

# Solvent Extraction of Uranium(VI) by Didodecylphosphoric Acid

Khaled Mousa and Fawwaz Khalili

Department of Chemistry, University of Jordan, Amman - Jordan.

## استخلاص اليورانيوم (VI) بواسطة حامض ثنائي دوديكيل الفسفوريك

خالد موسى وفواز الخليلي

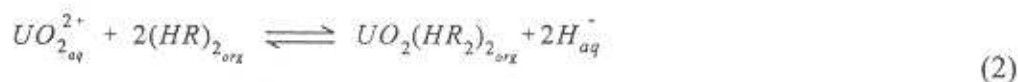
خلاصة : تم استخلاص اليورانيوم (VI) من محلول بيركلورات باستخدام حامض ثنائي دوديكيل الفسفوريك المذاب في التولوين . وقد درست تأثيرات العوامل التالية على عمليات الاستخلاص : تركيز حامض النيتريك ، زمن النزح ، زمن الاستخلاص ، تركيز المتصلة ، درجة الحموضة ، القوة الأيونية ، نوع الأنتروليت واختلاف درجات الحرارة . واستخدمت قيم معامل التوزيع عند درجات حرارة مختلفة لحساب التغير في المحتوى الحراري والطاقة الحرة ودرجة العشوائية المصاحبة لعملية الاستخلاص . وحددت كذلك صيغة المعقد المتكون عند الاستخلاص وهو  $UO_2(ClO_4)(HR)_2(HR)_2$  حيث  $(HR)_2$  تمثل الجزيء المزدوج من حامض ثنائي دوديكيل الفسفوريك .

ABSTRACT: Solvent extraction of uranium(VI) ion from perchlorate solution using didodecylphosphoric acid, DDPA, in toluene diluent was studied. The effects of stripping nitric acid concentration, stripping time, extraction time, DDPA concentration, pH, ionic strength, supporting electrolyte and temperature on the extraction processes have been studied. From the distribution coefficient values at different temperatures, the enthalpy, the free energy and the entropy changes associated with the extraction processes were determined. The composition of the complex formed was established to be  $UO_2(ClO_4)(HR)_2(HR)_2$  where,  $(HR)_2$  represents the dimer of DDPA.

Solvent extraction enjoys a favored position among separation techniques, due to its simplicity, speed and wide scope (Dean, 1969). The distribution coefficient ( $K_d$ ) of a solute (A) between an organic phase and an aqueous phase is given by

$$K_d = \frac{[A]_{org}}{[A]_{aq}} \quad (1)$$

Generally, dialkylphosphoric acids extract uranium(VI) ion in non polar diluents by a cation exchange mechanism (Baes *et al.*, 1958; Bunus *et al.*, 1978; Marcus *et al.*, 1976; Mason *et al.*, 1970; Sato, 1962) according to the following reaction



The extraction equilibrium constant is expressed as follows

$$K_{ex} = \frac{[UO_2(HR_2)_2]_{org}[H^-]_{aq}^2}{[UO_2^{2+}]_{aq}[(HR)_2]_{org}^2} \quad (3)$$

or

$$K_{ex} = K_d [H^+]_{aq}^2 / [(HR)_2]_{org}^2 \quad (4)$$

where

$$K_d = [UO_2(HR_2)_2]_{org} / [UO_2^{2+}]_{aq}$$

It is well known that di(2-ethylhexyl)phosphoric acid, D2EHPA, in many diluents is an effective extractant for actinides from mineral acid solutions (Sato, 1963; Baes, 1962; Kiwan *et al.*, 1973). Peppard *et al.* (1957a, b; 1959) have described the application of D2EHPA to the fractionation of the trivalent lanthanides plus yttrium, to the isolation of certain carrier-free radioactive M(III) nuclides, to the mutual separation of certain M(III) actinides and to the separation of Ce(IV) from M(III) actinides and lanthanides. Mason *et al.* (1981) studied the extraction of U(VI) and Th(IV) from an aqueous nitrate phase by bis(2,6-dimethyl-4-heptyl)phosphoric acid, HD(DIBM)P, in n-heptane and benzene diluents. The extraction stoichiometries and the corresponding expression for the extraction equilibrium constants were determined. The equilibrium study of extraction of lanthanide ions with didodecylphosphoric acid, DDPA, was carried out by Kondo *et al.* (1989). The extracted species into toluene diluent was found to be  $LnR_3 \cdot 3HR$  and the extraction equilibrium constants for the three lanthanide ions, that is, samarium(III), europium(III) and gadolinium(III) were obtained.

This work describes an investigation of the extraction of uranium(VI) by DDPA from perchlorate solution.

### Experimental

**REAGENTS:** The extractant, didodecylphosphoric acid, DDPA, was prepared and purified as described in the literature (Kondo *et al.*, 1989).

