Arabian Journal of Chemistry (2010) **3**, 115–119

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

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

M.A. Bayyari [a], **M.K. Nazal** [b], **F.I. Khalili** [c,*]

[a] *Queasmah-hi al maadi, 11183 Amman, P.O. Box 38905, Jordan*
[b] *Abdelsalam Kamal Street, Hay Al-Baraka, 11953 Amman, P.O. Box 11241, Jordan*
[c] *University of Jordan, Chemistry Dept., Amman 11942, Jordan*

Received 26 January 2009; accepted 16 July 2009
Available online 10 February 2010

KEYWORDS

Ionic strength;
Extraction;
Thorium(IV);
Perchlorate solution;
HDDPA

Abstract Extraction of Th(IV) ion from perchlorate media at high ionic strength (I = 1.00, 3.00 and 5.00 M) using didodecylphosphoric acid was studied. The effect of HDDPA concentration, ionic strength, pcH and temperature on the extraction processes have been studied in perchlorate 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 $X = ClO_4^-$, Y = 1 or 2, HR_2 is HDDPA molecule and R_2 is deprotonated HDDPA molecule.

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 application. 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 for separating trace constituents from large amounts of other substances (Stray, 1964).

It has been used in the laboratory and on industrial scale, because of the selectivity of this process in removing a solute from a liquid mixture by a solvent. As a separation technique, it is a partitioning process based on unequal distribution of the solute (A) between two immiscible solvents at equilibrium (US Environmental Protection Agency (EPA), 2004):

$$A_{(aq)} \leftrightarrow A_{(org)}$$

The process is often very selective and the isolation of the metal in aqueous can usually be made as complete as desired by carrying out successive extraction procedures (Stray, 1964).

---

* Corresponding author.
E-mail address: fkhalili@ju.edu.jo (F.I. Khalili).

1878-5352 © 2010 King Saud University. All rights reserved. Peer-review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.02.007

Production and hosting by Elsevier

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. 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:

$$D_c = \frac{[\mathrm{ML}_n]_{\mathrm{org}}}{[\mathrm{M}^{n+}]_{\mathrm{aq}}}$$

Extraction of thorium(IV) by acidic organophosphorus extractants from aqueous media is given by:

$$\mathrm{Th}(\mathrm{X}^-)_{4-n\,\mathrm{aq}} + y(\mathrm{HR}_2)_{\mathrm{org}} \leftrightarrow \mathrm{Th}(\mathrm{X})_{4-n}\mathrm{R}_n(\mathrm{HR}_2)_{y-n\,\mathrm{org}} + n\mathrm{H}^+_{\mathrm{aq}}$$

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

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, perchloric acid (70%) (Fluka Chemika) and hydrochloric acid (35%) (GCC), were used through out this work. Arsenazo(III) (BDH) was used as spectrophotometric reagent for Th(IV) ion.

All other compounds were of analytical grade. Deionized water was used in aqueous solutions, and for washing all glassware.

A variable-temperature shaker water bath (Memmert Co.) was used for shaking samples. The spectrophotometric measurements were carried out using Spectro Scan 80DV Spectrophotometer. All weighing were carried out with SHIMADZO AW120 balance.

A 250.0 mL of about 0.025 M thorium nitrate stock solution was prepared by dissolving 3.68 g of thorium nitrate hexahydrate $Th(NO_3)_4{\cdot}6H_2O$ 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).

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

One liter of HDDPA solution was pre-equilibrated by mixing it with 1.00 L of media solutions (perchlorate media $HClO_4$ and $NaClO_4$ solution at $I = 1.00$, 3.00, 5.00 M and pcH 1 and 2). 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 that contain HDDPA with the suitable concentration in toluene as a diluent was placed in 50 mL glass 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 as follows:

The spectrophotometric determination of Th(IV) concentration 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. Then, volume was adjusted to 25.0 mL through the addition of water. Spectral measurements were recorded at $\lambda_{\max} = 660$ nm (Khalili et al., 2003), each experiment was repeated at least twice (Savvin, 1961).

