Thermodynamic Study of Uranium Extraction from Tunisian Wet Process Phosphoric Acid

N. Khleifia, A. Hannachi, N. Abbes

Abstract—In the present paper, an experimental investigation was conducted to study the thermodynamic of uranium extraction from Tunisian wet phosphoric acid using the synergistic solvent mixture of di-2-ethylhexyl phosphoric acid (DEHPA) and trioctyl phosphine oxid (TOPO) diluted in kerosene. The effect of different factors affecting the extraction process (temperature, TOPO and DEHPA concentrations) has been investigated. The obtained data of temperature effect on the extraction showed that the enthalpy change is -35.8 kJ.mol^{-1}. The slope analysis method was used for determining the stoichiometry of the extracted species.

Keywords—DEHPA-TOPO, extraction, phosphoric acid, stoichiometry, uranium.

I. INTRODUCTION

DESPITE the Fukushima Daiichi nuclear accident of March 2011, the development of nuclear power looks set to continue in the coming decades. Indeed, many countries maintain their project to build new nuclear power plants. Nuclear energy is presently the world's third largest source of electricity following coal and hydroelectric power [1]. However, the increased growth of nuclear energy has a direct impact on the growing interest of uranium extraction to face to the increase of the energy demand. As the uranium primary resources are getting depleted, the beneficiation of secondary resources has become more important in recent years [1]. Among unconventional resources, phosphate rocks, which are chemically processed for phosphoric acid and fertilizer production, attract a great attention as they contain 30-200 ppm of uranium, depending of the origin of rocks [2]-[4]. During the phosphoric acid production by the dihydrate process, the phosphate mineral reacts with a mineral acid, generally sulfuric acid. In this process, more than of 80% of the uranium contained in the raw material passes into the phosphoric acid in the form of U(IV) and U(VI) ions. The separation of uranium from Wet Process Phosphoric Acid (WPA) has gained considerable importance. It is practiced for two main reasons: to produce uranium as a by-product and to prevent the contamination of soil by the radionucleide elements and rare earth metals through fertilizers.

Tunisia, one of leading countries in phosphate production, currently processes annually an average of 8 million tons of commercial phosphates. The average uranium content in Tunisian phosphate ores is above 50 ppm. Phosphate reserves in these deposits are estimated to several hundreds of million tons. Nearly 80% of processed phosphate rocks are transformed into phosphoric acid and mineral fertilizers in the Tunisian Chemical Group (GCT). Because of the huge quantities of processed phosphate ores in Tunisia, the corresponding uranium quantities are large.

Several techniques have been developed to extract uranium from phosphoric acid like precipitation, ionic exchange, and membrane separation. These techniques have their own limitations and drawbacks such as scaling, fooling, low selectivity and high production cost. To overcome these drawbacks, solvent extraction seems to be the most successful process, which is well capable to be practiced by the uranium industry on a large commercial scale [5]-[9].

Synergistic extraction is an important method to enhance the solvent extraction efficiency. Among the extraction systems developed to recover uranium from WPA, the synergistic solvent mixture of di-2-ethylhexyl phosphoric acid (DEHPA) and trioctyl phosphine oxid (TOPO) has been the favored because of its high efficiency and selectivity for uranium extraction. Several research studies have been conducted on the solvent extraction of uranium from phosphoric acids where DEHPA-TOPO system was used as the extractant [10]-[12]. However, most reported studies were focused on uranium recovery from synthetic phosphoric acid solutions. Uranium extraction studies from industrial solutions are very scarce. Experimental studies on the thermodynamic of uranium extraction from phosphoric acid by DEHPA/TOPO are limited. The synergism mechanism has not been well understood. Although, synergistic extraction of species with the mixture of acidic and neutral solvents was explained by the mechanism of addition, substitution, and solvation, the information given about the parameters affecting the synergism mechanism of DEHPA–TOPO couple is limited. Therefore, in the present paper, the uranium extraction process from Tunisian WPA using DEHPA in combination with synergistic reagent TOPO was considered. The uranium extraction thermodynamics was investigated by studying the influence of temperature and extractants concentrations on the distribution coefficient (D). The slope analysis method was used for determining the stoichiometry of the extracted species.

II. EXPERIMENTAL

The phosphoric acid sample used in this study (25% P_2O_5) was provided by the Tunisian Chemical Group (GCT). Its

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World Academy of Science, Engineering and Technology
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Vol:7, No:11, 2013

average chemical composition is shown in Table I. Analytical grade TOPO and DEHPA were used as organic solvents. The commercial grade kerosene was used as diluent after acid washing followed by alkaline solution neutralization and alkaline stripping with water.