The organic solution was prepared by dissolving DDPA into toluene. The aqueous solution was prepared by dissolving uranyl perchlorate into perchloric acid - sodium perchlorate solution. The pH of the aqueous solution was adjusted using a 1.0-M perchloric acid and the ionic strength was adjusted using a 1.0-M sodium perchlorate solution. All other chemicals were of AR grade. Doubly distilled water was employed to make up aqueous solutions, and distilled water was employed for washing all glassware.

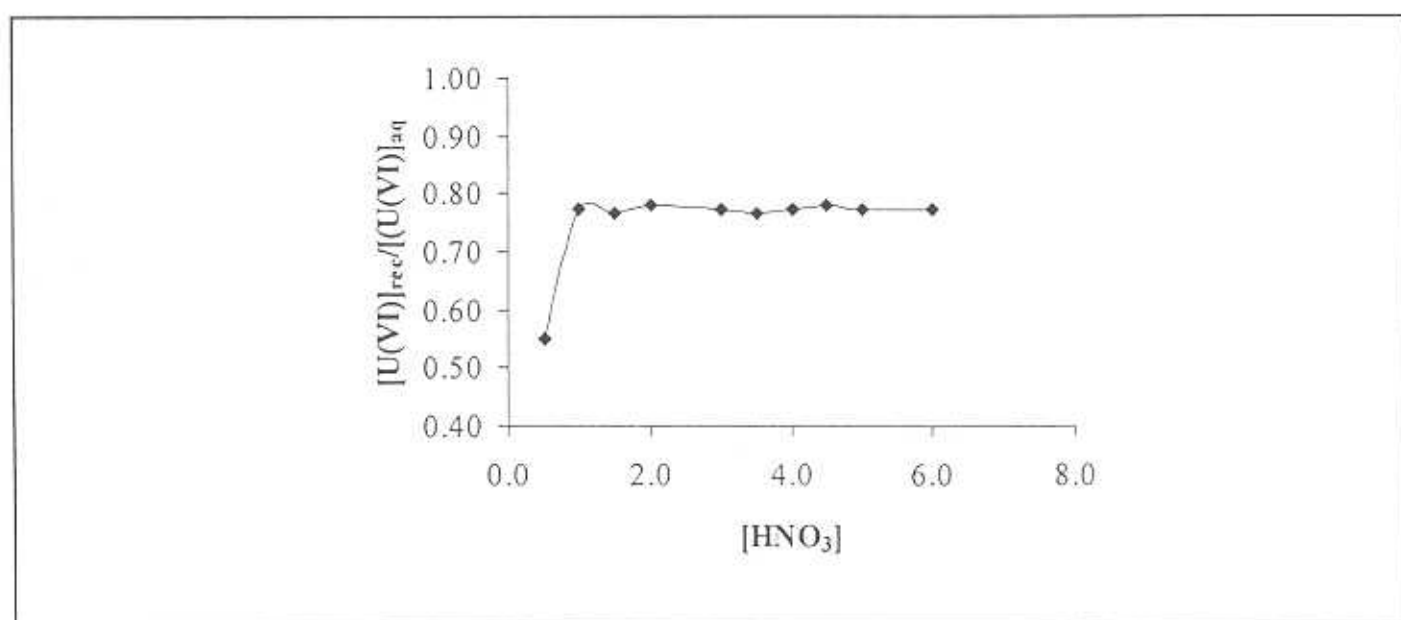


Figure 1. Variation of  $[U(VI)]_{rec}/[U(VI)]_{aq}$  with  $HNO_3$  concentration.