3. Results and discussion

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 ionic strengths (1.00, 3.00 and 5.00 M $HClO_4$ and $NaClO_4$) and constant pcH (−log Molar concentration of H^+) 1.00 and 2.00 in perchlorate media. The D_c value increases with increase in the HDDPA concentration. The logarithms of the D_c values obtained were plotted versus the corresponding logarithm of the HDDPA concentration. A straight line was obtained with slopes as shown in Figs. 1 and 2 (1.75 at $I = 1.00$ M, 1.76 at $I = 3.00$ M and 1.76 at $I = 5.00$ M at pcH 1.00 and 1.72 at $I = 1.0$ M, 1.75 at $I = 3.00$ M and 1.71 at $I = 5.00$ M at pcH 2.00) approximately 1.75 in perchlorate media.

This means that at least two complexes are formed in organic phase between Th(IV) and didodecylphosphoric acid from perchlorate media, 25% contain one molecule of HDDPA, and 75% contain two molecule of HDDPA, which involved in the formation of the thorium–HDDPA complex in perchlorate media.

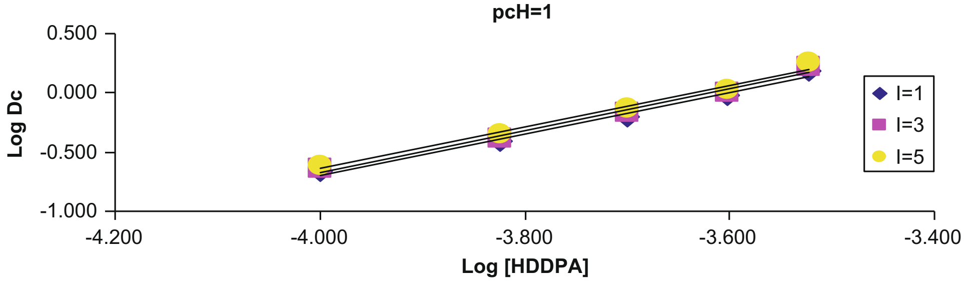

Figure 1 Variation of Log D_c with Log [HDDPA] in perchlorate media ($I = 1.00$, 3.00 and 5.00 M, pcH 1.00, $T = 30$ °C).

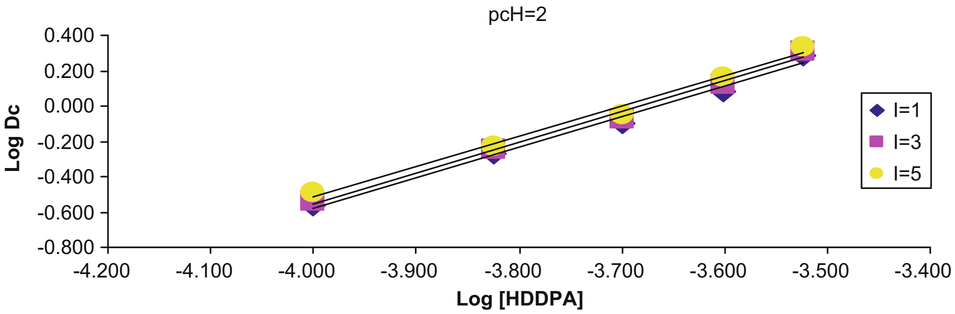

Figure 2 Variation of Log D_c with Log [HDDPA] in perchlorate media (I = 1.00, 3.00 and 5.00 M, pcH 2.00, T = 30 °C).

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

The effect of pcH on the extraction of thorium(IV) ion from perchlorate media of ionic strength (I = 1.00 and 3.00 M) has been studied, the logarithm of the D_c values obtained were plotted against the corresponding pcH values. A straight line with a slope of about 0.17 and 0.20 was obtained at I = 1.00 and 3.00, respectively, as shown in Fig. 3. These values represent the number of hydrogen ions released during the formation of thorium–HDDPA complex.

