



Separation of cerium(IV) and yttrium(III) from citrate medium by solvent extraction using D2EHPA in kerosene

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Abstract

The extraction and separation of cerium(IV) and yttrium(III) from citric acid solution using Di-2-ethylhexyl phosphoric acid, D2EHPA, in kerosene was investigated. The effects of the different parameters on the extraction process, including the shaking time, extractant concentration, phase ratio, acid concentration as well as, temperature, were separately investigated to achieve the maximum possible separation between Ce(IV) and Y(III). The extraction constant was modeled based on the most predominant citrate cationic species at pH 4.0. The stoichiometry of the extracted species was found to be $[\text{Ce}(\text{H}_2\text{Cit})_2 \cdot 2\text{A}(\text{HA})]$ and $[\text{Y}(\text{H}_2\text{Cit}) \cdot 2\text{A}(\text{HA})]$, (where HA denotes D2EHPA), based on the slope analysis method applied on the obtained results. The mean conditional extraction constants values $K_{\text{C,ex}}$ were found to be $4.15 \times 10^2 \pm 0.05$ and $5.36 \pm 0.28 \times 10^3$ for Ce(IV) and Y(III), respectively. The thermodynamic functions associated with the extraction reaction were evaluated and discussed. It was found that the extraction process is spontaneous and exothermic for both metal ions. Possible separation of Y(III) from Ce(IV) was given in terms of the separation factors at different extraction conditions.

Keywords Extraction · REEs · Citric acid · D2EHPA · Separation

Introduction

Cerium and yttrium are rare earth elements (REEs) that find many applications and uses in new technology. Cerium oxide is considered as one of the most effective agents for polishing of optical components. Cerium metal is typically added to aluminum to enhance aluminum corrosion resistance (Emsley 2011). Yttrium oxide is used in the composition of phosphors emitting wavelengths of red, blue and green (Smets 1987). It is additionally utilized in the production of alloys, electrodes, electrolytes, electronic filters, lasers and superconductors. Among organophosphorus extractants, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA) and D2EHPA are the most effective extractants for the separation of REEs. Solvent extraction processes for separation and purification of rare earths have been reviewed (Li 2017, 2019; Yang et al. 2017; Jha et al. 2016; Binnemans et al. 2015; Xie et al. 2014; Binnemans et al. 2013). The separation between Nd(III), Dy(III), and Y(III)

from hydrochloric acid solution by D2EHPA and EHEHPA separately and in mixtures has been investigated by Mohammadi et al. (2015). They reported that a mixture of D2EHPA and EHEHPA provides a better separation of Y(III) from Dy(III). Khaironiel et al. (2014) investigated the extraction of certain lanthanides using D2EHPA from nitric acid and sulphuric acid solutions. They found that the extraction ability of the investigated lanthanides by D2EHPA decreased in the sequence of Ce(IV) > Nd(III) > La(III). Yin et al. studied the separation of certain lanthanides using lactic acid and citric acid with D2EHPA. They showed that it could not only improve the extraction efficiency, but also increases the separation factor between certain lanthanides (Yin et al. 2013, 2014). The extraction of lanthanides La, Pr and Er from citric acid solutions using D2EHPA in kerosene has been studied by Abu Elgoud et al. (2019). They concluded that the extraction depends on the acid and extractant concentration. The order of the conditional extraction constants follows the sequence, Er(III) \gg La(III) \geq Pr(III). The separation factor of Er(III) from La(III) and Pr(III) increases by the increase of extractant concentration from 1.0 mol/L citric acid solution at pH 4.0 and decreases by the increase of citric acid concentration. The recovery of Y(III) by pseudo-emulsion-hollow fiber strip dispersion (PEHFSD) system

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using D2EHPA as a carrier has been investigated by Pirom et al. (2018). Results indicated that, the PEHFSD system was found to be suitable for the simultaneous extraction and recovery of Y(III) from acidic nitrate medium in a single contactor using D2EHPA in kerosene as the carrier. The PEHFSD system exhibited 99% extraction and 98% stripping. Davarkhah et al. (2018), investigated the selective separation of yttrium(III) through a liquid membrane system using 2-thenyltrifluoroacetone (HTTA) as an extractant carrier. They reported that yttrium(III) ions are liable to be separated effectively from strontium ions in aqueous solutions by the chloroform liquid membrane containing HTTA as a carrier. The optimum conditions for the transport of yttrium include: the donor phase of pH 5.4 with 1% (v/v) n-propylamine PA, the liquid membrane containing 0.02 M HTTA in dichloromethane, and 1.0 M nitric acid solution as a receiving phase. Extraction kinetics of Ho(III) and Y(III) with D2EHPA using a Hollow Fiber were reported by Yoshizuka et al. (1990). Results showed that the diffusional effects were reasonably explained by the diffusion model accompanied by an interfacial reaction, taking into account of the velocity distributions of the aqueous and organic phases through the inner and outer sides of a hollow fiber. Lim et al. (1996), described kinetic studies of solvent extraction of rare earths into DEHPA using radiotracers (^{141}Ce , ^{152}Eu , ^{153}Gd , ^{160}Tb and ^{88}Y) in a modified Lewis cell. The initial rate extraction was first order with respect to individual RE concentration. At low acidities, the extraction rates of REs were equal and independent of pH. TOPS 99, an equivalent to di-2-ethylhexyl phosphoric acid has been employed for the extraction and separation of a mixture of rare earths (four LREs La, Ce, Pr, Nd, and seven HREs like Tb, Dy, Y, Ho, Er, Yb and Lu) into some fractions from phosphoric acid solutions. From the acid and extractant effects, 0.1 and 1 mol/L TOPS 99 were suitable for the separation of a mixture of REs into three concentrates at 3 mol/L acid, which is similar to wet phosphoric acid solutions (Radhika et al. 2011). Wang and Sun et al. studied the selective extraction and separation of yttrium from heavy lanthanide by sec-nonylphenoxy acetic acid (CA-100) in the presence of the complexing agent such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). They concluded that the separation factors of yttrium with respect to heavy lanthanide increased in the presence of the complexing agent (Sun 2005; Wang et al. 2004; Sun et al. 2006).

