

## ARTICLE

**Solvent Extraction Properties of Lipophilic Thiophene-Based Trifluoromethyl-Substituted  $\beta$ -Diketone Ligands for Uranium(VI) and Thorium(IV) Ions****Samir A. Al-Taweel<sup>a\*</sup>, Elham A. Al-Qudah<sup>a</sup>, Salah A. Al-Trawneh<sup>a</sup> and Fawwaz I. Khalili<sup>b</sup>**<sup>a</sup> Chemistry Department, Faculty of Science, Mu'tah University, Al-Karak 61710, Jordan.<sup>b</sup> Chemistry Department, Faculty of Science, The University of Jordan, Amman, Jordan.Received on: 23<sup>rd</sup> Sep. 2019;Accepted on: 16<sup>th</sup> Jun. 2020

**Abstract:** [4,4,4-trifluoro-1-(5-chloro-2-thienyl)-1,3-butanedione H(5-chloro-TTA) and 4,4,4-trifluoro-1-[5-methyl-2-thienyl]-1,3-butanedione H(5-methyl-TTA) were prepared according to literature. The extraction behavior of H(5-chloro-TTA) and H(5-methyl-TTA) diketones with Uranyl(VI) and Thorium(IV) ions was studied under different experimental conditions; namely, extraction time, ligand concentration, stripping time, stripping acid concentration, pH and temperature. From the distribution coefficients ( $K_d$ ) at different temperatures, the enthalpy ( $\Delta H^\circ$ ), Gibbs free energy ( $\Delta G^\circ$ ) and entropy changes ( $\Delta S^\circ$ ) associated with extraction processes for these ions were determined.

**Keywords:** Solvent extraction, Trifluoromethyl- $\beta$ -Diketone, Uranium(VI), Thorium(IV), thermodynamics, Synergism.

**Introduction**

Solvent extraction has attracted extensive attention due to its simplicity, speed and wide scope<sup>[1-3]</sup>. In the context of increasing energy demands and the threat of global warming due to CO<sub>2</sub> emission, the nuclear energy may be an attractive option. Selective extraction of uranium as uranyl ion complexes is of special interest in nuclear fuel reprocessing as well as in the extraction of uranium from its ores. 2-Thenoyltrifluoroacetone (**1**), H(TTA), is a very popular extracting agent and was developed for the extraction of rare-earth elements from nuclear fuel wastes<sup>[4-6]</sup>. H(TTA) extracts uranium(VI) and thorium(IV) ions from acidic aqueous solutions into non-polar solvents *via* the formation of metal-chelate complexes<sup>[7-10]</sup>. H(TTA), with a pK<sub>a</sub> value of 6.23, was designed to provide a better extraction performance of metal ions from acidic solutions than other chelating  $\beta$ -diketones, like acetylacetonate H(ACAC) (pK<sub>a</sub>=8.82). For example, zirconium

could be separated from hafnium using a benzene solution of H(TTA)<sup>[11-14]</sup>.

A mixture of two extractants can show enhanced separating properties greater than the sum of the actions of the individual reagents used alone. This combined action of two extractants is known as synergic extraction. Synergism was first reported in the literature for the extraction of uranium(VI) with organophosphorus compounds<sup>[15-20]</sup>. A system that has been shown to exhibit such a behavior is that of tri-n-butyl phosphate (TBP) and di-n-butyl phosphoric acid (HDBP) as synergists often combine neutral phosphorus-containing extractants with acidic reagents like H(TTA). In addition to organophosphorus compounds, heterocyclic bases, sulfoxides, carboxylic acids, phenols and amines show a synergic effect<sup>[18-20]</sup>.

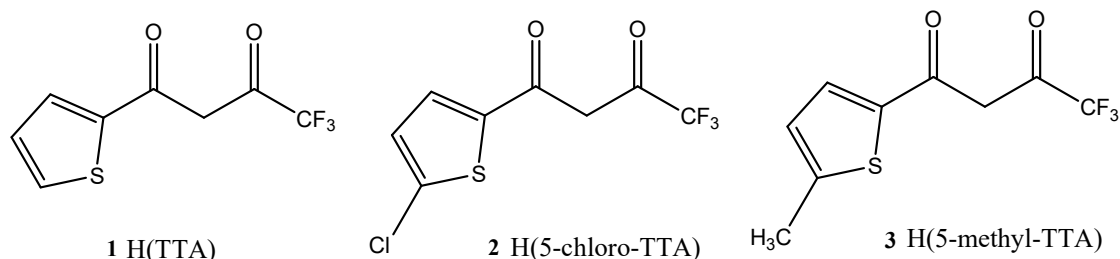
The substituents on the  $\beta$ -diketone can influence the properties of corresponding rare-earth metal complexes. Alkyl chains, for example, increase the volatility and the solubility in organic solvents. Perfluorinated alkyl groups

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increase the Lewis acidity by increasing the percentage of enol form in solution, thus enhancing the extractive performance of the chelating ligand. This work addresses the efficiency of 4,4,4-Trifluoro-1-(5-chloro-2-thienyl)-1,3-butanedione (**2**), H(5-chloro-TTA),

with chlorine as electron-withdrawing substituent and 4,4,4-Trifluoro-1-[5-methyl-2-thienyl]-1,3-butanedione (**3**), H(5-methyl-TTA), with the methyl group as electron-releasing substituent in the extraction of U(VI) and Th(IV) ions from aqueous acidic solutions.