## SOLVENT EXTRACTION OF URANIUM (VI) BY DIDODECYLPHOSPHORIC ACID

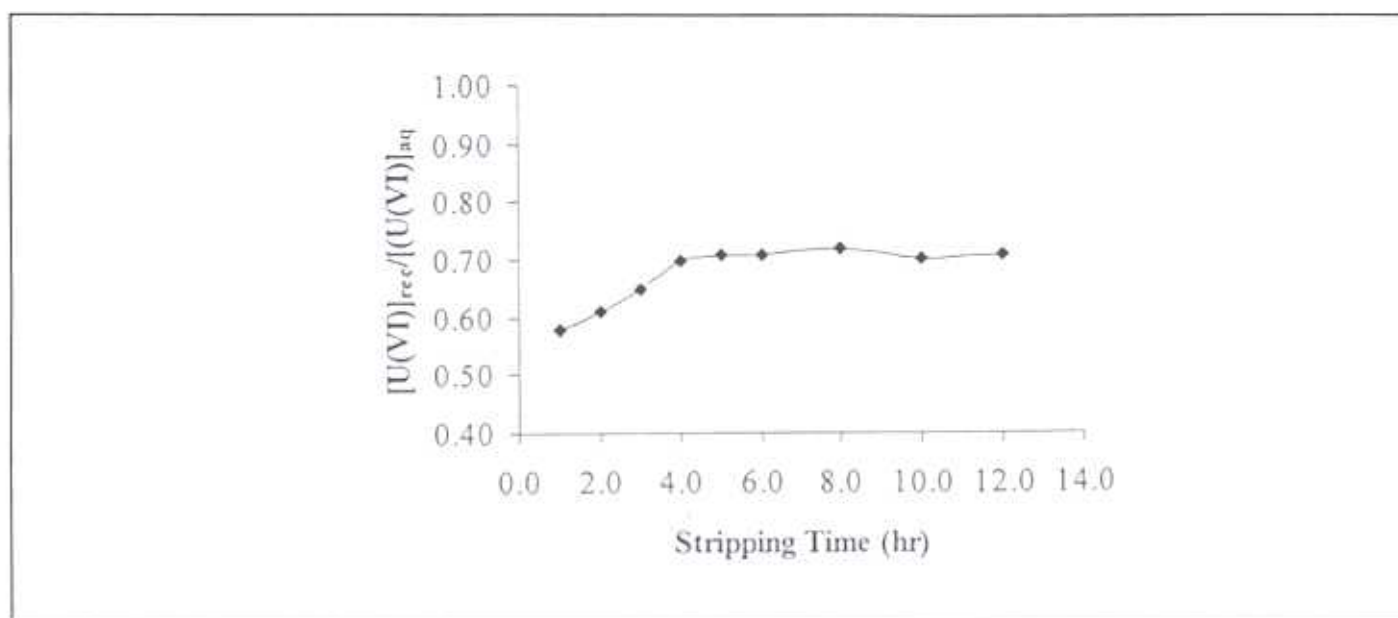


Figure 2. Variation of  $[U(VI)]_{rec}/[U(VI)]_{aq}$  with stripping time.

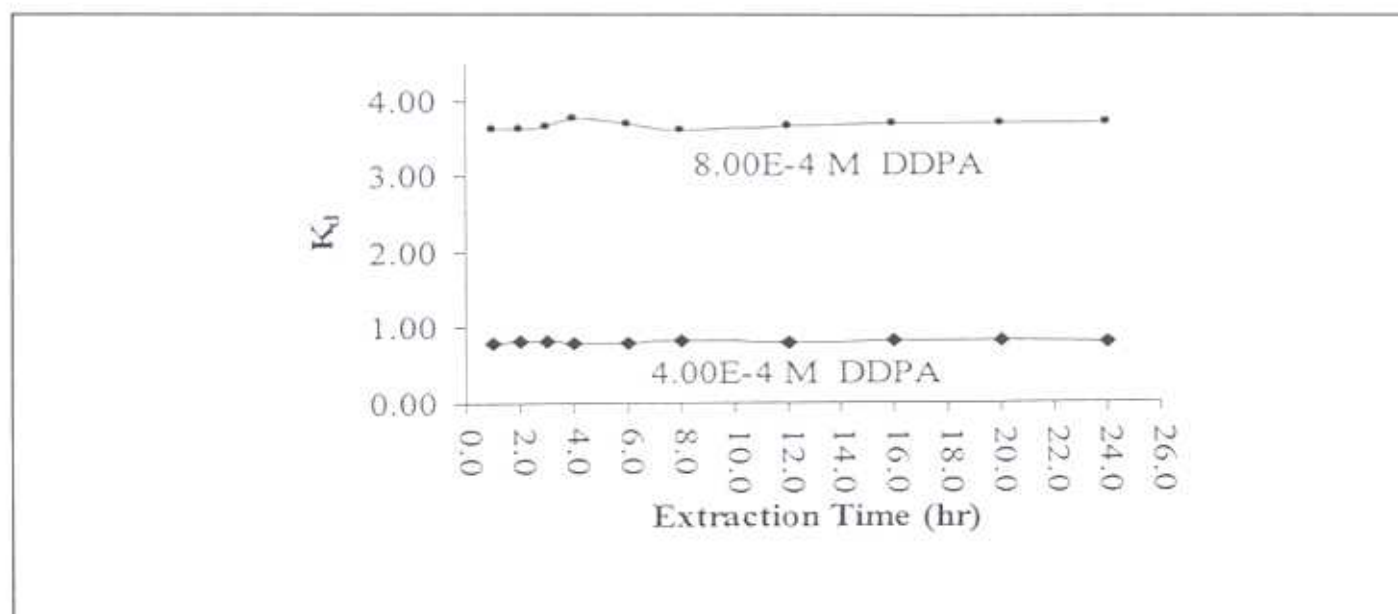


Figure 3. Variation of  $K_d$  with extraction time at 25 C.

