Asian Journal of Chemistry; Vol. 28, No. 3 (2016), 687-690

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19467

# Extraction Studies of Uranium(VI) from Sodium Perchlorate Medium

R.R. LAKHAN and S.D. PAWAR*

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai-400 098, India

*Corresponding author: Fax: +91 22 26528547; E-mail: sureshpawar2004@gmail.com

*Received*: 11 July 2015; *Accepted*: 14 August 2015; *Published online*: 5 December 2015; AJC-17676

Cyanex-923, extractant has been used for the extraction of U(VI) from sodium perchlorate medium. This metal ion was quantitatively extracted with Cyanex-923 extractant in toluene at pH 1.0. From the organic phase containing the extracted metal ion is stripped back with 4 M HCl solution. The effect of pH, reagent concentration, sodium perchlorate concentration, stripping agent, diluent and equilibration period on the extraction of U(VI) has been studied. The stoichiometry of the extracted species was determined on the basis of slope analysis method.

**Keywords: Uranium(VI), Sodium perchlorate, Extraction, Cyanex-923, Stripping.**

## INTRODUCTION

Liquid liquid extraction of U(VI) using extracting ligand, 2-(4-chlorophenyl)-8,9-dihydro-7*H*-pyrazolo[1,5-a]quinazolin-6-one has been studied [1]. Synthesis and characterization of N,N'-di-*p*-tolylpyridine-2,6-dicarboxamide (DTPDA) was carried out and used for extraction of U(VI) and Th(IV) from nitric acid solution [2]. Solvent extraction of U(VI) and V(V) separation from sulfate solutions using alamine 336 as an extractant in kerosene was also carried out [3]. Selective separation and preconcentration of U(VI) using tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-butylphosphate (TBP) were studied in strongly acidic conditions [4]. The extraction behaviour of U(VI) from an aqueous nitric acid medium employing a 2-hydroxy-1-naphthaldehyde thiosemicarbazone in ethyl acetate has been studied in presence of different extractant like trioctyl phosphine oxide (TOPO), DMSO and trioctyl amine (TOA) [5]. Solvent extraction of U(VI) from aqueous solutions of $NH_4SCN$ was studied in the presence of dibenzo-18-crown-6 [6]. The extraction behaviour of U(VI) and Th(IV) from nitrate solution was studied using Cyanex 923 (TRPO) in xylene. The metal ions are extracted into xylene as $Th(NO_3)_4 \cdot 2TRPO$ and $UO_2(NO_3)_2 \cdot 2TRPO$ [7]. N,N,N',N'-Tetrabutyladipamide (TBAA) was synthesized and used for the extraction of U(VI) and Th(IV) from $HNO_3$ solution in a diluent of 1,2,4-trimethyl benzene and kerosene [8]. The extraction behaviour of uranium(VI) from mixed organo-aqueous solution containing water-miscible protic aliphatic alcohols and several aprotic solvents was investigated by using dicyclohexano-18-crown-6 (DC18C6) as an extractant [9]. Studies on solvent extraction of U(VI) by chelating extractant LIX-54 and its mixtures with tri-*n*-butyl phosphate (TBP) in benzene diluent showed quantitative extraction at pH 4.3 [10]. A method was proposed for extraction of U(VI) at pH 5.5-6.0 from acetate solution using Versatic 911. The composition of the extracted species was $UO_2R_2 \cdot 2RH$ (RH = Versatic 911) [11].

## EXPERIMENTAL

Cyanex-923 extractant supplied by Cytec Industries Inc. Canada, were used without further purification. A known amount of Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved and diluted with double distilled water as per requirement. All other chemical used were of analytical grade. Elico model LI 120 pH meter with combined glass electrode was used for $H^+$ ions concentration studies and Shimadzu UV-visible recording spectrophotometer model UV-2401PC with 10 mm cortex quartz cuvettes for absorbance measurements.

**Procedure:** An aliquot of solution containing 200 µg of uranium(VI) and sodium perchlorate was adjusted to pH 1 with dilute HCl and $NH_4OH$ solutions. The solution was transferred to a separating funnel and equilibrated for 10 min with 10 mL of Cyanex-923 dissolved in toluene. The two phases were allowed to separate, the organic phase containing the metal extracted species was stripped with 4.0 M HCl and determine spectrophotometrically by Arsenozo-I [12]. All the experiment were carried out at room temperature except the effect of temperature on distribution equilibria.

