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EXTRACTION OF URANIUM (VI) FROM NITRIC ACID AND NITRATE SOLUTIONS BY TRIBUTYLPHOSPHATE/KEROSENE

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Abstract

The extraction of nitric acid and hexavalent uranium from nitric acid and nitric acid containing uranium (VI) media by tributyl phosphate (TBP)/kerosene has been studied, and all factors affecting the extraction process (time of mixing, uranium concentration, nitric acid concentration, TBP concentration, temperature) have been investigated. The equilibrium constant of the extraction reaction of uranium by TBP:

$$\mathrm{UO_2^{2+} + 2NO_3^- + 2TBP \leftrightarrows UO_2(NO_3)_2 \cdot 2TBP}$$

was found to be $10^{2.464}$, $10^{2.668}$ L^4/mol^4 at 25 °C, and the enthalpy was -16.47, -23.07 kJ/mol for 0.5 M and 1 M nitric acid concentrations, respectively.

The purification of the yellow cake produced at the pilot plant of uranium extraction from the Syrian wet phosphoric acid was investigated using TBP/kerosene.

Keywords: extraction, uranium (VI), nitric acid, tributyl phosphate/kerosene.

1. Introduction

The purification of crude uranium recovered from its ores at plant-scale using tributyl phosphate (TBP) started in the early 1950s in Canada and U.K, then in U.S. in 1953 [1]. Today, TBP extraction technology and processes are applied world-wide for the purification of crude uranium and also thorium. The success of TBP solvent extraction compared to other processes for purification of uranium is due to:

- TBP is highly selective for uranium, and provides excellent decontamination from most impurities.
- TBP is relatively stable against degradation under conditions normally used to purify uranium. Simple washing techniques are available to remove solvent degradation products.
- TBP/kerosene solutions have low vapor pressure and can be stored and handled without elaborating precautions against fires [1].

Organophosphoric compounds such as alkyl phosphine oxide and phosphonate, phosphinate, and also ethers, ketones are considered more polar than tributyl phosphate. So, the stripping of uranium from these compounds will be very difficult [2].

T. SATO [3] studied the extraction of uranium (VI) from nitric acid solutions using TBP. He found that 6 M nitric acid was the best concentration for uranium extraction. Moreover he found that, 97% of uranium can be recovered from 6 M nitric acid solution containing < 0.042 M of uranium using 19% TBP/kerosene.

The present work investigates the extraction of nitric acid and uranium (VI) from nitric acid solutions by TBP/kerosene and the purification of the yellow cake resulted from the secound cycle of uranium extraction from wet-process phosphoric acid by DEHPA-TOPO process using TBP/kerosene as extractant.

2. Experimental

Tributyl phosphate used as an extractant was from FLUCKA with purity 99%. The diluent used was the kerosene PEMCO SOLV 110 from PEMCO Chemicals company, which has a density of 800–810 kg/m^3 at 15 °C, its boiling point range is $200 - 250$ °C, and flash point > 70 °C, with aromatic content of max 0.5% (v/v).

The aqueous solutions of nitric acid were prepared by diluting concentrated nitric acid (from RIEDEL–DE HAËN, 65%) with double distilled water.

The aqueous solutions of uranium (VI) were also prepared by dissolving the necessary amount of uranyl nitrate hexahydrate (from MERCK with purity $>$ 98 %) with the appropriate amount of concentrated nitric acid, then diluted with double distilled water.

The yellow cake was obtained from a pilot plant of phosphoric acid purification by DEHPA-TOPO process in Homs, then dissolved in concentrated nitric acid, and diluted with double distilled water.

The extraction was carried out by stirring equal volumes (25 mL) of aqueous and organic phases in a thermostated water bath, the mixtures were separated after 30 min. of decantation. It is very important to note that no third phase or any precipitation was observed during the extraction process.

Uranium was determined in the aqueous and organic phases by γ-spectroscopic method, while iron was determined by atomic absorption spectroscopy. The concentration of nitric acid in the aqueous phase solutions was measured using an automatic potentiometric titrator (AT-420N-WIN) from KYOTO ELECTRONICS, Japan. The viscosity of the organic phases after the extraction process was measured using CANNON-FENSKE viscometer.

3. Results and Discussion

3.1. Extraction of Nitric Acid by TBP

3.1.1. Mixing Time Effect

Equal volumes (25 mL) of 0.363 M TBP/kerosene and 1 M nitric acid were mixed together at 25 °C for various time intervals. *Fig. 1* shows the variation of nitric acid concentration in the organic phase against time. It is clear that 1/2 minute is the minimum time to reach the equilibrium.

