

Actinide separation using solubility difference of the TBP complexes with their nitrates in supercritical carbon dioxide

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The uranium separation from the mixture of tri-*n*-butylphosphate (TBP) complexes of uranyl and neodymium nitrates was carried out in CO₂ at 313 K, 11 MPa. The concentration ratio of uranium to neodymium increased up to 1.5 times of the initial ratio, and it agreed well with the ratio estimated based on their solubilities in CO₂.

INTRODUCTION

In the nuclear fuel cycle, reprocessing of spent nuclear fuels is one of the key processes. The conventional method for the reprocessing, PUREX process, is well established one, but further development for a new process of reducing cost and minimizing waste amount is required as the next generation reprocessing.

In order to decrease the waste amount from the reprocessing, the use of supercritical CO₂ has been proposed[1-6]. The supercritical CO₂ has the appropriate properties as an extracting solvent, *i.e.*, low viscosity and high diffusivity, and its density can be easily adjusted to a suitable value for the extraction by changing its pressure and temperature [7]. The generation of waste solvents can be remarkably reduced compared with the ordinary solvent extraction processes, since the supercritical CO₂ becomes a gas by depressurization [8]. Some experiments of uranium extraction from simulated spent fuel have been carried out using CO₂ and tri-*n*-butylphosphate (TBP).

Figure 1 shows an example of the solubility data for the two TBP complexes in CO₂ [9]. The abscissa represents TBP mole fraction, x_{TBP} , defined as the following equation:

$$x_{TBP} = \frac{n_{TBPinComplex}}{n_{CO_2} + n_{TBPinComplex}} . \quad (1)$$

In this figure, the area over the curve shows the conditions where the complex and CO₂ are mixed homogeneously, on the other hand, the area below the curve, the complex and CO₂ cannot form a single phase. There were TBP mole fractions, x_{TBP} , which gave the maximum pressures for single phase formation for complexes, at approximately 0.03. When x_{TBP} was larger than 0.03, CO₂ was dissolved in the complex. On the other hand, the complex was dissolved in CO₂ when x_{TBP} was smaller than 0.03.

Two phases were generated from a single phase by decreasing the pressure of the fluid below the single formation pressure. The values of x_{TBP} attributing to the two phases are

considered to equal to those of intersection points of the solubility curve and the pressure line. As shown in Figure 1, the solubility curve of TBP uranyl nitrate complex was different with that of TBP neodymium nitrate complex. The difference of the solubility might be useful for the separation of the elements dissolving in CO₂.

In this study, we performed the uranium separation from the mixture of TBP complexes of uranyl and neodymium nitrates in CO₂ at 313 K, 11 MPa.

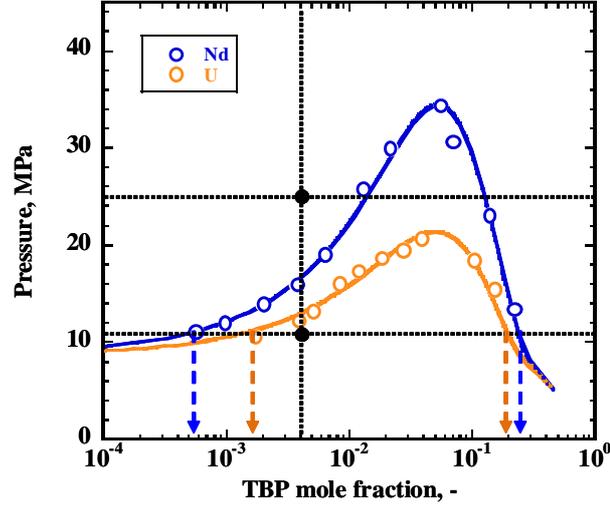


Figure 1 Phase diagram for TBP complexes of neodymium nitrate and uranyl nitrate in CO₂ at 313 K

CALCULATION

Before carrying out the experiment, we calculated the concentration ratios of neodymium and uranium, [Nd]/[U], in the samples, which would be obtained, from the experimental condition and the solubility data[9].

