

Dicyclohexano-18-crown-6 Ether: A New Selective Extractant for Nuclear Fuel Reprocessing

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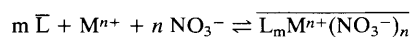
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Isomers of dicyclohexano-18-crown-6 ether (DCH 18C6) are used as a selective extractant of plutonium contained in high and medium activity solutions of nuclear fuel reprocessing; this extractant exhibits both higher stability and better selectivity towards plutonium separation than the tributyl phosphate used in the Purex process.

Tributyl phosphate (TBP) has been used in solvent extraction for decades with considerable industrial applications such as the Purex process in nuclear fuel reprocessing.¹ This solvent has received much interest from both academic and industrial research centres and thus, nuclear fuel reprocessing using this extractant has reached a maximum in efficiency, selectivity and safety. Although the proposal of a new, more efficient, extractant appears to be a rather ambitious goal, the development of molecular engineering furnishes new tools and concepts to meet this challenge. In particular, the discovery of crown ethers and other macrocycles permits the design and synthesis of specific ligands exhibiting high association constants and high selectivities for nearly all kinds of cations.² Indeed, in the last two decades thermodynamic and kinetic data for the association of, and extraction by, macrocycles with most of the metallic cations has been described.³ This basic research has already led to the proposal of many analytical applications.⁴ However, restricted availability and, above all, difficulties in the experimentation involving highly irradiated and concentrated solutions have somewhat inhibited the evaluation of macrocycles as new extractants in industrial nuclear fuel reprocessing. The use of macrocycles for the removal of high activity cations from concentrated fission products solutions has been claimed in patents and

publications.⁵ DCH 18C6 was described by Yaskin⁶ *et al.* to be an efficient complexing agent of plutonium, with a stoichiometry of 2 macrocycles : 1 plutonium atom. Use of DCH 18C6 as a specific extractant of traces of plutonium was recently proposed for concentration and analytical sample preparations.⁷ Nevertheless, these authors were using highly diluted solutions and/or pure element solutions which in turn does not demonstrate the feasibility of the separation of plutonium from concentrated industrial solution mixtures. The proposal of a macrocycle as a specific extractant in replacement of tributyl phosphate during nuclear fuel reprocessing is also difficult due to the numerous constraints of the actual process. For example, nitric acid is used for the dissolution of the irradiated fuel and this counter anion is known to have a rather poor efficiency for cation extraction with macrocycles. On the other hand, the high concentration of nitrate in the nuclear fuel reprocessing solutions may favour the extraction of a multicharged cation such as Pu⁴⁺ over mono- or di-cations (Scheme 1). In addition the Pu⁴⁺ forms a 2 : 1 'sandwich like' complex with DCH 18C6 and the partition coefficient will depend strongly on the concentration of macrocycle. High concentration will favour the extraction of plutonium over most of the other cations which give 1 : 1 complexes with this macrocycle such as Sr²⁺ and Cs⁺.

Scheme 1 Definition of the constant extraction (K_{ex}) and distribution coefficient (D_m) of cation (M^{n+}) by a specific extractant (L) with a stoichiometry L/M^{n+} of n ; $[L]$ and $[L_mM^{n+}(NO_3^-)_n]$ indicate the concentrations in organic solutions; $[M^{n+}]$ and $[NO_3^-]$ indicate the concentrations in aqueous solutions



$$k_{ex} = \frac{[\overline{L_m M^{n+} (NO_3^-)_n}]}{[L]^m [M^{n+}] [NO_3^-]^n}$$

$$D_m = \frac{[\overline{L_m M^{n+} (NO_3^-)_n}]}{[M^{n+}]} = k_{ex} [L]^m [NO_3^-]^n$$

