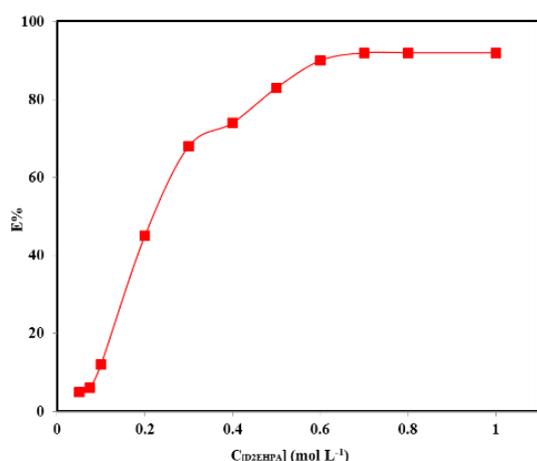


Fig. 2. Effect of extractant concentration on the extraction percentage (E%) of Ce (IV) from 0.01M sulfuric acid solution.

From the slope analysis of the log-log plot of the distribution coefficient *versus* extractant concentration (Fig. 3) it was concluded that two molecules of D2EHPA dimers are associated with an extractable complex.

Thermodynamic analysis and effect of temperature

The effect of temperature on the extraction of 0.006 M Ce (IV) by 0.4M D2EHPA in kerosene from 0.01M sulfuric acid was studied in the temperature range of 20-50 °C. The results represented graphically in Fig. 4 indicate the decrease in the percentage of extracted metal ion with the increase in temperature. Therefore, the Ce (IV) extraction process follows an exothermic reaction.

Thermodynamic parameters Gibbs free energy, enthalpy and entropy were calculated using the following equations [57-60]:

$$\log D = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (4)$$

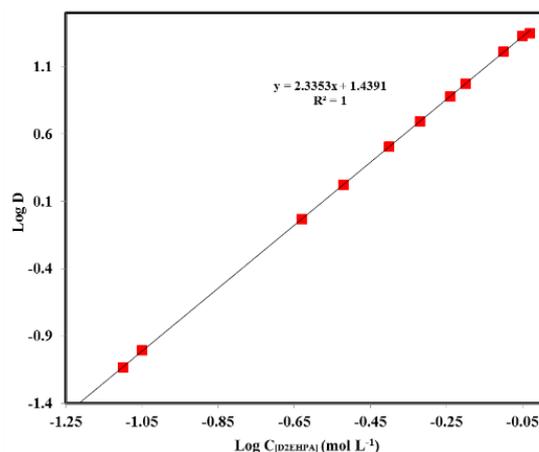


Fig. 3. Logarithm of the distribution coefficient (D) *versus* logarithm of the extractant concentration.

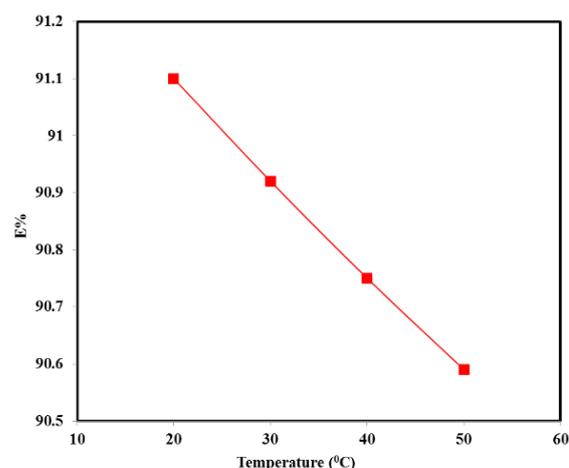


Fig. 4. Effect of temperature on the extraction percentage of 0.006M Ce(IV) with 0.4M D2EHPA from 0.01M sulfuric acid solution.

where R (8.31 J mol⁻¹ K⁻¹) and T are the universal gas constant and absolute temperature, respectively. According to the Van't Hoff equation (Eq. 4), the values of ΔH and ΔS can be determined by plotting the logarithm of the distribution coefficient (D) *versus* inverse temperature (Fig. 5).

