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Dissolution of Metal Species in Supercritical Fluids—Principles and Applications

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Metal species in solid and liquid materials can be extracted into supercritical CO_2 containing organic complexing agents. The solubility of metal complexes in CO_2 is an important factor in determining the extraction efficiency. A spectroscopic method utilizing a high-pressure fiber optic system for determination of solubility of metal complexes in supercritical CO_2 is described. Fluorination of the ligand, replacement of the coordinated H_2O with a lipophilic Lewis base, and formation of ion pairs with a fluorinated counteranion are some of the techniques that can be used to enhance the solubility of metal complexes in supercritical CO_2. Direct dissolution of uranium oxides and selective extraction of aqueous strontium are two examples given in this paper to illustrate the capability of this in situ chelation/supercritical fluid extraction technology. Potential applications of the extraction technology for treatment of metal-contaminated wastes including mixed wastes and nuclear wastes are discussed.

Introduction

Direct extraction of metal ions by supercritical CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute−solvent interactions. However, when metal ions are chelated with organic ligands, they may become quite soluble in supercritical CO_2. Wai and co-workers first reported in 1991 that fluorine substitution in a chelating agent could greatly enhance the solubility (by 2−3 orders of magnitude) of its metal complexes in supercritical CO_2.[1] These authors further demonstrated that, by using a fluorinated dithiocarbamate reagent [bis-(trifluoroethyl)dithiocarbamate] dissolved in supercritical CO_2, effective extraction of copper ions spiked in solid and liquid samples could be accomplished.[2] Later, fluorinated β-diketones were used by several groups to extract lanthanides and actinides from solid and liquid samples in supercritical CO_2.[3−5] Many papers appeared in the late 1990s using this in situ chelation/supercritical fluid extraction (SFE) approach for extracting metal species in supercritical CO_2 utilizing different chelating agents.[6−8] According to the literature, the following factors are important for effective extraction of metal species in supercritical CO_2: (1) solubility of the chelating agent, (2) solubility of the metal chelate, (3) density, (4) chemical form of the metal species, (5) water, and (6) matrix. The solubility of metal chelates in supercritical CO_2 appears to be the most important factor in determining the SFE efficiency. This paper describes a spectroscopic technique developed in our laboratory for measurement of the solubility of metal chelates in supercritical CO_2. Some molecular parameters that show significant influence on the solubility of metal chelates in supercritical CO_2 have been identified. Two examples are given in this paper to illustrate the usefulness of such information for designing supercritical fluid dissolution/extraction processes for metal species. One example is the dissolution of solid UO_3 in supercritical CO_2 using an adduct formation approach involving a fluorinated β-diketone and an organophosphate ligand. Another example is the selective extraction of strontium from aqueous solutions using a macrocyclic ligand and a fluorinated counteranion dissolved in supercritical CO_2. Potential applications of the SFE method for treating metal-contaminated wastes including mixed wastes and nuclear wastes are discussed.

Solubility Measurement Using Spectroscopic Techniques

The following three techniques are commonly used for solubility determination in supercritical fluids: gravimetric, chromatographic, and spectroscopic methods. Spectroscopic methods generally offer more rapid determination of solubility, with increased sensitivity, and require small amounts of samples. If a metal complex has characteristic absorption bands in the UV−vis region, the spectroscopic method is a good choice for determining the complex's solubility in supercritical CO_2. A stainless steel high-pressure view cell with quartz windows was used by Laintz et al. in 1991 for determination of the solubilities of a number of metal dithiocarbamate complexes in supercritical CO_2.[1] One drawback of using the high-pressure view cell for solubility measurement is its fixed path length (e.g. about 5 cm in the case of Laintz's original work) which limits the concentration range of its measurement. For highly soluble metal complexes, the absorbance may be out of the linear range of the Beer−Lambert law. In addition, the high-pressure view cells are expensive to fabricate. Recently, the use of a high-pressure fiber optic system for measurement of the solubility of a uranyl complex in supercritical CO_2 was reported.[9] The fiber optic system, consisting of three fiber optic cells with path lengths ranging from 38 μm to 1 cm, enables compounds of high or low solubility to be measured over a concentration range of several orders of magnitude. The system is capable of withstanding pressure in excess of 300 atm, and spectra over the entire UV−vis range (200−900 nm) can be obtained. The cost of fabricating the fiber optical system is about one tenth of that for a typical high-pressure stainless steel view cell.