In a previous work, the leaching efficiency for different lanthanides present in phosphogypsum fertilizer (PGF) by 1.0 mL/L citric acid solution, was found to be in the order Ce (88.3%) > Y (40.7%) (Gasser et al. 2019). In this system, the different parameters affecting the extraction process of Ce(IV) and Y(III) was investigated such as; shaking time, extractant concentration, phase ratio, acid concentration as well as,

temperature were investigated. Based on the data obtained, the data was successfully modeled by empirical equation for conditional extraction constant, which verify the experimental results. Furthermore, the separation feasibility of the studied rare earth elements based on the difference in their extraction behaviors was also assessed

Experimental

Materials

Cerium(IV) (1.0 g/L) stock solution was prepared by dissolving a certain amount of cerium ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) obtained from Aldrich in double distilled water, whereas stock solution of Y(III) (1.0 g/L) was prepared by dissolving a known amount of the metal oxide produced by Aldrich in a minimum amount of concentrated nitric acid. The obtained yttrium solution was evaporated to near dryness, washed with double distilled water until it became almost free from nitrate ions, then completed to 1 L. Required concentrations of the investigated metal ions were prepared from the stock solutions by dilution. The extractant D2EHPA was purchased from Aldrich. The odorless kerosene was used as a diluent for the extractant and obtained from Misr Petroleum Company, Egypt. The total lanthanide concentrations in the studied samples were determined spectrophotometrically by the Arsenazo III method (Marczenko 1976). All other reagents were used as supplied without further purification.

Extraction procedure

Solvent extraction was performed by shaking equal volumes (5.0 mL) of aqueous and organic phases until equilibrium using a water-thermostated shaker of the type G.F.L 1083, Germany at 298 ± 1 K. The concentration of rare earth ions in the aqueous phase was determined spectrophotometrically using a UV–visible spectrophotometer model Shimadzu, UV-160A, Japan. The distribution coefficient (D), extraction efficiency (E) and separation factor (SF) were obtained from the following equations (Rydberg et al. 1992):

$$D = \frac{[M]_t - [M]_a}{[M]_a}, \quad (1)$$

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

$$SF = \frac{D_1}{D_2}, \quad (3)$$

where $[M]_t$ is the original metal concentration in the aqueous phase before extraction, $[M]_a$ is the metal concentration after

extraction, V_{aq} is the volume of the aqueous solution and V_{org} is the volume of the organic solution.

Results and discussion

Extraction of Ce(IV) and Y(III) with D2EHPA extractant in kerosene

Effect of shaking time

The effect of shaking time on the extraction of Ce(IV) and Y(III) (500 mg/L each) from 1.0 mol/L citric acid using 0.02 mol/L D2EHPA in kerosene was studied in shaking time range of 5.0–60.0 min, Fig. 1. The results illustrated that as the time increases from 5.0 to 10.0 min, the % E increased from about 13.2–15.84% and from 57.22 to 68.34 for Ce(IV) and Y(III), respectively. After that, the % E slightly decreases as time increases for both metal ions. Therefore, the required time for extraction of the studied metal ions was adjusted at 10.0 min in the following experiments.

Effect of D2EHPA concentration

The effect of extractant concentration in kerosene in the range 0.01–0.08 mol/L on the extraction of 0.5 g/L Y(III) from 1.0 mol/L citric acid medium was studied. In case of Ce(IV) the change of D2EHPA concentration was within the range 0.02–0.08 mol/L. The obtained results are given in Fig. 2. It is clear that the extraction efficiency increased with the increase in concentration of D2EHPA. However,

