SYNTHESIS AND EVALUATION OF *N,N*-DI-ALKYL-2-HYDROXYACETAMIDES FOR THE MODIFIER- FREE SEPARATION OF TRIVALENT ACTINIDES FROM NITRIC ACID MEDIUM

By

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CHEM 02 2012 04 004

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A thesis submitted to the

Board of Studies in Chemical Sciences

In partial fulfillment of requirements

for the Degree of

DOCTOR OF PHILOSOPHY

of

HOMI BHABHA NATIONAL INSTITUTE

March 2018

Homi Bhabha National Institute

Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by **T Prathibha** entitled **Synthesis and evaluation of *N,N*-di-alkyl-2-hydroxyacetamides for the modifier- free separation of trivalent actinides from nitric acid medium** and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

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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.

Prathi
29/06/2018

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List of Publications arising from the thesis

Journal

1. "*N,N*-dialkyl-2-hydroxyacetamides for modifier-free separation of trivalent actinides from nitric acid medium". **T Prathibha**, R Kumaresan, B. Robert Selvan, K. A Venkatesan, M. P Antony and P. R. Vasudeva Rao. *Radiochimica Acta* (**2016)** 104: 173–181.
2. "Radiolytic stability of *N, N*-di-alkyl-2-hydroxyacetamides". **T Prathibha**, B Robert Selvan, K A Venkatesan, S Rajeswari and M P Antony. *Journal of Radioanalytical and Nuclear Chemistry* (**2017**) 311(3): 1929-1935.
3. "Modifier-free separation of trivalent actinides and lanthanides from fast reactor simulated high-level liquid waste using *N,N*-di-octyl-2-hydroxyacetamide".**T Prathibha**, R Kumaresan, P.K Nayak, K.A Venkatesan, G.G.S Subramanian, S Rajeswari, T Kalaiyarasu, R Karunakaran and M.P Antony. *Journal of Radioanalytical and Nuclear Chemistry* **(2017)** 314: 2365-2375.
4. "Comparison in the aggregation behaviour of amide extractant systems by dynamic light scattering and ATR-FTIR spectroscopy". **T Prathibha**, K.A Venkatesan and M.P Antony. *Colloids and Surfaces-A: Physicochemical and Engineering Aspects.* **(2018)** 538: 651-650.

Conferences

1. "Vibrational spectroscopic and dynamic light scattering analysis of some of the selected nuclear extractants during extraction of nitric acid and metal ions." "**T Prathibha**, K A Venkatesan and M P Antony, In: International Conference on Molecular Spectroscopy (ICMS-2017), December 8-10, M.G University, Kottayam, Kerala.

2. "Analysis of degradation products of *N,N*-di-octyl-2-hydroxyacetamide using dynamic light scattering and ATR-FTIR spectroscopy.**"T Prathibha**, B Robert Selvan, K.A Venkatesan and M.P Antony. Presented in: Emerging trends in separation science and technology (SESTEC-2018), May 23-26. BITS Pilani, K K Birla Goa campus, Goa.

Others

1. "A novel 2-oxy-*N,N*-dioctylacetamide grafted resin for the separation of trivalent actinides from nitric acid medium". B Robert Selvan, **T Prathibha**, K. A Venkatesan, M. P Antony and P.R Vasudeva Rao. *Radiochimica Acta* (**2015**) 103(2): 91-99.
2. "Synthesis and evaluation of *N,N*-di-alkyl-2-methoxyacetamides for the separation of U(VI) and Pu(IV) from nitric acid medium". R Kumaresan, **T Prathibha**, B Robert Selvan, K.A Venkatesan and M.P Antony. *Radiochimica Acta* (**2017**) 105(9): 699-707.

Prathi
29/06/2018
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DEDICATIONS

TO THE CONSTANT SUPPORT FROM MY PARENTS AND MY
HUSBAND

ACKNOWLEDGEMENTS

I express sincere thanks to my Ph.D supervisor **Dr. M. P. Antony,** for his guidance and valuable suggestions to improve the quality of work throughout the tenure. The moral support and constant encouragement provided by him has immensely helped me in each and every step of my work.

I am extremely grateful to **Dr. K.A Venkatesan**, whose continuous encouragement, suggestions and guidance has made this work possible. I am pleased to express my deep sense of gratitude to my doctoral committee chairman, **Dr. N. Sivaraman** and members **Dr. V. Jayaraman, Dr. C Mallika** and **Dr. R. V. Subba Rao**, for their valuable suggestions. I extend my sincere thanks to **Dr. M Joseph**, Director, MC&MFCG and **Dr. K Ananthasivan**, Associate director, MFCG for their constant support.

I express my heartfelt thanks for **Dr. R Kumaresan** and **Sri B. Robert Selvan** for their valuable support and suggestions during the experimental works. I wish to put a special note of thanks to **Smt Amudha Suba** for her sincere assistance during the course of my work. I also wish to express my special thanks to **Smt K.V Syamala**, **Smt S Rajeswari** and **Sri M Karunanithi** for their timely support and encouragement.

I am grateful to my section colleagues **Dr. P Manoravi**, **Dr. A.S Suneesh, Dr. Alok Rout, Dr. Prasant Kumar Nayak, Dr. G Panneerselvam, Sri G Ganapathy Sankara Subramanian, Sri T Bapuji, Sri R Karunakaran, Sri T Kalaiyarasu, Sri A Amalraj and Smt Amrita Sen** for their co-operation which has helped me to complete the work. I am also thankful to the support from research scholars **Sri T Ramaswamy**, **Sri B Murali Krishna, Sri P Amesh**, **Sri Venkateswara Rao** and **Dr. R Rama.**

I would like to acknowledge **Sri H Krishnan**, Radiological dosimetry division for providing the ^{60}Co gamma irradiation facility and **Dr. Subramanian** & **Dr. T Sairam**, DAE-UGC CSR for recording the nmr spectra of samples. I am thankful for the sincere co-

operation of MSc project students, **Smt. Amanah M Muhammed**, **Smt. Dymphna George Sebastian**, **Smt. Anjali K.P** and **Ms Athira Ravi** during some of the experiments.

Finally, I would like to express my extreme gratitude to my family members for all their sacrifice and prayers.

Prathi 29/06/2018

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SYNOPSIS

The development of mankind was always associated with the inventions leading to better methods of living, which is directly related to the availability of electrical energy. The process of generation of electricity by different available resources usually lead to several impacts on the surroundings, such as emission of green house gases by fossil fuels and geographical imbalances due to hydroelectric projects. It is high time now, to think about a sustainable development wherein the utilization of natural resources would not harm the environment with a high impact. Nuclear energy is slowly evolving as an inevitable option for the generation of electricity world-wide, especially due to its high energy efficiency without the emission of green house gases [1]. A robust technology back-up and proper handling of nuclear materials are important factors for the choice of nuclear energy. The significance of nuclear energy option for India was identified in 1950's and the country has a three-stage nuclear power programme aimed at the utilization of vast resources of available thorium in nuclear reactors for electricity generation by 2050 [2].

The spent fuel discharged from the nuclear reactor contains highly radioactive fission products and actinides. Many of the leading countries in the world where nuclear energy contributes a major share of the total electricity production have chosen to send the spent nuclear fuel directly to deep geological repositories isolated from the biosphere. This option is usually described as an open-end nuclear fuel cycle. It would require repositories with millions of years of surveillance. The spent fuel from a thermal reactor using 4% enriched uranium fuel having a burn-up of 45000 MWD/Te contains more than 95% of the fertile depleted uranium fuel (^{238}U with reduced amounts of ^{235}U) along with other useful fissile elements such as ^{239}Pu. Therefore, many other countries in the world including India choose to reprocess the spent fuel for recovery of these fissile materials. This option, usually described as a ‘closed-end nuclear fuel cycle’ is particularly attractive for our country which is poor in uranium resources. The recovered uranium and plutonium would be employed as fuel in the fast breeder reactors in the second stage of our nuclear power programme. It is envisaged that the fast breeder reactors would generate more amount of fissile ^{239}Pu, along with generating fissile ^{233}U from natural ^{232}Th loaded in their core blankets [2].

At present, aqueous reprocessing methods are adopted for the recovery of uranium and plutonium from the spent nuclear fuel. Other reprocessing technologies such as pyroprocessing methods are also being developed as part of India’s three stage nuclear power programme involving advanced metallic fuels. Aqueous reprocessing is relatively less expensive than pyroprocessing and it offers a technology that is well developed in all parts of the world. The PUREX (Plutonium Uranium Recovery by EXtraction) process makes use of the extractant, tri-*n*-butylphosphate (TBP) dissolved in a non-polar diluent such as *n*-dodecane for selective extraction of uranium and plutonium from a solution of spent nuclear fuel in 3- 4 M nitric acid. The aqueous raffinate of PUREX process is usually described as the ‘high level liquid waste’ (HLLW). Although a major share of the radiotoxicity of spent fuel is removed with the separation of plutonium, the remaining raffinate contains other radiotoxic elements including some of the fission products and actinides.

The nuclear fuel cycle shall be considered as ‘partially closed’, if the HLLW is directly sent to geological repositories. It has been identified that the long-lived alpha emitting radio nuclides including neptunium, americium and curium contribute a major share of its radiotoxicity, although these are present in very small quantities in HLLW. These are usually described as ‘minor actinides’. Selective removal of minor actinides would reduce the waste storage timelines of HLLW to a considerable extent and the nuclear fuel cycle shall be considered as ‘fully closed’ only under such circumstances. The strategy of ‘partitioning and transmutation (P&T)’ aims at the selective separation of minor actinides and their transmutation into elements having shorter half lives in accelerator driven systems (ADS) or fast reactors [3]. The separation technologies for the selective removal of minor actinides still require a great deal of development, so as to avail the benefits of a fully closed nuclear fuel cycle.

There are a number of considerations involved in the development of a suitable extractant for selective metal ion extraction from highly radioactive waste solutions in industrial scales. These factors vary from optimum physical and chemical properties to the ease of synthesis of extractants. While it is important to have good distribution values for metal ions, it is equally important to have good aggregation behaviour and radiolytic stability so as to avoid the formation of third phase and deleterious degradation products during extraction [4, 5]. A good number of studies have been reported for the development of extractants and processes for minor actinide partitioning in the last four decades [6]. The basic studies in this direction have been actively pursued by many countries in the world including the United States, Germany, Japan, India and Russia.

The major studies in this direction in late 1980’s were focussed on the development of a trans-uranic extraction (TRUEX) process based on octyl(phenyl)-*N*,*N*-di-isobutylcarbamoylmethyl phosphineoxide (CMPO) as extractant. A mixture of 0.2 M CMPO and 1.2 M TBP was employed for extraction of trivalent lanthanides and actinides from high level waste solutions. Hot demonstration runs of TRUEX process was carried out in USA, Japan and India. The major disadvantages reported for the TRUEX process was the formation of deleterious degradation products, requirement of complexing agents for stripping and the use of a non-incinerable extractant. Totally incinerable amide based extractants were chosen for later studies aimed at minor actinide partitioning. They had the added advantage of innocuous degradation products, which did not affect the distribution values of extractants during the extraction process. Malonamides and diglycolamides are two important classes of extractants in this category. Amongst several malonamides studied, *N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA) and *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy malonamide (DMDOHEMA) were found to be promising extractants. Demonstration runs of the DIAMEX processes involving both the extractants were carried out in Germany. The distribution values and third phase behaviour was better for DMDOHEMA extractant, however the values were still smaller requiring the use of high concentrations (1 M) of extractants.

Recently, the studies on minor actinide partitioning are focussed on diglycolamides (DGA), which showed very good distribution values for extraction of trivalent metal ions from high level waste solutions. *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), *N,N,N',N'*-tetraethylhexyldiglycolamide (TEHDGA) and *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D^3DODGA) are some of the promising DGA derivatives. The use of TODGA or TEHDGA required a phase modifier, whereas D^3DODGA was a modifier-free extractant. Batch studies and counter-current extraction studies using genuine fuel solution reported for TODGA extractant systems have shown promising results. Literature reports show that further studies are in progress using DGAs for optimization of extraction properties.

Scope of the present work

The DGA extractants required very low aqueous acidities (< 0.1M HNO_3) for back extraction, which was disadvantageous in view of phase disengagement problems and crud formation. The use of TODGA required a phase modifier so as to avoid third phase formation during extraction from high level waste solutions. The malonamide extractant systems showed better back extraction properties and modifier-free extraction as compared to diglycolamides; however the distribution values of various metal ions were smaller in these systems. In this context, it was desirable to develop an extractant system which showed good extraction and stripping properties without the use of a modifier. Critical evaluation of the structure of DGA extractants shows that the property of extraordinary extraction of trivalent metal ions in diglycolamides is essentially due to the presence of etheric oxygen sandwiched between a couple of amidic sites. Due to the presence of these two amidic sites, the polarity of the diglycolamide seems to be significantly high, and this factor leads to poor compatibility of its metal-solvate in a nuclear diluent, *n*-dodecane leading to third phase formation [7]. Moreover, the presence of more number of polar groups increases the extraction of nitric acid during the extraction of metal ions leading to difficulties during back extraction. The third phase formation tendency and extraction of nitric acid can be minimized by redesigning the structure of DGA with a single amidic functionality and retaining the etheric oxygen at the required position in the structure. Accordingly, a new class of extractants, *N, N*-di-alkyl-2-hydroxyacetamides (DAHyA) with a single amide group and hydroxyl group at alpha position were chosen for the present study [8]. Preliminary investigations on the extraction behaviour and radiation stability of DAHyA derivatives showed promising results for separation of Am(III) from nitric acid medium. Along with these results, the detailed studies on third phase formation, aggregation behaviour and extraction & stripping of metal ions from fast reactor simulated high level waste (FR-SHLLW) solution using this new class of extractant form the subject matter of the present thesis.

Organization of the thesis

The thesis is organized in 7 chapters. A brief summary of each chapter is given below.

Chapter-1: Introduction

Chapter 1 briefly describes the role of nuclear energy in satisfying the energy demand of a constantly developing world. The significance of reprocessing of spent fuel in the three-stage nuclear power programme of India is discussed with emphasis on aqueous reprocessing methodologies. The key role of minor actinide partitioning and some of the important extractant systems for minor actinide partitioning are discussed with regard to advantages and disadvantages of each system. Brief introductory remarks are made on the third phase formation, radiolytic degradation and aggregation properties of extractants during liquid-liquid extraction. Finally, the scope of the present work is presented in light of the above discussion.

Chapter 2: Experimental

Chapter 2 contains a description of the materials, instruments, methods and conditions used in the present study. The details of instrumental facilities employed in the present study and the experimental conditions are discussed. The detailed procedures involved for the preparation of standard solutions and FR-SHLLW is mentioned. The equipments and methods used during liquid-liquid extraction studies employed throughout the studies have also been described in detail. A step-wise description of the organic synthesis of extractants involved in the present study is given along with the characterization data of all the intermediate products and final products. Some of the selected NMR and FT-IR spectra are also attached.

Chapter 3: Studies on the extraction of Am(III) and Nd(III) from nitric acid medium using *N,N*-di-alkyl-2-hydroxyacetamides

Chapter 3 contains the results of preliminary investigations using three DAHyA derivatives, namely *N,N*-di-hexyl-2-hydroxyacetamide (DHHyA), *N,N*-di-octyl-2-hydroxyacetamide (DOHyA) and *N,N*-di-decyl-2-hydroxyacetamide (DOHyA) for the extraction of Am(III) and Nd(III) from nitric acid medium. Tracer studies using Am(III) was carried out for determining the stoichiometry of extraction and the effect of aqueous nitric acid concentration on extraction. The nitric acid extraction isotherms were determined for all the three DAHyA derivatives. The values of limiting organic concentration (LOC) and critical aqueous concentration (CAC) values of nitric acid were reported in each case. In all the above studies, the results were compared with literature reports available for other extractant systems including the DGAs, malonamides and CMPO. Compared to other extractant systems, the distribution values for Am(III) was found to increase gradually for DAHyA derivatives with increase in aqueous nitric acid concentration. The nitric acid extraction in DAHyA systems were lesser compared to other extractant systems and hence the CAC values of nitric acid was higher for DOHyA and DDHyA. The bulk extraction capacities of all the three DAHyA derivatives were studied during the extraction of Nd(III) ions from 3 M and 4 M nitric acid solutions. The results showed that stoichiometric extraction of Nd(III) could be achieved in DOHyA and DDHyA systems without the formation of third phase, even when the initial aqueous concentration of metal ion was around 500 mM. Among the three DAHyA derivatives studied, the hexyl derivative, DHHyA was found to be not suitable for liquid-liquid extraction processes; however both DOHyA and DDHyA were identified as promising candidates for modifier free extraction of trivalent metal ions from nitric acid medium.

Chapter 4: Radiolytic stability of *N,N*-di-alkyl-2-hydroxyacetamides

Chapter 4 deals with the evaluation of radiolytic stability of DAHyA extractant systems under gamma irradiation up to a dose of 750 kGy. All the three DAHyA derivatives were irradiated as neat as well as solutions in n-dodecane. The influence of nitric acid on radiolytic degradation was also studied by carrying out the irradiation in the presence of 4 M nitric acid. The Am(III) distribution studies using the irradiated samples revealed that the distribution values decreased with increase in absorbed dose. The samples irradiated in solution showed more radiolytic degradation compared to neat samples. However, the distribution values measured for samples irradiated to the same doses in the presence and absence of 4 M nitric acid did not show considerable difference. These observations confirmed the hydrolytic stability of the DAHyA extractants. The irradiated samples of DOHyA were subjected to stripping studies using 0.1 M and 1 M nitric acid solutions. It was found that radiolytic degradation even under an absorbed dose of 500 kGy did not affect the stripping of Am(III) using 0.1 M and 1 M nitric acid solutions. Measurement of physical properties of irradiated samples revealed that the density of extractant solutions did not change considerably, however the viscosities of the samples showed an increasing trend with increase in absorbed dose. The phase disengagement time recorded for irradiated samples was found to be higher compared to un-irradiated samples during stripping conditions. The results of degradation studies were comparable for all the three DAHyA derivatives. ATR-FTIR spectroscopy and dynamic light scattering were employed for the study of effect of gamma irradiation on 0.4 M DOHyA/ *n*-dodecane system and the results revealed only minimal effects on structure and properties of DOHyA for absorbed dose up to 500 kGy.

Chapter 5: Comparison of *N, N*-di-octyl-2-hydroxyacetamide with other extractant systems using dynamic light scattering and infrared spectroscopy

In this chapter, dynamic light scattering (DLS) has been employed for a comparative evaluation of the aggregation properties of DOHyA system with other extractant systems in the literature including TODGA-DHOA and TODGA-octanol. ATR-FTIR spectroscopy has also been used for explaining the changes in aggregation properties as a function of concentration of nitric acid and metal ions in the aqueous phase. The quantitative extraction of both nitric acid and Nd(III) ions were measured for different extractant systems involved in the study. The metal ion extraction in DOHyA was comparable with DGA systems, while the nitric acid extraction was lower. The average sizes of reverse micellar aggregates formed in DOHyA system were always smaller compared to other extractant systems. Among the two TODGA-modifier systems, the reverse micellar aggregates were bigger in TODGA-octanol system compared to TODGA-DHOA system. The sizes of reverse micellar aggregates formed during extraction from FR-SHLLW were found to be smaller than those formed during the extraction of Nd(III) ions. In all the cases, slow aggregation and formation of smaller aggregates with reduced mutual interactions were found to be responsible for avoiding third phase formation in DOHyA system.

Chapter 6: Counter-current extraction and stripping of metal ions from FR-SHLLW using *N,N*-di-octyl-2-hydroxyacetamide.

This chapter discusses the results of batch studies and mixer-settler studies carried out for the demonstration of modifier-free extraction and stripping of trivalent lanthanides and actinides from FR-SHLLW. A solution of 0.4 M DOHyA in n-dodecane was chosen as extractant for the demonstration run, based on the results of batch studies involving the determination of distribution values of different metal ions in FR-SHLLW during liquid-liquid extraction using this extractant. Studies were done in the presence of different complexing agents in the aqueous phase, so as to minimize the extraction of unwanted fission product elements such as Mo(VI), Zr(IV) and Pd(II). It was proposed to add 0.05 M CyDTA to the feed based on the results of these studies. Batch stripping studies were done on cross-current mode so as to optimize the concentration of nitric acid solution to be used for stripping of loaded metal ions. 0.5 M nitric acid solution was chosen as strippant for the demonstration run based on the results obtained. A 20-stage ejector mixer-settler facility housed in a negative atmosphere glove box was employed for the demonstration runs for both extraction and stripping of metal ions from FR-SHLLW spiked with $^{(152+154)}$Eu and ^{241}Am tracers. The results of the analysis of stage samples from the mixer-settler revealed that quantitative extraction and stripping of Am(III) could be achieved in less than five stages along with all the trivalent lanthanides and Y(III). The co-extraction of Zr(IV) and Pd(II) could be efficiently masked by the addition of CyDTA to the feed. The extraction of Mo(VI), however could not be prevented and also, it was not stripped back during the 20 stages of stripping. The results of both batch studies and counter-current studies for DOHyA have been compared with the results available for other extractant systems in the literature.

Chapter 7: Conclusions and future perspectives

Chapter 7 summarizes the results of the above studies and discusses the scope of future studies using hydroxyacetamide extractants.

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Chapter 1

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INTRODUCTION

1.1 The growing demand on nuclear energy

The human development index (HDI) of a nation depends largely on the per capita availability of electricity to the citizens. In a constantly developing world, the demand of energy increases day by day and the impact of extracting energy from the natural resources reflect in various aspects of climatic changes. It is high time to think about a sustainable development wherein utilization of natural resources would not harm the environment with a high impact. According to the reports of International Energy Agency (IEA France), major world energy resources were petroleum (32.4%), coal (27.3%), natural gas (21.4%), bio fuels (10%) nuclear power (5.7%) and hydroelectric power (2.3%) as of 2010. Among them, the prospect of nuclear energy has remained positive. A total of 72 nuclear reactors were under construction at the beginning of 2014, the highest number in 25 years. The statistical reports of Nuclear Energy Institute (NEI Washington) show that 30 countries worldwide are operating 449 nuclear reactors for electricity generation as of April 2017. About 11% of the worlds' electricity production in the year 2014 was contributed by nuclear power plants [1]. Based on life-cycle emissions intensities for nuclear (20 tonnes CO_2 emission per TWh^{-1}) and coal (>1,000 tonnes CO_2 emission per TWh^{-1}) power, this is an effective saving of at least 2.4 billion tons of carbon dioxide emissions annually, as well as avoidance of a toxic brew of heavy metals, black carbon, sulphates, and numerous other aerosols [2, 3]. Forgoing nuclear power therefore means overlooking an already large global contributor to low carbon electricity, especially given its use as a direct substitute for coal. Currently, nuclear energy has evolved as a mature low carbon technology which has followed a trend towards increased safety levels and power output to benefit from economies of scale.

1.2 Nuclear power programme in India

India has a three-stage nuclear power programme formulated by Homi Jehangir Bhabha in the 1950's to secure the country's long term energy independence, through the use of its limited uranium resources and abundant thorium reserves found in the monazite sands of coastal regions of South India. The ultimate focus of the programme is on enabling the thorium reserves of India to be utilised in meeting the country's energy requirements [4-6]. Thorium is particularly attractive for India, as we have only around 1–2% of the global uranium reserves, but one of the largest shares of global thorium reserves (about 25% of the world's known thorium reserves, 365000 tons approximately) [7]. The first stage of the programme has been successfully running in India by the generation of electricity using pressurized heavy water reactors (PHWR) fuelled by natural uranium (^{238}U along with 0.7% ^{235}U) fuel. As of 2017, India has 22 nuclear reactors in operation in eight nuclear power plants, having an installed capacity of 6780 MWe and producing a total of 30,292.91 GWh of electricity. There are six more reactors are under construction and are expected to generate an additional 4,300 MWe [8]. At present, 3.4 % of the total electricity generation in India is contributed by these nuclear plants. The second stage of the programme is envisaged by the construction of fast breeder reactors (FBR) utilising the fissile plutonium (^{239}Pu) and depleted uranium (^{238}U along with 0.3% ^{235}U) generated in the PHWRs. The first prototype fast breeder reactor (PFBR) of the nation is under construction at Kalpakkam [9]. The energy density of FBRs would be much higher compared to PHWRs and also they would be producing more fissile material than they consume. In these second generation breeder reactors, natural thorium (^{232}Th) would be introduced in a core blanket where it will undergo transmutation with fast neutrons generating another fissile isotope of uranium (^{233}U). The fast breeder reactors in the third stage of our nuclear programme would be fuelled by both ^{233}U and ^{232}Th and during their operation more of fissile ^{233}U would be generated by the transmutation of thorium [10].

Many countries in the world including the U.S, France, China, Russia, Germany and Sweden generate a major share of their total electricity using fast reactors. In India, the fast reactor programme was initiated in 1975 and a fast breeder test reactor (FBTR) fuelled by uranium-plutonium mixed carbide was commissioned in 1985 [11]. The experience gained from the construction, commissioning and operation of FBTR as well as worldwide FBR operational experience have provided us the necessary confidence to launch PFBR of 500 MWe capacity. In addition, it is proposed to construct six more units of 500MWe reactors based on uranium-plutonium mixed oxide (MOX) fuel and twin unit design with improved economy and enhanced safety. Metallic fuel reactors of 1000 MWe capacity, with emphasis on breeding will be deployed in future fast reactors [12, 13].

The Integrated Energy Policy of India forecasts that the installed capacity requirement of electricity generation in 2031-32 would be about ~ 800 GWe against present installed capacity of 164.5 GWe. The projection for installed capacity requirement in 2051-52 is ~ 1350 GWe. In the Indian energy scenario projections for the future, the nuclear power through fast reactors is expected to play an important role of ~ 20% of total installed capacity by 2052 [14-16].

1.3 Significance of closed fuel cycle operation for nuclear energy

In the United States, Canada, Sweden, Finland, Spain and South Africa the spent nuclear fuel is directly sent to storage in geological repositories, isolated from the biosphere. The Yucca mountain nuclear waste repository in the United States is one of the proposed major geolological repositories in the world [17]. This method is usually described as an ‘open fuel cycle’ or ‘once through fuel cycle’ operation and is adopted by countries rich in natural uranium resources. Among them, some other countries such as Finland, Sweden and Canada have designed repositories to permit the future recovery of the spent nuclear fuel, in case it is needed. However, several countries including Japan, Switzerland, France, India, Spain and Germany have chosen to reprocess the spent nuclear fuel. During reprocessing, uranium and plutonium in the spent nuclear fuel is separated from fission products and other actinides either by aqueous (solvent extraction) or by non-aqueous (pyrometallurgical) separation methods. In this way, more than 95% of the spent fuel is recovered and used again in nuclear reactors. In countries with limited uranium resources such as India, it is essential to follow a closed nuclear fuel cycle to sustain the nuclear power programme beyond the availability of fissile ^{235}U. The capital requirement for reprocessing is not small [18], but it offers a way for cleaner energy production and utilisation of other available nuclear materials as discussed in the previous section.

Over the past four decades, nuclear industry has generated 76,340 metric tons of spent fuel in storage worldwide, most of it at reactor sites [19, 20]. The annual spent fuel generated is approximately 2000-2300 tons of heavy metal, with roughly 85% - 90% going into long term storage and less than 15% allocated for reprocessing, but much of it in interim storage [21]. Though only few countries in the world have actively taken up the reprocessing programme as of now, many countries are actively involved in the R & D activities related to the separation of metals from spent nuclear fuel, due to the potential benefits associated with it [22].

1.4 Aqueous reprocessing of spent nuclear fuel

Nuclear reprocessing separates the components of spent nuclear fuel. The reprocessing of nuclear fuel is done either by aqueous or non-aqueous routes. Non-aqueous route of reprocessing also referred to as pyrometallurgical reprocessing or pyroprocessing is usually preferred for metallic fuels. During this process, the spent fuel is dissolved in a suitable electrolytic medium at high temperatures (400^0C- 500^0C) and the individual components are separated by electrodeposition under suitable conditions. Oxide fuels are usually reprocessed by aqueous route after dissolving the spent fuel in a suitable acidic medium. Although HCl, HNO_3 and HF are employed for dissolution, HNO_3 is the most preferred medium due to its less corrosive nature and feasibility of adjustment of the feed acidity by de-nitration. Aqueous reprocessing leads to a cleaner separation of the components of spent fuel compared to pyroprocessing. Availability of a range of extractants and feasibility of batch-wise operation for efficient separation are two important attractions for aqueous reprocessing as compared to pyroprocessing. The aqueous reprocessing of spent nuclear fuel is done in several stages by different processes [23].

Aqueous reprocessing involves liquid-liquid extraction of various components in spent fuel dissolver solution using organic extractants usually dissolved in a non-polar medium such as *n*-dodecane or similar paraffinic hydrocarbons. The extractants employed in liquid–liquid extractions are usually amphiphilic in nature, containing both polar functional groups for metal coordination and non-polar organophilic alkyl moieties for increasing the solubility of extractants in non-polar diluents. Tri-*n*-butyl phosphate (TBP) is one of the most widely used extractants in nuclear reprocessing. **PUREX**, the current method for first stage of aqueous reprocessing, is an acronym standing for **P**lutonium and **U**ranium **R**ecovery by **EX**traction. The PUREX process uses TBP in order to extract uranium and plutonium, independent of each other, from the fission products in spent fuel dissolver solution. The process was invented by Herbert H. Anderson and Larned B. Asprey at the metallurgical Lab at the University of Chicago, as a part of the Manhattan Project under G. T. Seaborg [24]. It is the most developed and widely used process in the nuclear industry at present.

1.4.1 Methods in aqueous reprocessing

Industrially, the liquid-liquid extraction process is usually carried out either in a cross-current mode or counter current mode. In cross- current method of extraction, the aqueous raffinate after the extraction in a single stage is contacted again with a fresh solvent. The first and second extracts are then combined to give a better overall recovery than that could be achieved in a single stage. The number of stages may be added depending on the requirement of recovery of the solute from aqueous medium. Cross-current mode of extraction is advisable whenever the requirement of percentage recovery and purity of the product is high. However, it will result in a mixed extract solution “too dilute” to be processed without further treatment. Also, large volumes of solvents are required, which should be avoided in nuclear industry. Therefore, cross-current mode of extraction is mostly limited to small scale operations in aqueous reprocessing studies.

In counter-current extraction mode [25], the extract from first stage becomes the solvent to the next stage, where the aqueous concentration is higher. The number of successive stages can be added in this way until the solvent becomes saturated, leading to efficient extraction of solutes from aqueous phase. The feed stream enters the n^{th} stage and the extracting solvent stream enters the 1^{st} stage. The raffinate phase is collected from the 1^{st} stage while the extract phase is collected from the n^{th} stage. Using this scheme, the concentration driving force is maintained more or less uniform in all the stages comprising the cascade. Counter-current extraction provides a greater overall recovery in a fewer stages with minimum phase ratio for a given degree of extraction and can yield both high recoveries and concentrated extracts. Equipment used for counter-current extraction varies widely. Functional requirements of such liquid-liquid extractors are to develop a sufficient interfacial area, turbulence to promote mass transfer and to facilitate counter-current flow of two phases without excessive entrainment. Industrial extractors are mainly classified into two types, namely, stage-wise and differential extractors [26]. The design of stage-wise extractors allows equilibrium conditions in all the stages of extraction. Mixer-settler extractors and centrifugal extractors are the leading examples of this category. In differential extractors, equilibrium is never achieved between the aqueous and organic phases in any part of the stage. Liquid-pulsed column is an example of a differential extractor. In nuclear reprocessing plants, all the three types of extractors are used depending on the requirements. The differences, advantages and limitations of the above three extractors are briefly detailed below.

1.4.1 i) Mixer-settler

Mixer-settlers are mostly individual stage units, simple to construct & operate and also cost effective. Effective phase dispersion is usually achieved in a mixer settler by impellers or by air pulsing. An ejector mixer-settler developed by Koganti et al. [28, 29] was employed in the present study. They can handle wide range of flow ratios and liquids with high viscosity. Mixer-settlers have the advantages of low headroom, high efficiency, many stages, reliable scale-up, low maintenance etc. The disadvantages are the problems associated with large hold-up volume, large floor area, high solvent inventory, inter-stage pumping (which is required in some designs), large residence time etc.

1.4.1 ii) Centrifugal Extractor (CE)

Centrifugal extractors are small in size, have lesser hold-up volume for a given throughput and operate with low inventory of solvents. CE have shorter contact time (5-10 sec) compared to mixer-settlers and liquid pulsed columns, making it useful for spent fuel reprocessing where radiation doses are expected to be higher, especially for fast reactor fuel reprocessing. CE can handle systems that have smaller density difference between organic and aqueous phases. However, CEs have higher initial cost, higher operating cost, higher maintenance cost etc. Koganti et al. developed remotely maintainable centrifugal contactors of capacities varying from 5 to 1000 L/h, employing a unique liquid seal [27].

1.4.1 iii) Liquid pulsed column (LPC)

These are differential extractors simple to construct and operate. LPC provides high interfacial area and high degree of turbulence. LPC has a contact time of about 1/3 to 1/2 that of mixer-settler resulting in lesser solvent damage. LPC has low solvent inventory, short residence time, high efficiency and low maintenance. Contact time of LPC lies between that of mixer-settler and centrifugal extractors. LPC has limited throughput and cannot handle wide flow ratios. Liquid pulsed columns are also largely used in nuclear fuel reprocessing for specific applications where required throughput is less [27].

1.5 The back-end of closed fuel cycle:

The major challenges in the field of nuclear energy are associated with the proper treatment of spent nuclear fuel as well as with ensuring of proper safety measures while handling radioactive materials. Table-1 gives the compositions of the spent nuclear fuel from a thermal reactor and fast reactor [30].

Table 1 Elemental compositions of spent nuclear fuel from thermal and fast reactors. The amounts are expressed in grams per ton of fuel [30].

Type of fuel	**LWR-UOX, 60 GWd/t, 4.5 wt.% ^{235}U, 5 years cooling**	**FBR-MOX, 120 GWd/t, 30 wt.% ^{239}Pu, 5 years cooling**
Fission products (g/t of U + Pu)		
Kr	607	770
Sr	1370	1536
Y	779	816
Zr	6290	9356
Mo	5990	11008
Ru	4130	10900
Rh	739	3235
Pd	2820	8624
Te	870	2427
I	383	1070
Xe	9650	16455
Cs	4560	13619
Ba	3110	5477
La	2150	4094
Ce	4200	7497
Pr	1970	3549
Nd	7200	12562
Sm	582	2664
Actinides (g/t of U + Pu)		
U	923,339	633,910
Pu	13000	236,689
Np	889	318
Am	928	4426
Cm	193	86.2

From the table, it is clear that the spent nuclear fuel is composed primarily of the largely unconsumed remains of the original fuel (typically ^{238}U and other isotopes of uranium). In addition there are other actinides, created when one isotope is transmuted into another by a reaction involving neutron capture, ^{239}Pu is the leading example. There may be some amounts of fission products which can be any of the elements in the periodic table having mass numbers between 80 and 160. It is estimated that after the extraction of uranium and plutonium from the spent nuclear fuel, remaining fission products and minor actinides (americium, curium and neptunium) constitute 5.2% and 0.2% respectively for thermal reactor fuel, while the amounts are 11.3% and 0.5% respectively for fast reactor fuel.

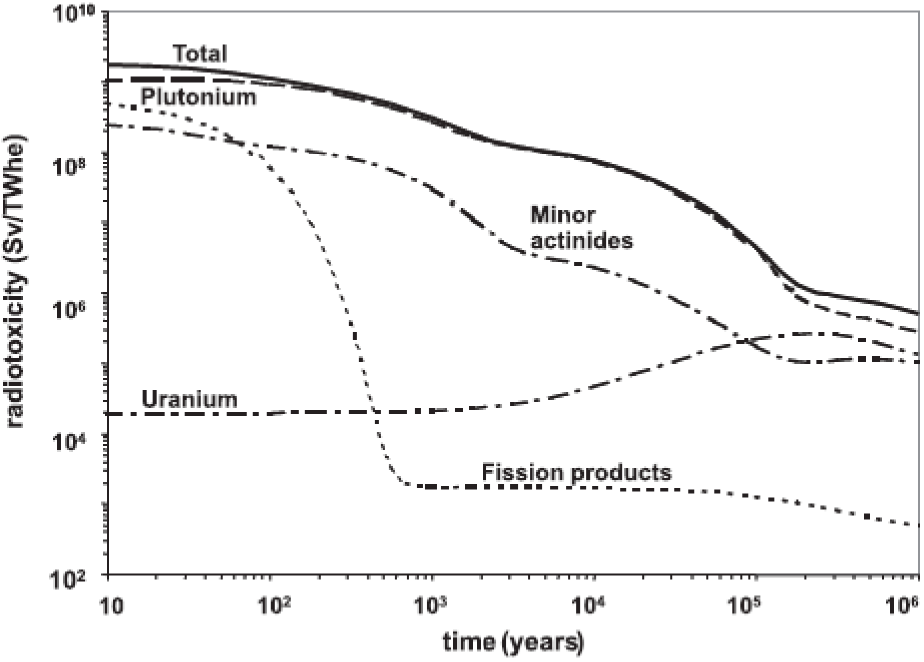


Figure 1.1: Relative radio-toxicity of the different components in spent nuclear fuel from a light water reactor irradiated to 33 GWd/t of initial uranium with respect to the radio-toxicity of the corresponding uranium ore [32].

The raffinate from the PUREX cycle containing minor actinides, fission products, activation products and process/structural materials is concentrated to obtain the high-level liquid waste (HLLW). The current strategy is to immobilize this HLLW in glass/ceramic matrices prior to their disposal in deep geological repositories [31]. Figure 1.1 shows how the relative radio-toxicity of the different components of spent nuclear fuel varies over time [32]. The major share of the radiotoxicity of spent fuel is due to plutonium (^{239}Pu, $t_{1/2}$ ~ 24065 yrs). If the plutonium is removed, the minor actinides and some of the fission products contribute maximum to the radiotoxicity. Within a few hundreds of years after spent fuel is discharged, the radio-toxicity due to medium-lived fission products such as caesium and strontium (^{137}Cs, $t_{1/2}$: 30.2 yrs, ^{90}Sr, $t_{1/2}$: 28.8 yrs) gradually gets removed and thereafter, the long term radiotoxicity of spent fuel is mainly due to the minor actinides. There are some of the long lived fission products in HLLW such as ^{99}Tc ($t_{1/2}$ ~ 2.11*10^{5} yrs), ^{135}Cs ($t_{1/2}$ ~ 2.3*10^{6} yrs), ^{107}Pd ($t_{1/2}$ ~ 6.5*10^{6} yrs) and ^{93}Zr ($t_{1/2}$ ~ 1.53*10^{6} yrs) which are beta emitters and hence considered as less radiotoxic. The minor actinides are some of the long-lived alpha active radioisotopes of americium, curium and neptunium including ^{241}Am ($t_{1/2}$ ~ 432.2 yrs), ^{243}Am ($t_{1/2}$ ~ 7380 yrs), ^{245}Cm ($t_{1/2}$ ~ 8500 yrs) and ^{237}Np ($t_{1/2}$ ~ 2.14*10^{6} yrs). These are termed as ‘minor actinides’ as their concentration in the spent fuel is very small (0.2%-0.5%), and yet they are significant contributors to the total alpha activity and hence the radiological toxicity of HLLW [33].

Some of the nuclear reactions leading to the formation of minor actinides are given below:

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

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

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

$${}^{239}\mathrm{Np}(\mathrm{n},\gamma)\,{}^{240}\mathrm{Np}\xrightarrow[62\ \mathrm{min}]{\beta}{}^{240}\mathrm{Pu}(\mathrm{n},\gamma)\,{}^{241}\mathrm{Pu}$$

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

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

$${}^{243}\mathrm{Pu}\xrightarrow{\beta}{}^{243}\mathrm{Am}\ (\mathrm{n},\gamma)\,{}^{244}\mathrm{Am}\xrightarrow{\beta}{}^{244}\mathrm{Cm}\ (\mathrm{n},\gamma)\,{}^{24\cdot}\ \mathrm{Cm}$$

Since the half lives of the minor actinides concerned range from a few hundred to millions of years, the surveillance of this high active vitrified waste is rather difficult. In order to reduce this long surveillance period, the concept of partitioning and transmutation (P&T) is being recommended. This involves the complete separation of minor actinides from HLLW and their transmutation into elements having shorter half lives in accelerator driven systems (ADS) or fast reactors [34, 35].

1.6 Minor actinide partitioning

The success of P&T technology depends on the efficient separation of minor actinides. Among the minor actinides, neptunium exists in spent fuel dissolver solution showing different oxidation states varying from +4 to +6. Advanced PUREX process flow sheets are being designed, optimizing the recovery of neptunium along with uranium and plutonium in the spent nuclear fuel [36]. Therefore, the minor actinides present in the HLLW are only the long-lived alpha emitting isotopes of americium and curium. The solution chemistry of Am^{3+} and Cm^{3+} resemble the solution chemistry of trivalent lanthanides, and hence any extractants or separation processes aimed for the separation of these trivalent actinides co-extracts the trivalent lanthanides in HLLW, unless they are extremely selective. The neutron absorption cross-sections of Ln(III) elements under the conditions of fast neutron flux employed in accelerator driven systems would be so high that the effective transmutation of trivalent actinides would be difficult in the presence of lanthanides [34]. Therefore, the partitioning of minor actinides would require a separation process in two stages, the first stage involving the group separation of trivalent lanthanides & actinides and the second stage involving the mutual separation of actinides and lanthanides. Recent studies have also been directed towards the development of single-stage separation methods by suitable combination of extractants [37].