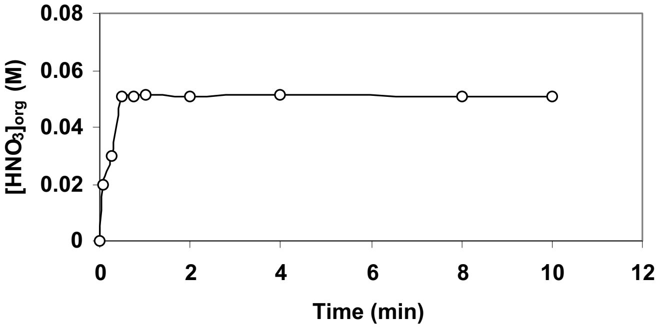

Fig. 1. Variation of $[HNO_3]_{org}$ against time. $[TBP]_i = 0.363$ M, $[HNO_3]_i = 1.13$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

3.1.2. *Effect of Nitric Acid Concentration*

The extraction of nitric acid in the range of (0.5 – 6.35 M) by 0.363 M tributyl phosphate/kerosene at an organic to aqueous phase ratio ($V_{org}/V_{aq} = 1$), and at 25 °C was examined. The results are shown in *Fig. 2*. The concentration of nitric acid in the organic phase increases with increasing the concentration of nitric acid in the aqueous phase.

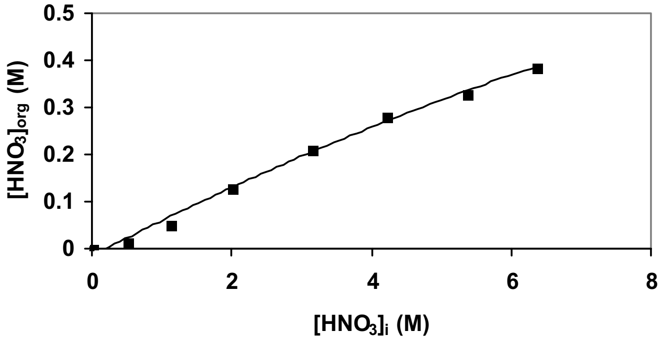

Fig. 2. Variation of $[HNO_3]_{org}$ against $[HNO_3]_i$. $[TBP]_i = 0.363$ M, $V_{org}/V_{aq} = 1$, $t = 25$ °C.

3.1.3. *Effect of TBP Concentration on HNO_3 Extraction*

The effect of the tributyl phosphate concentration in kerosene on the extraction of 1.125, 3.15, 6.35 M nitric acid at $V_{org}/V_{aq} = 1$ and at 25 °C was studied. *Fig.* 3 shows the variation of nitric acid concentration in the organic phase against initial tributyl phosphate concentration. It can be seen that the concentration of nitric acid in the organic phase increases linearly with increasing initial tributyl phosphate concentration.

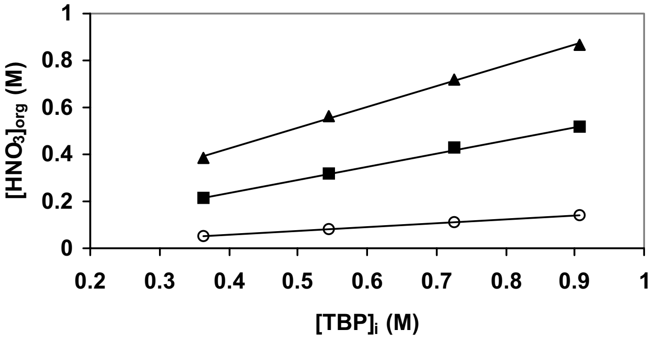

Fig. 3. Variation of $[HNO_3]_{org}$ against $[TBP]_i$. ○ $[HNO_3]_i = 1.125$ M. ■ $[HNO_3]_i = 3.15$ M, ▲ $[HNO_3]_i = 6.35$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

The extraction mechanism of nitric acid by tributyl phosphate can be expressed by the following equation [1]:

$$H^+ + NO_3^- + TBP \leftrightarrows TBP \cdot HNO_3 \tag{1}$$

The equilibrium constant of *Eq.* (1) can be written as:

$$K_{HNO3} = \frac{[TBP \cdot HNO_3]}{[H^+][NO_3^-][TBP]}. \tag{2}$$

Taking into account the dimerization of TBP in the organic phase [4]:

$$2TBP \leftrightarrows (TBP)_2 \qquad K_{dim} = [(TBP)_2]/[TBP]^2 = 2.6. \tag{3}$$

From the mass balance of tributyl phosphate the following expression can be written:

$$[TBP] = [TBP]_i - 2[(TBP)_2] - [TBP \cdot HNO_3] \tag{4}$$

In consequence:

$$[TBP] = \frac{-1 + \sqrt{\Delta}}{4K_{dim}}, \tag{5}$$

where:

$$\Delta = 1 - 8K_{dim}[HNO_3]_{org} + 8K_{dim}[TBP]_i. \tag{6}$$

Taking the logarithm of both sides of *Eq.* (2) and rearranging, we obtain:

$$\mathrm{Log}\frac{[HNO_3]_{(org)}}{[H^+][NO_3^-]} = \mathrm{Log}K_{HNO3} + \mathrm{Log}[TBP],$$

where

$$[TBP \cdot HNO_3] = [HNO_3]_{org}. \tag{7}$$

The Log-Log plots of $[HNO_3]_{(org)}/[H^+][NO_3^-]$ against [TBP] gave two straight lines, with a slope of 1.3 and 1.18 and regression coefficients of 0.9995 and 0.997 for 1.13 M and 3.15 M nitric acid concentration, respectively (*Fig. 4*), suggesting that one molecule of HNO_3 was extracted with one molecule of TBP.