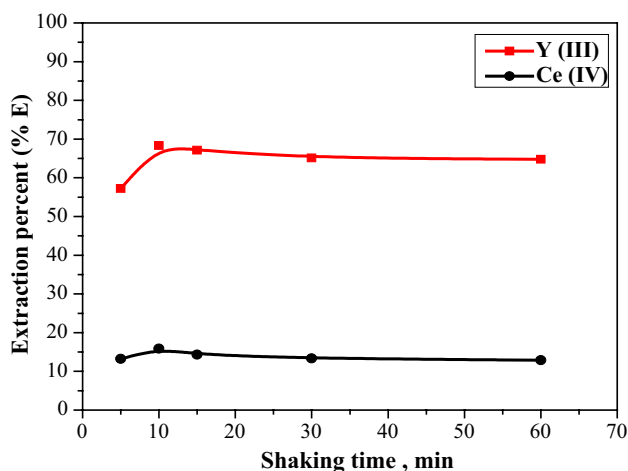


Fig. 1 Effect of shaking time on the extraction of Ce(IV) and Y(III) (500 mg/L each) from 1.0 mol/L citric acid solution using 0.02 mol/L D2EHPA in kerosene at pH 4.0, $A/O=1.0$ and 25 °C

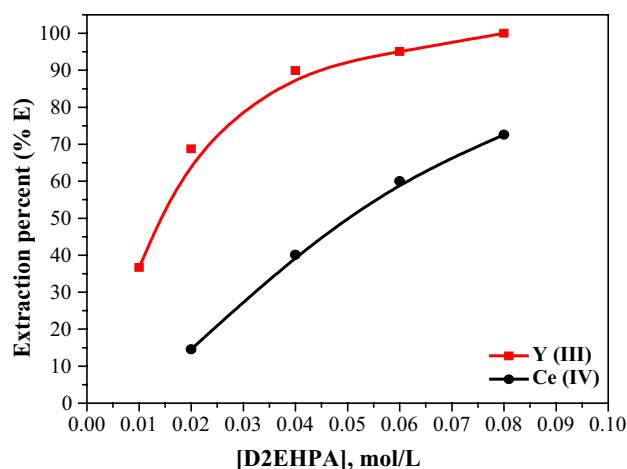


Fig. 2 Effect of D2EHPA concentration on the extraction of Ce(IV) and Y(III) from 1.0 mol/L citric acid solution at pH 4, $A/O=1.0$ and 25 °C

0.02 mol/L D2EHPA was used as it enables separation between Ce(IV) and Y(III).

Effect of phase ratio

The effect of changing aqueous to organic phase ratio (A/O) on the extraction of Ce(IV) and Y(III) from 1.0 mol/L citric acid with 0.02 mol/L D2EHPA in kerosene was investigated. The obtained results are given in Fig. 3. For Y(III), as the phase ratio increased from 1:1 to 1:6, the extraction efficiency (% E) decreased from 68.1 to 11.0%. In case of Ce(IV), as the phase ratio increased from 1:1 to 1:4, the % E decreased from about 14.97–3.08%. Therefore, the phase

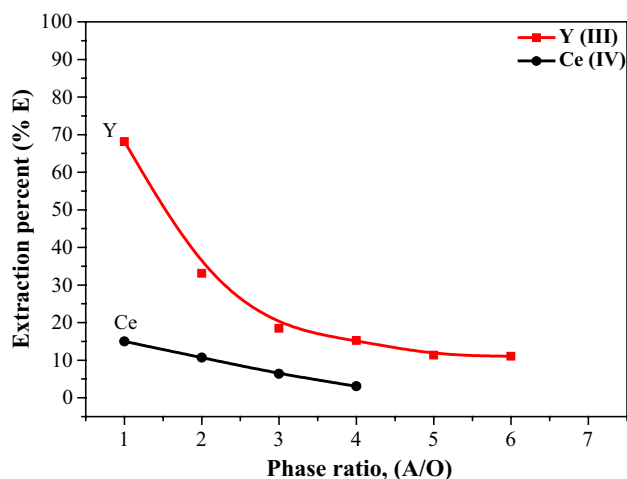


Fig. 3 Effect of phase ratio on the extraction of Ce(IV) and Y(III) from 1.0 mol/L citric acid solution using D2EHPA in kerosene at pH 4.0 and 25 °C

ratio of 1.0 was selected as a suitable ratio for the extraction process.

Effect of citric acid concentration

The extraction behavior of Ce(IV) and Y(III) by D2EHPA (0.02 mol/L) from citric acid solution of different concentrations ranging from 0 to 1.5 mol/L was investigated. While for Ce(IV), the investigated concentration range was from 0.5 to 1.5 mol/L due to its precipitation at pH equals to 2.50 (in the absence of citric acid). The obtained results indicated that, as the citric acid concentration increases the extraction of metals decreases, Fig. 4. This decrease is related to the formation of less extracted metal ions citrate complexes in the aqueous phase.

Modeling of the extraction equilibrium

The aforementioned results indicated that the extraction of the investigated Ce(IV) and Y(III) from 1.0 mol/L at pH 4.0 citric acid solution increased by the increase of D2EHPA molar concentration and decreased by the increase of citric acid molar concentration. Furthermore, due to the buffering effect of citric acid, the pH of citric acid solution has limited effect on the extraction for metal ions investigated. This behavior can be modeled based on the reaction between the main metal cationic ion species at pH 4.0 and the main species of citric acid at the same pH.