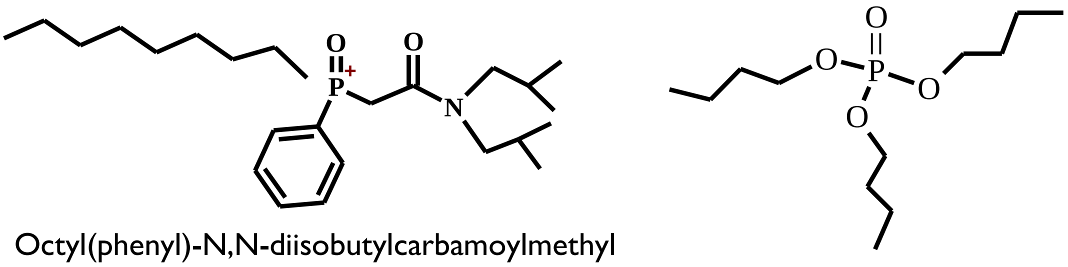
The choice of extractants employed for separation processes depends on a number of factors including physical, chemical and economical aspects. To be used for nuclear reprocessing, the criteria are more stringent compared to other industrial applications, as the systems should be stable in a high radiation field. Some of the important points in this regard may be summarized in the following [81]:

- Minimal solubility in water and high solubility in paraffinic solvents such as *n*-dodecane
- Low toxicity, low volatility, non- flammability and incinerability.
- Optimum viscosity and interfacial tension of solutions.
- Good distribution values for extraction from 3-4 M nitric acid medium.
- Good selectivity for the metal ions of interest, less extraction of unwanted species.
- Good extraction capacity without third phase formation
- Ease of stripping of metal ions after extraction i.e using moderately acidic solutions (˜1 M) and without the use of complexing agents.
- Good hydrolytic and radiolytic stability
- Ease of synthesis and availability at a reasonable cost

It is the driving force for all the researchers in this field to identify better extractant systems without compromising any of the above points. Monodentate extractants such as tri-alkyl phosphates (eg TBP) and long chain monoamides have been proposed for the extraction of metal ions which exists in nitric acid solutions with oxidation states +4 or higher (eg U(VI), Pu(IV)). The literature survey on the studies related to trivalent actinide separation indicates that trivalent actinides require strong field bidentate or tridendate ligands in organic phase for efficient co-ordination and separation from the HLLW. There are a number of extractant systems for minor actinide partitioning proposed by various research groups all over the world from time to time [38, 39]. Some of the important systems available in the literature are described in the following.

1.6.1 The carbamoylmethylphosphonates (CMP) and carbamoylmethylphosphineoxides (CMPO)

The ability of bi-dentate carbamoylmethylphosphonate compounds to extract trivalent americium and lanthanides was first reported by T. H Siddal in 1964 [40]. Thereafter, several groups in the United States and many other countries have synthesized and studied –CH_2- bridged carbamoylmethylphosphonates for extraction of Am(III) from HNO_3 and HCl media [41]. Later carbamoylmethylphosphine oxides were identified as better extractants in this category, due to the more basic nature of phosphine oxide functional group. The extraction properties and phase compatibility of CMPO was greatly influenced by the alkyl chains in the molecule.



Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphineoxide (CMPO)

Tri-n-butylphosphate (TBP)

Figure 1.2: Structures of CMPO and TBP

Among the various structures, octyl(phenyl)-*N*,*N*-di-isobutylcarbamoylmethyl phosphineoxide (figure 1.2) was chosen for detailed studies for actinide extraction [42]. A mixture of 0.2 M CMPO and 1.2 M TBP in paraffinic hydrocarbon was used for the extraction of actinides (Np, Am, Cm, Pu, U), fission products (lanthanides, Zr, Ru, Pd) and Fe from nitric acid medium. High distribution ratio (D) values of tri-, tetra-, and hexavalent actinides from solutions of moderate acid concentration and good selectivity over most fission products were the key feature of this extractant which made it a suitable candidate for actinide partitioning from HLW. The Trans Uranic EXtraction process (TRUEX) employing CMPO-TBP mixture in paraffinic hydrocarbon was developed by the Argonne National Laboratory, USA and later demonstrated using genuine waste solution from the Hanford site [43,44]. The most extensive pilot-scale testing of the TRUEX process was done at the Idaho National Engineering and Environmental Laboratory (INEEL).

At Karlsruhe, Germany, actinide partitioning was demonstrated with the reprocessing raffinate of light water reactor (LWR) fuels using TRUEX solvent [45]. A mixture of 0.2 M CMPO and 1.4 M TBP was used as the extractant and stripping was carried out using 0.05 M nitric acid solution in the presence of inorganic complexants. The results showed good extraction, but poor stripping of trivalent actinides. Russians developed a TRU extraction process based on a somewhat simpler derivative of CMPO (diphenyl-*N*,*N*-di-*n*-butyl CMPO) employing a fluoroether diluent (Fluoropol-732). This process behaved similar to the TRUEX process in terms of its efficiency for actinide extraction, showed little tendency towards third-phase formation, and avoided the interferences caused by degradation of TBP. However, formation of corrosive products due to the degradation of diluent was a serious draw-back of this process [46]. At Japan's Power Reactor and Nuclear Fuel Development Corporation, batch and counter–current runs with real high–active raffinate from FBR spent fuel reprocessing was carried out using 0.2 M CMPO + 1.2 M TBP in *n*-dodecane [47, 48]. Oxalic acid was added in the feed and scrubbing solutions to improve decontamination of Ru, Zr and Mo. In India, basic solvent extraction data was generated for the extraction of actinides and few fission / corrosion products and structural elements using TRUEX solvent [49-53]. Recently, the TRUEX process was demonstrated with genuine fast reactor fuel solution in hot cells [54].

The major draw-backs associated with the TRUEX process, as evidenced from all the above studies were:

1) Early third phase formation of CMPO in non-polar diluents during extraction conditions necessitated the use of TBP as phase modifier in good amounts.

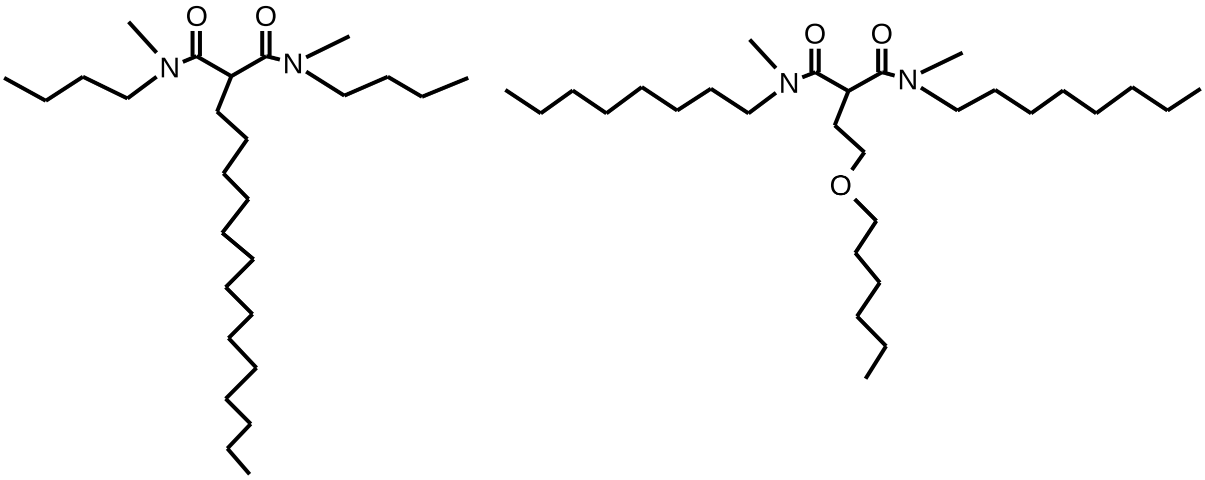
2) Degradation products of both TBP and CMPO caused problems during stripping and also during the re-cycling of solvent [55-59].

3) Either very low aqueous acidities or good amounts of inorganic or organic complexing agents were required during stripping of extracted metal ions, which increased the salt content of the product [51, 52].

4) As both CMPO and TBP contained phosphorus, the incineration of the spent solvent generated solid phosphate residue, which had to be treated as active waste.

1.6.2 Alkyl and alkoxy substituted malonamides

Amide based extractants are preferred over phosphorous based extractants for applications related to nuclear reprocessing, obviously due to the total incinerability of amides [60, 61]. Also, the degradation products generated by amide extractants have been shown to be innocuous (non-interfering) under the conditions of both extraction and stripping. Substituted malonamides were proposed for minor actinide partitioning in the so called DIAMEX (DIAmide EXtraction) process. Extensive studies were carried out during last two decades on this class of extractants under the programme commonly referred to as "EUROPART" [62-67]. Amongst several malonamides studied, *N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA) and *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy malonamide (DMDOHEMA) were found to be promising extractants (figure 1.3).



N,N'-Dibutyl-N,N'-dimethyl
tetradecylmalonamide
(DBDMTDMA)

N,N'-Dimethyl-N,N'-di-octyl
hexylethoxymalonamide
(DMDOHEMA)

Figure 1.3: Structures of malonamides

The relative extractability of the actinides by diamides followed the order Pu(IV) > U(VI) > Am(III), while fission product ions such as zirconium, technitium, molybdenum, rhuthenium, palladium and iron also were significantly extracted in the acidity range of 3– 4 M HNO_3.Initially, DMDBTDMA was proposed as the reference molecule for DIAMEX process and HOT demonstration of DIAMEX process was carried out at Karlsruhe, Germany using 0.5 M DMDBTDMA in NPH [62, 63]. It was found that 6 extraction stages were sufficient to achieve quantitative extraction of lanthanides and actinides. Co-extraction of molybdenum and zirconium was prevented by a scrubbing cycle using oxalic acid. Salient feature of this process was that the back extraction proved to be very efficient, yielding more than 99.9% recovery of both the lanthanides and the actinides in 4 stages. Authors reported the need for process optimization to prevent co-extraction of technetium, ruthenium, palladium and neptunium which were accumulated in the product during back-extraction. The use of a phase modifier was proposed for process applications with more concentrated waste solutions [63].

Later, DMDOHEMA was selected as the new reference molecule for the DIAMEX process, because: (i) introduction of hexyl ethoxy group on the central alkyl chain slightly enhanced the affinity for trivalent actinides and lanthanides, (ii) presence of bulky alkyl group on the amide group increased the lipophilicity and, therefore, limited the third phase phenomena, and (iii) shortening of the length of the alkyl chain at centre carbon atom shortened the chain length of the degradation products and, therefore, facilitated their elimination by alkaline scrubbing [65]. A hot demonstration of the DIAMEX process with a genuine high-level PUREX raffinate (45 GWd/Te) using 1 M DMDOHEMA in NPH was reported at ITU, Karlsruhe [66]. It was demonstrated that quantitative extraction of lanthanides and actinides was achieved in less number of stages compared to DMDBTDMA. Co-extraction of Mo and Zr, as well as that of Pd, was efficiently prevented using oxalic acid and HEDTA scrubbing, respectively. However, Tc, Y, and to some extent Ru, were co-extracted. The back-extraction of Am and Cm proved to be very efficient, yielding more than 99.9% recovery in 4 stages.

Berthon et al. [67] reported the radiolytic and hydrolytic stability of malonamides using potentiometric titrations and gas chromatography techniques. The radiolytic stability studies showed that the concentration of the malonamide extractants decreased strongly with the irradiation dose. However, effect of HNO_3 on the radiolytic stability of malonamides was not significant. The acids and secondary amines formed during the degradation, however, did not interfere during stripping and could be easily removed by acidic and basic solvent washings for re-cycling of the spent solvent.

1.6.3 Diglycolamides

Due to the relatively weak affinity of the carbonyl groups of malonamide for the actinide / lanthanide ions, the DIAMEX process required high concentration of the extractant (0.5–1 M) solvent for actinide partitioning, which was responsible for the co-extraction of many unwanted fission products. During the last few years, diglycolamides (DGA), developed at the Japan Atomic Energy Research Institute (JAERI) have caught the attention of radiochemists all around particularly in the countries like Japan, Germany and India. DGA based extractants are capable of extracting trivalent actinides from moderately acidic feeds (3 – 4 M HNO_3), with very high distribution values [68-71]. Among different derivatives of DGAs, tetraoctyl diglycolamide (TODGA) was found to be the most promising with reference to its free solubility in *n*-dodecane and significantly high distribution coefficient values for trivalent actinides [72, 73]. Extensive solvent extraction studies with TODGA have been pursued at Japan, India and Germany [74–80].

The use of TODGA for extraction processes required the use of a phase modifier [74]. Initial studies from Germany reported the use of TBP as phase modifier. However, TBP was later replaced with CHON modifiers such as DHOA (*N*,*N*-di-hexyloctanamide) and long chain alcohols. The TODGA process using 1-octanol as phase modifier was demonstrated recently at ITU with genuine PUREX raffinate [80]. Promising results were reported from India during counter-current extraction runs using TODGA-DHOA systems and TODGA-decanol systems [79, 85]. The main features identified in these studies may be summarized in the following:

1) All the trivalent lanthanides and actinides were quantitatively extracted in 3-4 stages.

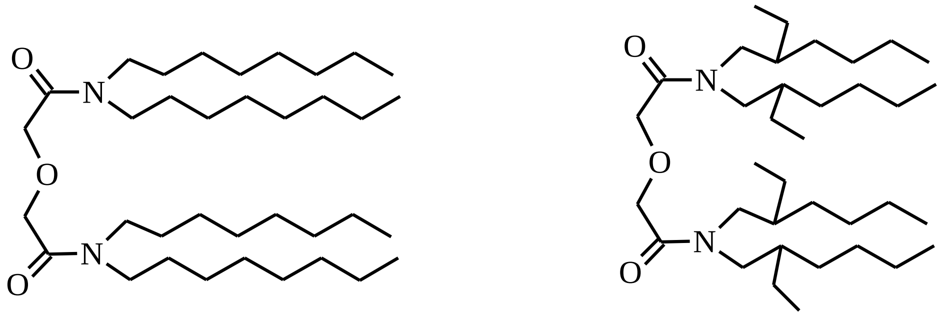
2) Quantitative stripping required more number of stages even with 0.01 M nitric acid, whenever TBP or DHOA was used as modifier [78, 79]. However, use of long chain alcohols such as octanol or decanol resulted in comparatively less number of stages.

3) The high extraction efficiency of TODGA lead to the significant co-extraction of troublesome fission products such as Zr(IV), Pd(II), Mo(VI) and Ru(III) from HLLW. For minimizing the co-extraction of these elements, suitable complexing agents were to be added along with the feed or suitable scrubbing cycles were to be introduced during the extraction process [77, 135].

4) The hydrolytic degradation of TODGA was negligible, even after keeping TODGA solutions in contact with 3 M HNO_3 for 3 months [96].

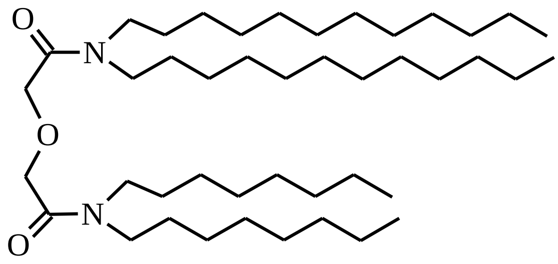
5) The radiolytic degradation studies showed only minimal changes in the extraction and stripping behaviour of TODGA even after irradiating up to 600 kGy dose [96, 106].

Actinide partitioning studies have been reported with other diglycolamide extractants such as *N,N,N',N'*-tetra (bis)-2-ethylhexyldiglycolamide (TEHDGA) which is a branched chain isomer of TODGA [81-84]. Engineering scale studies on the extraction of metal ions from real radioactive waste solutions using TEHDGA have been reported by BARC, India [84]. The stripping of metal ions was found to be better with TEHDGA as compared to TODGA. Previous studies from our group reported the synthesis of *N,N*-di-2-ethylhexyl-*N',N'*-dioctyl diglycolamide (DEHDODGA), which combined the alkyl chains of both TODGA and TEHDGA in a single molecule [87]. However, the use of TEHDGA or DEHDODGA also required a phase modifier [94]. Unsymmetrical diglycolamides which combined octyl chains and decyl or dodecyl chains in a single molecule were proved to be promising candidates showing good distribution values for extraction of Am(III) with better third phase limits compared to TODGA [88-90]. Studies with *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D^3DODGA) showed that this extractant can be employed for the extraction of metal ions from FR-SHLLW without the use of a phase modifier [89, 108]. The structures of some of the important diglycolamides are shown in figure 1.4.



N,N, N', N'-Tetraoctyldiglycolamide
(TODGA)

N,N, N', N'-Tetraethylhexyldiglycolamide
(TEHDGA)



N,N-Didodecyl-*N', N'*-dioctyldiglycolamide
(D^3DODGA)

Figure 1.4: Structures of diglycolamides

1.7 Radiolytic stability

It is important to measure the radiolytic degradation of extractant systems before their deployment for the treatment of spent fuel solutions from the reactor [101]. The radiation dose during actinide partitioning from actual HLLW can be estimated with the knowledge of (a) the burn-up and cooling of spent fuel, (b) volume reduction from PUREX raffinate to HLLW, (c) concentrations, and energies of the beta/gamma emitters, and (d) the contact time during each cycle of actinide partitioning. Typically, the radiation dose in HLLW solutions emanating from Pressurized Heavy Water Reactor (PHWR; burn up 7000 MWD/Te) and Pressurized Water Reactor (PWR; burn up 33000 MWD/Te) with 3 years' cooling are expected to be ˜20 kGy and ˜100 kGy during the process conditions of liquid-liquid extraction [39]. Fast reactor high level liquid waste solutions (FR-HLLW; 80000 MWD/Te) are expected to generate a radiation dose not more than ˜ 250 kGy. The solvent systems in contact with such highly radioactive solutions must be robust towards radiolytic degradation in an irradiated mixed-organic/aqueous acidic environment with the formation of only benign products.

A study of irradiation in aqueous reprocessing systems should take in to consideration of the diluents, presence of extracted water, nitric acid and nature of extractants. Their direct radiolysis results in the formation of electronically excited states, free radicals, and ions in spurs along the track of the incident particle. These produced reactive species may then undergo recombination to recreate their parent compound or other molecular species, or they may diffuse away from their point of origin to react with solutes. The probability of recombination or diffusion depends on the linear energy transfer (LET) of the incident particle, which is much higher for alpha radiation as compared to gamma and beta radiations. Massive, highly charged, alpha particles have short ranges and therefore deposit energy in closely-spaced overlapping spurs. This results in high localized concentrations of reactive species, many of which undergo recombination before they can diffuse into the bulk solution. This results in higher yields of molecular species and lower yields of radicals. On the other hand, the carbon centred radicals, hydrogen atoms and electrons formed by gamma irradiation are carried off to the bulk of the solution. These activated species attack more of the solvent molecules resulting in more amount of radiolytic damage [99]. This leads to undesirable effects such as a decrease in the selectivity of solvents and poorer phase separation due to the formation of degradation products [96, 102-105].

Radiolytic degradation studies are usually performed under irradiation of gamma rays, with subsequent analysis of the degradation products by chromatographic techniques [99, 100, 110]. The degradation of the system is expressed by its G-value which is defined in units of number of molecules degraded by the absorption of 100 eV of energy [96, 99]. The impact of irradiation can also be assessed by methods such as measurement of the decrease in distribution values, alterations in viscosity and phase disengagement time [102-107].

1.8 Third phase formation during liquid-liquid extraction

Among the problems to be solved in designing a liquid-liquid extraction process, third phase formation is considered as most crucial, especially during nuclear reprocessing applications. Evidently, it is the undesirable formation of a new phase in between the aqueous and organic phases, where most of the extractant, metal ions and significant amount of nitric acid get accumulated. This happens at high loadings of nitric acid and metal ions, when the extracted metal solvate complex becomes less soluble in the organic phase. The limits of third phase formation for a given extractant vary depending on polarity of functional groups present. Availability of more polar groups in a single molecule induces the immiscibility of extracted metal solvates even with low amounts of extracted metal ions. It is usually observed that, long alkyl chains in the extractants help to increase the third phase limits during extraction [88]. It is obviously due to the better stabilization of the extracted complexes in non-polar diluents due to the increased non-polar nature of extractants.

Normally, third phase formation is investigated empirically by measurement of third phase boundaries according to various chemical and physical parameters, such as the concentrations of extracted solutes and extractant, type of diluents, temperature etc. The maximum aqueous concentration of nitric acid or metal ion in aqueous phase in equilibrium with the extractant, without third phase formation, is usually described as the 'critical aqueous concentration' (CAC). Similarly, the maximum concentration of extracted nitric acid or metal ions in the organic phase, without forming a third phase is denoted as the 'limiting organic concentration' (LOC). The formation of third phase can be identified by monitoring the changes in concentration of extracted metal ions and or nitric acid in the organic phase as a function of aqueous concentration of metal ions and or nitric acid [91-94]. At the point of third phase formation, a sudden drop in the concentration of organic phase is observed. During process conditions, the formation of a third phase is indicated by a simultaneous drop in concentrations of both aqueous and organic outlets under the same feed conditions. During the extraction of fissile metal ions, such an accumulation of metal may lead to criticality hazards. Therefore, the study of third phase formation plays a major role in designing the liquid-liquid extraction processes for nuclear reprocessing applications.

Thus it is equally important to have better distribution values and high LOC and CAC values for a good extractant. An extractant with very high distribution values for trivalent metal ions (e.g TODGA) forms third phase easily with nitric acid metal ions. The use of a phase modifier is essential for process applications involving such extractants. As discussed, TBP was employed as phase modifier in CMPO systems. For TODGA and TEHDGA systems, studies have been reported with a number of phase modifiers including TBP, DHOA, octanol, decanol and isodecanol [74, 83, 106]. Addition of such phase modifiers to organic phase usually increases the extraction of unwanted metal ion present in HLLW and decreases the selectivity of trivalent actinide. The chemical and radiolytic degradation of modifier also complicates the recovery of extracted actinides and burdens the management of spent organic waste. Studies have shown that the use of TBP and DHOA also increases the extraction of nitric acid which adds to the difficulty in back extraction of metal ions in such systems [78, 79]. The use of long chain alcohols as phase modifier did not contribute towards nitric acid extraction; however, they have been reported to affect the radiation stability of extractant systems at high radiation fields [103, 107]. It is always desirable to choose an extractant which resists third phase formation without the assistance of a phase modifier. Diamide extractants such as DMDOHEMA did not form third phase, however showed much lower distribution values, which necessitated the use of high concentrations of extractants [63, 66]. A modifier free extractant system showing sufficiently good distribution values for target metal ions at reasonable concentration levels would be an ideal choice for extraction processes.

1.9 Aggregation of extractants in non-polar diluents

The extractants, used to complex and impart organic phase solubility to the metal ions are generally surface-active amphiphiles, containing both polar metal binding functionalities and non-polar moieties such as alkyl groups which are required to make the resulting metal-ligand complexes organophilic. The chemical and thermodynamic models used to describe biphasic metal extraction systems are often approached from the standpoint of metal ion coordination chemistry, generally considering inter-ligand interactions as perturbations to the metal-ligand complexation and extraction equilibria. The studies of metal ion-extractant complexes in organic solvents sometimes present unusual features that are difficult to reconcile within the framework of the traditional coordination chemistry interpretations of solvent extraction behaviour. Because of the amphiphilic nature of the extractant molecules, applications of approaches that combine the concepts of coordination chemistry and surfactant chemistry have been fruitful for understanding the chemical species and driving forces in such cases [120].

For example, in diglycolamide systems, measurements based on simple equilibrium thermodynamics suggest the participation of more number of extractant molecules in the extraction of An(III) or Ln(III) nitrates, which is more than that can be reasonably accommodated in the inner coordination sphere of these cations. Also, the nature of extracted metal complexes changes with the change in nitric acid concentration in the aqueous phase. These observations are difficult to explain in terms of the concepts of classical co-ordination theory. They are explained on the basis of self assembling of extractants in non-polar diluents forming reverse micelles having a polar core with their polar functional groups, surrounded by the non-polar tails of alkyl groups. The polar cores co-extract water, nitric acid and metal ions and interact mainly via dispersion forces. These polar cores interact attractively through the non-polar diluents due to van der Waals attractions, while protruding chains sterically stabilize the aggregates [119]. The interactive forces between the reverse micellar aggregates is the sum of these two contributions, which can be calculated using Baxter’s sticky hard sphere approximation[114,115].

Aggregation studies of the extractants help to quantify the interactive forces between the aggregates in a given extractant system. These attractive interactions increase continuously with increase in concentration of extracted nitric acid and metal ions. When the concentration of extracted species in the organic phase is more than LOC, the attractive forces between the aggregates lead to a de-mixing of organic phase into a heavy concentrated reverse micellar phase containing most of the extractant, extracted species & smaller quantity of diluent, and a second lighter organic phase consisting mostly of diluents. This organic phase splitting is described as "third phase formation". In view of the similarity of these phase separations with the liquification of the Van der Waals gases in the presence of an attractive inter-particle interaction; they have been termed in the literature as gas–liquid type phase transition modelled in the framework of Baxter adhesive hard sphere theory [118].

Interfacial tensiometry is often used to determine the critical micellar concentration (CMC) in micellar systems [119, 120]. Theoretical calculations based on Small Angle X-ray and Neutron Scattering (SAXS and SANS) techniques have been successfully used for determining the size of reverse micellar aggregates and interaction parameters between these aggregates in extractant systems [119-121]. Dynamic light scattering (DLS) and viscometry based techniques are useful in measuring the size of reverse micellar aggregates and micellar volume fractions for deriving information on the aggregation behaviour extractants under different conditions [124-126]. Co-relation of such experimental observations with theoretical calculations and other experimental techniques such as FT-IR spectroscopy has been useful in studying the aggregation phenomena of extractant systems [119-124, 128]. The insights provided by the above studies have become useful in designing extractant systems with better performance.

1.9.1 The dynamic light scattering (DLS) technique

The dynamic light scattering technique is typically used for measuring the size of particles in sub-micron region, dispersed in a liquid. The reverse micellar aggregates of extractants in non-polar medium can be identified and their apparent hydrodynamic diameter can be measured using DLS. These reverse micelles undergo brownian motion as a result of their interactions with each other. In DLS, the sample is illuminated by a monochromatic, coherent beam of light and the fluctuations in the intensity of scattered light due to brownian motion of the particles is measured as a function of time. The correlator used in the instrument generates a correlation function for the scattered intensity, $G(\tau)$ defined as,

$$G(\tau) = <I(t).I(t+\tau)/ I(t)^2> \qquad (1)$$

where τ is the time difference of the correlator. Assuming a large number of monodisperse particles in brownian motion, the correlation function is an exponential decaying function of the correlator time delay τ and is determined by the cumulant analysis. It is related to the translational diffusion coefficient of the particles, D by the relation,

$$G(\tau) = A[\ 1+ B \exp(-2\ Dq^2\tau)] \qquad (2)$$

where A is the baseline correction factor, B is the intercept of the correlation function and q is the scattering vector which is constant for a given observation angle and wavelength of light. Now, by assuming the reverse micelles as hard spheres, their hydrodynamic diameter d_H can be calculated by substituting the value of translational diffusion coefficient, D in the Stokes-Einstein equation,

$$d_H = k_BT/(3\pi\eta D) \qquad (3)$$

where, k_B is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the dispersion medium [129].

1.10 Scope of the present work

Among the various extractant systems studied for group separation of trivalent actinides and lanthanides from nitric acid medium, diglycolamides such as TODGA and D^3DODGA have been identified as promising candidates. However, the diglycolamides require very low aqueous acidities (< 0.1M HNO_3) for back extraction, which is disadvantageous in view of phase disengagement problems. The use of TODGA requires a phase modifier so as to avoid third phase formation during extraction from high level waste solutions. The malonamide extractant systems show better back extraction properties and modifier-free extraction as compared to diglycolamides; however the distribution values of various metal ions are smaller in these systems.

Critical evaluation of the structure of DGA extractants show that the property of extraordinary extraction of trivalent metal ions in diglycolamides is essentially due to the presence of etheric oxygen sandwiched between a couple of amidic sites. Due to the presence of these two amidic sites, the polarity of the diglycolamide seems to be significantly high, and perhaps this factor leads to poor compatibility of its metal-solvate in a nuclear diluent, *n*-dodecane leading to third phase formation. Moreover, the presence of more number of polar groups increases the extraction of nitric acid during the extraction of metal ions leading to difficulties during back extraction. The third phase formation tendency and extraction of nitric acid can be minimized by redesigning the structure of DGA with a single amidic functionality and retaining the etheric oxygen at the required position in the structure.

Accordingly, a new class of extractants, *N*, *N*-di-alkyl-2-hydroxyacetamides (DAHyA) with a single amide group and hydroxyl group at alpha position (figure 1.5) were chosen for the present study as alternative extractants for minor actinide partitioning devoid of the complications of DGAs.

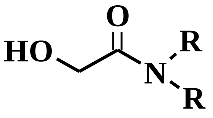


Figure 1.5: General structure of *N,N*-di-alkyl-2-hydroxyacetamide

A series of DAHyA derivatives with different alkyl side chains were synthesized during the present study and evaluated their use as extractants for the separation of Am (III) from nitric acid medium. Based on the preliminary investigations on various alkyl substituted hydroxyacetamides, *N*,*N*-di-octyl-2- hydroxyacetamide (DOHyA) was chosen for further studies on extraction and stripping of metal ions from FR-SHLLW. The aggregation behaviour of DOHyA was studied using dynamic light scattering spectroscopy and the results compared with other diglycolamide systems under loading of nitric acid and metal ions. The results were co-related with ATR-FTIR measurements under the same conditions, probing the better third phase formation behaviour of DOHyA compared to others.

Chapter 2

EXPERIMENTAL

2

This chapter contains a description of the materials, methods and conditions used in the present study. The instrumental facilities for different analytical techniques employed in the study such as dynamic light scattering, gamma counting and atomic spectrometry are briefly discussed. The procedures involved in the preparation of reagents and steps in the organic synthesis of extractants are mentioned. The equipments and methods used during liquid-liquid extraction studies employed throughout the studies have been described in detail. The results of characterisation of synthesized compounds by FT-IR and NMR techniques are also presented. All the experiments in the present study were conducted at 298 K.

2.1 Solvents and reagents

2.1.1 Solvents

Petroleum ether (L.R grade, boiling range: 60^0C-80^0C) procured from M/s Impex chemical corporation, Mumbai was purified by distillation before use. A. R grade solvents ethyl acetate, acetone, dimethylformamide, methanol and *n*-hexane obtained from M/s Merck, India were used as such. Tri-ethylamine (A.R grade, procured from M/s RFCL, India) was freshly distilled from calcium hydride before each use. Chloroform (A.R grade, procured from M/s RFCL, India) was distilled over anhydrous P_2O_5 and stored over 4 A^o molecular sieves. Chloroform-D (99.8 atom% D containing 0.03% TMS) for NMR analysis was procured from M/s Aldrich, India. *n*-dodecane (99% Alfa aesar) and 1-octanol (99%, Alfa aesar) obtained from M/s Thermofischer scientific, India were used without any further purification.

2.1.2 Acids

Commercial stocks of concentrated hydrochloric acid (37%, ACS grade) and nitric acid (69%, ACS grade) procured from M/s Merck India were diluted and used without any further purifications.

2.1.3 Inorganic salts

ACS grade salts of sodium hydroxide, potassium hydrogen phthalate, sodium bicarbonate, sodium sulphate, sodium acetate and re-sublimed iodine procured from M/s Merck, India were used in the present study. The details of the salts used in the preparation of FR-SHLLW is mentioned in section 2.3.7

2.1.4 Organic salts

The complexing agents, di-sodium dihydrogen ethylenediaminetetraaceticacid dihydrate (> 99.5%), N-(2-hydroxyethyl) ethylenediamine-N,N’,N’-triacetic acid(HEDTA, > 98%), trans-1,2-cyclohexanediaminetetraaceticacid monohydrate (CyDTA, > 99%) and hexamethylenetetramine (HMTA, > 99%) were procured from M/s TCI chemicals, Japan. Oxalic acid dihydrate, (ACS grade, Alfa aesar) and potassium oxalate monohydrate (ACS grade, Alfa aesar) were supplied by M/s Thermofischer scientific India. The indicators phenolphthalein (ACS grade) and methylthymolblue sodium salt (ACS grade) were procured from M/s Merck India.

2.1.5 Organic reagents

N,*N*-di-hexylamine (97%), *N,N*-dioctylamine (97%) and *N*,*N*-didecylamine (98%) were procured from M/s Sigma Aldrich, India and used as such. The acid chlorides chloroacetylchloride (98%) and acetoxyacetylchloride (97%) procured from M/s

Thermofischer scientific, India also were used without any purification. *N*,*N*-di-hexyloctanamide (DHOA) procured from M/s Thermax Ltd, Pune and *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) procured from M/s Orion chemicals, Mumbai were purified by column chromatography before using for the studies.

2.1.6 Radioactive tracers

The radioisotope $^{(152+154)}$Eu dissolved in hydrochloric acid was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai, India. The HCl was evaporated off and the tracer solution was prepared by re-dissolving in dilute nitric acid. The radioisotope ^{241}Am was received from Oak Ridge National Laboratory (ORNL) as Am_2O_3. It was dissolved in concentrated nitric acid and diluted for tracer studies.

2.2 Instrumental facilities

2.2.1 Organic synthesis and characterization

2.2.1 i) Organic reactor

'*Easymax*' Organic reactor from *Mettler Toledo* was employed for some of the steps in the organic synthesis of extractants. The reactions were carried out in 100 ml reaction flasks equipped with mechanical stirrers having stirring speed up to 1200 rpm. The jacket temperature varied from -5^{0}C to 80^{0}C depending on the reaction.

2.2.1 ii) Rotary evaporator

IKA RV 10 Digital model rotary evaporator was used for distilling off volatile solvents from the reaction mixtures and from fractions collected during the column chromatography.

2.2.1 iii) NMR spectrometer

Brucker Avance III 500 MHz (AV 500) multi nuclei solution NMR spectrometer was used for recording the ^{1}H and ^{13}C nmr spectra of synthesized samples. The samples for NMR analysis were prepared by dissolving approximately 25 µL of each compound in 400 µL of deuterated chloroform containing 0.03% of TMS as internal standard.

2.2.1 iv) FT-IR spectrometer

The Fourier transformed infrared (FT-IR) spectra of the samples were recorded using *Bruker Tensor-II FT-IR spectrometer* equipped with an ATR (Attenuated Total Reflectance) diamond crystal. 10 - 20 µL of organic phase was placed on the diamond disk and the spectrum was recorded from 600 cm^{-1} to 4000 cm^{-1}. For each sample, the data was acquired for about 16 scans with a resolution of 4 cm^{-1}.

A *Bomem MB-100 FT-IR spectrometer* with a resolution of 4 cm^{-1} and spectral range 4000-650 cm^{-1} was also used for the measurement of IR spectra in the initial stages of study. The samples to be scanned were sandwiched between two zinc-selenide windows in this case. The sample compartment was purged with nitrogen for a sufficient period prior to scan.

2.2.2 Determination of metal ion extraction

2.2.2 i) High Purity Germanium (HpGe) Detector

The gamma emitting radionuclides $^{(152+154)}$Eu and ^{241}Am were characterized and estimated by gamma spectrometry. In this technique, a planar high pure germanium (HpGe) crystal semiconductor detector obtained from Baltic Scientific Instruments, Latvia was used. It was coupled with multichannel analyzer (MCA).

2.2.2 ii) Gamma counter

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

2.2.2 iii) Inductively coupled plasma-optical emission spectrometer (ICP-OES)

Ultima C spectroanalyser (Jobin Yvon, France) equipped with Inductively Coupled Plasma excitation source was used for analysis of several non-radioactive elements. The spectrometer provided 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. The instrument was calibrated using standard reference solutions (MBH analytical Ltd, U.K) of individual elements in the sample, before each analysis.

2.2.3 Aggregation studies

2.2.3 i) Dynamic light scattering (DLS) spectrometer

The aggregate size measurements in the organic phase were performed using Zetasizer-nano ZS-90 spectrometer (Malvern Instrument Company, UK) with a 4 mW He–Ne laser beam operating at a wavelength of 632.8 nm. All the measurements were performed at a scattering angle of 90^0 in a cell of 4 mm path length at 298 K. The instrument was calibrated using standard colloidal suspension (polystyrene latex) before the size measurement of the actual samples. The samples for DLS measurements were prepared by mixing of equal volumes of aqueous and organic phases in a vortex mixer for 15 minutes at 298 K. The solutions were then kept overnight before making the aggregate size measurements. The average value of five repeated measurements was reported along with standard deviation. The values of polydispersity index (PDI) values varied from 0.03 to 0.07 for extractant phases containing metal ions and from 0.05 to 0.35 for extractant phases containing only nitric acid.

2.2.4 Complexometric titrations

2.2.4 i) pH meter

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

2.2.4 ii) Electronic single pan balance

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

2.2.4 iii) Milli-Q integral water purifier system

De-ionised water from milli-Q water purifying system (Merck-millipore) was used for all the experiments.

2.2.5 Measurement of physical properties

The densities and viscosities of extractant samples were measured using Anton Paar Microviscometer Lovis 2000 ME combining densitometer DMA 4500M.

2.2.6 Mixer-settler Facility in glove box

The counter current extraction and stripping studies were performed using a 20 stage air-pulsed ejector mixer settler system made of stainless steel. This facility was housed in a negative pressure glove box (Figure 2.1). Each stage of the system was comprised of a separate mixer (M) and settler (S), indicated in the figure by numbers 1 to 20.

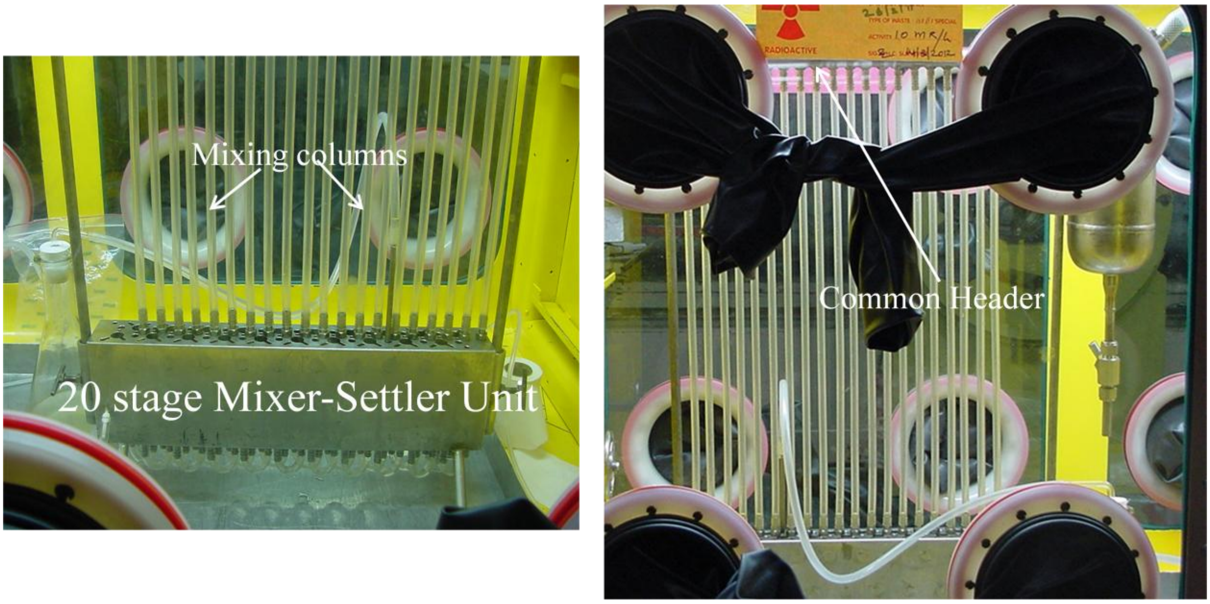


Figure 2.1: Photograph of the 20-stage mixer-settler facility in glove-box employed for the counter-current extraction and stripping studies.

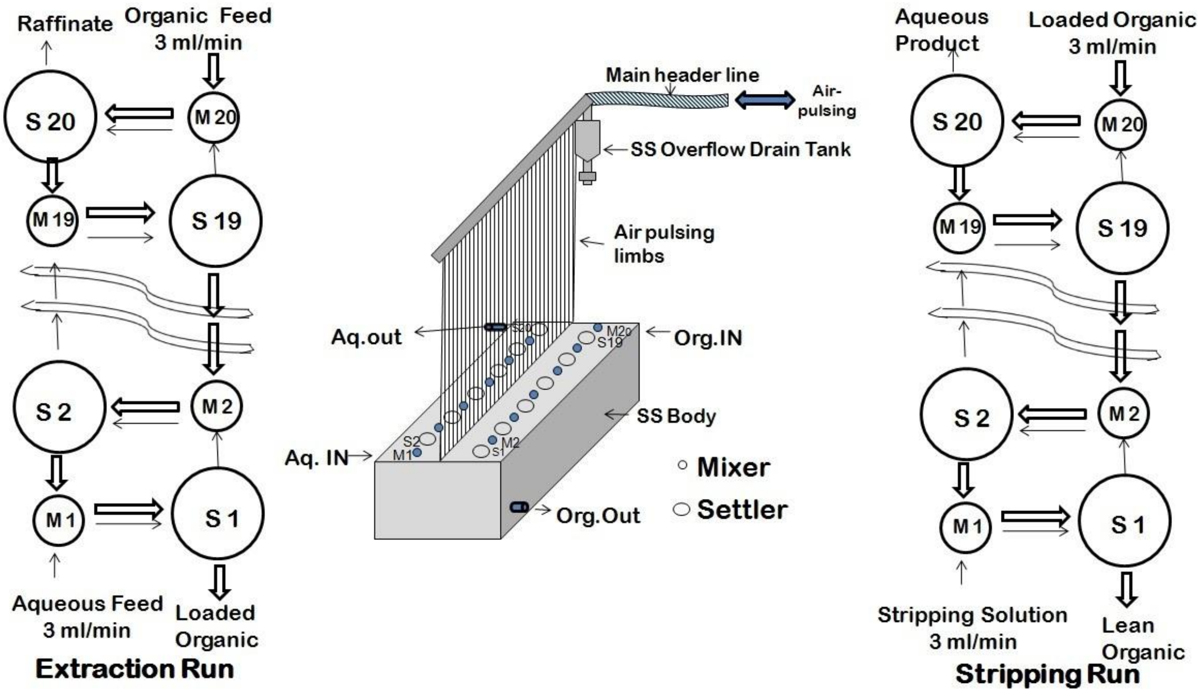


Figure 2.2: Illustration of the mixer-settler facility employed in the present study.