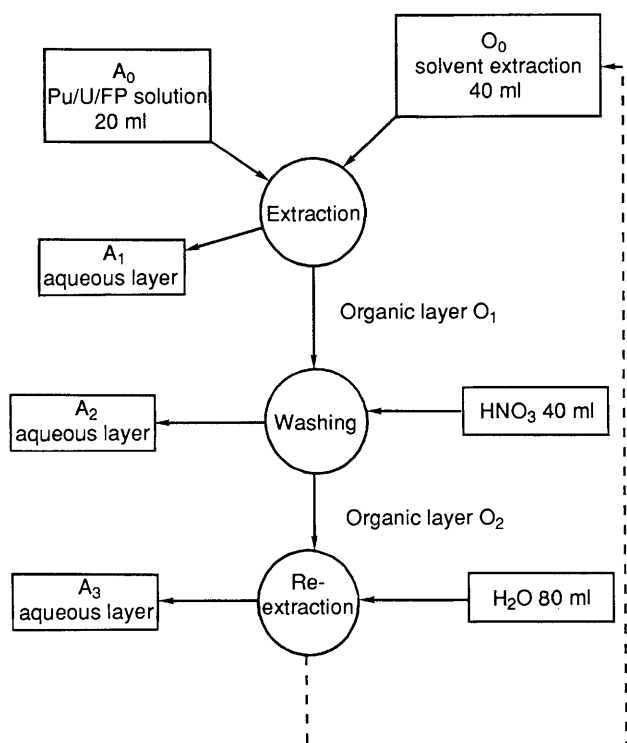


Fig. 1 Extraction of plutonium from irradiated nuclear fuel solutions

Here, we describe the use of isomers of DCH 18C6 for the separation of plutonium from solutions with medium and high activities arising in nuclear fuel reprocessing.

Various solutions containing uranium(vi), plutonium(iv) and fission products with high (1.85 TBq l^{-1}) activity were extracted with 18C6, 15C5, B 15C5, DB 18C6, DCH 24C8 and DCH 18C6 solutions (Fig. 1); only the last two exhibited a significant extraction of the plutonium and the DCH 18C6 was chosen for the study owing to the lower solubility of this macrocycle in nitric acid. Results described in Table 1 show that a single extraction of the aqueous solution by 0.67 mol l^{-1} of DCH 18C6 in CHCl_3 permits the separation of the plutonium leaving only part of the uranium and little of the fission products. Simply washing the organic layer with 1 mol dm^{-3} nitric acid improves the separation of Pu^{IV} from both fission products and U^{VI} . Re-extraction by using neutral water allows the recovery of the plutonium. Thus, in one step, 93% of Pu^{IV} can be separated from both uranium and fission products of a high activity solution. In comparison, use of a classical solution of TBP 30% in dodecane for the separation of the same solution led to an aqueous solution containing only 12.5% of the Pu^{IV} , 34% of the U^{VI} and 0.01% of the initial activity of the fission products. These results illustrate the efficiency of DCH 18C6 as a specific extractant of plutonium from nuclear waste, which demonstrates the

Table 1 Extraction of plutonium from high activity solutions by using DCH 18C6^a

Initial organic solutions	Initial aqueous solutions	Extraction	Washing aqueous solutions	Re-extraction
O_0	A_0	A_1 init. (%)	A_2 init. (%)	A_3 init. (%)
DCH 18C6- CHCl_3	Pu 1.1 g l^{-1} U 267 g l^{-1} Pf 1.1 TBq 1^{-1}	Pu 6 U 42 Pf 92	Pu 1.6 U 21 Pf 1.1	Pu 93 U 38 Pf 0.14

^a Composition of aqueous solutions and initial organic phase, uranium concentrations was determined by potentiometric titration using $\text{Fe}^{2+}/\text{K}_2\text{Cr}_2\text{O}_7$; plutonium titration is obtained by using visible spectroscopy after oxidation of plutonium by cerium(IV). Fission products were characterized by their γ emission.

Table 2 Extraction of plutonium using DCH 18C6 as extractant from medium activity solution

O_0 0.67 mol l^{-1}	A_0	A_1 init. (%)	A_2 init. (%)	A_3 init. (%)
DCH 18C6 <i>cis-syn-cis</i>	Pu 1.36 g l^{-1}	Pu 2 U 35 Pf 98	Pu 6 U 31 Pf 1	Pu 92 U 34 Pf 0.2
DCH 18C6 <i>cis-anti-cis</i>	U 0.96 g l^{-1}	Pu 4.6 U 40 Pf 98	Pu 18 U 40 Pf 1	Pu 80 U 20 Pf 0.2
DCH 18C6 mixture	Pf 177 MBq 1^{-1}	Pu 4.2 U 40 Pf 99.8	Pu 10 U 40 Pf 1.1	Pu 85 U 17 Pf 0.2

