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Liquid–liquid extraction studies for the separation and recovery of plutonium from acidic medium with novel ligand Benzodioxodiamide (BenzoDODA)

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ABSTRACT

Detailed liquid–liquid extraction studies of Pu(IV) with BenzoDODA have been carried out to evaluate the efficacy of BenzoDODA in the separation and recovery of Pu(IV) from acidic solutions. Acid uptake constant (K_H) was determined to be 0.44. Incorporation of tertiary butyl group in the aromatic moiety of BenzoDODA resulted in the increase in extractability of Pu(IV) but at the expense of decrease in the selectivity for Pu(IV) vis a vis other metal ions. Among the various diluents studied, the normal paraffinic hydrocarbons, namely, n-dodecane/kerosene were found to be the most preferred diluents. BenzoDODA was found to be stable in radiation environment, with good extraction ability up to 20 MRad. Number of stages required for the effective recovery of plutonium from the feed solution has been determined by McCabe Thiele's plot. It was found that even at higher loadings of Pu(IV), there is no third formation which is remarkable since at these loading TBP/n-dodecane solvent system has shown considerable third phase formation. Thus, BenzoDODA/n-dodecane solvent system can be used for recovery of Pu(IV) from concentrated processing streams as well.

1. Introduction

Spent nuclear fuel arising from power reactors mainly consists of residual uranium (~95 wt.%), plutonium (~1 wt.%), minor actinides (neptunium, americium and curium, 0.1%) and various short/long lived fission products (~4 wt.%) [1]. Among the various strategies being adopted for spent fuel management, the most preferred one involves (i) Separation and recovery of major actinides, namely, U and Pu, (ii) Partitioning of long lived actinides and fission products and their transmutation to either short lived or stable products, (iii) Separation of heat emitting radionuclides like ^{137}Cs, and ^{90}Sr, (iv) Separation and recovery of valuable radionuclides for their use in various possible applications and, (v) Immobilization of residual concentrated activity in suitable matrix. In this regard, the first and the foremost step, that is, the extraction and per-concentration of uranium and plutonium becomes extremely important not only from the point of view of the fissile/fertile nature of the elements, but also to reduce their quantum for disposal as radioactive wastes [2]. Thus the dissolver solution, obtained by dissolution of the spent fuel, is processed to recover Pu and the residual U for use in the next generation of nuclear reactors. PUREX (Plutonium Uranium Reduction Extraction) process is the only commercial scale process used for separation and purification of plutonium from nuclear spent fuel [3,4]. However, this process faces a major limitation, tributyl phosphate (TBP) does not selectively extract 'Pu' and therefore adjustments have to be made for the further purification of Pu from other co-extracted metal ions. Additionally, TBP is known to have low limiting organic concentration for 'Pu' and therefore shows a tendency to form third phase at slightly higher concentrations of Pu [4]. Further, the high level liquid waste (HLW) generated during the reprocessing of spent fuel contains a few mg of Pu per liter of waste volume. This has necessitated the development of novel class of ligands for selective separation of plutonium from dissolver solution and other waste streams. Various ligands, including, tertiary and quaternary amines [5], sulphoxide [6], alkylated monoamides [7], carbamoyl methylene phosphine oxides [8], catecholamides [9], terepthalimides [9], pyrolidones [10], etc. have been explored for this purpose. The use of these extractants is mainly hampered by co-extraction of other actinides and fission products in appreciable fractions. Recently, we have reported the novel ligand, namely, BenzoDODA which has shown high extractability and excellent selectivity for Pu over other metal ions present in dissolver solution [11]. These

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preliminary investigations have shown BenzoDODA quite a promising ligand for selective separation of 'Pu'. Therefore, it becomes necessary to carry out detailed liquid–liquid extraction studies to determine its efficacy in separation and recovery of plutonium from various acidic streams.

In the present work extensive liquid–liquid extraction studies of Pu(IV) with BenzoDODA/n-dodecane have been carried out. Further the effect of radiolytic degradation of the extractant on the extraction behavior of Pu(IV) has also been studied to evaluate its effectiveness in the treatment of Pu(IV) bearing radioactive acidic solutions.

2. Experimental

2.1. Reagents

BenzoDODA and tert. butyl BenzoDODA (Fig. 1) were synthesized as per the procedure reported earlier [11]. The n-paraffin mixture (C-10 to C-16) from Aldrich Inc. (USA) containing 90% n-dodecane was used for the preparation of desired concentrations of BenzoDODA and tert. butyl BenzoDODA. However, for the diluent effect studies BenzoDODA was dissolved in given diluent to form corresponding concentrations. All other reagents used were of analytical grade.

2.2. Radionuclides

In house plutonium stock solution having ^{239}Pu as a major constituent (>93%), was used in its nitrate form in liquid–liquid extraction studies. The tetravalency of plutonium was maintained by adding sodium nitrite in the stock solution and checked for its radiochemical purity by alpha-spectrometry.

