



ORIGINAL ARTICLE

The effect of ionic strength on the extraction of Thorium(IV) from nitrate solution by didodecylphosphoric acid (HDDPA)

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Abstract Extraction of Th(IV) ion from nitrate media at high ionic strength ($I = 1.00, 3.00, 5.00$ and 7.00 M) using didodecylphosphoric acid was studied. The effect of HDDPA concentration, ionic strength, pH and temperature on the extraction processes have been studied in nitrate media. From the equation of the extraction process, (K_{ex}) extraction constant can be calculated from the distribution ratio D_c values at different temperatures. Enthalpy, free energy and entropy changes were determined. The composition of the complex formed were established to correspond to $[Th(X)_4(HR_2)_Y]_{org}$, where $X = NO_3^-$ and $Y = 1$ or 2 , $HR_2 =$ HDDPA molecule and $R_2 =$ deprotonated HDDPA molecule.

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1. Introduction

Solvent extraction of metal chelate complexes has been recognized as an excellent separation method for a long time, because

of its simplicity, speed, and its wide scope of applications. As solvent extraction does not involve co-precipitation, which is such an undesirable feature of separations based on precipitation, it is frequently appears to be the ideal method of separating trace constituents from large amounts of other substances (Stray, 1964).

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Solvent extraction or (liquid–liquid extraction) is a technique used both in the laboratory and on industrial scale; refers to selectivity of this process in removing a solute from a liquid mixture by solvent. As a separation technique, it is a partitioning process based on the unequal distribution of the solute (A) between two immiscible solvents in equilibrium, usually water (aq) and an organic liquid (org) (EPA, 2004)

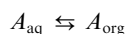
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The process is often very selective and the isolation of the metal in question can usually be made as complete as desired by several repetition of the extraction procedure (Stray, 1964).

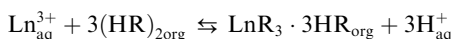
The ratio of the total concentration of solute in the extract form (regardless of its chemical form) to its total analytical concentration in the other phase called distribution ratio in liquid–liquid extraction, which it is an experimental parameter and its value does not necessarily imply that distribution equilibrium between the phases has been achieved (Inczédy, 1994), it is expressed by

$$D_c = \frac{[ML_n]_{\text{org}}}{[M^{n+}]_{\text{aq}}}$$

Khaled (1996) studied the extraction of Uranium(VI) and Thorium(IV) ions from perchlorate solution by HDDPA in toluene and chloroform as a carrier diluents. The composition of the formed complex were established to be $\text{UO}_2(\text{ClO}_4)(\text{HR}_2)(\text{HR})_2$ and $\text{Th}(\text{ClO}_4)_{4-n}\text{R}_n(\text{HR})_{5-n}$ where $n = 1$ or 2 , respectively. Th(IV) has been found to be more extractable than U(VI) (Khalili et al., 2003).

Ehsan (2002) studied the synergistic effect of didodecylphosphoric acid with tri-*n*-butylphosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO) on the extraction of Uranium(VI) and Thorium(IV). The composition of the formed complex were established to be $\text{UO}_2(\text{ClO}_4)_2[(\text{HDDPA})_2]_3(\text{TOPO})$, $\text{UO}_2(\text{ClO}_4)_2[(\text{HDDPA})_2]_3(\text{TBP})$, $\text{Th}(\text{ClO}_4)_4[(\text{HDDPA})_2]_3(\text{TOPO})$ and $\text{Th}(\text{ClO}_4)_4[(\text{HDDPA})_2]_3(\text{TBP})$ (Soudani et al., 2001).

Didodecylphosphoric Acid extractant, HDDPA, has proved to be very useful in the extraction of lanthanide ions. Konodo et al. (1989) studied the extraction of europium(III), samarium(III), and gadolinium(III) ions from nitrate solution by HDDPA in toluene as a carrier diluent. It was found that lanthanides ions (Ln^{3+}) are extracted according to the following reaction equilibrium:



This work aim at studying the extraction behavior of Thorium(IV) from nitrate media at high ionic strength ($I = 1.00, 3.00, 5.00$ and 7.00 M) using didodecylphosphoric acid. In addition, the effect of HDDPA concentration, ionic strength, pcH and temperature on the extraction processes will be studied.

2. Experimental

Thorium nitrate (BDH) was used without further purification. Didodecylphosphoric acid (HDDPA) was prepared and recrystallized three times from ethyl acetate (Konodo et al., 1989).