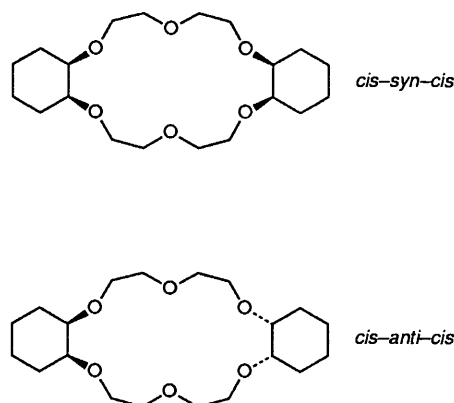


Fig. 2 Structures of the two main isomers of commercially available DCH 18C6

possibility of separation of Pu^{IV} from U^{VI} without the need of valence exchange as required in the Purex process. The lower decontamination obtained after re-extraction in the case of the macrocycle solution must be related to the better extraction of the plutonium (93% compared to 12%). Indeed if very high decontamination is to be obtained with the TBP solution, numerous extraction steps are required if complete extraction of Pu^{IV} is wanted. Increase of the number of washing steps in the case of macrocycle extraction may provide both a good decontamination and a direct separation of Pu/U .

Commercial DCH 18C6 is a mixture of *cis-syn-cis*- and *cis-anti-cis*-isomers (Fig. 2). Wen-Ji Wang *et al.*⁸ have demonstrated the higher efficiency of the *cis-syn-cis*-isomer for the extraction of thorium. The two isomers can be separated using the method described by Izatt *et al.*,⁹ and used as extractants in conditions described in Fig. 1 with a solution of medium activity (Table 2). Selectivity of the plutonium extraction appears to be much higher when using the *cis-syn-cis*-isomer than the *cis-anti-cis*-isomer or the com-

Table 3 Selectivity of the extraction of plutonium towards uranium with commercial and highly irradiated DCH 18C6

DCH 18C6 0.134 mol l ⁻¹	Isolated Pu (%)	Isolated U (%)
Commercial mixture	92	17
Irradiated	90	13

mercial mixture. The extraction constants were then calculated to be 480 and 140 mol⁻³ l³ with the *cis-syn-cis* and the *cis-anti-cis* respectively and using the 2:1 stoichiometry for the complex DCH 18C6/Pu⁴⁺ as demonstrated previously (Scheme 1).⁶ The distribution coefficient is directly proportional to the k_{ex} (Scheme 1) and a maximum D_m twice as large for the *cis-syn-cis*-isomer as for the *cis-anti-cis*-isomer can be expected. Thus, if a highly selective extractant of plutonium is required then concentrated solutions of the isomer *cis-syn-cis* DCH 18C6 could be proposed.

Interest in using DCH 18C6 in nuclear fuel reprocessing has improved by taking into account the high stability of such macrocycles in highly active solutions. A solution of 10% DCH 18C6 in CHCl₃ was irradiated by a caesium-137 source which produced 1.2 kGy h⁻¹ during 140 h without any modifications observed by UV, IR, ¹H and ¹³C NMR spectroscopy or by HPLC (SiO₂: CHCl₃, heptane); this result is consistent with those recently published¹⁰ by Matel *et al.* on the stability of an analogue system undergoing irradiation with a ⁶⁰Co source. DCH 18C6 used for extraction of a high activity solution remained bound to a solution of Pu^{IV}, U^{VI} and fission products corresponding to an ambient activity of 50 MGy h⁻¹ for 8 months. This contact which corresponds to a total energy of 611 kJ mol⁻¹ with 80.5 kJ mol⁻¹ of α emission can be estimated to be equivalent to 5000 extractions of high activity solutions as described above. The macrocycles were then washed in nitric acid and reused. The irradiated and commercial macrocycle was used comparatively for the extraction of plutonium from medium activity solutions. Results in Table 3 indicate that the selectivity of the plutonium extraction was barely if at all affected by strong irradiation of macrocycle DCH 18C6. In similar conditions Isaac¹¹ has already demonstrated that TBP led to a significant production of di- and

mono-butyl phosphate; these two products dramatically decrease the selectivity of plutonium extraction in the Purex process.

In conclusion DCH 18C6, specifically the *cis-syn-cis*-isomer of this macrocycle, is an efficient extractant capable of performing the separation Pu^{IV} from fission products and Pu^{IV} from U^{VI} without valence exchange as required in the Purex process. Stability under irradiation and selectivity of crown ethers may lead to the development of a new industrial technique for the reprocessing of nuclear fuel.¹²

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