The change in Gibbs free energy is obtained from the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The values of the calculated thermodynamic parameters are shown in Table 1. Negative ΔH values indicate the exothermic reaction of Ce (IV) extraction by D2EHPA. Therefore, increasing the temperature will reduce Ce (IV) extraction from the aqueous phase. The negative ΔG value also indicates that the extraction reaction is spontaneous.

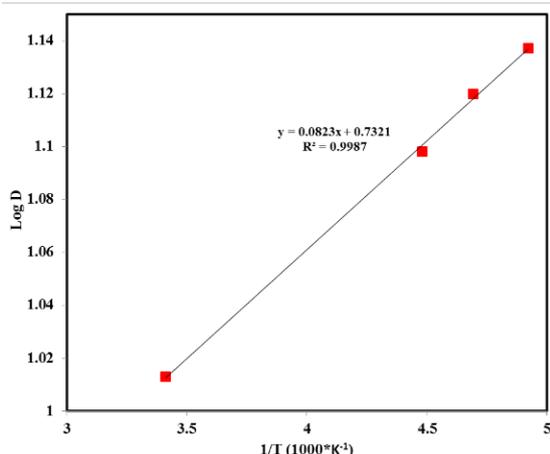


Fig. 5. Logarithm of the distribution coefficient (D) vs. inverse temperature.

Table 1. Standard molar thermodynamic quantities for the Ce (IV) extraction process at a temperature of 298.15 ± 1 K

| ΔG (kJ mol ⁻¹) | ΔS (J mol ⁻¹ K ⁻¹) | ΔH (kJ mol ⁻¹) |
|---------------------------------------|------------------------------------------------------|---------------------------------------|
| -2.47 | -1.51 | -2.02 |

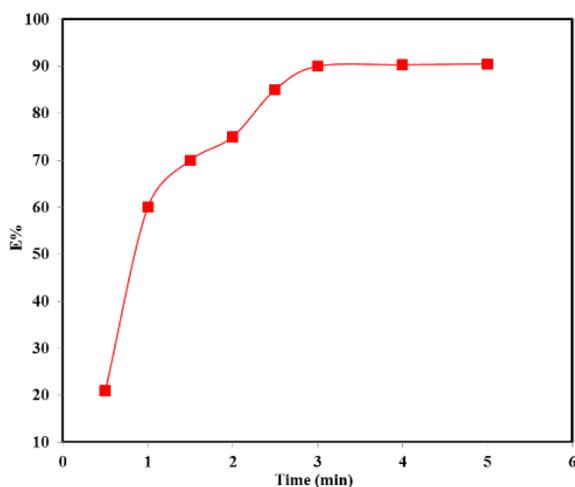


Fig. 6. Effect of contact time between aqueous and organic phases on cerium extraction at $C_{Ce(IV)} = 0.006$ mol L⁻¹.

Effect of phase contact time

The time needed to reach equilibrium between the amount of metal ions in aqueous and organic phases was investigated within the range of 3-10 min for the following constant parameters: pH 2.1; $C_{[Ce(IV)]} = 0.006$ mol L⁻¹; $C_{[D2EHPA]} = 0.4$ mol L⁻¹ in kerosene; $V_{aq}:V_{org} = 1:1$; and temperature, 25 ± 1 °C. The obtained results (Fig. 6) showed that the time required to reach equilibrium is ~ 3 min. Obviously, a 5-minute contact time is more than sufficient for the effective extraction of Ce (IV). Increasing the contact time beyond 3 minutes causes only slight changes in Ce (IV) extraction.

Effect of initial metal ion concentration

The increase in Ce (IV) concentration in the range 0.2×10^{-3} -0.011M decreased the extraction percentage of Ce (IV). The results shown in Fig. 7 depict a sharp decrease in Ce (IV) extraction percentage with the increase in its concentration. This could be attributed to the formation of other metal ion species which are not extracted by the used extraction system or to the capacity insufficiency of the extractant to extract metal ions of high initial concentrations.

