DEVELOPMENT OF ADVANCED REAGENTS AND METHODS FOR THE SEPARATION OF ACTINIDES FROM NITRIC ACID MEDIUM

By

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution/University.

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DEDICATION

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SYNOPSIS

1. Introduction

The demand for energy is steadily increasing with ever increasing 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 etc, makes nuclear option inevitable for the future energy demand. Nuclear reactors employ natural or enriched uranium as the fuel [1]. The spent nuclear fuel discharged from nuclear reactor contains substantial quantities of fissile elements such as plutonium, depleted uranium, and several other elements formed by fission reaction, known as fission products. The spent nuclear fuel is therefore reprocessed for recovery of these fissile elements for further use in the reactors as fuel.

Two different technologically viable methods are available for the reprocessing of spent nuclear fuel discharged from nuclear reactor. They are (i) Aqueous reprocessing, (ii) Non-aqueous reprocessing. The first one is industrially well-established and being employed in many countries. In this method, the spent nuclear fuel is dissolved in nitric acid medium and the fissile elements such as uranium and plutonium are recovered by a process known as PUREX (Plutonium Uranium Recovery by EXtraction) process. This involves the liquid-liquid extraction of U(VI) and Pu(IV) present in the dissolver solution by a solution of 1.1 M tributyl phosphate (TBP) in *n*-dodecane [2]. The raffinate rejected after the PUREX process is known as “high-level liquid waste” (HLLW). The HLLW is a complex mixture of several elements such as minor actinides, lanthanides, other fission products, corrosion products of structural materials and the additives etc, present in 3-4 M nitric acid medium.

The radiotoxicity of HLLW is essentially arising due to the presence of long-lived radiotoxic minor actinides such as ^{237}Np, ^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm, ^{243}Cm and fission products such as ^{99}Tc, ^{107}Pd, ^{93}Zr, ^{129}I, ^{135}Cs, ^{137}Cs, and ^{90}Sr. Since the half-lives of these isotopes vary from few years to several hundred years, HLLW poses long-term risks to the public health and the environmental safety. Therefore, the success 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. However, it demands the long-term surveillance due to the presence of these minor actinides. In case of accidental ground-water invasion into these repositories, the radiotoxic actinide metal ions can get dispersed far and wide due to their high mobility in aqueous medium. Such repositories thus require continuous long-term surveillance for thousands of years, making it a very expensive option. Alternatively, partitioning (P) of these radiotoxic elements followed by transmutation (T) of them into stable or short-lived products by neutron bombardment in accelerators or fast-breeder reactors is also envisaged. P&T reduces the radiotoxicity of HLLW enormously and minimises the surveillance period and therefore, it is being considered as one of the viable options for the safe management of HLLW [3].

The transplutonium actinides essentially exhibit trivalent oxidation state and chemically behave like trivalent lanthanides (Ln(III)) [4]. Due to the close chemical similarity of minor actinides (Am, Cm) with Ln(III), and the bulk concentration of Ln(III) in HLLW, it is difficult to separate the trivalent actinides (An(III)) directly from HLLW. Therefore, in general it is proposed to separate the minor actinides from HLLW by means of two extraction cycles: the first cycle separates the (An(III)) and (Ln(III)) together from bulk of the fission products and the second cycle aims to separate the Ln(III) from An(III). The separation of Ln(III) from An(III) prior to the transmutation of actinides is essential. Owing to high neutron absorption cross sections, lanthanides capture the neutrons, and reduce the efficiency of actinide transmutation. As most of the lanthanide isotopes are stable, there is no much additional advantage in transmuting them. Moreover, only a limited amount of elements can be incorporated in the targets. In addition, Ln(III) do not form solid solutions in metal alloys or in mixed oxide transmutation targets, and as a result they segregate into separate phases with a tendency to grow under thermal treatment. Thus, the minor actinides tend to concentrate in these phases and this will lead to an unacceptable non-uniform heat distribution in the transmutation fuel matrix under irradiation. In view of these, the complete separation of Ln(III) from An(III) is very important prior to the actinide transmutation [5].

For the co-extraction of trivalent An(III) and Ln(III) from HLLW, several processes were developed in various countries. For example, TRUEX (TRans-Uranic element EXtraction) process in USA, DIAMEX (DIAmide EXtraction) in France, DIDPA (Di-Iso Decyl Phosphoric Acid) in Japan and TRPO (Trialkyl Phosphine oxide) in China etc, [6,7]. 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 [8]. 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 [8].

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 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. To overcome these issues, additional process such as scrubbing, addition of complexing agents to the feed etc., need to be carried out during the separation of actinides, this ultimately increases the waste generation. Apart from this, a two cycle separation of actinides from HLLW is associated with generation of secondary waste and high cost effects.

In view of these limitations, the development of advanced reagents and simplified process for actinide partitioning from HLLW are desirable. The present work involves the synthesis of various DGA class of extractants and their evaluation for trivalent actinides separation from nitric acid medium. This study also consists of identification of advanced DGAs which do not form third phase during the trivalent metal ion extraction from fast reactor HLLW, and development of a novel and simplified flow-sheet for single-cycle separation of actinides using completely incenerable reagents.

2. Organization of the thesis

This thesis is divided into seven chapters. The first chapter deals with a brief introduction to reprocessing of spent nuclear fuel and the safe management of HLLW. This chapter also describes the survey of literature on the development of new reagents and methods for the separation of long-term radiotoxic actinides from HLLW. Chapter 2 provide details regarding the chemicals, reagents, instrumentation used, and experimental methods adopted in the present work. Chapter 3 deals with the evaluation of a new unsymmetrical diglycolamide (UDGA), *N*,*N*-di-2-ethylhexyl-*N',N*'-di-octyl-3-oxapentane-1,5-diamide trivially known as di-ethylhexyl-di-octyl diglycolamide (DEHDODGA) for the trivalent actinide separation from HLLW. Chapter 4 discusses the tuning of DGA structure to obtain the desired solvent extraction properties for the efficient partitioning of An(III). Chapter 5 describes the development of a novel single-cycle separation methodology for the actinide separation from HLLW. Chapter 6 deals with the evaluation of radiolytic stability of the UDGAs developed in the present work under actinide partitioning conditions. Chapter 7 summarizes and concludes the important observations and results of the present work and give the directions for the future works.

Chapter 1 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. It also explains the importance of safe management of HLLW, in view of its long-term radiotoxicity. 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/reagents proposed for the separation of long-lived radiotoxic actinides from HLLW, and the scope for further developments.

Chapter 2 details the various chemicals and reagents used for the synthesis of various diglycolamic acids, and DGAs in the present work. This also includes the detailed synthetic and purification procedures. A brief description of various experimental tools used for characterization of synthesised diglycolamic acids and DGAs such as FT-IR, NMR, Mass spectroscopic techniques are presented. The characterization details such as assignment of spectral lines and their correlation with the structure of the reagents etc., are provided. Methodologies adopted for the measurement of radioactivity of various radioisotopes using α-scintillation counting, NaI(Tl) detector, high purity germanium detector(HpGe) are discussed. Experimental set up, and the procedure adopted for the determination of third phase limits such as limiting organic concentration (LOC) and critical aqueous concentration (CAC) are also given. Usage of inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the determination of concentration of various metal ions presents in HLLW, and thereby the distribution ratio measurements etc., are explained.

Chapter 3 deals with the evaluation of a new UDGA, di-ethylhexyl-di-octyl-diglycolamide (DEHDODGA) for partitioning of minor actinides from HLLW. This compound contains 2-ethylhexyl group in one arm, and the octyl moiety in the other. It is prepared with a view to enjoy the properties of both TEHDGA, and TODGA, with an expection to minimize the limitations of TEHDGA, and TODGA. The extraction behaviour of various metal ions that are expected to present in HLLW such as Am(III), Eu(III), Y(III), Zr(IV), Fe(III), Co(II), Sb(III), Mn(II), Cs(I), Cd(II), Ru(III), Pd(II), Mo(VI), Cr(VI), Ba(II), Ni(II), and Sr(II) was studied in DEHDODGA/*n*-dodecane as a function of various parameters. The third phase formation behaviour of DEHDODGA during the extraction of trivalent f-elements from nitric acid medium was studied under various conditions. The solvent composition was modified to 0.1 M DEHDODGA-0.5 M *N*,*N*-dihexyl octanamide (DHOA)/*n*-dodecane to prevent the third phase formation. The extraction behaviour of various metal ions from nitric acid medium as well as from fast-reactor simulated HLLW in modified solvent was examined. The conditions needed for the quantitative recovery of trivalents from the loaded organic phase were optimized with the use of diethylenetriaminepentaacetic acid (DTPA)-citric acid at pH 3 to facilitate the mutual separation of lanthanides-actinides in the subsequent step. In addition, the basicity constant, the stoichiometry of Am(III)–DEHDODGA by slope analysis of extraction data, and the enthalpy change accompanied by the extraction of Eu(III), Pu(III), and Am(III) were determined. The extraction behavior of metal ions, third phase formation behavior of Nd(III) etc., were studied in 0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane and the results are discussed in this chapter.

Chapter 4 describes the tuning of DGA structure. This chapter consists of two parts. The first part deals with the studies on UDGAs containing octyl group on one amidic nitrogen atom and the alkyl group on the other nitrogen atom was varied. Several UDGAs such as *N*,*N*-dihexyl-*N*’,*N*’-dioctyl-3-oxapentane-1,5-diamide (DHDODGA), *N*,*N*-didecyl-*N*’,*N*’-dioctyl-3-oxapentane-1,5-diamide (D^2DODGA), *N*,*N*-didodecyl-*N*’,*N*’-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) were evaluated for the extraction of Am(III), Eu(III), Sr(II) from nitric acid medium, and third phase formation behaviour during the extraction of Nd(III). These studies indicated the presence of dodecyl groups on amidic nitrogen atom of DGA prevents third phase formation during the trivalent extraction. Based on those observations, second part of tuning has been carried out by studying several dodecyl group containing UDGAs such as *N*,*N*-di-butyl-*N’,N’*-di-dodecyl-3-oxapentane-1,5-diamide (DBD^3DGA), *N*,*N*-di-dodecyl-*N’,N’*-di-hexyl-3-oxapentane-1,5-diamide (D^3DHDGA), *N*,*N*-di-decyl-*N’,N’*-di-dodecyl-3-oxapentane-1,5-diamide (D^2D^3DGA), and *N*,*N*-di-dodecyl-*N’,N’*-di-2-ethylhexyl-3-oxapentane-1,5-diamide trivially known as di-dodecyl-di-ethylhexyl diglycolamide (D^3DEHDGA). All these UDGAs were evaluated for the trivalent actinide and lanthanide extraction from nitric acid medium and for the third phase formation tendency during the extraction. The results are intercompared and correlated to their structure.

However, extensive studies were carried out using D^{3}DODGA including the extraction and stripping behavior of Am(III) from simulated HLLW of fast reactor fuel, and the results are discussed in this chapter.

Chapter 5 deals with the studies related to mutual separation of Ln(III) and An(III) from the feed composition of 0.1 M HNO_3 and 0.1 M citric acid (CA), which was employed for back extraction from the An(III)-Ln(III) loaded TRUEX solvent. A solvent of composition of 0.1 M HDEHP-TBP (10 wt%/V) in *n*-dodecane was used as the organic phase for the selective separation of Ln(III). The separation factor of Eu(III) over Am(III) was measured as a function of various parameters. The results regarding these studies are discussed in this chapter. This chapter also involves the development of a novel approach "Single-cycle process for Minor Actinide partitioning using completely incinerable ReagenTs (SMART process)" for the partitioning of long-lived actinides from HLLW in a single-cycle. The SMART solvent was a combination of D^{3}DODGA and an acidic extractant, *N,N*-di-2-ethylhexyldiglycolamic acid (HDEHDGA), in *n*-dodecane, and DTPA was used for the selective stripping of An(III) from the loaded organic phase. The extraction mechanism of Eu(III) and Am(III) in combined solvent system was compared with that in individual solvents. Optimization studies of organic phase and aqueous phase compositions for holding Ln(III) in the organic phase and for selective stripping of An(III) are discussed in detail in this chapter.

Chapter 6 describes the radiolytic stability of UDGAs proposed 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 [9]. Therefore, the reagents used for the actinide separations need to be robust with respect to high radiation.

In this context, the radiolytic stability of DEHDODGA, D^3DODGA, and D^3DEHDGA have been evaluated under various process conditions. The influence of diluent (*n*-dodecane), phase modifier (in the case of DEHDODGA), and nitric acid on the radiolysis of UDGAs was investigated. The distribution ratio of Am(III), Eu(III), and Sr(II) in the irradiated solvents was determined as a function of absorbed dose of γ-radiation. The stripping behaviour of Am(III) from the degraded organic phase was studied as a function of absorbed dose. Third phase formation tendency of irradiated D^3DODGA, D^3DEHDGA was examined as a function of absorbed γ-dose during Nd(III) loading from 4 M nitric acid medium. The influence of the presence of degradation products on the back extraction of trivalent actinides has been investigated. The results related to these studies are described in detail in this chapter.

Chapter 7 summarises 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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Introduction

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. Studies point that to achieve eight percent Gross Domestic Product (GDP) growth per annum, electricity generation needs to grow around twelve percent annually [1]. Being one of the fast growing countries, India certainly needs huge quantity of energy for its sustainable growth in terms of GDP. The total energy demand of our country by 2050 is estimated to be around 1000 GWe[2]. This can be met only by the appropriate use of all available fuel resources. Nearly 75 % of the world energy production is mainly from the fossil fuels such as coal, gas, and oil [3]. The use of these fossil fuels leads to the generation of greenhouse gases, which pollute the environment. Moreover, their availability is very limited. 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 from the present 3% to at least 25% in coming years for a sustained development of our nation. Nuclear energy has several advantages over the others as follows,

1. Nuclear power plants need very less fuel than the ones which burn fossil fuels. One ton of natural uranium produces much higher energy than that produced by two to three million tons of coal or oil.
2. Nuclear plants do not generate any greenhouse gases.
3. It is an extremely reliable source of energy because most nuclear reactors have a life cycle of 40 years which can be easily extended further by 20 more years.
4. Using breeding technology, it is possible to produce more fuel than that consumed in the nuclear reactor.

1.1. Nuclear fuel cycle

All the nuclear power plants currently operating in the world are based on nuclear fission. Many types of nuclear reactors have been designed and built to convert the heat produced from a nuclear fission chain reaction to electrical energy. Several stages are involved in the production of electricity through nuclear fission reactors-right from mining of uranium to management of waste. All these stages are collectively called as nuclear fuel cycle, and it can be divided into two parts. From mining of uranium to fuel loading into nuclear reactor is called as "front end of the fuel cycle" and from discharging of spent fuel to waste management is called as "back end of the nuclear fuel cycle". The fuel that is discharged from a nuclear reactor, known as 'spent nuclear fuel', contains valuable materials such as depleted uranium (U), plutonium (Pu) and several radionuclides formed by the fission reaction, known as "fission products"(FPs). There are two options existing worldwide for the nuclear fuel cycle and they are: the once through fuel cycle (or open fuel cycle) and closed fuel cycle. In the once-through fuel cycle, spent nuclear fuel as such is disposed as waste; whereas in the closed fuel cycle, it is chemically processed to recover the fissile materials for fueling the future reactors. Therefore, the closed fuel cycle, enables effective utilization of the fuel resources and also reduces gently the waste volume. Figure 1.1 illustrates the various stages involved in nuclear fuel cycle.

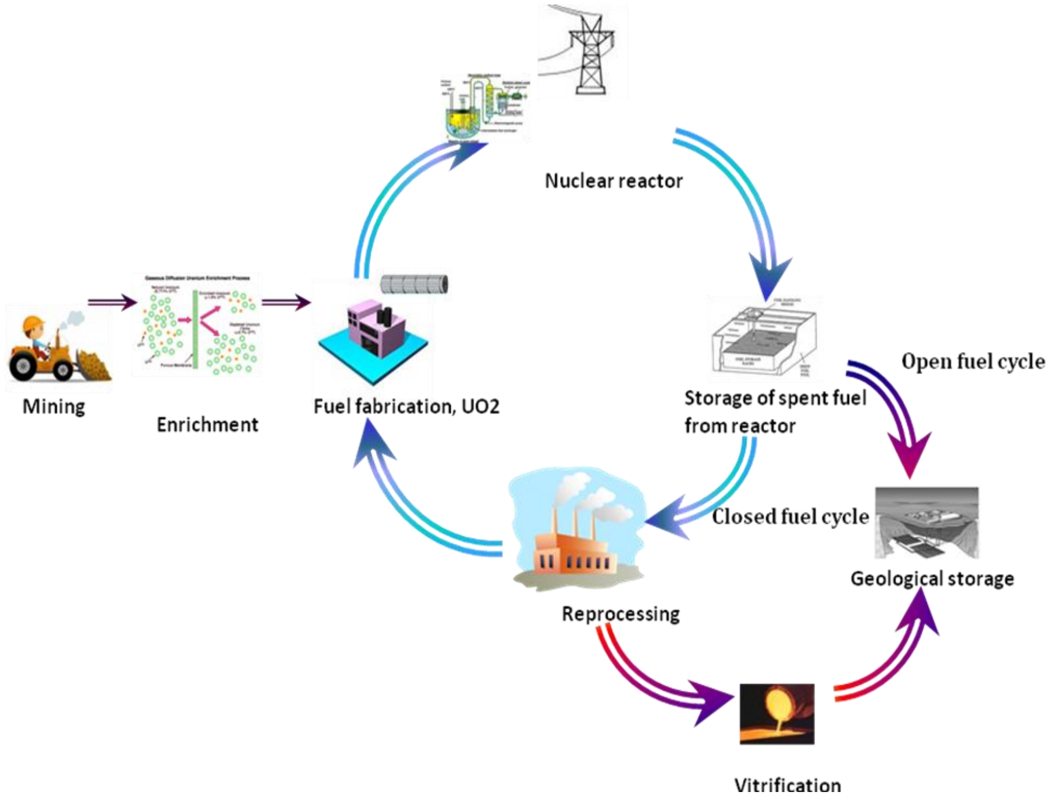


Figure 1.1. Illustration of nuclear fuel cycle

1.2. Indian nuclear power programme

As early as in 1954, Dr. Homi Jehangeer Bhabha charted a three stage nuclear power programme based on a closed nuclear fuel cycle in order to meet the nation's energy demands and also considering the available resources. The first stage of Indian nuclear power programme came on track with the building up of Pressurized Heavy Water Reactors (PHWRs) and the allied fuel cycle facilities. These reactors use natural uranium as fuel. Part of the uranium fuel is converted to fissile plutonium by a series of nuclear reactions in the nuclear reactor as shown in scheme 1.1. At present, 15 PHWRs are in operation. The second stage is based on the setting up of Fast Breeder Reactors (FBRs) by utilizing plutonium recovered from the reprocessing of spent fuel of PHWRs. A 40 MWt Fast Breeder Test Reactor (FBTR) is in operation at Kalpakkam since 1985[4] to demonstrate the second stage. In the second stage nuclear power reactors, thorium (Th) is kept as blanket for converting the fertile Th into fissile ^{233}U, by the reactions shown in scheme 1.1. 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. A 30 kWt reactor, KAMINI at kalpakkam, India is the only reactor in the world, which uses ^{233}U as fuel [5].

1.3. Nuclear reactions in the reactor

The fissile element used as fuel in the nuclear reactor undergoes fission to generate around thirty two elements and their isotopes as FPs and tremendous amount of energy. Depending upon the type of nuclear reactor, composition of fuel, and burn-up *etc*., the extent of fission may vary, in turn the composition of FPs. In addition to the nuclear fission reactions, several neutron absorption reactions also occur resulting in the formation of activation products. Some of those nuclear reactions are shown in the scheme 1.1.

$$^{232}\mathrm{Th}(n,\ \gamma)\ ^{233}\mathrm{Th} \xrightarrow[22\ \mathrm{min}]{\beta} {}^{233}\mathrm{Pa} \xrightarrow[27\ \mathrm{d}]{\beta} {}^{233}\mathrm{U}$$

$$^{238}\mathrm{U}(n,2n)\ ^{237}\mathrm{U} \xrightarrow[7\ \mathrm{d}]{\beta} {}^{237}\mathrm{Np}$$

$$^{238}\mathrm{U}(n,\ \gamma)\ ^{239}\mathrm{U} \xrightarrow[23\ \mathrm{min}]{\beta} {}^{239}\mathrm{Np}$$

$$^{235}\mathrm{U}(n,\ \gamma)\ ^{236}\mathrm{U}(n,\ \gamma)\ ^{237}\mathrm{U} \xrightarrow[7\ \mathrm{d}]{\beta} {}^{237}\mathrm{Np}$$

$$^{239}\mathrm{Np} \xrightarrow[3\ \mathrm{d}]{\beta} {}^{239}\mathrm{Pu}$$

$$^{241}\mathrm{Pu} \xrightarrow[15\ y]{\beta} {}^{241}\mathrm{Am} \xrightarrow[433\ y]{\alpha} {}^{237}\mathrm{Np}$$

$$^{239}\mathrm{Np}(n,\gamma)\ ^{240}\mathrm{Np} \xrightarrow[62\ \mathrm{min}]{\beta} {}^{240}\mathrm{Pu}(n,\ \gamma)\ ^{241}\mathrm{Pu}(n,\ \gamma) \xrightarrow[15\ y]{} {}^{242}\mathrm{Pu}(n,\ \gamma) \xrightarrow[4X10\text{^}5\ y]{} {}^{243}\mathrm{Pu}$$

$$^{241}\mathrm{Am}\ (n,\gamma)\ ^{242}\mathrm{Am} \xrightarrow[16\ \mathrm{h}]{\beta} {}^{242}\mathrm{Cm}$$

$$^{243}\mathrm{Pu} \xrightarrow[5\ \mathrm{h}]{\beta} {}^{243}\mathrm{Am}\ (n,\gamma)\ ^{244}\mathrm{Am} \xrightarrow[10\ \mathrm{h}]{\beta} {}^{244}\mathrm{Cm} \xrightarrow[18\ y]{\alpha} {}^{240}\mathrm{Pu}$$

$$^{232}Th(n,\gamma)^{233}Th \xrightarrow{\beta} {}^{233}Pa \xrightarrow{\beta} {}^{233}U$$

$$^{238}\mathrm{U(n,2n)}^{237}\mathrm{U} \xrightarrow{\beta} {}^{237}\mathrm{Np}$$

$$^{238}\mathrm{U(n,\gamma)}^{239}\mathrm{U} \xrightarrow{\beta} {}^{239}\mathrm{Np}$$

$$^{235}\mathrm{U(n,\gamma)}^{236}\mathrm{U(n,\gamma)}^{237}\mathrm{U} \xrightarrow{\beta} {}^{237}\mathrm{Np}$$

$$^{239}\mathrm{Np} \xrightarrow{\beta} {}^{239}\mathrm{Pu}$$

$$^{239}\mathrm{Np(n,\gamma)}^{240}\mathrm{Np} \xrightarrow{\beta} {}^{240}\mathrm{Pu(n,\gamma)}^{241}\mathrm{Pu(n,\gamma)} \longrightarrow {}^{242}\mathrm{Pu(n,\gamma)} \longrightarrow {}^{243}\mathrm{Pu}$$

$$^{241}Pu \xrightarrow{\beta} {}^{241}Am \longrightarrow {}^{237}Np$$

$$^{241}\mathrm{Am\,(n,\gamma)}^{242}\mathrm{Am} \xrightarrow{\beta} {}^{242}\mathrm{Cm}$$

$$^{243}\mathrm{Pu} \xrightarrow{\beta} {}^{243}\mathrm{Am\,(n,\gamma)}^{244}\mathrm{Am} \xrightarrow{\beta} {}^{244}\mathrm{Cm} \xrightarrow{\alpha} {}^{240}\mathrm{Pu}$$

Scheme 1.1. Nuclear reactions that take place in the nuclear reactor in addition to nuclear fission reaction.

The actinides Np, Am, and Cm that are formed by the above mentioned reactions are called minor actinides (MA) as their concentration in the fuel is very less.

1.4. Radiotoxicity of spent nuclear fuel

The fuel discharged from the nuclear reactor is referred as spent nuclear fuel which consists of FPs and MAs. Figure 1.2 shows the variation in the relative radiotoxicity of different components of spent nuclear fuel with time. For the first 100 years after discharge from nuclear reactor, spent fuel radiotoxicity is determined by the FPs [6]. It is then determined by Pu and other minor actinides such as Np, Am and Cm. Plutonium is being recovered quantitatively from the spent nuclear fuel by reprocessing. Thus, the radiotoxicity contribution of Pu is minimized. The raffinite obtained from reprocessing of spent nuclear fuel is called high-level liquid waste (HLLW), and its radiotoxicity is mainly determined by the presence of MAs.

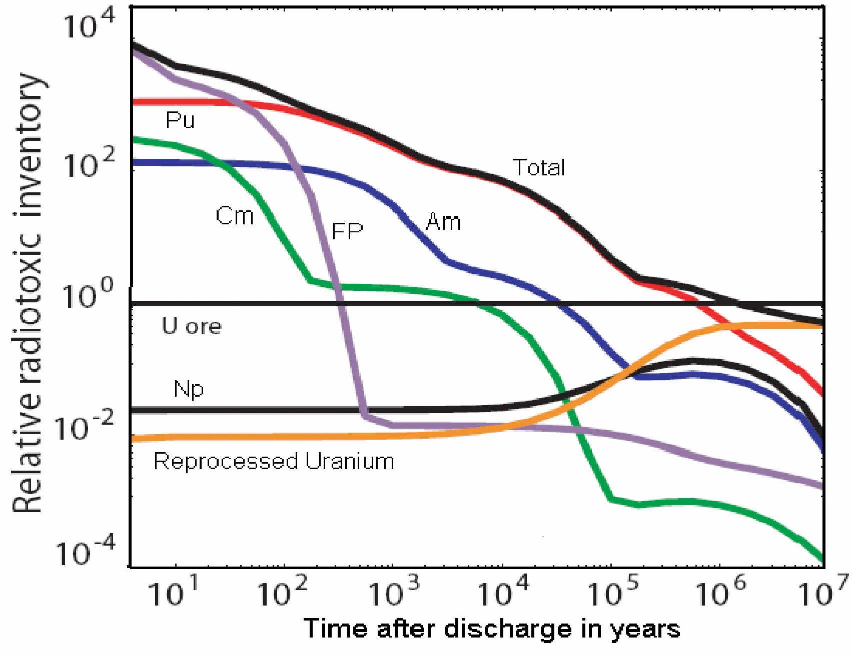


Figure 1.2. Relative radiotoxicity of different components in the spent nuclear fuel from a light water reactor irradiated to 41 M Wd/kg U with respect to the radiotoxicity of the corresponding uranium ore [6].

1.5. Reprocessing of spent nuclear fuel

The spent nuclear fuel discharged from nuclear power reactors contain substantial amounts of fertile U and fissile Pu that can be reprocessed and recycled as fuel. Reprocessing and recycling of the separated U and Pu in fast reactors has been the favored strategy at the back end of the fuel cycle. In comparison with direct disposal of spent nuclear fuel, reprocessing and recycling provides several advantages. These include:

1. Better utilization of natural resource by recycling the remaining U and Pu, thus reducing demands on fresh U mining and milling and ensuring a more sustainable and long-term use of nuclear energy. Reprocessing and recycling in fast reactors has the potential to reduce the U demand per kWh by a factor of 50-100[7].
2. Long term radiotoxicity of spent nuclear fuel is reduced. This reduces the concerns for the repository, and simplifies the repository design.

3. Long term heat production is reduced, which increases the capacity of a repository, as the packaging density in most cases is determined by the heat load.
4. The volume of high level waste is reduced.

In addition, some valuable fission products such as cesium, strontium, and platinum group metals such as Pd can be extracted for industrial use. In this context, reprocessing of spent nuclear fuel is very useful not only for the safe disposal of radiotoxic materials but also for obtaining valuable radionuclides.

The spent nuclear fuel can be reprocessed in two ways, using aqueous and non-aqueous reprocessing methods. A brief view of non-aqueous reprocessing is given below and aqueous reprocessing will be dealt in detail in the subsequent sections.

1.5.1. Non-aqueous reprocessing (Pyrochemical process)

A family of high temperature chemical processes that utilize oxidation - reduction reaction to effect chemical separations are called as pyrochemical processes [8]. Among the several pyrochemical processes that are known, three are currently under development in different countries. They are: (a) the oxide electrowinning process, developed by Research Institute of Atomic Reactors (RIAR), Russia, suitable for reprocessing of oxide fuel, (b) the electrorefining process, developed by Argonne National Laboratory (ANL), USA, suitable for reprocessing of metallic fuel and (c) the fluoride volatility process developed by Russia and USA, suitable for the oxide as well as molten salt reactor fuels.

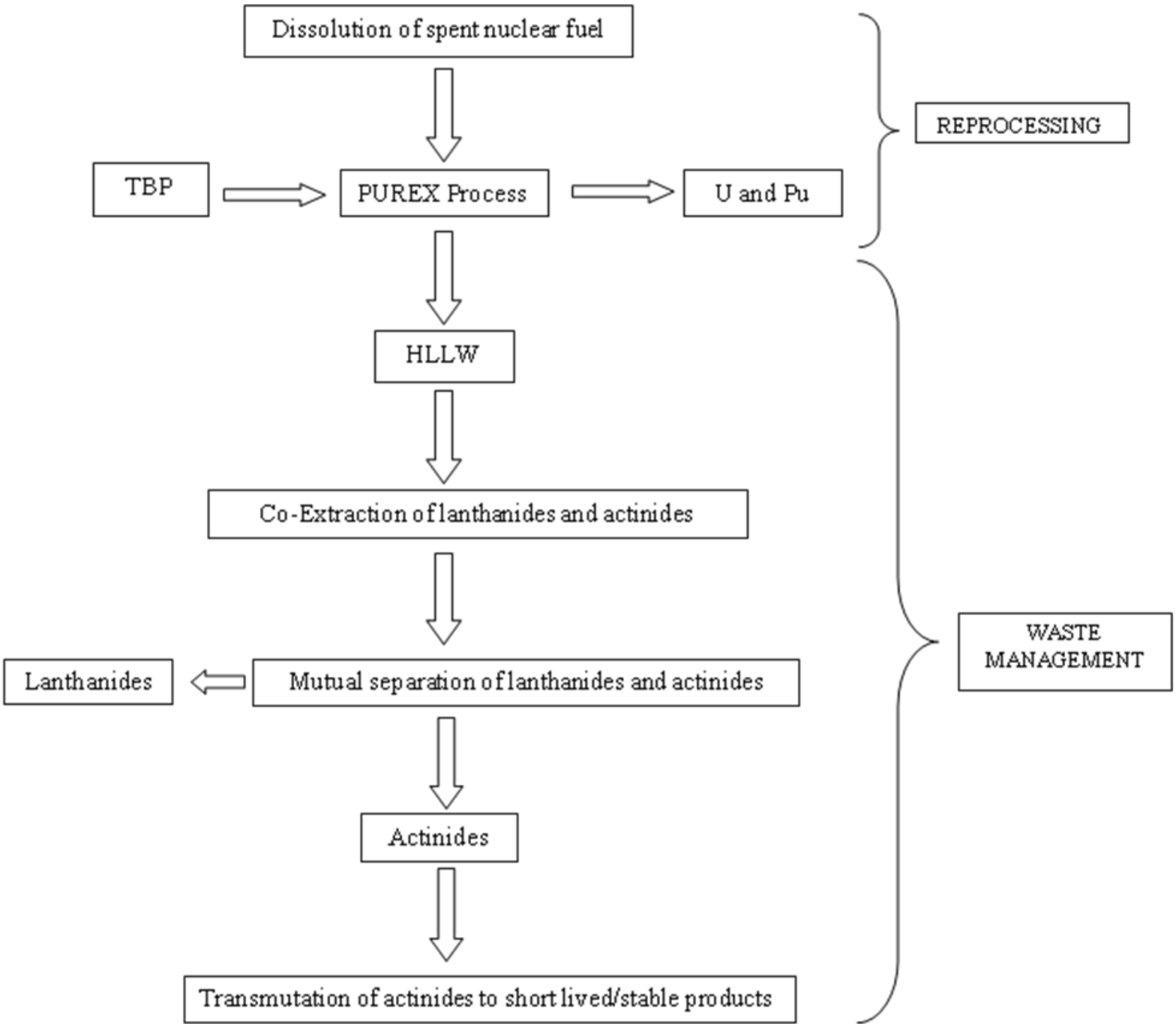
Though, Pyrochemical process has attractive features such as less number of process steps, less criticality problems, lower volumes of waste generated and easier waste management etc, it has several limitations compared to aqueous reprocessing such as lower separation factors for fission products, need for remotisation, need for sophisticated equipment, need for high purity inert atmosphere to enable handling of hygroscopic salts and reactive metals, high temperature operation etc,. In addition, pyro process is a batch process, and the chloride salts pose challenges in selection of container materials. Therefore, the aqueous reprocessing is being used for the recovery of U and Pu from spent nuclear fuel worldwide.

1.5.2. Aqueous Reprocessing of spent nuclear fuel

Aqueous reprocessing of spent nuclear fuel and allied waste management is designed to have many processes for various purposes as shown in the flow chart 1.1. All these stages are explained in the subsequent sections.

1.5.2.1. Plutonium Uranium Reduction EXtraction (PUREX) process

"Inner transition elements" a series of fourteen elements following actinium (Ac), starting from thorium (Th) and ending with lawrencium (Lr) are known as "Actinides". Actinide elements are unique among the elements in the periodic table. This uniqueness and many interesting properties that arise are essentially due to the delocalized 5f electrons of actinides which have energies close to those of 6d and 7s electrons. This feature enables actinides to exhibit multiple valence states both in solids and in solution and easy conversion of one state to another. These valence states also have widely differing charge densities or "ionic potentials" enabling them to form complexes of differing stoichiometry and widely varying stability with various inorganic and organic ligands.



Flow chart 1.1. Various stages of aqueous reprocessing, and allied waste management of spent nuclear fuel.

Thus, the ability of actinides to form strong solvation type complexes with extractants such as Tri-*n*-butyl phosphate (TBP) resulted in the evolution of successful separation schemes not only in laboratory scale but also in plant scale for the separation of actinides from fission products and was exploited in PUREX process. PUREX process is a TBP based solvent extraction process used for the recovery of U(VI) and Pu(IV) consisting of the following steps [9].

1. Initial cooling to get rid of most of the short-lived fission products such as Zr, Nb, Ru, I, *etc*.
2. Decladding of the fuel, dissolution in nitric acid and adjustment of the valance state of Pu to Pu(IV) making it amenable for solvent extraction.
3. Solvent extraction of U(VI) and Pu(IV) by 1.1 M TBP in *n*-dodecane.
4. Scrubbing of loaded organic phase once or twice with different concentration of nitric acid to remove the unwanted fission products.
5. Partitioning of Pu(IV) by selective reduction in organic phase to Pu(III), which goes with aqueous phase and stripping of U(VI) with dilute nitric acid.
6. Final purification of U and Pu which is ready to use as fuel in nuclear reactors
7. Treatment of the solvent for its reuse in the process.

Thus, PUREX process not only reduces the radiotoxicity of spent nuclear fuel, but also provides pure uranium and plutonium which can be used as fuel in the future reactors.

1.5.2.2. Waste management

The acidity of high-level liquid waste (HLLW) is expected to be ~ 3-4 M and contains significant amounts of lanthanide fission products and transplutonium elements. The long-term radiotoxicity of HLLW is essentially due to the presence of long-lived minor actinides (MAs) such as Np, Am, and Cm, whose half-lives are given in the table 1.1 and discussed in section 1.9. Some of the fission products such as ^{135}Cs, ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{107}Pd, ^{93}Zr, and ^{129}I contribute to the source of HLLW. Currently, this HLLW is vitrified in the form of borosilicate glass and stored in deep geological repositories. Since the half-lives of the minor actinides concerned, range between a few hundred and millions of years, the surveillance of canisters for such a long period is debatable from economical as well as environmental safety considerations. On the other hand, the vitrified mass of HLLW will have to withstand the heat and radiation damages caused by the decay of beta/gamma emitting fission products, such as ^{137}Cs and ^{90}Sr for about 200 years. Consequently, it may cause the risk for the migration of long-lived alpha emitting minor actinides from repository to the aquatic environment. The residual activity level of 4000 Bq per gram (in terms of alpha activity) is considered benign enough to be treated as Low Level Waste (LLW), which can be disposed of in sub-surface repositories [10, 11]. Thus, the safe management of nuclear waste plays an important role in the success of nuclear energy. Details regarding the removal of major and minor actinides from HLLW will be discussed in the section 1.9.

Solvent extraction process is widely used for the aqueous reprocessing and allied waste management all over the world.

1.6. Solvent extraction for aqueous reprocessing and waste management

Solvent extraction is considered as the most efficient method for the separation of desired products from a complex mixture, and plays a very important role in various industries such as nuclear, metallurgical, pharmaceutical, food and beverage, chemical, petrochemical, biochemical, catalysis, polymers, etc,.

Solvent extraction essentially depends on the distribution of a solute (for example a desired metal ion, M) between two immiscible/partially miscible liquids 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 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.

$$D_M = [M]_{org} / [M]_{aq} \tag{1.1}$$

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 mixed with an immiscible organic phase containing the active extractant. The extractant transfers metal ion from aqueous phase into organic phase by a series of chemical reactions. The organic phase loaded with the solute is then transferred to the stripping section and is mixed with stripping aqueous solution containing a suitable reagent that provides the driving force required to strip (back extract) the solute. The “stripped organic” is called lean organic phase and is recycled back to extraction and the aqueous phase containing metal now goes to final metal recovery.

At the front end of nuclear fuel cycle, solvent extraction process is usually employed for the recovery of U and Th in the pure form from various primary and secondary sources. Solvent extraction plays an important role even in the reprocessing of spent nuclear fuel and allied waste management at the backend of nuclear fuel cycle. Most of the extractants used for the separation of valuable materials in solvent extraction are high viscous organic substances. In most of the solvent extraction processes, extractants are dissolved in a non-reactive second organic medium in which they are completely miscible, is called as diluent. The physical properties of the extractant are modified by diluting the extractant with diluents. The addition of diluent confers appropriate hydrodynamic properties on the resultant solvent, and 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. The most widely used diluent in the nuclear fuel reprocessing is *n*-dodecane. In view of these, and for applications in nuclear industry, the extractant is expected to have the following properties[12]

1. High solubility in paraffinic solvents.
2. Low solubility in the aqueous phase.
3. Non-volatility, non-toxicity and non-inflammability.
4. High complexation ability with the metal ions of interest.
5. No third phase formation (will be discussed in the following section) during the solvent extraction.
6. High solubility of the metal-ligand complex in the organic phase, i.e. high metal loading capacity in the organic phase.
7. Ease of stripping of metal ions from the loaded organic phase.
8. High selectivity for the metal ion of interest over the other species present in the aqueous solution.
9. Optimum viscosity for the ease of flow and optimum inter-facial tension to enable fast phase disengagement.
10. Ease of regeneration of the extractant for recycling.
11. High thermal, radiolytic and hydrolytic stability during operation.
12. Ease of synthesis or availability at a reasonable cost.
13. 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, for many researchers to synthesize an ideal solvent, which can exhibit most of the above mentioned properties.

1.7. Third phase formation in solvent extraction

Third phase formation is a phenomenon of great importance and concern in the reprocessing of spent nuclear fuel by solvent extraction process. It is the splitting of organic phase into two phases, with the heavier one, rich in metal–solvate (or metal complex) and extractant, and the lighter phase rich in diluent [13]. Usually, it occurs due to the excess loading of metal complexes into organic phase, where polar metal-solvate is no longer soluble in non-polar diluent such as *n*-dodecane. The concentration of metal ion in the organic phase above which third phase formation take places is called the limiting organic concentration (LOC) and the corresponding aqueous phase concentration of metal ion is known as critical aqueous concentration (CAC). The occurrence of third phase formation during the solvent extraction can be explained briefly as follows.

Generally the hydrophilic parts of extractant are compatible enough to be soluble in non-polar diluents such as *n*-dodecane. During the extraction of metal ions from aqueous phase, the polar parts of the extractant molecule involve in complexation with metal ions to result in the formation of polar metal-solvate complexes which in turn, rise in the polarity difference between extractant and diluent. It is observed that above a particular concentration of metal ion (LOC) in the organic phase, the polarity differences between polar metal-solvate complexes and non-polar diluent molecules increases to an extent that the polar metal-solvates are no longer soluble in diluent. Therefore, it results in the splitting of organic phase into two. Often third phase formation can be explained by the formation of reverse micelles of extractant metal complexes in non-polar diluents. It is believed that the splitting is essentially due to higher attractive interactions among polar metal-solvates than that of metal-solvate and diluent. Formation of a third phase creates inhomogeneous density and viscosity in organic phase and complicates the mixing of organic and aqueous phases. Accumulation of fissile materials such as Pu in the third phase can cause criticality hazard. To avoid these complications it is desirable to operate the solvent extraction process much below the limit which usually accompanied by very less amount of loading than the theoretical loading and reduce the efficiency of solvent extraction. Therefore, it is essential to avoid the third phase formation during solvent extraction of actinides.

The minimisation of undesirable third phase formation can be achieved by reducing the polarity differences between metal-solvate complexes and diluent molecules. It can be accomplished by enhancing the compatibility between extractant and diluent. Sometimes, to minimise the polarity differences between the metal-solvate complexes and diluent molecules, another polar reagent, which is called as phase modifier is added. There are 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., that influence third phase formation behaviour [13]. The addition of phase modifier changes the physico-chemical and extraction properties of extractant and increases waste generation. Therefore, a solvent system which is devoid of third phase formation is desirable.

1.8. Characteristics of extractants

Extractants (or reagents) are organic molecules generally which posses both hydrophilic and hydrophobic structural parts. Usually polar hydrophilic groups take part in the complexation with metal ions present in the aqueous phase. The hydrophobic character provided by the organic part of the reagent molecule is required to maximize the solubility of metal-complex in the organic phase and to reduce the aqueous solubility of the reagent in aqueous phase. An extractant to be employed for commercial solvent extraction process has to satisfy the properties as described in the section 1.6.

1.8.1. Types of extractants

To transfer a metal ion from an aqueous solution in which it exists as a hydrated ion, to an organic phase, it has to be converted to an extractable species. Such a conversion requires the charge neutralization of the metal species and replacement of some or all of its water of hydration by extractants. Hence, chemical reactions between the metal ions present in the aqueous phase and the extractants present in the organic phase are involved in the solvent extraction of metals. Therefore, complexation of a metal ion can be viewed as a conversion of a hydrophilic species into a hydrophobic species. Since it involves the replacement of hydrated water molecules by extractants or ligands, complexing reactions are substitution reactions. Based on the complexing reactions which involve compound formation, ion association and solvation of a metal ion, extractants can be broadly classified into four groups as acidic (cation extractants), basic (anion extractants), neutral (solvating agents) and chelating extractants [14]. 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.

1.8.1.1. Acidic extractants

Acidic extractants extract the metal ions by cation-exchange mechanism, in which hydrogen atoms of the extractant are exchanged with metal ions as shown in equation 1.2.

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

Since the extraction takes place with the release of hydrogen ions, usually the extraction of metal ions by acidic extractants takes place at lower acidity. Extracted metal can be stripped at higher acidity. These extractants can have functional groups such as -COOH, >P(O)OH and -SO_3H. For example, organic derivatives of phosphorous acids and monocarboxylic acids belong to this category of extractants [15]. Alkyl or aryl groups present in the extractant can influence its acidic nature, and the distribution ratio for the extraction increases with increase in the acid strength of the extractant. Among the esters of phosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups, alkylphosphoric acids are the most promising, especially di(2-ethylhexyl) phosphoric acid (HDEHP). HDEHP has been used for the extraction of many metals such as uranium, cobalt, nickel, rare earths and vanadium on commercial scale. Di(2-ethylhexyl) phosphonic acid (PC-88A) is another important acidic extractant and has been employed for several metal recovery applications.

1.8.1.2. Basic extractants

Basic extractants extract metal ions by ion association resulting from the physical attractive forces between oppositely charged species. Hence, ion association enhances with decrease in the distance between the centers of oppositely charged ions which are in contact. It increases also with decrease in the dielectric constant (ε) of the medium. Hence, water with high ε tends to inhibit ion association, whereas organic solvents with low ε enhance ion association. Long chain primary (RNH_2), secondary (R_2NH), tertiary (R_3N) amines and quaternary ammonium salts $(R_4N)^+ X^-$ belong to this category [15]. The nature of alkyl chain as well as the number of carbon atoms in the alkyl chain can influence the metal extraction by amines. Aliphatic amines are preferred as compared to amines with aromatic substituents. High degree of branching of the alkyl chain leads to a decrease in extractive properties, probably due to the steric effects. The anionic metal species (MY^-) present in the aqueous phase is exchanged with the anion of the amine salt which is formed by the amine and an acid (HX) and these reactions are 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.

1.8.1.3. Neutral extractants

Neutral extractants are reagents containing donor atoms with lone pair of electrons for the solvation of neutral inorganic species. Extraction involves the formation of an addition complex comprising undissociated electrically neutral salt and the extractant. The addition 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.,[15]. 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. More details regarding this class of extractants are discussed in the subsequent chapters.

1.8.1.4. Chelating extractants

The essential feature of chelating extractants is that they show chelation behaviour, the formation of ring structures involving the extractant molecule as a ligand to the metal ion. Reagents such as 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 [15].

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. For example, for the recovery of U(VI) and Pu(IV) from spent nuclear dissolver solution a neutral extractant TBP is used.

1.9. Partitioning of minor actinides

The HLLW resulted from the aqueous reprocessing spent nuclear fuel poses long term challenges to the environment and mankind due to the presence of long-lived alpha emitters such as MAs. Currently, HLLW is vitrified in the form of borosilicate glass and stored in deep geological repositories. However, this practice needs long term surveillance as the half-lives of MA are very high. On the other hand, the partitioning (P) of MAs from HLLW, and their subsequent transmutation (T) into stable or short-lived products by using advanced reactors or accelerated driven systems (ADS) reduces the radiotoxicity to a large extent, and simplifies the management of HLLW. In this context, P&T of MAs is being considered as the best strategy for the safe management of HLLW [16]. Figure 1.3 depicts advantage of P&T strategy in minimizing the radiotoxicity of HLLW [17]. Table 1.1 compares the natural half-lives of actinides before and after transmutation. It is very interesting to note that the half-lives of these minor actinides can be dramatically reduced by the transmutation process [18]. However, the selective separation of MAs from HLLW containing substantial amounts of lanthanide FPs is difficult due to their chemical similarity. It may be possible to separate lighter actinides such as Th, U, Pu and Np by exploiting the greater extractability of the higher oxidation states of these lighter 5f elements. However, the transplutonium actinides do not have stable higher oxidation states (with minor exceptions such as Am(VI), Bk(IV), both of which are powerful oxidants), and majority of them exhibit +3 oxidation states [19]. This may be due to the increase of effective nuclear charge experienced by f- electrons with increase in atomic number which arises from poor shielding of f-electrons (actinide contraction). Majority of the lanthanides formed as fission products also exhibit +3 oxidation state and posses similar chemical and extraction behavior as that of trivalent actinides

(An(III)). Due to the large concentration of lanthanides (Ln(III)) in HLLW and their close extraction properties with An(III), it is very difficult to separate An(III) selectively from HLLW. Therefore, it is proposed to extract the An(III) along with Ln(III) in one cycle, and their mutual separation in the second cycle. The strategy for a two cycle separation of actinides is shown in the flow chart 1.1. The necessity for the separation of Ln(III) from An(III)s, prior to the transmutation of An(III) will be discussed in detail in the section 1.10. For the co-extraction of An(III) and Ln(III) from HLLW several reagents were proposed as extractants and evaluated in various processes such as TRans Uranium element EXtraction (TRUEX) process developed in USA using Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (OΦCMPO) [20-23], TriAlkyl Phosphine Oxides (TRPO) developed by Chinese [24-27], Di-IsoDecyl-Phosphoric Acid (DIDPA) developed in Japan [28-31], *N*,*N*´-DiMethyl-*N*,*N*´-DiButylTetraDecyl MalonAmide (DMDBTDMA) [32-34], *N,N'*-DiMethyl-*N,N'*-DiOctyl-2-HexylEthoxyMalonAmide(DMDOHEMA)[35-39] developed by French scientists, diglycolamides (DGAs) such as TODGA, TEHDGA are extensively being studied by Japanese and others [40-69], and in the recent past *N,N,N',N'*-tetraalkyl-3,6-dioxaoctane diamides (DOODA) such as DOODA-C_8 and DOODA-C_{12} are also being developed by Japanese etc, [70]. The structures of these reagents are shown in figure 1.4.

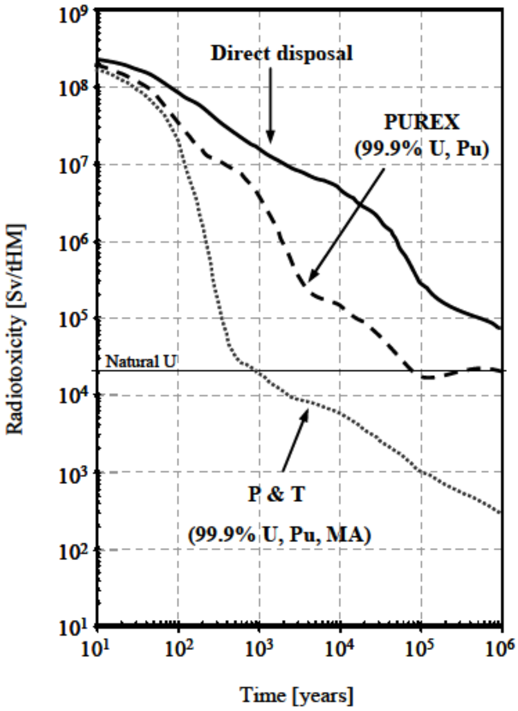
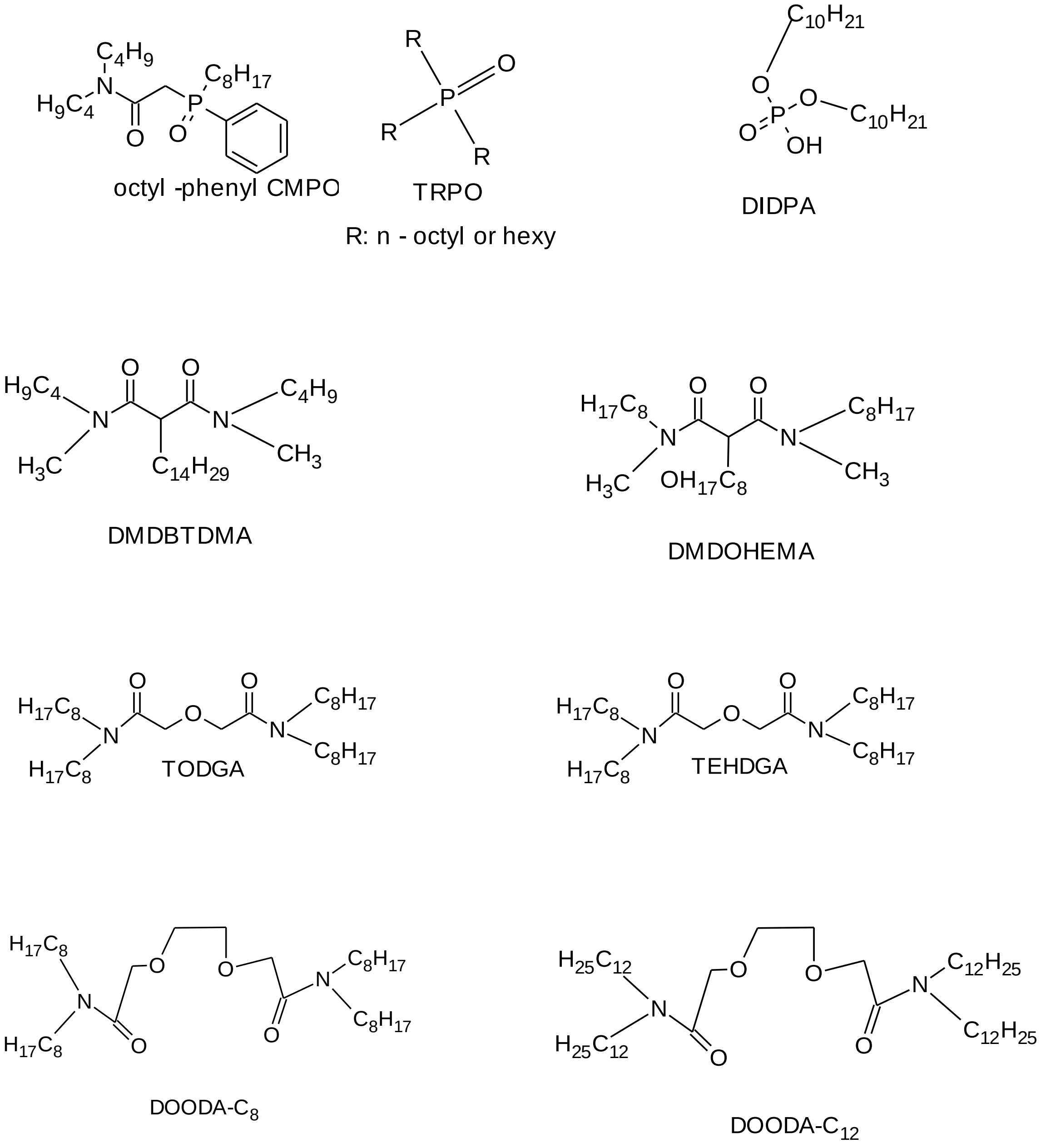


Figure 1.3. Depiction of the advantage of P&T strategy over direct disposal of HLLW in minimizing the radiotoxicity [17].

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}[18].

Actinide	$t_{1/2}$ (natural decay)	$\tau_{1/2}$ (transmutation)
^{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


octyl -phenyl CMPO

TRPO

R: n - octyl or hexy

DIDPA

DMDBTDMA

DMDOHEMA

TODGA

TEHDGA

DOODA-C_8

DOODA-C_{12}

Figure 1.4. The structure of various reagents proposed for partitioning of minor actinides.

TRUEX process[20-23] was employed by several researchers for the partitioning of minor actinides from simulated as well as from genuine HLLW. However, it has several limitations such as

1. 0.2 M OΦCMPO/*n*-dodecane forms third phase during the solvent extraction and demands the addition of high concentration of phase modifier, (1.2 M TBP).
2. The distribution ratios of trivalent actinides from 3-4 M nitric acid medium (acidity of a typical HLLW) are not high. Therefore, more number of extraction stages are needed for the complete extraction.
3. The distribution ratios of trivalent actinides are relatively higher at lower acidities (~0.1 M HNO_3), which make the back-extraction from the loaded organic phase difficult.
4. The TRUEX solvent undergoes radiolytic degradation during actinide separation and degradation products interfere during stripping.

Another extractant, namely trialkyl phosphine oxide (TRPO) has been developed and tested by China for the partitioning of trivalent actinides. The structure of TRPO is given in figure 1.4, where the alkyl group R is either octyl or hexyl alone, and a mixture of hexyl, heptyl and octyl groups. A 30% TRPO in *n*-dodecane was evaluated for the metal ion extraction from nitric acid medium [26,27]. However, this solvent system suffers from many limitations such as,

1. 30% TRPO solution in *n*-dodecane forms third phase even with 3 M nitric acid. Therefore, addition of siginificant amount of phase modifier (20% TBP) is essential.
2. The distribution ratio of Am(III) is less than 1 at 3-4 M nitric acid, and reasonable values are achieved only at lower concentrations of nitric acid medium(less than 1 M). In view of this, aqueous phase acidity of HLLW has to be lowered several times by multiple dilutions.

3. Co -Extraction of U and Np is significantly higher [27].

Di-isodecyl phosphoric acid (DIDPA) (figure 1.4) is another reagent proposed by Japanese scientists for the partitioning of minor actinide from HLLW. Being acidic reagent, DIDPA is not efficient for the metal ion extraction from 3-4 M nitric acid medium. Therefore, the aqueous phase acidity of HLLW needs to be reduced either by de-nitration or by dilution so as to make it 0.5 M, prior to the extraction. Moreover, the third phase formation during the course of extraction demands the addition of phase modifier (0.1 M TBP) into the organic phase [30, 31].

In addition, OΦCMPO, TRPO, and DIDPA are phosphorous containing reagents and give solid residue upon their inceneration at the end of their useful life. In view of these, French researchers developed an extractant based on CHON principle (avoiding the use of S, P containing reagents) to minimize the generation of wastes from extractant destruction. This novel approach for the extractant design has 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) [32-34] has shown promising results. Extensive studies were carried out using DMDBTDMA as a reference molecule in the DIAMEX process. Later several malonamide molecules containing etheric oxygen atom into the bridging alkyl chains of diamides were synthesized and evaluated for the actinide partitioning. *N,N'*-Di-Methyl-*N,N'*-Di-Octyl Hexyl-Ethoxy MalonAmide(DMDOHEMA) emerged as the promising alternate extractant to DMDBTDMA in the DIAMEX process, in view of increased extraction efficiency, less the third phase formation tendency (due to increased lipophilicity) and the possibility of easy elimination of degradation products (due to the presence of shorter alkyl groups) etc,. DIAMEX process with genuine radioactive waste has demonstrated using DMDBTDMA and DMDOHEMA [35-38] at Institute for Trans Uranium elements (ITU), Karlsruhe, Germany.

