



Extraction of Tetravalent Uranium by Certain Acidic Organophosphorus Extractants from Phosphate Medium

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خلاصة

تنطوي صناعة الاسمدة على مخلفات تحتوى على كميات ضئيلة من اليورانيوم مختلطا مع بعض اللانثانيدات وحيث ان عنصر اليورانيوم قد يتواجد فى الحالة رباعية التكافؤ أو سداسية التكافؤ أو كلتا الحالتين معا ، فان أساليب الاستخلاص تعتمد على الاستخلاص الانتقائى لحالات الأكسدة المختلفة .

تم فى هذا البحث دراسة استخلاص اليورانيوم رباعى التكافؤ من وسط فوسفاتى حمضى بواسطة ثمانى الفينيل لحمض الفوسفات (OPAP) أو ثنائى - 2 - إيثيل هكسيل حمض الفوسفوريك (HDEHP) المخفف بالكيروسين . وقد تم فحص تأثير العوامل المختلفة على عملية الاستخلاص 0 وفى هذا الخصوص تم فحص تأثير تركيز كل من حمض الفوسفوريك والمستخلصات المستخدمة و اليورانيوم ، وايون الحديدوز وايون الحديدى ، وكذلك تأثير درجه الحرارة . وقد تم فحص تأثير استخدام مختلف المحاليل الكيميائية فى عملية نزع اليورانيوم رباعى التكافؤ وقد أوضحت النتائج أن الاستخلاص بواسطة ثنائى - 2 - إيثيل هكسيل حمض الفوسفوريك (HDEHP) (أفضل من الاستخلاص بواسطة ثمانى الفينيل لحمض الفوسفات (OPAP) كما تم الحصول على اعلى نسبة نزع لليورانيوم باستعمال حمض الفوسفوريك المركز عند درجة حرارة منخفضة .

Abstract

The extraction of U(IV) by octylphenyl acid phosphate (OPAP) or di-2-ethylhexyl phosphoric acid (HDEHP) in kerosene from phosphoric acid was carried out. The effect of extractant , phosphoric acid , uranium, Fe(II) and Fe(III) concentration on the extraction process was separately investigated. The effect of different reagents and temperature on the stripping of U(IV) was also investigated. The results obtained for the extraction of U(IV) by HDEHP showed that the extraction increases with

the increase in HDEHP and Fe(III) concentration while it decreases with the increase in phosphoric acid, uranium and Fe(II) concentration. In case of extraction with OPAP, the extraction of U(IV) was found to decrease with the phosphoric acid, Fe(II) and initial uranium concentration while the increase in OPAP concentration slightly affected the extraction. The use of high phosphoric acid concentration as stripper at low temperature was found to give the best stripping results.

Introduction

The tailing of phosphate fertilizers manufacture produces wastes which contain traces of uranium, rare earths and heavy metals in phosphate medium. The wet-process phosphoric acid produced as by-product of these industries also contains traces of uranium mixed with trivalent lanthanides. In addition, phosphate salts are a common species in radioactive wastes solutions in which uranium and other actinides represent the long-term hazard of these wastes.

As uranium can be found as U(IV) or U(VI) or their mixtures, recovery techniques are based on selective separation of the different oxidation states. Octylphenyl acid phosphate (OPAP) was used for the extraction of U(VI) and some trivalent lanthanides from nitric acid medium (1). Chen et al(2) used HDEHP and dibutyl butyl phosphonate (DBBP) mixture in kerosene for the synergic extraction of uranium from wet-process phosphoric acid. The synergic extraction of U(VI) by HDEHP and TOPO in kerosene from phosphoric acid (3) or by HDEHP, PMBP (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) and TBP in benzene media (4) from nitrate medium was reported. Tsai and Chang (5) studied the extraction of U(IV) from wet-process phosphoric acid by OPAP-kerosene solution and used concentrated phosphoric acid for the stripping of uranium from loaded OPAP solution. Arnold et al (6) studied the effect of different components found in phosphoric acid on the extraction of U(IV) from wet-process phosphoric acid.