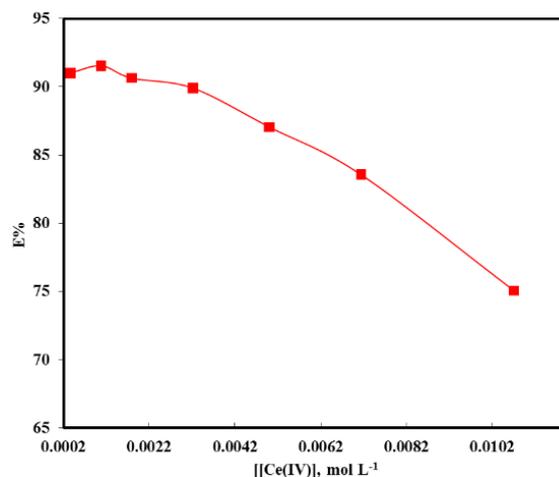


Fig. 7. Effect of Ce (IV) concentration on its extraction from 0.01M sulfuric acid by 0.4M D2EHPA /kerosene extraction system.

Effect of the nature of diluent

Three diluents, namely n-hexane, kerosene and benzene were selected to examine the influence of the diluent type on Ce (IV) extraction. As depicted in Table 2, the extraction percentage vigorously depends on the diluent nature. Diluents with low dielectric constant had better extraction performance for Ce (IV), so Ce (IV) extraction can be improved if kerosene is used as the diluent.

Table 2. Effect of diluent type on Ce (IV) extraction percentage. Aqueous solution pH 2, Contact time = 10 min, Temperature: 25 ± 1 °C, $V_{aq}:V_{org} = 1:1$, $C_{[D2EHPA]} = 0.4$ mol L⁻¹, and $C_{[Ce(IV)]} = 0.006$ mol L⁻¹

| Diluent | Dielectric constant at 20 °C | E% |
|----------|------------------------------|------|
| Hexane | 1.9 | 91.1 |
| Kerosene | 1.8 | 93 |
| Benzene | 2.3 | 81 |

Number of steps required to perform Ce (IV) extraction

Based on the obtained experimental results, McCabe-Thiele diagram was applied to determine the number of steps of the Ce (IV) solvent extraction.

The number of steps has been concluded graphically from the McCabe-Thiele diagram that consists of the equilibrium curve and the operating line. The equilibrium curve comprises a series of experimental points which represent the cerium content in the aqueous phase and the Ce content in the organic extract for different volumetric ratios and residence times. After contact, both phases are in equilibrium. The operating line sets the operating conditions and its slope is the A/O ratio. The McCabe-Thiele diagrams of Ce (IV) extraction process in the H₂SO₄/ D2EHPA system for A/O ratio of 1 and 2 are shown in Figures 8 and 9, respectively.