Scheme 1. Chemical structure of extractants applied in this study (**2** and **3**).

## Materials and Methods

### Reagents and Equipment

Analytical grade reagents and solvents were used. Uranyl acetate dihydrate (BDH) and thorium(IV) nitrate pentahydrate (BDH) were used without further purification. 2-Chlorothiophene, 2-methylthiophene, acetyl chloride, potassium t-butoxide and 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione and hydrochloric acid were purchased from Aldrich, perchloric acid, nitric acid and Arsenazo(III) from BDH and toluene from Merck. Deionized water was used to prepare all aqueous solutions. Solvents were dried according to standard procedures. Ethyl trifluoroacetate, 2-acetyl-5-chlorothiophene and 2-acetyl-5-methylthiophene were prepared according to literature procedure ([22], [23] and [24], respectively) and characterized by melting point measurement (Electrothermal),  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  (Bruker AC-200 spectrometer) in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ . Spectronic-Genesys-5 (Milton Roy) spectrophotometer was used for spectrophotometric measurements.

### Preparation of Solutions

A  $6.00 \times 10^{-2}$  M uranyl perchlorate stock solution was prepared by treating 6.36 g of uranyl acetate with 6.00 mL of 9.00 M perchloric acid, adding distilled water and heating with stirring for about one hour until the clear yellow solution of uranyl perchlorate was obtained, followed by dilution to 250 mL. The exact concentration of the solution was determined gravimetrically using the quantitative precipitation of uranium(VI) by pyridine as diuranic acid ( $\text{H}_2\text{U}_2\text{O}_7$ )<sup>[25]</sup>.  $2.50 \times 10^{-2}$  M thorium

nitrate stock solution was prepared by dissolving the appropriate amount of thorium nitrate tetrahydrate in distilled water. The exact concentration of the solution was determined by titration with EDTA solution at  $\text{pH}=2-3$ , using xylenol orange as an indicator<sup>[26]</sup>. H(5-chloro-TTA) solution (0.1 M) was prepared by dissolving 6.4148 g of it in 250 mL toluene. The resulting solution was equilibrated with 250 mL of  $\text{HClO}_4$  and  $\text{NaClO}_4$  solution ( $I=1.00$  M,  $\text{pH}=2.00$ ). The mixture was stirred for 12 h and the organic layer was separated from the aqueous layer. Same procedure was applied to prepare 0.1 M solution of H(5-methyl-TTA).

### Extraction of Uranyl(VI) and Thorium(IV) Ions

To extract the uranyl(VI) ion, a 10.0-mL sample of  $6.00 \times 10^{-5}$  M uranyl perchlorate solution and 10.0 mL of toluenic H(5-chloro-TTA) or H(5-methyl-TTA) solution were shaken (GFL-mbh-1083 shaker) for 6.0 h or 8 h, respectively. A 4.0 mL-sample of the toluenic layer was shaken with 10.0 mL of 0.10 M  $\text{HNO}_3$  for 6.0 h (H(5-chloro-TTA)) or 8 h (H(5-methyl-TTA)). The uranyl ion concentration in the aqueous layer was determined, in duplicate, spectrophotometrically at  $\lambda=650$  nm by the Arsenazo (III) method<sup>[27]</sup>.

To extract the thorium(VI) ion, the same procedure was adopted starting with 10.0 mL of  $1.085 \times 10^{-4}$  M thorium(IV) solution. 2 M HCl was used to strip the thorium(IV) ions instead of  $\text{HNO}_3$ . Thorium(IV) concentration in both aqueous layers was determined in duplicate spectrophotometrically by the Arsenazo(III) method at  $\lambda=659$  nm<sup>[28]</sup>.

## Results and Discussion

### Extraction of Uranyl(VI)

For the distribution of uranyl(VI) ions or thorium(IV) ions between the organic and aqueous layers, the coefficient  $K_d$  is defined as the equilibrium concentration quotient for extracted species (after 6 h / 8 h of shaking, equilibrium is assumed to be established):

$$A_{(aq)} \rightleftharpoons A_{(org)} \quad K_d = \left( \frac{[A]_{org}}{[A]_{aq}} \right)_{eq}$$

The effect of the concentration of H(5-chloro-TTA) on the extraction of uranyl(VI) ion was investigated. The ionic strength of the aqueous phase was kept constant at 1.0 M using  $\text{NaClO}_4$  and pH equal to 2.60. As can be seen in Figure 1, the value of  $K_d$  increases with increased H(5-chloro-TTA) concentration. A double-logarithmic plot of  $K_d$  versus the concentration of H(5-chloro-TTA) gives a straight line of a slope of  $2.13 \pm 0.04$ . This value represents the number of ligand molecules participating in extracting a single uranyl(VI) ion (i.e., 2).