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 [39,40].

To further increase the extraction efficiency of completely incinerable diamide based extractants, a new class of extractants called diglycolamides (DGAs), with an introduction of etheric oxygen between two amide groups was synthesized [41-44]. DGAs are *N,N,N',N'*-alkyl derivatives of 3-oxapentane-1,5 diamides containing three oxygen donor atoms for complexation with the metal ions, and hence act as tridentate ligands (figure 1.4). Sasaki *et al.,* [41] synthesized and studied the physico-chemical and extraction properties of various DGAs. It was realized that the properties of DGAs strongly depend on the nature of alkyl groups attached to amidic nitrogen atom. Among the various DGAs studied, the octyl based *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) has shown promising nature for partitioning of MAs [46-53]. 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 [54-57]. Extensive studies on these DGAs proved that the DGAs aggregate in *n*-dodecane to form reverse micelles, above 0.7 M nitric acid and enhance the extraction of trivalent f-elements [58-62]. Among these two symmetrical DGAs, TODGA showed higher extraction affinity towards trivalent actinides over the TEHDGA [46,63]. This was explained based on basicity differences and variation in the extent of aggregation [63-66].

However, the diglycolamides, TODGA and TEHDGA also suffer from a few limitations. Their solutions in *n*-dodecane form third phase during the extraction of trivalent metal ions from nitric acid medium. A 0.1 M TODGA/*n*-dodecane solution formed third phase when the Nd(III) concentration more than 8 mM in 3 M nitric acid medium with an LOC of 6.4 mM [67,68]. The concentration of An(III) and Ln(III) in the HLLW varies from

0.5 to 8 g/L (~50 mM) depending upon the nature of fuel type, burn–up, etc.[51]. Therefore, it is necessary to add a phase modifier in 0.1 M TODGA/*n*-dodecane to prevent the third phase formation while the extraction of trivalent metal ions from high concentrated feed such as HLLW of fast reactor. However, 0.1 M TODGA/*n*-dodecane solution may be employed for the extraction of trivalent metal ion from HLLW of PHWRs where the concentration of trivalents is low. Similarly, a 0.2 M TEHDGA/*n*-dodecane (the recommended concentration for the actinide partitioning) forms third phase when it is equilibrated with equal volume of 4 M nitric acid alone [57]. The limiting organic concentration (LOC) and critical aqueous concentration (CAC) of trivalent metal ions are lower in TEHDGA than that of TODGA. Thus, both TODGA and TEHDGA solutions in *n*-dodecane cannot be used for the trivalent actinide separation from HLLW arising from the reprocessing of fast reactor fuel, without phase-modifiers. In addition to third phase formation, the solutions of these symmetrical DGAs in *n*-dodecane co-extract other metal ions such as Mo(VI), Sr(II), Pd(II) and Zr(IV), which is undesirable due to the β, γ activity associated with these elements. 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.

In the recent past, another class of extractants, namely *N,N,N',N'*-tetraalkyl-3,6-dioxaoctane diamide (DOODA) are being studied for actinide partitioning. These extractants contain two etheric oxygen atoms in the back bone alkyl chain carrying the two amide groups and thus act as tetradentate ligands [69,70]. DOODAs have shown sufficient solubility in nuclear diluents, *n*-dodecane. Among various DOODAs studied, DOODA-C_8 and DOODA-C_{12} have shown promising features for actinide partitioning due to (1) efficient extraction of actinides and (2) poor extraction of fission products. The structure of these DOODAs is given in figure 1.4. Though, the LOC of Nd(III) during the extraction from 3 M nitric acid is more for DOODA-C_8 (19 mM) than TODGA (6.4 mM), the distribution ratios are lower in DOODA. On the other hand, 0.1 M DOODA-C_{12}/*n*-dodecane did not form third phase during the Nd(III) loading from 3 M nitric acid medium containing 100 mM Nd(III).

However, the distribution ratios of An(III) in the case of DOODA class of extractants are much lower (< 10) than that observed in DGA class of extractants. These values may further reduce when the extraction is carried out from HLLW. Therefore, DGA class of extractants appear to be more promising for the partitioning of minor actinides from HLLW.

1.10. Mutual separation of lanthanides and actinides

The An(III) and Ln(III) separated together from HLLW are further separated from each other. This separation is necessary for the effective transmutation of An(III) because Ln(III) act as neutron poisons. i.e. they tend to absorb neutrons efficiently. For instance, the neutron capture cross section for ^{157}Gd is > 2,50,000 barns, for ^{143}Nd is 330 barns, and for ^{149}Sm is > 40,000 barns etc., since most of the lanthanide isotopes are stable, and only a few are long-lived radioisotopes, there is no much gain in transmuting them, and further more only a limited amount of elements can be incorporated in the targets. In addition, Ln(III) do not form solid solutions in metal alloys or in mixed oxide transmutation targets, and as a result they segregate in separate phases with the tendency to grow under thermal treatment. Minor actinides tend to concentrate in these phases and this will lead to an unacceptable non-uniform heat distribution in the transmutation fuel matrix under irradiation. Therefore, the minor actinide fraction should not contain more than 0.2 % of Ln(III) [71].

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) is being exploited for their mutual separations. Although, both An(III) and Ln(III) are classified as hard acids, according to Pearson’s hard-soft acid base theory, the An(III) have slightly softer nature than the Ln(III) [72,73]. Being lighter ions, Ln(III) act as relatively hard acids and form complexes preferably with relatively shorter 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 [74]. However, neither nitrogen based ligands nor oxygen based ligands can extract either An(III) or Ln(III) preferably. Therefore, a suitable complexing agent is added to the aqueous phase to hold actinide group of elements and the Ln(III) are exctracted using their preferential ligand or vice versa. For example in the TALSPEAK process (Trivalent Actinides Lanthanide Separation Phosporous based reagent Extraction from Aqueous Komplexes), 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 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), with multiple stages of such extractions yielding better separation factors [75].

However, in TALSPEAK process, a phosphorous based reagent HDEHP is employed and this process needs the maintenance of constant pH in the aqueous phase. 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. To overcome these limitations, Suneesh *et al.,* [76,77] developed a completely incinerable acidic extractant, *N,N*-di-2-ethyl hexyl diglycolamic acid (HDEHDGA) and studied for the Ln(III)–An(III) separations. This extractant has shown promising nature for the efficient separation of Ln(III) from An(III).

1.11. Single-cycle separation of minor actinides from HLLW

Considering the difficulties in the selective and direct separation of An(III) from HLLW, the An(III) are proposed to be separated in two extraction cycles. i.e. the first cycle separates the An(III) and Ln(III) from the bulk of the fission products and the second cycle aims to separate selectively the An(III) from Ln(III) as shown in the flow chart 1.1. In general, a neutral extractant is employed in the first cycle and an acidic extractant in the second cycle. However, researchers in Europe have carried out extensive investigations to develop the reagents for the selective An(III) extraction over the Ln(III) such as 2,6-bis(5,6-dialkyl- 1,2,4-triazine-3-yl)-pyridine (BTP) 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine ($CyMe_4$-BTBP) [78-82]. The poor hydrolytic and radiolytic stability, slow extraction kinetics, low back extraction of An(III) from the loaded organic phase etc., limit the usage of nitrogen based soft ligands for the selective An(III) separation from HLLW.

Alternatively, the combination of neutral extractant and acidic extractant may facilitate the direct An(III) separation in a single-cycle. That is, minor actinide partitioning cum Ln(III)-An(III) separation can be achieved in a single step. This strategy reduces the waste generation, the human efforts and be more economical. The concept of combining the neutral and acidic extractants for the separation of Ln(III) from the transuranic elements is reviewed by Lumetta *et al* [83]. The authors indicate the promising nature of combining neutral and acidic extractants to achieve a single-cycle separation of trivalent actinides alone from HLLW. Dhami *et al.*, [84] 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. The distribution ratio of these metal ions was reported to decrease with increase in the concentration of nitric acid. The extracted metal ion was stripped using a unique solution composed of 0.4 M hydrazine hydrate, 0.4 M formic acid and 0.05 M DTPA to achieve a separation factor of ~3 for americium over europium. They also reported that lowering HDEHP concentration improves the extraction efficiency of trivalents from nitric acid solution; however, it showed an adverse effect on the lanthanide/actinide separation factor. However, these separation factors are very low to achieve the complete separation of lanthanides from actinides.

A new process, namely Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants (PALADIN)[85] process was developed by CEA, France to produce a single solvent for separating lanthanides from actinides based on the reagents diamides and HDEHP. However, in this process 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. It was reported that tetramethylammonium citrate solution was used for the scrubbing. 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 a selective stripping of An(III) into aqueous phase containing DTPA by retaining the Ln(III) in organic phase.

1.12. Radiolytic stability of extractants

The solvent systems employed for the extraction of radioactive metal ions such as minor actinides will be exposed to the high energy alpha, beta, and γ radiation. The Cleavage of chemical bonds in the solvent results in the formation of 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 [86-90]. 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. The formation and presence of these degradation products alter the physico-chemical and solvent extraction properties of the reagents to a significant extent [91-95]. 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 under biphasic, acidic conditions.

1.13. Scope of the present work

The literature survey on diglycolamide (DGA) class of reagents indicates that they are promising candidates for partitioning of minor actinides from HLLW. The survey also indicates that the DGAs studied so far are symmetrical, i.e. the alkyl groups attached to the both amidic nitrogen atom are identical. Among the various DGAs studied, the octyl derivatives, TODGA and TEHDGA received much attention in the previous decade and they are explored extensively for the separation of trivalent actinides form nitric acid medium and HLLW. However, these reagents also have some limitations. They form third phase during the extraction of trivalent metal ions from nitric acid medium and demand the addition of phase modifiers, in significant concentration, to avoid third phase formation. The formation of third phase is an undesirable event especially occurs during the treatment of HLLW arising from fast reactor fuel reprocessing, where the concentration of trivalents are quite high. In addition, these reagents, TODGA and TEHDGA, also co-extract other metal ions such as Zr(IV), Sr(II), Mo(VI) and Pd(II) etc. along with trivalent metal ions to a significant extent. Co-extraction of these metal ions during minor actinide partitioning complicates stripping of metal ions from the loaded organic phase during recovery. This can be obviated by the employment of scrubbing the organic phase before stripping. However, this practice leads to the generation of large volumes of secondary wastes. Therefore, the literature survey on diglycolamides indicate that there is a need to develop advanced class of diglycolamides, which can resolve these issues and suitable for the treatment of HLLW arising from fast reactor fuel reprocessing.

The advanced class of diglycolamides can be prepared by modifying the nature of alkyl groups attached to amidic nitrogen atom. It is quite likely that the structure of DGAs can be turned to avoid third phase formation during the extraction of trivalent actinides from HLLW. One way of preparing these advanced class reagents is to introduce unsymmetry in DGAs, where the alkyl groups attached to amidic nitrogen atom are different. In this context, the present work is aimed at the synthesis of several unsymmetrical diglycolamides (UDGAs) and studied for the feasibility of using them for partitioning of minor actinides from fast reactor-HLLW. Using these UDGAs the extraction behaviour of actinides and other metal ions, third phase formation behavior, basicity, metal to ligand stoichiometry during the extraction, and their radiation stability etc., were studied, and correlated to the nature of alkyl groups attached to the amidic nitrogen atoms. Based on the results, the UDGA suitable for the minor actinide partitioning from FR-HLLW was identified.

Moreover, the current approach for partitioning of trivalent actinides from the HLLW is carried out in a two-step process, where the actinides and lanthanides are co-extracted in the first cycle, followed by their mutual separation in the second cycle. Using the UDGA and diglycolamic acid synthesized in the present work, a novel approach namely, SMART (Single-cycle process for Minor Actinide partitioning using completely incinerable ReagenTs), was developed for the separation of trivalent actinides in a single processing step.

Experimental

This chapter describes the synthesis and characterization of various diglycolamic acids and unsymmetrical diglycolamides (UDGAs). The spectroscopic techniques such as FT-IR, ^{1}H & ^{13}C-NMR and mass spectrometry used for characterization of various organic compounds synthesized are presented. Experimental procedures such as liquid- liquid extraction of actinides and other metal ions, third phase formation studies, methods and materials employed for the analysis of radioactive and non-radioactive samples along with instruments such as NaI(Tl) detector, alpha scintillation counter, gamma-spectrometer, inductively coupled plasma-optically emission spectrometry (ICP-OES) etc employed for the above studies have been explained in detail.

2.1. Chemicals and reagents

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

2.1.1. Radioactive tracers

The radioisotopes such as $^{(152+154)}Eu$, $^{(85+89)}Sr$, ^{133}Ba, and ^{137}Cs were procured from Board of Radiation and Isotope Technology, Mumbai, India. ^{88}Y was procured from Cerca Lea, France. ^{241}Am tracer was obtained from Bhabha Atomic Research Centre, Mumbai. ^{233}U tracer was obtained from reprocessing group, Indira Gandhi Centre for Atomic Research, Kalpakkam, and used after purification by solvent extraction using tri-*n*-butyl phosphate (TBP).

2.1.2. Preparation of HLLW tracer

The dissolver solution was obtained by the dissolution of irradiated fast breeder test reactor fuel of composition $(U_{0.71}Pu_{0.29})O_2$ with burn-up of 112 GWd/Te in concentrated nitric acid. The dissolver solution (0.2 mL) was taken in 4 M HNO_3 (3 mL). The oxidation state of plutonium was adjusted to Pu(IV) by adding few drops of concentrated sodium nitrite solution. The aqueous phase was then contacted with equal volume of 1.1 M TBP/*n*-dodecane. After equilibration, the organic phase was removed and the aqueous phase contacted again with equal volume of fresh organic phase. The organic phase was then removed. This procedure was repeated 3-4 times to remove uranium(VI) and plutonium(IV) quantitatively. The aqueous phase obtained after the extraction of U(VI) and Pu(IV) as an equivalent of HLLW to monitor the radioisotopes such as ^{95}Zr, ^{106}Ru, ^{125}Sb, ^{60}Co, ^{54}Mn and ^{144}Ce.

2.1.3. Plutonium tracer

Plutonium was purified by anion-exchange. The isotopic composition of the plutonium is as follows (values in atom%) ^{238}Pu: 0.017, ^{239}Pu: 93.60, ^{240}Pu: 6.24, ^{241}Pu: 0.12, ^{242}Pu: 0.023. The specific activity of this plutonium tracer was 1.665×10^5 dpm/μg. The plutonium (IV) tracer was prepared by the following procedure. The acidity of the plutonium solution was adjusted to 1 M HNO_3 and about 0.2 – 0.4 mL of 2.5 M $NaNO_2$ solution was added drop-wise with constant shaking. The resulting Pu(IV) was extracted with 0.5 M thenoyltrifluoroacetone(TTA)/xylene solution. The organic phase was scrubbed with 1 M HNO_3 solution to remove the impurities. The loaded plutonium was stripped by 8 M HNO_3 and used as a stock solution. For the Pu(III) extraction studies, the oxidation state of plutonium was adjusted to Pu(III) by adding freshly prepared ferrous sulfamate, and hydroxylamine hydrochloride [96].

2.1.4. Organic materials and solvents

Diglycolic anhydride and dialkyl amines

Diglycolic anhydride (technical grade, 90%) dibutylamine, dihexylamine, dioctylamine, didecylamine and di-2-ethylhexylamine were procured from Sigma Aldrich Chemie GmbH, Steinheim, Germany. Diglycolic anhydride, obtained from Alfa Aesar was also used in some experiments. Didodecylamine was obtained from Fluka.

Dicycolhexylcarbodiimide (DCC)

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

Alkanes

The alkanes such as *n*-decane, *n*-dodecane, *n*-tetradecane were purchased from Aldrich. *n*-Hexane was obtained from Ranbaxy Fine Chemicals Limited, New Delhi, India.

Dihexyloctanamide

N,*N*- Dihexyloctanamide (DHOA) was obtained from Heavy Water Plant, Tuticorin, India.

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.

Tri-n-butyl phosphate (TBP)

Tri-*n*-butyl phosphate (TBP) was obtained from M/s. Fluka Chemie GmbH, Buche, Switzerland. It was washed with dilute sodium carbonate solution (~ 0.2 M) followed by distilled water and then dried under vacuum.

Thenoyltrifluoroacetone (TTA)

TTA (M/s Tokyo Kasei Kogyo, Japan) was recrystallized from benzene. A 0.5 M of TTA solution in xylene was prepared and stored in amber glass bottle covered with black paper.

Naphthalene

Scintillation grade naphthalene was procured from Loba Chemie Pvt. Ltd,Mumbai, India.

1, 4-Dioxane

1,4-Dioxane was procured from Merck Specialities Private Limited, Mumbai, India and purified prior to use to remove the peroxides that are normally present as quenching impurities. About 2 litres of 1,4-Dioxane was refluxed with ~ 80 g of NaOH pellets for four hours. The dioxane was then distilled and the fraction that distilled between 373 – 375 K was collected after discarding the initial 100 mL fraction. This purified 1, 4 - Dioxane was used for the preparation of cocktail for liquid scintillation counting.

2,5- Diphenyl Oxazole (PPO)

Scintillation grade 2,5-diphenyl oxazole (PPO) was obtained from Loba Chemie Pvt. Ltd., Mumbai, India.

1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP)

Scintillation grade 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP) was obtained from Koch-Light Laboratories Ltd. Colnbrook Buch, England.

Tri-n-octyl phosphinoxide (TOPO)

Tri-*n*-octyl-phospinoxide (TOPO) obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany.

Ethylacetate

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

Methanol

Methanol was obtained from Ranbaxy Fine Chemicals Limited, New Delhi, India.

Silica-gel

Silica-gel of mesh 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.

2.1.5. Aqueous solutions and complexing agents

Diethylenetriaminepentaaceticacid(DTPA)

Diethylene triaminepentaacetic acid was procured from Acros Organics, Geel, Germany. The solution of DTPA was prepared by first dissolving with NaOH (1:5) in millipore water and the pH of the solution was adjusted by HNO_3 to desired value.

Acid solutions

The acid solutions (HNO_3, HCl, GR grade, Merck Specialities Private Limited, Mumbai, India) were prepared by the dilution of concentrated acids, and were standardized by standard acid-base titration methods using standardized NaOH solution using phenolphthalein as indicator.

Sodium hydroxide solution

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

Phenolpthalein

Phenolpthalein (Merck Specialities Private Limited, Mumbai, India) solution 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.

Ammonia Solution

Ammonia Solution (about 25% NH_3, specific gravity 0.91) was obtained from Qualigens Fine Chemicals, Mumbai, India.

Citric acid

Citric acid, anhydrous was obtained from Otto Chemie, Mumbai, India.

Acetohydroxamic Acid

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

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.

Methyl Thymol Blue

Methyl thymol blue was obtained from s.d. fine – CHEM Limited, Mumbai, India. The solution of methyl blue was prepared by dissolving ~20 – 25 mg of it in 10 mL of distilled water for using as indicator for the standardization of neodymium solution.

Neodymium nitrate

Neodymium nitrate was purchased from Alfa Aesar, Mumbai.

2.2. Instrumentation

2.2.1. Liquid scintillation counter

An in-house fabricated liquid scintillation counter was used for measuring alpha activity. In liquid scintillation counting, the energy of alpha particles is absorbed by the cocktail (solvent containing organic scintillators) and converted into photons in the visible region which in turn are converted into photoelectrons by photomultiplier tube and subsequently measured as an electronic pulse. 1,4-dioxane was used as the primary solvent, 2,5-diphenyloxazole (PPO) was used as the primary scintillator. 1,4-di-2-(5-phenyloxazolyl)benzene (POPOP) was used as a wavelength shifter and tri-*n*-octylphosphine oxide (TOPO) as the complexing agent. The liquid scintillation counter consists of a machined perspex vial holder, coupled to a single low noise photo multiplier tube. The discriminator was set with ^{241}Am source and the efficiency was verified with a plutonium source.

In addition, the α-radioactivity of various radioisotopes was also estimated by using α-β discriminating liquid scintillation counter (300SL TDCR liquid scintillation analyzer, Hidex, Finland). The known amount of sample from both organic and aqueous phase was taken in ultima gold AB cocktail (Perkin Elmer) for liquid scintillation counting.

2.2.2. High Pure Gamma Spectrometer (HpGe Detector)

Gamma Spectrometry was used to identify fission products and their concentration. In this technique, a planar high pure germanium (HpGe) crystal semiconductor obtained from OXFORD Instruments, USA was used as the detector.

2.2.3. Gamma counter

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

2.2.4. Gamma chamber

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 resin 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.

2.2.5. 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 from fractions collected during the column chromatography.

2.2.6. 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.

2.2.7. Thermostatted rotary water bath shaker

A refrigerated water bath (PolyScience, Model-9100, USA) with a temperature controlling accuracy of ± 0.010 K was used for the solvent extraction experiments. A JULABO (F33-HE) refrigerated circulator with a temperature controlling accuracy of ± 0.010 K and a heating immersion circulator with a temperature controlling accuracy of ± 0.010 K were also used for the experiments.

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. Spectrophotometer

UV-VIS-NIR spectrophotometer (Shimadzu model UV-3600) was used for absorbance measurements.

2.2.10. Mass spectrometer [Time-of- Flight mass spectra (TOF-MS)]

A home built reflectron time of flight mass spectrometer was used for the mass analysis. Nicotinic acid was used as a matrix and a fourth harmonic of Nd-YAG laser (266 nm) was used for the desorption/ionization. Fine graphite powder mixed uniformly as the matrix for the mass analysis of organic compounds to enhance the absorption of laser [97].

2.2.11. NMR spectrometer

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

2.2.12. Inductively coupled plasma-optical emission spectrometer

Ultima C spectroanalyser (Jobin Yvon, France) equipped with Inductively Coupled Plasma excitation source was used for several non-radioactive elemental analysis. 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.

2.2.13. Electronic single pan balance

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

2.2.14. Thin Layer Chromatrography

Thin-Layer Chromatography (TLC) of reactants and reaction mixture during and after reaction 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 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.

2.3. Methods

2.3.1. Preparation of scintillation Cocktail

The scintillation cocktail is composed of a mixture of solvents and solutes. The solvents act as a medium for absorbing the energy of the nuclear radiation and for dissolving the sample. The solutes act as an efficient source of photons after accepting energy from the excited solvent molecules. Generally, dioxane based cocktail is used for counting both aqueous and organic solution [98]. Dioxane, the primary solvent was refluxed over NaOH for

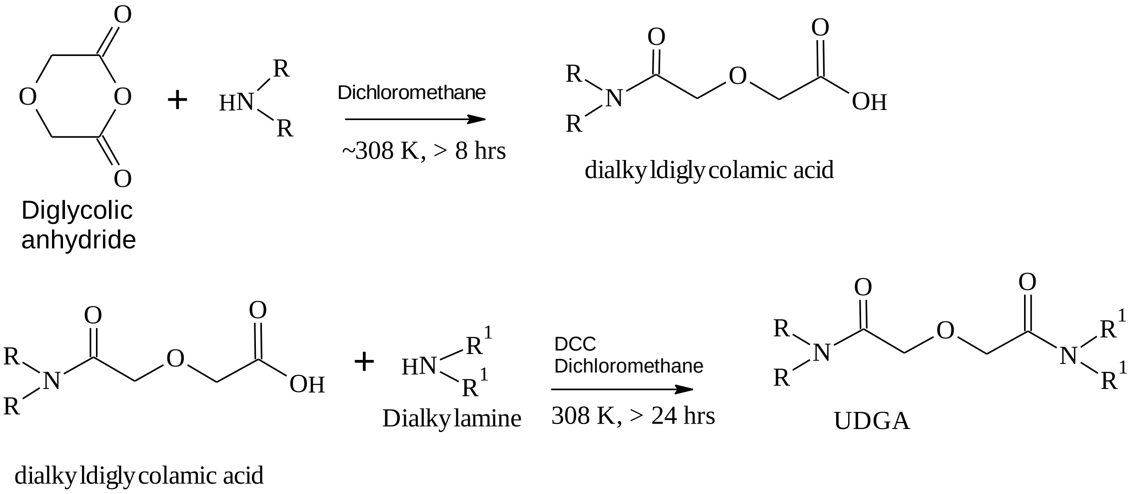
6 hours and distilled to remove peroxide impurities. The following compositions of scintillation grade chemicals (in wt/vol%) were used for the preparation of cocktail [99]. Naphthalene: 10% (secondary solvent), 2,5-Diphenyl oxazole: 0.7% (PPO, primary solute), 1,4-Bis(5-phenyloxazol-2-yl) benzene: 0.03% (POPOP, wavelength shifter) and a complexing agent tri-*n*-octyl phosphine oxide: 4% (TOPO). Naphthalene acts as an intermediate solvent that is capable of transmitting the energy from the primary solvent to the scintillator, thereby by-passing the quenching agent [100]. The prepared cocktail was stored in an amber coloured bottle. Acid quenching [101] is one of the major problems encountered during the liquid scintillation counting, and hence the quenching of scintillation by nitric acid was also studied. Steps were taken to avoid quenching by aliquoting only 50 μL, in the case of samples containing concentrated nitric acid. Samples containing lower activities were counted for longer time.

2.3.2. Column chromatography

The reaction products were purified by column chromatography. A column was packed with silica gel of mesh size 100-200. 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 (5-6 cm long). Hexane or petroleum ether was used as the mobile phase.

2.3.3. Organic synthesis

Several diglycolamic acids and unsymmetrical diglycolamides (UDGAs) were synthesized by the procedure described elsewhere [102]. Synthesis of UDGAs consist two steps. The first step involved the reaction between diglycolic anhydride and dialkylamine to obtain 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 UDGA. The reaction scheme for the synthesis of a typical UDGA is shown in scheme 2.1. The details of synthesis are given below.



Scheme 2.1. The synthetic procedure of UDGAs

Synthesis of dialkyl-diglycolamic acids

Diglycolic anhydride (1eq.) was mixed with dichloromethane (30 mL), which was taken 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 six hours to two days depending up on the nature of alkyl group, to obtain the corresponding dialkyl-diglycolamic acid (see the first step of the scheme 2.1). 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, 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 2.1. Recrystalization of these diglycolamic acids results in white powder (di-octyl diglycolamic acid (DODGAA)/di-dodecyl diglycolamic acid (D^{3}DGAA) or pale yellow colored di-2-ethylhexyl diglycolamic acid (HDEHDGA)). The products were then characterized by IR, NMR, and mass 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.

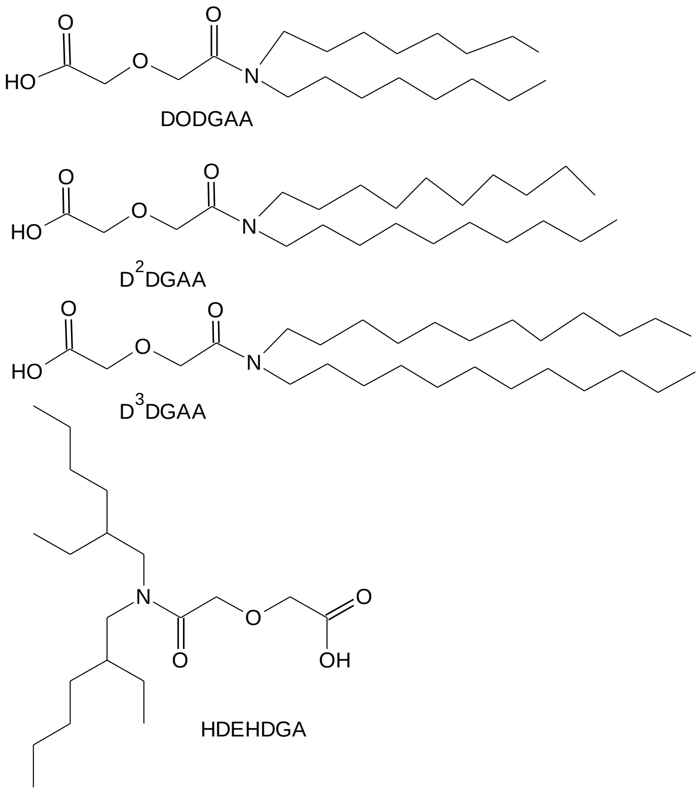


Figure 2.1. The structure of *N,N*-di-alkyl diglycolamic acids.

DODGAA: ^{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 ^{1}H-NMR spectrum of

DODGAA is given in figure 2.2. It is interesting to note from figure 2.2 that the two methelene protons present in between two carbonyl groups of DODGAA appeared at two different positions due to their different chemical environment. The IR spectrum (figure 2.3) 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. The molecular ion peak in the mass spectrum was found at m/z 357.4 as shown in figure 2.4.

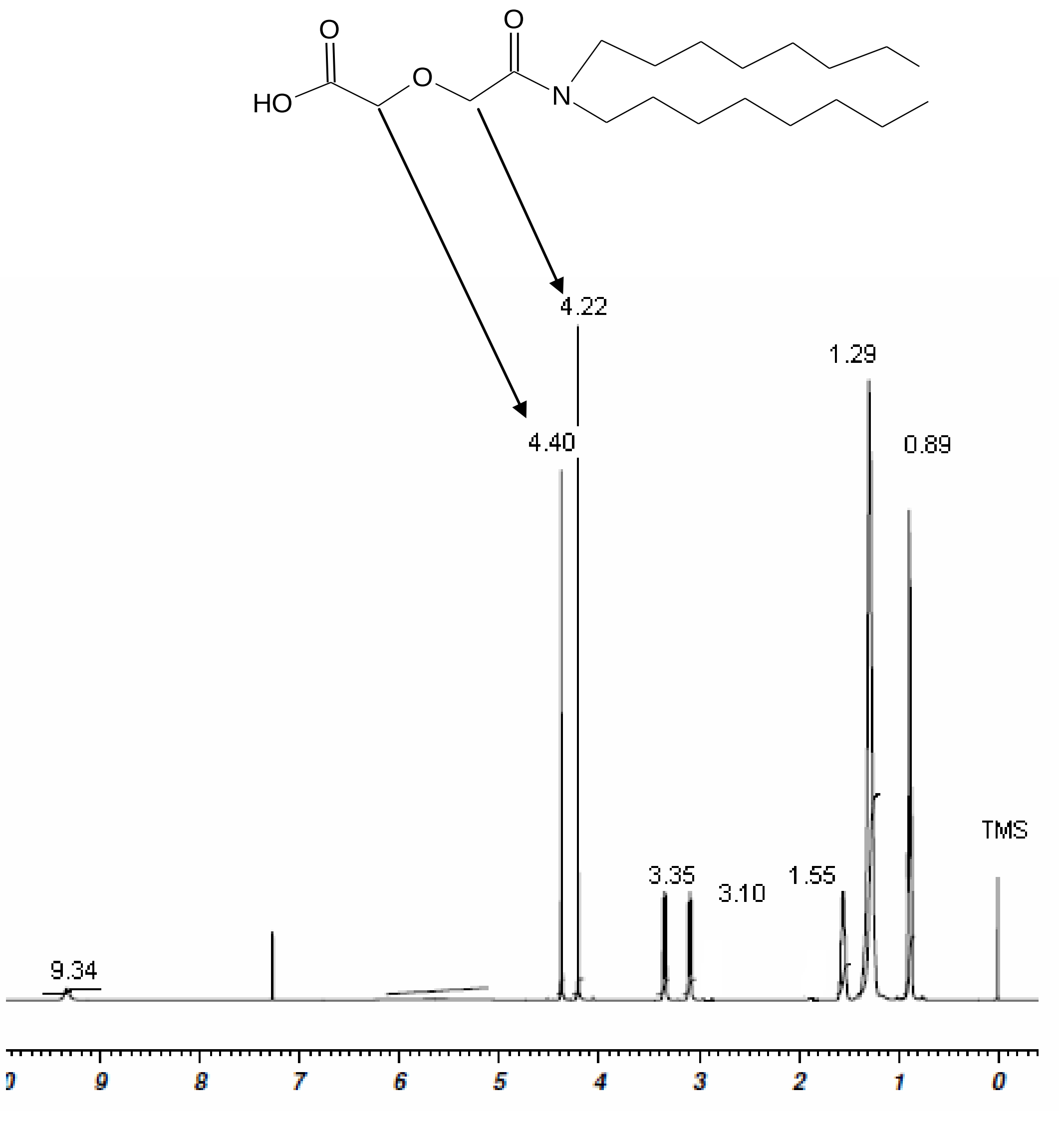


Figure 2.2. ^{1}H-NMR spectrum of DODGAA

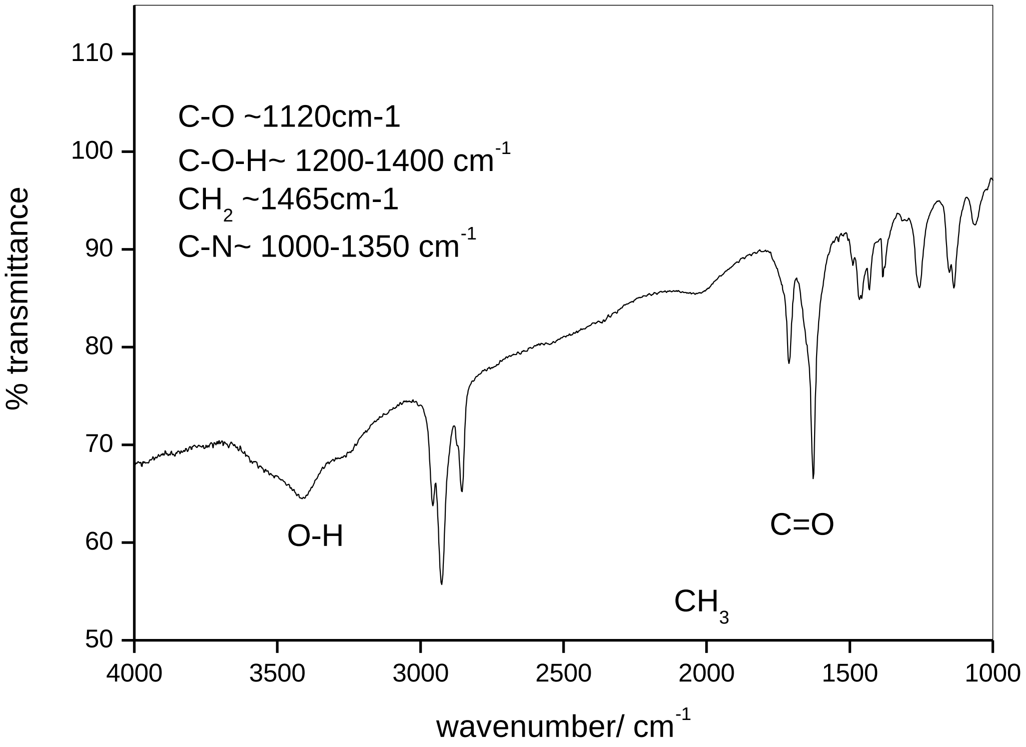


Figure 2.3. IR-spectrum of DODGAA

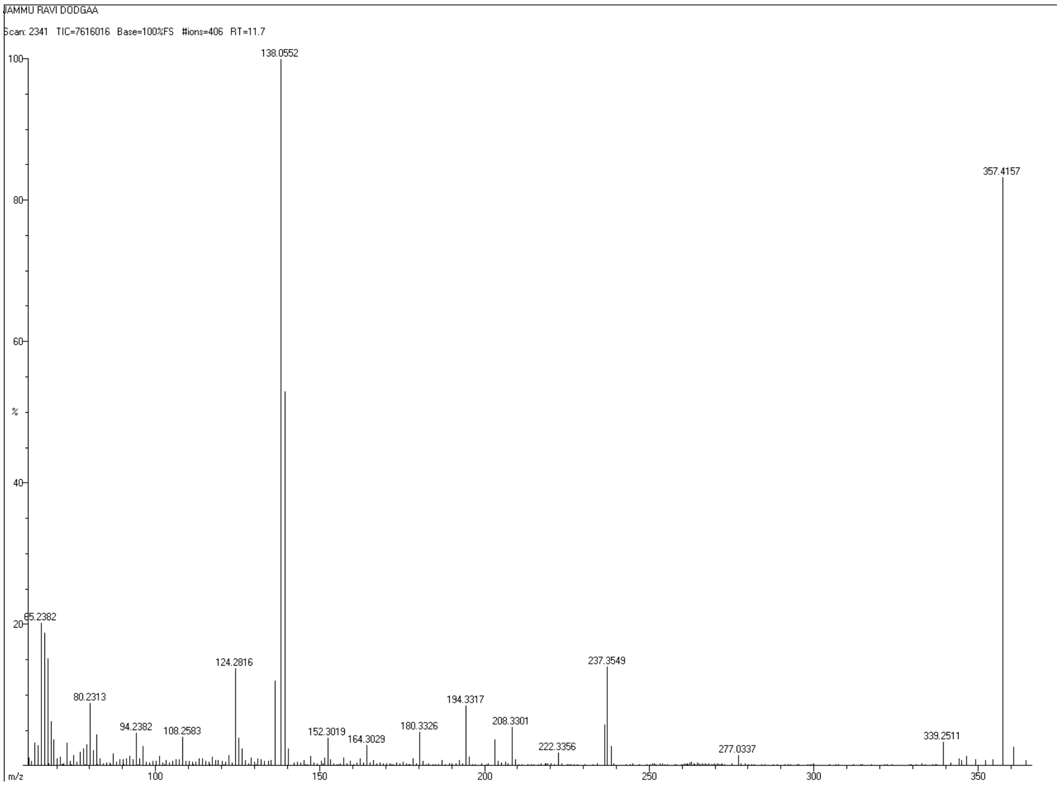


Figure 2.4. Mass spectrum of DODGAA

Similar characteristic features of other diglycolamic acids are seen in their NMR, IR and mass spectra and the details are given below.

D^{3}DGAA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K), δ 0.89 (t, 6H, N-$(CH_2)_{11}$-CH_3), 1.27, 1.56 (s, 40 H, -N-CH_2-$(CH_2)_{10}$-CH_3), 3.11, 3.36 (t, 4 H, -N-CH_2-$(CH_2)_{10}$-CH_3), 4.22 (s, 2H,-N-CO-CH_2-O-), 4.40(s, 2H,-CH_2-COOH). ^{13}C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) 170.59, 77.28, 77.03, 76.78, 71.17, 46.88, 31.90, 29.61, 29.58, 29.52, 29.50, 29.33, 29.31, 29.23, 28.62, 27.41, 26.94, 26.8, 22.67, 14.09. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 3424 (broad, O-H stretching) 2918, 2849 (-CH3-stretching), 1749 (C=O stretching), 1598 (C=O stretching), 1465 (CH_2-bending), 1355 (–C-N- stretching), 1360 (–CH_3-bending), 1126 (C-O-stretching). The molecular ion peak in the mass spectrum was found at m/z 468.6.

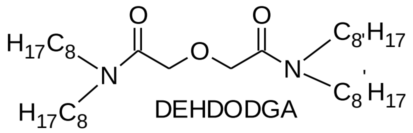
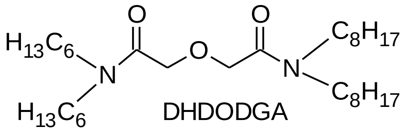
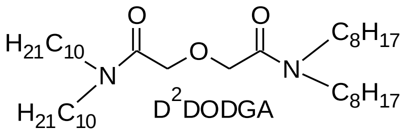
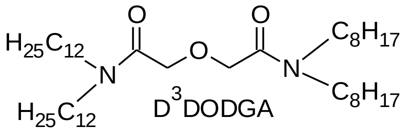
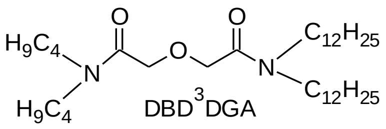
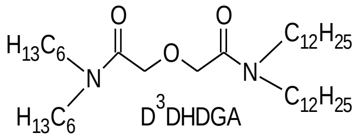
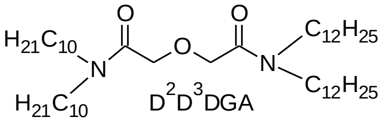
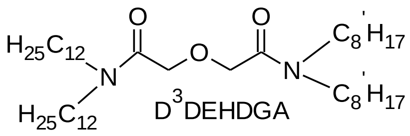
HDEHDGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K), δ 10.67 (s, 1H, COO$\underline{H}$), 4.32 (s, 2H, -OCH_2-), 4.11(s, 2H, $^{-}$C$\underline{H}_2$O^{-}), 3.17-3.31 (m, 4H, 2 C$\underline{H}_2$ - N), 2.96-2.98 (m, 2H, C$\underline{H}$), 1.15-1.24 (m, 16H, C$\underline{H}_2$-R), 0.77-0.84(m, 12H, C$\underline{H}_3$). ^{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 specrum showed the transmittance bands at the following frequencies (cm^{-1}): 3454 (COOH), 1739 (-CO in COOH), 1622(-CO in –CON). A home built reflectron time of flight mass spectrometer was used for mass analysis. The Electron ionization mass spectrum shows a peak corresponding to the mass of 356.5. This results are in good agreement with those reported by Suneesh *et al*.[76].

Synthesis of UDGAs

The diglycolamic acid obtained 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 drop-wise to the diglycolamic acid solution and mixed usingmagnetic stirrer for about fifteen minutes. The desired di-alkylamine was then added drop-wise to the reaction mixture and stirred for about seven days to ten days at constant temperature, 298 K depending upon the alkyl chain length of the reactants. The temperature was seen slightly get elevated to 303 K when the reactants have dodecyl groups (see the second step of the scheme 2.1). 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. The yield of this reaction varied from 60-70 % depending upon the alkyl chain length attached to amidic nitrogen atom of UDGA.

A series of UDGAs namely, *N*,*N*-di-2-ethylhexyl-*N’*,*N’*-di-octyl-3-oxapentane-1,5-diamide or di-ethylhexyl-di-octyl-diglycolamide (DEHDODGA), *N*,*N*-dihexyl-*N’*,*N’*-dioctyl-3-oxapentane-1,5-diamide or di-hexyl-di-octyl-diglycolamide (DHDODGA, *N*,*N*-didecyl-*N’*,*N’*-dioctyl-3-oxapentane-1,5-diamide or di-decyl-di-octyl diglycolamide (D^2DODGA), *N*,*N*-didodecyl-*N’*,*N’*-dioctyl-3-oxapentane-1,5-diamide or di-dodecyl-di-octyl diglycolamide (D^3DODGA), *N*,*N*-di-butyl-*N’*,*N’*-di-dodecyl-3-oxapentane-1,5-diamide or di-butyl-di-dodecyl diglycolamide (DBD^3DGA), *N*,*N*-di-dodecyl-*N’*,*N’*-di-hexyl-3-oxapentane-1,5-diamide or di-dodecyl-di-octyl diglycolamide (D^3DHDGA), *N*,*N*-di-decyl-*N’*,*N’*-di-dodecyl-3-oxapentane-1,5-diamide or di-dodecyl-di-decyl diglycolamide (D^3D^2DGA). *N*,*N*-di-dodecyl-*N’*,*N’*-di-2-ethylhexyl-3-oxapentane-1,5-diamide, or di-dodecyl-di-ethylhexyl diglycolamide (D^3DEHDGA) were synthesized and characterized by using NMR, IR, and mass spectral techniques. The structures of these UDGAs are given in table 2.1. The characterization details for each compound are given below.

Table 2.1. The structures of UDGAs synthesized

S.No	Name of the diglycolamide	Structure
1	*N*,*N*-di-ethylhexyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or Di-ethylhexyl-di-octyl-diglycolamide	
2	*N*,*N*-di-hexyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or di-hexyl-di-octyl-diglycolamide	
3	*N*,*N*-di-decyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or di-decyl-di-octyl-diglycolamide	
4	*N*,*N*-di-dodecyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or di-dodecyl-di-octyl- diglycolamide	
5	*N*,*N*-di-butyl-*N*′,*N*′-di-dodecyl-3-oxapentane-1,5-diamide or di-dodecyl-di-butyl- diglycolamide	
6	*N*,*N*-di-dodecyl-*N*′,*N*′-di-hexyl-3-oxapentane-1,5-diamide or di-dodecyl-di-hexyl- diglycolamide	
7	*N*,*N*-di-decyl-*N*′,*N*′-di-dodecyl-3-oxapentane-1,5-diamide or di-decyl-di-dodecyl- diglycolamide	
8	*N*,*N*-di-dodecyl-*N*′,*N*′-di-ethylhexyl-3-oxapentane-1,5-diamide or di-dodecyl-di-ethylhexyl- diglycolamide	

DEHDODGA: ^{1}H nmr (500 MHz, $CDCl_3$, TMS, 298 K): 4.30 (S, 2H), 4.27 (S, 2H), 3.32-3.20 (m, 4H), 3.17- 3.14 (m, 2H), 3.06 (d, 2H, J=7.5), 1.77-1.65 (m, 2H), 1.50-1.49(m, 6H), 1.25 (m, 34H), 0.86-0.85 (m, 18H). ^{13}C nmr (500 MHz, $CDCl_3$, TMS, 298 K): 169.53, 168.49, 69.15, 69.07, 50.06, 47.98, 47.96, 46.94, 45.78, 37.95, 36.69, 31.78, 31.72, 30.56, 30.49, 29.34, 29.29, 29.20, 29.17, 28.95, 28.81, 28.70, 28.69, 27.58, 27.01, 26.82, 23.80, 23.78, 23.05, 22.98, 22.59, 22.58, 14.02, 13.98, 10.91, 10.59, 10.58. Figure 2.5 shows the of ^{1}H-NMR spectrum of DEHDODGA. The IR spectrum has bands at ν (cm^{-1}): 2928 (C-H stretch), 2857(C-H), 1657(C=O), 1457 (-CH_2-_), 1381 (C-N), and 1119(C-O-C). Figure 2.6 shows the IR spectrum of DEHDODGA. The EI mass spectrum shows the peak corresponding to M$^+$ at 580.6.

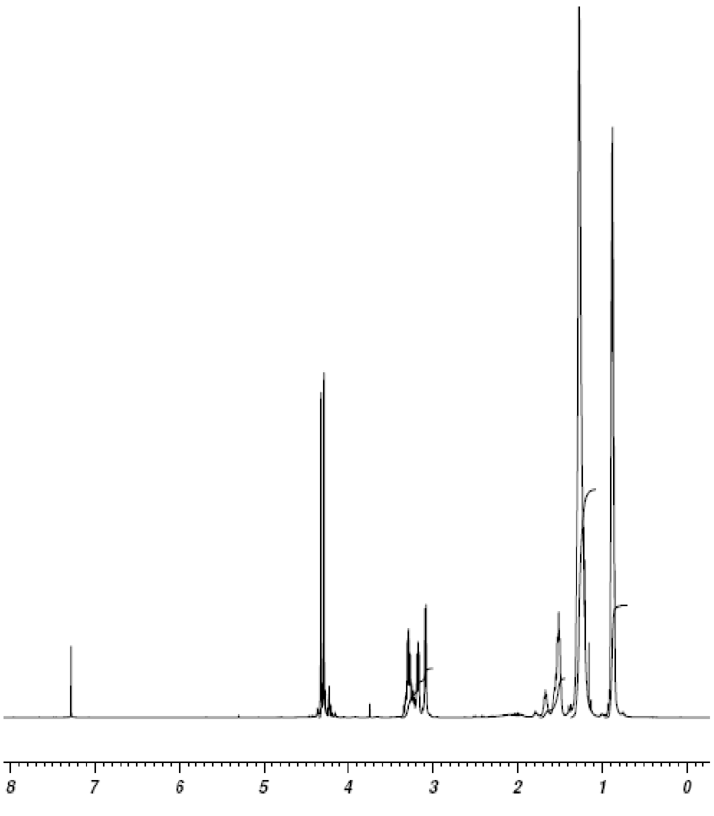


Figure 2.5. ^{1}H-NMR spectrum of DEHDODGA.

Figure 2.6. IR-spectrum of DEHDODGA

DHDODGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.34 (s, 2H), -O-CH_2-CO-N-, 4.30 (s,2H), -O-CH_2-CO-N-, 3.31-3.24 (m, 4 H), -CO-N-CH_2-R, 3.20-3.11(m, 4 H)- -CO-N-CH_2-R, 1.52 (m, 8 H), CH_3-CH_2-$(CH_2)_n$-N-, 1.33-1.28(m, 32 H) CH_3-CH_2-$(CH_2)_n$-CH_2-N-, 0.89-0.86 (m, 12 H) CH_3-$(CH_2)_n$-N. ^{13}C-NMR (500 MHz, CDC_{l3}, TMS, 298 K) at δ 169.04, 168.43, 69.07, 68.48, 50.08, 47.27, 46.90, 45.75, 34.04, 32.24, 31.80, 30.56, 29.37, 29.33, 29.28, 29.20, 29.16, 28.93, 28.78, 28.55, 27.56, 27.47, 27.00, 26.97, 26.86, 26.66, 25.71, 25.32, 25.01, 24.69, 22.59, 14.02, 13.96. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 2928, 2851 (C-H stretching), 1654 (C=O stretching), 1376 (C-N stretching), 1120 (C-O stretching). The molecular ion peak in the mass spectrum of DHDODGA was found at m/z 524.3. Yield was >65 % and the purity was >98%.

D^{2}DODGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.35 (s, 2H) $-O-CH_2-CO-N-$, 4.309 (s, 2H) $-O-CH_2-CO-N-$, 3.20-3.17(m, 4H) $-CO-N-CH_2-R$, 3.19-3.11(m, 4 H) $-CO-N-CH_2-$, 1.54-1.51(m, 8 H) $CH_3-CH_2-(CH_2)_n-CH_2-N-$, 1.28-1.27(m,48 H) $CH_3-CH_2-(CH_2)_n-CH_2-N$, 0.89-0.87 (m, 12 H) $CH_3-(CH_2)_n-N$. ^{13}C-NMR (500 MHz, CDC_{l3}, TMS, 298 K) δ 169.08, 168.47, 77.29, 77.04, 76.79, 71.59, 69.09, 68.48, 54.61, 50.09, 47.03, 46.93, 46.22, 45.78, 32.29, 31.89, 31.88, 31.83, 31.80, 31.74, 30.50, 29.58, 29.55, 29.51, 29.41, 29.37, 29.32, 29.30, 29.24, 29.20, 28.96, 28.80, 27.59, 27.0, 26.87, 26.09, 25.4, 24.7, 22.6, 14.75. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 2921, 2859 (C-H stretching), 1654 (C=O stretching), 1355 (C-N stretching), 1112 (C-O stretching). The molecular ion peak in the mass spectrum was found at m/z 637.8. Yield was >65 % and the purity of the compound was >98%.

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, CDC_{l3}, 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). The molecular ion peak in the mass spectrum was fond at m/z 692.7. Yield was >60 % and the purity was >98%.

DBD^{3}DGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.33 (s, 2H, $-O-CH_2-CO-N-$), 4.30 (s, 2H, $-O-CH_2-CO-N-$), 3.93-3.3 (m, 4 H, $-CO-N-CH_2-R$), 3.18-3.11 (m, 4 $H-CO-N-CH_2-R$), 1.78-1.59 (m, 8 H, $CH_3-CH_2-(CH_2)_n-N-$), 1.26(m, 40 H- $CH_3-CH_2-(CH_2)_n-CH_2-N-$), 0.877 (m, 12 H -$CH_3$-$(CH_2)_n$-N). ^{13}C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 169.04, 168.43, 69.07, 68.48, 50.08, 47.27, 46.90, 45.75, 34.04, 32.24, 31.80, 30.56, 29.37, 29.33, 29.28, 29.20, 29.16, 28.93, 28.78, 28.55, 27.56, 27.47, 27.00, 26.97, 26.86, 26.66, 25.71, 25.32, 25.01, 24.69, 22.59, 14.02, 13.96. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 2928, 2851 (C-H stretching), 1654 (C=O stretching), 1376 (C-N stretching), 1120 (C-O stretching). The molecular ion peak in the mass spectrum of D^3DBDGA was found at m/z 524.3. Yield was >65 % and the purity was >98%.

D^3DHDGA: ^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.35 (s, 2H) -O-CH_2-CO-N-, 4.31 (s, 2H, -O-CH_2-CO-N-), 3.20-3.17 (m, 4H, -CO-N-CH_2-R), 3.19-3.11(m, 4 H,-CO-N-CH_2-), 1.54-1.51(m, 8 H, CH_3-CH_2-$(CH_2)_n$-CH_2-N-), 1.28-1.27(m,48 H, CH_3-CH_2-$(CH_2)_n$-CH_2-N), 0.89-0.87 (m, 12H, CH_3-$(CH_2)_n$-N). 13C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) δ 169.08, 168.47, 77.29, 77.04, 76.79, 71.59, 69.09, 68.48, 54.61, 50.09, 47.03, 46.93, 46.22, 45.78, 32.29, 31.89, 31.88, 31.83, 31.80, 31.74, 30.50, 29.58, 29.55, 29.51, 29.41, 29.37, 29.32, 29.30, 29.24, 29.20, 28.96, 28.80, 27.59, 27.0, 26.87, 26.09, 25.4, 24.7, 22.6, 14.75. The IR spectrum showed the transmittance bands at the following frequencies (cm-1) 2921, 2859 (C-H stretching), 1654 (C=O stretching), 1355 (C-N stretching), 1112 (C-O stretching). The molecular ion peak in the mass spectrum was found at m/z 637.8. Yield was >65 %.

D^2D^3DGA: ^{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, 4H, -CO-N-CH_2-R), 3.15-3.12 (m, 4H,-CO-N-CH_2-R), 1.56-1.51(m, 8H, CH_3-CH_2-$(CH_2)_n$-N-), 1.27-1.27 (m, 56H, CH_3-CH_2-$(CH_2)_n$-CH_2-N-), 0.90-0.88 (m, 12H, CH_3-$(CH_2)_n$-N). 13C-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). The molecular ion peak in the mass spectrum was fond at m/z 692.7. Yield was >60 %.

D^{3}DEHDGA:^{1}H-NMR (500 MHz, $CDCl_3$, TMS, 298 K) at δ 4.30 (s, 2H), -O-C$\underline{H}_2$-CO-N-, 4.16 (s,2H), -O-C$\underline{H}_2$-CO-N-, 3.28-3.24 (m, 4 H), -CO-N-C$\underline{H}_2$-R, 3.15-3.12(m, 4 H)-CO-N-C$\underline{H}_2$-R, 1.79-1.77(m, 10 H) CH_3-C$\underline{H}_2$-$(CH_2)_n$-N-, 1.30-1.26 (m, 44 H) CH_3-CH_2-(C$\underline{H}_2$)$_n$-CH_2-N-, 0.89-0.87 (m, 18 H) C$\underline{H}_3$-$(CH_2)_n$-N. ^{13}C-NMR (500 MHz, $CDCl_3$, TMS, 298 K) δ 169.09, 168.47, 153.57, 77.29, 76.78, 71.03, 69.10, 68.49, 47.04, 46.93, 46.23, 45.79, 37.94, 36.68, 32.29, 31.90, 30.56, 30.51, 29.61, 29.54, 29.45, 29.41, 29.37, 29.33, 29.29, 28.97, 28.81, 27.60, 27.51, 27.04, 27.01, 26.89, 26.84, 26.09, 25.52, 25.34, 24.71, 23.78, 23.07, 22.99, 22.67, 14.09,14.01, 10.93. The IR spectrum showed the transmittance bands at the following frequencies (cm^{-1}) 2927 (C-H stretching), 1762(C=O stretching), 1647(C=O stretching), 1350(C-N stretching), 1128 (C-O stretching). The molecular ion peak in the mass spectrum was found at m/z 692.7.

2.3.4. Extraction of nitric acid and K_H determination

The basicity of the ligand (K_H) is an important parameter that decides the extraction of metal ions. The basicity of the UDGAs synthesized in the present study was determined by the procedure, based on the extraction of nitric acid, is described below [43]. To determine the basicity of UDGA, the extraction of nitric acid from 1 M nitric acid medium was studied as a function of concentration of UDGA in *n*-dodecane at 298 K. The interaction of nitric acid with UDGA is given by equilibrium expression 2.1.

$$H^+_{(aq)} + NO_3^-{}_{(aq)} + n\mathrm{UDGA}_{(org)} \rightleftharpoons HNO_3.n\mathrm{UDGA}_{(org)} \qquad (2.1)$$

where the subscripts (aq), and (org) denote the aqueous, and organic phases respectively, and K_H, the “conditional acid extraction constant” , defined as

$$K_H = \frac{[HNO_3.nUDGA]_{(org)}}{[H^+]_{(aq)}[NO_3^-]_{(aq)}[UDGA]^n_{(org.free)}} \tag{2.2}$$

Taking logarithm, and rearranging equation 2.2,

$$\log [H^+]_{(org)} - 2\log [H^+]_{(aq)} = n \log[UDGA]_{(org.\ free)} + \log K_H \tag{2.3}$$

where, $[UDGA]_{(org.free)} = [UDGA]_{initial} - [H^+]_{(org)}$, and $[H^+]_{(org)} = [HNO_3.nUDGA]_{(org)}$. The value of $[H^+]_{(aq)}$ can be obtained from the titre value (T), and dissociation constant of HNO_3 (K_a = 23.5) using the following equation 2.4.

$$K_a = \frac{[H^+]_{(aq)}.[NO_3^-]_{(aq.)}}{[HNO_3]_{(aq)}} = \frac{[H^+]^2{}_{(aq)}}{T-[H^+]_{(aq)}} \tag{2.4}$$

where T = $\{[H^+]_{(aq)} + [HNO_3]_{(aq)}\}$ in aqueous phase (i.e. dissociated, and undissociated HNO_3), and $[H^+]_{(aq)} = [NO_3^-]_{(aq)}$. Thus, the equation 2.4 is modified to

$$[H^+]^2_{(aq)} + K_a.[H^+]_{(aq)} - K_a.T=0 \tag{2.5}$$

From equation 2.3, the plot of $\{\log[H^+]_{(org)}-2\log[H^+]_{(aq)}\}$ against $\log[UDGA]_{(org.,free)}$ results in a straight line. The slope, *n*, gives the number of molecules of UDGA involved in the formation of an adduct with HNO_3, and the intercept ($\log K_H$) gives the basicity of the ligand. The K_H values were determined for the UDGAs synthesized in the present work from the plots $\{\log[H^+]_{(org)}-2\log[H^+]_{(aq)}\}$against $\log[UDGA]_{(org,\ free)}$ at 1 M nitric acid medium.