The mixer compartment was cylindrical with a short diffuser fixed at the bottom. The aqueous and organic phases diffusing through the bottom dispersed in the mixer compartment with the help of ejectors connected to the mixer column from a common header. Efficient mixing of aqueous and organic phases in the mixers was achieved by alternatively applying pressure and vacuum with the help of a solenoid valve operated by a cyclic timer.

The illustration of mixer-settler shown in Figure 2.2 indicates that each mixer (M2) is connected to three settlers (S1, S2 and S3) and each settler (S2) is connected to three mixers (M1, M2 and M3). The volume of each mixer unit was 7 mL and the volume of each settler unit was 15 mL.

2.3 Preparation of solutions

2.3.1 Acidimetry

2.3.1.i) Phenolphthalein solution

About 0.25 g of phenolphthalein was dissolved in 50 mL of 1:1 mixture (volume ratio) of de-ionised water and ethanol to prepare the indicator solution for acid-base titrations.

2.3.1. ii) Standard sodium hydroxide solution

Sodium hydroxide solution (0.1 M) was prepared by dissolving approximately 10 g of sodium hydroxide crystals in 250 mL of de-ionised water. It was standardized by acid-base titration with potassium hydrogen phthalate (KHP).

2.3.1. iii) Nitric acid solutions

Nitric acid stock solutions (8 M and 12 M) were prepared from the commercial (69 wt. %) nitric acid and standardized by acid-base titration against standard sodium hydroxide solution.

2.3.2 Complexometry

2.3.2. i) Methylthymol blue solution

About 25 mg of methylthymol blue sodium salt was dissolved in 10 mL de-ionised water to prepare the indicator solution for complexometric titrations.

2.3.2. ii) EDTA solution

EDTA solution (0.02 M) was prepared by dissolving approximately 1.86 g of EDTA disodium salt dihydrate in 250 mL de-ionised water. It was standardized by complexometric titration against standard lanthanum reference solution (MBH analytical Ltd, U.K).

2.3.2. iii) Neodymium solutions

A stock solution of neodymium (0.35 M) was prepared by dissolving approximately 15.2 g of neodymium nitrate hexahydrate crystals in 0.1 M nitric acid. This stock solution was standardized by complexometric titration using standard EDTA solution and then diluted to required concentrations in 3 M or 4 M nitric acid. More concentrated solutions of neodymium (up to 1.3 M) were prepared by directly dissolving the required amount of the salt in 4 M nitric acid followed by estimation.

2.3.3 Fast reactor simulated high level liquid waste solution (FR-SHLLW)

The FR-SHLLW was prepared by mixing different elements in 4 M nitric acid,based on the literature report on the reprocessing of spent fast reactor fuel irradiated to the burn-up of 80,000 MWd/Te with 2 year cooling [131]. The reported elemental composition of FR-SHLLW is shown in table 2.1.

All the rare earth metals used for the preparation of FR-SHLLW were procured from Sigma Aldrich, India. Eu(III) and Pr(III) were procured as oxides (Sigma Aldrich) and converted into their nitrate salts by digestion of oxide salts with concentrated nitric acid followed by evaporation of excess nitric acid. Pd(II) and Rh(III) stock solutions in nitric acid procured from Sigma Aldrich were directly used for preparation. The nitrate salts of La (III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III) and Tb(III)) and Y(III) used were 99.999% pure on trace metals basis and were available as hexahydrate salts. ACS grade nitrate salts of Ba(II), Sr (II), Cs (I), Rb(I), Na(I), Ag(I), Fe(III) and Ni (II) were procured from M/s Merck, India.

Table 2.1 Composition of the high-level liquid waste from the reprocessing of fast reactor fuel irradiated to the burn-up of 80,000 MWd/Te and 2 year cooling [131]. Medium: 4 M HNO_3.

Element	Concentration (g/Litre)	Element	Concentration (g/Litre)	Element	Concentration (g/Litre)
La	0.342	Mo	1.092	Rh	0.262
Ce	0.684	Fe	0.500	Sn	0.163
Pr	0.339	Cr	0.101	Cs	1.125
Nd	1.125	Te	0.163	Rb	0.055
Sm	0.306	Cd	0.038	Se	0.002
Pm	0.053	Ni	0.100	Na	3.000
Eu	0.032	Sr	0.147	Ag	0.109
Gd	0.065	Ba	0.414	Tc	0.262
Tb	0.011	Ru	0.813	Sb	0.007
Dy	0.006	Pd	0.600	Am	0.218
Y	0.074	Zr	0.822		

Mo(VI) was added as ammonium heptamolybdate teterahydrate (Alfa Aesar), zirconium was added as zirconyl nitrate (Sigma Aldrich) and Te(II) was added as sodium tellurite (Sigma Aldrich). Pm (III) was substituted by La(III) and Tc(VII) was not added. The elements Ru(III), Se(IV), Sb(III) and Sn(II) were also not added, as the commercially available salts of these elements were showing miscibility problems in the medium.

The procedure for the preparation of FR-SHLLW involved the preparation of approximately 100 mg/ mL stock solutions of individual elements in 0.1 M nitric acid, followed by standardisation using ICP-OES analysis. Required quantities of individual stock solutions were mixed together followed by diluting with 6 M nitric acid solution and de-ionised water so as to obtain 3.5 litres of the final solution in 4 M nitric acid. The aqueous phase acidity of the final solution was estimated by acid-base titration against standard sodium hydroxide solution, in the presence of potassium oxalate as masking agent for preventing the interference from hydrolysable cations.

2.4 Experimental Procedures

2.4.1 Measurement of distribution (D) values

The distribution ratio (*D*) of a metal ion is defined as ratio of the concentration of metal ion in the organic phase to the concentration of metal ion in the aqueous phase at equilibrium. All the *D* values were measured in duplicate after pre-equilibration of organic phases with the required concentration of nitric acid. Depending upon the nature of experiment, organic phase was either DAHyA or TODGA with phase modifiers dissolved in *n*-dodecane. The aqueous phase was either nitric acid or FR-SHLLW spiked with radioisotopes. In some experiments involving FR-SHLLW, complexing agents were added to the aqueous phase. The extraction experiments involved equilibration of equal volumes (1 mL or 3 mL) of organic phase and aqueous phase for about 1 hour. The mixing of organic and aqueous phases was performed in 5 mL or 15 mL stoppered glass tubes by up-side down rotation (100 rpm) in a tube rotator. The distribution ratio of the metal ions was determined by measuring the radioactivity of these isotopes in aqueous and organic phases using a well-type NaI (Tl) scintillation detector coupled with single channel analyzer, and using Eq. (1)

$$D_{\mathrm{M}} = \frac{[M]_{org}}{[M]_{aq}} \tag{1}$$

where [M] is the radioactivity of ^{241}Am or $^{(152+154)}$Eu. When the radioactivity of a mixture of radionuclides was assayed, HpGe detector coupled with multi channel analyzer was employed. The distribution ratios of other metal ions were measured using the same equation, by substituting their concentrations in aqueous and organic phases as determined by ICP-OES analyses. In this case, the concentration of the metal ion in aqueous phase was measured directly and concentration in the organic phase was indirectly calculated from the difference in the initial concentration and final concentration of the metal ion in aqueous phase after extraction. The average error in the measurement of D_M, by both the methods, was estimated to be within ± 5%.

2.4.2 Co-current extraction and stripping studies

For co-current extraction and stripping studies, the organic phase (5 mL) was first loaded with metal ions from 4 M nitric acid or FR-SHLLW spiked with the required radiotracers. After equilibration, the radioactivity present in an aliquot (100 µL) of the loaded organic and aqueous phases were determined using NaI (Tl) scintillation counter coupled with a single channel analyzer. The loaded organic phase was subsequently used for co-current stripping studies while the lean aqueous phase was employed for co-current extraction studies.

During co-current extraction studies, the lean aqueous phase was equilibrated with equal amount of fresh organic phase. The radioactivity in the organic phase was then measured. The organic phase was discarded and the lean aqueous phase was again equilibrated with equal volume of fresh organic phase. This procedure was repeated until the radioactivity extracted to the organic phase was negligible.

During co-current stripping studies, the loaded organic phase obtained after the first contact with FR-SHLLW or 4 M nitric acid was equilibrated with equal amount of the stripping solution. The radioactivity in the aqueous phase was determined in this case. The aqueous and organic phases were then separated and the organic phase was again equilibrated with equal volume of fresh stripping solution. The procedure was repeated until the radioactivity measured for the aqueous phase was negligible.

2.4.3 Mixer settler studies

A schematic description of conditions used for the 20-stage counter-current extraction and stripping runs with the mixer-settler facility was described in figure 2.2

(section 2.2.6). The aqueous phase was flowing from 1st stage to 20th stage and the organic phase was flowing in the reverse direction during the counter-current extraction experiments. The total volume of organic solution used in the run was 2.2 liters and the same volume of feed and stripping solution was also used. The flow rates for both the runs were maintained at 3 mL/minute with the help of metering pumps equipped with precise flow control (± 0.05 mL/min). The attainment of steady state at the end of 4 hours was confirmed by measurement of gamma activities of the samples from the exit points of aqueous and organic streams. Once the steady state was achieved, the stage samples were collected and the radioactivity of ^{241}Am and $^{(152+154)}$Eu at each stage in organic and aqueous phases was measured by a high purity germanium (HPGe) detector coupled with multichannel analyzer. The concentration of other metal ions in the aqueous phase was estimated using ICP-OES.

2.4.4 Column Chromatography

Column chromatography was performed using manually packed silica gel (100-200 mesh, Merck) columns. The compounds were separated by gradient elution using mixtures of petroleum ether (boiling range: 60^0C-80^0C) and ethyl acetate. The elution of different components of the product mixture was monitored by thin layer chromatography (TLC). It was done using silica gel 60 F_{254} aluminium sheets procured from Merck. 30% ethyl acetate/ petroleum ether mixture was used as the mobile phase and the TLC plates were developed using iodine vapours.

2.4.5 Irradiation with gamma rays

All the samples were irradiated under static condition using a gamma chamber facility equipped with a ^{60}Co source generating a dose rate of 3.4 kGy/h. The dose of the chamber was calibrated by Fricke dosimetry. The extractant samples were irradiated in three different forms such as (1) neat (2) dissolved in *n*-dodecane and (3) dissolved in *n*-

dodecane in contact with equal volume of 4 M nitric acid. At calculated time intervals, samples of different levels of irradiation were withdrawn from the chamber and stored as such till the irradiation of 700 kGy was over in 20 days. The irradiated neat samples were dissolved in *n*-dodecane and employed for the extraction studies. All the irradiated samples were used for extraction studies without any pre-treatment.

2.4.6 Measurement of phase disengagement time

The phase disengagement time (PDT) is the time taken for the disappearance of all the dispersed primary droplets at the interface formed after a vigorous shaking of organic and aqueous phases. Typically, 2.5 mL of organic phase was shaken vigorously for 60 seconds with 2.5 mL of 4 M or 0.1 M nitric acid solution in a graduated 20 mL stoppered test tube (150 mm X 15 mm). The two phases were allowed to disengage with the tube kept vertically and the time required for the disengagement was measured using a stop-watch of 0.01 seconds resolution. The measured PDT values are the average of three independent experiments and reported with the standard deviation of ±5%.

2.4.7 Extraction of nitric acid

During the study of extraction of nitric acid by various extractant systems, the extractants dissolved in *n*-dodecane were equilibrated with equal volumes of nitric acid solutions for one hour. The concentration of nitric acid in aqueous phase was varied from 0 M to 12 M. The amount of nitric acid present in organic and aqueous phases was then determined by standard acid-base titration.

The extractant organic phases were equilibrated with aqueous nitric acid solutions with gradually increasing concentrations. Once a third phase is observed at a particular concentration of nitric acid, the aqueous phase was diluted by slow, drop-wise addition of de-ionised water under constant stirring so as to dissolve the third phase. The aqueous acidity of the resulting two phase system was then reported as the critical aqueous concentration (CAC) of nitric acid for that system. The concentration of nitric acid in the organic phase at this point was reported as the limiting organic concentration (LOC) of nitric acid. During the above experiments, third phase was formed with initial aqueous nitric acid concentrations just above the third phase limits and only minimum amount of de-ionised water was added for dissolution of third phase.

2.4.8 Extraction of Neodymium

The extraction of neodymium for various extractant systems was studied at equilibrium aqueous phase acidities 3 M and 4 M. The concentration of Nd(III) in the aqueous phase was varied from 5 mM to 1300 mM depending on the nature of extractant systems involved in the study. Initially, the organic phase was pre-equilibrated with desired concentration of nitric acid. Equal volumes of pre-equilibrated organic phase and nitric acid solutions containing Nd (III) were equilibrated by upside down rotation in test-tube rotor at 100 rpm. The extracted phases were then allowed to settle for an hour and the amount of Nd(III) in aqueous and organic phases were estimated by complexometric titration against standard EDTA solution.

Some of the organic extractants form third phase during solvent extraction process. For such extractant systems, the limiting organic concentration (LOC) of Nd(III) was determined by a similar method which was discussed above for nitric acid extraction. In this case, the third phase formed after equilibrating with minimum excess of metal ions in the aqueous phase was dissolved by slow, drop-wise addition of pre-equilibrated organic phase. The concentration of Nd(III) estimated in the organic phase of the two phase system after dissolution of third phase was reported as the limiting organic concentration.

2.4.9 Synthesis and characterisation of *N*, *N*-di-alkyl-2-hydroxyacetamides

2.4.9 i) Route 1: Synthesis starting with chloro acetylchloride

N,*N*-di-alkyl-2-hydroxyacetamides were initially synthesized by a three-step procedure described elsewhere [134]. The scheme of synthesis according to this route is given in figure 2.3. The details of the synthesis procedures adopted and the characterisation data for each product are described in the following paragraphs.

Step 1: Synthesis of *N*,*N*-dialkyl-2-chloro acetamides

A 250 mL single-neck round bottom flask was charged with dry chloroform (20 mL) and diglycolyl chloride (0.19 moles) and partially immersed in an ice-bath maintained at 0-5^{0}C.

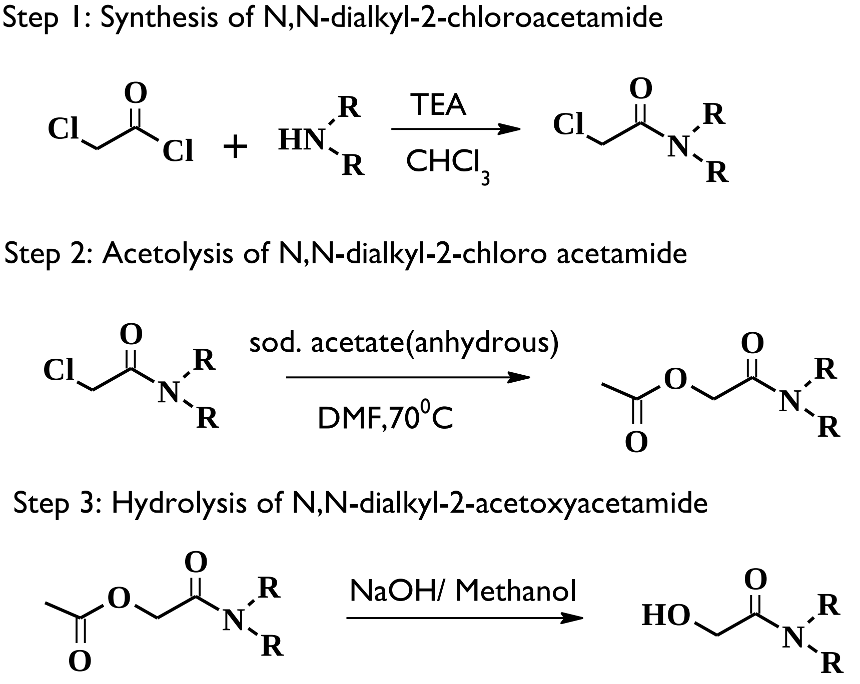


Figure 2.3: Scheme 1- Synthesis of *N*,*N*-di-alkyl-2-hydroxyacetamides

To this, a solution of tri-ethylamine (0.21 moles) and the corresponding *N*,*N*-di-alkylamine (0.19 moles) in dry chloroform (50 mL) was added drop wise over a period of one hour. An exothermic reaction was initiated with the formation of a precipitate. The reaction mixture was stirred for two more hours at room temperature and then the chloroform was removed by rotary evaporation. The slurry was then extracted with n-hexane (100 mL) and washed with water (100 mL) to remove all the precipitated tri-ethylaminehydrochloride. The hexane extract was then successively washed with 1 M HCl (100 mL X 2), water (100 mL X 1) and saturated sodium bi-carbonate solutions (100 mL X 2).It was finally dried over anhydrous sodium sulphate and concentrated in vacuo to get the corresponding 2-chloro acetamide. The yields obtained in all the three reactions were quantitative. Structural characterization data for the three chloroacetamide derivatives are given below.

N,N-di-hexyl-2-chloroacetamide(DHCA): (dark brown liquid, yield: >98%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.059(s, 2H), 3.317 (t, 2H, J=7.6Hz), 3.268 (t, 2H, J=7.6Hz), 1.556 (m,4H), 1.299 (m,12H), 0.882 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 166.07, 48.36, 46.27, 41.33, 31.58(d), 29.14, 27.33, 26.58(d), 22.57, 14.01(d).

IR (neat, ν cm^{-1}): 2930, 2844(strong, C-H stretch), 1655(C=O stretch), 1458 ($-N-CH_2-CO-$bend), 1370 (strong, C-Cl stretch), 1110(weak).

N,N-di-octyl-2-chloroacetamide (DOCA): (dark brown liquid, yield: >98%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.060(s, 2H), 3.313 (t, 2H, J=7.6Hz), 3.265 (t, 2H, J=7.6Hz), 1.574 (m,4H), 1.282 (m,20H), 0.882 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 166.06, 48.36, 46.27, 41.33, 31.81(d), 29.35, 29.28, 29.22(m), 27.37, 26.93(d), 22.65(d), 14.01(d).

IR (neat, ν cm^{-1}): 2930, 2856(strong, C-H stretch), 1655(C=O stretch), 1459 ($-N-CH_2-CO-$bend), 1370 (strong, C-Cl stretch), 1110(weak).

N,N-di-decyl-2-chloroacetamide (DDCA): (dark brown liquid, yield: >98%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.055(s, 2H), 3.312 (t, 2H, J=7.6Hz), 3.264 (t, 2H, J=7.6Hz), 1.536(m,4H), 1.258 (m,28H), 0.878 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 166.01, 48.32, 46.24, 41.29, 31.87(d), 29.52(m), 29.36, 29.28(d), 29.13, 27.34, 26.89(d), 22.64, 14.06(d).

IR (neat, ν cm^{-1}): 2930, 2854(strong, C-H stretch), 1655(C=O stretch), 1459 (-N-CH_2-CO-bend), 1370 (strong, C-Cl stretch), 1110(weak).

Step 2: Synthesis of *N,N*-dialkyl-2-acetoxy acetamides

The 2-chloro acetamide (0.15 moles) was mixed with anhydrous sodium acetate (0.3 moles) and DMF (150 mL) and the mixture was heated at 80^{0}C for four hours. It was then cooled and transferred to a separating funnel by washing the reaction vessel several times with n-hexane (150 mL). The DMF was separated by repeated washing with distilled water (150 mL X 3) followed by washing with 1M HCl (150 mL X 1). The hexane extract was again washed with water (150 mL), dried over anhydrous sodium sulphate and concentrated in vacuo. As per TLC analysis, the product thus obtained was found to be a mixture of acetoxy and hydroxy derivatives of the corresponding 2-chloroacetamide and this crude product as such was used for the next hydrolysis step. Structural characterization data for one of the acetoxy derivative is given below.

N,N-di-decyl-2-acetoxy acetamide (DDAA): (pale yellow liquid, yield: 72%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.703(s, 2H), 3.301 (t, 2H, J=8Hz), 3.139 (t, 2H, J=8Hz), 2.181 (S, 3H), 1.561(m,4H), 1.267 (m,28H), 0.880 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 170.64, 165.84, 61.25, 46.97, 46.26, 31.86(d), 29.52(m), 29.27(m), 28.87, 29.13, 27.58, 26.98, 26.86, 22.64, 20.63, 14.06.

IR (neat, ν cm^{-1}): 3494 (medium, broad), 2928, 2858 (strong, C-H stretch), 1754 (strong, -O-C=O stretch) 1671 (strong, C=O stretch), 1467 (strong, -CH_2-scissoring), 1402 (medium, C-N stretch), 1375 (medium, -CH_3 bend), 1234 (medium, -CH_2-wagging), 1074 (strong, C-O stretch of acetoxyl).

Step 3: Hydrolysis of *N, N*-dialkyl-2-acetoxyacetamides

Sodium hydroxide (0.2 moles) was dissolved in methanol (50 mL) and cooled to room temperature. The crude product mixture from step-2 (0.15 moles) dissolved in methanol (50 mL) was added to it and stirred at room temperature for 2 hours. At the end of two hours, methanol was evaporated off at 50^0C and the product mixture was transferred to a separating funnel after extracting with *n*-hexane (150 mL). It was then washed with distilled water (150 mL X 3) and 1 M HCl (150 mL). The hexane extract was once again washed with water (150 mL), dried over anhydrous sodium sulphate and concentrated in vacuo. The crude product was then purified by column chromatography over silica gel using 7% ethyl acetate-petroleum ether as eluent. The structural characterization data for all the three hydroxyacetamide derivatives are given below.

N,N-di-hexyl-2-hydroxy acetamide (DHHyA): (pale yellow liquid, yield: 76%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.142(d, 2H, J=4Hz), 3.727 (t, 1H, J=4Hz), 3.365 (t, 2H, J=8Hz), 3.055 (t, 2H, J=8Hz), 1.542 (m,4H), 1.255 (m,12H), 0.892 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 170.98, 59.68, 46.07, 45.79, 31.58, 31.47, 28.52, 27.53, 26.65, 26.51, 22.58(d), 14.02(d).

IR (neat, ν cm^{-1}): 3410 (medium, broad, O-H stretch), 2926, 2858 (strong, C-H stretch), 1646 (very strong, C=O stretch), 1462 (medium, -CH_2-scissoring), 1402 (medium, C-N stretch), 1278 (medium, -CH_2-wagging), 1083 (strong, C-O stretch of hydroxyl).

N,N-di-octyl-2-hydroxy acetamide(DOHyA): (pale yellow liquid, yield: 74%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.138 (d, 2H, J=4Hz), 3.706 (t, 1H, J=4Hz), 3.361 (t, 2H, J=8Hz), 3.047 (t, 2H, J=8Hz), 1.538 (m,4H), 1.286 (m,20H), 0.883 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 171.01, 59.71, 46.11, 45.82, 31.77(d), 29.31, 29.22(d), 29.12, 28.52, 27.54, 26.96, 26.81, 22.60(d), 14.03(d).

IR (neat, ν cm^{-1}): 3410 (medium, broad, O-H stretch), 2926, 2858 (strong, C-H stretch), 1646 (very strong, C=O stretch), 1462 (medium, -CH_2-scissoring), 1402 (medium, C-N stretch), 1278 (medium, -CH_2-wagging), 1083 (strong, C-O stretch of hydroxyl).

N,N-di-decyl-2-hydroxy acetamide (DDHyA): (pale yellow liquid, yield: 67%)

^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.138(s, 2H), 3.716 (bs, 1H), 3.359 (t, 2H, J=7.6Hz), 3.046 (t, 2H, J=7.6Hz), 1.537 (m,4H), 1.262 (m,28H), 0.880 (m, 6H).

^{13}C NMR ($CDCl_3$, δ relative to TMS): 171.0, 59.71, 46.11, 45.83, 31.86(d), 29.53(d), 29.46, 29.35, 29.26(d), 28.51, 27.54, 26.96, 26.81, 22.64, 14.06.

IR (neat, ν cm^{-1}): 3410 (medium, broad, O-H stretch), 2926, 2858 (strong, C-H stretch), 1646 (very strong, C=O stretch), 1462 (medium, -CH_2-scissoring), 1402 (medium, C-N stretch), 1278 (medium, -CH_2-wagging), 1083 (strong, C-O stretch of hydroxyl).

2.4.9 ii) Route 2: Bulk synthesis of DOHyA starting with acetoxy acetylchloride

The over-all yield of hydroxyacetamide derivatives synthesized by route-1 was 60% to 70%. Therefore, the bulk synthesis of DOHyA for mixer-settler studies was carried out by a modified method starting with acetoxyacetylchloride. The scheme of synthesis according to this route is given in figure 2.4. The yield of DOHyA using the modified route was > 98%.

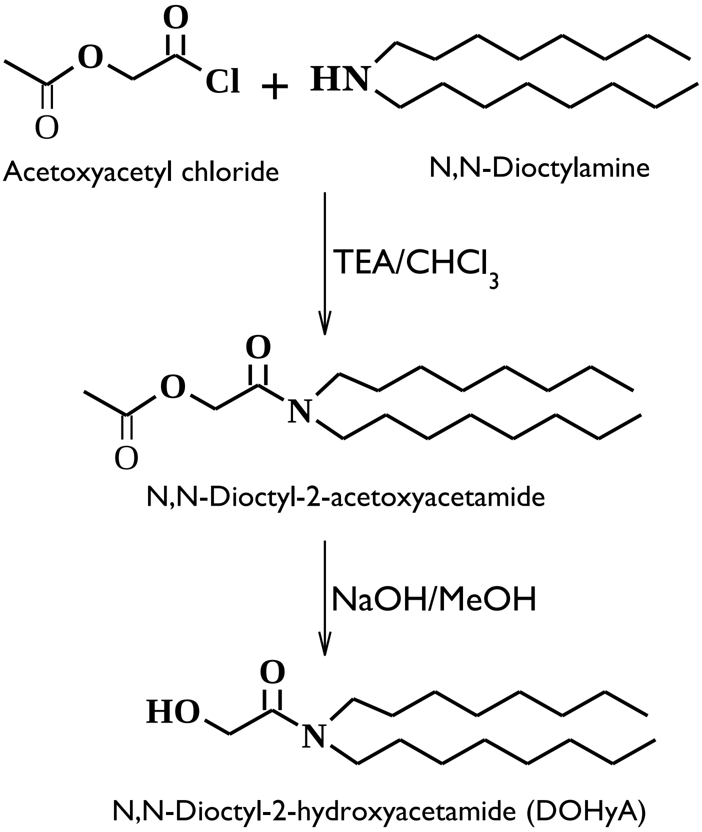
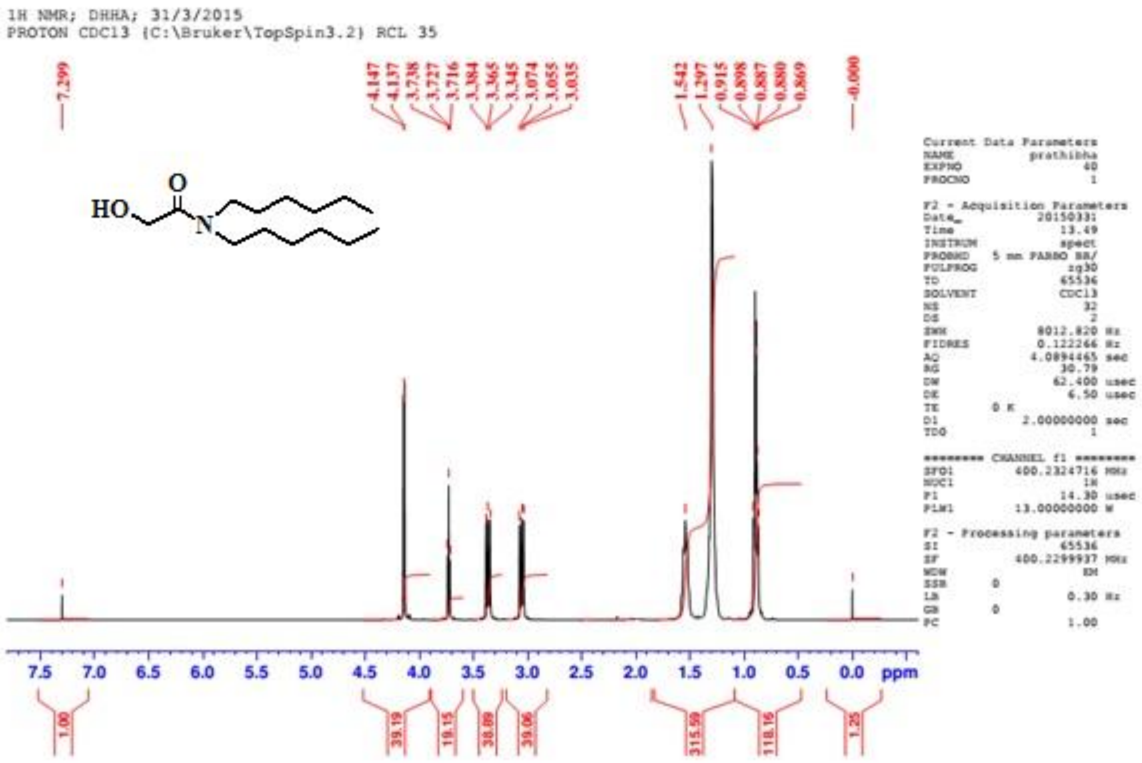


Figure 2.4: Scheme 2- Synthesis of *N,N*-di-octyl-2-hydroxyacetamide (DOHyA)

2.4.10 Selected nmr and IR spectra of the synthesized compounds

The ^{1}H and ^{13}C nmr spectra of all the three *N,N*-di-alkyl-2-hydroxyacetamides are attached in figures from 2.5 to 2.11. The FT-IR spectra of these neat compounds recorded over Zn-Se windows are also attached in figures from 2.12 to 2.15.



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DE                   6.50 usec
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TD0                     1

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PLW1          13.00000000 W

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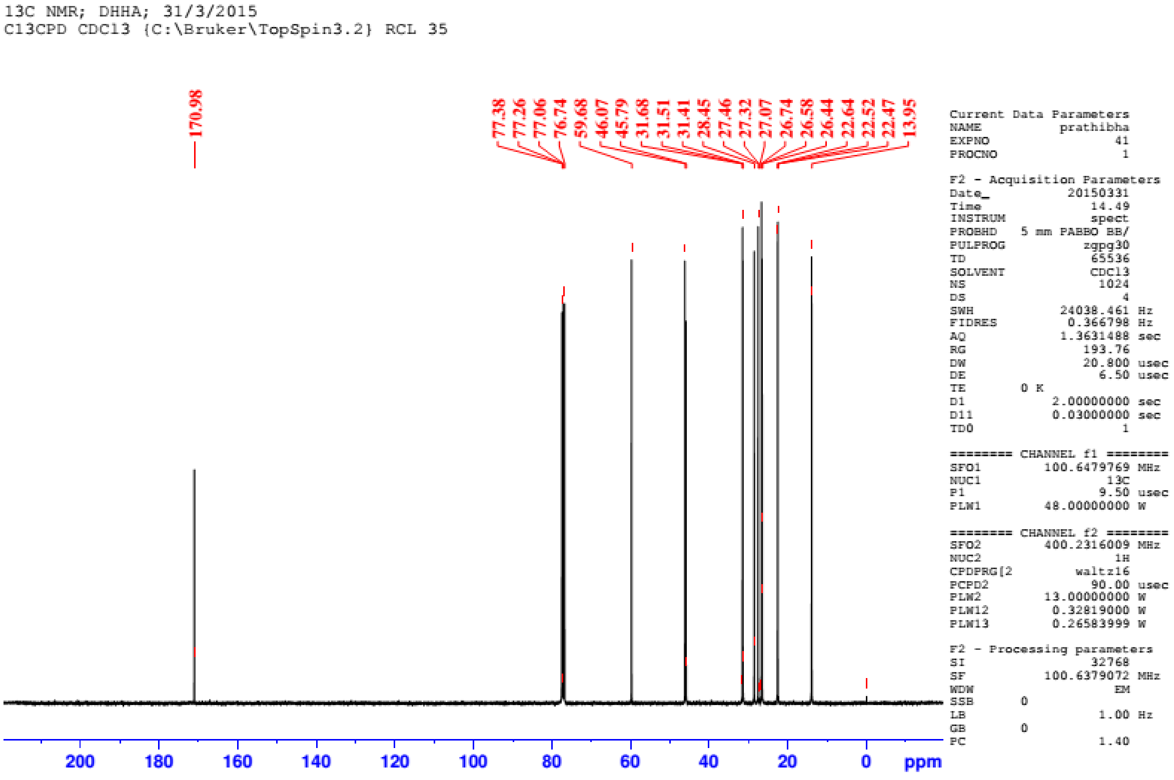
Figure 2.5: ^{1}H nmr spectrum of *N,N*-di-hexyl-2-hydroxy acetamide



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TE          0 K
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D11          0.03000000 sec
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P1                   9.50 usec
PLW1          48.00000000 W

======== CHANNEL f2 ========
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NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          13.00000000 W
PLW12          0.32819000 W
PLW13          0.26583999 W

F2 - Processing parameters
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SSB         0
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GB          0
PC                   1.40
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Figure 2.6: ^{13}C nmr spectrum of *N,N*-di-hexyl-2-hydroxy acetamide