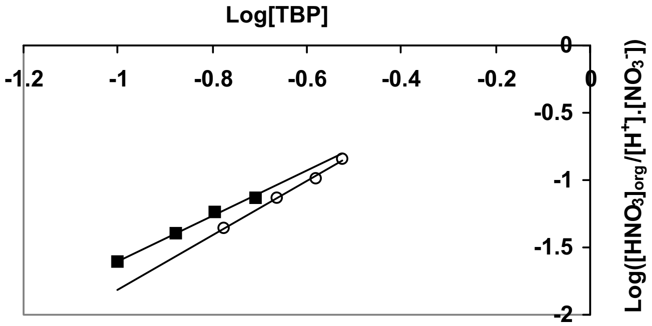

Fig. 4. Variation of Log $\{[HNO_3]_{org}/[H^+][NO_3^-]\}$ against Log [TBP]. ○ $[HNO_3]_i$ = 1.125 M. ■ $[HNO_3]_i$ = 3.15 M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

The equilibrium constant for the extraction reaction of nitric acid by TBP/kerosene was found to be 0.347 ± 0.077 L^2/mol^2 for 1.13 and 3.15 M nitric acid concentration.

3.2. Extraction of Uranium by TBP/Kerosene

3.2.1. Mixing Time Effect

The mixing time was investigated by extracting 0.126 M uranium from 3 M nitric acid using 0.726 M TBP/kerosene at $V_{org}/V_{aq} = 1$ and 25 °C for various time intervals. *Fig. 5* shows that 1/2 minute is the minimum time to reach the equilibrium. All experiments were given 10 minutes of stirring to ensure equilibrium.

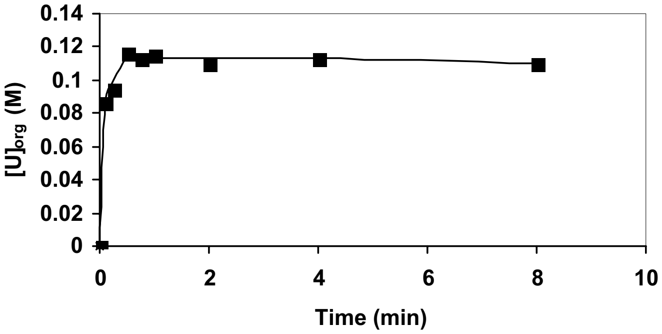

Fig. 5. Variation of $[U]_{org}$ against time. $[HNO_3]_i = 3$ M, $[U]_i = 0.126$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

3.2.2. *Uranium and Nitric Acid Concentration Effect*

For this purpose uranium was extracted from HNO_3 solutions of 0.5 to 7.0 M, and each solution contained different uranium concentrations from 0.025 to 0.63 M, using 0.726 M TBP/kerosene, at phase ratio of $V_{org}/V_{aq} = 1$ and at fixed temperature of 25 °C. Results are shown in *Fig. 6*, where it could be concluded that the extraction of uranium increases with increasing both uranium and nitric acid concentration to reach the maximum at 5 M HNO_3. The decrease of uranium concentration in the organic phase after this maximum can be explained by the fact that nitric acid will compete with $UO_2(NO_3)_2$.

The viscosity (η) of the organic phases resulted from the extraction of uranium at 1 and 3 M nitric acid concentrations were measured. The plot of Log η against Log $[U]_{org}/[TBP]$ gives two straight lines with slopes of 0.068 and 0.114 and correlation coefficients 0.989 and 0.9899, respectively (*Fig. 7*). So the two following empirical relationships can be written:

$$\text{Log}\ \eta = \text{Log}\ \{[U]_{org}/[TBP]\}^{0.068} + 0.341 \text{ for 1 M nitric acid concentration.}$$

$$\text{Log}\ \eta = \text{Log}\ \{[U]_{org}/[TBP]\}^{0.114} + 0.362 \text{ for 3 M nitric acid concentration.}$$

The small changes in the viscosity vs. $[U]_{org}/[TBP]$ confirm that no polymerization of uranium in the organic phase is occurred.

3.2.3. *TBP Concentration Effect*

To examine the effect of TBP concentration on the extraction of 0.126 M uranium from 0.5 M and 1 M nitric acid solution, two series of organic solutions containing 0.18 to 1.26 M TBP in kerosene were prepared, the first series was equilibrated with