## RESULTS AND DISCUSSION

**Effect of pH:** Extraction of U(VI) with Cyanex-923 diluted in toluene was carried out in the pH range 1-7. With the decreasing pH extraction increases and it becomes quantitative in the pH range 1-2. Hence all the extractions carried out at pH 1 (Fig. 1).

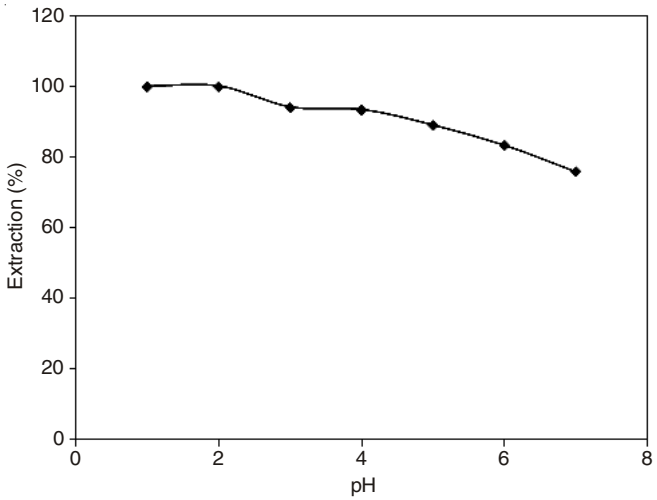


Fig. 1. Effect of pH on percentage extraction of U(VI) with Cyanex-923 in toluene

**Effect of reagent concentration:** Uranium was extracted with various concentration of Cyanex-923 in toluene from $0.25 \times 10^{-4}$ to $1 \times 10^{-2}$ M, keeping other parameters like sodium perchlorate concentration, period of equilibration, diluent and temperature constant. It was found that the extraction increased with increase in the reagent concentration. The extraction of U(VI) was quantitative in the range $2.5 \times 10^{-3}$ M to $1 \times 10^{-1}$ M Cyanex-923 in toluene. Hence all the extractions were carried out at fixed concentration of $2.5 \times 10^{-3}$ M Cyanex-923. The minimum reagent concentration required for the complete extraction of U(VI) was $2.5 \times 10^{-3}$ M in toluene which is less compared to other extractants (Table-1).

TABLE-1
COMPARISON OF CYANEX-923 EXTRACTANT WITH OTHER EXTRACTANTS

| Extractants | Reagent concentration | Ref. |
|---|---|---|
| Synergistic mixture of PC88A and octyl(phenyl)-N-N-diisobutyl carbamoyl methyl phosphine oxide | 0.9 M and 0.1 M respectively | [13] |
| Dibenzo-18-crown-6 | 0.01 M | [6] |
| Petroleum sulfoxide | 0.3 - 0.4 M | [14] |
| Mixture of PC88A and Cyanex-923 in dodecane | 0.6 M and 0.15 M respectively | [15] |
| Mixture of aliquat 336 and TBP | 0.1 M and 0.06 M respectively | [16] |

**Effect of sodium perchlorate concentration:** The effect of sodium salicylate concentration on the percentage extraction of U(VI) with 0.0025 M Cyanex-923 in toluene at fix pH of 1 was studied in the sodium perchlorate range from $0.5 \times 10^{-3}$ to $1.0 \times 10^{-2}$ M. As the sodium perchlorate concentration increases the extraction goes on increasing and becomes quantitative in the range $5 \times 10^{-3}$ M to $1.0 \times 10^{-2}$ M with Cyanex-923 in toluene. Hence all the extractions were carried out at $5 \times 10^{-3}$ M sodium perchlorate with Cyanex-923.

**Effect of stripping agents:** The extracted uranium(VI) in the organic phase of Cyanex-923 was stripped with different strengths of acids like HCl, $HNO_3$, $H_2SO_4$ and $HClO_4$. The complete recovery of U(VI) from metal loaded Cyanex-923 was found with 4 M HCl solution (Table-2).

