DEVELOPMENT OF A SINGLE-CYCLE APPROACH FOR MINOR ACTINIDE PARTITIONING

By

PRASANT KUMAR NAYAK
CHEM02201104006

Indira Gandhi Centre for Atomic Research
Kalpakkam

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N. Sivaraman 19/9/17
Chairman – Dr. N. Sivaraman **Date:**

19.9.2017
Guide / Convener – Dr. M. P. Antony **Date:**

Ashok Khanna
Examiner - Prof. Ashok Khanna **Date:** 19/9/17

Member 1- Dr. S. Rangarajan **Date:**
19.09.2017

Member 2- Dr. T. R. Ravindran **Date:**
T R Ravindran 19.9.2017

Tech. Adviser- Dr. K. A. Venkatesan **Date:**
K.A. Venkatesan 19/9/17

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Date: 19.9.2017

Place: kalpakkam

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List of Publications arising from the thesis

Journal

1. "A new method for partitioning of trivalent actinides from high-level liquid waste", P. K. Nayak, R. Kumaresan, K. A. Venkatesan, M. P. Antony, P. R. Vasudeva Rao, *Separation Science and Technology,* **2013**, *48 (9)*, 1409-1416.

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3. "Single-cycle separation of americium (III) from simulated high-level liquid waste using tetra-bis (2-ethylhexyl) diglycolamide and bis (2-ethylhexyl) phosphoric acid solution", P. K. Nayak, R. Kumaresan, K. A. Venkatesan, S. Rajeswari, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao, *Journal of Environmental Chemical Engineering*, **2013,** *1 (3),* 559-565.

4. "Studies on the Radiochemical Degradation of Tetraethylhexyl Diglycolamide and Ethyhexylphosphoric Acid in n-Dodecane Solution", P. K. Nayak, Shivkumar Chaurasia, R. Kumaresan, K. A. Venkatesan, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao, B. M. Bhanage, *Separation Science and Technology,* **2015,** *50 (5),* 646-653.

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2. Single-step separation of trivalent actinides from nitric acid medium R.Kumaresan, Prasant Kumar Nayak, K.A.Venkatesan, M.P.Antony, P.R.Vasudeva Rao Proceedings of nuclear and radiochemistry symposium held at Jabalpur, M.P, India Eds. R.Tripathi, G.A.R.Rao, B.S.Tomar, K.L.Ramakumar Page 187.

3. Demonstration of Single-Cycle Partitioning of Trivalent Actinides from SHLLW. P. K. Nayak, R. Kumaresan, K. A. Venkatesan, S. Rajeswari, G. G. S. Subramanian, M. P. Antony, P. R. Vasudeva Rao. Proceedings of DAE-BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2014), Mumbai, India, p-55.

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Prasant Kumar Nayak

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Synopsis

1. Introduction

The demand for energy is steadily increasing with increase in population and rapid industrialization all over the world. Huge consumption of natural energy resources, such as oil and gas, and the uncertainty in the development of renewable resources such as solar, tidal, wind etc, makes nuclear option inevitable for the future energy demand. At present, the nuclear energy contributes nearly 11% of the global electricity demand [1]. Natural or enriched uranium is used as the fuel for thermal nuclear reactors where as uranium-plutonium mixed oxide is used in fast reactors for energy production. The fuel discharged from a reactor after energy production is called as spent nuclear fuel (SNF). The spent nuclear fuel contains substantial quantities of fissile elements, which can undergo nuclear fission such as plutonium, depleted (unused) natural uranium, and several fission products formed during fission reaction. Therefore, it is necessary to reprocess the spent nuclear fuel for the recovery of the fissile elements for further use in the reactors as fuel.

Aqueous reprocessing of the spent nuclear fuel is being adopted for the recovery of uranium and plutonium. This is industrially well-established and being employed in many countries. In this method, the spent nuclear fuel is dissolved in nitric acid, and the uranium and plutonium are recovered by a well-known process called Plutonium Uranium Recovery by EXtraction (PUREX) process [2]. The PUREX process consists of three major steps namely (i) the head end step, which includes decladding, dissolution, and feed preparation, (ii) solvent extraction using tri-*n*-butyl phosphate (TBP), and (iii) final purification and conversion of uranium and plutonium to their respective oxides.

The raffinate rejected after the PUREX process is known as “high-level liquid waste” (HLLW), which is a complex mixture of several elements such as minor actinides (MA), lanthanides, other fission products, corrosion products of structural materials and additives present in 3-4 M nitric acid medium. Among the various elements, the radiotoxicity of HLLW is essentially contributed by long-lived and alpha emitting radiotoxic minor actinides and heat emitting fission products like ^{137}Cs and ^{90}Sr. Since the half-lives of these isotopes vary from a few years to several hundred years, HLLW poses long-term risks to public health and environmental safety. Therefore, the future of nuclear energy depends on the safe management of HLLW. Currently, immobilization of HLLW in a suitable ceramic or glass matrix, followed by the deposition in deep geological repositories is being practiced [3]. However, it demands the long-term surveillance due to the presence of these minor actinides making it a very expensive option. Alternatively, partitioning (P) of these radiotoxic elements followed by transmutation (T) of radiotoxic element into stable or short-lived products by neutron bombardment in accelerated driven systems (ADS) or fast-breeder reactors (FBR) called P&T strategy is a viable option for the safe management of HLLW. P&T reduces the radiotoxicity of HLLW significantly and minimizes the surveillance period and therefore, it is being pursed as one of the viable options for the safe management of HLLW [4].

Partitioning of trivalent actinides from HLLW involves a complex chemical process. The transplutonium actinides (Am and Cm) essentially exhibit trivalent oxidation state in nitric acid and chemically behave like trivalent lanthanides (Ln(III)) in nitric acid medium [5]. The trivalent actinides are known as minor actinides. The lanthanides (Ln(III)) are fission products having close similarity in their chemical properties, size and extractive properties with trivalent actinides (An(III)), which makes it difficult to separate the An(III) alone from HLLW. The mutual separation of Ln(III) and An(III) prior to the transmutation of actinides is essential, owing to high neutron absorption cross sections of lanthanides. Presence of lanthanides reduces the efficiency of actinide transmutation. The complete separation of Ln(III) from An(III) is very important prior to the actinide transmutation.

Generally, a two cycle process is proposed for minor actinide partitioning. First cycle involves co-extraction of An(III) and Ln(III) from HLLW using neutral extractants known as group separation. Whereas, the second cycle aims for the separation of An(III) from Ln(III) using acidic extractants known as mutual separation of An(III) from Ln(III). For the co-extraction of trivalent An(III) and Ln(III) from HLLW, several processes were developed in various countries. For example, *n*-Octyl(phenyl)-*N,N*-diisobutylCarbamoylMethyl Phosphine Oxide (CMPO) is used as an extractant in TRans-Uranic element EXtraction (TRUEX) process, developed in USA [6], *N,N'*-DiMethyl-*N,N'*-DiOctyl-2-HexylEthoxy Malon Amide (DMDOHEMA) in DIAMide EXtraction (DIAMEX) process developed in France, and TriAlkylPhosphineOxides (TRPO) in Trialkyl Phosphine oxide process developed in China etc, [6-8]. Later Japanese developed a new class of extractants namely, diglycolamdies (DGAs), which are being widely studied for the partitioning of An(III) due to the several advantages they offer over the other reagents [9]. Among various DGAs studied so far, *N,N,N',N'*-tetra-octyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) received much attention for the group separation of An(III) and Ln(III) from the HLLW [9]. For the second cycle namely for lanthanide – actinide separation, acidic extractants such as Di(2-ethylhexyl) Phosphoric Acid (HDEHP) is used in Trivalent Actinides Lanthanide Separation Phosphorous based reagent Extraction from Aqueous Komplexes (TALSPEAK) process [10] and *N,N*-di-2-ethylhexyl diglycolamic acid (HDEHDGA) used for the mutual separation of An(III) from Ln(III) [11].

The reagents proposed for the co-extraction of An(III) and Ln(III) from HLLW suffer from certain limitations such as i) third phase formation i.e. splitting of organic phase into two phases during extraction ii) co-extraction of other metal ions present in HLLW such as Zr(IV), Mo(VI), Sr(II), Pd(II) along with the trivalent actinides. Third phase formation can be avoided by adding suitable polar organic phase to solvent phase called as phase modifier, in significant concentration. The phase modifier was usually another extractant, such as tri-*n*-butyl phosphate (TBP), *N,N*-dihexyloctanamide (DHOA), or long chain alkyl alcohol. The co-extraction of other metal ions can be minimized using aqueous soluble complexing agents to the feed solution. This ultimately increases the waste generation. Apart from this, a two cycle separation of actinides from HLLW is associated with more secondary waste generation and not economical for the waste treatment.

In view of these limitations, a single-cycle process for minor actinide partitioning is being developed by combining a neutral extractant with an acidic extractant [12, 13]. In this case, the extractant for group separation and mutual separation are combined to achieve single-cycle process for minor actinide partitioning. In single-cycle process, the trivalent actinides and lanthanides are extracted from HLLW using combined solvent formulation and the recovery of actinides alone from the loaded solvent phase was carried out using aqueous soluble and actinide selective diethyltriamminepentaaceticacid (DTPA)-citric acid (CA) solution. TRUSPEAK process is a combination of TRUEX and TALSPEAK process, where CMPO and HDEHP together used for the extraction of Am(III) and Eu(III) and 0.4 M hydrazine hydrate, 0.4 M formic acid - 0.05 M DTPA was used for mutual separation of Am(III) from Eu(III) [13].

2. Scope of the present study

Generally, the extractant used for the group separation of trivalent metal ions from HLLW that originate from FBRs forms third phase. In order to avoid third phase formation, some phase modifier was used along with the extractant. However, addition of phase modifier results in increase in the extraction of other fission products. The presence of phase modifier in solvent phase also burdens the management of spent organic waste. These problems can be avoided by using modifier free extractant for the group separation of trivalent metal ions from HLLW. In this context, a modifier free extractant *N*,*N*,-didodecyl-

N',*N'*-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) being developed and demonstrated the separation of minor actinide from a Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW) solution in a 20 stage mixer-settler.

The aim of the present study is to develop a single-cycle process for minor actinide partitioning by combining a neutral extractant with an acidic extractant. A method known as **S**ingle-cycle method for **M**inor **A**ctinide partitioning using completely incinerable **R**eagen**T**s (SMART), for the separation of trivalent actinides by combining D^3DODGA and *N,N*-di-2-ethylhexyl diglycolamic acid (HDEHDGA) was developed in the present study and the extraction behavior of the metal ions present in FR-SHLLW studied extensively. The extraction and stripping conditions are optimized. The minor actinide partitioning in a single-cycle was demonstrated in a 20 stage mixer-settler using 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD from FR-SHLLW. In this case, both An(III) and Ln(III) are extracted to organic phase using combined solvent system followed by the selective stripping of An(III) using diethylenetriaminepentaacetic acid (DTPA)-Citric Acid (CA) solution.

Similarly, the extraction behavior of Am(III) and Eu(III) was studied in TODGA - HDEHP, and TEHDGA - HDEHP in a single-cycle process. The mutual separation of Am(III) from Eu(III) is difficult in case of TODGA - HDEHP system whereas the batch stripping studies indicate the selective separation of Am(III) from Eu(III) in TEHDGA - HDEHP solvent system. The extraction behavior of metal ions present in FR-SHLLW was studied extensively using 0.1 M TEHDGA - 0.25 M HDEHP. The extraction and stripping were carried out in a 16 stage mixer-settler. The results indicate the mutual separation of An(III) from trivalent lanthanides. In this process, An(III) are selectively stripped using DTPA-CA solution where as Ln(III) are held in the combined organic phase. Finally trivalent lanthanides were stripped from organic solution using aqueous soluble *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) in nitric acid medium. The radiation stability of TEHDGA

- HDEHP solvent was also studied. A novel and simplified flow-sheet for separation of actinides was developed for single cycle process.

3. Organization of the thesis

3.1. Chapter 1

The first chapter deals with a brief introduction to reprocessing of spent nuclear fuel and the safe management of HLLW. Also describes the need of nuclear energy for sustainable development of the Nation, and importance of spent nuclear fuel reprocessing to utilize the nuclear materials effectively. This chapter provides a detailed literature survey on various strategies proposed for the safe management of HLLW. It points out the merits and demerits of various processes and reagents proposed for the separation of long-lived radiotoxic actinides from HLLW, and the scope for further developments.

3.2. Chapter 2

This chapter deals with the details of various chemicals and reagents used for the synthesis of different diglycolamic acids, and DGAs in the present work. This also includes the detailed synthetic and purification procedures. Methodologies adopted for the measurement of radioactivity of various radioisotopes using NaI(Tl) detector, high purity germanium detector (HpGe) are discussed. Details of mixer-settler are discussed. Usage of inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the determination of concentration of various metal ions presents in FR-SHLLW, and thereby the distribution ratio measurements etc., are explained.

3.3. Chapter 3

This chapter deals with conventional two-cycle process for minor actinide partitioning. In the first cycle, partitioning of trivalent metal ions from FR-SHLLW has been demonstrated, using an unsymmetrical diglycolamide, *N*,*N*,-didodecyl-*N*’,*N*’-dioctyl-3-oxapentane-1,5-

diamide (D^3DODGA), in *n*-dodecane (*n*-DD). The extraction behavior of various metal ions present in the FR-SHLLW was studied using a solution of 0.1 M D^3DODGA/*n*-DD, by batch equilibration mode. The extraction of Am(III) was accompanied by the co-extraction of all lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II) from FR-SHLLW. The co-extraction of unwanted metal ions is minimized by adding trans-1,2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA) to FR-SHLLW, prior to extraction. A counter-current mixer-settler run is performed in a 20-stage mixer-settler. Quantitative extraction of Am(III), Ln(III) and Y(III) from FR-SHLLW in 0.1 M D^3DODGA/*n*-DD was achieved in 20 contacts and the recovery of Am(III) and other trivalents from the loaded organic phase was achieved in 5 contacts using 0.01 M nitric acid.

3.4. Chapter 4

This chapter discusses single-cycle process for minor actinide partitioning by using a combined solution of unsymmetrical diglycolamide (D^3DODGA) and *N,N*-di-2-ethylhexyl diglycolamic acid (HDEHDGA) from FR-SHLLW. These extractants were used separately in two cycle process. In order to achieve the minor actinide partitioning in a single cycle, both the extractants were combined and the extraction and stripping behavior of various metal ions present in the FR-SHLLW were studied. The third phase formation behavior of the solvent formulation D^3DODGA - HDEHDGA/*n*-DD, was studied with FR-SHLLW. The distribution ratio of various metal ions present in FR-SHLLW was measured in a solution of 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD. The results indicate that the extraction of Am(III) was accompanied by the co-extraction of lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II). The extraction of unwanted metal ions was minimized using aqueous soluble complexing agent. Based on the results, the counter current mixer-settler run was performed in a 20-stage mixer-settler. Quantitative extraction of Am(III), Ln(III), Y(III), and Sr(II) in 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD was observed. The recovery of

Am(III) from the loaded organic phase was carried out by the optimized aqueous formulation composed of 0.01 M DTPA + 0.5 M citric acid (CA) at pH 1.5. The stripping of Am(III) was accompanied by co-stripping of some early lanthanides.

3.5. Chapter 5

This chapter deals with the extraction behavior of Am(III) and Eu(III) in the combined solvent consisting of (a) TODGA - HDEHP system and (b) THEDGA - HDEHP system. In the first case, the role of TODGA and HDEHP in the combined solvent system was studied. The extraction behavior of Am(III) and Eu(III) was compared with those observed in TODGA/*n*-DD and HDEHP/*n*-DD. The effect of various parameters such as concentrations of HNO_3, TODGA, HDEHP on the distribution ratio of Am(III) and Eu(III) was studied. Synergistic extraction of both the metal ions observed at lower acidities. However, the extraction of Am(III) and Eu(III) in the combined solvent was comparable with that observed in TODGA at higher acidities. The slope analysis of the extraction data confirmed the involvement of both the extractants at all acidities investigated in the present study. In the second case, the extraction behavior of Am(III) and Eu(III) in a solution of TEHDGA - HDEHP was studied from nitric acid medium. The distribution ratio of Am(III) and Eu(III) in TEHDGA - HDEHP/*n*-DD was measured as a function of various parameters such as concentrations of nitric acid, TEHDGA, HDEHP and nitrate ion. The synergistic extraction of Am(III) and Eu(III) observed in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was attributed to the involvement of both TEHDGA and HDEHP for extraction. Slope analysis of the extraction data indicated the predominant participation of HDEHP for extraction at low acidities and TEHDGA and nitrate ion at higher acidity.

3.6. Chapter 6

This chapter describes the development of a single-cycle method for the actinide separation from FR-SHLLW by using TEHDGA - HDEHP solution. In this solvent both

Am(III) and Eu(III) were synergistically extracted to organic phase. The stripping behavior of Am(III) and Eu(III) from the extracted organic phase was investigated using DTPA - citric acid (CA) solution. Also the extraction behavior of Am(III) and various metal ions present in FR-SHLLW was studied in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. The extraction of Am(III) was accompanied by the co-extraction of lanthanides and unwanted metal ions such as Zr(IV), Mo(VI), Y(III), Fe(III) and Pd(II). Extraction of unwanted metal ions was minimized by using aqueous soluble complexing agent in FR-SHLLW. Based on these studies, a counter current mixer-settler run was performed to separate Am(III) from FR-SHLLW. Quantitative extraction of Am(III), Ln(III), Y(III), and Mo(VI) in 0.1 M - 0.25 M HDEHP/*n*-DD was observed. The recovery of Am(III) from the loaded organic phase was carried out by using 0.05 M DTPA - 0.5 M citric acid at pH 3. The study, thus, indicated the possibility of separation of Am(III) from FR-SHLLW. After stripping of Am(III), the lean organic contains all the lanthanides. A procedure was developed for the back extraction of lanthanides from the lean organic phase. An aqueous soluble reagent i.e. tetraethyldi-glycolamide (TEDGA) in nitric acid medium was used for the back extraction of lanthanides.

3.7. Chapter 7

This chapter describes studies on the radiolytic stability of TEHDGA - HDEHP/*n*-DD used for actinide partitioning in the present work. The extractants to be employed for the separation of radioactive elements such as actinides and long-lived fission products invariably exposed to the high energetic radiation associated with them. Under these conditions, the covalent bonds in extractant may undergo cleavage to generate degradation products. Presence of degradation products in organic phase alters the physico-chemical properties [14]. The radiochemical degradation of a solution of TEHDGA - HDEHP/*n*-DD was investigated by irradiating the solvent to various absorbed dose levels of γ-radiation. The neat extractants or a solution of extractants in *n*-dodecane was irradiated in the presence and absence of nitric acid. The degree of degradation was assessed by measuring the variation in the extraction behavior of Am(III), Eu(III) and other metal ions in irradiated solvent systems. The distribution ratio of Am(III) and Eu(III) decreased with increase of absorbed dose. The presence of *n*-dodecane enhanced the radiolytic degradation of the solvent, however, the role of nitric acid during degradation was insignificant. The recovery of Am(III) and Eu(III) from the irradiated solvent system was studied.

3.8. Chapter 8

This chapter summarizes the results and conclusions obtained in the present work. This chapter also discusses about scope for the future work in this field.

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Chapter 1: Introduction

1.1. Introduction

The global demand for energy is increasing steeply with ever increasing population, economy and rapid industrialization all over the world [1]. Electricity is one of the basic requirements of day-to-day life and it is a critical component of infrastructure that determines the economic development of a country. The per capita energy consumption is usually taken as an index for the development of a nation. In India per capita energy is less than the developed countries. In order to become a developed country, the energy production should be increased such that per capita energy consumption will increase. The choice of fuel for energy production is essentially dictated by the availability and accessibility of the source, its economic viability, and the convenience it offers. At present, the energy is produced essentially from the fossil fuels such as natural gas, oil and coal owing to their widespread availability [2]. However, there are several issues associated with the use of these fuels even though they provide reliable source of energy. The energy production from fossil fuels generates wide variety of gases that can cause water and air pollution. Combustion of oil, gas and coal produces green house gases such as carbon dioxide and also burning of coal produces sulfur dioxide. Consequently, burning of all these fossil fuels contributes heavily to global warming, pollution of air, water and land, acid rain and there by deteriorates the health of people and destroys the environment and ecosystem. Being one of the fast growing countries, India certainly needs huge quantity of energy for its sustainable growth in terms of Gross Domestic Product (GDP). The total energy demand of our country by 2050 is estimated to be around 1000 GWe [3, 4]. This can be met only by the appropriate use of all available fuel resources. In view of this as well as due to the uncertainty in the development of renewable energy technologies such as solar, tidal and wind etc., the dependence on nuclear energy seems to be inevitable for meeting the future energy demand. Therefore, the contribution of nuclear energy to the total energy demand needs to be increased in coming years for a sustained development of our nation. Nuclear energy is nearly carbon-free source of power as it is not generating any greenhouse gases. It has several advantages over the other sources of energy. They are,

1. Nuclear plants do not generate any greenhouse gases.
2. The quantity of fuel required for nuclear power plants is very less as compared to other plants which burn fossil fuels. The energy production from one ton of natural uranium is much higher than that two to three million tons of coal or oil.
3. Production of more fuel than that consumed in the nuclear reactor using breeding technology is feasible. In this way the nuclear energy can solve the energy demand in future.

1.2. Nuclear fuel cycle

The principle of generating power in nuclear power plants is based on controlled chain reaction i.e. nuclear fission. In fission reaction, the heavier nuclei such as uranium (^{235}U or ^{233}U) or plutonium (^{239}Pu) are split into lighter fragments with the release of large amount of energy (~200 MeV per fission). The lighter fragments are called as fission products. The heat energy liberated during fission is then converted into electrical energy. Several stages are involved in the production of electricity through nuclear fission reactors starting from mining of uranium from the ore to management of waste. All these stages are collectively called as nuclear fuel cycle. The fuel discharged from a nuclear reactor after irradiation is known as spent nuclear fuel (SNF). This contains valuable materials such as depleted uranium (U), plutonium (Pu) and several radionuclides formed by the fission reaction, known as fission products (FPs). Apart from this, some transuranium elements such as neptunium, americium and curium are also formed in small concentrations (~0.1%) by nuclear activation reaction. These elements are known as minor actinides (MA). Once through fuel cycle (or open fuel cycle) and closed fuel cycles are two options available for the disposal of spent nuclear fuel. In the once-through fuel cycle, spent nuclear fuel as such is disposed as waste in deep geological repository; whereas in the closed fuel cycle, the SNF is processed for the recovery of unused fissile materials such as uranium and plutonium which can be used for the future reactor. Therefore, the closed fuel cycle provides the effective utilization of the fuel resources.

1.3. Indian nuclear power programme

The nuclear power programme in India was initiated by the great visionary Dr. Homi Jehangeer Bhabha [5]. A three stage nuclear power programme was conceived by Bhabha in the year of 1954 to meet the nation's energy demand. The objective of the programme was to judiciously utilize the uranium and thorium resources of the country to the maximum extent. This was based on the closed fuel cycle concept. In the first stage, natural uranium is used as fuel in pressurized heavy water reactors (PHWR). Currently, there are eighteen PHWRs operating with a total capacity of 4280 MWe in India [6]. The element which can undergo fission reaction directly by neutron is called fissile element where as the element which can be converted into fissile element by nuclear reaction is called fertile element. For example ^{235}U, ^{239}Pu, ^{233}U are the fissile elements where as ^{238}U and ^{232}Th are fertile elements. ^{238}U and ^{232}Th can be converted into ^{239}Pu and ^{233}U subsequently by nuclear reactions which are fissile elements. In first stage reactors, ^{235}U under goes nuclear fission and ^{238}U is converted to ^{239}Pu. The SNF from PHWR contains significant quantities of ^{239}Pu, along with residual uranium (depleted uranium i.e. ^{238}U). The SNF was processed for the recovery of fissile and fertile elements. In the second stage reactors, plutonium recovered from first stage is used as fuel in Fast Breeder Reactors (FBRs). In this context a Fast Breeder Test Reactor (FBTR) facility was built at Kalpakkam and it has been in operation since 1985 [7]. Huge resource of thorium is present in the coastal India. This thorium was used as a blanket in the second stage of reactor to convert them into fissile ^{233}U. The ^{233}U thus produced, is processed, and used as fuel in the thermal breeder reactors of third stage. Thus the third stage of Indian nuclear power programme is purely based on the usage of plentiful resources of thorium available in India.

1.4. Reprocessing of spent nuclear fuel

The spent nuclear fuel discharged from nuclear power reactors contains substantial amounts of fertile uranium and fissile plutonium that can be reprocessed and recycled as fuel for future reactors. Plutonium Uranium Recovery by EXtraction (PUREX) process has been widely employed for reprocessing of spent nuclear fuel [8, 9]. The PUREX process was developed in early fifties and has been industrially employed as the primary process for the recovery of uranium and plutonium from spent nuclear fuel in worldwide. The PUREX process consists of three major steps. These are (i) head end step, which includes decladding of fuel, dissolution, and feed preparation, (ii) solvent extraction using tri-n-butyl Phosphate (TBP), which involves co-extraction and partitioning of uranium and plutonium, and (iii) final purification and conversion of uranium and plutonium to their respective oxides. The flow sheet for PUREX process is shown in Figure 1.1.

In PUREX process, the spent nuclear fuel was chopped mechanically to small pieces and dissolved in 8-10 M nitric acid. The final acidity was adjusted to 3-4 M and the valence state of plutonium was adjusted to Pu(IV) using $NaNO_2$. The second step involves the liquid-liquid extraction of uranium and plutonium from the dissolver solution followed by partitioning of uranium and plutonium. The solvent extraction of U(VI) and Pu(IV) from the feed adjusted solution (3-4 M HNO_3) is carried out by a solution of 1.1 M tri-*n*-butyl phosphate in *n*-dodecane. The partitioning of Pu(IV) from the loaded organic phase was carried out by reducing Pu(IV) to Pu(III) using reducing agents such as ferrous sulfamate or uranous nitrate stabilized with hydrazine. In this way, Pu(III) distributes to aqueous phase and thus enables the separation of uranium and plutonium. The reducing agent, uranous

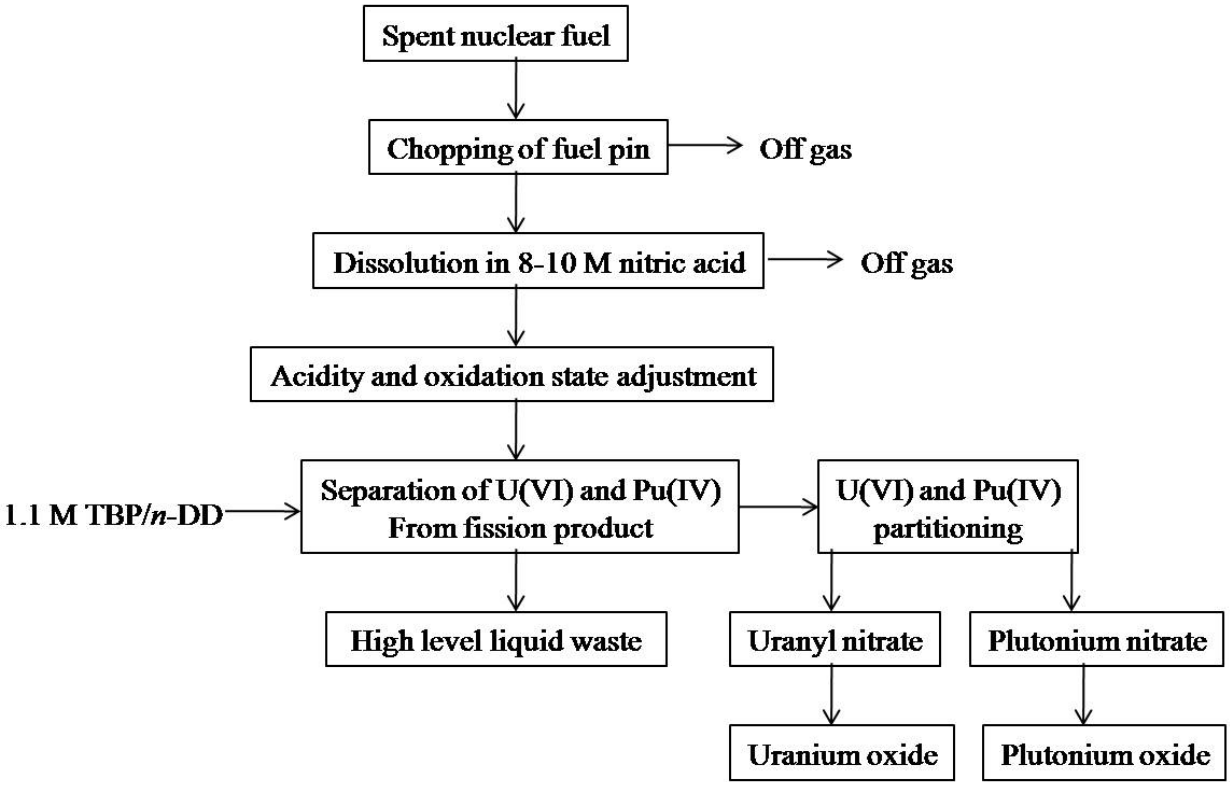

Figure 1.1. Flow sheet for PUREX process

nitrate stabilized with hydrazine is preferred instead of ferrous sulfamate for partitioning step, since ferrous sulfamate introduces additional metal ions into the process stream. The uranium present in the organic phase is back extracted using dilute nitric acid. In the final step, the uranium present in the aqueous phase is precipitated as ammonium diuranate and calcined to obtain uranium oxide. Similarly, the purification of plutonium product is carried out by either solvent extraction or ion exchange process [10]. The plutonium product obtained is precipitated as plutonium oxalate and calcined to plutonium oxide. By this method both uranium and plutonium are converted to their corresponding oxides.

The PUREX raffinate i.e. aqueous solution rejected after the extraction of uranium and plutonium by PUREX process is known as high-active waste (HAW). The HAW is a complex mixture of several elements such as minor actinides, lanthanides, other fission products, corrosion products and the additives etc., present in 3-4 M nitric acid medium. This high active waste is generally concentrated to obtain high-level liquid waste (HLLW).

1.5. Radiotoxicity of spent nuclear fuel

The radiotoxicity of SNF is due to the presence of plutonium, fission products and the minor actinides. The decay of radioactivity of SNF in different processess is shown in Figure 1.2. In case of direct disposal of SNF, the estimated time for the decay of radiotoxicity to the background level (equal to natural uranium) is 10^5-10^6 years. In the first few hundred years after discharge from nuclear reactor, the radiotoxicity of SNF is essentially contributed by fission products such as ^{137}Cs, and ^{90}Sr [11]. After the decay of ^{137}Cs, and ^{90}Sr, the radiotoxicity is determined by ^{239}Pu, ^{240}Pu and other minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am and ^{245}Cm. The decay of radiotoxicity for SNF after PUREX process is also shown in Figure 1.2 [12]. During PUREX process, plutonium was recovered from the SNF, so that the long-term radiotoxicity of HLLW is essentially contributed by the long lived minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm, ^{243}Cm. The half-lives of these isotopes vary from few years to several hundred years. The half-lives of some actinides are tabulated in Table 1.1 [13]. Due to long half-life of minor actinides, the HLLW poses a long-term risk to the public health and safety of environment. In this case, the radiotoxicity of SNF decays to background level in 10^5 years.

The current practice for waste management is immobilization of HLLW into a suitable non-leachable ceramic or glass matrix, followed by deposition in deep geological repositories [14]. However, these repositories need to be monitored for long term (10^5 Year) surveillance due to the presence of minor actinides. In the event of a ground-water invasion into these repositories, the radiotoxic metal ions may get leached and released in to the environment owing to their significant solubility and higher mobility in aqueous medium. Such repositories need long-term surveillance over thousands of years, thus making this disposal practice a very expensive option. If the radiotoxicity of the spent fuel is reduced by some method, the waste management of HLLW can be simplified. In this context, partitioning and transmutation is one of the methods for the safe disposal of nuclear waste.

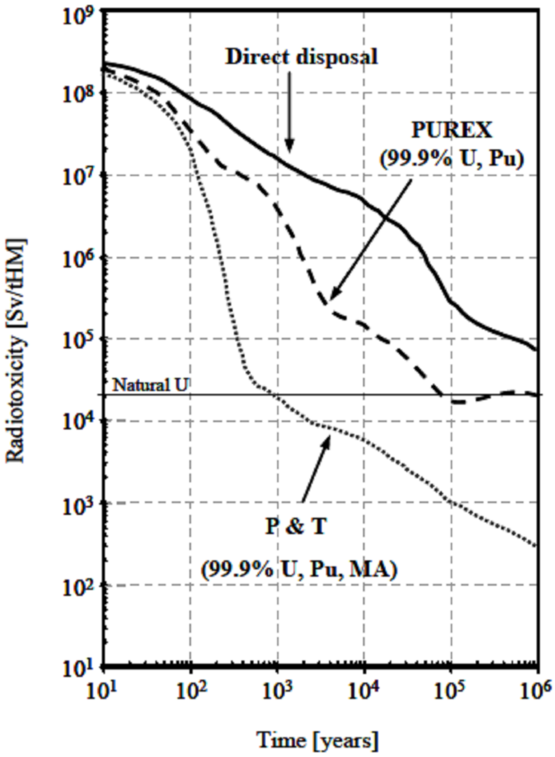

Figure 1.2. Depiction of the advantage of P&T strategy over direct disposal of SNF for minimizing the radiotoxicity [12].

1.6. Partitioning and transmutation for waste management

Partitioning (P) means separation and Transmutation (T) means conversion of long lived radionuclei to stable or short lived product. Generally transmutation is achieved in fast reactors or in acceleration driven system (ADS). In Partitioning and Transmutation (P&T) strategy, the separation of minor actinides from the HLLW followed by transmutation of these minor actinides is carried out [12, 13]. This strategy reduces the radiotoxicity of HLLW to a large extent, and simplifies the management of HLLW. The dacay of radiotoxicity for P&T process is shown in Figure 1.2. By adopting P&T strategy, the radiotoxicity of the HLLW decays to back ground level in few hundred years. The radiotoxicity is due to the presence of fission products such as ^{137}Cs, and ^{90}Sr. The great decrease in radiotoxicity is because of the removal of plutonium as well as the complete burning of minor actinides in the fast reactor. Table 1.1 compares the natural half-lives of actinides before and after transmutation. It is interesting to note that the half-lives of these minor actinides can be dramatically reduced to very small values by transmutation [13] and thereby reduces the radiotoxicity burden to the environment. Partitioning of the minor actinide can be achieved in solvent extraction process.

Table 1.1. Half lives (Y) of actinides due to natural decay and by fission with fast neutrons. The fission half-life was calculated using the relation $\tau_{½} = 2/ (\sigma, \Phi)$ where σ and Φ are the fission cross section and the neutron flux respectively. The cross section data is based on the JEF 2. 2 data file. The values used for a fission spectrum were taken from JEF report 14, NEA/OECD1994. The neutron flux was assumed to be 5 x 10 ^{15} cm^{-2} s^{-1}[13].

Actinide	$t_{1/2}$ (natural decay) in years	$\tau_{1/2}$ (transmutation) in years
^{237}Np	2.14x 10^{6}	2.46
^{238}Pu	88	1.61
^{239}Pu	2 x 10^{4}	1.76
^{240}Pu	6 x 10^{3}	2.35
^{241}Pu	14	1.95
^{242}Pu	4 x 10^{5}	2.83
^{241}Am	433	2.40
^{242m}Am	152	1.72
^{243}Am	7 x 10^{3}	2.89
^{242}Cm	0.44	1.93
^{243}Cm	30	1.46
^{244}Cm	18	1.97
^{245}Cm	8 x 10^{3}	1.60

1.7. Solvent extraction process for metal recovery

The liquid-liquid extraction, commonly known as solvent extraction, is considered as the most efficient method for the separation of metal ions from a complex mixture in liquid medium. It plays a very important role in various industries such as nuclear, metallurgical, pharmaceutical, food and beverage, chemical, petrochemical, biochemical, catalysis, polymers, etc,. Solvent extraction is the preferential distribution of a solute (for example a desired metal ion, M) between two immiscible/partially miscible liquids i.e. generally aqueous and organic liquids in contact with each other. A solute M, dissolved in one liquid distributes into another immiscible liquid until its chemical potential becomes equal in both the phases. This condition is referred to as equilibrium. The distribution ratio of a solute M (D_M) is defined as the ratio of its concentration in the organic phase ($[M]_{org}$) to that in the aqueous phase ($[M]_{aq}$) at equilibrium as shown in equation 1.1.

$$D_M = [M]_{org} / [M]_{aq} \qquad (1.1)$$

The distribution ratio of solute is constant for given pair of liquids at constant temperature. In metal recovery operations, the valuable component is a metal ion or metal complex contained in aqueous solution. This aqueous solution is equilibrated with an immiscible organic phase containing coordinating ligand known as extractants. The extractants present in organic phase transfers metal ion from aqueous phase into organic phase under certain conditions is called as “extraction” process. The process for recovery of the metal ions present in loaded organic phase is known as “back extraction or stripping” using aqueous solution. The aqueous solution used for the stripping of metal ions is called stripping solution. Due to the low distribution ratio of metal ions in stripping solution, the metal ions facilitate to come to the aqueous phase from the organic phase. The organic phase after stripping of metal ions is called lean organic phase and is recycled back to extraction stage.

Solvent extraction plays an important role in spent nuclear fuel reprocessing and waste management at the backend of nuclear fuel cycle. In PUREX process, uranium and plutonium were recovered from the dissolver solution by solvent extraction process. In case of waste management, solvent extraction helps in separation of minor actinide from HLLW. Most of the extractants used in solvent extraction are high viscous organic substances. Therefore, extractants are dissolved in a non-reactive organic in which they are completely miscible, is called as “diluents”. The physical properties of the extractant are modified by addition with diluents. By diluting the extractant, the hydrodynamic property of the resultant solvent changes, reduces the extracting power, and hence improves the selectivity. Several advantages such as improved mass transfer, improved phase separation, decreased solubility into the aqueous phase and vice versa are obtained as a result of the addition of diluent. Sometimes, other components such as phase modifiers and synergists are also added to alter physicochemical characteristics and to increase extraction. The mixture of extractant with other components such as diluent, modifier and synergists is called the solvent phase. The most widely used diluent in the nuclear fuel reprocessing industry is *n*-dodecane. Some important properties of the extractants are given below [15].

1. High complexation ability and selectivity with the metal ions.
2. High solubility of the metal-ligand complex in the organic phase.
3. No third phase formation (to be discussed below) during the solvent extraction.
4. High solubility in paraffinic solvents and low solubility in the aqueous phase.
5. Non-volatility, non-toxicity and non-inflammability.
6. Ease of stripping of metal ions from the loaded organic phase.
7. Optimum viscosity for the ease of flow.
8. Ease of regeneration of the extractant for recycling.
9. Adequate thermal, radiolytic and hydrolytic stability during operation.
10. Ease of synthesis or availability at a reasonable cost.

11. Contain C, H, N, O atoms preferably for the complete incineration after the usage.

However, there is no single extractant which exhibits all these desirable properties. Therefore, it is challenging and interesting to synthesize noval extractants, which can exhibit most of the above mentioned properties.

1.8. Third phase formation in solvent extraction

During solvent extraction process, the extractant phase come in contact with aqueous phase containing metal ions. Some cases, extraction of metal ions by the extractant results in the splitting of organic phase into two phases. The heavier phase is rich in metal–solvate (or metal complex) and extractant, and the lighter phase rich in diluent [16]. The heavier phase is known as third phase. Usually, it occurs due to the excess loading of metal complexes into organic phase, where polar metal-solvate is no longer compatible in non-polar diluent such as *n*-dodecane. By this way the metal-solvates separated out from polar diluent phase formed third phase. The concentration of metal ion in the loaded organic phase above which third phase formation take places is called the limiting organic concentration (LOC) and the corresponding metal ion concentration in aqueous phase is known as critical aqueous concentration (CAC). The occurrence of third phase formation during the solvent extraction can be explained briefly as follows.

The extractant is having a polar group for the extraction of metal ions where as the diluent is a non-polar molecule (*n*-dodecane). Initially the extractant is soluble in non-polar diluents, *n*-dodecane. During solvent extraction, metal ions are extracted from aqueous phase. The polar parts of the extractant molecule involve in complexation with metal ions form polar metal-solvate complexes. As a result the polarity of the metal-solvate complex increases in the organic phase. After a certain concentration of metal ion (LOC) loaded in the organic phase, the polarity differences between polar metal-solvate complex and non-polar diluent molecule increase such that the polar metal-solvates are no longer soluble in non-polar diluent. As a result the organic phase splits into two phases. The heavier organic phase mostly contains all metal-solvate complexes, called as third phase, where as the lighter phase contains mostly non-polar diluents. Third phase creates inhomogeneous density and viscosity in organic phase and complicates the mixing of organic and aqueous phases. The density of third phase is intermediate between aqueous phase and diluents phase. Third phase formation is an undesirable event in solvent extraction procedures.

The third phase formation can be avoided by adding some polar organic known as phase modifier or polar diluents such as iso-decanol to the solvent phase. Several parameters such as temperature, nature of diluent, equilibrium aqueous phase acidity, structure of the extractant, concentration of extractant, presence of phase modifier and its concentration etc., can influence the tendency of third phase formation [16,17]. However, the addition of phase modifier changes the physico-chemical and extraction properties of extractant and increases waste generation. Therefore, a solvent system without third phase formation is desirable in nuclear reprocessing plant.

1.9. Types of extractants

Extractants are organic molecules which posses both polar hydrophilic and non-polar hydrophobic structural parts. The polar hydrophilic groups help to complex with metal ions present in the aqueous phase where as the hydrophobic group provides the solubility of metal-complex in the diluent phase and also reduce the aqueous solubility of the extractant in aqueous phase. In general, extractants can be broadly classified into four groups according to the nature of the extractants. 1) Acidic (cation extractants), 2) Basic (anion extractants), 3) Neutral (solvating agents) 4) Chelating extractants [18]. Acidic extractants extract cations by compound formation, basic extractants extract anionic species by ion-pair formation, neutral extractants extract neutral species by solvation, and chelating extractants belong to the category of acidic extractants, extract metal ions by chelation with the formation of ring structures involving the extractant molecule and metal ion.

1.9.1. Acidic extractants

Acidic extractants form complexes with metal ion by cation-exchange mechanism. The hydrogen ion of the extractant is replaced by exchanging with metal ions as shown in equation 1.2.

$$M^{n+}_{(aq)} + n\ HA_{(org)} \Leftrightarrow M(A)n_{(org)} + n\ H^{+}_{(aq)} \qquad (1.2)$$

The extraction of metal ion takes place with the release of hydrogen ions. At lower acidity, the extractants dissociates and form metal complex solvates easily. So the extraction of metal ions is favorable at lower acidity according to Le Chatelier principle. Back extraction of metal ions is carried out using higher acid solution because in the presence of higher acidity, the metal complex is not stable in organic phase and transferred to aqueous phase. Generally, acidic extractants have functional groups such as -COOH, >P(O)OH and $-SO_3H$. The hydrogen present in the extractant is replaced by metal ions during extraction. For example, organic derivatives of phosphorous acids and monocarboxylic acids belong to this category of extractants [9]. The phosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups and alkylphosphoric acids are the most promising acidic extractant. Di(2-ethylhexyl) phosphoric acid (HDEHP) has been used for the extraction of many metals such as uranium, cobalt, nickel, rare earths and vanadium on commercial scale.

1.9.2. Basic extractants

Basic extractants extract metal ions by anion exchange mechanism. The long chain primary (RNH_2), secondary (R_2NH), tertiary (R_3N) amines and quaternary ammonium salts ($(R_4N)^+\ X^-$) belong to this category [9]. The anionic metal species (MY^-) present in the aqueous phase is exchanged with the anion of the quaternary amine salt. The metal solvate complex formation reaction is shown in equations 1.3 and 1.4.

$$R_3N_{(org)} + HX_{(aq)} \Leftrightarrow R_3NH^+X^-_{(org)} \qquad (1.3)$$

$$R_3NH^+\,X^-_{(org)} + MY^-_{(aq)} \Leftrightarrow R_3NH^+MY^-_{(org)} + X^-_{(aq)} \qquad (1.4)$$

Tri-*n*-octylamine (Alamine 336) and tri-octylmethylammonium chloride (Aliquat 336) are the two important basic extractants used for several applications.

1.9.3. Neutral extractants

Neutral extractants are reagents containing donor atoms with lone pair of electrons for the co-ordination to the metal ions. The metal ions combine with anions form a neutral metal complex. Neutral extractants only extract the electrically neutral metal complex. The metal complex thus formed is soluble in the organic phase than in the aqueous solution. Two main groups of extractants in this category are organic reagents containing oxygen bonded to carbon such as ethers, esters, ketones, and amides and those containing oxygen or sulphur bonded to phosphorus, such as alkyl phosphates or alkyl thio phosphates etc. [9]. Organic reagents such as amides, diamides, triesters of phosphoric, phosphonic, phosphinic acids, organic sulphoxides, sulfides etc., belong to the family of neutral extractants. The solvating power depends strongly on the basicity of the reagent. TBP is the most widely used neutral extractant in nuclear reprocessing plant.