Analytical grade toluene (Merck) was purified by distillation, hydrochloric acid (35%) (GCC) and nitric acid (69%) (BDH) were used throughout this work. Arsenazo (III) (BDH) was used as spectrophotometric reagent for Th(IV) ion.

All other compounds were of analytical grade. Deionized water was employed to make up aqueous solutions, and for washing all glassware.

A mechanical shaker was used to shake all samples in all experiments. The spectrophotometric measurements were carried out using Spectro Scan 80DV Spectrophotometer. SHIMADZO AW120 (Japan) analytical balance was also used.

A 250.0 mL of about 0.025 M thorium nitrate stock solution was prepared by dissolving 3.68 g of thorium nitrate hexahydrate $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ in 250.0 mL of water. The exact concentration of the solution was determined by titration with EDTA solution at pH 2–3, using xylenol orange as indicator (Savvin, 1961).

The HDDPA stock solution was prepared by dissolving 4.34 g of HDDPA, in 2.00 L toluene as a diluent to give 5.00×10^{-3} M of HDDPA solution.

A 1.00 L of HDDPA solution was pre-equilibrated by mixing it with 1.00 L of media solutions (nitrate media HNO_3 and NaNO_3 solution $I = 1.00, 3.00, 5.00$ and 7.00 M and pcH = 1.00, 2.00), the mixture was stirred for 24 h, and then the aqueous layer was separated.

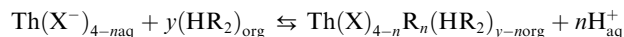
A 10.0 mL of 9.81×10^{-5} M thorium solution, and 10.0 mL of the organic layer, which contain HDDPA with the suitable concentration in toluene as a diluent, was placed in 50 mL vial, and the mixture was shaken for 3.0 h. A 0.5 mL of the aqueous solution was drawn in which concentration of Th(IV) was directly determined by spectrophotometer, each experiment was repeated at least twice (Khalili et al., 2003).

The spectrophotometric determination of Th(IV) samples was carried out by introducing 0.50 mL of Arsenazo(III) indicator solution (0.1%), 10.0 mL of 9.0 M HCl solution, and 0.50 mL of the Thorium(IV) solution in a 25.0 mL volumetric flask, the volume was then adjusted to 25.0 mL through the addition of water. A wavelength $\lambda = 660$ nm was chosen as the optimum wavelength of measurement absorbance of Thorium(IV)–Arsenazo(III) complex (Savvin, 1961).

A calibration graph was done for every run using 1.626, 3.252, 6.505, 9.757, 13.01, 16.262, 19.515, 22.767 and 26.019 $\mu\text{g/mL}$ of Th(IV) solution, Fig. 1.

3. Results and discussion

The general equation for the reaction of extraction Thorium(IV) by acidic organophosphorus extractant from aqueous media is given by:



where (X^-) is an anion which found in aqueous phase, (HR_2) is the didodecylphosphoric acid (HDDPA) extractant dissolved in the organic phase which is toluene, (R_2) is deprotonated didodecylphosphoric acid. The charge of Th ion is $4+$, ($4 - n$) is the number of moles of the anion which shared in the formation of extracted complex in organic phase, (y) number of moles of ligands in the extracted complex and (n) the number of hydrogen ion released from didodecylphosphoric acid during formation of the complex in the organic phase (Khalili et al., 2003).

3.1. Effect of HDDPA concentration on D_c

The effect of didodecylphosphoric acid (HDDPA) concentration, on the extraction of Thorium(IV) ion was studied at constant ionic strength (1.00, 3.00, 5.00 and 7.00 M HNO_3 and NaNO_3) and constant pcH (1.00 and 2.00). The D_c (distribution ratio in liquid–liquid extraction) value increases with the increase of the HDDPA concentration. The logarithms of the D_c values obtained were plotted versus the corresponding logarithm of the HDDPA concentration, a straight line of a slope around 1.50. This means that at least two complexes

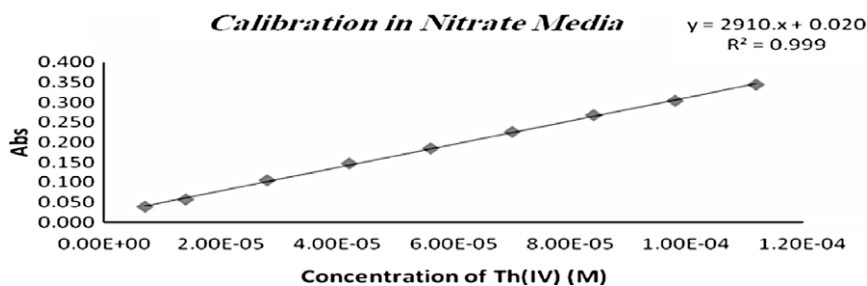


Figure 1 Calibration curve in nitrate media.

are formed in organic phase between Th(IV) and didodecylphosphoric acid, (1.00 (50%) or 2.00 (50%) molecules of HDDPA are involved in the formation of the Thorium–HDDPA complex). This is shown in Figs. 2 and 3.