MEASUREMENT OF EXTRACTION EQUILIBRIUM: Equal volumes (10.0 ml) of the organic and aqueous solutions of known concentrations were shaken in a 30-ml vial at a required temperature, and allowed to attain equilibrium. The uranium(VI) ion concentration in the aqueous solution was 8.0 ppm. After about 4 hours, the two solutions were separated and aliquotes (4.0 ml) were taken for analysis. Concentration of uranium(VI) was determined spectrophotometrically with a DU-7 spectrophotometer using 4-(2-pyridyl azo) resorcinol, PAR, as a spectrophotometric reagent (Florence *et al.*, 1963). Scanning was performed for a standard solution of the uranium-PAR complex against a reagent blank in the range  $\lambda = 400 - 800$  nm. A wavelength of  $\lambda = 530$  nm was chosen to be the optimum wavelength of measurement. Best extraction time was chosen by extraction of several samples of the same solution for different periods (Fig. 3). Best stripping nitric acid concentration was determined by shaking 4.0 ml of the equilibrated organic solution ( $4.0 \times 10^{-4}$  M DDPA) and 5.0 ml of nitric acid at different concentrations for 24 hours (Fig. 1) while best stripping time was chosen by shaking 5.0 ml of 1.0 M nitric acid solution and 4.0 ml of the equilibrated organic solution of the same concentration ( $4.0 \times 10^{-4}$  M DDPA) for different periods (Fig. 2). The best DDPA concentration was chosen by extraction of several solutions of uranium(VI) ion by extractant solutions at different concentrations (Fig. 4). The optimum pH was chosen by extraction samples at pH values of 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 1.8, 1.9 and 2.0 (Fig. 5). The effect of the ionic strength



was studied by extraction of several samples at ionic strength of 0.1, 0.5, 1.0, 1.5, and 2.0 M (Fig. 6). The effect of the supporting electrolyte was studied by extraction of several samples of different supporting electrolytes of  $\text{NaClO}_4$ ,  $\text{NaCl}$ , and  $\text{NaNO}_3$  (Fig. 7). The thermodynamic parameters were obtained by studying the extraction of several samples of uranium(VI) ion at the temperatures of 15.0, 20.0, 25.0, 30.0, 35.0, and  $45.0 \pm 0.2$  °C (Figure 8). All experimental data are obtained with only one variable in each experiment; the other variables kept constant.

### Results and Discussion

**STRIPPING OF URANIUM(VI) FROM THE ORGANIC PHASE:** Nitric Acid solution was used for stripping of U(VI) from the organic phase. Figs. 1 and 2 demonstrated that a 1.0 M nitric acid is sufficient for stripping of U(VI) with stripping time of at least four hours, and can be confirmed by the material balance with a percentage error of about 2% or less.

**EFFECT OF EXTRACTION TIME:** From Fig. 3, it was established that equilibrium was attained in one hour, a time of four hours was selected.

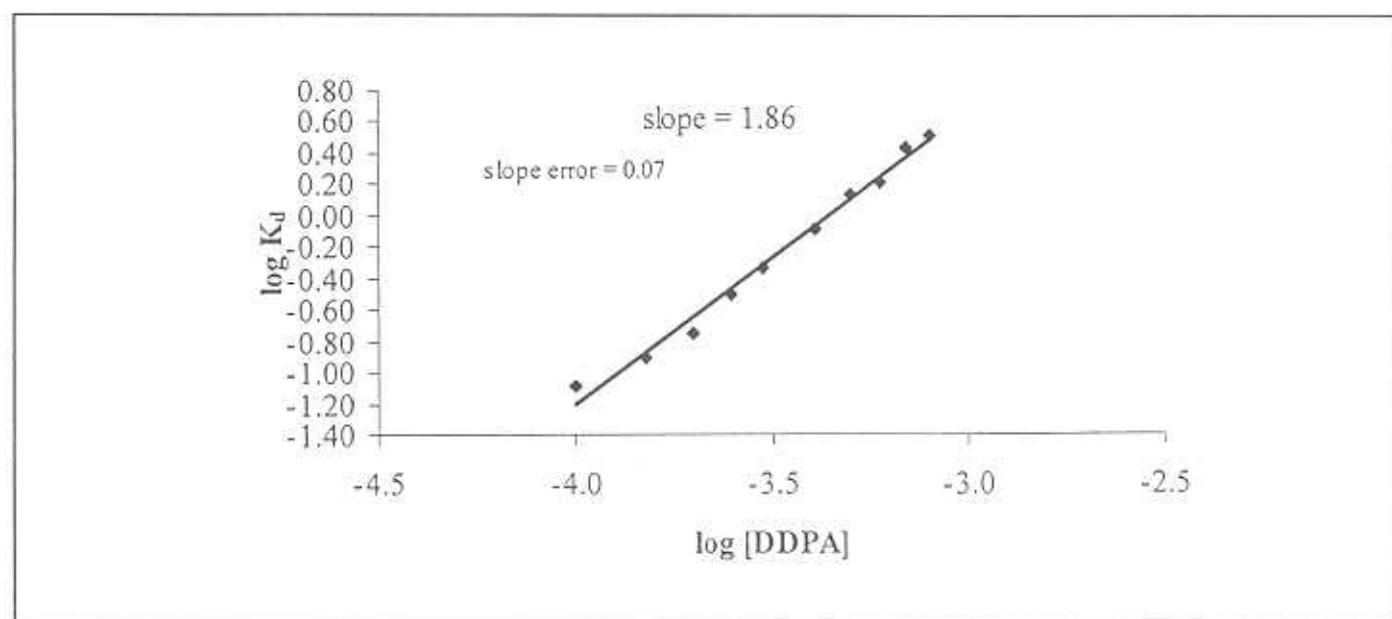


Figure 4. Variation of  $K_d$  with  $\log [\text{DDPA}]$  at 25 °C.