1.9.4. Chelating extractants

Chelating extractants extract metal ions by chelation i.e. the formation of ring structures with the metal ions by the extractant molecule. Some examples of these types of extractants are hydroxyoximes and diketones especially. 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63), 2-hydroxy-5-dodecylbenzophenone oxime (LIX 64), thenoyltrifluoro acetone (TTA) etc., belong to this family of extractants [9]. Depending upon the feed type, nature of metal ions, and process conditions different types of extractants are employed at different stages of nuclear reprocessing and allied waste management.

1.10. Partitioning of minor actinides from HLLW

The success of P&T strategy depends on efficient separation of minor actinides. Partitioning of trivalent actinides from HLLW involves a complex chemistry. The stable oxidation state of transplutonium actinides (Am and Cm) in HLLW is +3. Trivalent lanthanides are formed as fission product and present in HLLW. The concentration level of these actinides is very small as compared to trivalent lanthanides (Ln(III)) in HLLW. Both trivalent actinides and lanthanides have similar chemical and extractive properties due to the similarity in size and oxidation state. It is difficult to separate the An(III) alone from HLLW. Therefore, the current approach for minor actinide partitioning involves a two-cycle process. The first cycle involves the liquid-liquid extraction of An(III) and Ln(III) together from HLLW called as group separation, followed by lanthanide-actinide mutual separation in the second cycle. Mutual separation of Ln(III) and An(III) is necessary prior to the transmutation, since the Ln(III) act as neutron poisons. Presence of these trivalent lanthanides reduces the efficiency of transmutation process. In addition, the lanthanides do not form solid solutions easily with americium and curium during the fabrication of targets for transmutation in the form of metal-alloy or oxide. In view of these, the complete separation of Ln(III) from An(III) is very important prior to the actinide transmutation.

1.11. Group separation: Lanthanide-Actinide (III) co-extraction

Several reagents have been proposed for the co-extraction of An(III) and Ln(III) from HLLW and number of flow-sheets based on those reagents have been developed world wide. TRans Uranium element EXtraction (TRUEX) process developed in USA involves *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) as extractant [19-22], TriAlkyl Phosphine Oxides (TRPO) developed by Chinese [23-26], Di-IsoDecyl-Phosphoric Acid (DIDPA) developed in Japan [27-30], *N,N′*-DiMethyl-*N,N′*-DiButylTetraDecyl MalonAmide (DMDBTDMA) [31-33], *N,N'*-DiMethyl-*N,N'*-DiOctyl-2-

HexylEthoxyMalonAmide (DMDOHEMA) [34-38] developed in France, Octyl derivatives of diglycolamides (DGAs) developed in Japan [39-66], and in the recent past *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D^3DODGA) [67-69] are some of the processes proposed for minor actinide partitioning. The structures of these reagents are shown in Figure 1.3. These extractants are used for co-extraction of An(III) and Ln(III) in the first cycle of minor actinide partitioning as discussed below.

1.11.1. TRUEX Process

The TRans Uranium EXtraction (TRUEX) process was developed by USA researchers in the 1980s for the partitioning of trivalent actinides from the PUREX raffinate. The extractant developed by Horwitz *et al.* for this process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) [19-22]. The TRUEX process solvent consists of a standard PUREX process solvent to which CMPO is added for trivalent actinide extractions. The composition of TRUEX solvent is 0.2 M CMPO-1.2 M TBP in normal paraffinic hydrocarbon diluents. This solvent can extract trivalent actinides and lanthanide from HLLW. The extracted trivalent metal ions can be stripped from the loaded organic phase using dilute nitric acid. During the extraction process, Zr(IV) and Mo(VI) are co-extracted along with trivalent actinides and lanthanides.

Generally CMPO forms third phase with HLLW. In order to avoid third phase formation, the polar phase modifier TBP was added to extractant phase. This solvent also contains phosphorous, which is not satisfying the CHON principle. Another drawback of the TRUEX process is that the degradation products of the extractant complicate the efficient back extraction of the trivalent metals.

1.11.2. TOPO and TRPO process

In TRPO process, trialkyl phosphine oxide (TRPO) was used as extractant. The extractants trioctylphosphine oxide (TOPO) and trialkyl phosphine oxide (TRPO, $R_3P=O$ with R=C6-C8) were developed by Chinese researchers and tested for the partitioning of trivalent actinides. [23-25]. TOPO and TRPO extract trivalent actinides and lanthanides quite well from low nitric acid medium. The An(III) and Ln(III) can be stripped by 5 M nitric acid. A 30% TRPO in *n*-dodecane was evaluated for the metal ion extraction from nitric acid medium [25, 26]. One of the disadvantages is that certain fission products e.g. Zr(IV), Mo(VI) were extracted along with trivalent actinide and lanthanides. Formation of third phase, incomplete extraction and back extraction of trivalent An(III) and Ln(III) are some of the other major issues.

1.11.3. Diisodecylphosphoric acid (DIDPA) process

Di-isodecyl phosphoric acid (DIDPA) process was proposed by Japanese scientists for the partitioning of minor actinide from HLLW. DIDPA was used as extractant in this process. It is very difficult for DIDPA to extract metal ions from 3-4 M nitric acid medium. All trivalent actinides and lanthanides were extracted from 0.5 M HNO_3 into DIDPA solvent consisting of 0.5 M DIDPA and 0.1 M TBP in n-dodecane. Addition of TBP makes the phase separation faster. Trivalent actinides and lanthanides were then stripped with 4 M HNO_3. [27-30]. Therefore, HLLW needs to be de-nitrated or diluted so as to bring down the acidity to 0.5 M nitric acid, prior to the extraction. By this way secondary waste generation is more and phosphorous containing reagents such as CMPO, TRPO, and DIDPA are producing solid residue upon their inceneration which complicates the waste management.

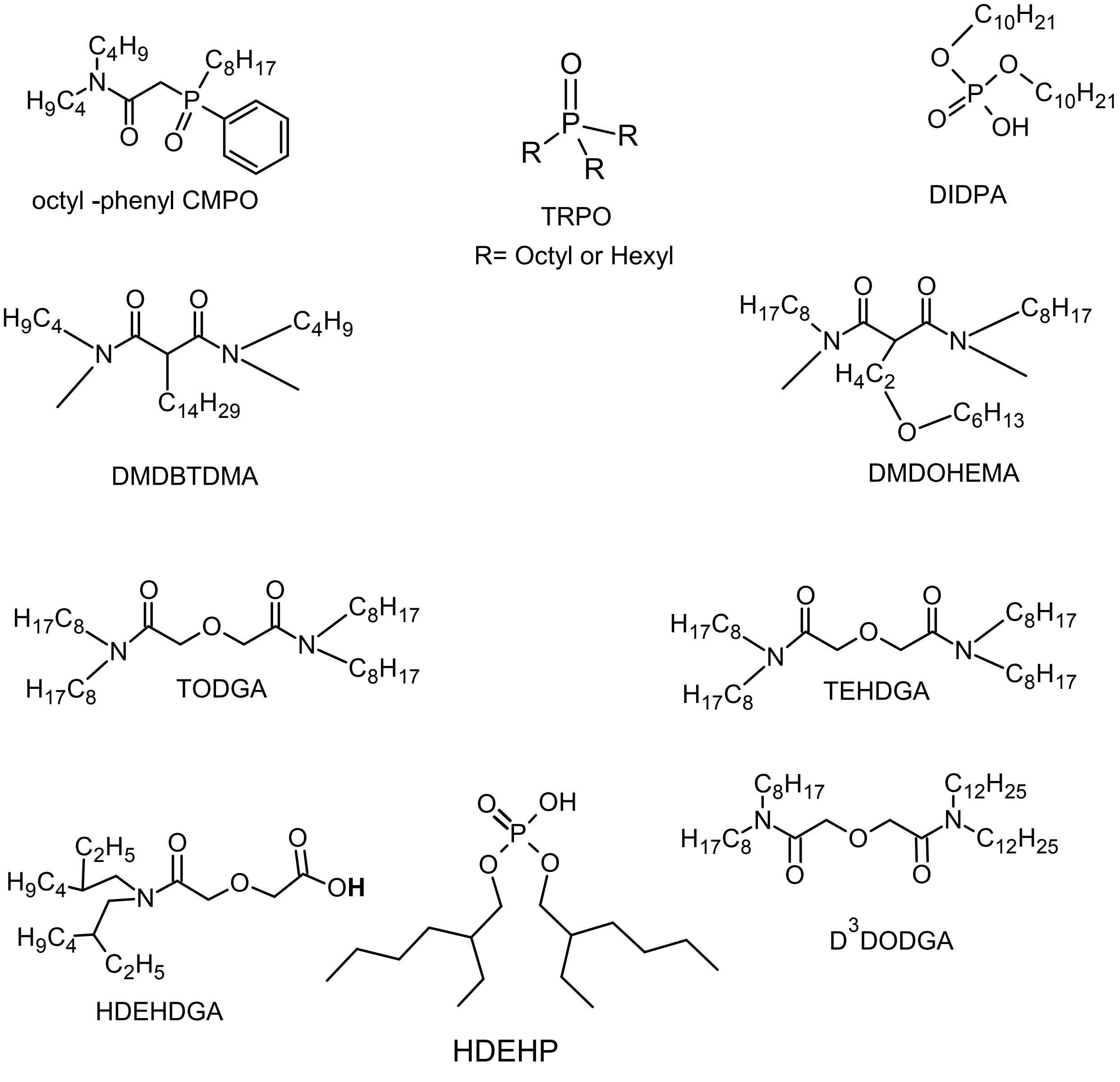

Figure 1.3. The structure of various reagents proposed for partitioning of minor actinides.

1.11.4. DIAMEX process

French researchers developed extractants based on CHON principle for the recovery of trivalent actinides from HLLW. These extractants can be incinerated completely for the minimization of waste production. During the inceneration, the extractants are converted in to gaseous products. This novel approach for the extractant design has been received much attention from various research groups. Numerous CHON based diamides were synthesized and employed for the extraction of trivalent actinides from nitric acid media. Among these, *N,N'*-Di-Methyl-*N,N'*-Di-Butyl-2-Tetra-Decyl MalonAmide (DMDBTDMA) [31-33] has shown promising results. Extensive studies were carried out using DMDBTDMA as extractant for minor actinide partitioning in DIAMide EXtraction (DIAMEX) process. Trivalent actinides and lanthanides are extracted from nitric acid solutions with an acid concentration >2 M by 0.5 M DMDBTDMA. The distribution ratios for the extraction of Am, Cm and Ln from HLLW were studied. Unfortunately Zr and Mo were extracted to a much higher extent.

A new malonamide containing ether functions on the central carbon atom has been studied in France. These malonamides, especially the N,N'dimethyl-N,N'dioctyl-hexylethoxy-malonamide (DMDOHEMA), exhibit better affinities for actinide and lanthanide ions in comparison with other malonamides. DMDOHEMA emerged as the promising alternate extractant to DMDBTDMA in the DIAMEX process, in view of increased extraction efficiency, less third phase formation tendency (due to increased lipophilicity) and the possibility of easy elimination of degradation products etc,. DIAMEX process with genuine radioactive waste was demonstrated using DMDBTDMA and DMDOHEMA [34-37]. However, the distribution ratios of trivalent actinides are low in the DIAMEX solvents, therefore, high concentration of extractant (0.5 M-1 M) needs to be employed for the actinide partitioning. The use of excess concentration of extractant causes the co-extraction of many undesirable metal ions, and complicates the extraction and stripping behavior of actinides [38].

1.11.5. Diglycolamides for minor actinide partitioning

A new class of extractants called diglycolamides (DGAs), *N,N,N',N'*-alkyl derivatives of 3-oxapentane-1,5 diamides containing three oxygen donor atoms were synthesized and studied the extraction behavior of An(III) from nitric acid medium. Sasaki *et al.* synthesized and studied the physico-chemical and extraction properties of various DGAs [40]. The properties of DGAs strongly depend on the nature of alkyl groups attached to amidic nitrogen atom. Diglycolamides (DGA) contain three oxygen atoms which co-ordinate the metal ions, so they act as tridentate ligands. Because of these three functional groups, the extraction of trivalent actinide ions was improved compared to conventional extracting agents containing only one or two functional groups. The hydrophobicity of DGA extractants is controlled by the length of the carbon chains attached to the amidic N atoms. Among the various DGAs studied, *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) has shown promising behavior for partitioning of MAs [45-52]. Later studies on its isomer, *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) showed that it is also a promising extractant for MA partitioning from HLLW [53-56]. Among these two symmetrical DGAs, TODGA showed higher extraction affinity towards trivalent actinides over the TEHDGA [45, 62].

1.11.5.1. TODGA solvent

Tetraoctyl-3-oxapentane-1,5-diamide or N,N,N',N'-tetraoctyldiglycolamide (TODGA) has been proposed for the extraction of trivalent actinide and lanthanides from HLLW. The n-octyl group attached to the N atoms gives enough lipophilicity to the TODGA molecule, to dissolve satisfactorily in n-dodecane at any ratio. On the other hand, TODGA exhibits better extraction of the actinides than DGA with longer alkyl chains. For separation of trivalent actinides from HLLW, phase modifier such as TBP, dihexyloctanamide (DHOA) was added to TODGA phase. Hot runs were carried out using 0.2 M TODGA - 0.5 M TBP in n-DD, 0.1 M TODGA - 0.5 M DHOA in n-DD [46, 47, 50].

However, the diglycolamides, TODGA and TEHDGA having more advantages over other extractants also suffer from a few limitations such as third phase formation during the extraction of trivalent metal ions from nitric acid medium. *Sasaki et al.* reported 0.1 M TODGA/*n*-dodecane solution formed third phase when the Nd(III) concentration was more than 8 mM in 3 M nitric acid medium with an LOC of 6.4 mM [66]. Therefore, a phase modifier was added to prevent the third phase formation during the extraction of trivalent metal ions from HLLW. Thus, these extractants could not be used without phase-modifiers for the trivalent actinide separation from HLLW arising from the reprocessing of fast reactor fuel. In addition to third phase formation, these symmetrical DGAs in *n*-dodecane also co-extract other fission products such as Mo(VI), Sr(II), Pd(II) and Zr(IV). This can be minimized either by employing complexing agents to aqueous feed or by scrubbing the loaded organic phase, which ultimately increases the waste generation. Therefore, elimination of third phase formation and suppression of undesirable metal ion extraction by DGAs is an important requirement.

The radiolytic stability of TODGA has been studied and the main degradation products are amines and monoamides because the amide bonds and the bonds in the vicinity of the ether oxygen are relatively weak with respect to radiation. The radiolytic effect on the extraction of the actinide and lanthanide ions in a partitioning process of the HLLW is negligibly small, although radiolytic degradation products are observed.

1.11.5.2. Unsymmetrical diglycolamide solvent

The symmetrical diglycolamide (TEHDGA, TODGA) forms third phase with HLLW. So phase modifier was added to the extractant phase. In order to avoid the drawbacks of symmetrical diglycolamide, several unsymmetrical diglycolamides (UDGA) were developed and studied for the extraction of trivalent metal ions from nitric acid medium [67, 68]. In contrast to symmetrical DGAs such as TODGA and TEHDGA, the alkyl groups attached to the N atoms of UDGAs are different. Among the various UDGAs studied, the *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D^3DODGA) is a promising reagent for trivalent actinide partitioning [67]. The dodecyl group in conjunction with the octyl group present in D^3DODGA, not only retained the excellent extraction properties of TODGA, but also surmounted the problem of third phase formation during the extraction of trivalent metal ions from 3-4 M nitric acid [68]. The extraction behaviors of several metal ions that are present in HLLW were studied in a solution of 0.1 M D^3DODGA /*n*-DD as a function of concentration of nitric acid, in detail [69]. The results revealed the possibility of using 0.1 M D^3DODGA /*n*-DD for the separation of trivalent actinides from simulated and genuine wastes without any phase modifier.

1.12. Mutual separation of lanthanides and actinides

Both trivalent actinides and lanthanides, co-extrated in the first cycle from HLLW are further mutually separated from each other in the second cycle. This mutual separation is necessary for the effective transmutation of An(III) because Ln(III) act as neutron poisons and reduces the neutron economy during transmutation process. However, the separation of Ln(III) from An(III) is a challenging task due to their similarities in chemical and extraction properties. A marginal size difference between Ln(III) and An(III) plays an important role for their mutual separations. According to Pearson's hard-soft acid base theory, both An(III) and Ln(III) are classified as hard acids. But the An(III) have slightly softer nature than the Ln(III) [70,71]. Being lighter ions, Ln(III) act as relatively hard acids and form complexes preferably with oxygen atom based ligands over nitrogen based ones. On the other hand, An(III) being relatively larger in size prefers nitrogen based soft donor ligands over oxygen based ligands

[72]. However, neither nitrogen based ligands nor oxygen based ligands can extract either An(III) or Ln(III) preferably. Therefore, the An(III) can be held in aqueous phase using suitable complexing agents and the Ln(III) are exctracted using a suitable extractant or vice versa. For the mutual separation of trivalent lanthanides from actinides, so many processes have been developed. Some processes are discussed below.

1.12.1. TALSPEAK process

A more efficient approach for mutual separation of lanthanide and actinide is known as Trivalent Actinide Lanthanide Separation by Phosphorous Reagent Extraction from Aqueous Komplexes (TALSPEAK) process [73]. In this process, diethylenetriaminepentaacetic acid (DTPA) containing soft donor nitrogen atoms is added in the aqueous phase to preferentially hold An(III), and Ln(III) extraction is carried out using di-2-ethylhexyl phosphoric acid (HDEHP), containing hard donor oxygen atoms. This facilitates the preferential extraction of Ln(III) over the An(III). Selective extraction of trivalent lanthanides is carried out using 0.5 M di(2-ethylhexyl) phosphoric acid (HDEHP) from a 0.05 M DTPA+1 M lactic acid solution at pH 3. The lactic acid serves as a buffering reagent. The DTPA complexes of the actinides remain in the aqueous phase.

However, TALSPEAK processes also have some limitations as the pH should be maintained in aqueous phase which is very difficult. The poor solubility of HDEHP in *n*-dodecane, high phase disengagement time and the need of phase modifier limit its usage in the process applications.

1.12.2. Reverse TALSPEAK

The reverse TALSPEAK process has been developed to overcome the drawback of the large amounts of troublesome secondary waste created by the TALSPEAK process. Trivalent actinides and lanthanides are first extracted together by 1 M HDEHP in n-dodecane from 0.1 M HNO_3 and the mutual separation of trivalent lanthanides from actinide is achieved using a mixture of 0.05 M DTPA and 1.5 M lactic acid. DTPA helps in selective co-ordination with trivalent actinides where as lactic acid is used as a buffering reagent. Finally, the lanthanides can be stripped from the organic solvent with 6 M HNO_3. The demerit of reverse TALSPEAK is similar to TALSPEAK process.

1.12.3. Bis(2-ethylhexyl)diglycolamic acid (HDEHDGA)

Diglycolamic acid is an acid derivative of alkyl-3-oxapentane, emerging as promising candidate for lanthanide-actinide mutual separations [74,75]. Unlike the other reagents in use, the diglycolamic acids are made up of CHON- atoms and they are completely miscible in n-dodecane. Bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) was studied for the extraction of Eu(III) and Am(III) from nitric acid medium [74]. The results revealed that HDEHDGA exhibited superior selectivity for Eu(III) over Am(III). The mutual separation of Eu(III) and Am(III) from 0.1 M citric acid-nitric acid medium was studied. The extraction behavior of Eu(III) and Am(III) in a solution of HDEHDGA in n-DD from citric acid medium was studied and the conditions for the selective stripping of Am(III) from the loaded organic phase were optimized. The mutual separation of Eu(III) and Am(III) was demonstrated in a counter-current mixer-settler by employing the optimized conditions [75]. This extractant is evolving as a promising reagent for the efficient separation of Ln(III) from An(III).

1.13. Single-cycle separation of minor actinides from HLLW

The extractants such as CMPO, DGA and malonamides have been proposed for group separation (i.e. step 1) and extractants such as HDEHP, HDEHDGA have been proposed for lanthanide-actinide separation (i.e. step 2). However in the recent past, single-cycle methods for the separation of trivalent actinides are receiving increased attention. There are a couple of approaches reported in literature. The first one is the direct separation of trivalent actinides from HLLW [76-80]. The methods such as Selective ActiNide Extraction (SANEX) concept, Actinide reCycling by SEParation and Transmutation (ACSEPT) and 1-cycle SANEX concept [76, 77] were developed for direct separation of actinides from HLLW. In contrast to this, the second approach involves the extraction of both the trivalent actinides and lanthanides together in organic phase followed by selective stripping of actinides alone from the loaded organic phase [81-83]. Based on this approach, both TRUEX and TALSPEAK process solvents were combined to form TRUSPEAK process [81,82], and by combining DIAMEX and TALSPEAK process solvents to form Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN) [83] process were developed.

1.13.1. Direct separation of trivalent actinides from lanthanides

The direct separation of actinides from HLLW is possible using actinide selective extractants as compared to trivalent lanthanides. Actinides are softer acids as compared to lanthanides. Extractant having multiple soft doner atoms can be used for the selective separation of actinides. Some processes are discussed below.

1.13.1.1. BTP process

Recently, Kolarik *et al.* developed 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (named BTPs, Bis Triazine Pyridine) for the trivalent actinide – lanthanide separation [76]. Very efficient separations have been obtained with 2,6-bis(5,6-n-propyl-1,2,4-triazin-3-yl)pyridine (nPr-BTP), which is considered as the reference molecule of the bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines. The BTP extractants are CHON molecules and capable to extract actinides selectively from moderate nitric acid concentration.

The radiation stability of the nPr-TBP extractant is less. Its synthesis is tedious; it has a low solubility in organic diluents and slow extraction kinetics. The extraction kinetics of nPr-BTP is too slow for practical applications. Several attempts have been made to accelerate the extraction kinetics by using co-extractants, such as TBP or DMDOHEMA. These modifiers, however, lower the selectivity towards An(III).

1.13.1.2. BTBP process

New Bis Triazine Bis Pyridine (BTBP) ligands, which are structurally related to the BTP family, have been prepared and extraction behavior of actinides was studied in Europe. 2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazy-3-yl)-[2,2']bipyridine, which is called CyMe4-BTBP is reported to be very effective for the actinide - lanthanide separation [76-80]. The problem of $CyMe_4BTBP$ is due to very low kinetics of metal extraction. In order to enhance the kinetics, the malonamide DMDOHEMA or TODGA has been used as phase transfer catalyst. The limitation of these extractants are poor hydrolytic and radiolytic stability, slow extraction kinetics, low back extraction of An(III) from the loaded organic phase etc.

1.13.2. Single-cycle separation using a combination of solvents

In two-cycle process, both neutral and acidic extractants are used in individual cycle. But the combination of neutral extractant and acidic extractant may facilitate the direct An(III) separation in a single-cycle. The pictorial representation of single cycle is shown in Figure 1.4. In single-cycle process, the trivalent actinides and lanthanides are co-extracted from HLLW using combined solvent formulation and recovery of actinides alone from the loaded solvent phase was carried out by aqueous soluble and actinide selective diethyltriamminepentaaceticacid (DTPA)-citric acid (CA) solution. This strategy reduces the waste generation, the human efforts and be more economical. Lumetta *et al.* introduced the concept of combining the neutral and acidic extractants for the separation of Ln(III) from the transuranic elements [81]. The authors indicate the promising nature of combining neutral and acidic extractants to achieve a single-cycle separation of trivalent actinides alone from HLLW. Some single -cycle process for minor actinide partitioning is described here.

1.13.2.1. TRUSPEAK process

The TRUSPEAK process is a combination of TRUEX and TALSPEAK process. The solvent used in individual process is combined here. The solvent is CMPO - HDEHP in n-dodecane. Dhami *et al.* studied the extraction and stripping behavior of Am(III) and Eu(III) using a solution composed of HDEHP - CMPO dissolved in *n*-paraffinic diluents [82]. The extracted metal ion was stripped using a unique solution composed of 0.4 M hydrazine hydrate, 0.4 M formic acid + 0.05 M DTPA and achieved a separation factor of ~3 for americium over europium. However, these separation factors are very low to achieve the complete separation of lanthanides from actinides.

1.13.2.2. PALADIN process

A new process, namely Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN) process was developed in France to produce a single solvent for separating lanthanides from actinides based on the reagents diamides and HDEHP [83]. Some undesirable metal ions such as Mo, Zr, Fe, Pd and to some extent Ru were also extracted due to the presence of both diamide and HDEHP which make it essential to scrub the loaded organic phase for removing those metal ions prior to the stripping of actinides. In addition, the extractants used are also not completely incinerable due to the presence of phosphorous based reagent, HDEHP. The combination of neutral and acidic extractants facilitates the extraction of An(III) and Ln(III) from 3-4 M nitric acid medium, and also favors the selective stripping of An(III) into aqueous phase containing DTPA by retaining the Ln(III) in organic phase.

Similarly, Gannaz *et al.* studied the extraction of Eu(III) and Am(III) by a mixture of extractants consisting of a malonamide (DMDOHEMA) and di-n-hexylphosphoric acid (HDHP) [84]. During extraction from nitric acid medium, the solvent behaves primarily like a malonamide that extracts both trivalent actinides and lanthanides. However, selective stripping of trivalent actinides from the loaded organic phase was controlled by HDHP present in organic phase as well as the aqueous complexing formulation developed by the authors. This process has the drawback that two different extractants are used in the organic phase, which will complicate the solvent clean-up and that the pH of the aqueous phase must be carefully adjusted. Furthermore, numerous ions are co-extracted to the solvent phase.

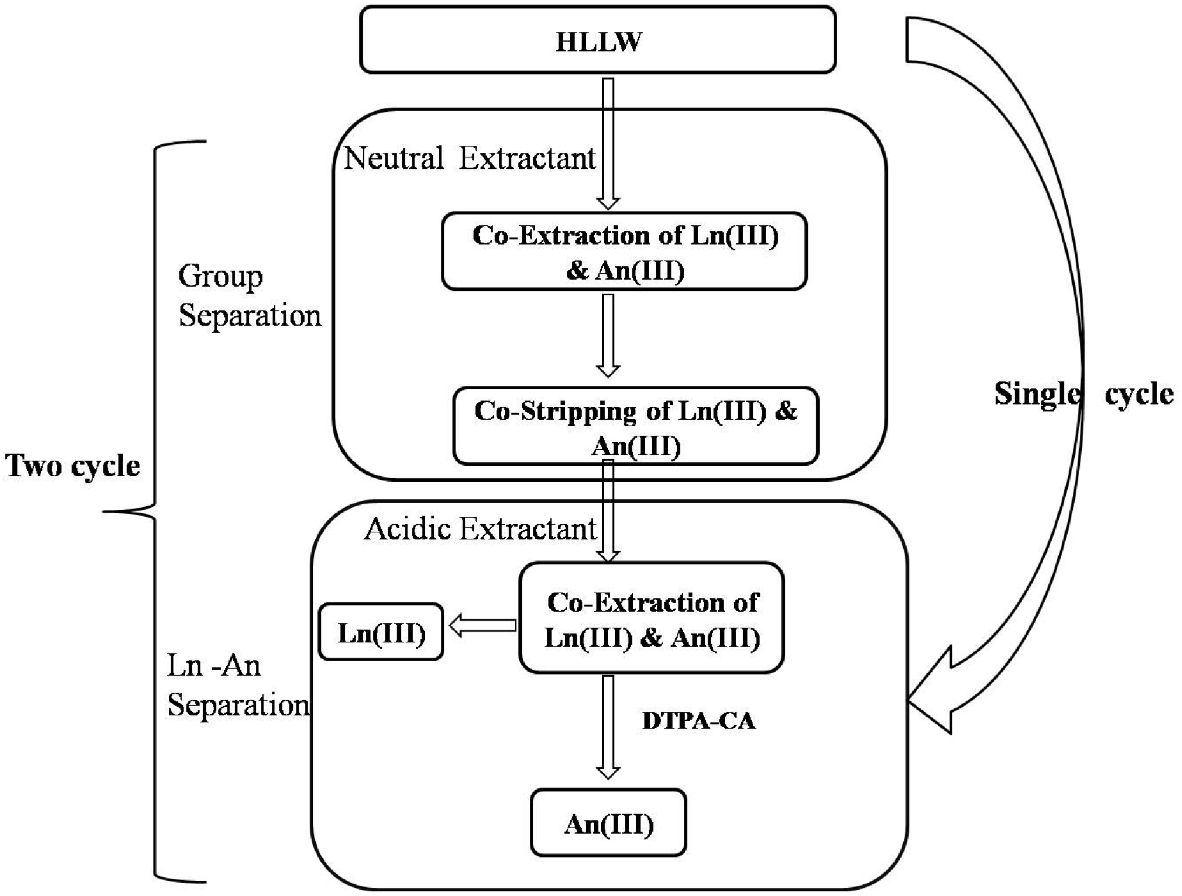

Figure 1.4. Graphical representation of two cycle and single cycle process.

1.14. Radiolytic stability of extractants

During the solvent extraction process, the solvent is exposed to the high energy alpha, beta, and γ radiations. As a result, the cleavage of chemical bonds in the solvent ocures and hence forms chemically active species such as free radicals and ions. Some of these species may recombine or react with other molecules depending on the energy and type of radiation [85-89]. The chemically active species such as free radicals, ions, and other neutral molecules which are produced as a result of interaction of radiation with solvent are collectively called as degradation products. These degradation products alter the physico-chemical and solvent extraction properties of the reagents to a significant extent [90-94]. Degradation products present in the organic phase may interfere in the complex formation of extractants with the metal ions. Therefore, the extraction and stripping properties of actinide metal ions may vary. Thus, the degradation of solvent not only reduces the extraction efficiency, but also alters the separation factors, physical and chemical properties. In addition, the re-usability of its solvent strongly depends on the radiolytic stability. Therefore, the components of the solvent formulation to be employed in the nuclear solvent extraction process must have adequate radiolytic stability. In this context, it is very important to understand radiation chemistry and evaluation of radiation stability of a solvent proposed for the extraction of actinides from HLLW.

1.15. Scope of the present work

The current approach for partitioning of trivalent actinides from HLLW is a two-cycle approach, namely, i) the group separation i.e., the separation of trivalent actinides together with lanthanides from HLLW in first cycle, followed by ii) lanthanide-actinide separation in the second-cycle. The literature survey indicates that CMPO, TEHDGA, TODGA, DMDOHEMA, DMDOTDMA etc. are used for the the group separation of trivalent metal ions from HLLW. But these extractants forms third phase with HLLW and some extractants are phosphorous based extractants. These problems can be avoided by using modifier free extractant containing C, H, O, N atoms for the group separation of trivalent metal ions from HLLW. In this context, an unsymmetrical diglycolamide N,N,-didodecyl-N',N'-dioctyl-3-oxapentane-1,5-diamide, (D^3DODGA) was developed for the extraction of actinides and fission products from nitric acid medium. The studies have shown that D^3DODGA does not require any phase modifier during the extraction of trivalent actinides. Separation of trivalent actinides from FR-SHLLW was demonstrated using a modifier-free organic phase composed of D^3DODGA in n-dodecane.

In contrast to this traditional approach, a single-cycle approach has been developed in which the actinides are separated directly from HLLW in a single processing cycle. The solvent formulation in this approach is composed of neutral and acidic extractant. A novel approach namely Single cycle method for Minor Actinide partitioning using completely incinerable ReagenTs (SMART) has been developed. This method uses the applications of D^3DODGA as neutral extractant and di-2-ethylhexyl diglycolamic acid (HDEHDGA) as acidic extractant for the single-cycle separation of trivalent actinides from FR-SHLLW. The extractants are made up of CHON- atoms and they are completely miscible with n-dodecane. The extraction behavior of various metal ions present in FR-SHLLW was studied in a solution of D^3DODGA - HDEHDGA/*n*-DD. The extraction of Am(III) was accompanied by the co-extraction of lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II). The extraction of unwanted metal ions was minimized by addition of suitable aqueous soluble complexing agents. The extraction and stripping conditions were optimized for the selective separation of lanthanide from actinide. The counter-current mixer-settler run was performed using a 20-stage mixer-settler. The results obtained from these studies are reported.

A new solvent composition of DGAs - HDEHP was studied for a single-cycle process for minor actinide partitioning. Symmetrical DGAs (TEHDGA & TODGA) were studied for the group separation of actinides from HLLW where as HDEHP was used for lanthanide-actinide separation in TALSPEAK process. The extraction behavior of Am(III) and Eu(III) was studied in TODGA - HDEHP, and TEHDGA - HDEHP in a single-cycle process. The batch studies revealed that the mutual separation of Am(III) from Eu(III) is difficult in case of TODGA - HDEHP system whereas the selective separation of Am(III) from Eu(III) is possible in TEHDGA - HDEHP solvent system. The extraction behavior of metal ions present in FR-SHLLW was studied extensively using TEHDGA - HDEHP solvent. The extraction and stripping were carried out in a 16 stage mixer-settler. The results indicate the mutual separation of An(III) from trivalent lanthanides. In this process, An(III) were selectively stripped using DTPA-CA solution where as Ln(III) were held in the combined organic phase. The trivalent lanthanides present in organic phase were stripped using aqueous soluble *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) in nitric acid medium. The radiochemical degradation of a solution of TEHDGA - HDEHP/*n*-DD was investigated by irradiating the solvent to various absorbed dose levels of γ-radiation. The radiolytic degradation of combined solvent system resulted in the formation of innocuous products that do not hold Am(III) during back extraction. A novel and simplified flow-sheet for separation of actinides was developed for single cycle process.

The aim of the present work is to demonstrat 1) trivalent actinide partitioning from simulated high-level liquid waste using modifier-free unsymmetrical diglycolamide in *n*-dodecane, 2) Partitioning of minor actinide using completely incinerable reagents (D^3DODGA – HDEHDGA) in a single-cycle to separate americium(III) from simulated high-level liquid waste, 3) Development of single-cycle process for minor actinide partitioning using Diglycolamide – HDEHP solvent system, 4) Demonstration of single-cycle separation of americium (III) from fast reactor simulated high-level liquid waste using TEHDGA - HDEHP solution in a mixer-settler, 5) study the radiochemical degradation of TEHDGA - HDEHP solution. The results generated from these studies are reported in this thesis.

1.16. References

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Chapter 2: Experimental

This chapter describes the synthesis of diglycolamic acid, symmetrical and unsymmetrical diglycolamides used for the studies. Experimental procedures such as liquid-liquid extraction of actinides, other metal ions and third phase formation studies are discussed in details. The materials and methods used for the analysis of radioactive and non-radioactive samples along with instruments such as NaI(Tl) detector, gamma-spectrometer, inductively coupled plasma-optically emission spectrometry (ICP-OES) etc employed for the above studies have been explained in detail. All the experiments were conducted at 298 K unless otherwise mentioned.

2.1. Chemicals and reagents

All the chemicals and reagents used in this study were of analytical grade and used as received unless otherwise mentioned.

2.1.1. Radioactive tracers

The radioisotope $^{(152+154)}$Eu(III) tracer was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai, India. Initially the radioisotope was in hydrochloric acid medium. The hydrochloric medium was changed into nitric acid medium by continuous evaporation and addition of nitric acid. Finally the solution was prpared in nitric acid medium using dilute nitric acid. ^{241}Am(III) was received from Oak Ridge National Laboratory (ORNL) as Am_2O_3 and dissolved in nitric acid. This ^{241}Am(III) tracer was also diluted using dilute nitric acid. Both radioactive tracers were in dilute nitric acid medium.

2.1.2. Organic materials and solvents

Diglycolic anhydride and dialkyl amines

Diglycolic anhydride (technical grade, 90%) dioctylamine, and di-2-ethylhexylamine were procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany. Didodecylamine was obtained from Fluka.

Dicycolhexylcarbodiimide (DCC)

Dicyclohexylcarbodiimide (DCC) was procured from spectrochem, Mumbai, India.

Alkanes

n-dodecane was purchased from Aldrich. *n*-Hexane was obtained from Ranbaxy Fine Chemicals Limited, New Delhi

Bis (2-ethylhexyl)phosphoric acid

Bis(2-ethylhexyl)phosphoric acid (HDEHP) was obtained from M/s. Fluka Chemie GmbH, Buche, Switzerland.

Dichloromethane

Dichloromethane was obtained from Fischer Inorganics and Aromatics Limited, Chennai, India.

Ethylacetate

Ethylacetate was obtained from Fischer Inorganics and Aromatics Limited, Chennai, India.

Silica-gel

Silica-gel of mesh size 60-120 and 100-200 for column chromatography were obtained from Sisco Research Lab Private Limited, Mumbai, India and dried at 373 K for one hour prior to use.

2.1.3. Aqueous solutions and complexing agents

Acid solutions

The acid solutions (GR grade HNO_3 and HCl,) were procured from Merck Specialities Private Limited, Mumbai, India. Different concentrations of acid solutions were prepared by the dilution of concentrated acids, and standardized using standardized NaOH solution and phenolphthalein indicator.

Diethylenetriaminepentaaceticacid (DTPA)

Diethylene triaminepentaacetic acid was procured from Acros Organics, Geel, Germany. The solution of DTPA was prepared by dissolving DTPA in millipore water with the addition of NaOH pellets and the pH of the solution was adjusted using HNO_3 to desired value.

Sodium hydroxide

Sodium hydroxide (AR grade) was obtained from Ranbaxy Fine Chemicals Limited, New Delhi, India.

Phenolpthalein

Phenolpthalein (Merck Specialities Private Limited, Mumbai, India) indicator was prepared by dissolving ~ 500 mg of solid in 100 mL of 1:1 mixture of distilled water and ethanol.

Sodium nitrite

Sodium nitrite was obtained from S.D. fine Chemicals, Mumbai, India.

Citric acid

Unhydrous citric acid was obtained from Otto Chemie, Mumbai, India.

Oxalic Acid

Oxalic acid was procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany.

EDTA

EDTA [bis(ethylenediaminetetraacetic acid)] was obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany.

CyDTA

Trans-1,2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA) was obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany.

HEDTA

N-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid tri-sodium salt (HEDTA) was obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany.

2.2. Instrumentation

2.2.1. High Pure Gamma Spectrometer (HpGe Detector)

The gamma emitting radio nuclei were characterized and estimated by gamma spectrometry. In this technique, a planar high pure germanium (HpGe) crystal semiconductor detector obtained from Baltic Scientific Instruments, Latvia was used. It was coupled with multichannel analyzer (MCA).

2.2.2. Gamma counter

The activity of ^{241}Am, $^{(152+154)}$Eu was measured independently using a gamma counter with single channel analyzer and well type NaI(Tl) detector. The NaI(Tl)-photo multiplier tube (PMT) integral assembly was procured from M/S Harshaw, U.S.A and other electronic modules were obtained from Electronic Corporation of India Limited (ECIL), Hyderabad, India.

2.2.3. Gamma chamber for irradiation

An indigenous, compact, self-shielded (Gamma Chamber 5000, BRIT) gamma chamber was used in the present study. The radiation field was provided by a set of stationary cobalt-60 gamma sources placed in a cylindrical cage. The samples were placed in an irradiation chamber located in the vertical drawer inside the lead flask. The volume of irradiation chamber was about 5 L. The gamma chamber was calibrated using Fricke dosimeter.

2.2.4. Rotary evaporator

A rotary evaporator (Model R-3000 from M/s. Buchi Laboratory Technique AG, Switzerland) was used for distilling off volatile solvents from the reaction mixture and fractions collected during the column chromatography.

2.2.5. pH meter

All pH measurements were made with Cyberscan 500 pH, Metrohm. The meter was calibrated at 298 K with standard buffers of pH 4, 7 and 10.

2.2.6. Inductively coupled plasma-optical emission spectrometer

Ultima C spectroanalyser (Jobin Yvon, France) equipped with Inductively Coupled Plasma excitation source was used for analysis of several non-radioactive elements. The spectrometer provides a resolution of 0.015 nm with a polyscan facility of ±2 nm. RF generator of 40.68 MHz with a maximum output power of 1550 W was used for plasma generation. Samples were injected by the in-built peristaltic pump with the flow rate of 1mL/min. The emission lines chosen for the given metal analysis were the most sensitive lines having no interference from other elements in the group.

2.2.7. NMR spectrometer

A Brucker Avance III 500 MHz (AV 500) multi nuclei solution NMR spectrometer was used for the structure analysis of synthesized diglycolamic acids and diglycolamides. $CDCl_3$ was used as the solvent.

2.2.8. FT-IR spectrometer

A BOMEM MB-100 FT-IR spectrometer with a range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1} was used for the measurement of IR spectra. The samples to be scanned were sandwiched between two zinc-selenide windows. The sample compartment was purged with nitrogen for a sufficient period prior to scan. For solid sample analysis, a thin pellet of sample was prepared in dry KBr salt and recorded.

2.2.9. Electronic single pan balance

A calibrated electronic single pan balance with a sensitivity of 0.01 mg was used to weigh chemicals and solutions.

2.2.10. Thin Layer Chromatography

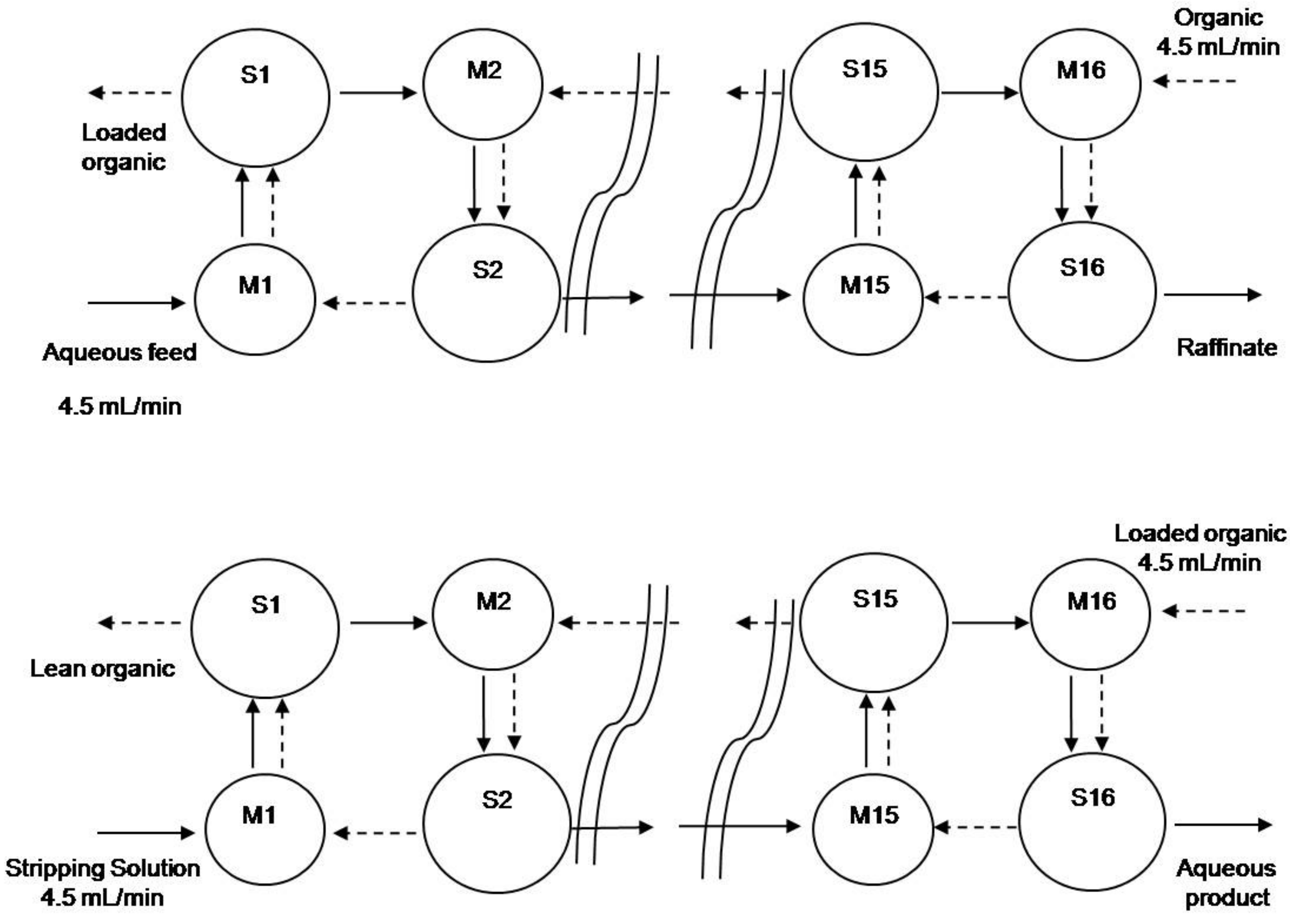
Thin-Layer Chromatography (TLC) of reactants and reaction mixture during and after reactions were performed using TLC Aluminum Silica-gel 60 F254 Sheets (Merck) cut into small pieces of approx. 4 × 10 cm size. Fine capillaries were used to spot the compounds or reaction mixture and the TLC was performed in a solvent containing 15-30 % of ethyl acetate in petroleum ether or hexane. The sheets were subsequently air-dried and placed in an iodine chamber for spot visualization.

