

Supercritical carbon dioxide extraction of caesium from aqueous solutions in the presence of macrocyclic and fluorinated compounds

Chen M. Wai,^a Yuriy M. Kulyako^{*b} and Boris F. Myasoedov^b

^a Department of Chemistry, University of Idaho, Moscow, ID, 83844-2343, USA. Fax: +1 208 885 6173

^b V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975 Moscow, Russian Federation. Fax: +7 095 938 2054

Supercritical fluid extraction of caesium, potassium and sodium from aqueous solutions in the presence of dicyclohexano-21-crown-7, pentadecafluoro-*n*-octanoic acid (PFOA) and tetraethylammonium perfluoro-1-octanesulfonate (TPFOS) has been investigated at different temperatures of supercritical carbon dioxide, ratios between reagent concentrations and initial concentrations of caesium in the solution.

The long-lived fission products of nuclear fuel ¹³⁷Cs and ⁹⁰Sr are among the most hazardous components of radioactive high-level wastes (HLW). Current extraction technology for the recovery of caesium and strontium from HLW involves macrocyclic polyethers (crown ethers) as extractants and paraffinic or halogenated hydrocarbons as solvents. One of the main drawbacks of these processing systems is the generation of large amounts of harmful organic wastes. In connection with increased environmental requirements restricting the use of conventional solvents, the development of alternative extraction methods that exclude or decrease drastically the amount of wastes has been carried out very intensively in recent years.

Supercritical fluid extraction (SFE) with CO₂ is one of the most promising techniques capable of solving environmental problems because fluid carbon dioxide as a solvent precludes the use of toxic organic liquids. Since Laintz *et al.*¹ have demonstrated the possibility of metal (copper) chelate extraction with supercritical CO₂, this method has attracted interest of researchers involved in the extraction of actinides.^{2–5} Until recently, no data on the SFE of caesium were published.

It is well known that crown ethers are primarily used for the extraction of alkali and alkaline earth metals, which do not form complexes with other types of reagents. Crown ethers extract metals as ion pairs in which the metal enters into the cationic part of the complex. Counteranions are usually required for creating these ion pairs capable of being transferred through a phase boundary. Under SFE conditions, when a crown ether is in the aqueous phase, the solubility of compounds that serve as a source of counteranions in such a non-polar solvent as supercritical CO₂ is crucial for the transport of the resulting complex into the CO₂ phase. Fluorinated organic compounds and metal complexes with fluorinated ligands are known to be highly soluble in supercritical CO₂. The solubility of the compounds increases with increasing number of fluorine substituents.⁶ Therefore, pentadecafluoro-*n*-octanoic acid (PFOA) and tetraethylammonium perfluoro-1-octanesulfonate (TPFOS) have been chosen as a source of counteranions. In this work, we report on the first results of the SFE of caesium with crown ethers in the presence of the above compounds.

The experiments were performed on an SFE unit involving a high-pressure pump, a thermostatted oven and a 10 ml stainless steel extraction cell. Certain amounts of dicyclohexano-21-crown-7 (DCH21C7), PFOA or TPFOS dissolved in chloroform were introduced into the cell. The contents of the cell were evaporated to dryness on a water bath (*T* = 60 °C) in a nitrogen flow. Next, 2 ml of an aqueous solution containing a mixture of alkali metal ions (Cs⁺, K⁺ and Na⁺) was added to the cell. The cell was placed in the oven connected to the CO₂ line and heated to a required temperature. Next, the system was pressurised by CO₂ to 100 atm. The contents of the cell was held under static conditions for 20 min. Thereafter, the dynamic stage of the extraction was conducted at a fluid CO₂ flow rate of 1.0–2.0 ml min⁻¹ (the total CO₂ volume was 50 ml). The CO₂ flow leaving the cell passed through a restrictor dipped into a vessel with chloroform (a trap for the collection of extracted

Table 1 Extraction of alkali metals with various crown ethers in the presence of PFOA. Initial alkali metal concentrations: [Cs⁺] = 1.67×10⁻⁴ mol dm⁻³ (22.2 g ml⁻¹); [K⁺] = 1.73×10⁻⁴ mol dm⁻³ (6.8 g ml⁻¹); [Na⁺] = 1.76×10⁻⁴ mol dm⁻³ (4.1 g ml⁻¹); *P* = 100 atm; *T* = 40 °C; the molar ratio [Cs⁺]:[crown ether]:[PFOA] = 1:100:100.