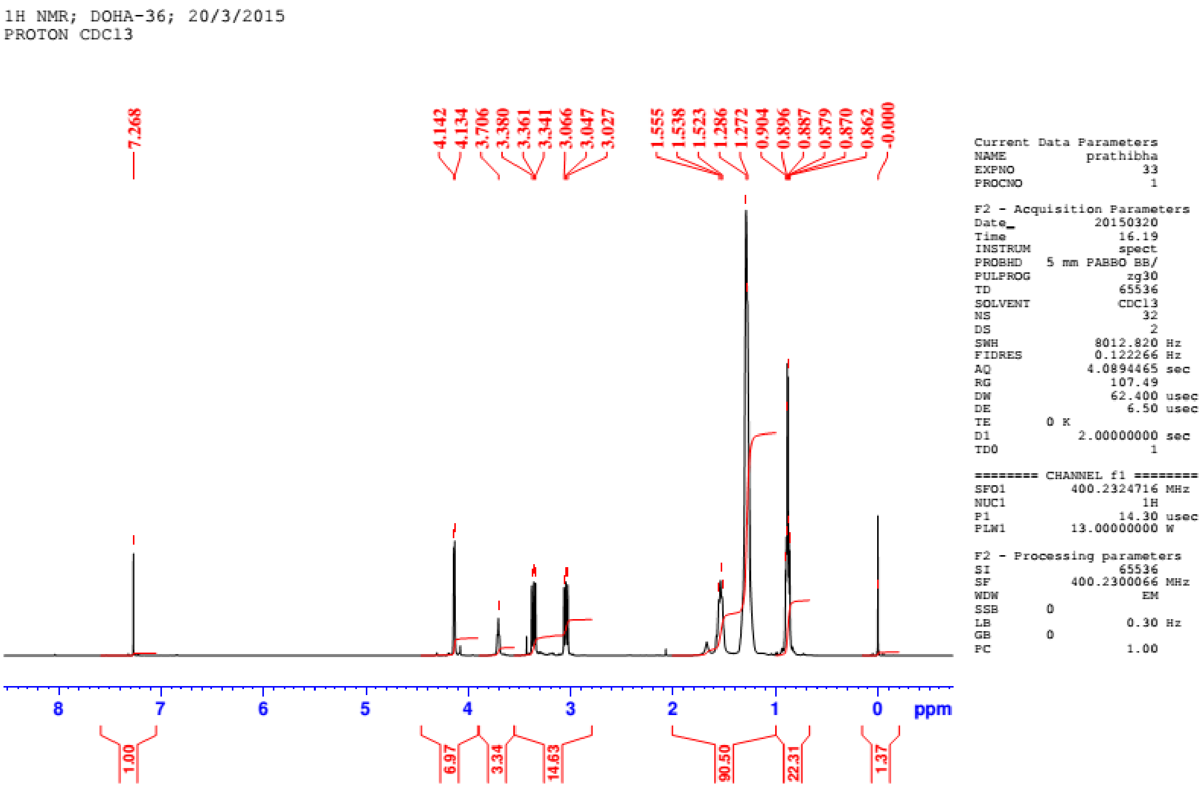

Figure 2.7: ^{1}H nmr spectrum of *N,N*-di-octyl-2-hydroxy acetamide

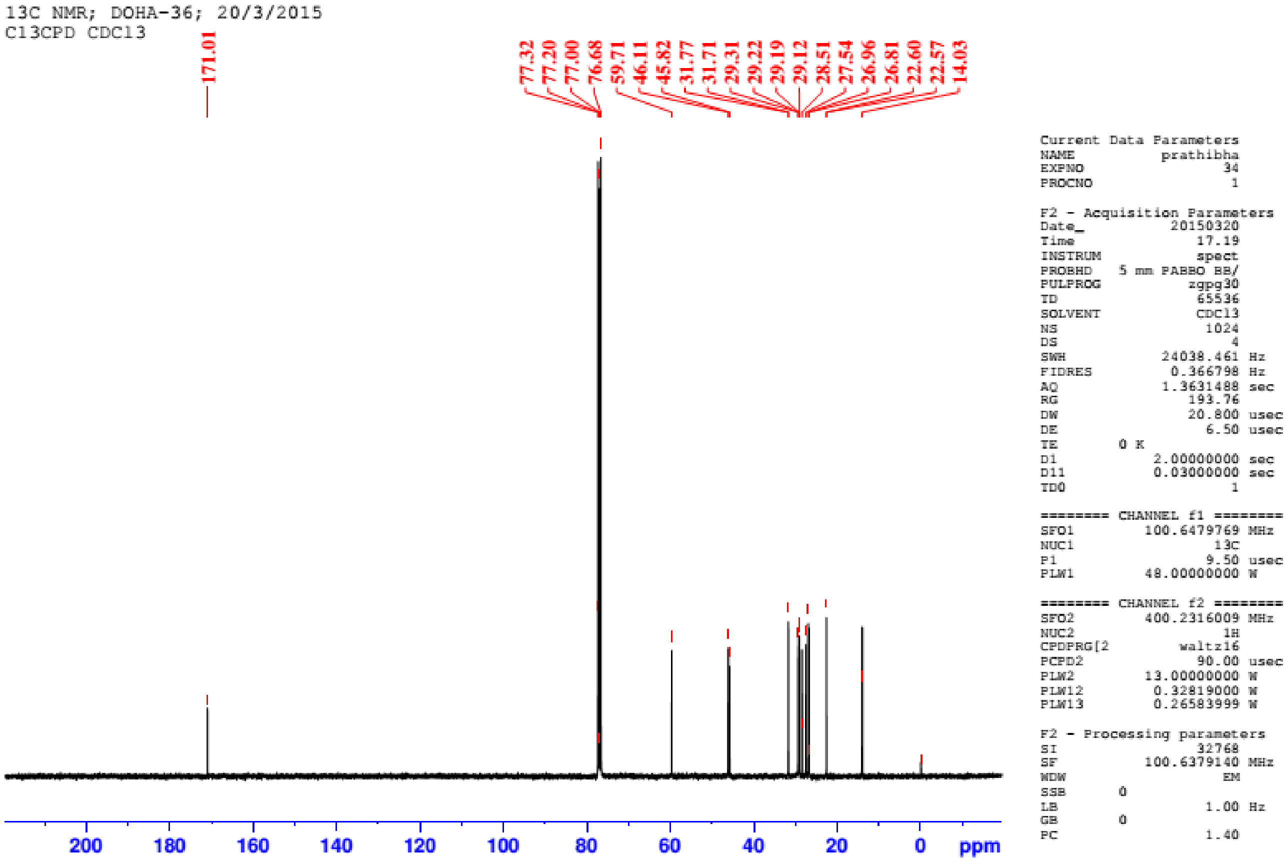

Figure 2.8: ^{13}C nmr spectrum of *N,N*-di-octyl-2-hydroxy acetamide

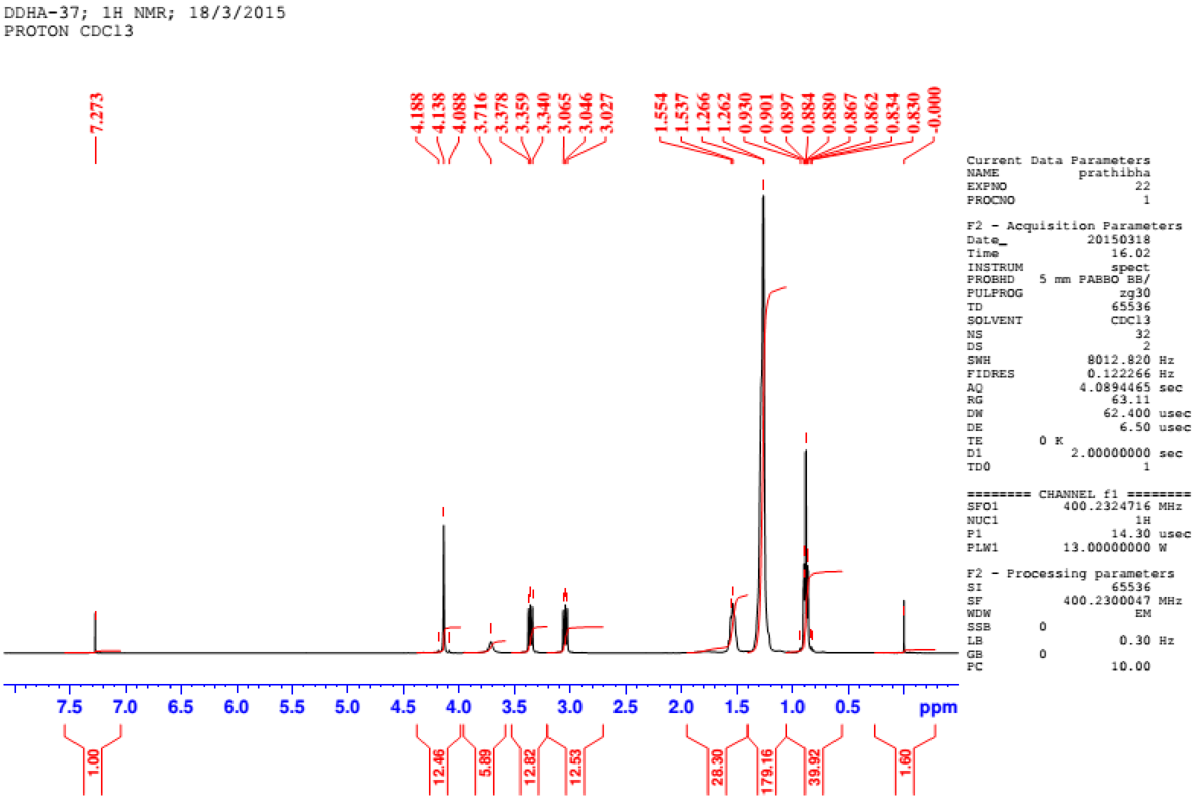

Figure 2.9: ^{1}H nmr spectrum of *N*,*N*-di-decyl-2-hydroxy acetamide

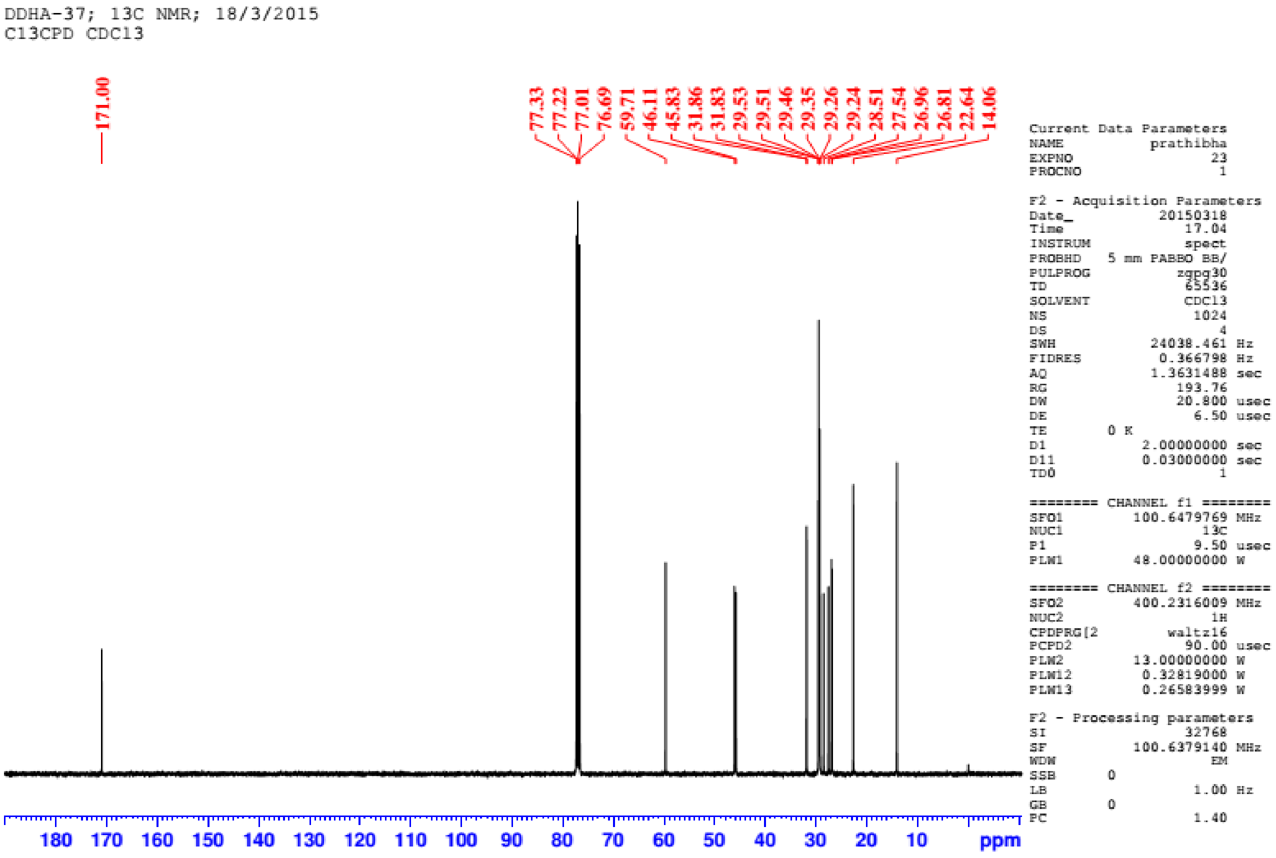

Figure 2.10: ^{13}C nmr spectrum of *N*,*N*-di-decyl-2-hydroxy acetamide

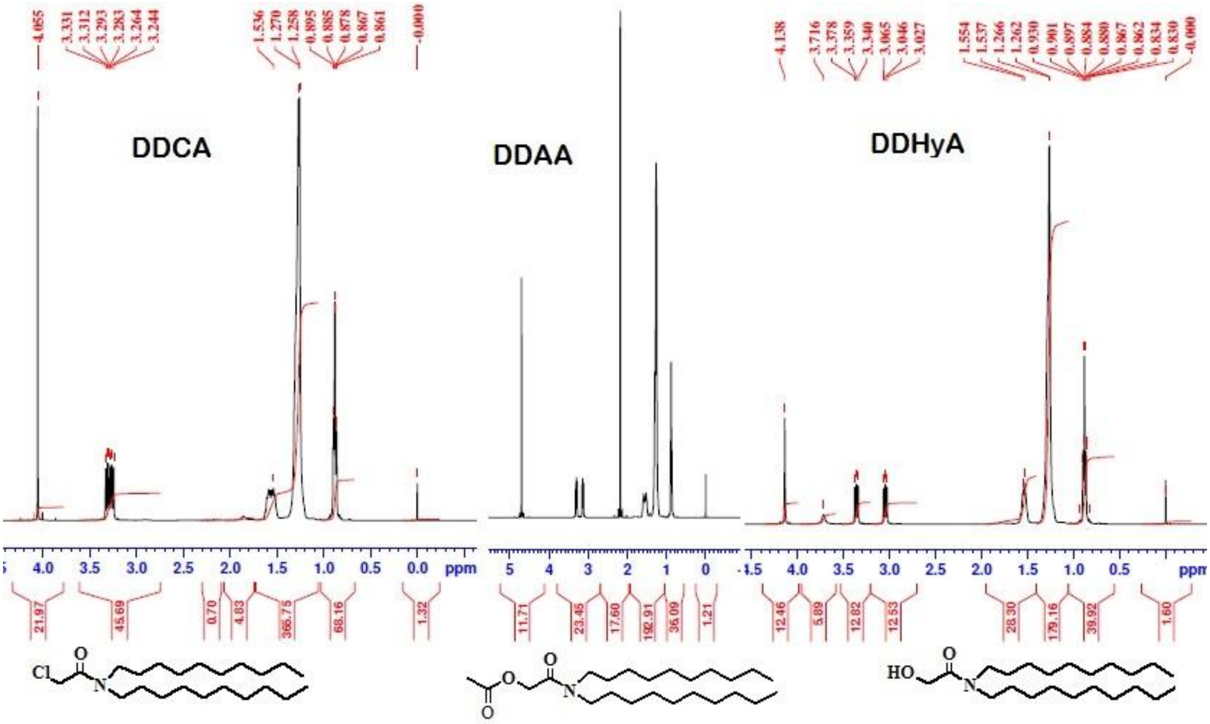

Figure 2.11: Comparison of ^{1}H nmr spectra of the products at three steps of route-1 during the synthesis of *N,N*-di-decyl-2-hydroxyacetamide (DDHyA)

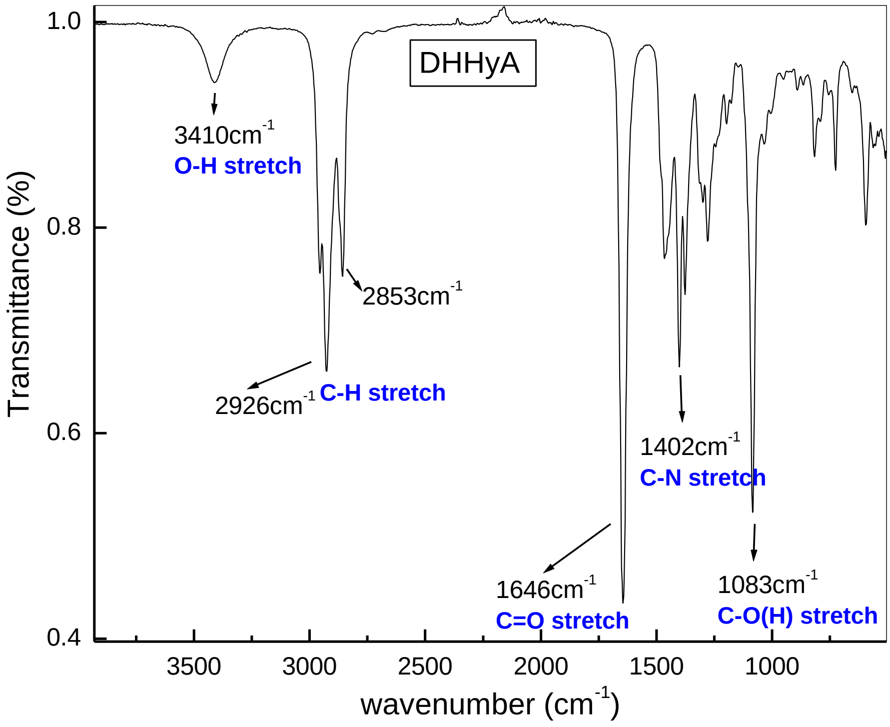

Figure 2.12: I.R spectrum of *N,N*-di-hexyl-2-hydroxy acetamide

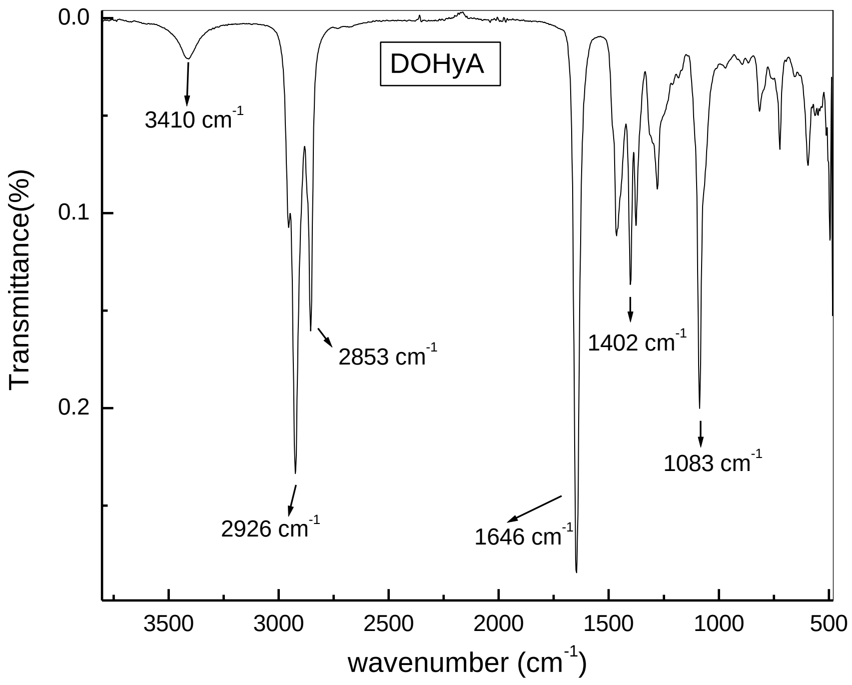

Figure 2.13: I.R spectrum of *N,N*-di-octyl-2-hydroxy acetamide

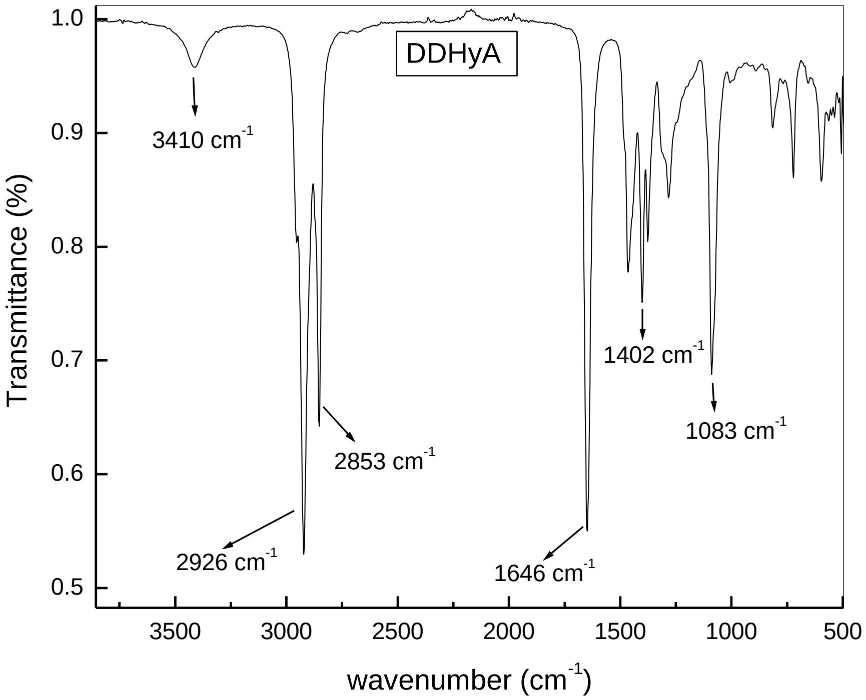

Figure 2.14: I.R spectrum of *N,N*-di-decyl-2-hydroxy acetamide

3

STUDIES ON THE EXTRACTION OF Am(III) AND Nd(III) FROM NITRIC ACID MEDIUM USING *N,N*-DI-ALKYL-2-HYDROXYACETAMIDES

3.1 Introduction

Even though the process flow-sheets based on many reagents have been developed and demonstrated for the separation of trivalent minor actinides from high level liquid waste (Section 1.6, Chapter 1), it is important to note that all these reagents are suffering from some major drawbacks such as third phase formation. However, the problem due to third phase formation was manoeuvred by adding phase modifiers to the organic phase in significant concentrations, even though the organic phase without any modifier was preferred. The phase modifiers are usually another extractant such as *N*,*N*-dihexyl octanamide (DHOA), tri-*n*-butyl phosphate (TBP) or long chain alcohol etc. Addition of such phase modifiers to organic phase usually increases the extraction of unwanted metal ion present in HLLW and decreases the selectivity of extractant towards trivalent actinides. The chemical and radiolytic degradation of the modifier also complicates the recovery of extracted actinides and burdens the management of spent organic waste. Therefore, it is always desirable to develop extractants which can operate without a phase modifier for trivalent actinide separation from HLLW.

The literature survey on the studies related to trivalent actinide separation indicates that trivalent actinides require strong field bidentate or tridendate ligands in organic phase for efficient co-ordination and separation from the HLLW. For instance, the simple monodendate amides exhibit poor selectivity for trivalent actinides. The selectivity could be improved to a significant extent, by designing bidendate amides such as dialkyl malonamides (DMDOHEMA) for extraction. Moreover, the literature also shows that the extraction efficiency could be improved dramatically by introducing an oxygen atom at the 2-position from the amidic functional group as in diglycolamides (DGA). However, the presence of two amidic groups and etheric oxygen in a single molecule in DGAs resulted in high polarity of these ligands and poor miscibility of their metal-solvates in organic phase. The miscibility of metal solvates can be enhanced by reducing the number of carbonyl groups in the structure of DGAs. In this regard, a ligand with one amidic group and ethereal oxygen in 2-position (2-hydroxyacetamides) was identified as a better choice of extractant for trivalent actinide separation from HLLW.

Sugo et al. [96] identified hydroxyacetamides as one of the major hydrolytic and radiolytic degradation products of diglycolamides. A detailed study of the extraction behaviour of hydroxyacetamide produced during the gamma irradiation of TEHDGA by Sinharoy et al. [111] showed that trivalent actinides and some other fission products were extracted by these compounds. Robert Selvan et al. [112] reported efficient recovery of Am(III) and Eu(III) from nitric acid medium using 2-oxy acetamide anchored Merrifield resin. Parallel to these reports, solvent extraction studies of *N,N*-di-octyl-2-hydroxyacetamide for extraction of some selected actinides and fission products were reported by Kannan et al.[113]. The promising results reported in all these studies projected the potential of *N,N*-di-alkyl-2-hydroxyacetamides (DAHyA) as extractants for minor actinide partitioning.

Therefore, a detailed study was undertaken to explore the advantages and possible limitations of this new class of extractants. Three DAHyA derivatives with hexyl, octyl and decyl side chains (Fig 3.1) were chosen so as to study the influence of alkyl side chains on the properties of DAHyA. The detailed description of synthesis and characterisation of *N,N*-di-alkyl-2-hydroxyacetamides was given in section 2.4.9 of chapter-2 . These DAHyA derivatives have been used for the extraction of Am(III) and

Nd(III) which are selected as representatives for trivalent actinides and lanthanides respectively.

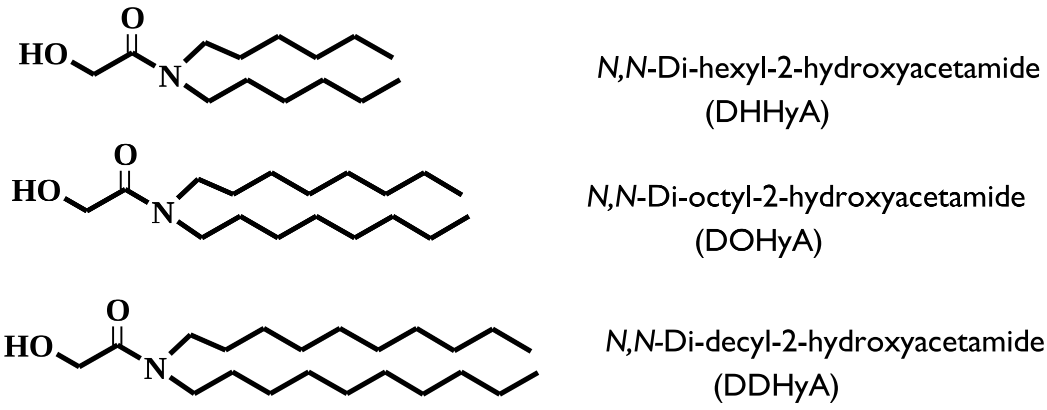

Figure 3.1: Structures of *N,N*-di-alkyl-2-hydroxyacetamides employed in the present study.

The results of the investigations carried out in the present chapter have been compared with other extractant systems in the literature, bringing out the advantages of DAHyA extractants in terms of nitric acid extraction, D-values for Am(III) and extraction capacity for Nd(III). The potential of long chain derivatives of DAHyA for modifier-free separation of trivalent actinides has been identified by these studies.

3.2 Extraction of Am(III) from nitric acid medium

Initially, 0.1 M solutions of DAHyA extractants in *n*-dodecane was employed for extraction of Am(III) ($D_{Am(III)}$) from aqueous nitric acid medium. Figure 3.2 shows the results of the extraction of Am(III) for all the three DAHyA compounds. As the figure was drawn on logarithmic scale, the data of the figure is shown in table 3.1 for easy reference. 0.1 M DHHyA/*n* –dodecane solution showed comparatively higher $D_{Am(III)}$ values and formed third phase upon equilibration with aqueous nitric acid solutions whose concentrations were above 6 M.

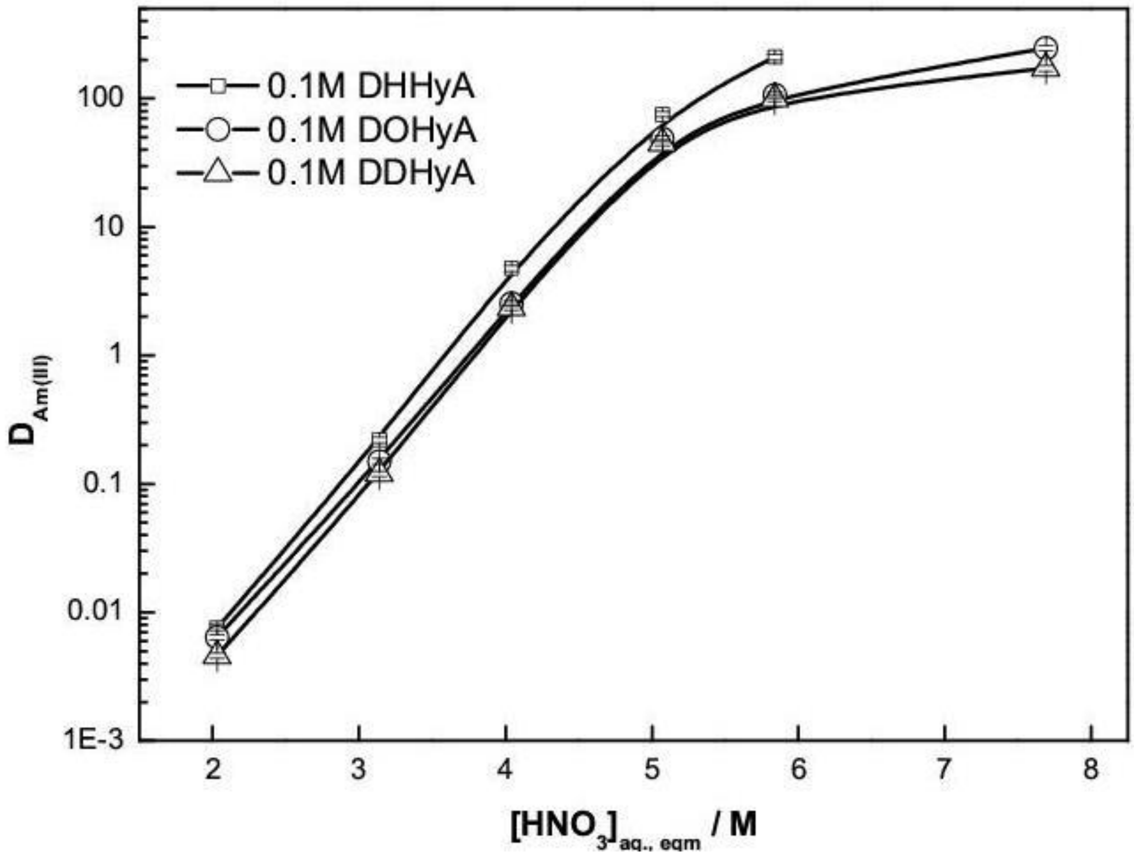

Figure 3.2: Variation in $D_{Am(III)}$ values as a function of nitric acid concentration for *N,N*-di-alkyl-2-hydroxyacetamides at 298 K. Diluent: *n*-dodecane. Aqueous phase: nitric acid solutions spiked with ^{241}Am tracer.

Table 3.1 Data table for figure 3.2

	$D_{Am(III)}$		
$[HNO3]_{aq., eqm}$ / M	DDHyA	DOHyA	DHHyA
2.03	0.0046	0.0064	0.0076
3.14	0.12	0.15	0.22
4.04	2.36	2.54	4.77
5.07	45.16	48.59	75.42
5.84	99.9	106.79	209.62
7.69	171.63	246.27	*

*Not determined due to third phase formation

The $D_{Am(III)}$ values were measured for DOHyA and DDHyA using equilibrium aqueous nitric acid concentrations up to 8 M, without any third phase. The results showed that $D_{Am(III)}$ values increased gradually with increase in aqueous nitric acid concentration and reached a value of ~100 at 6 M nitric acid followed by saturation.

The difference in values among the different DAHyA derivatives was less, as compared to the literature results for different diglycolamide derivatives with differing chain lengths [70-73]. The values were very small (less than 0.01) at 2 M nitric acid and sufficiently higher (near to 100) above 5 M nitric acid concentrations. However, the $D_{Am(III)}$ values varied between 0.1 and 5 for nitric acid concentration range 3 M to 4 M. The concentration of nitric acid prevailing in HLLW ranges from 3 – 4 M. Under these conditions the distribution ratio of Am(III) achieved in 0.1 M DAHyA/*n*-dodecane was quite low, and inadequate for efficient extraction of trivalent metal ions from HLLW. As it was desirable to have higher $D_{Am(III)}$ values at 3 M and 4 M nitric acid concentrations, it was decided to use 0.2 M concentrations of extractants in further studies.

3.2.1 Comparison with other extractants

Figure 3.3 shows the variation of $D_{Am(III)}$ values as a function of nitric acid concentration for 0.2 M DOHyA/*n*-dodecane. The results are compared with other extractant systems reported in the literature including CMPO, DMDBTDMA and TODGA [75]. The figure clearly shows that the $D_{Am(III)}$ values increase only gradually for DOHyA, but for all the other systems, the values start increasing at low nitric acid concentrations. The $D_{Am(III)}$ values of 0.2 M DOHyA/*n*-dodecane system was comparable with CMPO and DMDBTDMA systems when the aqueous acidity was 3 - 4 M. Also, the values were comparable with TODGA system at still higher aqueous acidities (5 – 6 M). The data of figure 3.3 is presented in table 3.2 for easy reference.

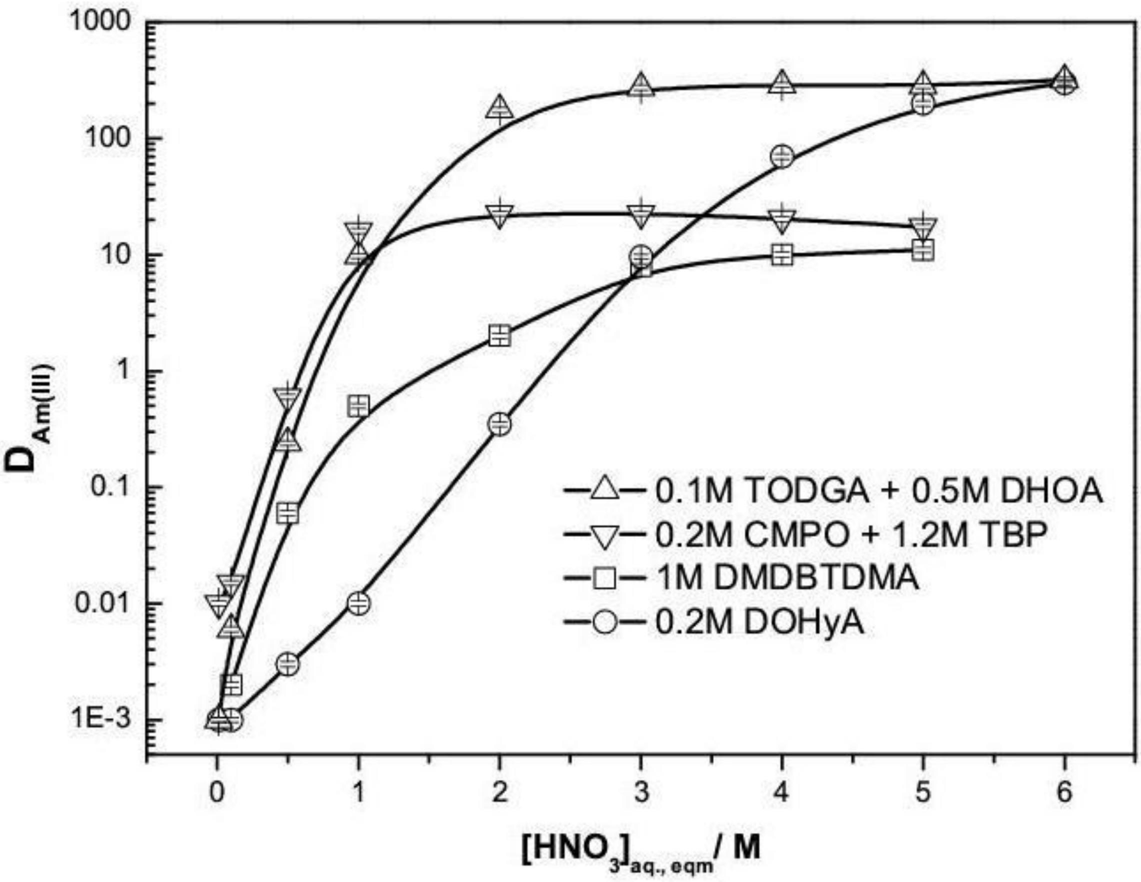

Figure 3.3: Variation in $D_{Am(III)}$ for different extractants as a function of nitric acid concentration at 298 K. Diluent: *n*-dodecane. Aqueous phase: nitric acid solutions spiked with ^{241}Am tracer.

Table 3.2 Data table for figure 3.3

	$D_{Am(III)}$			
$[HNO_3]_{aq., eqm}$ / M	CMPO[75]	TODGA[75]	DOHyA	DMDBTDMA[75]
0.01	0.01	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
0.1	0.015	0.006	$< 10^{-3}$	0.002
0.5	0.6	0.24	0.003	0.06
1	16.1	9.8	0.01	0.5
2	22.7	176	0.35	2
3	22.6	274	9.6	8
4	20.4	289	70	10
5	17.3	284	200	11
6	*	319	300	*

*Not reported

These results indicate that 0.2 M DOHyA/*n*- dodecane extractant system can be successfully employed for the extraction of Am(III) from nitric acid solutions at high acidities (above 3 M).

After extraction, the recovery of Am(III) is achieved by using dilute nitric acid. Usually the concentration of nitric acid for back extraction is chosen in such a way that the distribution ratio of Am(III) is lower than 10^{-2}. From figure 3.3, it is evident that all the other extractant systems would require aqueous nitric acid solutions having acidities around 0.1 M or less for back extraction of loaded metal ions. However, the use of such low concentration of nitric acid in a mixer-settler during back extraction could lead to the hydrolysis of the metal ions present in the extracted phase. In fact, such crud formation has been reported in TRUEX solvent system during recovery of Am(III) [54]. To overcome this problem, the stripping formulations containing one or two complexing agents have been employed for back extraction in those systems even though the stripping solution without any complexing agent was preferable. During solvent extraction process, the use of a higher acidity aqueous phase is always desirable so as to avoid all these problems. The $D_{Am(III)}$ values for DOHyA system was less nearly 0.01 even when the aqueous phase acidity was 1 M and it indicates that efficient stripping of Am(III) with DOHyA would be possible using 1 M or 0.5 M nitric acid solutions. The observations in the present study therefore point out that the DAHyA extractants can be used for the separation of Am(III) from high level liquid waste solutions with efficient back extraction of loaded metal ions using nitric acid solutions at higher acidities compared to other extractant systems.

3.3 Extraction stoichiometry

The increase in the distribution ratio of Am(III) with increase in the concentration of nitric acid observed in DAHyA indicates that the extraction of Am(III) is governed by the formation of neutral metal–solvate complex in organic phase. This is the general trend of extraction of metal ions from nitric acid shown by any neutral ligand. The extraction by DAHyA can be represented by the equilibrium reaction shown in equation 1. This shows that increasing the concentration of DAHyA or nitrate ion should increase the distribution ratio of Am(III) and the logarithmic plot of $D_{Am(III)}$ against concentration of DAHyA should reveal the stoichiometry of metal-solvate complex according to equation 3.

$$Am^{3+}_{aq} + 3\,NO_3^- + x\,DAHyA_{org.} \Leftrightarrow Am(NO_3)_3.(DAHyA)_{x\,org.} \qquad (1)$$

The equilibrium constant (K) for the above reaction can be written as

$$K = \frac{[Am\,(NO_3)_3.(DAHyA\,)_x]_{org\,.}}{[Am^{\,3+}]_{aq\,.} + 3\,[NO_3^-]_{aq\,.} + x\,[DAHyA\,]_{org\,.}} \qquad (2)$$

However, the ratio of concentration of Am(III) in the organic phase to that in the aqueous phase is described as the distribution ratio ($D_{Am(III)}$) [section 2.4.1, chapter-2].

Upon rearranging and substituting $D_{Am(III)}$ results in equation (3)

$$\log D_{Am\,(III)} = \log K + 3\,\log[NO_3^-] + x\,\log[DAHyA_{org}] \qquad (3)$$

Therefore, a logarithmic plot of $D_{Am(III)}$ against [DAHyA] for the extraction of Am(III) at constant nitrate ion concentration should result in a straight line plot whose slope value (x) would indicate the number of DAHyA molecules involved in the extraction of a single metal ion.

Figure 3.4 shows the variation of $D_{Am(III)}$ values for all the three DAHyA derivatives as their concentrations were varied from 0.1 M to 0.3 M in *n*-dodecane during extraction from 3 M nitric acid medium. The data table for the figure is also attached for easy reference of the values. It can be seen that the distribution ratio of Am(III) increases with increase in the concentration of DAHyA as expected. Linear regression analysis of the extraction data results in a slope of 5 to 6 for all the extractants. This indicates that about 5 molecules of DAHyA are coordinated to Am(III) ion in the metal-solvate present in organic phase. Similar studies have revealed a metal to ligand stoichiometry of 1:3 for TODGA [75] and other diglycolamides [87] for extraction of Am(III) from 3-4 M nitric acid solutions. For DAHyA extractants, co-ordination of more number of extractant molecules can be explained on the basis that these are bidentate extractants and diglycolamides are tridentate extractants.

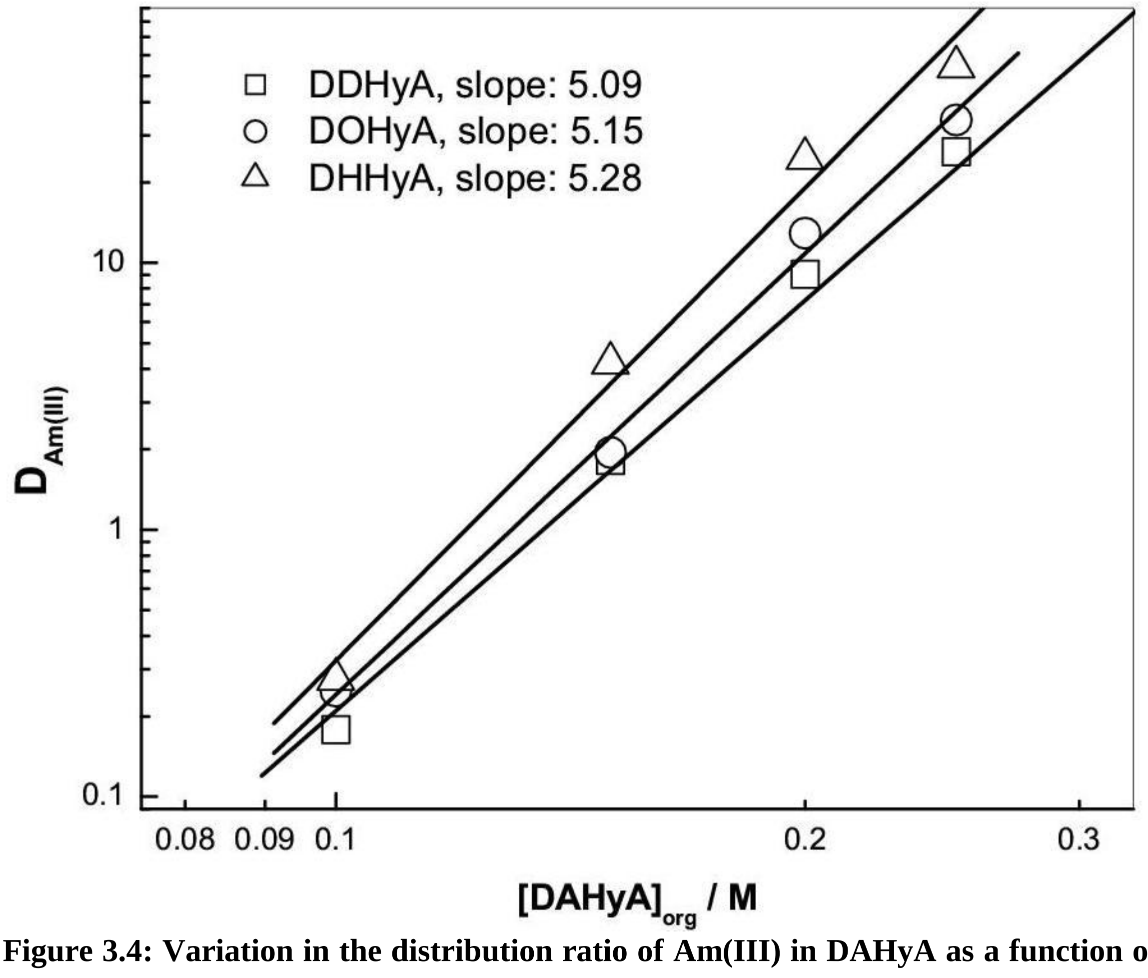

Figure 3.4: Variation in the distribution ratio of Am(III) in DAHyA as a function of extractant concentration at 298 K. Diluent: *n*-dodecane. Aqueous phase: 3 M nitric acid spiked with ^{241}Am tracer.

Table 3.3 Data table for figure 3.4

$[\text{DAHyA}]_{org}$ / M	DHHyA	DOHyA	DDHyA
0.1	0.275	0.249	0.178
0.15	4.207	1.947	1.818
0.2	24.563	12.934	9.059
0.25	54.135	34.234	26.033

Figure 3.5 shows the variation of $D_{Am(III)}$ values for all the three DAHyA derivatives as their concentrations were varied from 0.1 M to 0.3 M in *n*-dodecane during extraction from 4 M nitric acid medium. Though both the scales are logarithmic, the data obtained in this case (table 3.4) did not result in straight line plots as in the case of extraction from 3 M nitric acid medium.

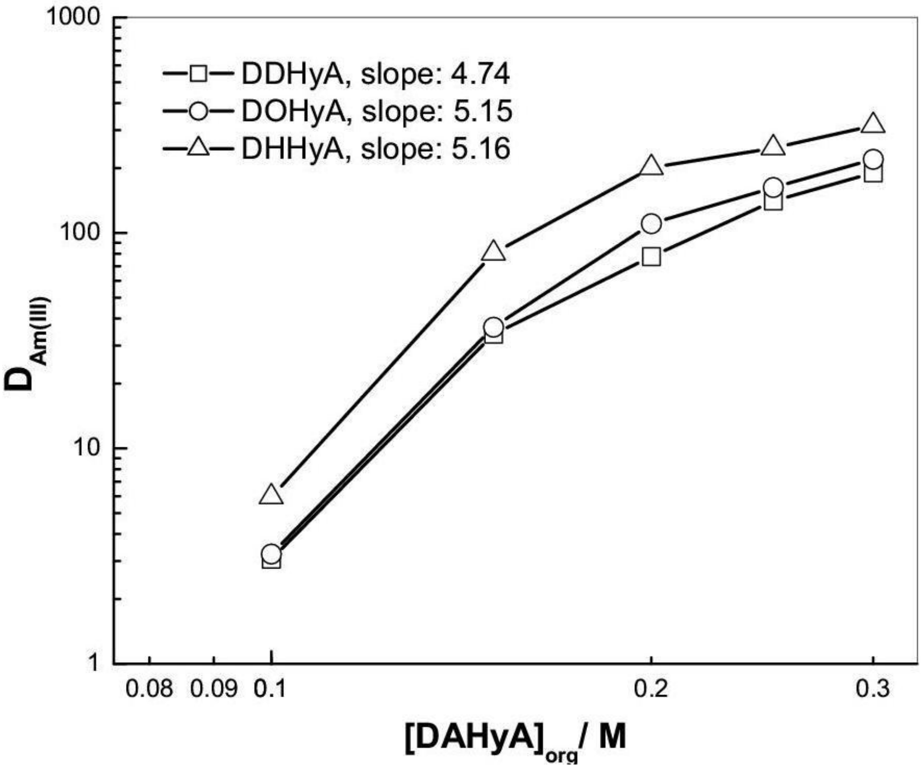

Figure 3.5: Variation in the distribution ratio of Am(III) in DAHyA as a function of extractant concentration. Diluent: *n*-dodecane. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer.