2.2.11. Description of mixer-settler

A high efficiency air pulsed ejector mixer-settler used in the present study was developed by Koganti et al. [1, 2]. Two mixer settlers with a) 16 stages b) 20 stages were used in the present study. A 16-stage stainless steel mixer-settler unit used in the present studies is illustrated in Figure 2.1. The mixer-settler contains a cylindrical mixer with a short diffuser, fixed at the bottom of the mixer compartment. The aqueous and organic phases were passed through the diffuser section and the dispersion was achieved in the rest of the mixer section. The ejectors were connected independently to a mixer and mixer column to a common header. The photograph of a 20 stage mixer-settler unit used for the experiment in glove box is shown in Figure 2.2. The common header was connected to pressure and vacuum sources through a 2 way 3 port solenoid valves. The illustration of mixer-settler shown in Figure 2.1 indicates that each mixer (M2) is connected to three settlers (S1, S2 and S3) and each settler (S2) is connected to three mixers (M1, M2 and M3). The volume of the mixer and settler unit was 30 and 50 mL respectively.

Extraction and stripping behavior of trivalent lanthanides and actinides were performed in a counter current mode using this 16-stage ejector mixer settler. Mixing of the organic and aqueous phases was achieved by air pulsing in the column by applying vacuum and pressure alternatively with the help of a solenoid valve operated by a cyclic timer. The

Extraction run



Stripping run

M – Mixer chamber, S – Settler chamber, 1,2 ….15, 16 – represents the number of stages, Solid arrow represents the flow of aqueous phase whereas dotted arrow represents the flow of organic phase

Figure 2.1. Illustration of a 16-stage mixer settler and conditions employed during extraction and back extraction.

aqueous and organic solutions were fed to the mixer settler at a constant flow rate of 4.5 ml per minute by means of metering pumps equipped with precise flow control. The system was operated for ~7 hrs. Steady state was attained in four hours. The stage samples of organic and aqueous phase were collected for analysis. The loaded organic and raffinate were collected separately in a 2 L container. The lanthanides and actinides were back extracted from the loaded organic in a counter current extraction process using the same mixer settler in a separate run. Extraction and stripping behavior of ^{241}Am(III) and $^{(152+154)}$Eu(III) was monitored in various streams by HpGe-MCA detector.

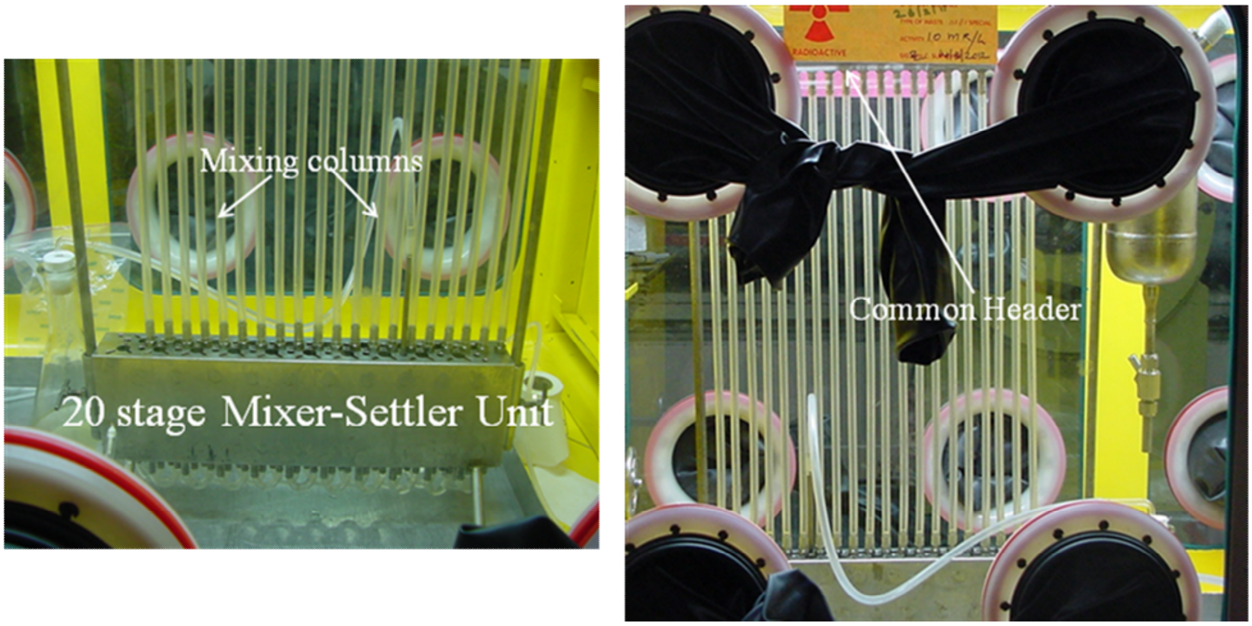


Figure 2.2. Photograph of 20 stage mixer-settler used for the experiment inside the glove box

2.3. Preparation of Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW)

The composition of FR-SHLLW of the fuel with burn-up of 80,000 MWd/Te and cooled for two years was shown in Table 2.1[3]. For the preparation of FR-SHLLW solution, stock solution of different metal ions was prepared. The stock solution for nitrate salt was prepared by dissolving of individual metal ion in nitric acid (≤ 1 M). The oxide salts were initially dissolved in nitric acid twice under IR lamp and finally the stock solutions were prepared using nitric acid. The concentration of metal ion in its stock solution was estimated using ICP-OES and complexometric titration. Simulated HLLW was prepared by adding the appropriate amount of stock solution of each metal ion together in nitric acid. Finally the nitric acid concentration was adjusted to 3M using nitric acid. The final acidity was determined by standard acid-base titrations using standard NaOH and phenolphthalein indicator. During titration, saturated potassium oxalate solution was added to prevent interfaces from hydrolysable ions.

Table 2.1. The simulated composition of fast reactor high-level liquid waste (FR-SHLLW). The composition is based on the HLLW arising from reprocessing of spent fast reactor fuel with a burn-up of 80,000 MWd/Te and 2 year cooling.

Element	Concentration [g/L]	Element	Concentration [g/L]	Element	Concentration [g/L]
La	0.342	Mo	1.092	Cs	1.125
Ce	0.684	Cr	0.101	Rb	0.055
Pr	0.339	Te	0.163	Se*	0.002
Nd	1.125	Cd	0.038	Na	3.000
Sm	0.306	Ni	0.1	Ag	0.109
Pm*	0.053	Sr	0.147	Tc*	0.262
Eu	0.032	Ba	0.414	Sb*	0.007
Gd	0.065	Ru	0.813	^{241}Am	0.218
Tb*	0.011	Pd	0.600	$^{(152+154)}$Eu	Tracer
Dy	0.006	Zr	0.822	[HNO_3]	~ 3 M
Y	0.074	Rh	0.262		
Fe	0.5	Sn*	0.163		

* Sb, Sn, Se – were not added as they are sparingly soluble. La was added for Tb, and Pm. Mo was added for Tc.

2.4. Synthesis of extractants

Diglycolamic acids and diglycolamides (DGA) were synthesized by the procedure described elsewhere [4, 5]. Synthesis of DGAs consists of two steps. The first step involved the reaction between diglycolic anhydride and dialkylamine to obtain the corresponding diglycolamic acid. In the second step, the diglycolamic acid was reacted with another (desired) dialkylamine in the presence of dicyclohexylcarbodiimide (DCC) to obtain the DGA. Symmetrical diglycolamide was synthesized by addition of same dialkylamine in both the step whereas unsymmetrical diglycolamide was synthesized by addition of different dialkylamine in the second step. The reaction scheme for the synthesis of a typical DGA is shown in Figure 2.3. The details of synthesis are given below.

2.4.1. Synthesis of dialkyl-diglycolamic acids

Diglycolic anhydride (1eq.) was mixed with dichloromethane (30 mL), in a round bottom flask equipped with a $CaCl_2$ guard tube. A solution of desired di-alkylamine (1eq.) in dichloromethane (10 mL) was added drop-wise to diglycolic anhydride solution. The reaction mixture was stirred at room temperature for four to eight hours depending upon the nature of the dialkyl amine, to obtain the corresponding dialkyl-diglycolamic acid (see the first step of reaction in Figure 2.3). The resulting clear solution was then washed with distilled water followed by ~1 M HCl and again by distilled water in order to remove the unreacted reactants, if any. The diglycolic anyhydride is water soluble and can be washed out. To ensure the complete consumption of dialkylamine, a bit excess amount of anhydride was added. The organic phase was dried with anhydrous sodium sulphate, and the solvent was removed under vacuum. The residue was recrystallised from hexane to obtain the corresponding diglycolamic acids. The structures of diglycolamic acids synthesized in the present study are shown in Figure 2.4. Recrystalization of these diglycolamic acids results pale yellow colored di-2-ethylhexyl diglycolamic acid (HDEHDGA). The products were then characterized by IR and NMR spectroscopic techniques. The yield of the reaction was varied from > 90% to 95% depending up on the alkyl chain length attached to the nitrogen atom of amine. The characterization details of the compounds are given below.

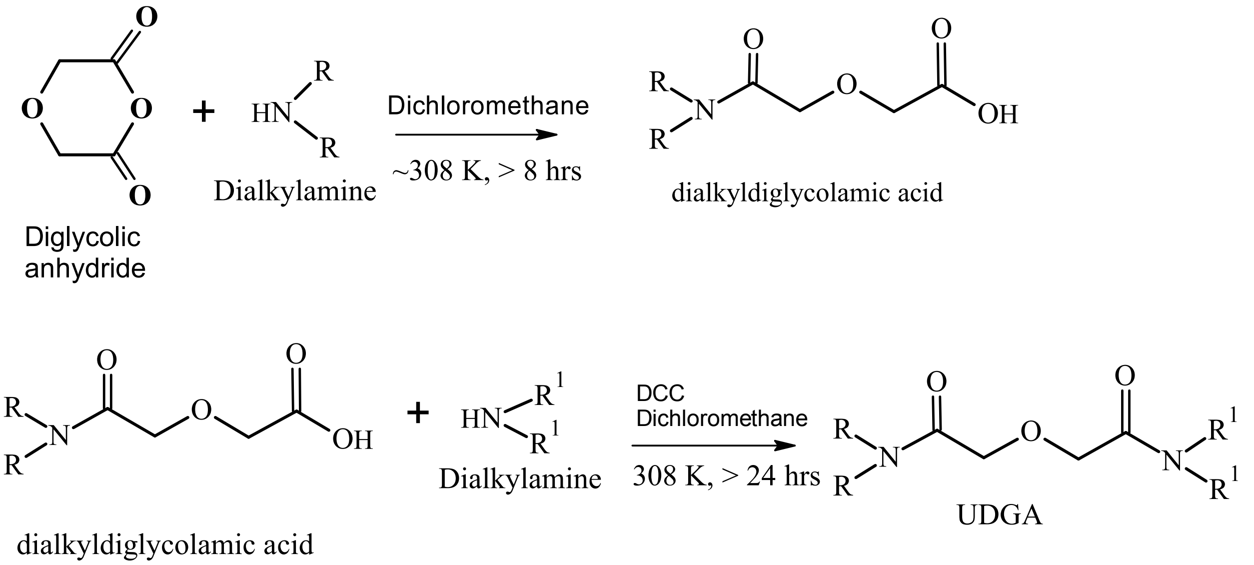
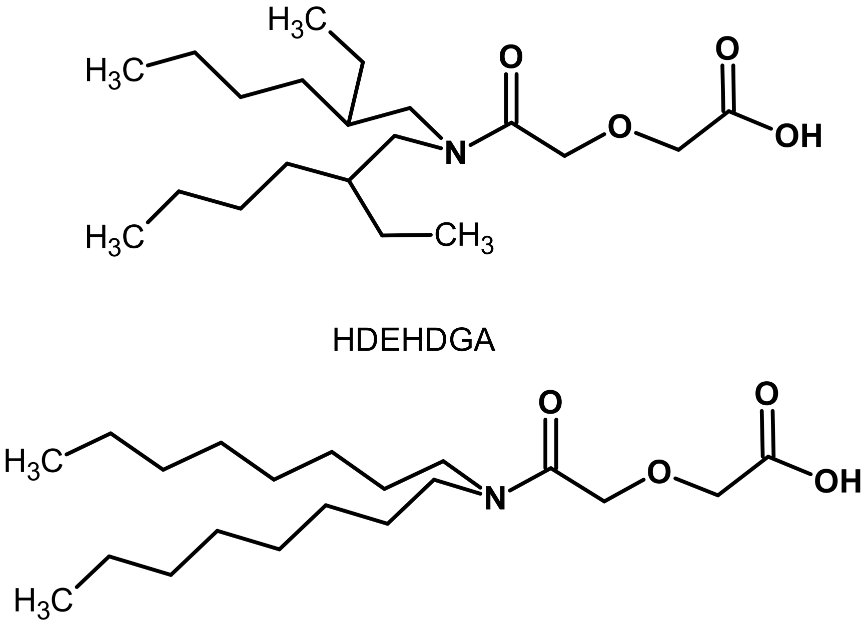


Figure 2.3. The synthetic procedure of diglycolamic acid and DGAs



HDEHDGA

Dioctyl diglycolamic acid

Figure 2.4. The structure of Dialkyl diglycolamic acids

Dioctyl diglycolamic acid (HDODGA): ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K), δ 0.89 (t, 6H, N-$(CH_2)_7$-CH_3), 1.29, 1.55 (s, 24 H, -N-CH_2-$(CH_2)_6$-CH_3), 3.10, 3.35 (t, 4 H, -N-CH_2-$(CH_2)_6$-CH_3), 4.21 (s, 2H,-N-CO-CH_2-O-), 4.38(s, 2H,-CH_2-COOH), 9.34(s, 1H, -COOH). ^{13}C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) 171.93, 170.42, 77.29, 77.05, 72.63, 70.98, 46.88, 46.79, 31.75, 31.71, 29.18, 29.17, 29.11, 29.06, 28.62, 26.92, 26.87, 25.89, 22.59, 22.57. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 3413 (broad, O-H stretching) 2926 (-CH_3-stretching), 1713 (C=O stretching), 1628 (C=O stretching), 1466 (CH_2-bending), 1400 (–C-N- stretching), 1375 (–CH_3-bending), 1120 (C-O-stretching). The two bands for C=O groups are clearly seen in the IR spectrum for two carbonyl groups.

Di-2-ethylhexyl diglycolamic acid (HDEHDGA): ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K), δ 10.67 (s, 1H, COO$\underline{H}$), 4.32 (s, 2H, -OCH_2-), 4.11(s, 2H, -C$\underline{H}_2$O-), 3.17-3.31 (m, 4H, 2 C$\underline{H}_2$ - N), 2.96-2.98 (m, 2H, C$\underline{H}$), 1.15-1.24 (m, 16H, C$\underline{H}_2$-R), 0.77-0.84(m, 12H, C$\underline{H}_3$). ^{13}C NMR (500MHz, $CDCl_3$, TMS , 298K): 172.22 , 172.14 ,77.21(-OCH_2), 71.1,49.34, 37.16 ,30.35, 28.47, 23.58 , 22.86, 13.93 ,10.47. IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}): 3454 (COOH), 1739 (-CO in COOH), 1622(-CO in –CON).

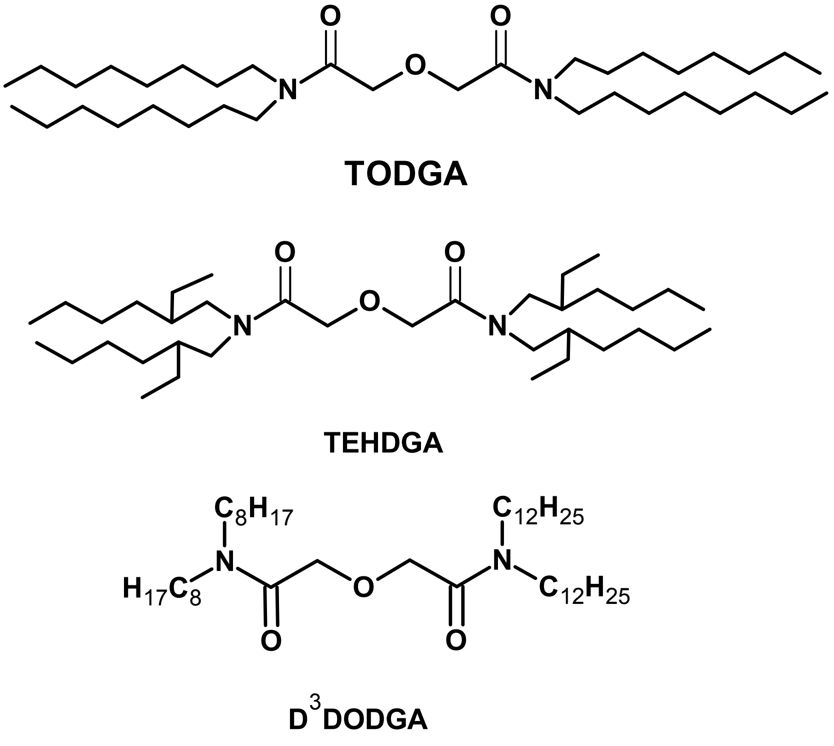
2.4.2. Synthesis of diglycolamides

Synthesis of diglycolamide is shown in the second step of the reaction in Figure 2.3. The diglycolamic acid obtained in first step was dissolved in dichloromethane taken in a round bottom flask equipped with $CaCl_2$ guard tube. A solution of dicyclohexylcarbodiimide (DCC) in dichloromethane was added (1.1 eq.) drop-wise to the diglycolamic acid solution and mixed using magnetic stirrer for about fifteen minutes. The desired di-alkylamine was then added drop-wise to the reaction mixture and stirred for about five days to seven days at room temperature, depending upon the alkyl chain length of the reactants. The progress of the reaction was monitored using thin layer chromatography. The excess solvent was removed by heating the reaction mixture in water bath after the completion of the reaction. The crude reaction mixture was dissolved in either petroleum ether or in *n*-hexane and filtered using Whatmann filter paper to remove the by-product, dicyclohexyl urea. The filtrate in hexane was taken in separating funnel and washed thoroughly with distilled water followed by ~1 M HCl several times to remove the unreacted amine, if present. Excess solvent was removed from using rotary evaporator and then the product was purified by column chromatography using silica gel. For the synthesis of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), dioctylamine was added in both the steps where as di-2-ethylhexylamine was added for the synthesis of *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA). For the synthesis of *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D^{3}DODGA), dioctylamine was added in the first step where as didodecylamine was added in the second step. Since different amines were present in both side of the diglycolamide, this diglycolamide is termed as unsymmetrical diglycolamide. The structures of these diglycolamides are shown in Figure 2.5. The final products were characterized by IR and NMR spectroscopic techniques. The characterization details of the compounds are given below.

TODGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.307 (s, 4 H), 3.291 (t, 4 H, J=8.0 Hz), 3.177 (t, 4 H, J=8.0 Hz), 1.519 (m, 8 H), 1.272 (br, 40 H), 0.885 (t, 6 H, J=6.0 Hz), 0.876 (t, 6 H, J=6.0 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 168.32, 68.97, 46.92, 45.68, 31.80, 29.38, 29.29, 29.20, 28.89, 27.56, 27.02, 26.87, 22.64, 22.63, 13.93. IR (neat, ν cm^{-1}): 2958 (C-H stretch), 2924(C-H stretch), 2874(weak, C-H stretch), 1651(C=O stretch), 1464 (-CH_2-bend), 1380 (C-N stretch) and 1116(C-O-C stretch). Yield was >94.

TEHDGA: ^{1}HNMR ($CDCl_3$, δ relative to TMS): 4.330 (s, 4 H); 3.370 (m, 4 H); 3.043 (d, 4 H, J=7.0 Hz); 1.669 (m, 3 H); 1.560 (m, 3 H); 1.250 (m, 30 H); 0.880 (m, 24 H). ^{13}C NMR ($CDCl_3$, δ relative to TMS): 169.52, 68.72, 49.94, 47.89, 37.91, 36.63, 30.52, 28.81, 28.79, 23.81, 23.06, 14.07, 14.03, 10.90, 10.61. IR (neat, ν cm^{-1}): 2958 (C-H stretch), 2924(C-H stretch), 2874(weak, C-H stretch), 1651(C=O stretch), 1464 (-CH$_2$-bend), 1380 (C-N stretch) and 1116 (C-O-C stretch). Yield was >94 %.

D^{3}DODGA: ^{1}H-NMR (500 MHz, CDCl$_3$, TMS, 298 K) at δ 4.35 (s, 2H), -O-CH$_2$-CO-N-, 4.17 (s,2H), -O-CH$_2$-CO-N-, 3.28-3.25 (m, 4 H), -CO-N-CH$_2$-R, 3.15-3.12(m, 4 H)- -CO-N-CH$_2$-R, 1.56-1.51(m, 8 H) CH$_3$-CH$_2$-(CH$_2$)$_n$-N-, 1.27-1.27 (m, 56 H) CH$_3$-CH$_2$-(CH$_2$)$_n$-CH$_2$-N-, 0.90-0.88 (m, 12 H) CH$_3$-(CH$_2$)$_n$-N. ^{13}C-NMR (500 MHz, CDCl$_3$, TMS, 298 K) δ 169.11, 167.79, 153.57, 77.03, 76.78, 71.59, 69.09, 68.49, 54.62, 50.11, 47.05, 46.94, 45.84, 45.79, 32.29, 31.91, 30.51, 29.64, 29.57, 29.55, 29.50, 29.47, 29.43, 29.39, 29.35, 29.30, 28.99, 28.97, 27.60,27.52,27.05, 27.02, 26.90, 26.84, 26.50, 26.09, 25.52, 25.34,24.72, 23.86, 22.68, 20.81, 17.49, 14.11. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 2924 (C-H stretching), 1651(C=O stretching), 1350(C-N stretching), 1126 (C-O stretching). Yield was >60 % and the purity was >98%.


TODGA

TEHDGA

D^{3}DODGA

Figure. 2.5. Structures of diglycolamides

2.4.3. Synthesis of aqueous soluble *N,N,N'N'*-tetraethyl diglycolamide (TEDGA)

Diglycolic anhydride (1eq.) mixed with dichloromethane (30 mL), was taken in a round bottom flask in an ice bath equipped with a $CaCl_2$ guard tube. A solution of di-ethylamine (1eq.) in dichloromethane (10 mL) was added drop-wise to diglycolic anhydride solution. The reaction mixture was stirred for one hour to obtain the diethyldiglycolamic acid. The synthetic procedure is shown in Figure 2.6. Here both reacants and product are water soluble. To ensure the complete consumption of diglycolic anhydide, bit excess amount of diethylamine was added. In the second step, dicyclohexylcarbodiimide (DCC) in dichloromethane was added drop-wise to the diglycolamic acid solution and mixed using magnetic stirrer for about fifteen minutes. After that, the excess of di-ethylamine was added drop-wise to the reaction mixture and stirred for about six hour such that the reaction should complete. The crude reaction mixture was washed with double distilled water and filtered using Whatmann filter paper to remove the by-product, dicyclohexyl urea. The excess of distilled water and diethylamine were removed from the filtrate using rotary evaporator in reduced atmosphere. Same TEDGA was used for the experiment without any further purification.

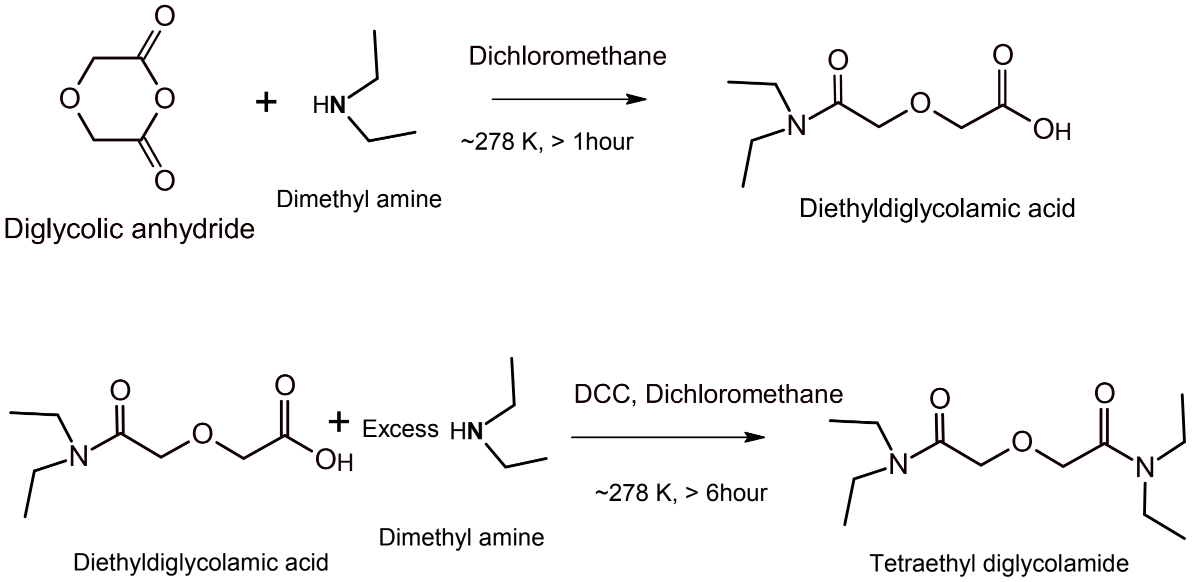


Figure 2.6. The synthetic procedure of tetraethyl diglycolamide

2.4.4. Column chromatography

The crude product obtained after the reaction contains both reactants, products intermediate compounds, bi-products and solvents. This complex mixer was purified using column chromatography to get the purified product. The column was packed with silica gel of mesh size 100-200 with the help of ether. For faster elution of the compounds from the column, the top and bottom of the column was packed with silica gel of mesh size 60 to 120 to a small extent. The crude product was loaded at the top of the column. Products were eluted from the column using hexane or petroleum ether as the mobile phase. The polarity of the mobile phase was increased by addition of ethyl acetate, such that diglycolamides eluted faster as compared to diglycolamic acid. The diglycolamic acid is more polar and the interaction with silica is more because of the presence of –COOH group as compared to diglycolamide. So diglycolamide elutes faster than diglycolamic acid in the column. The eluted fraction was collected in conical flask and TLC was checked for all the eluted fractions in each time. All eluted fractions showing single spot in TLC collected in a round bottom flask and hexane and ethyl acetate solvent was removed using rotary evaporator under reduced pressure. The product was dried completely using rotary evaporator for 2-3 hour continuously under reduced pressure to remove the excess solvent.

2.5. Extraction of metal ions

All the extraction experiments were conducted in duplicate at 298 K with 1:1 aqueous: organic phase ratio. The organic phase consisted of the desired concentration of extractant in *n*-dodecane like DGA/n-DD, UDGA/*n*-DD and combination of extractant/*n*-DD depending upon the nature of experiment. The aqueous phase consisted of either nitric acid or FR-SHLLW spiked with a radioactive tracer. The organic phase was pre-equilibrated with desired concentration of nitric acid prior to metal ion extraction. The extraction experiments involved equilibration of equal volumes of organic phase and aqueous phase unless otherwise mentioned for about one hour in a constant temperature water bath. After equilibration the radioactivity present in both organic and aqueous phases was measured. The γ-radioactivity of radioactive metal ion was measured using a well-type NaI(Tl) scintillation detector when they are present alone. The distribution ratio (D_M) of the metal ion was determined by using the equation 2.1.

$$D_M = \frac{\text{Radioactivity of metal ion in organic phase}}{\text{Radioactivity metal ion in aqueous phase}} \tag{2.1}$$

The relative standard deviation (RSD) associated with the measurement of distribution ratio is about ± 5 % in the range of distribution ratio values 0.01 to 100 in radiometric technique. At high distribution ratio ($D_M > 100$), organic phase contains significant radioactivity compared to the aqueous phase (near to background level). Therefore, it is difficult to measure the radioactivity present in the aqueous phase which leads to the uncertainty in the measurement. Similarly at low distribution ratio ($D_M < 0.01$), aqueous phase contains significant radioactivity compared to the organic phase (near to background level). This leads to the error in measurements of distribution ration in radiometric method.

In case of non radioactive metal ions, the concentration of metal ions present in aqueous phase before and after equilibration was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The concentration of metal ions in organic phase was calculated by mass balance. The distribution ratio (D_M) of the metal ion was determined by using the equation 2.2.

$$D_M = \frac{\text{Initial aq. metal ion conc. - aq. metal ion conc. after equilibration}}{\text{aq. metal ion conc. after equilibration}} \qquad (2.2)$$

The relative standard deviation (RSD) associated with the measurement of distribution ratio is about ± 5 % in the range of distribution ratio values 0.01 to 50 in ICP-OES measurement. The distribution ratio depends upon the initial concentration of the metal ions as well as the metal ion concentration after extraction. In FR-SHLLW so many elements are present in various concentrations as shown in table 2.1. Some metal ion such as Dy (6 ppm) and Gd (65 ppm) is present in low concentration in FR-SHLLW solution. The metal ion concentration becomes very low in aqueous phase after extraction. Therefore, the quantification of the metal ions in aqueous phase after extraction is difficult by ICP-OES. The results obtained from the ICP-OES are presented in the thesis. However, the distribution ratio of Dy and Gd are associated with more uncertainty. The distribution ratio > 50 reported in the thesis is associated with more uncertainty but indicates the complete extraction by the extractant.

2.5.1. Metal to ligand stoichiometry for a neutral extractant

Being neutral reagents, DGAs extracts metal ions in neutral species from nitric acid medium. For example, the extraction of Am(III) from nitric acid medium is shown in equation 2.3. In this case, Am(III) forms a neutral species by combining with 3 molecules of nitrates. This neutral species can be extracted to organic phase by diglycolamide. The equilibrium constant (K) for the extraction of Am(III) from nitric acid is shown in equation 2.4. The equation 2.4 can be rearranged to equation 2.5 using equation 2.1.

$$\mathrm{Am}^{+3} + 3NO_3^- + xDGA \Leftrightarrow Am(NO_3)_3(DGA)_x \qquad (2.3)$$

$$K = \frac{[\mathrm{Am(NO_3)_3(DGA)_x}]_{\mathrm{org.}}}{[\mathrm{Am^{3+}}]_{\mathrm{aq}}[\mathrm{DGA}]^{\mathrm{x}}_{\mathrm{org}}\ [\mathrm{NO_3^-}]^3_{\mathrm{aq.}}} \qquad (2.4)$$

$$K = \frac{D_{\mathrm{Am}}}{[\mathrm{DGA}]^{\mathrm{x}}_{\mathrm{org.}}\ [\mathrm{NO_3^-}]^3_{\mathrm{aq.}}} \qquad (2.5)$$

Where K is equilibrium constant

By taking the logarithm of both the side and rearranging the equation 2.5,

$$\log D_{\mathrm{Am}} = \log \mathrm{K} + x \log \left[\mathrm{DGA}\right]_{\mathrm{org.}} + 3\log[NO_3^-] \qquad (2.6)$$

At constant acid concentration [NO_3^-] and log K are constant. So, equation 2.6 can be rearranged as shown in equation 2.7.

$$\log D_{\mathrm{Am}} = \log \mathrm{K'} + x \log \left[\mathrm{DGA}\right]_{\mathrm{org.}} \qquad (2.7)$$

From the equation 2.7, by varying the DGA concentration during the extraction of metal ions keeping the nitric acid concentration constant, a plot logD vs log[DGA], the slope indicates, the dependence of [DGA] for the extraction of metal ion. This slope analysis method was used for the determination of dependency of extractant during extraction of metal ions using neutral extractant.

2.5.2. Metal to ligand stoichiometry for an acidic extractant

Acidic extractants form complexes with metal ions by cation exchange mechanism. These extractants can extract metal ions from dilute nitric acid medium because in dilute acid medium the extractant will be in dissociated form and can complex with metal ions. HDEHP is an acidic extractant. The following equation can be written for the complex formation of Am(III) with HDEHP.

$$\mathrm{Am}^{+3} + xHDEHP \Leftrightarrow Am(DEHP)_x + xH^+$$

$$K = \frac{[\mathrm{Am(DEHP)_{x\ org.}}][H^+]^x_{aq.}}{[\mathrm{Am^{3+}}]_{\mathrm{aq}}[\mathrm{HDEHP}]^{\mathrm{x}}_{\mathrm{org}}}$$

$$K = \frac{D_{\mathrm{Am}}[H^+]^x_{aq.}}{[HDEHP]^{\mathrm{x}}_{\mathrm{org.}}}$$

By taking logarithm both side and rearranging the above equation will be

$$\log D_{\mathrm{Am}} = \log\mathrm{K}' + x\log\left[\mathrm{HDEHP}\right]_{\mathrm{org.}} - x\log\left[\mathrm{H}^+\right]_{\mathrm{aq.}} \qquad (2.8)$$

At a fixed concentration of [HDEHP], by linear regression plot of logD vs log[H^+], shows the slope of -x. This indicates x molecules of H^+ are released to aqueous phase during metal ions extraction. On the other hand at a fixed acidity, when [HDEHP] is varied, the linear regression plot of log D vs log[HDEHP] shows the slope x, which indicates the involvement of x number of HDEHP molecules during extraction of metal ion. Similarly, in a combined extractant system, the slope of the plot logD vs log [extractant] indicates the number of extractant molecules involving in the extraction step.

2.6. Batch experiment studies

Batch studies were conducted to optimize the conditions required for complete extraction and complete recovery of metal ions. The experiments involved equilibration of equal volumes (5 ml) of organic and aqueous phase spiked with desired isotope for one hour. After one hour the organic phase was removed and fresh organic was introduced until the concentration of metal ions become negligible in the aqueous phase. By this way, number of stages required for the complete extraction of metal ions can be optimized. The organic phase was pre-equilibrated with the corresponding nitric acid concentration prior to the metal ion loading.

During the batch stripping studies, a known volume (5 ml) of loaded organic phase was equilibrated with equal volume of a stripping solution. The stripping solution was used depending upon the nature of experiment. After equilibration, the aqueous phase was removed and the organic phase was contacted again with fresh stripping solution. This procedure was repeated until the metal ion present in organic phase was recovered quantitatively. The aqueous phase collected after each stage was analyzed for the metal ion by the procedure described above. This will indicate the number of stages required for the complete stripping of metal ions from loaded organic phase.

2.7. References

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Chapter 3: Demonstration of trivalent actinide partitioning using unsymmetrical diglycolamide

3.1. Introduction

PUREX process is being adapted worldwide, for the recovery of uranium and plutonium from the spent nuclear fuel. PUREX process basically consists of solvent extraction of U(VI) and Pu(IV) from nitric acid medium by a solution of 1.1 M tri-*n*-butylphosphate (TBP) in *n*-dodecane. The raffinate rejected after extraction of U(VI) and Pu(IV) during PUREX process is known as high-level liquid waste (HLLW), which contains significant amounts of lanthanides, other fission products, and minor actinides. Since these lanthanides, and actinides, exist in trivalent oxidation state in HLLW, they are inextractable by TBP during PUREX process. These trivalent actinides existing in small concentration levels need to be separated from HLLW for the management and safe disposal of HLLW. In this context, partitioning and transmutation (P&T) strategy is being considered as a viable method for the safe disposal of HLLW.

At present, partitioning of minor actinides from HLLW is a two-cycle process. In the first cycle, the trivalent lanthanides (Ln(III)) and actinides (An(III)) are co-extracted into the organic phase using a neutral extractant present in n-dodecane from HLLW followed by the co-stripping of lanthanides and actinides from the loaded organic phase by using dilute nitric acid. In the second cycle, mutual separation of actinides from lanthanides is performed by using acidic extractant. In this cycle, both trivalent lanthanides and actinides are extracted from the aqueous product of the first cycle using the acidic extractant and the selective stripping of actinides using a buffer solution of diethylenetriamminepenta acetic acid (DTPA) -citric acid at pH 3 condition. Several neutral extractants such as carbamoylorganophoshorous compounds (TRUEX process), trialkylphosphine oxides (TRPO process), diisodecylphosphoric acid (DIDPA), and diamides (DIAMEX process) etc are used for the separation of trivalent actinides and lanthanides in first cycle [1-3]. During the last decade, diglycolamides (DGA) are emerging as superior candidates for the separation of trivalents from high-level liquid waste. The diglycolamides are alkyl derivatives of 3-oxapentane-1,5-diamides containing three oxygen donor atoms in a molecule, for efficient co-ordination to the metal ions [4]. Among the various diglycolamides, the symmetrical derivatives, namely *N*,*N*,*N*',*N*'-tetraoctyl diglycolamide (TODGA) and *N*,*N*,*N*',*N*'-tetra-2-ethylhexyl diglycolamide (TEHDGA) have been extensively studied in the previous decade for the separation of trivalent actinides (Am(III) and Cm(III)) from nitric acid medium [5-7]. Using these reagents, several authors have demonstrated the separation of trivalent actinides from simulated as well as genuine PUREX raffinate, and developed flow-sheets for trivalent actinide partitioning [8-11]. However, these diglycolamides have some drawbacks such as third phase formation during solvent extraction operation and extraction of unwanted fission product metal ions. Nevertheless, these problems have been maneuvered by developing suitable procedures such as conditioning of the feed as well as modifying the solvent phase with organic phase modifiers for trouble-free separation of actinides from PUREX raffinate [8-11].

The third phase formation is an undesirable event in solvent extraction procedures [12]. It is the splitting of organic phase in to two phases, with heavier one rich in metal-solvate complex, and the lighter one rich in diluent. The splitting of organic phase occurs at a particular concentration of metal ion in the organic phase, referred as limiting organic concentration (LOC) and the corresponding equilibrium aqueous phase metal ion concentration is known as critical aqueous concentration (CAC) [12]. The third phase formation has been observed in all reagents reported so far in literature as promising candidates for partitioning of trivalent actinides from nitric acid medium [8,10]. This is in fact due to the co-extraction of chemically similar trivalent lanthanides and the low LOC exhibited by these reagents for third phase formation during the extraction of trivalent metal ions. The limiting organic concentration of Nd(III) in 0.1 M TODGA/*n*-DD is only 5 mM from 3 M nitric acid medium [13], where as the actual concentration of trivalents in HLLW could vary from 10 mM to 50 mM depending upon the type of fuel and burn-up [14, 15]. Similarly, the concentration of nitric acid in HLLW could vary from 3 to 4 M. In view of this, the third phase formation is the one of the major issues during partitioning of trivalent actinides from HLLW in various systems in the early developmental stage.

Third phase formation can be avoided by adding a suitable polar organic phase to solvent phase called as phase modifier, in significant concentration. The phase modifier is usually another extractant, such as tri-*n*-butyl phosphate (TBP) [9], *N,N*-dihexyloctanamide (DHOA) [6] etc., or a long chain alkyl alcohol [11]. In TRUEX process, 1.2 M TBP is added as phase modifier to 0.1 M CMPO solvent phase. Although the addition of phase modifier averted the problem of third phase formation, it resulted in increase in the extraction of other fission products [8, 10]. Moreover, it is also expected that the chemical and radiolytic degradation of phase modifier in conjunction with radiolytic products of the extractant and diluent could complicate the hydrodynamics of the solvent and recovery of metal ions. The presence of phase modifier in solvent phase also burdens the management of spent organic waste. In addition, the alcohol based modifiers could pose explosion risks when the organic phase contacts with oxidising nitric acid during extraction [16, 17]. Therefore, it is desirable to employ an extractant that operates without any phase modifier for minor actinide partitioning from HLLW.

In this connection, several unsymmetrical diglycolamides (UDGA) were developed and studied for the extraction of trivalent metal ions from nitric acid medium [18, 19]. In contrast to symmetrical DGAs such as TODGA and TEHDGA, the alkyl groups attached to the N atoms of UDGAs are different. Among the various UDGAs studied, the *N*,*N*,-

didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D^3DODGA) is a promising reagent for trivalent actinide partitioning [18 20]. The dodecyl group in conjunction with the octyl group present in D^3DODGA, not only retained the excellent extraction properties of TODGA, but also surmounted the problem of third phase formation during the extraction of trivalent metal ions from 3-4 M nitric acid [18 - 20]. The extraction behavior of several metal ions that are present in HLLW was studied in a solution of 0.1 M D^3DODGA /*n*-DD as a function of concentration of nitric acid, in detail [20]. The results revealed the possibility of using 0.1 M D^3DODGA /*n*-DD for the separation of trivalent actinides from simulated and genuine wastes.

The present chapter deals with the extraction and stripping behavior of various metal ions present in the fast reactor simulated high-level liquid waste (FR-SHLLW) using a modifier-free solvent phase composed of 0.1 M D^3DODGA in *n*-DD. The structure of D^3DODGA and other aqueous complexing agents are shown in Figure 3.1. The distribution ratio of metal ions was determined and the number of stages needed for extraction and stripping was optimized. A procedure was developed to minimize the extraction of unwanted metal ions. Based on those results, a counter-current mixer-settler run was performed in a 20-stage mixer-settler and a flow-sheet for trivalent actinide partitioning from HLLW was developed.

3.2. Third phase formation behavior of D^3DODGA

Third phase formation is an important parameter in solvent extraction. The solvents used in solvent extraction process should not form a third phase upon metal ion loading. In this context, Ravi *et al.* extensively studied the third phase formation behavior of D^3DODGA in *n*-dodecane and indicated that the solvent phase could load stoichiometric levels of trivalent metal ions from 3-4 M nitric acid medium without leading to third phase formation

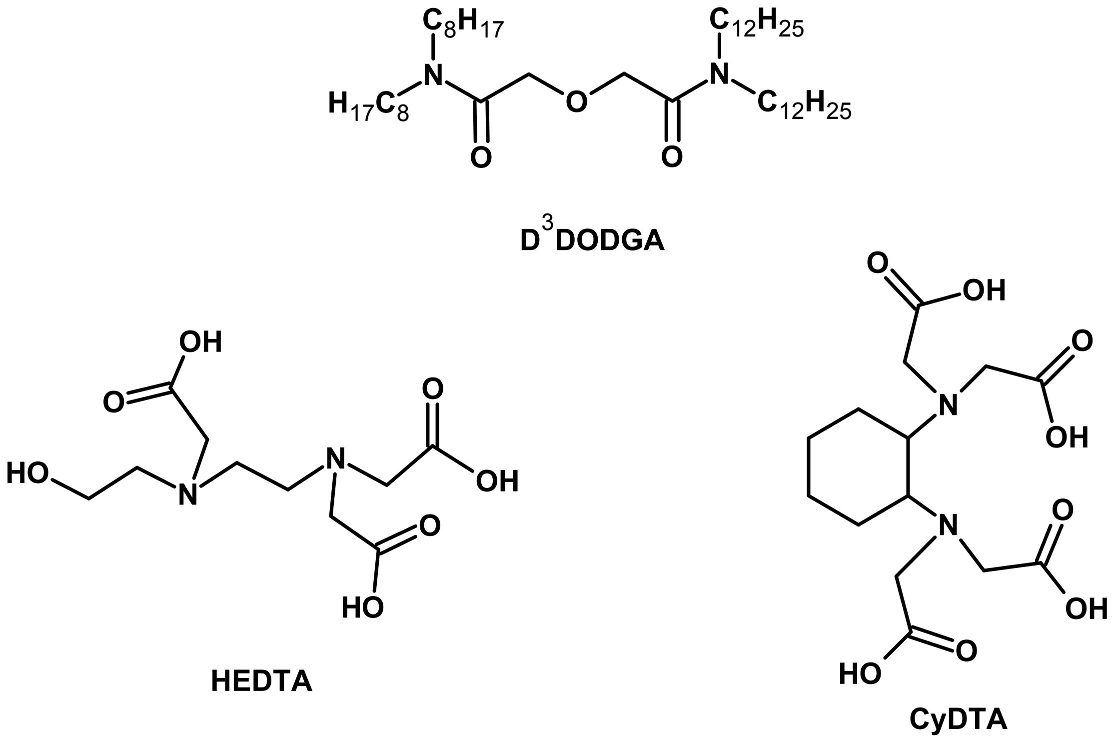

Figure 3.1. Structures of D^{3}DODGA, HEDTA and CyDTA.

[18-20]. They observed the quantitative extraction of metal ions into D^{3}DODGA/*n*-DD from high concentrated solutions of Nd(III) (>600mM) without leading to any third phase formation. They also reported that D^{3}DODGA forms a 3:1 complex with Am(III) during the extraction from 1 M nitric acid. Therefore, a 0.1 M D^{3}DODGA/*n*-DD (100 mM) is expected to extract a maximum of 33 mM of trivalent metal ion. The study thus indicates that Nd(III) could be loaded to near stoichiometric levels in 0.1 M D^{3}DODGA/*n*-DD without any third phase formation. Thus, it is possible to use 0.1 M D^{3}DODGA/*n*-DD for the partitioning of minor actinides from HLLW without any phase modifier. The third phase formation of 0.1 M D^{3}DODGA/*n*-DD was studied by contacting several times with FR-SHLLW in 1:1 volume ratio and the solvent phase extracts the trivalent metal ions without any third phase formation. It can be understood from these observations that the presence of dodecyl groups on the DGA prevents third phase formation and presence of octyl group also retains the extraction behavior of trivalent metal ions comparable to that of TODGA. In view of these

extraordinary properties of D^3DODGA/*n*-DD, this solvent can be used for partitioning of minor actinides without any phase modifier.

