

Selective extraction of strontium with supercritical fluid carbon dioxide

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Strontium (Sr²⁺) can be selectively extracted from aqueous solutions into supercritical fluid CO₂ at 60 °C and 100 atm with dicyclohexano-18-crown-6 (DC18C6) using CF₃(CF₂)₆CO₂⁻ (PFOA⁻) or CF₃(CF₂)₆CF₂SO₃⁻ (PFOSA⁻) as a counter anion; at a mole ratio of Sr²⁺ : DC18C6 : PFOA⁻ = 1:10:50, the extraction of Sr (5.6 × 10⁻⁵ M) from water at pH 3 is near quantitative whereas Ca²⁺ and Mg²⁺ at equal concentration are only extracted to a level of 7 and 1%, respectively; PFOSA⁻ is an effective counter anion for selective extraction of Sr²⁺ from 1.3 M HNO₃ with DC18C6 in supercritical CO₂.

Research in selective transport of metal ions in supercritical (sc)-CO₂ is of considerable current interest because of its potential applications in a variety of chemical processes which may be carried out in this environmentally friendly solvent.^{1,2} Selective extraction of alkali metal and alkaline earth metal ions from aqueous solutions to organic solvents with crown ethers is well established in the literature. Extraction of these hard metal ions with crown ethers in scCO₂ is expected to be difficult because of limited solubilities of the resulting metal complexes in CO₂.³ It is known that fluorinated metal chelates are CO₂-philic.⁴ Thus, fluorination of ligands is one method of increasing solubility of metal complexes in CO₂. 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 scCO₂ utilizing fluorinated counteranions. We report for the first time the successful extraction of Sr²⁺ from aqueous media into scCO₂ utilizing a macrocyclic compound and a fluorinated counter anion.

It is known that 18-membered crown ethers with cavity diameters in the range 2.6–2.8 Å are the most suitable hosts for Sr²⁺ (2.2 Å).⁵ For example, ⁹⁰Sr 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 counter anion.⁶ This macrocyclic system is currently being evaluated for removing ⁹⁰Sr (t_{1/2} = 30 years), a major uranium fission product, from the high level acidic nuclear wastes stored at the Idaho DOE site. However, disposal of organic liquid wastes generated from any solvent extraction process is a problem of environmental concern today because of changing government regulations. Supercritical fluid extraction provides several advantages over conventional solvent extraction including minimization of waste generation, allowing rapid separation of extracted metal complexes, and enhancement of transport speed due to high diffusivity of the supercritical fluid.

The high-pressure apparatus for supercritical fluid extraction of aqueous systems has been described previously.⁷ A measured amount of DC18C6 and a fluorinated counter anion, both dissolved in chloroform, was loaded into a 10 mL stainless steel extraction vessel and evaporated to dryness on a water bath at 60 °C with flowing nitrogen gas. 5 mL of an aqueous solution containing a mixture of Sr²⁺, Ca²⁺ and Mg²⁺ at 5.6 × 10⁻⁵ M each were then added to the vessel. The vessel was pressurized with CO₂ and heated to the desired temperature. After 20 min of static extraction, the exit valve was opened and the system was flushed with scCO₂ for 20 min. The aqueous solution before and after extraction was analyzed by an ICP/AES instrument for metal contents.

DC18C6 is quite soluble in scCO₂, with a solubility estimated to be > 10⁻² mol L⁻¹ at 60 °C and 100 atm, according to our experiments. Direct extraction of Sr²⁺ (5.6 × 10⁻⁵ M) with an excess of DC18C6 (5.4 × 10⁻⁴ M) in supercritical CO₂ showed virtually no detectable extraction of Sr²⁺ from water (Table 1) or from a 1.3 M nitric acid solution (Table 2). With the addition of a fluorinated carboxylic acid such as pentadecafluoro-*n*-octanoic acid (HPFOA), extraction of Sr²⁺ from water with DC18C6 in scCO₂ became significant. The pH of water in equilibrium with scCO₂ under the experimental conditions should be *ca.* 2.9 according to a previous study.⁸ Because of the inductive effect of the fluorinated group in HPFOA, the pK_a value of this perfluorinated acid is *ca.* 1. Therefore, HPFOA is expected to exist as the anionic form PFOA⁻ under the specified experimental conditions of this water/scCO₂ system. With a concentration of Sr²⁺ = 5.6 × 10⁻⁵ M and a mol ratio of Sr²⁺ : DC18C6 : PFOA⁻ = 1 : 5 : 10, *ca.* 36% of the Sr²⁺ was removed from the water after 20 min of static extraction

