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Bis-(2-ethylhexyl) carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide [BenzoDODA]—first selective extractant for plutonium(IV) recovery (SEPUR) from acidic media

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ABSTRACT

A novel extractant, namely, Benzodioxodiamide (BenzoDODA) has been synthesized and evaluated for its extraction behaviour towards plutonium and other elements present in the spent nuclear fuel. High separation factors for plutonium over other elements were observed, indicating the high selectivity of the extractant for plutonium. The extractant is quite promising for the selective separation of plutonium from dissolver solution and various acidic waste streams.

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Plutonium is the only artificial element which has been produced in thousands of metric tons during the last 60 years owing to its strategic importance as well as its use in fast reactors for electricity production. Every ton of uranium fuel, upon burning in the reactor, results in the production of about 1–3 kg of Pu in the spent fuel. The dissolver solution, obtained by dissolution of the spent fuel, is processed to recover Pu and the remaining U for use in the next generation of nuclear reactors. Further, the high level liquid waste (HLW) generated during the reprocessing of spent fuel contains a few mg of Pu per litre of waste volume. Therefore, there is a need for selective separation of Pu from the dissolver solution as well as HLW and other waste streams.¹

During the last five decades various ligands have been proposed for the recovery of plutonium from reprocessing waste streams of diverse nature. O'Boyle et al. and Gorden et al. have reviewed, in detail, the various ligands/methods available for the separation of Pu from various waste streams.^{2,3} To date, the only commercial scale process used for the separation and purification of plutonium from spent nuclear fuel is the well known PUREX process which involves the bulk extraction of uranium along with plutonium in the organic phase comprising of tributyl phosphate and aliphatic diluents.⁴ The extracted metal ions are later separated by reducing the oxidation state of plutonium and stripping it into aqueous phase thereby retaining uranium in the organic phase. This process, though simple to use, offers several disadvantages, namely, (i) the use of organophosphorous extractants which are non-incinerable, (ii) the use of various reducing agents which tend to increase the waste volume and (iii) the co-extraction of other fission products, such as, Zr, Tc, Ru, etc. either with the extractant or with the degradation products formed after radiolysis of the extractant. Likewise several other extractants which include tertiary and guaternary amines,⁵ sulphoxide,⁶ alkylated monoamides,⁷ carbamoyl methylene phosphine oxides,⁸ catecholamides,⁹ terepthalimides,⁹ pyrolidones,¹⁰ etc. have been explored in various laboratories. The use of these extractants is mainly hampered by co-extraction of other actinides and fission products in appreciable fractions. So far there is no reagent available which can selectively extract Pu from various acidic waste streams.

With this in view we have focused on the designing of ligands based on (1) incorporation of only C, H, N and O in the extractant to maintain its incinerability, (2) incorporation of appreciable number of hard donor oxygen atoms appropriately placed in the extractant to provide better chelation and (3) incorporation of amidic functionality which serves the dual purpose of providing effective chelation as well as solubility of the metal extractant complex in paraffinic diluents. In this Letter we report the synthesis and evaluation of Pu selective extractant, namely, bis-(2-ethylhexyl)





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Figure 1. Reaction scheme for the synthesis of BenzoDODA.



Figure 2. Kinetics of extraction of Pu(IV) by 0.1 M BenzoDODA/*n*-dodecane from 3.0 M HNO₃ solution.



Figure 3. Effect of initial nitric acid concentration on Pu(IV) extraction by 0.1 M BenzoDODA/*n*-dodecane.

carbamoyl methoxy phenoxy-bis-(2-ethylhexyl) acetamide, commonly named as Benzodioxodiamide (BenzoDODA) for the separation of Pu from different acidic solutions.

The extractant (Fig. 1) has been synthesized from commercially available and tailor-made materials.¹¹ All other chemicals used in this study were of reagent grade.

The extraction studies of metal ions were carried out at $25 \pm 1 \,^{\circ}C.^{12}$ Equilibration time was determined by contacting 0.1 M BenzoDODA/*n*-dodecane with aqueous solution containing Pu(IV) (3.0 M HNO₃) for different time periods. Figure 2 shows the variation of $D_{Pu(IV)}$ as a function of contact time. It is evident that the minimum contact time required to reach the equilibrium is less than 10 min, which is considered to be fast enough to be used at a plant scale.



Figure 4. Effect of ligand concentration (BenzoDODA) on extraction of Pu(IV) in 3.0 M HNO₃.

With a view to optimise the conditions for extraction and stripping, $D_{Pu(IV)}$ was determined at varying nitric acid concentrations. $D_{Pu(IV)}$ was found to increase with the increase in acidity (Fig. 3). This could be attributed to the salting out effect (of nitrate ions), which facilitates the extraction reaction in forward direction.

The stoichiometry of metal to ligand in the extracted complex was determined using slope analysis method. Figure 4 shows the variation of $D_{Pu(IV)}$ as a function of concentration of extractant at fixed metal ion and acid concentration. The stoichiometry of plutonium to ligand is determined to be 1:1.