3.3. Extraction behavior of metal ions from FR-SHLLW

Ravi *et al.* studied the extraction behavior of Am(III) and Eu(III) in 0.1 M D^3DODGA/*n*-DD [20]. Since, 0.1 M D^3DODGA/*n*-DD does not form any third phase during the extraction of Nd(III) from high concentrated solutions and FR-SHLLW solution, this solvent can be used for the extraction of trivalent actinides from HLLW without any phase modifier. When D^3DODGA is proposed for the separation of trivalent actinides from HLLW, it is necessary to understand the extraction behavior of various elements present in HLLW. Therefore, FR-SHLLW solution was prepared as discussed in chapter 2, and the extraction behavior of trivalent lanthanides, actinides, and other fission products present in FR-SHLLW, in a solution of 0.1 M D^3DODGA/*n*-DD was studied. The composition of FR-SHLLW is shown in Table 2.1. FR-SHLLW is composed of trivalent actinide Am(III) in addition to trivalent lanthanides in a matrix of several other metal ions present in 3 M nitric acid medium. The solvent 0.1 M D^3DODGA/*n*-DD was equilibrated with FR-SHLLW. After equilibration for one hour, solvent phase was separated and the aqueous phase was analyzed using ICP-OES for the measurement of metal ions present. The radioactive elements, ^{241}Am(III) and $^{(152+154)}$Eu(III) were analyzed by NaI(Tl) gamma detector. The distribution ratio of all metal ions was calculated as discussed in section 2.5. of experimental chapter. The distribution ratio of the metal ions present in FR-SHLLW is tabulated in Table 3.1 using 0.1 M D^3DODGA/*n*-DD from FR-SHLLW. It can be seen that the distribution ratio of Am(III), lanthanides and fission products such as Zr(IV), Y(III) and Pd(II) are higher than the distribution ratios observed for other metal ions ($<10^{-2}$). It is also interesting to observe that the distribution ratio of trivalent metal ions increases in the order of their charge (z) to radius (r) ratio i.e. in lanthanide series. Since all these metal ions are existing in trivalent state, the radius of these ions decreases in the order of La(III) > Ce(III) > Pr(III) > Nd(III) > Am(III) > Sm(III) > Eu(III). Therefore, the ratio, z/r, increases in the reverse order and the distribution ratio follows in the order of La(III) < Ce(III) < Pr(III) < Nd(III) < Am(III) < Sm(III) < Eu(III). Ravi *et al.* studied the extraction behavior of various metal ions in 0.1 M D^3DODGA/*n*-DD and reported that the distribution ratio reached a maximum value when the ionic radii of the metal ion were in the range 80 -100 pm [20]. Prior to this, Zhu *et al.* reported a correlation between the distribution ratio of various metal ions in diglycolamide, TODGA, and ionic radii of metal ions [21]. The distribution ratio was reported to increase from 10^{-2} to >200 with increase of ionic radius from 60 pm to 100 pm. Since the ionic radii of metal ions namely Am(III), Ln(III), Y(III) and Zr(IV) are of the order 80-100 pm and extraction is carried out from 3 M nitric acid, the distribution ratio is essentially governed by the diglycolamide, D^3DODGA, present in the solvent.

The distribution ratio of metal ions generally decreases in the order M(IV) > M(III) > M(II) > M(I), which is characteristic to diglycolamides [20]. So the distribution ratio of tetravalent zirconium is more as compared to trivalent lanthanides. The distribution ratio of Zr(IV), Pd(II), Sr(II) and Mo(VI) are 363, 1.23, 0.1 and 0.07 respectively as shown in Table 3.1 in 0.1 M D^3DODGA/*n*-DD. This indicates that Zr(IV) and Pd(II) can be extracted to 0.1 M D^3DODGA/*n*-DD phase along with trivalent lanthanides and actinides. Due to the low distribution ratio Sr(II) and Mo(VI) are not extracted to the solvent phase. The other trivalent metal ions present in FR-SHLLW are Fe(III), Ru(III) Rh(III), etc. It is observed that their distribution ratios are less than 10^{-2}. The lower distribution ratio observed for Fe(III), Rh(III), and Ru(III) could be attributed to the lower ionic radii of these metal ions than trivalent lanthanides. This indicates these trivalent, divalent and monovalent metal ions have negligible extraction to solvent phase.

Table 3.1. Distribution ratios of metal ions present in fast reactor simulated high-level liquid waste in the presence and absence of complexing agents. Organic phase = 0.1 M D^3DODGA/*n*-DD, Aqueous phase = FR-SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer in the presence of complexing agent. Organic/Aqueous phase ratio = 1 Temperature = 298 K.

Elements	Distribution ratio (D_M)			
	Without reagent	In the presence of reagent		
		0.2 M oxalic acid	0.05 M HEDTA	0.05 M CyDTA
La(III)	1.6	1.5	0.9	0.9
Ce(III)	1.7	2.2	2.1	2.0
Pr(III)	6.6	6.5	7.0	6.0
Nd(III)	16	12	15	13
Sm(III)	63	64	51	58
Eu(III)	80	87	91	96
Gd(III)	38	53	38	44
Dy(III)	49	57	51	53
Y(III)	11	10	11	10
Mo(VI)	0.07	0.03	0.05	0.04
Sr(II)	0.1	0.1	0.1	0.1
Pd(II)	1.23	0.80	0.01	0.02
Zr(IV)	363	0.02	33	0.05
Fe(III)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Cr(VI)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ni(II)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Te(VI)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ru(III)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Rh(III)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Cs(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Rb(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ag(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Na(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
^{241}Am(III)	21	22	20	19

3.4. Elimination of unwanted metal ions

The extraction of unwanted fission products such as Zr(IV), Pd(II) and Y(III) in 0.1 M D^3DODGA/*n*-DD could pose some problems during recovery of trivalent actinides from organic phase. It was reported that the presence of Zr(IV) and Pd(II) in the extracted organic phase results in the formation of crud-type precipitate during stripping with dilute nitric acid [22]. A similar behavior was also observed in the present case when the loaded organic phase was contacted successively with aqueous 0.01 to 0.1 M nitric acid. Several authors have maneuvered this problem by scrubbing the extracted organic phase with aqueous reagents and others have conditioned the feed by adding appropriate complexing agents to prevent the extraction of unwanted metal ions [8, 10]. Since it is desirable to eliminate the extraction of unwanted metal ions, the studies were conducted on the extraction of metal ions from FR-SHLLW in the presence of various complexing agents such as oxalic acid, *N*-(2-hydroxyethyl) ethylenediamine-triacetate (HEDTA) and trans-1,2-Cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CyDTA). The distribution ratio of metal ions present in FR-SHLLW in the presence of complexing agent is shown in Table 3.1. Among the various complexing agents studied, oxalic acid has reduced the distribution ratio of Zr(IV) from 363 to 0.02 where as 0.05 M CyDTA eliminates the extraction of Zr(IV) (D = 0.05) and palladium (D = 0.02) in the solvent phase. HEDTA selectively complexes with Pd(II) in aqueous phase and reduces the distribution ratio to 0.01. Since CyDTA prevents the extraction of problematic Zr(IV) and Pd(II), it was decided to add CyDTA in FR-SHLLW and perform the further batch and mixer-settler studies. Addition of these aqueous soluble complexing agents to FR-SHLLW does not affect the extraction of trivalent actinides and lanthanides.

3.5. Batch extraction studies from FR-SHLLW

The distribution ratio of Am(III) and lanthanides in 0.1 M D^3DODGA/*n*-DD in the presence of CyDTA ranges from 1 to ~100 as shown in Table 3.1. Therefore, it is necessary to understand the number of contacts of organic phase needed for complete extraction of trivalent metal ions from FR-SHLLW for optimization of hydrodynamics in counter-current solvent extraction procedure. Batch extraction studies were carried to understand the number of contacts required for complete extraction of trivalent lanthanides and actinides. Equal volumes of FR-SHLLW containing 0.05 M CyDTA and 0.1 M D^3DODGA/*n*-DD were equilibrated for one hour. After equilibration, organic phase was removed and fresh solvent was poured into the same aqueous phase. This process continued till the concentration of trivalent actinide and lanthanide become negligible in the aqueous phase. Figure 3.2 shows the variation in the cumulative extraction of metal ions from FR-SHLLW as a function of number of contacts of organic phase with feed solution. It is observed that Am(III) is extracted in 4 contacts. The lanthanides were extracted to the solvent phase according to the increasing order of the distribution ratio. The metal ions having low distribution ratio, requires more number of contacts for extraction. The elements La(III) and Ce(III) exhibiting low distribution ratio in 0.1 M D^3DODGA/*n*-DD require 8 contacts for complete extraction, whereas the other lanthanides and Y(III) are extracted in 3 contacts. This indicates within 8-10 contacts, all trivalent lanthanides along with actinides will get extracted to 0.1 M D^3DODGA/*n*-DD.

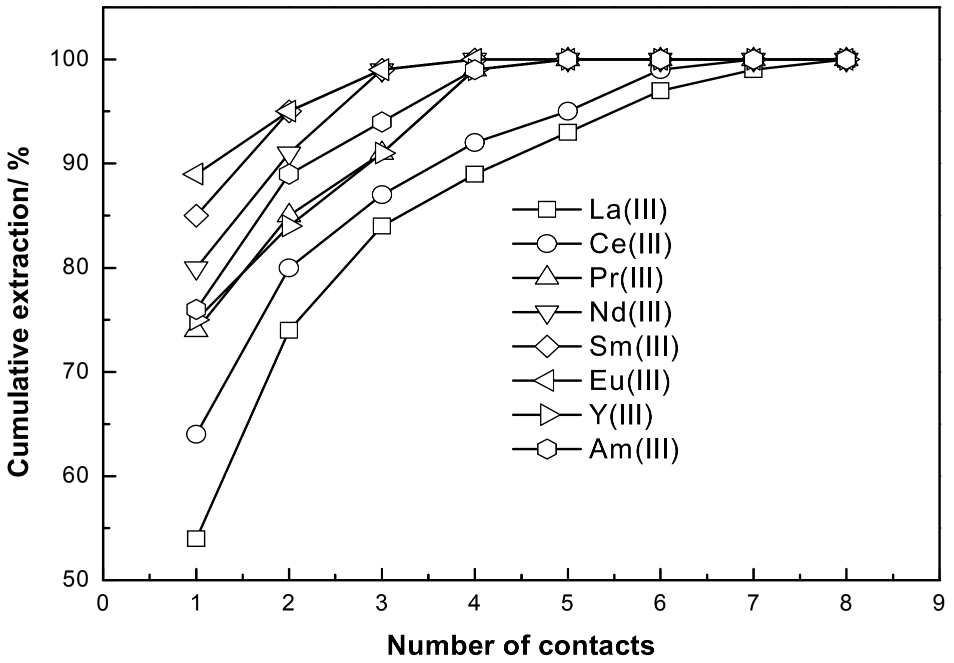

Figure 3.2. Batch extraction of Am(III), Ln(III) and Y(III) from FR-SHLLW. Organic phase = 0.1 M D^3DODGA/*n*-DD. Aqueous phase = FR-SHLLW + 0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer. Temperature = 298 K.

3.6. Batch stripping studies

In this case, trivalent actinides and lanthanides were extracted from FR-SHLLW containing 0.1 M CyDTA using 0.1 M D^3DODGA/*n*-DD. The stripping study was carried out using 0.01 M nitric acid from loaded organic phase. The loaded organic phase was equilibrated with 0.1 M nitric acid. After equilibration aqueous phase was separated out and fresh aqueous phase was added and equilibrated. This process was continued until the loaded organic phase was free from trivalent actinide and lanthanides. Batch stripping of actinides and lanthanides depends on the distribution ratio of the metal ions. Metal ions having higher distribution ratio during extraction, also show higher distribution during stripping and decrease the stripping efficiency. Since Am(III) and Eu(III) have higher distribution ratio during extraction, the batch stripping profile of these metal ions were studied. The batch stripping profile of Am(III) and Eu(III) is shown in Figure 3.3. The stripping of Eu(III) completed in 4 contacts whereas stripping of Am(III) completes in 3 contacts. This indicates that other lanthanides stripped easily as compared to Eu(III).

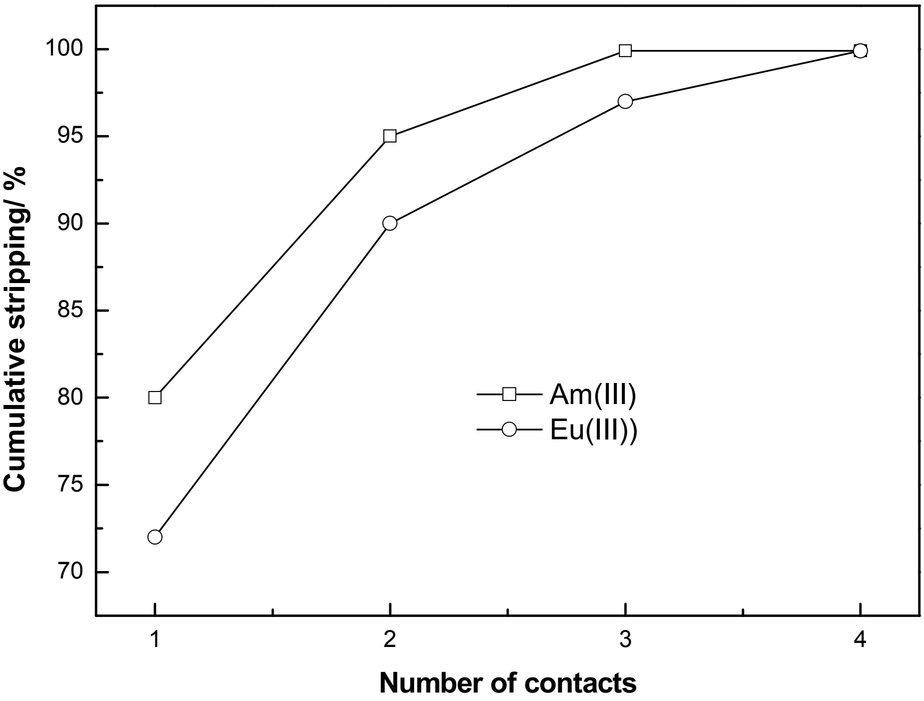

Figure 3.3. Batch stripping of Am(III) and Eu(III) from loaded organic phase. Organic phase = 0.1 M D^{3}DODGA/*n*-DD loaded with Am(III) and Eu(III) from FR-SHLLW + 0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer. Aqueous phase = 0.01 M nitric acid. Temperature = 298 K.

3.7. Mixer-settler studies - Extraction

The extraction profile of Am(III) and Ln(III) in 0.1 M D^{3}DODGA/*n*-DD, in a 20-stage mixer-settler is shown in Figure 3.4. The extraction was carried out from FR-SHLLW containing 0.05 M CyDTA spiked with $^{(152+154)}$Eu(III) and ^{241}Am(III) tracer. The organic and aqueous phases were passed in a counter-current direction at the flow rate of 3 mL/min in a 20-stage mixer-settler. The FR-SHLLW was passed from the 1st stage to 20th stage and the organic phase was passed in reverse direction. The organic and aqueous phases were assayed for $^{(152+154)}$Eu(III) and ^{241}Am(III) radioactivity and the other metal ions were determined by the analysis of aqueous phase (FR-SHLLW) using ICP-OES. The aqueous phase makes the first contact with organic phase in stage 1, where the trivalents are expected to be extracted/loaded into organic phase. It is observed from Figure 3.3 that the percentage of Eu(III) in aqueous phase decreased sharply in the first contact and the percentage of Eu(III) is negligible after 4 contacts. This indicates that more than 90% Eu(III) is extracted in the first contact itself and within 4 contacts quantitative extraction of Eu(III) from FR-SHLLW is achieved. Similarly, quantitative extraction of Am(III) is achieved in 7-8 stages.

The Figure 3.4 shows that Nd(III) is extracted from aqueous phase only after complete or near complete extraction (~80%) of Eu(III), Sm(III) and Am(III) from aqueous phase. This could be due to the lower distribution ratio exhibited by Nd(III) (D = 13) as compared to Eu(III) (D = 96), Sm(III) (D = 58) and Am(III) (D = 19) as shown in Table 3.1. A similar behavior was also observed for other trivalent metal ions that exhibit lower distribution ratio than others as shown in Figure 3.3. The distribution ratio of La(III) and Ce(III) is lower than other trivalents and hence they were extracted from aqueous phase only after complete or near complete extraction of other lanthanides. From the mixer-settler run, the preferential extraction of trivalents in 0.1 M D^3DODGA/*n*-DD follows the order Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). From Table 3.1, the distribution ratio of trivalents from FR-SHLLW (in the presence of CyDTA) also follows the same order namely Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). Therefore, the study indicates that the solvent phase is preferentially loaded with the metal ion that exhibits higher distribution ratio.

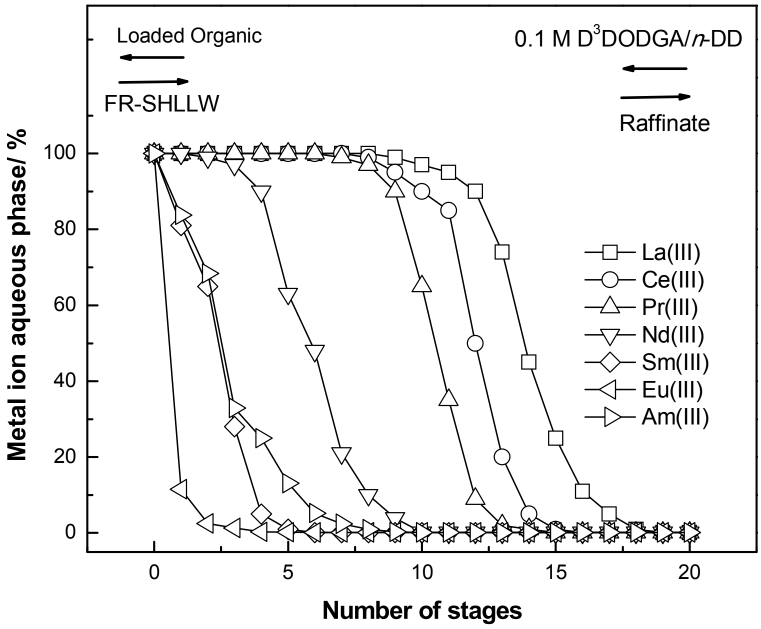

Figure 3.4. Stage profile of Am(III), and Ln(III) in a 20-stage mixer-settler during the extraction of trivalent metal ions from FR-SHLLW. Organic phase = 0.1 M D^{3}DODGA /*n*-DD. Aqueous phase = FR-SHLLW+0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer.

In view of this, the lanthanides Pr(III), Ce(III) and La(III) exhibiting lower distribution ratio than other lanthanides remain in aqueous phase even at 8th stage. They are extracted only beyond 10th stage and the extraction of La(III) completed only in 19th stage. The extraction behavior of Gd(III) and Dy(III) are not shown in Figure 3.3 due to the large uncertainty in the measured values by ICP-OES as their concentration in FR-SHLLW is significantly low. However, they are expected to behave similar to Eu(III) and Sm(III) as their distribution ratios are comparable to that of Eu(III) and Sm(III). The organic phase coming out at 1st stage of mixer-settler is known as loaded organic phase, which contains trivalent lanthanides and actinides along with Y(III).

The aqueous phase obtained after 20-stages known as raffinate, was analyzed by ICP-OES. The results are shown in Table 3.2. The concentration of lanthanides, Y(III) are negligible in raffinate. This indicates the trivalent actinides and lanthanides were extracted to the solvent phase. The cumulative extraction of these metal ions is > 99.9 % in 20 stage mixer-settler. Other metal ions having low distribution ratio (D = 10^{-2}) in 0.1 M D^3DODGA/*n*-DD (Table 3.1.) remained in the raffinate phase and the extraction of these metal ions were negligible (<1 %) as shown in Table 3.2. This indicate that Am(III), Ln(III) and Y(III) are extracted quantitatively from FR-SHLLW in 0.1 M D^3DODGA/*n*-DD. However, it is important to note the troublesome metal ions such as Zr(IV), Mo(VI), Sr(II), Fe(III), Cr(VI), Ni(II), Pd(II), Ru(III), Rh(III) are rejected to raffinate in addition to other elements.

3.8. Mixer-settler studies - Stripping from loaded organic phase

The cumulative back extraction of Am(III) and Ln(III) from the loaded organic phase was studied as a function of number of contacts of 0.01 M nitric acid in batch mode. It was found that all the trivalent metal ions are quantitatively recovered in 3-5 contacts. Based on this, a counter current stripping run was performed and the stripping profile of Am(III) and other lanthanides obtained in a 20-stage mixer-settler is shown in Figure 3.5. The loaded organic phase was passed from 20th stage to 1st stage and the stripping solution was passed from 1st stage to 20th stage (Figure 3.5). It is observed that significant amount of trivalents are back extracted into the aqueous phase at 20th stage itself, where the loaded organic phase makes a first contact with aqueous stripping solution and the recovery increases with number of stages. The stripping profiles clearly indicate that all the trivalent metal ions are quantitatively back extracted into aqueous phase in 5 stages. Table 3.2 shows the data for the recovery of metal ions from the loaded organic phase obtained after 20-stages. It can be seen that the recovery is quantitative (>99.9). Therefore, the study clearly demonstrated the possibility of using D^3DODGA for modifier-free partitioning of trivalent actinides from FR-HLLW.

Table 3.2. Cumulative extraction and stripping of metal ions in a 20-stage mixer-settler. Extraction condition: Organic phase = 0.1 M D^{3}DODGA/*n*-DD. Aqueous phase = FR - SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer + 0.05 M CyDTA.
Back extraction: Organic phase = Loaded organic. Aqueous phase = 0.01 M HNO_3 Temperature = 298 K.

Metal ion	Cumulative extraction of metal ions (%) after 20 stages	Cumulative stripping of metal ions (%) after 20 stages
La(III)	> 99.9	> 99.9
Ce(III)	> 99.9	> 99.9
Pr(III)	> 99.9	> 99.9
Nd(III)	> 99.9	> 99.9
Sm(III)	> 99.9	> 99.9
Eu(III)	> 99.9	> 99.9
Gd(III)	> 99.9	> 99.9
Dy(III)	> 99.9	> 99.9
Y(III)	> 99.9	> 99.9
Sr(II)	< 1	B.D.L
Mo(VI)	< 1	B.D.L
Cr(VI)	< 1	B.D.L
Te(VI)	< 1	B.D.L
Cd(II)	< 1	B.D.L
Ni(II)	< 1	B.D.L
Fe(III)	< 1	B.D.L
Ba(II)	< 1	B.D.L
Ru(III)	< 1	B.D.L
Pd(II)	< 1	B.D.L
Zr(IV)	< 1	B.D.L
Rh(III)	< 1	B.D.L
Cs(I)	< 1	B.D.L
Rb(I)	< 1	B.D.L
Ag(I)	< 1	B.D.L
^{241}Am(III)	> 99.9	> 99.9

B.D.L. – Below Detection Limit (< 0.1 ppm)

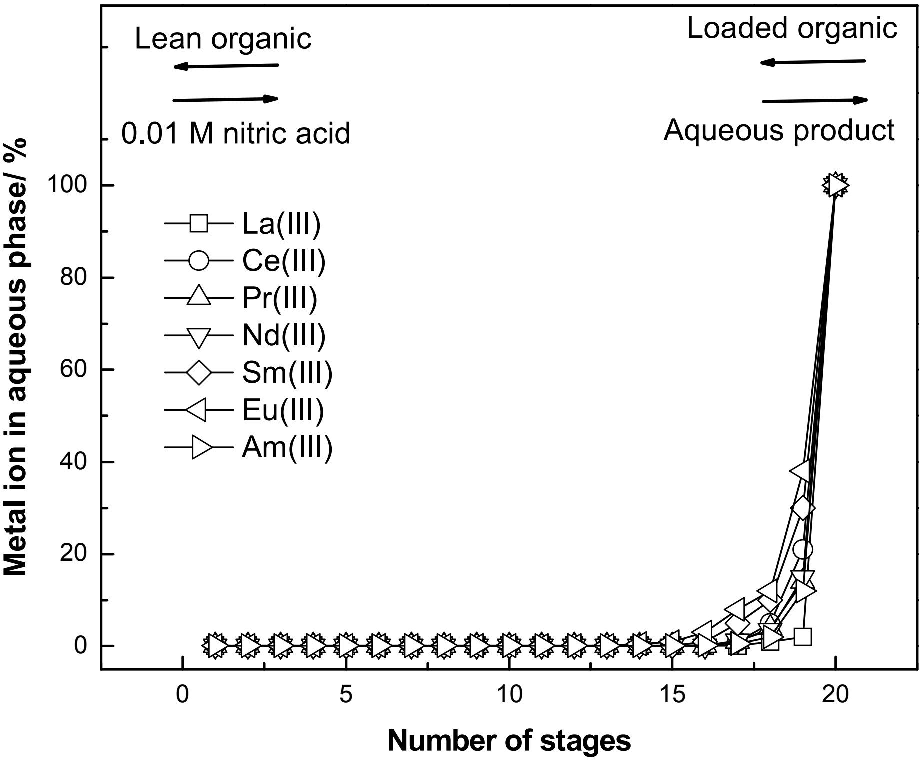

Figure 3.5. Stage profile of Am(III), and Ln(III) in a 20-stage mixer-settler during the back extraction of trivalent metal ions from loaded organic phase. Organic phase = Loaded organic. Aqueous phase = 0.01 M nitric acid.

Based on the above study, a flow-sheet shown in Figure 3.6 could be proposed for the separation of trivalent metal ions from FR-SHLLW using 0.1 M D^{3}DODGA/*n*-DD. The flow-sheet is simple as compared to other flow-sheets developed for trivalent actinide partitioning. It requires 20 stages for quantitative extraction of trivalents and 3-5 stages for stripping. It is important to note that this method does not demand any scrubbing stages before stripping, which otherwise generates large volume of secondary waste. Perhaps scrubbing was needed in other flow-sheets where the solvent phase extracts significant concentration of unwanted metal ions and acid. In addition, the phase modifier used in other flow sheets also extracts substantial amount of nitric acid from aqueous phase leading to the requirement of scrubbing and large number of stages for back extraction of target metal ions. The study also indicated that the problems due to crud-formation or precipitation was not observed during the entire run, thus confirming the clean separation of trivalent metal ions from FR-SHLLW using 0.1 M D^3DODGA/*n*-DD. Therefore, D^3DODGA is a promising candidate for the separation of Am(III) from FR-SHLLW.

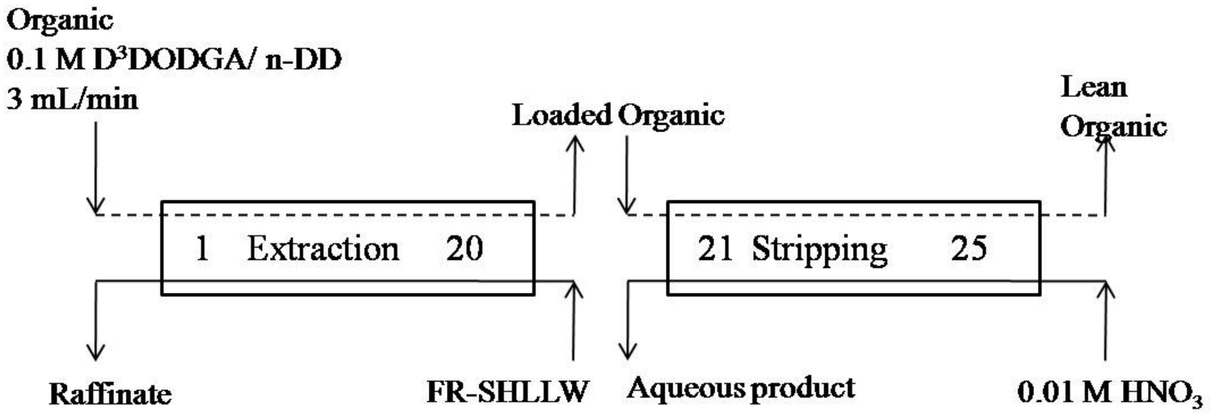

Figure 3.6. Proposed flow-sheet for partitioning of trivalent actinides from FR-HLLW using modifier-free unsymmetrical diglycolamide, 0.1 M D^3DODGA/*n*-DD. The numbers 1 to 25 represents each mixer and settler.

3.9. Conclusion

The modifier-free partitioning of Am(III) from FR-SHLLW was demonstrated using an unsymmetrical diglycolamide, D^3DODGA, in *n*-dodecane in a 20-stage mixer-settler. The extraction of Am(III) was accompanied by the co-extraction of trivalent lanthanides, Zr(IV), Y(III), Pd(II). However, the co-extraction of problematic metal ions (Zr(IV), Pd(II)) in to organic phase was prevented by the addition of CyDTA. The stage profiles in a mixer-settler showed that Am(III) was extracted in 7-8 contacts. Depending upon the distribution ratio of trivalents the preferential loading of lanthanides in 0.1 M D^3DODGA/*n*-DD was achieved in the order Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). All the extracted metal ions were quantitatively back extracted in 3-5 contacts using 0.01 M nitric acid. The proposed flow-sheet based on D^3DODGA is simple and offered significant advantages such as waste minimization, easy disposal of spent solvent etc. The study demonstrated the possibility of using unsymmetrical diglycolamide, 0.1 M D^3DODGA/*n*-DD, for trivalent actinide partitioning from FR-SHLLW in a modified free manner and therefore, D^3DODGA is a promising candidate for the separation of trivalent actinides from genuine wastes.

3.10 References

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Chapter 4: Single-cycle process for minor actinide partitioning using *N*,*N*,-didodecyl-*N'*,*N'*-dioctyl-3-oxapentane-1,5-diamide-*N*,*N*,-di-2-ethylhexyl diglycolamic acid as solvent

4.1. Introduction

The current approach for partitioning of trivalent actinides from High-Level Liquid Waste (HLLW) is a two-cycle approach [1, 2], namely, i) the group separation i.e., the separation of trivalent actinides along with lanthanides from HLLW, followed by the mutual separation of lanthanides and actinides. The mutual separation of trivalent actinides and lanthanides is necessary prior to transmutation, since the lanthanides act as neutron poisons during transmutation. The presence of lanthanides with actinides reduces the efficiency of transmutation. Thus, the extractants indicated in previous chapter such as CMPO, DGA and malonamides are proposed for group separation (i.e. step 1) [1-4] and extractants such as bis(2-ethylhexyl)phosphoric acid (HDEHP), bis-triazinylpyridine (BTP) have been proposed for lanthanide-actinide separation (i.e. step -2) [1]. However in the recent past, single-cycle methods for the separation of trivalent actinides are receiving increased attention. There are a couple of approaches reported in literature. The first one is the direct separation of trivalent actinides from HLLW [5-8]. The methods such as Selective ActiNide Extraction (SANEX) concept, Actinide reCycling by SEParation and Transmutation (ACSEPT) and 1-cycle SANEX concept were developed for direct separation of actinides from HLLW [5-8]. In contrast to this, the second approach involves the extraction of both the trivalent actinides and lanthanides together into the organic phase followed by selective stripping of actinides alone from the loaded organic phase [9, 10]. This approach requires a combination of neutral extractant and an acidic extractant. The neutral extractant helps the extraction of both trivalent actinides (An(III)) and lanthanides (Ln(III)) and acidic extractant helps for the mutual separation of actinides, during stripping. In this case, both An(III) and Ln(III) are extracted into organic phase followed by the selective stripping of An(III) using diethylenetriamine pentaacetic acid (DTPA)-citric acid (CA) solution. Based on this approach, the methods such as TRUSPEAK, PALADIN were developed [9, 10].

The literature survey shows limited studies on the direct separation of trivalent actinides from HLLW [5-8]. Musikas *et al.* developed a Selective ActiNide Extraction (SANEX) concept for the separation of trivalent actinides employing nitrogen and sulfur based extractants [7]. Kolarik *et al.* studied the selective extraction of trivalent actinides from 1 M nitric acid using a mixture of tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2']-bipyridine ($CyMe_4BTBP$) and dimethyldioctylhexaethoxymalonamide (DMDOHEMA) or tetraoctyldiglycolamide (TODGA) as phase transfer catalyst in a counter-current solvent extraction mode [5]. Separation of >99.9% Am(III), >99.7% Cm(III) and >99.9% Cf(III) was achieved with the contamination of less than 0.1% of the initial lanthanides. Lanthaniden Und Curium Americum separation (LUCA) process, aimed for Am(III)/Eu(III) separation was studied using the synergistic mixture composed of bis(4-chlorophenyl)-dithiophosphinic acid [$(ClPh)_2PSSH$] and tris(2-ethylhexyl) phosphate (TEHP) [8]. The separation factor greater than 3000 was reported for Am(III) over Eu(III). Actinide reCycling by SEParation and Transmutation (ACSEPT), an European research project envisages the innovative-SANEX (i-SANEX) concept and 1-cycle SANEX approach for the development of new extractants and innovative separation processes with a reduced number of cycles. In this context, Wilden *et al.* demonstrated a laboratory scale counter-current extraction using 0.015 M CyMe4BTBP + 0.005 M TODGA in hydrogenated tetrapropylene (TPH)/1-octanol for the direct selective separation of the trivalent actinides americium and curium from a simulated PUREX raffinate solution [6]. The resultant aqueous product contained 99.8% of the initial americium and 99.4% of the initial curium content. The above methods are based on the selective separation of trivalent actinides alone directly from HLLW.

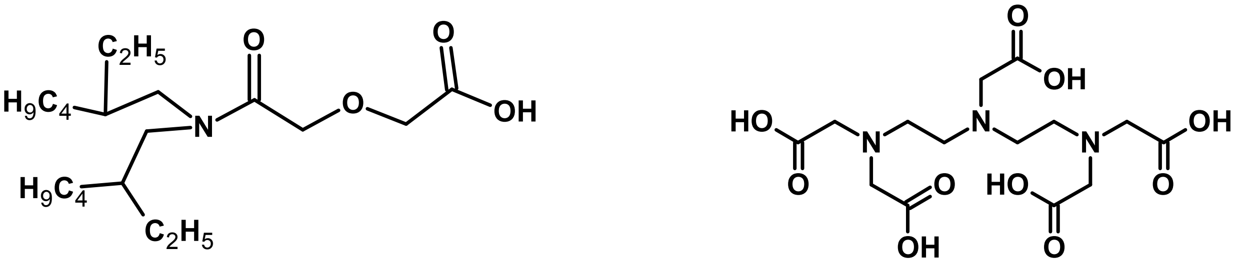
In Another approach, a combination of neutral and acidic extractants is used for the separation of minor actinides from HLLW. Here, both trivalent actinides and lanthanides were extracted to the combined organic phase followed by selective stripping of actinides from the organic phase [9-11]. In this context, Lumetta *et al.* studied the extraction of Am(III) and Eu(III) using a solvent composed of 0.1 M *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) and 1 M bis(2-ethylhexyl) phosphoric acid (HDEHP) in *n*-dodecane from 1 M nitric acid medium [9]. Usually, the hydrophilic complexing agents are added to the aqueous phase for selective stripping of actinides. Selective stripping of Am(III) from the loaded organic phase was achieved by using an aqueous formulation composed of citric acid (CA) and DTPA at pH 3.5. The Am(III) to Eu(III) separation factor of ~12 was reported. Gannaz *et al.* reported the extraction of Eu(III) and Am(III) by a mixture of extractants composed of DMDOHEMA and dihexyl phosphoric acid (HDHP) [11]. Hérès *et al.* reported a process namely, Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN), for a single-cycle separation of trivalent actinides [10]. The solvent used in PALADIN was composed of 0.5 M DMDOHEMA and 0.3 M bis(2-ethylhexyl)phosphoric acid (HDEHP) in hydrogenated tetrapropylene (TPH). The aqueous complexing agents such as lactate or citrate buffered solutions (pH 3 to 4) of *N*-(2-hydroxyethyl) ethylenediamine-triacetate (HEDTA) or DTPA were used for selective stripping of An(III) from the loaded organic phase. A separation factor of 12.5 was achieved for Eu/Am in PALADIN process. Geist *et al.* synthesized an aqueous soluble triazine derivative, 2,6-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)pyridine (SO_3-Ph-BTP), and studied for the selective back-extraction of Am(III) from the loaded organic phase, which is composed of 0.2 M TODGA - 5% iso-octonol in TPH [12]. A very similar approach was explored recently by Lumetta *et al.* and a separation factor of 20-30 for Am(III)/Ln(III) was reported [13,14]. However, the studies reported on single-cycle methods indicate that the solvent used for extraction was not completely incinerable. During the incineration of these solvents for the management or organic waste, these solvents leave phosphrous based solid residue. Moreover, the diluents used for these methods were unconventional diluents, other than *n*-dodecane. Now a days, researchers are investigating on the solvents containing C,H,O,N atoms such that the solvent is converted to gaseous products without leaving any solid residue. In contrast to the above, the present study deals with the solvent phase which is completely incinerable.

In the chapter 3, the group separation was demonstrated using *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) as extractant. During this process An(III) and Ln(III) were extracted from FR-SHLLW using 0.1 M D^3DODGA/*n*-DD and both An(III) and Ln(III) were stripped using 0.01 M nitric acid solution [15]. Now trivalent An(III) and Ln(III) are present in the dilute nitric acid solution. Suneesh *et al.* developed a process for the mutual separation of An(III) from Ln(III) using an acidic extractant, di-2-ethylhexyl diglycolamic acid (HDEHDGA) from dilute nitric acid [16]. They also demonstrated the mutual separation of Am(III) and Eu(III) from 0.1 M nitric acid - 0.1 M citric acid medium by using a solution of 0.1 M HDEHDGA/*n*-DD in a 20-stage mixer-settler [17]. Quantitative extraction of Am(III) and Eu(III) from 0.1 M citric acid medium was achieved in 2-3 contacts with the use of 0.1 M HDEHDGA/*n*-DD, at pH 3. The selective recovery of Am(III) from the loaded organic phase was achieved using 0.01 M DTPA-0.025 M CA at pH 1.5. More than 96% of Am(III) was recovered from the loaded organic phase after 20-stages in a mixer-settler. However, the stripping of Eu(III) was only 2% after 20 stages of stripping. The results, therefore, confirmed the feasibility of using HDEHDGA/*n*-DD for the mutual separation of Eu(III) and Am(III) from citric acid medium. In addition, Ravi *et al.* explored a novel approach, namely **S**ingle-cycle method for **M**inor **A**ctinide partitioning using completely incinerable **R**eagen**T**s (SMART), for the separation of trivalent actinides by combining D^3DODGA and HDEHDGA as extractants [18]. The extractants used in the SMART approach are completely incinerable reagents. They also studied the extraction behavior of Am(III) and Eu(III) using D^3DODGA - HDEHDGA in n-dodecane from nitric acid medium. The selective stripping of Am(III) was studied using DTPA-CA solution. The batch stripping studies conducted using these reagents showed excellent results for the mutual separation of Am(III) from Eu(III) [18]. However, these studies were limited only to representative actinide and lanthanides element namely Am(III) and Eu(III) respectively. The extraction and stripping behavior of all lanthanides and the other elements present in HLLW was unknown. The performance of Am(III) separation in the presence of these interferences during the counter-current extraction is essential for the further development of this approach.

In view of the above, the present chapter deals with the extraction and stripping behavior of various metal ions present in the fast reactor simulated high-level liquid waste (FR-SHLLW) by using a solvent phase composed of *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) and di-2-ethylhexyl diglycolamic acid (HDEHDGA). The structures of extractants and stripping reagents are shown in Figure 4.1. The distribution ratios of various metal ions present in FR-SHLLW were measured and the number of stages needed for extraction and stripping of Am(III) was optimized. Based on these results, the counter-current mixer-settler run was performed using a 20-stage mixer-settler. The results obtained from these studies are reported in this chapter.

4.2. Third phase formation studies with FR-SHLLW

Third phase formation is an undesirable event in solvent extraction procedure [19]. It is the splitting of organic phase in to two phases during the course of solvent extraction. It occurs due to the poor solubility and incompatibility of polar metal-solvate complex in a non-polar diluent. Ravi *et al.* studied the third phase formation behavior of nitric acid and Nd(III) in various unsymmetrical diglycolamides present in *n*-dodecane [3]. The third phase was not observed in a solution of 0.1 M D^3DODGA/*n*-DD even at the stoichiometric levels of loading of Nd(III) from 3-4 M nitric acid medium. However, the present solvent formulation is composed of a mixture of neutral extractant, D^3DODGA, and an acidic extractant diglycolamic acid, HDEHDGA. Therefore, it is necessary to study the third phase formation behavior of the present solvent formulation when contacted with HLLW. In the present case, the third phase formation was studied in the presence of FR-SHLLW. Table 4.1 shows the third phase formation behavior of D^3DODGA - HDEHDGA in *n*-dodecane at various molar ratios of D^3DODGA and HDEHDGA when contacted with FR-SHLLW. It is interesting to note that the third phase is not observed when the ratio of acidic to neutral extractant is maintained below 2. Since it is desirable to employ 0.1 M D^3DODGA to achieve higher throughputs during extraction, further studies were conducted with a solvent formulation composed 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-dodecane.



HDEHDGA **DTPA**

Figure 4.1. Structures of HDEHDGA and DTPA.

Table 4.1. Third phase formation behavior of D^{3}DODGA - HDEHDGA /*n*-DD with FR-SHLLW
Organic phase = Various molar ratios of D^{3}DODGA - HDEHDGA in *n*-dodecane
Aqueous phase = FR-SHLLW, Organic to Aueous phase ratio=1, Temperature = 298 K

Solvent composition	Ratio of acidic extractant to neutral extractant	Third phase formation with FR-SHLLW
0.05 M D^{3}DODGA -0.2 M HDEHDGA/*n*-DD	4	Yes
0.1 M D^{3}DODGA -0.3 M HDEHDGA/*n*-DD	3	Yes
0.05 M D^{3}DODGA-0.1 M HDEHDGA/*n*-DD	2	No
0.1 M D^{3}DODGA -0.2 M HDEHDGA/*n*-DD	2	No
0.1M D^{3}DODGA -0.1 M HDEHDGA/*n*-DD	1	No
0.1 M D^{3}DODGA -0.05 M HDEHDGA/*n*-DD	0.5	No

4.3. Extraction from FR-SHLLW

The extraction behavior of various metal ions present in FR-SHLLW was studied and their distribution ratios in 0.1 M D^{3}DODGA/*n*-DD and combined solvent 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD are summarized in Table 4.2. The distribution ratio of trivalent lanthanides (Ln(III)) and Am(III) is always more in combined solvents as compared to 0.1 M D^{3}DODGA/*n*-DD. HDEHDGA is an acidic extractant and the extraction of these metal ions are negligible at 3 M nitric acid. The distribution ratio of these metal ions in the combined extractant is more as compared to individual solvent. This indicates the metal ions are synergistically extracted to the combined solvent. The distribution ratio of other elements is comparable in both solvents. The distribution ratio of elements is increasing in the lanthanide series. The distribution ratio follows the order La(III) < Ce(III) < Pr(III) < Nd(III) < Am(III) < Sm(III) < Eu(III). It can be seen that the $D_{Am(III)}$, $D_{Ln(III)}$ and fission products such as $D_{Zr(IV)}$, $D_{Y(III)}$ and $D_{Pd(II)}$ are higher than the distribution ratios observed for other metal ions ($< 10^{-1}$). This indicates that Am(III), Ln(III), Zr(IV), Y(III) and Pd(II) metal ions could be significantly extracted from FR-SHLLW by the combined solvent in a few contacts. Ravi *et* *al.* studied the extraction behavior of various metal ions in 0.1 M D^{3}DODGA/*n*-DD and reported that the distribution ratio reached a maximum value when the ionic radii of the metal ion were in the range 80 -100 pm [20]. Prior to this, Zhu *et al.* reported a correlation between the distribution ratio of various metal ions in diglycolamide, TODGA, and ionic radii of metal ions [21]. The distribution ratio was reported to increase from 10^{-2} to >200 with increase of ionic radius from 60 pm to 100 pm. Since the ionic radii of metal ions namely Am(III), Ln(III), Y(III) and Zr(IV) are of the order 80-100 pm and extraction is carried out from 3M nitric acid, the distribution ratio is essentially governed by the diglycolamide, D^{3}DODGA, present in the solvent. The other metal ions having lower distribution ratios are inextractable to combined solvent. This could be due to the lower ionic radii of the elements.

4.4. Elimination of unwanted metal ions

The extraction of unwanted fission products in the solvent formulation could pose some complications during selective stripping of trivalent actinides from organic phase. Therefore, it is desirable to eliminate or minimize the extraction of unwanted metal ions without affecting the extraction of trivalent lanthanides and actinides. To maneuver this problem, several authors have added suitable complexing agents to FR-SHLLW and retained the unwanted metal ions in FR-SHLLW [22, 23]. Therefore, the extraction behavior of the metal ions present in FR-SHLLW in the presence of various complexing agents such as oxalic acid, *N*-(2-hydroxyethyl) ethylenediamine-triacetate (HEDTA) and trans-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CyDTA) was studied and the results are shown in Table 4.2. The results indicate that oxalic acid holds selectively Zr(IV) and HEDTA holds Pd(II). CyDTA holds both Zr(IV) and Pd(II) without altering the distribution ratio of other metal ions. So 0.05 M CyDTA eliminates the extraction of problematic fission products such as Zr(IV) and Pd(II) in the solvent phase. In view of this, CyDTA was added to FR-SHLLW for successive studies.