3.3. Effect of ionic strength on D_c

The effect of ionic strength was studied at constant pcH, a plot of the D_c values versus the corresponding ionic strength values give a straight line with a slope of 0.03 and 0.06 at pcH 1.00 and 2.00, respectively. The data indicate that the D_c value increases with the increasing of ionic strength in perchlorate. This is explained by the increase of the thermodynamic activity of the metal salt extracted and decrease in the activity of water as the ionic strength increases (Kolarik, 1982), this is shown in Fig. 4, which means that perchlorate anion is functioning as a salting out agent.

The effect of salt variation upon UO_2^{2+} extraction by 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) was studied. The distribution ratio increases with the increase in salt concentration of $NaClO_4$, or $NaNO_3$ in ternary extraction system. But it decreases with the increase of salt concentration of NaCl, and this is explained by the complexing ability of the anion which is in the order $Cl^- > NO_3^- \gg ClO_4^-$ (Bagawde et al., 1978).

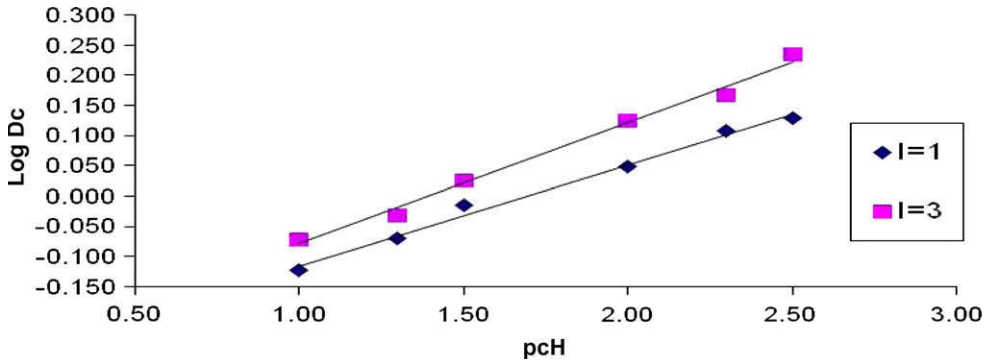

Figure 3 Variation of Log D_c with pcH in perchlorate media (T = 30 °C).

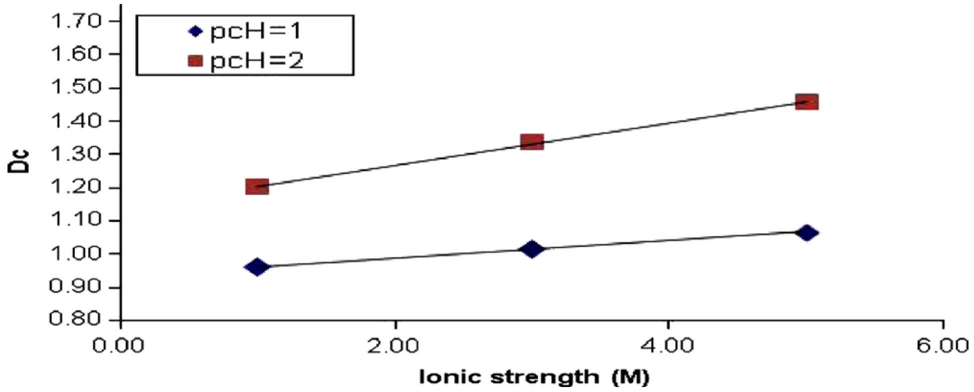

Figure 4 Variation of D_c with ionic strength at pcH 1.00 and 2.00 in perchlorate media, T = 30 °C.

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 $X = ClO_4^-$ and $Y = 1$ or 2 in perchlorate media. This means that didodecylphosphoric acid in toluene as a carrier diluent extracted thorium(IV) ion from perchlorate solution by a solvation mechanism. This mechanism can be represented by the following equilibrium equations:

$$Th(X)_{4\,aq} + Y(HR_2)_{org} \leftrightarrow Th(X)_4(HR_2)_{Y\,org}$$

where $X = ClO_4^-$, $Y = 1.0$ or 2.0, (HR_2) is the didodecylphosphoric acid (HDDPA) extractant dissolved in the organic phase which is toluene.