Citric acid (H_3Cit) is considered as a tribasic acid with $pK_{a1} = 3.13$, $pK_{a2} = 4.76$ and $pK_{a3} = 6.40$ at 25 °C (Lide 2004). According to MEDUSA software (www.kemi.kth.se/medusa), the speciation diagram for 1.0 mol/L citric acid as function of pH is given in Fig. 5. From this figure,

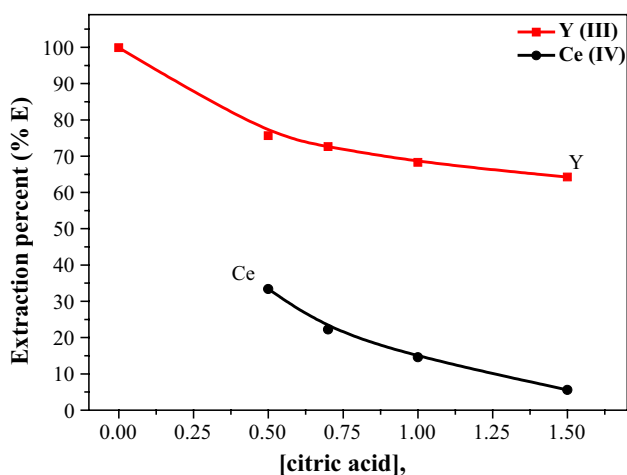


Fig. 4 Effect of citric acid concentration on the extraction of Ce(IV) and Y(III) using 0.02 mol/L D2EHPA in kerosene at pH 4, $O:A = 1.0$ and $T = 25$ °C

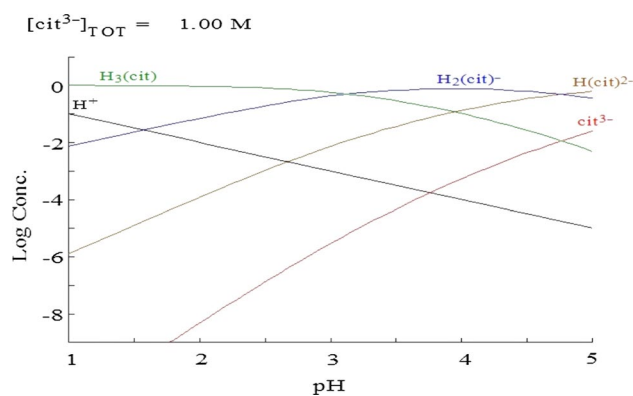
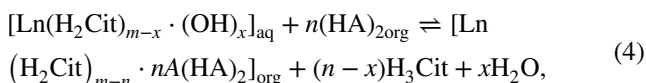


Fig. 5 Equilibrium diagram of 1.0 mol/L citric acid in pH range (1.0–5.0)

more than 77.0% of the citric acid solution is present as $[H_2Cit]^-$ at pH 4.0. Therefore, it is expected that this species represents the main ligand responsible for complex formation with the different lanthanides ions.

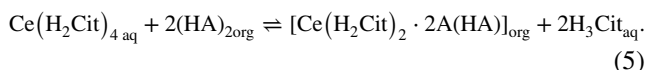
In aqueous solution of pH 4.0, Ce(IV) is present mainly in the free cationic form (Charles and Rabert 1976). In case of yttrium, under the same conditions, a main hydrolyzed species is in the form $[Y(OH)]^{2+}$. Therefore, we can assume that in 1.0 mol/L citric acid solution at pH 4.0, interaction of $(H_2Cit)^-$ with tetravalent cerium and yttrium ions results in formation of $[Ce(H_2Cit)_4]$ and $[Y(H_2Cit)_2 \cdot OH]$, respectively.

Providing that D2EHPA is a dimer in kerosene, and extracts cationic species in the organic phase, we can assume that the extraction of the former species will follow the general extraction equilibrium for the investigated metal ions:



where $n = 2.0$ or 3.0 , $x = 0$ or 1.0 and $m = 3.0$ or 4.0 . $(HA)_2$ denotes D2EHPA in dimer form.

In case of Ce(IV), the extraction from 1.0 mol/L citric acid solution and pH 4.0 by 0.02 mol/L D2EHPA in kerosene could be represented at equilibrium by



The conditional extraction constant $K_{C.ex}$ can be expressed as

$$K_{C.ex} = \frac{[Ce(H_2Cit)_2 \cdot 2A(HA)]_{org} [H_3Cit]_{aq}^2}{[Ce(H_2Cit)_{4aq}] [(HA)_2]_{org}^2}, \quad (6)$$

and the distribution ratio is considered as

Table 1 Conditional extraction constants $K_{C,ex}$ for Ce(IV) and Y(III) extraction by different concentrations of D2EHPA in kerosene

| D2EHPA, mol/L | $K_{C,ex}$ | |
|--------------------|----------------------|----------------------|
| | Ce(IV) $\times 10^2$ | Y(III) $\times 10^3$ |
| 0.01 | – | 5.8 |
| 0.02 | 4.25 | 5.50 |
| 0.04 | 4.19 | 5.6 |
| 0.06 | 4.17 | 5.34 |
| 0.08 | 4.14 | |
| K_{ex} (average) | 4.19 ± 0.05 | 5.56 ± 0.19 |