Table 4.2. Distribution ratios of metal ions present in simulated high-level liquid waste with and without complexing agents

Organic phase = 0.1 M D^{3}DODGA/*n*-DD or 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD, Aqueous phase = FR- SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer in the presence of complexing agent. Organic/Aqueous phase ratio = 1 Temperature = 298 K.

Metal ion	Distribution ratio (D_M)						
	In 0.1 M D^{3}DODGA/*n*-DD	In 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD					
		Without reagent	0.05 M CyDTA	0.05 M HEDTA	0.2 M oxalic acid	0.2 M oxalic acid + 0.05 M HEDTA	0.05 M HEDTA + 0.05 CyDTA
La(III)	1.6	1.9	2.8	2.5	2.2	3.3	3.2
Ce(III)	1.7	4.2	6.5	4.6	4.9	7.2	6.4
Pr(III)	6.6	9.4	15	10	12	16	14
Nd(III)	16	21	25	21	25	34	29
Sm(III)	63	51	55	54	58	52	55
Eu(III)	80	75	79	72	80	82	76
Gd(III)	38	85	80	82	90	78	84
Dy(III)	49	60	66	93	68	57	48
Y(III)	11	>100	>100	>100	>100	>100	>100
Mo(VI)	0.07	0.06	0.15	0.14	0.05	0.27	0.23
Fe(III)	$<10^{-2}$	0.06	0.12	0.14	0.08	0.13	0.10
Cr(VI)	$<10^{-2}$	0.10	0.18	0.21	0.14	0.40	0.33
Te(VI)	$<10^{-2}$	0.01	0.07	0.06	0.05	0.22	0.14
Cd(II)	$<10^{-2}$	0.16	0.23	0.26	0.19	0.46	0.38
Ni(II)	$<10^{-2}$	0.08	0.19	0.17	0.13	0.25	0.23
Sr(II)	0.1	0.32	0.51	0.52	0.44	0.88	0.71
Ba(II)	$<10^{-2}$	0.11	0.19	0.17	0.13	0.21	0.18
Ru(III)	$<10^{-2}$	0.30	0.32	0.37	0.30	0.39	0.35
Pd(II)	1.23	1.34	0.14	0.13	0.45	0.18	0.13
Zr(IV)	363	95	0.02	80	0.02	0.07	0.06
Rh(III)	$<10^{-2}$	0.04	0.12	0.09	0.12	0.13	0.09
Rb(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ag(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
^{241}Am(III)	21	36	38	40	34	35	40

Table 4.3. Distribution ratio values of Am(III) and Eu(III) as a function of pH. Organic phase = 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD. Aqueous phase = 0.01 M DTPA + 0.5 M citric acid at various pH.

$pH_{eqm.}$	Distribution ratio		Separation factor S.F. = $D_{Eu(III)}/D_{Am(III)}$
	Am(III)	Eu(III)	
1	2.6	23	8.8
1.5	0.8	7.5	9.4
2	0.06	0.6	10
2.5	~0.01	0.09	-
3	~0.01	0.06	-

4.5. Back extraction from loaded organic phase

The trivalent actinides and lanthanides co-extract from FR-SHLLW in 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD. The present approach envisages the mutual separation of actinides and lanthanides from the organic phase to facilitate transmutation of actinides. Previously, the stripping behavior of Am(III) alone from D^{3}DODGA - HDEHDGA/*n*-DD was studied by Ravi *et al.* They proposed that the aqueous formulation composed of DTPA and citric acid (CA) for efficient back extraction of Am(III) [18]. Even though, DTPA alone could recover Am(III) from organic phase, the CA was added to the aqueous phase for maintaining the pH of aqueous phase during stripping. Table 4.3 shows distribution ratio of Am(III) and Eu(III) from FR-SHLLW containing 0.01 M DTPA+0.5 M CA at various pH. It is observed that distribution ratio of Am(III) and Eu(III) decreases with increase of pH, due to the more dissociation of DTPA at higher pH. So, DTPA forms complex with metal ions in aqueous phase which indicates the distribution ratio of metal ions is less. The very low distribution ratios of both metal ions in pH 2 to 3 indicate that these metal ions report to aqueous phase during stripping. The separation factor (SF) for Eu(III) over Am(III) is also shown in Table 4.3. The separation factor is ~10 at pH 1 to 2 whereas after pH 2, mutual separation is difficult due to the low distribution ratio of both metal ions. At pH 1, the distribution ratios of both metal ions are more such that both are extracted to organic phase. Since it is necessary to retain Eu(III) in organic phase while stripping Am(III), it is desirable to choose pH 1.5 for mutual separation, where the $D_{Am(III)}$ is quite low compared to $D_{Eu(III)}$.

Table 4.4. Back extraction of Am(III) and Eu(III) from the loaded organic phase. The loaded organic phase was obtained by extraction of Am(III) and Eu(III) in 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD from FR-SHLLW. Stripping formulation was composed of 0.01 M DTPA + citric acid at pH 1.5.

Number of contacts	0.1M CA		0.5M CA		0.7 M CA	
	% Am stripping	% Eu stripping	% Am stripping	% Eu stripping	%Am stripping	% Eu stripping
1	25.91	4.77	23.96	3.91	18.43	3.68
2	41.53	9.06	47.06	8.68	36.70	9.23
3	52.02	12.72	62.49	13.02	49.69	14.02
4	60.55	15.67	74.99	16.46	59.53	17.69
5	66.73	18.07	83.40	19.97	68.05	22.35

The variation in the back extraction of Am(III) and Eu(III) at different concentration of citric acid in aqueous phase is shown in Table 4.4. In this case, both the metal ions were individually loaded to a combined organic phase followed by the stripping of metal ions using various concentrations of citric acid with 0.01 M DTPA in aqueous phase at pH 1.5. The percentage of cumulative stripping with number of contacts of aqueous phase for both metal ions is shown in Table 4.4. It is observed that increase in concentration of citric acid (from 0.1 M to 0.5 M), increases the stripping of both metal ions. When the citric acid concentration increased from 0.5 M to 0.7 M, the cumulative stripping of metal ions is reduced. This could be due to the increased solubility of citric acid in organic phase at 0.7 M citric acid and thereby holding the metal ions in organic phase itself which makes it difficult to strip. In this case citric acid behaves like a buffering reagent. At higher concentrations of citric acid, the equilibrium pH is stable as compared to low citric acid concentration. At 0.1M citric acid, cumulative stripping of metal ions is less as compared to 0.5 M citric acid due to the acid stripping from the loaded organic phase. The equilibrium pH may be decreasing less than the initial pH 1.5 and hence holds the metal ions in organic phase. At 0.5 M citric acid concentration, after five contact ~84 % of Am(III) was stripped whereas ~20% of Eu(III) was reporting to aqueous phase. At 0.01 M DTPA+0.5M CA at pH 1.5, significant amount of Am(III) is back extracted into aqueous phase, where as Eu(III) is retained in organic phase. Therefore, for mixer-settler studies, 0.1 M DTPA+0.5 M CA at pH 1.5 was chosen as stripping condition from the loaded organic phase.

4.6. Mixer-settler studies - Extraction

The extraction profile of Am(III) and Eu(III) in 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD, in a 20-stage mixer-settler is shown in Figure 4.2. The extraction was carried out from FR-SHLLW containing 0.05 M CyDTA spiked with $^{(152+154)}$Eu(III) and ^{241}Am(III) tracer. These solutions were passed in a counter-current direction at the flow rate of 3 mL/min in a 20-stage mixer-settler. The aqueous phase was passed from the 1st stage to 20th stage and the organic phase was passed in reverse direction. The organic and aqueous phases were assayed for $^{(152+154)}$Eu(III) and ^{241}Am(III) radioactivity and the other metal ions were determined by the analysis of aqueous phase (FR-SHLLW) using ICP-OES. The Figure 4.2 is plotted percentage of metal ion in aqueous phase (%) against number of stages of mixer-settler. It is observed from Figure 4.2 that initially all the metal ions are present in FR-SHLLW aqueous phase and entering to mixer-settler unit at stage 1. As the aqueous phase passes through the mixer-settler the concentration of metal ions is coming down in aqueous phase. This indicates that the metal ions are extracted to organic phase. The extraction of metal ions depends on the distribution ratio of the metal ions. Metal ions having higher the distribution ratio get extracted to the solvent phase quite easily. The distribution ratio of metal ions is in the order of Eu(III) > Am(III) > Nd(III) > Ce(III) > La(III) as shown in Table 4.2. So loading of the metal ions follows the same order in mixer-settler as shown in Figure 4.2. The concentration of Eu(III) and Am(III) in aqueous phase become negligible in stage 3 and 4 successively indicating the quantitative extraction of these metal ions in 3- 4 stages. A similar extraction profile was also observed for the extraction of other lanthanides (only few lanthanides are shown in Figure 4.2 for clarity) except lanthanum which required 8 -10 stages for complete extraction. The aqueous raffinate obtained after 20-stages was analyzed by ICP-OES and the results are shown in Table 4.5. The concentration of Am(III), Ln(III) and Y(III) is negligible in the raffinate after 20 stage of extraction. This indicates that Am(III), Ln(III), and Y(III) are extracted quantitatively from FR-SHLLW in 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-DD. But Sr(II) is extracted to the extent of 90%. However, it is important to note the troublesome metal ions such as Zr(IV), Mo(VI), Fe(III), Cr(VI), Ni(II), Pd(II), Ru(III), Rh(III) are rejected to raffinate in addition to other elements.

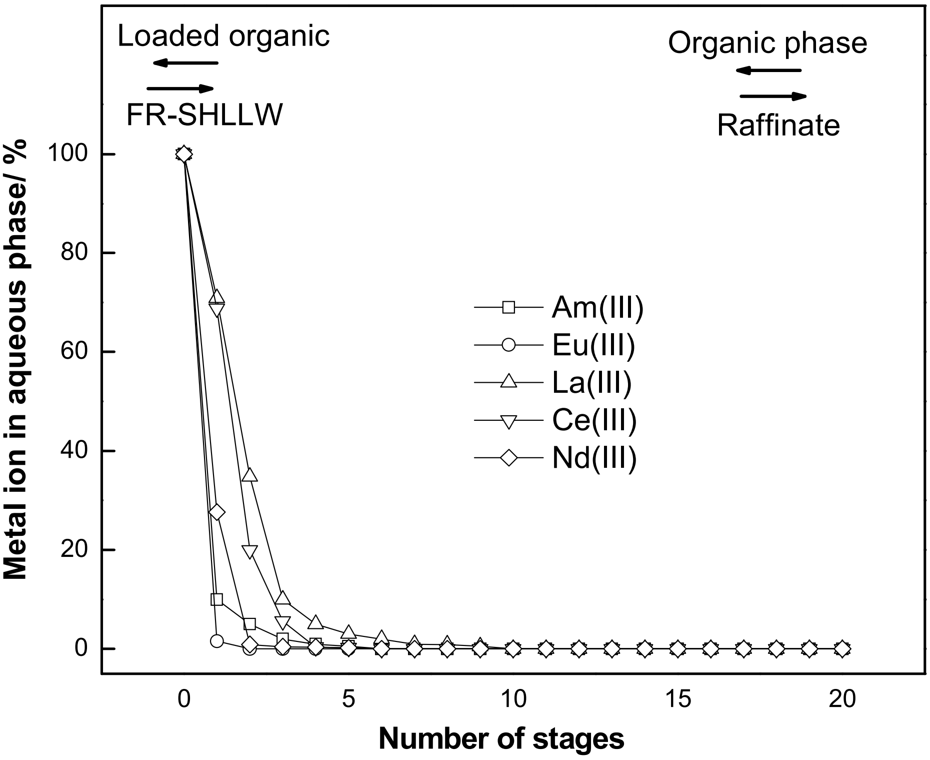


Figure 4.2. Profiles of ^{241}Am(III), $^{(152+154)}$Eu(III), La(III), Ce(III) and Nd(III) extraction from FR-SHLLW using a 20-stage mixer-settler. Organic phase: 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD. Aqueous phase: FR-SHLLW+0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer.

Table 4.5. The extraction and stripping of metal ions in a 20-stage mixer-settler. Temperature = 298 K. Extraction condition: Organic phase = 0.1 M D^{3}DODGA - 0.2 M HDEHDGA/*n*-DD. Aqueous phase = FR- SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer + 0.05 M CyDTA.
Back extraction: Organic phase = Loaded organic. Aqueous phase = 0.01 M DTPA + 0.5 M CA at pH 1.5

Metal ion	Concentration (g/L)	Cumulative extraction of metal ions (%) after 20 stage	Cumulative stripping of metal ions (%) after 20 stage
La(III)	0.342	> 99.9	86
Ce(III)	0.684	> 99.9	97
Pr(III)	0.339	> 99.9	75
Nd(III)	1.125	> 99.9	47
Sm(III)	0.306	> 99.9	25
Eu(III)	0.032	> 99.9	< 5
Gd(III)	0.065	> 99.9	< 4
Dy(III)	0.006	> 99.9	< 2
Y(III)	0.074	> 99.9	< 5
Sr(II)	0.147	90	50
Mo(VI)	1.092	< 1	B.D.L
Cr(VI)	0.101	< 1	B.D.L
Te(VI)	0.163	< 1	B.D.L
Cd(II)	0.038	< 1	B.D.L
Ni(II)	0.1	< 1	B.D.L
Fe(III)	0.5	< 1	B.D.L
Ba(II)	0.414	< 1	B.D.L
Ru(III)	0.813	< 1	B.D.L
Pd(III)	0.6	< 1	B.D.L
Zr(IV)	0.822	< 1	B.D.L
Rh(III)	0.262	< 1	B.D.L
Cs(I)	1.125	< 1	B.D.L
Rb(I)	0.055	< 1	B.D.L
Na(I)	3	< 1	B.D.L
Ag(I)	0.109	< 1	B.D.L
^{241}Am(III)	0.218	> 99.9	55

B.D.L. – Below Detection Limit (<0.1 ppm)

4.7. Mixer-settler studies - Stripping

The recovery of Am(III) from the loaded organic phase was carried out using an aqueous formulation, 0.01 M DTPA+0.5 M CA at pH 1.5. The stripping profile of Am(III) and some lanthanides obtained in a 20-stage mixer-settler is shown in Figure 4.3. The loaded organic phase was passed from the 20th stage to 1st stage and the stripping solution was passed from the 1st stage to 20th stage. Based on the nature of stripping profile obtained in the present study (shown in Figure 4.3), the lanthanides can be classified in to "early lanthanides" to represent the lanthanides from lanthanum to samarium and "later lanthanides" to represent the lanthanides beyond samarium. At the 20th stage, the loaded organic makes a first contact with aqueous stripping formulation and it is expected to recover Am(III) alone from the loaded organic phase during striping. It is observed that significant amount of Am(III) is back extracted in to aqueous phase at 20th stage and stripping of Am(III) is observed in all 20 stages. The concentration of metal ions in the stripping solution phase was measured by ICP-OES. Trivalent actinides and lanthanides were stripped continuously from 1st stage to 20th stages of the mixer settler. About 55% of the Am(III) was recovered in 20 stages (product stream). However, the batch studies shown in Table 4.4 indicate the recovery of ~85% Am(III) during stripping. The difference observed in batch and mixer-settler run could be due to the re-extraction of Am(III) in a mixer-settler run when operated in a counter-current mode. Nevertheless, the trend observed in the present study shows that it is possible to recover Am(III) quantitatively when the stripping is continued for more than 20 stages. Figure 4.3 also shows the stripping profile of Eu(III) in a 20 stage mixer settler. As expected, the stripping of Eu(III) is negligible in 20 stages. The cumulative stripping of europium is less than 5% after 20 stages. Therefore, the contamination of Eu(III) in the Am(III) product is negligible. However, it is necessary to understand the stripping behavior of other lanthanides during the recovery of Am(III).

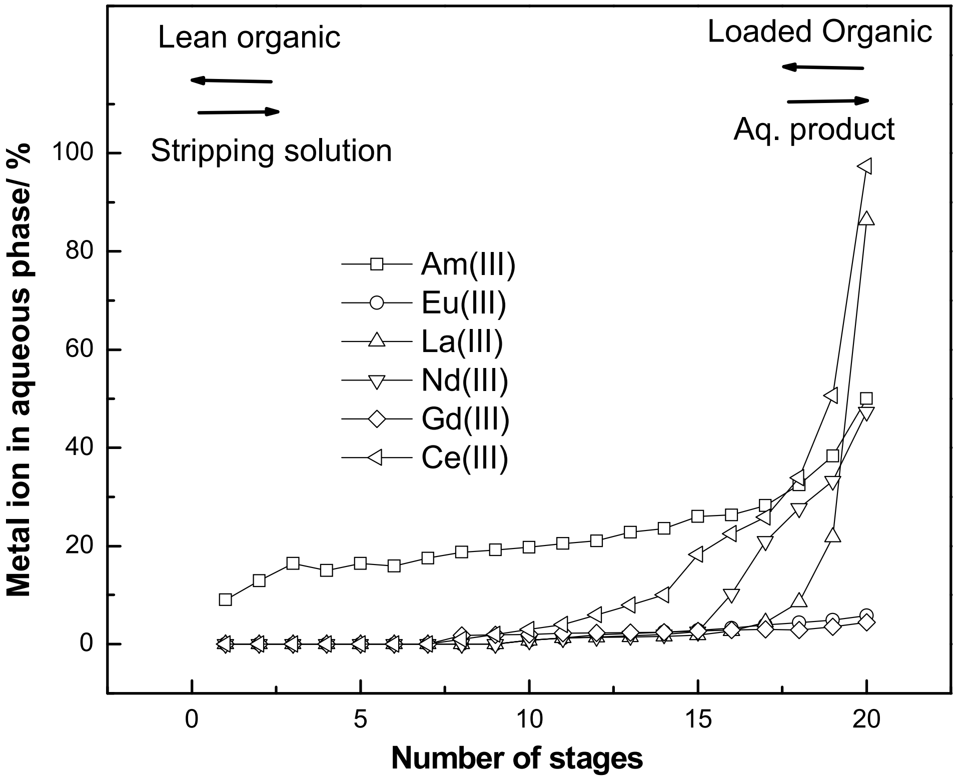


Figure 4.3 Profiles of ^{241}Am(III), $^{(152+154)}$Eu(III), La(III), Ce(III), Nd(III) and Gd(III) stripping from the loaded organic phase using a 20-stage mixer-settler. Organic phase: Loaded organic. Aqueous phase: 0.01 M DTPA + 0.5 M CA at pH 1.5.

Figure 4.3 also shows the stripping behavior of some “early lanthanides” and “later lanthanides” (only few lanthanides are shown in the Figure for clarity). It is important to observe that significant amount of “early lanthanides” are stripped to the aqueous phase along with Am(III), where as the “later lanthanides” behave similar to Eu(III). The cumulative stripping of lanthanides and other metal ions after 20 stages is shown in Table 4.5. Depending upon the nature of lanthanides, the stripping of “early lanthanides” is determined to be 60 - 85% in 5 -10 contacts (from 20th to 10 stages, Figure 4.3). It is also important to note that the recovery of “early lanthanides” is more than Am(III) recovery (~55%), perhaps due to low distribution ratio of "early lanthanides", as shown in Table 4.2. In contrast, the cumulative recovery of "later lanthanides" is lower than 5%.

Therefore, the study clearly shows that stripping of Am(III) is accompanied by the stripping of "lighter lanthanides". Even though, the separation of Am(III) from lanthanides is not clean, as it is envisaged, the study is important from the point of view of single cycle separation, and lanthanide and actinide separation. Previously, we carried out the primary batch studies with a trivalent actinide and lanthanide representatives namely Am(III) and Eu(III) for determining the behavior of Am(III) and other lanthanides during lanthanide-actinide separation. Since the separation of Am(III) and Eu(III) was excellent in those studies, a similar behavior was expected for all lanthanides. However, the present study clearly indicated that investigations carried out merely with Am(III) and Eu(III) representatives are not adequate for understanding the behavior other lanthanides. In addition, the present study indicates the feasibility of "intra-lanthanide" separations apart from lanthanide-actinide separation. Since the distribution ratio of "early lanthanides" are quite low, as discussed above, it is quite possible that they can be easily separated from "later lanthanides" as well as from Am(III). Based on the present study, it is possible to visualize a novel separation approach in which the trivalent lanthanide and actinide ions present in organic phase can be recovered in three groups, namely, the "early lanthanides", trivalent actinides and "later lanthanides". This kind of approach may create other opportunities such as "intra-lanthanides" separation.

4.8. Conclusion

The extractants, D^3DODGA and HDEHDGA, are CHON based completely incinerable reagents. The extraction and stripping behavior of Am(III) and other metal ions present in the FR-SHLLW was studied using a solution of D^3DODGA - HDEHDGA/*n*-DD to develop a single-cycle processing approach for the separation of Am(III) from FR-SHLLW.

The third phase formation was not observed with FR-SHLLW when the ratio of acidic to neutral extractant was maintained below 2. Therefore, the extraction studies were carried out using a solvent formulation composed of 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-dodecane. The extraction of metal ions was governed by the neutral extractant, D^3DODGA and stripping controlled by the acidic extractant, HDEHDGA. The extraction of Am(III) and lanthanides was accompanied by the co-extraction of unwanted metals such as Zr(IV), Pd(II), Sr(II) and Y(III) from FR-SHLLW. Since it was desirable to retain these troublesome metal ions in aqueous phase, complexing agent CyDTA, was added to FR-SHLLW and the extraction and stripping conditions were optimized. Based on those optimized conditions, a counter-current extraction run was performed to separate Am(III) from FR-SHLLW using a 20-stage mixer-settler. As expected the Am(III), lanthanides, Y(III) were quantitatively extracted in 4 stages. Strontium was extracted to the extent of 90% in 20 stages. However, it was noted that the troublesome metal ions such as Zr(IV), Mo(VI), Fe(III), Cr(VI), Ni(II), Pd(II), Ru(III), Rh(III) were rejected to raffinate in addition to other elements. The stripping of Am(III) from the loaded organic phase was performed by using the aqueous formulation composed of 0.01 M DTPA+0.5 M CA at pH 1.5. About 55% of Am(III) was recovered in 20 stages (product stream). This was accompanied by the co-stripping of significant amounts of "early lanthanides". However, the "later lanthanides" behave similar to Eu(III). Since the distribution ratio values of "early lanthanides" were quite low as compared to Am(III) and "later lanthanides", it could be possible to separate "early lanthanides" from both Am(III) and "later lanthanides". Therefore, the present study indicates the feasibility of "intra-lanthanide" separations apart from lanthanide-actinide separation.

4.9. References

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Chapter 5: Single-cycle process for minor actinide partitioning using diglycolamide - di-2-ethylhexyl phosphoric acid solvent

5.1. Introduction

In the recent past, a single-cycle process has been developed by combining two or more extractants in a single solvent formulation to achieve extraordinary extraction as well as to develop a simple processing method for minor actinide partitioning [1-6]. Lumetta *et al.* reported the merits of combining the neutral and acidic extractants to achieve single-cycle separation of trivalent actinides from HLLW [2]. The authors studied the extraction behavior of Am(III) and Eu(III) in a TRUSPEAK solvent formulation consisting of 0.1 M *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) + 1 M bis(2-ethylhexyl)phosphoric acid (HDEHP) in *n*-DD from 1 M nitric acid medium [3]. Selective stripping of Am(III) alone from the organic phase was reported using an aqueous formulation composed of 0.05 M diethylenetriaminepentaacetic acid (DTPA) + 1.5 M citrate at pH 3.5. The Am(III) to Eu(III) separation factor of ~12 was reported.

Gannaz *et al.* investigated the extraction behavior of Eu(III) and Am(III) in a solution of dimethyldioctylhexaethoxymalonamide (DMDOHEMA) and dihexylphosphoric acid (HDHP) [4]. The extraction of metal ion in this case was reported to be governed by DMDOHEMA and the selective stripping of Am(III) alone from organic phase was controlled by the differential complexing ability of HDHP present in organic phase and a polycarboxylic acid, namely DTPA present in aqueous phase during stripping. Dhami *et al.* studied the extraction and stripping behavior of Am(III) and Eu(III) using a solution composed of HDEHP and CMPO dissolved in *n*-paraffinic diluents [5]. Modolo *et al.* studied the synergistic selective extraction of Am (III) over Ln(III) from nitric acid solution using dithiophosphinic acid (R_2PSSH) and neutral organophosphorous compounds such as, tributylphosphate (TBP), trioctylphosphinic oxide (TOPO) etc [6]. The authors reported the possibility of separating actinides from lanthanides using the above synergistic mixture from 1 M nitric acid medium.

The alkyl derivatives of diglycolamides (DGAs) are being regarded as promising reagents for the separation of trivalent actinides and lanthanides from nitric acid medium [7-10]. The exceptional feature in DGA responsible for efficient extraction of trivalents is the etheric oxygen present between the two amidic moieties. This feature facilitates the DGA molecule to form a stable tridentate coordination with metal ions during extraction [11]. Among the various alkyl derivatives investigated so far, the octyl containing substituents such as *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) [12-14] and *N,N,N',N'*-tetra-2-ethylhexyldiglycolamide (TEHDGA) [15,16] are studied extensively for trivalent actinide partitioning and they are accepted choice of solvents for actinide partitioning.

Chapter 4 describes the combination of D^3DODGA - HDEHDGA extractant for minor actinide partitioning in single-cycle process. The results indicated that the stripping of americium was accompanied with lighter lanthanides from a combined solvent phase [17]. For the improvement of the single-cycle process, several combinations of neutral and acidic extractants were studied. *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) was the promising candidate as compared to TEHDGA for minor actinide partitioning in the first cycle because TODGA has a good distribution ratio for actinides and lanthanides and extraction of other fission products is less. So, TODGA was chosen as the neutral extractant. For the mutual separation of actinides from lanthanides, the well known process, Trivalent Actinides Lanthanide Separation Phosphorous based reagent Extraction from Aqueous Komplexes (TALSPEAK), di(2-ethylhexyl) phosphoric acid (HDEHP) was used as extractant [18]. In the TALSPEAK process diethylenetriamine pentaacetic acid (DTPA) containing soft donor nitrogen atoms is used as the complexing agent in the aqueous phase to preferentially hold An(III), and Ln(III). Extraction was carried out using di-2-ethylhexyl phosphoric acid

(HDEHP), containing hard donor oxygen atoms. This facilitates the preferential extraction of Ln(III) over the An(III), with multiple stages of such extractions yielding better separation factors. However, in TALSPEAK process, a phosphorous based reagent HDEHP is employed and this process needs the maintenance of a constant pH in the aqueous phase. Del Cul *et al.* developed a citric acid based TALSPEAK process for the mutual separation of Ln(III) from An(III) [19]. Citric acid in this process acted as a buffer and enhanced the separation factor (SF) of Am(III) from Eu(III). TODGA and HDEHP showed better results in the individual process. So the combination of TODGA - HDEHP was studied for a single-cycle process for minor actinide partitioning.

In this chapter, the extraction behavior of Am(III) from Eu(III) in a combined solution composed of *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) - HDEHP and tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) - HDEHP in *n*-dodecane was studied separately as a function of various parameters such as variation in nitric acid and extractant concentration. The results of combined extractant were compared with that of the individual extractant and the involvement of the number of molecules during extraction was deduced from the slope analysis of the extraction data. Since TODGA is a powerful extractant than TEHDGA for the separation of trivalent actinides, TODGA - HDEHP combined solvent system was studied initially. The structures of extractants are shown in Figure 5.1.

5.2. Studies with TODGA - HDEHP solution

5.2.1. Third phase formation studies

Diglycolamides form third phase with nitric acid and trivalent metal ions, such as lanthanides and actinides [7]. However, the formation of a third phase can be prevented by the addition of phase modifiers to the organic phase [7, 12]. The phase modifier is usually another extractant such as tri-*n*-butylphosphate (TBP) and dihexyloctanamide (DHOA) or a polar diluent like 1-octanol. In the present study, HDEHP was added to TODGA for the separation of actinides from lanthanides in a single-cycle process as the co-solvent. The effect of HDEHP in a solution of 0.1 M TODGA/*n*-DD on the third phase formation of nitric acid and Nd(III) was studied. Since the maximum concentration of HNO_3 and trivalent metal ions (Ln(III) and An(III)) in high-level liquid waste does not exceed 4 M and 50 mM [8] respectively, the present study involved equilibration of the organic phase with aqueous solution containing 70 mM Nd(III) in 4 M HNO_3. Table 5.1 shows the third phase formation behavior of nitric acid and Nd(III) in a solution of 0.1 M TODGA - HDEHP/*n*-DD. It can be seen that there is no third phase formation when the concentration of HDEHP was kept at 0.25 M. Therefore, the solvent formulation composed of 0.1 M TODGA - 0.25 M HDEHP/*n*-DD was used for all subsequent studies.

Table 5.1. Dependence of HDEHP concentration on third phase formation with nitric acid and Nd(III) in 0.1 M TODGA - HDEHP/*n*-DD. T = 298 K.

Solvent composition	Third phase formation with	
	$[HNO_3]_{ini}$ /M	70 mM Nd in 4 M HNO_3
0.1 M TODGA/*n*-DD	6 M	Yes
0.1 M TODGA - 0.2 M HDEHP/*n*-DD	Above 8 M	Yes
0.1 M TODGA - 0.25 M HDEHP/*n*-DD	Above 10 M	No

5.2.2. Extraction in individual solvent

TODGA is a neutral extractant, and HDEHP is an acidic extractant. Therefore, the extraction behavior of Am(III) and Eu(III) in these extractants would be different if they are used alone. To understand this, the extraction behavior of Am(III) in a solution of 0.25 M HDEHP/*n*-DD or 0.1 M TODGA/*n*-DD was studied as a function of nitric acid concentration and the results are shown in Figure 5.2. It is observed that the distribution ratio of Am(III) in HDEHP/*n*-DD decreases with increase in the concentration of nitric acid.

Linear regression of the extraction data obtained in case of 0.25 M HDEHP/*n*-DD results in a slope of –3. This indicates the transfer of three equivalents of H^+ to the aqueous phase during the extraction of Am(III), as shown in equation 5.1. The magnitude of slope and the distribution ratios obtained in this system are in good agreement with the results reported by others [18, 20]. A similar result is also observed for the extraction of Eu(III) in 0.25 M HDEHP/*n*-DD as shown in Figure 5.3. However, the distribution ratios of Eu(III) are always higher than the values obtained for Am(III) at all acidities [20]. Figures 5.2 and 5.3 also show the variation in the distribution ratio of Am(III) and Eu(III) in 0.1 M TODGA/*n*-DD as a function of nitric acid concentration. Since, TODGA is a neutral extractant, the distribution ratio of these metal ions increases with increase in the concentration of nitric acid in both cases. This extraction behavior can be explained by the mechanism shown in equation 5.2, as discussed elsewhere [7, 8, 10]. The distribution ratios observed for Eu(III) is higher than Am(III) in this system also, which is characteristic to diglycolamides.

$$\mathrm{Am^{3+} + 3HDEHP \Leftrightarrow Am(DEHP)_3 + 3H^+} \qquad (5.1)$$

$$\mathrm{Am^{3+} + 3NO_3^- + 4TODGA \Leftrightarrow Am(NO_3)_3(TODGA)_4} \qquad (5.2)$$

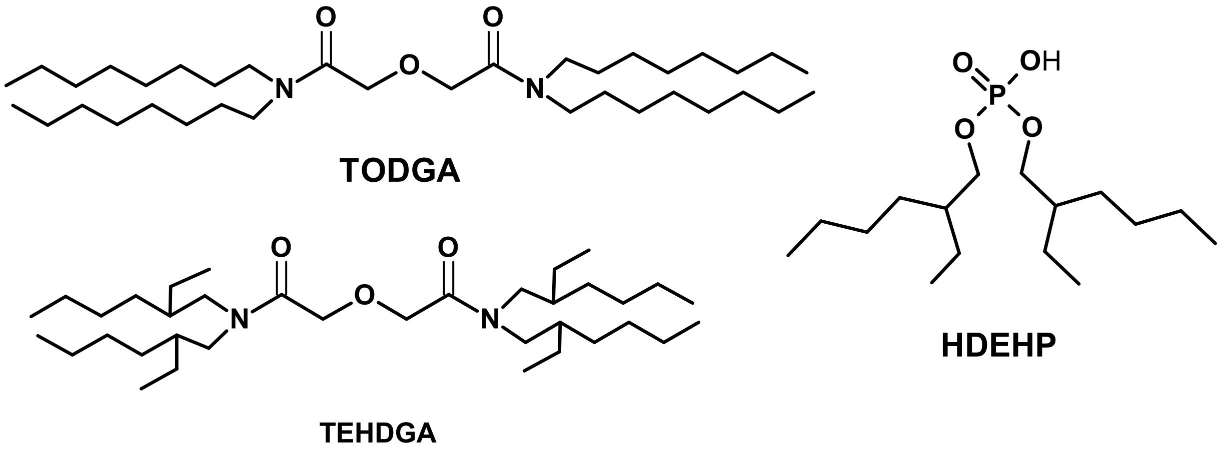

Figure 5.1. Structures of TODGA, TEHDGA and HDEHP

5.2.3. Extraction in combined solvent

The distribution ratio of Am(III) in a solution of 0.1 M TODGA - 0.25 M HDEHP/*n*-DD is also shown in Figure 5.2. It was observed that the distribution ratio of Am(III) in this case is much higher than that observed in individual solutions at lower acidities (< 2.0 M). This indicates that Am(III) is synergistically extracted by the mixture of HDEHP and TODGA. A similar synergistic extraction is also observed for Eu(III) in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD, as shown in Figure 5.3. However, the synergism is observed at nitric acid concentrations lower than 1 M. In contrast to the synergistic extraction observed at lower acidities, the distribution ratios of Am(III) and Eu(III) in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD are comparable to that observed in 0.1 M TODGA/*n*-DD, at higher acidities. This indicates the predominant role of TODGA in extraction at higher acidities.

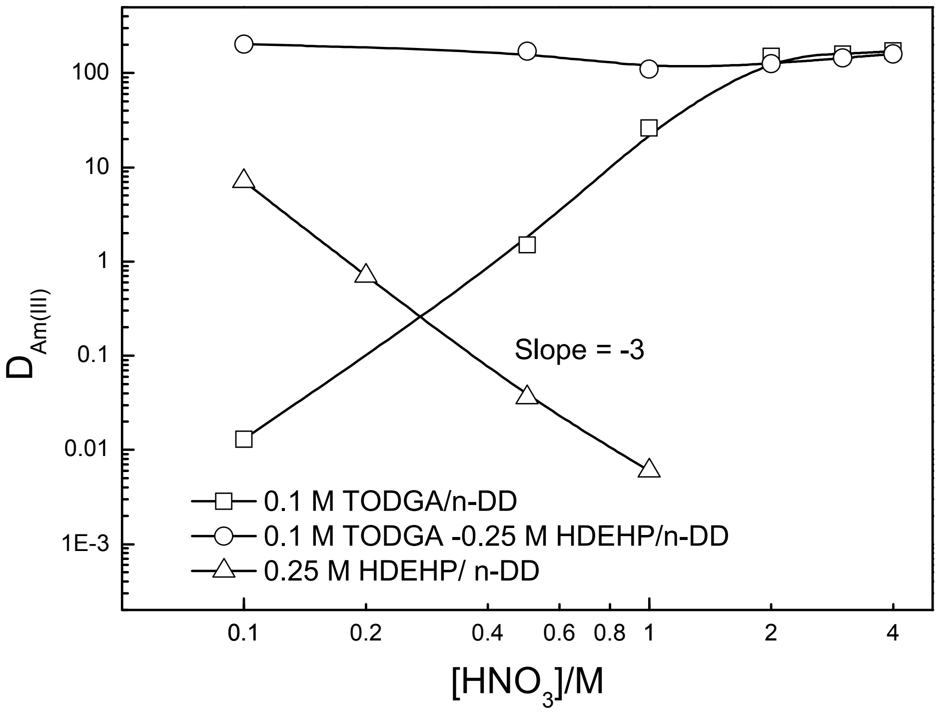

Figure 5.2. Distribution ratio of Am(III) as a function of nitric acid concentration. Organic phase: 0.1 M TODGA/*n*-DD or 0.25 M HDEHP/*n*-DD or 0.1 M TODGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: Various concentrations of nitric acid spiked with ^{241}Am(III) tracer.

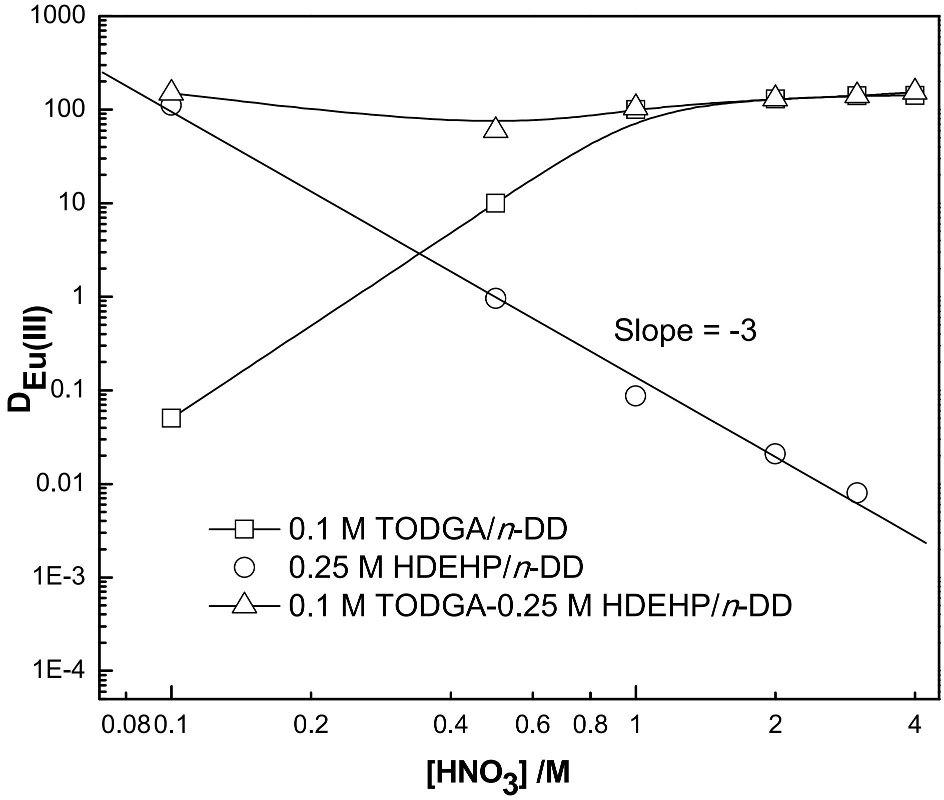

Figure 5.3. Distribution ratio of Eu(III) as a function of nitric acid concentration. Organic phase: 0.1 M TODGA/*n*-DD or 0.25 M HDEHP/*n*-DD or 0.1 M TODGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: Various concentrations of nitric acid spiked with $^{(152+154)}$Eu(III) tracer.

5.2.4. Extraction at 0.5 M nitric acid

The synergistic extraction of Am(III) and Eu(III) observed in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD at lower acidities indicate that the extraction is governed by both TODGA and HDEHP. A marginal decrease in distribution ratio of Am(III) and Eu(III) is observed, as shown in Figure 5.2 and 5.3 which show that the extraction is likely to be governed by the cation exchange property of HDEHP. Therefore, the effect of HDEHP concentration on the distribution ratio of Am(III) and Eu(III) in a solution of 0.02 M TODGA - HDEHP/*n*-DD was studied and the results are shown in Figure 5.4. It is observed that the distribution ratio of Am(III) and Eu(III) increases with increase in the concentration of HDEHP. Linear regression analysis of the extraction data results in a slope of 1.7 and 1.9 for Eu(III) and Am(III) respectively. This result confirms that ~2 molecules of HDEHP are involved in extraction. Comparing this value with a slope value of 3 obtained in the absence of TODGA, the study indicates that the dependence of HDEHP is reduced by the presence of TODGA in the solvent.

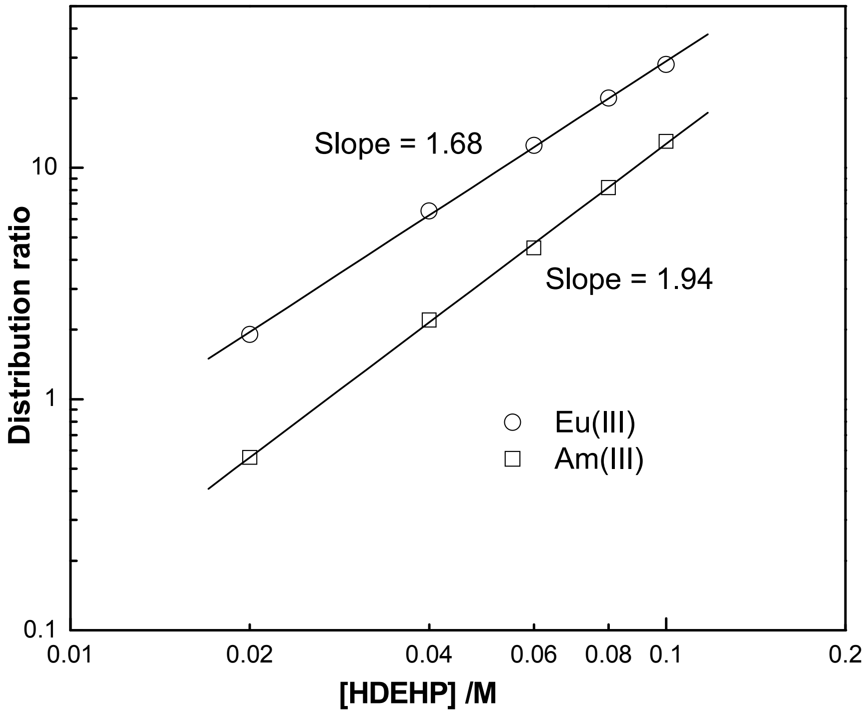

Figure 5.4. Influence of HDEHP concentration on distribution ratio of Am(III) and Eu(III) in 0.02 M TODGA - HDEHP at 0.5 M nitric acid concentration. Organic phase: 0.02 M TODGA - HDEHP/*n*-DD, varying concentration of HDEHP. Aqueous phase: 0.5 M nitric acid spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracers.

To study the effect of TODGA under these conditions, the distribution ratio of Am(III) and Eu(III) in a solution of TODGA - 0.04 M HDEHP/*n*-DD at 0.5 M nitric acid was measured and the results are shown in Figure 5.5. It is observed that the distribution ratio of both these metal ions increases with increase in the concentration of TODGA. Linear regression analysis of the extraction data results in a slope of 1.24 for Eu(III) and 1.1 for Am(III). This indicates that about one molecule of TODGA is involved in the extraction step.

Based on these observations the mechanism of trivalent metal ion extraction in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD can be proposed by the mechanism shown in equation 5.3. A similar extraction mechanism could be applicable at lower nitric acid concentrations (< 0.5 M). However, the composition of HDEHP and TODGA involved in the extraction step could be different depending upon the concentration of nitric acid. It is quite likely that the involvement of HDEHP would be more at lower nitric acid concentrations.

$$\mathrm{M^{3+} + 2HDEHP + NO_3^- + TODGA \Leftrightarrow M(NO_3)(DEHP)_2TODGA + 2H^+} \qquad (5.3)$$

5.2.5. Extraction at 3 M nitric acid

The effect of HDEHP concentration on the extraction of Am(III) and Eu(III) in a solution of 0.02 M TODGA - HDEHP/*n*-DD at 3 M nitric acid is shown in Figure 5.6. The concentration of HDEHP was varied from 0.01 M to 0.2 M. It is observed from Figure 5.6, that the distribution ratio of both the metal ions increases with increase in the concentration of HDEHP. Linear regression analysis of the extraction data results in a slope value of ~0.1 in both cases, indicating the involvement of HDEHP molecules in the extraction of Am(III) and Eu(III) even at 3 M nitric acid however, to a limited extent. Comparing this slope value with a slope of 2 obtained at 0.5 M nitric acid, the results indicate that the involvement of HDEHP decreases remarkably with increase in the concentration of nitric acid. Since the magnitude of slope obtained at 3 M nitric acid is small and the involvement of HDEHP is also less, the distribution ratios of Am(III) and Eu(III) in the combined solvent merges with the extraction behavior observed in TODGA/*n*-DD.