Table 3.4 Data table for figure 3.5

$[DAHyA]_{org}$ / M	DHHyA	DOHyA	DDHyA
0.1	5.949	3.229	3.059
0.15	80.300	36.416	33.859
0.2	200.735	110.468	77.550
0.25	247.243	162.322	140.690
0.3	314.500	219.376	189.782

The slope values obtained for three points between 0.1 M and 0.2 M concentrations varied from 4.7 to 5.16 indicating that around 5 molecules of DAHyA are co-ordinated to Am(III) ion in the metal solvate formed under these conditions. However, the slope values obtained for joining three points corresponding to concentrations of extractants between 0.2 M and 0.3 M were different, showing the formation of metal solvates with less number of extractant molecules. The slope values were 1.10 for DHHyA, 1.69 for DOHyA and 2.2 for DDHyA. It can be inferred that as the nitric acid concentration of aqueous phase increases from 3 M to 4 M, less number of extractant molecules are involved in the extraction of each metal ion from aqueous phase using organic phases with extractant concentrations above 0.2 M. It can be seen that the $D_{Am(III)}$ values are also higher ($>10^2$) under these conditions.

Therefore, the stoichiometry of extraction from 4 M nitric acid medium using DAHyA extractants at concentrations higher than 0.2 M was different from the stoichiometry observed for extraction from 3 M nitric acid solution. The non-linearity of the curves clearly indicates that the stoichiometry of extraction varies depending on the acidity of aqueous phase and concentration of extractant. Also, our later studies on extraction of Nd(III) ions (section 3.5 in this chapter and section 5.3 in chapter-5)) have shown that the stoichiometry varies as the concentration of metal ions increases in the aqueous phase.

3.4 Extraction of nitric acid

It is found that all the neutral extractants studied for the extraction of metal ions from HLLW solutions co-extract significant quantities of nitric acid along with metal ions during the solvent extraction process. The extracted nitric acid plays a vital role in the stabilization of extracted metal ion complexes in the organic phase. Therefore, the study of nitric acid extraction is important during the evaluation of any extractant used for this purpose. Usually, it is desirable that the co-extraction of nitric acid is not too much or too less.

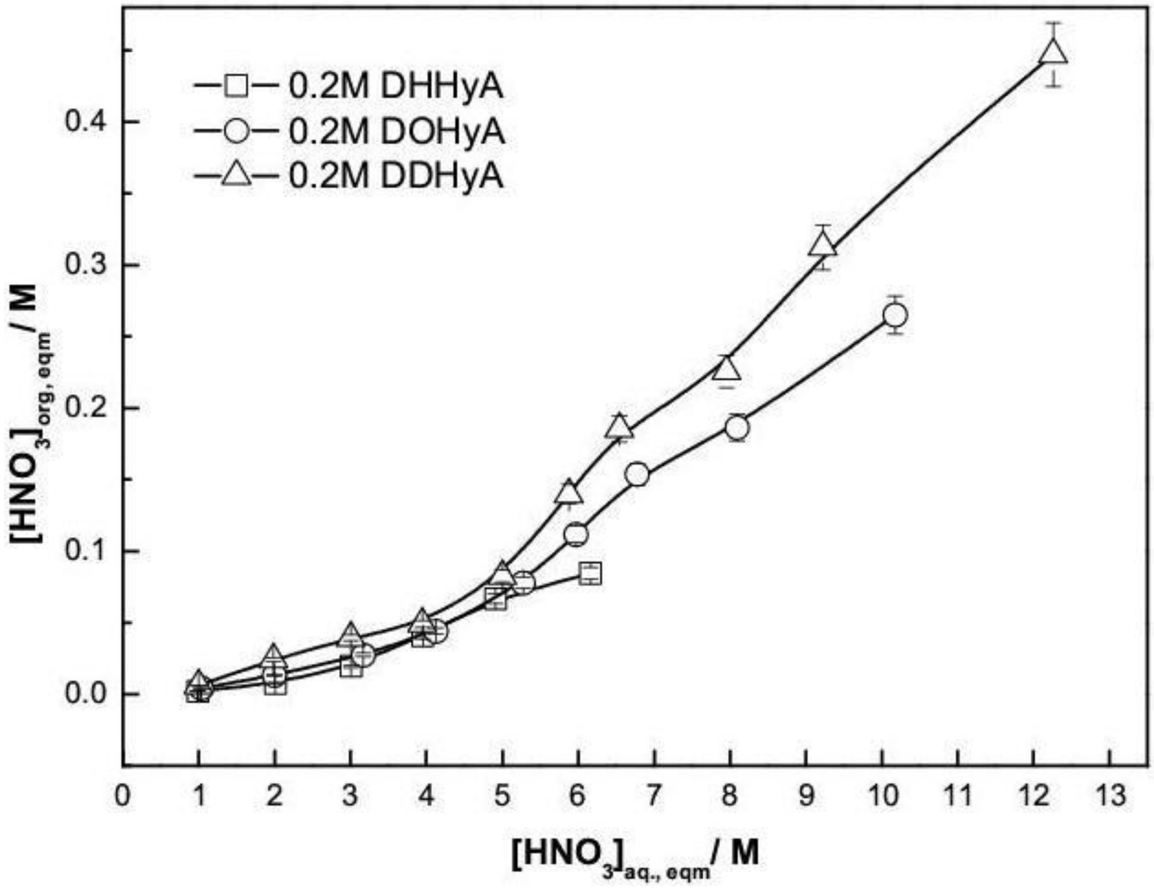

Figure 3.6: Nitric acid extraction isotherms for *N,N*-di-alkyl-2-hydroxyacetamides at 298 K. Diluent: *n*-dodecane.

Figure 3.6 gives the nitric acid extraction isotherms at 298 K for all the three *N,N*-di-alkyl-2- hydroxyacetamides in the present study. The extraction of nitric acid by all the three DAHyA derivatives was comparable up to an equilibrium aqueous phase acidity of 6 M. When the equilibrium aqueous phase acidity was increased beyond 6 M, the extraction of nitric acid was found to vary in the order DDHyA> DOHyA> DHHyA. A third phase was observed for DHHyA system on equilibration with aqueous phase of higher acidities. It was found that as the chain length of the extractant was increased, more amounts of nitric acid could be extracted to the organic phase, without the formation of third phase. Similar observations have been reported for other amide extractant systems such as the diglycolamides [88].

The extraction of nitric acid in an extractant system is a measure of the basicity of the extractant. The relative basicities of all the three DAHyA derivates should be similar as per the results shown in figure 3.6. To understand the relative basicity of DOHyA, the extraction of nitric acid at various concentrations (0.2 M-0.8 M) of DOHyA in *n*-dodecane was studied. The concentration of nitric acid was fixed at 4 M. The results of the study are summarized in table 3.5.

Table 3.5: The equilibrium nitric acid concentrations measured for different concentrations of DOHyA/*n*-dodecane system at 298 K. Aqueous phase: 4 M nitric acid.

$[DOHyA]_{org}$ / M	$[HNO_3]_{org}$ / M	$[HNO_3]_{aq}$ / M
0.2	0.0453	3.8945
0.4	0.1218	3.8484
0.6	0.2232	3.7742
0.8	0.3217	3.6858

The extraction of nitric acid in DOHyA/*n*-dodecane extractant system can be represented by the equilibrium reaction shown in equation 4.

$$H^{+}_{(aq.)} + NO^{-}_{3\,(aq.)} + n\,DOHyA_{(org.)} \Leftrightarrow [(DOHyA)_{n}.HNO_{3}]_{(org.)} \qquad (4)$$

The equilibrium constant is defined by,

$$K_{H} = \frac{[(DOHyA)_{n}.HNO_{3}]_{(org.)}}{[H^{+}]_{(aq.)}.[NO_{3}^{-}]_{(aq.)}.[DOHyA]^{n}_{(org.)}} \qquad (5)$$

Here, the equilibrium constant is also known as the 'conditional acid extraction constant' (K_H). Re-arranging equation (5) in logarithmic form gives equation (6) as,

$$\log[H^{+}]_{(org.)} - 2\log[H^{+}]_{(aq.)} = n\log[DOHyA]_{(org.,free)} + \log K_{H} \qquad (6)$$

In the above equation, $[DOHyA]_{(org.free)}$ was calculated from the difference in the initial extractant concentration and concentration of extracted nitric acid in organic phase. The value of $[H^+]_{(aq)}$ in the above equation was calculated from the initial acidity of aqueous phase and the known dissociation constant of nitric acid (K_a=23.5). The values of {log $[H^+]_{(org)}$ − 2log$[H^+]_{(aq)}$ } were plotted against log$[DOHyA]_{(org.free)}$ to get straight line plot which is shown in figure 3.7. The slope value calculated for the curve is 1.84, indicating the formation of 1:2 adduct of nitric acid with DOHyA at 4 M. The Y-intercept of the plot gives the magnitude of log K_H. From this, the value of K_H is calculated to be 0.092 for DOHyA.

The K_H values for TODGA and CMPO were reported as 4.1 and 2.0, when the nitric acid concentration of aqueous phase was 1 M [75]. For DMDBTDMA extractant, K_H value of 0.32 is reported for extraction from 3 M nitric acid medium [65]. Recently, our group has reported the extraction behaviour of a novel extractant system, namely *N*,*N*-di-alkylmethoxyacetamides in which the –OH group of DAHyA was replaced with –

OCH$_3$ group. The K$_H$ value for *N*,*N*-di-octyl-2-methoxyacetamide (DOMeOA) for extraction from 4 M nitric acid medium was calculated to be 0.208 [147].

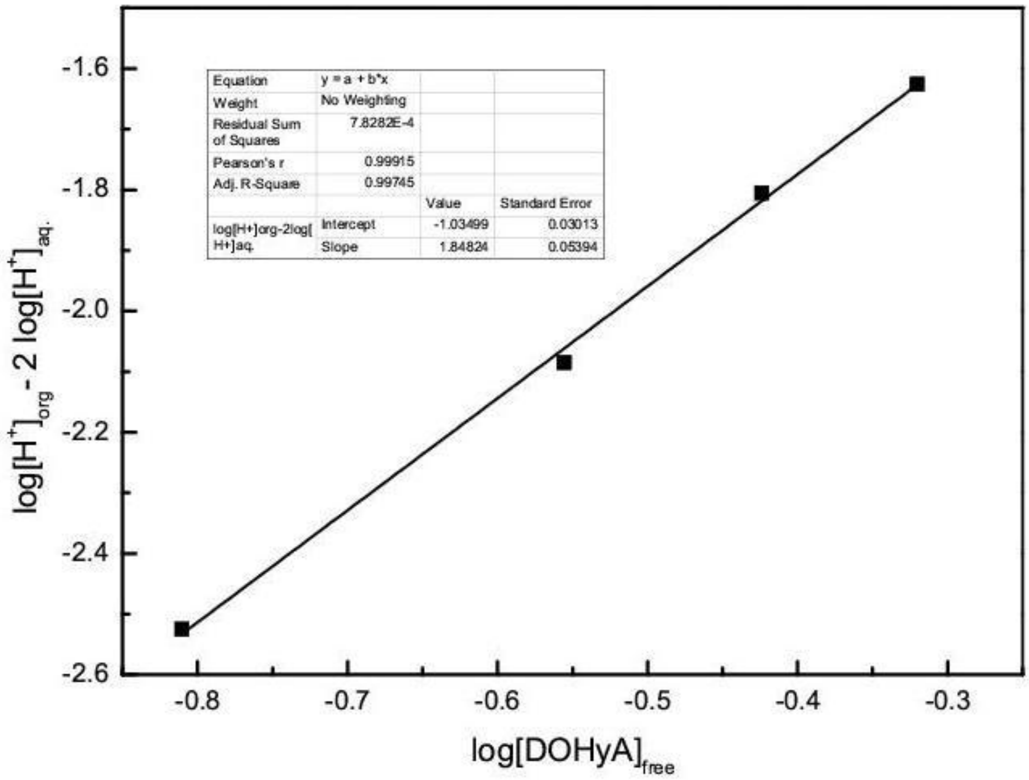

Figure 3.7: Determination of conditional acid uptake constant (K$_H$) for DOHyA at 298 K. Aqueous phase: 4 M nitric acid. Diluent: *n*-dodecane.

The lower extraction of nitric acid in hydroxyacetamides compared to the corresponding methoxyacetamides points out the less availability of protonation sites in hydroxyacetamides. The reason for this can be attributed to the intramolecular hydrogen bonding in hydroxyacetamides [139]. The intramolecular hydrogen bonding structures of DAHyA are discussed in detail in Chapter-4 (section 4.4, under 'Effect of irradiation on hydrodynamic parameters').

The limiting organic concentration (LOC) and critical aqueous concentration (CAC) values of nitric acid for all the three DAHyA derivatives are given in table 3.6. It was found that DHHyA having hexyl side chains extracted minimum amount of nitric acid at LOC and formed a third phase, when the equilibrium aqueous phase acidity was above 6 M . The DOHyA and DDHyA derivatives formed third phase only when equilibrium aqueous phase acidity was above 10 M.

For DOHyA, the LOC value of nitric acid observed was corresponding to a stoichiometry of approximately 1:1 for the extractant-nitric acid complex in the organic phase. It can be assumed that carbonyl group of each DOHyA molecule is co-ordinated to each HNO_3 molecule under these conditions. For DDHyA extractant, the LOC value of nitric acid indicated the formation of 1: 2 extractant nitric acid complexes in the organic phase under these conditions. Higher stoichiometry observed in DDHyA indicates that the carbonyl group as well as the nitrogen of amide or –OH groups is protonated in this case.

Table 3.6: LOC and CAC values for *N*,*N*-di-alkyl-2-hydroxyacetamides for extraction of nitric acid.

Extractant	Concentration of nitric acid (M)		
	Initial	CAC	LOC
0.2 M DHHyA/*n*-DD	7.6	6.16	0.082
0.2 M DOHyA/*n*-DD	11.6	10.17	0.25
0.2 M DDHyA/*n*-DD	15.7	12.26	0.45

The observations in the present study thus indicate that DAHyA derivatives with octyl and decyl side chains resisted third phase formation on contacting with nitric acid solutions having acidities around 10 M, without the use of any phase modifiers.

3.4.1 Comparison with other extractants

The extraction of nitric acid by DOHyA was compared with other extractant systems including CMPO and TODGA. Figure 3.8 gives a comparison of the nitric acid extraction of some of these extractant systems in *n*-dodecane with 0.4 M DOHyA/ *n*-dodecane system, when the initial nitric acid concentration of the aqueous phase was varied up to 12 M.

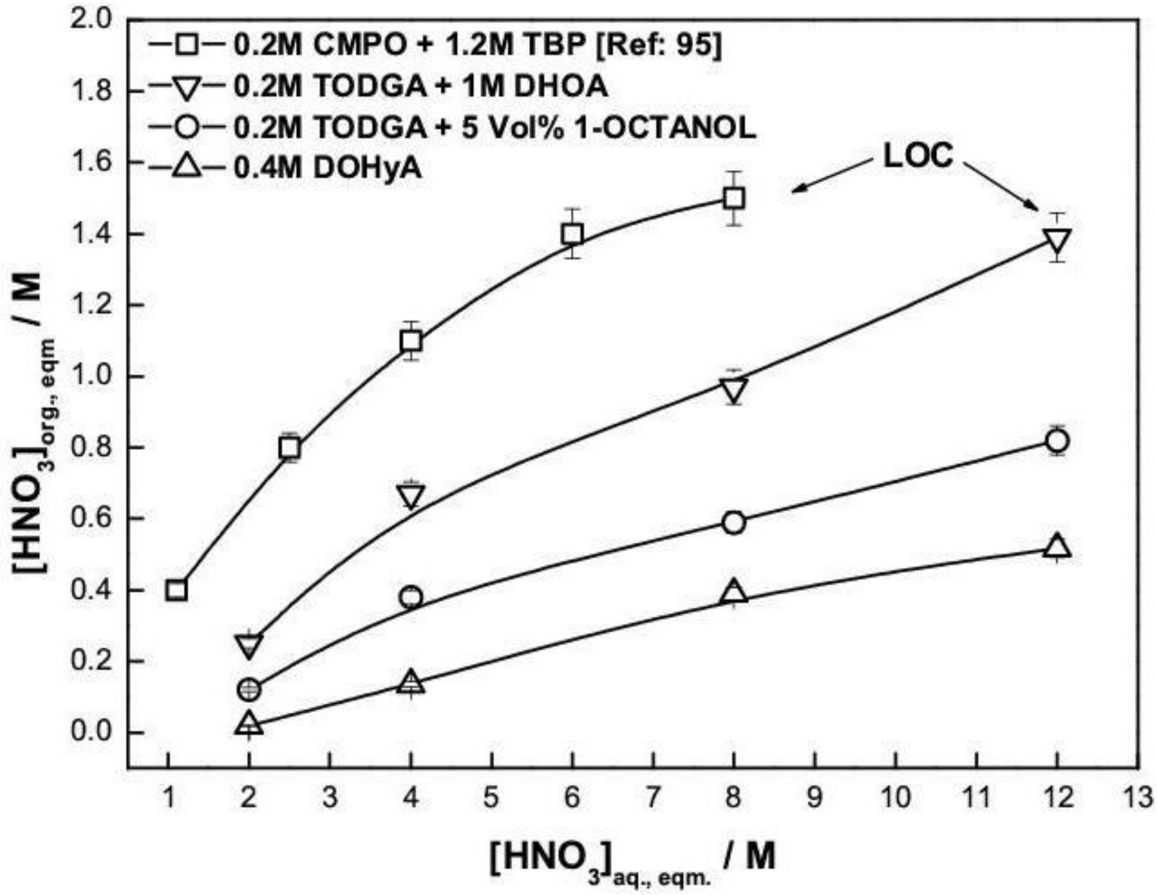

Figure 3.8: Nitric acid extraction in different extractant systems at 298 K. Diluent: *n*-dodecane.

The CMPO and TODGA extractants were widely studied in the process scale applications for minor actinide partitioning in the presence of suitable phase modifiers. It was found that the presence of phase modifiers resulted in the extraction of more amounts of nitric acid in those systems. For comparison with literature reports of 0.2 M CMPO systems, acid uptake studies were carried out with 0.2 M TODGA and 0.4 M DOHyA solutions in *n*-dodecane. Even though 0.2 M DOHyA/*n*-dodecane formed third phase when the initial aqueous phase concentration exceeded 10 M, no third phase was observed in 0.4 M DOHyA system up to 12 M. It is reported that CMPO-TBP extractant system formed third phase on equilibration with aqueous phase acidities above 8 M [95]. For TODGA-DHOA system also, third phase was observed at aqueous phase nitric acid concentrations above 9 M [75]. However, the TODGA-octanol system and DOHyA system did not show a third phase even when the initial aqueous phase acidity was 12 M. The extraction of nitric acid by DOHyA was found to be lower than all the other extractants.

If we analyze the stoichiometry of nitric acid extraction at the maximum organic concentration (MOC), it shows the formation of a 1:1 extractant: nitric acid complex in DOHyA, while the nitric acid content is equivalent to 1:3 stoichiometry in TODGA-octanol system. These observations may be accounted according to the number of polar groups in each molecule of these extractants, i.e one carbonyl group in DOHyA and two carbonyl groups along with one ethereal oxygen in TODGA, which co-ordinate with the extracted HNO_3 molecules. For the other two systems, the phase modifiers containing carbonyl or phosphoryl groups also extracted nitric acid and third phase was formed earlier. However, it should be noted that no third phase was formed in all these systems when the aqueous nitric acid concentration was around 4 M, which is the aqueous acidity expected for high level liquid waste solutions.

At all the aqueous phase acidities studied, DOHyA showed the minimum extraction of nitric acid compared to other extractant systems. The nitric acid present in the extracted phase dictates the number of stages/contacts required for stripping of extracted metal ions. Usually the nitric acid present in the organic phase is also back extracted into aqueous phase during stripping of metal ions. Thus higher concentration of extracted acid increases the acidity of stripping solution leading to the requirement of large number of stages for quantitative back extraction of metal ions. Therefore, minimal extraction of nitric acid is always advantageous for any extractant system and DOHyA can be regarded as a better candidate for extraction in view of its lower nitric acid extraction compared to other existing extractant systems.

3.5 Extraction of Nd(III) ions

The aqueous chemistry of Ln(III) and An(III) ions closely resemble each other due to the participation of f-orbitals in bonding for both these groups of metal ions in a similar way. Among the inner transition elements, the early actinides in the periodic table up to plutonium exhibit higher valancies in aqueous nitric acid solutions. However, americium and later actinides preferentially exhibit +3 oxidation state similar to lanthanide ions. Therefore, extraction of Am(III) ions from nitric acid medium would be invariably accompanied by the co-extraction of Ln(III) ions which exist in good amounts in high level liquid waste. The approximate composition of spent fuel was discussed in chapter-1 (Table-1.1). It shows that the total amount of lanthanides may be ten times or higher than the amount of minor actinides in high level waste solutions. Therefore, it becomes essential to study the extraction of lanthanide ions by any extractant proposed for minor actinide partitioning. The extraction of Ln(III) ions are studied mainly with respect to the extraction capacity of the extractant. Among the Ln(III) ions, the preferred prototype is Nd(III) for studies related to the extraction capacity as it is the most abundant metal ion among the lanthanides present in HLLW. Literature reports are available on the study of third phase formation [83, 93-95] aggregation behaviour [120-122, 128] and stability of solid complexes [113,116] of various extractant systems with Nd(III) ions.

In the present study, the extraction of Nd(III) ions by the three DAHyA derivatives was studied by equilibrating 0.2 M solutions of DAHyA in *n*-dodecane with 3 M and 4 M nitric acid solutions containing Nd(III) ions. The concentrations of Nd(III) ions were varied from 25 mM to 600 mM. It was found that the hexyl derivative DHHyA formed a third phase with Nd(III) ions at both the acidities, even when the concentration of metal ion was as low as 3 mM. This behaviour was similar to that of diglycolamides such as TODGA or TEHDGA [74] systems, requiring a phase modifier for extraction of metal ions at these acidities. However, further studies with DHHyA were not carried out in this direction.

On the other hand, both DOHyA and DDHyA did not form any third phase under the conditions of present study. The Nd(III) extraction isotherms for these two systems are shown in figure 3.9.

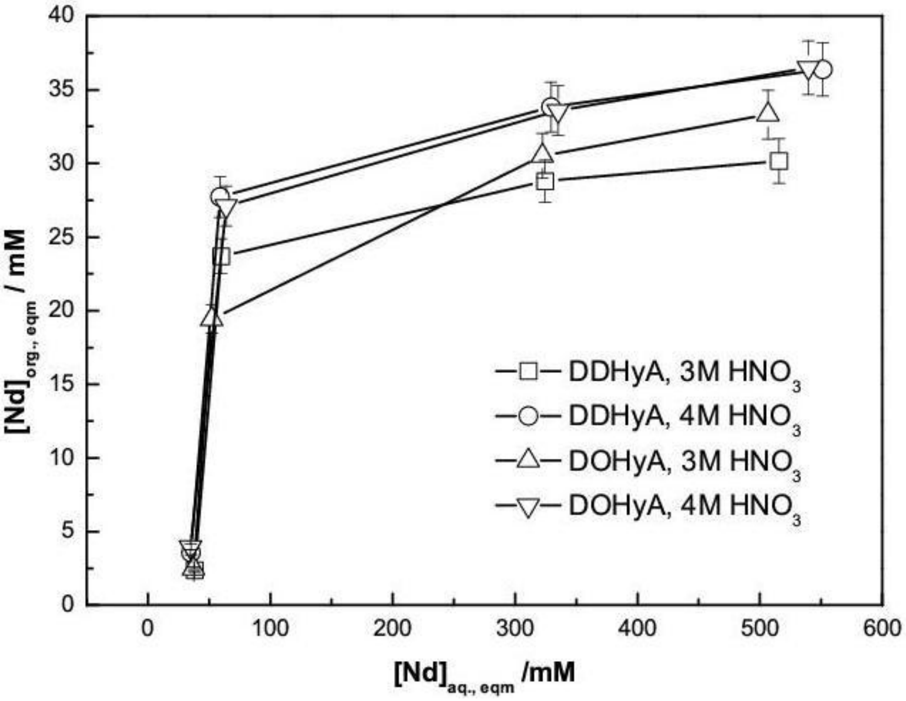

Figure 3.9: Nd (III) extraction isotherms for *N,N*-di-alkyl-2-hydroxyacetamides at 298 K. Organic phase: 0.2 M DAHyA in *n*-dodecane. Aqueous phase: 3 M or 4 M nitric acid containing Nd(III).

As per the literature reports, the total concentration of Ln(III), minor actinides and other extractable metal ions in HLLW by these extractants shall not exceed 50 mM [32,133]. The aqueous concentration of Nd(III) employed in the present studies varied up to 600 mM and both these extractants did not show a third phase during the extraction of metal ions from 3 M and 4 M nitric acid solutions, which is the acidity range of HLLW. It was found that the extraction of Nd(III) was more at 4 M as compared to the extraction from 3 M nitric acid solutions. In both the cases, the extraction was nearly similar for both the DAHyA derivatives.

As the aqueous concentration of Nd(III) was increased, the extraction of metal ions to the organic phase increased sharply in the beginning and the loading of Nd(III) in organic phase reached a saturation limit at ~ 40 mM. Under this condition, the stoichiometry of Nd: DAHyA corresponds to ~ 1:5, which is in good agreement with the stoichiometry determined by slope analysis of the extraction data (figure 3.4). The study, thus, indicates that neodymium(III) could be loaded to near stoichiometric levels from 3-4 M nitric acid medium in 0.2 M DOHyA and 0.2 M DDHyA in *n*-dodecane without the formation of third phase.

As a part of aggregation studies discussed in chapter-5, the Nd(III) extraction of DOHyA from 4 M nitric acid medium was studied by varying the initial concentration of Nd(III) up to 1300 mM (Figure 5.5). In those studies, the concentration of DOHyA employed was 0.4 M in *n*-dodecane and no third phase was formed under those conditions also. All the above results point out that extraction of trivalent lanthanides and actinides from nitric acid medium by long chain DAHyA derivatives (DOHyA and DDHyA) would not require the use of a phase modifier.

3.6 Summary

The alkyl derivatives of *N,N*-dialkyl-2-hydroxyacetamide were studied for the extraction of Am(III) from nitric acid medium to evaluate the suitability of using them for partitioning of trivalent actinides from HLLW. The alkyl group in DAHyA was varied from hexyl to decyl. The distribution ratio for the extraction of Am(III) in 0.1 M DAHyA/*n*-dodecane was less than 10^{-2} at nitric acid concentrations ranging from 0.01 to 1 M and the $D_{Am(III)}$ reached a value of ~100 at 6 M nitric acid followed by saturation. The $D_{Am(III)}$ decreased in the order DHHyA > DOHyA > DDHyA. The $D_{Am(III)}$ of 10 to 70 obtained in 0.2 M DAHyA/*n*-dodecane at 3 -4 M nitric acid, was adequate for efficient extraction of trivalent metal ions from HLLW in few contacts. Also, the results showed that even 0.5 M or 1 M nitric acid solution can be employed for back extraction of loaded Am(III) ions, whereas other extractants required aqueous nitric concentrations around 0.1 M for efficient back extraction. About five molecules of the DOHyA were coordinated to Nd(III) when loaded from 3 -4 M nitric acid medium and it was in good agreement with the slope analysis of the Am(III) extraction in DAHyA/*n*-dodecane. DAHyA formed third phase with nitric acid at concentrations, much above the concentration of nitric acid prevailing in HLLW. The stoichiometry of DAHyA: HNO_3 increased in the order DHHyA (1: 0.4) < DOHyA (1: 1) < DDHyA (1: 2). The third phase was not observed in octyl and decyl derivatives even when the initial concentration of Nd(III) was up to ~ 600 mM in 4 M nitric acid, which was far above the concentration of trivalent metal ions (5 mM to 50 mM) present in HLLW. Therefore, the solvents DOHyA and DDHyA did not require any phase modifier. In view of these, the DAHyA derivatives are promising candidates for the separation of trivalent actinides from high-level liquid waste.

RADIOLYTIC STABILITY OF *N*, *N*-DI-ALKYL-2-HYDROXYACETAMIDES

4

4.1 Introduction

As discussed in section 1.7 of chapter-1, the solvent systems employed in nuclear reprocessing applications must be stable towards radiolytic degradation in an irradiated, organic/aqueous acidic environment with the formation of only benign products. Therefore, the evaluation of radiolytic stability is an important step before proposing a novel extractant system for process applications. The present chapter discusses the studies on radiolytic degradation of all the three *N*,*N*-di-alkyl-2-hydroxyacetamides under gamma irradiation. The different samples of extractants were irradiated with gamma rays from a ^{60}Co source up to an absorbed dose of 750 kGy. The distribution values of Am(III) were measured as a function of absorbed dose and reported. The variation in physical properties such as density, viscosity and phase disengagement time also were measured and reported. The effect of irradiation on the stripping behaviour of these extractants was also assessed by stripping studies in cross-current mode. An attempt was made for the analysis of degradation products of DOHyA by FT-IR analysis. The effect of irradiation of DOHyA on the bulk extraction of Nd(III) and its aggregation behaviour under irradiated conditions was also studied. The results of all these studies are discussed in the following sections in this chapter.

4.2 Effect of gamma irradiation on the extraction of Am(III)

In the present study, the distribution ratio of Am(III) in the irradiated *N*,*N*-di-alkyl-2-hydroxyacetamides (DAHyA) was measured from 4 M nitric acid solutions. The results of the measurements are summarized in the figures 4.1, 4.2 and 4.3. Figure 4.1 shows the variation in distribution ratio of Am(III) as a function of absorbed dose for all the three extractants irradiated as neat samples.

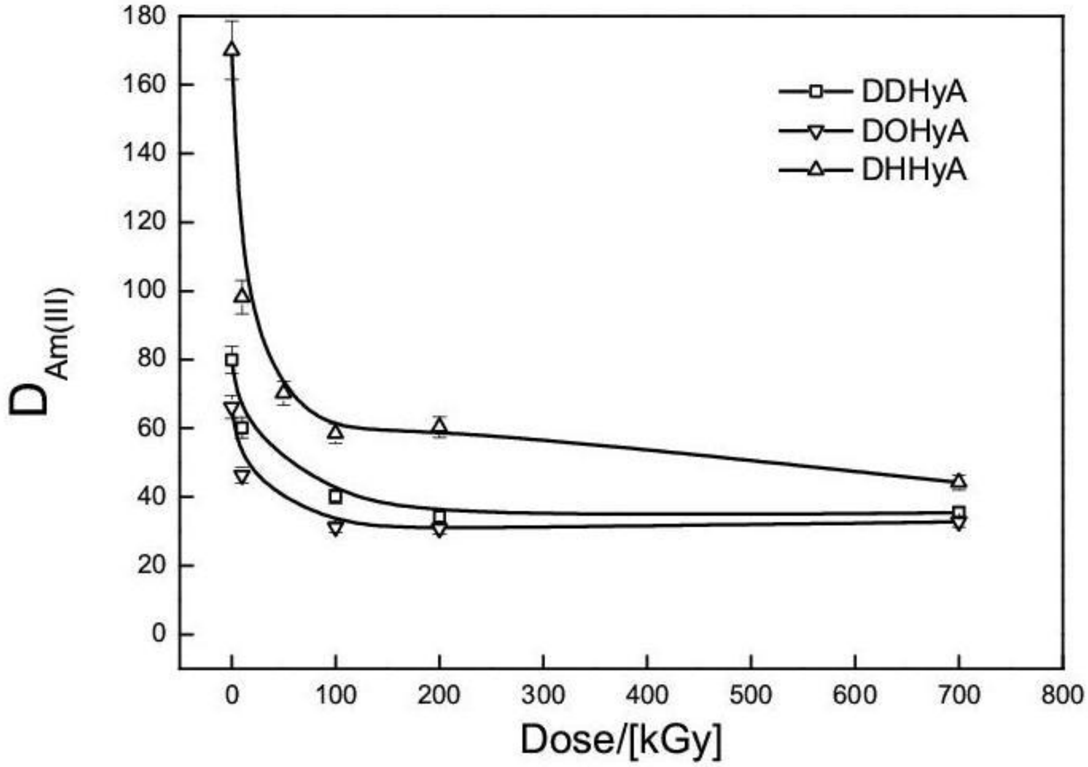

Figure 4.1: Variation in the distribution ratio of Am(III) with absorbed dose for neat extractants at 298 K. Neat DAHyA were irradiated to different dose levels, diluted to 0.2 M with *n*-dodecane and employed for extraction studies without any pre-treatment. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer.

It can be observed that $D_{Am(III)}$ decreased with increase of absorbed dose for all the three extractants. This indicates that the degradation of *N*,*N*-di-alkyl-2-hydroxyacetamides increases with increase of absorbed dose. The similar decreasing trend of $D_{Am(III)}$ values observed for all the three extractants point out that changes in chain length of DAHyA has insignificant effect on the radiation stability. The variation in distribution ratio of Am(III) as a function of absorbed dose for all the three extractants irradiated as 0.2 M solutions in *n*-dodecane, in the presence and absence of 4 M nitric acid is shown in figures 4.3 and 4.2 respectively. Similar decreasing trend of $D_{Am(III)}$ values was observed under all the three conditions. However, higher distribution ratios were obtained when the samples were irradiated as neat, as compared to their 0.2 M solutions in *n*-dodecane.

The $D_{Am(III)}$ values for neat samples at 700 kGy were about 100 times higher than the $D_{Am(III)}$ values observed for samples in *n*-dodecane irradiated to the same dose level. The larger decrease in distribution values as compared to neat extractants is a common observation for most of the extractants in solution and it is generally explained as a result of the sensitization effect due to radiolysis of the diluents. The radical cations generated from *n*-dodecane as a result of irradiation abstract H-atoms from the dissolved extractant molecules, thereby increasing the chances of electron transfer reactions and radiolytic degradation [99].

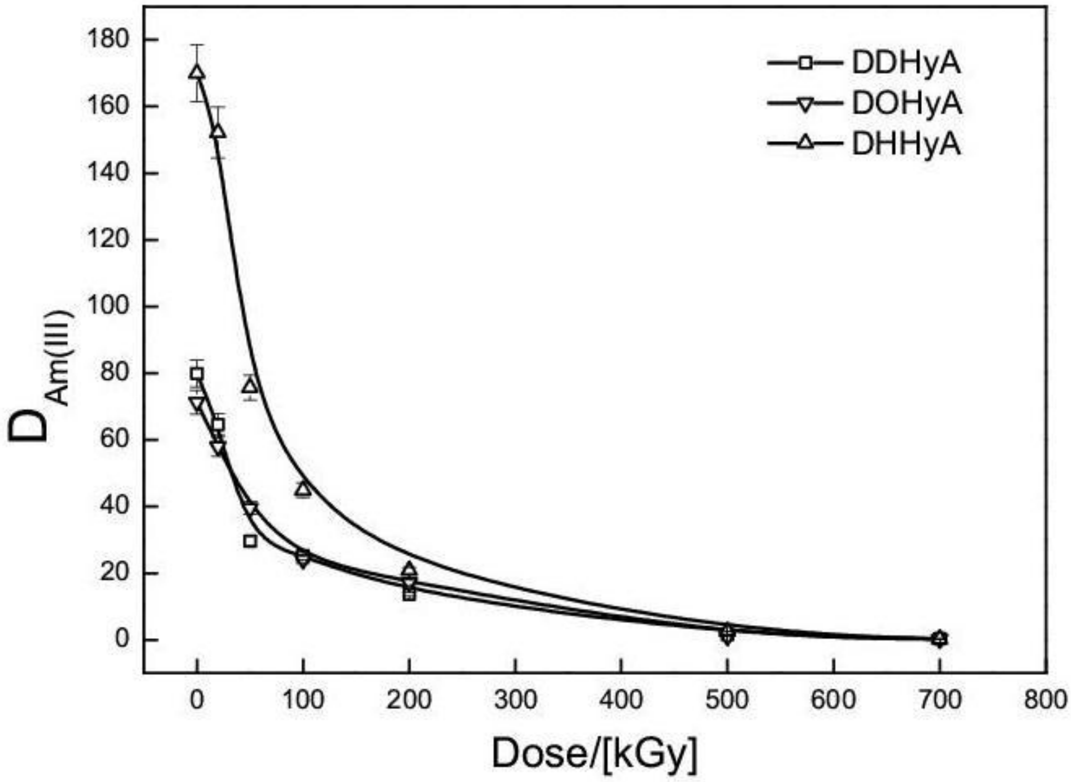

Figure 4.2: Variation in the distribution ratio of Am(III) with absorbed dose for extractants in *n*-dodecane at 298 K. 0.2 M DAHyA in *n*-dodecane were irradiated to different dose levels and employed for extraction studies without any pre-treatment. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer.

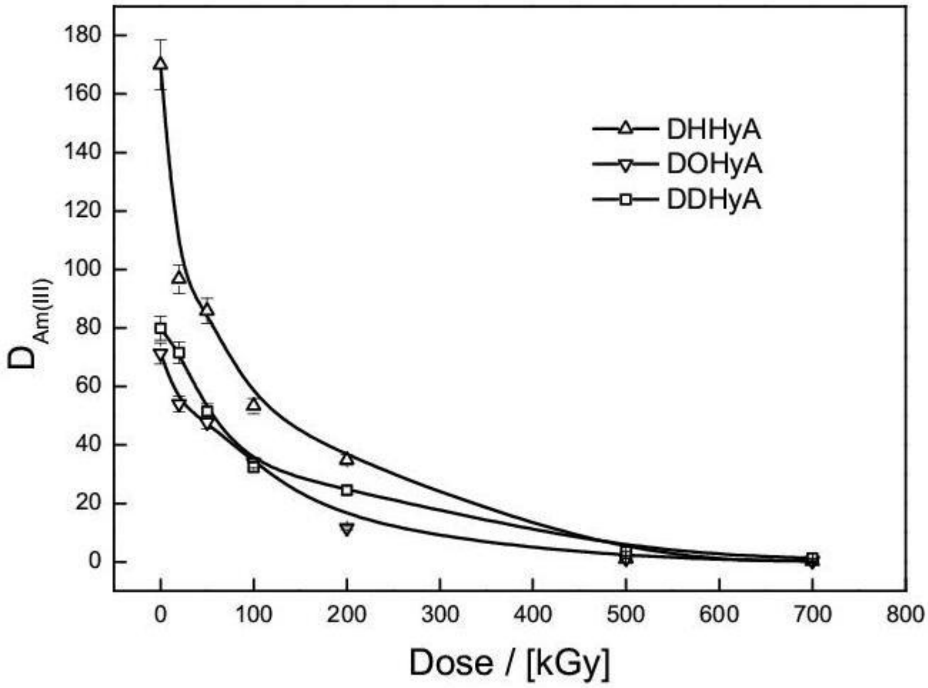

Figure 4.3: Variation in the distribution ratio of Am(III) with absorbed dose for extractants in *n*-dodecane at 298 K. 0.2 M DAHyA in *n*-dodecane in contact with 4 M nitric acid were irradiated to different dose levels and employed for extraction studies without any pre-treatment. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer.

The $D_{Am(III)}$ values were fairly good (> 30) at absorbed dose around 100 kGy and thereafter the values were smaller. The results show that these reagents can be successfully used for the process level applications where the total absorbed dose would be less than 100 kGy. Based on the residence time of the solvents in process equipments such as centrifugal contactors, the expected dose levels during the process conditions are less than 100 kGy for high level waste solutions from thermal reactors [39, 102]. The results also show that the $D_{Am(III)}$ values for DAHyA were > 10 when the absorbed dose was around 200 kGy which is the expected dose for fast reactor fuel solutions.

The radiolytic stability of amide extractants is better than CMPO systems during extraction as well as stripping conditions [55-59]. Among the amide based extractants, the radiolytic stability of DAHyA systems studied in this work was found to be comparable with the malonamide extractant systems and TEHDGA systems reported in the literature [67,103]. The decrease in distribution values of Am(III) reported for all these systems follow a similar trend. If we compare the decrease in $D_{Am(III)}$ values for TODGA systems as a function of gamma irradiation, the values are higher than DAHyA systems at higher absorbed doses[106]. However, the $D_{Am(III)}$ values showed by DAHyA systems (˜10) when the absorbed dose is 200 kGy are good enough for extraction of metal ions in a multi-stage extraction process.