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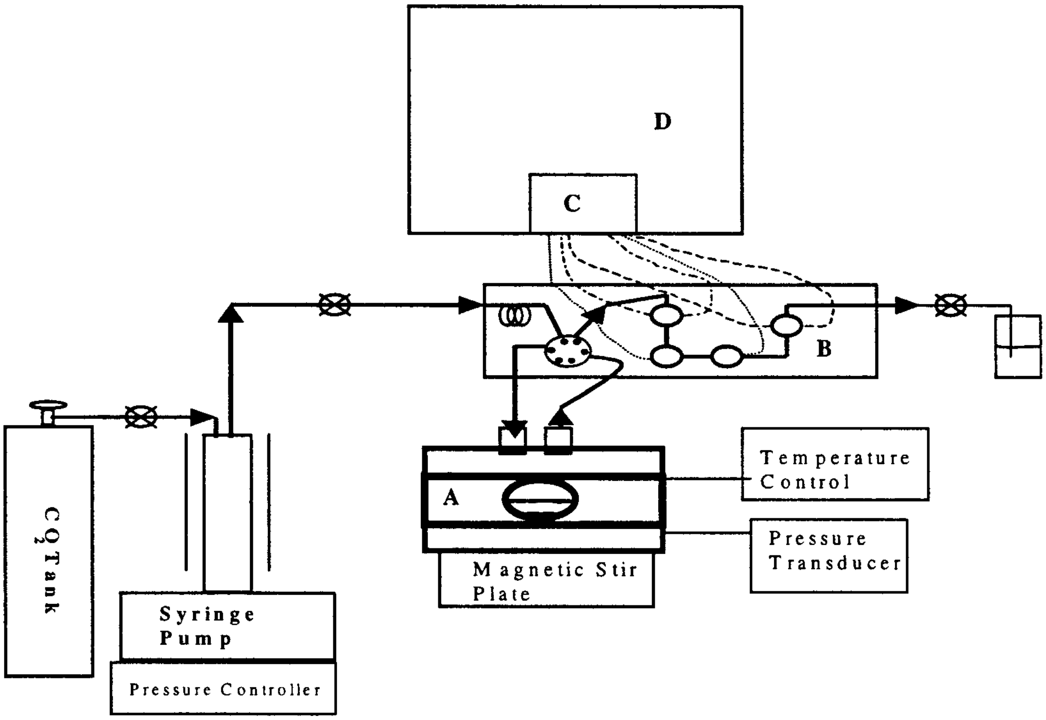

Figure 1. A high-pressure fiber optic system for solubility measurement in supercritical CO2: (A) view cell, (B) fiber optical cells in an oven, (C) fiber optic interface, and (D) UV−vis spectrometer.

The schematic diagram of a fiber optic system used in our laboratory for solubility measurement is illustrated in Figure 1. The fiber optic system is similar to that described by Carrott and Wai,[9] but a high-pressure view cell was used to dissolve the sample. Using the view cell allowed the phase behavior of the metal complex under supercritical conditions to be observed. An ISCO syringe pump, model 260D (ISCO, Lincoln, NE), was used to supply CO_2 at the desired pressure. Supercritical CO_2 was introduced to the saturation cell containing the test compound via a 1.5-m ($^{1}/_{16}$-in. o.d. × 0.03-in. i.d.) stainless steel equilibration coil to ensure that the CO_2 was at the correct temperature prior to entering the cell. Either a 3.5-mL saturation vessel or a 14.9-mL view cell (5-cm path length) was connected to a Rheodyne six-port valve to contain the sample. The switching valve enabled the sample cell to be switched in or out of the flow path without the need for depressurizing the entire system and also facilitated the cleaning and flushing of the fiber optic cells. Three high-pressure UV−vis cells, with path lengths of 38 μm, 733 μm, and 1 cm, were used for the solubility measurements. All components of the apparatus, except the view cell, were housed in an HPLC oven (Figure 1, component B) to allow precise control of the temperature. A digital temperature controller maintained heating of the external view cell. A Cary 1E UV−vis spectrometer and fiber optic interface (Varian Instruments) were used for spectroscopic measurements.

