

Ternary Complex Formation of Uranium(VI) and its Extraction with Tri-n-butyl phosphate and 8-Hydroxyquinoline

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1. Introduction

The ternary complex formation of metal ions with ligand in an aquatic solution has been of interest in various research fields such as synergistic extraction, spectrophotometry, spectrofluorometry, solubility and sorption of radionuclides in an environment. When the metal ion extraction based on its formation of a ternary complex with two additives shows much higher extraction efficiency as compared to the extractions by an individual additive, it is classified as a synergistic extraction. Synergistic extraction uses a neutral donor in combination with an acidic chelating ligand. The chelating ligand neutralizes the charge of a metal ion to form an uncharged extractable complex having sites for water molecules, which can be replaced by the neutral donors to form an organophilic adduct. The most common acidic chelating ligands are β -diketones or organophosphorous acids, and neutral donors are amine derivatives or organophosphorous compounds such as alkylphosphates and alkylphosphine oxides.

Development of sensitive and selective analytical instruments such as ICP-AES and ICP-MS makes an analyst be free from the trouble to separate analyte. However, sometimes, the removal of matrix from an analyte is required to increase sensitivity and to decrease background level and hysteresis of an instrument. Solvent extraction is one of the most important techniques in concentration and purification of U(VI).

The purpose of this study is an understanding of a ternary complex formation of U(VI) in the presence of pyridine derivatives and TBP. The solvent extraction technique was used, and the results was explained by a stability of U(VI)-chelating ligand complexes. The result of this study could be applied to the concentration and separation of U(VI) from the sea water.

2. Experimental

Except for the experiments for a diluent influence, cyclohexane was used as an organic solvent. U(VI) of 1.0×10^{-4} mol/L in 0.1 mol/L (Na,H)ClO₄ was extracted with the organic phase containing oxine (8-hydroxyquinoline) and TBP (tri-n-butyl phosphate) at various pHs (2 to 5), concentrations of TBP (0.05 to 1 mol/L) and of oxine (0.5×10^{-4} to 5×10^{-4} mol/L), and kinds of organic solvent. The extraction coefficient was determined by shaking equal volume of two phases for 30 minutes. After phase separation by using centrifuge (IEC Centra-4B, 3500 rpm for 30 min), pH (Orion

720A+) was measured, U(VI) concentration in the aqueous phase was determined by ICP-AES (ULTIMA2C, Jobin Yvon) and that in the organic phase was calculated by a mass balance. Extraction coefficient was calculated as the ratio of uranium concentration in an organic phase to that in an aqueous phase.

3. Results and discussion

3.1. Design of the synergistic extraction system. The design of extraction system in an analysis of metal ion should consider various factors such as high separation efficiency for a concentration of trace metal ion, easy stripping for a determination in aqueous phase, group, element or species separation corresponding to the selectivity of a determination instrument, small additives for an economical efficiency and the protection of the environment, and an acceleration of a separation reaction for a numerous sample.

TBP has been used for several decades as the most successful extractant for a recovery of uranium from various matrices. Oxine has been used for the U(VI) separation by using a precipitation of a self adduct or by extracting the adduct into an organic phase. The stability of a synergistic adduct in the system of oxine and neutral donors is influenced by the basicity of an additive, and shows the trend of TBP < DBBP (di-butylbutyl phosphonate) < DOSP (di-octyl sulphoxide) < TOPO (tri-octylphosphine oxide) in NaCl and benzene media [1]. This trend suggests TOPO as the most effective synergist with oxine for the extraction of U(VI). However, to be applied to an analysis of U(VI) from a natural water on the premises, other factors should be considered such as the extraction capacity, stability and reusability of a reagent, easiness in a stripping or back extraction, applicability to various techniques such as a column extraction. Generally, TOPO has a lower extraction capacity than TBP, and TOPO requires a solvent to be used in a column extraction. The low extraction efficiency of TBP could be increased by dissolving a small amount of TOPO. The effect of NaCl and property of diluent are to be studied for the application to the uranium separation from a seawater.

3.2. Diluent effect. The effect of diluent on the extraction efficiency of U(VI) was measured and the result was shown at Fig. 1. Cyclohexane shows the highest efficiency in the measured diluents.

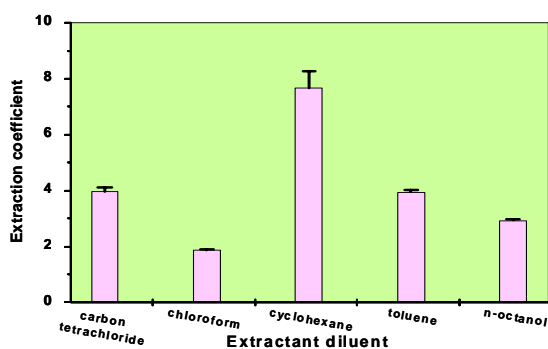


Fig. 1. U(VI) extraction coefficient at various diluents. [TBP]=2.0 mol/L, [oxine]= 2×10^{-4} mol/L, [U]= 1.0×10^{-4} mol/L, pH 4.0.