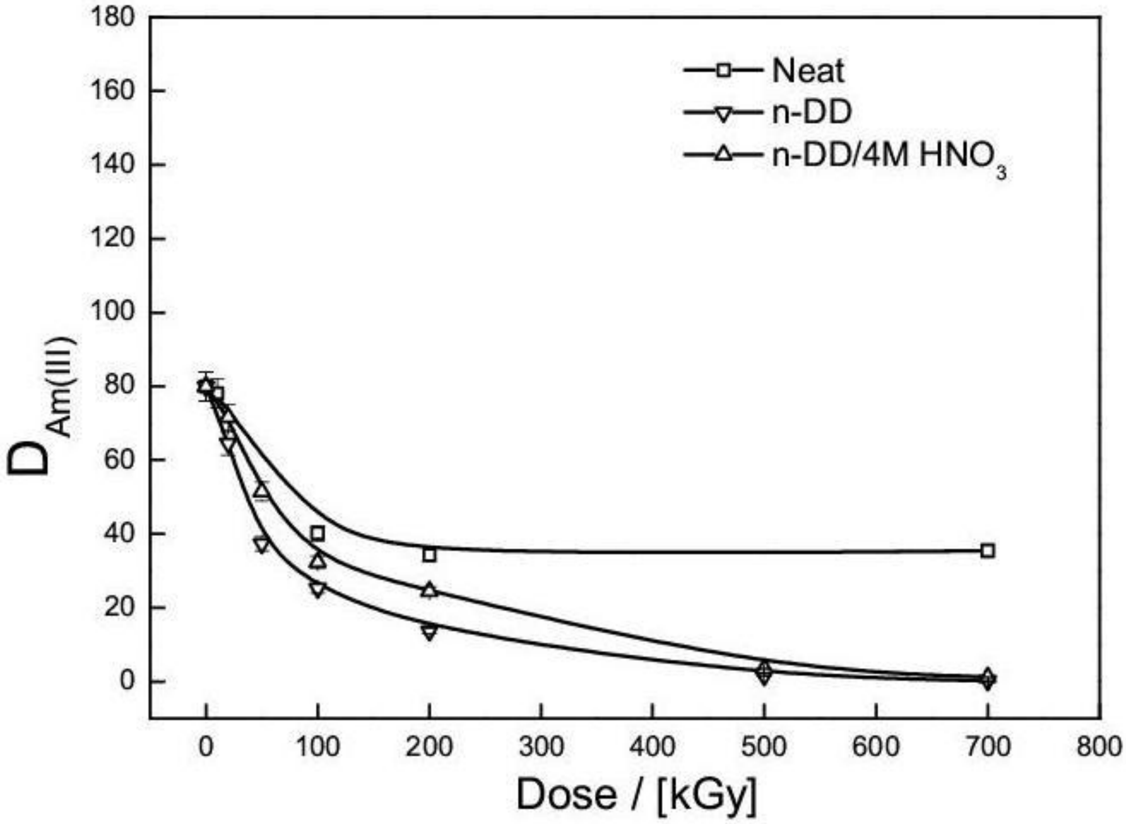

Figure 4.4: Variation in the distribution ratio of Am(III) with absorbed dose for DDHyA at 298 K. DDHyA was irradiated to different dose levels as neat, as well as 0.2 M solution in *n*-dodecane, in the presence and absence of equal volume of 4 M nitric acid. The neat samples were diluted to 0.2 M in *n*-dodecane and used for extraction studies. The other samples were used as such for extraction studies without any pre-treatment. Aqueous phase: 4 M nitric acid spiked with ^{241}Am tracer.

During the measurement of $D_{Am(III)}$ values of un-irradiated DAHyA extractants (figure 3.2 chapter-3), the hexyl derivative was found to have slightly higher distribution values compared to octyl and decyl derivatives. In the present study also, the distribution values obtained for hexyl derivative were higher than the values obtained for octyl and decyl derivatives up to 200 kGy irradiation. At higher levels of irradiation (> 500 kGy), the values were equally lower for all the extractants. In figure 4.4, a comparison is made between the effect of irradiation on the distribution values of Am(III), for neat irradiated samples along with samples irradiated in *n*-dodecane with and without the presence of 4 M nitric acid for one of the extractants (DDHyA).

The results show that irradiation in the presence of nitric acid does not have a deleterious effect on the system. The presence of co-existing nitric acid, in fact, improved the distribution values to a small extent. Similar results were observed for all the three *N*,*N*-di-alkyl-2-hydroxyacetamides employed in the present study. The results are in line with the observations reported for diglycolamides in the literature by different groups [96, 108].

The *N*,*N*-di-alkyl-2-hydroxyacetamides were identified as one of the major degradation products of the diglycolamides during radiolytic degradation [96, 111]. These compounds are expected to be chemically stable as they are the derivatives of hydroxy acids which are found in many naturally occurring compounds and are stabilized by intramolecular hydrogen bonding. However, they undergo radiolytic degradation and it has been reported that the radiolytic degradation in hydroxy compounds initiate with the abstraction of H-atom from the alpha carbon [100]. Based on the observations in the present study, it can be concluded that the observed radiation stability and hydrolytic stability of hydroxyacetamides is comparable with diglycolamides.

4.3 Stripping studies

The studies on the effect of aqueous nitric acid concentration on the extraction of Am(III) by DAHyA extractants (Chapter-3, Section 3.2) have pointed out the possibility of efficient stripping of metal ions from loaded organic phases of DAHyA using 0.5 M or 1 M nitric acid solutions. Therefore, the stripping behaviour of Am(III) from DOHyA was studied in detail using both irradiated and un-irradiated samples. Figure 4.5 shows the cumulative stripping behavior of Am(III) from the loaded 0.2 M DOHyA/ *n*-dodecane.

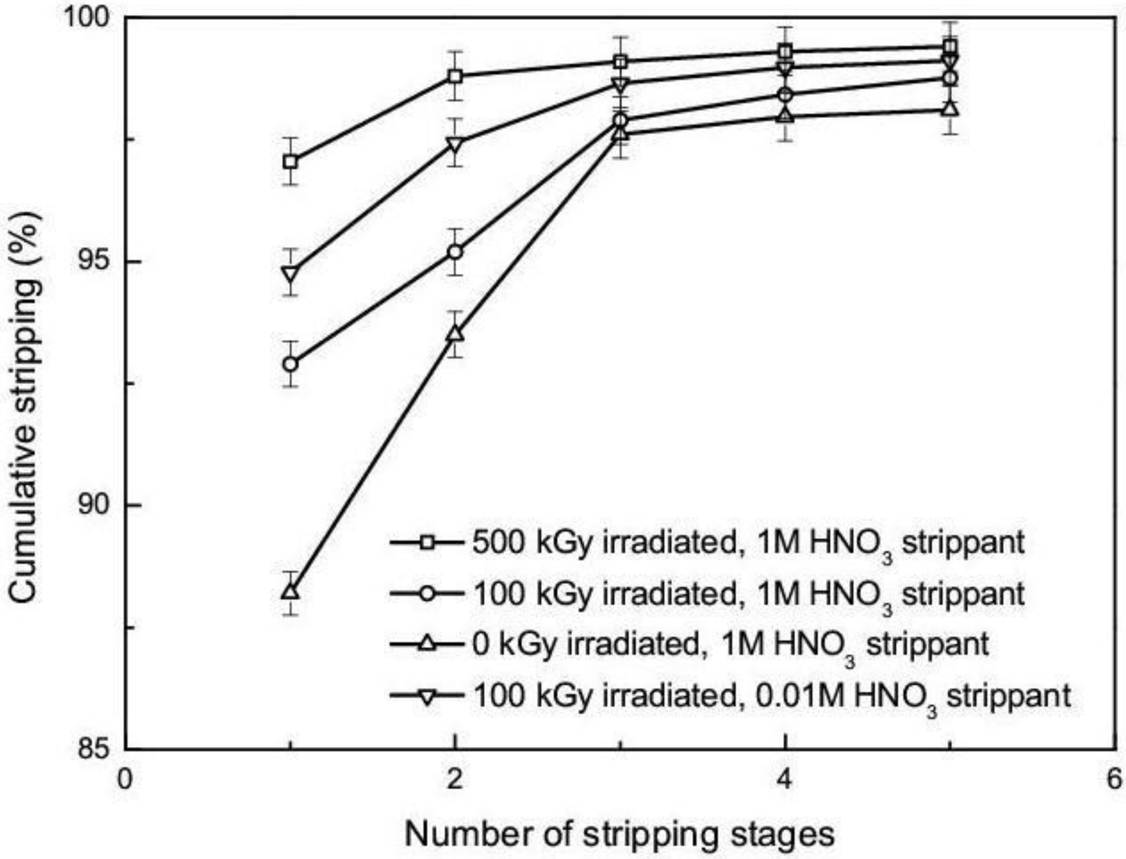

Figure 4.5: Cumulative stripping of Am (III) from loaded 0.2 M DOHyA in *n*-dodecane as a function of number of contacts with dilute nitric acid. The metal ions were loaded from 4 M nitric acid solution and then stripped back using either 0.01 M or 1 M nitric acid.

The stripping behavior was studied for the solvent irradiated at 100 kGy and 500 kGy in the presence of 4 M nitric acid and the results were compared with that of un-irradiated solvent. In all the above cases, 1 M nitric acid was used as the stripping solution. It can be seen that quantitative recovery of Am(III) was possible in 3 - 4 contacts using both 0.01 M and 1 M nitric acid solutions. From figure 4.5, it is also evident that the stripping behavior of the extractant is not affected by irradiation even at 500 kGy absorbed dose. After three successive contacts with the stripping solutions, the recovery of Am(III) was similar in all the cases.

Stripping studies were also done using 0.01 M HNO_3 as stripping solution for 100 kGy irradiated solvent and the results are compared in the same figure. The radiolytic degradation of the extractants such as tri-alkyl phosphates usually result in acidic degradation products which interfere during stripping with low nitric acid concentrations such as 0.01 M or 0.1 M [102]. Quantitative recovery of Am(III) with 3 contacts of 0.01 M nitric acid for 100 kGy irradiated DOHyA indicates the absence of such acidic degradation products. A similar behavior was reported for diglycolamides and other amide based extractants also [67, 108]. However, the $D_{Am(III)}$ values for diglycolamides at 1 M nitric acid are comparatively higher and it was not possible to carry out stripping at this nitric acid concentration. Therefore it becomes one of the important advantages of *N*, *N*-di-alkyl-2-hydroxyacetamide systems to recover the loaded metal ion with 1 M nitric acid, even after irradiating up to 500 kGy.

4.4 Effect of irradiation on hydrodynamic parameters

During solvent extraction process, the hydrodynamic properties of the organic solvent play a very important role in delivering good extraction performance. The process involves the dispersion of organic and aqueous phases into each other followed by settling again in two different phases. The radiolytic degradation of the solvent changes the nature of molecules and this may lead to changes in the density and viscosity of the system. Some of the degradation products formed may be having poor compatibility with the organic phase leading to poor separation between aqueous and organic phases. Therefore, it is essential to assess the variation in physical properties of the solvents such as density, viscosity and phase disengagement time as a function of absorbed dose.

The density and viscosity of 0.2 M solutions of *N*,*N*-di-alkyl-2-hydroxyacetamides were measured for fresh and irradiated solvents and the results are shown in table 4.1. When subjected to a radiation dose of 500 kGy, both densities and viscosities increase for all the extractants. It is essential that the viscosity of the organic phase be sufficiently low (~2 cP) to permit the ready flow of solutions in low-power agitators for phase dispersion and efficient phase separation. Similarly, a good difference in density between aqueous and organic phases (~0.2 g/mL or more) is recommended for efficient phase separation [23]. It can be seen that, though the values are increasing with absorbed dose, they are within the operational limits even for samples irradiated up to 500 kGy.

Table 4.1 Hydrodynamic properties of irradiated and un-irradiated *N*,*N*-di-alkyl-2-hydroxyacetamides. Organic phase: 0.2 M of DAHyA in *n*-dodecane irradiated to different dose levels.

	Density /g.mL^{-1}			**Viscosity /cP**		
	0 kGy	100 kGy	500 kGy	0 kGy	100 kGy	500 kGy
DHHyA	0.752	0.754	0.756	1.423	1.465	1.532
DOHyA	0.755	0.756	0.759	1.518	1.543	1.632
DDHyA	0.757	0.757	0.758	1.619	1.650	1.720

The increase in densities is only marginal, and the increase in viscosities is more. The viscosity is mainly associated with the self association of the molecules due to inter molecular bonding properties. It is seen from the literature [139] that the hydroxyacetamides are stabilized by intramolecular hydrogen bonding in their molecules as shown in figure 4.6.

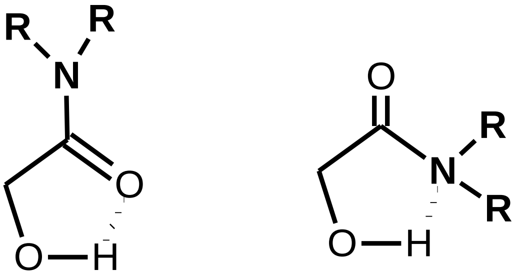

Figure 4.6: Intramolecular hydrogen bonding in *N,N*-di-alkyl-2-hydroxyacetamides

As a result of irradiation, the stabilizing intramolecular forces are weakened leading to inter molecular interactions dominating between the molecules, thereby increasing the cohesive forces which accounts for the increase in viscosities in *N*,*N*-di-alkyl-2-hydroxyacetamides. As per the literature reports, the diglycolamide systems or other monoamide systems do not show an increase in viscosity upon irradiation as they do not have such hydrogen bonding effects [103, 106, 107].

In table 4.2, the phase disengagement times (PDT) observed for *N*,*N*-di-alkyl-2-hydroxyacetamides from two different acidities at different doses of irradiation are compared. An increase in PDT is observed with increase in chain length of the extractants in the case of irradiated samples. However, such an increase is only marginal in the case of un-irradiated sample. Also, PDT increases with increase in absorbed dose at both the acidities, 4 M and 0.1 M of nitric acid. The increase is small with 4 M nitric acid solution, but significant increase is observed with 0.1 M nitric acid solution. These two acidities of nitric acid are usually employed for loading (4 M) and stripping of the metal ions (0.1 M).

Table 4.2 The phase disengagement time (PDT), in seconds, observed for irradiated and un-irradiated *N*,*N*-di-alkyl-2-hydroxyacetamides. Organic phase: 0.2 M of DAHyA in *n*-dodecane irradiated to different dose levels.

	0 kGy		**100 kGy**		**500 kGy**	
	0.1M HNO_3	4 M HNO_3	0.1M HNO_3	4M HNO_3	0.1M HNO_3	4 M HNO_3
DHHyA	20	17	27	23	36	24
DOHyA	23	17	28	26	38	26
DDHyA	25	14	34	24	47	26

The presence of degradation products affects more in stripping cycles when the metal ions are brought to the aqueous phase from the loaded organic phase. The problem of slow phase disengagement can be solved by the use of higher nitric acid concentrations during stripping which is described in stripping studies in the following section. As discussed earlier, the advantage of using *N*,*N*-di-alkyl-2-hydroxyacetamides in solvent extraction is that the loaded metal ions can be stripped from the organic phase by using 1 M nitric acid. Neverthless, the increase in PDT at 0.1 M nitric acid indicates the formation of degradation products such as hydroxyaceticacid and di-alkylamines which interact more with the aqueous phase at this acidity. The exact nature of the degradation products have to be confirmed by detailed investigations.

4.5 Effect of irradiation on the bulk extraction of Nd(III)

The bulk extraction of Nd(III) ions by irradiated samples of DOHyA was studied so as to analyse the effect of irradiation on the loading of metal ions in the organic phase. The Nd(III) extraction isotherms for DOHyA samples irradiated to different absorbed doses are given in figure 4.7. A higher concentration of extractant (0.4 M DOHyA/*n*-

dodecane) was employed in these studies so that the comparison of results was easier. The initial aqueous concentration of Nd(III) in these studies was varied from 0.025 M to 0.3 M and the free acidity of aqueous phase was fixed at 4 M. It was found that the extraction of Nd(III) decreased linearly with increase in absorbed doses. As it was found for Am(III) extraction during tracer studies (section 4.1), the extraction of Nd(III) by 100 kGy irradiated samples showed satisfactory results, though the extraction was lowered at higher absorbed doses (> 500 kGy).

For the un-irradiated sample, the extraction of Nd(III) increased rapidly with increase in aqueous Nd(III) concentration up to 0.1 M. Thereafter, the extraction values showed only a small change with increase in aqueous Nd(III) concentration indicating saturation of the organic phase. The samples irradiated to 100 kGy also showed a similar trend, though the extraction of Nd(III) was less in this case.

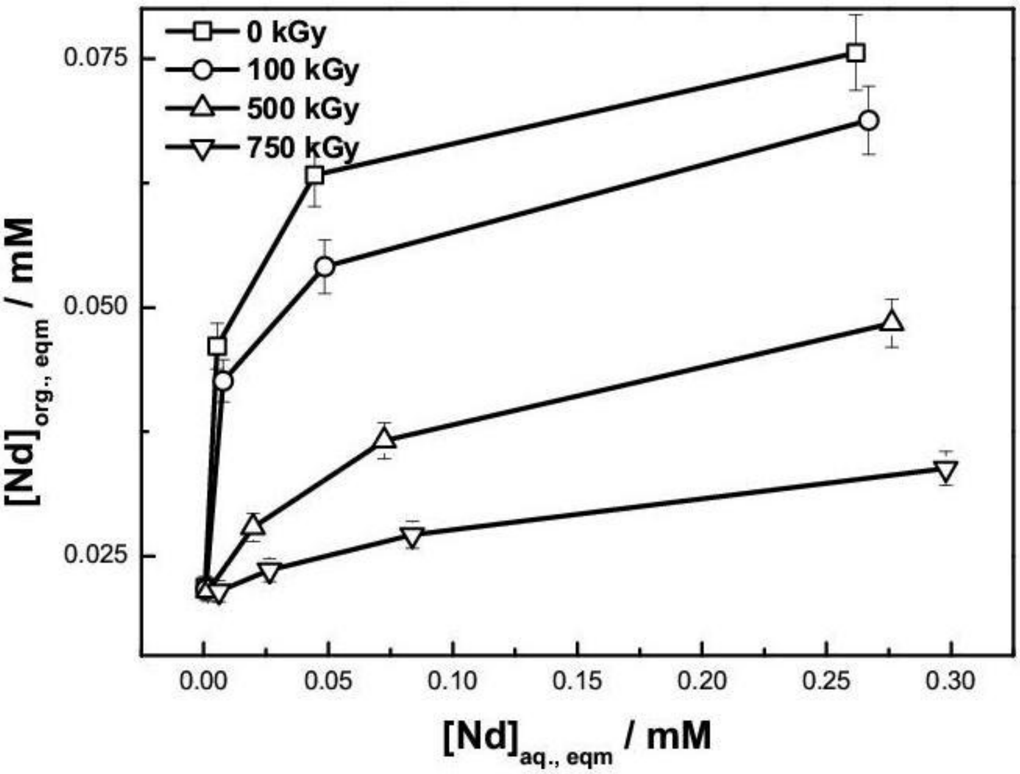

Figure 4.7: The Nd(III) extraction isotherm for irradiated and un-irradiated DOHyA samples at 298 K. Organic phase: 0.4 M DOHyA/ *n*-dodecane. Aqueous phae.: 4 M nitric acid containing Nd(III).

Lesser extraction at higher absorbed doses evidently indicates the availability of less number of DOHyA molecules in the organic phase which can extract the metal ions. It can be inferred that the extraction capacity of the system is lowered as a result of irradiation by gamma rays. However, it should be mentioned that there was no undesirable effects like third phase formation observed for samples at high loadings, even after irradiation up to 750 kGy.

4.6 Effect of irradiation on aggregation behaviour of extractants

The formation of reverse micellar aggregates in the organic phase of amphiphilic extractants have been studied in detail, especially in relation to the third phase formation in various extraction systems [117-125]. In chapter-5, the aggregation behaviour of DOHyA during the extraction of nitric acid and Nd(III) has been studied and compared with TODGA systems. The results of aggregation studies of irradiated samples using dynamic light scattering is discussed in this chapter.

Figure 4.8 compares the average sizes of reverse micellar aggregates measured for irradiated and un-irradiated 0.4 M DOHyA/ *n*-dodecane samples during the extraction of Nd(III) ions from 4 M nitric acid solutions. These measurements were done on the same samples studied for bulk extraction of Nd(III) ions which was described in the previous section. It is reported that aggregate sizes in the organic phase increase with increase in extraction of metal ions [118], and it is evident in the present study also. However, there was only minimal variations in aggregate sizes as a function of absorbed dose when the concentration of Nd(III) in the aqueous phase was around 100 mM (0.1 M). At higher absorbed doses, a decrease in aggregate size was observed for the organic phase loaded from 300 mM Nd(III) solutions.

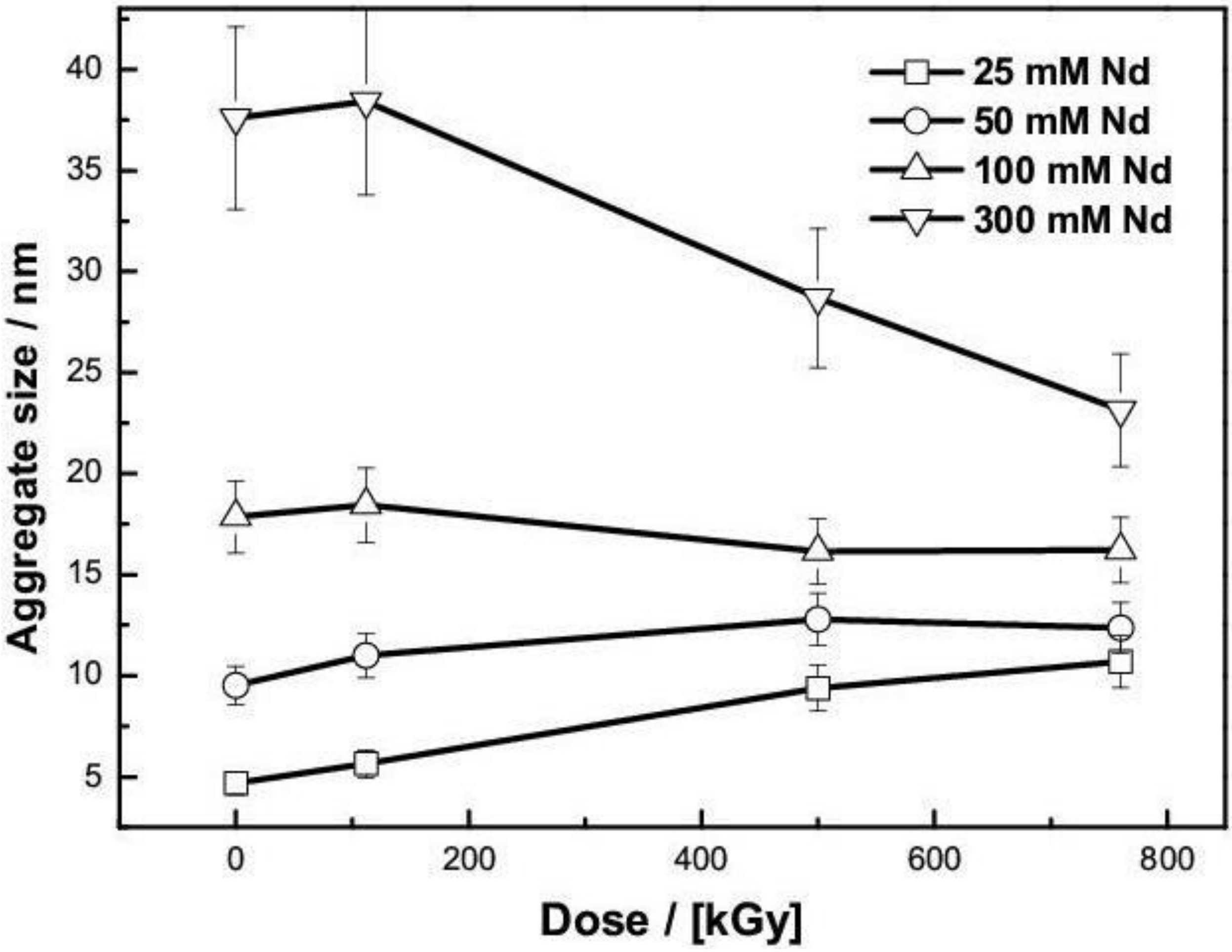

Figure 4.8: Average aggregate sizes of reverse micellar aggregates in 0.4 M DOHyA/*n*-dodecane as a function of absorbed dose during extraction of Nd(III) ions from aqueous solutions of different concentrations at 298 K. Aqueous phase: 4 M nitric acid containing Nd(III).

Figure 4.9 gives a comparison of the aggregate size distribution as a function of loading of Nd(III) ions at different absorbed doses. The results showed that the aggregate size distribution was similar for un-irradiated and 100 kGy irradiated samples. When the absorbed dose was 750 kGy, both the aggregate sizes and the intensity of distribution were found to be reduced. It should be noted that these effects were more visible only at higher loadings of the organic phase.

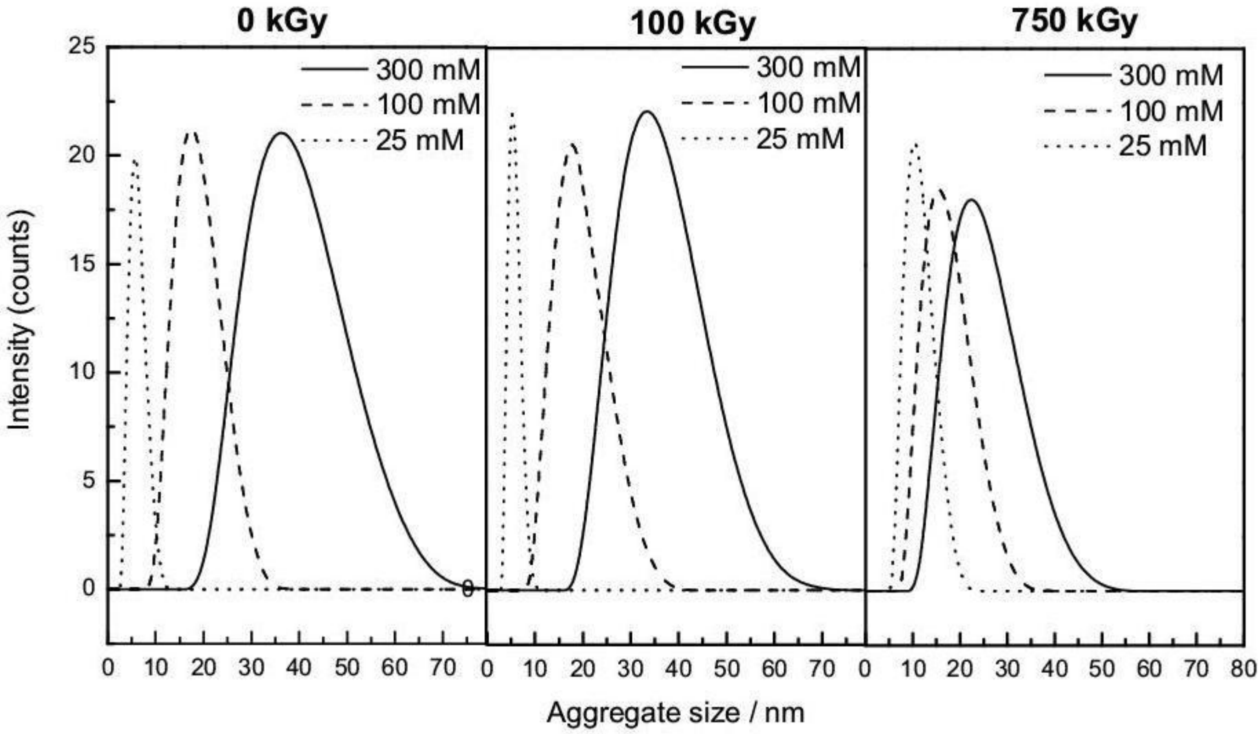

Figure 4.9: Comparison in the aggregate size distribution for DOHyA as a function of loading of Nd(III) ions at different absorbed doses at 298 K. Aqueous phase Nd(III) nitrate dissolved in 4 M nitric acid.

Figure 4.10 gives a comparison of the aggregate size distribution for DOHyA as a function of absorbed dose at different loadings of Nd(III) ions. It can be seen that the distribution curves at different absorbed dose levels were similar when the initial concentration of Nd(III) in the aqueous phase was 100 mM (0.1 M). As the initial concentration of Nd(III) in aqueous phase was increased to 300 mM (0.3 M), the aggregate sizes and intensity of size distribution were found to decrease with increase in absorbed dose. Thus it can be inferred from figure 4.9 and 4.10 that the aggregation behaviour of DOHyA extractant remains mostly unchanged for absorbed doses up to 100 kGy, when the initial concentration of Nd(III) in the aqueous phase is up to 100 mM.

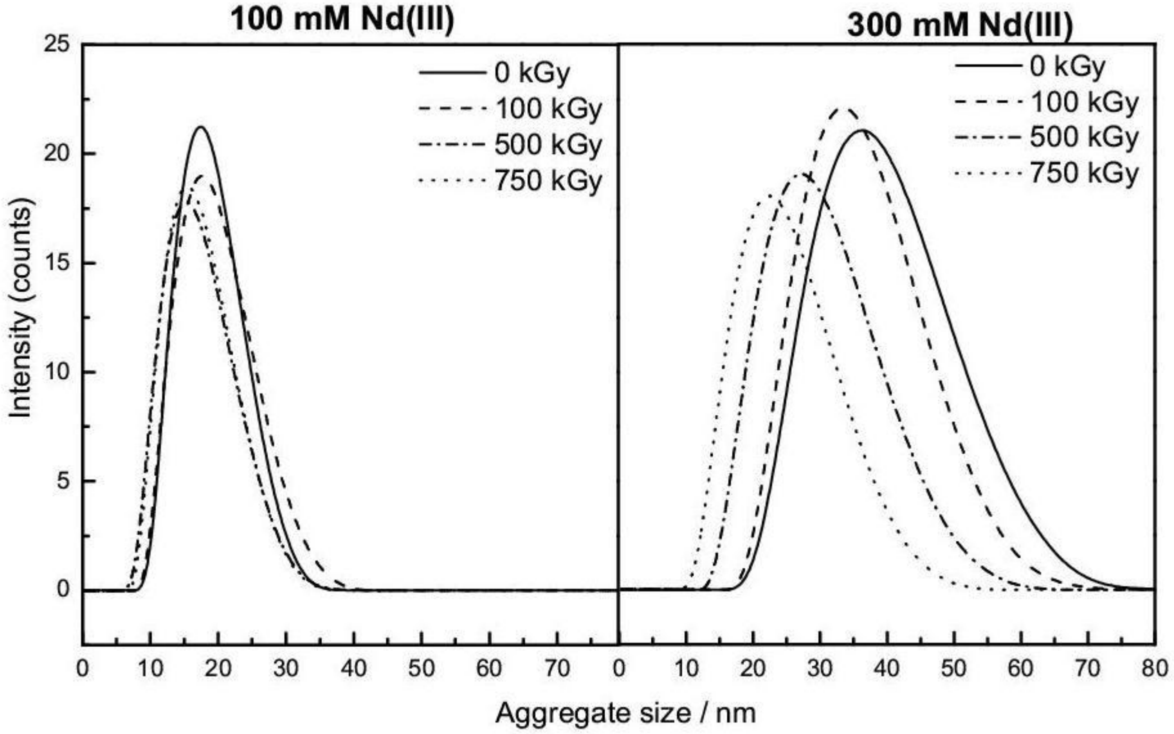

Figure 4.10: Comparison in the aggregate size distribution for DOHyA as a function of absorbed dose at different loadings of Nd(III) ions at 298 K. Aqueous phase: Nd(III) nitrate dissolved in 4 M nitric acid.

The observed decrease in the sizes of aggregates with increase in absorbed dose can be explained on the basis of reduced extraction of metal ions by irradiated samples. The results of the present study clearly shows that the aggregation behaviour of DOHyA was not significantly affected during loading of metal ions from Nd(III) solutions having concentrations up to 100 mM, when the absorbed dose was around 100 kGy. As the total concentration of extractable metal ions in high level waste solutions shall not exceed 100 mM [131], the DOHyA aggregates are expected to be stable under process conditions where the adsorbed dose would be around 100 kGy. At higher values of absorbed doses and under higher loadings, the aggregate sizes were smaller. It has been reported that the increase in aggregate sizes usually result in incompatibility of aggregates in organic phase leading to undesirable effects such as third phase formation during extraction of metal ions [118]. As the aggregate sizes are smaller at higher absorbed doses, it can be inferred that the chances of third phase formation are reduced as a result of irradiation.

4.7 ATR-FTIR studies using irradiated samples

From the above discussions, it is clear that metal ion extraction in DAHyA extractant systems decrease with increase in absorbed dose of gamma radiation. It is usually explained on the basis of formation of degradation products, which reduces the availability of extractant molecules. In the present study, the irradiated and un-irradiated DOHyA samples were analyzed by ATR-FTIR spectroscopy after extraction of metal ions from a simulated high level liquid waste solution of fast reactor origin (section 2.3.7, chapter-2). The spectra are compared in figure 4.11. It was found that the intensity of vibrational bands at 1615 cm^{-1} and 1190 cm^{-1} decreased with increase in absorbed dose. These bands are assigned for the stretching vibrations due to the bonded carbonyl group and C-O of hydroxyl group respectively. The decrease in intensity of both these bands is clearly indicative of the weakening of metal-ligand interactions in the organic phase, as the extracted metal ions are attached to the carbonyl group and hydroxyl group in the molecule.

Usually, it is observed that vibrational frequency of carbonyl group in amides decreases as a result of bonding with metal ions. As a result of irradiation, no shifting of vibrational bands was observed in the entire spectral region from 650 cm^{-1} to 3400 cm^{-1}. Also, no extra peaks were recorded in the spectra of irradiated samples. Thus the results of ATR-FTIR analysis did not reveal the presence of degradation products in the system under the conditions studied. However, the decreased intensity of carbonyl and hydroxyl groups are indicative of lesser availability of these groups in the organic phase after irradiation. Also, the decrease in ‘D’ values is also essentially due to the degradation of extractant molecules.

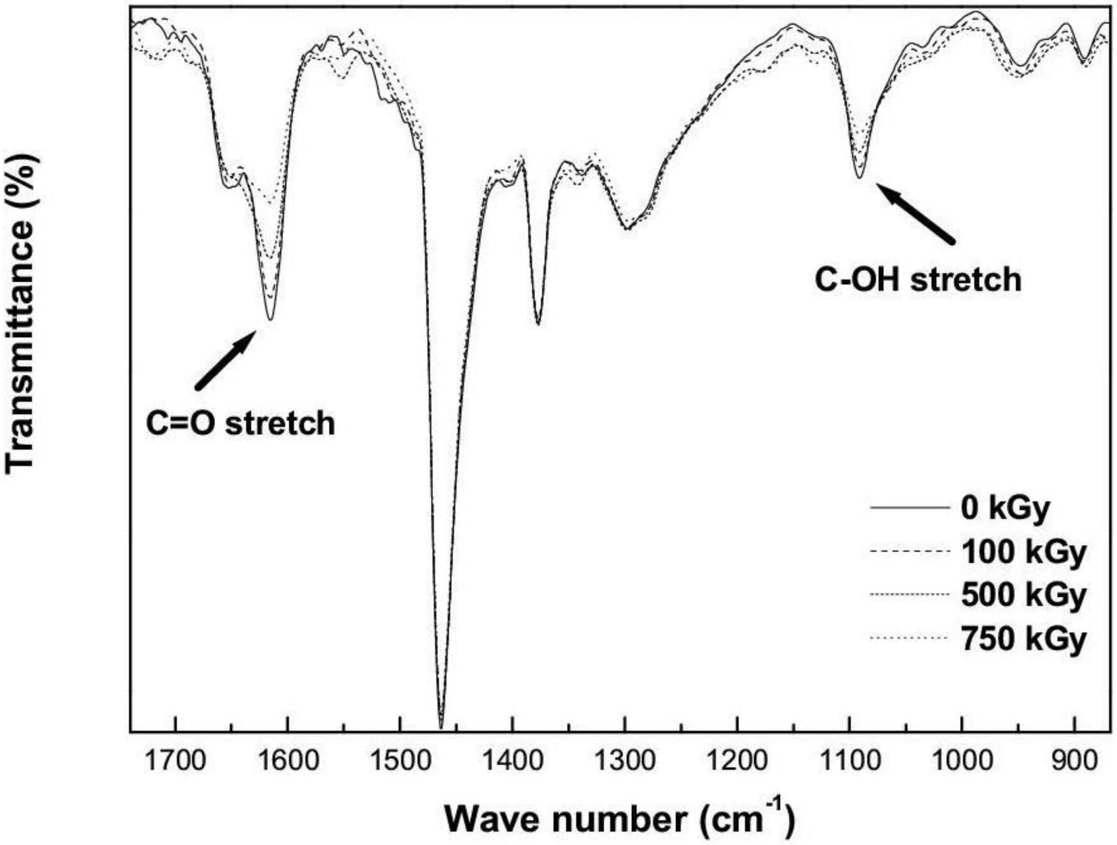

Figure 4.11: ATR-FTIR spectra of irradiated samples after extraction of metal ions from FR-SHLLW. Organic phase: 0.4 M DOHyA/*n*-dodecane.

The FT-IR spectra were recorded after equilibration with FR-SHLLW in the present study. It can be inferred that the degradation products are soluble in the aqueous phase and therefore removed from the organic phase during the mixing with aqueous phase. Future studies in this direction shall be directed towards the analysis of dissolved organics in the aqueous phase after irradiation. Also, further studies involving more sensitive techniques like mass spectrometry are necessary for detailed analysis of the degradation products. The stretching vibration of hydroxyl group of DAHyA compounds in *n*-dodecane solution is usually masked by the effect of hydrogen bonding. Therefore, the absorption band at 3410 cm^{-1} visible for neat DAHyA extractants is usually absent, when the FT-IR spectra are recorded in *n*-dodecane medium. Detailed studies for the analysis of degradation products have been planned as a part of the future work in this direction.

4.8 Summary

The radiolytic stability of three *N*,*N*-di-alkyl-2-hydroxyacetamides having alkyl side chains varying from hexyl to decyl was assessed by gamma irradiation upto 700 kGy under different conditions. The $D_{Am(III)}$ values of radiolytically degraded samples decreased with increase in absorbed dose. The samples in *n*-dodecane were found to undergo more degradation as compared to the neat samples. The presence of nitric acid during irradiation did not affect the degradation of DAHyA. The stripping properties were similar to un-irradiated DAHyA and quantitative recovery of Am(III) was achieved even with 1 M nitric acid solution. The densities and viscosities of irradiated samples were found to increase upon irradiation. An increase in phase disengagement time was observed for irradiated samples, especially when used with 0.1 M nitric acid solution. The bulk extraction of Nd(III) ions from nitric acid medium was studied using DOHyA and the results showed that the extraction of Nd(III) decreased linearly with increase in absorbed dose. The average sizes of reverse micellar aggregates in DOHyA showed only minimal variations as a result of irradiation, when the initial Nd(III) concentration in the aqueous phase was around 100 mM. Also, the aggregation behavior of samples irradiated to 100 kGy was similar with un-irradiated samples. At higher loadings of metal ions in the organic phase, the aggregate sizes decreased at higher absorbed doses. No third phase was observed during extraction of metal ions by irradiated samples under the conditions of the present study. The ATR-FTIR studies of the irradiated samples after extraction of metal ions from FR-SHLLW showed a decrease in intensity of the vibrational bands of bonded >C=O group and C-OH group in the molecule, pointing out the weakening of metal-ligand interactions as a result of irradiation.

COMPARISON OF *N*, *N*-DI-OCTYL-2-HYDROXYACETAMIDE WITH OTHER EXTRACTANT SYSTEMS USING DYNAMIC LIGHT SCATTERING AND INFRARED SPECTROSCOPY

5

5.1 Introduction

From the discussions in chapters 3 and 4, the ability to extract trivalent metal ions from nitric acid medium without the use of a phase modifier was identified as one of the distinct advantages of long chain DAHyA extractants (DOHyA and DDHyA) over the existing extractant systems such as DGA or CMPO. Based on the ease of synthesis and better availability of synthetic pre-cursors, the octyl derivative (DOHyA) was chosen for further studies described in chapter-5 and chapter-6. The third phase formation limit of DOHyA was far higher than TODGA or TEHDGA under similar conditions of extraction of nitric acid and/or metal ions.

The factors which affect the formation of a triphasic system during liquid-liquid extraction cannot be explained on the basis of classical co-ordination chemistry concepts alone. As discussed in chapter-1 (section 1.9), the properties of biphasic and triphasic extractant systems are better explained by combining the principles of co-ordination chemistry with surfactant chemistry [120]. During extraction of nitric acid and metal ions from the aqueous phase, extractants behave as non-ionic surfactants forming reverse micellar aggregates whose apparent hydrodynamic radii usually vary between 1 nm and 100 nm, depending on the conditions of extraction [124-128]. The aggregation behaviour of extractants can be studied by measuring the variation in sizes of these aggregates as a function of various parameters which affect the extraction.

The studies by Yaita et al. [122] have revealed that the nitric acid driven aggregation of TODGA becomes important when the aqueous phase acidity exceeds 0.7 M and the aggregate sizes increase with increase in the concentration of nitric acid. An average number of 6 - 7 TODGA molecules were reported per aggregate at the highest aqueous phase acidity. The reverse micelle formation in TODGA/ *n*-dodecane system during the extraction of Nd(III) ions was studied by Jensen et al. [120]. These studies have shown that the inter-particle interaction between the polar cores of reverse micelles increased with increase in concentration of both nitric acid and metal ions. In the absence of a phase modifier, these interactions usually result in the separation of a third phase in TODGA systems.

The phase modifiers used along with the extractants play the role of co-surfactants, which help to stabilize the reverse micelles of extractants in non-polar diluents, without forming a triphasic system. In the present chapter, the aggregation behaviour of biphasic systems of TODGA in the presence of two phase modifiers, viz 1-octanol and DHOA has been studied under high loadings of nitric acid and metal ions from aqueous phase and the results have been compared with DOHyA system under similar conditions. The structure of extractants and phase modifiers involved in the study is given in figure 5.1.

Dynamic light scattering (DLS) technique has been used for the measurement of average aggregate size and size distribution under different conditions, and the results have been co-related with ATR-FTIR measurements. Similar studies are reported in the literature for ionic surfactant systems which form reverse micelles in non-polar solvents [137, 138]. However, only a few literature reports are available on the use of DLS for studying the aggregation behaviour of extractant systems consisting of neutral molecules

[124-126]. The observations in the present study have been used to explain the modifier-free extraction of DOHyA system.