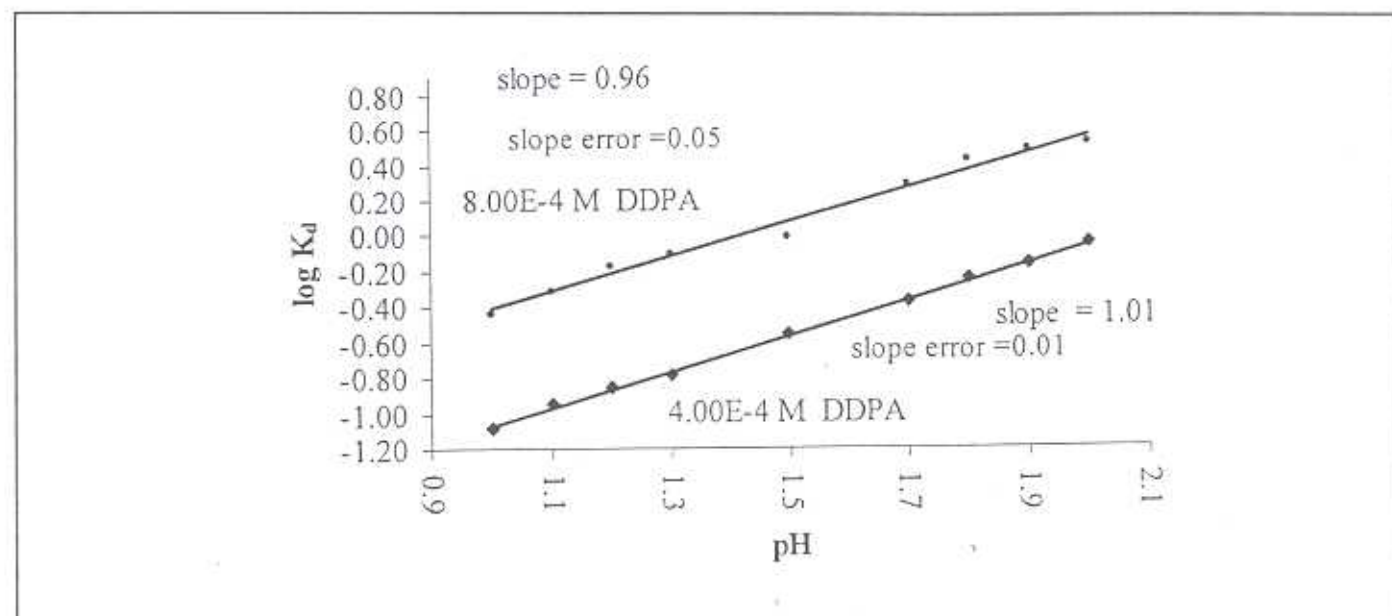


Figure 5. Variation of  $\log K_d$  with pH at 25 °C.

## SOLVENT EXTRACTION OF URANIUM (VI) BY DIDODECYLPHOSPHORIC ACID

**EFFECT OF EXTRACTANT CONCENTRATION:** From Fig. 4 it is seen that the  $K_d$  for U(VI) is directly second power dependent upon the DDPA concentration in the organic phase. However, since DDPA has been shown to be dimeric in toluene (Kondo *et al.*, 1989) then two dimer extractant molecules are involved in the formation of the uranium-DDPA complex.

**EFFECT OF pH:** From Fig. 5 it is seen that the  $K_d$  for U(VI) is directly first power dependent upon the pH. This dependence is shown for two different concentrations of DDPA ( $4.0 \times 10^{-4}$  M and  $8.0 \times 10^{-4}$  M) against an aqueous perchloric acid - sodium perchlorate solution of constant ionic strength of 0.10 M.