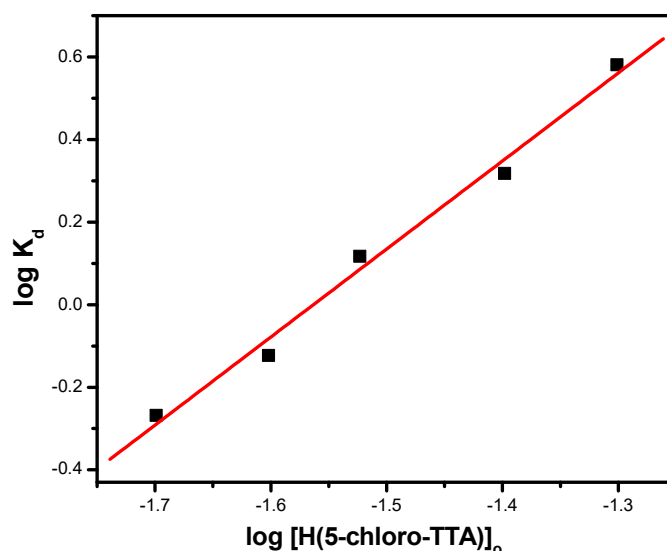
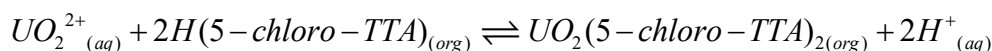


Figure 1. Variation of  $\log K_d$  with  $\log [H(5\text{-chloro-TTA})]_0$  for uranyl(VI) ion at 25°C

Figure 2 shows the effect of pH on the extraction of uranyl(VI) ion from perchloric acid-perchlorate solution of an ionic strength of 1.0 M using the  $2.70 \times 10^{-2}$  M H(5-chloro-TTA) in toluene as carrier diluent. A linear relationship is observed with a slope of  $2.14 \pm 0.32$ . This means

that two hydrogen ions were released during the formation of uranyl-H(5-chloro-TTA) complex in the organic phase. Consequently, the extraction process can be represented by the following equation:



The equilibrium constant  $K_{ex}$  for the extraction process can thus be given by Equation 1:

$$K_{ex} = \left( \frac{[UO_2(5\text{-chloro-TTA})_2]_{org} [H^+]_{aq}^2}{[UO_2^{2+}]_{aq} [H(5\text{-chloro-TTA})]_{org}^2} \right)_{eq} \quad (1)$$

or

$$K_{ex} = K_d \left( \frac{[H^+]_{aq}^2}{[H(5\text{-chloro-TTA})]_{org}^2} \right)_{eq} \quad \text{where} \quad K_d = \left( \frac{[UO_2(5\text{-chloro-TTA})_2]_{org}}{[UO_2^{2+}]_{aq}} \right)_{eq}$$

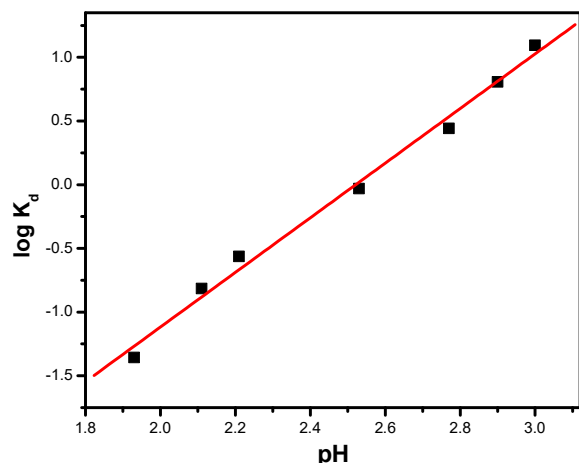


Figure 2.  $\log K_d$  versus pH for uranyl(VI) ion using H(5-chloro-TTA) as extractant at 25°C.

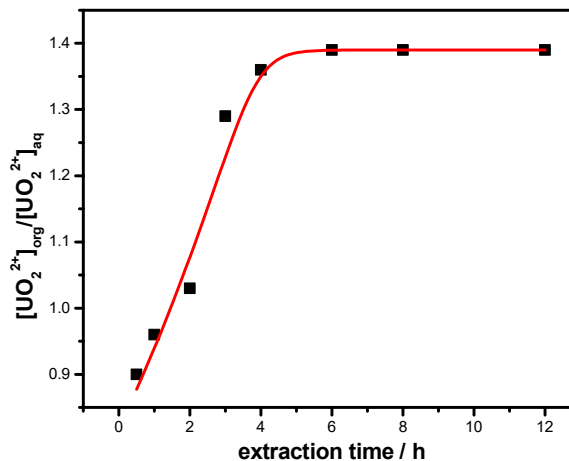


Figure 3. Variation of  $[\text{UO}_2^{2+}]_{\text{org}}/[\text{UO}_2^{2+}]_{\text{aq}}$  with extraction time using H(5-chloro-TTA) at 25°C.