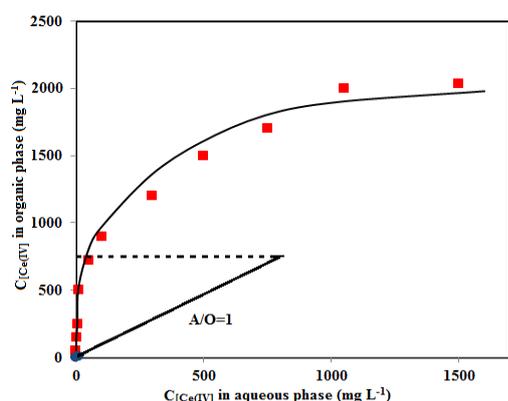


Fig. 8. McCabe-Thiele diagram of Ce (IV) extraction system with A/O =1

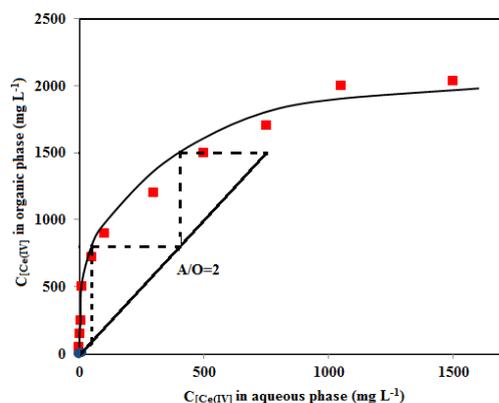


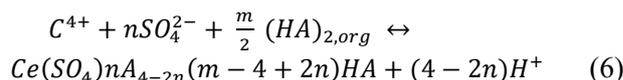
Fig. 9. McCabe-Thiele diagram of Ce (IV) extraction system with A/O =2.

As shown in Fig. 8, with one theoretical step, the extraction percentage is more than 90%. From Figure 9 is seen that three theoretical steps are required, and the extraction percentage achieved is 98%. According to Cox and Musikas [61], the number of real steps should be the theoretical number multiplied by 1.5–2. So, the real number of extraction steps should be two and five, respectively.

Extraction mechanism

It is well-established that organophosphorous-based acidic extractants exit as dimmers in nonpolar

organic diluents [62]. Fig. 1 shows that by decreasing the solution acidity, the extraction of cerium in its tetravalent state by organophosphorous-based acidic extractants like D2EHPA from aqueous sulfuric media is enhanced. This phenomenon indicates that the mechanism of cerium (IV) extraction, especially at low acidities, is generally cation exchange [57]. Therefore, the mechanism of Ce (IV) extraction in sulfuric solutions can be expressed by the following cation exchange reaction [63]:



Accordingly, the distribution coefficient (D) and the equilibrium constant (K) of the reaction are obtained from the following equations:

$$D = \frac{[Ce(SO_4)_n A_{4-2n} (m-4+2n)HA]_o}{C^{4+}} \quad (7)$$

$$K = \frac{[Ce(SO_4)_n A_{4-2n} (m-4+2n)HA][H^+]^{(4-2n)}}{[C^{4+}][SO_4^{2-}]^n [(HA)_2]^{\frac{m}{2}}} \quad (8)$$

The logarithmic form of Equation (8) is:

$$\log D = \log K + (4-2n)pH + n \log [SO_4^{2-}] + \left(\frac{m}{2}\right) \log [(HA)_2] \quad (9)$$

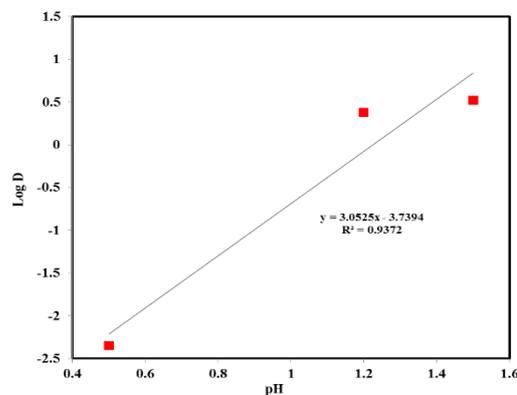


Fig. 10. Plot of log D vs. equilibrium pH for the extraction of cerium (IV) with D2EHPA.

The linear relationship between the log D values and pH (Fig. 10) shows that the distribution coefficient, D, of Ce (IV) increased with the increase in equilibrium pH value with a slope of about 3.0, indicating the release of 3 mol of H⁺ ions in the aqueous medium with 1 mol of cerium (IV). Therefore, the value of n in Equation (6) is 0.5, which results in 0.5 mol of sulfate in the extracted complex.