TABLE-2
EFFECT OF STRIPPING AGENTS ON PERCENTAGE RECOVERY OF URANIUM(VI) FROM METAL LOADED ORGANIC PHASE OF CYANEX-923 IN TOLUENE

| Molarity ($mol/dm^3$) | Percentage recovery of U(VI) with strippants | | | |
|---|---|---|---|---|
| | HCl | $HNO_3$ | $H_2SO_4$ | $HClO_4$ |
| 1 | 67.0 | 12.9 | 18.8 | 2.3 |
| 2 | 73.8 | 11.9 | 17.5 | 5.9 |
| 3 | 80.3 | 7.8 | 13.6 | 8.3 |
| 4 | 99.9 | 0.0 | 10.3 | 9.8 |

**Influence of diluents and effect of equilibration period:** The extraction of U(VI) with Cyanex-923 was carried out using different aliphatic and aromatic diluents like toluene, carbon tetrachloride, chloroform, xylene, *n*-hexane and cyclohexane. Quantitative extraction of U(VI) was observed with all the above diluents except that of chloroform (96.9 %) and carbon tetrachloride (69.6 %). Toluene is preferred as the best diluents because of its better phase separation.

Extraction equilibrium was studied for different periods of shaking ranging from 1 to 30 min. It was observed that 1 min of shaking period was sufficient for quantitative extraction of U(VI) with $2.5 \times 10^{-3}$ M Cyanex-923 in toluene. However there was no adverse effect by increasing the extraction period upto 30 min.

**Stoichiometry of the extracted species:** It was necessary to evaluate the distribution coefficient (D) while varying the extractant concentration to ascertain the nature of the extracted species. In order to determine the stoichiometry of the extracted species a graph of log D *versus* log R (R = Cyanex-923) at the fixed pH of 1 was plotted (Fig. 2). The slope obtained was 2.98, which is around 3 indicating that three molecules of Cyanex-923 react with one molecule of U(VI) ion. Hence the probable stoichiometric ratio of U(VI) to Cyanex-923 is 1:3. The slope of log $D_{U(VI)}$ *versus* log $[ClO_4^-]$ is 1.98 indicating two molecules of perchlorate react with one molecule of U(VI) (Fig. 3). The probable extracted species of U(VI) in the organic phase is $UO_2(ClO_4)_2$. 3Cyanex-923, similar to the earlier reported with TOPO [17].

**Influence of temperature:** Extraction of uranium(VI) with $2.5 \times 10^{-3}$ M Cyanex-923 in toluene at a pH 6 having sodium perchlorate concentration of $5 \times 10^{-3}$ M, were carried out at different temperature (303-343 K). The distribution ratio decreased with increase in temperature. The van't Hoff equation is, $\log D_{U(VI)} = -(\Delta H/2.303RT) + C$, where $D_{U(VI)}$ represent the distribution ratio, $\Delta H$ is the enthalpy change for the reaction and C is the constant. The slope obtained from plot of log $D_{U(VI)}$ *vs.* $1/T \times 1000$ is 0.312 (Fig. 4). The $\Delta H$ values obtained is -5.974 kJ/mol, indicating that the reaction is exothermic in nature.

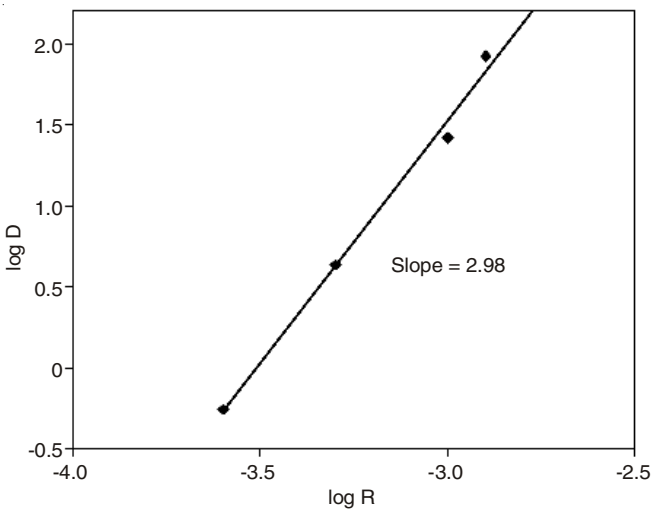


Fig. 2. Effect of reagent concentration on distribution ratio of U(VI)