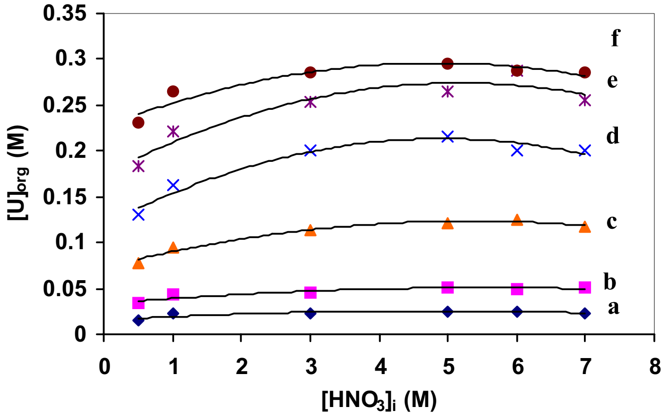

Fig. 6. Variation of $[U]_{org}$ against $[HNO3]_i$. a: $[U]_i = 0.02521$ M, b: $[U]_i = 0.05041$ M, c: $[U]_i = 0.12604$ M, d: $[U]_i = 0.25207$ M, e: $[U]_i = 0.37811$ M, f: $[U]_i = 0.63$ M. $[TBP]_i = 0.726$ M, $V_{org}/V_{aq} = 1$, $t = 25$ °C.

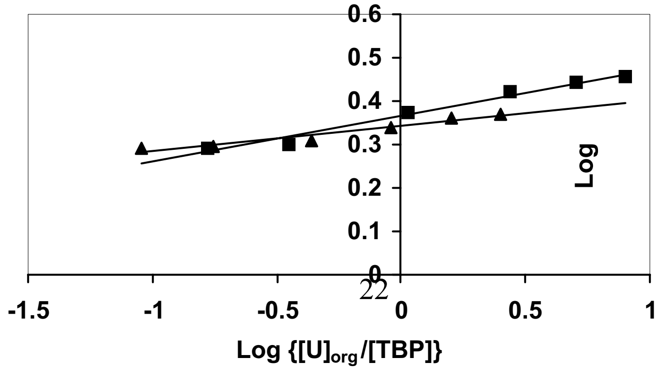

Fig. 7. Variation of Log η against Log $\{[U]_{org}/[TBP]\}$. ▲ $[HNO_3] = 1$ M, ■ $[HNO_3] = 3$ M. $[TBP]_i = 0.726$ M, $V_{org}/V_{aq} = 1$.

0.5 M nitric acid, while the other series was equilibrated with 1 M nitric acid. The extraction was carried out by mixing the equilibrated TBP/kerosene solutions with the aqueous phases mentioned previously at $V_{org}/V_{aq} = 1$ and 25 °C. The results are represented in *Fig. 8* in the form of Log-Log plots of $K_d = [U]_{org}/[U]_{aq}$ against $[TBP]_i$ for 0.5 M and 1 M nitric acid concentrations.

Uranyl ions (UO_2^{2+}) are complexed in the presence of HNO_3 to give $UO_2NO_3^+$,

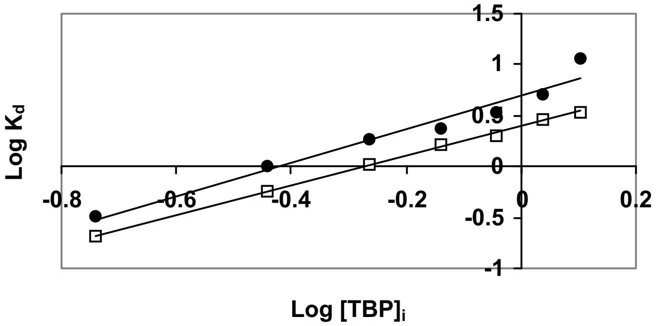

Fig. 8. Variation of Log K_d against Log $[TBP]_i$. □ $[HNO_3] = 0.5$ M, ● $[HNO_3] = 1$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

$UO_2(NO_3)_2$, $UO_2(NO_3)_3^-$ and $HUO_2(NO_3)_3$ as described in the following *Eqs.* [5]:

$$UO_2^{2+} + NO_3^- \leftrightarrows UO_2NO_3^+ \qquad K_1 = [UO_2NO_3^+]/[UO_2^{2+}][NO_3^-], \tag{8}$$

$$UO_2^{2+} + 2NO_3^- \leftrightarrows UO_2(NO_3)_2 \qquad K_2 = [UO_2(NO_3)_2]/[UO_2^{2+}][NO_3^-]^2, \tag{9}$$

$$UO_2^{2+} + 3NO_3^- \leftrightarrows UO_2(NO_3)_3^- \qquad K_3 = [UO_2(NO_3)_3^-]/[UO_2^{2+}][NO_3^-]^3, \tag{10}$$

$$UO_2^{2+} + 3NO_3^- + H^+ \leftrightarrows HUO_2(NO_3)_3 \qquad K_4 = [HUO_2(NO_3)_3]/[UO_2^{2+}][NO_3^-]^3[H^+]. \tag{11}$$

The Log values of K_1, K_2, K_3 and K_4 were 0.38, −1.4, 0.5, −1.74, respectively [5].