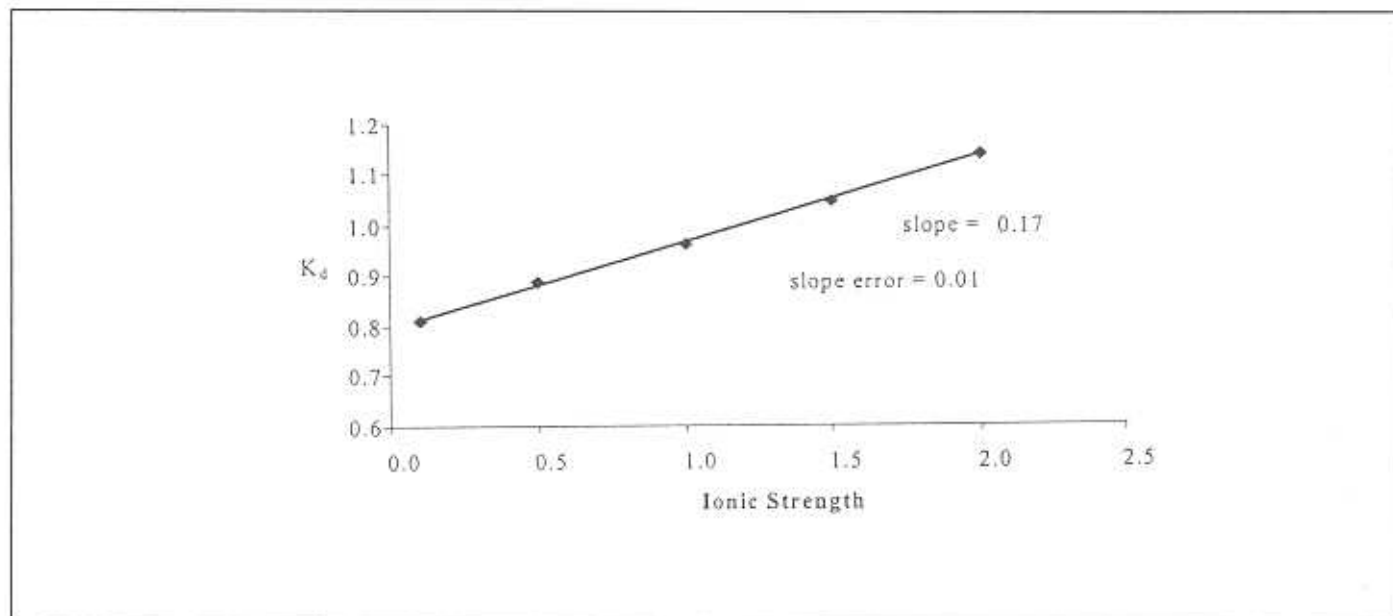


Figure 6. Variation of  $K_d$  with ionic strength,  $[DDPA] = 4 \times 10^{-4}$  M at 25C.

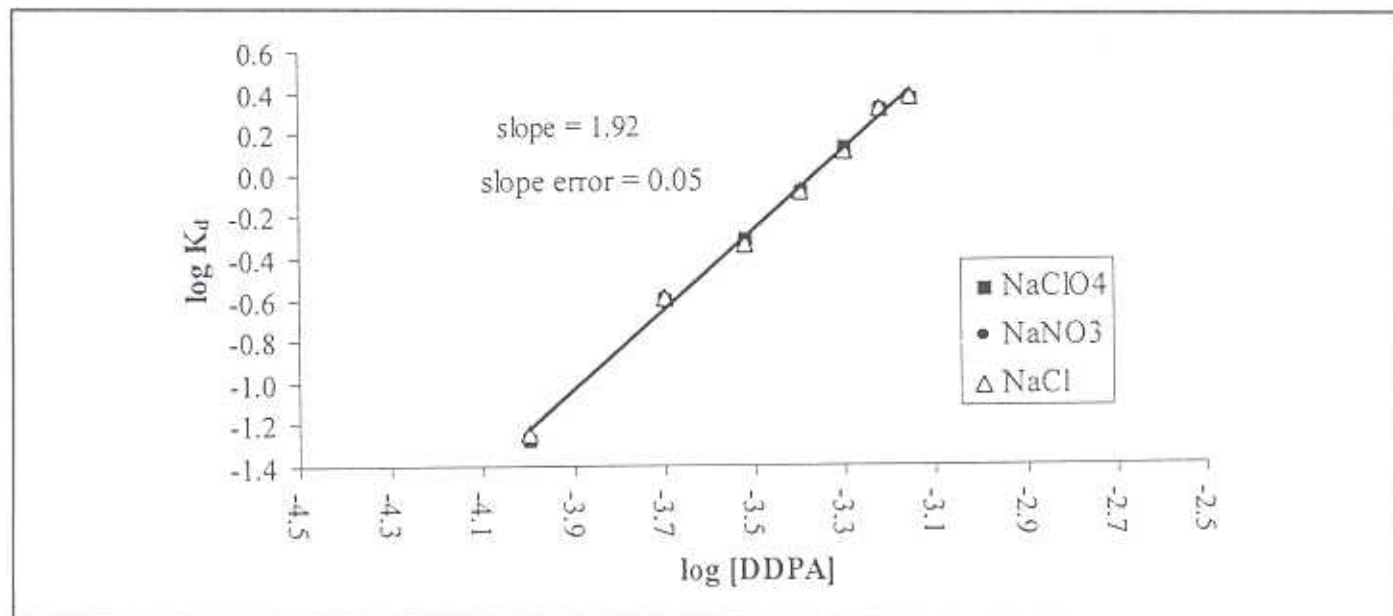


Figure 7. Variation of  $\log K_d$  with  $\log [DDPA]$  for different supporting electrolyte,  $[DDPA] = 4 \times 10^{-4}$  M at 25C.