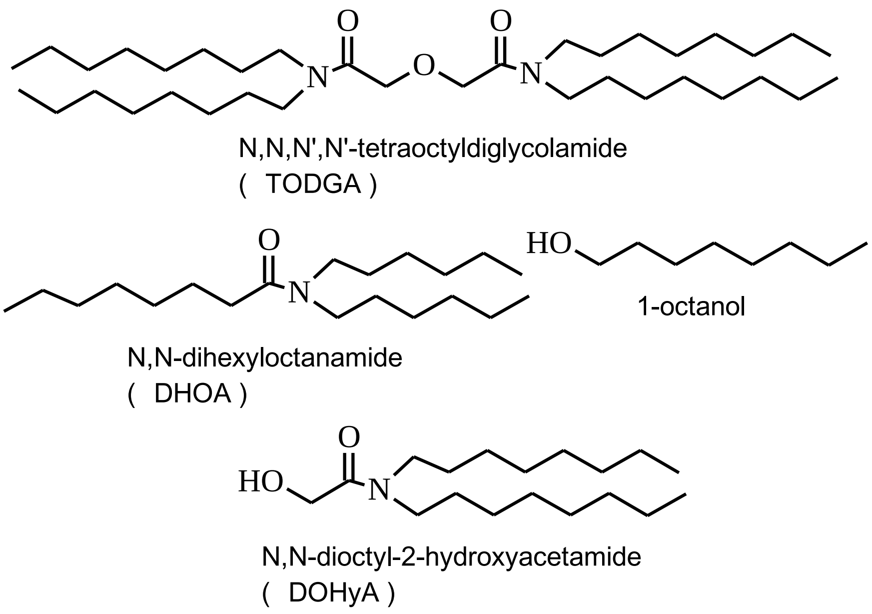

Figure 5.1: Structures of extractants and phase modifiers used in the present study.

5.2 Effect of nitric acid extraction on aggregation

Pathak et al.[125] have reported the sizes of reverse micellar aggregates for 0.1 M TODGA in *n*-dodecane after contacting with aqueous phases having nitric concentrations less than 4 M. At higher acidities more than 4 M, the data were not available due to third phase formation. In the present studies, a 0.2 M solution of TODGA in *n*-dodecane was employed for DLS studies along with phase modifiers, 0.5 M DHOA or 5 vol% 1-octanol. As seen from figure 5.1, DOHyA consists of half of the TODGA molecule and hence a 0.4 M solution of DOHyA in *n*-dodecane was used in the studies. Figure 5.2 shows the extraction of nitric acid for these three extractant systems when the aqueous nitric acid concentration was varied up to 12 M. Among them, the TODGA-DHOA system formed third phase with nitric acid when the initial nitric acid concentration was 12 M, and hence the last point shown in the acid extraction plot for this system corresponds to the acid extracted to the third phase. However, no third phase was observed for TODGA-octanol system and DOHyA system even after equilibration with 12 M nitric acid solution. It can be seen from the figure that the presence of DHOA enabled higher extraction of nitric acid at a given initial nitric acid concentration.

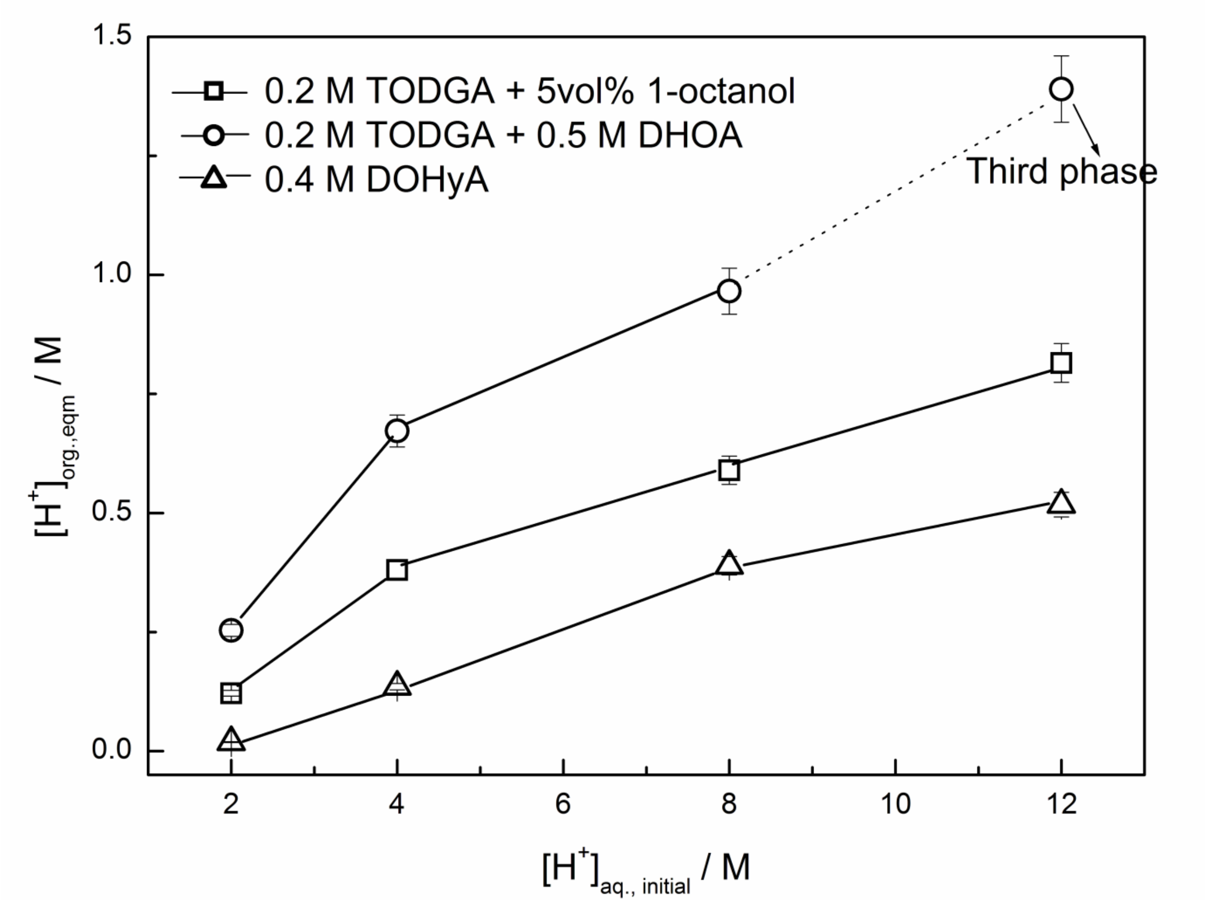

Figure 5.2: The nitric acid extraction plots for different extractant systems in *n*-dodecane at 298 K.

The extracted nitric acid may cause problems during stripping and facilitate third phase formation. Therefore, researchers in this field preferred the use of long chain alcohols such as 1-octanol as phase modifiers. It can be seen from figure 5.2 that the extraction of nitric acid is much lower for TODGA-octanol system as compared to TODGA-DHOA system. The maximum extraction of nitric acid in TODGA-octanol system is nearly 0.6 M, which corresponds to the extraction of three HNO_3 molecules per each TODGA molecule. For TODGA-DHOA system, the maximum extraction of nitric acid (without third phase) is around 1.1 M, indicating that along with the extraction of three HNO_3 molecules by each TODGA molecule, one HNO_3 molecule is extracted by each DHOA molecule. The extractant DOHyA did not require any phase modifier and also had the lowest extraction of nitric acid among the three systems studied. Here, the maximum observed extraction of nitric acid (nearly 0.4 M) corresponds to the extraction of only one molecule of HNO_3 per DOHyA molecule.

The extraction of nitric acid by DOHyA was found to be lower compared to other extractant systems including TODGA, CMPO, DMDBTDMA and even the methoxy acetamides studied previously by our group. It was found that if the –OH group of DAHyA was replaced with $–OCH_3$ group, the extraction of nitric acid was increased [143]. It can be inferred that the lone pairs of both ‘N’ and ‘O’ atoms in the molecule are less available for protonation due to intramolecular H-bonding in these molecules. (The possibility of intramolecular hydrogen bonding was discussed in section 4.4 of chapter-4). Therefore lower availability of protonation sites can be the reason for lower extraction of nitric acid in DAHyA system.

Figure 5.3 shows the results of DLS measurements for the three extractant systems at different acidities. The measurements were done after equilibration with nitric acid solutions having concentrations up to 8 M for TODGA-DHOA system and up to 12 M for other two systems. It can be seen that the reverse micellar aggregates formed in DOHyA system are smaller as compared to the TODGA systems at a particular acidity. In the case of DOHyA, both the average size and the intensity distribution of reverse aggregates increased with increase in nitric acid concentration. A similar behaviour was also reported for diglycolamide systems in the absence of phase modifiers [128].

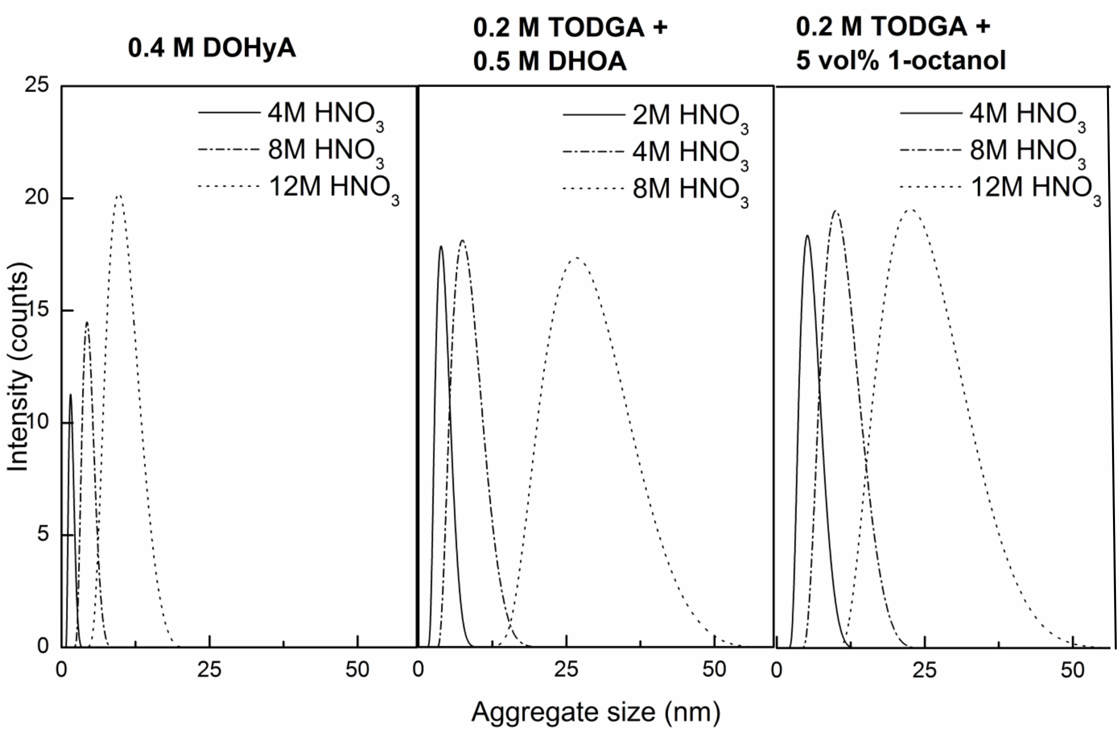

Figure 5.3: Distribution of aggregate sizes for various extractant systems in *n*-dodecane under successive loading of nitric acid at 298 K. Aqueous phase: Nitric acid at concentrations varying from 2 M to 12 M.

Therefore, it can be concluded that in pure extractant solutions aggregation increases with increase in extraction of nitric acid. For TODGA systems in the presence of modifiers, the DLS measurements show that the maximum intensity of aggregate distribution remained nearly the same and only the sizes of reverse aggregates and width of their size distribution increased with increase in concentration of nitric acid in the aqueous phase. The results indicate that in TODGA systems, the intensity of reverse micellar aggregates is reasonable even at very low equilibrium aqueous concentrations of nitric acid. As per literature reports, the interaction between TODGA reverse micelles leads to the de-mixing of organic phase at higher acidities of the aqueous phase in the absence of phase modifiers [119]. It has been reported that the phase modifiers act as co-surfactants which adsorb onto the reverse micellar aggregates formed by the extractants, thereby increasing the surface per extractant polar head [127]. This helps to reduce the dispersion forces in the polar cores of the aggregates under high loadings. In view of this, the inter particle interaction is quenched and third phase formation is avoided.

In Figure 5.4, the average sizes of reverse micellar aggregates measured for the three extractant systems are plotted as a function of extracted nitric acid in the organic phase.

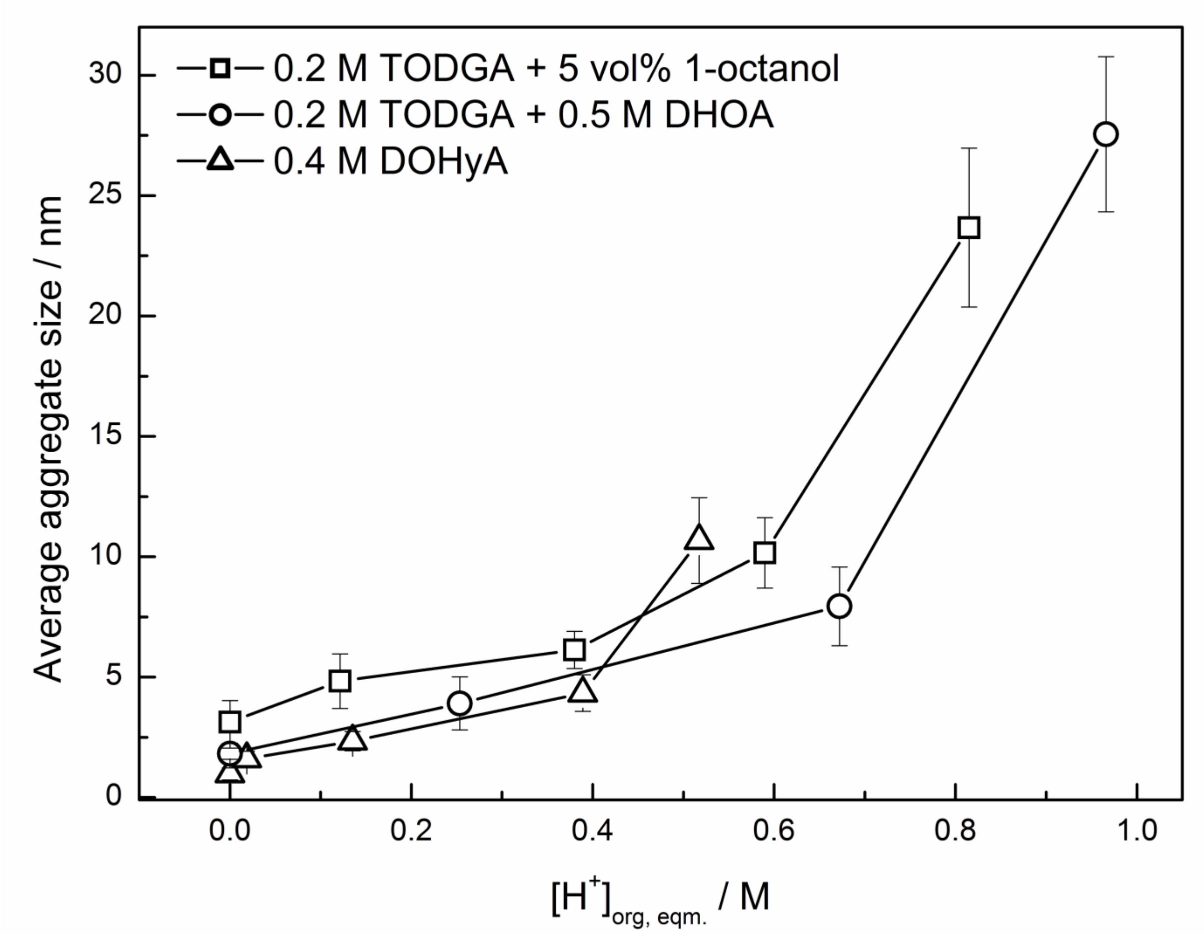

Figure 5.4: Aggregation behaviour of various extractant systems under successive loading of nitric acid at 298 K. Aqueous phase: Nitric acid at concentrations varying from 2 M to 12 M. Organic to aqueous phase ratio= 1:1.

It can be seen that though the extraction of acid was more in TODGA-DHOA system, the average sizes of reverse aggregates were smaller in TODGA-DHOA system compared to TODGA-octanol system for the same amount of extracted nitric acid. It should be noted that the DHOA molecule having the amidic carbonyl group interacts more with nitric acid in the reverse micelle as compared and octanol molecule, which contains a less polar hydroxyl group. Due to such strong interaction operating between DHOA molecule and nitric acid, the size of the reverse micelle of TODGA-DHOA is compact/small as compared to the TODGA-octanol system for the same amount of nitric acid extracted in to organic phase.

The average aggregate size observed for DOHyA system was marginally smaller than TODGA systems for the same amount of extracted nitric acid concentration till the concentration of nitric acid in the organic phase was 0.4 M. Extraction of nitric acid beyond this point resulted in a sharp increase in aggregate size in DOHyA system compared to TODGA systems. This was observed only at a high initial concentration of nitric acid of 12 M. It should be noted that the amount of nitric acid extracted in to 0.4 M DOHyA/n-dodecane is marginally more than 0.4 M, when the initial concentration of nitric acid was 12 M. Even under these conditions, third phase was not observed for DOHyA system. Since the amount of nitric acid extracted into organic phase is less as compared to TODGA systems (figure 5.2), the polarity induced in the reverse micelles due to nitric acid extraction is also less for the DOHyA system. In view of this, the inter-particle interactions in the organic phase is lower as compared to TODGA systems and third phase formation was not observed in DOHyA system.

5.3 Effect of metal ion extraction on aggregation.

As the extractants, TODGA and DOHyA are proposed for the group separation of actinides and lanthanides from high level liquid waste solutions, the aggregation behaviour of all the three extractant systems were studied during the extraction of metal ions. Nd(III) was chosen as the prototype metal ion and the extractant solutions were equilibrated with Nd(III) solutions in 4 M nitric acid in which the concentrations of metal ions varied from 0.025 M (3.6 g/L) to 1.3 M (187 g/L). Jensen et al. [120] reported the aggregation behaviour of TODGA after equilibration with aqueous solutions of low acidities (< 0.5 M) containing Nd(III) ion less than 0.015 M. It was also reported that TODGA showed third phase at higher concentrations of nitric acid and metal ions in the absence of a phase modifier [74]. The extraction of Nd(III) by different extractant systems used in the present study are shown in figure 5.5. No third phase was observed in all the three systems even when the initial concentration of Nd(III) was as high as 1.3 M and the extraction behaviour was similar for all the three systems. The extraction of metal ions increased sharply with increase in initial concentration of metal ions in the aqueous phase up to 0.15 M and thereafter the increase was small.

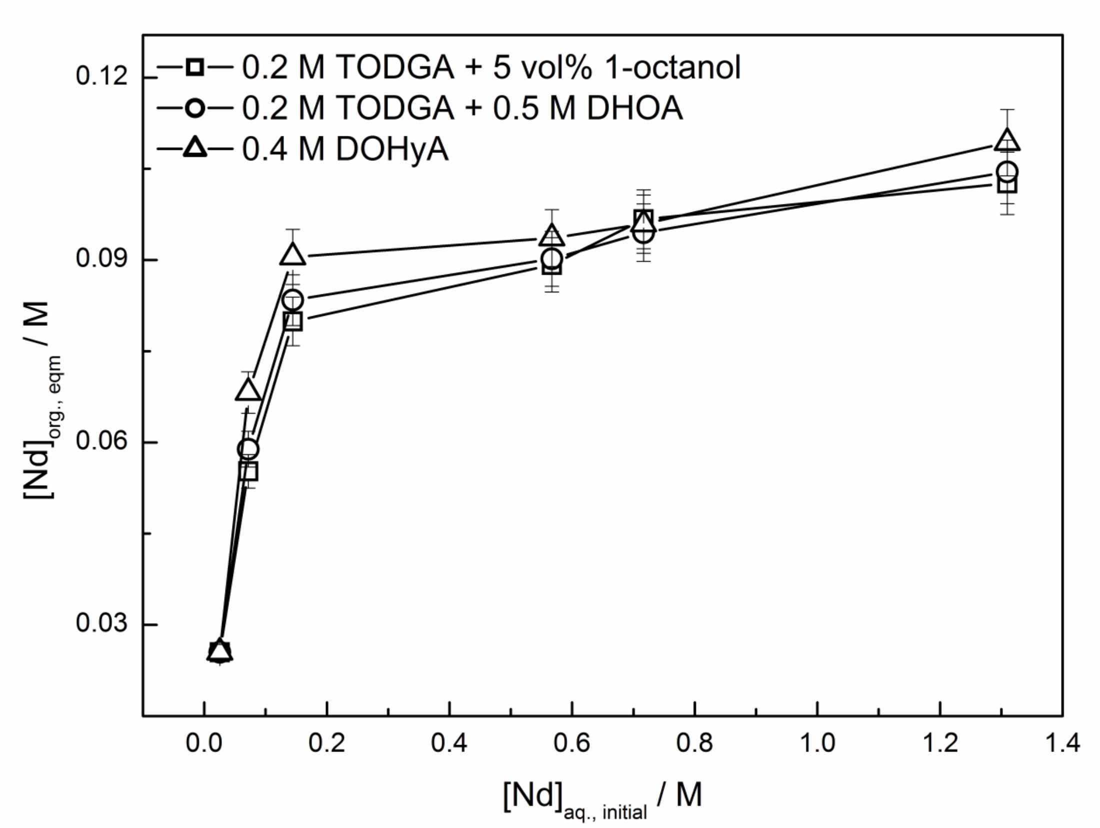

Figure 5.5: The Nd extraction isotherms for different extractant systems in *n*-dodecane at 298 K. Aqueous phase: Solutions of Nd(III) in 4 M nitric acid.

At high concentrations of metal ions in aqueous phase, the concentration of Nd(III) in organic phase was near to 0.1 M indicating that two TODGA molecules (2:1) or four DOHyA molecules (4:1) were involved in the extraction of a single metal ion. The observed stoichiometry is in good agreement with our previous studies using DAHyA (Chapter-3) and literature reports for diglycolamides [86].

Figure 5.6 shows the size distribution of reverse aggregates at different initial concentrations of Nd(III) in aqueous phase for all the three extractant systems. The aggregation behaviour was found to be similar for the extraction of both nitric acid and metal ions except that relatively bigger reverse micellar aggregates were formed with metal ions, as they are extracted along with nitric acid.

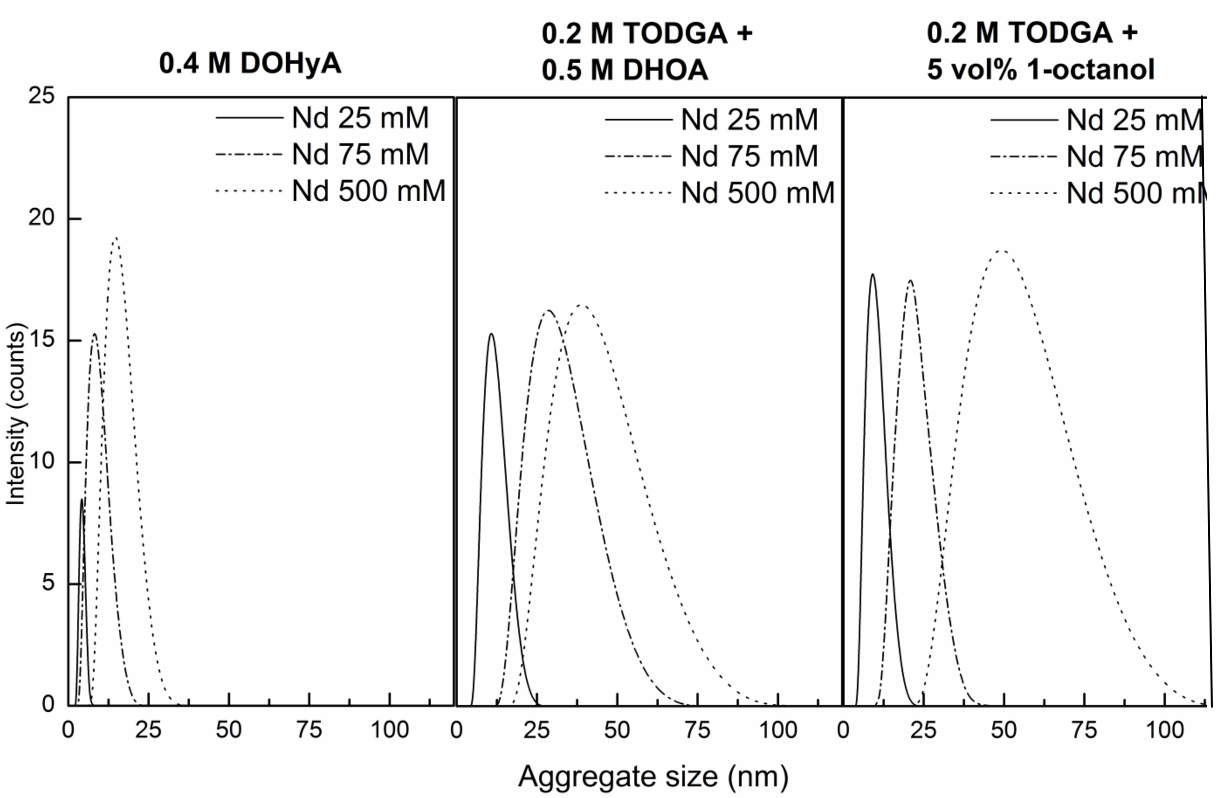

Figure 5.6: Distribution of aggregate sizes for various extractant systems in *n*-dodecane under successive loading of Nd(III) ions at 298 K. Aqueous phase: 4 M Nitric acid containing different concentrations of metal ions. Organic to aqueous phase ratio= 1:1. Temperature: 298 K.

The average size of the reverse aggregates was smaller for DOHyA system compared to TODGA system and both the size and intensity of these aggregates increased for DOHyA system with increase in aqueous metal ion concentration as compared to only increase in size of aggregates in the case of TODGA systems. Here also, the observations point out that the intensity of reverse micellar aggregates is reasonable for TODGA-modifier systems, even at very low concentrations of the metal ions in aqueous phase.

As described in the previous section, the dispersion forces in the polar cores of reverse micellar aggregates in these systems are effectively quenched by the phase modifier molecules, thereby preventing the de-mixing of organic phases at high loadings of metal ion. In DOHyA system, both the number and size of reverse aggregates increases gradually with increase in amount of extracted metal ions. In all the cases, the width of aggregate size distribution curves increases at high loadings of Nd(III) ions, showing the presence of more number of reverse micellar aggregates of different sizes.

The variation of average sizes of reverse micellar aggregates as a function of extracted Nd(III) concentration for all the three extractant systems is shown in figure 5.7. When the extracted Nd(III) concentration was low (< 0.06 M), the average aggregate sizes observed for both the TODGA systems were comparable. However, at higher concentrations of metal ions in the organic phase, bigger aggregates were formed in TODGA-octanol system as compared to TODGA-DHOA system. As it was discussed in the case of nitric acid extraction (section 5.1), the reason for the formation of relatively smaller aggregates in TODGA-DHOA system could be due to the presence of carbonyl group in DHOA molecule, which seems to interact with extracted Nd(III) at high loadings in the organic phase. Due to such strong interaction operating between DHOA and Nd(III) ions, the size of the reverse micelles of TODGA-DHOA are compact/small as compared to the TODGA-octanol system for the same amount of metal extraction in the organic phase.

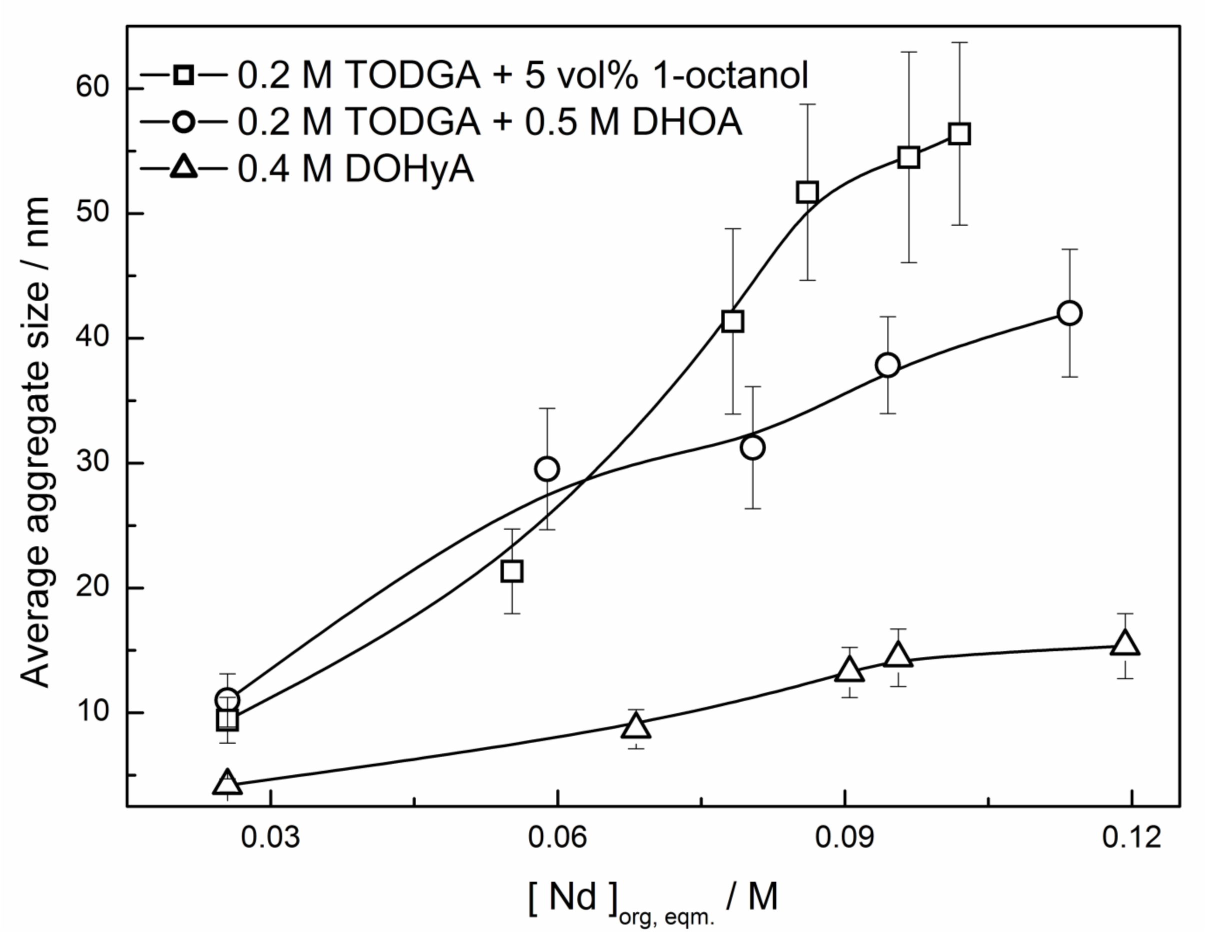

Figure 5.7: Aggregation behaviour of various extractant systems in *n*-dodecane under successive loading of Nd(III) ions at 298 K. Aqueous phase: Solutions of Nd(III) in 4 M nitric acid.

However, the above effect of carbonyl group of DHOA was prominent, only when the concentration of metal ions in the organic phase was quite high (> 0.06 M). Above 0.06 M Nd(III) in organic phase, the metal ion appears to be associated with less than three TODGA molecules as per the stoichiometry of extraction as shown in figure 5.5.

From figure 5.4, it can be seen that the reverse micellar aggregates formed in DOHyA system were marginally smaller than those observed in TODGA systems, for the extraction of same amount of nitric acid. However, during the extraction of same amounts of metal ion, the reverse micellar aggregates formed in DOHyA system were found to be much smaller as compared to the TODGA systems, as shown in figure 5.7. To obtain this data, it should be noted that the extraction of Nd(III) was carried out from 4 M nitric acid medium. Under this condition, significant amount of nitric acid is also co-extracted along with the metal ion in organic phase. From figure 5.2, it can be seen that the extraction of nitric acid in TODGA phase was about three times higher than that observed in DOHyA system. Therefore, the amount of nitric acid present in the DOHyA reverse micelle is lower than that observed in TODGA system. Since the amount of nitric acid extracted in to DOHyA is less, the polarity induced in the DOHyA reverse micelle core is also less. In view of this, the reverse micellar aggregates formed in DOHyA system is small as compared to TODGA system. However, the extraction of metal ions in all the three systems were comparable showing that the same amount of metal ions were accommodated in the smaller reverse micellar aggregates in DOHyA system.

5.4 ATR-FTIR studies

The ATR-FTIR spectroscopy was used for monitoring the changes in extractant systems during extraction of nitric acid and metal ions. The FTIR spectra recorded for the three extractant systems after equilibration with nitric acid solutions (4 M and 8 M) and Nd(III) solutions (25 mM and 500 mM) in 4 M nitric acid are shown figures 5.8, 5.9 and 5.10. Major changes were observed in the carbonyl (>C=O) portion of the amide group as well as the etheric (C-O-C) group in TODGA systems after extraction. For DOHyA system, the changes were observed only in the amidic carbonyl group and the C-OH group was unchanged during extraction. A peak at 950 cm^{-1} was observed in the FT-IR spectra of all theextractant samples after extraction of nitric acid and it is identified as due to the N-(OH) stretching of free nitric acid molecules in the organic phase [137]. The intensity of this peak increased when the organic phases were equilibrated with nitric acid at higher concentrations. During extraction of nitric acid and Nd(III) nitrate, the nitrate ($[NO_3]^-$) ions in the organic phase are identified by the O-N-O symmetric stretching bands which usually appear in the frequency region around 1300 cm^{-1} [137]. While a free nitrate band appears around 1300 cm^{-1}, co-ordinated nitrate bands are observed at lower frequencies. The nitrate absorption bands were observed for DOHyA system at 1297 cm^{-1}, for TODGA-octanol system at 1288 cm^{-1} and for TODGA-DHOA system at 1283 cm^{-1}. These values reflect the extent of co-ordination of extracted nitrate ions or nitric acid in the organic phase. It can be seen that the co-ordination of nitrate ions in TODGA-DHOA system is stronger compared to TODGA-octanol system, as the DHOA molecule also contributes to the co-ordination. The DOHyA molecule with a single carbonyl group in the molecule recorded the maximum stretching frequency due to extracted nitrate ions, showing the minimum co-ordination environment in this system.

There were no major changes observed in the FT-IR spectrum of DOHyA recorded after equilibrating with 4 M nitric acid, except the appearance of a new band at 1297 cm^{-1} due to the extraction of nitric acid (figure 5.8). When the spectrum was recorded after equilibration with 8 M nitric acid, the carbonyl absorption peak at 1657 cm^{-1} was found to be broadened with a small shoulder at 1633 cm^{-1} and the intensity of 1297 cm^{-1} band increased. When the spectrum was recorded after equilibration with 25 mM Nd(III) solution in 4 M nitric acid, the carbonyl absorption band was showing a partial shift to 1614 cm^{-1} from 1657 cm^{-1} and this shift was almost complete in the spectrum recorded after equilibration with 500 mM Nd(III) solution. The C - O stretching band of the C-OH group (1092 cm^{-1}) remained unchanged during the extraction of both nitric acid and metal ions. Thus only gradual changes were observed in the system during the extraction. Only at high loadings of metal ions or nitric acid, all the extractant molecules in the system were involved in extraction. These observations are in line with the increase in aggregate intensities with increase in extraction for DOHyA system observed in DLS studies.

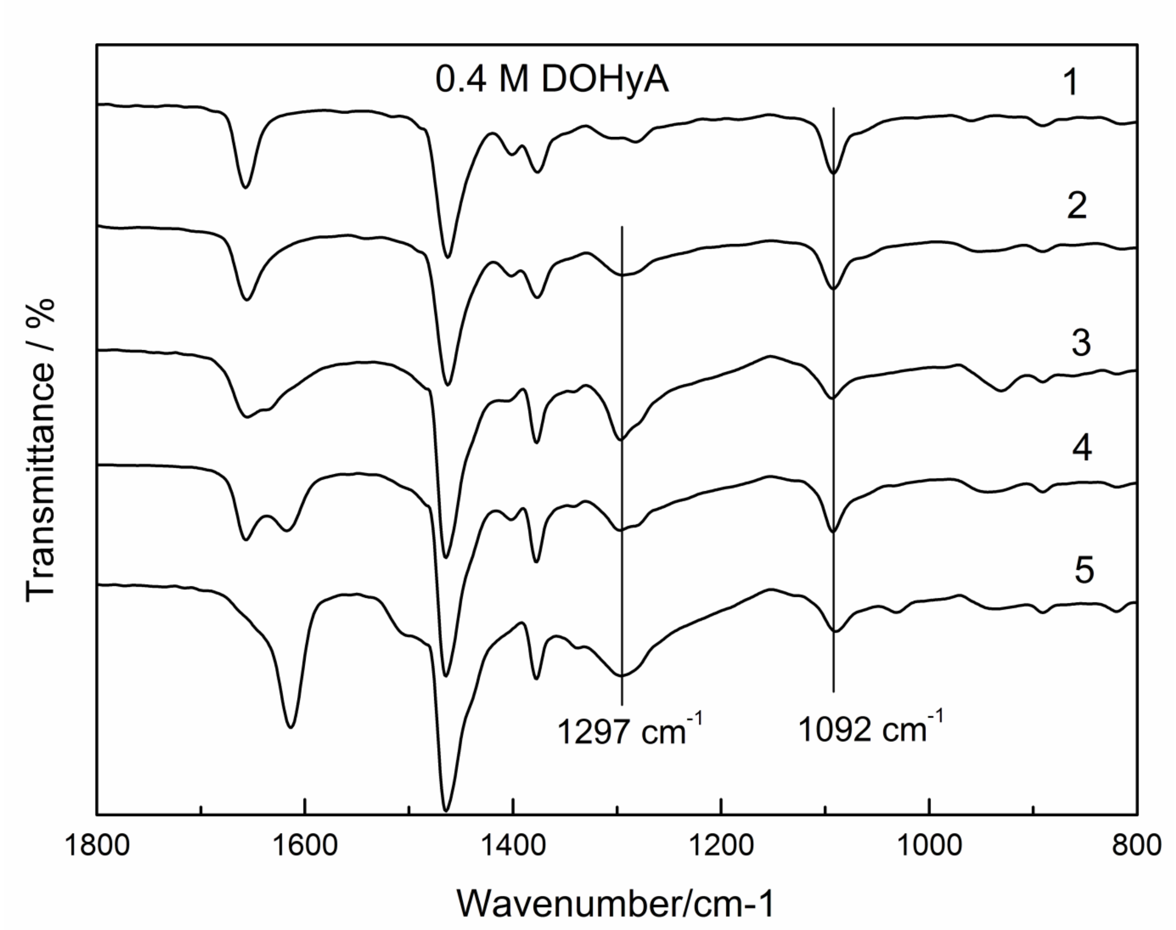

Figure 5.8: ATR-FTIR spectra of DOHyA system in *n*-dodecane under loading of nitric acid and Nd(III) ions. Aqueous phase: 1) No aqueous phase, 2) 4 M HNO_3, 3) 8 M HNO_3, 4) 25 mM Nd(III) nitrate + 4 M HNO_3, 5) 500 mM Nd(III) nitrate + 4 M HNO_3. Temperature: 298 K.

The FT-IR spectra recorded after equilibration with nitric acid solutions for TODGA systems showed changes in both the carbonyl group and the ether group in the molecule. For TODGA-DHOA system (figure 5.9), the combined carbonyl absorption band for both TODGA and DHOA was observed at 1651 cm^{-1} with good intensity. This band was shifted to two bands at 1643 cm^{-1} (due to TODGA) and 1594 cm^{-1} (due to

DHOA) after extraction of nitric acid. The absorption band due to the etheric group was broadened and partially shifted from 1122 cm^{-1} to 1165 cm^{-1} after equilibration with 4 M nitric acid and the shift was nearly complete after equilibration with 8 M nitric acid.