Taking a mass balance of nitrate and uranium:

$$\begin{aligned}[HNO_3]_i &= [NO_3^-] + [UO_2NO_3^+] + 2[UO_2(NO_3)_2] + 3[UO_2(NO_3)_3^-] \\ &\quad + 3[HUO_2(NO_3)_3], \end{aligned} \tag{12}$$

$$\begin{aligned}[U]_i &= [UO_2^{2+}] + [UO_2NO_3^+] + [UO_2(NO_3)_2] + [UO_2(NO_3)_3^-] \\ &\quad + [HUO_2(NO_3)_3]. \end{aligned} \tag{13}$$

Ion balance gives:

$$[H^+] = [NO_3^-] + [UO_2(NO_3)_3^-]. \tag{14}$$

Substituting, the values of uranyl nitrate complexes from *Eqs.* (8), (9), (10), (11) into *Eq.* (13) leads to:

$$[U]_i = [UO_2^{2+}] \cdot \{1 + K_1[NO_3^-] + K_2[NO_3^-]^2 + K_3[NO_3^-]^3 + K_4[NO_3^-]^3[H^+]\} \tag{15}$$

Then:

$$[UO_2^{2+}] = [U]_i/\{1 + K_1[NO_3^-] + K_2[NO_3^-]^2 + K_3[NO_3^-]^3 + K_4[NO_3^-]^3[H^+]\}. \tag{16}$$

In similar way, substituting the values of uranyl nitrate complexes from *Eqs.* (8), (9), (10) and (11) into *Eq.* (12) leads to:

$$[\mathrm{HNO_3}]_i = [\mathrm{NO_3^-}] + [\mathrm{UO_2^{2+}}] \cdot \{1 + \mathrm{K_1}[\mathrm{NO_3^-}] + 2\mathrm{K_2}[\mathrm{NO_3^-}]^2 + 3\mathrm{K_3}[\mathrm{NO_3^-}]^3 + 3\mathrm{K_4}[\mathrm{NO_3^-}]^3[\mathrm{H^+}]\}. \tag{17}$$

Substituting the value of $\mathrm{UO_2(NO_3)_3^-}$ from *Eq.* (10) into *Eq.* (14) leads to:

$$[\mathrm{H^+}] = [\mathrm{NO_3^-}] + \mathrm{K_3}[\mathrm{UO_2^{2+}}][\mathrm{NO_3^-}]^3. \tag{18}$$

Moreover, substituting the value of $[\mathrm{UO_2^{2+}}]$ from *Eq.* (16) into *Eq.* (18), leads to:

$$[\mathrm{H^+}] = ([\mathrm{NO_3^-}]) + ((\mathrm{K_3}[\mathrm{NO_3^-}]^3[\mathrm{U}]_i)/(1 + \mathrm{K_1}[\mathrm{NO_3^-}] + \mathrm{K_2}[\mathrm{NO_3^-}]^2 + \mathrm{K_3}[\mathrm{NO_3^-}]^3 + \mathrm{K_4}[\mathrm{NO_3^-}]^3[\mathrm{H^+}])). \tag{19}$$

Rearranging *Eq.* (19), gives:

$$\mathrm{K_4}[\mathrm{NO_3^-}]^3[\mathrm{H^+}]^2 + \{1 + \mathrm{K_1}[\mathrm{NO_3^-}] + \mathrm{K_2}[\mathrm{NO_3^-}]^2 + \mathrm{K_3}[\mathrm{NO_3^-}]^3 - \mathrm{K_4}[\mathrm{NO_3^-}]^4\} \cdot [\mathrm{H^+}] - \{[\mathrm{NO_3^-}] + \mathrm{K_1}[\mathrm{NO_3^-}]^2 + \mathrm{K_2}[\mathrm{NO_3^-}]^3 + \mathrm{K_3}[\mathrm{NO_3^-}]^4 + \mathrm{K_3}[\mathrm{NO_3^-}]^3[\mathrm{U}]_i\} = 0. \tag{20}$$

At constant nitrate and uranium concentration, it is possible to solve this second order equation for $[\mathrm{H^+}]$, consequently, knowing the concentration of $[\mathrm{H^+}]$, $[\mathrm{NO_3^-}]$ and $[\mathrm{U}]_i$ it is also possible to calculate the concentration of uranyl ions from *Eq.* (16), then all uranyl nitrate complexes from *Eqs.* (8), (9), (10) and (11).

The mechanism of uranium extraction from nitric acid by tributyl phosphate can be expressed by the following stoichiometric relation [6]:

$$\mathrm{UO_2^{2+}} + 2\mathrm{NO_3^-} + 2\mathrm{TBP} \leftrightarrows \mathrm{UO_2(NO_3)_2} \cdot 2\mathrm{TBP} \tag{21}$$

The equilibrium constant of *Eq.* (21) can be expressed as:

$$\mathrm{K}_U = \frac{[\mathrm{UO_2(NO_3)_2} \cdot 2\mathrm{TBP}]}{[\mathrm{UO_2^{2+}}][\mathrm{NO_3^-}]^2[\mathrm{TBP}]^2}. \tag{22}$$

Since $[\mathrm{UO_2(NO_3)_2} \cdot 2\mathrm{TBP}] = [\mathrm{U}]_{\mathrm{org}}$ and $[\mathrm{U}]_{\mathrm{org}}/[\mathrm{UO_2^{2+}}] = K_{d'}$, this expression can be rearranged to yield:

$$\mathrm{Log}\ \mathrm{K}_{d'} = \mathrm{Log}\ \mathrm{K}_U + 2\mathrm{Log}\ [\mathrm{NO_3^-}] + 2\mathrm{Log}\ [\mathrm{TBP}]. \tag{23}$$

Fig. 9 shows the Log-Log plots of $\mathrm{K}_{d'}$ against [TBP] which gave two straight lines with good correlation coefficients 0.999 and 0.977 and slopes equal to 2.09 and 2.14 for 0.5 M and 1 M nitric acid concentration, respectively. The logarithm of the equilibrium constant of uranium extraction was calculated from the intercept and found to be 2.464 and 2.668 $\mathrm{L^4/mol^4}$ for 0.5 M and 1 M nitric acid concentration.

