Extraction of Uranium Ions from Nitric Acid Solution using N,N,N',N'-tetrabutyl-3-oxapentanediamide(TBOD) into Supercritical Carbon Dioxide

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1. Introduction

To extract uranium ions, we applied to N,N,N',N'-tetrabutyl-3-oxapentanediamide (TBOD) as a alternative ligand in supercritical CO_2. Generally, tributylphosphate (TBP) as an organophosphorous ligand was used to extract the uranium ions or oxides in supercritical CO_2 [1-4]. There are several problems such as secondary radioactive wastes and vulnerability to high radiation fields [5, 6]. Diamides can be completely incinerated, resulting in the advantages of no secondary wastes. Additionally, diamides have high irradiation stability and a strong affinity to metallic ions such actinides in acidic solutions [7, 8]. CO_2 is a good solvent for the minimization of the organic wastes because of its easy recycle [9]. This study deals with the solubility of TBOD, TBOD-HNO_3 and TBOD-HNO_3-UO_2(VI) and the extraction of uranium ions using TBOD in supercritical CO_2.

2. Experimental and Results

2.1 Chemicals

TBOD was synthesized by modification of the procedures given by a previously published method[10]. The uranium nitrate (1,000 ppm, atomic absorption standard solution) was obtained from Aldrich. The uranium oxides powder, which is non-irradiated, was obtained from Korea Atomic Energy Research Institute. TBOD-HNO_3 complex and TBOD-HNO_3-UO_2(VI) complex were prepared by the same method reported for the preparation of TBP complexes[11]. All other cited chemicals used were of analytical reagent grade.

2.2 Solubility of TBOD and its complexes in liquid / supercritical CO_2

A variable volume cell was used for solubility measurements. A desired amount of TBOD (or its complexes) was loaded into the cell, and sealed. After the temperature of the cell was raised up to a desired value, liquid CO_2 was inserted the cell through a syringe pump. TBOD (or its complexes), placed inside, was mixed with CO_2 by a magnetic bar inside. When the mixture turned into a clear single phase, we measured the applied pressure and the volume of the cell. These cloud points of TBOD in liquid and supercritical CO_2 were recorded at various temperatures (20, 40, 60℃). The figure 1 illustrates the single-phase limit in liquid and supercritical CO_2. TBOD turned out to be very soluble in CO_2 (mole fractions of 1×10^{-3} ~ 5.5×10^{-2} in CO_2). The solubility decreases with increasing temperature due to the density decrease and decreased solvating power of the fluid at higher temperature.

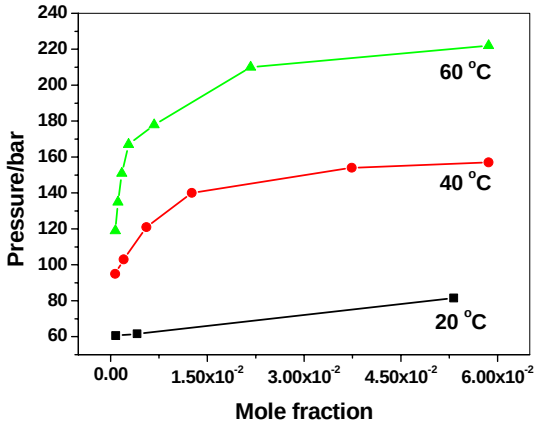

Figure 1. Solubility of TBOD at various temperatures (20, 40, 60 °C) in liquid / supercritical CO_2.

We also measured the solubility of TBOD-HNO_3 complex and TBOD-HNO_3-UO_2(VI) complex in broad ranges (temperature : 20, 40, 60 °C, pressure : 70~350 bar). The solubility of the complexes increases dramatically with the pressure, particularly at low temperatures. By compared with TBOD, the solubility pressure of its complexes was higher.

2.3 Extraction of uranium ions in nitric acid to supercritical CO_2 using TBOD

Uranium ions in the nitric acid solution were extracted using TBOD in supercritical CO_2. 5 ml of nitric acid solution containing uranium ions (250 μg) was taken into the 20 ml cell (Hanwoul Eng., Korea) and extraction test was performed. The supercritical CO_2 –TBOD mixture was supplied continuously into the cell. This dynamic extraction was done for 30 min. And then, neat CO_2 (without TBOD) was flushed for 30 min. After the extraction, the amount of U ions in nitric acid solution and that in the collecting solution were analyzed by ICP (ULTIM2C, JOBINYVON/HORIBA).

Figure 2 shows the extraction rate of U ions with respect to nitric acid molarity.

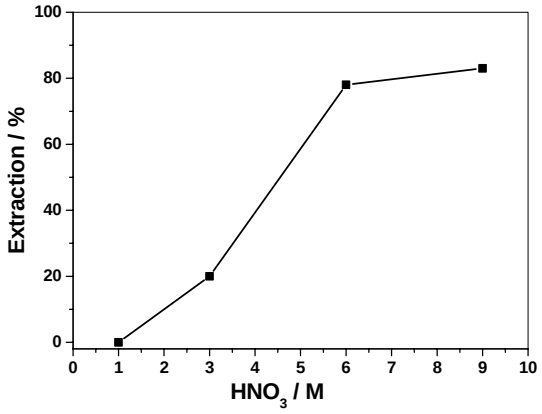

Figure 2. Extraction efficiency of uranium ion as a function of HNO_3 mol-concentration. (2.1×10^{-4} M U(VI), 2.7 mmol TBOD, 40℃, 150 bar)

Although the solubility of TBOD in supercritical CO_2 was lower than TBP, the extraction efficiency was found to be higher than TBP. The extraction efficiency of TBOD (83%) was superior to that of TBP (< 40%) in extracting uranium ions. TBOD looks better affinity to metal ions than TBP does.

The main extraction reaction of M^{n+} by diamide derivatives is expressed HNO_3 concentration as

$$M^{n+} + n(NO_3^-) + aDA \leftrightarrow M(NO_3)_n(DA)_a$$

Where, DA is diamide derivatives such as TBOD. The reaction tends to shift to the right direction at a higher concentration of nitric acid. The figure 2 shows the shift trend to the right direction in stronger nitric acid solution under liquid/supercritical CO_2. The extraction efficiencies of uranium ions using TBOD increase with increasing concentration of nitric acid.

3. Conclusion

A new chelating ligand, N,N,N',N'-tetrabutyl-3-oxapentanediamide(TBOD), was applied to the extraction of uranium ions into supercritical CO_2. TBOD is an environmentally favorable (non-phosphorous) extractant with the affinity to strong acid solution. TBOD forms a complex with HNO_3, and this complex can extract uranium ions in HNO_3 and dissolve into liquid and supercritical CO_2. We measured the solubility of TBOD and its complexes, and they turned out to be very soluble in liquid and supercritical CO_2. Uranium ions in nitric acid were extracted using TBOD into supercritical CO_2. TBOD seemed the better in extracting U ions in nitric acid than TBP.

ACKNOWDGEMENT

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