Table 1 Extraction of Sr²⁺, Ca²⁺ and Mg²⁺ from water by sc fluid CO₂ containing DC18C6 and perfluorinated counter anion PFOA⁻ or PFOSA⁻ at 60 °C and 100 atm^a

Mol ratio			Extraction (%)		
Sr ²⁺ :DC18C6:HPFOA			Sr ²⁺	Ca ²⁺	Mg ²⁺
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
NET ₄ PFOSA					
1	0	10	12 ± 2	6 ± 2	2 ± 1
1	5	10	98 ± 2	45 ± 4	2 ± 1
1	10	10	99 ± 1	66 ± 5	2 ± 1
KPFOSA					
1	10	10	97 ± 2	8 ± 2	2 ± 1

^a The aqueous solution contained a mixture of Sr²⁺, Ca²⁺ and Mg²⁺ with a concentration of 5.6 × 10⁻⁵ M each; pH of water under equilibrium with scCO₂ = 2.9; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL min⁻¹. HPFOA = CF₃(CF₂)₆CO₂H; NET₄PFOSA = NET₄[CF₃(CF₂)₆CF₂SO₃]; KPFOSA = CF₃(CF₂)₆CF₂SO₃K.

Table 2 Extraction of Sr²⁺, Ca²⁺ and Mg²⁺ from 1.3 M HNO₃ by scCO₂ containing DC18C6 and HPFOA or PFOSA salt at 35 °C and 200 atm^a

Mol ratio			Extraction (%)		
Sr ²⁺ :DC18C6:HPFOA			Sr ²⁺	Ca ²⁺	Mg ²⁺
1	10	0	1	0	0
1	10	50	18 ± 2	2 ± 1	1 ± 1
KPFOSA					
1	10	50	60 ± 3	8 ± 2	2 ± 1
1	20	50	76 ± 3	8 ± 2	1 ± 1
NET ₄ PFOSA					
1	10	50	61 ± 3	7 ± 2	2 ± 1

^a The acid solution contained a mixture of Sr²⁺, Ca²⁺ and Mg²⁺ 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⁻¹.

followed by 20 min of dynamic flushing at 60 °C and 100 atm. The percentage extraction of Ca²⁺ and Mg²⁺ (at equal concentration as Sr²⁺) under the same conditions was negligible (3% or less). By doubling the concentration of DC18C6 (*i.e.* at a mol ratio of Sr²⁺: DC18C6: PFOA⁻ = 1:10:10), *ca.* 52% of the Sr²⁺ in the water phase was removed at 60 °C and 100 atm. Assuming the percentage Sr extraction from water represents equilibrium partition, we may estimate the distribution coefficient D_{Sr} (concentration of Sr in the CO₂ phase over that in the aqueous phase) from the extraction data using the relationship $D_{Sr} = (C_i - C_f)/C_f$, where C_i and C_f are the concentration of Sr in water before and after the extraction, respectively. The D_{Sr} value appears to double (from 0.56 to 1.08) when the Sr²⁺: DC18C6: PFOA⁻ ratio is increased from 1:5:10 to 1:10:10, suggesting the stoichiometry of Sr to DC18C6 in the complex is most likely 1:1. In the absence of DC18C6, extraction of Sr²⁺ was negligible at 60 °C and 100 atm (Sr²⁺: PFOA⁻ = 1:10). Pressure has a minor effect on Sr²⁺ extraction. At 60 °C and 300 atm, the percentage extraction of Sr²⁺ was increased to 58% at a mol ratio of Sr²⁺: DC18C6: PFOA⁻ = 1:10:10.