U–Al alloy was irradiated in DHRUVA reactor (neutron flux $\sim 5 \times 10^{13}$ neutron sec^{-1} cm^{-2}). After appropriate cooling, the alloy was dissolved in concentrated alkali solution at 150 °C in quartz beaker in a glove box. The solution and the residue were centrifuged and separated; then the residue was dissolved in 2.0 M nitric acid solution. Aliquots (tracer level) were taken from the acidic solution to study the extraction behavior of the various radionuclides with BenzoDODA.

2.3. Measurement of distribution ratios

Single-stage batch experiments were carried out to obtain the distribution ratios of nitric acid, Pu(IV) and other elements under the given experimental conditions. Liquid–liquid extraction studies were carried out by equilibrating equal volume of the organic and aqueous phases for 30 min at room temperature (ca. 298 K) followed by centrifugation for phase separation. 100–500 μl of each phase was taken for radiometric assay of various radionuclides using High Purity Germanium (HPGe) detector based gamma spectrometry system (Table 1). Independent experiments with plutonium and uranium were carried out. Plutonium and uranium (^{233}U) were assayed by alpha counting in a ZnS(Ag) based alpha counter. The results were reported as distribution ratio (D_M) and are calculated as radioactivity of the corresponding radionuclide in the organic phase divided by that in the aqueous phase. Each experiment was done in duplicate and results agree within ±5%.

Acid uptake studies were carried out by contacting 0.1 M BenzoDODA/n-dodecane with nitric acid of varying concentrations and estimating the amount of acid extracted into the organic phase using methodology reported earlier [12].

Table 1
'γ' energy of ^{241}Am and some of the fission products present in dissolver solution.

Element	'γ' energy (keV)
^{241}Am	59.5
^{144}Ce	133
^{103}Ru	497.1
^{140}La	328.6
^{147}Nd	91.1
^{95}Zr	724.1
^{95}Nb	765.8

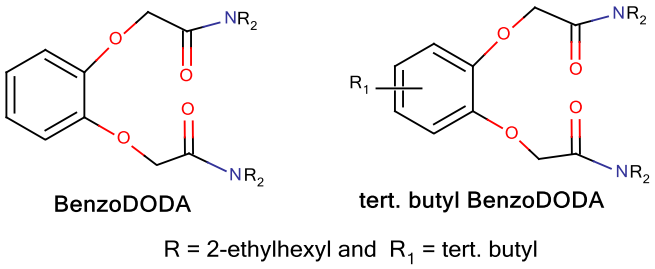

Fig. 1. BenzoDODA and tert. butyl BenzoDODA.

2.4. Radiolytic stability studies

Two types of samples were taken in glass vials for irradiation, namely, (1) 0.1 M BenzoDODA in n-dodecane and, (2) 0.1 M BenzoDODA/n-dodecane in contact with equal volume of 3.0 M nitric acid, the later one being occasionally shaken during irradiation. These samples were irradiated with γ rays from ^{60}Co source at a dose rate of 22 Gy/min in air at room temperature. After a particular absorbed dose the samples were removed from the chamber and analyzed for distribution ratios of plutonium from 3.0 M nitric acid solution.

3. Results and discussions

3.1. Acid uptake studies

Nitric acid uptake is a property exhibited by most of the amidic extractants. Since BenzoDODA contains two amidic moieties, it is expected to possess significant acid uptake. It was observed that uptake of acid increases with the increase in initial nitric acid concentration. In order to compare the basicity of BenzoDODA with other amidic extractants, it becomes imperative to have the quantitative knowledge of its basicity in terms of conditional acid uptake constant.

BenzoDODA interacts with the nitric acid according to the following mechanism.

$$E_{(\text{org.})} + n \cdot H^{+}_{(\text{aq.})} + n \cdot NO^{-}_{3(\text{aq.})} \rightleftharpoons E \cdot n\text{HNO}_{3(\text{org.})} \quad (1)$$

where E is the extractant and n is the number of nitric acid molecules involved in the formation of the adduct. The acid uptake constant K_H is given by

$$K_H = \frac{[E \cdot n\text{HNO}_3]_{\text{org.}}}{[E]_{\text{org.}}[H^+]^n_{\text{aq.}}[NO^-_3]^n_{\text{aq.}}} \quad (2)$$

where $[E]_{\text{org.}}$ is the concentration of free organic extractant and is determined as

$$[E]_{\text{org.}} = [E]_{\text{initial}} - [E \cdot n\text{HNO}_3]_{\text{org.}}$$

As the data for the activities of nitric acid and free BenzoDODA in the organic phase are not available, therefore, the equilibrium constant is referred to as conditional acid uptake constant.