Selective Chelation-Supercritical Fluid Extraction of Metal Ions from Waste Materials

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Introduction

The removal of toxic organics, metals, and radioisotopes from solids or liquids is of major concern in the treatment of industrial and nuclear wastes. For this reason, developing methods for selective separation of toxic metals and radioactive materials from solutions of complex matrix is an important problem in environmental research. Recent developments indicate supercritical fluids are good solvents for organic compounds.[1] Many gases become supercritical fluids under moderate temperatures and pressures. For example, the critical temperature and pressure of carbon dioxide are 31°C and 73 atm, respectively. The solubilities of some organic compounds in carbon dioxide have been shown to increase by several orders of magnitude as the pressure is changed from atmospheric to the supercritical region. The high diffusivity, low viscosity, and T-P dependence of solvent strength are some attractive properties of supercritical fluid extraction (SFE).[1,2] Since CO_2 offers the additional benefits of stability and non-toxicity, the SFE technique avoids generation of organic liquid waste and exposure of personnel to toxic solvents.

While direct extraction of metal ions by supercritical fluids is highly inefficient, these ions when complexed with organic ligands become quite soluble in supercritical fluids.[3,4] Specific ligands can be used to achieve selective extraction of metal ions in this process. After SFE, the fluid phase can be depressurized for precipitation of the metal chelates and recycled. The ligand can also be regenerated for repeated use. The success of this selective chelation-supercritical fluid extraction (SC-SFE) process depends on a number of factors including the efficiencies of the selective chelating agents, solubilities of metal chelates in supercritical fluids, rate of extraction, ease of regeneration of the ligands, etc. In this report, we present our recent results on the studies of the solubilities of metal chelates in supercritical CO_2, experimental SC-SFE approaches to the extraction of metal ions from aqueous solution, and the development of selective chelating agents (ionizable crown ethers) for the extraction of lanthanides and actinides.

Solubilities of Metal Dithiocarbamate Complexes in Supercritical CO_2

Supercritical fluid extraction of metal chelates in CO_2 has received little attention in the literature. This is believed to be caused by low solubilities of these compounds in supercritical fluids. Several studies have been reported on the separation of metal chelates by supercritical fluid chromatography using CO_2 as a mobile phase, but no solubility data were given.[5,6] In a recent study, we observed that a number of metal-diethyldithiocarbamates (DDC) exhibit limited solubilities in supercritical CO_2 as reflected by their poor chromatographic behavior.[3,7] It was demonstrated that if fluorine is substituted for hydrogen in the ligand, as in the case of bis(trifluoroethyl)dithiocarbamate (FDDC), the chromatograms of the fluorinated metal chelates are drastically improved, suggesting enhanced solubilities for the FDDC chelates. The effect of fluorine on the solubilities of metal-chelates in supercritical CO_2 was studied spectroscopically using a Varian Cary model 2200 UV/VIS spectrometer and a high pressure cell with quartz windows. The results are given in Table 1.

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Table 1. Solubilities of Metal-FDDC and DDC Complexes in Supercritical CO_2 at 100 atm and 50°C

Metal Chelate	Solubility (mol/L)
NA (FDDC)	$(4.7 \pm 0.3) \times 10^{-4}$
Na (DDC)	$(1.5 \pm 0.1) \times 10^{-4}$
Cu (FDDC)$_2$	$(9.1 \pm 0.3) \times 10^{-4}$
Cu(DDC)$_2$	$(1.1 \pm 0.2) \times 10^{-6}$
Ni(FDDC)$_2$	$(7.2 \pm 0.1) \times 10^{-4}$
Ni(DDC)$_2$	$(8.5 \pm 0.1) \times 10^{-7}$
Co(FDDC)$_3$	$(8.0 \pm 0.6) \times 10^{-4}$
Co(DDC)$_3$	$(2.4 \pm 0.4) \times 10^{-6}$
Bi(FDDC)$_3$[a]	$(7.3 \pm 0.1) \times 10^{-4}$
Bi(DDC)$_3$[a]	$(9.0 \pm 0.6) \times 10^{-6}$

(a) Measured at 150 atm and 50°C.