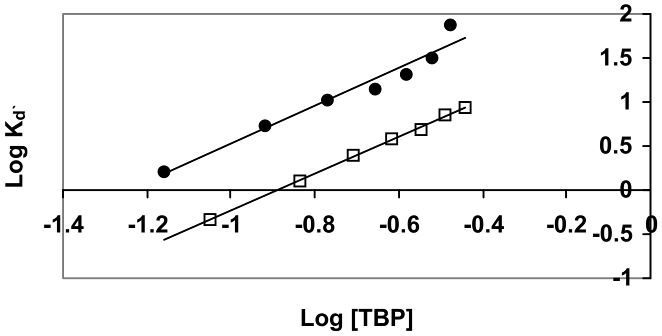

Fig. 9. Variation of Log $K_{d'}$ against Log [TBP]. □ $[HNO_3] = 0.5$ M, ● $[HNO_3] = 1$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

3.2.4. *Temperature Effect on Uranium Extraction*

To study the effect of temperature, the extraction of uranium was carried out by 0.363 M TBP in kerosene which was pre-equilibrated with 0.5 M and 1 M nitric acid. Uranium concentration was 0.126 M in 0.5 M and 1 M HNO_3.

The extraction was carried out in a thermostatic bath, and the mixture was stirred for 10 minutes at $V_{org}/V_{aq} = 1$ at different temperatures. The results are shown in *Fig. 10*.

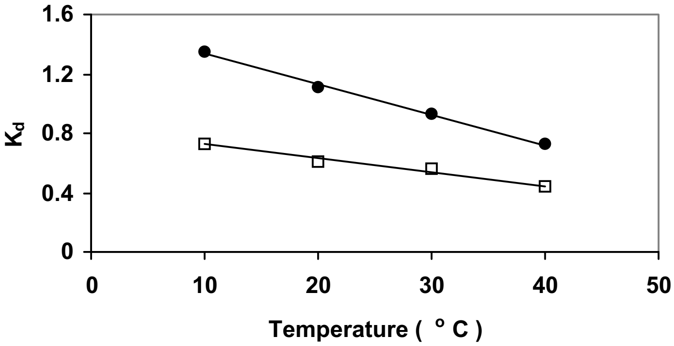

Fig. 10. Variation of K_d against temperature. □ $[HNO_3] = 0.5$ M, ● $[HNO_3] = 1$ M. $[TBP]_i = 0.363$ M, $V_{org}/V_{aq} = 1$.

The distribution coefficient decreases with increasing temperature. So the extraction reaction is exothermic. The decline of the extraction at 1 M HNO_3 is larger than that at 0.5 M HNO_3.

To determine the value of ΔH°, we plotted Log K_U against (1/T) for two concentrations of nitric acid of 0.5 M and 1 M (*Fig. 11*). Two straight lines have been obtained, these two straight lines have correlation coefficients equal to 0.99 and 0.995 with slopes equal to 860.509 and 1204.79, respectively.

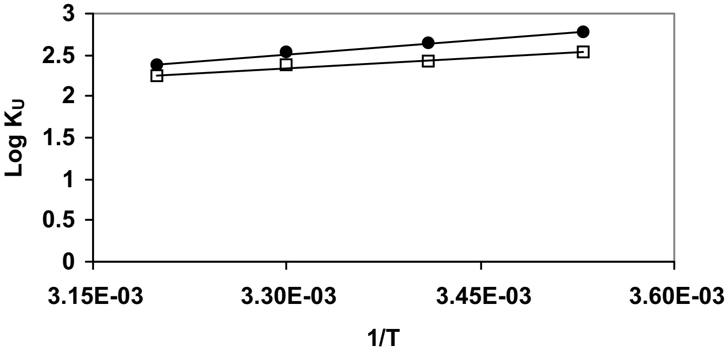

Fig. 11. Variation of Log K_U against 1/T. □ $[HNO_3] = 0.5$ M, ● $[HNO_3] = 1$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

Applying the integration of Van't Hoff's equation [7]:

$$\text{Log } K_{U\ (T2)} - \text{Log } K_{U\ (T1)} = -\Delta H^\circ/19.145[1/(T_2 - T_1)],$$

where, ΔH° is practically constant within the temperature range $T_1 - T_2$, the value of the enthalpy ΔH° for the extraction reaction was found to be:

$$\Delta H^\circ = -18.78 \text{ kJ/mol for 0.5 M nitric acid concentration.}$$
$$\Delta H^\circ = -26.64 \text{ kJ/mol for 1 M nitric acid concentration.}$$

3.2.5. Isotherm of Uranium Extraction from Y.C.

A stock solution of uranium (200 g/L) was prepared by dissolving 350 g of yellow cake produced from a pilot plant of wet-process phosphoric acid purification in 415.5 mL of concentrated nitric acid (65%) at 80 °C it was then diluted to 1 L with double distilled water. Uranium, iron and nitric acid concentration were determined by γ-spectroscopy, atomic absorption spectrometry and potentiometric method and found to be 200 g/L, 1 g/L, 5.75 M, respectively.