3.3. *Effect of chelating ligands.* Pyridine-2,6-dicarboxylic acid (PDA) and picolinic acid were tested as a chelating ligands in the extraction of U(VI) with TBP. In the case of picolinic acid, although the extraction coefficient increased with its increasing concentration, the synergism was much lower than the case of oxine. PDA shows a different dependence on its concentration in an extraction coefficient as shown at Fig. 2. Extraction coefficient increased with increasing PDA concentration within the range of $[PDA] \leq [U(VI)]$ where 1:1 neutral species of $\{UO_2L\}^0$ is extracted by forming an adduct with TBP. If the PDA concentration is larger than that of U(VI), the formation of negatively charged species ($\{UO_2L_n\}^{2-2n}$, $n=2$ or 3) hinders the extraction.

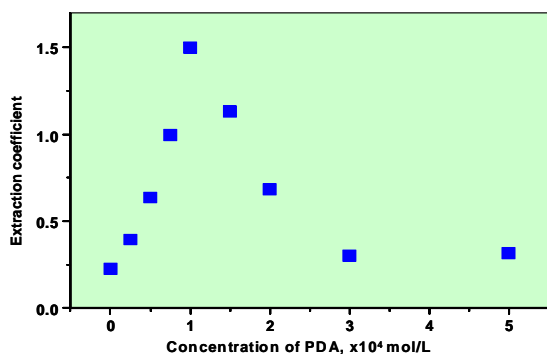


Fig. 2. Effect of PDA concentration on the extraction coefficient of U(VI) in the presence of TBP. [TBP]=1.0 mol/L, [U(VI)]= 1.0×10^{-4} mol/L, pH=3.5 \pm 0.3

3.4. *Extraction by oxine and TBP in NaClO₄ and cyclohexane media.* The plots of the logarithmic extraction coefficients of U(VI) against the logarithmic concentrations of TBP and oxine showed the slope of 1 and 2, respectively. This indicates that the species extracted into an organic phase has a structure of $\{UO_2(OX)_2(TBP)\}^0_{org}$. The plot of the logarithmic extraction coefficients of U(VI) against pH was shown at Fig. 3. The slope is 2 at pH>3. It supports the coordination of two deprotonated oxines in a neutral U(VI)-chelating ligand complex formation. TBP enhances the extraction by coordinating its oxygen of a

phosphoryl group to the U(VI) ion in a neutral complex and replacing a water molecule. TBP does not release any hydrogen ions as a result of a dissociation, therefore, the extraction is not affected by the acidity of the solution. The formation of $\{UO_2(OX)_2(TBP)\}^0_{org}$ in NaClO₄ and cyclohexane media coincides with the species formation in NaCl and benzene media[1].

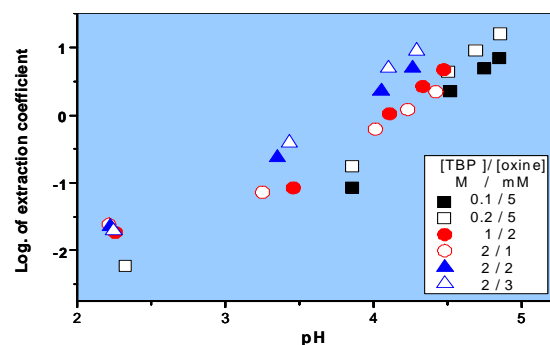


Fig. 3. U(VI) extraction coefficient at various pHs. [TBP]=0.1 to 2.0 mol/L, [oxine]=1 to 5×10^{-4} mol/L, [U]= 1.0×10^{-4} mol/L.

Synergism is the largest for oxine compared to picolinate and PDA. This can be understood as a result of the stability difference in the U(VI)-chelating ligand complexes. The stability of the U(VI) complex with picolinate is too small to form a large amount of neutral species of $\{UO_2L_2\}^0$ prior to the $\{UO_2L_2(TBP)\}^0_{org}$ formation, while that with PDA is so large that the coordination of TBP should compete with the formation of the hydrophilic species of $\{UO_2L_n\}^{2-2n}$ ($n=2$ or 3).

4. Summary

Ternary complex formation of U(VI) in the presence of pyridine derivatives and TBP was studied by an extraction technique. The difference of the synergistic effect in the extraction (picolinate < PDA < oxine) was explained by the difference in the stability of the U(VI)-chelating ligand complexes. The stability should be appropriate to form a large amount of neutral species prior to the formation of an organophilic adduct.

Acknowledgements

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REFERENCE

- [1] A.G. Godbole, R. Swarup, S.K. Patil, J. Radioanal. Nucl. Chem., Letters 94 (1985) 321.