Prior to uranium extraction, WPA must undergo several pre-treatment steps. It was cooled to an optimum processing temperature, treated with activated carbon to remove both the suspended solids and the organic matter present in the acid, and finally oxidized with hydrogen peroxide till Electromotive Force (EMF) > 700 mV.

Extraction experiments were carried out by equilibrating aqueous and organic phases in cover glass beakers using magnetic stirrer. The mixture was vigorously shaken for 15min to achieve equilibrium and was then allowed to settle for 15min. The uranium concentration in the aqueous phase was determined using a Jobain Yvon ICP 2000 spectrometer. The concentration of uranium in organic phase was estimated by mass balance.

The distribution coefficient, D, is defined as the ration of uranium concentration in organic phase to that in the aqueous phase.

TABLE I
TYPICAL ANALYSIS OF TUNISIAN WPA

P_2O_5	U	Fe	Mg	Cd	Al	SO_4^{2-}
(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
25	37	1500	2900	14	1860	0,91

III. RESULTS AND DISCUSSION

A. Effect of DEHPA and TOPO Concentrations on Uranium Extraction

The effect of DEHPA and TOPO concentrations on uranium extraction efficiency was studied. A series of extraction experiments was performed using mixture of DEHPA and TOPO diluted in kerosene in various concentrations (0.2–0.5 M) and (0.08–0.3 M) for DEHPA and TOPO, respectively. In these experiments, the operating conditions of extraction were fixed at an O/A ratio of 1/2 and using 15min shaking time at room temperature. From the obtained results, shown in Fig. 1, it is clearly that the uranium distribution coefficient increases with increasing extractant concentrations. It is then preferable to have high extractant concentrations for a better loading of the organic phase with uranium.

B. Nature of Extracted Species

The synergistic mixture of DEHPA and TOPO is a mixture of acidic extractant (DEHPA) and neutral extractant (TOPO). The extractant DEHPA is a derivative of orthophosphoric acid whose two hydrogen atoms are substituted with two radicals. Hexavalent uranium was extracted by acidic extractants in a dimeric form of $UO2(HA)_2A_2$, where A represents the alkyl and phosphoryl groups of a typical organophosphorus acidic extractant and HA is the organophosphorus acidic extractant itself. Furthermore, whether the metal-extractant complex formed will be a monomer or polymer depends on metal loading level of the extractant. TOPO is a neutral extractant.

Uranium is extracted by TOPO through the coordination with the oxygen of the phosphoryl group (P=O) in the structure. TOPO does not release any hydrogen ions as a result of dissociation. Therefore, extraction is not affected by the acidity of the solution as opposed to the case of DEHPA [13].
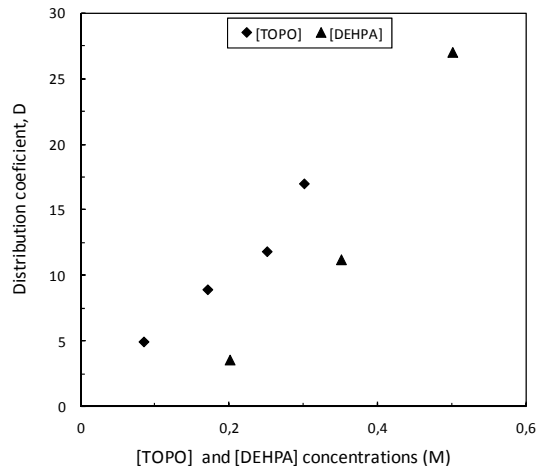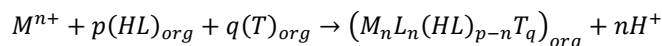

Fig. 1 Effect of TOPO and DEHPA concentrations on uranium distribution coefficient

The reaction of uranium extraction by mixture of acidic and neutral solvents may be written as:

$$M^{n+} + p(HL)_{org} + q(T)_{org} \rightarrow \left(M_nL_n(HL)_{p-n}T_q\right)_{org} + nH^+$$

where $M^{n+}=UO_2^{2+}$, HL=DEHPA, T=TOPO and $M_nL_n(HL)_{p-n}T_q$ represents the metal-extractant complex in the organic phase.