A set of uranium solutions of 5, 10, 20, 40, 80, 120, 160, 200 g/L was prepared previously with 5.75 M nitric acid. Equal volumes (25 mL) of aqueous phase as well as 0.363 M and 0.726 M TBP/kerosene at $V_{org}/V_{aq} = 1$ were shaken at 25 °C for 20 min, phases were then separated after 1 hour of decantation.

Fig. 12 shows the variation of uranium concentration in the organic phase against uranium concentration in the aqueous phase. It is clear that uranium concentration in the organic phase increases with increasing uranium concentration in the aqueous phase. The saturation of 0.363 M TBP/kerosene was achieved by contacting it twice with the highest uranium concentration (200 g/L). From *Fig.12* we can see that at 0.7 M uranium concentration in the aqueous phase the uranium concentration in the organic phase is 0.159 M, so the ratio $[TBP]_i/[U]_{org} \approx 2$. This means that two molecules of tributyl phosphate associate with one molecule of $UO_2(NO_3)_2$, this result is in a good agreement with that obtained by HEALY et al. [8] during the saturation of TBP with a solid uranyl nitrate.

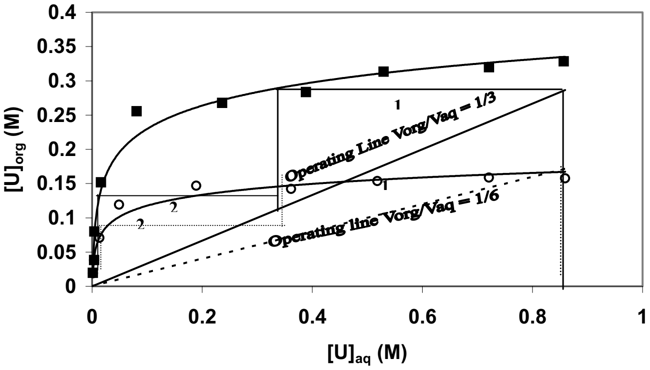

Fig. 12. Extraction isotherm for uranium from nitric acid by TBP/kerosone. ○ $[TBP]_i = 0.363$ M, ■ $[TBP]_i = 0.726$ M, $[HNO_3]_i = 5.75$ M, $V_{org}/V_{aq} = 1$, $t = 25$ °C.

The number of stages for uranium extraction from 5.75 M nitric acid solution using 0.363 M and 0.726 M TBP/kerosene was determined by McCabe and Thiele diagram at operating lines ($V_{org}/V_{aq} = 1/6$ and $1/3$). We concluded that 2 stages are enough to extract 98% of uranium using 0.363 M and 0.726 M TBP/kerosene respectively.

The worst element which pollute the yellow cake produced as a by product in the second extraction cycle of phosphoric acid purification using DEHPA-TOPO process is the iron. We found that TBP/kerosene is very selective vs. uranium and no iron was transferred to the organic phase during the extraction process. The concentration of iron in the organic phase was less than the detection limit of the atomic absorption spectrometry ($< 0.08\mu$g/mL). In consequence, stripping of uranium from the organic phase with a dilute nitric acid will give a solution containing only the uranium, then the precipitation of uranium will give an iron free uranyl nitrate.

3.2.6. *Effect of NaNO$_3$ on Uranium Extraction from Y.C.*

The effect of nitrate ions on uranium extraction from Y.C. at 25 °C was investigated by shaking equal volumes (25 mL) of the aqueous phase which contains 0.126 M uranium and different samples of NaNO$_3$ solutions with concentrations ranging from (0 – 7 M) and constant nitric acid concentration of 1 M with 0.363 M TBP/kerosene. As shown in *Fig. 13* the plot of Log K$_d$ against Log [NO_3^-] gave a straight line with a slope of ≈ 2 until [NO_3^-] = 0.7 M, then Log K$_d$ decreases with increasing [NO_3^-] concentration.