Extraction of nitric acid by a solution of UDGA/*n*-dodecane was studied by equilibrating equal volumes (1 mL) of organic phase and 1 M HNO_3 for about 1 hour at 298 K. The amount of nitric acid extracted by organic phase was determined by titrating a known volume of organic phase in methanol-water solution with standardised sodium hydroxide, using phenolphthalein as an indicator. A similar procedure was adopted for determining the concentration of nitric acid present in aqueous phase. However, methanol was not added in this case.

2.3.5. 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 was the solution of extractant in *n*-dodecane in the desired concentration. Depending upon the nature of experiment, organic phase consisted either UDGA/*n*-dodecane alone or mixed with a phase modifier, or co-solvant etc,. The aqueous phase was either desired concentration of nitric acid or simulated high-level liquid waste (HLLW) spiked with a radioisotope or a metal ion. In the case of non-radioactive metal ion extraction studies, the concentration of metal ion in aqueous phase was fixed at 20-200 ppm. 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 (1 mL) 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 for ^{241}Am(III), ^{88}Y(III), $^{(152+154)}$Eu(III), $^{(82+85)}$Sr(II), ^{137}Cs(I), ^{95}Zr(IV), ^{106}Ru(III), ^{125}Sb(III), ^{60}Co(II), ^{54}Mn(II) and ^{144}Ce(III) isotopes was measured using a well-type NaI(Tl) scintillation detector when they are present alone. If more than one isotope was added as in the case of HLLW tracer, the γ-radioactivity of various isotopes was measured using HPGe detector coupled with MCA. The characteristic γ energies of various isotopes used for their quantitative measurement are given in table 2.2. The alpha radioactivity of ^{233}U(VI) and ^{239}Pu was estimated by alpha-beta discriminating liquid scintillation counter (300SL TDCR liquid scintillation analyzer, Hidex, Finland). A known amount of sample from both organic and aqueous phase was taken in ultima gold AB cocktail (Perkin Elmer) for liquid scintillation counting.

The radioisotopes were identified by their characteristic gamma energy, as shown in table 5.1. The concentration of individual metal ions such as Mo(VI), Pd(II), Ba(II), Cd(II), Cr(VI), Ni(II), and Fe(III) present in aqueous phase before and after equilibration was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Their concentration in the organic phase was calculated by mass balance. The distribution ratio (D_{M}) of the metal ion was determined by using the equation 2.6.

$$D_{\mathrm{M}} = \frac{[M]_{org}}{[M]_{aq}} \tag{2.6}$$

where M_{org} and M_{aq} are the radioactivity (or concentration) of radionuclide (or metal ion) in organic and aqueous phases respectively.

Table 2.2. Characteristic γ-energy of various radioisotopes used for the assay.

Radioisotope	γ-energy (keV)
^{54}Mn	834
^{60}Co	1173
^{95}Zr	756
^{106}Ru	621
^{125}Sb	427
^{137}Cs	661
^{144}Ce	133
^{154}Eu	1274

2.3.6. Metal to ligand stoichiometry

Being neutral reagents, UDGAs extracts americium from nitric acid medium by the reaction represented by equation 2.7. Therefore, at constant nitrate concentration, variation of log D_{Am} with log $[\mathrm{UDGA}]_{\mathrm{org.}}$ for the extraction of Am(III) can result in a slope of x according to the equation 2.10.

$$\mathrm{Am}^{+3} + 3\,\mathrm{NO_3}^{-} + x\,\mathrm{UDGA} \rightleftharpoons \mathrm{Am(NO_3)_3.(UDGA)}_x \tag{2.7}$$

$$K = \frac{[Am(NO_3)_3(UDGA)]_{org.}}{[Am^{3+}]_{aq}[UDGA]^{x}_{org}\;[NO_3^-]^{3}_{aq.}} \tag{2.8}$$

$$K' = \frac{D_{Am}}{[UDGA]^{x}_{org.}\,[NO_3^-]^{3}_{aq.}} \tag{2.9}$$

Where K' is constant at constant nitrate concentration.

$$logD_{Am} = logK' + x\,log\,[UDGA]_{org.} \tag{2.10}$$

2.3.7. Preparation of simulated HLLW

The simulated HLLW was prepared by the procedure described elsewhere for the burn-up of 100 GWd/Te and the composition is given in table 2.3 [103]. The nitrate salt or oxide of individual metal ion was dissolved in nitric acid (≤ 1 M) to prepare their stock solutions. 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. The final acidity was determined by standard acid-base titrations using standard NaOH and phenolphthalein indicator. A potassium oxalate solution was added during the titrations to prevent interferences from hydrolysable ions.

Table 2.3. Elemental composition of simulated high-level liquid waste (SHLLW) arising from reprocessing of fast reactor spent fuels (100 GWd/Te) cooling period 1 year.

Metal ion	Quantity (g/L)
Zr(IV)	0.89
Sn(IV)	0.02
Se(IV)	0.01
Sb(III)	0.01
Ce(III)	0.69
Dy(III)#	0.005
La(III)	0.48
Eu(III)	0.31
Gd(III)	0.07
Nd(III)	1.13
Pr(III)	0.34
Pm(III)#	0.05
Sm(III)	0.05
Tb(III)#	0.01
Rh(III)	0.26
Ru(III)	0.81
Y(III)#	0.08
Fe(III)	0.50
Ba(II)	0.41
Sr(II)	0.14
Pd(II)	0.60
Cd(II)	0.04
Ni(II)	0.10
U(VI)	2.64
Mo(VI)	1.09
Cr(VI)	0.10
Te(VI)	0.16
Tc(VI)	0.26
Cs(I)	1.12
Rb(I)	0.06
Ag(I)	0.13
Na(I)	3
Nitric acid	4 M

La added for Y, Pm, Tb, Dy

2.3.8. Stripping studies

Batch studies were conducted to optimize the conditions required for complete recovery of trivalent metal ions from the loaded organic phase. The experiment involved equilibration of equal volumes of organic and aqueous phase spiked with desired isotope/HLLW tracer for one hour. The organic phase was either 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane or irradiated 0.1 M UDGA/*n*-dodecane or other solvent composition of interest. Aqueous phase was either 3 M nitric acid or 4 M nitric acid or simulated HLLW. The organic phase was pre-equilibrated with the corresponding aqueous phase prior to the metal ion loading.

After equilibration, a known volume of loaded organic phase was equilibrated with equal volume of a stripping solution. The stripping solution was either 0.1 M nitric acid or a solution of DTPA at desired acidity or DTPA-citric acid formulation depending upon the nature of experiment. The stripping solution composed of DTPA and citric acid at various pH values. 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.

2.3.9. Third phase formation studies

The third phase studies were carried out in various UDGAs synthesized in the present work by equilibrating desired concentration of UDGA in desired diluents with equal volume of desired aqueous phase. Various diluents such as *n*-decane, *n*-dodecane, *n*-tetradecane etc., were used in the present study. The aqueous phase may be desired concentration of nitric acid alone or known concentration of Nd(III) in desired concentration of nitric acid. In some experiments, the organic phase was added with desired concentration of phase modifier such as DHOA. The concentrations of various components in the organic phase were varied depending upon the nature of experiment. In all the third phase formation studies, the organic phase was pre-equilibrated twice with desired concentration of nitric acid and separated from aqueous phase. The experimental setup for the third phase formation studies consisted of a equilibration tube immersed in a double walled glass container. The temperature of the container was maintained at a desired temperature by circulating the water from a constant temperature water bath. The equilibration was carried out by mixing equal volumes(1mL) of doubly pre-equilibrated organic phase with aqueous phase containing neodymium (III) nitrate in nitric acid at a fixed temperature. The concentration of the nitric acid in this case is similar to that used for pre-equilibration. However, pre-equilibration was not carried out in the third phase formation studies of nitric acid. The mixing was carried out by using a magnetic stirrer. The third phase formed, was then carefully dissolved by a drop-wise addition of the pre-equilibrated organic phase until the third phase/ turbidity was dissolved. The formation as well as the disappearance of the third phase was monitored visually. The concentrations of neodymium in organic and aqueous phases were determined by complexometry to obtain the limiting organic concentration (LOC) and critical aqueous concentration (CAC) of neodymium respectively. To determine the LOC and CAC of nitric acid, the organic phase was equilibrated with nitric acid until the third phase was formed. It was then dissolved by the addition of distilled water. The concentration of nitric acid in organic and aqueous phase was measured by standard acid-base titration.

2.3.10. Effect of temperature of extraction of metal ions

Enthalpy change accompanied by the extraction of Am(III), Eu(III), and Pu(III) in 0.03 M DEHDODGA/*n*-dodecane from 3 M nitric acid medium was determined by measuring the distribution ratio of individual metal ions at various temperatures ranging from 293 K – 323 K.

DEHDODGA for minor actinide partitioning

3.1. Introduction

PUREX process is being adapted worldwide, for the recovery of uranium, and plutonium from the spent nuclear fuel. It 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 [15]. The raffinate rejected after extraction is known as high-level liquid waste (HLLW), which contains significant amounts of lanthanides, other fission products, and transplutonium elements. Since these lanthanides, and actinides (example ^{241}Am), exist in trivalent state in HLLW, they are inextractable by TBP during PUREX process. These trivalent α-emitting 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 in several countries for managing HLLW [16].

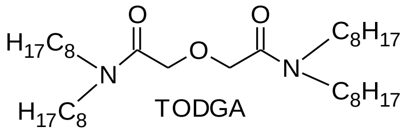
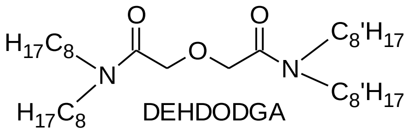
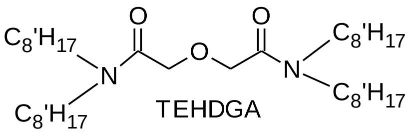
Partitioning of minor actinides is generally carried out by using reagents such as carbamoylorganophoshorous compounds (TRUEX process) [20-23], trialkylphosphine oxides (TRPO process) [24-26], diisodecylphosphoric acid (DIDPA) [28-30], and diamides (DIAMEX process) [34-38] etc. Recently, diglycolamides (DGA) are emerging as superior candidates for the separation of trivalents from high-level liquid waste [40]. Introduction of an etheric oxygen between the two amide groups, as in DGAs, increases the extraction of minor actinides due to enhanced tridentate complex formation with trivalents [45]. Sasaki *et al.*[41] studied physico-chemical and extraction properties of DGAs as a function of alkyl chain length attached to the amidic nitrogen atom of DGA. The solubility of DGAs in aqueous phase decreased and that in organic diluents (such as *n*-hexane and *n*-dodecane) increased with increase of alkyl chain length. When the number of carbon atoms in the alkyl chain was eight or more, the solubility of DGA in aqueous phase was quite low and that in *n*-dodecane, was high. Their study also revealed that the distribution ratio (*D*) of Am(III) and Eu(III) decrease with increase in the alkyl chain length on amidic nitrogen atom. Thus, the physico-chemical and extraction properties of DGAs are strongly dependent on the nature of alkyl groups attached to the amidic nitrogen atom. Based on those studies, the octyl derivative, *N,N,N',N*'-tetraoctyl diglycolamide (TODGA) was proposed as the promising reagent for the trivalent actinide separation from nitric acid medium. Later studies have shown that its isomer, *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) was also a potential candidate for the partitioning of trivalent actinides [55-57]. The extensive studies using these reagents, confirmed their capability for the extraction of trivalent actinides (An(III)) and lanthanide (Ln(III)) from nitric acid medium [40-57].

Even though, TEHDGA is a promising candidate for minor actinide partitioning, the $D_{\mathrm{Am(III)}}$ in TEHDGA/*n*-dodecane is lower than TODGA/*n*-dodecane under similar conditions[26]. Therefore, most of the data generated with TEHDGA use 0.2 M solution, while TODGA is employed as 0.1 M solution. In addition, early formation of third phase in 0.2 M TEHDGA/*n*-dodecane (occurs at 3.9 M HNO_3) with nitric acid demands the requirement of organic phase modifiers, in significant concentration[57]. Recently, Magnusson *et al*. [49] demonstrated a TODGA based extraction process for partitioning of minor actinides from a genuine PUREX raffinate in a centrifugal contactor and reported that significant amount of strontium was extracted by TODGA, and required more stages of scrubbing. On the other hand, TEHDGA is reported to have more selectivity towards the extraction of trivalent metal ions over the other metal ions [52]. Higher extraction of strontium, and other elements in TODGA was attributed to the higher basicity (K_H) of the TODGA/*n*-dodecane (K_H = 4.1 [53]) as compared to TEHDGA (K_H = 0.19 [64]). Arisaka *et al.*[65] reported the K_H of TODGA/*n*-dodecane as 0.38. Mowafy *et al*. [42] reported the K_H value of 0.27 for TODGA/benzene.

The information available in the literature thus indicates that the extraction behaviour is strongly dependent on the nature of alkyl groups. Considering the advantages and limitations of *n*-octyl group in TODGA, and 2-ethylhexyl- moiety in TEHDGA, the synthesis of a new unsymmetrical diglycolamide, namely, *N*,*N*-di-2-ethylhexyl-*N',N*'-di-octyl-3-oxa-pentane-1,5-diamide, trivially known as di-ethylhexyl-di-octyl-digylcolamide (DEHDODGA) which will have better extraction properties with lower third phase formation tendency is envisaged in the present study. This compound contains 2-ethylhexyl groups in one arm, and the octyl groups in the other arm. It is realized that, the alkyl groups present in DGAs studied for minor actinide partitioning are symmetrical i.e. all the alkyl groups attached to the diglycolamide are structurally identical. For instance, in TODGA all alkyl groups are octyl, and in TEHDGA it is 2-ethylhexyl moiety. Since the extraction and stripping behavior of trivalents are strongly dependent on the structure and properties of alkyl group attached, and thus the separations are unique to substituents. Moreover the hydrophilic and lipophilic properties of DGA can be manipulated by varying substituents [19, 21]. In view of these the extractant DEHDODGA is prepared to have the properties of both TEHDGA, and TODGA, and expected to minimize the limitations of TEHDGA, and TODGA. The structures of these reagents are shown in table 3.1.

The present chapter deals with the evaluation of DEHDODGA for the separation of Ln(III) and An(III) from nitric acid medium. These studies include determination of extractant (DEHDODGA) basicity, optimization of extractant concentration for the extraction, investigation of third phase formation limits during the extraction, modification of solvent composition to prevent third phase formation, extraction behavior of actinides, fission products and other metal ions in the modified solvent, interference of these metal ions on the extraction of trivalent metal ions, the influence of phase modifier on the extraction behavior of metal ions, and the development of stripping formulation for the quantitative back extraction of trivalent metal ions from the loaded organic phase etc.

Table 3.1. The structures and names of the DGAs

S.No.	Name	Structure
1.	*N,N,N',N'*-tetra-octyl-3-oxapentane-1,5-diamide (or) tetra-octyl diglycolamide	
2.	*N,N*-di-2-ethylhexyl-*N',N'*-di-octyl-3-oxapentane-1,5-diamide (or) di-ethylhexyl-di-octyl-diglycolamide	
3.	*N,N,N',N'*-tetra-2-ethylhexyl-3-oxapentane-1,5-diamide (or) tetra-ethylhexyl-diglycolamide	

3.2. Determination of basicity of DEHDODGA

Neutral ligands such as DGAs generally extract nitric acid to a significant extent from the aqueous phase. The "basicity" or "conditional acid extraction constant", (K_H) of a ligand is the measure of amount of nitric acid extraction by the ligand, which determines its complexing ability with metal ions. Figure 3.1 shows the extraction of nitric acid by a solution of DEHDODGA in *n*-dodecane as a function of nitric acid concentration in the aqueous phase at constant temperature 298 K. It is observed that the amount of nitric acid extracted into organic phase increases with increase in concentration of DEHDODGA in the organic phase as well as nitric acid concentration in the aqueous phase. When the equilibrium concentration of nitric acid in the aqueous phase exceeds 9 M and 4 M, there was a third phase formation in case of 0.03 M and higher concentrations of DEHDODGA (0.1 M or

0.2 M) respectively. Therefore, the amount of nitric acid extracted into organic phase was estimated below those limits.

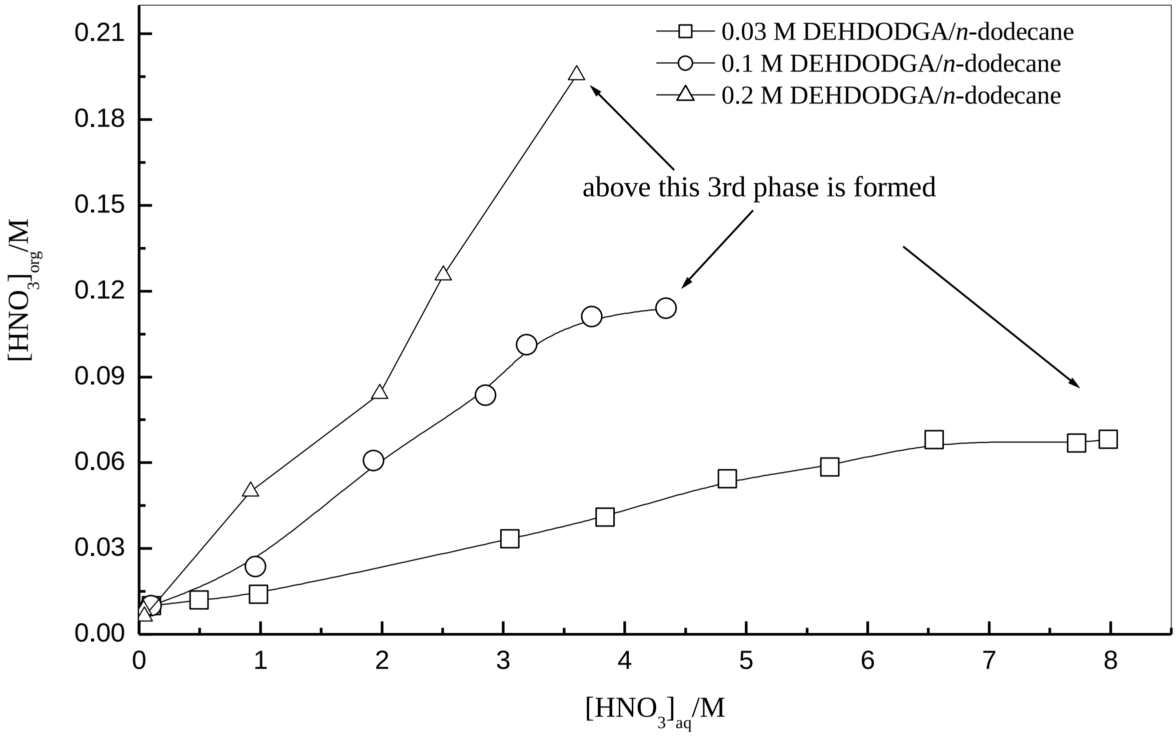


Figure 3.1. Nitric acid extraction isotherm of DEHDODGA/*n*-dodecane at 298 K.

Basicity of DEHDODGA was determined by the procedure described in section 2.3.4. The extraction of nitric acid into organic phase was monitored by equilibrating various concentrated solutions of DEHDODGA in *n*-dodecane with 1 M nitric acid at a constant temperature, 298 K. Figure 3.2 shows the variation in $\{\log[H^+]_{(org)} - 2 \log [H^+]_{(aq)}\}$ with $\log[DEHDODGA]_{(org.free)}$. Slope of the straight line obtained in the plot, *n*, gives the number of molecules of DEHDODGA involved in the formation of an adduct with HNO_3, and the intercept ($\log K_H$) gives the conditional acid extraction constant or basicity of the ligand. From the intercept, K_H was determined to be 0.24. Deepika *et al*. [64] reported a K_H of 0.19 for TEHDGA/*n*-dodecane and Makoto Arisaka *et al*. [65] reported a K_H value of 0.38 for

TODGA/*n*-dodecane. The K_H value of 0.24 obtained for DEHDODGA indicates that its basicity is in between to that of TODGA and TEHDGA.

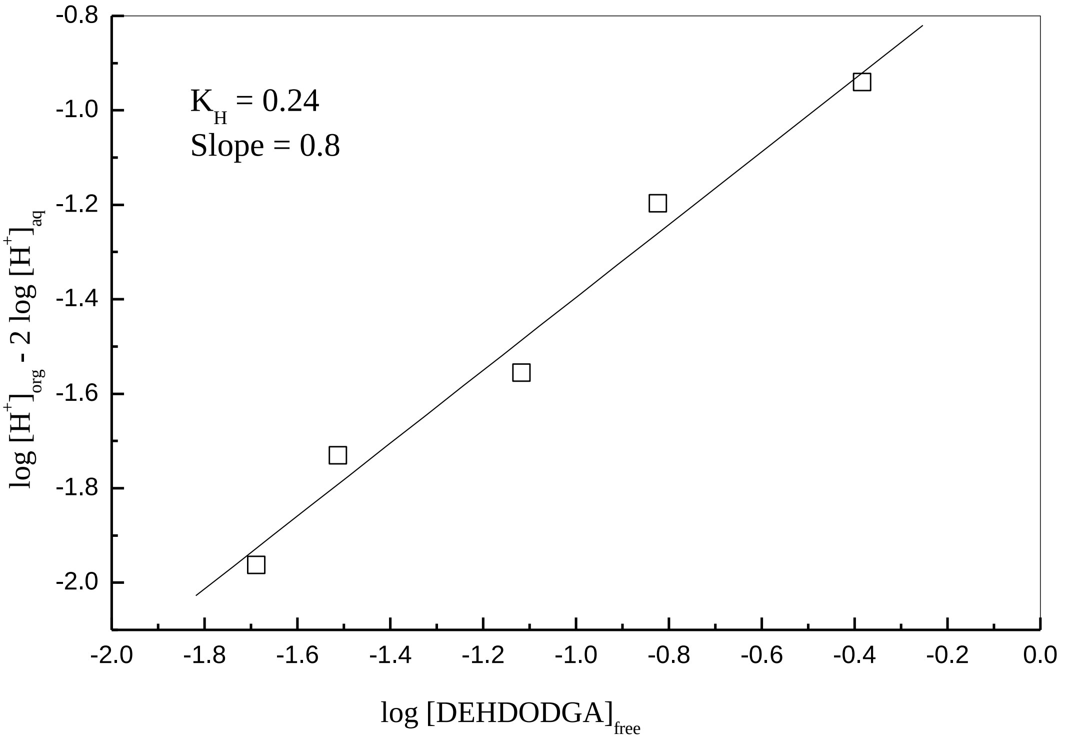


Figure 3.2. Plot of {log $[H^+]_{org}$ - 2 log $[H^+]_{aq}$} against log $[\mathrm{DEHDODGA}]_{free}$ for the extraction of nitric acid by DEHDODGA/*n*-dodecane at 298 K. Aqueous phase : 1 M HNO_3.

3.3. Extraction of metal ions by DEHDODGA

Table 3.2 shows the distribution ratio of Am(III) ($D_{\mathrm{Am(III)}}$) as a function of equilibrium concentration of nitric acid in various concentrated solutions of DEHDODGA in *n*-dodecane at 298 K. It can be seen that $D_{\mathrm{Am(III)}}$ increases with increase in the concentration of DEHDODGA concentration in organic phase at a fixed concentration of nitric acid in the aqueous phase. This could be due to higher availability of extractant molecules for the complexation with the metal ion at higher concentrations. Table 3.2 also indicates that the $D_{\mathrm{Am(III)}}$ increases with increase in aqueous phase acidity at all concentrations of DEHDODGA studied. This behavior is expected for the neutral ligands and it can be explained by equilibrium equation 3.1.

$$Am^{+3}_{(aq)} + 3\ NO^{3-}_{(aq)} + x\ DEHDODGA_{(org)} \rightleftharpoons Am(NO_3)_3.(DEHDODGA)_{x\ (org)} \quad (3.1)$$

Increase in the concentration of nitric acid in the aqueous phase, shifts the equilibrium towards forward direction, and thus increases complex formation. Therefore, at higher nitric acid concentrations, the distribution ratios are higher and at lower acidities they are low. This behavior is indeed desirable for complete extraction of trivalents from 3-4 M nitric acid medium (HLLW acidity) and quantitative back extraction from the loaded organic phase using dilute nitric acid or other stripping solution.

Table 3.2. Comparison in the $D_{Am(III)}$ in a *n*-dodecane solution of DEHDODGA, TODGA[43] and TEHDGA[54] at 298 K.

$[HNO_3]_{eq}$ /M	$D_{Am(III)}$				
	[DEHDODGA]			[TEHDGA]	[TODGA]
	0.01 M	0.03 M	0.1 M	0.2 M	0.1 M
0.1	Nil	4×10^{-4}	6×10^{-3}	--	0.013
0.5	1×10^{-4}	3×10^{-3}	0.14	--	0.78
1	1×10^{-4}	0.03	2.3	3.4	24.1
2	0.06	2.42	108	32.1	171
3	1.00	30.13	279	87.1	297

Table 3.2 also compares the extraction behaviour of Am(III) in various isomeric DGAs. It is interesting to note from table 3.2 that the extraction of Am(III) increases in the order TEHDGA < DEHDODGA < TODGA. This indicates that branching in alkyl groups attached to amidic nitrogen atom suppresses the extraction of metal ions. For a good extraction and stripping of metal ions, a *D* of 10-40 is desirable. It is observed from table 3.2 that this range is obtained at 3 M nitric acid, when the concentration of DEHDODGA is 0.03

M in *n*-dodecane. Therefore, the metal ion extraction behavior was studied by employing 0.03 M DEHDODGA in *n*-dodecane and the results are discussed below.

The extraction behavior of some trivalent metal ions, and Pu(IV) was studied in 0.03 M DEHDODGA as a function of concentration of nitric acid in the aqueous phase and the results are given in table 3.3. The distribution ratios of An(III) and Ln(III) increase with increase of concentration of nitric acid in the aqueous phase and exceeds a value of 300 at higher acidities. These extraordinary high *D* values observed for Ln(III) and An(III) in DGA class of extractants was attributed to the formation of reverse micellar aggregates of appropriate cavity at higher acidities (> 0.7 M HNO_3) [58-62]. It is interesting to note that the *D* values of these metal ions increased in the order of Pu(III) < Am(III) < Eu(III), which is the increasing order of ionic potential (charge to radius ratio (z/r)) for these metal ions (ionic radii of Pu(III) = 0.1 nm, Am(III)=0.099 nm, Eu(III)= 0.095 nm[104]. Among the actinide ions studied, the extraction of tetravalent plutonium is much higher. Moreover, a third phase was observed in the case of Pu(IV) extraction from 7 M nitric acid medium. The extraction of Cs(I) by 0.03 M DEHDODGA/*n*-dodecane was negligible at all acidities studied and therefore, it is not included in the table 3.3.

Table 3.3. Distribution ratio of Am(III), Eu(III), Pu(III), and Pu(IV) in 0.03 M DEHDODGA/*n*-dodecane at 298 K. Aqueous phase: Varied concentration of nitric acid. Organic to aqueous phase ratio= 1:1.

$[HNO_3]_{eq}$ /M	D_M			
	Am(III)	Eu(III)	Pu(III)	Pu(IV)
0.1	4×10^{-4}	9×10^{-4}	2×10^{-4}	0.02
0.5	3×10^{-3}	6×10^{-3}	3×10^{-3}	0.34
1.0	0.03	0.17	0.03	2.28
2.0	2.42	19.5	2.17	19.2
3.0	30.1	116	22.9	56.1
4.0	94.8	152	38.6	105
5.0	>300	>300	75.9	138
6.0	>300	>300	83.5	210
7.0	>300	>300	102	*
8.0	>300	>300	ND	*

*- not determined due to third phase formation, ND- not determined

The extraction of Sr(II) was studied in both 0.03 M DEHDODGA and 0.1 M DEHDODGA as a function of concentration of nitric acid in the aqueous phase and the *D*s are given table 3.4. It is interesting to note that the distribution ratio of Sr(II) ($D_{Sr(II)}$) in 0.03 M DEHDODGA/*n*-dodecane increases from 10^{-3} at 0.1 M nitric acid to a maximum value of 0.18 at 4 M, followed by decrease. In 0.1 M DEHDODGA/*n*-dodecane a maximum $D_{\mathrm{Sr(II)}}$ value of 3.6 is obtained at 4 M nitric acid. Tachimori *et al.*[52] reported a similar behavior in 0.1 M TODGA/*n*-dodecane, and 0.1 M TEHDGA/*n*-dodecane systems. In both cases, the $D_{\mathrm{Sr(II)}}$ values increased with increase in the concentration of nitric acid, reached a maximum value of ~5 at 3 M nitric acid followed by a decrease. Table 3.4 also shows the separation factor of americium over strontium (SF=D_{Am}/D_{Sr}) achieved in DEHDODGA. It is observed that SF increases continuously with increase of nitric acid concentration in case of 0.03 M DEHDODGA/*n*-dodecane. A separation factor of 300 to 500 is achieved during the extraction from 3, and 4 M nitric acids respectively in 0.03 M DEHDODGA/*n*-dodecane.

Table 3.4. Variation in the $D_{Am(III)}$ and $D_{Sr(II)}$, and their separation factors (SF) with DEHDODGA concentration at various nitric acid concentrations. T = 298 K, SF= D_{Am}/D_{Sr}. Organic to aqueous phase ratio= 1:1.

$[HNO_3]_{eq}$ / M	*D*				SF	
	Am(III)		Sr(II)			
	0.03 M	0.1 M	0.03 M	0.1 M	0.03 M	0.10
0.1	4×10^{-4}	6×10^{-3}	3.7×10^{-3}	3.4×10^{-3}	0.10	2
0.5	2.8×10^{-3}	0.14	2.6×10^{-3}	5×10^{-3}	1.0	24
1	0.03	2.3	8×10^{-3}	0.03	3.5	80
2	2.4	108	0.03	0.7	81	144
3	30.1	246	0.09	2.7	324	91
4	95	>300	0.18	3.6	520	>83
5	> 300	*	0.17	*	~1700	*
6	> 300	*	0.10	*	> 2000	*
7	> 300	*	0.04	*	> 6900	*
8	> 300	*	0.01	*	> 20000	*

* indicates the corresponding values are not determined due to third phase formation with nitric acid.

However, the SF decreased to < 100 when the concentration of DEHDODGA/*n*-dodecane increased to 0.1 M at 3 M nitric acid, indicating increase in Sr(II) extraction with increase of DEHDODGA concentration. The separation factor achieved in the present study is higher than the value reported for 0.1 M TEHDGA/*n*-dodecane (SF~22), and marginally higher than the value reported for 0.1 M TODGA/*n*-dodecane (SF~75) system under similar conditions [52, 105].

3.3.1. Enthalpy of extraction

The enthalpy change accompanied by the extraction of Am(III), Eu(III), and Pu(III) from 3 M nitric acid medium using a solution of 0.03 M DEHDODGA/*n*-dodecane was determined by studying the uptake of these metal ions as a function of temperature using Van't Hoff equation of the form shown in equation 3.2.

$$\frac{\partial\, lnD}{\partial\, (1/T)} = \frac{-\Delta H_{tot}}{R} \tag{3.2}$$

The plot of ln*D* against (1/T) for the extraction of these metal ions is shown in figure 3.3. The enthalpy of extraction can be calculated from the slope of straight lines obtained by the linear regression of extraction data. It can be seen from the table 3.5, that extraction is exothermic.

Burger [106] has suggested that several factors control the overall enthalpy change (ΔH_{tot}) in solvent extraction. Essentially it consists of the enthalpy changes is associated with (a) the dehydration of M(III), which requires energy, (b) formation of metal- solvate complex which may be endothermic or exothermic (c) transfer, and dissolution of metal-solvate complex in the organic phase which requires energy which may exothermic or endothermic. Thus the overall enthalpy change observed is the combination of various enthalpies mentioned above, and whichever factor predominates will govern the magnitude and sign of overall enthalpy change. The exothermicity observed in the present case indicates that the extraction is driven by complex formation of DEHDODGA with the metal ions.

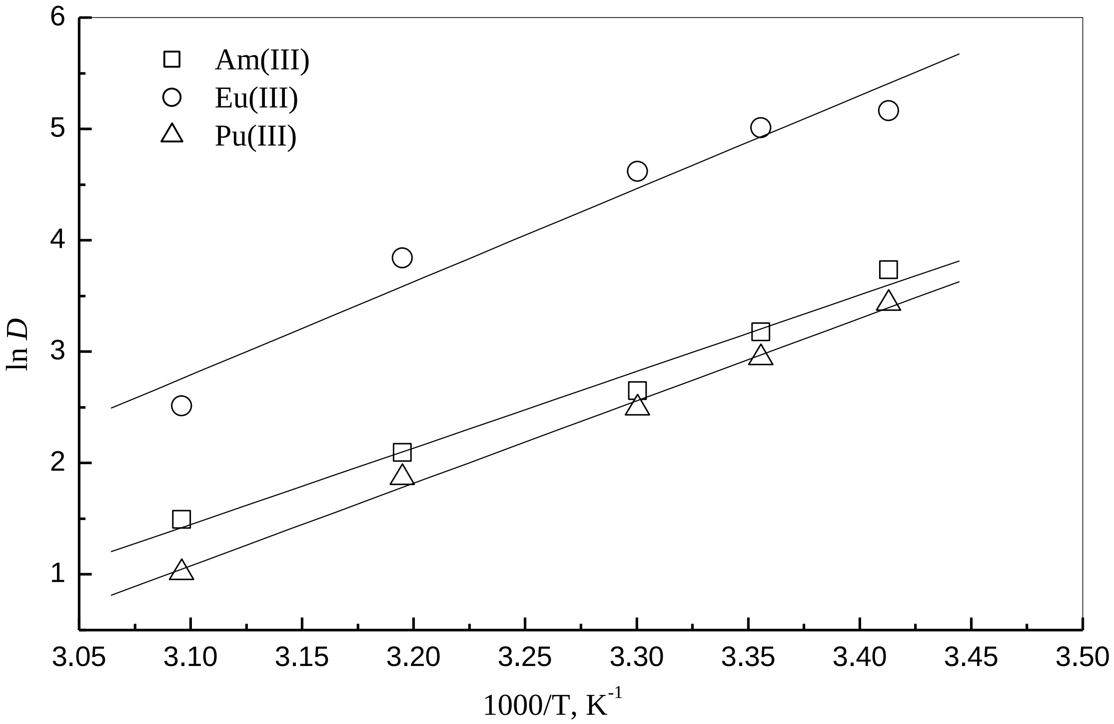


Figure 3.3. Plot of ln *D* against 1/T for the extraction of some trivalents from 3 M nitric acid medium. Organic phase: 0.03 M DEHDODGA/*n*-dodecane. Organic to aqueous phase ratio=1:1.

Table 3.5. Enthalpy change accompanied by the extraction of some trivalents in 0.03 M DEHDODGA/*n*-dodecane, Aqueous phase: 3 M HNO_3. Organic to aqueous phase ratio= 1:1.

Metal ions	ΔH_{tot}, kJ/mol
Pu(III)	-61.5 ± 13.2
Am(III)	-57.1 ± 6.7
Eu(III)	-69.7 ± 8.8

3.3.2. Extraction of metal ions by 0.1 M DEHDODGA/n-dodecane

The above studies were carried out using a 0.03 M DEHDODGA in *n*-dodecane. However, to achieve higher throughput and higher metal loading in organic phase, the extractant concentration should be more in the organic phase. Therefore, a 0.1 M DEHDODGA/*n*-dodecane solution seems to be better option over the 0.03 M solution for the trivalent metal ion extraction from HLLW. In this context, the extraction behavior of metal ions that are present in HLLW was studied using 0.1 M DEHDODGA/*n*-dodecane as a function of concentration of nitric acid and the results are given in table 3.6.

It is interesting to note that the distribution ratios of trivalent metal ions such as Am(III) and Eu(III) are high during the extraction from 3-4 M nitric acid medium by 0.1 M DEHDODGA/*n*-dodecane. In addition to these metal ions, the other undesirable fission products such as Y(III), Zr(IV) also exhibited high *D*s at 3-4 M nitric acid medium. Sr(II) exhibiting a *D* ~4 at 4 M nitric acid medium is likely to be extracted completely in 3-4 contacts. Mo(VI) and Ba(II) extraction also increased with increase of nitric acid concentration and reached a maximum of 0.2 and 0.1 respectively. The co-extraction of these metal ions along with actinides indicates the possibility of complications during the recovery of trivalent actinides from the loaded organic phase, and in the subsequent lanthanide-actinide separation step. This needs the scrubbing of loaded organic phase to improve decontamination. Even though these results are quite similar to other symmetrical diglycolamides, the distribution ratios of Pd(II), Cd(II), Ba(II), Sr(II), and Cr(VI) are smaller than that observed in TODGA/*n*-dodecane. However, this difference is marginal in most of the cases. It is important to note that the extraction of Mn(II), Sb(III), Co(II) and Cs(I) is insignificant at all the acidities studied. The distribution ratios of these metal ions are lower than 1 x 10^{-3} and hence, there is practically no extraction. It is noteworthy that the extraction of U(VI) is much less when compared with trivalent metal ions. Poor extraction of U(VI) could be due to the steric hindrance created by linear UO_2^{2+} species during the complexation with nonlinear DEHDODGA. A similar behavior is also seen in the symmetrical DGAs such as TODGA and TEHDGA [9,43].

Thus, the distribution ratios of metal ions (D_M) are strongly dependent on the oxidation state and size of the metal ion. In general, the D_M value decreases in the order $M^{4+} \sim M^{3+} >> M^{2+} \sim MO_2^{2+} >> M^+$, which is in good agreement with the order observed for symmetrical diglycolamide, TODGA [50].

Table 3.6. Variation in the *D* of Am(III), fission products and structural component metal ions with nitric acid concentration at 298 K. Organic phase: 0.1 M DEHDODGA/*n*-dodecane; Aqueous phase: nitric acid. Organic to aqueous phase ratio=1:1.

$[HNO_3]$/ M	Am(III)	Eu(III)	Y(III)	Zr(IV)	Pd(II)	Fe(III)	Ni(II)	Mo(VI)	Cr(VI)	Cd(II)	Ba(II)	U(VI)	Sr(II)
0.1	$6x10^{-3}$	$6x10^{-3}$	$6x10^{-3}$	0.02	0.06	0.07	$< 10^{-3}$	0.19	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	3×10^{-3}	3.4×10^{-3}
0.5	0.14	0.12	-	0.18	0.04	0.01	-	-	-				5×10^{-3}
1	2.3	1.99	3.3	77	0.06	0.04	$< 10^{-3}$	0.04	0.1	0.16	0.05	0.15	0.03
3	279	272	>300	>300	0.07	-	0.05	0.14	0.1	0.14	0.83	2.3	2.7
4	>300	>300	>300	>300	0.09	-	0.03	0.22	0.1	0.25	0.91	5.3	3.6

Note: Mn(II), Sb(III), Co(II), Cs(I) were found to have a $D < 1 \times 10^{-3}$ at all the acidities

3.4. Third phase formation behavior of DEHDODGA

3.4.1. Third phase formation with nitric acid

Sasaki *et al.* [67] studied the third phase formation behaviour of various DGAs and reported that the LOC and CAC values increase with increase of alkyl chain length attached to amidic nitrogen atom of DGAs. DGAs extract significant amount of nitric acid and some of them form third phase even with nitric acid alone. For example, 0.1 M TODGA/*n*-dodecane and 0.2 M TEHDGA/*n*-dodecane form third phase when they equilibrated with equal volume of 6 M and 4 M nitric acids respectively at 298 K.

Table 3.7. Critical aqueous concentration (CAC) of nitric acid for third phase formation in DEHDODGA/*n*-dodecane at 298 K. Organic to aqueous phase ratio=1:1.

[DEHDODGA] in *n*-dodecane/ M	CAC of $[HNO_3]_{eq}$/M
0.03	9.5
0.1	5.5
0.2	4.9
0.5	4.0

In this context, the third phase formation behaviour of DEHDODGA/*n*-dodecane was studied with nitric acid as a function of its concentration, and results are presented in table 3.7. It is important to note that DEHDODGA also form third phase with nitric acid and CAC of nitric acid decreases with increase in the concentration of DEHDODGA. The third phase was formed at the critical aqueous nitric acid concentration of 9.5 M for 0.03 M DEHDODGA/*n*-dodecane which decreases to the value of 4 M when the concentration of DEHDODGA is 0.5 M. However, the third phase formation limits can be shifted to higher CAC levels by the addition of modifiers such as *N, N*-dihexyloctanamide (DHOA). Table 3.8 shows the variation in the third phase formation behaviour of DEHDODGA-DHOA in *n*-dodecane with initial concentration of nitric acid. It is observed that the formation of third phase is shifted to higher nitric acid concentrations with increase in the concentration of DHOA.

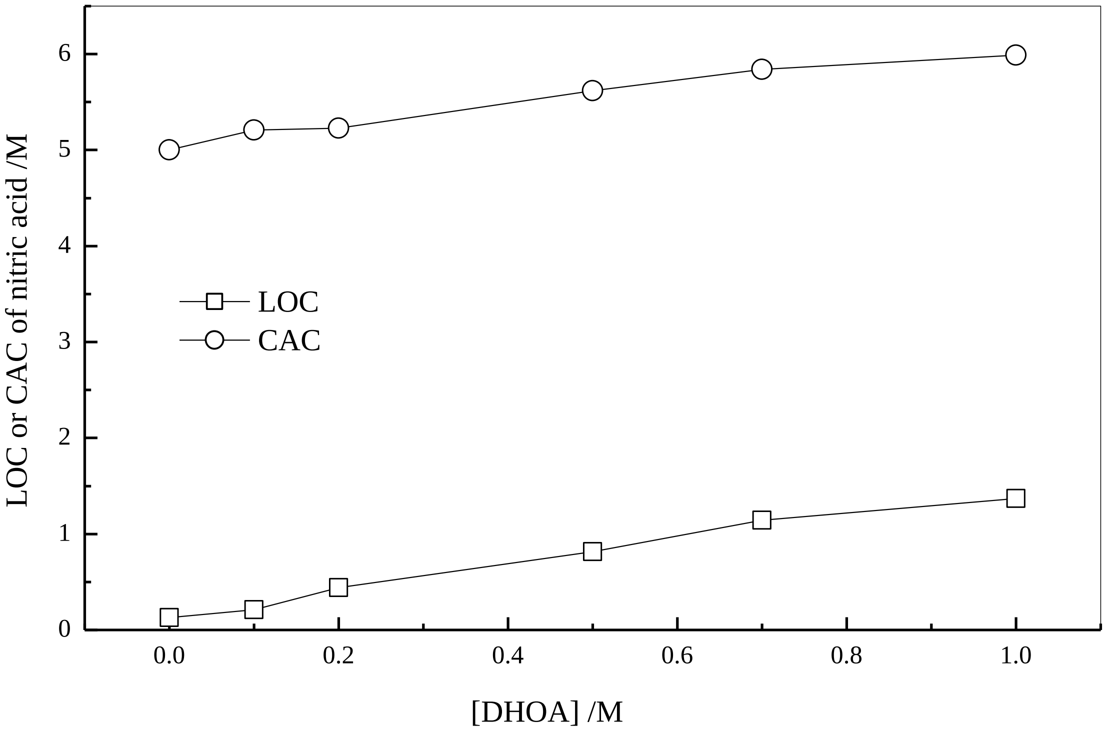


Figure 3.4. Variation in the LOC and CAC of nitric acid with DHOA concentration in 0.1 M DEHDODGA-DHOA in *n*-dodecane at 298 K.

The third phase formed at the initial nitric acid concentration of 6 M in case of 0.1 M DEHDODGA/*n*-dodecane is shifted to 7 M when 0.2 M DHOA is added in 0.1 M DEHDODGA/*n*-dodecane. Further increase in DHOA shifts the third phase formation to higher nitric acid concentrations. Figure 3.4 shows the variation in LOC and CAC of nitric acid with concentration of DHOA in 0.1 M DEHDODGA-DHOA/*n*-dodecane at 298 K. It is observed that both LOC and CAC increase with increase in the concentration of DHOA, as expected.

Table 3.8. Third phase formation in 0.1 M DEHDODGA-DHOA/*n*-dodecane at 298 K as a function of $[HNO_3]_{ini.}$ N-No third phase, T–Third phase. Organic to aqueous phase=1:1.

DEHDODGA/ M	DHOA/ M	Initial concentration of nitric acid /M						
		4	5	6	7	8	9	10
0.1	0	Up to 4 M there is no third phase formation	N	T	T	T	T	T
0.1	0.16		N	T	T	T	T	T
0.1	0.20		N	N	T	T	T	T
0.1	0.33		N	N	T	T	T	T
0.1	0.5		N	N	N	T	T	T
0.1	0.7		N	N	N	N	T	T
0.1	1		N	N	N	N	N	T

3.4.2. Third phase formation with neodymium

The LOC of Nd(III) in 0.1 M DGA/*n*-dodecane at various acidities are shown in table 3.9. It is observed that the LOC of Nd(III) decreases with increase of aqueous phase acidity, and increases with increase of extractant concentration. At 3 M nitric acid medium, the LOC of Nd(III) in 0.1 M DEHDODGA is 4.1 mM, whereas for 0.1 M TODGA/*n*-dodecane and 0.1 M TEHDGA/*n*-dodecane the LOC values are 6.4 and 2.6 mM respectively. Figure 3.5 shows the variation in the LOC of neodymium(III) with the concentration of DEHDODGA/*n*-dodecane measured at different acidities. The LOC values increase with increase in concentration of DEHDODGA and decrease with increase in nitric acid concentration. For instance, at 1 M nitric acid, the LOC of neodymium(III) increases from 8 mM to 110 mM with the increase in the concentration of DEHDODGA from 0.1 M to 0.5 M, whereas the LOC in 0.5 M DEHDODGA decreases from 110 mM to 30 mM with increase in the nitric acid concentration from 1 M to 3 M. This shows that nitric acid and neodymium(III) are competing for extraction by DEHDODGA/*n*-dodecane. However, the LOC of neodymium can be increased, similar to the LOC increase observed in case of HNO_3, by adding DHOA in organic phase. Figure 3.6 compares the LOC of neodymium(III) in the presence and absence of DHOA in 0.1 M DEHDODGA/*n*-dodecane solution. As expected the LOC increases with increase in the concentration of DHOA and decreases with increase of nitric acid concentration. Addition of DHOA permits the determination of LOC of Nd(III) even at the equilibrium acidity of 5–6 M. For instance, at 5 M nitric acid, the LOC of Nd(III) increases from 3 mM to 5.5 mM by the addition of 0.1 M and 0.2 M DHOA respectively, in 0.1 M DEHDODGA in *n*-dodecane. This indicates that the concentration of DHOA in 0.1 M DEHDODGA-DHOA-*n*-dodecane needs be manipulated to avoid the third phase formation during the mixing of solution containing 8 g/L lanthanide (~50 mM Nd) in 4 M nitric acid. In the present study the concentration of neodymium(III) and nitric acid was varied up to 100 mM and 5 M respectively. It was found that by adding 0.3 M of DHOA in 0.1 M DEHDODGA/*n*-dodecane the third phase was formed when the initial concentration of neodymium, $[Nd(III)]_{ini}$, is 15 mM in 5 M nitric acid. Increasing the DHOA concentration to 0.4 M also resulted in third phase formation above 25 mM of Nd(III). However, by using 0.5 M DHOA in 0.1 M DEHDODGA/*n*-dodecane, the third was not observed at 50 mM $[Nd(III)]_{ini}$. Increasing the initial concentration of neodymium to 100 mM also does not result in the formation of third phase. Thus, the present study suggests that it is desirable to use 0.5 M DHOA to avoid third phase formation during minor actinide partitioning from HLLW. Based on the above results, the extraction of lanthanides (III) using 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane from simulated high-level liquid waste corresponding to a burn-up of 100 GWd/Te was studied to confirm the suitability of this proposed composition for minor actinide partitioning. The composition of simulated HLLW is described in section 2.3.7.

Table 3.9. The limiting organic concentration of neodymium(III) in 0.1 M DGA/*n*-dodecane at 303 K.

$[HNO_3]$/M	[Extractant]/M	LOC of Nd(III) (mM)	
		TODGA	DEHDODGA
1 M	0.1	14	7.0
2 M	0.1	12	5.3
3 M	0.1	6.0	4.1
	0.2	12.2	11.3
	0.3	31.4	14.3
	0.4	--	28.9
	0.5	60.0	33.3

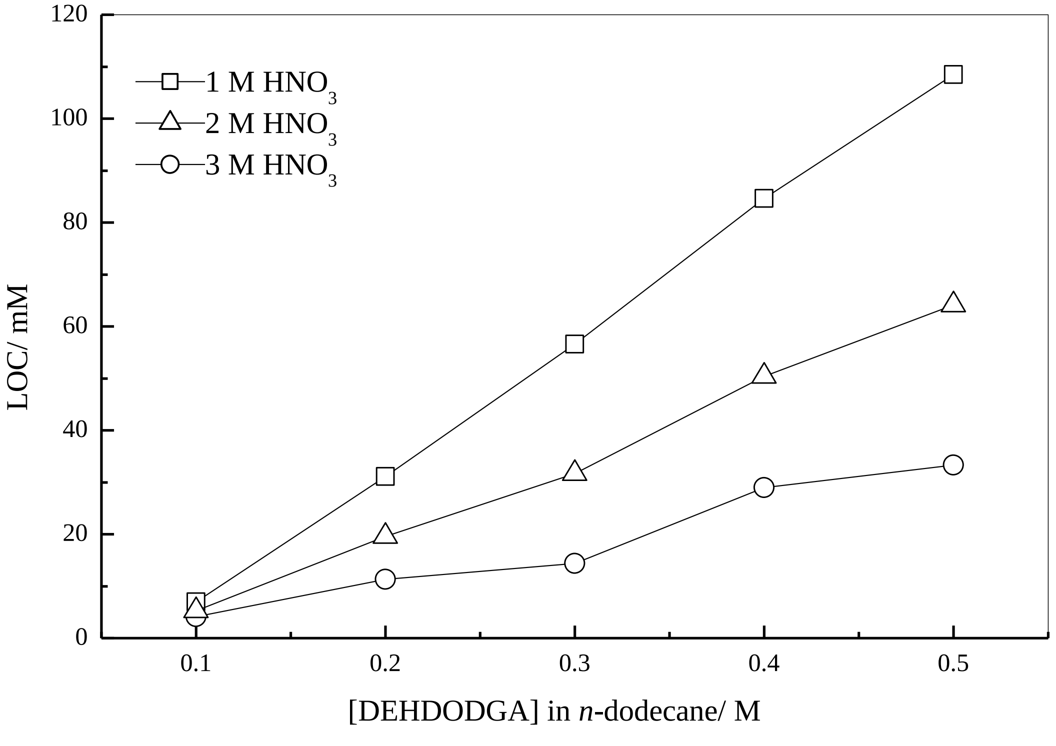


Figure 3.5. Variation in the LOC of neodymium(III) with concentration of DEHDODGA in *n*-dodecane at 303 K at different concentrations of nitric acid.

The simulated HLLW was spiked with $^{(152+154)}$Eu(III) tracer to monitor the extraction of trivalent lanthanides. The results confirmed the absence of third phase formation during the extraction of lanthanides(III) from simulated HLLW using the optimized solvent, namely 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. However, the $D_{Eu(III)}$ decreased from a value of ~300 for its extraction from 4 M nitric acid medium to the value of 170 from simulated HLLW. The reduction in the *D* could be attributed to the extraction of other metal ions apart from the trivalents that are present in simulated HLLW.

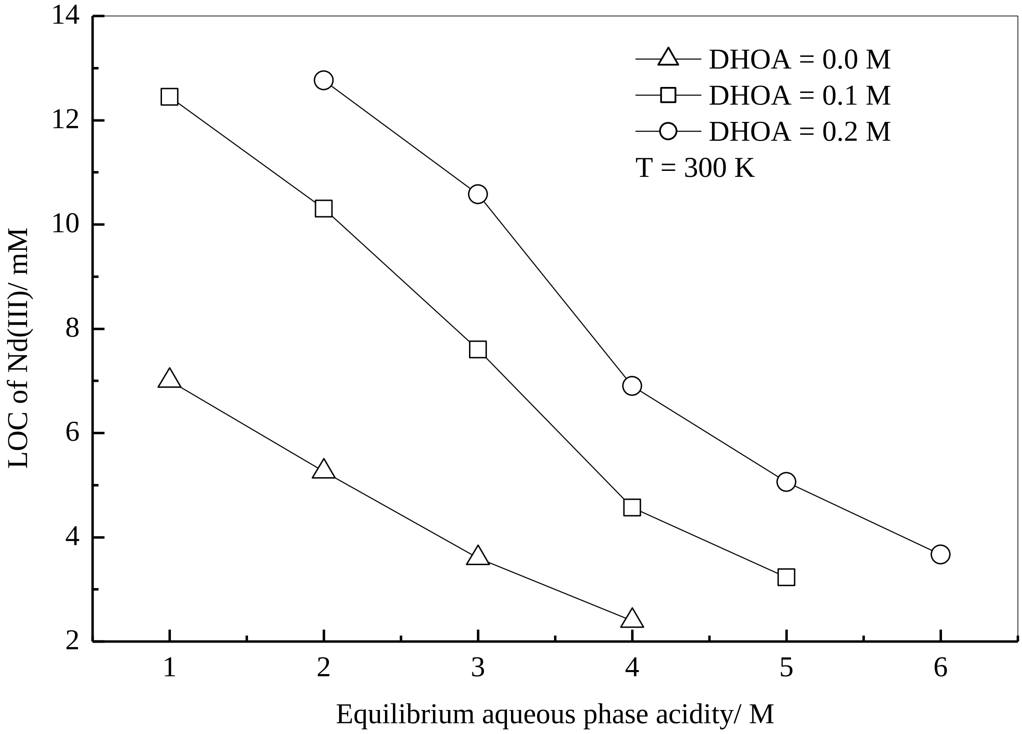


Figure 3.6. Variation in the LOC of Nd(III) with equilibrium aqueous phase acidity at different DHOA concentrations. Extractant: 0.1 M DEHDODGA-DHOA/*n*-dodecane, T = 300 K.

3.4.3. Effect of temperature on third phase formation

Figure 3.7 shows variation in LOC of neodymium(III) with temperature at various concentrations of DHOA in 0.1 M DEHDODGA/*n*-dodecane. A couple of factors seem to determine the magnitude of slope obtained in figure 3.7 and 3.8. While the increase of temperature increases the solubility of polar metal-solvate complexes and increases the metal loading, it also lowers the *D*, as the extraction equilibrium was exothermic (see section 3.3.1). The LOC observed in the present study is the net effect of these two opposing factors. In the absence of DHOA, higher slope obtained at 3 M nitric acid could be attributed to the higher *D* of metal ions achievable in this case as compared to lower acidities (< 3 M). As a result, the variation in LOC at 3 M in the absence of DHOA is more with increase of temperature as indicated in figure 3.7.

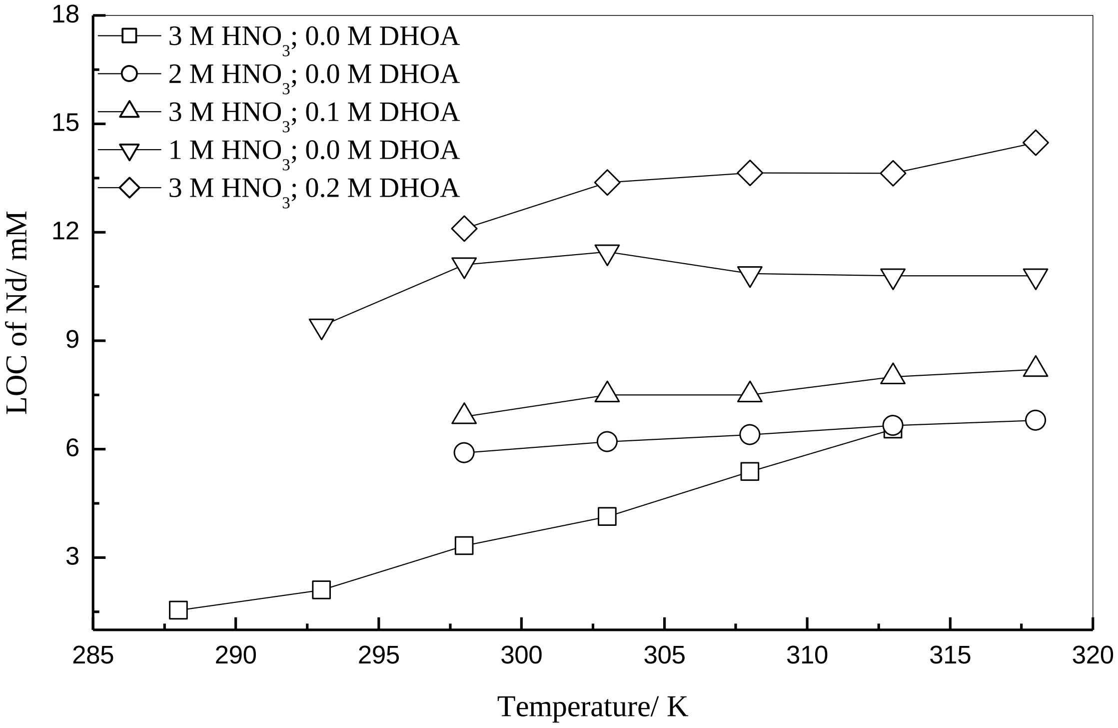


Figure 3.7. Variation in the LOC of Nd(III) with temperature and DHOA concentration. Organic phase: 0.1 M DEHDODGA-DHOA/*n*-dodecane. Organic to aqueous phase ratio=1:1.