$NaDDC = (CH_3CH_2)NCS_2Na$;

$NaFDDC = (CF_3CH_2)_2NCS_2Na$

As shown in Table 1, the substitution of fluorine for hydrogen on the ethyl substituent of the ligand dramatically increased the solubility of these complexes in supercritical CO_2. The solubility of the sodium salt of the ligands showed only a slight increase (a factor of 3) on the addition of fluorine. However, for the metal chelates, the results are much different. In the case of the copper and nickel complexes, the solubility increased by almost three orders of magnitude on the addition of fluorine to the ligand. The cause of such large enhancement in solubility is unknown. Perfluorinated compounds (PFCs) are known to exhibit high gas-dissolving capacities, a reason such compounds are used as blood substitutes and artificial blood.[8] The reverse appears to be true for the solubility of fluorinated metal chelates in CO_2.

The solubilities of metal chelates in supercritical CO_2 increase with fluid density as shown in Figure 1. The solubility of Cu(FDDC)$_2$ quadrupled when the density of the fluid phase increased by a factor of 3. The strong dependence of solubility on density, a parameter which can be easily adjusted in SFE, is an attractive feature of this separation technique.

Fluorination of a ligand may provide a solution to the solubility problem of metal chelates in supercritical CO_2 which is a major obstacle to the development of a practical SC-SFE process. Research is currently in progress to synthesize and test the solubilities of different fluorinated ligands in supercritical CO_2, particularly the ionizable macrocycles, for selective extraction of metal ions.

The Rate of Extraction of Metal Ions by FDDC in Supercritical CO_2

The rate of extract of metal ions in aqueous solution by supercritical CO_2 containing fluorinated DDC was studied spectroscopically with a high pressure view-cell. Figure 2 shows the extraction of 5×10^{-5} M of Cu^{2+} in water with CO_2 saturated with FDDC as a function of time at 350°C. There is a significant increase in extraction efficiency moving from subcritical CO_2 (71.5 atm, d = 0.25 g/mL) into supercritical region (74.8 atm, d = 0.29 g/mL), illustrating that a small change in
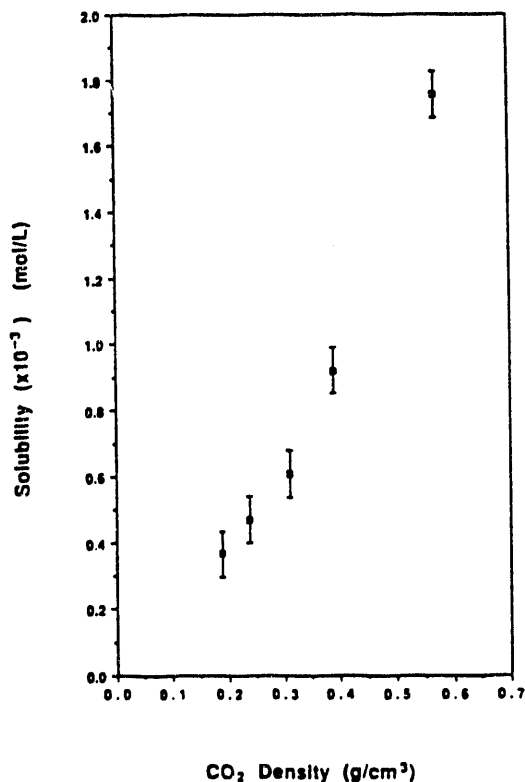
Figure 1. Solubility of $Cu(FDDC)_2$ in Supercritical CO_2 as a Function of Fluid Density

Figure 2. Rate of Extraction of Aqueous Cu^{2+} into Supercritical CO_2 Containing LiFDDC

density can have a dramatic effect on solubility. Furthermore, the extraction was about 90% complete at 78.3 atm (d = 0.37 g/mL) in 5 minutes. Clearly, the rapid extraction rate and high efficiency demonstrated in this experiment suggest the suitability of this SC-SFE technique for treatment of liquid wastes.