1.0 mol/L citric acid at pH 4.0

Table 2 Conditional extraction constants $K_{C,ex}$ for Ce(IV) and Y(III) extraction by D2EHPA in kerosene at different citric acid concentrations

| Citric acid, mol/L | $K_{C,ex}$ | |
|--------------------|----------------------|----------------------|
| | Ce(IV) $\times 10^2$ | Y(III) $\times 10^3$ |
| 0.5 | 4.06 | 3.88 |
| 0.7 | 4.17 | 4.64 |
| 1 | 4.20 | 5.38 |
| 1.5 | 3.94 | 6.75 |
| K_{ex} (average) | 4.10 ± 0.12 | 5.16 ± 1.22 |

0.02 mol/L D2EHPA at pH 4.0

$$D = \frac{[\text{Ce}(\text{H}_2\text{Cit})_2 \cdot 2\text{A}(\text{HA})]_{\text{org}}}{[\text{Ce}(\text{H}_2\text{Cit})_4]_{\text{aq}}} \quad (7)$$

Therefore, the conditional extraction constant, $K_{C,ex}$, is given as

$$K_{C,ex} = \frac{D[\text{H}_3\text{Cit}]_{\text{aq}}^2}{[(\text{HA})_2]_{\text{org}}^2} \quad (8)$$

This model can be linearized to give

$$\log D = \log K_{C,ex} + 2 \log [(\text{HA})_2]_{\text{org}} - 2 \log [\text{H}_3\text{Cit}]_{\text{aq}} \quad (9)$$

Different values of the conditional extraction constant were calculated from Eq. (8) at different D2EHPA and citric acid concentrations and given in Tables 1 and 2. The mean value of $K_{C,ex}$ for Ce(IV) extraction by D2EHPA was found to be $(4.15 \pm 0.05) \times 10^2$.

Using this average conditional extraction constant obtained for Ce(IV), $K_{C,ex}$, the distribution coefficient, D , was calculated based on Eq. (8) and compared with that obtained from experimental procedures and presented in Tables 3 and 4, respectively. The calculated values were

Table 3 Calculated and experimental values of the distribution ratio for Ce(IV) and Y(III) at different D2EHPA concentrations

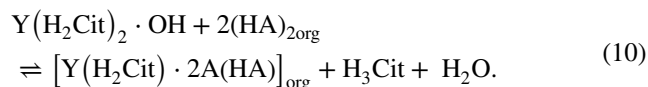
| D2EHPA, mol/L | Ce(IV) | | Y(III) | |
|---------------|---------------------------|-------------------------|---------------------------|-------------------------|
| | $D_{\text{experimental}}$ | $D_{\text{calculated}}$ | $D_{\text{experimental}}$ | $D_{\text{calculated}}$ |
| 0.005 | – | – | – | – |
| 0.01 | – | – | 0.58 | 0.54 |
| 0.015 | – | – | – | – |
| 0.02 | 0.17 | 0.17 | 2.20 | 2.14 |
| 0.04 | 0.67 | 0.66 | 8.90 | 8.58 |
| 0.06 | 1.5 | 1.49 | 19.21 | 19.30 |
| 0.08 | 2.65 | 2.66 | – | – |

Table 4 Calculated and experimental values of the distribution ratio for Ce(IV) and Y(III) at different citric acid concentrations

| Citric acid, mol/L | Ce(IV) | | Y(III) | |
|--------------------|---------------------------|-------------------------|---------------------------|-------------------------|
| | $D_{\text{experimental}}$ | $D_{\text{calculated}}$ | $D_{\text{experimental}}$ | $D_{\text{calculated}}$ |
| 0.5 | 0.65 | 0.66 | 3.1 | 4.29 |
| 0.7 | 0.34 | 0.34 | 2.65 | 3.01 |
| 1 | 0.168 | 0.166 | 2.15 | 2.14 |
| 1.5 | 0.07 | 0.07 | 1.8 | 1.43 |

found to be within the values experimentally determined. This supports the proposed extraction equilibrium.

On the other hand, At pH 4.0, Y(III) suffers from hydrolysis and may be presented as $[\text{Y}(\text{OH})]^{+2}$. Therefore, the extraction equilibrium of Y(III) from 1.0 mol/L citric acid solution and pH 4.0 by 0.02 mol/L D2EHPA in kerosene is represented by



The conditional extraction constant $K_{C,ex}$ can be expressed as

$$K_{C,ex} = \frac{D[\text{H}_3\text{Cit}]}{[(\text{HA})_2]^2} \quad (11)$$

and linearized to give

$$\log D = \log K_{C,ex} + 2 \log [(\text{HA})_2] - \log [\text{H}_3\text{Cit}] \quad (12)$$

As shown in Tables 1 and 2, the mean value of $K_{C,ex}$ for Y(III) extraction by D2EHPA was found to be $(5.36 \pm 0.28) \times 10^3$

The distribution ratios for Y(III) are calculated from Eq. (11) at different D2EHPA and citric acid concentrations. The calculated and corresponding experimental values at different D2EHPA and citric acid concentrations are

presented in Tables 3 and 4, respectively. There is a great agreement between the experimental and calculated values which supports the assumed extraction mechanism.