The effect of extraction time on the value of  $[\text{UO}_2^{2+}]_{\text{org}}/[\text{UO}_2^{2+}]_{\text{aq}}$  is shown in Figure 3, where it is shown to increase with increased time of extraction. Equilibrium is established in less than 6 hours of shaking.

Figure 4a shows the effect of  $\text{HNO}_3$  concentration on the fraction of uranyl(VI) ion recovered from the organic phase,  $[\text{UO}_2^{2+}]_{\text{rec}}/[\text{UO}_2^{2+}]_{\text{org}}$ . It decreases with increasing

$\text{HNO}_3$  concentration due to the formation of uranyl nitrate compound  $\text{UO}_2(\text{NO}_3)_2$ . The plateau is reached at 3.0 M  $\text{HNO}_3$ . A 0.10 M  $\text{HNO}_3$  concentration is considered suitable for stripping of uranyl(VI) ion from the organic phase. Figure 4b shows that at least 6 h of stripping with  $\text{HNO}_3$  are thereby necessary to reach maximum recovery (97.7%).

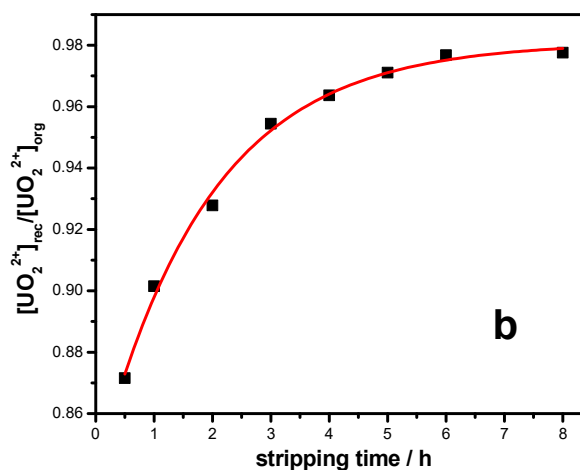
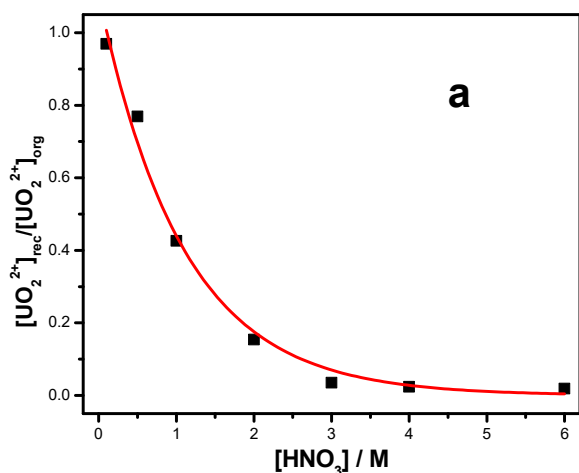


Figure 4. a) Variation of  $[\text{UO}_2^{2+}]_{\text{rec}}/[\text{UO}_2^{2+}]_{\text{org}}$  ratio with  $[\text{HNO}_3]$  using H(5-chloro-TTA) as an extractant at 25°C, b) effect of stripping time on recovery;  $[\text{HNO}_3]=0.10$  M.

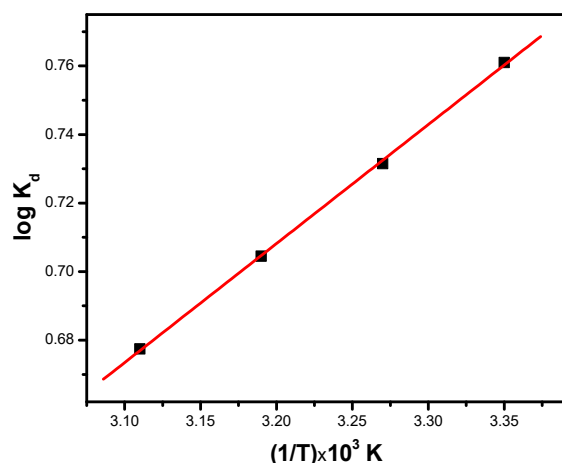
The temperature effect on the  $K_d$  value was studied by extracting 10.0 mL of  $6.0 \times 10^{-5}$  M uranyl(VI) ion at  $\text{pH}=2.80$  and  $I = 1.0$  M with 10.0 mL of  $2.70 \times 10^{-2}$  M solution of H(5-chloro-TTA) at 298.15, 305.65, 313.15 and 321.15 K for 6.00 hours. The value of  $K_d$  decreases with increased temperatures and a plot of  $\log K_d$  against  $1/T$  (Figure 5) gives a straight line, the slope of which yields for  $\Delta H$  of the process a value of  $-6.65 \pm 0.53$  kJ  $\text{mol}^{-1}$ . The extraction

equilibrium constant  $K_{\text{ex}}$  can be calculated by Equation 1. The concentration of H(5-chloro-TTA) in the organic phase at equilibrium,  $[\text{H(5-chloro-TTA)}]_{\text{(org)}}$ , can be calculated as the difference between the initial concentration of H(5-chloro-TTA) and the complexed concentration of H(5-chloro-TTA) and is equal to  $2.70 \times 10^{-2}$  M. From  $K_{\text{ex}}$ , the Gibbs free energy of extraction,  $\Delta G_{\text{ex}}^{\circ}$ , can be calculated (Equation