To determine the solubilities of metal chelates in supercritical CO_2, both the path length of the fiber optic cells and the molar absorptivity of the complex must be known. First, the path length of each of the optical cells was determined. The 1-cm-path-length cell was constructed simply by measuring the distance between the fibers during assembly; however, this is impossible for the cells with a path length less than 1 mm. The path lengths of these cells were determined using a series of standard anthracene solutions with a known molar absorptivity. The molar absorptivity of anthracene at 359 nm was calculated using the Beer−Lambert law where the path length was 1 cm. The path lengths for the two remaining cells were calculated from the slope of linear calibration curve of absorbance (at 359 nm) vs concentration using the calculated molar absorptivity. The molar absorptivity for each complex was determined by using standards of the metal chelate in hexane in the 1-cm-path-length cell. Hexane was used because it has a polarity similar to that of CO_2 and because solutes exhibit similar extinction coefficients and negligible wavelength shifts in absorption maxima. The molar absorptivities for all complexes measured were calculated from the slope of a linear calibration curve of absorbance [at 376 nm for the $UO_2(TTA)_2{\cdot}X$ complex] vs concentration. The relative standard deviation of the uranium complex solubility measurements was estimated to be less than 10%.

Recently, a high-pressure fiber optic reactor was constructed in our laboratory for measurement of the dissolution rate of various compounds in supercritical CO_2.[10] The fiber optic reactor can be connected to a CCD array UV−vis spectrometer to obtain absorption spectra rapidly. The high-pressure fiber optic reactor reported by Hunt et al. is capable of obtaining one UV−vis spectrum per second over the entire UV−vis range.[10] This type of fiber optic reactor system is very useful for studying the rates of metal dissolution processes and chemical reactions in supercritical fluids.

Solubility Data and Modeling

Fluorinated β-diketones form soluble complexes with uranyl ions in supercritical CO_2.[11] A positive synergistic effect for uranium extraction was observed when a mixture of a fluorinated β-diketone and TBP (tributyl phosphate) was used as the extractant in supercritical CO_2.[12,13] However, solubility data of these uranyl com-

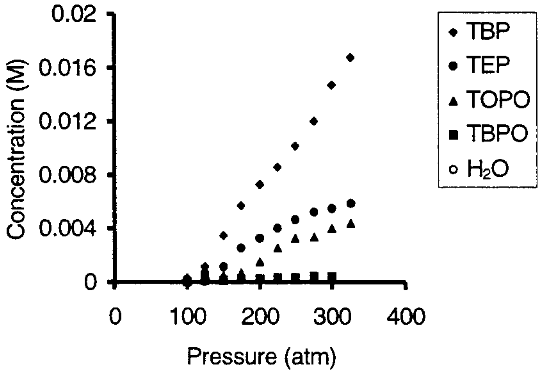

Figure 2. Solubility of $UO_2(TTA)_2{\cdot}X$ adduct complexes in supercritical CO_2 at 40 °C and various pressures.

plexes in supercritical CO_2 are not known in the literature. The solubilities of several uranyl−TTA (thenoyltrifluoroacetone) complexes in supercritical CO_2 at 40 °C and various pressures were measured recently in our laboratory, as shown in Figure 2. The data are intended to illustrate the effect of adduct formation on the solubility of the uranyl−TTA−X complexes in CO_2, where X = TBP, TEP (triethyl phosphate), TOPO (trioctylphosphine oxide), TBPO (tributylphosphine oxide), and H_2O. Among this group of uranyl−TTA adduct complexes, $UO_2(TTA)_2{\cdot}TBP$ is the most soluble in supercritical CO_2 at each pressure, followed by $UO_2(TTA)_2{\cdot}TEP$ and $UO_2(TTA)_2{\cdot}TOPO$.