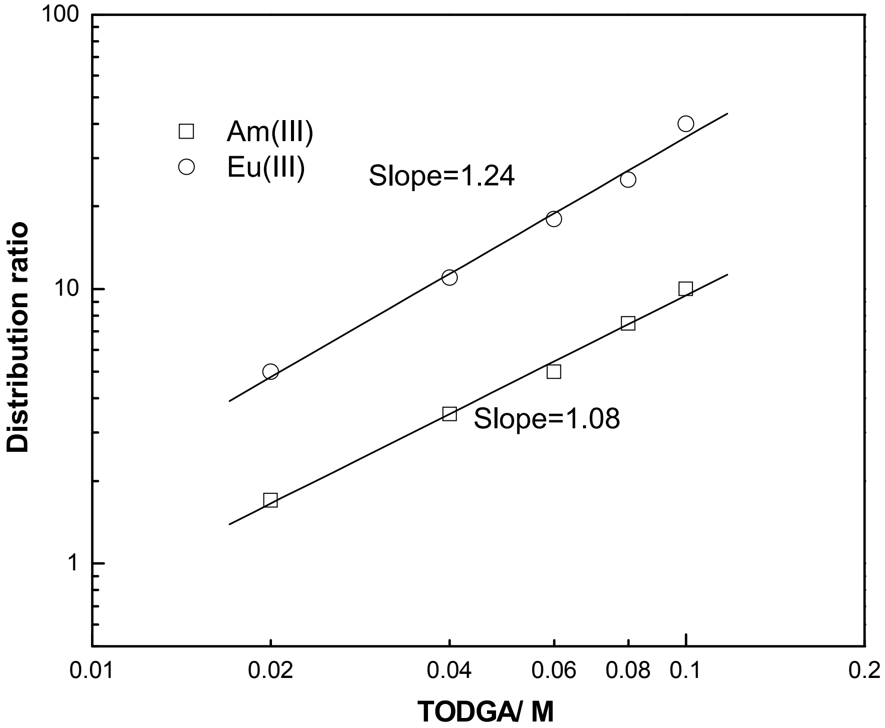

Figure 5.5. Influence of TODGA concentration on distribution ratio of Am(III) and Eu(III) in TODGA - 0.04 M HDEHP at 0.5 M nitric acid concentration. Organic phase: TODGA - 0.04 M HDEHP/*n*-DD, varying concentrations of TODGA. Aqueous phase: 0.5 M nitric acid spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracers.

Similarly the dependence of TODGA concentration on the extraction of Am(III) and Eu(III) is plotted in Figure 5.7. It is observed that the distribution ratio of Am(III) and Eu(III) increases with increase in the concentration of TODGA. Linear regression analysis of the extraction data results in a slope of ~3. This indicates the involvement of 3 molecules of TODGA in the extraction step. Comparing this value and the slope of 4 generally reported in the absence of HDEHP in *n*-DD solution [7.10], the study shows that the dependence of TODGA for extraction decreases in the presence of HDEHP. The reason for the involvement of 3 molecules of TODGA observed in the present case could be due to the additional involvement of HDEHP to some extent along with TODGA during the extraction of Am(III) and Eu(III) at 3 M nitric acid. Sasaki *et al.* reported the stoichiometry of M(III) - TODGA complexes when Eu(III) and Am(III) were extracted in TODGA present in various diluents [21]. The stoichiometry was reported to vary from 1:4 for *n*-dodecane to 1:2 in 1,2-dichloro ethane and 1-octanol. This was attributed to the increase in polarity of the extracted organic medium. Increasing the polarity of the organic solvent decreased the stoichiometry of the M(III) - TODGA complex. It is quite likely that there could be a change in polarity of organic phase (TODGA/*n*-dodecane) by the presence of HDEHP. Therefore, three molecules of TODGA are involved for the extraction of metal ions from 3 M nitric acid medium.

Based on the above observations, the mechanism of M(III) extraction in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD at various nitric acid concentrations can be represented by the equation 5.4.

$$M^{3+} + (3-x)NO_3^- + xHDEHP + (3-y)TODGA \Leftrightarrow M(NO_3)_{(3-x)}(DEHP)_x(TODGA)_{(3-y)} + xH^+$$
$$x = 0.1-2,\ y = 1-3 \qquad (5.4)$$

In this equation the magnitude of x and y increases with decrease in the concentration of nitric acid. At low acidities, the extraction of trivalent metal ion is predominantly governed by HDEHP molecules. However, the participation of TODGA and hence the nitrate ion is also significant due to the observation of synergism. The dependence of HDEHP for extraction decreases and that on TODGA and nitrate ion increases with increase in the concentration of nitric acid. Comparable extraction of trivalents observed at higher acidities (>2 M) is essentially due to the dominant role of TODGA for participation in the extraction. Moreover, the contribution of HDEHP (~0.1 molecule) is low at higher acidities. Therefore, the extraction behavior observed in the combined solvent is similar to that observed for TODGA at higher acidities. Nevertheless, the studies confirmed that extraction is contributed by both HDEHP and TODGA at all acidities investigated in the present study.

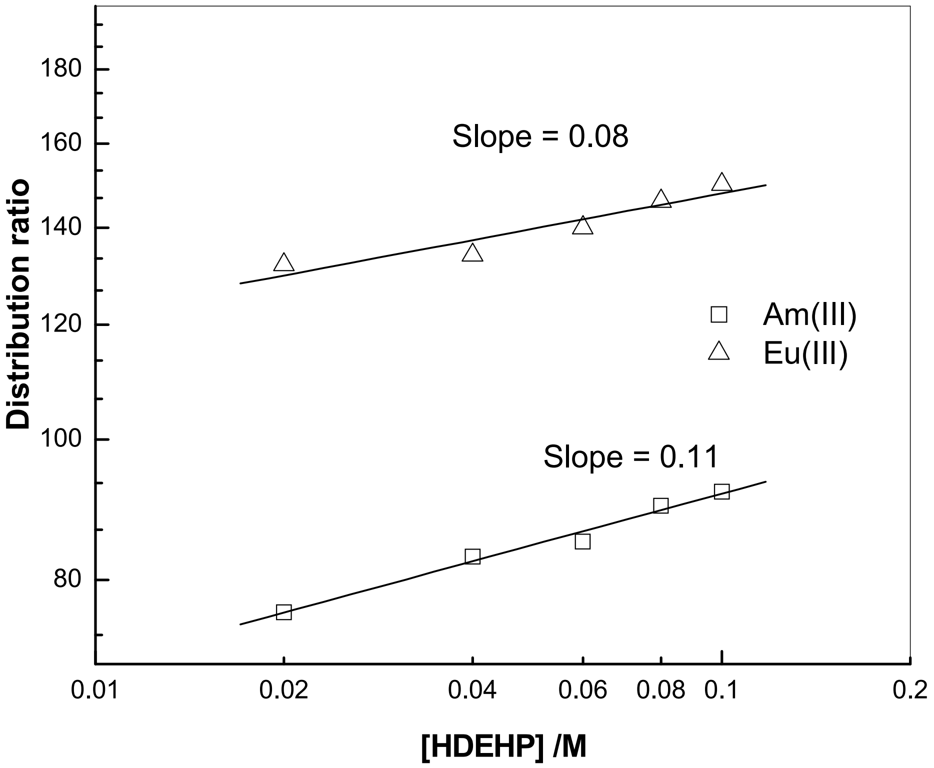

Figure 5.6. Influence of HDEHP concentration on distribution ratio of Am(III) and Eu(III) in 0.02 M TODGA - HDEHP at 3 M nitric acid concentration. Organic phase: 0.02 M TODGA - HDEHP/*n*-DD, varying concentration of HDEHP. Aqueous phase: 3 M nitric acid spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracers.

5.2.6. Stripping of Am(III)

The trivalent actinides and lanthanides are extracted along with the lanthanides in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD. Mutual separation of actinides from lanthanides from organic phase is necessary to facilitate transmutation of actinides. The TALSPEAK process developed for the mutual separation of lanthanides and actinides exploits the differential complexing ability of HDEHP present in organic phase and DTPA present in aqueous phase. Therefore, the back extraction of Am(III) from 0.1 M TODGA - 0.25 M HDEHP/*n*-DD phase was attempted using DTPA. The stripping behavior of Am(III) and Eu(III) from loaded organic phase is shown in Table 5.2. This indicates that the back extraction was negligible even after six contacts, when the concentration of DTPA was 0.05 M at pH 3, perhaps due to the release of nitric acid from organic phase. This indicates that the aqueous phase requires phase modifier for mutual separation. Del Cul *et al.* developed a citric acid based TALSPEAK process for the mutual separation of lanthanides and actinides [19]. Citric acid in this process acted as a buffer and to enhance the phase disengagement and separation factor of Am(III) from Eu(III). Therefore, citric acid could be combined with DTPA in the present case also, to study Am(III)-Eu(III) separation from the loaded organic phase.

5.2.7. Effect of citric acid, pH and DTPA during stripping of Am(III)

The effect of citric acid concentration and pH of the aqueous phase on stripping of Eu(III) and Am(III) from the loaded organic phase is shown in Table 5.2. In this experiment, the loaded organic phase was contacted with a fresh aqueous solution of 0.01 M DTPA+citric acid each time. This procedure was repeated up to six contacts. It is observed from Table 5.2 that the stripping of Am(III) and Eu(III) is negligible when the DTPA concentration is 0.01 M. However, the stripping of Am(III) increases with increase of DTPA concentration as DTPA is complexing with the metal ions in aqueous phase. It is observed that the stripping of both the metal ions increases with increase in the concentration of citric acid because the aqueous phase behaves as a better buffer solution in the presence of more citric acid. The stripping pattern for both Am(III) and Eu(III) is similar in six contacts. However, the mutual separation of Am(III) over Eu(III) is difficult because of high complexing power of TODGA.

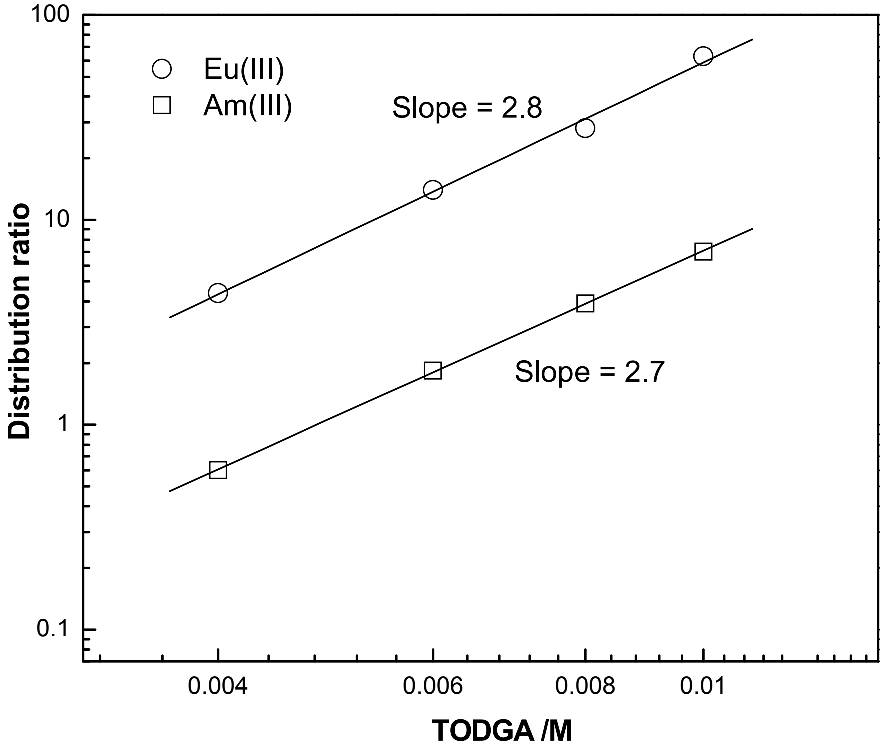

Figure 5.7. Influence of TODGA concentration on distribution ratio of Am(III) and Eu(III) in TODGA - 0.04 M HDEHP at 3 M nitric acid concentration. Organic phase: TODGA - 0.04 M HDEHP/*n*-DD, varying concentrations of TODGA. Aqueous phase: 3 M nitric acid spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracers.

Table 5.2. Stripping of Am(III) and Eu(III) from the loaded organic phase. Extraction of Am(III) and Eu(III) in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD from 3M nitric acid. Stripping formulation was composed of DTPA + citric acid at pH 3.

No of contact	0.01 M DTPA-0.1 M CA		0.05 M DTPA-0.5 M CA		0.05 M DTPA-1 M CA	
	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)
1	0.30	0.50	1.5	0.81	2.60	0.83
2	1.4	0.89	3.1	2.01	6.14	2.41
3	2.2	1.65	5.2	3.37	9.45	3.87
4	3.43	2.14	7.4	4.10	14.78	5.79
5	5.22	2.92	9.1	5.14	18.35	7.16
6	6.22	3.19	11.8	6.01	22.5	10.1

5.3. Studies with TEHDGA- HDEHP solvent

In TODGA - HDEHP system both Am(III) and Eu(III) were synergistically extracted to the organic phase but the mutual separation was very difficult. In order to get mutual separation, the extraction and stripping studies were carried out with a different combination of extractants. TEHDGA, is also a promising candidate for separating the trivalents (An(III) and Ln(III)) from nitric acid medium [7]. So in this study TEHDGA is used as a neutral extractant and the extraction behavior of these metal ions was studied in a combined solvent TEHDGA - HDEHP system. The extraction behavior of Am(III) and Eu(III) in TEHDGA - HDEHP/*n*-DD as well as in a solution of TEHDGA/*n*-DD and HDEHP/*n*-DD was studied as a function of various parameters. The dependence of Am(III) and Eu(III) extraction on TEHDGA, HDEHP were deduced from the slope analysis of the extraction data. The back extraction of Am(III) and Eu(III) from the loaded organic phase was investigated by using various concentrations of stripping reagents composed of DTPA and citric acid (CA) to obtain a suitable aqueous formulation for mutual separation.

5.3.1. Third phase formation studies

The diglycolamide, TEHDGA/*n*-DD, forms third phase with nitric acid and trivalent metal ions (Ln(III) and An(III)) [7]. The formation of third phase is usually prevented by the addition of phase modifiers such as tri-n-butylphosphate (TBP) and dihexyloctanamide (DHOA) etc. to the organic phase [7-9]. The solution of 0.2 M TEHDGA/n-DD forms third phase with 4 M nitric acid as shown in Table 5.3. HDEHP was added to TEHDGA, and the third phase formation was studied. It was observed that the presence of HDEHP in TEHDGA prevented the third phase formation. The acidic extractant, HDEHP was added into TEHDGA, for the selective stripping of actinides. So, it is desirable to employ the required concentration of HDEHP in the solvent formulation. Therefore, studies were carried out to optimize the concentration of HDEHP required in a solution of 0.1 M TEHDGA - HDEHP/*n*-DD to facilitate the extraction of trivalents (Ln(III) and An(III)) from HLLW without leading to third phase formation. Table 5.3 shows the third phase formation behavior of nitric acid and Nd(III) in a solution of 0.1 M TEHDGA - HDEHP/*n*-DD. The concentration of HDEHP was increased from 0.1 M to 0.25 M. When 0.1 M HDEHP was added to 0.1 M TEHDGA, the third phase was observed at nitric acid concentration above 8 M as well as with 70 mM Nd(III) solution in 4 M nitric acid. However, when the concentration of HDEHP was increased to 0.25 M, the third phase was not observed in 8 M nitric acid as well as 70 mM Nd(III) solution. Therefore, for all subsequent studies the solvent formulation composed of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was employed.

Table 5.3. Third phase formation behavior of nitric acid and Nd(III) in 0.1 M TEHDGA - HDEHP/*n*-DD. T = 298 K.

Solvent composition	Third phase formation with	
	$[HNO_3]_{ini}$ /M	70 mM Nd in 4 M HNO_3
0.2 M TEHDGA/*n*-DD	4 M	Yes
0.1 M TEHDGA-0.1 M HDEHP/*n*-DD	Above 8 M	Yes
0.1 M TEHDGA-0.2 M HDEHP/*n*-DD	Above 8 M	Yes but insignificant
0.1 M TEHDGA-0.25 M HDEHP/*n*-DD	Above 10 M	No

5.3.2. Extraction studies

The extraction behavior of Am(III) in a solution of 0.1 M TEHDGA/*n*-DD or 0.25 M HDEHP/*n*-DD is shown in Figure 5.8. It is observed that the distribution ratio of Am(III) in HDEHP/*n*-DD decreases, and that in TEHDGA/*n*-DD increases with increase in the concentration of nitric acid. Linear regression of the extraction data obtained in case of 0.25 M HDEHP/*n*-DD results in a slope of -3. This indicates the transfer of three equivalents of H^+ to the aqueous phase during the extraction of Am(III). Similar result is also observed for the extraction of Eu(III) in 0.1 M TEHDGA/*n*-DD and 0.25 M HDEHP/*n*-DD as shown in Figure

5.9. However, the distribution ratios of Eu(III) are always higher than the values obtained for Am(III) at all acidities.

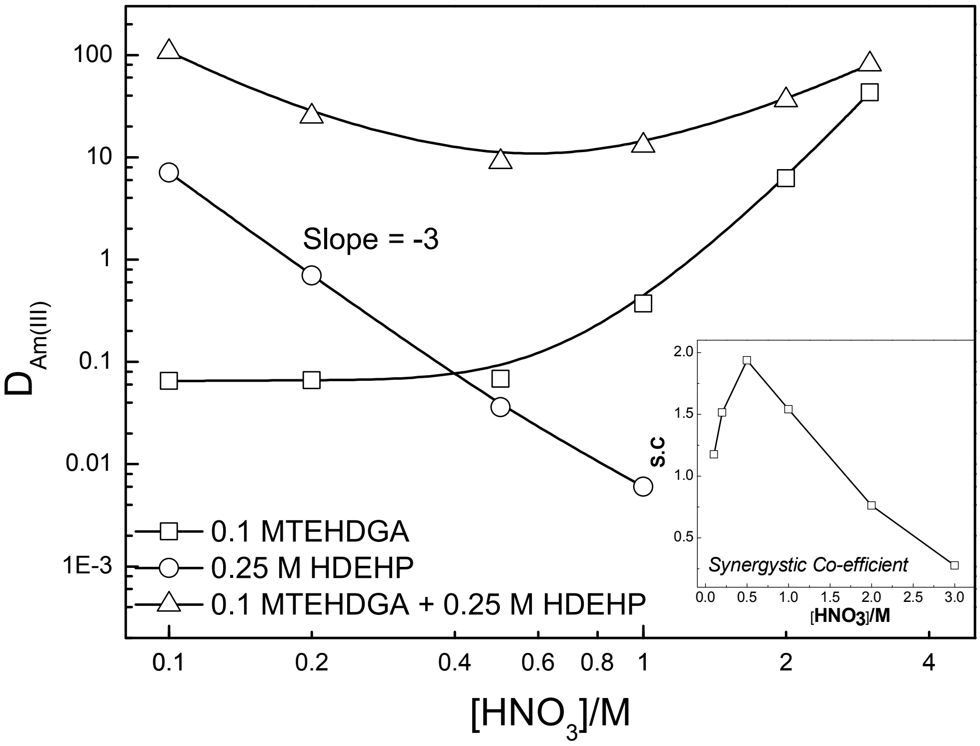

Figure 5.8. Variation in the distribution ratio of Am(III) and synergystic co-efficient as a function of nitric acid concentration. Organic phase: 0.1 M TEHDGA/*n*-DD or 0.25 M HDEHP/*n*-DD or 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: Nitric acid spiked with ^{241}Am(III) tracer.

The distribution ratio of Am(III) and synergistic co-efficient (S.C.) in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD is also shown in Figure 5.8. It was observed that the distribution ratio of Am(III) in this case is much higher than that observed in individual solutions at all acidities. This indicates that Am(III) is synergistically extracted by the mixture of HDEHP and TEHDGA. The synergistic co-efficient is more at 0.5 M indicates more synergism at 0.5 M nitric acid. A similar synergistic extraction of Eu(III) is also observed in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD, as shown in Figure 5.9. Such synergistic extraction of metal ions by neutral and acidic extractants has been reported by others [1, 4]. Synergism observed for the extraction of Am(III) and Eu(III) requires detail understanding of the mechanism of extraction. The mechanism of extraction is studied at low as well as high nitric acid concentrations.

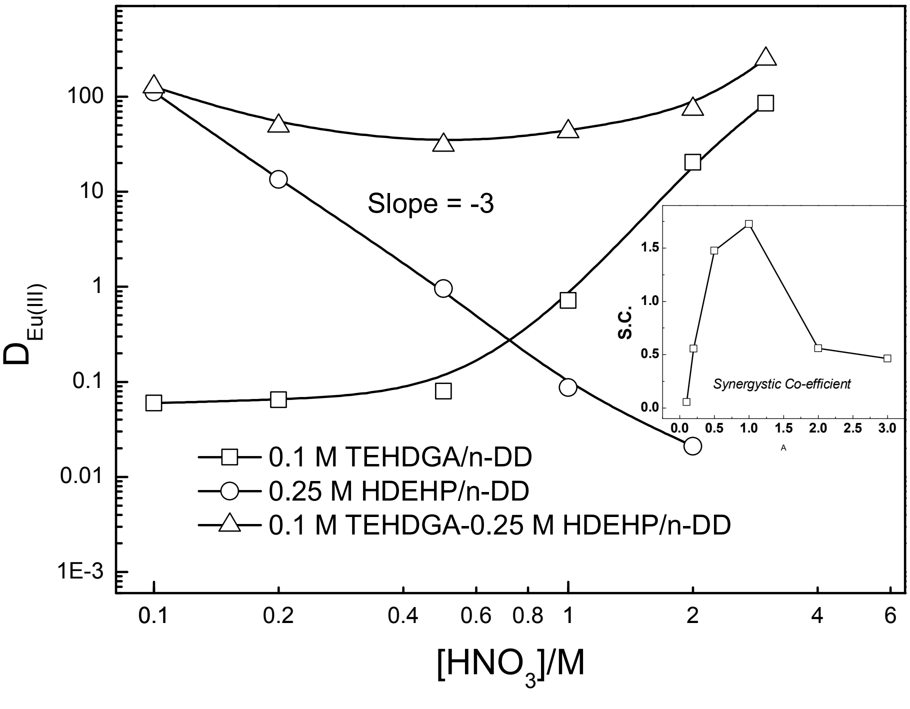

Figure 5.9. Variation in the distribution ratio of Eu(III) and synergistic co-efficient as a function of nitric acid concentration. Organic phase: 0.1 M TEHDGA/*n*-DD or 0.25 M HDEHP/*n*-DD or 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: Nitric acid spiked with $^{(152+154)}$Eu(III) tracer

5.3.3. Extraction at 0.5 M nitric acid

The extraction of Am(III) and Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was studied at 0.5 M nitric acid. The variation in the distribution ratio of Am(III) and Eu(III) as a function of nitric acid concentration, ranging from 0.1 M to 0.5 M, is shown in Figures 5.8 and 5.9 respectively. It is observed that the distribution ratio in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD decreases with increase in concentration of nitric acid from 0.1 M to 0.5 M. This shows that the extraction of Am(III) and Eu(III) in this acid range is predominantly governed by the ion exchange property of HDEHP, rather than TEHDGA. At 0.5 M nitric acid concentration, the effect of HDEHP concentration in a solution of 0.1 M TEHDGA - HDEHP/*n*-DD, on the distribution ratio of Am(III) and Eu(III) was studied and the results are shown in Figure 5.10. It is observed that the distribution ratio of both metal ions increases with increase in the concentration of HDEHP. Linear regression of the extraction data results in a slope of 1.3. These results confirm that 1-2 molecule of HDEHP could be involved in the extraction of trivalents at 0.5 M nitric acid. However, Takayama *et al.* reported a slope of 3 for the extraction of Am(III) and Eu(III) in HDEHP/benzene under similar conditions [22]. Comparing a slope of 3 obtained in the absence of TEHDGA [22] with a slope of 1.3 obtained in the present study indicates that the dependence of HDEHP concentration on extraction decreases in the presence of TEHDGA.

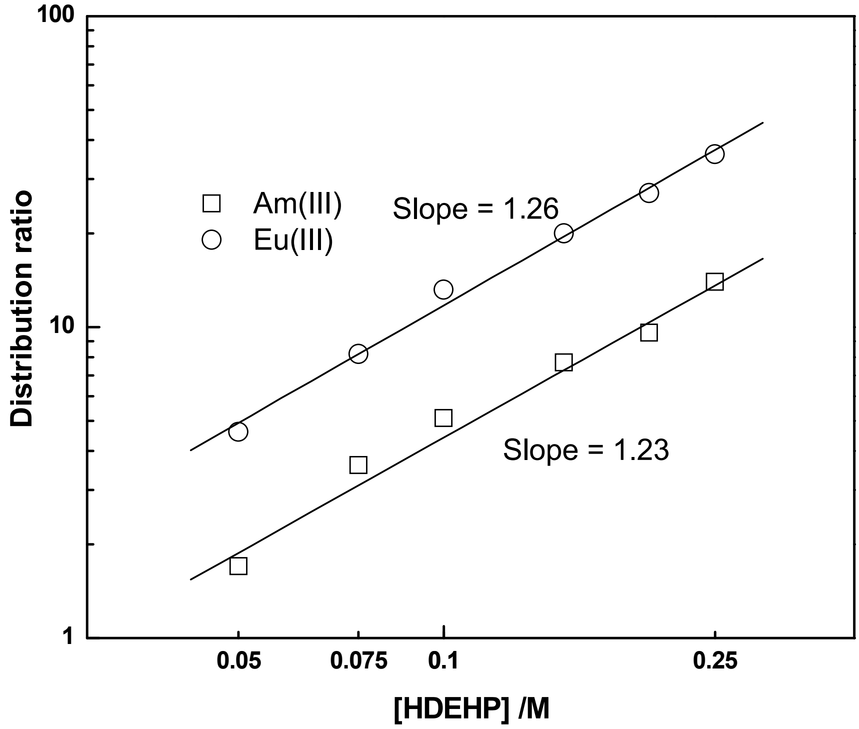

Figure 5.10. Variation in the distribution ratio of Am(III) and Eu(III) as a function of HDEHP concentration. Organic phase: 0.1 M TEHDGA - HDEHP/*n*-DD. Aqueous phase: 0.5 M Nitric acid spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer.

The variation in the distribution ratio of Am(III) and Eu(III) as a function of sodium nitrate concentration at a fixed aqueous phase nitric acid concentration of 0.5 M is shown in Figure 5.11. It is observed that the distribution ratio increases with increase in the concentration of nitrate ion. Linear regression analysis of the extraction data results in a slope of 1, indicating the dependence of one molecule of nitrate ion for extraction. Similarly, the variation in the distribution ratio of Am(III) and Eu(III) with TEHDGA concentration at 0.5 M nitric acid, shown in Figure 5.12, indicate that the dependence of one molecule of TEHDGA for extraction. All the above observations indicate the involvement of HDEHP, TEHDGA and nitrate ion for extraction at 0.5 M nitric acid.

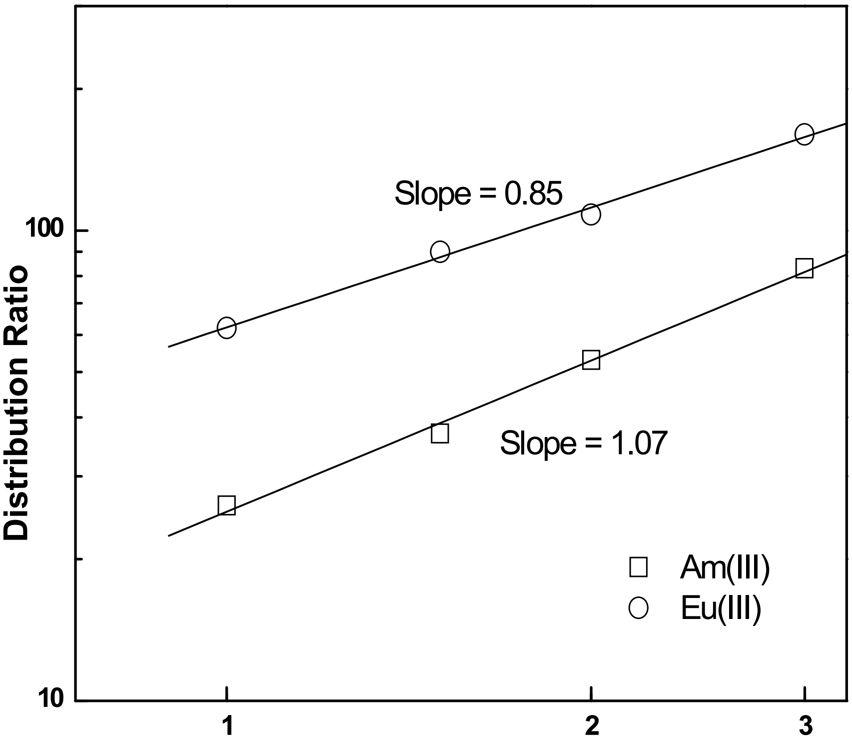

Figure 5.11. Variation in the distribution ratio of Am(III) and Eu(III) as a function of nitrate ion concentration. Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: $NaNO_3$ present in 0.5 M nitric acid spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer.

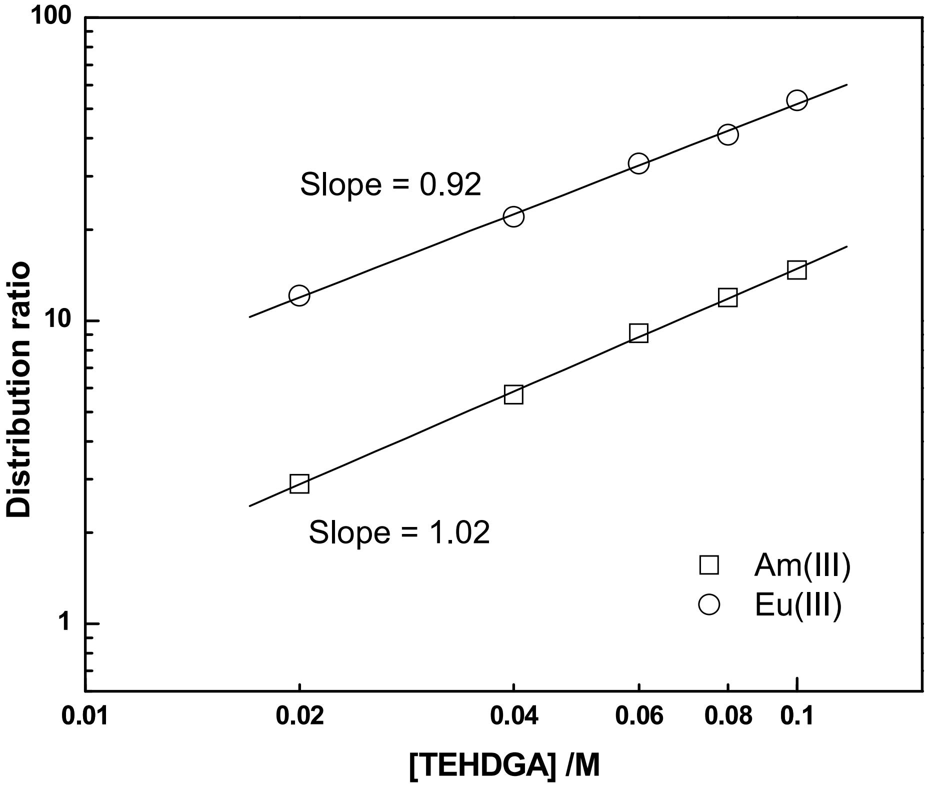

Figure 5.12. Variation in the distribution ratio of Am(III) and Eu(III) as a function of TEHDGA concentration. Organic phase: TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: 0.5 M Nitric acid spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer.

5.3.4. Extraction at 3 M nitric acid

Above 0.5 M nitric acid, the distribution ratio of Am(III) and Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD increases with increase in the concentration of nitric acid as shown in Figure 5.8 and 5.9. The extraction of Am(III) and Eu(III) is governed predominantly by TEHDGA in higher acid range due to the similarity in the extraction trend observed in 0.1 M TEHDGA/*n*-DD. Therefore, the effect of TEHDGA concentration on the extraction of these metal ions at 3 M nitric acid was studied and the results are shown in Figure 5.13. It is observed that the distribution ratio of Am(III) and Eu(III) increases with increase in the concentration of TEHDGA, resulting in a slope of 1.4 for Am(III) and 1.2 for Eu(III). These values are much lower than the value of 3 reported for the extraction of these metal ions in 0.1 M TEHDGA/*n*-DD solution [23]. The effect of HDEHP concentration on the extraction of Am(III) and Eu(III) at 3 M nitric acid was studied and the results are shown in Figure 5.14. It is observed that the distribution ratio of both metal ions increase with increase in concentration of HDEHP. Linear regression analysis of the extraction data results in the slope of 0.28 for Am(III) and 0.78 for Eu(III). These results confirm the involvement of HDEHP for extraction even at 3 M nitric acid. All the above results indicate the synergistic extraction of Am(III) and Eu(III) in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. The dependence of HDEHP concentration on extraction decreases and that of TEHDGA and nitrate ion concentration increases with increase in the concentration of nitric acid.

The above results indicate that the extraction of trivalent metal ions is predominantly governed by HDEHP at low nitric acid medium (<0.5 M). The nitrate ion and TEHDGA also participate in the extraction at lower acidity to some extent due to synergism. The dependence of HDEHP on extraction decreases and that on TEHDGA and nitrate ion increase with increase in the concentration of nitric acid. The present study presumes that the contribution of TEHDGA at low acidity was negligible and that of HDEHP was negligible at higher acidity. Nevertheless, the study confirmed the involvement of both HDEHP and TEHDGA for the extraction of trivalent metal ions in the acidity range investigated in the present study. A similar mechanism was also proposed by Muller *et al.* for the extraction of trivalent lanthanides and actinides in ethoxymalonamide (DMDOHEMA) + HDEHP system [24]. The authors reported the formation of $Eu(DMDOHEMA)_x(DEHP)_2NO_3$ ($1 \leq x \leq 3$) in extracted phase at 3 M NO_3^- ions in aqueous phase and confirmed by ESI mass spectrum. Gannaz *et al.* studied the extraction of Ln(III) and Am(III) in a mixture of DMDOHEMA and dialkylphosphoric acid (HDHP) and suggested a similar mechanism for extraction [4]. However at very low acidities, where the concentration of nitrate was less, Muller *et al.* also proposed the involvement of more HDEHP molecules for charge neutralization of metal ions and proposed complexes such as Eu(DMDOHEMA)$_x$(DEHP)$_3$ ($1 \le x \le 3$) etc. for metal ion extraction [24].

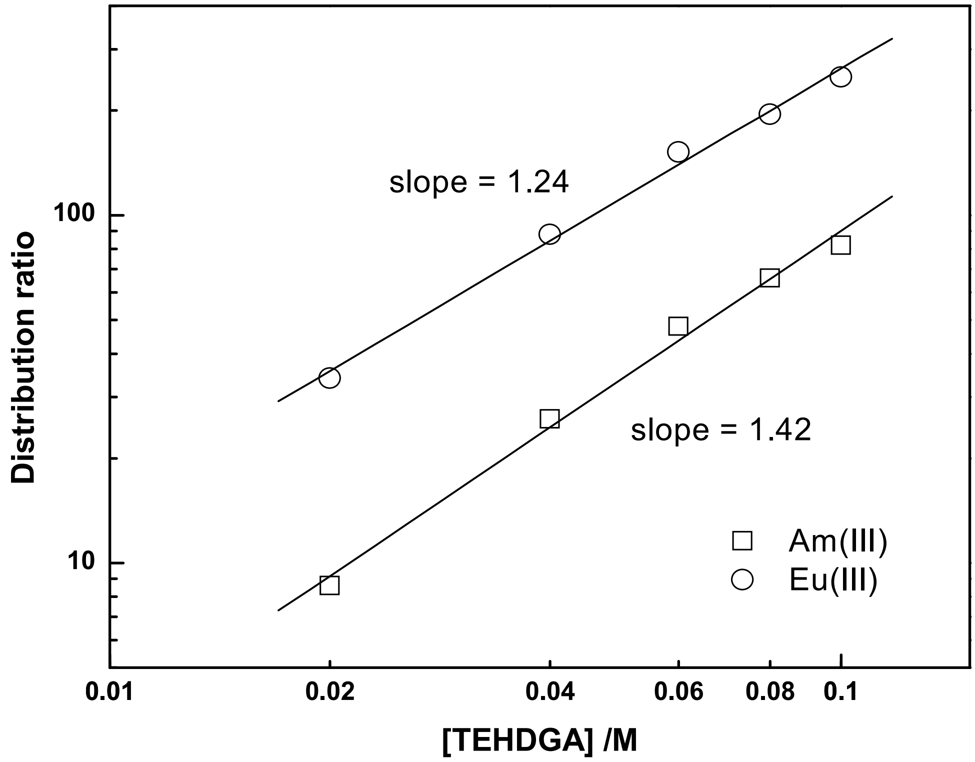

Figure 5.13. Variation in the distribution ratio of Am(III) and Eu(III) as a function of TEHDGA concentration. Organic phase: TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: 3 M Nitric acid spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer.

Based on the above observations, the mechanism of M(III) extraction in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD at various nitric acid concentration can be represented by the following equation 5.5.

$$M^{3+} + (3-x)NO_3^- + xHDEHP + (3-y)TEHDGA \Leftrightarrow M(NO_3)_{(3-x)}(DEHP)_x(TEHDGA)_{(3-y)} + xH^+$$
$$X = 0.3-2,\ Y = 1-2 \qquad (5.5)$$

In this equation the magnitude of x and y increases with decrease in the concentration of nitric acid. At 0.5 M nitric acid, the extraction of trivalent metal ion is predominantly governed by HDEHP molecules. However, one molecule of TEHDGA and one nitrate ion is also involved due to the observation of synergism. The dependence of HDEHP for extraction decreases and that of TODGA and nitrate ion increases with increase in the concentration of nitric acid. Comparable extraction of trivalents observed at higher acidities is essentially due to the dominant role of TEHDGA for participation in the extraction. Moreover, the contribution of HDEHP (~ 0.78) is low at higher acidities. Therefore, the extraction behavior observed in the combined solvent is similar to that observed for TEHDGA at higher acidities. Nevertheless, the studies confirmed that extraction is contributed by both HDEHP and TEHDGA at all acidities investigated in the present study.

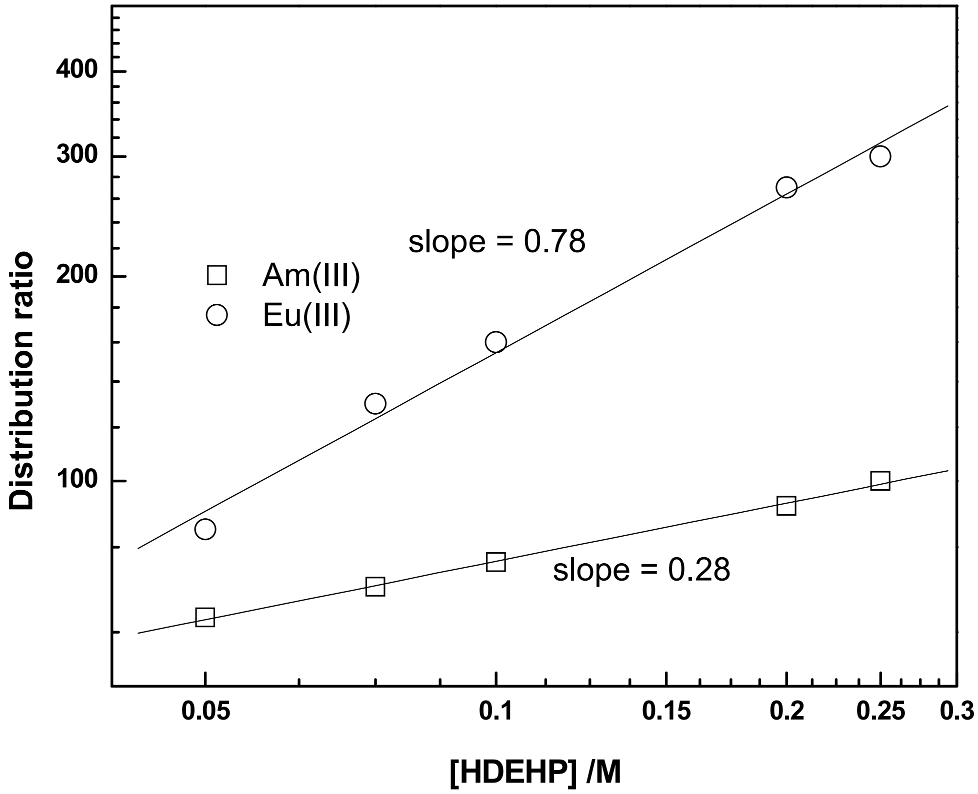

Figure 5.14. Variation in the distribution ratio of Am(III) and Eu(III) as a function of HDEHP concentration. Organic phase: 0.1 M TEHDGA - HDEHP/*n*-DD. Aqueous phase: 3 M Nitric acid spiked with ^{241}Am(III) or $^{(152+154)}$Eu(III) tracer.

5.4. Conclusions

The extraction behavior of Am(III) and Eu(III) in a solution of 0.1 M TODGA - 0.25 M HDEHP/*n*-DD and 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was studied as a function of various parameters. In case of 0.1 M TODGA - 0.25 M HDEHP/*n*-DD, the distribution ratio of these metal ions obtained in this solution was compared with those obtained in individual solutions. Synergistic extraction of Am(III) and Eu(III) was observed at acidities lower in the combined solvent, whereas, the distribution ratios were comparable with that of TODGA at higher acidities. The dependence of HDEHP decreased and that of TODGA increased with increase in the concentration of nitric acid. Slope analysis of the extraction data indicates that extraction is predominantly governed by HDEHP at low nitric acid concentrations and by TODGA at higher acidities. The studies confirmed the involvement of both the TODGA and HDEHP at all acidities investigated in the present study. The mutual separation is difficult in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD because of the stripping pattern for both metal ions are similar.

The extraction behavior of Am(III) and Eu(III) in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD from 0.1 M to 3 M nitric acid medium was studied to examine the feasibility of using the combined extractants for separating minor actinides from HLLW. Extraction behavior of these metal ions in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was compared with individual solvents, namely 0.1 M TEHDGA/*n*-DD and 0.25 M HDEHP/*n*-DD. The synergistic extraction observed in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD solvent formulation indicated the involvement of TEHDGA and HDEHP for extracting Am(III) and Eu(III) from nitric acid medium. The dependence of extraction of Am(III) and Eu(III) on HDEHP concentration decreased and that on TEHDGA and nitrate ion concentration increased with increase in the concentration of nitric acid in aqueous phase.

5.5. References

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Chapter 6: Demonstration of minor actinide partitioning in mixer-settler using tetra-2-ethylhexyl diglycolamide - di-2-ethylhexyl phosphoric acid solvent

6.1. Introduction

The synergistic extraction behavior of Am(III) and Eu(III) in a single-cycle process using 0.1 M TODGA - 0.25 M HDEHP/*n*-DD and 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD as solvent from nitric acid medium were studied in details [1,2]. When partitioning of minor actinide is to be demonstrated in plant scale using this solvent, then solvent comes in contact with actual High Level-Liquid Waste (HLLW). However, the real HLLW contains significant quantities of other fission products in addition to Eu(III) and other lanthanides. The composition of Fast Reactor Simulated High-Level Liquid Waste (FR-SHLLW) is shown in Table 2.1[3]. It is observed that the concentration of Am(III) is very small in comparison to chemically similar lanthanides. Among the lanthanides, the concentrations of Nd(III), La(III), Ce(III), Pr(III) are significant. In addition, the concentrations of Zr(IV), Fe(III), Mo(VI) are also large. Therefore, it is necessary to understand the extraction behavior of Am(III) and other fission products present in HLLW using 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD as solvent.

In view of this, the present chapter deals with the extraction and stripping behavior of various metal ions present in FR-SHLLW using the solvent composed of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. The distribution ratio of metal ions present in FR-SHLLW was measured and the number of stages needed for extraction and stripping of Am(III) was optimized. Based on these results, the counter-current run was performed in a 16-stage mixer-settler. The results obtained from these studies are reported in this chapter.

6.2. Extraction from FR-SHLLW

The distribution ratios of various metal ions present in FR-SHLLW using 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD are given in Table 6.1. It is observed that the distribution ratio of Am(III), lanthanides and fission products such as Zr(IV), Y(III), and Mo(VI) are higher than the distribution ratios observed for other metal ions. The distribution ratios of the trivalent actinides and lanthanides range from 2.5 to 54. This indicates that trivalent actinide and lanthanides are quantitatively extracted from FR-SHLLW by the solvent in a few contacts. Along with the trivalent lanthanides, some fission products such as Zr(IV), Y(III), and Mo(VI) also show higher distribution ratio. Zhu *et al.* reported a correlation between the distribution ratio of various metal ions in diglycolamide, TODGA, and ionic radii of metal ions [4]. The distribution ratio was reported to increase from 10^{-2} to >200 with increase of ionic radius from 60 pm to 100 pm. A maximum distribution ratio was observed for the metal ions having ionic radii 80 pm to 100 pm. Since the ionic radii of metal ions discussed above namely Am(III), Ln(III), Y(III) and Zr(IV) are of the order 80 - 100 pm. These metal ions are easily extracted by the diglycolamide from nitric acid medium. Therefore, distribution ratio observed for Am(III), Ln(III), Y(III) and Zr(IV) metal ions are higher than the other metal ions present in FR-SHLLW.

6.3. Elimination of unwanted metal ions

The distribution ratios of Zr(IV), Y(III), Pd(II) and Mo(VI) metal ions are 73, 47, 0.78 and 26 respectively from FR-SHLLW using 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD as solvent as shown in Table 6.1. This indicates the extraction of Zr(IV), Y(III), Pd(II) and Mo(VI) in addition to trivalent actinides and lanthandes to the solvent phase. The extraction of these unwanted fission products may pose some complications during stripping and subsequent lanthanide-actinide separations. Therefore, it is desirable to eliminate or minimize

Table 6.1. Distribution ratios of metal ions present in simulated high-level liquid waste with and without complexing agents
Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD, Aqueous phase: FR-SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer in the presence of complexing agent in 3 M nitric acid. Organic/Aqueous phase ratio = 1 Temperature = 298 K.