The equilibrium constant for the extraction process can be given by:

$$K_{ex} = \frac{[Th(X)_4(HR_2)_Y]_{org}}{[Th(X)_4]_{aq}[HR_2]_{org}^Y}$$

$$K_{ex} = \frac{D_c}{[HR_2]_{org}^Y}$$

where

$$D_c = \frac{[Th(X)_4(HR_2)_Y]_{org}}{[Th(X)_4]_{aq}}$$

Thorium was extracted quantitatively with the neutral ligand 1-phenyl-2,3-dimethyl-5-pyrazolone (Apy) in the presence of perchlorate (ClO_4^-), di- and tri-chloroacetates (DCA/TCA) at pH 2.5 into an organic solvent by solvation mechanism (Roopa et al., 2005).

The suggested mechanisms for the three complexes were as follows:

$$Th_{aq}^{4+} + 2Apy_{aq} \leftrightarrow [Th(Apy)_2(ClO_4)_4]_{org}$$

$$Th_{aq}^{4+} + 2Apy_{aq} + 4TCA_{aq} \leftrightarrow [Th(Apy)_2(TCA)_4]_{org}$$

$$Th_{aq}^{4+} + Apy_{aq} + 4DCA_{aq}H_2O \leftrightarrow [Th(Apy)(H_2O)(DCA)_4]_{org}$$

The extraction of thorium(IV) ion from perchlorate medium by HDDPA in chloroform diluents followed the mixed ion exchange–solvation mechanism (Savvin, 1961). The equilibrium reaction was found to be:

$$Th(ClO_4)_{4-n\,aq}^{n+} + 2.5(HR)_{2\,org} \leftrightarrow Th(ClO_4)_{4-n}R_n(HR)_{5-n\,org} + nH_{aq}^+$$

where n is 1 or 2.

3.4. Effect of temperature on extraction of Th(IV) ion

Effect of temperature on the K_{ex} value was investigated at pcH 2.00. From the data shown in Fig. 5, it is clear that the K_{ex} value decreases by increasing temperature.

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

The K_{ex} can be calculated based on the following proposed equations for the reactions:

$$Th(X)_{4\,aq} + Y(HR_2)_{org} \leftrightarrow [Th(ClO_4)_4(HR_2)_Y]_{org}$$

$$K_{ex} = \frac{D_c}{[HR_2]_{org}^Y} \quad \text{(I)}$$

where $X = ClO_4^-$ and $Y = 2$. The hydrogen ion concentration can be calculated from pcH = $-\mathrm{Log}[H^+]$.

The HDDPA concentration in the organic phase at equilibrium $[HR]_{equ\ org}$, can be calculated from the difference between the initial HDDPA concentration and the amount used for complexation. Substituting the previous values in Eq. (I) to calculate K_{ex} as shown in Table 1. From this, we can see that K_{ex} increases with the increase of ionic strength in perchlorate solution. This could be explained by the increase in dehydration of Th(IV) ion upon formation of complex.

3.6. Calculation of the thermodynamic parameters

From the van't Hoffs equation

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

ΔH can be calculated by plotting Log D_c against $1/T$. The change in free energy (ΔG) can by calculated at 303 K by using the equation $\Delta G = -RT \ln K_{ex}$, while ΔS can be calculated at 303 K from ΔG and ΔH. All the thermodynamic values are shown in Table 1.

From the data in Table 1, it is clear that the extraction at different ionic strengths from perchlorate solutions behave

Table 1 Thermodynamic parameters of thorium(IV) in perchlorate media at pcH 2.00.