Crown ether	Cavity size/Å	Extraction efficiency, <i>E</i> (%)		
		Cs ⁺ (3.34 Å)	K ⁺ (2.66 Å)	Na ⁺ (1.90 Å)
18C6	2.67–2.86	4	0	0
DCH18C6	2.67–2.86	28	68	7
DCH21C7	3.40–4.30	42	46	0
DB24C8	>4.3	27	17	0

solutes). On completion of the extraction process, the cell was depressurised to 1 atm. The extraction efficiency was calculated by difference between the metal concentrations in the aqueous phase before and after extraction. The metal concentration was determined by ICP–MS. Each series of test solutions included samples with known Cs⁺, K⁺ and Na⁺ concentrations for controlling the accuracy of determination. It was found that PFOA, TPFOS and DCH21C7 caused no interference in the ICP–MS determination of the elements.

It is considered that the selectivity of crown ethers for metal ions is primarily determined by the so-called ionic diameter–cavity size comparability concept.^{7,8} For example, the 21-crown-7 host with a cavity diameter of 3.4–4.3 Å was found to be selective for caesium (the cationic diameter 3.34 Å) under conventional liquid–liquid extraction conditions. To be certain in the validity of this concept for SFE, we examined the effect of the crown ether structure on the efficiency of caesium extraction. The experimental results are presented in Table 1.

The data in Table 1 show that, in general, the extraction efficiencies are maximum for cations whose ionic diameters are closest to the cavity size of the crown ether; this fact is consistent with the above-mentioned concept. Thus, DCH18C6 exhibits appreciable selectivity for K⁺ ions, and DCH21C7 removes caesium most effectively in comparison with the other crown ethers. Therefore, the latter was chosen for the further investigation.

As can be seen in Table 1, the efficiency of caesium extraction is no higher than 50% even with a large excess of reagents.

Table 2 Effect of temperature on the extraction efficiency of alkali metals in the presence of PFOA or TPFOS. Initial concentrations of alkali metals: [Cs⁺] = 1.67×10⁻⁴ mol dm⁻³ (22.2 g ml⁻¹); [K⁺] = 1.73×10⁻⁴ mol dm⁻³ (6.8 g ml⁻¹); [Na⁺] = 1.76×10⁻⁴ mol dm⁻³ (4.1 g ml⁻¹). The molar ratio [Cs⁺]:[DCH21C7]:[counteranion] = 1:100:100. *P* = 100 atm.

<i>T</i> /°C	Counteranion	Extraction efficiency, <i>E</i> (%)		
		Cs ⁺	K ⁺	Na ⁺
21	PFOA	60	72	0
40		43	53	0
60		16	19	0
21	TPFOS	67	73	0
40		63	69	0
60		55	39	0

Table 3 Comparison of the extraction behaviour of caesium in the recovery from solutions containing equal molar (about 1.7×10^{-4} mol dm⁻³; solution I) and weight amounts (about 5 g ml⁻¹; solution II) of alkali metals. $P = 100$ atm. The molar ratio [Cs⁺]:[DCH21C7]:[PFOA] = 1:100:100. Initial concentrations: (I) [Cs⁺] = 1.67×10^{-4} mol dm⁻³ (22.2 g ml⁻¹); [K⁺] = 1.73×10^{-4} mol dm⁻³ (6.8 g ml⁻¹); [Na⁺] = 1.76×10^{-4} mol dm⁻³ (4.1 g ml⁻¹). (II) [Cs⁺] = 4.87 g ml⁻¹; [K⁺] = 5.0 g ml⁻¹; [Na⁺] = 5.1 mg ml⁻¹.