Ionizable Crown Ethers for Selective Chelation of Lanthanides and Actinides

Properly designed macrocyclic polyethers containing ionizable functional groups such as the carboxylic acid or hydroxamic acid group can be made highly selective for complexation with the f-block elements in solvent extraction processes.[9-12] In the case of sym-dibenzo-16-crown-5-oxyacetic acid, the extraction of
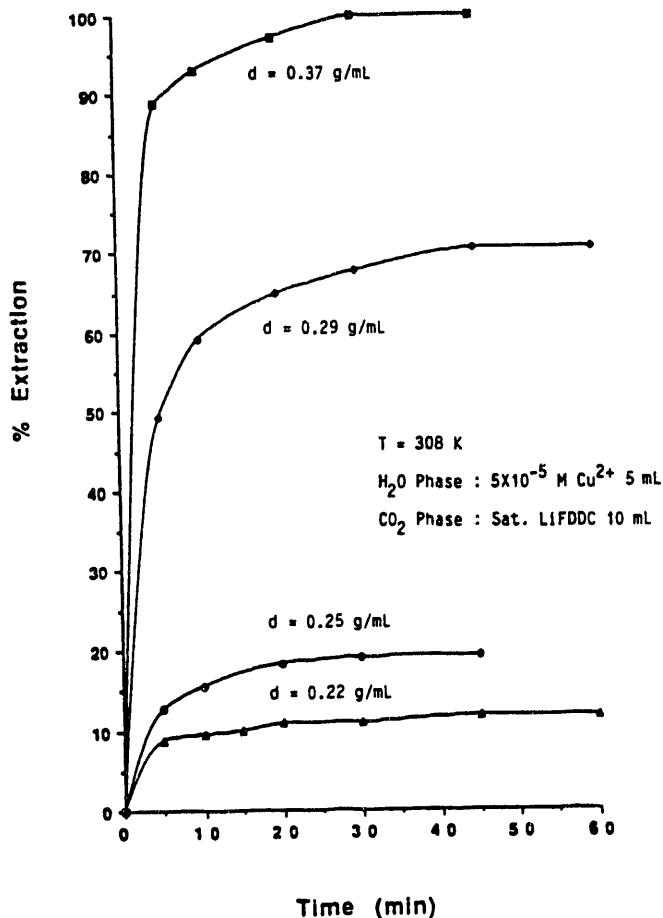
lanthanides was found independent of counteranions, quantitative, and reversible with repect to pH. The distribution coefficients (D) for the extraction of trivalent lanthanide ions are several orders of magnitude higher than those for the alkali metal and the alkaline earth metal ions (Table 2). Spectroscopic evidence indicates that both the cavity and the carboxylate group of the macrocycle are involved in the complexation with a possible sandwich formation for the trivalent lanthanide ions. This type of ionizable crown ether behaves like a bifunctional ligand that forms chelates with cations according to their size as well as their chemical nature. Sym-dibenzo-16-crown-5-oxyacetic acid and its analogues have been used to extract lanthanides from seawater for

Table 2. D Values of Selected Lanthanides and Other Metal Ions During Solvent Extraction with Sym-dibenzo-16-crown-5-oxyacetic Acid

Cation	Ionic Radius (A)	D Value
Na^+	1.02	0.01
Sr^{2+}	1.26	0.01
Ba^{2+}	1.42	0.01
Y^{3+}	1.02	15.0
Zr^{4+}	0.84	0.01
La^{3+}	1.16	6.8
Lu^{3+}	0.98	25.2

Metal ion: $1x10^{-4}$ M; Ligand: $5x10^{-3}$ M; pH: 6.0.
Ionic radii from Reference 13, C. N. VI for Na^+,
VIII for others.

quantitative analysis[10] and to separate ^{90}Y from ^{90}Sr in paper chromatography.[11] The selectivity of Lu/La (D_{Lu}/D_{La}) was found $>10^2$ under certain conditions when a hydroxamic acid group is attached to the macrocyclic host. These ionizable crown ethers also show high efficiencies for the extraction of actinides as illustrated in Figure 3 for Th(IV), U(VI), and Am(III). Other actinides including Pu(VI), Np(VI), and Cm(III) also showed high extractibility by the ionizable crown ethers.

