



Effect of degradation products of TEHDGA on actinide partitioning process



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ABSTRACT

Degradation products of TEHDGA, obtained on γ -radiolysis of 0.2 M TEHDGA + 30% isodecyl alcohol/*n*-dodecane in the presence of nitric acid, were isolated and studied for their extraction behaviour with americium and other metal ions of high level waste. It was observed that two degradation products, *N,N*-bis(2-ethylhexyl)glycolamide (BEHGA) and diglycolic acid monoamide (DGAMA), considerably affect actinide partitioning process. BEHGA a neutral extractant, similar to TEHDGA, showed extraction for americium, lanthanides, Zr(IV) and Mo(VI) at higher (extraction) acidities, while, DGAMA an acidic extractant showed extraction at lower (stripping) acidities. BEHGA extract by solvation through a bidentate pre-organised five membered ring formed due to intramolecular hydrogen bonding between its α -OH and C=O groups, and DGAMA having pK_a of 1.8, extracts metal ions through cation exchange in pH medium. Their presence in the degraded solvent significantly affects the performance of the solvent with respect to loss of selectivity during extraction and insufficient stripping.

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1. Introduction

High level liquid wastes (HLLW) generated during the reprocessing of the spent nuclear fuels consist of extremely long-lived radiotoxic minor actinides such as ^{241}Am , ^{243}Am , ^{245}Cm , and ^{237}Np . The safe disposal of this radiotoxic waste is a matter of great environmental concern, and crucial to the success and public acceptance of the nuclear-energy program. Presently, the HLLW is being immobilized in glass matrix and stored in geological storage facilities. However, due to the very long half-lives of these minor actinides, the matrix will remain radioactive for millions of years, therefore, such storage require continuous long-term surveillance making this an expensive, unsafe and un-acceptable practice. However, as an alternative method, the strategy of partitioning, i.e., the complete removal of minor actinides from HLW, and their subsequent transmutation in high flux reactors/accelerator driven subcritical systems is being adopted, thereby, making the HLW more safe, suitable and acceptable for geological storage by largely reducing its minor actinide load [1].

Selective separation of trivalent minor actinides is difficult owing to the presence of a large amount of trivalent lanthanide fission products which have chemical properties similar to those of the trivalent minor actinides. In this context, several extractants

and processes have been developed for lanthanide–actinide co-extraction from the HLLW in the past few decades, such as TRUEX, TRPO, DIDPA, and DIAMEX based on extractants such as *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), trialkylphosphine oxides (TRPO), diisodecylphosphoric acid (DIDPA), *N,N'*-dimethyl-*N,N'*-dibutyltetradecyl malonamide (DMDBTDMA), and *N,N'*-dimethyl-*N,N'*-dioctyl-2-hexylethoxy-malonamide (DMDOHEMA) [2]. Recently, diglycolamide based extractants such as *N,N,N,N'*-tetraoctyl diglycolamide (TODGA) and *N,N,N,N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) have attracted considerable interest in the field of actinide partitioning due to their superior extraction properties than the earlier proposed extractants [3].

Of the two diglycolamide extractants, TEHDGA is known to have low extraction for fission products from acidic HLW due to the branching in its alkyl side chain, and also is commercially more viable solvent for large scale operations due to the use of a less expensive precursor, bis(2-ethylhexyl)amine, in its synthesis [4]. Several studies have been carried out on TEHDGA for actinide partitioning [4–7], for uranium and thorium separations [8], for separations using flat sheet supported liquid membrane [9–11], for strontium separations [12–14] and for the extraction of trace concentrations of actinides, lanthanides and fission products using impregnated resins by extraction chromatography [15].

Since the solvents used for actinide partitioning are continuously exposed to high radiation dose in contact with high aqueous

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nitric acid concentrations, therefore, understanding of radiolytic and hydrolytic stabilities of these solvents and the effect of degradation products of solvents on the separation process is extremely important for complete process development. In this context, detailed investigations have been carried out on the hydrolytic and radiolytic stability of TEHDGA [16–18]. From our studies on the radiolytic degradation of TEHDGA [18], we were able to identify and isolate several radiation degradation products of TEHDGA such as bis(2-ethylhexyl) amine (BEHA), *N,N*-bis(2-ethylhexyl) formamide (BEHFA), *N,N*-bis(2-ethylhexyl)acetamide (BEHAA), *N,N*-bis(2-ethylhexyl)glycolamide (BEHGA), diglycolic acid monoamide (DGAMA) and *N,N*-bis(2-ethylhexyl)-*N,N'*-dipropyl diglycol amide (BEHDPDGA), formed mainly through the cleavage of its etheric and amidic bonds. Upon examining the effect of each degradation products on extraction process, it was observed that BEHGA and DGAMA have good potentials for extraction for Am(III) in extraction and stripping acidities respectively. Therefore, extraction behaviour of Am(III) and some of the selected fission products present in HLLW was also studied to establish the effect of these degradation products on overall actinide partitioning process.