3.2. Effect of *pcH* on extraction of Th(IV) ion

The effect of *pcH* on the extraction of Thorium(IV) ion from nitrate media of ionic strength (1.00 M), has been studied. From this, we can see little effect of *pcH* on extraction of Th(IV) ion from nitrate media (slope around 0.03). This means the number of hydrogen ions released during the formation of Thorium–HDDPA is zero (distribution ratio is independent of the *pcH* of the aqueous phase). This can be shown in Fig. 4.

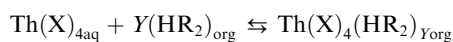
3.3. Effect of ionic strength on D_c

The effect of ionic strength was studied at constant *pcH*; the data indicate that the D_c value increases with increase of ionic strength. This is explained by the increase of the thermodynamic activity of the metal salt extracted and decrease the activity of water as the ionic strength increases, this is shown

in Fig. 5, which means that they are working as salting out agent (Kolarik, 1982).

The effect of salt variation upon extraction of UO_2^{2+} ion by 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) showed that the distribution ratio increases with the increase in salt concentration of $NaClO_4$ or $NaNO_3$ in ternary extraction system. However, it decreases with the increase of salt concentration of $NaCl$, and explain that by the complexing ability of the anion in the order $Cl^- > NO_3^- \gg ClO_4^-$ (Banerjee et al., 2003).

By considering both the HDDPA concentration effect and the *pcH* effect on the D_c value, the extracted species can be written in this form $Th(X)_4(HR_2)_Y$, where $X = NO_3^-$ and $Y = 1$ or 2 in nitrate media. This means that didodecylphosphoric acid in toluene as a carrier diluent extracted Thorium(IV) ion from nitrate solutions by a solvation mechanism. This mechanism is according to the following equilibrium equation:



where $X = NO_3^-$, $Y = 1.0$ or 2.0 , (HR_2) is the didodecylphosphoric acid (HDDPA) extractant dissolved in the organic phase which is toluene.

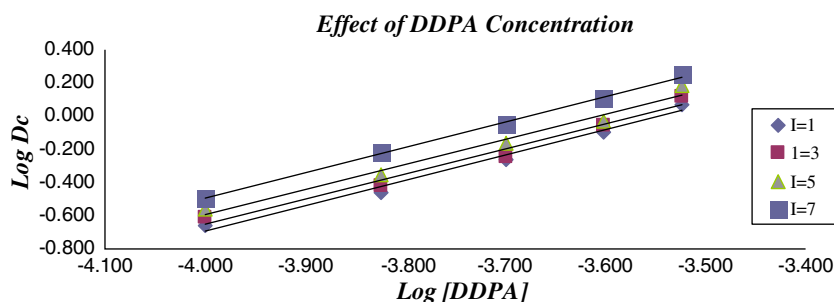


Figure 2 Variation of $\text{Log } D_c$ with $\text{Log}[\text{HDDPA}]$ in nitrate media, ($I = 1.00, 3.00, 5.00$ and 7.00 M, $\text{pcH} = 1.00$, $T = 30^\circ\text{C}$).

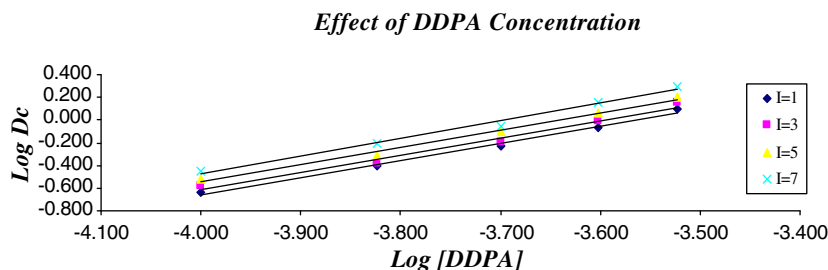


Figure 3 Variation of $\text{Log } D_c$ with $\text{Log}[\text{HDDPA}]$ in nitrate media, ($I = 1.00, 3.00, 5.00, 7.00$ M, $\text{pcH} = 2.00$, $T = 30^\circ\text{C}$).