Counteranion	$T/^\circ\text{C}$	Extraction efficiency, E (%)					
		I			II		
		Cs ⁺	K ⁺	Na ⁺	Cs ⁺	K ⁺	Na ⁺
PFOA	21	60	72	0	36	29	0
	40	43	53	0	21	12	0
	60	16	19	0	0	0	0
TPFOS	40	63	69	0	40	56	0
	60	55	39	0	25	32	0

The solubility of the resulting complexes in the CO₂ phase, which mainly depends on temperature and pressure,⁶ is a primary prerequisite to the effective extraction with supercritical CO₂. We examined the temperature effect on the extraction of alkali metals (Table 2). As a rule, the solubility of a compound in supercritical CO₂ increases with temperature.⁶ However, in our case (Table 2), the opposite dependence is observed, *i.e.*, an increase in the temperature results in a decrease of the caesium extraction efficiency. Note that this dependence is more clearly pronounced with the use of PFOA.

The extraction of caesium with supercritical CO₂ was found to depend on the initial concentration in the solution. Table 3 shows that in the recovery of caesium from solution with a concentration of 5 g ml⁻¹ the caesium extraction efficiency decreases markedly as compared to the case with a concentration of caesium of about 22 g ml⁻¹.

In studies of the dependence of the extraction efficiency for alkali metals on the ratio between reagents, we found that an excess of counteranions rather than the crown ether is a more important factor affecting the extraction efficiency (Table 4).

Thus, the SFE of caesium can be performed with the crown ether DCH21C7 in the presence of fluorinated compounds as counteranions. The SFE temperature, the concentration of

Table 4 Effect of the ratio between crown ether (DCH21C7) and counteranion (TPFOS) concentrations on the efficiency of alkali metal extraction. $P = 100$ atm; $T = 60$ °C.

Molar ratio [Cs ⁺]:[DCH21C7]:[TPFOS]	Extraction efficiency, E (%)		
	Cs ⁺	K ⁺	Na ⁺
1: 0:100	7	2	0
1: 10:100	24	32	0
1: 50: 50	14	20	0
1: 50:100	25	37	0
1:100:100	25	32	0

counteranions and the initial caesium concentration in the solution were found to be crucial factors determining the extraction behaviour of caesium.

This work was supported by a grant from the USA National Research Council's Radioactive Waste Management Program.

References

- 1 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *Anal. Chem.*, 1992, **64**, 2875.
- 2 C. L. Phelps, N. G. Smart and C. M. Wai, *J. Chem. Educ.*, 1996, **73**, 1163.
- 3 Yuche Lin, N. G. Smart and C. M. Wai, *Trends Anal. Chem.*, 1995, **14**, 123.
- 4 Yuche Lin, N. G. Smart and C. M. Wai, *Environ. Sci. Technol.*, 1995, **29**, 2706.
- 5 Yuche Lin, C. M. Wai, F. M. Jean and R. D. Brauer, *Environ. Sci. Technol.*, 1994, **28**, 1190.
- 6 N. G. Smart, T. Carleson, T. Kast, A. A. Clifford, M. D. Burford and C. M. Wai, *Talanta*, 1997, **44**, 148.
- 7 *Makrotsiklicheskie soedineniya v analiticheskoj khimii (Macrocyclic compounds in analytical chemistry)*, eds. Yu. A. Zolotov and N. M. Kuz'min, Nauka, Moscow, 1993, p. 41 (in Russian).
- 8 *Separation Techniques in Nuclear Waste Management*, eds. T. E. Carlson, N. A. Chipman and C. M. Wai, 1996, p. 47.

Received: 24th February 1999; Com. 99/1446