The log–log plot between the D2EHPA concentrations and the corresponding distribution ratios, Fig. 6, gave linear relations with positive slopes of 2.0 for both Ce(IV) and Y(III). This indicates that two dimers are involved in the extracted species for the two metal ions. On the other hand, a plot between $\log D$ against the citric acid concentrations gives linear relations, Fig. 7. The slope of these lines were found to be -2.0 and -1.0 for Ce(IV) and Y(III), respectively. This indicates that two moles of citric acid are released in the aqueous medium during the extraction of Ce(IV) and one mole is released in case of Y(III). Therefore, the data obtained from the slopes of Figs. 6 and 7 confirm the proposed extraction mechanism.

Effect of temperature

The influence of temperature on the extraction of Ce(IV) and Y(III) (500 mg/L each) from 1.0 mol/L citric acid solution by D2EHPA was investigated through the temperature range of 15–65 °C. The obtained results show that with increasing temperature, the extraction percent of metal ions decreases, Fig. 8. The conditional extraction constant values, $K_{C,ex}$, of the extracted species were evaluated at the respective temperature degrees according to Eqs. (8 and 11).

Using the following Van't Hoff equation (Van't Hoff 1995), the standard enthalpy change (ΔH°) associated with the extraction can be calculated by

$$\ln K_{C,ex} = \frac{-\Delta H^\circ}{RT} + C, \quad (13)$$

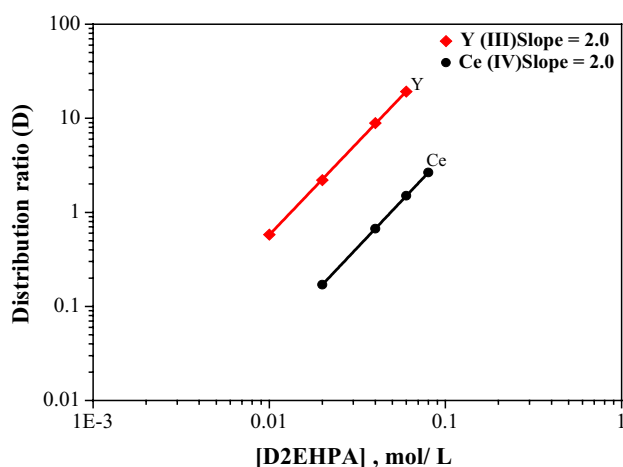


Fig. 6 Log–log linear relationships between the extractant concentrations with the corresponding distribution ratios in the extraction of Ce(IV) and Y(III) from 1.0 mol/L citric acid solution at pH 4.0, $O:A=1$ and 25 °C

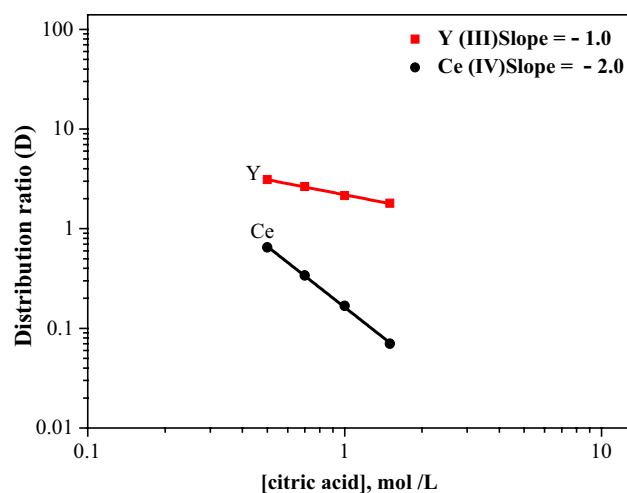


Fig. 7 Log–log relationship between the citric acid concentrations and the corresponding distribution ratios in the extraction of Ce(IV) and Y(III) using 0.02 mol/L D2EHPA in kerosene at pH 4, $O:A=1$ and 25 °C

where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (in Kelvin) and C is a constant. As shown in Fig. 9, $\ln K_{C,ex}$ is linearly related to the reciprocal of the temperature ($1/T$) K^{-1} ; the slopes obtained from this figure were used to calculate (ΔH°). The standard free energy change (ΔG°) and the standard entropy change (ΔS°) were calculated from the following equations:

$$\Delta G^\circ = -RT \ln K_{ex}, \quad (14)$$

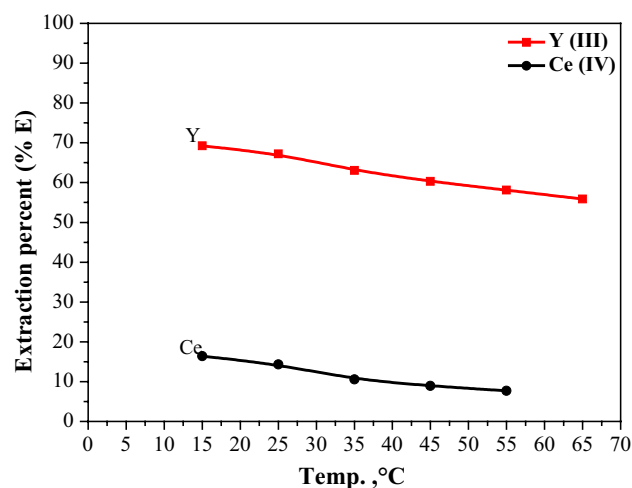


Fig. 8 Effect of temperature on the extraction of Ce(IV) and Y(III) with 0.02 mol/L D2EHPA in kerosene from 1.0 mol/L citric acid solution at pH 4, $O:A=1$