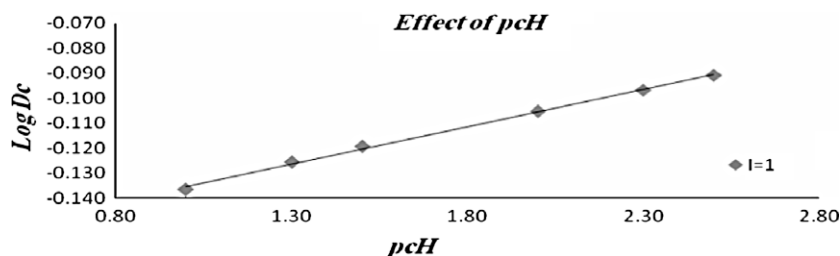


Figure 4 Variation of Log D_c with pcH in nitrate media, ($T = 30^\circ\text{C}$).

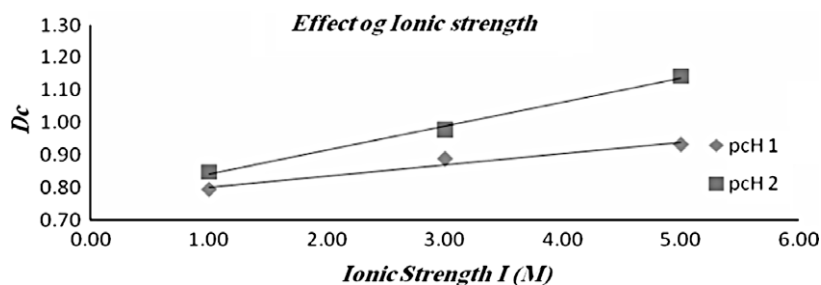


Figure 5 Variation of D_c with ionic strength at pcH = 1.00 and 2.00 in nitrate media, $T = 30^\circ\text{C}$.

The equilibrium constant equation for the extraction process is:

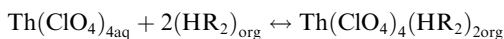
$$K_{\text{ex}} = \frac{[\text{Th}(\text{X})_4(\text{HR}_2)_Y]_{\text{org}}}{[\text{Th}(\text{X})_4]_{\text{aq}}[\text{HR}_2]_{\text{org}}^Y}$$

$$K_{\text{ex}} = \frac{D_c}{[\text{HR}_2]_{\text{org}}^Y}$$

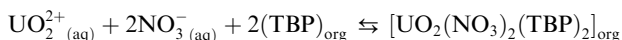
where

$$D_c = \frac{[\text{Th}(\text{X})_4(\text{HR}_2)_Y]_{\text{org}}}{[\text{Th}(\text{X})_4]_{\text{aq}}}$$

The same mechanism, solvation mechanism, was found for the extraction of Thorium(IV) ion from aqueous medium such as perchlorate media by neutral ligands in organic diluent (Bayyari et al., 2010):

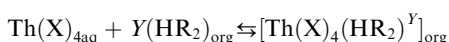


Stas et al. (2005) studied the extraction of UO_2^{2+} from nitric acid and nitrate solution by tributylphosphate (TBP) in kerosene. The equilibrium reaction was found to be:



3.4. Calculation of the extraction equilibrium constant (K_{ex})

The K_{ex} calculation is based on the following proposed equation for the reaction:



$$K_{\text{ex}} = \frac{D_c}{[\text{HR}_2]_{\text{org}}^Y}$$

where $\text{X} = \text{NO}_3^-$ and $Y = 1.5$.

The hydrogen ion concentration can be calculated from $\text{pcH} = -\text{Log}[\text{H}^+]$.

The HDDPA concentration in the organic phase at equilibrium $[\text{HR}]_{\text{equ,org}}$, can be calculated from the difference between the initial HDDPA concentration and the amount used for complexation. Substituting the previous values in K_{ex} equation gives the values shown in Tables 1 and 2. From this, we can see K_{ex} increases with the increase of ionic strength in perchlorate and nitrate solutions. This is explained by the dehydration of Th(IV) ion due to formation of the complex.

3.5. Effect of temperature on the extraction of Th(IV) ion

The temperature effect on the D_c value was investigated. The data is shown in Fig. 6. From the data, it is clear that the D_c value decreases with increasing temperature.

