The solubility of TBOD (N,N,N'N'-tetra-butyl-3-oxa-pentanediamide) and its complex in liquid/supercritical carbon dioxide

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1. Introduction

Current decontamination methods consist of many techniques such as surface decontamination, which separate contaminants from the subject surface, and melting decontamination that uses the difference of density of contaminants and that of subjects. However, most of decontamination methods produce lots of secondary wastes. We need more environmentally-friendly processes for decontamination that results in the reduction of the amount of the secondary wastes. Carbon dioxide has been one of the alternative green solvents, because it is non-toxic, non-flammable, inexpensive and easy to handle [1]. Additionally, the tunable property of carbon dioxide through pressure and temperature control is very useful for its diverse use in extracting many organic materials [2]. However, carbon dioxide is non-polar solvent that cannot dissolve polar, ionic, or oxide contaminants. To resolve this limit of carbon dioxide solvent, we are developing CO_2–soluble chelate ligands that can extract metal ions into CO_2.

TBP(tri-n-butylphosphate) is a well-known chelating ligand that can extract metallic ions such as uranium and plutonium from the nitric solution into organic solvent [3]. TBP shows some weaknesses such as radiation instability under the strong gamma radiation and not-incinerable due to hazardous phosphate formation. We suggest another ligand, TBOD(N,N,N'N'-tetra-butyl-3-oxa-pentanediamide) for extraction of actinides and fission products. Compared to TBP, the diamide, TBOD has a high irradiation stability and a strong affinity to metallic ions, and it can be completely incinerated because TBOD consists of C, H, O and N elements only [4]. In this paper, we examine the properties of TBOD under the supercritical CO_2 solvent conditions and discuss about possible usages in decontamination.

2. Methods and Results

We used a variable cell in order to measure the solubility of TBOD in supercritical CO_2. The apparatus diagram is shown in figure 1. Dead volume of variable cell is 4.2ml and the change of the volume per rotation is 0.61 ml. After inserting a known amount of TBOD into the variable cell at a given temperature, we measured the pressure of CO_2 (or the cloud point) above which TBOD and supercritical CO_2 became single phase. Near the cloud point, we applied a fine control of the volume change. By inserting the amount of CO_2 with volume expansion, we can measure the cloud points continuously.

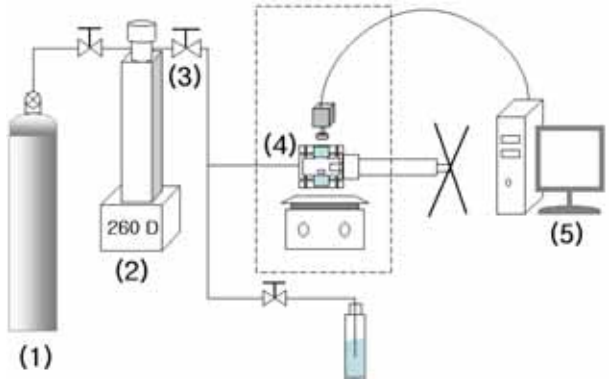

Figure 1. Solubility measurement apparatus;
(1) Cylinder of CO_2 (2) Syringe pump
(3) Inlet valve (4) Variable cell (5) Monitor.

2.1 Solubility limit of TBOD

The solubility limits of TBOD in liquid and supercritical CO_2 at 20, 40 and 60℃ are shown in figure 2. In this figure, single phase exists above the limit line of pressures. The pressure limit of the single phase increases with the concentration of TBOD. Higher pressure is also needed at higher temperature.

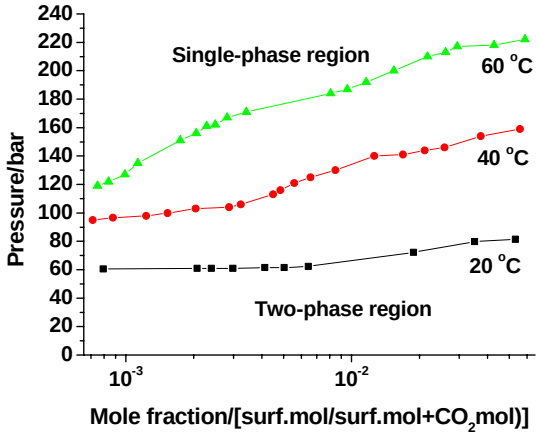

Figure 2. The solubility limits of TBOD.

2.2 Solubility limit of TBOD complex

When TBOD is applied to extract uranium ions dissolved in the nitric acid, TBOD forms two kinds of complexes with nitric acid and uranium ions – TBOD-HNO_3 and TBOD-NO_3-UO_2. The same volume of TBOD and HNO3 (65% purity) were mixed together by an agitator, then the complex, TBOD-HNO_3 was physically separated by a centrifugal separator. An agitator mixed nitric acid containing uranium ions (0.2 M) with TBOD of the same volume. Then the complex, TBOD-NO_3-UO_2 was physically separated from the mixture by a centrifuge. The solubility limit of each complex was measured at different temperatures. The measured pressure limits are shown in figure 3.

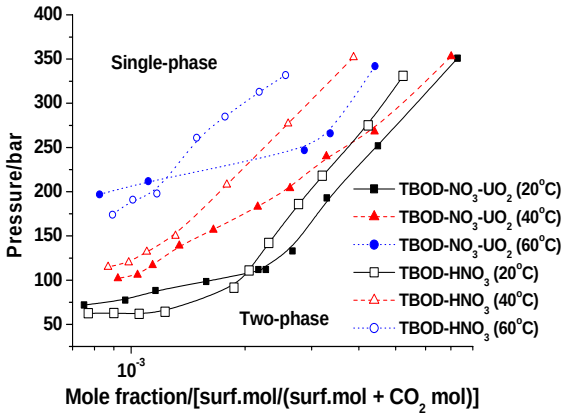

Figure 3. Solubility limits of TBOD complex.

For comparison, the solubility limits of TBOD and its complexes at 40°C are drawn in figure 4. The limit pressures for dissolution of the complexes are somewhat larger than that of TBOD. We need high CO_2 pressure when TBOD is applied to solvent extraction of uranium in CO_2 medium.

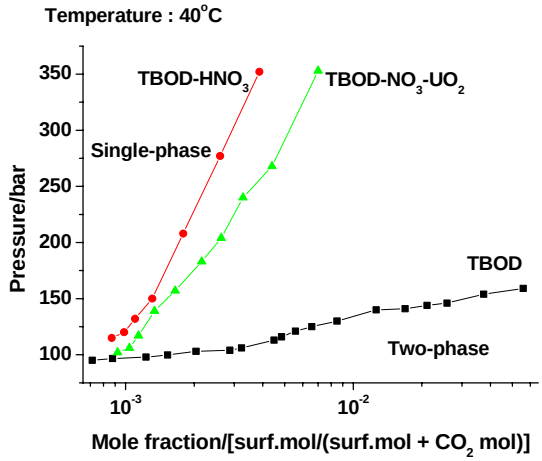

Figure 4. Comparison of TBOD and TBOD complex.

3. Conclusion

The solubility limits of TBOD and its complexes in liquid and supercritical CO_2 were measured by a variable cell method. Dissolution of TBOD needs higher pressure as temperature increases. TBOD complexes, TBOD-HNO_3 and TBOD-NO_3-UO_2 are also soluble to liquid and supercritical CO_2. However, high pressure may be needed when TBOD is applied to solvent extraction of uranium in CO_2 medium, since the complex containing uranium ions has low solubility.

Acknowledgment

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