As mentioned above, the solubility data was summarized as the function of x_{TBP} defined as the ratio of TBP and CO₂. However, the mole fraction of metal and CO₂, x_{metal} , is more understandable and convenience than x_{TBP} in order to calculate separation. Therefore, metal fraction, x_{metal} , in the sample was calculated from x_{TBP} as follows:

$$x_{metal,G} = \frac{x_{TBP,G}}{\left[\frac{[TBP]}{[Metal]} \right]_{Initial\ Sample}}, \quad (2)$$

$$x_{metal,L} = \frac{x_{TBP,L}}{\left[\frac{[TBP]}{[Metal]} \right]_{Initial\ Sample}} \quad (3)$$

where the subscript G and L represents the gas phase sample and the liquid phase sample, respectively. To calculate [Nd]/[U], we introduced a correction value, $V_{Nd/U}$, which was the volume mixing ratio of TBP-neodymium nitrate and TBP-uranyl nitrate at the preparation of

the complex. The value of [Nd]/[U] for each phase sample was calculated as follows:

$$\left[\frac{[\text{Nd}]}{[\text{U}]} \right]_{\text{G}} = V_{\text{Nd/U}} \frac{x_{\text{Nd,G}}}{x_{\text{U,G}}}, \quad (4)$$

$$\left[\frac{[\text{Nd}]}{[\text{U}]} \right]_{\text{L}} = V_{\text{Nd/U}} \frac{x_{\text{Nd,L}}}{x_{\text{U,L}}}. \quad (5)$$

We determined the experimental condition as follows: the molar ratio of neodymium and uranium in the initial complex were set at 0.181 to be the near ratio of uranium and other elements in spent fuel. Because of the pressure capacity of our experimental apparatus, the pressure for dissolving and separation were set at 25 and 11 MPa, respectively. The TBP mole fraction was 0.04 that was an enough fraction to dissolve all complexes in CO₂ at 313 K.

The values of [Nd]/[U] obtained from by using Eqs. (4) and (5) was summarized in Table 1. As for the solubility data, we used the solubility data at 313 K in Figure 1, which were for the two TBP complexes shown in Table 2 in the next section. The values of denominator in Eqs. (2) and (3) were the ratio of TBP and metal shown in Table 2. As shown in Table 1, it estimated that uranium, whose complex has a higher solubility in CO₂ than that of neodymium complex, would be concentrated in the gas phase sample, while neodymium would be concentrated in the liquid phase sample.

Table 1 Calculated concentration ratio of neodymium and uranium

Sample	[Nd]/[U]
Gas phase sample	0.13
Liquid phase sample	0.29

MATERIAL AND METHOD

TBP Complex

A TBP complex containing neodymium and uranium was prepared by mixing two complexes containing neodymium nitrate or uranyl nitrate. The each complex was prepared as follows: an excess amount of neodymium nitrate hexahydrate (Wako Chemical Pure Industries, Ltd., Japan) or uranyl nitrate was dissolved in TBP (Wako Chemical Pure Industries, Ltd., Japan) in a centrifuging tube. To separate residue of nitrate as well as aqueous phase generated from solvating water, the mixture was centrifuged at 2000 rpm for 10 min. The upper organic solution layer in the tube was collected. Metal concentration in the obtained sample was determined with an ICP-AES (ICPS-7000, Shimadzu, Japan) followed by a back-extraction with 3.0 mol dm⁻³ nitric acid. From the metal concentration and water content measured by a Karl-Fisher titrator (AQ-7, Hiranuma, Japan), TBP concentration in the sample was calculated. Table 2 shows the compositions of the complexes.

For the separation experiment, TBP-neodymium nitrate was mixed with TBP-uranyl nitrate with the ratio of 1:3.5 in volume in order that the molar ratio of neodymium and uranium in the complex equaled to 0.181.

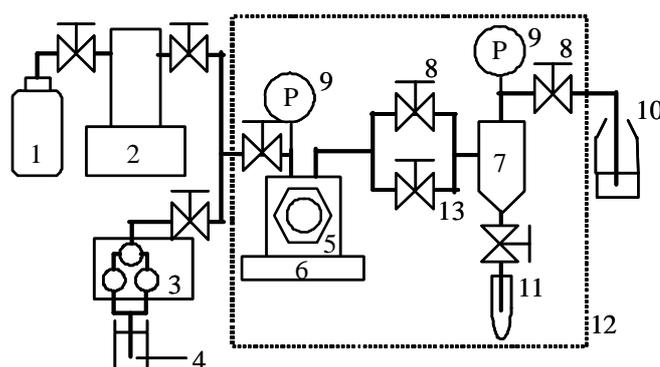
Table 2 Composition of the complexes

Sample	Concentration, mol dm ⁻³		
	TBP	Nd or U	H ₂ O
TBP-Nd(NO ₃) ₃	3.30	1.02	0.19
TBP-UO ₂ (NO ₃) ₂	3.25	1.48	0.12