All of these compounds showed an increase in solubility in CO_2 with an increase in pressure. The solubilities of $UO_2(TTA)_2{\cdot}TBPO$ and $UO_2(TTA)_2{\cdot}H_2O$ are significantly less than those of the other three complexes. $UO_2(TTA)_2{\cdot}H_2O$, the least soluble uranyl−TTA complex in this series, was actually used as the starting material to prepare the rest of the $UO_2(TTA)_2{\cdot}X$ adduct complexes for this study. Replacing the coordinated water molecule with an organophosphorus ligand apparently can significantly increase the solubility of the resulting complex. The most soluble adduct complex, $UO_2(TTA)_2{\cdot}TBP$, has a solubility about 2 orders of magnitude higher than that of $UO_2(TTA)_2{\cdot}H_2O$.

A simple solvato-complex model, which relates the solubility (*S*) of a compound to the solvent density (*D*), was used to model the solubility of these uranium complexes.[14] According to this model, the molecules of the solute A and those of the solvent B would associate with one another to form a solvato complex represent by the reaction

$$A + kB \rightarrow AB_k \qquad (1)$$

The equilibrium constant *K* can be expressed by

$$K = [AB_k]/[A][B]^k \qquad (2)$$

Rearranging eq 2 into logarithmic form, we have

$$\ln [AB_k] = k \ln [B] + \ln [A] + \ln K \qquad (3)$$

The equilibrium constant is a function of the enthalpy of solvation (ΔH_{solv}) and temperature. The concentration of the solvato complex (or solubility *S*) can be related to the density (*D*) of the fluid phase by the relation

$$\ln S = k \ln D + C \qquad (4)$$

where *k* is a constant indicating the degree of solvation of the solute in a supercritical fluid and *C* is a constant related to the enthalpy of solvation. Equation 4 predicts a linear relation between ln *D* and ln *S*, with the slope and intercept determining *k* and *C*, respectively.

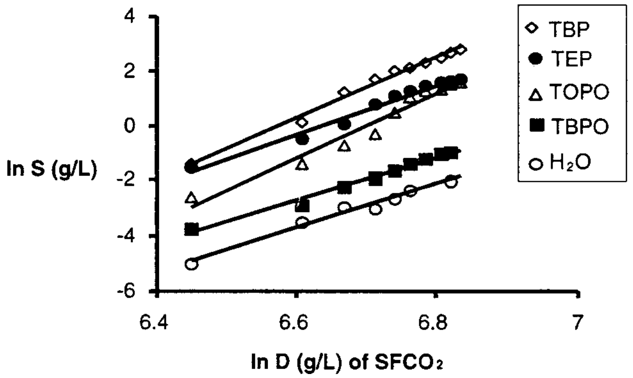

Figure 3. ln *S* versus ln *D* plot for the $UO_2(TTA)_2{\cdot}X$ adduct complexes in supercritical CO_2.

When the $UO_2(TTA)_2{\cdot}X$ solubility data are plotted in terms of ln *S* versus ln *D* as shown in Figure 3, a linear relationship is observed for each of the compounds. All of the complexes studied give a positive value for *k* and a negative value for *C*. The *k* value can be related to the average number of solvent molecules associated with the metal complex. The highly soluble complexes appear to have high *k* values. For the phosphate adducts, the one with the higher *k* value [$UO_2(TTA)_2{\cdot}TBP$, $k = 11$] is more soluble than the one with the lower *k* value [$UO_2(TTA)_2{\cdot}TEP$, $k = 9$]. This is also true for the phosphine oxide adducts. $UO_2(TTA)_2{\cdot}TOPO$, having a *k* value of 11.8 is more soluble than $UO_2(TTA)_2{\cdot}TBPO$ with a *k* value of 7.6. The results suggest that it is the nature of the adduct molecule and the *k* value that determine the solubility of the uranyl−TTA complexes in supercritical CO_2. Using this simple model, the solubility of a uranium complex in supercritical CO_2 can be predicted over a wide density range based on a few experimental measurements. According to Figure 2, the solubility of $UO_2(TTA)_2{\cdot}TBP$ is sufficiently high to warrant the use of TTA and TBP as extractants for uranium extraction in supercritical CO_2.