2) and  $\Delta S_{ex}^{\circ}$  as well (Equation 3). The thermodynamic parameters are listed in Table 1.

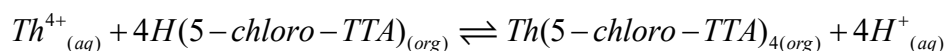
$$\Delta G_{ex}^{\circ} = -RT \ln K_{ex} \quad (2)$$

$$\Delta S_{ex}^{\circ} = (\Delta H_{ex}^{\circ} - \Delta G_{ex}^{\circ})/T \quad (3)$$



**Figure 5.** Log  $K_d$  versus  $1/T$  for uranyl(VI) ion extracted by H(5-chloro-TTA).

H(5-methyl-TTA) (3) was used to extract uranyl(VI) ion under similar conditions to those applied in the extraction with H(5-chloro-TTA). The optimum conditions thereby were determined to be: 4 h of extraction at pH 2.53 with a ligand concentration of  $5.0 \times 10^{-2}$  M, followed by stripping with 0.10 M  $\text{HNO}_3$  for 8 h, compared to 6 h of extraction at pH 2.80 with a ligand concentration of  $2.7 \times 10^{-2}$  M, followed by stripping with 0.10 M  $\text{HNO}_3$  for 6 h in the case of H(5-chloro-TTA). The effect of temperature on the  $K_d$  value was also studied by extracting 10.0 mL of  $6.0 \times 10^{-5}$  M uranyl(VI) ion at pH = 2.53 and  $I = 1.0$  M with 10.0 mL of  $5.00 \times 10^{-2}$  M solution of H(5-methyl-TTA) in the temperature range 300–320 K for 4.00 hours. By plotting  $\log K_d$  versus  $1/T$  and from the slope of obtained straight line,  $\Delta H$  of the process was determined to be  $-5.67 \pm 0.28$  kJ.mol<sup>-1</sup>.  $K_{ex}$ ,  $\Delta G_{ex}^{\circ}$  and  $\Delta S_{ex}^{\circ}$  were also calculated by Equations 1, 2



The equilibrium constant  $K_{ex}$  for the extraction process can thus be given by equation 4:

$$K_{ex} = \left( \frac{[\text{Th}(5\text{-chloro-TTA})_4]_{org} [\text{H}^+]_{aq}^4}{[\text{Th}^{4+}]_{aq} [\text{H}(5\text{-chloro-TTA})]_{org}^4} \right)_{eq} \quad (4)$$

and 3, respectively. The thermodynamic parameters are listed in Table 1.

The substituent effect on the extraction efficiency of H(TTA)-derived ligands is considered by comparing the  $K_d$  values for the extraction of uranyl(VI) ion with H(5-chloro-TTA), H(5-Me-TTA) and H(TTA) under the same conditions (temperature, ligand concentration, pH and extraction time). The extraction coefficient,  $K_d$ , shows thereby the following trend: H(5-chloro-TTA) > H(TTA) > H(5-methyl-TTA) with corresponding values of 2.30 : 1.23 : 1.05, confirming that electron-withdrawing substituents enhance the extraction efficiency of the H(TTA) ligands.

### Extraction of Thorium(IV) Ion

By determining the value of  $K_d$  for different periods ( $\frac{1}{2}$ –8 h) of extraction of thorium(IV) ion with H(5-chloro-TTA), it could be shown that equilibrium is reached in 5 hours, which has been chosen hereafter as the suitable time to ensure equilibration in the extraction process. The effect of H(5-chloro-TTA) concentration on the extraction of thorium(IV) ion was investigated at a constant ionic strength of 1.0 M and pH 1.60. The double-logarithmic plot of  $K_d$  versus  $[\text{H}(5\text{-chloro-TTA})]$  gives a straight line ( $R^2=0.99$ ) with a slope of  $4.23 \pm 0.048$ , suggesting that four ligand molecules are involved in the formation of the thorium–(5-chloro-TTA) complex in the organic phase. This conclusion is supported by the results of the investigation of pH effect on the extraction of thorium(IV) ions in the pH range 1.45–1.95 ( $[\text{H}(5\text{-chloro-TTA})]_{\text{toluene}} = 5.00 \times 10^{-3}$  M,  $I=1.0$  M). The logarithmic plot of  $K_d$  versus pH gives a straight line ( $R^2=0.99$ ) with a slope of  $4.22 \pm 0.13$  corresponding to the release of four hydrogen ions during the formation of thorium(IV)–(5-chloro-TTA) complex in the organic phase. Consequently, the extraction process can be represented by the following Equation:

$$\text{or } K_{ex} = K_d \left( \frac{[H^+]_{aq}^4}{[H(5-chloro-TTA)]_{org}^4} \right)_{eq}$$