Experimental Apparatus and Procedure

Figure 2 shows a schematic diagram of the experimental apparatus. It consisted of four parts; two feeding pumps (a syringe pump for CO₂, No. 2, and a plunger pump for the complex, No. 3), a dissolving cell (a view cell whose volume was 60 cm³, No. 5), a separator (a cyclone whose volume was 7 cm³, No. 7), and two collection vessels (a vessel for gas phase, No. 10, and one for liquid phase, No. 11). The cell and cyclone were set in a thermostatic chamber kept at 313 K. The fluid in the syringe pump was kept at 278 K.

In advance, the discharging pressures of two back pressure regulation valves were set at 25 and 11 MPa so as to keep the pressure of the cell and the cyclone at 25 and 11 MPa, respectively. In the cell, 1.68 cm³ of the TBP complex was absolutely dissolved in CO₂ at 25 MPa. By opening a valve (No. 13), a certain amount of the mixed fluid was flown into the cyclone, and the pressure of the cell decreased from 25 MPa to 11 MPa while that of the cyclone increased at 11 MPa. After closing the valve, the TBP complex and CO₂ was fed into the cell via pumps at 0.067 and 2.0 cm³, respectively. The fluid started to flow into the cyclone through the regulating valve after the pressure of the cell increased up to 25 MPa. In the cyclone, two phases, a gas and a liquid phase, were observed. The gas phase sample was collected in the collection vessel after depressurization with the regulating valve. On the other hand, the liquid phase sample was collected carefully not to make a big decrease of the pressure in the cyclone. We kept the decrease of the pressure of the cyclone within 0.5 MPa. Metal concentration in the obtained sample was determined with the ICP-AES (ICPS-7000, Shimadzu, Japan) followed by a back-extraction with 3.0 mol dm⁻³ nitric acid.



1. CO₂ cylinder, 2. syringe pump, 3. plunger pump, 4. sample,
5. view cell, 6. stirrer, 7. cyclone, 8. back pressure regulation valve, 9. pressure gage, 10. collecting vessel for gaseous phase,
11. collecting vessel for liquid phase, 12. thermostatic chamber, 13. valve

Figure 2 Experimental apparatus

RESULTS AND DISCUSSION

Tables 3 and 4 show the concentration ratios of neodymium and uranium in the gas phase sample and the liquid phase sample, respectively. The state in the cyclone seemed to become in a steady state after approximately 50 min. The ratios in Sample G5 and L5 were 0.12 and 0.27, respectively, and they were almost same with the calculated values shown in Table 1.

Table 3 Concentration ratio of neodymium and uranium in the gas phase sample

Sample No.	Time, min	U, mmol	Nd, mmol	[Nd]/[U], -
Sample G1	10-18	1.0×10^{-1}	1.9×10^{-2}	0.18
Sample G2	20-28	3.8×10^{-1}	6.4×10^{-2}	0.17
Sample G3	30-38	3.3×10^{-1}	5.0×10^{-2}	0.15
Sample G4	40-48	3.3×10^{-1}	4.9×10^{-2}	0.15
Sample G5	50-58	3.2×10^{-1}	4.6×10^{-2}	0.12

Table 4 Concentration ratio of neodymium and uranium in the liquid phase sample

Sample No.	Time, min	U, mmol	Nd, mmol	[Nd]/[U], -
Sample L1	19	2.2×10^{-2}	8.2×10^{-3}	0.37
Sample L2	29	2.3×10^{-2}	5.5×10^{-3}	0.24
Sample L3	39	1.8×10^{-2}	4.7×10^{-3}	0.26
Sample L4	49	1.9×10^{-2}	5.4×10^{-3}	0.29
Sample L5	59	2.9×10^{-2}	7.8×10^{-3}	0.27

The concentration ratio of uranium to neodymium increased up to 1.5 times of the initial ratio. For the further separation, it is effective to do the separation with a higher pressure and a higher x_{TBP} (~ 0.03).

CONCLUSION

The uranium separation from the mixture of TBP complexes of uranyl and neodymium nitrates was carried out in CO_2 at 313 K, 11 MPa, and compared with the calculation based on their solubilities in CO_2 . The concentration ratio of uranium to neodymium increased up to 1.5 times of the initial ratio, and it agreed well with the estimated ratio based upon their solubilities in CO_2 .

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