SFE of Uranium

Extraction of uranyl ions from mine waters and from contaminated soil using TTA and TBP as extractants in supercritical CO_2 has been reported.[13] The possibility of dissolving solid uranium oxides in supercritical CO_2 using TTA and TBP as complexing agents has been evaluated recently in our laboratory.[15] According to our experiments, uranium trioxide reacts with HTTA effectively according to the following reaction:

$$UO_{3\,(solid)} + 2HTTA_{(in\ SF\ CO2)} \rightarrow UO_2(TTA)_2{\cdot}H_2O_{(solid)}$$

Because of the low solubility of $UO_2(TTA)_2{\cdot}H_2O$, the complex formed on solid UO_3 surfaces prevents rapid dissolution of the oxide in supercritical CO_2. In the presence of both HTTA and TBP in supercritical CO_2, the dissolution of solid UO_3 becomes much faster because of the formation of the highly soluble adduct complex $UO_2(TTA)_2{\cdot}TBP$.

$$UO_{3\,(solid)} + 2HTTA_{(in\ SF\ CO2)} + TBP_{(in\ SF\ CO2)} \rightarrow UO_2(TTA)_2{\cdot}TBP_{(in\ SF\ CO2)} + H_2O$$

Table 1. Sequential Extraction of Mixed Wastes [PCB(BZ#54) + Uranium] with Supercritical CO_2[a]

sample	first extraction neat CO_2 for PCB	second extraction CO_2 + TTA + TBP for uranium
sand	98	94
Idaho soil	97	82
UTS-4 tailings	98	80

[a] 200 μg of BZ#54 (2,2′,6,6′-tetrachlorobiphenyl), 200 μg of U, 300 mg of TTA, and 200 μL of TBP; 1 g of soil; 100 mg of UTS-4 tailings containing 1010 μg of uranium/g of tailings (from CANMET). 150 °C and 200 atm for PCB extraction, 80 °C and 200 atm for uranium extraction; 30 min static followed by 30 min dynamic extraction at a flow rate of 1.5 mL/min.

Table 2. Extraction of Sr^{2+}, Ca^{2+}, and Mg^{2+} from Water by Supercritical Fluid CO_2 Containing DC18C6 and a Perfluorinated Counteranion $PFOA^-$ or $PFOSA^-$ at 60 °C and 100 atm

mole ratio	% extraction		
	Sr^{2+}	Ca^{2+}	Mg^{2+}
Sr^{2+}:DC18C6:PFOA-H			
1:10:0	1	0	0
1:0:10	4 ± 1	1 ± 1	1 ± 1
1:5:10	36 ± 2	1 ± 1	1 ± 1
1:10:10	52 ± 2	2 ± 1	1 ± 1
1:10:50	98 ± 2	7 ± 2	2 ± 1
Sr^{2+}:DC18C6:PFOSA-K			
1:10:10	97 ± 2	8 ± 2	2 ± 1

The aqueous solution contained a mixture of Sr^{2+},Ca^{2+}, and Mg^{2+} with a concentration of 5.6×10^{-5} M each; pH of water under equilibrium with SF CO_2 = 2.9; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min. PFOA-H = $CF_3(CF_2)_6COOH$; PFOSA-K = $CF_3(CF_2)_6CF_2SO_3K$.