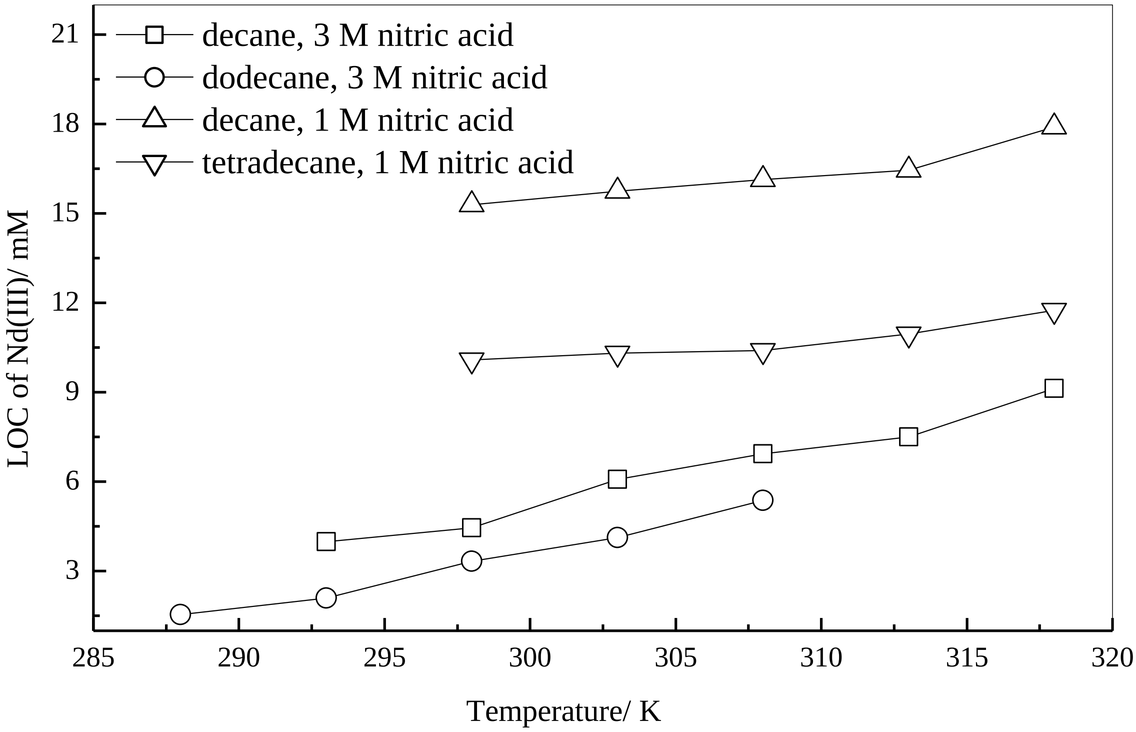


Figure 3.8. Variation in the LOC of neodymium (III) with temperature. Organic phase: 0.1 M DEHDODGA in various diluents. Aqueous phase: 1 M or 3 M nitric acid with neodymium (III).

3.4.4. Effect of diluent on third phase formation

It was reported that the nature of diluent shows significant influence on the third phase formation behavior. In this context, the third phase formation behavior of DEHDODGA was studied in various diluents such as decane, dodecane and tetradecane at different temperatures. The effect of the diluent nature on the LOC of Nd(III) in 0.1 M DEHDODGA is shown in figure 3.8. It is observed that LOC values decrease with increase in alkyl chain length of diluent. Suresh *et al*. [12] observed a similar trend in the LOC of Th(IV) in various trialkylphosphate extractants. Studies by Nave *et al*. [59] indicated the formation of tetrameric reverse micelles in TODGA in *n*-dodecane systems at different nitric acid concentrations.The loading capacities of the solvent depends not only on the aqueous phase acidity and temperature but also on the molecular size of the diluent[24]. The decrease in

LOC values with increase in alkyl chain length of the diluent could be due to the lower polarity with increase of alkyl chain length of the diluent. Moreover the LOC values increases with the increase in temperature in all the diluents, as expected.

3.5. Nitric acid extraction by modified solvent

The extraction of metal ions from nitric acid solution by a neutral extractant is usually accompanied by the co-extraction of nitric acid. The co-extracted nitric acid causes difficulties during back extraction of metal ions from the loaded organic phase. The presence of phase modifier in the solvent phase usually increases the acid extraction further. Figure 3.9 compares the extraction isotherm of nitric acid in 0.1 M DEHDODGA/*n*-dodecane in the presence and absence of phase modifier, 0.5 M DHOA. It is observed that the extraction of nitric acid in organic phase increases with increase in the concentration of nitric acid in aqueous phase in both the cases. When the equilibrium concentration of nitric acid in aqueous phase was ~6 M, the third phase formation was observed in case of 0.1 M DEHDODGA/*n*-dodecane. However, the extraction of nitric acid is much higher in case of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. About 0.6 M nitric acid is extracted into the organic phase when the concentration of nitric acid in aqueous is ~6 M, without leading to any third phase formation.

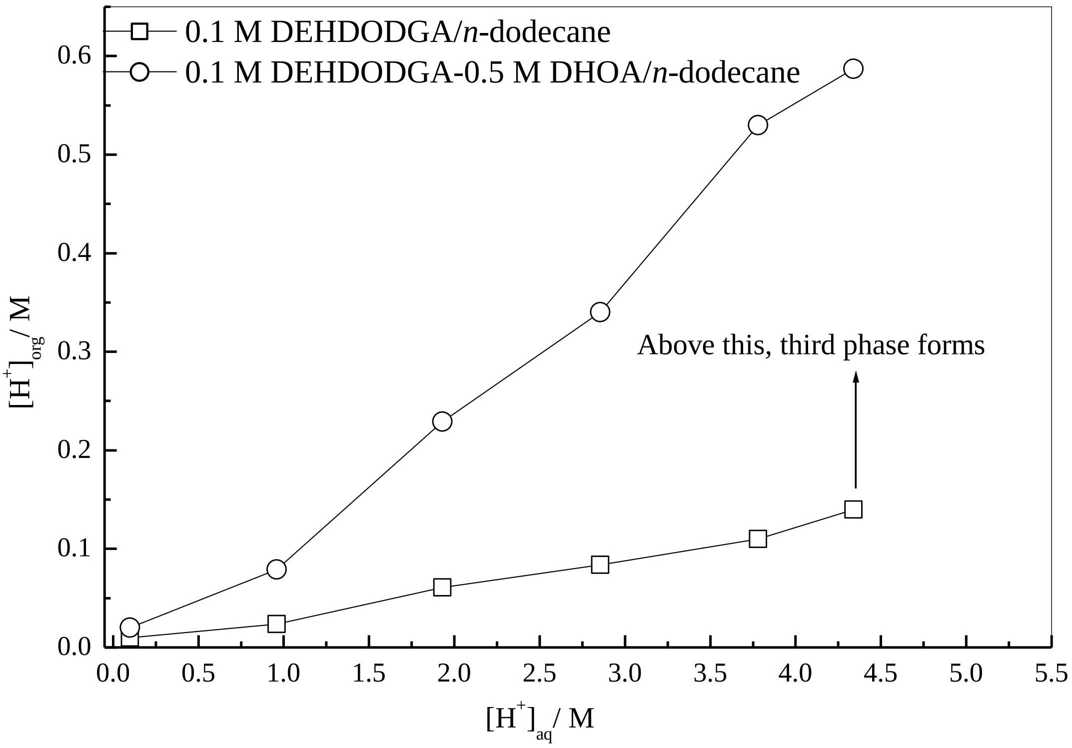


Figure 3.9. Nitric acid extraction isotherm at 298 K. Organic phase: 0.1 M DEHDODGA/*n*-dodecane or 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. Aqueous phase: varying concentration of nitric acid. Organic to Aqueous phase ratio= 1:1.

3.6. Effect of phase modifier on the extraction of metal ions

Since the solvent composition is optimized to 0.1 M DEHDODGA-0.5 M DHOA in *n*-dodecane for partitioning of minor actinides from HLLW, the extraction behavior of various metal ions was studied in this solvent, and the results are shown in table 3.10. It is interesting to note that the *D* of trivalent lanthanides and actinides are greater than 300 above 4M nitric acid media. Comparing table 3.6 and table 3.10, one can notice that the distribution ratios of Am(III), Eu(III), Y(III), and Zr(IV) decrease with the addition of 0.5 M DHOA to 0.1 M DEHDODGA/*n*-dodecane. A similar behavior was also reported in the symmetrical diglycolamide, TODGA. This could be attributed to the breakage of reverse micelles of DGA aggregates in the presence of DHOA [68]. However, the magnitude of *D* observed for these metal ions are quite high for complete extraction in 1-2 contacts from 3-4 M nitric acid medium. It is also observed that the distribution of other metal ions is lowered in the presence of DHOA, which is desirable for the minimization of other fission products extraction to organic phase. However, the *D*s of Pd(II), Ni(II) increase in the presence of DHOA. It is interesting to note that the *D* of metal ions decrease in the order of $M^{4+} > M^{3+} >> M^{2+} \sim MO_2^{2+} >> M^{+}$ in this case also. The distribution ratios of Mn(II), Co(II), Sb(II), Cs(I) are negligible in both 0.1 M DEHDODGA/*n*-dodecane and 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane solvent systems. The extraction of Ru(III), Sr(II), and Mo(VI) is less in the present system as compared to the symmetrical diglycolamides such as TODGA and TEHDGA [50,56]. Consequently, the scrubbing stages required for the removal of these unwanted metal ions from the loaded organic phase would be less if DEHDODGA is employed for the counter-current extraction. Poor extraction of fission products and corrosion products in the unsymmetrical diglycolamide, DEHDODGA, would minimize the generation of secondary waste during the scrubbing of loaded organic phase.

The extraction behavior of these metal ions observed above was studied individually from nitric acid medium, and it may be altered when the extraction was carried out from the mixture of several metal ions. Therefore, the extraction behavior of Am(III) and some fission products was studied from simulated HLLW by the modified solvent. Table 3.11 compares the extraction behavior of metal ions from 4 M nitric acid medium with that from simulated HLLW. It is observed that the extraction of these metal ions is lower in case of simulated HLLW than that from 4 M nitric acid medium. This could be due to the competitive extraction of other metal ions. However, the $D_{\mathrm{Am(III)}}$ is sufficient for its complete extraction even from simulated HLLW in a few contacts.

Table 3.10. Variation in the $D_{\mathrm{Am(III)}}$ and other metal ions present in SHLLW at 298 K. Organic phase: 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. Aqueous phase: nitric acid solution spiked with radioisotopes. Equilibration time: 1 hour; organic to aqueous ratio=1:1.

$[HNO_3]$ / M	Am(III)	Eu(III)	Y(III)	Zr(IV)	Pd(II)	Ni(II)	Mo(VI	Cr(VI)	Cd(II)	Ba(II)	Sr(II)	Ce(III)	Ru(III)
0.1	6×10^{-3}	0.03	7×10^{-3}	1.8	2.18	0.02	0.09	0.1	0.02	0.09	$< 10^{-3}$	$< 10^{-3}$	0.02
0.5	0.12	0.05	0.1	0.73	3.35	-	-	-	-		3×10^{-3}	0.03	0.03
1	1.6	10.6	2.9	1.76	4.11	0.04	0.05	0.02	0.01	$< 10^{-3}$	0.02	0.22	0.04
3	131	232	198	>300	2.0	0.1	0.15	0.04	0.01	0.08	0.36	14	0.06
4	>300	>300	>300	>300	1.84	0.1	0.12	0.02	0.02	0.3	0.44	27	0.04
6	>300	>300	>300	>300	1.46	-	-	-	-	-	0.28	72	0.01

Note: The distribution ratios of Sb(III), Mn(II), Co(II), and C(I) are $< 1 \times 10^{-3}$

Table 3.11. Variation in the *D* of Am(III), fission products and structural component metal ions with nitric acid concentration at 298 K. Organic phase: 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane; Aqueous phase: simulated HLLW spiked with HLLW tracer or radioisotope. Organic to aqueous phase ratio=1:1.

Aqueous phase	Am(III)	Eu(III)	Ru(III)	Zr(IV)	Ce(III)	Sr(II)
4 M HNO_3	>300	>300	0.024	>300	27	0.44
SHLLW	36	170	0.1	>300	7.4	0.07

Note: Mn(II), Sb(III), Fe(III), Co(II), Cs(I) were found to have a $D < 1 \times 10^{-3}$ at all the acidities

3.7. Stoichiometry of Am (III)-DEHDODGA

The ligand to metal ratio during the extraction was determined by the procedure described in section 2.3.6. Figure 3.10 shows the plot of log D_{Am} against log $[DEHDODGA]_{org}$ at various concentrations of nitric acid. The data were fit using linear least squares method. The slope values obtained vary in the range 2.5 – 3.1, indicating that three molecules are involved in the extraction of Am(III) by DEHDODGA. For TODGA, and TEHDGA, these values are 4, and 3, respectively [41, 54].

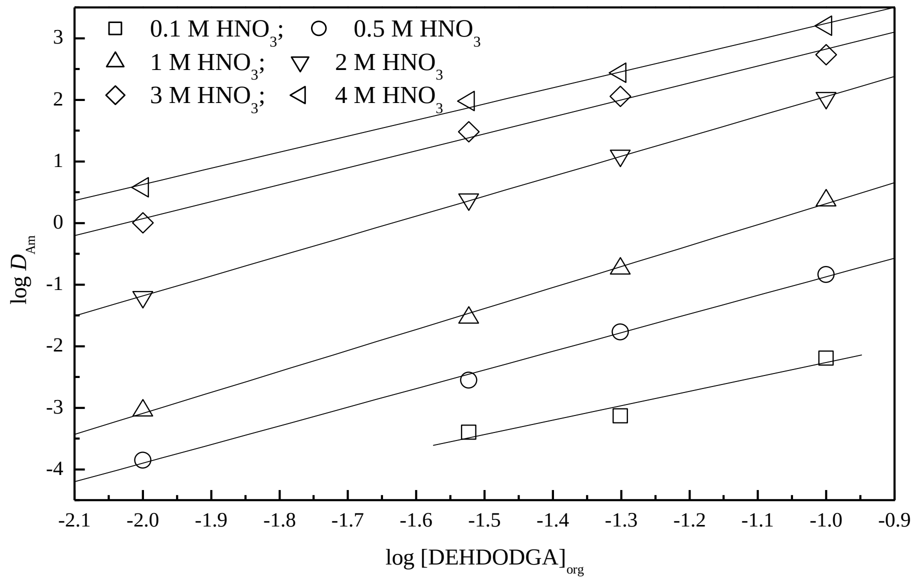


Figure 3.10. Variation of log D_{Am} with log$[DEHDODGA]_{org}$ from nitric acid medium at 298 K.

3.8. Stripping studies

The success of solvent extraction process depends on the efficient extraction of the desired metal ions, and quantitative back extraction in minimum contacts. Usually, dilute nitric acid is employed for back extraction(stripping) of trivalent metal ions from the loaded DGAs. Low *D* of trivalent actinides in DGAs at low nitric acid medium favours the better back extraction of them. In this context, the back extraction studies from the loaded 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane were carried out using low concentrated nitric acid solutions. In this study, the organic phase (0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane) was loaded with desired metal ions from 4 M nitric acid medium as well as from simulated HLLW. The loaded organic phase was then contacted with 0.1 M nitric acid for recovery. The aqueous phase was separated, and contacted again with 0.1 M nitric acid. This procedure was repeated several times until the metal ions present in organic phase were recovered quantitatively. Several such experiments were performed by loading individual metal ions or group of metal ions that are present in HLLW. The studies indicated that the trivalent lanthanides and actinides, when extracted individually from 4 M nitric acid, it was possible to recover them quantitatively in 4-5 contacts from 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane with 0.1 M nitric acid. Similarly, the fission products Zr(IV) and Y(III), when loaded from 3-4 M nitric acid medium they could be recovered back in 4 contacts with 0.1 M nitric acid. However, when the organic phase was loaded from the SHLLW, a crud type precipitate was observed in the second and third contact during stripping with 0.1 M nitric acid. This may be due to the hydrolysis of metal ions that are present in the loaded organic phase. To prevent the hydrolysis, the concentration of nitric acid in the stripping solution was increased to 0.5 M in nitric acid. Even then crud type of precipitate was observed in the third contact.

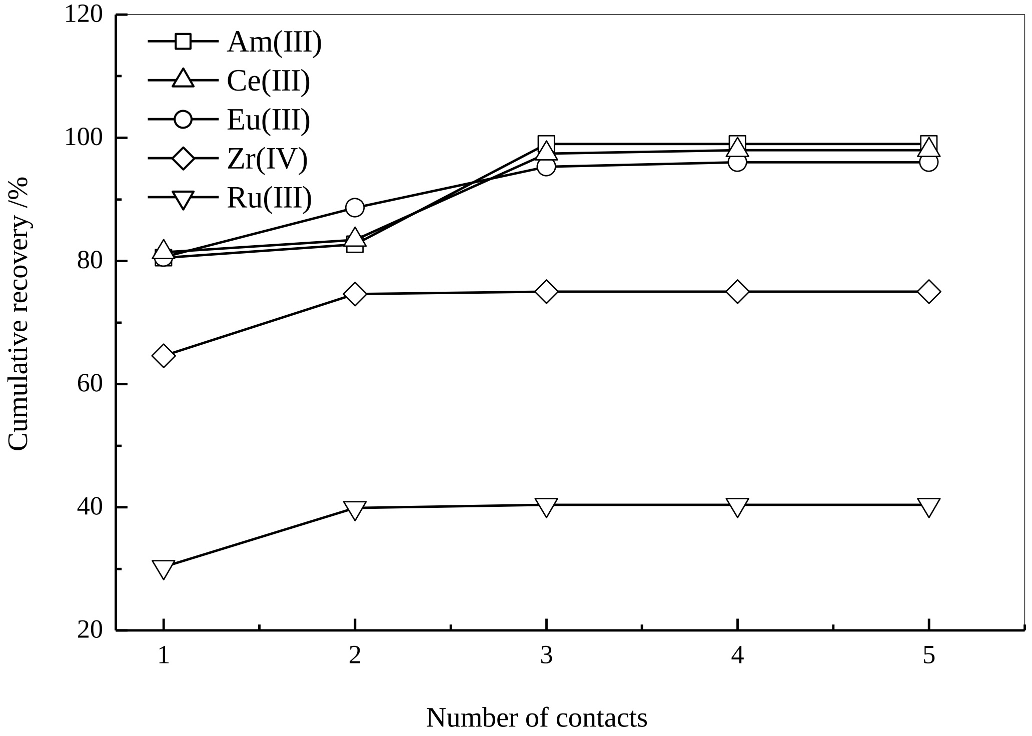


Figure 3.11. Cumulative stripping of trivalent and tetravalent metal ions from the loaded organic phase as a function of number of contacts at 298 K. Feed: simulated HLLW spiked with HLLW. Loaded organic phase: 0.1 M DEHDODGA- 0.5 M DHOA/*n*-dodecane. Stripping solution: 0.01 M DTPA-0.5 M citric acid at pH 3. Organic to Aqueous phase ratio= 1:1.

In the view of such observations, several researchers proposed scrubbing of loaded organic phase with complexing reagents to remove the unwanted metal ions prior to stripping. In addition, some researchers even added the complexing agents such as oxalic acid and ethylenediaminetetraacetic acid (EDTA) in the feed to minimize or exclude the extraction of undesired metal ions during loading [49, 56]. However, these procedures generate secondary waste and also it quite likely that the oxalates of certain metal ions precipitates in the feed. The stripping studies indicate that it is necessary to use a complexing agent for back extraction of actinides from the loaded organic phase. Diethylene triaminepentaacetic acid (DTPA) is an aqueous soluble complexing agent extensively used for the recovery of trivalent metal ions. The advantage of using DTPA over other reagents in the present study is due to the employment of DTPA in the subsequent lanthanide-actinide (Ln-An) separation. In trivalent actinide-lanthanide separation by phosphorus based extractants from aqueous complexes (TALSPEAK) process, developed for Ln-An separation, DTPA is used for the retention of trivalent actinides in aqueous phase [75]. Therefore, it is desirable to use DTPA for recovery of the metal ions from the loaded organic phase. Citric acid was added to keep pH constant and it may also act as complexing agent for trivalent metal ions. Addition of CA and DTPA played a crucial role in eliminating crud formation during the stripping. The stripping formulation was developed using DTPA and CA and optimized to 0.01 M DTPA-0.5 M CA at pH 3. The back extraction of metal ions was carried out from the loaded organic phase using this stripping formulation in several contacts and the results are shown in figure 3.11. It is observed that the stripping of metal ions increases with increase in the number of contacts. In 4-5 contacts, complete stripping of metal ion is achieved without leading to any crud-formation.

3.9. Studies on TODGA and TEHDGA mixture

The studies with unsymmetrical diglycolamide, DEHDODGA, indicate that majority of its properties are in between to the properties of TODGA and TEHDGA. Since the structure of DEHDODGA resembles the combination of TODGA and TEHDGA structures, its properties are also expected to be similar to that of combination of TODGA and TEHDGA. It is quite likely that the property of DEHDODGA can be obtained by mixing both TODGA and TEHDGA in the solvent system. Therefore, it is interesting to study and compare the extraction properties of 0.05 M TODGA+0.05 M TEHDGA/*n*-dodecane with that of 0.1 M DEHDODGA. Figure 3.12 shows the $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ as a function of equilibrium concentration of nitric acid in the aqueous phase in 0.05 M TODGA + 0.05 M TEHDGA in *n*-dodecane at 298 K. It is interesting to note that the $D_{\mathrm{Am(III)}}$ increases with increase in the nitric acid concentration similar to any other DGA/*n*-dodecane system.Figure 3.12 also compares the extraction behavior of trivalent metal ions in the solvent mixture with that of 0.1 M DEHDODGA/*n*-dodecane. Although, DEHDODGA is a structural combination of TODGA and TEHDGA, the extraction properties in 0.1 M DEHDODGA are not exactly same as that in 0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane.

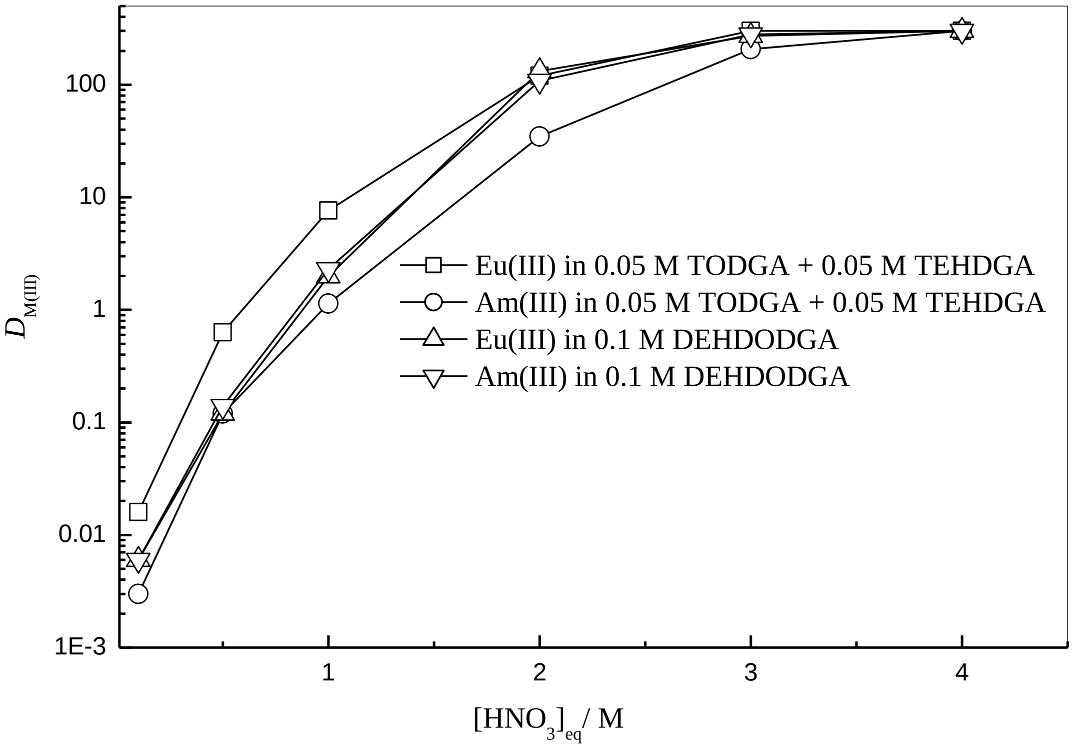


Figure 3.12. Extraction of trivalent metal ions as a function of nitric acid concentration in the aqueous phase at 298 K.

Figure 3.13 shows the extraction behavior of Ba(II) and Sr(II) as a function of nitric acid concentration in the mixture of solvents(0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane). The *D* of divalent metal ions increased with increase in nitric acid concentration up to 4 M nitric acid followed by decrease. This behavior is quite similar to that in DEHDODGA. Figure 3.13 compares the divalent metal ion extraction in the mixture of solvents with that in 0.1 M DEHDODGA. However, the *D* of divalent metal ions is lower in solvent mixture. In addition to the extraction of trivalent metal ions, the third phase formation studies were also carried out in 0.05 M TODGA+0.05 M TEHDGA/*n*-dodecane during the Nd(III) loading into organic phase from nitric acid medium. Table 3.12 shows the LOC and CAC of nitric acid and Nd(III) at 298K in solvent mixture as well as in 0.1 M DEHDODGA/*n*-dodecane. It is interesting to note that the LOC and CAC values of Nd(III) are also different in 0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane from that of 0.1 M DEHDODGA/*n*-dodecane. The LOC of Nd(III) are relatively smaller in the solvent mixture than that of DEHDODGA/*n*-dodecane under similar conditions.

Table 3.12. LOC and CAC of nitric acid and Nd(III) in mixture of solvents and in DEHDODGA/*n*-dodecane at 298 K.

Aqueous phase	Mixture of solvents		0.1 M DEHDODGA	
	Initial	LOC	initial	LOC
Nitric acid/ M	5.2	0.13	5.9	0.14
Nd(III) in 3 M HNO_3/ mM	5	3.13	5.7	4.1
Nd(III) in 4 M HNO_3/ mM	3.1	2	3.5	2.5

Thus the studies on 0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane indicate that the extraction behavior of metal ions is different in the mixture of solvents from that of UDGA. The properties of UDGAs are not likely to be achieved by mixing two solvents. Therefore, synthesizing the UDGA is necessary and is a better option over combining two solvents in order to obtain the mixed properties of two different DGAs.

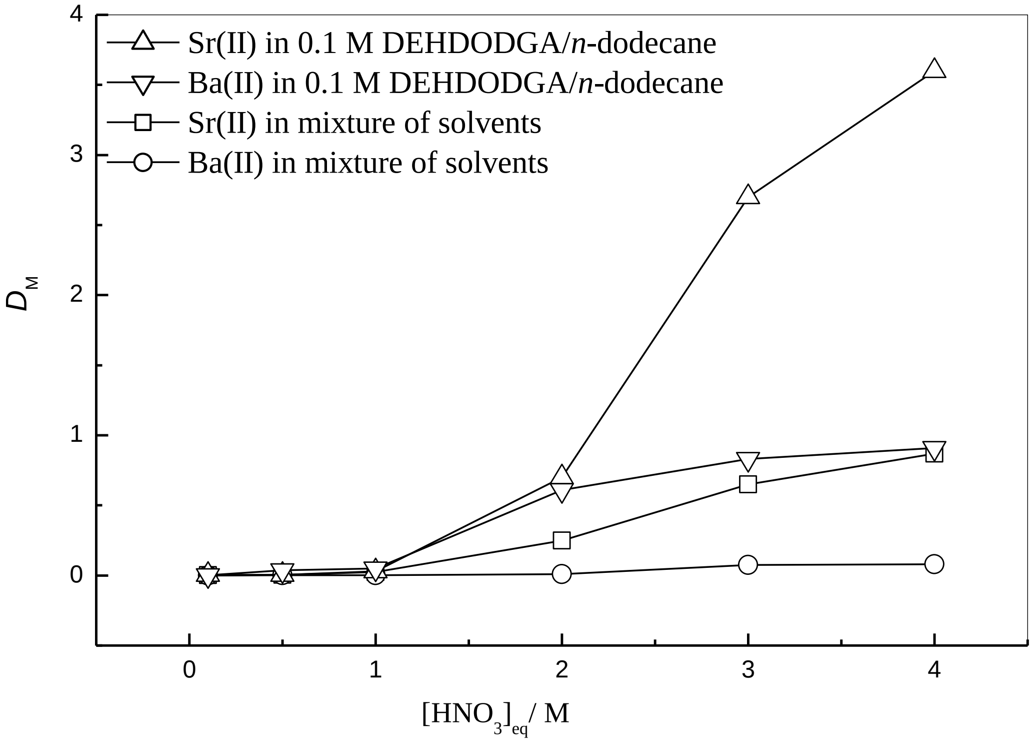


Figure 3.13. Variation in the *D* of divalent metal ions with nitric acid concentration at 298 K. Organic phase: either 0.05 M TODGA + 0.05 M TEHDGA/*n*-dodecane or 0.1 M DEHDODGA/*n*-dodecane. Organic to aqeuous phase ratio =1:1.

3.10. Conclusions

The unsymmetrical diglycolamide, *N*,*N*-di-2-ethylhexyl-*N*$'$,*N*$'$-di-octyl-3-oxa-pentane-1,5-diamide (DEHDODGA) was synthesized, and characterized by ^{1}H, and ^{13}C nmr, mass, and IR spectroscopy. The *D* of Am(III), Eu(III)), and Pu(IV) increased with increase in the concentration of nitric acid. The *D* increases in the order Pu(III) < Am(III) < Eu(III), which is the increasing order of *z/r* of these metal ions. Nearly three molecules of DEHDODGA are found to be involved in the complex formation of Am(III) from nitric acid medium. The separation factor of americium over strontium achieved with the use of DEHDODGA was higher than that obtained with the corresponding symmetrical diglycolamides TODGA and

TEHDGA. The studies also indicated that the basicity of the extractants are in the increasing order TEHDGA $\underset{\sim}{}$ DEHDODGA < TODGA.

The LOC and CAC values of neodymium (III) and nitric acid were determined in 0.1 M DEHDODGA–DHOA–paraffin diluent system as a function of various parameters such as temperature, aqueous phase acidity, extractant concentration, presence of phase modifier etc. The DHOA concentration required to avoid third phase formation during minor actinide partitioning of HLLW was optimised to 0.5 M in the solution of 0.1 M DEHDODGA-DHOA in *n*-dodecane. The extraction behaviour of various metal ions present in high-level liquid waste (HLLW) was studied in a solution of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. The *D* of metal ions decreased in the order $M^{4+} \geq M^{3+} >> M^{2+} \sim MO_2^{2+} > M^+$. The extraction of trivalent actinides and lanthanides is accompanied by complete extraction of Zr(IV) and Y(III). The distribution ratios of Sr(II), Cr(VI), Mo(VI), Pd(II), Ru(III), Ba(II), Cd(II) in DEHDODGA/*n*-dodecane are lower than the corresponding symmetrical DGA, TODGA. A crud-type precipitate was observed in the aqueous phase when the organic phase was loaded from simulated HLLW, indicating the need of aqueous soluble complexing agents for back extraction. Using a solution of DTPA-citric acid at pH 3, quantitative recovery of trivalent metal ions could be achieved within four contacts without leading to any crud formation. The use of DTPA-citric acid for recovery offers additional advantage during lanthanide-actinide separation in the subsequent step. The studies on a mixture of TODGA and TEHDGA solvents indicated that the properties observed from the UDGAs are different from that obtained by mixing two symmetrical DGAs. Therefore, use of UDGAs seems to be the inevitable option to achieve unique properties required in the DGAs.

Tuning the diglycolamides for actinide separation

4.1. Introduction

In the recent past, diglycolamide (DGA) class of extractants are being studied extensively for the separation of trivalent actinides from high-level liquid waste (HLLW). Among the many DGAs studied, the octyl based DGAs such as *N,N,N',N'*-tetra-octyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) received much attention[46]. However, the solutions of these DGAs in *n*-dodecane form third phase during the solvent extraction of trivalent actinides from equal volume of 3 M nitric acid if the trivalent metal ions concentration exceeds 8 mM at 298 K [57,68]. The concentration of trivalent lanthanides (Ln(III)) and actinides(An(III)) in fast reactor HLLW (composition of simulated HLLW is given in table 4.7) is higher than this limit. Therefore, the TODGA and TEHDGA solutions in *n*-dodecane result in third phase formation during the extraction from fast reactor HLLW. To avoid the third phase formation, it was suggested to add another organic solvent, known as phase modifier, in the organic phase [43,49,57]. The addition of phase modifier, however, alters the extraction properties of the solvent and increases the waste generation. In addition, these DGAs co-extract other metal ions such as Zr(IV), Sr(II), Pd(II) and Mo(VI) etc, along with An(III). The contamination of other metal ions in An(III) is undesirable for the effective transmutation of actinides. Several additional process modification such as feed adjustment, scrubbing of loaded organic phase etc., need to be carried out to minimize the extraction of these metal ions.

Therefore, the elimination of third phase formation and the suppression of undesirable metal ion extraction are the major challenging issues, which need to be addressed during partitioning of minor actinides by DGAs. It was reported that the physico-chemical, extraction, and third phase formation properties of DGAs strongly depend on the nature of alkyl groups attached to amidic nitrogen atom, and thus can be tuned with the appropriate selection of alkyl groups [41,42].

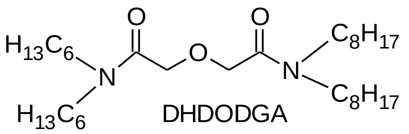
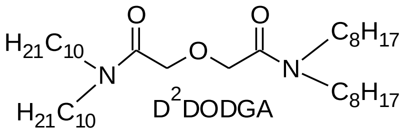
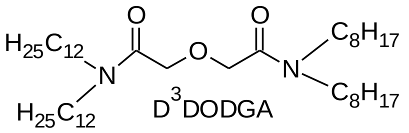
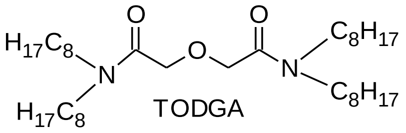
In this context, the present chapter deals with the tuning of DGA structure by varying the alkyl groups attached to the amidic nitrogen atom to suit partitioning of minor actinides from HLLW. The tuning of DGA structure has been carried out in two modes. In the first mode, octyl groups on one amidic nitrogen atom are kept constant and the alkyl group on the other amidic nitrogen atom varied from hexyl to dodecyl. The octyl groups were chosen to be fixed on one amidic nitrogen atom to retain the desirable extraction properties of TODGA. The alkyl groups on the other nitrogen atom varied to identify the most suitable alkyl groups for the realization of other desirable properties, for example prevention of third phase formation. In the second mode of tuning, dodecyl groups on one amidic nitrogen atom were kept constant, and the alkyl groups on other amidic nitrogen are varied from butyl to decyl. Dodecyl groups were chosen to retain the properties of tetra-dodecyl diglycolamide (TDdDGA), with respect to prevention of third phase formation. The alkyl groups on the other amidic nitrogen atom were varied from butyl to decyl to improve the other desirable properties. It was reported that the TDdDGA/*n*-dodecane extracts stoichiometric amount of trivalent metal ions from nitric acid medium without leading to any third phase formation [67]. Extraction behavior of actinides, fission products and other structural metal ions which are likely to present in HLLW has been studied in these unsymmetrical diglycolamide (UDGA) solutions, and correlated with the nature of alkyl group attached to amidic nitrogen atom.

PART A-Tuning the DGAs with octyl groups

In the present part, octyl groups on one amidic nitrogen atom were kept constant, and the alkyl groups on other amidic nitrogen atom were varied from hexyl to dodecyl. The structures and names of various UDGAs studied in this part are shown in table 4.1. The new

UDGAs, namely, *N*,*N*-di-hexyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide known as di-hexyl-di-octyl diglycolamide (DHDODGA), *N*,*N*-di-decyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide trivially called as di-decyl-di-octyl diglycolamide (D^2DODGA), *N*,*N*-di-dodecyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide commonly known as di-dodecyl-di-octyl diglycolamide (D^3DODGA) have been synthesized and evaluated for the actinide partitioning from nitric acid medium.

Table 4.1. The structures and names of the UDGAs

S.No.	Name of the diglycolamide	Structure
1.	*N*,*N*-di-hexyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide or di-hexyl-di-octyl-diglycolamide	
2.	*N*,*N*-di-decyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide or di-decyl-di-octyl-diglycolamide	
3.	*N*,*N*-di-dodecyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide or di-dodecyl-di-octyl- diglycolamide	
4.	*N*,*N*,*N'*,*N'*-tetra-octyl-3-oxapentane-1,5-diamide or tetra-octyl- diglycolamide	

4.2. Basicity of UDGAs

Basicity (K_H) also known as conditional acid extraction constant of ligands play an important role in the complex formation with metal ions. Therefore, the K_H values are determined for the present UDGAs synthesized in the present study by the procedure described in section 2.3.4. Figure 4.1 shows the $\log[H^+]_{org}$-2 $\log[H^+]_{aq}$ as a function of

$\log[\mathrm{DGA}]_{\mathrm{free}}$ at 298 K for the UDGAs. The K_H values from intercepts are found to be 0.08, 0.12, and 0.07 for DHDODGA, D^{2}DODGA, and D^{3}DODGA respectively. Excluding DHDODGA, the magnitude of K_H decreases with increase in chain length of alkyl group in the order TODGA (0.38) [65] > D^{2}DODGA (0.12) > D^{3}DODGA (0.07). This indicates that the K_H of DGA decreases with increase in alkyl chain length attached to amidic nitrogen atom, perhaps due to the steric hindrance during protonation.

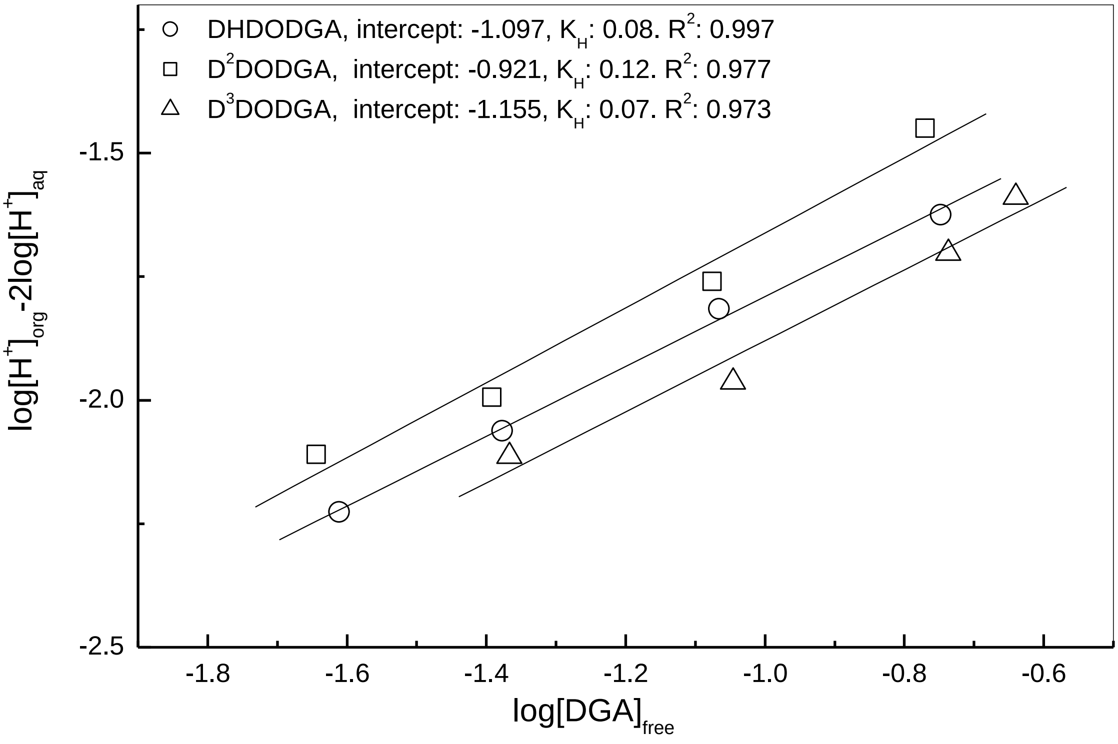


Figure 4.1. Plot of ($\log[H^+]_{(org)}$-2 $\log[H^+])]_{aq}$) vs $\log[\mathrm{DGA}]_{(free)}$ for the extraction of nitric acid by UDGAs at 298 K. Aqueous phase=1 M HNO_3.

4.3. Extraction of trivalent metal ions by UDGAs

The UDGAs namely DHDODGA, D^{2}DODGA and D^{3}DODGA were studied for the extraction of Am(III) from nitric acid medium and the results are compared with that of TODGA. The variation in the $D_{\mathrm{Am(III)}}$ in various 0.1 M UDGA and TODGA in *n*-dodecane solutions with equilibrium aqueous phase acidity is shown in figure 4.2. It is observed that the $D_{\mathrm{Am(III)}}$ increases with increase in the concentration of nitric acid as expected for DGA systems. A $D_{Am(III)}$ of > 300 is obtained in all the cases when the concentration of nitric acid is in the case of 4-7 M. High $D_{Am(III)}$ at 3-4 M nitric acid, and low D at low nitric acid concentrations are desirable properties for efficient extraction from HLLW and recovery of trivalent actinides respectively.

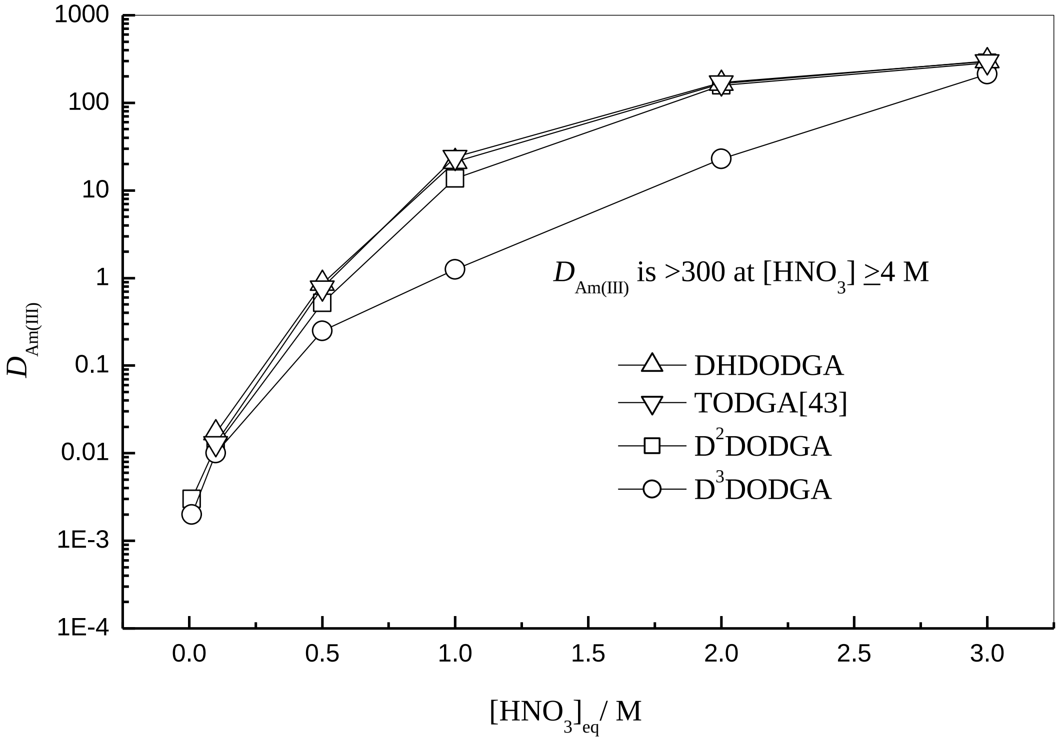


Figure 4.2. Variation in the $D_{Am(III)}$ with concentration of nitric acid in various DGAs at 298 K. Organic phase: 0.1 M DGA/*n*-dodecane. Aqueous phase: $[HNO_3]$ spiked with ^{241}Am tracer.

The $D_{Am(III)}$ in 0.1 M DHDODGA/*n*-dodecane could not be measured above 4 M nitric acid due to third phase formation. It is interesting to observe from figure 4.2, that the $D_{Am(III)}$ decreases in the order DHDODGA> D^2DODGA> D^3DODGA. The reduction in the D of metal ions with increase in the alkyl chain length attached amidic nitrogen atom of DGA was reported earlier [41]. The present results are in good agreement with the literature. The $D_{Am(III)}$ in 0.1 M TODGA/*n*-dodecane is comparable with the D obtained in the present UDGAs. Figure 4.3 shows the $D_{Eu(III)}$ as a function of equilibrium concentration of nitric acid in various UDGAs. The extraction behavior of Eu(III) is similar to that of Am(III). However, the $D_{Eu(III)}$ is higher than $D_{Am(III)}$ at all the acidities studied. The higher $D_{Eu(III)}$ than $D_{Am(III)}$ is common in DGA class of extractants, and attributed to higher charge to radius ratio of Eu(III).

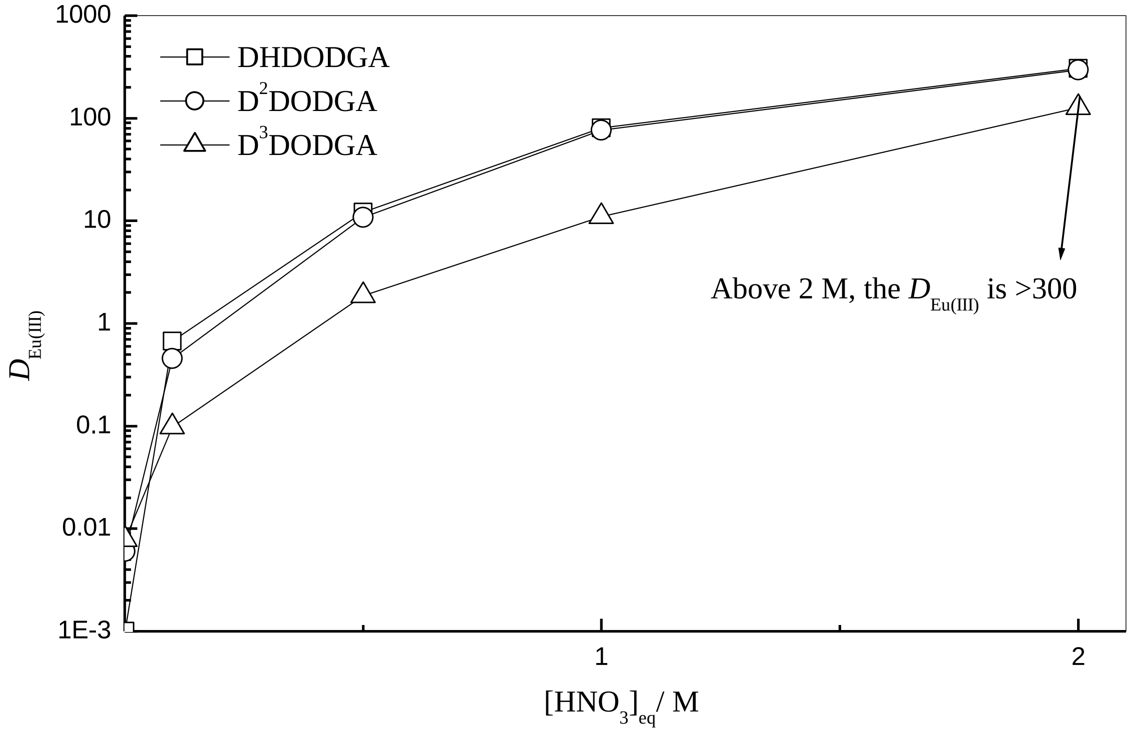


Figure 4.3. Variation in the $D_{Eu(III)}$ with concentration of nitric acid in UDGAs at 298 K. Organic phase: 0.1 M UDGA/*n*-dodecane. Aqueous phase: [HNO_3] spiked with $^{(152+154)}Eu$ tracer.

A similar extraction trend of trivalents was also reported by Sasaki *et.al.,* [41] in the case of symmetrical DGAs. However, Mowafy *et al.* [42] reported some deviations from the expected extraction trend. For instance, the extraction of Am(III) in symmetrical DGAs in benzene increased when the alkyl group attached to amidic nitrogen was varied in the order octyl < hexyl < propyl < butyl. However, the reason for such behavior was not reported. Nevertheless, the studies on DGAs carried out so far, in general, indicate that the *D* of metal ions decreased with the increase of alkyl chain length attached to amidic nitrogen atom. The extraction trend observed in the present study is also in good agreement with the trend reported by others.

A similar observation was also reported by others in symmetrical DGA systems [41,42]. The separation factors of Eu(III) over Am(III) ($D_{Eu(III)}/D_{Am(III)}$) in various DGA systems are shown in table 4.2. It is observed that the separation factor decreases with increase in the concentration of nitric acid. Above 2 M nitric acid, no separation observed in all cases, due to the comparable extraction of Eu(III) and Am(III) under these conditions.

Table 4.2. The separation factor of Eu(III) over Am(III) in various DGAs at 298 K. Organic phase: 0.1 M DGA in *n*-dodecane. Aqueous phase: Nitric acid spiked with $^{(152+154)}$Eu or ^{241}Am tracer. Organic to aqueous phase=1:1.

	SF= $D_{Eu(III)}/D_{Am(III)}$		
$[HNO_3]_{eq}$/M	**DHDODGA**	**D^2DODGA**	**D^3DODGA**
0.1	39	11	38
0.5	14	9	21
1	4	5	6
2	1.8	2	2

Table 4.3. $D_{Am(III)}$ in various UDGA/*n*-dodecane systems as a function of equilibrium concentration of nitric acid at 298 K. Organic phase: 0.03 and 0.1 M UDGA/*n*-dodecane. Aqueous phase: Nitric acid spiked with ^{241}Am tracer. Organic to aqueous phase=1:1.

$[HNO_3]_{eq}$/M	0.03 M DGA			0.1 M DGA		
	DHDODGA	D^2DODGA	D^3DODGA	DHDODGA	D^2DODGA	D^3DODGA
1	0.10	0.24	0.02	21	14	1.2
2	5.3	10	10	165	158	23
3	60	84	60	>300	285	214
4	96	>300	120	Third phase	>300	>300

4.4. Extraction stoichiometry of Am(III)-UDGA

UDGAs form complexes with Am(III) as shown in equation 4.1. Figure 4.4 shows the variation in the $D_{\mathrm{Am(III)}}$ with UDGA concentration. It is observed that the D increases with increase in the concentration of UDGA. Usually the magnitude of slope obtained from such a plot of log D vs log [UDGA] (figure 4.4) is regarded as the stoichiometry of metal-solvate complex in organic phase according to equation 4.1.

$$\mathrm{Am}^{+3}_{(aq)} + 3\ \mathrm{NO}^{3-}_{(aq)} + x\ \mathrm{UDGA}_{(org)} \rightleftharpoons \mathrm{Am(NO_3)_3.(UDGA)}_{x\ (org)} \quad (4.1)$$

It is interesting to note that the magnitude of slope varies in the order D^{3}DODGA (3) =D^{2}DODGA (3) < DHDODGA (4). Therefore, the number of UDGA molecules associated with Am(III) increase with decreasing the alkyl chain length attached to amidic nitrogen atom of UDGA. It is quite likely that the UDGA with higher alkyl chain length could be hindering the extraction and thus lowers the slope value. Due to the differences in slope, the straight line obtained for DHDODGA intersects the straight line of other UDGAs at two points as shown in figure 4.4. This indicates that the $D_{\mathrm{Am(III)}}$ in DHDODGA would be higher than that observed for both D^{2}DODGA and D^{3}DODGA when the concentration of UDGA is more than 0.1 M. On the other hand, when the concentration of UDGA is lower than 0.005 M the $D_{\mathrm{Am(III)}}$ in DHDODGA would be less than that observed for both D^{2}DODGA and D^{3}DODGA. When the concentration of UDGA is in between 0.005- 0.1 M, the $D_{\mathrm{Am(III)}}$ in DHDODGA would be intermediate between D^{2}DODGA and D^{3}DODGA systems. To confirm this, the $D_{\mathrm{Am(III)}}$ in 0.03 M, and 0.1 M UDGA/*n*-dodecane was measured, and the results are shown in table 4.3. It is observed that the $D_{\mathrm{Am(III)}}$ increases in the order D^{3}DODGA < D^{2}DODGA < DHDODGA when the concentration of UDGA is 0.1 M. The order changes to D^{3}DODGA < DHDODGA < D^{2}DODGA when the concentration of UDGA is 0.03 M. This explains the anomalous extraction behavior of Am(III) observed in DHDODGA as discussed in section 4.3. The $D_{\mathrm{Am(III)}}$ determined using 0.005 M were not adequate (10^{-4}) for comparing with other UDGAs (figure 4.4). The study, thus, shows that depending upon the concentration of UDGA employed for extraction, the order of selectivity is different.

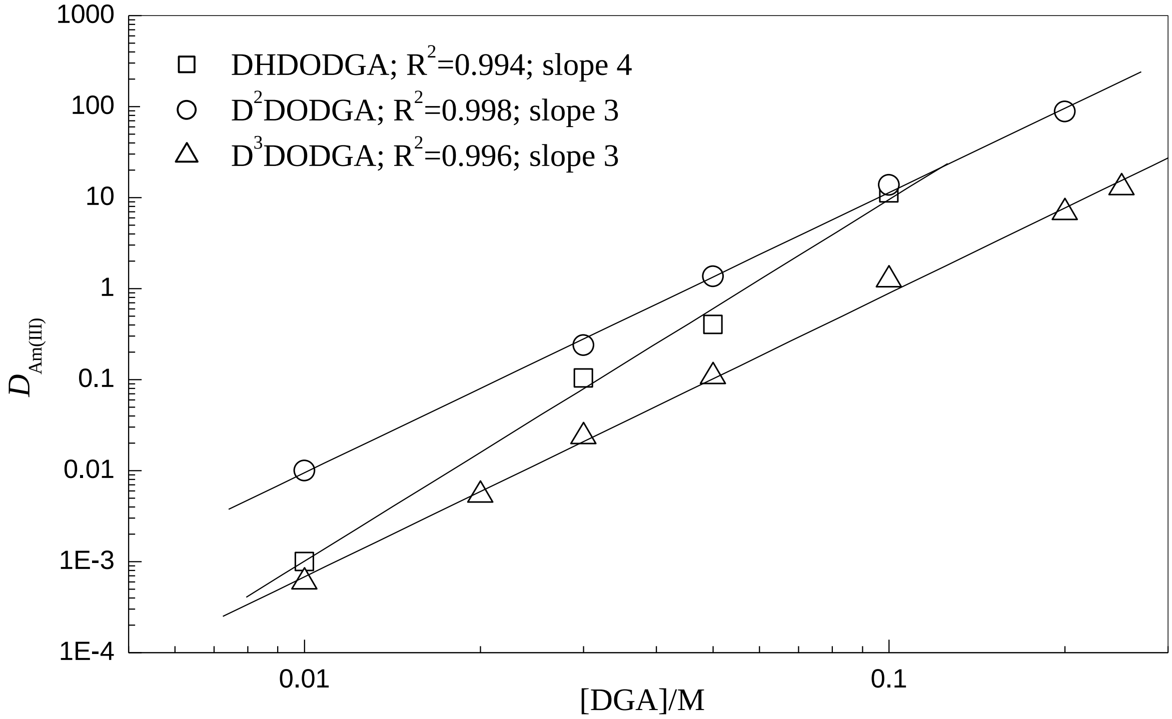


Figure 4.4. Variation in the $D_{Am(III)}$ with the concentration of UDGA at 298 K. Aqueous phase: 1 M HNO_3 spiked with ^{241}Am tracer. Organic to aqueous phase ratio=1:1.