Metal ion	Distribution ratio (D_M)						
	Without reagent	In the presence of reagent					
		0.2 M oxalic acid	0.05 M HEDTA	0.05 M CyDTA	0.2 M oxalic acid + 0.05 M HEDTA	0.2 M oxalic acid + 0.05 M CyDTA	0.2 M oxalic acid + 0.05 M HEDTA + 0.05 CyDTA
La(III)	2.5	2.1	2.1	3.3	2.8	2.1	1.9
Ce(III)	6.1	4.6	3.5	4.2	5.5	4.5	3.5
Pr(III)	12	8	9	12	11	8.1	7.4
Nd(III)	20	8	8	20	17	10	7.4
Sm(III)	54	43	44	53	57	44	38
Eu(III)	25	21	23	24	24	25	26
Gd(III)	39	33	36	38	32	31	30
Dy(III)	15	14	12	12	12	14	12
Y(III)	47	51	45	42	41	51	50
Mo(VI)	26	1.6	34	54	0.88	1.5	1.3
Fe(III)	1.2	1.3	1.1	1.3	1.3	1.3	1.4
Cr(VI)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Te(VI)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Cd(II)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ni(II)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Sr(II)	0.09	0.06	0.03	0.14	0.07	0.02	0.03
Ba(II)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ru(III)	0.07	0.06	0.02	0.08	0.04	0.05	0.01
Pd(II)	0.78	0.26	0.02	0.04	0.01	0.06	0.01
Zr(IV)	73	70	93	0.01	61	65	56
Rh(III)	0.09	0.10	0.07	0.13	0.09	0.12	0.10
Cs(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Rb(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
^{241}Am(III)	16	15	14	15	15	14	14

the extraction of these unwanted metal ions from HLLW without affecting the extraction of trivalent lanthanides and actinides. Several authors have maneuvered this problem by adding complexing agents to FR-SHLLW, and eliminated the extraction of Zr(IV) [5, 6]. Therefore, the extraction behavior of the metal ions present in FR-SHLLW in the presence of various complexing agents was studied and the results are shown in Table 6.1. In the presence of 0.2 M oxalic acid in FR-SHLLW, it was observed that the extraction of Mo(VI) was suppressed to a significant extent, whereas the extraction of problematic cations such as Zr(IV), Pd(II) and Fe(III) remains unaffected. The presence of HEDTA in aqueous phase significantly lowers the extraction of palladium. However, the presence of CyDTA in FR-SHLLW, the distribution ratio of Zr(IV) was reduced from 73 to 0.01, indicating the elimination of extraction of Zr(IV). Similarly, CyDTA reduced the extraction of palladium (D=0.04) into the solvent phase. The study thus indicates that by combining oxalic acid and CyDTA, the extraction of Zr(IV), Pd(II) and Mo(VI) could be minimized. Therefore, the extraction behavior of metal ions from FR-SHLLW in the presence of these combined complexing agents was studied and the results are also shown in Table 6.1. It is observed that there was no advantage of combining the CyDTA and oxalic acid complexing agents to FR-SHLLW. The effect of CyDTA is nullified in the presence of oxalic acid. In view of this, it is desirable to add a single complexing reagent and eliminate the extraction of metal ion that poses more complication than others. Among these problematic metal ions, Zr(IV) and Pd(II) are prone to hydrolysis and pose severe complications during stripping as compared to Mo(VI) [7]. Therefore, it is desirable to retain Zr(IV) and Pd(II) in aqueous phase and permit the extraction of Mo(VI), which is unlikely to cause much problems. Thus, it was decided to add CyDTA in FR-SHLLW for the successive studies.

Table 6.2. Stripping of Am(III) and Eu(III) from the loaded organic phase. Extraction of Am(III) and Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/n-DD from 3M nitric acid. Stripping formulation was composed of 0.01 M DTPA + citric acid at different pH.

Number of contact	pH 1.5				pH 3	
	0.025 M CA		0.1 M CA		0.1 M CA	
	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)
1	0.56	0.45	0.5	0.2	2.3	0.8
2	1.1	0.7	1.1	0.5	4.6	1.2
3	1.6	0.9	1.6	0.84	6.4	1.9
4	2.2	1.3	2.3	1.1	8.7	2.1
5	2.7	1.7	3.0	1.5	11	2.9
6	3.1	2.6	3.7	1.9	14	3.9

6.4. Batch Stripping studies of Am(III) and Eu(III)

The extraction of trivalent actinides from FR-HLLW in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD results in co-extraction of lanthanides. Mutual separation of these metal ions from organic phase is necessary to facilitate transmutation of actinides. The back extraction of Am(III) and Eu(III) from 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD phase was attempted using DTPA. However, the back extraction was found to be negligible even after 6 contacts, when the concentration of DTPA was 0.01 M at pH 3. This indicated that the aqueous phase required phase modifier for mutual separation. As discussed previously, citric acid was added to the aqueous phase which acted as a buffer and also enhanced the phase disengagement and separation factor of Am(III) from Eu(III). Therefore, citric acid was combined with DTPA in the present case, for studying the Am(III) - Eu(III) separation from the loaded organic phase.

6.5. Effect of citric acid, pH and DTPA during stripping of Am(III)

The effect of citric acid concentration and pH of the aqueous phase on stripping of Eu(III) and Am(III) from the loaded organic phase is shown in Table 6.2. In this experiment, the loaded organic was contacted with a fresh aqueous solution of 0.01 M DTPA+citric acid each time, after equilibration aqueous phase was removed and fresh aqueous solution was added. This procedure was repeated up to six contacts. It can be observed from Table 6.2 that stripping of Am(III) and Eu(III) is negligible (<3%) when the aqueous phase is 0.01 M DTPA+0.1 M CA at pH 1.5. Further increase in pH of the aqueous phase to 3 also did not strip the metal ions significantly. The concentration of DTPA in aqueous phase was increased from 0.01 M to 0.05 M keeping the concentration and pH constant. The stripping of Am(III) and Eu(III) in 0.05 M DTPA + citric acid at pH 3 is shown in Table 6.3. It was observed that the stripping of both the metal ions increases with increase in the concentration of DTPA and citric acid. When 0.05 M DTPA+0.1 M CA at pH 3 was used as stripping agent, the cumulative stripping of Am(III) was 62% along with 7% of Eu(III) in 7 contacts. Here DTPA forms complex selectively with Am(III) in aqueous phase and stripping was more as compared to Eu(III) in 7 contacts. The concentration of citric acid was increased from 0.1 M to 0.05 M, about 85% of Am(III) was stripped from organic phase with the co-stripping of Eu(III) to the extent of 9.2% in seven contacts. The increase in CA in aqueous phase also increasees the stripping of Am(III) due to better buffer capacity. But further increase in the concentration of citric acid to 1M did not increase the stripping of metal ions. Therefore, the aqueous stripping formulation composed of 0.05 M DTPA+0.5 M CA at pH 3 could be proposed for the back extraction of Am(III) from the loaded organic phase. However, this is also accompanied by the co-stripping of Eu(III) (~10%). Nevertheless, in a counter current run, the stripped solution goes for contacting with the organic phase in a mixer-settler. Since Eu(III) exhibits higher distribution ratio than Am(III), the stripped Eu(III) could be extracted by the organic phase in the subsequent contacts. This indicates the possibility of mutual separation of Am(III) from Eu(III) from 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD phase in a single-cycle process.

Table 6.3. Stripping of Am(III) and Eu(III) from the loaded organic phase. Extraction of Am(III) and Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/n-DD from 3M nitric acid. Stripping formulation was composed of 0.05 M DTPA + citric acid at pH 3.

Number of contact	0.1 M CA		0.5 M CA		1 M CA	
	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)	% Am(III)	% Eu(III)
1	15	0.88	15	1.0	16	1.2
2	28	2.1	33	2.2	34	3.3
3	38	3.7	51	3.7	51	4.9
4	46	4.4	62	5.5	63	6.3
5	54	5.1	70	7	71	8.5
6	59	6.2	78	8.5	78	9.9
7	62	7.0	85	9.2	85	10

6.6. Mixer-settler studies - Extraction

For mixer-settler studies, the organic phase was composed of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD and the aqueous phase was composed of FR-SHLLW spiked with $^{(152+154)}$Eu(III) and ^{241}Am(III) tracer and 0.05 M CyDTA. These solutions were passed in a counter-current direction at the flow rate of 4.5 mL/min in a 16-stage mixer-settler. The organic and aqueous phases were assayed for $^{(152+154)}$Eu(III) and ^{241}Am(III) radioactivity and the other metal ions were determined by the analysis of aqueous phase (FR-SHLLW) using ICP-OES. The extraction profile of Am(III) and Eu(III) in a 16-stage mixer-settler in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD is shown in Figure 6.1. In Figure 6.1, number of stages of mixer-settler is plotted against percentage of metal ions in aqueous phase. The FR-SHLLW was passed from the 1st stage to 16th stage and the organic phase was passed in reverse

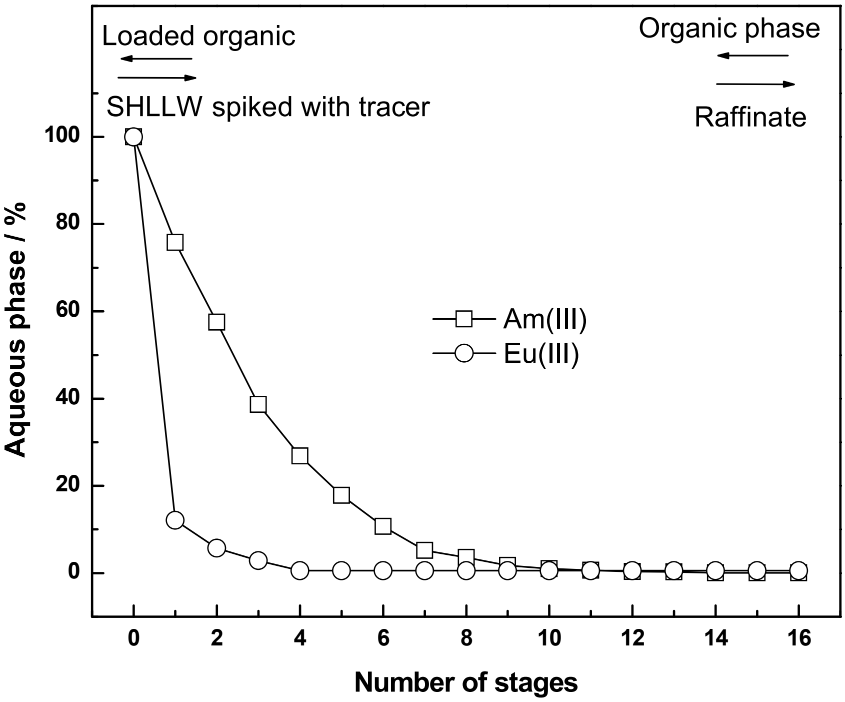

Figure 6.1. Profiles of ^{241}Am(III) and $^{(152+154)}$Eu(III) extraction from FR-SHLLW using a 16-stage mixer-settler. Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. Aqueous phase: FR-SHLLW+0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer.

direction. It is observed from the Figure 6.1 that the concentration of Eu(III) was negligible after 4th stage, indicating that Eu(III) extracted quantitatively to solvent phase in 4 stages. Where as Am(III) exhibiting lower distribution ratio than Eu(III) required about 11 stages for complete extraction. A similar extraction profile was observed for the extraction of other lanthanides from FR-SHLLW. The extraction of lanthanides and other metal ions was determined by the analysis of these metal ions in aqueous raffinate using ICP-OES. The results are shown in Table 6.4. The concentration of trivalent lanthanides and actinides in the aqueous after 16 stage extraction was negligible, indicating that these metal ions were extracted quantitatively to solvent phase. Along with the trivalent lanthanides and actinides some other fission products such as Y(III), Mo(VI) were extracted completely and Fe(III) was also extracted ~80% to the solvent phase. The extraction of Zr(IV) and Pd(II) was negligible due to the presence of CyDTA in FR-SHLLW phase. Other fission products except these metal ions were not extracted because of their low distribution ratio and present in raffinate phase. The gamma spectrum of FR-SHLLW spiked with ^{241}Am(III) and $^{(152+154)}$Eu(III) tracer and the loaded organic is shown in the Figure 6.2. The counts of ^{241}Am(III) and all the peaks corresponding to ^{152}Eu(III) and ^{154}Eu(III) are similar in both the graph. This indicates the metal ions initially present in the FR-SHLLW phase quantitatively loaded in to the organic phase.

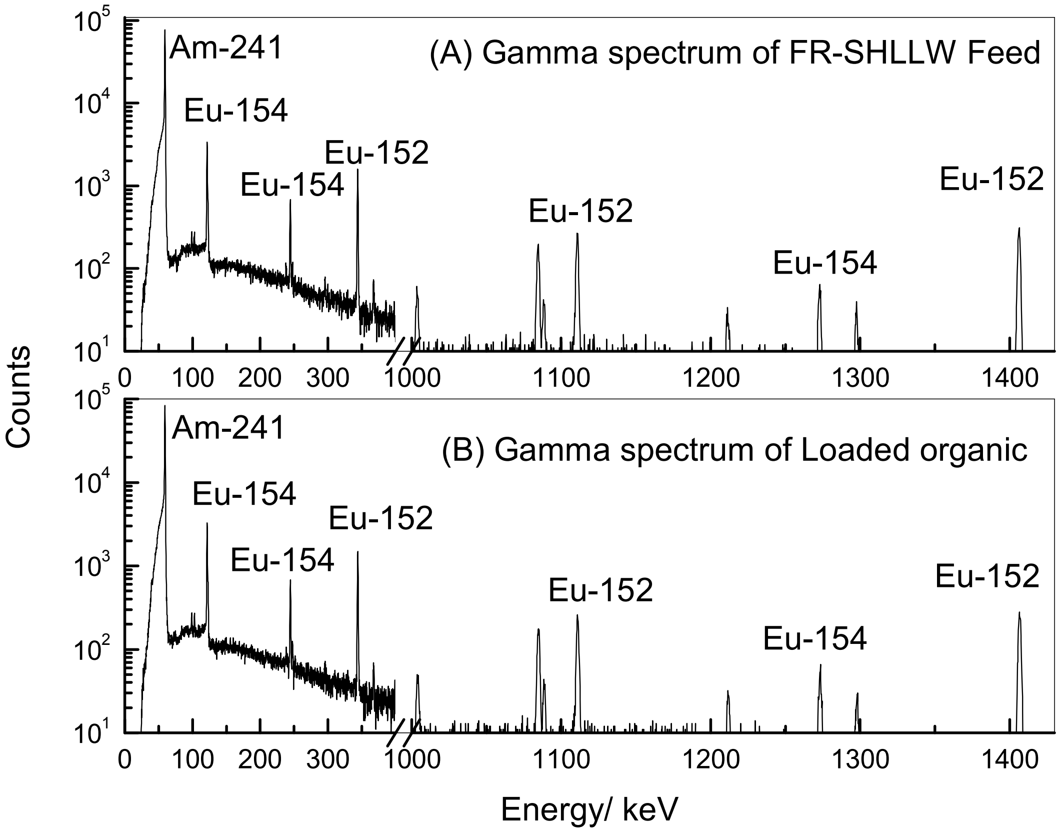

Figure 6.2. (A) Gamma spectrum of FR-SHLLW spiked with ^{241}Am(III) and $^{(152+154)}$Eu(III) . (B) Gamma spectrum of loaded organic phase.

6.7. Mixer-settler studies - Stripping

The recovery of Am(III) from the loaded organic phase was carried out by using an aqueous formulation, 0.05 M DTPA+0.5 M CA at pH 3, developed for stripping of Am(III) from other lanthanides present in organic phase. The stripping profile of Am(III) and Eu(III) in a 16-stage mixer-settler is shown in Figure 6.3. The loaded organic phase was passed from the 16th stage to 1st stage and the stripping solution was passed from the 1st stage to 16th stage. At the 16th stage, the loaded organic makes a first contact with aqueous stripping solution. Therefore, significant amount of Am(III) is back extracted in to aqueous phase at this stage and stripping continues upto 4 more stages (i.e from 16th to 12th stages). The radioactivity of ^{241}Am(III) was negligible thereafter from 12th stage to 1st stage. This indicated that Am(III) present in the loaded organic phase was recovered quantitatively in 4-contacts, in 12th to 16th stages. However, it is necessary to understand the stripping behavior of Eu(III) and other lanthanides during the recovery of Am(III). It was observed from the Figure 6.3 that stripping of Eu(III) from the loaded organic phase was seen in all stages. Moreover, the stripping of Eu(III) increased as the stripping formulation flows from 1st stage to 16th stage. Initially the stripping of Eu(III) was continuous from 1st stage to 12th stage because during this 12 stage loaded solvent phase was not containing Am(III). whereas after 12th stage the stripping of Eu(III) was reduced due to the selective stripping of Am(III) from loaded solvent phase. The stripping of Eu(III) reached a maximum value (~50%) at the 14th stage. From 14th to 16th stage, interestingly, a decrease in stripping was observed, which wass in contrast to Am(III) stripping. A similar behavior was also observed for all other lanthanides and Y(III) (not shown in the Figure for clarity). The decrease in stripping indicated that lanthanides undergo re-extraction in organic phase in 14th to 16th stages, perhaps, due to the decrease of pH in aqueous phase observed in 14th to 16th stages as shown in Figure 6.4.

Table 6.4. The extraction and stripping of metal ions in a 16-stage mixer-settler. Temperature = 298 K Extraction condition: Organic phase - 0.1 M TEHDGA - 0.25 M HDEHP/n-DD. Aqueous phase- FR-SHLLW spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer + 0.05 M CyDTA. Stripping condition: Organic phase – Loaded organic. Aqueous phase – 0.05 M DTPA + 0.5 M CA at pH 3.

Metal ion	% metal ion in aqueous phase after 16-stage extraction	% metal ion in aqueous phase after 16-stage stripping
La(III)	B.D.L	18
Ce(III)	B.D.L	12
Pr(III)	B.D.L	11
Nd(III)	B.D.L	12
Sm(III)	B.D.L	8
Eu(III)	B.D.L	6
Gd(III)	B.D.L	5.6
Dy(III)	B.D.L	3
Y(III)	B.D.L	29
Fe(III)	19	11
Mo(VI)	B.D.L	>99.9
Cr(VI)	>99.9	B.D.L
Te(VI)	>99.9	B.D.L
Cd(II)	>99.9	B.D.L
Ni(II)	>98	B.D.L
Sr(II)	>99.9	B.D.L
Ba(II)	>96	B.D.L
Ru(III)	>99	B.D.L
Pd(II)	>99.9	B.D.L
Zr(IV)	>99.9	B.D.L
Rh(III)	>99.9	B.D.L
Cs(I)	>99.9	B.D.L
Rb(I)	>99.9	B.D.L
Na(I)	>99.9	B.D.L
Ag(I)	>99.9	B.D.L
^{241}Am(III)	B.D.L	>99.9

B.D.L - Below Detection Limit. (<0.1 ppm)

The pH profile of aqueous phase in a 16-stage mixer-settler during stripping is shown in Figure 6.4. The initial pH of the aqueous stripping formulation was kept at 3. The pH of aqueous phase remained at 2.6 to 2.7 in 1st to 13th stages. However, a sharp fall in pH was observed in 14th to 16th stages. This could be due to stripping of nitric acid from loaded organic phase, which contained about 0.1 M nitric acid in organic phase. Therefore, the pH of aqueous phase decreased in 14th-16th stages. Since, the characteristic property of Eu(III) to exhibit higher distribution ratio in TEHDGA - HDEHP/*n*-DD at low pH, re-extraction of Eu(III) was observed in 14th - 16th stages. In view of this, the aqueous phase, which came out of the16th stage contained only 5% of Eu(III) in the Am(III) product.

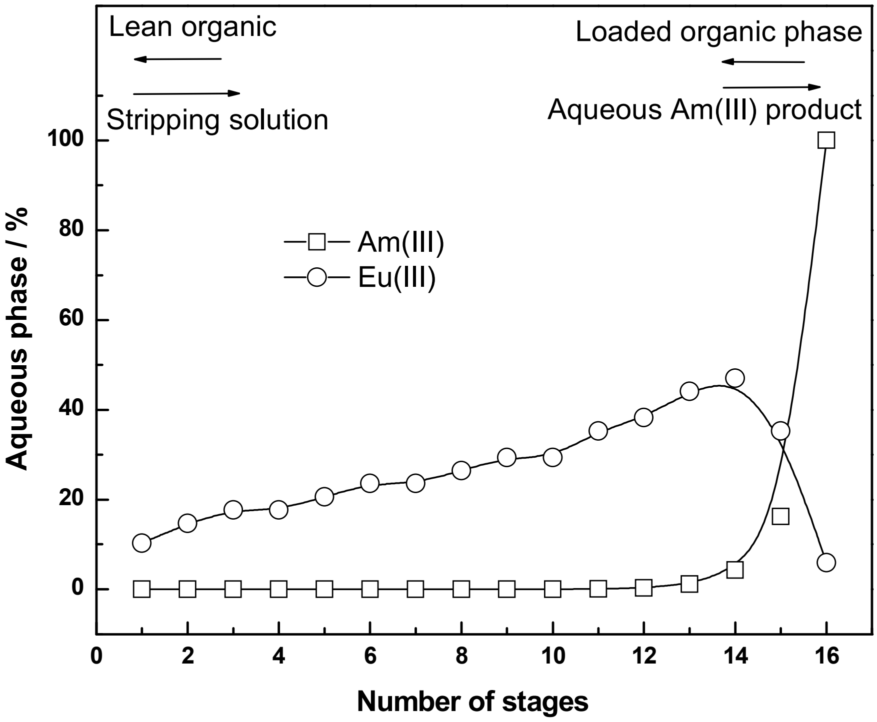

Figure 6.3. Profiles of ^{241}Am(III) and $^{(152+154)}$Eu(III) stripping from the loaded organic phase using a 16-stage mixer-settler. Organic phase: Loaded organic. Aqueous phase: 0.05 M DTPA+0.5 M CA at pH 3.

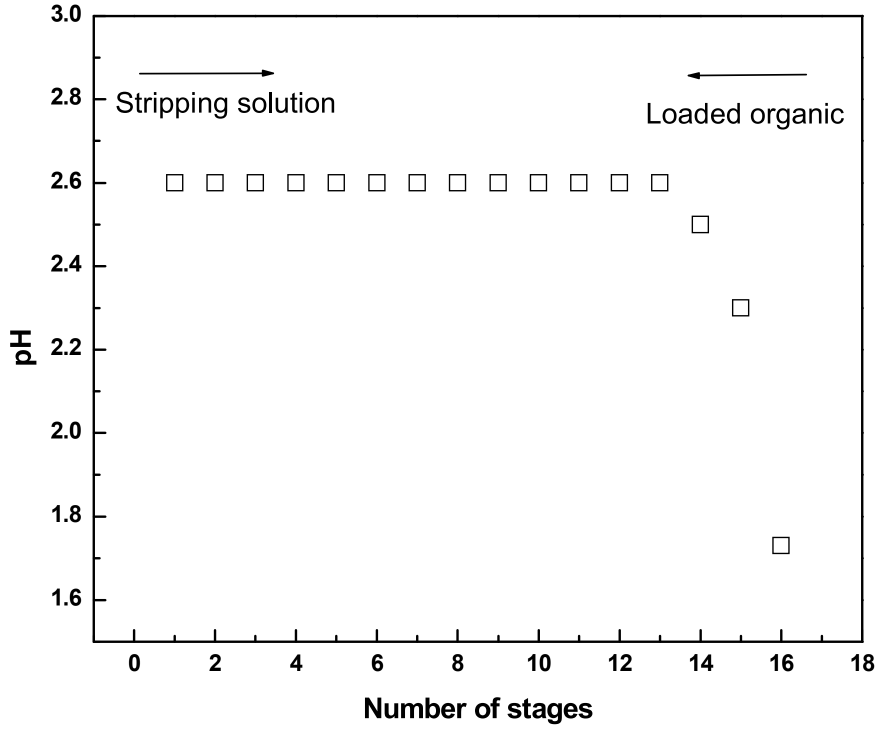

Figure 6.4. pH profile of aqueous phase during the stripping of Am(III) from the loaded organic phase in a 16-stage mixer-settler.

The gamma spectrum of aqueous product and lean organic is shown in the Figure 6.5. The aqueous spectrum indicates that the counts of ^{241}Am(III) is comparable with the loaded organic phase where as the counts of $^{(152+154)}$Eu(III) is less as compared to the counts of the corresponding peaks of loaded organic phase in Figure 6.2. This indicates that Am(III) is selectively stripped to the aqueous phase. But the counts of $^{(152+154)}$Eu(III) of lean organic phase is compared with the loaded organic phase. This indicates that $^{(152+154)}$Eu(III) is retained in the organic phase.

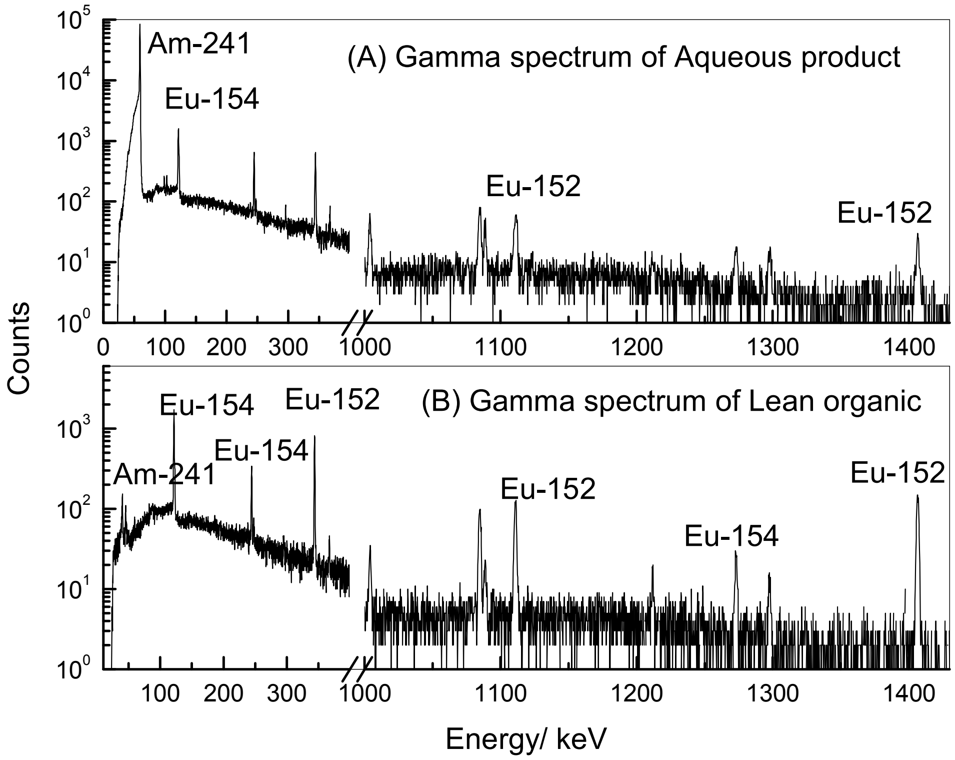

Figure 6.5. (A) Gamma spectrum of aqueous product. (B) Gamma spectrum of lean organic phase.

For clean separation of Am(III) from FR-SHLLW, it is necessary to understand the behavior of other lanthanides and metal ions also in the mixer-settler during stripping. The results on the stripping of lanthanides and other metal ions in aqueous phase (i.e in Am(III) product) are tabulated in Table 6.4. It was observed that stripping of many lanthanides in the Am(III) product was less than 10%. Maximum stripping was observed for the La(III) (~18%) as compared to other lanthanides. Higher stripping of lanthanides (La(III), Ce(III), Pr(III) and Nd(III)) in the Am(III) product could be due to the presence of these lanthanides in high concentration in FR-SHLLW. Since the simulated waste was prepared based on the fast reactor spent nuclear fuel composition corresponding to that seen a higher burn-up of 80,000 MWd/Te. The concentration of the lanthanides is much higher in this kind of waste than those observed in other high-level wastes. The study, thus, indicated the feasibility of separating Am(III) from FR-SHLLW as well as other lanthanides in a single-cycle processing step. However, a marginal contamination of some lanthanides such as La(III), Ce(III), Pr(III) and Nd(III) was observed in Am(III) product stream. The stripping of other lanthanides such as Sm(III), Gd(III) Dy(III) etc. having very large neutron absorption cross section into the Am(III) product was negligible. In addition to this Y(III) and Mo(VI) were stripped to the extent of 29% and >99.9% respectively. However, these elements do not interfere in the transmutation of Am(III) as their neutron absorption cross section is less. Our results, thus confirms the possibility of separating Am(III) directly from fast reactor HLLW in a single-cycle processing step, for facilitating transmutation of americium.

6.8. Separation of lanthanides from lean organic phase

The mixer-settler studies indicated that Am(III) was stripped along with 10% - 18% of lanthanides using 0.05 M DTPA + 0.5 M citric acid at pH 3 from loaded 0.1 M TEHDGA - 0.25 M HDEHP/n-DD solvent. Most of the lanthanides were present in lean organic phase. Retention of these lanthanides in organic phase could cause degradation of solvent, occupational exposure and solvent saturation during successive recycling. In view of this it is necessary to remove these lanthanides. Sasaki *et al.* studied several aqueous soluble DGA for the recovery of trivalent and tetravalent metal ions from loaded organic phase [8]. In this context, the aqueous soluble tetraethyldiglycolamide (TEDGA) was synthesized and the feasibility of back extraction of trivalent lanthanides present in TEHDGA - HDEHP phase was studied.

The distribution of Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was studied at various nitric acid concentration in presence and absence of TEDGA and the results are shown in Figure 6.6. It was noted that the distribution ratio of Eu(III) in the absence of TEDGA decreased with increase in nitric acid concentration and reaches a minimum at 0.5 - 1 M nitric acid followed by an increase upto 3 M nitric acid. But the distribution ratio was always high throughout all acidity. In the presence of TEDGA, the distribution values decreased drastically and reached a minimum value of about 10^{-3} at 0.5-1 M HNO_3. This indicated that the TEDGA present in the aqueous phase complexes Eu(III) efficiently and retained metal ions in the aqueous phase. The distribution ratio of lanthanides (La-Dy) in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD at 1 M nitric acid in presence of various concentration of TEDGA is shown in Table 6.5. The distribution ratio of lanthanides decreased with increase in TEDGA concentration and increased with increase in atomic number of lanthanides.

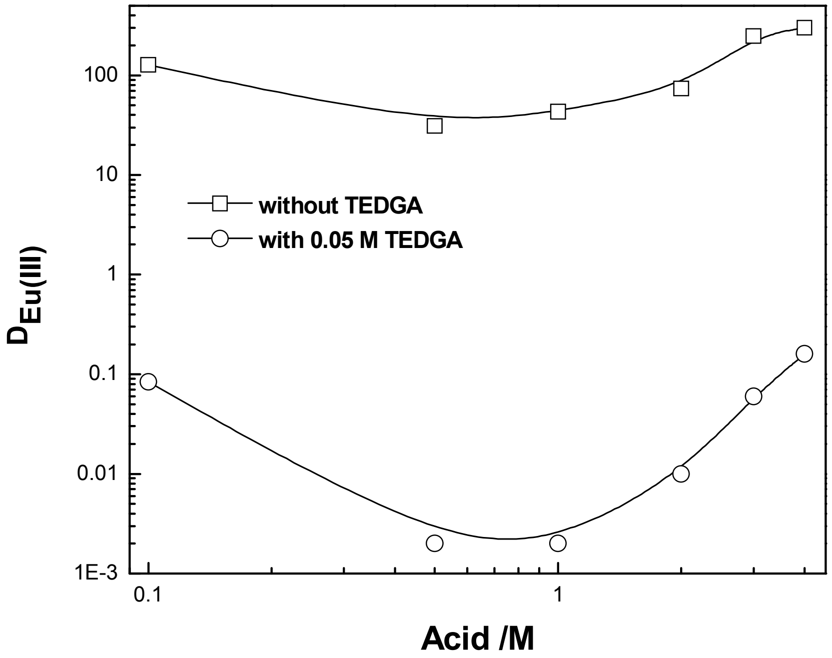

Figure 6.6. Distribution ratio of Eu(III) in the presence and absence of TEDGA at various HNO_3. Organic phase: 0.1M TEHDGA - 0.25M HDEHP/*n*-DD, Aqueous phase: HNO_3 +TEDGA.

Batch experiments were carried out for the back extraction of lanthanides from loaded organic phase using 0.2 M TEDGA at 1 M HNO_3. Initially lanthanides were loaded to 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD organic phase by equilibrating FR-SHLLW solution. After that these elements were stripped by batch equilibration mode using 0.2 M TEDGA in 1M nitric acid. The cumulative stripping of lanthanides from the loaded solvent phase is shown in Figure 6.7. The back extraction of trivalent lanthanides follows in the increasing order of lanthanide series. Lanthanum is having more distribution ratio (D=0.12) in the presence of 0.2 M TEDGA in 1 M nitric acid as compared to other trivalent lanthanides. So lanthanum took maximum number of contact for the back extraction from 0.1 M TEHDGA - 0.25 M HDEHP/n-DD solvent. The results indicated that about 99.9% of lanthanides can be back extracted within 3-4 contacts. Therefore, study indicated the possibility of recovery of lanthanides from the single-cycle organic phase.

Table 6.5. Distribution ratio of lanthanides in the presence and absence of TEDGA. Organic phase: 0.1M TEHDGA - 0.25M HDEHP/*n*-DD, Aqueous phase: 1 M HNO_3 +TEDGA.

Metal ions	Distribution ratio at various TEDGA concentration				
	Nil	0.05 M	0.1 M	0.15 M	0.2 M
La(III)	1.1	0.78	0.39	0.20	0.12
Ce(III)	1.8	0.81	0.28	0.10	0.06
Pr(III)	2.7	0.77	0.17	0.07	0.09
Nd(III)	6.1	1.5	0.71	0.75	0.04
Sm(III)	10	0.65	0.13	0.07	0.06
Eu(III)	18	0.57	0.12	0.08	0.06
Gd(III)	25	0.53	0.17	0.13	0.03
Dy(III)	110	0.29	0.06	0.03	0.04

Based on the work, a flow sheet for minor actinide partitioning in single-cycle process was proposed which is shown in Figure 6.8. In this process, both U(VI) and Pu(IV) can be separated from the spent fuel using PUREX process. HLLW contains all trivalent lanthanides and actinides along with other fission products. The trivalent actinides and lanthanides are extracted using 0.1 M TEHDGA - 0.25 M HDEHP in n-dodecane from HLLW. The extraction of trouble some fission products can be minimized using 0.05 M CyDTA in HLLW solution. CyDTA selectively forms complex with Zr(IV), Pd(II) and reduces the extraction of these metal ions. Other metal ions which were not extracted by the solvent phase remained in the aqueous phase known as high active raffinate. Selective stripping of actinides from the loaded solvent phase could be achieved using 0.05 M DTPA+0.5 M citric acid at pH 3. Most of the lanthanides will be present in the solvent phase after the selective stripping of actinides. In order to reuse same solvent in the successive steps, these lanthanides should be separated from organic phase. These lanthanides can be separated using aqueous soluble tetraethyldiglycolamide (TEDGA).

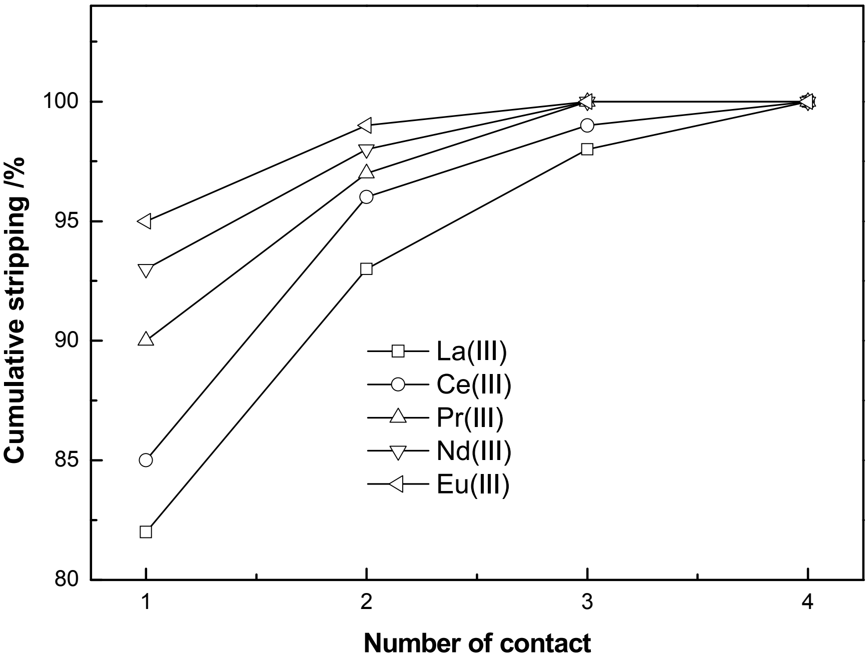

Figure 6.7. Cumulative stripping of lanthanides from the loaded 0.1 M TEHDGA - 0.25 M HDEHP/n-DD using 0.2 M TEDGA in 1 M nitric acid.

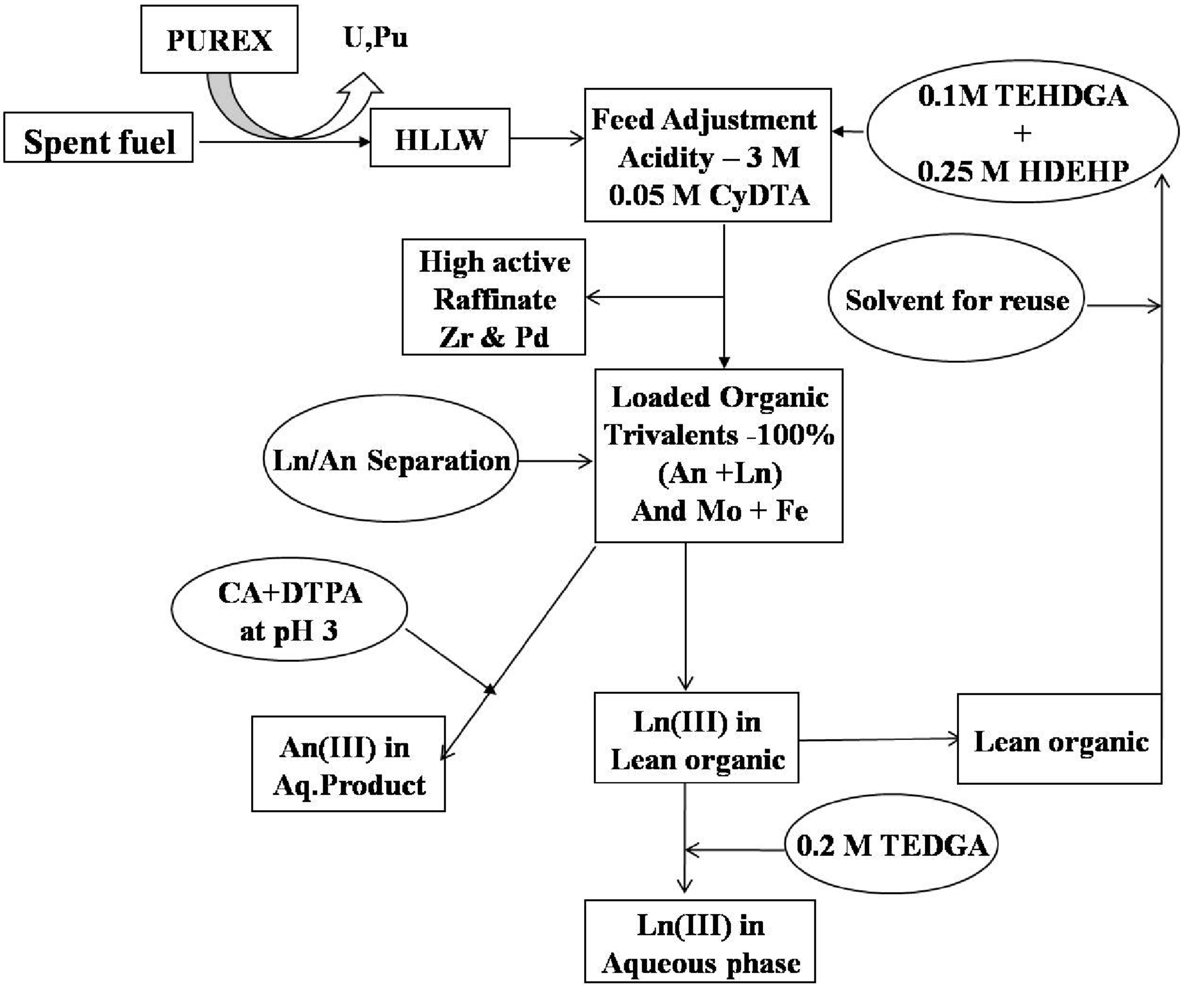

Figure 6.8. Proposed flow sheet for minor actinide partitioning in single-cycle process

6.9. Conclusion

The extraction and stripping behavior of Am(III) and other metal ions present in the fast reactor simulated high-level liquid waste was studied using a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD to develop a single-cycle processing approach for the separation of Am(III) from high-level liquid waste. The extraction of Am(III) in organic phase was accompanied by the co-extraction of lanthanides and other unwanted metals such as Zr(IV), Pd(II), Mo(VI) and Y(III) from FR-SHLLW. Since it was desirable to retain the troublesome metal ions, Zr(IV) and Pd(II), in FR-SHLLW, the aqueous soluble complexing agents CyDTA was added to FR-SHLLW, to eliminate the extraction of Zr(IV) and Pd(II) in organic phase. The selective stripping of Am(III) from the loaded solvent phase was accompanied by 10 % co-stripping of Eu(III) using DTPA and citric acid. The recovery of Am(III) increased with increase in the concentration of DTPA, citric acid and pH. Based on the optimized conditions, a counter-current extraction run was performed to separate Am(III) from FR-SHLLW using a 16-stage mixer-settler. The extraction was found to be accompanied by the co-extraction of chemically similar trivalent lanthanides, Mo(VI), Y(III), and Fe(III) along with Am(III). The lanthanides, Y(III) and Mo(VI) exhibited higher distribution ratio than Am(III) were quantitatively extracted in 4 stages, whereas Am(III) required 11 stages for complete extraction. The stripping of Am(III) from the loaded organic phase was performed by using the aqueous formulation composed of 0.05 M DTPA+0.5 M CA at pH 3. Quantitative recovery of Am(III) was observed in four stages. This was accompanied by the co-stripping of 18% La(III) and about 10% Ce(III), Pr(III),and Nd(III). The stripping of other lanthanides having very large neutron cross section was 5%. The lanthanides present in organic phase can be removed using 0.2 M TEDGA in 1 M nitric acid. The study, thus indicated the feasibility of separating of Am(III) from fast reactor HLLW in a single-cycle process.

6.10. References

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Chapter 7: Radiochemical degradation of tetra-2-ethylhexyl diglycolamide – di-2-ethylhexyl phosphoric acid solvent

7.1. Introduction

Generally, liquid-liquid extraction technique is adopted for the separation of radioactive metal ions from High Level-Liquid Waste in nitric acid medium (HLLW) [1]. It involves mixing of the hydrophobic organic phase with aqueous solution containing the target metal ion for separation. The organic phase, known as the solvent, is usually composed of an extractant diluted in an inert diluent, such as *n*-dodecane. The stability of the solvent towards radiation is one of the concerns when the solvent is proposed for the treatment of radioactive wastes [2]. During the extraction of metal ions from radioactive wastes, the organic phase is exposed to highly energetic, alpha, β, and γ- radiations. The energy associated with these radiations is partially or fully deposited in solvent molecules causing radiolytic degradation of the solvent. These include rupture of chemical bonds, formation of new degradation products etc. The presence of these degradation products alters the physico-chemical, extraction, and stripping properties of the solvent to a significant extent [2]. Therefore, it is very important to understand the radiation stability of the solvent when proposed for the separation of metal ions from radioactive wastes.

The earlier studies indicated that the combined solvent phase *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) and bis(2-ethylhexyl)phosphoric acid (HDEHP) in *n*-dodecane (*n*-DD) can be considered as a promising candidate for single-cycle separation of Am(III) from HLLW [3, 4]. The minor actinide partitioning has been demonstrated using a mixer-settler in single-cycle process using same combined solvent. Therefore, it is necessary to understand the radiolytic stability of the combined solution with respect to gamma radiation.

In view of this, the present chapter deals with evaluation of radiolytic stability of the combined solvent system, TEHDGA - HDEHP/*n*-DD. The solvent was irradiated to various dose levels by γ-radiation and the distribution ratio of various elements present in the FR-SHLLW was measured as a function of absorbed dose. The stripping behavior of Am(III) from organic phase was reported. The results were compared with un-irradiated solvent system.