The expression of equilibrium constant K is:

$$K = \frac{[M_nL_n(HL)_{p-n}T_q][H^+]^n}{[M^{n+}][HL]^p[T]^q} \quad (1)$$

Defining the distribution coefficient (D) as a ratio of uranium concentration in the organic phase to that in the aqueous phase:

$$D = \frac{[M_nL_n(HL)_{p-n}T_q]}{[M^{n+}]} = \frac{K[HL]^p[T]^q}{[H^+]^n} \quad (2)$$

Since the species extracted cannot be isolated, and furthermore, the equilibrium is shifted during the extraction, an indirect method based on slope-analysis is used for determining the stoichiometry of the extracted complexes. This method is an approximation. Hence, several interactions existing in solution have not been taken into consideration. Furthermore, the solution of the two phases is far from ideal. The distribution coefficient can be written in linearized form as:

$$ln(D) = ln(K) + pln[HL] + qln[T] - nln[H^+] \quad (3)$$

According to this relation, a formula for the complex

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:7, No:11, 2013

formed during the extraction can be suggested. The coefficients p and q give the numbers of extractants molecules, which are bound to the metallic cation. Graphically this represents, respectively, the slopes of straight lines on $\ln(D) = f(\ln[HL])$ plot for [H$^+$] and [T] being constants and $\ln(D) = f(\ln[T])$ plot for [H$^+$] and [T] being constants.

1. Effect of TOPO Concentration on Uranium Extraction at Constant DEHPA Concentration

The synergistic effect of TOPO concentration on the uranium extraction from Tunisian phosphoric acid, 25% P$_2$O$_5$, has been investigated. A set of experiments were performed by shaking the treated phosphoric acid with TOPO having different concentrations at constant DEHPA concentration (0,5 M) and O/A ratio equal to 0,5 for 15 min at room temperature. A plot of ln(D) versus ln[TOPO] at constant DEHPA concentration is presented graphically in Fig. 2. It is clear from this figure that the slope of the straight line is 1, which indicates that 1 mol of uranium in organic phase is associated with 1 mol of TOPO.
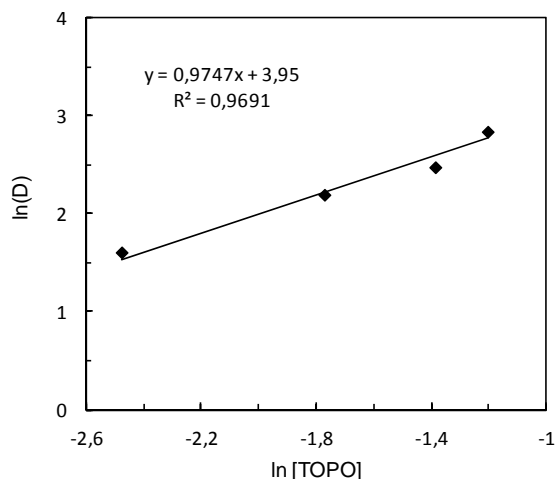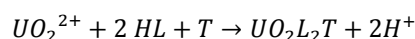
Fig. 2 Effect of TOPO concentration on distribution coefficient at constant DEHPA concentration

2. Effect of DEHPA Concentration on Uranium Extraction at Constant TOPO Concentration

To examine the effect of DEHPA concentration on the extraction of uranium from Tunisian phosphoric acid solution at constant TOPO concentration, two volumes of DEHPA and TOPO diluted in kerosene and wet process phosphoric acid were mixed together. The extraction was carried out by mixing the equilibrated DEHPA and TOPO in kerosene solutions with the phosphoric acid at O/A = 0.5 and T = 25 °C. Fig. 3 represents the plot of ln(D) versus ln[DEHPA]. According to this plot, the slope of the straight line is 2. Therefore, 1 mol of uranium in organic phase is associated with 2 mol of DEHPA.