4.5. Strontium extraction by UDGAs

The DGAs exhibit strong affinity towards strontium (II) and extract significant quantities of ^{90}Sr(II) along with trivalent actinides. The co-extraction of Sr(II) along with minor actinides poses several complications in obtaining pure actinides during the minor actinide partitioning. Therefore, the extraction of Sr(II) is undesirable, and needs to be minimized. In this context, the $D_{Sr(II)}$ in the present UDGAs was also determined and the results are shown in figure 4.5. It is observed that the $D_{Sr(II)}$ increases with increase in the equilibrium concentration of nitric acid and reaches a maximum at 4 M followed by a decrease. The $D_{Sr(II)}$ decreases in the order TODGA > D^2DODGA > DHDODGA > D^3DODGA.

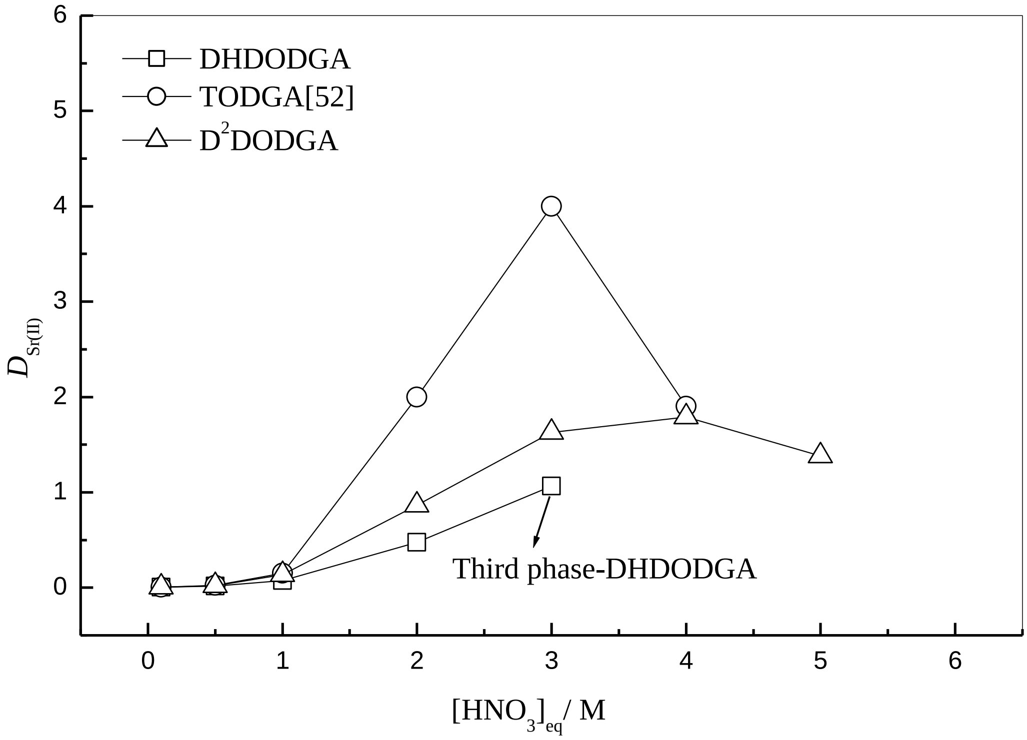


Figure 4.5. Variation in the $D_{Sr(II)}$ with concentration of nitric acid in various DGA systems at 298 K. Organic phase: 0.1 M DGA/*n*-dodecane. Aqueous phase: nitric acid spiked with $^{(85+89)}$Sr tracer. Organic to aqueous phase ratio=1:1.

It is interesting to observe that the $D_{Sr(II)}$ in DHDODGA/*n*-dodecane is much lower than all the other DGAs. Table 4.4 compares the separation factor of Am(III) over Sr(II) in various DGAs as a function of nitric acid concentration. It is observed that the separation factor increases with the increase in the equilibrium concentration of nitric acid in UDGA/*n*-dodecane systems. High separation factors are desirable to minimize the Sr(II) contamination in the actinides.

Table 4.4. Separation factor of Am(III) over Sr(II) in 0.1 M DGA/*n*-dodecane as a function of nitric acid concentration at 298 K.

HNO_3/ M	DHDODGA	TODGA	D^2DODGA	D^3DODGA
2	347	85	183	38
3	281	74	175	172
4	Third phase	>157	>166	>228
5	do	**	>217	>331

4.6. Third phase formation behavior of UDGAs

Table 4.5 shows the LOC and CAC of nitric acid in various 0.1 M DGA/*n*-dodecane systems at 298 K. It is interesting to note that the CAC values of nitric acid are quite high in D^3DODGA and D^2DODGA than that in TODGA system. It is noteworthy to mention that the HLLW acidity usually is in between ~ 3 and 4 M. Therefore, these reagents excepting DHDODGA can be employed for the extraction of actinides from 4 M nitric acid medium. However, this condition does not represent the real HLLW due to the absence of metal ions. Therefore, the LOC and CAC of trivalent metal ion, Nd(III) in 3-4 M nitric acid were estimated in these DGA solutions and the results are shown in table 4.6. It is interesting to note from table 4.6 that the LOC and CAC of Nd(III) also increased with increase of alkyl chain length attached to amidic nitrogen atom of DGA. The 0.1 M solution of DHDODGA in *n*-dodecane formed third phase with trace amount of metal ion in 3 M nitric acid, and even without metal ion from 4 M nitric acid. Therefore, DHDODGA may not be suitable for the metal ion extraction from 3-4 M nitric acid medium. On the other hand, the LOC of Nd(III) for 0.1 M TODGA/*n*-dodecane-4 M nitric acid system is found to be 2.8 mM, whereas for 0.1 M D^2DODGA/*n*-dodecane it is 8.1 mM. The CAC values of Nd(III) are too low to be determined by complexometric titrations, and therefore have not included in the table 4.6. The LOC and CAC values of Nd(III) for 0.1 M D^2DODGA/*n*-dodecane are higher than that of 0.1 M TODGA/*n*-dodecane. It is interesting and important to note that the quantitative amount of metal ion extracted into D^{3}DODGA/*n*-dodecane from high concentrated solutions of Nd(III) (> 600mM) without leading to any third phase formation. However, 0.1 M D^{2}DODGA/*n*-dodecane also forms third phase during the partitioning of trivalent actinides from HLLW. Therefore, 0.1 M D^{2}DODGA/*n*-dodecane also demands the addition of phase modifier to avoid third phase formation during the trivalent metal ion extraction from HLLW. However, 0.1 M D^{3}DODGA did not form third phase during the extraction from a 4 M nitric acid medium containing 600 mM of Nd(III) (more than ten times higher concentration of than that of HLLW).

Table 4.5. Third phase formation behavior in nitric acid extraction in various DGAs at 298 K. Organic phase: 0.1 M DGA in *n*-dodecane. Aqueous phase: Nitric acid. Organic to aqueous phase ratio=1:1.

DGA	$[HNO_3]_{ini}$/ M	LOC/ M	CAC/ M
DHDODGA	4	0.08	3.2
TODGA	6	0.18	5.1
D^{2}DODGA	7	0.20	5.6
D^{3}DODGA	12	0.28	9.3

It is interesting to observe from table 4.6 that the third phase in 0.1 M D^{3}DODGA/*n*-dodecane occurs only when the initial concentration of neodymium reaches 105 mM in 5 M HNO_3. The LOC and CAC of neodymium (III) are 24 mM and 69.5 mM respectively at 5 M HNO_3. The metal to ligand ratio (Nd: UDGA) observed at this LOC corresponds to ~1:4. At the nitric acid concentrations lower than 5 M, there was no third phase formation in 0.1 M D^{3}DODGA/*n*-dodecane even when the initial concentration of neodymium increased to 500 mM. Under these conditions, the neodymium(III) concentration in organic phase is ~ 31 mM. It was found that D^{3}DODGA forms a 3:1 complex with Am(III) during the extraction from 1 M nitric acid (see section 4.4). Therefore, a 0.1 M

D^3DODGA/*n*-dodecane (100 mM) is expected to extract a maximum of 33 mM. The study thus indicates that neodymium(III) could be loaded to near stoichiometric levels from 3-4 M nitric acid medium in 0.1 M D^3DODGA/*n*-dodecane without the formation of third phase. Thus, it is possible to use 0.1 M D^3DODGA/*n*-dodecane for the partitioning of minor actinides from HLLW without the need of any phase modifier.

Table 4.6. Third phase formation behavior of neodymium(III) in various DGA/*n*-dodecane systems at different nitric acid concentrations at 298 K. Organic phase: 0.1 M DGA/*n*-dodecane. Aqueous phase: Neodymium(III) in nitric acid. Organic to aqueous phase=1:1.

DGA	**3 M HNO_3**		**4 M HNO_3**		**5 M HNO_3**	
	$[Nd]_{ini}$/ mM	**LOC/ mM**	**$[Nd]_{ini}$/ mM**	**LOC/ mM**	**$[Nd]_{ini}$/ mM**	**LOC/ mM**
DHDODGA	Forms third phase even with trace level of Nd(III) at ≥ 3 M HNO_3					
TODGA[67]	8	6.4	6	2.8	< 1 mM	< 1 mM
D^2DODGA	15	13.2	10	8.1	7	3.5
D^3DODGA	>600	32	>600	31	105	24

It is interesting to note from the table 4.5 and 4.6 that the third phase formation limits for various DGAs are increasing with the increase of alkyl chain length attached to amidic nitrogen atom. The stoichiometric amount of trivalent metal ion can be extracted without any third phase formation when the dodecyl groups are present on the amidic nitrogen atom. Sasaki *et al.*[67] studied the third-phase formation of neodymium in various symmetrical DGAs. The LOC of neodymium(III) in symmetrical DGAs increased with increase in the chain length of alkyl group attached to amidic nitrogen atom. Interestingly, the authors also reported that the third phase was not formed in tetradodecyl diglycolamide/*n*-dodecane, (TDdDGA/*n*-dodecane) system during the loading of neodymium(III) from 3 M nitric acid. The stoichiometry of Nd:TDdDGA was as high as 1:3 was reported in this system. Despite the absence of third phase in TDdDGA system, several researchers employed a solution of TODGA along with a phase modifier in *n*-dodecane, for the separation of trivalent actinides from nitric acid medium. This was in fact due to the lower *D* of trivalents obtained in TDdDGA/*n*-dodecane (< 10 at 1 M HNO_3) as compared to the TODGA system [41]. It can be understood from these observations that the presence of dodecyl groups on the DGA prevents third phase formation. Thus, the studies on D^3DODGA indicated that its properties resemble with that of TODGA and of TdDGA. In view of these extraordinary properties of 0.1 M D^3DODGA/*n*-dodecane was studied in detail for partitioning of actinide and the results are described below.

4.7. Extraction studies using 0.1 M D^3DODGA/*n*-dodecane

Since there was no third phase formation during the extraction of trivalent actinides by 0.1 M D^3DODGA/*n*-dodecane from high concentrated solutions, it does not require any phase modifier for the extraction of trivalent actinides from nitric acid medium. When D^3DODGA is proposed for the separation of trivalent actinides from HLLW, it is necessary to understand the co-extraction behavior of various elements of HLLW. Therefore, present section reports the results on the extraction of fission products, and other metal ions that are present in HLLW, in a solution of 0.1 M D^3DODGA/*n*-dodecane. The effect of nitric acid concentration on the extraction behavior of various metal ions and their mutual interference were studied. It should be noted that the extractant D^3DODGA was employed in the present study without the presence of any phase modifier even for the simulated HLLW.

4.7.1. Trivalent metal ion extraction

Figure 4.6 shows the extraction behavior of several trivalent metal ions such as Y(III), Ce(III), Eu(III) and Am(III). It is observed that the *D* of these metal ions in 0.1 M D^3DODGA/*n*-dodecane increases with increase in the equilibrium concentration of nitric acid in the aqueous phase. The *D*s are greater than 300, when the extraction was carried out from higher nitric acid media (>4 M HNO_3). High *D* of An(III) and Ln(III) from 3-4 M nitric acid medium ensures their quantitative extraction of them in minimum number of contacts. However, this behavior is quite similar to that observed in other diglycolamides such as TODGA/*n*-dodecane [41].

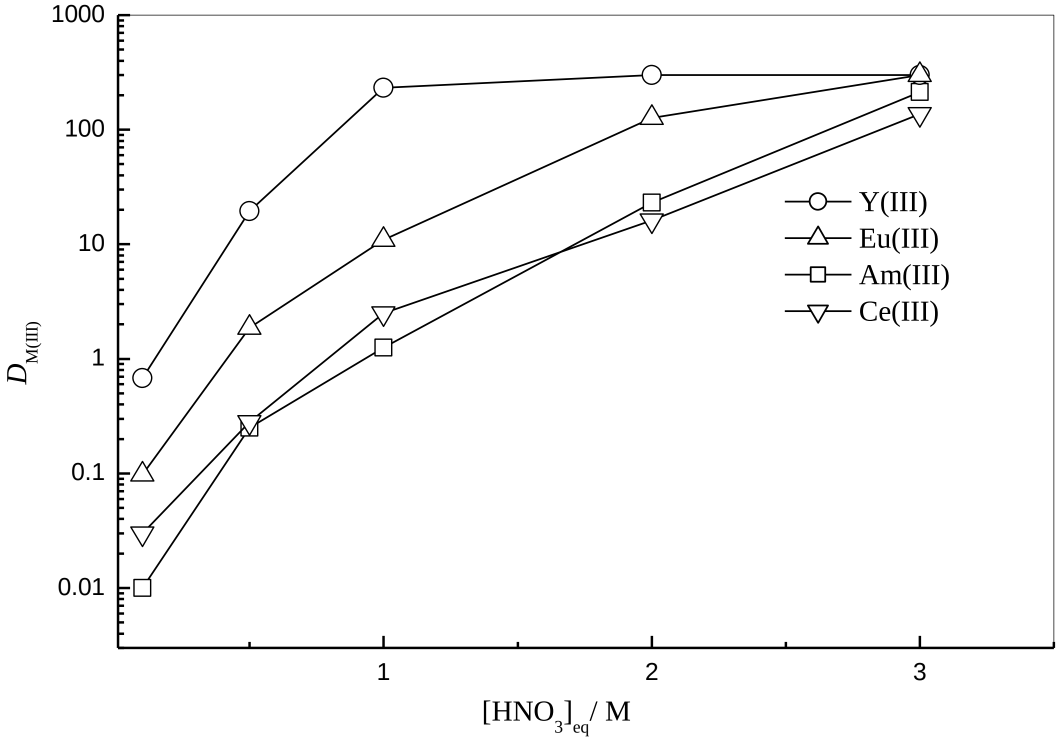


Figure 4.6. Variation in the *D* of trivalent metal ions with nitric acid concentration in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DODGA/*n*-dodecane, Aqueous phase: Nitric acid, Organic to aqueous phase ratio =1:1.

It is also interesting to observe that the *D* of trivalent metal ions increases in the order of their charge (z) to radius (r) ratio. Since all these metal ions are existing in trivalent state, the radius (given in parenthesis) of these ions decreases in the order of Ce(III) (0.103 nm) > Am(III) (0.099 nm) > Eu(III) (0.095 nm) > Y(III) (0.00093 nm). Therefore, the ratio, z/r, increases in the order Ce(III) < Am(III) < Eu(III) < Y(III). The unusual extraction efficiency of diglycolamides from the nitric acid medium (> 0.7 M) can be explained by the formation of reverse micelles of appropriate size suitable for the trivalent f-elements as reported elsewhere [59-62].

The other metal ions present in HLLW that exist in trivalent oxidation state are Fe(III), Ru(III), Sb(III) and Rh(III), etc. The extraction behavior of these metal ions in 0.1 M D^3DODGA/*n*-dodecane is shown in figure 4.7 as a function of nitric acid concentration. It is observed that their *D*s are lower than 0.05 at all the acidities studied. The contrasting extraction behavior observed for these metal ions as compared to the An(III) and Ln(III), could be attributed to either speciation of these metal ions in nitric acid medium or due to their charge to radius ratios. Since D^3DODGA is a neutral ligand, it extracts only the neutral species. Poor extraction of transition group elements in 0.1 M D^3DODGA/*n*-dodecane indicates that the formation of these neutral complexes in aqueous phase could be negligible as compared to An(III) and Ln(III). In addition, Zhu *et al*. [50] reported a correlation between the *D* of trivalent metal ions and ionic radii. The *D* was reported to increase from nearly 10^{-2} to ~ 10^3 with the increase of ionic radius from nearly 0.06 to around 0.1 nm. The *D*s reached a maximum at the radii of 0.0977 nm (Lu(III)). A similar correlation also holds good for the present UDGA. Therefore, the lower *D*s observed for Fe(III), Rh(III), Sb(III), and Ru(III) could be attributed to the lower ionic radii of these metal ions (~70) than trivalent lanthanides (0.090 –0.100 nm). However, the An(III) and Ln(III) having ionic radii 0.090-0.100 nm are extracted quantitatively by 0.1 M D^3DODGA/*n*-dodecane

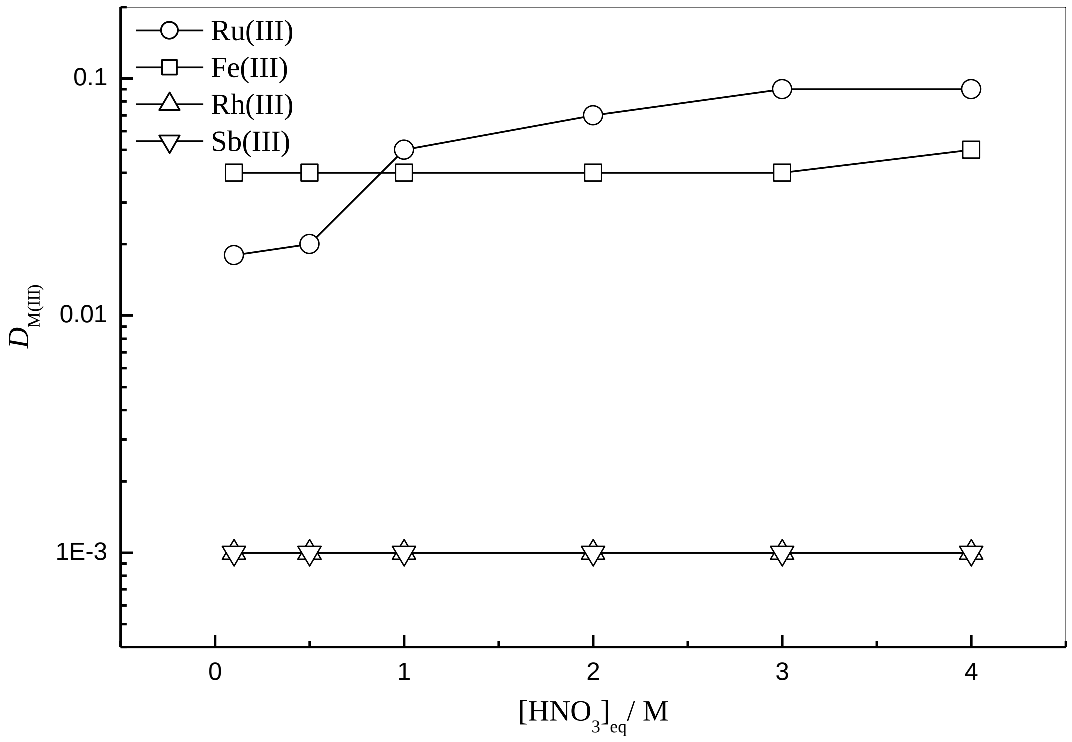


Figure 4.7. Variation in the *D* of trivalent metal ions with nitric acid concentration in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DODGA/*n*-dodecane Aqueous phase: Nitric acid containing metal ion. Organic to aqueous phase ratio= 1:1.

4.7.2. Extraction of Zr(IV)

The elements present in HLLW existing in tetravalent state include Zr(IV), Se(IV), Sn(IV), etc, The extraction behavior of Zr(IV) from nitric acid medium in a solution of 0.1 M D^3DODGA/*n*-dodecane is shown in figure 4.8. It is observed that the $D_{Zr(IV)}$ increases with increase in the equilibrium concentration of nitric acid as expected for any DGA systems. A *D* of >200 is achieved even at the nitric acid concentration of 1 M. This indicates that complete extraction of Zr(IV) is achieved in a single contact using 0.1 M D^3DODGA/*n*-dodecane. A *D* of >300 is obtained at nitric acid concentration greater than 2 M. Quantitative extraction of the fission product, Zr(IV), in 0.1 M D^3DODGA/*n*-dodecane may pose some complications during stripping and in the subsequent Ln(III)-An(III) separations.

Therefore, the study indicates the need for developing procedures for suppressing the extraction of Zr(IV), without affecting the extraction of trivalent actinides. However, such procedures are already reported for some of the symmetrical DGAs [79, 56]. The extraction of Se(IV), Sn(IV) was negligible. This behavior again attributed to the incompatible sizes of ions. It should be noted that the *D*s observed for Zr(IV) is higher than the *D* of trivalent metal ions. Thus, the extraction of undesirable radioactive fission products, such as ^{95}Zr(IV) and ^{90}Y(III) precautions steps to be taken in handling the loaded organic phase. However, complete extraction of Zr(IV) and Y(III) is a common observation in diglycolamide systems reported so far [50].

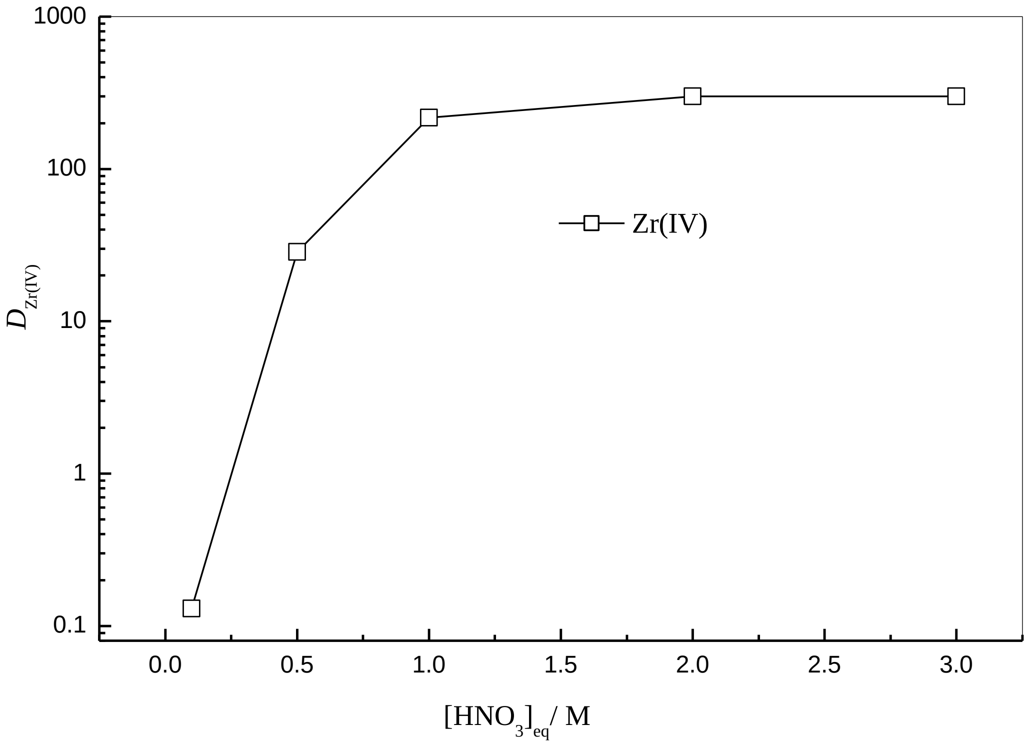


Figure 4.8. Variation in the $D_{Zr(IV)}$ with nitric acid concentration in the aqueous phase at 298 K. Organic phase: 0.1 M D^{3}DODGA/*n*-dodecane. Aqueous phase: Nitric acid containing Zr(IV). Organic to aqueous phase ratio= 1:1.

4.7.3. Extraction of divalent metal ions

The divalent metal ions present in HLLW include the fission products such as Ba(II), Cd(II), Sr(II), Pd(II) and corrosion products such as Mn(II), Ni(II), Co(II) (activation product). The *D* of Sr(II), Pd(II), Ni(II) and Ba(II) in 0.1 M D^3DODGA/*n*-dodecane as a function of equilibrium nitric acid concentration is shown in figure 4.9. It is observed that their *D*s increase with increase in the equilibrium concentration of nitric acid, and reaches a maximum at 3-4 M followed by decrease. This behavior is similar to the symmetrical DGAs. At 3-4 M nitric acid concentration prevailing in HLLW, the *D*s observed for these divalent metal ions are about 2-3 orders lower than that observed for trivalent actinides. However, the *D*s of Sr(II) and Pd(II) are not insignificant enough to be rejected into aqueous phase. The *D* of other metal ions such as Mn(II) and Co(II) in 0.1 M D^3DODGA/*n*-dodecane were lower than 10^{-3}.

It is quite interesting to compare the *D* of divalent metal ions in 0.1 M D^3DODGA/*n*-dodecane at 3 M nitric acid. The *D* of metal ions (given in parenthesis) increased in the order, Ni(II) (0.028) ~ Ba(II) (0.03) < Pd(II) (0.54) ~Sr(II) (1.2). This extraction trend is similar to that observed by, Zhu *et al.* [50]. The *D* of divalent metal ions was less than 0.1 when their ionic radii of divalent metal ions were in the range of 0.060-0.080 nm. However, the *D* increased to ~5 when the ionic radius was in the range 0.080-0.120 nm (Pd(II), Sr(II)). Therefore, the *D*s of Pd(II) and Sr(II) are relatively higher than that observed for other divalent metal ions.

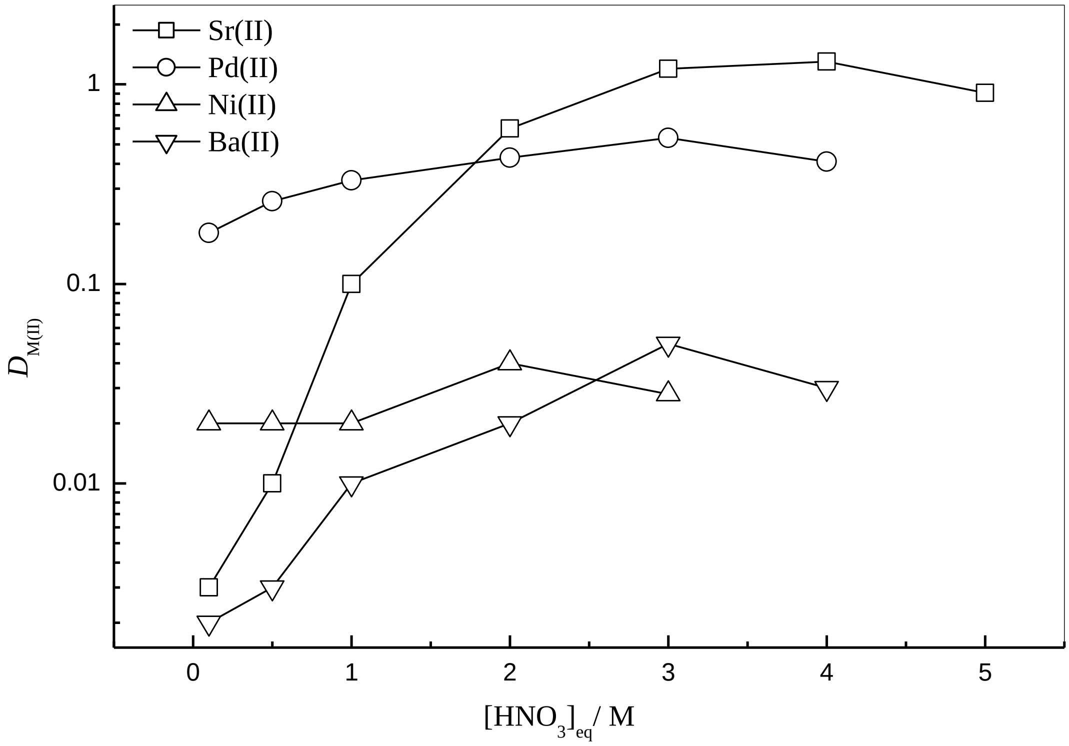


Figure 4.9. Variation in the *D* of divalent metal ions with nitric acid concentration in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DODGA/*n*-dodecane. Aqueous phase: Nitric acid containing metal ion. Organic to aqueous phase ratio= 1:1.

4.7.4. Extraction of hexavalent metal ions by D^3DODGA

The extraction behavior of some hexavalent metal ions is shown in figure 4.10 as a function of equilibrium nitric acid concentration. The $D_{U(VI)}$ increased from 10^{-3} to 4 with increase in nitric acid concentration from 0.1 to 5 M. The increase in *D* observed in this case could be attributed to the increased formation of neutral uranyl nitrate complex ($UO_2(NO_3)_2$), which is extractable, with increase in the concentration of nitric acid. However, the $D_{U(VI)}$ are much smaller when compared to the An(III) and Ln(III). In contract to this behavior, the *D* of other hexavalent metal ions such as Cr(VI), Mo(VI) and Te(VI) decreases with increase in the nitric acid concentration. A similar behavior was also observed in TEHDGA/*n*-dodecane system [55]. This behavior was attributed to the existence of these ions in anionic form.

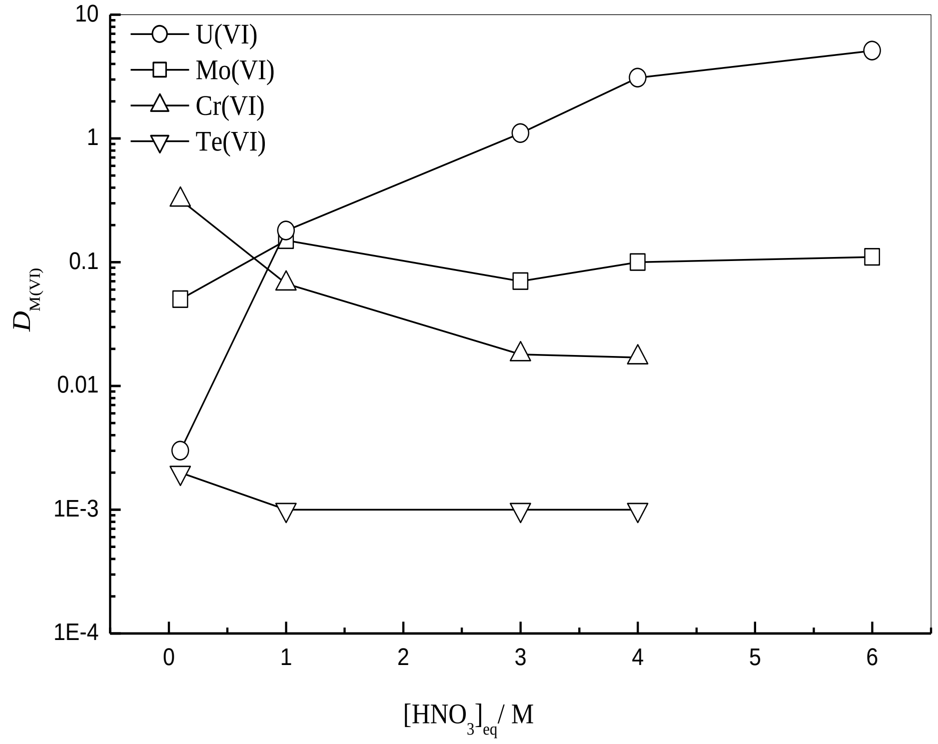


Figure 4.10. Variation in the *D* of hexavalent metal ions with nitric acid concentration in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DODGA/*n*-dodecane. Aqueous phase: Nitric acid containing metal ion. Organic to aqueous phase ratio=1:1.

4.8. Extraction of metal ions from simulated HLLW

The results presented in previous selections dealt with the extraction of individual metal ions in a solution of 0.1 M D^3DODGA/*n*-dodecane studied as a function of nitric acid concentration. However, the extraction behavior of metal ions may be different when they are extracted from HLLW. To understand the extraction behavior of metal ions in HLLW, studies were carried out from simulated HLLW (SHLLW). The SHLLW was prepared by the procedure described in section 2.3.7. The composition of fast reactor SHLLW of a burn up 100 GWd/Te is shown in table 4.7. The *D*s of various elements were measured from 4 M acid medium as well as from SHLLW and the results are included in table 4.7. It is quite interesting to compare the $D_{Am(III)}$ and some other metal ions obtained at 4 M nitric acid with those obtained in simulated high-level liquid waste (SHLLW).

It is observed that the *D* of several metal ions from SHLLW is lower when compared to those obtained from 4 M nitric acid. This could be attributed to the co-extraction of other metal ions present in SHLLW. However, the *D* obtained for Am(III) from SHLLW is sufficient for its complete extraction in a couple of contacts. The distribution ratios of Mn(II), Co(II), Cs(I), Sb(III) are negligible when they are extracted from 4 M nitric acid as well as SHLLW. This indicates that the extraction of undesirable metal ions in 0.1 M D^3DODGA/*n*-dodecane is less and therefore, the scrubbing stages required for the removal of unwanted metal ions from loaded organic phase would be less if 0.1 M D^3DODGA/*n*-dodecane is employed for the counter-current extraction. Thus, the extractant, D^3DODGA offer several advantages over TODGA such as (1) no third phase formation during the trivalent actinide partitioning from HLLW (2) complete extraction of trivalent actinides from 3-4 M nitric acid medium (3) quantitative recovery from the loaded organic phase in minimum contacts (4) poor extraction of unwanted metal ions. Our results with fast reactor (FR) simulated HLLW confirmed that the extraction of metal ions from real FR-HLLW would not lead to any undesirable third phase formation. Therefore, the results established the feasibility of using 0.1 M D^3DODGA/*n*-dodecane for partitioning of minor actinides from FR-HLLW without the requirement of any phase modifier.

Table 4.7. Elemental composition of simulated high-level liquid waste (SHLLW) arising from reprocessing of fast reactor spent fuels (100 GWd/Te) cooling period 1 year. The *D* of various elements in 0.1 M D^3DODGA/*n*-dodecane from SHLLW and 4 M nitric acid medium.

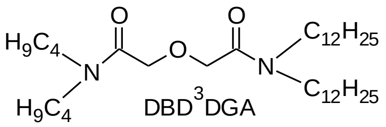
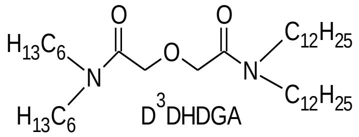
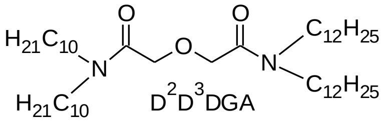
Metal ion	Quantity (g/L)	*D* of metal ions	
		4 M HNO_3	SHLLW
Zr(IV)	0.89	>400	136.7
Sn(IV)	0.02	10^{-2}	-
Se(IV)	0.01	10^{-2}	-
Sb(III)	0.01	$>10^{-3}$	-
Ce(III)	0.69	300	177
Dy(III)#	0.005	>300	43
La(III)	0.48	-	52
Eu(III)	0.31	-	11.4
Gd(III)	0.07	>300	197
Nd(III)	1.13	-	159
Pr(III)	0.34	-	63
Pm(III)	0.05	-	99
Sm(III)	0.05	-	-
Tb(III)#	0.01	-	>300
Rh(III)	0.26	-	-
Ru(III)	0.81	10^{-3}	<0.1
Y(III)#	0.08	>300	>300
Fe(III)	0.50	<0.1	<0.1
Ba(II)	0.41	<0.1	0.47
Sr(II)	0.14	1.3	0.28
Pd(II)	0.60	0.5	2.34
Cd(II)	0.04	<0.1	0.004
Ni(II)	0.10	-	<0.1
U(VI)	2.64	3.1	2.6
Mo(VI)	1.09	<0.1	$< 10^{-3}$
Cr(VI)	0.10	0.1	0.1
Te(VI)	0.16	<0.1	<0.1
Tc(VI)	0.26	<0.1	1.8
Cs(I)	1.12	10^{-3}	10^{-3}
Rb(I)	0.06	<0.1	<0.1
Ag(I)	0.13	<0.1	<0.1
Na(I)	3	<0.1	<0.1
Nitric acid	4 M	-	-

La added for Y, Pm, Tb, Dy

PART B-Tuning the DGAs with dodecyl groups

The present studies with D^{3}DODGA, and the studies with TDdDGA by Sasaki *et al.* [67] indicated that the presence of dodecyl groups on amidic nitrogen atom prevent the third phase formation during the extraction. To improve the extraction properties of diglycolamides further, the present study deals with the synthesis of various UDGA with dodecyl groups attached to one amidic nitrogen atom, and the alkyl groups at the other amidic nitrogen atom are varied from *n*-butyl to *n*-decyl moiety. Depending upon the nature of alkyl group varied, the UDGAs were designed as *N,N*-di-butyl-*N',N'*-di-dodecyl-3-oxapentane-1,5-diamide (DBD^{3}DGA), *N,N*-di-dodecyl-*N',N'*-di-hexyl-3-oxapentane-1,5-diamide (D^{3}DHDGA), *N,N*-di-decyl-*N',N'*-di-dodecyl-3-oxapentane-1,5-diamide (D^{2}D^{3}DGA). The extraction behavior of Am(III), Eu(III), and Sr(II) from nitric acid medium in a solution of these UDGAs in *n*-dodecane was studied as a function of various parameters. The third phase formation of nitric acid, and Nd(III) in 0.1 M UDGA/*n*-dodecane was a studied as function of nitric acid concentration.

Table 4.8. The structures and names of the UDGAs

S.No.	Name	Structure
1.	*N,N*-di-butyl-*N',N'*-di-dodecyl-3-oxapentane-1,5-diamide or di-dodecyl-di-butyl- diglycolamide	
2.	*N,N*-di-dodecyl-*N',N'*-di-hexyl-3-oxapentane-1,5-diamide or di-dodecyl-di-hexyl- diglycolamide	
3.	*N,N*-di-decyl-*N',N'*-di-dodecyl-3-oxapentane-1,5-diamide or di-decyl-di-dodecyl- diglycolamide	

4.9. Extraction of metal ions in modifier-free UDGAs

4.9.1. Trivalent metal ion extraction

The extraction behavior of Am(III) and Eu(III) was studied in the present UDGAs as a function of nitric acid concentration in the aqueous phase and the results are shown in figures 4.11 and 4.12 respectively. It is observed that the *D* increases with increase in the equilibrium concentration of nitric acid as expected for the DGA systems. The $D_{\mathrm{Am(III)}}$ in all UDGAs except for the D^2D^3DGA are greater than 300 at acidities greater than 3 M. It is interesting to observe from figure 4.12, that the $D_{\mathrm{Am(III)}}$ decreases in the order DBD^3DGA ~ D^3DHDGA > D^3DODGA > D^3D^2DGA. A similar trend is also observed for the extraction of Eu(III) as shown in figure 4.12.

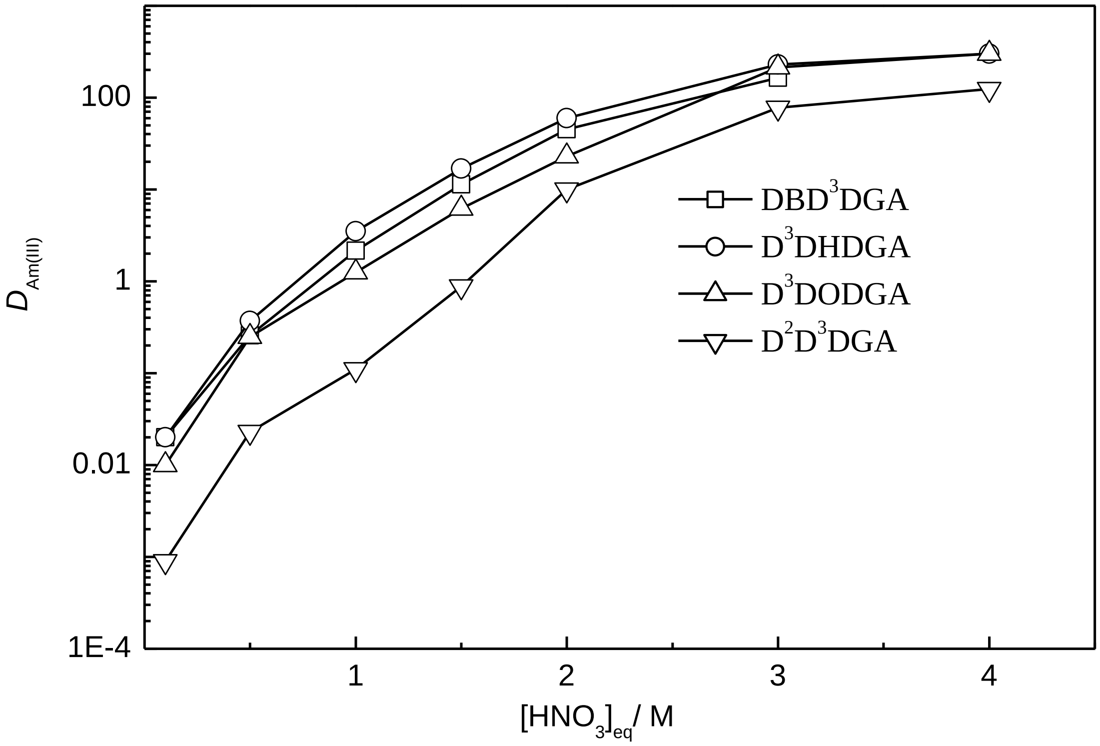


Figure 4.11.Variation in the $D_{\mathrm{Am(III)}}$ with equilibrium concentration nitric acid in the aqueous phase in various 0.1 M UDGA/*n*-dodecane solutions at 298 K. Organic to aqueous phase ratio= 1:1.

Increase in the alkyl chain length on the amidic nitrogen atom of DGA decreases the *D* of trivalent metal ions. This observation is in good agreement with the previous studies [41,42].

The separation factors of Eu(III) over Am(III) (=D_{Eu}/D_{Am}) in various DGA systems are shown in table 4.9. It is observed that the separation factor decreases, in general, with increase in concentration of nitric acid. Above 2 M nitric acid, the separation factor approaches unity in all cases, indicating that the extraction of Eu(III) and Am(III) is comparable under these conditions by these extractants.

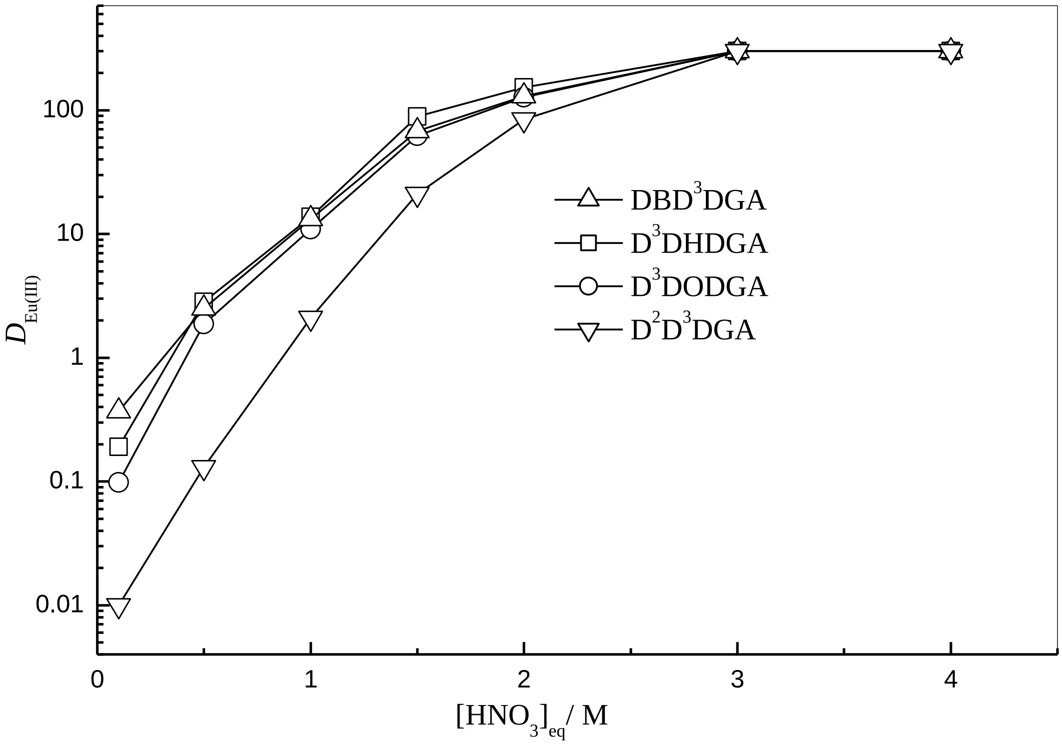


Figure 4.12.Variation in the $D_{Eu(III)}$ with equilibrium concentration of nitric acid in the aqueous phase in various 0.1 M UDGA/*n*-dodecane solutions at 298 K. Organic to aqueous phase ratio= 1:1.

Table 4.9. The separation factor of Eu(III) over Am(III) as a function of concentration of nitric acid in various 0.1 M UDGA/*n*-dodecane solutions at 298 K. Separation factor = $D_{Eu(III)}/D_{Am(III)}$.

$[HNO_3]$/ M	SF($D_{Eu(III)}/D_{Am(III)}$)			
	D^3DBDGA	D^3DHDGA	D^3DODGA	D^3D^2DGA
0.1	18.5	9.5	9.8	11.1
0.5	9.7	7.6	7.5	5.6
1	6.3	3.9	8.8	19.1
1.5	6.0	5.3	10	23.9
2	2.9	2.5	5.5	8.4
3	1.8	1.3	1.4	3.8

4.10. Extraction stoichiometry

The stoichiometry of metal-solvate was determined by slope analysis of the extraction data as discussed in the section 4.4 for these modifier-free UDGAs. The variation in the *D* of Am(III) with UDGA concentration in organic phase is shown in figure 4.13. In all the cases the slope was found to vary from 2.8 to 2.9. This indicates that about three molecules of UDGA are involved in the extraction of Am(III) from nitric acid medium. These results are consistent with other DGAs and UDGAs reported. It is interesting to note that the majority of DGAs form 1:3 complexes with Am(III) during extraction from 1 M nitric acid medium. The DGAs containing alkyl chains lower than or equal to octyl, form 1:4 complexes with Am(III). For example four molecules of TODGA and DHDODGA are involved in complexation with Am(III).

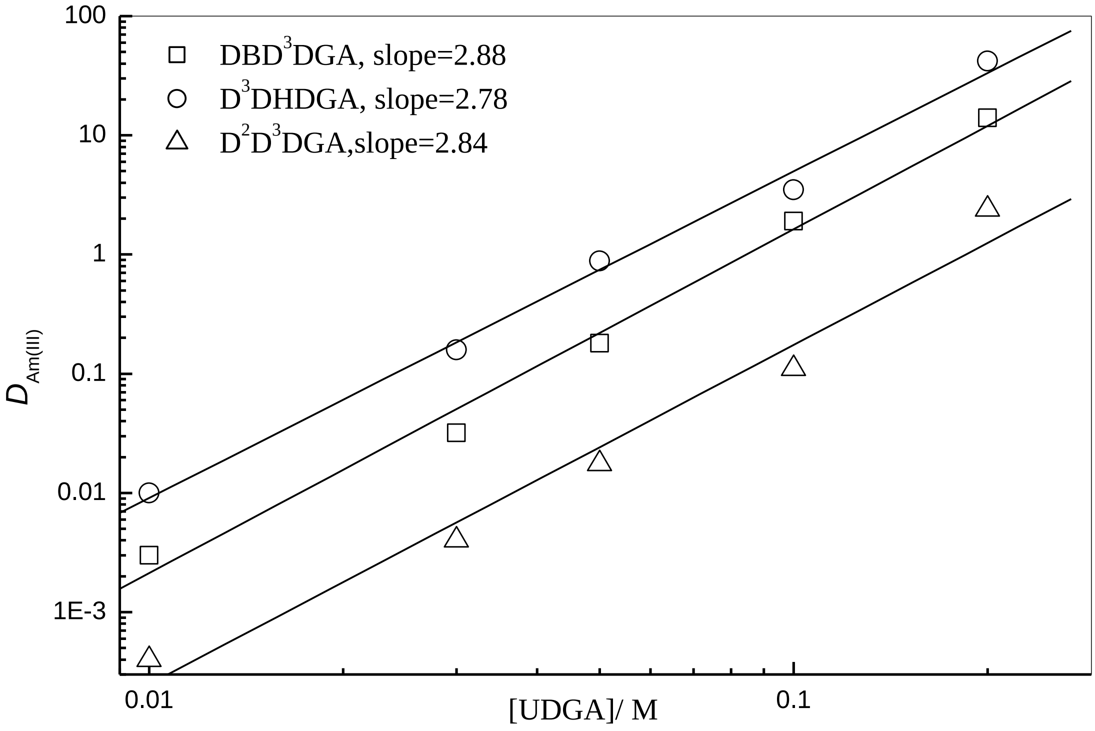


Figure 4.13. Variation in the $D_{Am(III)}$ with concentration of UDGA/*n*-dodecane at 298 K. Aqueous phase: 1 M nitric acid. Organic to aqueous phase ratio=1:1.

4.11. Strontium extraction

Figure 4.14 shows the variation in the $D_{Sr(II)}$ with concentration of nitric acid in various UDGAs. The $D_{Sr(II)}$ increased with increase of equilibrium concentration of nitric acid in the aqueous phase, and reached a maximum at 4 M nitric acid. This trend is quite similar to that observed in several DGAs studied so far. It is important to note from figure 4.14 that the $D_{Sr(II)}$ in the present UDGAs is quite lower than that in 0.1 M TODGA/*n*-dodecane. Table 4.10 shows the separation factor of Am(III) over Sr(II) in various 0.1 M DGA/*n*-dodecane as a function of concentration of nitric acid in the aqueous phase. The high separation factors of Am(III) over Sr(II) in the present UDGAs is the additional advantage for the partitioning actinides.

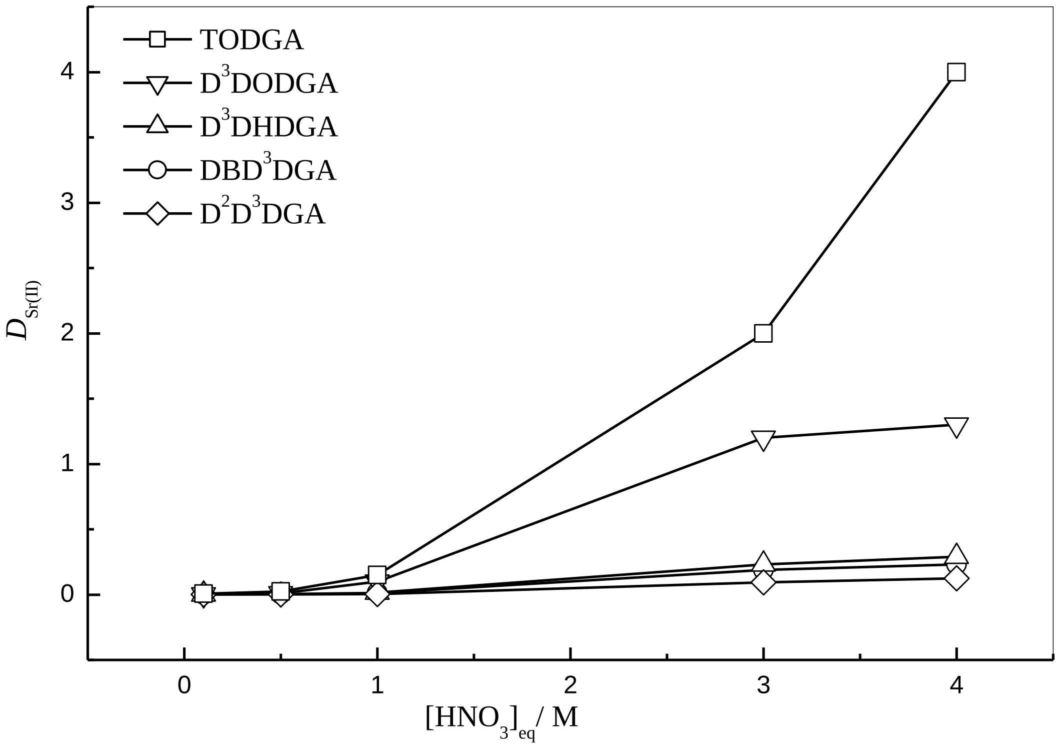


Figure 4.14. Variation in the $D_{Sr(II)}$with concentration of nitric acid in the aqueous phase in various 0.1 M UDGA/*n*-dodecane solutions at 298 K. Organic to aqueous phase ratio=1:1.

Table 4.10. Separation factor of Am(III) over Sr(II) achieved with the use of 0.1 M UDGA/*n*-dodecane as a function of equilibrium nitric acid concentration at 298 K. Organic to aqueous phase ratio=1:1.

HNO_3/ M	**SF($D_{Am(III)}$/$D_{Sr(II)}$)**			
	DBD^{3}DGA	**D^{3}DHDGA**	**D^{3}DODGA**	**D^{2}D^{3}DGA**
0.1	12.5	33.3	100	1.3
0.5	64.5	-	26	23
1	161	233	12.5	27.5
3	863	1000	177.5	830
4	1304	1034	231	984

4.12. Third phase formation behavior of UDGAs with dodecyl group

Table 4.11 shows the LOC of nitric acid in various 0.1 M UDGAs/*n*-dodecane at 298 K. It is observed that the LOC of nitric acid increases, in general, with increase in the chain length of alkyl group attached to amidic nitrogen atom. In addition, it is interesting to note the stoichiometry of UDGA: HNO_3 complex observed in organic phase at near limiting organic concentration. The stoichiometry of UDGA: HNO_3 at LOC increases with increase in the chain length of alkyl group attached. Figure 4.15 shows the variation in the stoichiometry of UDGA: HNO_3 complex as a function of total number of carbon atom in the alkyl chain length of UDGAs. It is interesting to observe that the stoichiometry of UDGA: HNO_3 complex at LOC increases with increase in the number of carbons, even though the coordinating atoms are same. The correct reason for this behavior is not clear at present, perhaps, it could be due to the stabilization of the UDGA-HNO_3 complex in *n*-dodecane phase by UDGAs having higher chain length.

Table 4.11. Limiting organic concentration (LOC), and critical aqueous concentration (CAC) of nitric acid in 0.1 M UDGA/*n*-dodecane at 298 K.

0.1M UDGA/*n*-dodecane	HNO_3 / M		
	Initial	LOC	CAC
DBD^3DGA	15.7	0.26	12.4
D^3DHDGA	10.9	0.23	8.3
D^3DODGA	12	0.29	9.3
D^3D^2DGA	12	0.30	9.4

From the application point of view, the present study (table 4.11) thus shows that the third phase is observed only when the initial concentration of nitric acid exceeds 10 M in all the

UDGAs. It is worthwhile to mention here that the concentration of nitric acid prevailing in HLLW is 3-4 M only. Therefore, the UDGAs studied in this section do not require any phase modifier during the extraction of trivalent actinides from HLLW, whereas the symmetrical DGAs such as TODGA and TEHDGA demand the addition of phase modifiers.

The third phase formation of Nd(III) from 3-4 M nitric acid was studied in the present UDGAs, containing dodecyl groups on one amidic nitrogen atom. The concentration of Nd(III) was varied up to 500 mM, which is about 10 times higher than the total concentration of all trivalent metal ions present in HLLW. Our studies revealed that all the UDGAs investigated in the present study do not lead to any third phase formation. Therefore, the studies confirmed that the UDGA with dodecyl group attached to one amidic nitrogen atom is inevitable for preventing third phase formation and the alkyl group at the other amidic nitrogen can be varied from butyl to decyl group for obtaining efficient extraction of trivalent actinides from nitric medium.

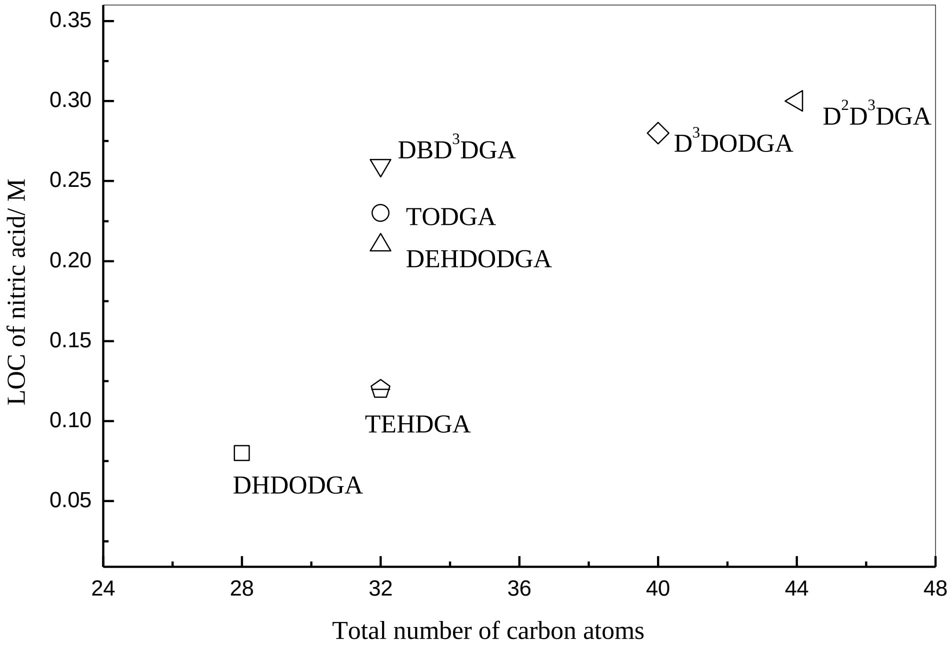


Figure 4.15. Variation in the LOC of nitric acid in various 0.1 M DGA/*n*-dodecane systems with the total number of carbon atoms in the alkyl groups at 298 K. Organic to aqueous phase ratio=1:1.