Considering the neutral character of the ligand the extraction reaction can be written as, $Pu_{aq.}^{4+} + 4.NO_{3aq.}^{+} L_{org.} \longrightarrow Pu(NO_{3})_4.L_{org.}$

Subsequently the ligand was evaluated for Pu separation from dissolver solution obtained by dissolving neutron irradiated uranium metal in 3.0 M HNO₃. Figure 5 shows the extraction behaviour of different elements with 0.1 M BenzoDODA/*n*-dodecane. From Figure 5 it is observed that among the elements studied only Zr and Nb are extracted, albeit in very less amounts, along with ~85% of plutonium in a single contact.

Table 1 shows the distribution ratio of Pu(IV) along with U(VI), Am(III) and some of the fission products. The separation factors of Pu(IV) over other elements are also shown in Table 1. The small, but finite D_M for some of the elements, namely, U, Zr, Te and Nb can be taken care by scrubbing the organic phase with the aqueous phase of similar acidity as that of the feed. Further, at higher loading of plutonium, the co-extraction of these metal ions will be reduced, thereby, giving still higher separation factors (SF).

Studies on the recovery of plutonium from the loaded organic phase were carried out with $0.2 \text{ M } N_2 H_4 + 0.6 \text{ M } H NO_3$ and 0.1 M oxalic acid. Table 2 shows the percentage back extraction of Pu in a single contact. Pu can thus be effectively recovered from the loaded organic phase in multiple stages thereby providing the option of recycling the solvent system.



Figure 5. γ Spectra of dissolver solution and 0.1 M BenzoDODA/n-dodecane after contacting with dissolver solution.

Table 1

Distribution ratio of Pu and other elements present in dissolver solution into 0.1 M BenzoDODA/n-dodecane

Element	Pu(IV)	U(VI)	²⁴¹ Am	¹⁴⁷ Nd	¹⁴¹ Ce	¹⁴⁰ La	¹⁰³ Ru	¹⁴⁰ Ba	⁹⁵ Zr	⁹⁵ Nb	¹³² Te	⁸⁹ Sr
D _M	6.74	0.11	0.005	0.002	0.005	0.019	0.011	0.0018	0.151	0.124	0.116	0.021
SF(D _{Pu} /D _M)	—	61.27	1348	3370	1348	354.7	612.7	3744.4	44.64	54.34	58.10	320.9

Table 2

Back extraction of Pu from loaded organic phase in different stripping agents

Extractant	0.2 M N ₂ H ₄ + 0.6 M HNO ₃	0.1 M Oxalic acid		
0.1 M BenzoDODA/n- dodecane	85% (1st Contact)	15% (1st Contact)		

In conclusion a novel extractant has been synthesized and evaluated for the selective separation of Pu from acidic media. It can be effectively used for the separation of Pu from dissolver solution, high level waste and other acidic waste streams. Detailed mixer settler studies with dissolver solution are under progress to assess the true potential of BenzoDODA/*n*-dodecane solvent system for the separation and recovery of Pu from spent nuclear fuel.

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- 11. General procedure for synthesis of extractant: To 50 ml of ethanol taken in a round bottom flask fitted with air condenser was added 0.1 mol of KOH. To this 0.05 mol of catechol was added and stirred for a while. About 0.1 mol of N.Nbis-(2-ethylhexyl)-2-chloroacetamide was added to the reaction mixture in one lot and was continuously stirred for 6 h. The temperature of the reaction mixture was raised to 50-60 °C and stirring was continued for 12 h. The resulting solution was filtered and evacuated to remove the solvent. Hexane was added to the residue and the resulting organic solution was washed several times with 2.5 wt% Na2CO3 solution till the aqueous phase became colorless. The organic phase was then treated successively with 0.5 M HCl and water, and dried over anhydrous Na₂SO₄. This was then concentrated in vacuum (0.01 mmHg) at 100-120 °C. The purity and yield of the product was 98.8% and 95% 'respectively'. Elemental Anal. Calcd for C42H76O4N2: C, 75.0; H, 11.31; O, 9.52; N, 4.16%. Found: C, 74.78; H, 11.17; O, 9.94; N, 4.11%. ¹H NMR (CDCl₃): 0.80–0.90 (m, 24H), 1.24 (m, 32H), 1.60–1.64 (m, 4H), 3.20–3.30 (m, 8H), 4.77 (s, 4H), 6.88 (s, 4H). GC–MS: 24.76 min, 1.24%, *m/z* 522 calculated for $(C_8H_{17})_2NCH_2CON(C_8H_{17})_2$ and 40.92 min, 98.76%, m/z 671 calculated for BenzoDODA($C_8H_{17})_2N-C(O)-CH_2-O-(Ar)-O-CH_2-C(O)-N(C_8H_{17})_2$.
- 12. Solvent extraction experiments: Plutonium was stabilized as Pu(IV) using NaNO₂. Solvent extraction studies were carried out by equilbrating equal volume of the organic and aqueous phases for 30 min followed by centrifugation for phase separation. 100–500 µl of each phase was taken for radiometric assay of Am(III) and fission products using High Purity Germanium (HPGe) detector based gamma spectrometry system. The results were reported as distribution ratio and are calculated as radioactivity of the corresponding radionuclide in the organic phase divided by that in the aqueous phase. Each experiments with plutonium and uranium were also carried out. Plutonium and uranium (²³³U) were assayed by alpha counting in a ZnS(Ag) based alpha counter.