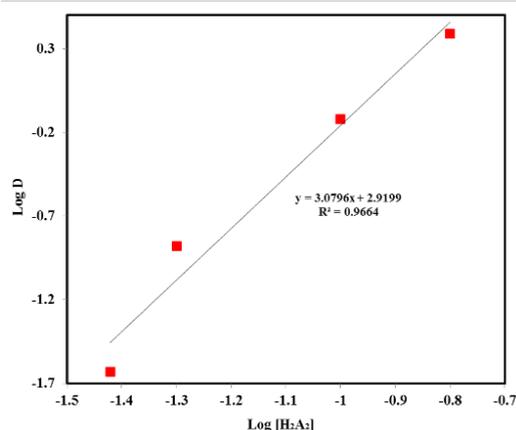
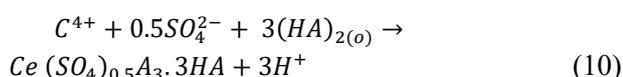


Fig. 11. Plot of log D vs. log[H₂A₂] for extraction of cerium (IV) with D2EHPA.

The plot of log D vs. log[H₂A₂] (Fig. 11) provides the metal-ion/extractant ratio of the extracted species. It can be seen from Fig. 11 that the plot of log D vs. log[H₂A₂] is linear with the slope of ~3.0 in the extraction system, indicating that the m value in Equation (6) is 6. This suggests the association of 3 mol of the monomer organophosphorus-based acidic extractant with the extracted species. Therefore, the overall cation exchange extraction reaction may be represented by the following reaction:



As Equation (10) indicates, even in this cationic range, part of the solvent in the form of HA solvates the extracted complex, and this is because the reactive oxygen of D2EHPA is much more basic than the reactive oxygen of H₂O. As a result, D2EHPA easily replaces part of the coordination water molecules in the extracted complex.

Separation of Ce (IV) from RE (III)

The parameters that affect the Ce (IV) extraction process were experimentally investigated. The optimum conditions for Ce (IV) extraction can be summarized as follows: D2EHPA concentration in kerosene, 0.5 mol L⁻¹; aqueous feed solution pH, 2.1; volume ratio of organic phase to aqueous phase, 1; temperature: 25±1 °C; extraction time, 5 min. The obtained extraction efficiency of Ce (IV) under the experimentally determined optimal conditions, was over 98%.

RE (III) elements such as La (III), Pr (III), Nd (III) and Sm (III) generally accompany Ce (IV) in solution. Under the derived optimum conditions, the separation of Ce (IV) from other RE (III) elements was investigated.

The separation factor for Ce/RE was calculated as follows:

$$SF_{Ce/RE} = \frac{(C_{Ce}/C_{RE})_{org}}{(C_{Ce}/C_{RE})_{feed}} \quad (11)$$

where C_{Ce} and C_{RE} are the concentrations of Ce (IV) and RE (III) in the organic and initial aqueous feed solution, respectively, in mol L⁻¹. The obtained results of the extraction of Ce (IV) and RE (III) are given in Table 3. Undoubtedly, the system is highly selective for Ce (IV), and the separation factors are relatively high.

Table 3. Standard molar thermodynamic quantities for the Ce (IV) extraction process at a temperature of 298.15±1 K

| Initial concentration in the feed solution (mol L ⁻¹) | Percent extraction (%E) | | SF _{Ce/RE} |
|-------------------------------------------------------------------|-------------------------|---------|---------------------|
| | Ce(IV) | RE(III) | |
| Ce 0.002 + La 0.002 | 98.15 | 0.55 | 175.27 |
| Ce 0.002 + Pr 0.002 | 97.68 | 0.88 | 109.75 |
| Ce 0.002 + Nd 0.002 | 98.44 | 0.74 | 131.25 |
| Ce 0.002 + Sm 0.002 | 98.70 | 0.44 | 219.33 |

CONCLUSIONS

The cerium (IV) extraction equilibria in the H₂SO₄-D2EHPA system were thoroughly studied using the organic ligand D2EHPA in kerosene as an extractant. The extracted species is Ce(SO₄)_{0.5}A₃·3HA. Thermodynamic functions of the extraction reaction were calculated and considered. Cerium (IV) extraction is essentially an exothermic and spontaneous process. The obtained experimental results illustrate that D2EHPA has good extractability for Ce (IV) in H₂SO₄ media. Thus, based on experiments, one can conclude that D2EHPA is a potential extractant for separating Ce (IV) from other RE (III) in binary initial solutions.

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