TBP, a stronger Lewis base, apparently can replace the polar H_2O molecule in the uranyl TTA, making the TBP adduct complex readily soluble in supercritical CO_2. A mixture of HTTA and TBP was also found effective for the dissolution of U_3O_8 in supercritical CO_2 but ineffective for the dissolution of UO_2. The feasibility of direct dissolution of solid uranium oxides in supercritical CO_2 suggests that the technique can be used for the treatment of uranium- and other actinide-contaminated wastes and for the reprocessing of spent nuclear fuels. Using the SFE technology, no liquid solvent wastes would be generated in the dissolution process.

The possibility of using the SFE technique for treatment of mixed wastes containing both organic pollutants and metals has also been evaluated recently. For a system containing both organic compounds and metal species, a sequential SFE procedure can be used to remove the organic components and the metal species separately from the mixed waste. The sequential extraction technique is illustrated by the following examples concerning the extraction of PCB and uranium from solid materials. Table 1 shows the results of sequential extraction of PCB and uranium from a spiked filter paper sample. The sample was first extracted with neat supercritical CO_2 to remove the PCB, followed by the addition of TTA and TBP to extract uranium. Near-quantitative recovery of the PCB and over 90% extraction of the spiked uranium from the paper according to the specified conditions were achieved. Good SFE efficiencies were also observed from a PCB- and uranium-spiked soil and from standard uranium mine tailings spiked with PCB.

The sequential SFE technique, in principle, is capable of removing organic pollutants, toxic metals, and radioactive elements from mixed solid wastes without involving any acid or organic solvent. This approach should result in significant reduction of secondary waste generation compared with conventional acid dissolution/solvent extraction processes. The matrix effect for the SFE of metals from solid materials such as soil may be more complicated than that of organic compounds. This is probably due to the fact that metals can usually be present in different oxidation states and chemical forms in various mineral phases of soil.

SFE of Strontium

Selective extraction of alkali metal and alkaline earth metal ions from aqueous solutions to organic solvents using crown ethers as extractants is well established in the literature. Extraction of these hard metal ions with crown ethers in supercritical CO_2 is expected to be difficult because of limited solubilities of the resulting metal complexes in CO_2. It is known that fluorinated metal chelates are CO_2-philic.[1] Thus, fluorination of ligands is one method of increasing the solubility of these metal complexes in CO_2. This approach requires the design and synthesis of specific fluorinated macrocyclic compounds. Another method is to extract crown ether−metal complexes as ion pairs into supercritical CO_2 utilizing fluorinated counteranions.[16] It is known that 18-membered crown ethers with cavity diameters in the range of 2.6−2.8 Å are the most suitable hosts for Sr^{2+} (2.2 Å). For example, ^{90}Sr can be selectively extracted from nitric acid solutions with dicyclohexano-18-crown-6 (DC18C6) dissolved in a paraffinic or halogenated solvent, where nitrate serves as the counteranion.[17]

DC18C6 is quite soluble in supercritical CO_2, with a solubility estimated to be $>10^{-2}$ mol/L at 60 °C and 100 atm. Direct extraction of Sr^{2+} (5.6×10^{-5} M) with an excess amount of DC18C6 (5.4×10^{-4} M) in supercritical CO_2 showed virtually no detectable extraction of Sr^{2+} from water (Table 2) or from a 1.3 M nitric acid solution. With the addition of a fluorinated carboxylic acid such as pentadecafluoro-*n*-octanoic acid (PFOAH), extraction of Sr^{2+} from water with DC18C6 in SF CO_2 became significant.[16] The pH of water in equilibrium with supercritical CO_2 under the experimental conditions should be around 2.9 according to a previous study.[18] Because of the inductive effect of the fluorinated group in PFOAH, the pK_a value of this perfluorinated acid is around 1. Therefore, PFOAH is expected to exist as the anionic form $PFOA^-$ under the specified experimental conditions of the water/supercritical fluid CO_2 system. With a concentration of $Sr^{2+} = 5.6 \times 10^{-5}$ M and a mole ratio of Sr^{2+}:DC18C6:$PFOA^-$ = 1:10:50, nearly quantitative extraction (98%) of Sr^{2+} from water into supercritical CO_2 was observed at 60 °C and 100 atm. Under these conditions, Ca^{2+} and Mg^{2+} were extracted at 7% and 1%, respectively. Selective transport of Sr^{2+} in the presence of Ca^{2+} and Mg^{2+} from an aqueous solution to the supercritical CO_2 phase apparently can be achieved using DC18C6 and $PFOA^-$ as a counteranion. The rate of extraction of Sr^{2+} from the aqueous phase into SF CO_2 with DC18C6 and PFOAH is reasonably fast, requiring about 20 min of static and 20 min of dynamic extraction to complete the extraction of Sr.