The present work is mainly concerned with the extraction of U(IV) by HDEHP and OPAP from phosphate medium to assess the conditions for the extraction and stripping of the loaded uranium in the organic phase.

Experimental

Chemicals

Octylphenyl acid phosphate (OPAP) was obtained from Mobil Chemical Company, USA. Bis (2-ethylhexyl) phosphoric acid (HDEHP) was a

product of Union Carbide Corporation, USA. Kerosene was obtained from Misr Petrol Ltd. Egypt, Uranyl nitrate was supplied by May & Baker Ltd., England. Ferrous sulfate was an Aldrich product while potassium permanganate and lithium carbonate were obtained from BDH, England. Sodium carbonate was supplied by Fluka while boric acid and ferric chloride were products of Merck.

Procedure

Preliminary experiments showed that in the investigated systems, equilibrium was reached after less than 30 min. After centrifugation and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured at 660 nm to determine the concentration of U(IV) in the aqueous phase while its concentration in the organic phase was determined by difference with the original concentration. The distribution ratio (D) was calculated from the relation

$$D = \frac{\bar{C}}{C} \cdot \frac{V}{\bar{V}}$$

where, \bar{C} and C are the concentrations of uranium in the organic and aqueous phases, respectively, while \bar{V} and V represent the volumes of the organic and aqueous phases, respectively.

Results and Discussion

The extraction of U(IV) by HDEHP and OPAP was separately investigated. The effect of the different parameters affecting the extraction process was studied.

Extraction of U(IV) by HDEHP

The effect of phosphoric acid concentration on the extraction of 10⁻²M U(IV) by 0.2M HDEHP was studied in the range 4 to 7 M. The results showed that the extraction process decreases with the increase in phosphoric acid concentration. Slope analysis of these results gave a straight line of slope -3, Fig.1.

The increase in HDEHP concentration from 0.05 to 0.375M increased the extraction of U(IV). The slope of the linear relation obtained from the log-log relation of the distribution ratio vs HDEHP concentration was found to be two, indicating that 2 HDEHP molecules participate in the extracted species, Fig.1.

The results of the effect of the initial U(IV) concentration represented in the same figure show that the increase in uranium concentration decreases the extraction process.

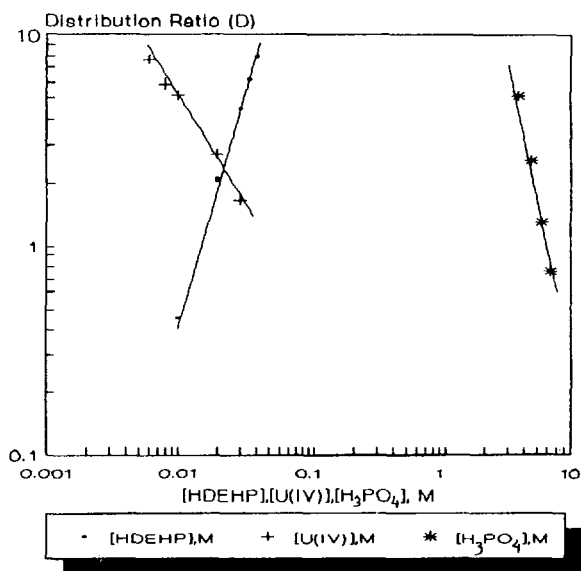
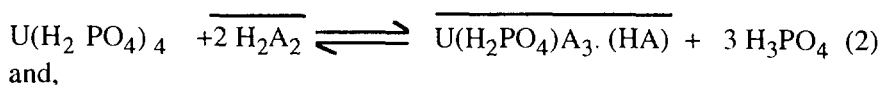


Fig.1. Effect of HDEHP, U(IV) and phosphoric acid concentration on the extraction of U(IV) by HDEHP in kerosene from 4 M phosphoric acid.

