

EXTRACTION OF TPE AND RE FROM NITRIC ACID SOLUTIONS BY MIXTURES OF CHLORATED COBALT DICARBOLLIDE WITH POLYOXOCOMPOUNDS

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ABSTRACT

The main data on development of a process for the extraction reprocessing of liquid highly radioactive wastes (HAW) to recover transplutonium and rare earth elements, strontium and cesium using chlorated cobalt dicarbollide (ChCoD) in the mixture with polyethylene glycol are considered. The extraction mixtures of ChCoD with crown ethers exhibit some advantages. By adding 15-crown-5 to ChCoD, the efficient recovery of TPE and RE could be improved; the mixture of ChCoD with 18-crown-6 provides increased selectivity towards actinides.

INTRODUCTION

Extraction systems based on ChCoD prove successful for reprocessing liquid HAW to recover, separate and purify strontium, cesium, TPE and RE fractions, as well as some other elements (1-4). These possibilities of extraction technology using ChCoD enable one to consider the latter as one of the most promising extractants for partitioning HAW in the program of long-lived radionuclide transmutation (5) and for recovering Cs and Sr from HAW for subsequent use (6).

Mathematical model for calculation of extraction cascades and automation of process control is a further development stage in HAW reprocessing technology using ChCoD (3, 4).

Successful tests of Sr and Cs recovery and purification technology were followed by elaboration of a process for recovery of TPE and RE from HAW. Concepts of extracting actinides and lanthanides by cobalt dicarbollide from nitric acid solutions were presented (7). The possibilities were checked under experimental conditions on a counter-flow test facility. The data on main extraction and technological characteristics of the flowsheet were obtained (2). The results of the conducted tests have shown that for the successful recovery of TPE and RE a higher concentration of extractant is required. It is also advisable to introduce a synergetic additive agent of linear polyether type (polyethylene glycols), for example SlovafoI-909 (n-non-ylphenylpolyethylene glycol with nine ethylene oxide groups in molecule).

The search for some other polyoxocompounds has been the subject of this investigation. These compounds in combination with a hydrophobic anion (ChCoD) could intensify the process of TPE and RE extraction (increase the

acidity of aqueous feed solution, decrease the concentration of ChCoD) and achieve efficient separation of actinide and lanthanide fractions. For this purpose, the extraction of americium and europium was investigated using the following polyoxocompounds: Dimethyl ether; tetraethylene glycol (DMT), SlovafoI-909; 3,6,9-trioxoundecane; 1,11-diol (TOUD), trihexaoxyethylamine (THoEA) and six crown ethers of different structure, 15-crown-5 (15-C-5), 18-crown-6 (18-C-6), dicyclohexyl-18-crown-6 (DC-18-C-6), dibenzo-18-crown-6 (DB-18-C-6) dibenzo-24-crown-8 (DB-24-C-6), diazo-18-crown-6 (DB-18-C-6) in the presence of a hydrophobic anion of chlorated cobalt dicarbollide.

Table I presents the distribution coefficients (D) and separation factors (β) for europium (III) and americium (III) in the systems mentioned above. It should be noted that the values of D^{Am} and D^{Eu} in the absence of ChCoD do not exceed 10^{-4} in all of the systems under investigation. As it is seen from Table I, non-additive increase of distribution coefficients is observed in the presence of SlovafoI-909 and 15-C-5, what agrees with the literature data (8, 9). In the systems using the crown-ethers 18-C-6, DC-18-C-6, DB-18-C-6, DB-24-C-6 and DMT, the values of D^{Am} and D^{Eu} decrease slightly. The addition of nitrogen-containing polyoxocompounds (DA-18-C-6, THoEA) suppresses the recovery of Eu (III) and Am (III) through the intensive extraction of onium cations.

The dependence of distribution coefficients on the concentration of 15-C-5 (Table II) has a maximum at molar ratio between reagents ChCoD : 15-C-5 = 1 : 1. Dependences of Eu (III) and Am (III) distribution coefficients on the concentration of polyoxocompounds in the systems containing ChCoD and SlovafoI-909 display a maximum also. However, its position corresponds to the molar ratio of reagents ChCoD : SlovafoI-909 = 3 : 1 (8). The increase of

TABLE I

Distribution Coefficients and Separation Factors for Microquantities of Am and Eu on Extraction by the Mixture of 0.16 M ChCoD and 0.06 M Polyoxocompounds from 1 M HNO₃

Compound	15-C-5	18-C-6	DC-18-C-6	DB-18-C-6	DB-24-C-8	DA-18-C-6	DMT	S1-909	THoEA	TOUD	
D ^{Am}	0.25±0.02	0.060±0.004	0.017±0.001	0.029±0.002	0.035±0.002	0.007±0.001	0.053±0.002	0.78±0.02	0.013±0.002	0.58±0.04	0.046±0.002
D ^{Eu}	0.18±0.01	0.019±0.006	0.012±0.001	0.020±0.002	0.025±0.002	0.004±0.001	0.060±0.002	0.42±0.02	0.009±0.002	0.30±0.02	0.039±0.002
β	1.4±0.1	3.2±0.3	1.4±0.1	1.4±0.1	1.4±0.1	1.5±0.1	0.8±0.1	1.9±0.2	1.4±0.1	1.9±0.2	1.2±0.1