2. Experimental

2.1. Chemicals and reagents

TEHDGA was synthesised in our laboratory according to previously reported procedure [19]. 0.2 M TEHDGA + 30% isodecyl alcohol/*n*-dodecane in contact with 3.5 M nitric acid was irradiated up to 1 MGy. After irradiation, the irradiated TEHDGA was separated and distilled to remove *n*-dodecane and isodecyl alcohol and finally distilled at 110 °C, 0.05 mmHg, to isolate BEHGA, the residue containing other degradation products including DGAMA and non-degraded TEHDGA was dissolved in *n*-hexane and passed through Brockmann type I basic alumina column. The acidic component, DGAMA, was trapped in the column leaving all the neutral components in the eluent phase. DGAMA was then eluted from the column by ethyl acetate (80%) and *n*-hexane (20%) mixture and obtained in pure form by distilling off the solvents. BEHGA and DGAMA (Fig. 1) were characterised by GC–MS and found to be more than 98% pure [18]. pK_a of DGAMA was determined by potentiometric titration using Henderson–Hasselbalch equation [20]. *N,N*-bis(2-ethylhexyl)-2-ethoxyacetamide and *N,N*-bis(2-ethylhexyl)-2-methoxyacetamide were synthesised by Williamson synthesis which involved the reaction between *N,N*-bis(2-ethylhexyl)-2-chloroacetamide and the corresponding alkoxide ions [21]. These were also characterised by GC–MS and IR prior to use. Isodecyl alcohol and *n*-dodecane were obtained from local companies and were used as received. All other chemicals used were of analytical grade. Radioactive tracer solutions of $^{241}\text{Am(III)}$, and $^{152,154}\text{Eu(III)}$ at an approximate concentration of 10^{-7} M in 1 M HNO_3 were used

as stock for extraction studies. Extraction studies for Sr(II), Ru(III), Zr(IV), and Mo(VI) were carried out using approximately 100 mg/L solution of each element, prepared by dissolving their respective inactive salts, strontium nitrate, ammonium molybdate, zirconium oxychloride, and ruthenium nitrosyl nitrate in 4 M HNO_3 .

2.2. Irradiation with gamma rays

Irradiation of 0.2 M TEHDGA + 30% isodecyl alcohol/*n*-dodecane was carried out at our ^{60}Co γ -irradiation facility. 500 mL of 0.2 M TEHDGA-30% isodecyl alcohol/*n*-dodecane in contact with 500 mL of 4 M nitric acid, was irradiated with γ -rays from a ^{60}Co source at a dose rate of 30 Gy/min in air at room temperature till a dose of 1 MGy was reached.

2.3. Distribution ratio measurements

For the determination of distribution ratios (D_M) of the metal ions, 2 mL of the organic solvent was contacted with an equal volume of aqueous nitric acid solution containing the metal ion at 25 ± 1 °C for 15 min. After phase separation by centrifugation, the organic and aqueous phases were separated and analysed for the metal ion concentration, and the D_M was calculated as the ratio of the concentration (or radioactivity) of the metal ion in the organic phase to the concentration of the metal ion in the aqueous phase. The estimation of Am(III) and Eu(III) in the organic and aqueous phases were carried out by analysing both the phases for the corresponding gamma activity using NaI(Tl) detector. The energy line used for the evaluation of ^{241}Am and $^{152,154}\text{Eu}$ were 59.8 and 121 keV respectively. Here Eu was chosen as the representative element for all the lanthanides. The distribution ratio measurements using radiometry have a maximum error of $\pm 5\%$. The estimation of other elements was carried out by the analysis of the aqueous phase before and after equilibration, after suitable dilution using ICP–AES. Metal concentration in organic phase was determined by difference in concentration in aqueous phase before and after equilibration. The quantification limit for ICP–AES analysis was 1.0 mg/L. Distribution ratios of all the metal ions were determined separately.

3. Results and discussion

3.1. Extraction studies with BEHGA

Prior to evaluating the distribution ratios with respect to various parameters, the time of equilibration for Am(III) from 4 M HNO_3 for 0.3 M BEHGA/*n*-dodecane was investigated. It was observed that the extraction equilibrium was attained within 5 min of contact time, and the $D_{\text{Am(III)}}$ remained constant thereafter. Therefore, all other extraction experiments were carried out for a contact time of 15 min to ensure that the equilibrium is

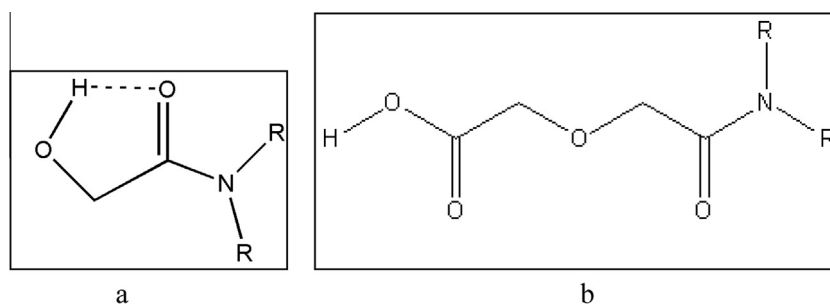


Fig. 1. Structures of (a) bis(2-ethylhexyl)glycolamide (BEHGA) and (b) diglycolic acid monoamide (DGAMA); where R = 2-ethylhexyl.

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