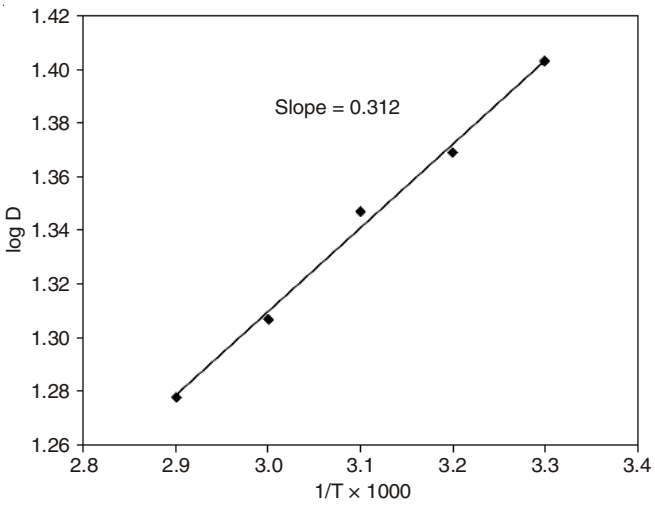


Fig. 4. Effect of temperature on distribution ratio of U(VI)

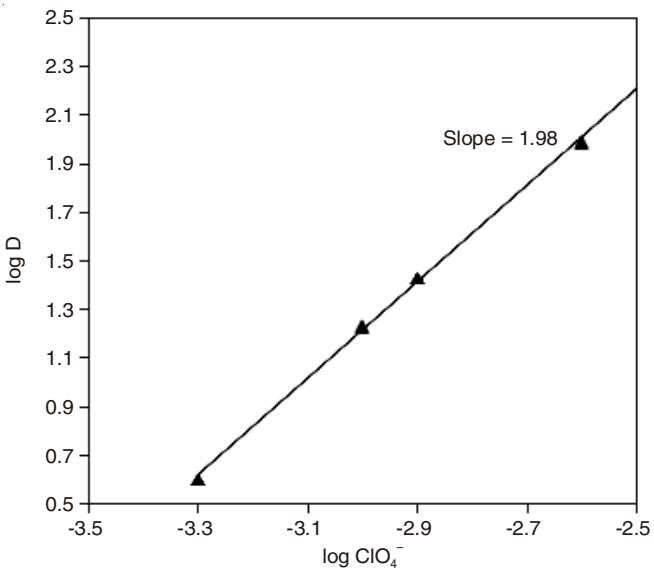


Fig. 3. Effect of sodium perchlorate concentration on distribution ratio of U(VI)

**Separation of uranium(VI) from other metal ions:** Uranium(VI) was separated mainly from Th(IV) and various other metal ions. This was made possible by exploiting the differences in their respective extracting and stripping conditions. In order to separate U(VI) and Th(IV), the difference in their pH and stripping agents were exploited. Uranium(VI) and Th(IV) were first extracted with $2.5 \times 10^{-3}$ M Cyanex-923 in toluene at a fixed pH of 1 and the solution having sodium perchlorate concentration of $5 \times 10^{-3}$ M when both the metal ions get simultaneously extracted. Uranium(VI) was first stripped completely with 4 M HCl and then Th(IV) was stripped with 7 M $HClO_4$. Thus U(VI) was separated from Th(IV). Uranium(VI) was also separated from various other metal ions such as Be(II), Ni(II), Ce(IV) and La(III) (Table-3).

## Conclusions

• The results obtained show that Cyanex-923 in toluene can be used effectively for quantitative extraction of U(VI) from sodium perchlorate media at pH 1. The U(VI) was extracted quantitatively in the sodium perchlorate range of $5 \times 10^{-3}$ M to $1 \times 10^{-2}$ M using $2.5 \times 10^{-3}$ M Cyanex-923 in toluene.

• The thermodynamic study of the extraction reaction of U(VI) with Cyanex-923 in toluene revealed that the extraction reaction is exothermic in nature with an enthalpy change (ΔH) value of -5.974 kJ/mol.

• Stripping of U(VI) is observed with 4 M HCl at room temperature however 65 °C is required for stripping of U(VI) with concentrated phosphoric acid when synergistic mixture of di-nonyl phenyl phosphoric acid and tri-*n*-butyl phosphate is used [18].