7.2. Irradiation Studies

All the samples were irradiated under static condition using a ^{60}Co gamma chamber facility which provides a dose rate of 4.4 kGy/h. The dose rate of γ- chamber was calibrated by Fricke dosimetry. The samples were irradiated as follows.

There are four cases considered.

Case 1: Both TEHDGA and HDEHP were irradiated independently to a desired dose level. After irradiation both these extractants were mixed and diluted with *n*-dodecane to obtain a solution of 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane. The resultant organic phase was subjected to extraction studies without any pre-treatment.

Case 2: A solution of 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane was prepared and irradiated to various dose levels. After irradiation, it was subjected to extraction studies.

Case 3: A solution of 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane was pre-equilibrated with 4 M nitric acid. The organic phase was separated after acid extraction and irradiated to various dose levels. The irradiated solution thus obtained was subjected to extraction studies.

Case 4: A solution of TEHDGA and HDEHP in 1: 2.5 mole ratios was prepared and irradiated to various absorbed dose levels. The irradiated solution was dissolved in *n*-dodecane so as to obtain 0.1 M TEHDGA - 0.25 M HDEHP in *n*-DD. The resultant organic phase was subjected to extraction studies without any pre-treatment.

7.3. Extraction studies

The distribution ratio of metal ions was determined by equilibration procedure. Equal volumes of organic and aqueous phases were taken in glass tube and equilibrated at a constant temperature of 298 K using a constant temperature water bath for about an hour. The organic phase was pre-equilibrated with 4 M nitric acid before extraction studies. The extraction studies involved equilibration of irradiated organic phase with FR-SHLLW solution containing 0.05 M CyDTA, spiked with ^{241}Am(III) and $^{(152+154)}$Eu(III). The acidity of the FR-SHLLW was adjusted to 4 M nitric acid. Trans-1,2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA) was added to FR-SHLLW for avoiding the extraction of unwanted fission product such as Zr(IV) and Pd(II) into the organic phase. The radioactivity of ^{241}Am(III) and $^{(152+154)}$Eu(III) in organic and aqueous phase was measured using well-type NaI(Tl) detector. The concentration of other metal ions present in aqueous phase was measured by ICP-OES.

7.4. Batch stripping studies

The irradiated organic solvent was loaded with Am(III) and Eu(III) from FR-SHLLW as described above. Back extraction of Am(III) and Eu(III) was carried out by equilibrating a known volume (5 ml) of the loaded organic phase with equal volume of stripping solution formulation as 0.05 M DTPA+0.5 M citric acid at pH 3. The stripping formulation was developed for selective recovery of Am(III) alone from loaded organic phase. After equilibration, a known volume of aliquot was taken from aqueous phase. Then the remaining aqueous phase was removed and a fresh aqueous stripping solution was added to the organic phase. This procedure was repeated several times until the ^{241}Am(III) ions present in organic phase was recovered quantitatively. The gamma radioactivity of ^{241}Am(III) present in aqueous phase at each stage of back extraction was estimated by using a well-type NaI(Tl) detector.

7.5. Effect of radiation

The radiation stability of the combined solvent TEHDGA - HDEHP was evaluated by irradiating independently. The neat extractants wre irradiated to various dose levels by γ-radiation. The irradiated TEHDGA and HDEHP were then mixed to obtain a solution of 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane. The distribution ratio of Am(III), Eu(III) from FR-SHLLW was measured in the resultant solution to assess the degree of degradation. Figure 7.1 shows the variation in the distribution ratio of Am(III) and Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane (case1, see section 7.2) as a function of absorbed dose. The distribution ratio of both Am(III) and Eu(III) decreased with increase of absorbed dose. The distribution ratio of Am(III) decreased from 33 in the un-irradiated solution to the value of 12 at 500 kGy absorbed dose. Similarly the distribution ratio of Eu(III) decreased from 108 to 43 with increase in absorbed dose. This indicated the possible degradation of TEHDGA and HDEHP by γ- radiation. Since the extraction of Am(III) and Eu(III) from FR-SHLLW in the combined solvent was essentially governed by TEHDGA, the decrease in distribution ratio of Am(III) and Eu(III) in the present case confirmed the degradation of TEHDGA by γ- radiation.

7.6. Effect of *n*-dodecane - Sensitization

To assess the effect of diluent on the radiolytic degradation of TEHDGA and HDEHP, a solution of 0.1 M TEHDGA - 0.25 M HDEHP present in *n*-DD was irradiated to a various dose levels and the distribution ratio of Am(III) and Eu(III) was measured in the irradiated solution (i.e case 2, section 7.2). The results are shown in Figure 7.1. The distribution ratio of both Am(III) and Eu(III) decreased with increase of absorbed dose in this case also. However, it is important to note that the decrease in distribution ratio was more (as compared to case 1)

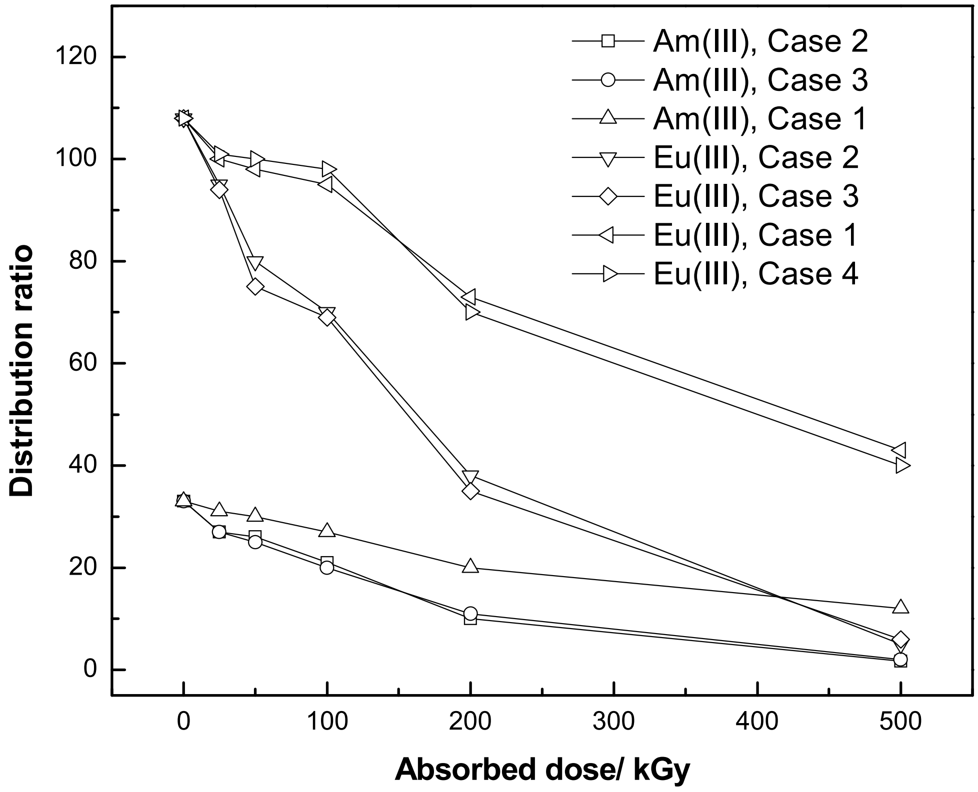

Figure 7.1. Variation in the distribution ratio of Am(III) and Eu(III) with the absorbed dose at 298 K. Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD irradiated under various conditions explained in section 7.2. Aqueous phase: FR-SHLLW + 0.05 M CyDTA spiked with ^{241}Am and $^{(152+154)}$Eu tracer. Organic to aqueous phase ratio = 1:1.

when irradiation was carried out in the presence of *n*-dodecane. This indicated that the radiolytic degradation of the solvent was more in the presence of *n*-dodecane. Since the separation of Am(III) and Eu(III) from FR-SHLLW was essentially governed by TEHDGA in the combined solvent system during extraction, the decrease in distribution ratio confirmed the higher degradation of TEHDGA in the presence of *n*-dodecane. A similar observation was also reported in several diglycolamides [5, 6]. It was reported that the major component, *n*-dodecane, present in the solvent system undergoes excitation upon irradiation and transfers its energy on to diglycolamide for facilitating degradation of diglycolamide. Such transfer of energy from the excited molecule to other was known as sensitization effect [5]. However, it is important to note that the distribution ratio of Am(III) and Eu(III) observed at 500 kGy are adequate for quantitative extraction of the trivalent metal ions from FR-SHLLW even at the absorbed dose level of 500 kGy.

7.7. Effect of HDEHP

The sensitization effect observed in the present study could be arising from the transfer of energy either from *n*-dodecane or HDEHP, which was also present in the solvent phase during irradiation. To investigate the role of HDEHP in sensitization, a solution of TEHDGA and HDEHP in 1: 2.5 mole ratio was irradiated to various absorbed dose levels. The irradiated solution was dissolved in *n*-dodecane so as to obtain 0.1 M TEHDGA - 0.25 M HDEHP in *n*-DD (i.e case 4, section 7.2). The distribution ratio of Eu(III) in the resultant solution was measured. The results are shown in Figure 7.1. It is observed that the distribution ratio of Eu(III) obtained at various dose levels compare well with the data obtained for the solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD when the extractants were irradiated independently (i.e case 1, section 7.2). This showed that the sensitization effect was observed only in the presence of *n*-dodecane.

The degradation observed in the solvent phase could be due to the degradation of either TEHDGA or HDEHP or both. To understand the degradation observed in the combined solvent system, the extractant TEHDGA alone was irradiated to various absorbed dose levels and mixed with HDEHP(un-irradiated) to obtain 0.1 M TEHDGA(irradiated) - 0.25 M HDEHP in *n*-DD. Similarly HDEHP alone was irradiated and mixed with TEHDGA to obtain 0.1 M TEHDGA - 0.25 M HDEHP (irradiated) in *n*-DD. The distribution ratio of Am(III) from FR-SHLLW in these two solutions was determined and compared with that obtained in 0.1 M TEHDGA(irradiated) - 0.25 M HDEHP(irradiated) in *n*-DD (i.e case 1, section 7.2). The results are shown in Figure 7.2. It was observed that the distribution ratio of Am(III) decreased with increase of absorbed dose in all cases. However, a marginal decrease in distribution ratio of Am(III) (from the un-irradiated condition) was observed in case of 0.1

M TEHDGA - 0.25 M HDEHP (irradiated) in *n*-DD as compared to others. Since the extraction of Am(III) from FR-SHLLW is governed essentially by TEHDGA, the degradation of HDEHP does not seem to affect the distribution ratio of Am(III) to a great extent, in this case. However, when TEHDGA was irradiated, the decrease in distribution ratio of Am(III) is more as shown in Figure 7.2. It also observed that the decrease in distribution ratio was more when both the extractants were irradiated. Even though the extraction of Am(III) from FR-SHLLW is essentially governed by TEHDGA, the synergistic participation of HDEHP to some extent was also reported during extraction. Therefore, the decrease in distribution ratio of Am(III) was more in the solution of 0.1 M TEHDGA(irradiated) - 0.25 M HDEHP(irradiated)/*n*-DD, as compared to other solutions.

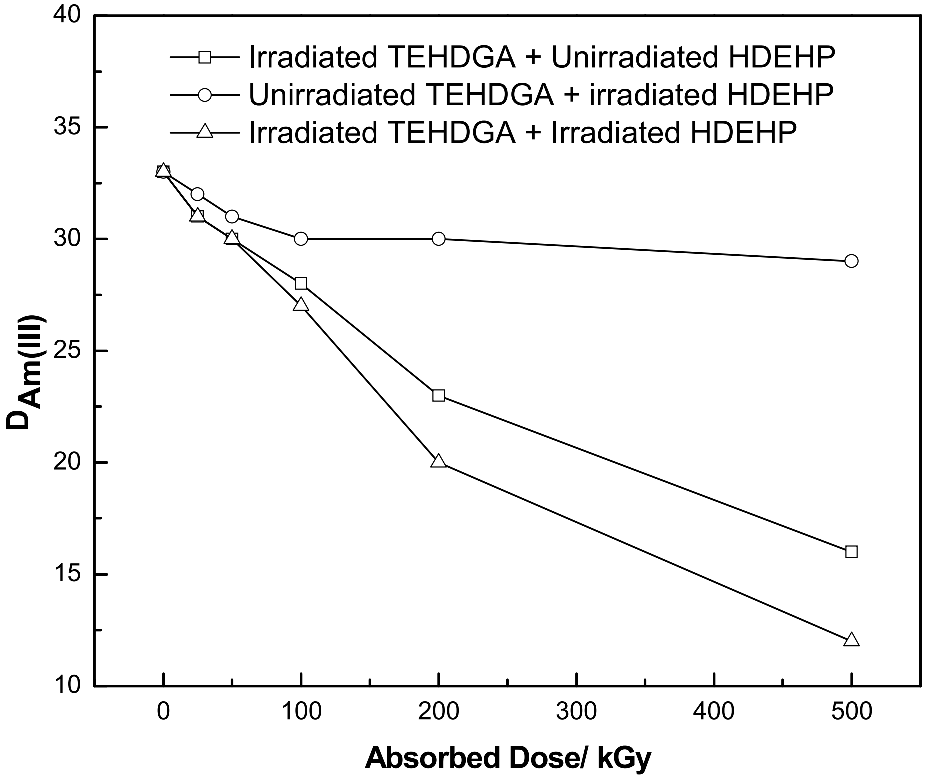

Figure 7.2. Variation in the distribution ratio of Am(III) with the absorbed dose at 298 K. Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP in *n*-DD irradiated to various absorbed dose level. Aqueous phase: FR-SHLLW + 0.05 M CyDTA spiked with ^{241}Am tracer. Organic to aqueous phase ratio = 1:1.

7.8. Effect of nitric acid

The extraction of Am(III) and other metal ions from FR-SHLLW in 0.1 M TEHDGA - 0.25 M HDEHP in *n*-DD was accompanied by the co-extraction of significant amount of nitric acid [5]. It was reported that ~0.2 M nitric acid was extracted in to organic phase [7]. It is a well-known fact that presence of nitric acid in organic phase could influence the radiolytic degradation of the solvent to a significant extent [8]. Therefore, the radiolytic degradation of acid extracted organic phase, 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD, was studied (i.e case 3, section 7.2). The organic phase was pre-equilibrated with 4 M nitric acid prior to irradiation in this case. Figure 7.1 also shows the variation in the distribution ratio of Am(III) and Eu(III) in the irradiated organic phase as a function of absorbed dose. The distribution ratio of Am(III) and Eu(III) decreased with increase of absorbed dose. However, it is noted that the distribution ratios are comparable with those observed for the irradiated 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD in the absence of nitric acid. This showed that the extracted acid does not play much role in degradation of organic phase.

7.9. Extraction from FR-SHLLW

The extraction behavior of various metal ions from FR-SHLLW in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD as a function of absorbed dose was investigated (i.e case 3 section 7.2). The organic phase was pre-equilibrated with 4 M nitric acid and subjected to irradiation in this case. The results are tabulated in Table 7.1. The distribution ratio of Am(III), all lanthanides and Y(III) decreased with increase of absorbed dose, as expected. The distribution ratio of Ba(II), Ru(III), Pd(II) and Zr(IV) were unaffected with absorbed dose as these metal ions are in-extractable ($D < 10^{-2}$). The distribution ratio of Cr(VI), Te(VII), Cd(II) and Mo(VI) increased marginally with increase of absorbed dose.

7.10. Stripping studies

Back extraction of Am(III) from the loaded organic phase is one of the important requirements for the recovery of metal ion from the loaded organic phase. If the degradation products are acidic and soluble in organic phase, the stripping of metal ions from the loaded organic phase is tedious and difficult [9]. Therefore, the distribution ratio of Am(III) in the degraded solvent under stripping condition (0.05 M DTPA + 0.5 CA pH 3) needs to be verified, for assessing the stripping behavior. Table 7.2 shows the distribution ratios Am(III) and Eu(III) in the irradiated (500 kGy) solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. The data are compared with un-irradiated system. It is interesting to observe that the distribution ratio of Am(III) was not changed to any significant extent with absorbed dose. This indicated that the degradation products does not seem to interfere in back extraction of Am(III) from loaded organic phase. However, the distribution ratio of Eu(III) decreased from 4.7 to 2.5 that results in a decrease of separation factor from 11 to 8.

The back extraction of Am(III) and Eu(III) from the irradiated organic solvent was carried out in batch mode, to understand the stripping behavior of Am(III) and Eu(III) from the irradiated solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD. The organic phase (i.e case 3, section 7.2) was irradiated to 500 kGy absorbed dose. The irradiated organic phase was taken for the extraction of Am(III) and Eu(III) from FR-SHLLW. Figure 7.3 shows the cumulative stripping of Am(III) and Eu(III) from the extracted organic phase as a function of number of contacts of stripping solution. It is observed that the cumulative stripping of Am(III) and Eu(III) increased with increase in the number of contacts of stripping solution, in all cases. Quantitative stripping of Am(III) was observed in 3 contacts. Since the distribution ratio of Eu(III) in 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was more as compared to Am(III), the stripping of Eu(III) was quite less in the un-irradiated solution. In fact, marginal stripping of Eu(III) only is needed for single-cycle separation of Am(III) from the extracted organic phase.

Table 7.1. Distribution ratio of metal ions present in fast reactor simulated high-level liquid waste. Organic phase = 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD irradiated to various dose levels (i.e case 3, section 7.2), Aqueous phase = FR-SHLLW in 4 M nitric acid + 0.05 M CyDTA spiked with ^{241}Am(III) & $^{(152+154)}$Eu(III) tracer Organic/Aqueous phase ratio = 1 Temperature = 298 K.

Metal ion	Distribution ratio of metal ion at various absorbed doses of					
	0 kGy	25 kGy	50 kGy	100 kGy	200 kGy	500 kGy
La(III)	3.1	2.5	2.5	1.8	1.2	0.35
Ce(III)	7.5	5.7	5.5	3.9	2.6	0.69
Pr(III)	14	10	9.8	6.8	4.3	1.1
Nd(III)	20	12	9.8	6.8	4.1	1.1
Sm(III)	83	62	59	38	21	3.7
Eu(III)	108	94	75	69	35	6.5
Gd(III)	69	64	61	50	34	7.3
Dy(III)	145	117	72	87	42	9.8
Y(III)	>100	>100	>100	>100	81	6.8
Sr(II)	0.12	0.12	0.10	0.11	0.14	0.14
Pd(II)	0.04	0.04	0.05	0.06	0.12	0.09
Zr(IV)	0.05	0.06	0.07	0.03	0.07	0.05
Mo(VI)	21	23	26	27	29	30
Fe(III)	0.25	0.38	0.65	0.68	1.06	2.17
Cr(VI)	0.02	0.02	0.04	0.04	0.08	0.09
Te(VI)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	0.06
Cd(II)	0.10	0.12	0.14	0.13	0.15	0.18
Ni(II)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	0.05
Ba(II)	0.06	0.04	0.07	0.07	0.04	0.07
Ru(III)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Rh(III)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Cs(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Na(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
Ag(I)	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$	$<10^{-2}$
^{241}Am(III)	33	27	25	20	11	5.2

However, the stripping of Eu(III) is increased in the irradiated solvent system, as shown in Figure 7.3. This could be due to the radiolytic degradation of TEHDGA and HDEHP. The radiolytic degradation resulted in decrease in the concentration of extractants and since the degradation products does not seem hold Eu(III) in organic phase, the stripping of Eu(III) is more in irradiated solution.

Table 7.2. Variation in the distribution ratio of Am(III) and Eu(III) and their separation factor (SF) with absorbed dose. Organic phase: 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane (un-irradiated or irradiated upto 500 kGy). Aqueous phase: 0.05 M DTPA + 0.5 M CA at pH 3 spiked with either ^{241}Am or $^{(152+154)}$Eu tracers.

Sample	Distribution ratio		SF =
	Am(III)	Eu(III)	$D_{Eu(III)}/D_{Am(III)}$
Un-irradiated solution	0.43	4.7	11
500 kGy irradiated	0.31	2.5	8

In the combined solvent system, the extraction of metal ion from FR-SHLLW is essentially governed by TEHDGA and stripping is governed by HDEHP, as discussed in previous chapters. To understand the role of irradiated (500 kGy) HDEHP in the combined system, the distribution ratio of Am(III) and Eu(III) was measured in 0.1 M TEHDGA (irradiated) - 0.25 M HDEHP/*n*-DD as well as 0.1 M TEHDGA - 0.25 M HDEHP(irradiated)/*n*-DD. The extractants were irradiated to 500 kGy absorbed dose. The results are shown in the Figure 7.4. It is observed that stripping of Am(III) and Eu(III) increases with increase in number of contacts of stripping solution, in both cases. However, it is noted that the stripping is comparable irrespective of the nature of irradiated solvent phase. Perhaps, this could be due to the fact that the degradation products of HDEHP do not seem to alter the stripping behavior of metal ions from the organic phase.

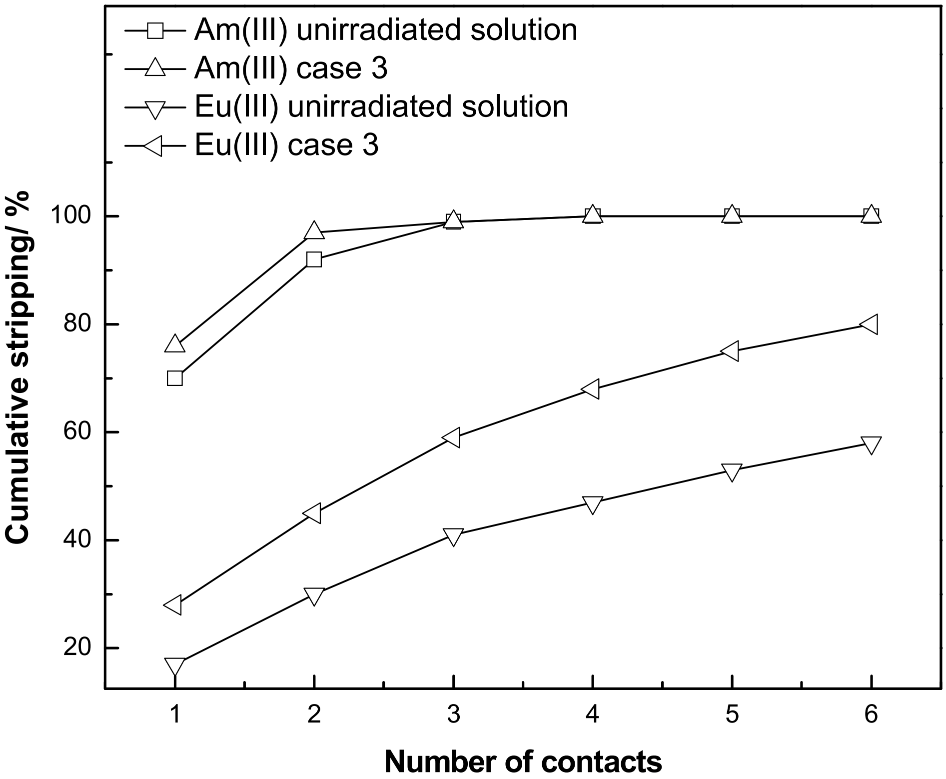

Figure 7.3. Cumulative stripping of Am(III) and Eu(III) as a function of number of contacts at 298 K. Loaded organic phase : 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane solution (un-irradiated or irradiated to 500 kGy, case 3, section 7.2) loaded with Am(III) or Eu(III). Stripping solution: 0.05 M DTPA + 0.5 M CA at pH 3.

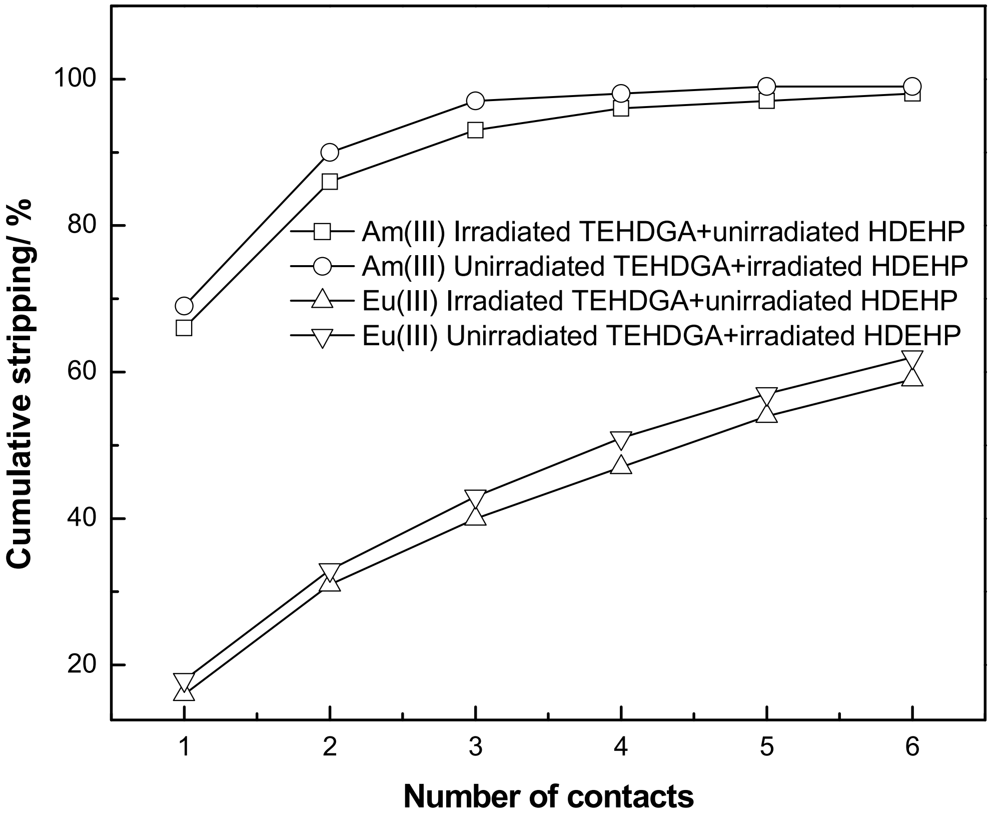

Figure 7.4. Cumulative stripping of Am(III) and Eu(III) as a function of number of contacts at 298 K. Loaded organic phase : 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane solution (un-irradiated or irradiated to 500 kGy) loaded with Am(III) or Eu(III). Stripping solution: 0.05 M DTPA + 0.5 M CA at pH 3.

7.11. Conclusions

The radiolytic stability of a solution of TEHDGA - HDEHP in *n*-DD towards γ-radiation was evaluated at various absorbed dose levels. The distribution ratio of Am(III), lanthanides and several other metal ions present in FR-SHLLW decreased with increase of absorbed dose. The presence of *n*-dodecane enhanced the radiolytic degradation; however, the degradation effect of nitric acid was negligible. Since the extraction of metal ions from FR-SHLLW in the combined solvent is essentially governed by TEHDGA, the decrease in distribution ratio of Am(III) and Eu(III) was more during extraction, when the TEHDGA underwent sensitization in the presence of *n*-dodecane. The recovery of Am(III) was quantitative in 3 contacts during back extraction, however, the stripping of Eu(III) was also quite more as compared to the un-irradiated condition. Since it is necessary to retain Eu(III) in organic phase during stripping of Am(III) in a single-cycle approach, the results indicate that the separation factor of Am(III) over Eu(III) could be lowered during stripping with increase of absorbed dose. Nevertheless, the results in the present study also indicate that radiolytic degradation of combined solvent system resulted in the formation of innocuous products that do not hold Am(III) during back extraction.

7.12. References

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Chapter 8: Summary and conclusions

This chapter summarizes the results of the studies on modifier free extractant for actinide partitioning using unsymmetrical diglycolamide (UDGA) from simulated fast reactor high level liquid-waste (FR-SHLLW). This chapter also describes the results on development of single-cycle method using various combinations of neutral and acidic extractants for minor actinide partitioning from FR-SHLLW. Several combinations of extractants such as D^3DODGA -HDEHDGA, TODGA - HDEHP and TEHDHA - HDEHP were studied for the minor actinide partitioning. The radiation stability of TEHDGA - HDEHP solvent was also studied. The summary of results is described below.

8.1. Actinide partitioning using D^3DODGA in mixer-settler

An unsymmetrical diglycolamide, *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) was synthesized. The distribution ratio of Am(III) and all metal ions present in FR-SHLLW in 0.1 M D^3DODGA/*n*-dodecane was determined. The results showed that, the solvent phase extracts trivalent actinides and lanthanides along with some fission products such as Zr(IV), Y(III), Pd(II). The co-extraction of these troublesome fission products was minimized by addition of aqueous complexing reagent CyDTA. Batch extraction studies were carried out to optimize the extraction condition. Finally, partitioning of Am(III) from FR-SHLLW was demonstrated in a 20-stage mixer-settler using above solvent without any addition of a phase modifier. The stage profiles in the mixer-settler showed that the extraction of metal ions followed decrease in distribution ratio of metal ions. The trivalent metal ions were preferentially loaded onto 0.1 M D^3DODGA/*n*-DD in the order of Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). Am(III) was extracted in 7-8 contacts. All the extracted metal ions were quantitatively back extracted in 3-5 contacts with 0.01 M nitric acid. The proposed flow-sheet based on D^3DODGA was simple and it offered significant advantages such as minimization of waste, modifier free extraction, easy disposal of spent solvent etc. The study demonstrated the possibility of using unsymmetrical diglycolamide, 0.1 M D^3DODGA/*n*-DD, for trivalent actinide partitioning from FR-SHLLW wastes.

8.2. Single-cycle process using D^3DODGA-HDEHDGA solvent

A single-cycle approach known as **S**ingle-cycle method for **M**inor **A**ctinide partitioning using completely incinerable **R**eagen**T**s (SMART), for the separation of trivalent actinides was developed by combining *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) and di-2-ethylhexyl diglycolamic acid (HDEHDGA). These extractants, D^3DODGA and HDEHDGA, are CHON based and completely incinerable reagents. The third phase formation behavior was studied in D^3DODGA - HDEHDGA in *n*-dodecane at various molar ratios of D^3DODGA and HDEHDGA with FR-SHLLW. The third phase formation was not observed with FR-SHLLW when the ratio of acidic to neutral extractant was maintained below 2. Therefore, the solvent formulation was optimized to 0.1 M D^3DODGA - 0.2 M HDEHDGA/*n*-dodecane. The extraction and stripping behavior of Am(III) and other metal ions present in the FR-SHLLW was studied by using a solution of D^3DODGA - HDEHDGA/*n*-DD for the separation of Am(III) from FR-SHLLW. It was observed that the $D_{Am(III)}$, $D_{Ln(III)}$ and fission products such as $D_{Zr(IV)}$, $D_{Y(III)}$ and $D_{Pd(II)}$ are higher than the distribution ratios observed for other metal ions ($< 10^{-1}$). This indicated that all these metal ions could be significantly extracted from FR-SHLLW by the solvent in a few contacts. The extraction of unwanted fission products was undesirable. The elimination or minimization of these fission products can be achieved by using aqueous soluble complexing agents. Among the various complexing agents studied, 0.05 M CyDTA eliminated the extraction of Zr(IV) ($D < 10^{-1}$) and palladium ($D < 10^{-1}$) in the solvent phase. The extraction of metal ions was governed by the neutral extractant, D^3DODGA and stripping controlled by the acidic extractant, HDEHDGA. The stripping behavior of Am(III) alone from D^3DODGA

- HDEHDGA/*n*-DD was optimized by the aqueous formulation composed of DTPA and citric acid (CA). Based on those optimized conditions, a counter-current extraction run was performed to separate Am(III) from FR-SHLLW using a 20-stage mixer-settler inside the glove box. As expected the Am(III), lanthanides, Y(III) were quantitatively extracted in 4 stages. Strontium was extracted to the extent of 90% in 20 stages, however, it was noted that the troublesome metal ions such as Zr(IV), Mo(VI), Fe(III), Cr(VI), Ni(II), Pd(II), Ru(III), Rh(III) were rejected to raffinate in addition to other elements. The stripping of Am(III) from the loaded organic phase was performed by using the aqueous formulation composed of 0.01 M DTPA+0.5 M CA at pH 1.5. About 55% of the Am(III) was recovered in 20 stages (product stream). This was accompanied by the co-stripping of significant amount of "early lanthanides". However, the "later lanthanides" behave similar to Eu(III). Since the D values of "early lanthanides" were quite low as compared to Am(III) and "later lanthanides", it could be possible to separate "early lanthanides" from both Am(III) and "later lanthanides". Therefore, this indicates the feasibility of "intra-lanthanide" separations apart from lanthanide-actinide separation.

8.3. Single-cycle process using TODGA - HDEHP and TEHDGA - HDEHP solvent

The combination of D^3DODGA - HDEHDGA extractant for separation of americium from lanthanides was not achieved up to the expectations. For the improvement of the single-cycle process, the combination of TODGA - HDEHP was studied because TODGA is one of the promising candidate for minor actinide partitioning and HDEHP was studied in the well known, Trivalent Actinides Lanthanide Separation Phosphorous based reagent Extraction from Aqueous Komplexes (TALSPEAK) process for the mutual separation of actinide from lanthanides. Since TODGA and HDEHP showed better results in the individual process, the combination of TODGA - HDEHP was studied for single-cycle minor actinide partitioning. The extraction behavior of Am(III) and Eu(III) in a solution of 0.1 M TODGA - 0.25 M

HDEHP/*n*-DD was studied as a function of various parameters. The distribution ratio of these metal ions obtained in the combined solution was compared with those obtained in individual solutions. Synergistic extraction of Am(III) and Eu(III) was observed at acidities lower than 2 M in the combined solvent. The dependence of HDEHP decreased and that of TODGA increased with increase in the concentration of nitric acid. Slope analysis of the extraction data indicated that extraction was predominantly governed by HDEHP at low nitric acid concentrations and by TODGA at higher acidities. The studies confirmed the involvement of both the TODGA and HDEHP at all acidities investigated in the present study. The mutual separation was difficult in 0.1 M TODGA - 0.25 M HDEHP/*n*-DD because the stripping pattern for both metals were similar.

Since TODGA - HDEHP solvent could not provide desirable results, a combination of TEHDGA and HDEHP was studied. The extraction behavior of Am(III) and Eu(III) in a solution of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD from nitric acid medium was studied as a function of various parameter. Synergistic extraction was observed in TEHDGA - HDEHP solvent. The selective stripping of Am(III) was optimized by varying the concentration of DTPA, citric acid at different pH. The stripping of Am(III) from the loaded organic phase was accompanied by 10 % co-stripping of Eu(III) in batch mode using DTPA and citric acid. The recovery of Am(III) increased with increase in the concentration of DTPA, citric acid and pH. The solvent phase as 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was better for extraction of metal ions and the aqueous phase 0.05 M DTPA + 0.5 M CA at pH 3 as stripping formulation for selective stripping of Am(III) was developed for the possibility of separating Am(III) from Eu(III) in a single cycle process.

8.4. Mixer-settler studies with FR-SHLLW using TEHDGA - HDEHP solvent

The possibility of separating Am(III) from Eu(III) present in nitric acid medium in a single-cycle process using TEHDGA - HDEHP as solvent and 0.05 M DTPA + 0.5 M CA at pH 3 as aqueous stripping formulation was investigated. However, the real HLLW contained significant quantities of other fission products in addition to Eu(III) and other lanthanides. The extraction and stripping behavior of various metal ions present in FR-SHLLW using the solvent composed of 0.1 M TEHDGA - 0.25 M HDEHP/*n*-DD was studied. The distribution ratio of metal ions present in FR-SHLLW was measured and the extraction and stripping of Am(III) was optimized. The extraction of Am(III) in organic phase was accompanied by the co-extraction of lanthanides and other unwanted metal ions such as Zr(IV), Pd(II), Mo(VI) and Y(III) from FR-SHLLW. The aqueous soluble complexing agent CyDTA was added to FR-SHLLW in order to eliminate the extraction of Zr(IV) and Pd(II) in organic phase. Based on the optimized conditions, a counter-current extraction run was demonstrated to separate Am(III) from FR-SHLLW using a 16-stage mixer-settler. The extraction was found to be accompanied by the co-extraction of chemically similar trivalent lanthanides, Mo(VI), Y(III), and Fe(III) along with Am(III). Eu(III) was quantitatively extracted in 4 stages, whereas Am(III) required 11 stages for complete extraction. The stripping of Am(III) from the loaded organic phase was performed by using the aqueous formulation composed of 0.05 M DTPA+0.5 M CA at pH 3. Quantitative recovery of Am(III) was observed in four stages. This was accompanied by the co-stripping of 18% La(III) and about 10% Ce(III), Pr(III),and Nd(III). The remaining lanthanides present in organic phase after stripping of Am(III) was removed by using 0.2 M TEDGA in 1 M nitric acid. The study, thus indicated the feasibility of separating Am(III) from fast reactors HLLW in a single-cycle process.

8.5. Radiation stability of TEHDGA - HDEHP solvent

The combined solvent phase 0.1 M TEHDGA - 0.25 M HDEHP in *n*-dodecane was regarded as a promising candidate for single-cycle separation of Am(III) from HLLW. Therefore, it is necessary to understand the radiolytic stability of the combined solution with respect to gamma radiation. In view of this, the solvent was irradiated to various dose levels by γ-radiation and the distribution ratio of various elements present in the FR-SHLLW was measured as a function of absorbed dose. The distribution ratio of Am(III), lanthanides and several other metal ions present in FR-SHLLW decreased with increase of absorbed dose. The presence of *n*-dodecane, HDEHP, nitric acid on irradiation of solvent was studied. The presence of *n*-dodecane enhanced the radiolytic degradation; however, the degradation effect of nitric acid and HDEHP was negligible. The recovery of Am(III) was quantitative in 3 contacts during back extraction, however, the stripping of Eu(III) was also quite high as compared to the un-irradiated condition. Since it was necessary to retain Eu(III) in organic phase during stripping of Am(III) in a single-cycle approach, the results indicated that the separation factor of Am(III) over Eu(III) could be lowered during stripping with increase of absorbed dose. Nevertheless, the results in the present study also indicated that radiolytic degradation of combined solvent system resulted in the formation of innocuous products that do not hold Am(III) during back extraction.

8.6. Scope for the future studies

The combined solvent phase such as D^3DODGA - HDEHDGA, TODGA - HDEHP and TEHDGA - HDEHP were extensively studied for the extraction of metal ions present in FR-SHLLW from nitric acid medium in single-cycle approach. The studies indicated that the third phase can be avoided using an acidic extractant such as HDEHP. The mutual separation of Am(III) from FR-SHLLW was demonstrated using mixer-settler in TEHDGA - HDEHP and D^3DODGA - HDEHDGA solvent system. In both the cases, the complete extraction of trivalent lanthanides and actinides was achieved whereas during stripping, early lanthanides strip easily from D^3DODGA - HDEHDGA combined solvent system, as compared to Am(III). But in the other solvent system, complete stripping of Am(III) was achieved along with 10-20% of early lanthanides. This process could not achieve the complete separation of trivalent actinides from lanthanides. For the better improvement of the mutual separation of Am(III) from FR-SHLLW, several other combined solvent system can be studied. In the present study, D^3DODGA, TODGA and TEHDGA as neutral extractant and HDEHDGA and HDEHP as acidic extractant were studied. Instead of these extractants, so many other neutral extractants such as CMPO, DMDOHEMA, and DMDOTDMA and some acidic extractant such as PC88A and CYANEX 272 can be combined and studied extensively for better separation factor for lanthanides over actinides. Also new combined solvent system can be developed for the complete separation of trivalent actinides from lanthanides and fission products.

The study also indicated that it is necessary to develop ligands that can minimize or eliminate the extraction of unwanted metal ions. These unwanted metal ions always interfere during stripping and subsequent lanthanide-actinide separation. Mixer-settler study indicated that complete stripping of Am(III) along with complete stripping of Mo(VI) using TEHDGA - HDEHP solvent system. Suitable complexing agents can be developed and added to FR-SHLLW during extraction run for selectively holding Mo(VI). The extraction of fission products can be minimized during extraction and stripping of lanthanides from organic phase during back extraction. Finally the trivalent actinides are present in aqueous phase having DTPA and citric acid after mixer-settler experiment. For further purification, the actinides should be back extracted to nitric acid medium. It is desirable to develop a necessary method for the destruction of DTPA and Citric acid in aqueous medium. By this way, the actinides can be converted easily into their corresponding oxide form directly from aqueous phase.

The extraction and stripping profile of Am(III), lanthanides and some fission product were studied in the combined solvent system from FR-SHLLW. But, HLLW contains trivalent minor actinides, lanthanides and fission products along with small concentrations of U(VI) and Pu(IV). The extraction and stripping behavior of U(VI), Pu(IV) and other minor actinide such as Np(V) and Cm(III) can be studied. The routing of U(VI), Pu(IV) and other actinides can be studied during minor actinide partitioning in combined solvent system.

The TEHDGA - HDEHP solvent have shown adequate radiation stability under various process conditions. However, the present work was restricted to examine only the influence of γ-dose. During the irradiation, the solvents form a wide variety of degradation products. No attempt was made to understand the degradation pattern, and nature of degradation products. The characterization of degradation product can be studied. The role of degradation products on extraction and stripping of metal ions can be studied. The radiation stability under alpha-exposure and the hydrolytic stability also can be studied.

Glossary

Abbrevation	Full name
ACSEPT	Actinide reCycling by SEParation and Transmutation
ADS	Accelerator Driven System
An(III)	Trivalent Actinides
BRIT	Board of Radiation and Isotope Technology
BTBP	Bis Triazine Bis Pyridine
BTP	Bis Triazine Pyridine
CA	Citric Acid
CAC	Critical Aqueous Concentration
CMPO	*n*-Octyl(phenyl)-*N,N*-diisobutylCarbamoylMethyl Phosphine Oxide
CyDTA	Trans-1,2-Cyclohexanediamine-*N,N,N',N'*-tetraacetic acid
CyMe4-BTBP	2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo [1,2,4]triazy-3-yl)-[2,2']bipyridine
DCC	Dicyclohexylcarbodiimide
DIAMEX	DIAMide EXtraction
D^3DODGA	*N,N*-di-dodecyl-*N',N'*-di-octyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-Octyl-DiGlycolAmide
DGAs	Diglycolamides
DHOA	*N,N* -diHexylOctanAmide
DIDPA	Di-IsoDecyl-Phosphoric Acid
D_M	Distribution ratio of Metal ion, M
DMDBTDMA	*N,N'*-DiMethyl-*N,N'*-DiButylTetraDecyl MalonAmide
DMDOHEMA	*N,N'*-DiMethyl-*N,N'*-DiOctyl-2-HexylEthoxy MalonAmide
DTPA	Diethylenetriamine pentaacetic acid

ECIL	Electronic Corporation of India Limited
FBRs	Fast Breeder Reactors
FBTR	Fast Breeder Test Reactor
FPs	Fission Products
FR	Fast Reactor
GDP	Gross Domestic Product
GWe	Giga Watt Electric
HAW	High Active Waste
HDEHDGA	*N,N*-di-2-ethylhexyl diglycolamic acid
HDHP	Di-n-hexyl Phosphoric acid
HDEHP	Di(2-ethylhexyl) Phosphoric Acid
HDODGA	Dioctyl diglycolamic acid
HEDTA	*N*-(2-hydroxyethyl) ethylenediamine-triacetate
HLLW	High Level Liquid Waste
HpGe	High pure Germanium
ICP-OES	Induced couple Plasma-Optical Emission Spectrometry
Ln(III)	Trivalent Lanthanides
LOC	Limiting Organic Concentration
LUCA	Lanthaniden Und Curium Americum separation
MAs	Minor Actinides
MCA	Multi Channel Analyzer
MeV	Mega electron Volt
MWd	Mega Watt days
n-DD	n-Dodecane
ORNL	Oak Ridge National Laboratory

PMT	photo multiplier tube
P&T	Partitioning and Transmutation
PALADIN	Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants
PHWRs	Pressurized Heavy Water Reactors
PUREX	Plutonium Uranium Recovery by Extraction process
SHLLW	Simulated High Level Liquid Waste
TALSPEAK	Trivalent Actinides Lanthanide Separation Phosphorous based reagent Extraction from Aqueous Komplexes
TBP	Tri-*n*-Butyl Phosphate
TEDGA	*N,N,N’N’*-tetraethyl diglycolamide
TEHDGA	*N,N ,N',N'*-ethylhexyl 3-oxapentane-1,5-diamide or *N,N,N’,N’*-tetra-2-ethylhexyl diglycolamide
TEHP	tris(2-ethylhexyl) phosphate
TLC	Thin-Layer Chromatography
Te	Tonne
TODGA	*N,N,N',N'*-tetra-octyl-3-oxapentane-1,5-diamide or *N,N,N’,N’*-tetra-octyl diglycolamide
TOPO	TriOctyl Phosphine Oxide
TPH	Hydrogenated tetrapropylene
TPO	TriAlkyl Phosphine Oxide
TUEX	TRans Uranium element EXtraction
TRUSPEAK	TRansUranic elements Separation by Phosphours based Extractants from Aqueous Komplexes
SANEX	Selective ActiNide Extraction
SF	Separation Factor
SMART	Single cycle method for Minor Actinide partitioning using completely incinerable ReagenTs

SNF	Spent Nuclear Fuel
UDGAs	Unsymmetrical Diglycolamides