Furthermore, optimum HCl concentration needed to recover thorium(IV) ions from the organic phase was determined by evaluating  $[Th^{4+}]_{rec}/[Th^{4+}]_{org}$  for a wide range of HCl concentrations extending from 0.1-6.0 M HCl. The optimum concentration was 3.00 M HCl, achieving thereby a recovery percentage of 97.5% after five hours of stripping.

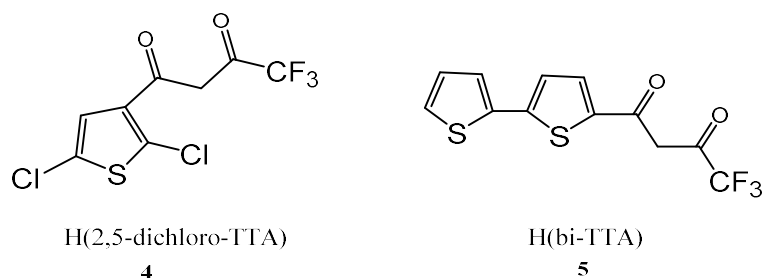
The temperature effect on the  $K_d$  value was studied by extracting 10.0 mL of  $1.085 \times 10^{-4}$  M thorium(IV) ion at pH 1.76 and  $I=1.0$  M for 5.00 h with 10.0 mL of  $7.00 \times 10^{-3}$  M solution of H(5-chloro-TTA) in the temperature range 300-320 K. The  $K_d$  value was found to decrease with increasing the temperature. Plotting  $\log K_d$  versus  $1/T$  gave a straight line.  $\Delta H$  of extraction was determined from this slope and found to be  $-4.66 \pm 0.20$  kJ mol $^{-1}$  which is slightly smaller than that of the extraction of uranyl(VI) ions with same ligand. The process is however still exothermic. The extraction equilibrium constant,  $K_{ex}$ , was calculated by Equation 4 ( $K_d$  at 25°C is 6.842; pH=1.76;  $[H(5-chloro-TTA)]_{(org)} = 7.00 \times 10^{-3}$  M) and found to be 260.  $\Delta G_{ex}^{\circ}$  and  $\Delta S_{ex}^{\circ}$  were also calculated by Equations 2 and 3, respectively and are listed in Table 1.

H(5-methyl-TTA) was also tested in the extraction of thorium(IV) ion under similar conditions to those applied in the extraction with H(5-chloro-TTA). The optimum conditions thereby were determined to be: five hours of extraction at pH 1.76 with a ligand concentration of  $1.0 \times 10^{-2}$  M, followed by stripping with 2.0 M HCl for 6 h, compared to 5 hours of extraction at pH 1.60 with a ligand concentration of  $5.0 \times 10^{-3}$  M, followed by stripping with 3.0 M HCl for 5 hours in the case of H(5-chloro-TTA). The effect of temperature on the  $K_d$  value was also studied by extracting 10.0 mL of  $1.085 \times 10^{-4}$  M uranyl(VI) ion at pH 1.76 and  $I=1.0$  M for 5.00 hours with 10.0 mL of  $1.00 \times 10^{-2}$  M solution of H(5-methyl-TTA) ligand in the temperature range 300-320 K. By plotting  $\log K_d$  versus  $1/T$ , and from the slope of obtained straight line,  $\Delta H$  of the process was determined to be  $-3.89 \pm 0.20$  kJ.mol $^{-1}$ .  $K_{ex}$  was calculated by Equation 4 ( $K_d$  at 25°C is 2.481; pH=1.76;  $[H(5-methyl-TTA)]_{(org)} = 1.00 \times 10^{-2}$  M) and found to be 22.6.  $\Delta G_{ex}^{\circ}$  and  $\Delta S_{ex}^{\circ}$  were calculated by Equations 2 and 3, respectively and are listed in Table 1. The

$$\text{where } K_d = \left( \frac{[Th(5-chloro-TTA)_4]_{org}}{[Th^{4+}]_{(aq)}} \right)_{eq}$$

substituent effect on the  $K_d$  value for the extraction of thorium(IV) ion with the H(TTA)-derived ligands was in the order: H(5-chloro-TTA) > H(TTA) > H(5-methyl-TTA) with corresponding values of 79.34 : 4.18 : 2.31, confirming that electron-withdrawing substituents enhance the extraction efficiency of the H(TTA) ligands.