TABLE-3
SEPARATION OF U(VI) FROM MULTICOMPONENT MIXTURES WITH CYANEX 923 IN TOLUENE

| Sr. No. | Metal ions | Amount taken (μg) | pH | Sodium perchlorate (M) | Extractant Cyanex-923 | Stripping agents | Recovery (%) |
|---|---|---|---|---|---|---|---|
| 1 | U(VI) | 200 | 1 | $5 \times 10^{-3}$ M | $2.5 \times 10^{-3}$ M | 4 M HCl | 99.5 |
| | Th(IV) | 100 | – | – | – | 7 M $HClO_4$ | 99.2 |
| 2 | U(VI) | 200 | 1 | $5 \times 10^{-3}$ M | $2.5 \times 10^{-3}$ M | 4 M HCl | 99.7 |
| | Be(II) | 50 | – | – | – | Un extracted | 99.1 |
| 3 | U(VI) | 200 | 1 | $5 \times 10^{-3}$ M | $2.5 \times 10^{-3}$ M | 4 M HCl | 99.5 |
| | Ni(II) | 50 | – | – | – | Unextracted | 99.4 |
| 4 | U(VI) | 200 | 1 | $5 \times 10^{-3}$ M | $2.5 \times 10^{-3}$ M | 4 M HCl | 99.6 |
| | Th(IV) | 100 | – | – | – | 7 M $HClO_4$ | 99.3 |
| | Ce(IV) | 50 | – | – | – | Unextracted | 99.4 |
| 5 | U(VI) | 200 | 1 | $5 \times 10^{-3}$ M | $2.5 \times 10^{-3}$ M | 4 M HCl | 99.4 |
| | La(III) | 50 | – | – | – | 2 M HCl | 99.3 |
| | Ce(IV) | 50 | – | – | – | Unextracted | 99.2 |

## ACKNOWLEDGEMENTS

The authors are thankful to Cytec Industries Inc. Canada for supplying Cyanex-923 as a gift sample.

## REFERENCES

1. G.M. Hussein and A.M.A. Morsy, *Chem. Technol. An Indian J.*, **9**, 140 (2014).
2. P. Hu, L. Qian, Y. He, H. Wang and W. Wu, *J. Radioanal. Nucl. Chem.*, **297**, 133 (2013).
3. J.R. Kumar, J.-S. Kim, J.-Y. Lee and H.-S. Yoon, *J. Radioanal. Nucl. Chem.*, **285**, 301 (2010).
4. A.R. Ghiasvand and E. Mohagheghzadeh, *Anal. Sci.*, **20**, 917 (2004).
5. S. Banerjee, M. Bhar and S. Basu, *Radiochim. Acta*, **91**, 593 (2003).
6. S.M. Sawant, *J. Radioanal. Nucl. Chem.*, **249**, 613 (2001).
7. S.K. Sahu, M.L.P. Reddy, T.R. Ramamohan and V. Chakravortty, *Radiochim. Acta*, **88**, 33 (2000).
8. Y.-S. Wang, G.-X. Sun, Y.-L. Li, B.-R. Bao, J.-W. Liu, X.-Y. Sun and J.-J. Mao, *Nucl. Sci. Technol.*, **8**, 103 (1997).
9. J.P. Shukla, A. Kumar and R.K. Singh, *Talanta*, **40**, 1261 (1993).
10. S. Singh, V. Chakravortty and K.C. Dash, *J. Radioanal. Nucl. Chem.*, **122**, 137 (1988).
11. U.S. Ray and S.C. Modak, *J. Indian Chem. Soc.*, **61**, 561 (1984).
12. Z. Marczenko, Spectrophotometric Determination of Elements, Ellis Horwood, p. 539 (1976).
13. S.K. Singh, P.S. Dhami, A. Dakshinamoorthy and M. Sundersanan, *Sep. Sci. Technol.*, **44**, 491 (2009).
14. S. Zhou, J. Ji, G. Chen, H. Du and J. Mao, *He Huaxue Yu Fangshe Huaxue*, **16**, 13 (1994).
15. S.K. Singh, S.K. Misra, S.C. Tripathi and D.K. Singh, *Desalination*, **250**, 19 (2010).
16. A. W. Lothongkum, P. Ramakul, W. Sasomsub, S. Laoharochanapan and U. Pancharoen, *J. Taiwan Inst. Chem. Eng.*, **40**, 518 (2009).
17. M. Konstantinova, *Dokl. Bolg. Akad. Nauk*, **30**, 1431 (1977).
18. H. Singh, S.L. Mishra and R. Vijayalakshmi, *Hydrometallurgy*, **73**, 63 (2004).