The extraction of Sr²⁺ showed a strong dependence on PFOA⁻ concentration. With a mol ratio of Sr²⁺: DC18C6: PFOA⁻ = 1:10:50, nearly quantitative extraction (98%) of Sr²⁺ from water into scCO₂ was observed at 60 °C and 100 atm. Under these conditions, Ca²⁺ and Mg²⁺ were extracted at 7 and 1%, respectively. Selective transport of Sr²⁺ in the presence of Ca²⁺ and Mg²⁺ from an aqueous solution to the scCO₂ phase apparently can be achieved using DC18C6 and PFOA⁻ according to the results shown in Table 1. Based on the extraction data, we also estimated the variation of D_{Sr} with respect to the HPFOA concentration. Values of D_{Sr} increase from 1.1 to *ca.* 49 when the concentration of the HPFOA is increased by a factor of five. This suggests that the Sr²⁺-crown complex extracted into the supercritical fluid probably involves 2 PFOA⁻. Accurate measurement of D values in supercritical fluids requires a different experimental design. The preliminary results obtained from this supercritical fluid extraction study appear consistent with the charge neutralization requirement and the general concept of crown ether extraction.

The rate of extraction of Sr²⁺ from aqueous phase into scCO₂ with DC18C6 and HPFOA is reasonably fast. At 60 °C, 100 atm and with a Sr²⁺: DC18C6: PFOA⁻ ratio of 1:10:10 in water, the supercritical fluid extraction of Sr was found to be 11, 49, 52 and 51, for 5, 11, 19 and 30 min of static extraction, respectively. The dynamic flushing time for these experiments was fixed at 20 min. Under the specified experimental conditions, 20 min of static extraction appear sufficient to reach equilibrium.

When perfluoro-1-octanesulfonic acid tetraethylammonium salt, NET₄PFOSA, was used instead of HPFOA, the extraction efficiency for Sr²⁺ from water became higher but the selectivity for Sr²⁺ over Ca²⁺ and Mg²⁺ was reduced. At a Sr²⁺: DC18C6: NET₄PFOSA ratio of 1:10:10, the percentage extraction of Sr²⁺, Ca²⁺ and Mg²⁺ were 99, 66, and 2%, respectively. If the potassium salt KPFOA was used in the extraction instead

of the NET₄⁺ salt, selective extraction of Sr²⁺ was observed. For KPFOA, the extraction of Sr²⁺, Ca²⁺ and Mg²⁺ were 97, 8 and 2%, respectively (Table 1). The cause of the unusual Ca²⁺ extraction from water with NET₄PFOSA and DC18C6 in supercritical CO₂ is not known.

Selective extraction of Sr²⁺ by scCO₂ with DC18C6 and a fluorinated counter anion was also observed in 1.3 M HNO₃ (Table 2). The extraction of Sr²⁺ in the acid solution with a Sr²⁺: DC18C6: KPFOA ratio of 1:10:50 was 60% whereas Ca²⁺ and Mg²⁺ were extracted at a level of *ca.* 8 and 2%, respectively. The extraction efficiency of Sr²⁺ increased to 76% when the crown ether concentration was doubled (Table 2). NET₄PFOSA did not show unusual Ca²⁺ extraction from the acid solution when it was used with DC18C6 in scCO₂. The fluorinated carboxylic acid HPFOA is less effective than the fluorinated sulfonic acid for Sr²⁺ extraction in the acid solution. In general, a high selectivity of extracting Sr²⁺ over Ca²⁺ and Mg²⁺ was observed in all 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 HNO₃.

The experimental results obtained from this study suggest that Sr²⁺ in water or in 1.3 M nitric acid can be selectively extracted as ion-pairs with DC18C6 and a fluorinated counter anion in supercritical fluid CO₂. Utilizing the same principle of synergism, other alkali metal and alkaline earth metal ions probably can also be extracted in supercritical CO₂ with proper selection of macrocyclic hosts and perfluorinated counter anions. The possibility of extracting and transporting alkali metals and alkaline earth metals selectively in supercritical CO₂ suggests a number of potential applications including removal of major fission products ¹³⁷Cs and ⁹⁰Sr from aqueous or acidic nuclear wastes and phase transfer catalysis for specific reactions in supercritical CO₂.

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