Thus, our studies revealed that the present UDGAs containing dodecyl groups on one amidic nitrogen atom do not form third phase during the extraction of trivalent metal ions from HLLW and therefore, do not need any phase modifier (modifier-free UDGAs).

It was reported that the presence of branching in alkyl groups attached to amidic nitrogen atom suppresses the undesirable metal ions [52]. Our studies with UDGAs indicated that the presence of dodecyl groups on amidic nitrogen atom prevents the third phase formation during the extraction of trivalent actinides from simulated HLLW. In this context, the present study also involves the synthesis evaluation of a new UDGA, containing dodecyl group on one amidic nitrogen atom and 2-ethylhexyl group on the other nitrogen. The structure of the new UDGA, *N*,*N*-di-dodecyl-*N*′,*N*’-di-2-ethylhexyl-3-oxapentane-1,5-diamide (D^3DEHDGA) is shown in figure 4.16.

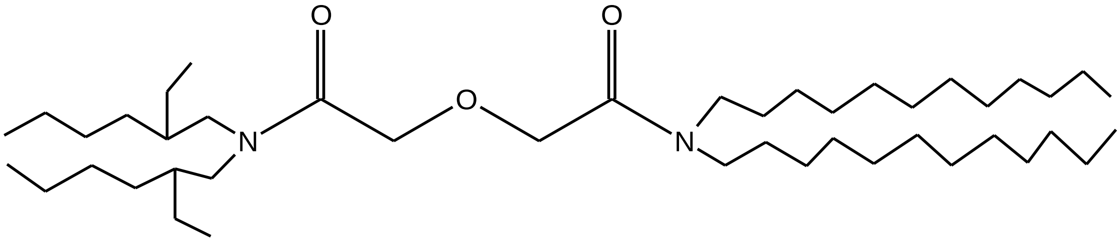


Figure 4.16. The structure of D^3DEHDGA

4.13. D^3DEHDGA for actinide partitioning

4.13.1. Trivalent metal ion extraction by D^3DEHDGA

Figure 4.17 shows the extraction behavior of Am(III) and Eu(III) in 0.1 M D^3DEHDGA/*n*-dodecane as a function of equilibrium concentration of nitric acid in the aqueous phase at 298 K. It is observed that the D of these metal ions increases with increase in the concentration of nitric acid. The $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ are $\geq$ 300 at nitric acid concentrations more than 3 M. The $D_{Eu(III)}$ is greater than that of $D_{Am(III)}$ at all the acidities studied as expected for the DGAs.

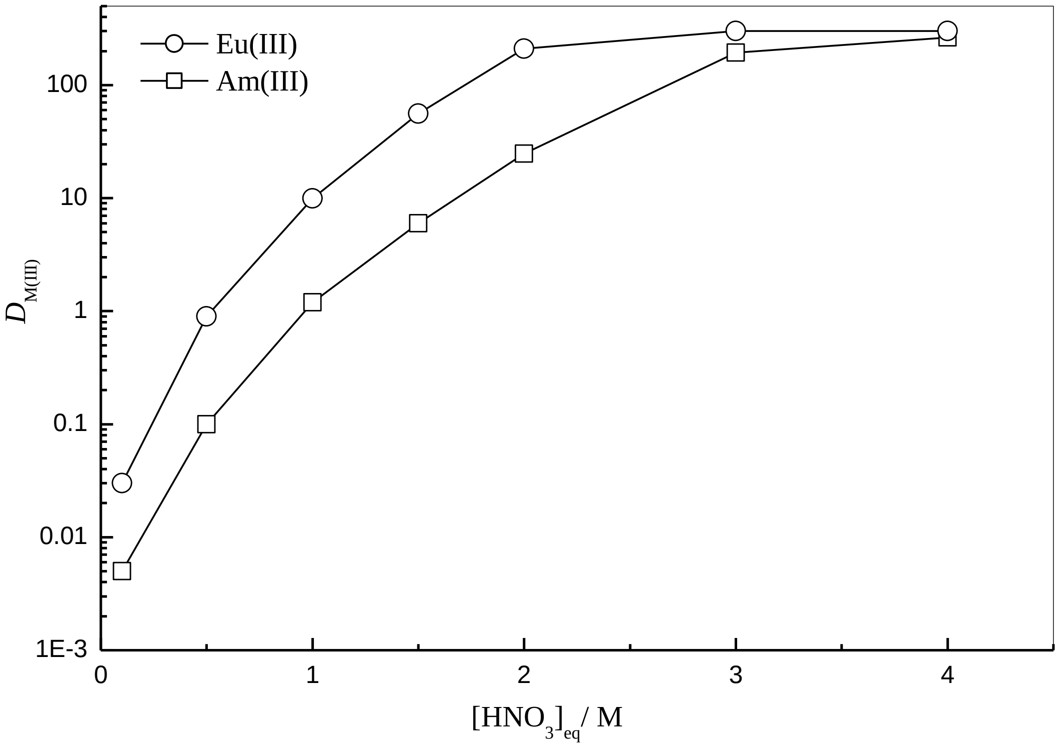


Figure 4.17. Variation in the $D_{Eu(III)}$ and $D_{Am(III)}$ with equilibrium concentration of nitric acid in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DEHDGA/*n*-dodecane. Organic to aqueous phase ratio= 1:1.

4.13.2. Stoichiometry of trivalents with D^3DEHDGA

In view of branching alkyl group on one amidic nitrogen atom and long alkyl chain length on the other amidic nitrogen, it is important to know the number of molecules of D^3DEHDGA involved in the complex formation with An(III) and Ln(III) during the extraction. Therefore, the stoichiometry of these metal ions (M(III)) with D^3DEHDGA was determined by using extraction data. The variation in the $D_{Am(III)}$ and $D_{Eu(III)}$ with D^3DEHDGA concentration in organic phase is shown in figure 4.18. The slopes of the straight line corresponding to Am(III) and Eu(III) are found to be 3.1 and 3.0 respectively.

This indicates that three molecules of D^{3}DEHDGA are involved in the extraction of trivalent f-elements from nitric acid medium.

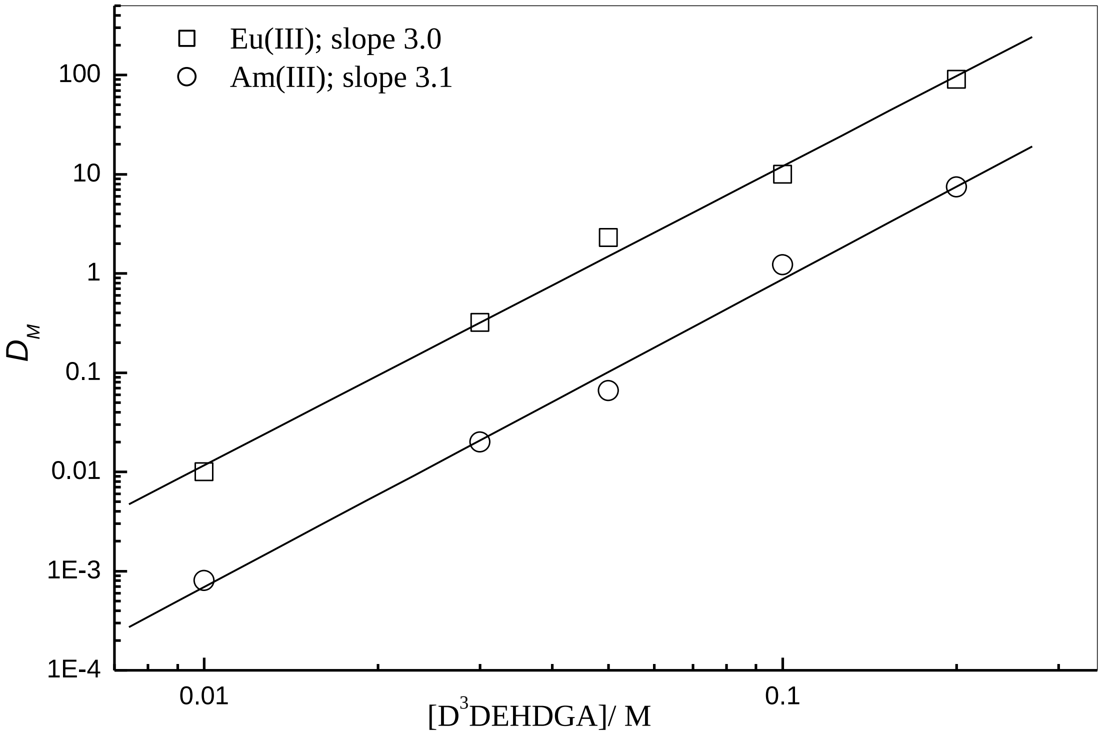


Figure 4.18. Variation in the $D_{Am(III)}$ and $D_{Eu(III)}$ with the concentration of D^{3}DEHDGA/*n*-dodecane at 298 K. Aqueous phase: 1 M nitric acid. Organic to aqueous phase=1:1.

4.13.3. Extraction of other fission products

The extraction behaviour of some fission products such as Ba(II), Sr(II), Ru(III), Cs(I), and Sb(III) was studied in 0.1 M D^{3}DEHDGA/*n*-dodecane from nitric acid medium, and results are shown in figure 4.19. It is observed that the $D_{Sr(II)}$ increases marginally with increase in the concentration of nitric acid. These *D*s are about 2-3 orders lower than that observed for An(III) and Ln (III). Figure 4.17 also compares the $D_{Sr(II)}$ in 0.1 M TODGA/*n*-dodecane with that in 0.1 M D^{3}DEHDGA. The $D_{Sr(II)}$ is quite lower in 0.1 M

D^3DEHDGA/*n*-dodecane than that in 0.1 M TODGA. Nevertheless, the $D_{Sr(II)}$s are not insignificant so as to be rejected into aqueous phase during minor actinide separation.

In contraction to the high extraction behavior of trivalent actinides and lanthanides, the $D_{Ru(III)}$ is quite low. It is interesting to note that the extraction of Sb(III), Cs(I) are less than 10^{-3} at all the acidities. The reasons for the poor extraction of these metal ions are explained in the section 4.6.3. In this context, the extraction behaviour of U(VI) in 0.1 M D^3DEHDGA/*n*-dodecane from nitric acid medium was studied and the results are shown in figure 4.19. It is observed that the $D_{U(VI)}$ increased with increase in equilibrium concentration of nitric acid. However, the *D*s observed for U(VI) are quite lower than that of observed for An(III) and Ln(III). A similar trend was also observed in the other DGAs studied in the literature.

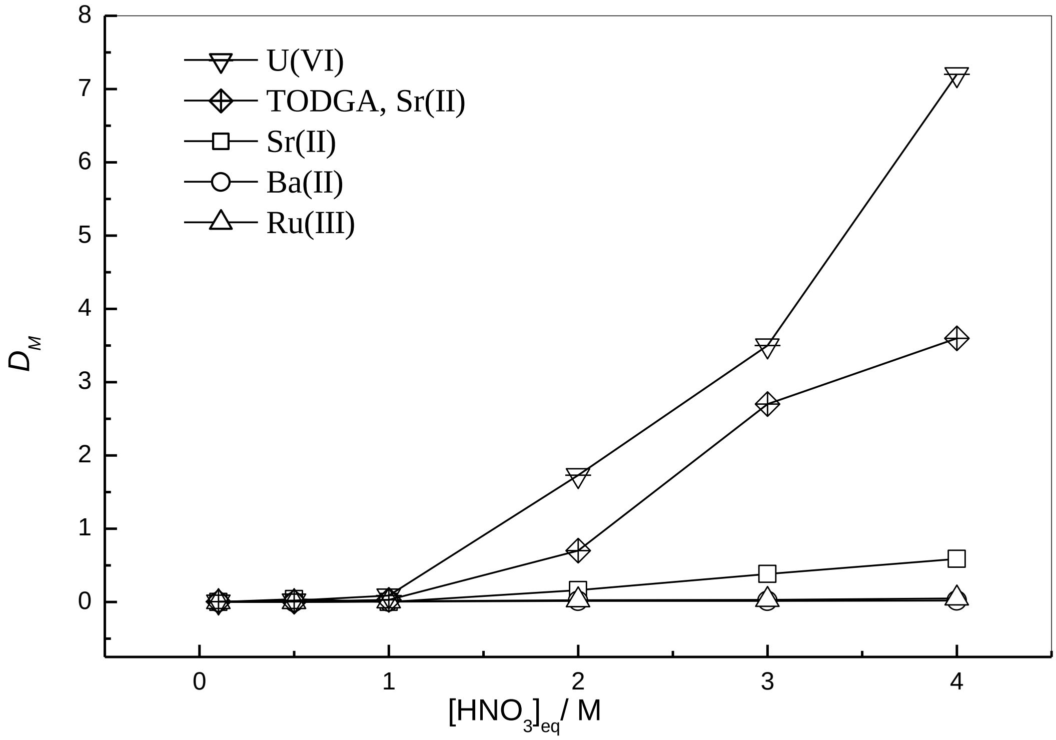


Figure 4.19. Variation in the *D* of some metal ions with equilibrium concentration of nitric acid in the aqueous phase at 298 K. Organic phase: 0.1 M D^3DEHDGA/*n*-dodecane. Aqueous phase: Nitric acid spiked with either $^{(85+89)}$Sr, ^{133}Ba, ^{106}Ru, ^{233}U tracer. Organic to aqueous phase ratio=1:1.

4.14. Third phase formation in D^3DEHDGA

The third phase formation behavior of 0.1 M D^3DEHDGA/*n*-dodecane was studied for the extraction of Nd(III) from nitric acid medium. The LOC and CAC of nitric acid in 0.1 M D^3DEHDGA/*n*-dodecane were determined and the results are shown in table 4.12. It is interesting to note that third phase formation was not observed in organic phase, even when ~11 M nitric acid was equilibrated with equal volume of 0.1 M D^3DEHDGA/*n*-dodecane. The LOC and CAC values for the extraction of Nd(III) in 0.1 M D3DEHDGA/*n*-dodecane at 298 K are given in table 4.12. The LOC and CAC values of Nd(III) decrease with increase of concentration in nitric acid in the aqueous phase. It is worthwhile to note that the third phase formation is observed when the Nd(III) concentration in 4 M HNO_3 exceeds 100 mM, which is much higher than the typical concentration of trivalent actinides and lanthanides present in HLLW(~50mM) in 3-4 M nitric acid medium. This indicates that 0.1 M D^3DEHDGA/*n*-dodecane does not require any phase modifier for the extraction of trivalent actinides from HLLW. In order to verify this, the extraction behavior of some metal ions, Am(III), Eu(III), Sr(II) and Ba(II), from fast reactor simulated HLLW was studied and the results are shown in table 4.13. It is observed that the *D* of all these metal ions are lowered as compared to that observed in 4 M nitric acid (figures 4.17 and 4.19), perhaps, due to competition of several metal ions present in simulated HLLW for the extraction. However, it is important to note that the *D* observed for Am(III) and Eu(III) is sufficient for complete extraction of these metal ions from SHLLW, in few contacts. Moreover, the distribution ratios of Sr(II) and Ba(II) are quite low during the extraction from simulated HLLW. In particular, no third phase formation was observed during the extraction of Am(III) and Eu(III) from simulated HLLW, confirming that 0.1 M D^3DEHDGA/*n*-dodecane is a promising candidate for minor actinide partitioning from fast reactor HLLW.

Table 4.12. The limiting organic concentration (LOC) and critical aqueous concentration (CAC) of neodymium (III) during the extraction from nitric acid medium by 0.1 M D^{3}DEHDGA/*n*-dodecane at 298 K. Organic to aqueous phase ratio= 1:1.

Aqueous phase	Initial	LOC	CAC
Nitric acid/ M	11.9	0.3	9.5
Nd(III) in 3 M HNO_3/ mM	295	24	225
Nd(III) in 4 M HNO_3/ mM	120	19	41.6
Nd(III) in 5 M HNO_3/ mM	40	17	11.5

Table 4.13. *D* of Am(III) and some fission products from simulated HLLW in 0.1 M D^{3}DEHDGA/*n*-dodecane at 298 K. $[H^+]_{SHLLW}$= 4 M. Organic to aqueous phase ratio = 1:1.

Metal ion	*D*
Am(III)	66
Eu(III)	126
Sr(II)	0.11
Ba(II)	10^{-3}

4.15. Conclusions

The diglycolamide structure has been tuned to obtain the desirable properties required for minor actinide partitioning from nitric acid medium. The tuning was carried out in two modes, in the first mode, with only octyl groups on one amidic nitrogen atom and different alkyl groups on the other nitrogen atom from hexyl to dodecyl groups. The UDGAs were synthesized to derive the advantage of high *D* and enhanced LOC of neodymium and nitric acid. The extraction behaviour of Am(III), Eu(III), and Sr(II) in these di-octyl-di-alkyl diglycolamides in *n*-dodecane was studied as a function of various parameters. The extraction of trivalents (Am(III) and Eu(III)) in UDGAs decreased in the order DHDODGA > D^2DODGA > D^3DODGA. The *D* of trivalents in TODGA was comparable with DHDODGA. However, the LOC of nitric acid and neodymium (III) increased in the order of DHDODGA < TODGA < D^2DODGA < D^3DODGA. Among these UDGAs, D^3DODGA offers several advantages such as (1) high *D* of trivalent lanthanides and actinides from nitric acid medium (>300 ~ 3-8 M HNO_3) (2) low $D_{Sr(II)}$ and thus high separation factor of americium over strontium (3) high LOC and CAC of nitric acid (4) no third phase formation with neodymium (III) even at the initial concentration of 600 mM from 3-4 M nitric acid medium at 298 K. Therefore, the solvent 0.1 M D^3DODGA/*n*-dodecane did not require any phase modifier. In view of these, D^3DODGA was studied extensively for the actinide partitioning. The extraction behavior of actinides, fission products, and corrosion products was studied in a solution of 0.1 M D^3DODGA in *n*-dodecane from nitric acid as well as from fast reactor high-level liquid waste. The extraction of metal ion in 0.1 M D^3DODGA/*n*-dodecane was strongly dependent on the charge to radius ratio and the distribution ratios followed the order M(IV) > M(III) >> M(VI) ~ M(II) >> M (I). Based on the *D*s obtained from 3–4 M nitric acid medium and simulated waste, the metal ions such as Zr(IV), Am(III), Ln(III) and Y(III) could be extracted quantitatively in to 0.1 M D^3DODGA/*n*-dodecane phase in 1–3 contacts. The metal ions such as Sr(II), Pd(II), U(VI), Te(VI), Ru(III) having *D* between 0.1–2 could also extracted in to organic phase in some contacts during counter-current extraction. The *D* of other metal ions was negligible ($\sim 10^{-2}$). The studies revealed that the extraction behaviour of various metal ions in 0.1 M D^3DODGA/*n*-dodecane was similar to TODGA/*n*-dodecane system. However, the exceptional difference was that D^3DODGA did not require any phase modifier for extraction from simulated HLLW. Therefore, it is advantageous to employ 0.1 M D^3DODGA/*n*-dodecane for partitioning of minor actinides from HLLW.

Considering the advantages with dodecyl groups on amidic nitrogen atom in preventing third phase formation during the extraction, several UDGAs containing dodecyl groups have been synthesised and evaluated in the second mode of tuning. The alkyl groups on the other amidic nitrogen atom are varied from *n*-butyl to *n*-decyl. The extraction behaviour of Am(III), Eu(III), and Sr(II) from was studied in these UDGAs from nitric acid medium. The $D_{Am(III)}$ and $D_{Eu(III)}$ decreased with increase in the chain length of alkyl group attached to amidic nitrogen atom of UDGA. The third phase formation of nitric acid in 0.1 M UDGA/*n*-dodecane indicated that the LOC values increased with increase in the chain length alkyl group attached to amidic nitrogen atom. The third phase formation was not observed during the extraction of Nd(III) from 3-4 M nitric acid medium even at the initial Nd(III) concentration of ~500 mM. Thus, the studies confirmed that the UDGAs with dodecyl group attached to one amidic nitrogen atom is inevitable for preventing third phase formation.

Another UDGA containing dodecyl groups and ethylhexyl groups namely, D^3DEHDGA was also synthesized, and evaluated for the extraction of trivalent actinides and lanthanides from nitric acid medium. Studies indicated that nearly three molecules of D^3DEHDGA were involved in the complexation with trivalents from 1 M nitric medium. Third phase formation was not observed when 0.1 M D^3DEHDGA/*n*-dodecane was employed for the extraction of Am(III) from fast reactor SHLLW, as well as from the nitric acid medium containing 100 mM Nd(III) in 4 M HNO_3. Therefore, these UDGAs are promising candidates for the separation of trivalent actinides from high-level liquid waste, which contain a maximum of ~50 mM trivalent metal ions in 3-4 M HNO_3 medium.

Development of SMART approach for the separation of actinides

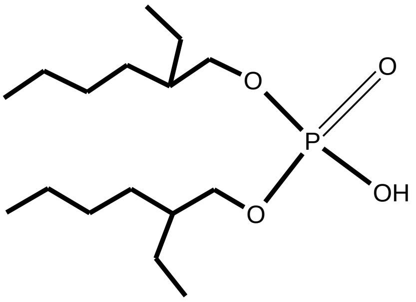
5.1. Introduction

Partitioning (P) and transmutation (T) of long-lived transplutonium actinides is being considered as the best strategy for the safe management of high-level liquid waste (HLLW). In this method, the long-term radiotoxic minor actinides are partitioned from HLLW and transmutated to short-lived or stable products using advanced reactors or accelerator driven sub-critical system. The transplutonium elements predominately exhibit +3 oxidation state and their concentration in HLLW is relatively less. The concentration of trivalent lanthanide fission products is much higher than the trivalent minor actinides (An(III)). Due to the similar oxidation state and marginal difference in ionic size, both An(III) and lanthanides (Ln(III)) exhibit similar chemical and extraction properties. In view of the large concentration of Ln(III) than An(III) in HLLW, and their similar extraction properties, it is very difficult to separate An(III) selectively from HLLW. However, the separation of Ln(III) from An(III) is necessary for effective transmutation of An(III) because Ln(III) act as neutron poisons i.e., they tend to absorb neutrons efficiently. Therefore, it is proposed to co-extract the An(III) along with Ln(III) in one cycle, and their mutual separation in the second cycle.

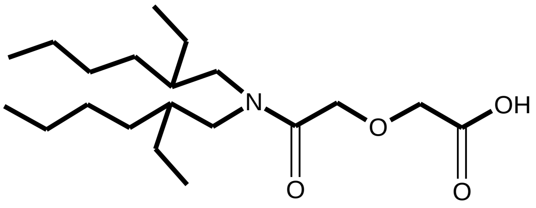
5.2. Ln(III)- An(III) separation by HDEHP from citric acid – nitric acid medium

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) is being exploited for their mutual separations. For example in the TALSPEAK process (Trivalent Actinides Lanthanide Separation Phosporous based reagent Extraction from Aqueous Komplexes), diethylenetriamine-*N,N,N',N'',N'''*-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 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), with multiple stages of such extractions yielding better separation factors [75].

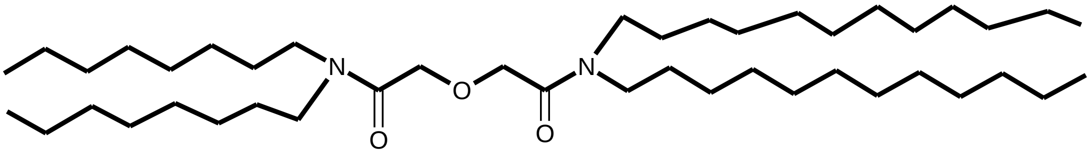
Recently Antony *et al.*[23] developed a method based on Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (OΦ-CMPO) based extraction process for partitioning of minor actinides and demonstrated with genuine fast reactor fuel solution. The extraction and stripping studies of trivalents lanthanides and actinides from simulated and real wastes suggested the use of 0.1 M citric acid (CA) -0.1 M nitric acid for stripping. The product stream thus obtained in a demonstration run with actual fuel solution was a mixture of trivalent actinides and lanthanides in CA-HNO_3 medium. Since this solution serves as the feed for Ln-An group separation, the inherent complexity of the feed calls for the development of a method or modify the exitsing method for separating lanthanides from actinides. Therefore, part of the present chapter describes studies on mutual separation of ^{241}Am(III) and $^{(152+154)}$Eu(III) from 0.1M CA-HNO_3 medium by a solution of bis-2-ethylhexylphosphoric acid (HDEHP) in *n*-dodecane. The present study aimed for the mutual separation of Ln(III) and An(III) from TRUEX product present in 0.1 M citric acid (CA)-0.1 M nitric acid using HDEHP as an extractant. The structures of HDEHP and DTPA are shown in figure 5.1.



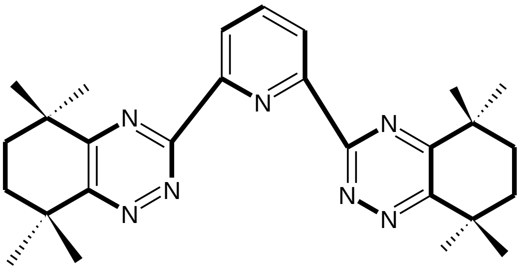
HDEHP



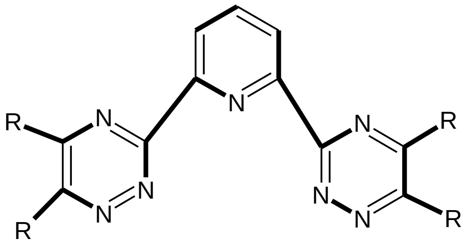
HDEHDGA



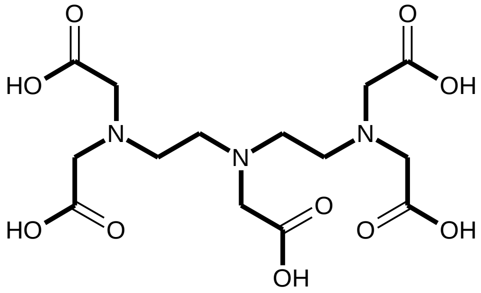
D^{3}DODGA



2,6-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)pyridine (CyMe$_4$BTP)



2,6-Bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTPs)



DTPA

Figure 5.1. The structure of some extractants and aqueous complexing agent

5.2.1. Phase Disengagement

The HDEHP solution in *n*-dodecane has poor phase disengagement especially when the aqueous phase acidity is low. Since the feed solution in the present case is composed of citric acid (0.1 M), dilute nitric acid (0.1 M) and DTPA (0.05 M), the phase disengagement time (PDT) required for the separation of organic and aqueous phase was measured and the results are shown in table 5.1. PDT is the time taken for the disappearance of all the dispersed primary globules at the interface formed after a vigorous shaking of organic and aqueous phases. It is observed that PDT is very high (> 1800 sec) when *n*-dodecane is used as diluent (0.1 M HDEHP/*n*-dodecane) for extraction.

However, PDT can be lowered by adding phase modifiers such as 1-octanol or TBP. It is interesting to note that PDT can be decreased to 45 sec. and 30 sec. by adding 10 wt.%/V of 1-octanol or 10 wt.%/V TBP respectively. Therefore, for all the subsequent studies organic phase contained 10 wt.% octanol or TBP added to the organic phase.

Table 5.1. Phase disengagement time(PDT) needed for separation of organic and aqueous phases. Organic phase: 0.1 M HDEHP/*n*-dodecane. TBP or 1-octanol is added as modifier. Aqueous phase: 0.05 M DTPA and 0.1 M Citric acid at pH= 3. T = 298 K.

[1-octanol]/ $\frac{\text{Wt}}{\text{Vol}}$ %	PDT/sec	[TBP]/ $\frac{\text{Wt}}{\text{Vol}}$ %	PDT/sec
0	>1800	0	>1800
2	120	2	55
5	60	5	41
10	45	10	<30

5.2.2. Effect of phase modifiers on the separation of Ln(III) and An(III)

Table 5.2 shows the influence of some phase modifiers such as 1-octanol, TBP, xylene, and OΦ-CMPO on the separation of Ln(III) and An(III). It is observed that presence of modifiers decreases the *D* of both these metal ions. However, the separation factors (SF) remained at 5-7. The SF as a function of concentration of TBP is shown in table 5.3. At a DTPA concentration of 0.005 M the SF increased with increase of TBP whereas it remained at a value of ~7 at 0.05 M DTPA. Therefore, for Ln(III)-An(III) separation it is desirable to fix the concentrtion of DTPA and TBP as 0.05 M and 10 wt./V% as the $D_{\mathrm{Eu}} \approx 3$ and $D_{\mathrm{Am}} \approx 0.47$.

Table 5.2. $D_{\mathrm{Eu(III)}}$ and $D_{\mathrm{Am(III)}}$ and their separation factors, at 298 K in 0.1 M HDEHP - 10 wt.%/V phase modifier/*n*-dodecane. Aqueous phase: 0.1 M CA+ 0.05 M DTPA+pH =3.

Phase modifiers	D_{Eu}	D_{Am}	SF=($D_{\mathrm{Eu(III)}}$/$D_{\mathrm{Am(III)}}$
1-octanol	12.2	2.33	5.23
TBP	3.12	0.47	6.64
Xylene	0.28	0.04	7
CMPO	4.0	0.74	5.38

Table 5.3. $D_{\mathrm{Eu(III)}}$ and $D_{\mathrm{Am(III)}}$ and their SFs as a function of concentration of TBP in the organic phase at 298 K. Organic phase: 0.1 M HDEHP-[TBP] (wt.%/V) in *n*-dodecane. Aqueous phase: 0.1 M CA+ [DTPA] at pH =3.

[TBP]/ $\frac{\mathrm{Wt}}{\mathrm{Vol}}$ %	0.005 M DTPA		SF=$D_{\mathrm{Eu(III)}}$ /$D_{\mathrm{Am(III)}}$	0.05 M DTPA		SF=$D_{\mathrm{Eu(III)}}$/ $D_{\mathrm{Am(III)}}$
	D_{Eu}	D_{Am}		D_{Eu}	D_{Am}	
2	7.7	41.2	1.16	15.8	2.18	7.25
5	37.9	10.3	3.69	6.3	0.82	7.68
10	17	3.8	4.47	3.1	0.47	6.64

5.2.3. Batch extraction and stripping studies

Figure 5.2 shows the extraction profiles of Eu(III) and Am(III) in 0.1 M HDEHP+10 wt% TBP/*n*-dodecane. The aqueous phase composed of 0.1 M citric acid and 0.05 DTPA at a pH 3. Extraction of both these metal ions increased with increase in the number of contacts of fresh organic phase. However, the extraction was rapid in the case of Eu(III). Near quantitative extraction of Eu(III) is achieved in 3 contacts, whereas extraction of Am(III) requires 8 contacts. The loaded organic phase, when contacted with a solution of 0.1 M CA + 0.05 M DTPA at pH 3, nearly 90% of Am(III) is stripped to aqueous phase (figure 5.3), where as 45% of extracted europium is stripped to aqueous phase under these conditions. This shows that separation of Am(III) from Eu(III) could be done with the use of multistage mixer-settlers in counter current mode.

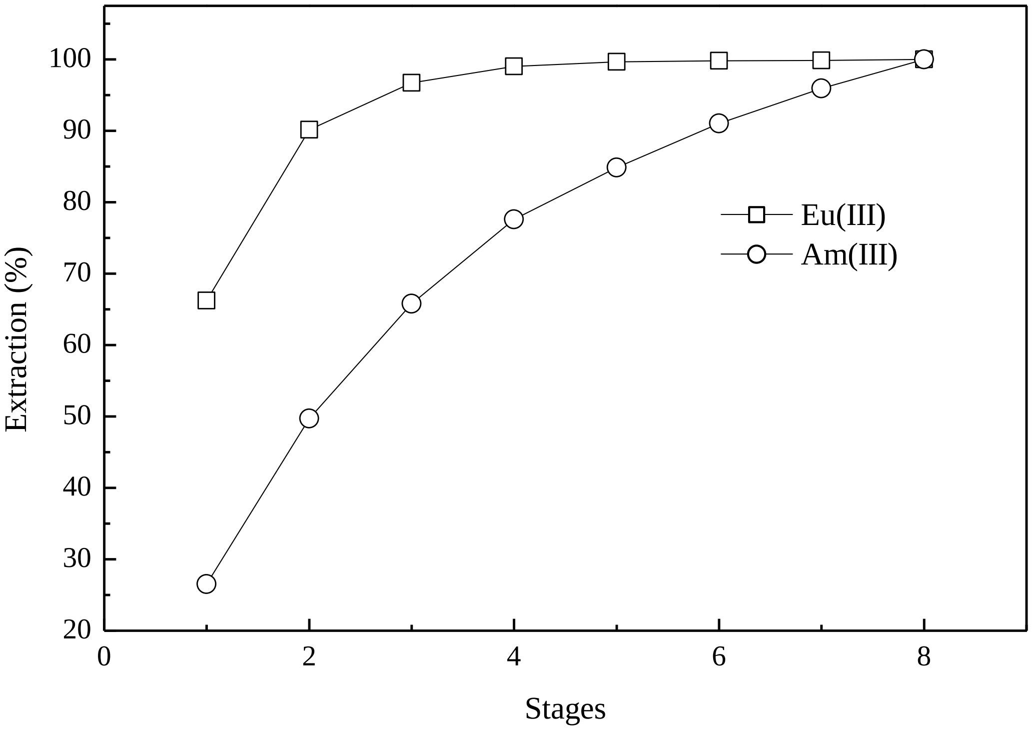


Figure 5.2. Cumulative extraction profile for the batch studies of Am(III) and Eu(III). Organic phase: 0.1 M HDEHP+10 wt.%/V [TBP]/*n*-dodecane, Aqueous phase: 0.1 M CA+0.05 M DTPA at pH 3 spiked with $^{(152+154)}$Eu or ^{241}Am tracer at 298 K.

Though the SF achieved in the present study is only moderate, separation of Am(III) from lanthanides could be achieved in the use of multistage mixer-settlers. Moreover, the present method avoids use of the diluents such as 1, 4-di-isopropylbenze, and external additives such as lactic acid or $NaNO_3$ used in TALSPEAK process, offering additional advantages.

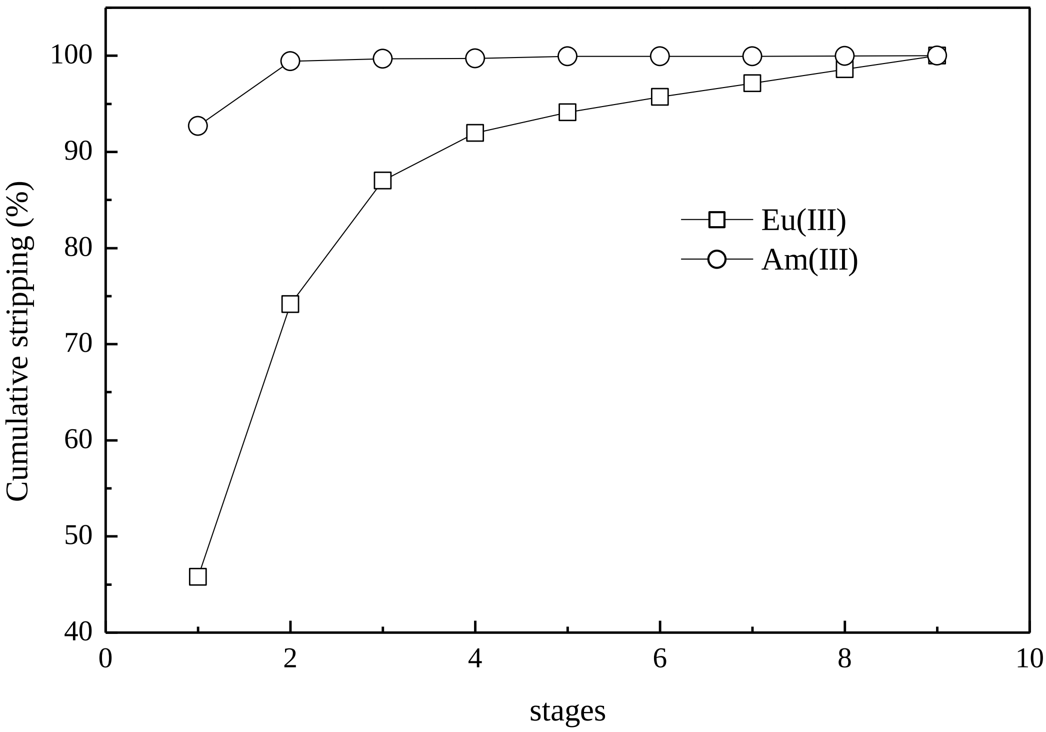


Figure 5.3. Cumulative stripping profile for Am(III) and Eu(III) in batch studies. Organic phase: 0.1 M HDEHP+10 wt.%/V TBP in *n*-dodecane. Aqueous phase: 0.1 M CA+0.05 M DTPA at pH 3 spiked with $^{(152+154)}$Eu or ^{241}Am tracer at 298 K.

5.3. Development of a single-cycle method for minor actinide partitioning

The studies so far carried out for the separation of trivalent minor actinides from HLLW consists two extraction cycles: the first cycle separates trivalent actinides and lanthanides from the bulk of other fission products and the second cycle aims to separate selectively the trivalent actinides from lanthanides. However, this strategy involves the usage of two different extractants in two separation processes, and generation of large volumes of waste solutions. Alternatively, a single cycle separation of trivalent actinides directly from the PUREX raffinate would reduce the number of cycles, making the nuclear waste management easier and more economical. In this context, Wilden *et al.* [81] developed a method based on 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridine ($CyMe_4$-BTBP) (figure 5.1) + tetraoctyldiglycolamide (TODGA) called as 1-cycle SANEX (Selective ActiNide EXtraction). In this work, the authors showed the feasibility of direct and selective extraction of trivalent actinides using 0.015 M $CyMe_4$BTBP + 0.005 M TODGA in hydrogenated tetrapropelene (TPH)/1-octanol (40/60 volume ratio). However, the diluent used in the study, TPH/1-octanol, was not a conventional diluent, *n*-dodecane, usually employed for reprocessing applications. Perhaps, it was employed to avoid the third phase formation and to enhance hydrodynamic properties. Moreover, the extraction kinetics in the 1-cycle SANEX process is quite slow. The kinetics of the extraction system plays an important role in the flow-sheet design with centrifugal contactors due to the short residence time [107,108]. In addition, the aqueous soluble complexing agents such as oxalic acid, amino acids were added to the feed solution prior to the extraction in order to suppress the extraction of undesirable metal ions such as Zr(IV), Mo(VI), Pd(II). The co-extraction of other metal ion such as Ag, Cd, Ni, Cu etc is significant in the proposed 1-cycle SANEX solvent. Although the extraction behavior of trivalent minor actinides was studied in 1-cycle SANEX, the stripping behavior was not studied extensively. Rather the distribution ratios of metal ions were determined under the scrubbing and stripping conditions.

Another approach for the separation of minor actinides/lanthanides is to extract, initially, both the trivalent actinides (An(III)) and lanthanides (Ln(III)) from HLLW. Once the trivalents are separated from 3-4 M nitric acid medium, prevailing in HLLW, it is easier to manipulate the mutual separation of An(III) and Ln(III) present in loaded organic phase. In this context, several studies have been reported in literature that combines the neutral and acidic extractants to accomplish the separation [83-85]. The extraction of trivalents from nitric acid medium, in such cases, was predominantly governed by the neutral extractant during extraction, and the mutual separation of An(III) and Ln(III) from the loaded organic phase was controlled by the acidic extractant, during stripping. Lumetta *et al.* [109] studied the extraction behavior of Am(III) and Eu(III) in a TRUSPEAK (TRUEX and TALSPEAK) solvent consisting of 0.1 M *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) + 1 M bis(2-ethylhexyl) phosphoric acid (HDEHP) in *n*-dodecane from 1 M nitric acid medium. Selective stripping of Am(III) from the loaded organic phase was achieved using an aqueous formulation composed of citric acid (CA) anddi ethylenetriaminepentaaceticacid (DTPA) at pH 3.5. The Am(III) to Eu(III) separation factor of ~12 was reported.

Gannaz *et al.* [110] reported the extraction behavior of Eu(III) and Am(III) by a mixture of extractants composed of DMDOHEMA and dihexyl phosphoric acid (HDHP). Once the trivalents were extracted to the organic phase by DMDOHEMA, the selective stripping of trivalents was controlled by the differential complexing ability of HDHP present in organic phase and polycarboxylic acid complexing reagent present in aqueous phase. Alternatively Hérès *et al.* [85] reported a PALADIN (Partition of Actinides and Lanthanides with Acidic extractant, Diamide, and INcinerable complexants) process for a single-step separation of trivalent actinide. The solvent used in PALADIN process was composed of 0.5 M DMDOHEMA and 0.3 M bis(2-ethylhexyl)phosphoric acid (HDEHP) in hydrogenated tetrapropylene (TPH). Completely incinerable 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 SF 12.5 was achieved for Eu/Am in PALADIN process. Recently, Nayak *et al.* [111] studied the feasibility of using tetra(2-ethylhexyl)diglycolamide (TEHDGA) and HDEHP extractants in *n*-dodecane for the separation of trivalent actinides from HLLW. The stripping of Am(III) alone from the loaded organic phase was accomplished by using DTPA and citric acid.

Thus, the literature indicates that the single-cycle processes reported so far either used solvents, which are not completely incinerable, or employed unconventional diluents, other than *n*-dodecane. In this chapter a novel approach namely, SMART (**S**ingle-cycle process for **M**inor **A**ctinide partitioning using completely incinerable **R**eagen**T**s) is being discussed, which exploits the favorable properties of the diglycolamide, especially the unsymmetrical diglycolamide (UDGA), and diglycolamic acid for the separation of trivalent actinides from HLLW. Unlike other systems, the diglycolamide and diglycolamic acid are made-up of CHON atoms, and thus completely incinerable, and are compatible with nuclear diluent, *n*-dodecane. In the present study, we have chosen the UDGA, *N*,*N*,-didodecyl-*N*',*N*'-dioctyl-3-oxapentane-1,5-diamide (D^3DODGA) and di-2-ethylhexyl diglycolamic acid (HDEHDGA) reagents (figure 5.1) for extraction due to some excellent and desirable properties [76,77]. These include optimum D for trivalents, no third phase formation during the extraction of trivalents from 3 M nitric acid containing more than 600 mM of Nd(III), and poor extraction of unwanted metal ions etc. Therefore, unlike other diglycolamides, D^3DODGA does not require any phase modifier during the extraction of trivalents from HLLW. Moreover, the acidic extractant, *N,N*-di-2-ethylhexyl diglycolamic acid (HDEHDGA), is a promising candidate developed for the mutual separation of Am(III) and Eu(III) from aqueous solution. In view of these, the $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ in a solution of D^3DODGA-HDEHDGA/*n*-dodecane was measured as a function of various parameters to evaluate the feasibility of using these extractants in a single-cycle process for the separation of trivalent actinides from HLLW.

5.3.1. Extraction by 0.05 M HDEHDGA/n-dodecane or 0.1 M D^3DODGA/n-dodecane

The present SMART approach deals with the extraction behavior of Am(III) and Eu(III) in a solution of combined extractants composed of a neutral extractant, D^3DODGA, and an acidic extractant, HDEHDGA, in *n*-dodecane. To understand the extraction behavior observed in these combined extractants, the extraction of Am(III) and Eu(III) in 0.05 M

HDEHDGA/*n*-dodecane was studied initially. Figure 5.4 shows the extraction of Am(III) in 0.05 M HDEHDGA/*n*-dodecane as a function of equilibrium concentration of nitric acid in aqueous phase. It is observed that the $D_{\mathrm{Am(III)}}$ decreases with increase in the concentration of nitric acid, as expected for an acidic extractant. Linear regression analysis of the extraction data yields a slope of 2, which is in good agreement with the slope reported by Suneesh *et al.* [76] for the extraction of trivalent metal ions in HDEHDGA/*n*-dodecane (the data at 10^{-3} M nitric acid could not be considered for linear regression due to complete extraction of Am(III) and large uncertainty in the distribution ratio values obtained). This indicates that two molecules of HDEHDGA are involved in the extraction step as shown in equation 5.1. The nitrate ion in equation 5.2 is included for charge neutralization. In contrast to this observation, the $D_{\mathrm{Am(III)}}$ in the neutral extractant, 0.1 M D^3DODGA/*n*-dodecane, shown in figure 5.4, increases with increase in the concentration of nitric acid. The mechanistic aspects of Am(III) extraction in 0.1 M D^3DODGA/*n*-dodecane was already described in chapter 4. Those results showed the involvement of three molecules of D^3DODGA for the extraction of trivalents from nitric acid medium, as shown in equation 5.2.

$$Am(III)_{aq} + 2\ HDEHDGA_{org} + NO^{-}_{3\ aq} \Leftrightarrow Am(DEHDGA)_2(NO^{-}_3)_{org} + 2\ H^{+}{}_{aq}\,. \tag{5.1}$$

$$Am(III)_{aq} + 3\ D^3DODGA_{org} + 3\ NO^{-}_{3\ aq} \Leftrightarrow Am(NO_3)_3(D^3DODGA)_{3\ org} \tag{5.2}$$

5.3.2. Extraction in combined extractants

The extraction behavior of Am(III) in 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane, is also shown in figure 5.4. It is interesting to observe that the $D_{\mathrm{Am(III)}}$ in combined extractants, initially decreased with increase in the concentration of nitric acid, reaches a minimum value at 0.1 M nitric acid followed by an increase. Below 0.1 M nitric acid, it is interesting to observe that the $D_{\mathrm{Am(III)}}$ in 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane are lower than those observed in 0.05 M HDEHDGA/*n*-dodecane. However, above 0.1 M nitric acid, the $D_{\mathrm{Am(III)}}$ are higher in combined extractants. The enhancement in the distribution ratios above 0.1 M nitric acid indicates the synergistic extraction of Am(III) in 0.1 M D^{3}DODGA-0.05 M HDEHDGA/*n*-dodecane and lowering of *D* below 0.1 M nitric acid indicating antagonism. A similar behavior was also reported by Gannez *et al*. [110] for the extraction of Am(III) in a solution containing the neutral (DMDOHEMA) and acidic extractant (HEHP) in *n*-dodecane.

Based on the work of Gannez et al. [110], the synergism observed in the present study could be attributed to the involvement of both the extractants for extraction, as shown in equation 5.3. However, the stoichiometry of extraction in such case could depend on several parameters such as equilibrium concentration of nitric acid and extractants. It is likely that increase in the concentration of nitric acid could decrease the involvement of the acidic extractant, HDEHDGA, and increases the participation of NO_3^- ion and D^{3}DODGA in extraction. In view of this, the $D_{\mathrm{Am(III)}}$ obtained in combined extractants tend to merge with that observed in D^{3}DODGA/*n*-dodecane alone at nitric acid concentrations more than 1 M, as shown in figure 5.4.

$$\mathrm{Am(III)_{aq} + x\ HDEHDGA_{org} + n\ D^3DODGA_{org} + (3-x)\ NO^-_{3\,aq} \Leftrightarrow Am(DEHDGA)_x(NO^-_3)_{3-x}(D^3DODGA)_{n\ org} + x\ H^+_{aq}}$$
$$\mathrm{x\ is > 0\ to\ 2\ and\ n = 1\ to\ 3} \tag{5.3}$$

$$Am(III)_{aq} + 3\ HDEHDGA_{org} \Leftrightarrow Am(DEHDGA)_{3\,org} + 3\ H^+{}_{aq}. \tag{5.4}$$

Figure 5.5 shows the extraction behavior of Eu(III) in 0.1 M D^{3}DODGA-0.05 M HDEHDGA/*n*-dodecane. The data are also compared with those obtained in individual extractants. The extraction behavior of Eu(III), and the synergism and antagonism observed in this case is similar to that observed for Am(III). However, the $D_{\mathrm{Eu(III)}}$ is higher in all the extractants at all the acidities, which is characteristic to DGAs and diglycolamic acid extractants.

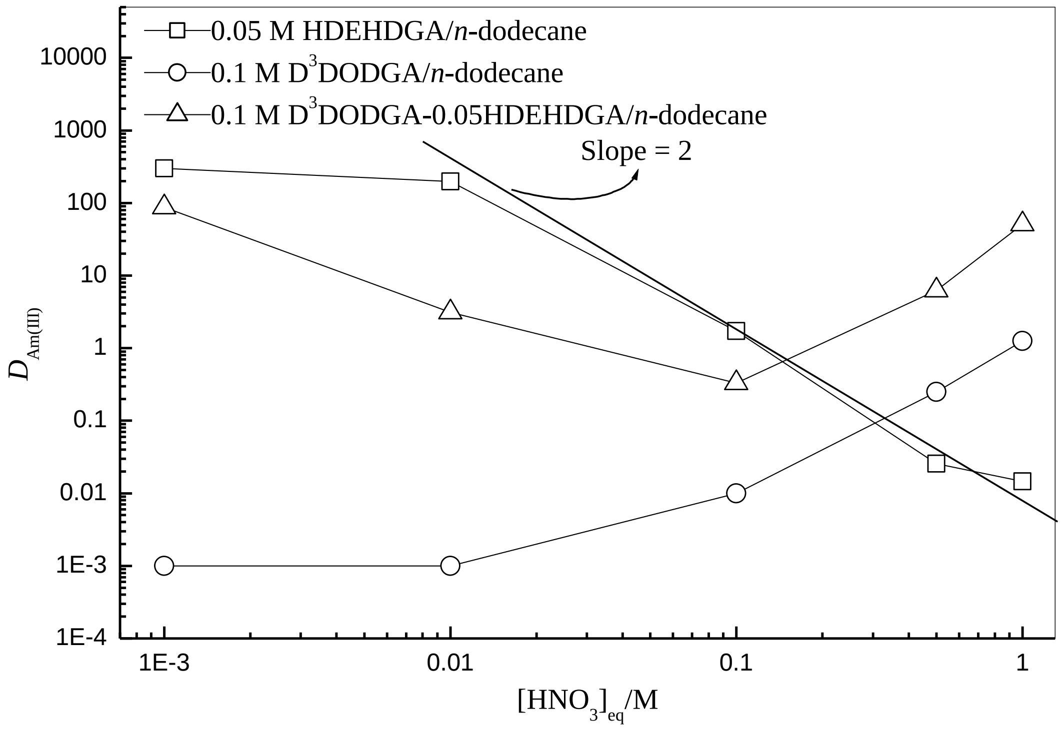


Figure 5.4. Variation in the $D_{Am(III)}$ with equilibrium aqueous phase acidity at 298 K. Aqueous phase: HNO_3 spiked with ^{241}Am tracer. Organic to aqueous phase ratio= 1:1.

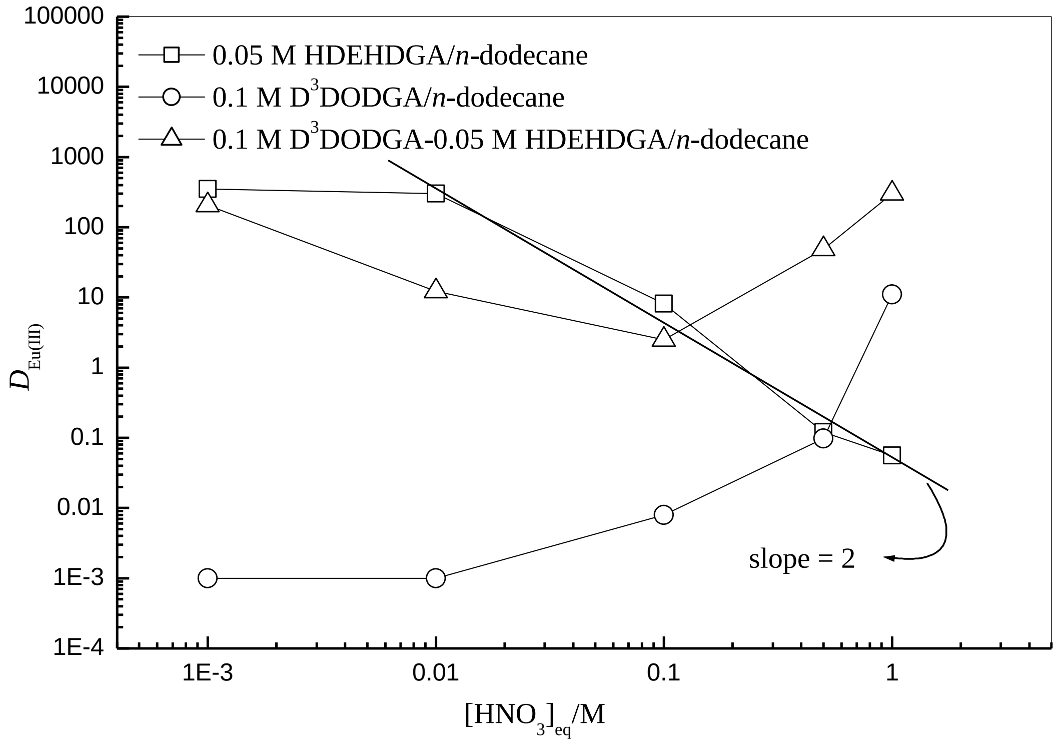


Figure 5.5. Variation in the $D_{Eu(III)}$ with equilibrium aqueous phase acidity at 298 K. Aqueous phase: HNO_3 spiked with $^{(152+154)}$Eu tracer. Organic to aqueous phase ratio= 1:1.

5.3.3. Extraction mechanism- Effect of HDEHDGA

To understand the mechanistic aspects of Am(III) and Eu(III) extraction in 0.1 M D^3DODGA- HDEHDGA/*n*-dodecane, the effect of HDEHDGA concentration on the $D_{Am(III)}$ and $D_{Eu(III)}$ was studied. Figure 5.6 shows the variation in the $D_{Am(III)}$ as a function of HDEHDGA concentration at different nitric acid concentrations. It is observed that the $D_{Am(III)}$ increases with increase in the concentration of HDEHDGA at all acidities (10^{-3}-1 M). A similar behavior was also observed for the extraction of Eu(III) in different concentrations of HDEHDGA. The magnitude of slope obtained by linear regression analysis of the extraction data at all acidities are tabulated in table 5.4 for Am(III) and Eu(III) extraction. It is interesting to observe a slope of ~3 at nitric acid concentrations ranging from 0.01 and 0.001 M. This indicates that three molecules of HDEHDGA are involved in the extraction of Am(III) and Eu(III) by 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane. However, suneesh *et al*. [76,77] reported the involvement of two molecules of HDEHDGA for the extraction of Am(III) and Eu(III) when the solvent was 0.05M HEHDGA/*n*-dodecane (equation5.1).

$$Am(III)_{aq} + 3\ HDEHDGA_{org} \Leftrightarrow Am(DEHDGA)_{3\,org} + 3\ H^{+}{}_{aq}. \qquad (5.5)$$

Moreover, the extraction of Am(III) and Eu(III) in 0.05 M HDEHDGA/*n*-dodecane alone, shown in figure 5.4 and 5.5, also indicated the involvement of two molecules of HDEHDGA for extraction. A slope of 3 obtained in 0.05 M HDEHDGA-0.1 M D^3DODGA/*n*-dodecane shows that the presence of D^3DODGA in combined system increases the participation of HDEHDGA. Based on these observations, equation 5.5 is proposed for the extraction of Am(III) and Eu(III) in 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane at low nitric acid concentrations (10^{-3}-10^{-2} M). Above 10^{-2} M nitric acid, the magnitude of slope, shown in table 5.4, decreases with increase in the concentration of nitric acid. This indicates that the involvement of HDEHDGA for extraction decreases at higher nitric acid concentrations. As the dissociation of the acidic extractant decreases with increase in the concentration of nitric acid, the involvement of HDEHDGA for extraction also decreases.

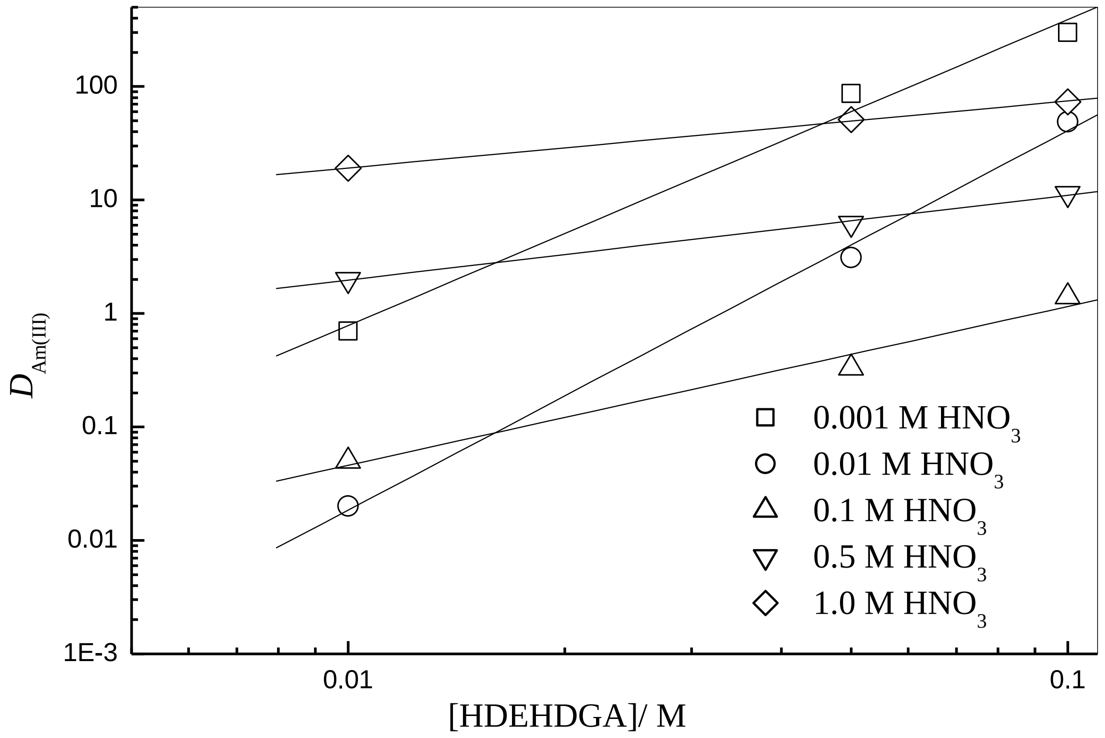


Figure 5.6. Variation in the $D_{Am(III)}$ in a solution of HDEHDGA -0.1 M D^3DODGA/*n*-dodecane with HDEHDGA concentration at 298 K. Aqueous phase: HNO_3 spiked with ^{241}Am tracer. Organic to aqueous phase ratio=1:1.