I (M)	Slope	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)	K_{ex}
1.00	3052	−58.45	−42.25	−53.47	1.92E+07
3.00	3258	−62.38	−42.45	−65.78	2.08E+07
5.00	3399	−65.08	−42.92	−73.14	2.51E+07

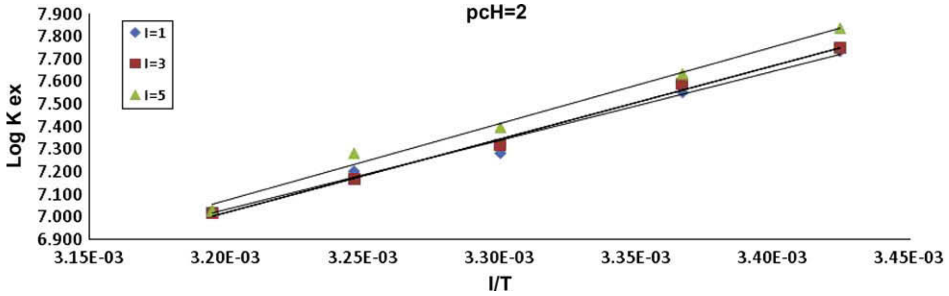

Figure 5 Variation of Log K_{ex} with $1/T$ in perchlorate media (I = 1.00, 3.00 and 5.00 M).

similarly. Since the enthalpy changes are exothermic, the extraction process is favored (spontaneous). In addition, the entropy changes decrease with increase in ionic strength (Yaftian et al., 2004).

4. Conclusion

The equilibrium study of the extraction of thorium(IV) ion with didodecylphosphoric acid was carried out. The extracted species from perchlorate media into toluene diluent was found to be $[Th(X)_4(HR_2)_Y]_{org}$, where $X = ClO_4^-$ and $Y = 1$ or 2 at different ionic strength. The extraction of Th(IV) ion increases with the increase in ionic strength. However, the distribution coefficient increased slightly with the increase in the pcH of the aqueous phase. The extraction equilibrium constant was obtained at different temperatures and the extraction system was found to be spontaneous due to the negative enthalpy change, which favors the extraction of Th(IV) ion.

References

Bagawde, S.V., Vasudava, P.R., Ramakrishna, V.V., Patil, S.K., 1978. The effect of temperature on the extraction of uranium(VI) from nitric acid by tri-*n*-butyl phosphate. J. Inorg. Nucl. Chem. 40, 1913.

Inczédy, J., 1994. Factors important in the selection and productions used in inorganic analytical chemistry description of liquid–liquid extraction. Pure Appl. Chem. 12 (66), 2501.

Khalili, F., Khaled, M., Soudani, E., 2003. Solvent extraction of thorium(IV) by didodecylphosphoric acid. Sci. Technol. 8, 107.

Kolarik, Z., 1982. Gemlin Handbook of Inorganic Chemistry, eighth ed. Springer-Verlag, Berlin, p. 34.

Konodo, K., Momoto, K., Nakashio, T., 1989. Equilibrium of solvent extraction of lanthanides with didodecylphosphoric acid. Solvent Extract. Ion Exchange 7 (6), 1027.

Roopa, Bose, Murty, D.S.R., Chakrapani, G., 2005. Extraction of thorium(IV) as perchlorate and chloroacetate complexes with 1-phenyl-2, 3-dimethyl-5-pyrazolone (antipyrine). J. Radioanal. Nucl. Chem. 265 (1), 115–122.

Savvin, S.B., 1961. Analytical use of arsenazo(III). Determination of thorium, zirconium, uranium and rare earth elements. Talanta 8, 673.

Stray, J., 1964. The Solvent Extraction of Metal Chelates, first ed. The MacMillan Company, p. 1.

US Environmental Protection Agency (EPA), 2004. Separation Techniques. USEPA.

Yaftian, M.R., Taheri, R., Zamani, A.A., Matt, D., 2004. Thermodynamics of the solvent extraction of thorium and europium nitrates by neutral phosphorylated ligands. J. Radioanal. Nucl. Chem. 262 (2), 455.