Some fluorinated crown ether carboxylic acids have been synthesized and tested using supercritical fluid chromatography. The retention times and elution peaks showed improvement over the non-fluorinated ones. We are currently in the process of testing the solubility of lanthanide complexes with the fluorinated ionizable crown ethers in supercritical CO_2. Applications of these special ligands for SC-SFE of rare earth fission products and transuranic elements in nuclear wastes will be discussed.
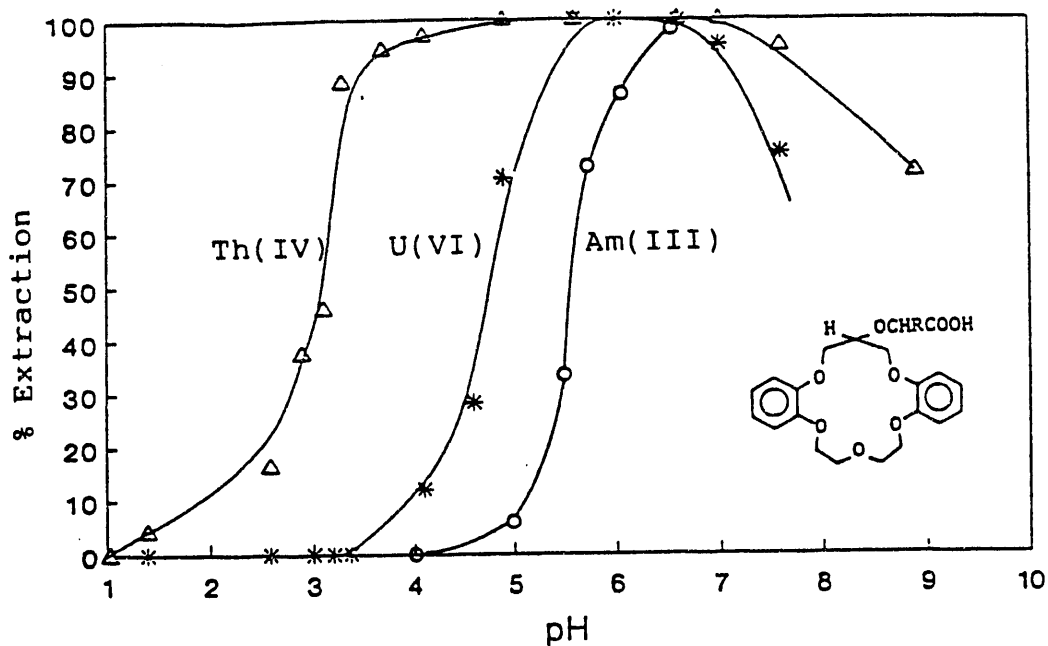
Figure 3. Solvent Extraction of Th(IV), U(VI), and Am(III) with Sym-dibenzo-16-crown-5-oxyacetic Acid as a Function of pH

References

1. Eckert, C. A., J. G. Van Alsten, and T. Stoicos. 1986. *Environ. Sci. Technol.* 20:319.

2. Hawthorne, S. B. 1990. *Anal. Chem.* 62:633A.

3. Laintz, K. E., and C. M. Wai. 1991. Presented at the Pittsburgh Conference, Chicago, Illinois, March 1991.

4. Laintz, K. E., C. M. Wai, C. R. Yonker, and R. D. Smith. 1991. *J. Supercrit. Fluids* 4:194.

5. Ashraf-Khorassani, M., J. W. Hellgeth, and L. T. Taylor. 1987. *Anal. Chem.* 59:2077.

6. Brickmann, F., and B. Wenclawiak. 1984. *Fresenius' Z. Anal. Chem.* 319:305.

7. Laintz, K. E., J. J. Yu, and C. M. Wai. 1991. *Anal. Chem.*, in press.

8. Riess, J. G., and M. LeBlanc. 1982. *Pure Appl. Chem.* 54:2383.

9. Tang, J., and C. M. Wai. 1986. *Anal. Chem.* 58:3233.

10. Tang, J., and C. M. Wai. 1989. *Talanta* 36:1129.

11. Wai, C. M., and H. S. Du. 1990. *Anal. Chem.* 62:2412.

12. Wai, C. M. 1991. "Selective Chelation and Separation of Lanthanides and Actinides with Ionizable Crown Ethers." Presented at the 201st ACS National Meeting, Atlanta, Georgia, April 1991.

13. Shannon, R. D., and C. T. Prewitt. 1969. *Acta Cryst.* B25:925.

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