Selective extraction of Sr^{2+} by supercritical CO_2 with DC18C6 and perfluoro-1-octanesulfonic acid tetraethylammonium salt (PFOSA-$N(C_2H_5)_4$) or its potassium salt (PFOSA-K) was observed in 1.3 M HNO_3 (Table 3).[16]

Table 3. Extraction of Sr^{2+}, Ca^{2+}, and Mg^{2+} from 1.3 M HNO_3 by Supercritical Fluid CO_2 Containing DC18C6 and PFOAH or PFOSA Salt at 35 °C and 200 atm[a]

mole ratio	% extraction Sr^{2+}	% extraction Ca^{2+}	% extraction Mg^{2+}
Sr^{2+}:DC18C6:PFOA-H			
1:10:0	1	0	0
1:10:50	18 ± 2	2 ± 1	1 ± 1
Sr^{2+}:DC18C6:PFOSA-K			
1:10:50	60 ± 3	8 ± 2	2 ± 1
1:20:50	76 ± 3	8 ± 2	1 ± 1
Sr^{2+}:DC18C6:PFOSA-$N(C_2H_5)_4$			
1:10:50	61 ± 3	7 ± 2	2 ± 1

[a] The acid solution contained a mixture of Sr^{2+},Ca^{2+}, and Mg^{2+} with a concentration of 5.6×10^{-5} M each; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min. PFOA-H = $CF_3(CF_2)_6COOH$; PFOSA-$N(C_2H_5)_4$ = $CF_3(CF_2)_6CF_2SO_3$-$[N(C_2H_5)_4]$; PFOSA-K = $CF_3(CF_2)_6CF_2SO_3K$.

The extraction of Sr^{2+} in the acid solution with a Sr^{2+}:DC18C6:PFOSA-K ratio of 1:10:50 was 60%, whereas Ca^{2+} and Mg^{2+} were extracted at about 8% and 2%, respectively. The extraction efficiency of Sr^{2+} increased to 76% when the crown ether concentration was doubled. The fluorinated carboxylic acid PFOAH is less effective than the fluorinated sulfonic acid for Sr^{2+} extraction in the acid solution. In general, a high selectivity of extracting Sr^{2+} over Ca^{2+} and Mg^{2+} was observed in all of the acid solution experiments. It should be pointed out that the high-level acidic nuclear wastes stored at the Idaho DOE site is in 1.3 M HNO_3. The solubility of the Sr-DC18−C-6 complex with PFOSA or PFOA as a counteranion has not been determined because of the difficulty involved in preparing the pure ion-pair complexes for solubility measurements.

Summary

The solubility of metal complexes in supercritical CO_2 can be significantly enhanced by the following methods: (1) fluorination of the ligand, (2) replacement of the coordinated water molecules with a lipophilic Lewis base, and (3) formation of ion pairs with a fluorinated counteranion. Using the in situ chelation/SFE technique, metal species in ionic form or even in oxide form can be extracted by supercritical CO_2 containing proper complexing agents. The extraction can be made selective using ion-recognition ligands such as crown ethers. The SFE technique can also be used to separate organic pollutants from toxic metals or radioisotopes from mixed wastes. The SFE technology offers several advantages over conventional liquid extraction methods, including direct removal of organic and metallic contaminants from solid materials with minimum liquid waste generation. This environmentally friendly extraction technology may have important applications for treatment and remediation of nuclear wastes and for other metal-related industrial manufacturing processes.

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