It is worth to mention that Eskandari reports  $K_d$  values of 0.03, 0.45 and 1.16 for uranyl(VI) ion extraction and values of 0.00, 4.19 and 38.44 for Th(IV) ion extraction using tributylphosphate (TBP), trioctylamine (TOA) and tricaprylyl methyl ammonium chloride (Aliquat 336) ligands, respectively<sup>[29]</sup>. In this work, we report  $K_d$  values of 2.3 and 79.3 for uranyl(VI) ion extraction and for thorium(IV) ion extraction, respectively, using H(5-chloro-TTA), indicating that H(5-chloro-TTA) is almost by a factor of two a more efficient extracting ligand than Aliquat 336. Table 1 shows however that H(5-chloro-TTA) shows a lower extraction potential than H(2,5-dichloro-TTA) (4) reported in a previous publication by us<sup>[21]</sup>. It is well-known that the  $pK_a$  values of  $\beta$ -diketones play a significant role in the extraction efficiency. An electron-withdrawing chlorine atom, for instance, makes H(5-Chloro-TTA) approximately 7 times more efficient than H(TTA) in extracting  $Th^{4+}$  ions from aqueous solutions, while two chlorine atoms in H(2,5-dichloro-TTA) make it approximately 410 times more efficient than H(TTA). In contrast, an electron-donating methyl group makes H-(5-methyl-TTA) less efficient than H(TTA) by a factor of 0.7. Nevertheless, the exceptionally high  $K_{ex}$  of another ligand we investigated in reference<sup>[21]</sup>, namely H(bi-TTA) (5), for the extraction of thorium(IV) ion, compared to that of H(TTA) (4900 times more efficient), cannot be explained based on  $pK_a$  argument, since the second thiophene ring is  $\pi$ -excessive and electron-rich aromatic  $\pi$ -system. Intermolecular synergism is believed to be responsible for this phenomenon, where the extra thiophene ring in H(bi-TTA), which is away from the  $Th^{+4}$  coordination sphere, acts as a donor ligand *via* sulfur atom, replacing the water of hydration and fulfilling the coordination number of the  $Th^{+4}$  metal ion.



**Scheme 2. Chemical structure of extractants 4 and 5 applied in reference [21].**

It is also important to notice in Table 1 that the extraction equilibrium constant,  $K_{\text{ex}}$ , of Th(IV) ion has a much higher value than that of uranyl(VI) (up to four orders of magnitude), making thorium(IV) more extractable than the uranyl(VI) ion, which can be attributed to the higher charge density of  $\text{Th}^{4+}$  ions.

The thermodynamic parameters of extraction listed in Table 1 deserve a closer look. The entropy change for  $\text{UO}_2^{2+}$  extraction,  $\Delta S^\circ$ , is negative (around  $-55.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), which is consistent with the formation of hydrated outer-sphere complex of uranyl ion, in which the water

molecules are less disrupted upon complexation of the uranyl ion with the TTA conjugate base as a bidentate ligand. On the other hand,  $\Delta S^\circ$  for the extraction of  $\text{Th}^{4+}$  is positive ( $13\text{-}31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), suggesting the formation of hydrated inner-sphere complex of  $\text{Th}^{4+}$  ion, in which the highly ordered water molecules surrounding  $\text{Th}^{4+}$  in aqueous solution in virtue of its high ionic potential are severely expelled from the metal coordinated sphere upon complexation, followed by transferring the lipophilic  $\text{Th}^{4+}$ -TTA complex to the organic phase.

**Table 1. The thermodynamic parameters of extraction for uranyl ion and  $\text{Th}^{4+}$  ion by H(TTA)-derived ligands at  $25^\circ\text{C}$**

Metal-ion	Ligand	$K_{\text{ex}}$	$\Delta H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta G^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\circ$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{UO}_2(\text{II})$	H(5-chloro-TTA)	$1.99 \times 10^{-2}$	$-6.65 \pm 0.53$	$9.71 \pm 1.06$	$-54.87 \pm 1.78$
	H(5-methyl-TTA)	$1.14 \times 10^{-2}$	$-5.67 \pm 0.28$	$11.09 \pm 0.56$	$-56.21 \pm 0.94$
	H(TTA)	$1.29 \times 10^{-2}$	$-6.18 \pm 0.49$	$10.78 \pm 0.98$	$-56.88 \pm 1.65$
		$*1.00 \times 10^{-2}$			
	H(2,5-dichloro-TTA)	$**2.41 \times 10^{-2}$	-	-	-
	H(bi-TTA)	$7.47 \times 10^{-2}$	$-8.84 \pm 0.64$	$6.43 \pm 0.30$	$-51.22 \pm 3.14$
Th(IV)	H(5-chloro-TTA)	$2.60 \times 10^2$	$-4.66 \pm 0.20$	$-13.78 \pm 0.40$	$30.59 \pm 0.67$
	H(5-methyl-TTA)	22.63	$-3.89 \pm 0.20$	$-7.73 \pm 0.40$	$12.88 \pm 0.67$
	H(TTA)	33.23	$-4.24 \pm 0.18$	$-8.68 \pm 0.36$	$14.89 \pm 0.60$
	H(2,5-dichloro-TTA)	$**1.37 \times 10^4$	-	-	-
	H(bi-TTA)	$1.63 \times 10^5$	$-7.89 \pm 0.59$	$-29.75 \pm 0.74$	$73.32 \pm 0.51$

\* Ref<sup>[8]</sup>; \*\* Ref<sup>[21]</sup>.