The reported models of the equilibrium behaviour of U(VI) with HDEHP from perchlorate (7), chloride (8), phosphate and sulfate (9) media indicate that either one or two extractant molecules could participate in the extraction of uranium. Assuming that at low pH, the predominating phosphate species in the aqueous phase is H_2PO_4 (10), the main uranium species in the aqueous phase are $U(H_2PO_4)_4$. Based on the above results and taking into consideration that HDEHP exist in a dimeric form in kerosene, (11), the extraction of U(IV) by HDEHP in kerosene could be represented at equilibrium by :



$$K_{ex} = D [H_3PO_4]^3 / [\overline{H_2A_2}]^2, \quad M \quad (3)$$

where K_{ex} is the extraction constant, bars refer to organic phase and HA denotes HDEHP.

The mean value of the extraction constant calculated at different phosphoric acid and HDEHP concentrations was found to be $2.7 \pm 0.3 \times 10^5 M$.

The effect of Fe(II) and Fe(III) which are present in the phosphate solutions on the extraction of U(IV) was investigated. In this context, Fe(II) concentration was varied in the range 2×10^{-2} - 0.2M. The results represented in Fig.2 show that the distribution ratio of U(IV) decreases with the increase in Fe(II). On the other hand, the increase in Fe(III) concentration from 5×10^{-5} to 1.5×10^{-2} M increased slightly the extraction of U(IV) from 4M phosphoric acid, Fig.2.

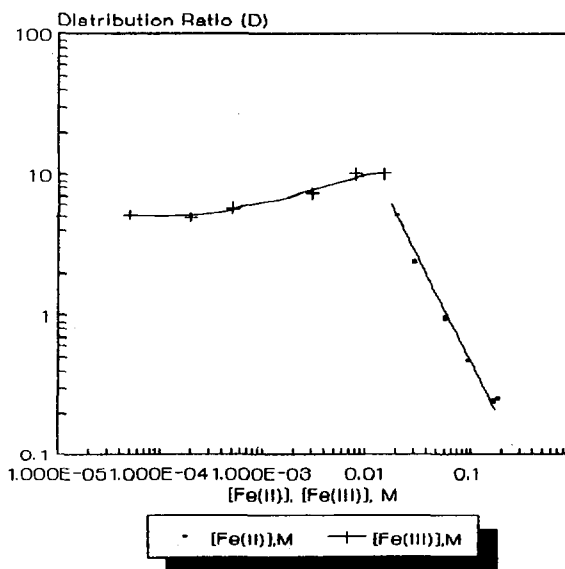


Fig.2. Effect of Fe(II) and Fe(III) on the extraction of U(IV) by HDEHP in kerosene from phosphoric acid;
 $T=25\text{ }^{\circ}\text{C}$, $[\text{H}_3\text{PO}_4] = 4\text{ M}$, $[\text{U(IV)}] = 0.01\text{ M}$ and $[\text{HDEHP}] = 0.035\text{ M}$

Extraction of U(IV) by OPAP

The effect of H_3PO_4 concentration on the extraction of 10^{-2} M U(IV) by 0.5 g/l OPAP was investigated in the range 4-7M. The extraction process was found to decrease sharply with the increase in acid concentration and a slope of -6 was obtained from the log-log relation of the distribution ratio (D) vs $[\text{H}_3\text{PO}_4]$, Fig.3. This effect could be related to the extraction of phosphoric acid by OPAP which leads to the marked decrease in the extraction of U(IV).

The effect of the extractant concentration on the extraction process of U(IV) from 4M phosphoric acid was investigated by varying the OPAP concentration in kerosene in the range 10^{-2} - 1.0 g/l. The results

represented in Fig.3 show a negligible effect of the variation of OPAP concentration on the distribution ratio.