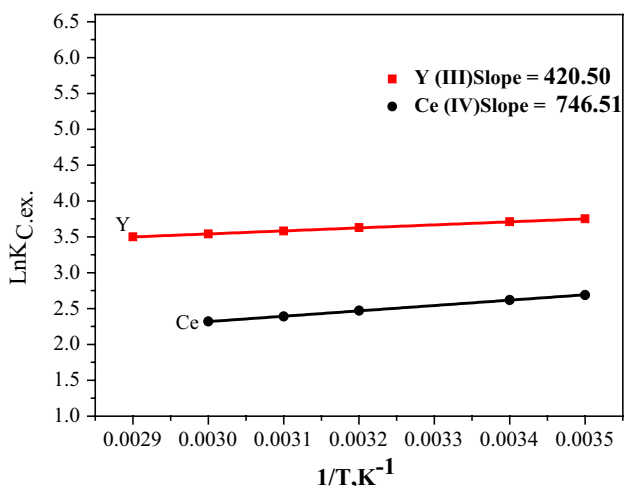


Fig. 9 Relation between ($\ln K_{C,ex}$) and ($1/T$) for the extraction of Ce(IV) and Y(III) with D2EHPA in kerosene from 1.0 mol/L citric acid solution

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{15}$$

The data in Table 5 represent the calculated thermodynamic functions for Ce(IV) and Y(III).

As given from the table, the extraction of Ce(IV) and Y(III) is exothermic as indicated by the negative values of ΔH° . The reaction of Ce(IV) and Y(III) with D2EHPA is spontaneous in nature as referred by the negative sign of ΔG° values, while the positive values of (ΔS°) show an increase in the randomness of the system during the formation of the extracted species.

Separation feasibility

The separation between Y(III) and Ce(IV) is represented by the separation factor (SF) which is given by the ratio of their distribution ratios at equilibrium as follows:

$$SF_{(Y/Ce)} = \frac{D_Y}{D_{Ce}} \tag{16}$$

where D_Y and D_{Ce} are the distribution ratios of Y (III) and Ce(IV), respectively.

Table 5 Calculated thermodynamic parameters of the extraction of Ce(IV) and Y(III) from 1.0 mol/L citric acid solution by D2EHPA in kerosene at $O:A = 1$

| Thermodynamic parameter | Y(III) | Ce(IV) |
|--|--------|--------|
| Enthalpy change (ΔH°), kJ mol ⁻¹ | -3.50 | -6.21 |
| Free energy change (ΔG°), kJ mol ⁻¹ | -9.19 | -6.49 |
| Entropy change (ΔS°), J mol ⁻¹ K ⁻¹ | 19.09 | 0.93 |

From Eqs. (8 and 11) the D values of Y (III) and Ce(IV) are given as

$$(D)_{Ce} = \frac{K_{C,Ce}[(HA)_2]^2}{[H_3Cit]^2} \tag{17}$$

$$D_Y = \frac{K_{C,Y}[(HA)_2]^2}{[H_3Cit]} \tag{18}$$

Substituting from Eqs. (17 and 18) in Eq. (16) gives

$$SF_{(Y/Ce)} = \frac{K_{C,Y}[H_3Cit]}{K_{C,Ce}} \tag{19}$$

Substituting with the mean $K_{C,ex}$ values:

$$SF_{(Y/Ce)} = \frac{5.36 \times 10^3 [H_3Cit]}{4.15 \times 10^2} \tag{20}$$

$$SF_{(Y/Ce)} = 12.92[H_3Cit] \tag{21}$$

It is clear that the $SF_{(Y/Ce)}$ calculated from Eq. (21) depends on the acid concentration. The plot of the relation between the SF and different citric acid concentrations at 0.02 mol/L D2EHPA, Fig. 10, shows that as the citric acid concentration increases, the separation between Y (III) and Ce(IV) increases.

The SF values given by the ratio of their extraction constants and listed in Table 6 show that the separation of Y(III) from Ce(IV) is 12.92.