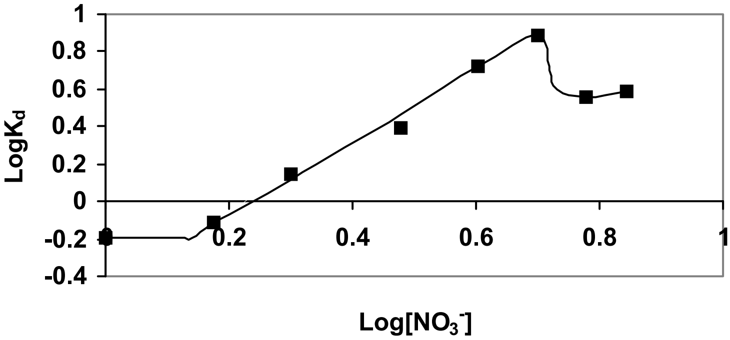

Fig. 13. Variation of Log K$_d$ against Log [NO_3^-]. [TBP]$_i$ = 0.363 M, [U]$_i$ = 0.126 M. [HNO3]$_i$ = 1 M, $V_{org}/V_{aq} = 1$, $t = 25$ °C.

3.2.7. *Effect of Nitric Acid Concentration on Uranium Extraction from Y.C.*

The effect of nitric acid concentration on uranium extraction from Y.C. at 25°C was studied by shaking equal volumes (25 mL) of the aqueous phase which contains 0.126 M uranium and different samples of nitric acid solutions with concentrations ranging from (1–8 M) with 0.363 M TBP/kerosene. *Fig. 14* shows that the distribution coefficient of uranium increases with increasing nitric acid concentration and reaches a maximum at 4 M nitric acid concentration, then decreases due to the competition between nitric acid and uranyl nitrate.

4. Conclusion

From the obtained results the following conclusions may be drawn:

- The partition of nitric acid between water and TBP/kerosene at 25 °C has been studied. The extracted nitric acid in the organic phase is in the form

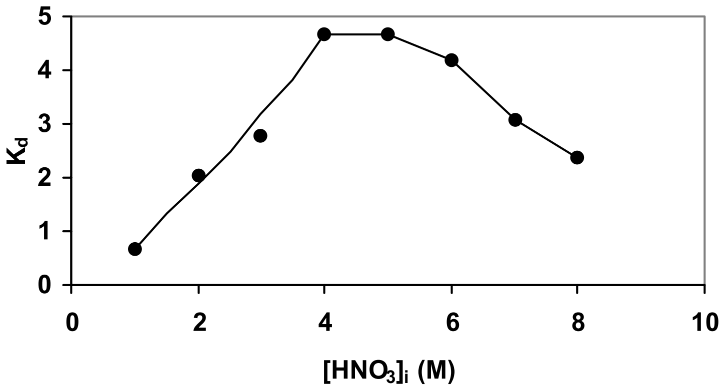

Fig. 14. Variation of K_d against initial nitric acid concentration. $[TBP]_i = 0.363$ M, $[U]_i = 0.126$ M. $V_{org}/V_{aq} = 1$, $t = 25$ °C.

of a 1:1 compound $HNO_3 \cdot TBP$. The equilibrium constant of the extraction reaction was found to be $K_{HNO3} = 0.347\ L^2/mol^2$.

- Uranium extraction from nitric acid solutions is fast, and increases with increasing both uranium and nitric acid concentration and reaches a maximum at 5 M HNO_3. The viscosity of the organic phase increases slightly with increasing uranium concentration in the organic phase. The equilibrium constant of uranium extraction was found to be $10^{2.464}$ and $10^{2.668}$ L^4/mol^4 for 0.5 M and 1 M nitric acid concentrations. Temperature has a negative effect on uranium extraction process, the ΔH° of the extraction reaction was found to be -18.78 and -26.64 kJ/mol for 0.5 M and 1 M nitric acid concentrations, respectively.
- Two stages are enough to extract more than 98% of uranium at 5.75 M nitric acid concentration using 0.363 and 0.726 M TBP/kerosene at operating lines ($V_{org}/V_{aq} = 1/6$ and 1/3) respectively.

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Nomenclature

M	Concentration in mol/L.
$[U]_i$	Initial uranium concentration in the aqueous phase (M).
$[U]_{org}$	Equilibrium uranium concentration in the organic phase (M).
$[U]_{aq}$	Equilibrium uranium concentration in the aqueous phase (M).
$[HNO_3]_i$	Initial concentration of nitric acid in the aqueous phase (M).
$[HNO_3]_{org}$	Equilibrium concentration of nitric acid in the organic phase (M).
$[HNO_3]$	Equilibrium concentration of nitric acid in the aqueous phase (M).
$[TBP]_i$	Initial tributyl phosphate concentration (M).
$[HNO_3 \cdot TBP]$	Equilibrium concentration of $HNO_3 \cdot TBP$ species (M).
K_{dim}	Equilibrium constant of tributyl phosphate dimerization (L/mol).
K_d	Distribution coefficient $= [U]_{org}/[U]_{aq}$.
$K_{d'}$	$= [U]_{org}/[UO_2^{2+}]$.
K_{HNO3}	Eqilibrium constant of nitric acid extraction (L^2/mol^2).
K_U	Eqilibrium constant of uranium extraction (L^4/mol^4).
ΔH°	Enthalpy of the extraction reaction (J/mol).
T	Thermodynamic temperature (K).
T_1, T_2	Initial and final thermodynamic temperature (K).
V_{org}	Volume of the organic phase.
V_{aq}	Volume of the aqueous phase.
η	Kinematic viscosity (CSt).
Y.C.	Yellow cake.

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