Thus, it can be concluded that the extraction reaction of uranium by DEHPA-TOPO system can be written as:

$$UO_2{}^{2+} + 2\,HL + T \rightarrow UO_2L_2T + 2H^+$$

A. Effect of Temperature on Uranium Extraction

The effect of temperature on the uranium extraction from Tunsian phosphoric acid was investigated. The extraction experiments were carried out by contacting phosphoric acid with mixture of DEHPA and TOPO diluted in kerosene for 15 min while the O/A phase ratio was fixed at 0.5. The temperature was varied from 30 to 60°C. Fig. 4 shows the temperature effect on uranium distribution coefficient. From the obtained data, it can be noticed that the distribution coefficient is decreased by increasing the temperature which demonstrates the exothermic nature of the uranium extraction process.
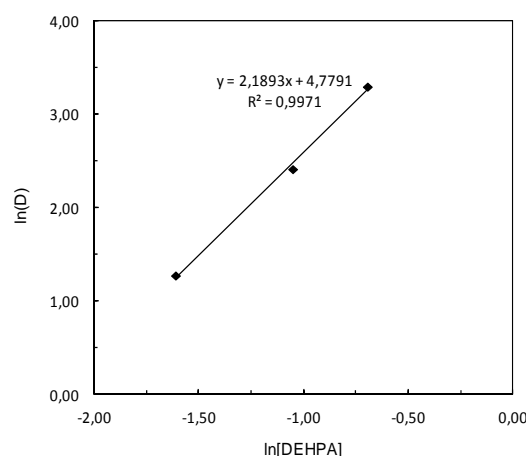
Fig. 3 Effect of TOPO concentration on distribution coefficient at constant DEHPA concentration
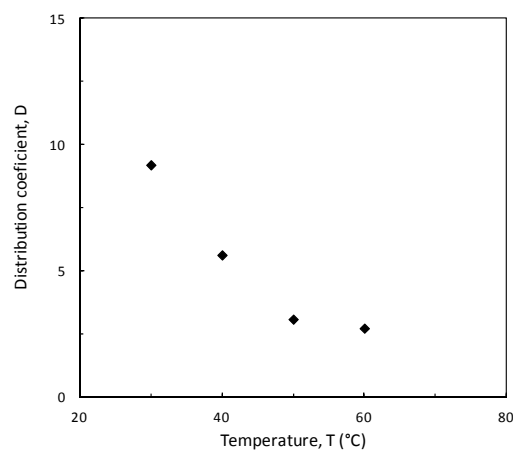
Fig. 4 Effect of temperature on uranium distribution coefficient

The temperature effect on the distribution coefficient can be quantified by making use of the Van't Hoff equation, which relates the chemical equilibrium constant with temperature:

$$\frac{d\ln(K)}{dT} = \frac{\Delta H}{RT^2} \tag{4}$$

By integration,

$$\ln(K) = -\frac{\Delta H}{RT} + c \tag{5}$$

World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:7, No:11, 2013

where c is constant.

And since the distribution coefficient D is related by definition to the equilibrium constant K. the previous equation can be written as:

$$\ln(D) = -\frac{\Delta H}{RT} + c \qquad (6)$$

The plot of ln(D) against $\frac{1}{RT}$ yields a straight line equation with slope equal to -ΔH. Fig. 5 shows the plot of ln(D) against $\frac{1}{RT}$. From this figure, an enthalpy change of −35.8 kJ.mol⁻¹ was obtained in the given range of temperature, which indicates that the extraction is an exothermic process.
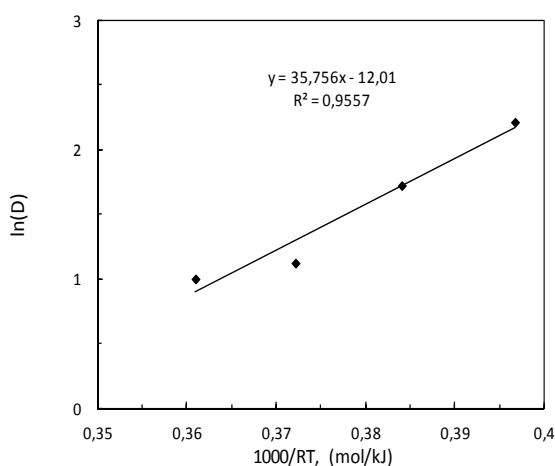

Fig. 5 ln(D) as a function of $\frac{1}{RT}$

IV. CONCLUSION

The DEHPA/TOPO in kerosene is the most suitable for the recovery of uranium from the wet phosphoric acid. An experimental investigation was developed to study the thermodynamic of uranium extraction by DEHPA-TOPO system. The effect of temperature and extractant concentrations was studied. Results show that temperature has a negative significant effect on the uranium extraction. However, the extractant concentrations enhance the uranium extraction performance. An enthalpy change of −35,8 kJ.mol⁻¹ was obtained in the given range of temperature, which indicates that the extraction is an exothermic process. The slope analysis method is used for determining the nature of extracted species.

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