On the other hand, the values of SF at different D2EHPA concentrations for Y(III) and Ce(IV) listed in Table 7 indicate that the highest SF between Y(III) and

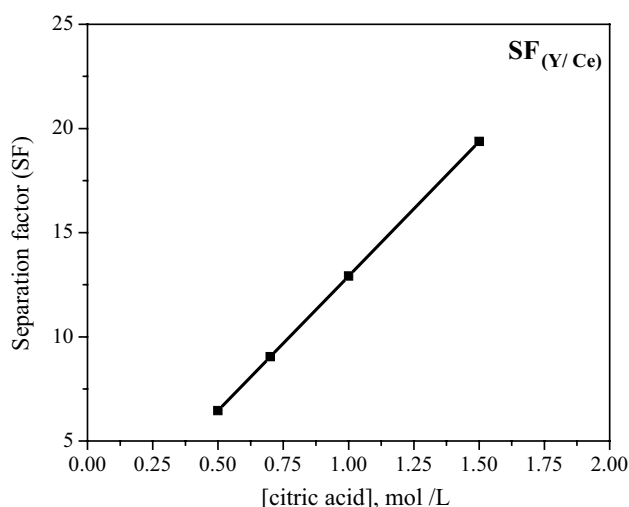


Fig. 10 Effect of citric acid concentration on the separation factor ($SF_{(Y/Ce)}$) with 0.02 mol/L D2EHPA

Table 6 Separation of Ce(IV) and Y(III) extracted from 1.0 mol/L citric acid solution using 0.02 mol/L D2EHPA in kerosene

| $K_{C,ex}$ (Ce) | $K_{C,ex}$ (Y) |
|--------------------|--------------------|
| 4.15×10^2 | 5.36×10^3 |
| $S_{Y/Ce}$ 12.92 | |

Table 7 Effect of D2EHPA concentration on the separation between Ce(IV) and Y(III)

| D2EHPA, mol/L | Separation factors Y/Ce |
|---------------|-------------------------|
| 0.02 | 12.94 |
| 0.04 | 13.28 |
| 0.06 | 12.81 |

Table 8 Effect of phase ratio on the separation between Ce(IV) and Y(III)

| A:O | Separation factors Y/Ce |
|-----|-------------------------|
| 1:1 | 12.94 |
| 2:1 | 4.13 |
| 3:1 | 3.78 |
| 4:1 | 5.59 |

Ce(IV) is 13.28 at D2EHPA concentration 0.04 mol/L. Also, the SF obtained from the values of distribution coefficient at various phase ratios are given in Table 8. Thus, the separation between Ce(IV) and Y(III) by varying the phase ratio could also be obtained under certain conditions. The separation for metal ions obtained during this work are compared with those of other reported extractants given in Table 9.

Conclusion

The extraction of Ce(IV) and Y(III) from citrate medium using D2EHPA mixed with kerosene has been performed. It was found that:

1. The extraction efficiency of Ce(IV) and Y(III) were found to increase by increasing D2EHPA concentration and decrease by the increase of citric acid concentration at pH 4.0.
2. The mean species in the organic phase are the following, $[Ce(H_2Cit)_2 \cdot 2A(HA)]$ and $[Y(H_2Cit) \cdot 2A(HA)]$.
3. The mean conditional extraction constants values $K_{C,ex}$ for Y(III) and Ce(IV) extraction by D2EHPA from 1.0 citric acid at pH 4.0 solution were calculated and found to be $(5.36 \pm 0.28) \times 10^3$ and $(4.15 \pm 0.05) \times 10^2$, respectively.
4. The experimental results showed that the extraction efficiency decreased with the increase in temperature, which indicates that the extraction of Ce(IV) and Y(III) ions is exothermic and the positive values of the calculated entropy change show an increase in the randomness of the system during the formation of the extracted species.
5. Separation feasibility in terms of the conditional extraction constant indicated that the separation factor of Ce(IV) and Y(III) increases by the increase of citric acid concentration.
6. Increasing the extractant concentration had almost no effect on the separation, while the highest separation between Y(III) and Ce(IV) can be performed at D2EHPA concentration of 0.04 mol/L. However, 0.02 mol/L was used and investigated through this work due to economic considerations.

Table 9 Extraction and separation for metal ions obtained during this work are compared with those of other reported extractants

| Author | Extractant | Medium | Metal ion | Separation factor (β) |
|----------------------------|--|--------------------------|-----------------------|---|
| In this work | 0.02 mol/L D2EHPA | Citrate medium | Ce, Y | 12.94 for $\beta Y/Ce$ |
| Wu et al. (2007) | Mixtures of Cyanex 302 and sec-nonylphenoxy acetic acid (CA-100) | | Ho, Y, Er | 3.24 for $\beta Y/Er$, 3.72 for $\beta Ho/Y$, 12.0 for $\beta Ho/Er$ |
| Sun et al. (2005) | Sec-octylphenoxy acetic acid (CA-12) and Cyanex 272 | Chloride medium | Ho, Y, Er, Tm, Yb, Lu | 1.58 for $\beta Er/Y$, 4.72 for $\beta Tm/Y$, 5.81 for $\beta Yb/Y$, 9.21 for $\beta Lu/Y$ |
| Michelsen and Smutz (1971) | D2EHPA | Hydrochloric acid medium | Ho, Y, Er | 1.39 for $\beta Er/Y$, 2.02 for $\beta Y/Ho$, 2.81 for $\beta Er/Ho$ |
| Thakur (2000) | D2EHPA | Hydrochloric acid medium | Tb, Dy, Ho, Y | 2.11 for $\beta Tb/Dy$, 1.94 for $\beta Dy/Ho$, 1.91 for $\beta Y/Ho$, 1.18 for $\beta Er/Y$ |

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