5.3.4. Extraction mechanism- Effect of D^3DODGA

The dependence of Am(III) and Eu(III) extraction on D^3DODGA was also investigated at different nitric acid concentrations. The variation in the $D_{Am(III)}$ and $D_{Eu(III)}$ as a function of D^3DODGA concentration in a solution of 0.05 M HDEHDGA- D^3DODGA/*n*-dodecane is shown in figure 5.7. At 0.5 M nitric acid concentration, it is observed that the *D* of both these metal ions increase with increase in the concentration of D^3DODGA. Linear regression of the extraction data yields a slope of 2, indicating the involvement of two molecules of D^3DODGA for extraction. In the absence of the acidic extractant, a slope of 3 was observed as described in chapter 4. Therefore, the presence of HDEHDGA in the solvent lowers the participation of D^3DODGA for extraction.

From table 5.4, the dependence of HDEHDGA at 0.5 M nitric acid is ~1. Therefore, the study confirms that both acidic and neutral extractants are involved in the synergistic extraction of trivalents as shown in equation 5.3. Further increase in the concentration of nitric acid decreases the participation of HDEHDGA (slope at 1 M is further reduced, table 5.4) and enhances the participation of D^3DODGA of extraction. At high nitric acid concentration (> 1M) when the $D_{\mathrm{Am(III)}}$ in combined extractants tend to merge with that observed in D^3DODGA/*n*-dodecane alone, the extraction would be expected to be governed exclusively by the neutral extractant, D^3DODGA, according to equation 5.2.

The dependence of Am(III) and Eu(III) extraction on D^3DODGA at lower nitric acid concentration (10^{-2} M) was also studied and the results on the variation of $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ with concentration of D^3DODGA is shown in figure 5.7. It is interesting to observe that the $D_{\mathrm{Am(III)}}$ and $\mathrm{D}_{\mathrm{Eu(III)}}$ decrease with increase in the concentration of D^3DODGA at 10^{-2} M nitric acid. Nayak *et al*. [111] studied the synergistic extraction of Am(III) and Eu(III) in a combined extractant system composed of TEHDGA-HDEHP/*n*-dodecane. A positive dependence of the neutral extractant, TEHDGA, reported at all acidities ranging from 10^{-3} M to 1 M was attributed to the synergistic extraction. However, the negative dependence of the neutral extractant observed in the present case is in good agreement with the antagonism observed at low acidity.

Table 5.4. Magnitude of slope obtained from the linear regression of the data obtained for the extraction of Am(III) and Eu(III) as a function of HDEHDGA concentration. Organic to aqueous phase ratio=1:1.

$[HNO_3]$/M	slope	
	Am(III)	Eu(III)
0.001	2.7	--*
0.01	3.0	3.1
0.1	1.4	1.5
0.5	0.74	0.8
1.0	0.58	--*

* could not be determined due to complete extraction of Eu(III)

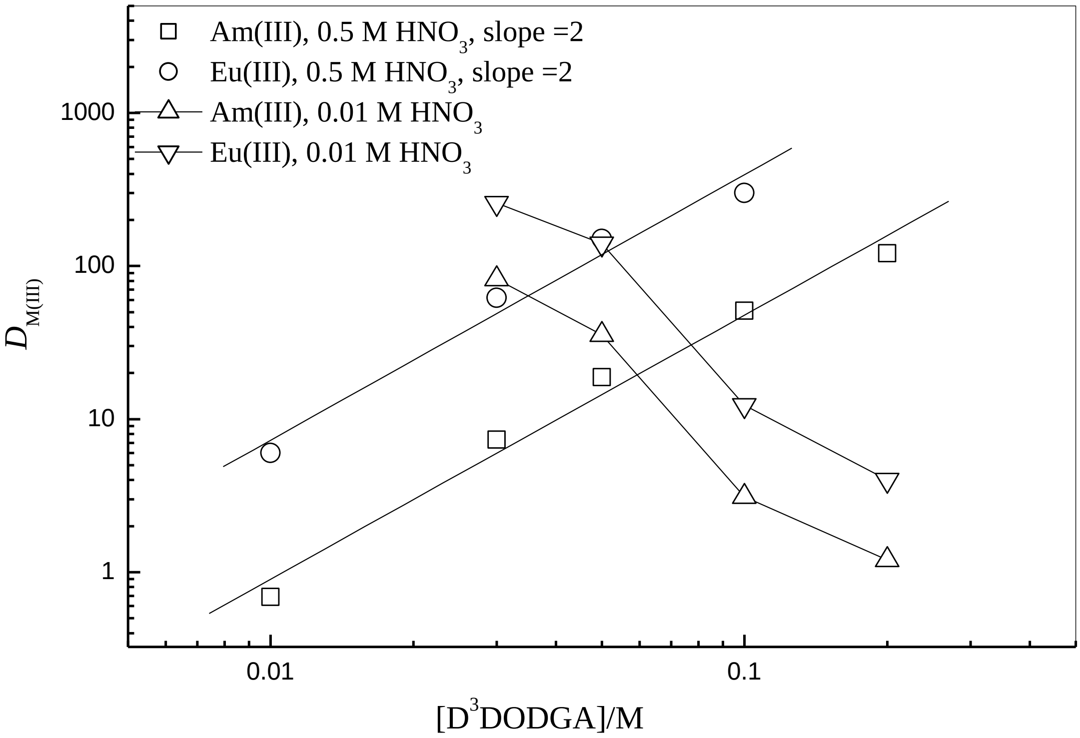


Figure 5.7. Variation in the $D_{Am(III)}$ and $D_{Eu(III)}$ in a solution of 0.05 M HDEHDGA-D^3DODGA/*n*-dodecane at 298 K with D^3DODGA concentration. Aqueous phase: Nitric acid spiked with ^{241}Am or $^{(152+154)}$Eu tracer.

5.3.5. Stripping studies

The extraction of trivalent actinides in 0.05 M HDEHDGA- 0.1 M D^{3}DODGA/*n*-dodecane from HLLW results in the co-extraction of chemically similar lanthanides. Mutual separation of actinides and lanthanides is necessary to facilitate efficient transmutation of actinides. Generally, the trivalent actinides are stripped from the organic phase using aqueous soluble polycarboxylic acids such as DTPA. This method exploits the differential complexing ability of the acidic extractant, HDEHDGA, present in organic phase and DTPA present in aqueous phase for selective stripping of trivalent actinides. Therefore, the extraction behavior of Am(III) and Eu(III) in a solution of 0.05 M HDEHDGA -0.1 M D^{3}DODGA/*n*-dodecane phase from DTPA solution was studied to explore the separation factor (SF $=D_{\mathrm{Eu(III)}}/D_{\mathrm{Am(III)}}$) of Eu(III) over Am(III). The $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ and the SF obtained in the presence of DTPA at various experimental conditions are included in table 5.5. It is observed that the $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ are lowered remarkably in the presence of DTPA.

This could be due to retention of Am(III) and Eu(III) by DTPA in aqueous phase. A separation factor of about ~10 is obtained at pH 3. Under this condition both the metal ions are inextractable. However, the $D_{\mathrm{Eu(III)}}$ and $D_{\mathrm{Am(III)}}$ increased to 3.5 and 0.3 respectively with decrease of pH to 1.5, leading to the SF of 10. Further decrease in pH to 1 led to poor extraction of both metal ions. Del Cul *et al*. [112] developed a citric acid based TALSPEAK process for the mutual separation of Ln(III) from An(III). The citric acid in this process acts as buffer and enhances the SF of Am(III) from Eu(III). Therefore, citric acid could be combined with DTPA in the present case also, to study the Am(III)-Eu(III) separation from the loaded organic phase. However, present studies, shown in table 5.5, indicate that the SFs do not improve to any significant extent with the addition of citric acid in the present case.

Figure 5.8 shows the stripping behavior of Am(III) and Eu(III) from the loaded organic phase, 0.1 M D^{3}DODGA-0.05 M HDEHDGA/*n*-dodecane. The extraction of Am(III) and Eu(III) was carried out from 3 M nitric acid medium. For back extraction, the loaded organic was contacted with equal volume of aqueous solution of 0.01 M DTPA at pH 1.5. After equilibration the aqueous phase was removed and the organic phase was contacted with fresh aqueous solution for stripping. This procedure was repeated up to 6-7 contacts. It is observed from figure 5.8 that both Am(III) and Eu(III) are back extracted to a significant extent using this aqueous formulation. However, for mutual separation, it is essential to retain Eu(III) in organic phase as much as possible during stripping. To minimize the stripping of Eu(III) the concentration of DTPA was reduced to 0.001M and the pH was maintained at pH 1.5. The stripping behavior of Am(III) and Eu(III) under this condition is also shown in figure 5.8. Again, the stripping of Am(III) and Eu(III) is significant with some improvement in mutual separation. To further improve the retention of Eu(III) in organic phase, the concentrations of HDEHDGA and D^3DODGA in organic were varied. Initially, the HDEHDGA concentration in organic phase was increased to 0.1 M at a constant D^3DODGA concentration of 0.1 M. The stripping behavior of Am(III) and Eu(III) from the loaded organic phase under this condition (0.1 M D^3DODGA -0.1 M HDEHDGA /*n*-dodecane) is shown in figure 5.8. It is observed that the stripping of Am(III) is about 85% with a co-stripping of 35% Eu(III) in six contacts. This indicates that 0.1 M D^3DODGA -0.1 M HDEHDGA /*n*-dodecane formulation is also not suitable for mutual separation.

To facilitate the stripping of Am(III) and retention of Eu(III), the concentration of D^3DODGA in organic phase was lowered to 0.05 M. Figure 5.9, shows the stripping behavior of Am(III) and Eu(III) from the loaded organic phase (0.05 M D^3DODGA-HDEHDGA/*n*-dodecane). The concentration of HDEHDGA was varied from 0.1 M to 0.2 M. It is observed that the stripping of Am(III) and Eu(III) increases with increase in the number of contacts. At 0.05 M D^3DODGA -0.1 M HDEHDGA/*n*-dodecane, the recovery of Am(III) is about 85% with the co-stripping 15% Eu(III) in six contacts. However, by using 0.05 M D^3DODGA -0.2 M HDEHDGA/*n*-dodecane, the stripping of Eu(III) is minimized to <8%

with 60% recovery of Am(III) in aqueous phase. The batch studies thus suggests that Am(III) could be back extracted quantitatively using a solution of 0.001 M DTPA at pH 1.5 from the solvent phase having a composition of 0.05 M D^3DODGA -0.2 M HDEHDGA/*n*-dodecane. Moreover, mutual separation would be more efficient in a counter-current run, where the stripped solution goes for contacting with the organic phase in the next stage. Since $D_{\mathrm{Eu(III)}}$ is higher than $D_{\mathrm{Am(III)}}$, it is quite likely that the stripped Eu(III) could be extracted by organic phase subsequently. Therefore, it is possible to achieve the mutual separation of Am(III) and Eu(III) using this stripping formulation in a mixer-settler.

Table 5.5. Variation in the $D_{\mathrm{Eu(III)}}$ and $D_{\mathrm{Am(III)}}$ and the separation factor (SF= $D_{\mathrm{Eu(III)}}/D_{\mathrm{Am(III)}}$) with concentration of HDEHDGA in organic phase, and aqueous phase conditions, at 298 K.

Aqueousphase condition	0.1 M D^3DODGA + 0.05 M HDEHDGA			0.1 M D^3DODGA + 0.1 M HDEHDGA		
	$D_{\mathrm{Eu(III)}}$	$D_{\mathrm{Am(III)}}$	SF	$D_{\mathrm{Eu(III)}}$	$D_{\mathrm{Am(III)}}$	SF
0.01 M DTPA+ pH 3	0.002	0.0003	6.66	0.014	0.0018	7.8
0.01 M DTPA+ pH 2	0.02	0.002	10	0.18	0.016	11.3
0.01 M DTPA+pH 1.5	3.35	0.35	9.6	11.57	1.39	8.3
0.01 M DTPA+ 0.05 M citric acid + pH 1.5	2.86	0.32	8.9	10.4	1.2	8.9
0.01 M DTPA+ 0.1 M citric acid + pH 1.5	2.87	0.33	8.9	9	1.16	7.6

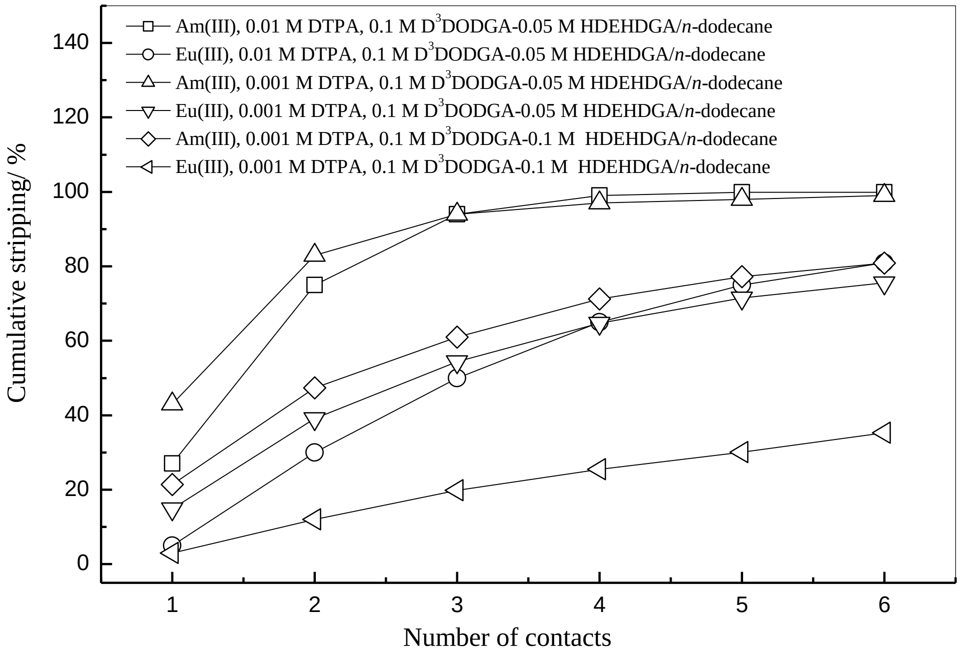


Figure 5.8. Cumulative stripping of Am(III) and Eu(III) from loaded organic phase using DTPA solution at pH 1.5. Organic to aqueous phase ratio=1:1.

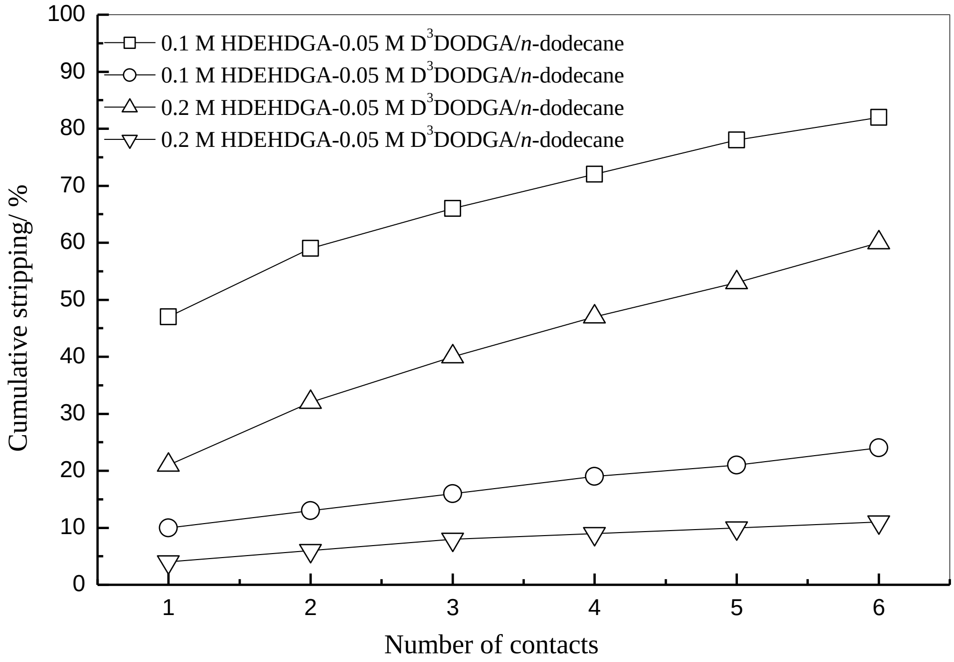


Figure 5.9. Cumulative stripping of Am(III) and Eu(III) from the loaded organic phase using 0.001 M DTPA at pH 1.5. Organic to aqueous phase ratio=1:1.

5.4. Conclusions

Separation of actinides from lanthanides was studied from citric acid -nitric acid medium. The method involves the use of 0.1 M HDEHP-TBP(10 wt.%/V) in *n*-dodecane as organic phase that gives as separation factor of 7 from pH 3 solution. Though the SF achieved with the present aqueous phase is only moderate, separation of Am(III) from lanthanides could be achieved with the use of multistage mixer-settler. A new approach, SMART, developed in the present study employed completely incinerable reagents, diglycolamide and diglycolamic acid compatible with *n*-dodecane, for the separation of trivalent actinides from nitric acid medium. The desirable properties of D^3DODGA and HDEHDGA were exploited to examine the feasibility of using these extractants together for a single-cycle separation of minor actinides from HLLW. Extraction behavior of these metal ions in 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane was compared with individual solvents, namely 0.1 M D^3DODGA/*n*-dodecane and 0.05 M HDEHDGA/*n*-dodecane. Synergistic extraction of Am(III) and Eu(III) observed in 0.1 M D^3DODGA-0.05 M HDEHDGA/*n*-dodecane at nitric acid concentrations above 0.1 M, was due to the involvement of both HDEHDGA and D^3DODGA for extraction. The dependence of Am(III) and Eu(III) on HDEHDGA concentration decreased and that on D^3DODGA increased with increase in the concentration of nitric acid in aqueous phase. The present SMART approach revealed that by using 0.05 M D^3DODGA-0.2 M HDEHDGA/*n*-dodecane as solvent, and 0.001M DTPA at pH 1.5 as aqueous formulation, it is possible to separate Am(III) from HLLW in a single-processing cycle. However, more studies with simulated and actual waste in a mixer-settler are needed to establish the robustness of the present approach.

Evaluation of radiation stability of unsymmetrical diglycolamides

6.1. Introduction

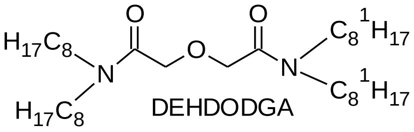
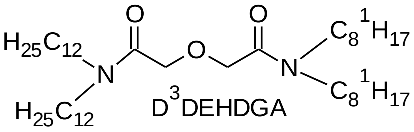
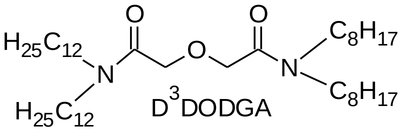
Diglycolamides (DGAs) are emerging as promising reagents for the separation of trivalent minor actinides from high level liquid waste (HLLW) arising from aqueous reprocessing of spent nuclear fuel [46]. The tunable nature of unsymmetrical diglycolamides (UDGAs) offer additional advantage in obtaining desired physico-chemical and extraction properties. In this context several UDGAs have been developed and evaluated for trivalent actinide partitioning from nitric acid medium in the present study. Radiation stability is another important requirement that needs to be evaluated while proposing for actinide partitioning. The solvent systems employed for the extraction of radioactive metal ions such as minor actinides will be exposed to the high amount of α, β, and γ-radiation. The energy associated with various radiations either partially or fully is deposited on the solvent molecules during the extraction, resulting in adverse effects to varying extents depending on the type of radiation, and duration of exposure. These effects include the rupture of chemical bonds present in the solvent molecules.

Cleavage of chemical bonds in the solvent results in the formation of chemically active species such as free radicals and ions. Some of these species may recombine or react with other surrounding species result in the formation of neutral molecules. The chemically active species which are produced as a result of interaction of high energy radiation with solvent molecules are collectively called as degradation products. The presence and formation of these degradation products alter the physico-chemical and solvent extraction properties of the solvent to a significant extent. The degradation products present in organic phase may interfere in the complex formation of extractants with the metal ions. Therefore, the extraction and stripping behavior of actinide metal ions may vary under the exposure. The degradation of solvent not only reduces the extraction efficiency, but also alters the separation factors to be achieved. Thus, the re-usability of solvent strongly depends on its radiolytic stability and the nature of degradation products. The ligand decomposition yield should be sufficiently low, and the nature of the decomposition products sufficiently benign, that significant process efficiency is not lost with time and absorbed radiation dose. In this context, it is very important to understand the radiation chemistry of a solvent proposed for the extraction under biphasic, acidic conditions.

Although the reagents used for the actinide partitioning from HLLW exposes to α-radiation of actinides and β, γ-radiation of other fission products, most radiation chemistry studies have been performed using γ-sources. Massive, highly charged α-particles have short ranges and deposit 156 eV nm^{-1} for energy of 5 MeV in water [113]. This energy deposition results in closely-spaced overlapping spurs, resulting in high localized concentrations of reactive species, many of which undergo recombination before they can diffuse into the bulk solution. The result is higher yields of molecular species and lower yields of radicals for α-radiation. Therefore, differences in the effects of irradiation between high and low LET sources might be expected. Despite of high LET of α-radiation, it resulted in the lower yield of reactive radical species than for γ-radiation in the case of CMPO and TODGA [90, 114]. This was attributed to the difference in the primary process induced by α and γ rays. It is well known that the activated species are formed locally at high density in a so called track irradiation with high LET α-radiation and large part of these species/ions formed recombine before the diffusion into bulk solution to result in the formation of extractant molecules. On the other hand, low LET γ-rays the activated species are individually formed in a so called spur. Thus, the radiation damage observed by α-radiation is generally less than that of γ radiation. In addition, α irradiation of samples is experimentally difficult. In this context, majority of the radiation chemistry studies carried out using γ radiation.

Even though the UDGAs studied in the present work shown the promising nature for the trivalent actinide partitioning from nitric acid medium, their radiation stability has not been discussed so far. The present chapter deals with the evaluation of radiation stability of three UDGAs namely *N*,*N*-di-2-ethylhexyl-*N'*,*N*'-di-octyl-3-oxapentane-1,5-diamide (DEHDODGA), *N*,*N*-di-dodecyl-*N'*,*N*'-di-octyl-3-oxapentane-1,5-diamide(D^{3}DODGA), *N*,*N*-di-dodecyl-*N'*,*N*'-di-2-ethylhexyl-3-oxapentane-1,5-diamide(D^{3}DEHDGA) under various process conditions. The structures of these UDGAs are given in the table 6.1. The important properties of UDGAs such as extraction, stripping, third phase formation etc., were examined as a function of absorbed dose of γ-radiation.

Table 6.1. Structures of UDGAs studied in this chapter

S.No.	Name of the diglycolamide	Structure
1.	*N*,*N*-di-2-ethylhexyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide or di-2-ethylhexyl-di-octyl-diglycolamide	
2.	*N*,*N*-di-dodecyl-*N'*,*N'*-di-2-ethylhexyl-3-oxapentane-1,5-diamide or di-dodecyl-di-ethylhexyl- diglycolamide	
3.	*N*,*N*-di-dodecyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide or di-dodecyl-di-octyl-diglycolamide	

6.2. Effect of γ- radiation on the extraction of trivalent metal ions

The radiation stability of UDGAs was studied by irradiating the neat extractants to various dose levels of γ-radiation. The irradiated UDGAs were diluted with *n*-dodecane, and the distribution ratio of Am(III) was measured to assess the degree of degradation in the solvent. Figure 6.1 and 6.2 shows the variation in the distribution ratio of Am(III) ($D_{\mathrm{Am(III)}}$) in irradiated DEHDODGA, and D^{3}DODGA and D^{3}DEHDGAs respectively as a function of absorbed dose. $D_{\mathrm{Am(III)}}$ decreased with increase in absorbed dose, indicating the degradation of UDGAs during γ-irradiation. The $D_{\mathrm{Am(III)}}$ decreased rapidly from ~300 to 71 with the increase of absorbed dose from 0 kGy to 50 kGy in the case of DEHDODGA (Figure 6.1). However, the change in $D_{\mathrm{Am(III)}}$ is negligible thereafter up to 1000 kGy. Though $D_{\mathrm{Am(III)}}$ values decreased with increase in the absorbed dose in the case of D^{3}DODGA and D^{3}DEHDGA, they are sufficient enough (183 and 79 respectively) for the process applications. To assess the influence of diluent *n*-dodecane and nitric acid on the radiolytic degradation of DEHDODGA, equal volume of 0.1 M DEHDODGA in *n*-dodecane together with 3 M nitric acid was irradiated to various absorbed doses. Prior to the irradiation, the organic phase was pre-equilibrated with 3 M nitric acid. The results on the variation in the $D_{\mathrm{Am(III)}}$ in the irradiated 0.1 M DEHDODGA/*n*-dodecane are shown in figure 6.3. It is observed that the $D_{\mathrm{Am(III)}}$ decreased with the increase of absorbed dose in this case also. It is interesting to compare the $D_{\mathrm{Am(III)}}$ observed when DEHDODGA irradiated alone (figure 6.1) and that irradiated in the presence of *n*-dodecane (0.1 M solution) and nitric acid (figure 6.3).

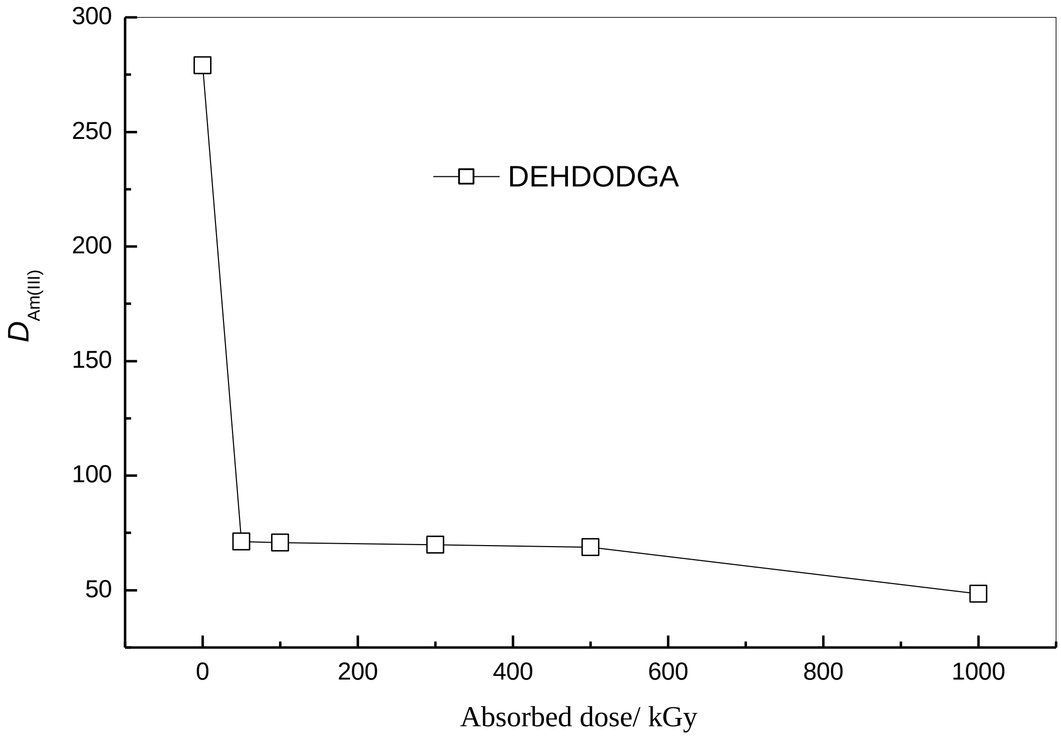


Figure 6.1. $D_{Am(III)}$ as a function of absorbed dose at 298 K in neat DEHDODGA system. Aqueous phase: 3 M nitric acid. Aqueous to organic phase ratio= 1:1. Equilibration time= 1 hour.

The $D_{Am(III)}$ decreased rapidly from 300 to ~70 with increase of absorbed dose from 0 kGy to 50 kGy in the case of neat DEHDODGA. The degradation of extractant is more when it was irradiated in the presence of *n*-dodecane and 3 M HNO_3 especially at irradiation doses greater than 300 kGy. Since 0.1 M DEHDODGA/*n*-dodecane forms third phase during the extraction of trivalent metal ions from HLLW, the solvent composition was modified to 0.1 M DEHDODGA- 0.5 M DHOA in *n*-dodecane. Therefore it is necessary to study the radiolytic degradation of 0.1 M DEHDODGA–0.5 M DHOA/*n*-dodecane. To understand the net effect of diluent, phase modifier, and nitric acid present in the aqueous phase, the organic phase, (0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane) was irradiated along with equal volume of 3 M nitric acid. Figure 6.3 shows the variation in the $D_{Am(III)}$ with the absorbed dose in 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. It is observed that the $D_{Am(III)}$ decreases from 80 to 0.4 with increase of absorbed dose from 0 kGy to 1000 kGy.

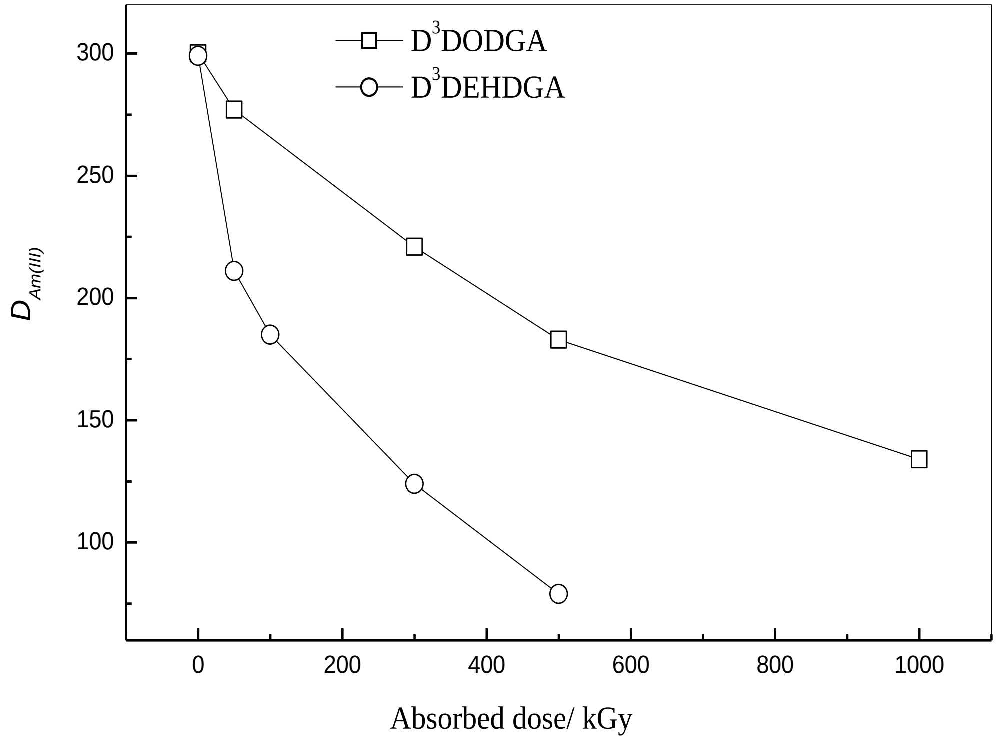


Figure 6.2. Variation in the $D_{Am(III)}$ with the absorbed dose at 298 K. Organic phase: 0.1 M UDGA in *n*-dodecane prepared by using neat irradiated UDGA. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer. Organic to aqueous phase ratio = 1:1.

It is interesting to compare the extraction behavior of Am(III) observed in the present case with that observed in symmetrical DGAs such as TODGA and TEHDGA. The $D_{Am(III)}$ at 3 M nitric acid in the irradiated solvents (500 kGy), such as 0.1 M TODGA-0.5 M DHOA/*n*-dodecane and 0.1 M TEHDGA-0.5 M DHOA/*n*- dodecane were reported to be 62 and ~12 respectively [92,93]. However the present case shows a $D_{Am(III)}$ of ~12 at absorbed dose of 500 kGy. The difference could be due to the fact that irradiation studies of TODGA and TEHDGA solutions were carried out in the absence of nitric acid. Figure 6.4 shows the variation in $D_{Eu(III)}$ from 3 M nitric acid with absorbed γ-dose. It is observed that the extraction of Eu(III) is quite similar to that of Am(III). However, the $D_{Eu(III)}$ values are higher as compare to $D_{Am(III)}$ at all the doses studied. This could be due to the characteristic property of the extractant DEHDODGA. A marginal reduction in the $D_{Eu(III)}$ is observed in the irradiated DEHDODGA with increase of absorbed dose. The presence of phase modifier, further reduced the $D_{\mathrm{Eu(III)}}$. However, the decrease in the $D_{\mathrm{Eu(III)}}$ is less as compared to that observed for Am(III) (figure 6.3). The influence of diluent *n*-dodecane on the radiolysis of D^3DODGA and D^3DEHDGA was studied by measuring the $D_{\mathrm{Am(III)}}$ in the irradiated 0.1 M solutions of these UDGAs in *n*- dodecane. Figure 6.5 shows the variation in the $D_{\mathrm{Am(III)}}$ with the absorbed γ-dose. It is interesting to note that the $D_{\mathrm{Am(III)}}$ was found to decrease with increase of absorbed dose in these systems also. Moreover, the $D_{\mathrm{Am(III)}}$ values in D^3DODGA and D^3DEHDGA are lower when they are irradiated along with diluent rather than in neat form at a particular dose (figure 6.2 and figure 6.5).

This indicates that the diluent, *n*-dodecane enhances the radiolytic degradation of D^3DODGA and D^3DEHDGA. A similar effect of diluent (*n*-dodecane) was reported in the case of other DGAs also. Sugo *et al.*,[88,89] reported that the presence of diluent, *n*-dodecane increases the radiolytic cleavage of TODGA due to sensitization effect, which essentially arises from a charge transfer from the radical cations of *n*-dodecane. However, the distribution ratios of 97 and 55 were observed at a high dose of 500 kGy for irradiated 0.1 M D^3DODGA/*n*-dodecane and 0.1 M D^3DEHDGA/*n*-dodecane respectively during the extraction from 4 M nitric acid medium. These values are quite high for process scale separation of trivalent actinides. In addition, it is interesting to note that the $D_{\mathrm{Am(III)}}$ is low in the case of 0.1 M D^3DEHDGA than that in 0.1 M D^3DODGA at all the doses studied. This may be due to the branching in alkyl groups present in D^3DEHDGA. It is well- known that the DGAs extract significant amount of nitric acid during the metal ion recovery from nitric acid medium.

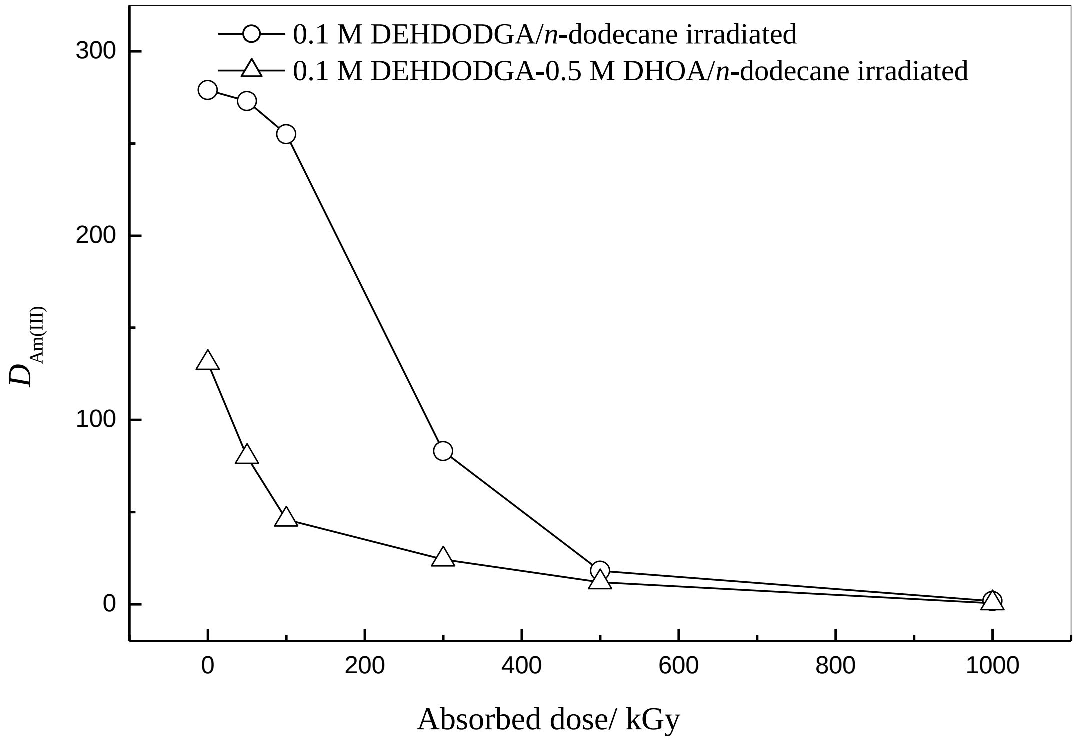


Figure 6.3. $D_{Am(III)}$ **as a function of absorbed dose at 298 K in various DEHDODGA systems. Aqueous phase: 3 M nitric acid. Aqueous to organic phase ratio= 1:1. Equilibration time= 1 hour.**

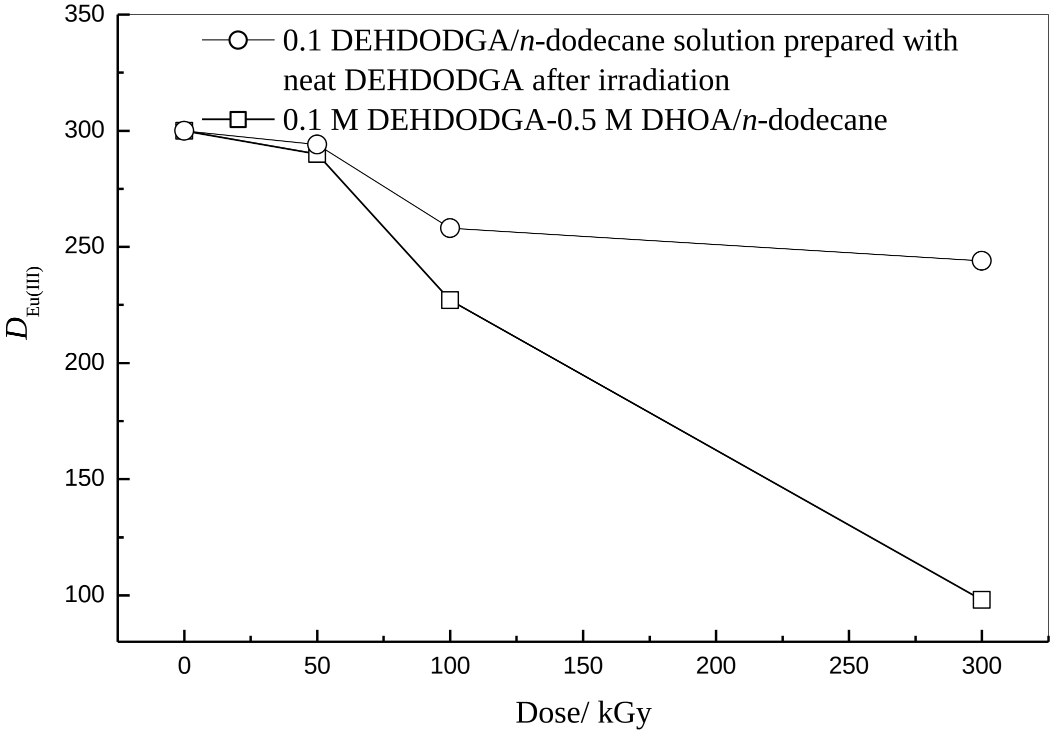


Figure 6.4. $D_{Eu(III)}$ **as a function of absorbed dose at 298 K in various DEHDODGA systems. Aqueous phase: 3 M nitric acid. Aqueous to organic phase ratio= 1:1. Equilibration time= 1 hour.**

Figure 6.6 shows the $D_{Am(III)}$ as a function of absorbed dose in 0.1 M D^3DODGA/*n*-dodecane and D^3DEHDGA /*n*-dodecane in contact with equal volume of 4 M nitric acid. It is observed that the $D_{Am(III)}$ decreases with increase of absorbed dose. However, the distribution ratios are quite high (>50) even at a high dose of 500 kGy in both the solutions, 0.1 M D^3DODGA and 0.1 M D^3DEHDGA indicating the possibility of process scale application of these UDGAs. From the comparison of figure 6.5 and figure 6.6, it is observed that there is no significant influence of nitric acid on degradation of these UDGAs.

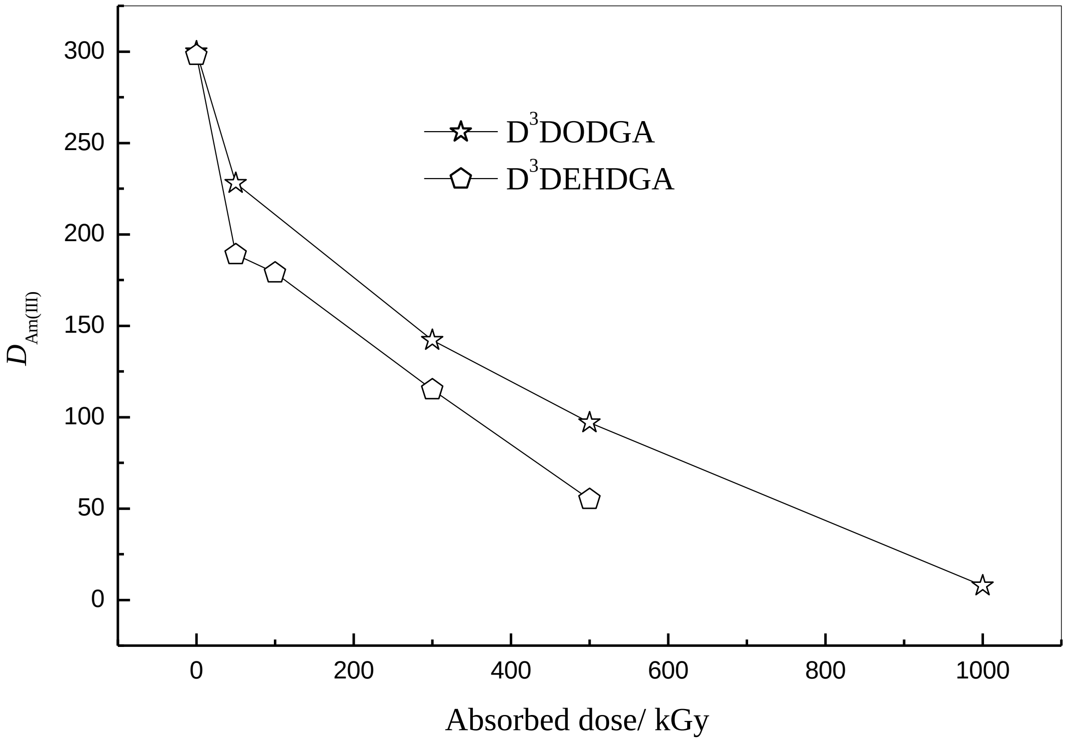


Figure 6.5. Variation in the $D_{Am(III)}$ with the absorbed dose at 298 K. Organic phase: irradiated 0.1 M UDGA in *n*-dodecane. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer. Organic to aqueous phase ratio = 1:1. Equilibration time = 1 hour.

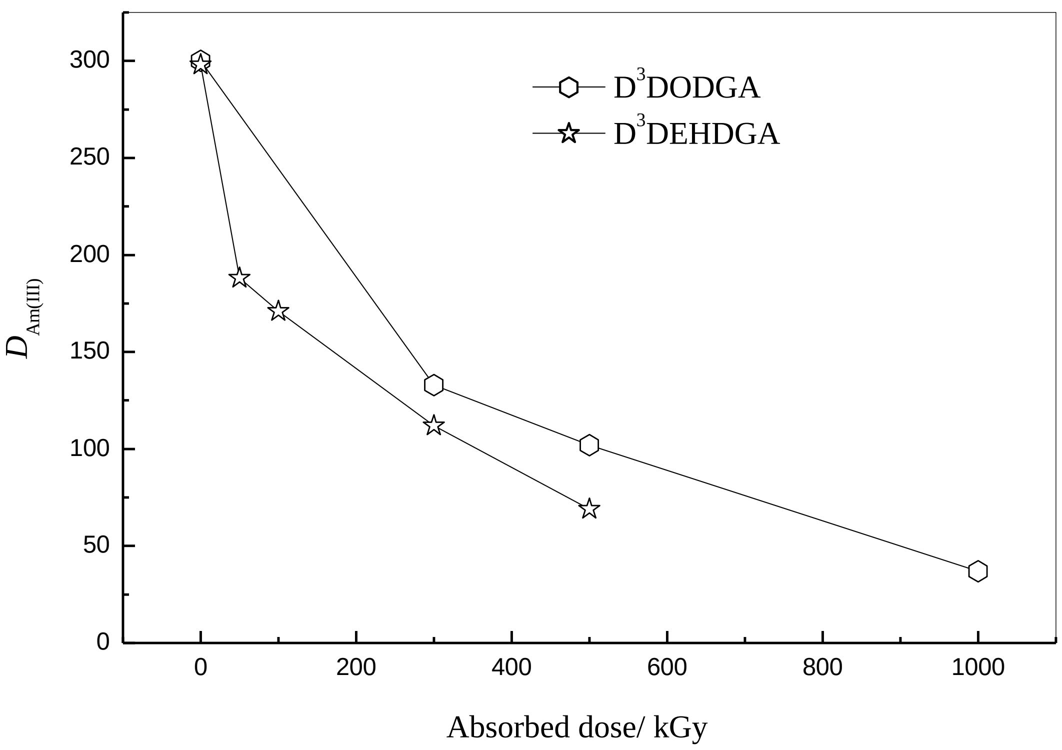


Figure 6.6. Variation in the $D_{Am(III)}$ with the absorbed dose at 298 K. Organic phase: 0.1 M UDGA in *n*-dodecane irradiated along with equal volume of 4 M nitric acid. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer. Organic to aqueous phase ratio = 1:1. Equilibration time = 1 hour.

6.3. Influence of absorbed dose on extraction of Sr(II)

The extraction of Sr(II) in 0.1 M DEHDODGA/*n*-dodecane was relatively lower than that observed in its symmetrical analogues such as TODGA and TEHDGA as discussed in chapter 3. However due to radiation effects, the extraction behavior of metal ions could be altered, and therefore the separation factor also could change upon irradiation. In this context, the extraction behavior of Sr(II) was studied in the irradiated solvents. Figure 6.7 shows the variation in the $D_{Sr(II)}$ with absorbed dose from 3 M nitric acid in the case of DEHDODGA/*n*-dodecane. The $D_{Sr(II)}$ decreases with increase of absorbed dose. The separation factor of Am(III) over Sr(II) achieved at various doses are shown in table 6.2. Even though, the $D_{Sr(II)}$ decreased with absorbed dose, the variation in separation factor is marginal. This is due to the reduction in the $D_{Am(III)}$ with increase in the exposed radiation dose. Though, the $D_{\mathrm{Sr(II)}}$ decreased with increase of absorbed dose, the increment in separation factor is marginal. However, the separation factors achieved under high radiation doses are higher than those observed for un-irradiated conditions. This is suggesting that high separation factor of Am(III) over Sr(II) retain in DEHDODGA even under high exposure doses. Similarly the extraction behavior of Sr(II) was studied in other UDGAs, namely D^3DODGA and D^3DEHDGA. Figure 6.8 shows the variation in the $D_{\mathrm{Sr(II)}}$ with absorbed dose from 4 M nitric acid. The $D_{\mathrm{Sr(II)}}$ decreased with increase of absorbed dose in both the cases. It is interesting to note that the separation factor is increasing with increase of absorbed dose up to 300 kGy. This may be due to the higher reduction in $D_{\mathrm{Sr(II)}}$ than $D_{\mathrm{Am(III)}}$. The separation factors of Am(III) over Sr(II) achieved at various doses are shown in table 6.3.

Table 6.2. Variation in the $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Sr(II)}}$, and the separation factor with the absorbed dose. Organic phase: irradiated solution of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. Aqueous phase: 3 M nitric acid. Organic to aqueous phase ratio=1:1.

Dose/ kGy	$D_{\mathrm{Am(III)}}$	$D_{\mathrm{Sr(II)}}$	Separation factor ($D_{\mathrm{Am(III)}}$/ $D_{\mathrm{Sr(II)}}$)
0	131	0.36	364
50	80	0.19	421
100	46	0.14	328
300	24	0.05	480
500	12	0.03	400

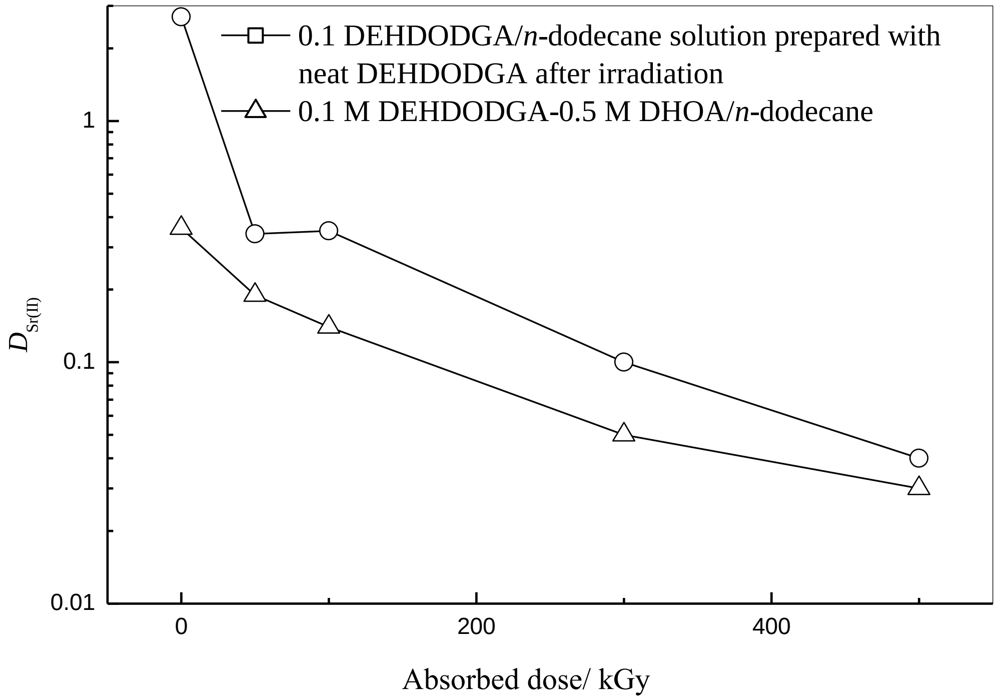


Figure 6.7. $D_{Sr(II)}$ as a function of absorbed dose at 298 K in various DEHDODGA systems. Aqueous phase: 3 M nitric acid spiked with $^{(85+89)}$Sr tracer. Aqueous to organic phase ratio= 1:1. Equilibration time= 1 hour.

Table 6.3.Variation in the separation factor of Am(III) over Sr(II) with absorbed dose. Organic phase: Irradiated 0.1 M solution of UDGA in *n*-dodecane. Aqueous phase: 4 M nitric acid spiked with either ^{241}Am or $^{(85+89)}$Sr tracers.

Dose/kGy	SF	
	D^3DODGA	D^3DEHDGA
0	269	516
50	616	279
100	1820	369
300	4850	942

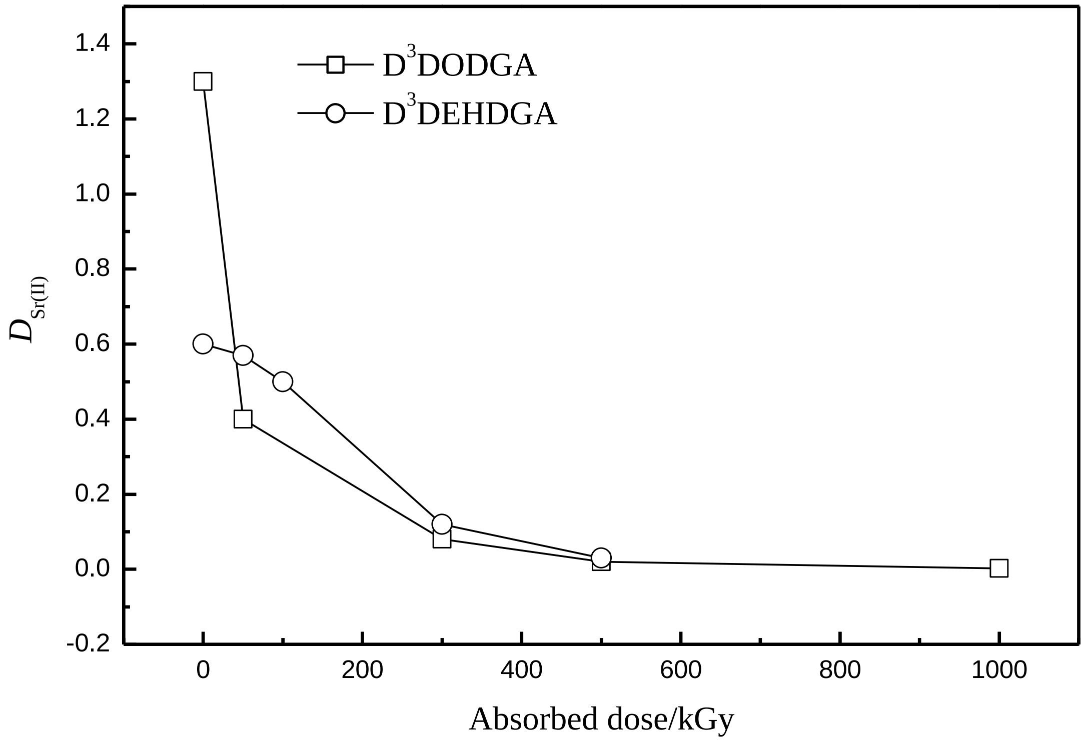


Figure 6.8. $D_{Sr(II)}$ as a function of absorbed dose at 298 K in 0.1 M UDGA/*n*-dodecane systems. Aqueous phase: 4 M nitric acid spiked with $^{(85+89)}$Sr tracer. Aqueous to organic phase ratio: 1:1. Equilibration time: 1 hour.

6.4. Extraction from simulated HLLW

The extraction behavior of trivalent metal ion, Am(III), has been studied in irradiated 0.1M D^{3}DODGA/*n*-dodecane and 0.1 M D^{3}DEHDGA/*n*-dodecane from simulated HLLW (SHLLW) as a function of absorbed dose and the results are shown in figure 6.9. It is interesting to compare the extraction behavior of Am(III) from nitric acid and HLLW. The $D_{Am(III)}$ values are lower when the extraction was carried out from SHLLW than from 4 M nitric acid medium. This may be due to the competition from several other metal ions present in SHLLW for the extraction. The $D_{Am(III)}$ are ~10 for the extraction from SHLLW by D^{3}DODGA irradiated to 1000 kGy. However, a *D* of only 0.2 was observed when the D^{3}DODGA was irradiated along with diluents to the same dose. Similarly a *D* of ~5 was observed when D^{3}DEHDGA was irradiated along with the diluent at a dosage of 300 kGy.

However, $D_{Am(III)}$ values further reduced to below 5 in the case of D^{3}DEHDGA with increase of absorbed dose above 300 kGy. This indicates that the radiolysis of D^{3}DEHDGA is more than D^{3}DODGA in all the cases.