TABLE II

Dependence of Am and Eu Distribution Coefficients on Initial Concentration of 15-crown-5 in Organic Phase Extraction by 0.16 M ChCoD from 1 M HNO₃

C _{15-C-5} ^M	0	0.06	0.1	0.2	0.3	0.4
D ^{Am}	0.046±0.002	0.25±0.01	0.48±0.02	0.65±0.03	0.32±0.02	0.17±0.01
D ^{Eu}	0.039±0.002	0.175±0.004	0.350±0.005	0.48±0.01	0.258±0.005	0.133±0.002
β	1.2+0.1	1.4+0.1	1.4+0.1	1.4+0.1	1.3+0.1	1.3+0.1

TABLE III

Dependence of Am and Eu Distribution Coefficients on Initial Concentration of 18-crown-6 in Organic Phase on Extraction by 0.03 M ChCoD in Nitrobenzene from 1 M HNO₃

C _{18-C-6} ^M	0	0.1	0.2	0.3	0.2*
D ^{Am}	0.35±0.03	0.25±0.02	0.16±0.01	0.0024±0.0006	1.96±0.08
D ^{Eu}	0.30±0.02	0.100±0.005	0.038±0.002	0.0008±0.0001	0.61±0.03
β	1.16±0.1	2.5±0.2	4.3±0.3	3.0±0.3	3.2±0.3

* - aqueous phase - 0.5 M HNO₃

TABLE IV

Dependence of Distribution Coefficients and Separation for Americium and Europium on Initial Concentration Europium Nitrate in Aqueous Phase on Extraction of the Mixture 0.2 M ChCoD and 0.2 M 15-crown-5 From 1 M HNO₃

$C_{Eu(NO_3)_3} \cdot M$	10^{-8}	0.01	0.05	0.1	0.5
D^{Am}	1.01 ± 0.05	0.88 ± 0.05	0.41 ± 0.02	0.32 ± 0.02	0.094 ± 0.005
D^{Eu}	0.74 ± 0.02	0.68 ± 0.02	0.34 ± 0.01	0.25 ± 0.01	0.065 ± 0.003
β	1.4 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.4 ± 0.1

TABLE V

Dependence of Distribution Coefficients and Separation Factors for Americium and Europium on Initial Concentration of Europium Nitrate in Aqueous Phase on Extraction by the Mixture 0.3 M ChCoD and 0.2 M 18-crown-6 in Nitrobenzene from 1 M HNO₃

$C_{Eu(NO_3)_3} \cdot M$	10^{-7}	0.01	0.05	0.1	0.3	0.5
D^{Am}	0.166 ± 0.008	0.157 ± 0.008	0.139 ± 0.008	0.120 ± 0.006	0.113 ± 0.006	0.103 ± 0.004
D^{Eu}	0.037 ± 0.002	0.041 ± 0.002	0.035 ± 0.002	0.028 ± 0.002	0.021 ± 0.001	0.017 ± 0.001
β	4.5 ± 0.4	3.8 ± 0.3	3.9 ± 0.3	4.3 ± 0.4	5.3 ± 0.4	6.0 ± 0.4

18-C-6 content leads to monotonous decreasing of Eu (III) and Am (III) distribution coefficients (Table III).

Maximum values of separation factors for pair "europium (III) - americium (III)" were obtained in the presence of 18-C-6 (Table III). It is interesting that nitrobenzene solutions of 18-C-6 possess the most selectivity towards the pair of Am (III)/Eu (III) as compared with other polyoxocompounds under consideration and in the presence of those different from ChCoD hydrophobic anions. The separation factors for the pairing of "europium (III) - americium (III)" in the systems of "picric acid - nitrobenzene," "dipicril amine - nitrobenzene," "higher isomer acids - nitrobenzene," "di-(2-ethyl hexyl) phosphoric acid - nitrobenzene" and "di-(2-ethyl hexyl) phosphoric acid - octane" in the presence of 18-C-6 are, as a rule, 1.5-2 times higher than in the same systems with the addition of 15-C-5.

The data presented in Tables I-III indicates that the mixtures of ChCoD with crown-ether 15-C-5 which afford the most efficient recovery of europium and americium and

the mixtures of ChCoD with crown-ether 18-C-6 and provides the separation factors for the Eu-Am pair with values $\beta = 4 - 6$ are of particular interest for HAW reprocessing. For these mixtures, the dependencies of distribution coefficients and separation factors on the concentration of europium nitrate in aqueous phase (Tables IV and V) were determined, which are indicative of retaining selective properties of the mixtures when passing from microconcentrations to macroconcentrations. These results allow the realization of the mixtures as useful for the reprocessing of highly active nitric acid Purex-raffinates which contain the small amounts of actinides and the macroconcentrations of lanthanides.

Therefore, the presented results have shown that the modified extraction systems, using ChCoD with the addition of crown-ethers, widen the potentialities of the proposed method for liquid HAW fractionation.

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