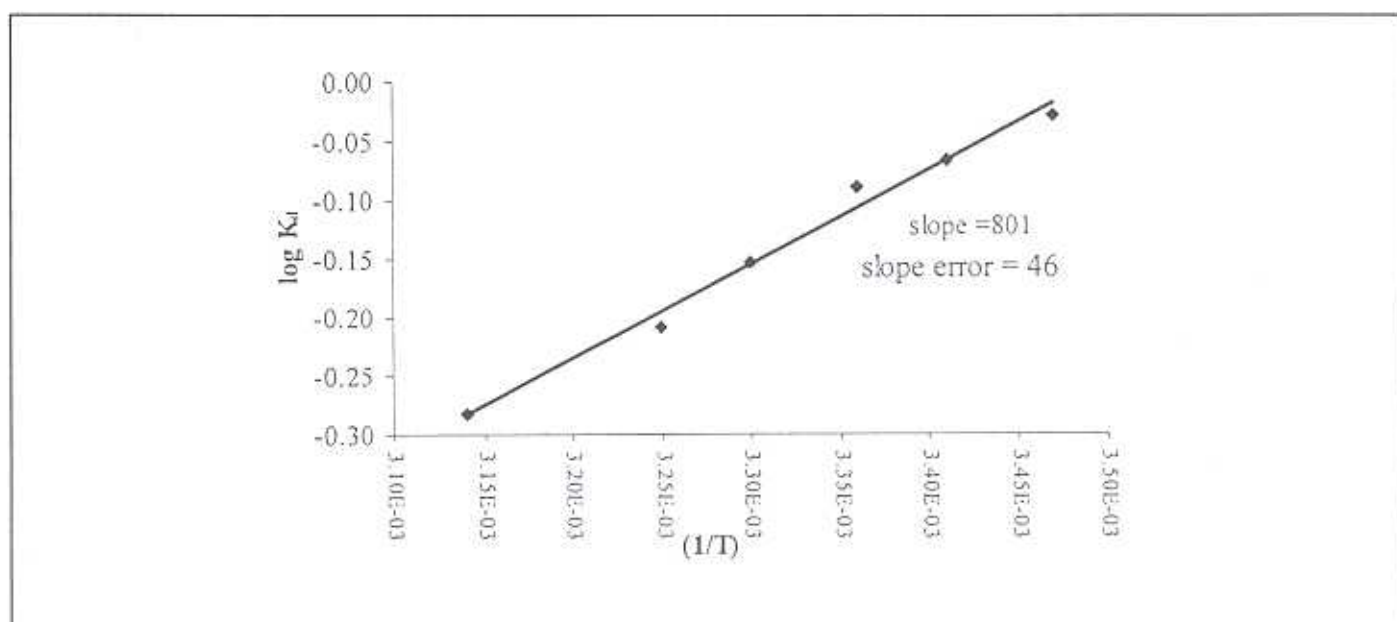
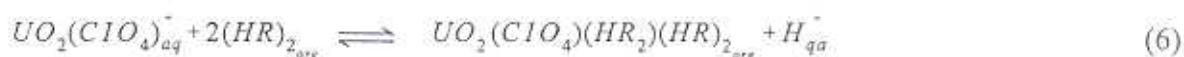
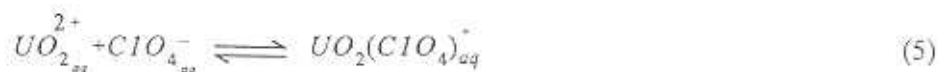


Figure 8. Variation of  $\log K_d$  with  $1/T$ ,  $[DDPA] = 4 \times 10^{-4}$  M.

From the extractant dependency and the pH dependency the extracted species can be written in the form  $UO_2(ClO_4)(HR)_2$  which means that a mixed ion exchange - solvation mechanism was involved in the extraction of U(VI) from perchlorate solution into DDPA solution according to the following equilibrium reactions.



Correspondingly, the extraction equilibrium constant is

$$K_{ex} = K_d [H^+]_{aq} / [(HR)_2]_{org}^2 \quad (7)$$

where,  $[H^+]$  is the concentration of the hydrogen ion in the aqueous phase,  $K_d$  is the distribution coefficient and  $[(HR)_2]_{org}$  is the concentration of DDPA dimer in the organic phase at equilibrium. Substitution of the previous values in equation (3) gives  $K_{ex} = 3.64 \times 10^{+5}$ . A similar mechanism was found by many authors (Luginin *et al.*, 1976; Rozen 1973; Schmid *et al.*, 1972) for the extraction of U(VI) by dialkylphosphoric acid extractants.

**EFFECT OF IONIC STRENGTH:** Fig. 6 shows that the  $K_d$  increases as the ionic strength ( $I$ ) increase. This is explained by the increase of the thermodynamic activity of the metal salt extracted and the decrease of the activity of water as the ionic strength increase (Kolarik, 1982).