Table 1 K_{ex} for the reaction in nitrate media at different ionic strength at pcH = 1.00, $T = 30^\circ\text{C}$.

D_c	I (M)	$[\text{HR}_2]_{\text{eq,org}}$	$[\text{HR}_2]_{\text{eq,org}}^Y$	K_{ex}
1.18	1.00	2.24E-04	3.35E-06	3.52E+05
1.31	3.00	2.21E-04	3.29E-06	3.98E+05
1.53	5.00	2.03E-04	2.89E-06	5.29E+05
1.77	7.00	1.98E-04	2.79E-06	6.34E+05

Table 2 K_{ex} for the reaction in nitrate media at different ionic strength at pcH = 2.00, $T = 30^\circ\text{C}$.

D_c	I (M)	$[\text{HR}_2]_{\text{eq,org}}$	$[\text{HR}_2]_{\text{eq,org}}^Y$	K_{ex}
1.24	1.00	2.19E-04	3.24E-06	3.83E+05
1.42	3.00	2.12E-04	3.09E-06	4.60E+05
1.57	5.00	2.02E-04	2.87E-06	5.47E+05
1.95	7.00	2.02E-04	2.87E-06	6.79E+05

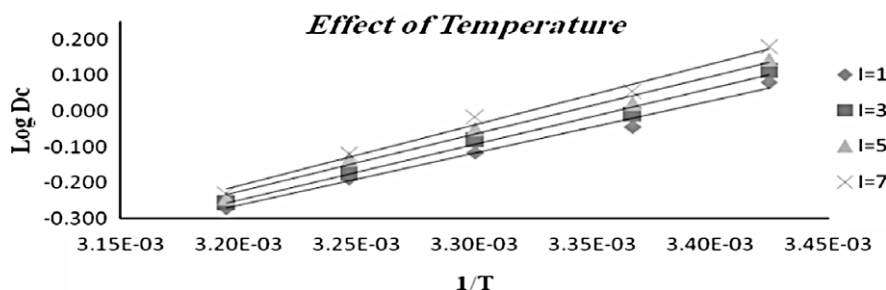


Figure 6 Variation of $\text{Log } D_c$ with $1/T$ in nitrate media, ($I = 1.00, 3.00, 5.00, 7.00 \text{ M}$).

Table 3 Thermodynamic parameters in nitrate media.

$I \text{ (M)}$	$\Delta H \text{ (kJ/mol)}$	$\Delta G \text{ (J/mol)}$	$\Delta S \text{ (J/mol K)}$	K_{ex}
1.00	-27.9	-32.4	14.8	3.83E+05
3.00	-29.7	-32.8	10.3	4.60E+05
5.00	-30.7	-33.3	8.6	5.47E+05
7.00	-32.6	-33.8	4.2	6.79E+05

3.6. Calculation of the thermodynamic parameters

From the van't Hoff's equation

$$\frac{\Delta \text{Log } D_c}{\Delta(1/T)} = \frac{-\Delta H}{2.303R}$$

ΔH can be calculated by plotting $\text{Log } D_c$ against $1/T$, where the slope equal to

$$\text{Slope} = \frac{\Delta \text{Log } D_c}{\Delta(1/T)} = \frac{-\Delta H}{2.303R}$$

The change in free energy (ΔG) can be calculated at 303 K by using the equation

$$\Delta G = -RTL \ln K_{\text{ex}}$$

While ΔS was calculated at 303 K from ΔG and ΔH . All the thermodynamic parameters are shown in Table 3.

From the data in Tables 1 and 2, it is clear that the extraction at different ionic strengths from nitrate solutions behave similarly. Since the enthalpy changes are exothermic and the entropy changes are positive, the extraction process is favored (spontaneous). In addition, the entropy changes decrease with increase ion exchange (Bagawde et al., 1978). This may be associated with the release of water molecules by Th(IV) in the process of complexation (Yaftian et al., 2004).

4. Conclusion

The Th(IV) extraction equilibrium constants were obtained, and the increase in ionic strength by nitrate anions or increasing the pH leads to increasing in the extraction efficiency from nitrate media.

The extraction system from nitrate was found to be spontaneous at different ionic strengths. The enthalpy changes are exothermic and the entropy changes are positive. This may be associated with the decrease in the release of water mole-

cules upon dehydration of Th(IV) ion during complexation with ionic strengths.

The extraction of Th(IV) ions from nitrate is more difficult than from perchlorate.

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