## Conclusion

Two lipophilic thiophene-based trifluoro-methyl-substituted  $\beta$ -diketone ligands were studied for their extraction behavior for  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  ions. The thermodynamic parameters

for the extraction process were measured. The  $K_d$  values were determined and found to be correlated with the inductive effect of substituent on the thiophene ring.

## References

- [1] Meera, R., Ph.D. Thesis, Cochin University of Science and Technology, Regional Research Laboratory (CSIR), Kerala, India, **2004**.
- [2] Musikas, C.; Schulz, W.W.; Liljenzin, J.O., *Principles and Practices of Solvent Extraction*. Second Edition, Revised and Expanded: Edited by Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G.R., Marcel Dekker: New York, **2004**, 760
- [3] Nazal, M. K.; Albayyari, M. A.; Khalili, F. I.; Asoudani, E., *J. Radioanal. Nucl. Chem.*, **2017**, 312, 133.
- [4] Graziani, R.; Forsellini, E., *J. Chem. Soc., Dalton Trans.*, **1972**, 2059.
- [5] Tabushi, Y.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E., *J. Am. Chem. Soc.* **1980**, 102: 5948.
- [6] Tabushi, Y.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E., *J. Am. Chem. Soc.*, **1984**, 106: 2481.
- [7] Tabushi, Y.; Kobuke, Y.; Ando, K.; Kishimoto, M.; Ohara, E., *J. Am. Chem. Soc.*, **1985**, 107 : 4585.
- [8] Day, R. A. Jr.; Powers, R. M., *J. Am. Chem. Soc.*, **1954**, 76: 3895.
- [9] Day, R. A. Jr.; Stoughton, R. W., *J. Am. Chem. Soc.*, **1950**, 72 : 5662.
- [10] Ahrland, S.; Liljenzin, J. O.; Rydberg, J., *Comprehensive Inorganic Chemistry*, 3<sup>rd</sup> Edition: Pergamon Press, Ltd; Oxford., **1973**.
- [11] Ranis, T. C.; House, H. P., *Analytical Chemistry*, **1961**, 33 : 1645.
- [12] Onishi, H.; Sekine, K., *Talanta.*, **1972**, 19 : 473.
- [13] Krishna C. J.; Viaji, N. P., *Coordination Chemistry Reviews.*, **1977**, 22 : 37.
- [14] Mustafa, Z. O.; Mark, D. B.; Anthony, A. C.; Keith, D. B.; Andrey, S.; Neil, G. S.; Nigel, D. T. *Analytica Chimica Acta.*, **1997**, 73 : 346.
- [15] Kassierer, E.F.; Kertes, A.S., *J. Inorg. Nucl. Chem.*, **1972**, 34 : 778.
- [16] Kolarik, Z., *Solvent Ext. Rev.*, **1971**, 1: 1-62.
- [17] Dyrssen, D.; Kuca, L., *Acta. Chem. Scand.*, **1960**, 14 : 1945.
- [18] Irving, H.; Edgington, D.N., *J. Inorganic. Nucl. Chem.*, **1960**, 15: 158.
- [19] Braatz, A.D.; Antonio M. R.; Nilsson, M., *Dalton Trans.*, **2017**, 46 : 1194.
- [20] Xing, X; Zhen, Q; Yao, H; Penghui, X; Zeng, H; Yiwu, M; Hongyuan, H; Liangang, Z., *Sci Rep.*, **2017**, 7 : 15735.
- [21] Al-Taweel, S. A.; Khalili, F.; Al-Tarawneh, S. A.; Yousef, Y. Y., *Journal of Saudi Chemical Society*. **2008**, 12(2): 165.
- [22] Reid, J.C., *J. Amer. Chem. Soc.*, **1947**, 69 : 2069.
- [23] Hartough, H. D; Kosak, A. I., *J. Am. Chem. Soc.*, **1947**, 69 (12) : 3093.
- [24] Lloyd, B.B; Robert, L., *J. Amer. Chem. Soc.*, **1951**, 73(9) : 4625.
- [25] Palei, P.N., *Analytical Chemistry of Uranium*. Arbor Press: London, **1970**.
- [26] Vogel, A.I., *A Text-book of Quantitative Inorganic Analysis*. Longman house: England, **1978**.
- [27] Hiroshi, O.; Kehichi, S. *Talanta.*, **1972**, 19 : 473.
- [28] Savvin, S.B., *Talanta.*, **1961**, 8 : 673.
- [29] Eskandari, M.N., *Fuel*, **2014**, 116 : 595.