**EFFECT OF SUPPORTING ELECTROLYTE:** In Fig. 7, the  $K_d$  for U(VI) is seen to vary directly with the second power of the DDPA concentration in the organic phase at a constant ionic strength of 0.10 M, the anion being  $ClO_4^-$ ,  $Cl^-$  or  $NO_3^-$ . From the data shown in Fig. 7 it is clear that the  $K_d$  value is independent of the type of the supporting electrolyte. This is explained by the fact that at 0.10 M ionic strength or less, the electrolyte effect is independent of the kind of ions and dependent only upon the ionic strength (Skoog *et al.*, 1990).

**EFFECT OF TEMPERATURE:** It is seen from the data in Fig. 8 that the  $K_d$  values decrease with increasing temperature and this is in agreement with the behavior reported for the extraction of U(VI) ion. The Van't Hoff's equation in the form



## SOLVENT EXTRACTION OF URANIUM (VI) BY DIDODECYLPHOSPHORIC ACID

given by equation (8) can be used to calculate the enthalpy change ( $\Delta H$ ) associated with extraction of U(VI)

$$\frac{\Delta \log K_d}{\Delta(1/T)} = \frac{-\Delta H^\circ}{2.303R} \quad (8)$$

The plot of  $\log K_d$  vs.  $1/T$  is shown in Fig. 8. The plot is linear in agreement with equation (8). The value of  $\Delta H$  obtained from this plot using least squares method is  $15.3 \pm 0.8 \text{ kJ mol}^{-1}$ . It is seen that extraction of U(VI) is exothermic. The values of free energy and entropy changes were calculated using equations (9) and (10)

$$\Delta G^\circ = -RT \ln K_{ex} \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

and these values were found to be  $\Delta G^\circ = -31.7 \pm 2.1 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 55.0 \pm 5.3 \text{ JK}^{-1} \text{ mol}^{-1}$ . A positive entropy change accompany the dehydration of U(VI) ion which is known to be highly hydrated. The extraction system was found to be spontaneous.

### Conclusion

The equilibrium study of the extraction of uranium(VI) ion with didodecylphosphoric acid was carried out. The extracted species into toluene diluent was found to be  $\text{UO}_2(\text{ClO}_4)(\text{HR}_2)(\text{HR})_2$ . The extraction equilibrium constant was obtained and the extraction system was found to be spontaneous due to the positive entropy change as well as the negative enthalpy change which favors the extraction of U(VI) ion.

### References

- BAES C. F. Jr., 1962. *J. Inorg. Nucl. Chem.* **24**, 707.  
BAES C. F. Jr., ZINGARO, R. A. and COLEMAN, C. F. 1958. *J. Phys. Chem.* **62**, 129.  
BUNUS F. T., DOMOCOS, V. C. and DUMITRESCU, P. 1978. *J. Inorg. Nucl. Chem.* **40**, 117.  
DEAN J. A., *Chemical Separation Methods*, pp. 18-44. Van Nostrand Reinhold, New York (1969).  
KIWAN A. M., and AMIN, R. S. 1973. *J. Inorg. Nucl. Chem.* **35**, 3315.  
KOLARIK Z., 1982. *Gmelin Handbook of Inorganic Chemistry*. Vol. D2, 8th. Edition, p. 34. Springer-Verlag, Berlin.  
KONDO K., MOMOTA, K. and NAKASHIO, T. 1989. *Solvent Ext. Ion Exch.* **7**, 1027.  
LUGININ V. A., and TSERKOVINTSKAYA, I. A. 1976. *Porb. Soverm. Anal. Khim.* **1**, 148.  
MARCUS Y., and KOLARIK, Z. 1976. *J. Inorg. Nucl. Chem.* **38**, 1069.  
MASON G. W., GRIFFIN, H. E. and LEWEY, S. M. 1981. *J. Inorg. Nucl. Chem.* **43**, 391.  
MASON G. W., SCHOFER, N. L. and PEPPARD, D. F. 1970. *J. Inorg. Nucl. Chem.* **32**, 3911.  
PEPPARD D. F., MASON, G. W. DRISCOLL, W. J. and MCCARTY, S. 1959. *J. Inorg. Nucl. Chem.* **12**, 141.  
PEPPARD D. F., MASON, G. W. MAIER, J. L. and DRISCOLL, W. J. 1957. *J. Inorg. Nucl. Chem.* **4**, 334.  
PEPPARD D. F., MASON, G. W. and MOLINE, S. W. 1957. *J. Inorg. Nucl. Chem.* **5**, 141.  
ROZEN A. M., MARTYNOV, B. V. ANIKIN, V. I. and MAMAIEV, L. A. 1973. *Soviet Radiochem.* **15**, 120.  
SATO T., 1963. *J. Inorg. Nucl. Chem.* **25**, 109.  
SATO T., 1962. *J. Inorg. Nucl. Chem.* **24**, 699.  
SCHMID E. R., 1972. *Mikrochem. Acta* **544**.  
SKOOG D. A., WEST, D. M. and HOLLER, F. J. 1990. *Analytical Chemistry*, 5th. Edition, p. 136, Saunders College Publishing, Philadelphia.

Received 18 August 1997  
Accepted 11 May 1999