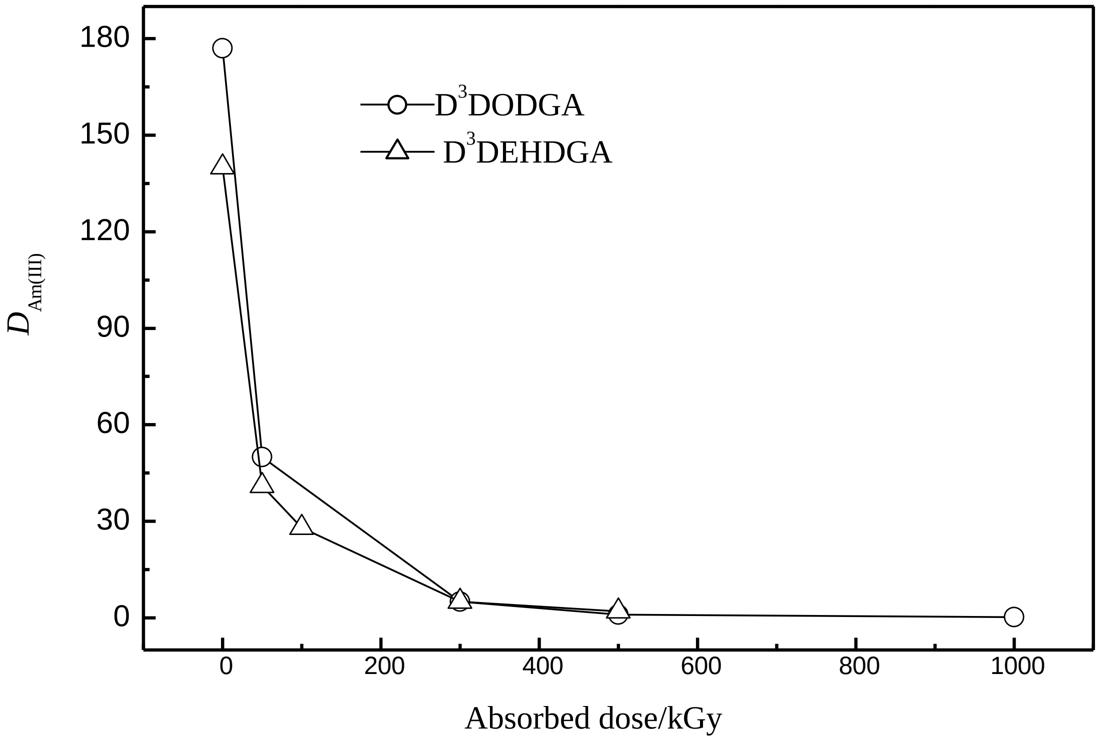


Figure 6.9. $D_{Am(III)}$ as a function of absorbed dose. Organic phase: irradiated 0.1 M solution of UDGA in *n*-dodecane. Aqueous phase: Simulated HLLW spiked with ^{241}Am tracer.

6.5. Stripping studies

One of the attractive properties of DGA class of extractants is the low *D* of trivalent metal ions at low concentrations of nitric acid, which is desirable for the back extraction of metal ions from the loaded organic phase. If the degradation products are acidic and soluble in organic phase, the stripping of metal ions from loaded organic phase become tedious [114]. Therefore, the $D_{Am(III)}$ in the degraded solvent at low concentrations of nitric acid (~0.1 M) need to be verified, for assessing the stripping behavior. In this context, the $D_{Am(III)}$ was measured using irradiated solvent (0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane-3 M nitric acid) from 0.1 M nitric acid medium, and the results are given in table 6.3. The $D_{Am(III)}$

values are not affected much with the increase of absorbed dose. This indicates the absence of any acidic degradation products in organic phase, which are quite likely to hold the metal ions.

Table 6.4. Variation in the $D_{Am(III)}$ with absorbed dose of γ-radiation at 298 K. Organic phase: irradiated solution of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. Aqueous phase: 0.1 M nitric acid spiked with ^{241}Am tracer. Organic to aqueous phase ratio=1:1. Equilibration time = 1 hour.

Dose/ kGy	$D_{Am(III)}$
0	$< 1 \times 10^{-3}$
50	$< 1 \times 10^{-2}$
300	$< 1 \times 10^{-2}$
500	$< 1 \times 10^{-2}$

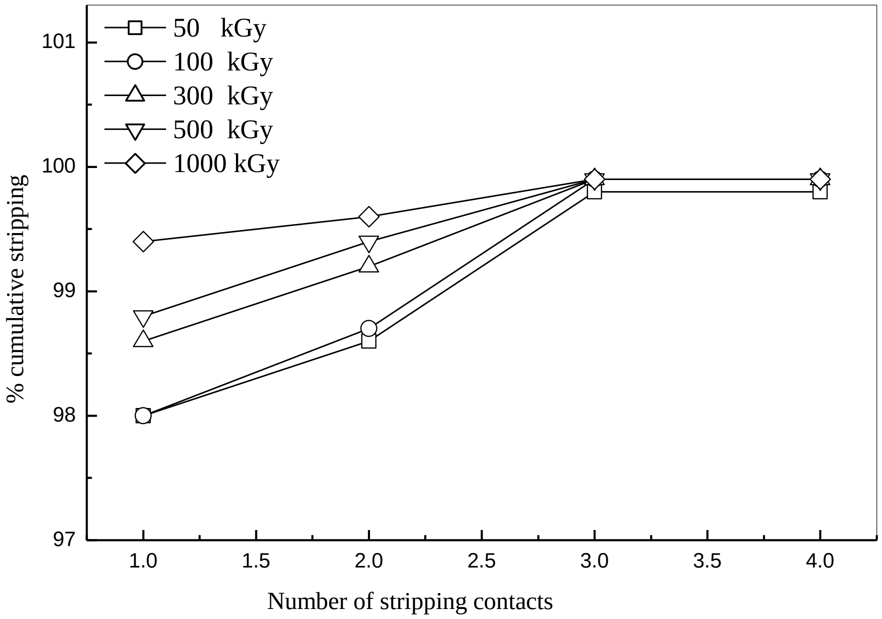


Figure 6.10. Percentage cumulative stripping of Am(III) from the solutions in *n*-dodecane made by irradiated neat DEHDODGA. Loaded organic phase : Irradiated DEHDODGA. Stripping solution: 0.01 M DTPA-0.5 M citric acid at pH 3. Aqueous to organic phase ratio= 1:1.

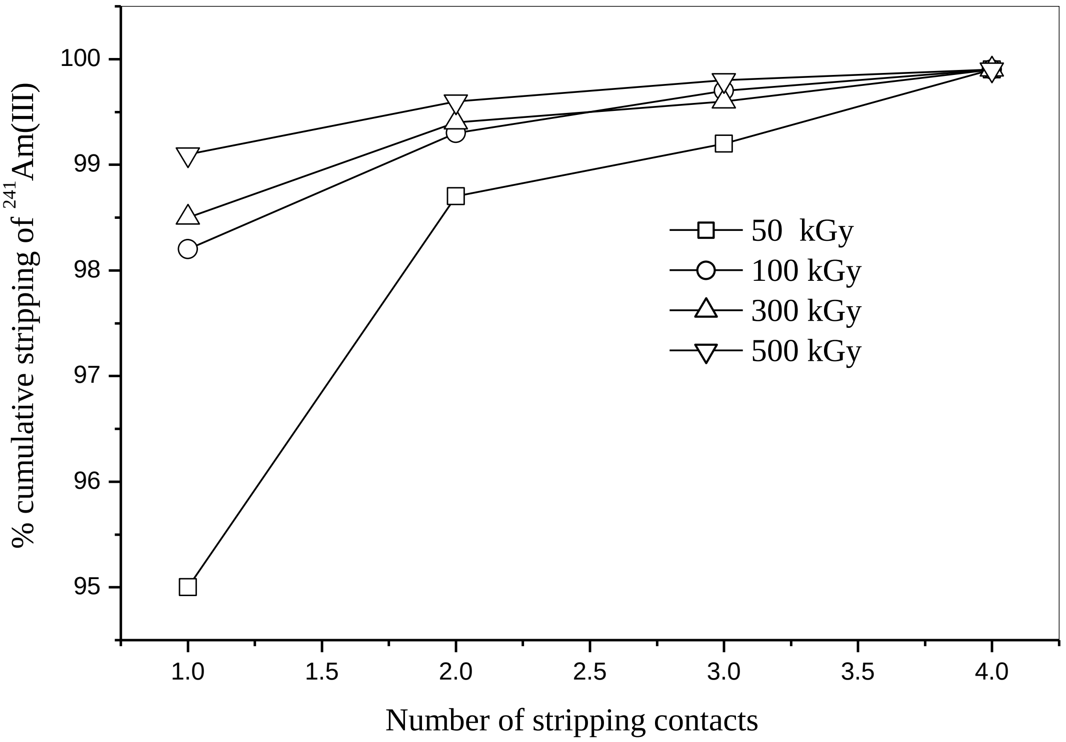


Figure 6.11. Percentage cumulative stripping of Am(III) from 0.1 M DEHDODGA/*n*-dodecane irradiated to various doses. Stripping solution: 0.01 M DTPA-0.5 M citric acid at pH 3. Aqueous to organic phase ratio= 1:1.

The stripping behavior of Am(III) from the loaded irradiated solvents has been studied at various doses. The influence of the diluent, phase modifier, on the stripping behavior of Am(III) from the loaded irradiated solvent were also evaluated. Figure 6.10 shows the percentage of Am(III) recovered from loaded organic phase as function of number of contacts of back extraction. The organic phase was prepared by dissolving the suitable amount of irradiated DEHDODGA in un irradiated *n*-dodecane and loaded with Am(III) from 3 M nitric acid medium by equilibration. Back extraction from this loaded organic phase was carried out using stripping formulation employed earlier. Quantitative amount of trivalent metal ion recovery in a couple of contacts was achieved using this stripping solution. The Am(III) was then back extracted using a stripping solution of 0.01 M DTPA- 0.5 M CA at pH 3. This stripping was developed for the recovery of trivalent metal ions from the loaded 0.1 M DEHDODGA–0.5 M DHOA/*n*-dodecane phase as described in chapter 3. This indicates degradation products are not interfering the stripping behavior of Am(III). The innocuous nature of degradation products of DGA class of extractant was reported earlier, and our results are in good agreement with literature [92, 93]. Complete metal ion recovery was achieved in three contacts from the loaded organic phase irrespective of the absorbed dose. However, it is interesting note the slight difference in the quantity of metal ion back extracted at first two contacts. The recovery was more from the solvent irradiated up to 1000 kGy was more when compared with that from the less irradiated solvent. This may be due to the lower concentration of metal ion present in the loaded organic phase irradiated to 1000 kGy, which can be completely back extracted by using strong complexing agent such as DTPA. Figure 6.11 shows the stripping behavior of Am(III) from the loaded irradiated 0.1 M. DEHDODGA/*n*-dodecane solution. In this case, 0.1 M DEHDODGA/*n*-dodecane was irradiated and loaded with metal ion prior to the back extraction. It is interesting to note that the quantitative recovery of metal ion was achieved at all doses, even in this system, which indicates that the presence of diluent is not influencing the stripping behavior of trivalent actinides. Figure 6.12 shows the stripping behavior of Am(III) from the loaded irradiated 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane solution.

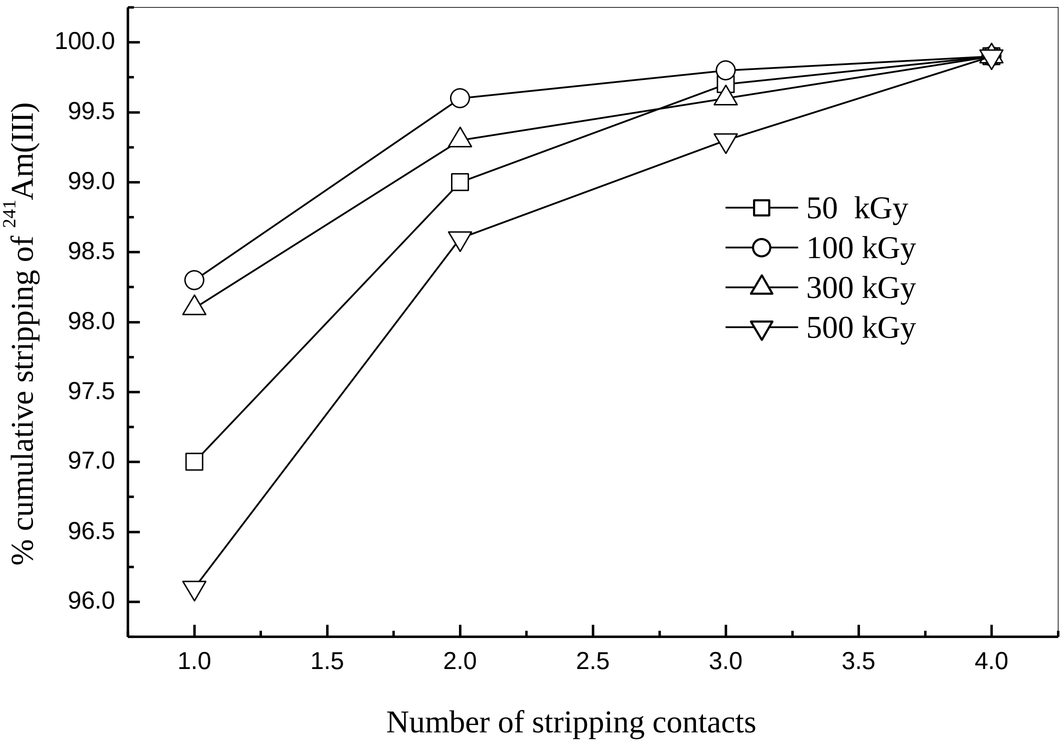


Figure 6.12. Percentage cumulative stripping of Am(III) from 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane irradiated to various doses. Stripping solution: 0.01 M DTPA-0.5 M citric acid at pH 3. Aqueous to organic phase ratio= 1:1.

Nearly 99 % was recovered from the loaded organic phase within two contacts of stripping. This clearly indicates that the innocuous nature of degradation products of DEHDODGA even in the presence of 0.5 M phase modifier, DHOA. Thus, the degradation products of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane-nitric acid are innocuous in nature and are not influencing stripping behavior of trivalent metal ions. Similarlly the stripping behavior of Am(III) from the loaded irradiated D^{3}DEHDGA and D^{3}DODGA was studied. In this case, the stripping was carried out using 0.1 M nitric acid solution.

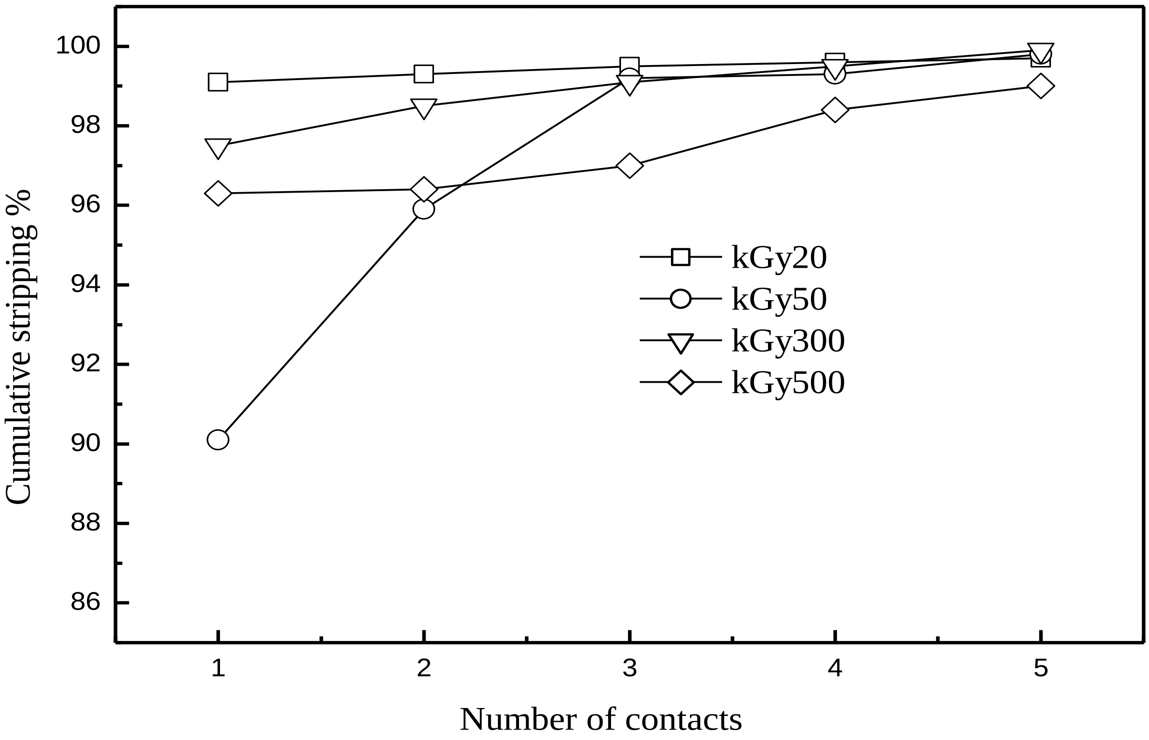


Figure 6.13. Cumulative stripping of Am(III) as a function of number of contacts at 298 K. Loaded organic phase : 0.1 M solution prepared by dissolving neat irradiated D^{3}DEHDGA in *n*-dodecane. Stripping solution: 0.1 M nitric acid.

Figure 6.13 shows the percentage cumulative back extraction of Am from the loaded irradiated D^{3}DEHDGA/*n*-dodecane. The neat D^{3}DEHDGA was irradiated to various dose levels and dissolved in *n*-dodecane to make 0.1 M solution. The Am(III) was loaded using this organic phase from 4 M nitric acid medium.It is interesting to note that the metal ion recovery is quantitative within 3-4 stripping contacts, indicating the absence of innocuous degradation products.

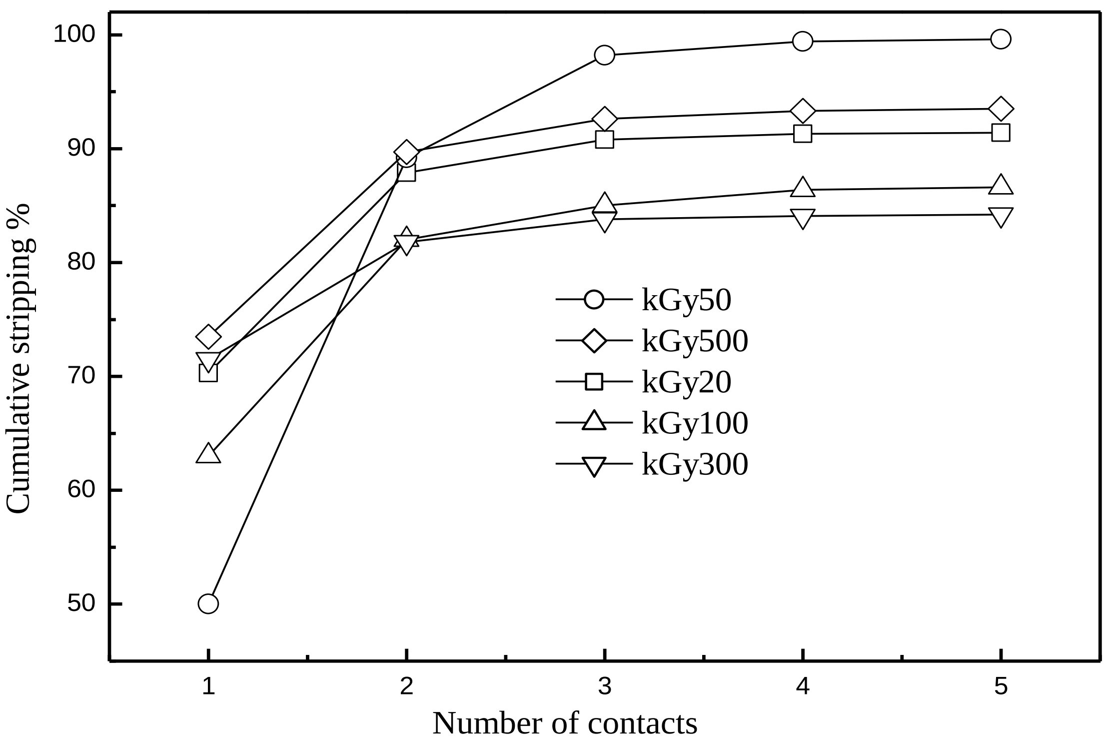


Figure 6.14. Cumulative stripping of Am(III) as a function of number of contacts at 298 K. Loaded organic phase : 0.1 M solution of irradiated D^{3}DEHDGA in *n*-dodecane. Stripping solution: 0.1 M nitric acid.

Even though, the difference in the back extraction of Am(III) at a specific absorbed dose is marginal, the stripping of Am(III) increases with increase of absorbed dose. Figure 6.14 shows the cumulative stripping of Am(III) from the solution of 0.1 M D^{3}DEHDGA/*n*-dodecane. The extractant was irradiated together with *n*-dodecane in this case. The cumulative stripping of Am(III) increases with number of contacts of stripping formulation, in all cases. However, it is interesting to note that back extraction of Am(III) is more when irradiated to higher dose levels. A similar stripping behavior was also observed when the extractant was irradiated with equal volume of 4 M nitric acid (figure 6.15).

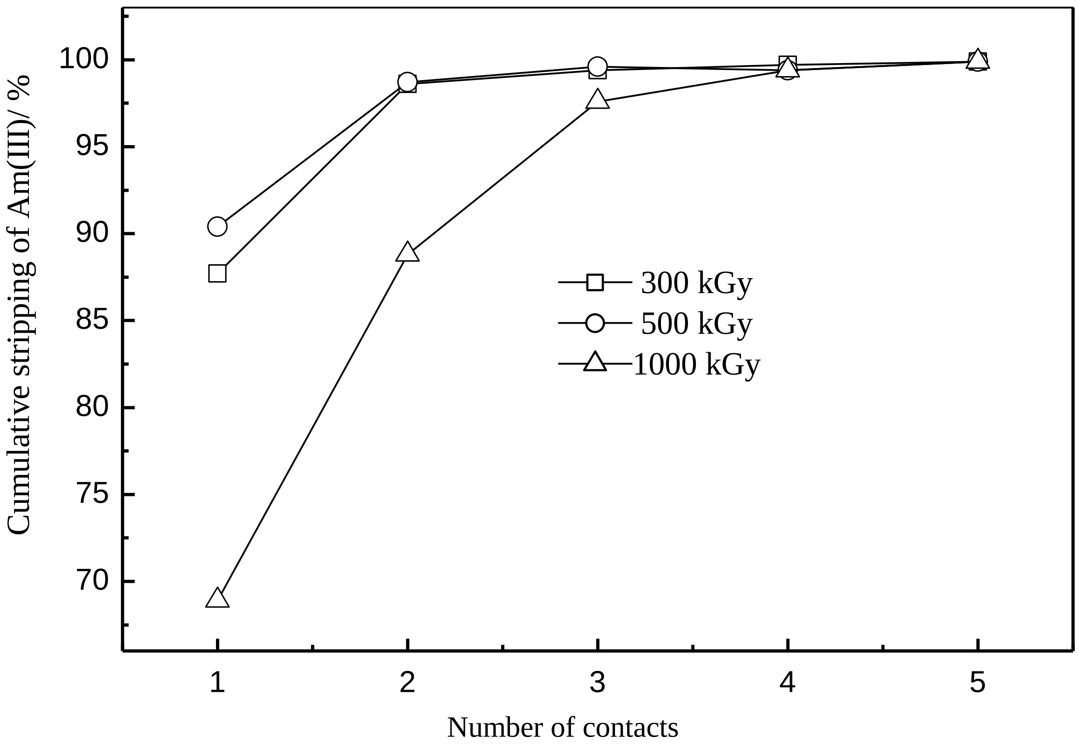


Figure 6.15. Cumulative stripping of Am(III) as a function of number of contacts at 298 K. Loaded organic phase: 0.1 M solution of irradiated D^3DEHDGA in *n*-dodecane with equal volume of 4 M nitric acid. Stripping solution: 0.1 M nitric acid.

Figure 6.16 shows the stripping behavior of Am(III) from the loaded irradiated D^3DODGA. The D^3DODGA was irradiated in neat form, in the presence of diluent, *n*-dodecane (0.1 M) and 0.1M solution of D^3DODGA/*n*-dodecane along with equal volume of 4 M nitric acid to various doses. The irradiated solvent was loaded with Am(III) from 4 M nitric acid medium and later back extracted using 0.1 M nitric acid. More than 95% of metal ion was recovered in three contacts of stripping. It is interesting to note that the percentage cumulative stripping is more from the highly irradiated solvent. These results indicating the absence of acidic degradation products even in the case of D^3DODGA/*n*-dodecane. The presence of diluents, *n*-dodecane, and nitric acid have no significant influence in the back extraction of metal ions.

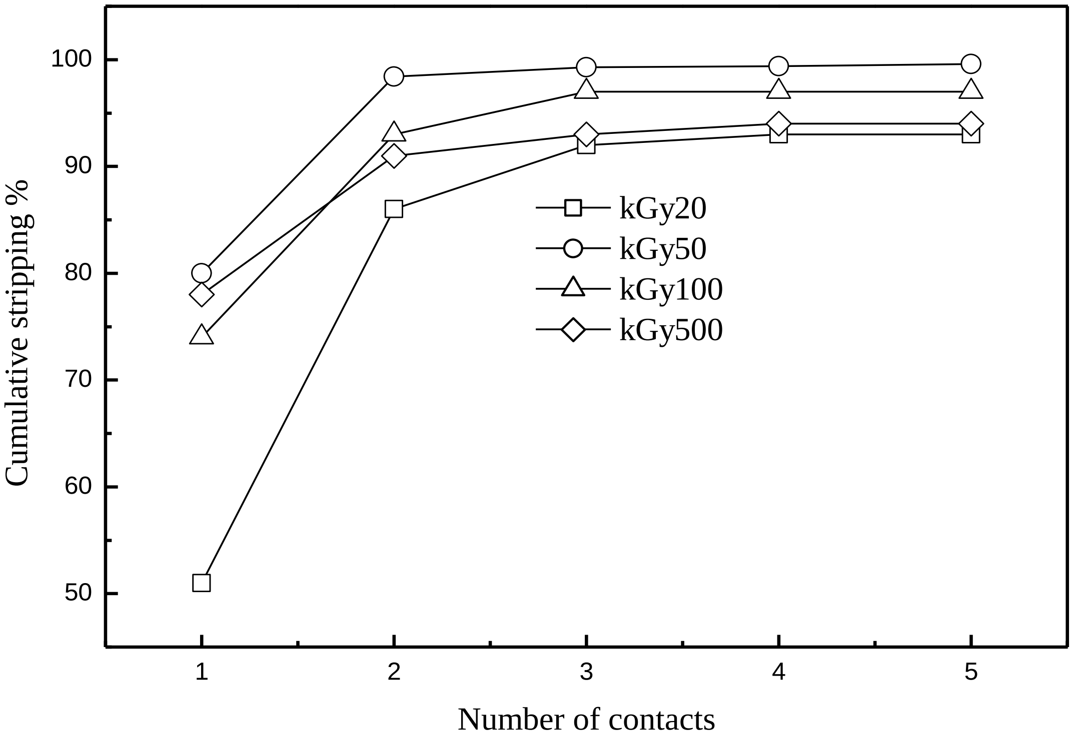


Figure 6.16. Cumulative stripping of Am(III) as a function of number of contacts at 298 K. Loaded organic phase :0.1 M solution of irradiated D^{3}DODGA in *n*-dodecane with equal volume of 4 M nitric acid. Stripping solution: 0.1 M nitric acid.

6.6. Third phase studies in irradiated solvent

The studies with D^{3}DODGA and D^{3}DEHDGA clearly indicated that 0.1 M D^{3}DODGA/*n*-dodecane and 0.1 M D^{3}DEHDGA/*n*-dodecane does not form third phase during the extraction of trivalent actinide from nitric acid medium as well as from fast reactor simulated HLLW, and proposed to use without the addition of phase modifier. However, under the irradiation conditions, the third phase formation behavior may alter due to the radiolytic cleavage of extractants and the formation of degradation products. Therefore, it is important to evaluate the third phase formation behavior of solvents under radiation exposure conditions. Therefore, the third phase formation tendency of D^{3}DEHDGA and D^{3}DODGA were studied during the extraction of Nd(III) from nitric acid medium as a function of absorbed dose. It is interesting to note that the extractants D^{3}DEHDGA and D^{3}DODGA are forming third phase under irradiation conditions. The dodecyl groups present on amidic nitrogen atoms of these UDGAs playing important role in preventing third phase formation during the extraction of trivalents of HLLW concentration under unirradiated conditions. The third phase formation in these solutions after the irradiation indicates the cleavage of dodecyl groups attached to the amidic nitrogen atoms. Table 6.5 and Table 6.6 shows the LOC of Nd(III) in irradiated 0.1 M D^3DEHDGA/*n*-dodecane and D^3DODGA/*n*-dodecane respectively as a function of absorbed dose at 298 K. It is interesting to note from the tables 6.4 and 6.5 that the LOC of Nd(III) increases with increase of absorbed dose. This may be due to the formation of polar degradation products in the organic phase. Moreover, the third phase formation was not induced at higher doses even the initial concentration of Nd(III) increased to as high as 1 M.

Table 6.5. Third phase formation limits of UDGA as a function of absorbed dose. Organic phase: Irradiated 0.1 M solution of D^3DEHDGA in *n*-dodecane. Aqueous phase: 4 M nitric acid. NT –No third phase.

Dose/	Nd(III) loading in irradiated 0.1 M D^3DEHDGA/*n*-dodecane		
	Initial	LOC/mM	CAC/mM
0	120	19	41.6
20	150	20	115
50	350	25	256
100	1000	NT	NT
300	1000	NT	NT
500	1000	NT	NT

Table 6.6. Third phase formation limits of UDGA as a function of absorbed dose. Organic phase: 0.1 M solution of D^{3}DODGA in *n*-dodecane, prepared using neat irradiated D^{3}DODGA. Aqueous phase: 4 M nitric acid. NT-No third phase.

Dose/kGy	Nd(III) loading in irradiated 0.1 M D^{3}DODGA/*n*-dodecane		
	Initial	LOC/mM	CAC/mM
0	630	17	610
300	730	25	710
500	880	27	810
1000	NT	NT	NT

At very high absorbed doses of γ- radiation, the concentration of extractant is less and therefore, concentration of metal-solvent complex will also be less. Since the concentration of metal-solvent complexes is low, there is no third phase formation at higher absorbed doses. It is important to mention here that the extractant, D^{3}DODGA was irradiated in neat form and used for 0.1 M D^{3}DODGA/*n*-dodecane solution preparation. The solvent irradiated even up to 1000 kGy dose, does not form third phase, when it is employed for the trivalent actinide extraction from the fast reactor HLLW.

6.7. Conclusions

The radiation stability of unsymmetrical diglycolamides DEHDODGA, D^{3}DEHDGA, and D^{3}DODGA was evaluated by measuring the $D_{\mathrm{Am(III)}}$ as a function of absorbed γ dose. The $D_{\mathrm{Am(III)}}$ decreased with increase in absorbed dose. The addition of diluent, *n*-dodecane, accelerated radiolytic cleavage of UDGAs and seems to act as a sensitizer. The influence of nitric acid on the radiolysis of UDGAs is marginal. However, the presence of nitric acid and *n*-dodecane has not influenced the degradation of DEHDODGA to a significant extent. On the other hand, the addition of phase modifier, 0.5 M DHOA in 0.1 M

DEHDODGA/*n*-dodecane increased the radiolytic damage of DEHDODGA. Though, the $D_{\mathrm{Am(III)}}$ decreased with increase in absorbed dose, they are sufficiently high for the partitioning of trivalent minor actinides from HLLW in all the UDGAs even up to a high dose of 500 kGy. The third phase formation tendency of 0.1 M D^3DEHDGA/*n*-dodecane and 0.1 M D^3DODGA/*n*-dodecane increased with increase of absorbed dose. However, the CAC values of trivalent f-element, Nd(III) are quite higher than their concentration in HLLW. The efficient extraction of Am(III) was achieved by irradiated D^3DEHDGA and D^3DODGA from the simulated HLLW of fast reactor fuel without the need of any phase modifiers indicating the robust nature of these UDGAs. The quantitative recovery of Am(III) from the loaded irradiated UDGAs suggesting the innocuous nature of the degradation products. Thus the radiolytic degradation studies of UDGAs clearly indicated their robust and promising nature for the separation of trivalent minor actinides from HLLW.

Summary and conclusions

This chapter summarizes the results of the studies aimed at the development of diglycolamide (DGA) class of extractants having desirable properties for the separation of trivalent actinides from high-level liquid waste (HLLW) arising from reprocessing of fast rector fuel. Several new unsymmetrical diglycolamides(UDGAs) having different alkyl groups attached to amidic nitrogen atom of UDGA were synthesized and studied. The summary of results is described below.

7.1. Actinide partitioning using DEHDODGA

A new unsymmetrical diglycolamide, *N*,*N*-di-2-ethylhexyl-$N^{'}$,$N^{'}$-di-octyl-3-oxa-pentane-1,5-diamide (DEHDODGA) was synthesized, and characterized by ^{1}H, and ^{13}C nmr, mass, and IR spectroscopic techniques. The distribution ratio (*D*) of Am(III), Eu(III)), and Pu(IV) in DHEDODGA/*n*-dodecane was determined and the *D* values increased with increase in the equilibrium concentration of nitric acid in the aqueous phase. The *D* increased in the order Pu(III) < Am(III) < Eu(III), which was in the increasing order of their ionic potentials (*z/r*). Nearly three molecules of DEHDODGA were involved in the complex formation of Am(III) from nitric acid medium. The separation factor (SF) of americium over strontium achieved with the use of DEHDODGA was higher than that obtained with the corresponding symmetrical diglycolamides such as TODGA and TEHDGA. The studies also indicated that the basicity of the extractants are in the order TEHDGA $\underset{\sim}{}$ DEHDODGA < TODGA.

The limiting organic concentration (LOC) and critical aqueous concentration (CAC) values of neodymium(III) and nitric acid were determined in 0.1 M DEHDODGA/*n*-dodecane and 0.1 M DEHDODGA–dihexyl octanamide (DHOA)–paraffin diluent system as a function of various parameters such as temperature, aqueous phase acidity, extractant concentration, phase modifier concentration etc. The phase modifier, DHOA, concentration required to avoid third phase formation during minor actinide partitioning from HLLW was optimized to 0.5 M in the solution of 0.1 M DEHDODGA-DHOA in *n*-dodecane. The extraction behaviour of various metal ions present in HLLW was studied in a solution of 0.1 M DEHDODGA-0.5 M DHOA/*n*-dodecane. The *D* of metal ions decreased in the order $M^{4+} \geq M^{3+} >> M^{2+} \sim MO_2^{2+} > M^{+}$. The extraction of trivalent actinides(An(III)) and lanthanides (Ln(III)) was accompanied by complete extraction of Zr(IV) and Y(III). The *D* of Sr(II), Cr(VI), Mo(VI), Pd(II), Ru(III), Ba(II), and Cd(II) in DEHDODGA/*n*-dodecane were lower than the corresponding symmetrical DGA, TODGA. A crud-type precipitate was observed in the aqueous phase during the back extraction when the organic phase was loaded from simulated HLLW, indicating the need of aqueous soluble complexing agents for back extraction. Using a solution of diethylenetriaminepentaaceticacid (DTPA)-citric acid at pH 3, quantitative recovery of trivalent metal ions from loaded organic phase could be achieved within four contacts without any crud formation. The use of DTPA-citric acid for recovery offers additional advantage during Ln(III)-An(III) separation in the subsequent step. The studies on a mixture of TODGA and TEHDGA solvents indicated that the properties observed from the UDGAs are different from that obtained by mixing two symmetrical DGAs. Therefore, use of UDGAs seems to be the inevitable option to achieve mixed properties of symmetrical DGAs.

7.2. Tuning the DGA structure

The DGA structure has been tuned to obtain the desirable properties required for minor actinide partitioning from nitric acid medium. The tuning was carried out in two modes, in the first mode, keeping only octyl groups on one amidic nitrogen atom and varying alkyl groups on the other nitrogen atom from hexyl to dodecyl groups namely, *N*,*N*-di-hexyl-*N',N'*-di-octyl-3-oxapentane-1,5-diamide known as di-hexyl-di-octyl diglycolamide

(DHDODGA), *N*,*N*-di-decyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide trivially called as di-decyl-di-octyl diglycolamide (D^{2}DODGA), *N*,*N*-di-dodecyl-*N'*,*N'*-di-octyl-3-oxapentane-1,5-diamide commonly known as di-dodecyl-di-octyl diglycolamide (D^{3}DODGA). All these UDGAs were synthesized and characterized by spectroscopic techniques and were aimed at obtaining the advantage of high *D* like TODGA and enhanced LOC for trivalent metal ions (neodymium(III)) and nitric acid. The extraction behaviour of Am(III), Eu(III), and Sr(II) in these di-octyl-di-alkyl DGAs in *n*-dodecane was studied as a function of various parameters. The extraction of trivalents (Am(III) and Eu(III)) in UDGAs decreased in the order DHDODGA > D^{2}DODGA > D^{3}DODGA. The *D* of trivalents in TODGA was comparable with DHDODGA. However, the LOC of nitric acid and neodymium(III) increased in the order of DHDODGA < TODGA < D^{2}DODGA < D^{3}DODGA. Among these UDGAs, D^{3}DODGA offers several advantages such as (1) high *D* of Ln(III) and An(III) from nitric acid medium (>300 ~ 3-8 M HNO_3) (2) low $D_{\mathrm{Sr(II)}}$ and thus high SF of americium over strontium (3) high LOC and CAC of nitric acid (4) no third phase formation with neodymium (III) even at the initial concentration of 600 mM from 3-4 M nitric acid medium at 298 K. Therefore, the solvent 0.1 M D^{3}DODGA/*n*-dodecane did not require any phase modifier. In view of these, D^{3}DODGA was studied extensively for the actinide partitioning.

The extraction behavior of actinides, fission products, and corrosion products was studied in a solution of 0.1 M D^{3}DODGA in *n*-dodecane from nitric acid medium as well as from fast reactor simulated HLLW. The extraction of metal ion in 0.1 M D^{3}DODGA/*n*-dodecane was strongly dependent on the charge to radius ratio and the distribution ratios followed the order M(IV) > M(III) >> M(VI) ~ M(II) >> M (I). Based on the distribution ratios obtained from 3–4 M nitric acid medium and from simulated waste, the metal ions such as Zr(IV), Am(III), Ln(III) and Y(III) could be extracted quantitatively in to 0.1 M D^{3}DODGA/*n*-dodecane phase in 3 contacts. The metal ions such as Sr(II), Pd(II), U(VI), Te(VI), Ru(III) having *D* between 0.1–2 could also be extracted in to organic phase in some contacts. The *D* of other metal ions was negligible (~10^{-2}). The studies revealed that the extraction behaviour of various metal ions in 0.1M D^3DODGA/*n*-dodecane was similar to TODGA/*n*-dodecane system. However, the exceptional difference was that D^3DODGA did not require any phase modifier for extraction from fast reactor simulated HLLW. Therefore, it is advantages to employ 0.1 M D^3DODGA/*n*-dodecane for partitioning of minor actinides from HLLW.

Considering the advantages with dodecyl groups on amidic nitrogen atom in preventing third phase formation during the extraction, several UDGAs containing dodecyl groups have been synthesised and evaluated in the second mode of tuning. The alkyl groups on the other amidic nitrogen atom were varied from *n*-butyl to *n*-decyl to obtain *N*,*N*-di-butyl-*N'*,*N'*-di-dodecyl-3-oxapentane-1,5-diamide (DBD^3DGA), *N*,*N*-di-dodecyl-*N'*,*N'*-di-hexyl-3-oxapentane-1,5-diamide (D^3DHDGA), *N*,*N*-di-decyl-*N'*,*N*'-di-dodecyl-3-oxapentane-1,5-diamide (D^2D^3DGA). The extraction behaviour of Am(III), Eu(III), and Sr(II) from nitric acid medium was studied in these UDGAs. The $D_{\mathrm{Am(III)}}$ and $D_{\mathrm{Eu(III)}}$ decreased with increase in the chain length of alkyl group attached to amidic nitrogen atom of UDGA. The third phase formation of nitric acid in 0.1 M UDGA/*n*-dodecane indicated that the LOC values increased with increase in the chain length of alkyl groups attached to amidic nitrogen atom. The third phase formation was not observed during the extraction of Nd(III) from 3-4 M nitric acid medium even at the initial Nd(III) concentration of ~500 mM. Thus, the studies confirmed that the UDGAs with dodecyl group attached to one amidic nitrogen atom is inevitable for preventing third phase formation.

Another UDGA containing dodecyl groups and ethylhexyl groups namely, *N*,*N*-di-dodecyl-*N'*,*N'*-di-2-ethylhexyl-3-oxapentane-1,5-diamide (D^3DEHDGA) was also synthesized, and evaluated for the extraction of Am(III) and Eu(III) from nitric acid medium. Studies indicated that nearly three molecules of D^3DEHDGA were involved in the complexation with trivalents from 1 M nitric medium. Third phase formation was not observed when 0.1 M D^{3}DEHDGA/*n*-dodecane was employed for the extraction of Am(III) from fast reactor SHLLW, as well as from the nitric acid medium containing 100 mM of Nd(III) in 4 M HNO_3. Therefore, these UDGAs are promising candidates for the separation of trivalent actinides from HLLW, which contain a maximum of ~50 mM trivalent metal ions in 3-4 M HNO_3 medium.

7.3. Development of advanced method for actinide partitioning from HLLW

Separation of Ln(III) from An(III) was studied from citric acid -nitric acid medium. The method involves the use of 0.1 M *N*,*N*-di-2-ethylhexyl diglycolamic acid (HDEHDGA)-Tri-*n*-butyl phosphate (TBP)(10 wt.%/V) in *n*-dodecane as organic phase that gives a SF of 7 from pH 3 solution. Even though the SF achieved with the present aqueous phase (0.1 M citric acid-0.05 M DTPA at pH 3) is only moderate, separation of Am(III) from lanthanides could be achieved with the use of multistage mixer-settlers. A new approach, SMART(**S**ingle-cycle process for **M**inor **A**ctinide partitioning using completely incinerable **R**eagen**T**s), developed using completely incinerable reagents, UDGA and diglycolamic acid compatible with *n*-dodecane, for the separation of An(III) from nitric acid medium. The desirable properties of D^{3}DODGA and HDEHDGA were exploited to examine the feasibility of using these extractants together for a single-cycle separation of minor actinides from HLLW. Extraction behavior of these metal ions in 0.1 M D^{3}DODGA-0.05 M HDEHDGA/*n*-dodecane was compared with individual solvents, namely 0.1 M D^{3}DODGA/*n*-dodecane and 0.05 M HDEHDGA/*n*-dodecane. Synergistic extraction of Am(III) and Eu(III) observed in 0.1 M D^{3}DODGA-0.05 M HDEHDGA/*n*-dodecane at nitric acid concentrations above 0.1 M, was due to the involvement of both HDEHDGA and D^{3}DODGA for extraction. The dependence of Am(III) and Eu(III) on HDEHDGA concentration decreased and that on D^{3}DODGA increased with increase in the concentration of nitric acid in aqueous phase. The present SMART approach revealed that by using 0.05 M

D^3DODGA-0.2 M HDEHDGA/*n*-dodecane as solvent, and 0.001 M DTPA at pH 1.5 as aqueous formulation, it is possible to separate Am(III) from HLLW in a single-processing cycle.

7.4. Radiation stability of UDGAs

The UDGAs are promising extractants for the partitioning of minor actinide from HLLW. The radiation stability of DEHDODGA, D^3DEHDGA, and D^3DODGA was evaluated by measuring the $D_{\mathrm{Am(III)}}$ as a function of absorbed γ dose. The $D_{\mathrm{Am(III)}}$ decreased with increase of absorbed dose in all the UDGAs under all the conditions studied. The addition of diluent, *n*-dodecane accelerated radiolytic cleavage of UDGAs and seems to act as sensitizer. The influence of nitric acid on the radiolysis of UDGAs was marginal. However, the presence of nitric acid and *n*-dodecane did not influence the degradation of DEHDODGA to a significant extent. On the other hand, the addition of phase modifier, 0.5 M DHOA in 0.1 M DEHDODGA/*n*-dodecane increased the radiolytic damage of DEHDODGA. Though the $D_{\mathrm{Am(III)}}$ decreased with increase of absorbed dose, they are sufficiently high for the partitioning of trivalent minor actinides from HLLW in all the UDGAs even up to a high dose of 500 kGy. The efficient extraction of Am(III) was achieved with the extraction by irradiated D^3DEHDGA and D^3DODGA even from the simulated HLLW of fast reactor fuel without the need of any phase modifiers indicating the robust nature of these UDGAs. The quantitative recovery of Am(III) during stripping from the loaded irradiated UDGAs suggests the innocuous nature of the degradation products.

7.5. Scope for the future studies

The UDGAs DEHDODGA and D^{3}DODGA were studied extensively for the extraction of actinides, lanthanides, other fission products, and corrosion products from citric acid medium as well as from fast reactor fuel simulated HLLW. However, the other UDGAs were examined only for the extraction of limited number of metal ions. The extraction behavior of other metal ions which are likely to be present in HLLW need to be studied in other UDGAs also. The studies using UDGAs in the present work clearly indicated that the extraction efficiency, and third phase formation tendency of DGAs decreases with increase in alkyl chain length attached to amidic nitrogen atom. A similar behavior was also reported in symmetrical DGAs by other researchers. Though, the high extraction efficiency of DGAs was attributed to aggregation to form reverse-micelles in the nitric acid medium (>0.7 M), a systematic understanding of the influence of alkyl group on aggregation behavior is not reported. Therefore, the study on the variation of aggregation behavior of DGAs with alkyl chain length attached to amidic nitrogen atoms can be carried out to improve the understanding.

Even though, the distribution ratio of An(III) and Ln(III) was quite low at lower nitric acid media (0.1 M) in DGAs, practically the stripping was not successful from the DEHDODGA-DHOA/*n*-dodecane phase when it was loaded with Am(III) from fast reactor HLLW. There was a crud formation during the back extraction even by using 0.5 M nitric acid solution. A similar observation was also made in the case of TODGA. The undesirable crud formation during the stripping, and factors influencing on it need to be understood clearly.

The SMART approach developed in the present study considered Am(III) and Eu(III) as the actinide and lanthanide representatives respectively. However, the HLLW consists several other lanthanides of which lighter lanthanides such as La(III) resembles Am(III) more and may contaminate the Am(III) product to a significant extent. In this context, future studies can be carried out to examine the extraction behavior of other fission products and corrosion products in the SMART solvent. The SFs achieved for Eu(III) to Am(III) are need to be improved for their efficient separation in the minimum number of contacts, and practical application of SMART process. The synergetic and antagonistic extraction in the SMART solvent was explained solely based on the influence of involvement of one extractant on the other. Future studies can be carried out to understand the influence of addition of one extractant on the aggregation behavior of the other. The aggregation pattern in the combined solvent systems and its influence on the extraction behavior under various conditions need to be understood.

The UDGAs, DEHDODGA, D^3DODGA and D^3DEHDGA have shown adequate radiation stability under various process conditions. However, the present work was restricted to examine only the influence of γ-dose on the performance of UDGAs. No attempt was made to understand the degradation pattern, and nature of degradation products. The radiation stability under alpha-exposure and the hydrolytic stability also can be studied.

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Glossary

Abbrevation	Full name
ADS	Accelerator Driven System
An(III)	Trivalent Actinides
ANL	Argonne National Laboratory
CAC	Critical Aqueous Concentration
CMPO	*n*-Octyl(phenyl)-*N*,*N*-diisobutylCarbamoylMethyl Phosphine Oxide
D^2D^3DGA	*N*,*N*-di-decyl-*N*′,*N*′-di-dodecyl-3-oxapentane-1,5-diamide or Di-Decyl-Di-DoDecyl-DiGlycolAmide
D^2DODGA	*N*,*N*-di-decyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or Di-Decyl-Di-Octyl-DiGlycolAmide
D^3DEHDGA	*N*,*N*-di-dodecyl-*N*′,*N*′-di-2-ethylhexyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-EthylHexyl-DiGlycolAmide
D^3DHDGA	*N*,*N*-di-dodecyl-*N*′,*N*′-di-hexyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-Hexyl-DiGlycolAmide
D^3DODGA	*N*,*N*-di-dodecyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-Octyl-DiGlycolAmide
DBD^{3}DGA	*N*,*N*-di-butyl-*N*′,*N*′-di-dodecyl-3-oxapentane-1,5-diamide or Di-DoDecyl-Di-Butyl-DiGlycolAmide
DEHDODGA	*N*,*N*-di-2-ethylhexyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or Di-EthylHexyl-Di-Octyl-DiGlycolAmide
DGAs	Diglycolamides
DHDODGA	*N*,*N*-di-hexyl-*N*′,*N*′-di-octyl-3-oxapentane-1,5-diamide or Di-Hexyl-Di-Octyl-DiGlycolAmide
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
DOODA	*N,N,N’,N’*-tetra alkyl-3,6-dioxaoctane diamide
DTPA	Diethylenetriamine pentaacetic acid
FBRs	Fast Breeder Reactors

FBTR	Fast Breeder Test Reactor
FPs	Fission Products
FR	Fast Reactor
GDP	Gross Domestic Product
GWe	Giga Watt Electric
HDEHDGA	*N*,*N*-di-2-ethylhexyl diglycolamic acid
HDEHP	Di(2-ethylhexyl) Phosphoric Acid
HLLW	High Level Liquid Waste
K_H	Basicity constant
kWh	Kilowatt hour
Ln(III)	Trivalent Lanthanides
LOC	Limiting Organic Concentration
MAs	Minor Actinides
MWd	Mega Watt days
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 Reduction Extraction process
RIAR	Russian’s Research Institute of Atomic Reactors
SHLLW	Simulated High Level Liquid Waste
TALSPEAK	Trivalent Actinides Lanthanide Separation Phosphorous based reagent Extraction from Aqueous Komplexes
TBP	Tri-*n*-Butyl Phosphate
TDdDGA	*N,N,N′,N′*-tetra-dodecyl-3-oxapentane-1,5-diamide or *N,N,N’,N’*-Tetra-Dodecyl DiGlycolAmide
TEHDGA	*N,N ,N′,N′*-ethylhexyl 3-oxapentane-1,5-diamide or *N,N,N’,N’*-tetra-2-ethylhexyl diglycolamide
TODGA	*N,N,N′,N′*-tetra-octyl-3-oxapentane-1,5-diamide or *N,N,N’,N’*-tetra-octyl diglycolamide
TRPO	TriAlkyl PhosphineOxides
TRUEX	TRans Uranium element EXtraction
UDGAs	Unsymmetrical Diglycolamides

Abstract of the thesis

Development of advanced reagents and methods for the separation of actinides from nitric acid medium

Partitioning of trivalent actinides and transmutation into stable innocuous products is being considered as a viable method for the safe management of high-level liquid waste (HLLW) arising from reprocessing of spent nuclear fuels. Among the various reagents studied for partitioning of trivalent actinides from HLLW by liquid-liquid extraction, diglycolamides (DGAs) are emerging as promising candidates. The DGA derivatives such as tetra-octyl diglycolamide (TODGA) and tetra 2-ethylhexyl diglycolamide (TEHDGA) received much attention in the recent past. However, their low metal loading capacity leading to third phase formation and co-extraction of undesirable metal ions limit their application for the industrial scale separations.

Present work involves the synthesis of some novel unsymmetrical diglycolamides (UDGAs), and their evaluation for the partitioning of minor actinides from HLLW. The alkyl group attached to the amidic nitrogen atom of UDGAs was to obtain desirable properties for efficient extraction of trivalents without leading to third phase formation and poor extraction of undesirable metal ions etc. In addition, a new approach namely "Single-cycle process for the Minor Actinide partitioning using completely incinerable ReagenTs(SMART)" for direct separation of trivalent actinides from HLLW has been developed by using a mixture of UDGA and diglycolamic acid. Since the UDGAs are proposed for solvent extraction applications of HLLW, the radiation stability of UDGAs were evaluated under process conditions. The study clearly indicated that the UDGAs reported in the present study are superior candidates for process scale applications as compared to the existing diglycolamides.

List of publications

a. Peer reviewed journals- published:

1. Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao. Co-extraction and stripping behavior of trivalent actinides and fission products in *N*,*N*-di-2-ethylhexyl-*N’*,*N’*-dioctyl-diglycolamide. *Radiochimica Acta*.101 (2013) 301-306.
2. Jammu Ravi, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao. *J Radioanal Nucl Chem*. 295 (2013) 1283-1292. Tuning the diglycolamides for modifier-free minor actinide partitioning.
3. Jammu Ravi, T. Prathibha, K.A. Venkatesan, M.P. Antony, T.G. Srinivasan, P.R. Vasudeva Rao. *Sep. Purif. Technol*. 85 (2012) 96–100. Third phase formation of neodymium(III) and nitric acid in unsymmetrical *N*,*N*-di-2-ethylhexyl *N’*,*N’*-dioctyldiglycolamide.
4. Jammu Ravi, A.S. Suneesh, T. Prathibha, K. A. Venkatesan, M. P. Antony, T.G.Srinivasan, P.R. Vasudeva Rao. *Solvent Extr. Ion Exch*, 29 (2011) 86–105. Extraction behavior of some actinides and fission products from nitric acid medium by a new unsymmetrical diglycolamide.
5. A.S. Suneesh, Jammu Ravi K.A. Venkatesan, M.P. Antony, T.G. Srinivasan, P.R. Vasudeva Rao. *J Radioanal Nucl Chem* 285 (2010) 653–658. Lanthanide-actinide separation by bis-2-ethylhexylphosphoric acid from citric acid-nitric acid medium.

b. Peer reviewed journals -Accepted:

1. Jammu Ravi, K.A. Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao. Unsymmetrical diglycolamide for the safe management of nuclear waste. (J. Environ. Chem. Eng. (2013), http://dx.doi.org/10.1016/j.jece.2013.07.002 .

2. Jammu Ravi, B. Robert Selven, K. A.Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao. Evaluation of radiation stability of *N,N*-didodecyl *N',N'*-di-octyl diglycolamide- a promising reagent for actinide partitioning. (J.Radioanal.Nucl.Chem. DOI 10.1007/s10967-013-2776-4).

3. Jammu Ravi, B. Robert Selven, K. A.Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao. Radiolytic stability of di-2-ethylhexyl-dioctyl diglycolamide. (Accepted in Radiochimica Acta).

c. Peer reviewed journal papers under review:

1. Jammu Ravi, K. A.Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao, Evaluation of modifier-free di-dodecyl-di-octyl diglycolamide for partitioning of minor actinides from fast reactor high-level liquid waste.

2. Jammu Ravi, K. A.Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao. Development of a single-cycle method for partitioning of trivalent actinides using completely incinerable reagents from nitric acid medium.

3. Jammu Ravi, K.A.Venkatesan, M. P. Antony, T. G. Srinivasan, P.R. Vasudeva Rao. Unsymmetrical diglycolamides for the separation of trivalent actinides from nitric acid medium.

International conferences

1. Unsymmetrical diglycolamides for minor actinides partitioning.
   Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao. Plutonium Futures- The Science 2012. Held at University of Cambridge, United Kingdom.(**Best presentation award**)

2. New usymmetrical diglycolamides for the extraction of americium(III) from nitric acid.
   Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao.International Conference on Vistas in Chemistry (ICVC)-2011, p 140-141. Edt by V. Ganesan, S. Anthonysamy, Kitheri Joseph. Held at Indira Gandhi Centre for Atomic Research, Kalpakkam.

National symposia

1. Superior diglycolamides for minor actinide partitioning
   Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao. In the Proceedings of Nuclear and Radiochemistry Symposium (NUCAR- 2013) held at Government Model Science College, R.D.University, Jabalpur, India, 2013.

2. Evaluation of unsymmetrical di-dodecyl-di-octyldiglycolamide for the separation of trivalent actinides from nitric acid medium valuation of didodecyl dioctyl diglycolamide for the partitioning of minor actinides.(**Best presentation award**)
   Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao. In the Proceedings of Nuclear and Radiochemistry Symposium (NUCAR-2013), held at Government Model Science College, R.D.University, Jabalpur, India, 2013.

3. Radiolytic stability of *N*,*N*,-di-2-ethylhexyl-*N’*,*N’*-di-octyl-diglycolamideadiation stability of di-2-ethylhexyl-di-octyl diglycolamide.
   B. Robert Selvan, Jammu Ravi, K.A.Venkatesan, M.P.Antony, T.G. Srinivasan, P.R. Vasudeva Rao. In Proceedings of Nuclear and Radiochemistry Symposium (NUCAR-2013), held at Government Model Science College, R.D.University, Jabalpur, India, 2013.

4. Co-extraction and stripping behaviour of various elements present in simulated high-level waste in unsymmetrical diglycolamide.
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5. Synthesis and characterization of unsymmetrical diglycolamides.
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6. Extraction behaviour of fission products in di-2-ethylhexyl-di-octyl-diglycolamide from simulated high-level liquid waste.
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7. Third phase formation of neodymium(III) in unsymmetrical diglycolamide.
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8. Extraction of Am(III) by octyl-based unsymmetrical diglycolamide.
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9. Lanthanide-actinide separation by a modified TALSPEAK process.
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Awards

1. Best poster presentation award by ***Royal Society of Chemistry*** in the international conference, “**Plutonium Futures-The Science 2012**” held at **University of Cambridge**, United Kingdom in July 2012.

2. Best Best poster presentation award in "Nuclear and Radiochemistry symposium (NUCAR)-2013" held at Government model science college, Jabalpur, India in February 2013.