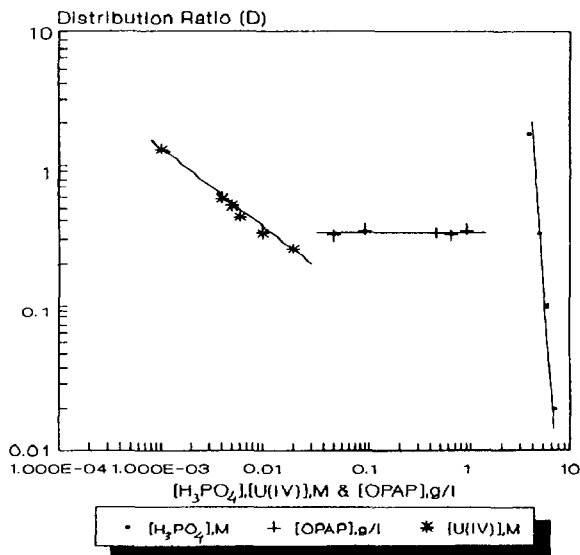


Fig.3. Effect of OPAP, U(IV) and phosphoric acid on the extraction of U(IV) by OPAP in kerosene from phosphoric acid.

The variation of initial U(IV) concentration in the range 10^{-3} - 2×10^{-2} M gave a linear decrease of the distribution ratio with the increase in uranium concentration. Slope analysis of the results obtained gave a slope of about -1.0, Fig.3. As in case of extraction with HDEHP, the increase in Fe(II) in the medium from 10^{-2} - 0.12 M leads to decrease in the extraction of U(IV), Fig.4. On the other hand, the increase in Fe(III) in the medium in the range 5×10^{-5} - 2×10^{-3} M was found to have a negligible effect on the distribution ratio, while further increase in Fe(III) till 1.5×10^{-2} M increased the extraction of U(IV), Fig.4.

Stripping of U(IV)

The stripping of U(IV) was tested by different strippers, namely; phosphoric acid, oxalic acid, boric acid, sodium carbonate and lithium carbonate at constant concentration of 2×10^{-2} M and at 25 ± 0.1 °C. Experimental results showed that phosphoric acid and lithium carbonate give better results compared with the other reagents tested.

The increase in phosphoric acid concentration from 4 to 10 M increased the stripping percentage of U(IV) from 3.98 to 96.22%, Fig.5. On the other

hand the increase in lithium carbonate from 10^{-5} - 2×10^{-2} M increased the percentage of the stripped uranium from 29.67 to 36.99%, Fig.5.

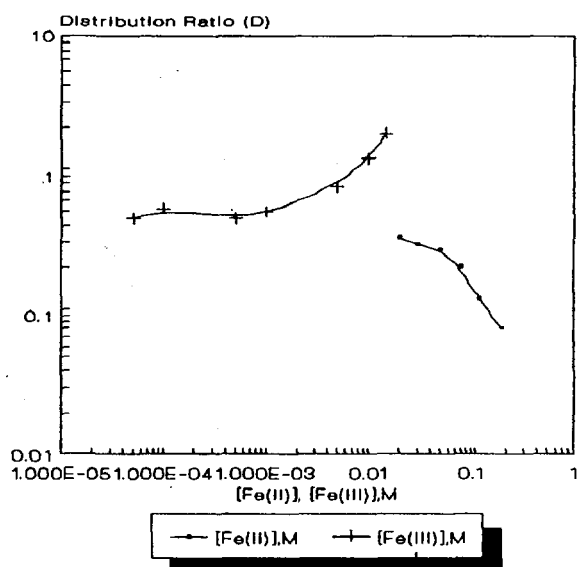


Fig.4. Effect of Fe(II) and Fe(III) on the extraction of U(IV) by OPAP in kerosene from phosphoric acid;

$T=25^{\circ}\text{C}$, $[\text{H}_3\text{PO}_4] = 4\text{M}$, $[\text{U(IV)}] = 0.01\text{M}$ $[\text{OPAP}] = 0.035\text{M}$

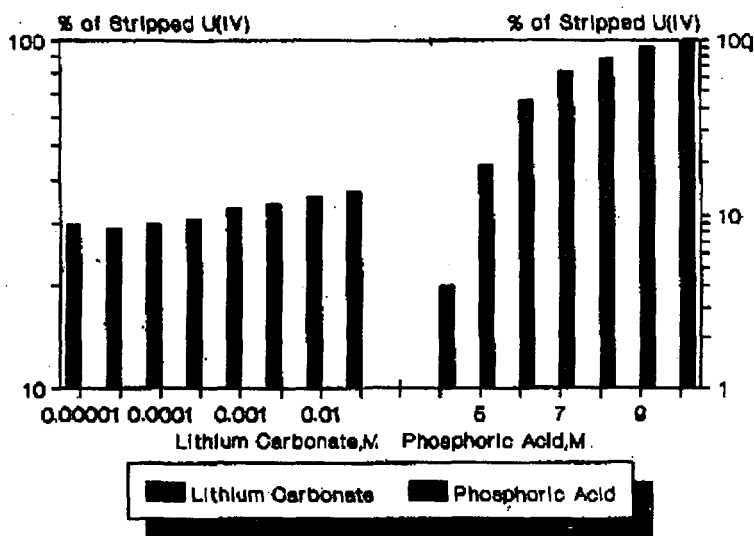


Fig.5. Effect of lithium carbonate and phosphoric acid on the stripping of U(IV) at 25°C

Effect of temperature on stripping

The effect of temperature on the stripping process was studied by varying the temperature from 15 to 60°C and from 20 to 60°C in case of phosphoric acid and lithium carbonate, respectively. The results represented on semi-log scale in Fig.6 show that in both cases the increase in temperature leads to decrease in stripping.

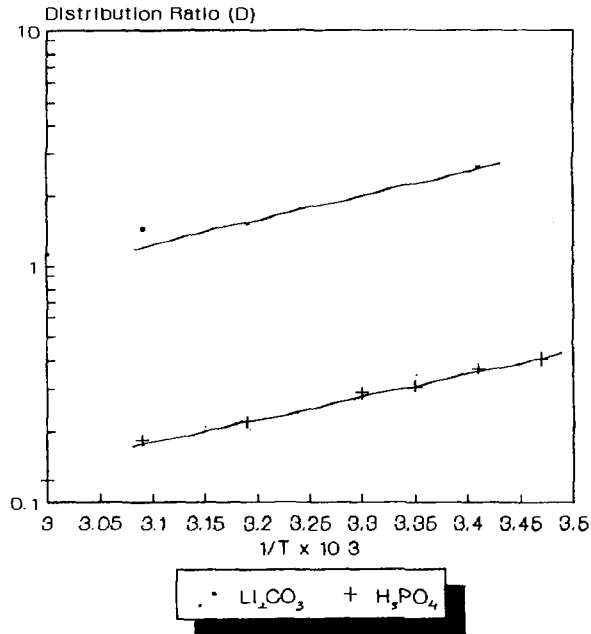


Fig.6. Effect of temperature on the stripping of U(IV) by lithium carbonate and phosphoric acid.

Conclusions

- The extraction of U(IV) from phosphoric acid was found to be higher by HDEHP in kerosene compared with OPAP.
- The extraction of U(IV) by HDEHP increased with the increase in the extractant concentration while in case of OPAP system, the extraction was nearly unaffected by the increase in OPAP concentration under the used experimental conditions.
- The increase in phosphoric acid concentration decreased the extraction of U(IV) by either HDEHP or OPAP in kerosene.
- The increase in Fe(II) concentration in the medium decreased the extraction of U(IV) by either extraction process.

- The stripping process was found to decrease with the increase in temperature. Best stripping results were obtained by 10 M phosphoric acid at temperature less than 25°C.

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