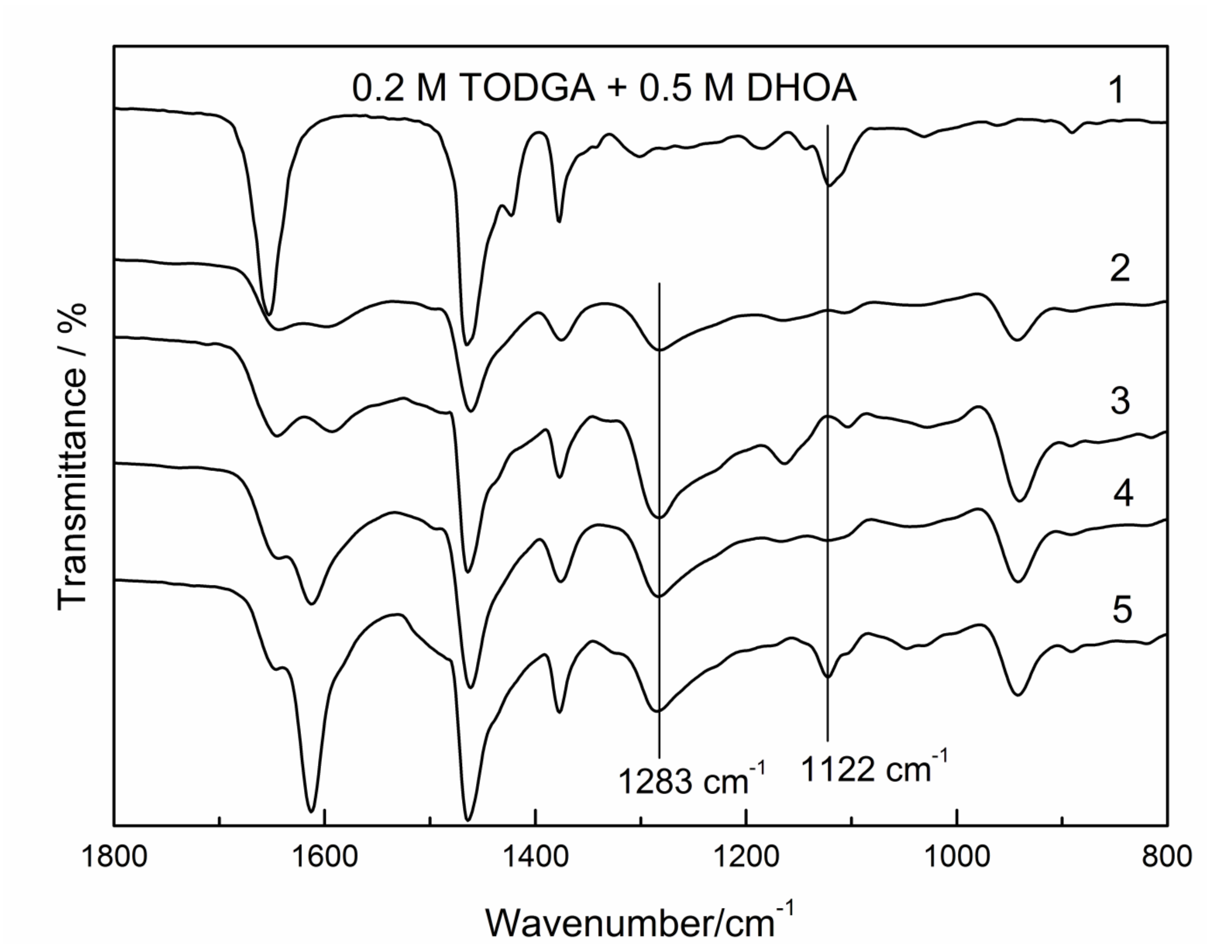

Figure 5.9: ATR-FTIR spectra of TODGA-DHOA system in *n*-dodecane under loading of nitric acid and Nd (III) ions. Aqueous phase: 1) No aqueous phase, 2) 4 M HNO_3, 3) 8 M HNO_3, 4) 25 mM Nd(III) nitrate + 4 M HNO_3, 5) 500 mM Nd(III) nitrate + 4 M HNO_3. Organic to aqueous phase ratio= 1:1. Temperature: 298 K.

The observations show that both the carbonyl groups and ether group of TODGA are involved in the extraction of nitric acid along with the carbonyl group of DHOA. When the spectra were recorded after the extraction of metal ions, the shift of carbonyl band from 1651 cm^{-1} to 1614 cm^{-1} due to Nd(III) co-ordination was nearly complete after equilibration with 25 mM Nd(III) solution. After equilibration with 500 mM Nd(III) solution, only the intensity of 1614 cm^{-1} band increased. In both the TODGA systems, however, the ether group showed only minimal changes during metal ion extraction; showing that it is not directly involved in extraction in this case, especially when the concentration of extracted metal ions is high. The small shoulders of carbonyl bands visible in the spectra after metal ion extraction was due to the presence of DHOA carbonyl group which did not take part in metal ion extraction. All the above observations show the active involvement of extractant molecules in extraction at all the studied extraction conditions.

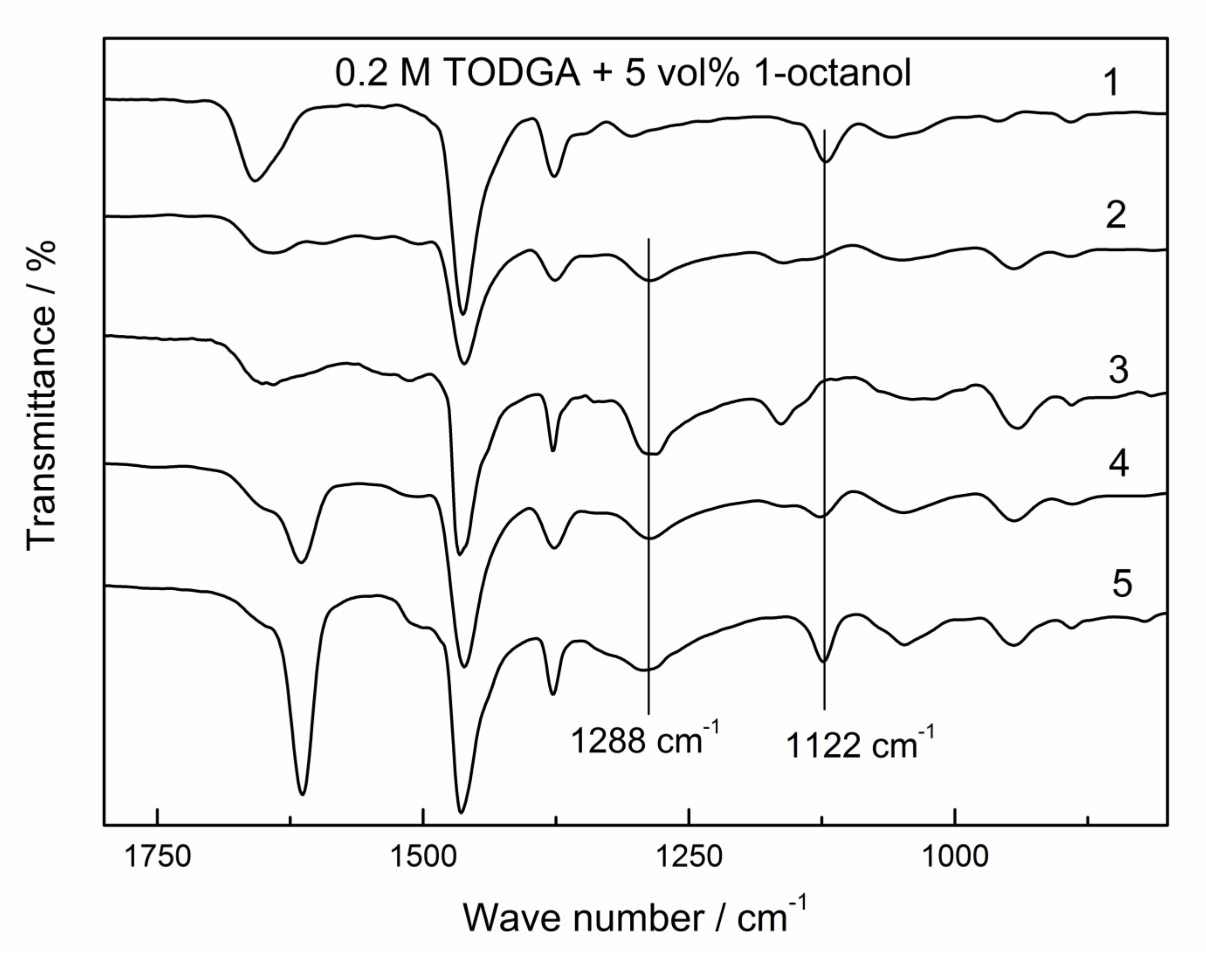

Figure 5.10: ATR-FTIR spectra TODGA-octanol system in *n*-dodecane under loading of nitric acid and Nd(III) ions. Aqueous phase: 1) No aqueous phase, 2) 4 M HNO_3, 3) 8 M HNO_3, 4) 25 mM Nd(III) nitrate + 4 M HNO_3, 5) 500 mM Nd(III) nitrate + 4 M HNO_3. Organic to aqueous phase ratio= 1:1. Temperature: 298 K.

The changes in FT-IR spectra after extraction of nitric acid and Nd (III) ions were similar for both the TODGA-modifier systems. The carbonyl absorption band observed at 1659 cm^{-1} for TODGA-octanol system (figure 5.10) was broadened and shifted to 1643 cm^{-1} after extraction of nitric acid. The shift in etheric group was similar to that for TODGA-DHOA system, showing the active involvement of this group during nitric acid extraction. The involvement of etheric group during metal ion extraction was found to be less during metal ion extraction in these systems. After equilibration with 25 mM Nd (III) solution, the shift of carbonyl absorption band to 1614 cm^{-1} was nearly complete, with only a very small shoulder at 1659 cm^{-1} due to the free extractant molecules. After equilibration with 500 mM Nd(III) solution, the 1614 cm^{-1} band was stronger and the shift was complete. The observations showed the active involvement of TODGA molecules in extraction at all the studied conditions. The DOHyA system, on the other hand, showed more involvement in extraction only at comparatively high initial concentrations of nitric acid and metal ions.

5.5 Aggregation behavior with FR-SHLLW

The proposed end use of all the extractants employed in the present study is the group separation of lanthanides and actinides from the high level liquid waste (HLLW) solution. Therefore, the aggregation behavior of extractants was studied after equilibration with a fast reactor simulated high level waste solution (FR-SHLLW) prepared in our laboratory [Chapter 2, section 2.3.7] as per the literature reports [131]. The total concentration of metal ions in FR-HLLW was estimated to be below 12 g/L and the acidity was 3 - 4 M. The aggregate sizes were measured after five successive contacts with FR-SHLLW in co- current mode, replacing with fresh aqueous phase each time. The results are shown in figure 5.11.

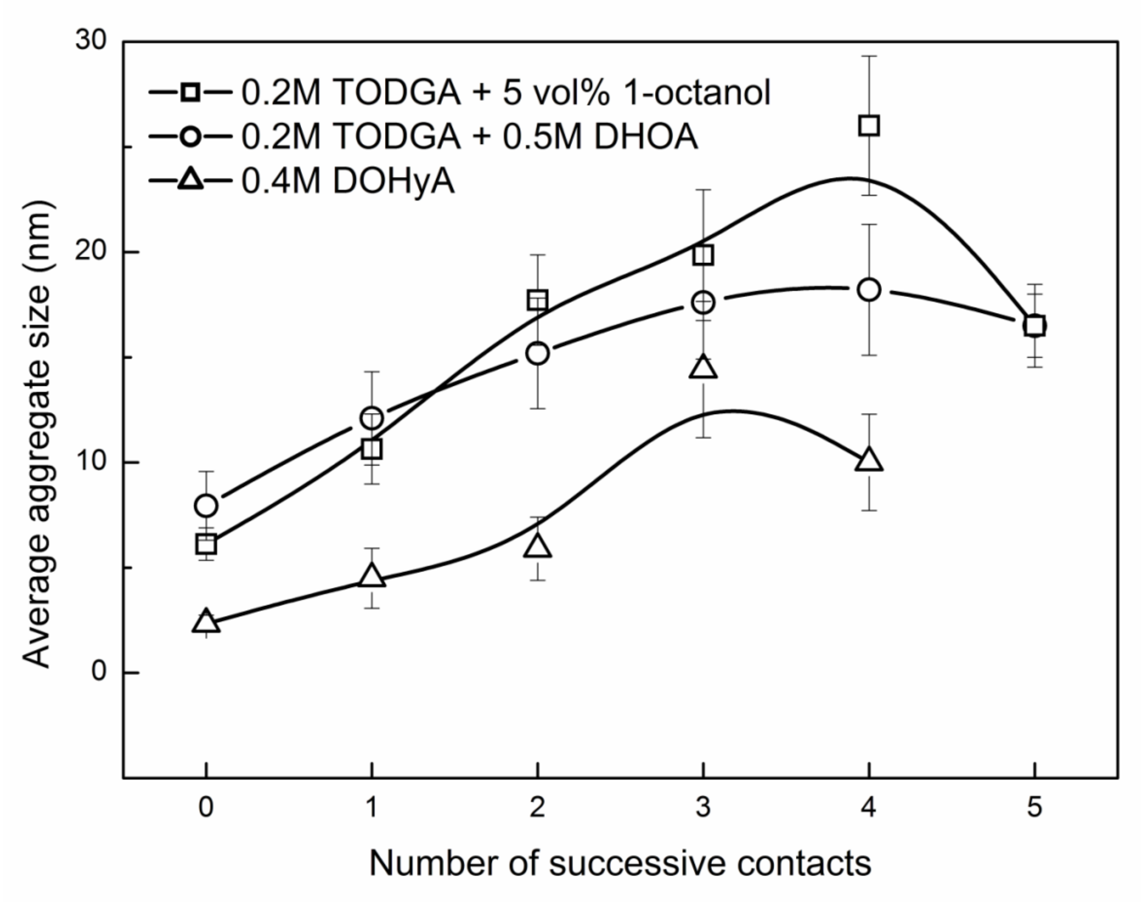

Figure 5.11: Aggregation behaviour of various extractant systems in *n*-dodecane under successive loading of metal ions from FR-SHLLW at 298 K. The first contact was given with 4 M nitric acid solution. Organic to aqueous phase ratio= 1:1.

It was observed that the sizes of reverse micellar aggregates formed during extraction from the simulated waste solution were smaller compared to the sizes of reverse aggregates observed during extraction from Nd(III) solutions. However, the trend in aggregate sizes were similar under both the conditions, i.e the reverse aggregates in DOHyA were smaller than those in TODGA systems and in the two phase modifiers, use of octanol resulted in the formation of bigger reverse aggregates compared to DHOA at high loadings of metal ions. Both TODGA and DOHyA shows good extraction of all trivalent lanthanides and other fission products in FR-SHLLW such as Y(III), Mo(VI), Zr(IV), Ru(III) and Pd(II) [5,12]. The aggregation behavior during the cumulative extraction of these different metal ions was found to be different compared to the extraction of a single metal ion (Nd(III)) for all the three extractant systems. It was observed that the average size of reverse aggregates gradually increased after each successive contact with FR-SHLLW and then decreased. In the previous section, it was observed that the average sizes of reverse micellar aggregates increased with increase in Nd(III) concentration in the aqueous phase up to very high initial concentrations (187 g/L) for all the systems. However, co-current extraction studies with FR-SHLLW showed the formation of a third phase in DOHyA system and crud formation in TODGA-modifier systems at high loadings of metal ions. For DOHyA, third phase was observed after three contacts with FR-SHLLW and the aggregate size for the light phase is reported in the figure. The average size of reverse aggregates in the heavy phase was very high (table 5.1).

Table 5.1 Aggregate sizes observed in the heavy phases of TODGA and DOHyA in *n*-dodecane after third phase formation with FR-SHLLW. Organic to aqueous phase ratio= 1:1.

Extractant	Concentration	Number of successive contacts with SHLLW for third phase formation	Aggregate size (nm)
TODGA	0.2 M	1	41.17 ± 14.63
DOHyA	0.4 M	3	38.89 ± 10.31

When a 0.2 M solution of TODGA/*n*-dodecane was equilibrated with FR-SHLLW solution, third phase was visible in the first contact itself. The average aggregate size in the third phase was comparable for both the systems. No third phase was separated in the case of TODGA-modifier systems, but a decrease in size of the aggregates was observed after four successive contacts with FR-SHLLW along with the formation of a precipitate or crud at the interface.

The study thus showed that though the third phase formation in TODGA system was absent in the presence of phase modifiers, undesirable effects like crud formation still occurred at very high loading of different metal ions. However, it should be mentioned here that the third phase or crud was observed only under co-current conditions. These effects can be effectively prevented during counter-current extraction of metal ions where the aqueous/organic ratio will be less than or equal to one.

5.6 Summary

The aggregation behavior of DOHyA in *n*-dodecane was compared with the aggregation behavior of TODGA in *n*-dodecane in the presence of two modifiers, DHOA and 1-octanol. The dispersive forces in the polar cores of the reverse micellar aggregates in TODGA systems were sufficiently quenched in the presence of phase modifiers and third phase formation was not observed in these systems even at very high loadings of nitric acid and Nd(III) ions. The aggregation behavior was found to be different for DOHyA/*n*-dodecane system which showed good extraction properties similar to TODGA with similar concentrations of nitric acid and Nd(III) ions in the aqueous phase. DOHyA, being a small molecule having a single carbonyl group extracts less amount of nitric acid and forms smaller reverse micellar aggregates in the organic phase as compared to TODGA, which is a bigger molecule having two carbonyl groups. As the dispersion forces among the reverse micellar aggregates of DOHyA system was sufficiently smaller, they were stable in the absence of a phase modifier in non-polar medium.

The intensity of reverse aggregates in the organic phase was found to increase with increase in extraction for DOHyA system whereas nearly similar intensities of aggregates were seen in the case of TODGA-modifier systems. The observations could be co-related with the results of ATR-FTIR measurements. The extraction of Nd(III) by

DOHyA was comparable with TODGA modifier systems, even though smaller reverse micellar aggregates were formed during extraction using DOHyA. The average sizes of reverse aggregates observed in both the TODGA-modifier systems were comparable at lower concentrations of nitric acid and metal ions in the aqueous phase; however the sizes of reverse micellar aggregates formed in the presence of DHOA were relatively small at high loadings due to the interaction of carbonyl group of DHOA with the extracted acid and metal ions. The results showed that the presence of 1-octanol, which interacts less with the extracted nitric acid and metal ion resulted in the formation of bigger stable reverse micellar aggregates in TODGA system at high loadings. The observations in the present study point out that a phase modifier which interacts less with the extracted nitric acid and metal ions would stabilize the reverse micellar aggregates in a better way.

Smaller reverse aggregates were observed in all the above extractant systems during extraction studies with FR-SHLLW. Though there was no indication of third phase during extraction of Nd(III) ions in all the three extractant systems even at very high initial aqueous concentrations, a third phase was observed in DOHyA system and crud formation was observed in TODGA-modifier systems after 3 - 4 successive contacts with FR-SHLLW.

COUNTER-CURRENT EXTRACTION AND STRIPPING OF METAL IONS FROM FR-SHLLW USING *N,N*-DI-OCTYL-2-HYDROXYACETAMIDE

6

6.1 Introduction

The studies on *N,N*-di-alkyl-2-hydroxyacetamides discussed in the previous chapters have identified the potential of this new class of extractants for use in minor actinide partitioning. The extraction and stripping of metal ions by a given extractant depends largely on the composition of the feed solution. The distribution ratio for the extraction of a given metal ion from a solution containing a mixture of different metal ions would always be lower than the distribution ratio measured with a single metal in solution. Therefore, it is essential to study the extraction and stripping behaviour of extractants from simulated waste solutions before proposing its use for extraction of metal ions from genuine waste solutions. In this context, extraction and stripping of metal ions from FR-SHLLW using 0.4 M DOHyA/*n*-dodecane was studied using a 20-stage ejector mixer-settler system and the results are reported in this chapter. Around 350 gms of DOHyA was synthesized and purified for mixer-settler studies. The detailed description of this synthesis was given in chapter-2 (section 2.4.9 ii).

The details of preparation of FR-SHLLW (section 2.3.7) and description of mixer-settler facility in glove-box (section 2.2.6) were also described in Chapter-2. Initially, batch studies were done so as to optimize the concentration of extractants, concentration of nitric acid used for stripping and also for the selection of proper complexing agents for the feed. The conditions for the counter-current runs were fixed based on the results of batch studies. The results obtained in the present studies have also been compared with the results available in literature for counter-current studies using other extractants.

6.2 Batch extraction studies

Initially, the extraction behaviour of various elements present in FR-SHLLW was studied by using a solution of 0.2 M DOHyA in *n*-dodecane. A distribution ratio of 2.44 was obtained for extraction of Am(III) and the distribution ratio of lanthanides varied from 0.5 to 10. Among the lanthanides, a gradual increase in the distribution ratios was observed with increase in atomic weight. In addition, the other metal ions such as Y(III), Mo(VI), Zr(IV) and Pd(II) also showed reasonable to high distribution ratios. The distribution ratio of selected fission products in FR-SHLLW during extraction using 0.2 M DOHyA is shown in table 6.1. Thus, it was observed that Am(III) was extracted along with all lanthanides, Y(III), Mo(VI), Zr(IV) and Pd(II). The extraction of all the remaining fission products in FR-SHLLW using DOHyA was negligible.

Partitioning of trivalent minor actinides (Am(III) and Cm(III)) is the ultimate aim of all the separation processes employing HLW. However, the extractant systems proposed so far for minor actinide partitioning (DGA, CMPO, malonamides, hydroxy acetamides etc.) co-extract the trivalent lanthanides and some other fission products along with trivalent actinides. In general, the co-extraction of all the metal ions other than minor actinides is undesirable. It is difficult to prevent the co-extraction of trivalent lanthanides while using the above extractants. Among the other fission products which are co-extracted, Zr(IV), Mo(VI) and Pd(II) are present in significant concentrations in HLW (Chapter-2, Table 2.1). Therefore, specific complexing agents are identified for masking the extraction of these elements. As per literature reports, complexing agents such as trans-1,2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA), *N*-(2-hydroxyethyl)-ethylenediamine- *N,N',N'*-triacetic acid tri-sodium salt (HEDTA) and oxalic acid were used by various researchers for suppressing the extraction of unwanted fission products [76-79]. Among the unwanted metal ions, it is desirable to minimize the extraction of

Zr(IV) and Pd(II), as these metal ions pose major complications during stripping of trivalent metal ions These metal ions also cause problems during Ln-An separation. For diglycolamide systems such as TODGA and TEHDGA, the literature showed that the use of oxalic acid and HEDTA in the feed was useful for suppressing the extraction of Mo(VI), Zr(IV) and Pd(II) to a significant extent [9-13]. Similarly, the addition of CyDTA to the SHLLW feed was useful for suppressing the extraction of Zr(IV) and Pd(II) [135]. In view of this, the extraction of various metal ions present in FR-SHLLW was studied in the presence of these complexing agents. The results are shown in table 6.1.

Table 6.1 Distribution ratio of Am(III) and troublesome fission products present in FR-SHLLW in the presence and absence of complexing agents. Organic phase = 0.2 M DOHyA/*n*-dodecane, Aqueous phase = FR-SHLLW spiked with ^{241}Am tracer in the presence of complexing reagents. Organic to aqueous phase ratio = 1:1 Temperature = 298 K

Elements	Distribution ratio (D_M)			
	Without reagent	In the presence of reagent		
		0.2 M oxalic acid	0.05 M HEDTA	0.05 M CyDTA
Mo	129	215	259	99
Pd	0.44	0.19	< 0.1	< 0.1
Zr	2.62	0.81	6.88	< 0.1
Am	2.44	6.48	2.93	5.26

It can be seen that the distribution ratio of Zr(IV) and Pd(II) was suppressed to a considerable extent in the presence of 0.2 M oxalic acid in aqueous phase, however the extraction of Mo(VI) was still high. The addition of 0.05 M HEDTA in FR-SHLLW was useful for reducing the distribution ratio of Pd(II) to less than 0.1, but the extraction of Zr(IV) and Mo(VI) was high. However, the addition of 0.05 M CyDTA was useful to bring down the distribution ratio of both Zr(IV) and Pd(II) to less than 0.1, and the distribution ratio of Mo(VI) was lowered to ~90. Therefore, the extraction of the troublesome elements such as Zr(IV) and Pd(II) could be minimized to a significant extent with the use of CyDTA. However, the extraction of Mo(VI) in 0.2 M DOHyA/*n*-dodecane phase could not be avoided irrespective of the nature of complexing agents investigated in the present study. In view of this, it is proposed to carry out further studies with FR-SHLLW solution containing 0.05 M CyDTA. As the distribution ratio of americium in 0.2 M DOHyA/*n*-dodecane system was less (D_{Am}= 5.26), it was also decided to increase the concentration of DOHyA from 0.2 M to 0.4 M.

The distribution ratio for extraction of various metal ions from FR-SHLLW containing 0.05 M CyDTA in 0.4 M DOHyA/*n*-dodecane is shown in table 6.2. The values are compared with the results reported by Modolo et al. [76] for extraction of various metal ions from synthetic high active raffinate (HAR) using 0.2 M TODGA + 0.5 M TBP dissolved in total petroleum hydrocarbon (TPH). The composition of HAR was based on the spent UO_2 fuel irradiated to the burn up of 33000 MWd/t_{HM} and 3 year cooling. It was found that the concentration of the metal ions present in HAR was nearly comparable with the composition of FR-SHLLW reported in table 2.1 (Chapter-2). The results shown in table 6.2 indicate that the distribution ratio of trivalent metal ions (Am(III) and Ln(III)) in DOHyA system was comparatively lower than those observed in TODGA system. However, it should be noted that the distribution ratio of trivalents obtained in DOHyA system was adequate for complete extraction of these metal ions in few contacts. It is important to note that the extraction of the troublesome fission product, Sr(II) was negligible in DOHyA (D_{Sr}< 0.01), while TODGA exhibits some extraction (D_{Sr}

= 0.42). In contrast to this, the distribution ratio of Mo(VI) in DOHyA was very high ($D_{Mo} > 200$), but it was significantly low in TODGA system ($D_{Mo} = 0.04$).

Table 6.2 Comparison of distribution values of TODGA and DOHyA from simulated waste solutions.

Extractant	0.2 M TODGA + 0.5 M TBP in TPH [76]	0.4 M DOHyA in *n*-dodecane
Feed	Synthetic HAR + 0.2 M $H_2C_2O_4$ + 0.05 M HEDTA	FR-SHLLW + 0.05 M CyDTA
La	>200	25.54
Ce	>200	20.17
Pr	>200	27.82
Nd	>200	31.18
Sm	>200	52.24
Eu	>200	67.83
Gd	>200	137
Tb	>200	>200
Dy	>200	>200
Y	>200	>200
Mo	0.04	>200
Fe	<0.03	<0.01
Cr	<0.03	<0.01
Te	<0.03	<0.01
Ni	<0.03	<0.01
Sr	0.42	<0.01
Pd	0.03	0.12
Zr	0.06	0.38
Rh	<0.03	<0.01
Cs	<0.03	<0.01
Rb	<0.03	<0.01
Na	<0.03	<0.01
Ag	<0.03	<0.01
Am	>200	47.26

Though the distribution ratio of Zr(IV) and Pd(II) was lower than 0.1 in 0.2 M DOHyA/*n*-dodecane system, these elements were extracted to some extent in 0.4 M DOHyA/*n*-dodecane ($D_{Zr} = 0.38$, $D_{Pd} = 0.12$). In contrast, the distribution ratio of these elements were significantly less in TODGA system (D_{Zr} = 0.06, D_{Pd} = 0.03) in the presence of 0.2 M oxalic acid and 0.05 M HEDTA as complexing agents in the aqueous phase.

In view of the above, some researchers proposed to add complexing agents directly to HLLW for minimizing or eliminating the extraction of unwanted metal ions in a mixer-settler run or to introduce scrubbing stages after extraction, for back extracting the unwanted metal ions from the loaded organic phase in a mixer-settler run [76-82].

Since the distribution ratios obtained for all the elements in DOHyA system was low as compared to the TODGA system, co-current extraction studies were carried out for determining the number of stages required for complete extraction of americium from FR-SHLLW using 0.4 M DOHyA in *n*-dodecane. The results revealed that americium present in FR-SHLLW was quantitatively extracted into organic phase in three contacts.

Table 6.3 gives a comparison in the co-current extraction of Am(III) in DOHyA system with a couple of diglycolamide systems reported by Ansari et al., [85] who studied the co-current extraction of Am(III) from PHWR-SHLLW in a solution of 0.05 M TODGA + 5 vol% isodecanol in *n*-dodecane as well as 0.1 M TEHDGA + 5 vol% isodecanol in *n*-dodecane. The concentration of the extractant employed by Ansari et al. in the co-current study was lower (0.05 M TODGA or 0.1 M TEHDGA) as compared to the DOHyA concentration (0.4 M) employed in the present study, owing to the fact that the concentration of various metal ions present in the PHWR-SHLLW was lower than those in FR-SHLLW. It can be seen from table 6.3 that in all the three systems, the cumulative extraction of Am(III) was nearly quantitative in three co-current stages.

Table 6.3 Comparison of co-current extraction and stripping of americium from SHLLW in different extractant systems in *n*-dodecane. Organic to aqueous phase ratio=1:1 Temperature 298 K

	Solvent composition		
	0.05 M TODGA + 5 % isodecanol [85]	0.1 M T2EHDGA + 5 % isodecanol [85]	0.4 M DOHyA
	Feed composition		
	PHWR-SHLLW + 0.1 M $H_2C_2O_4$ + 0.05 M HEDTA	PHWR-SHLLW + 0.1 M $H_2C_2O_4$ + 0.05 M HEDTA	FR-SHLLW + 0.05 M CyDTA
Extraction stages	Cumulative extraction to organic phase (%)		
I	99	85	83
II	> 99.9	> 99.9	99
III	> 99.9	> 99.9	> 99.9
	Stripping phase		
	0.1 M HNO_3 + 0.1 M citric acid	**0.1 M HNO_3 + 0.1 M citric acid**	**0.5 M HNO_3**
Stripping stages	Cumulative stripping to aqueous phase (%)		
I	89.79	91.73	90
II	> 99.9	> 99.9	98
III	> 99.9	> 99.9	> 99.9

6.3 Batch stripping studies

The recovery of the loaded metal ions from the organic phase is usually carried out by contacting the loaded organic phase with dilute nitric acid. The literature showed that nitric acid concentration less than 0.1 M was generally employed for the recovery of metal ions from the loaded diglycolamide and TRUEX solvent systems [76-79]. This was essentially due to the extraction of significant quantities of nitric acid by these solvent systems during the extraction of trivalent metal ions [136]. In addition, the presence of a phase modifier also facilitates the extraction of nitric acid. When a significant quantity of nitric acid is loaded in the organic phase during extraction, efficient stripping of metal ions from such acid loaded organic phase requires an aqueous phase with acidity less than 0.1 M [78]. However, the use of very low concentration of nitric acid generally leads to poor phase disengagement during stripping and also facilitate hydrolysis of some troublesome metal ions such as Zr(IV), Pd(II) and Fe(III) although these metal ions show very low distribution ratio during extraction. To overcome such complications several authors have employed complexing agents such as citric acid and hydroxamic acid for the recovery of trivalent metal ions from loaded organic phase [85].

Our previous studies on DOHyA [Chapter 3] showed that the extraction of nitric acid was significantly low in 0.2 M DOHyA/*n*-dodecane as compared to other extractant systems reported in literature. In addition, the most important advantage of using DOHyA/*n*-dodecane for trivalent actinide separation was that it showed significant extraction of Am(III) only when the concentration of nitric acid exceeded 1 M. The distribution ratio of Am(III) was negligible (< 0.01) in the nitric acid concentration range 0.01 M to 1 M [Chapter 3]. On the other hand, the extraction of Am(III) was significant even at 0.5 M nitric acid in other solvent systems reported in literature. Therefore, it should be possible to recover the trivalent metal ions from loaded DOHyA phase even with 1 M nitric acid. In view of this, batch stripping studies were performed using nitric acid solutions having acidities 0.1 M, 0.5 M and 1 M. The loading of metal ions in 0.4 M DOHyA in *n*-dodecane was carried out by contacting the organic phase with FR-SHLLW. The loaded organic phase was separated and contacted with various stripping solution in a co-current stripping mode. A comparison of the results on recovery of americium and selected lanthanides in the first contact of stripping is shown in figure 6.1. It can be seen that more than 95% of lanthanides and americium was recovered in the first contact with 0.1 M nitric acid, whereas the recovery was 80% - 90 % with 0.5 M nitric acid. When the concentration of nitric acid was increased to 1 M, the recovery of various metals was in the range of 80% to 60%. The co-current stripping studies indicate that three contacts of the loaded organic phase with 0.5 M or 1 M nitric acid could be sufficient for quantitative recovery of americium and lanthanides from the loaded organic phase.

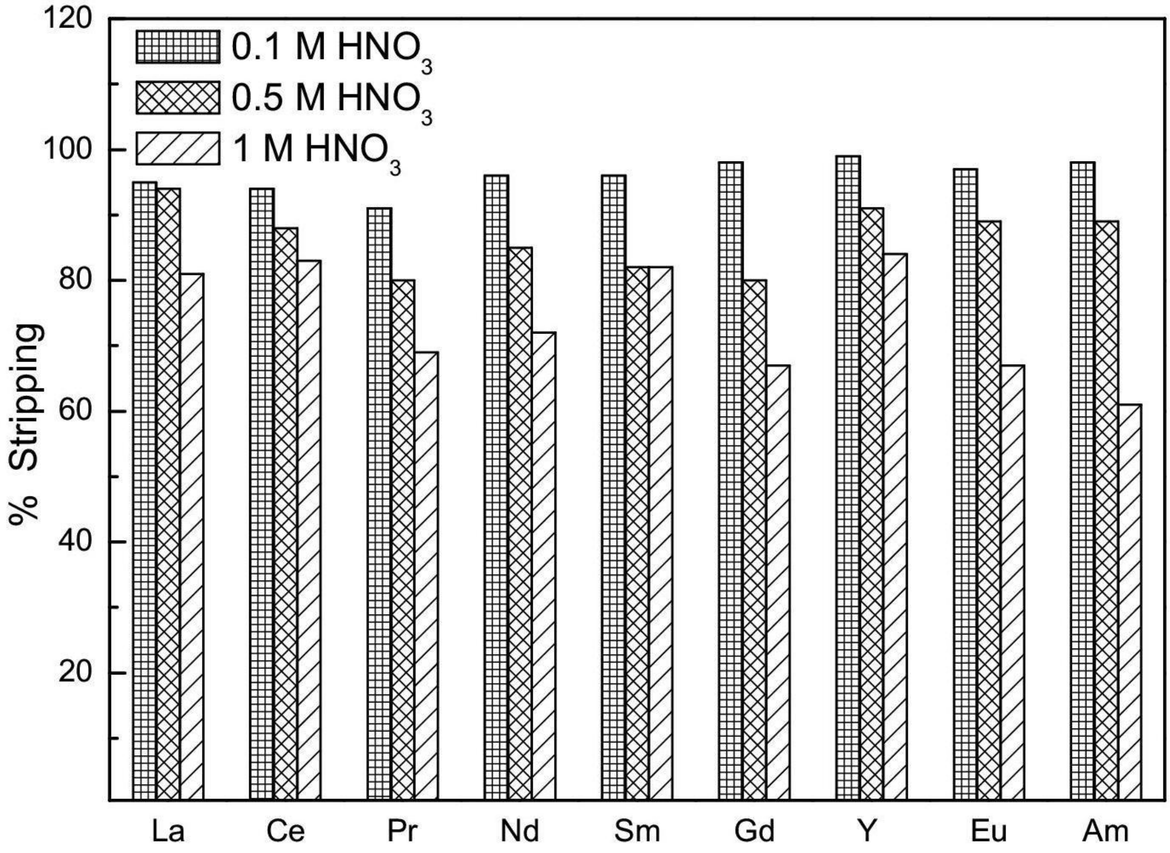

Figure 6.1: Comparison of stripping of various metal ions using different nitric acid solutions at 298 K. Organic phase: 0.4 M DOHyA in *n*-dodecane loaded with metal ions from FR-SHLLW spiked with ^{241}Am and $^{(152+154)}$Eu tracers.

Table 6.4 also shows the comparison in the co-current stripping of Am(III) from DOHyA/*n*-dodecane system using 0.5 M nitric acid with those reported by Ansari et al. for stripping of Am(III) from TODGA and TEHDGA systems using a solution of 0.1 M citric acid in 0.1 M nitric acid. The results revealed that three co-current stages were sufficient for quantitative transfer of Am (III) from loaded organic phase into aqueous phase for both the diglycolamides as well as for DOHyA employed in the present study. Based on these results, it was decided to use 0.5 M nitric acid for stripping of trivalent metal ions during counter-current stripping run.

6.4 Counter-current extraction studies

Counter-current extraction of various metal ions present in FR-SHLLW was studied using 0.4 M DOHyA in *n*-dodecane in a 20-stage ejector mixer settler system. The feed was FR-SHLLW containing 0.05 M CyDTA, spiked with ^{241}Am and $^{(152+154)}$Eu tracers. The feed solution was flowing from 1st stage to 20th stage, while the solvent was flowing from 20th stage to the first stage [Figure 2.2, Chapter 2]. The steady state extraction profile of Am(III), major lanthanides and other fission products is shown in figure 6.2. The extraction of Am(III) and Eu(III) was monitored by the radioactivities of ^{241}Am and $^{(152+154)}$Eu respectively in both aqueous and organic phases. For the remaining elements, the extraction was assessed by determining the concentration various metal ions present in aqueous phase before and after extraction. The concentration of metal ions in aqueous phase was determined by ICP-AES analysis. The profiles revealed that the extraction of Am(III) and all lanthanides present in FR-SHLLW was nearly quantitative in first three stages. Along with Am(III), Y(III) and Mo(VI) were also quantitatively (>99.9%) extracted in the first three stages. Among the other elements, the extraction of Zr(IV) and Pd(II) was about 26% and 5% respectively at the end of 20 stages. However, the extraction of these elements was nearly 10% and 2% after five stages and their extraction increased gradually with number of stages. The extraction of all other elements was negligible, as the concentrations of those metals were unaltered in the feed and raffinate. It should be noted that the extraction profile was studied up to 20 stages even though the extraction of trivalents was complete in three stages. This was carried out to understand the extraction behaviour of various unwanted metal ions such as Zr(IV) and Pd(II). The results from the present study showed that five stages of extraction was good enough for the extraction of Am(III) in 0.4 M DOHyA/ *n*-dodecane system from FR-SHLLW.

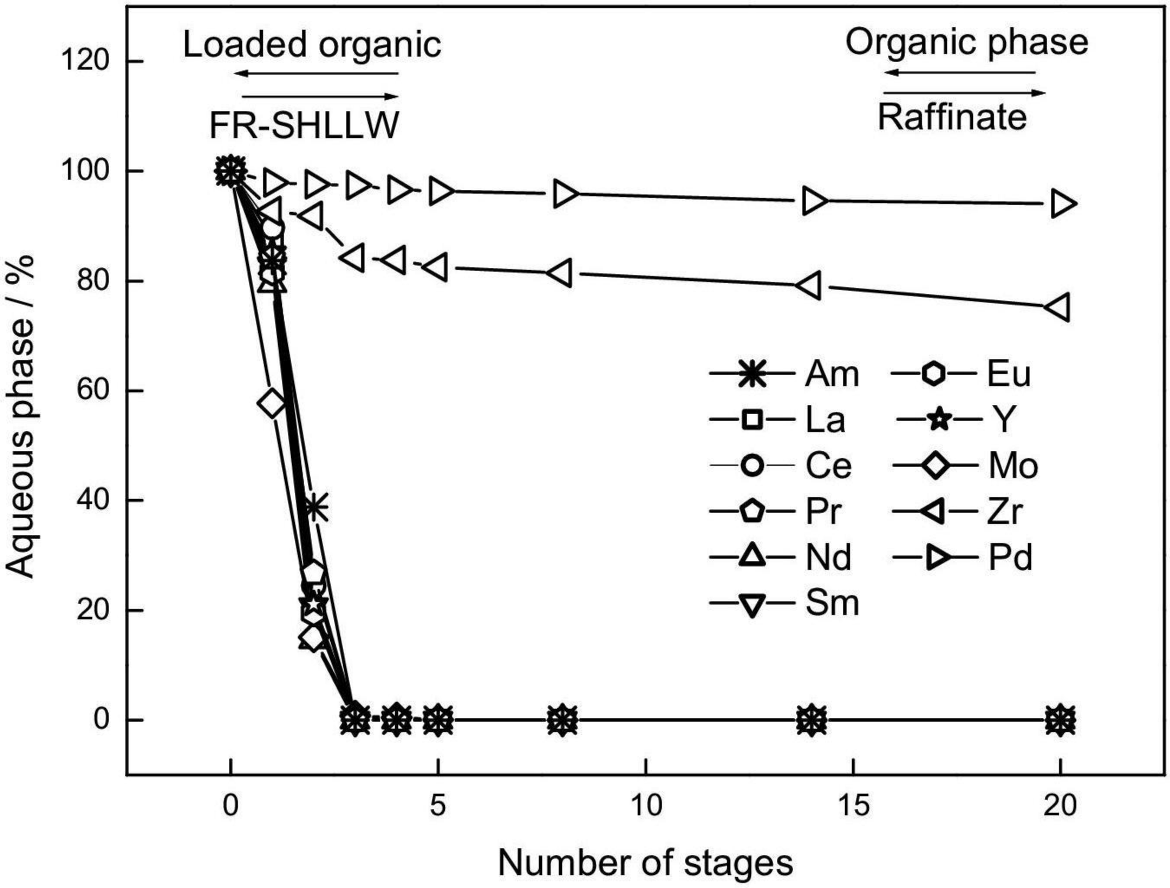

Figure 6.2: Counter-current extraction profiles for Am(III) and fission products using 20-stage mixer-settler. Organic phase: 0.4 M DOHyA in *n*-dodecane. Aqueous phase: FR-SHLLW + 0.05 M CyDTA spiked with ^{241}Am and $^{(152+154)}$Eu tracers. Organic to aqueous phase ratio 1:1, Temperature 298 K.

6.5 Counter-current stripping studies

The loaded organic solution obtained after 20 stages was collected together and it was subjected to a 20 stage counter current stripping run. The stripping reagent was 0.5 M nitric acid. The stripping profile for Am(III) and all the extracted lanthanides is shown in figure 6.3. It can be seen that, similar to the extraction profile, the recovery of all the extracted lanthanides and americium was nearly quantitative in three stages.

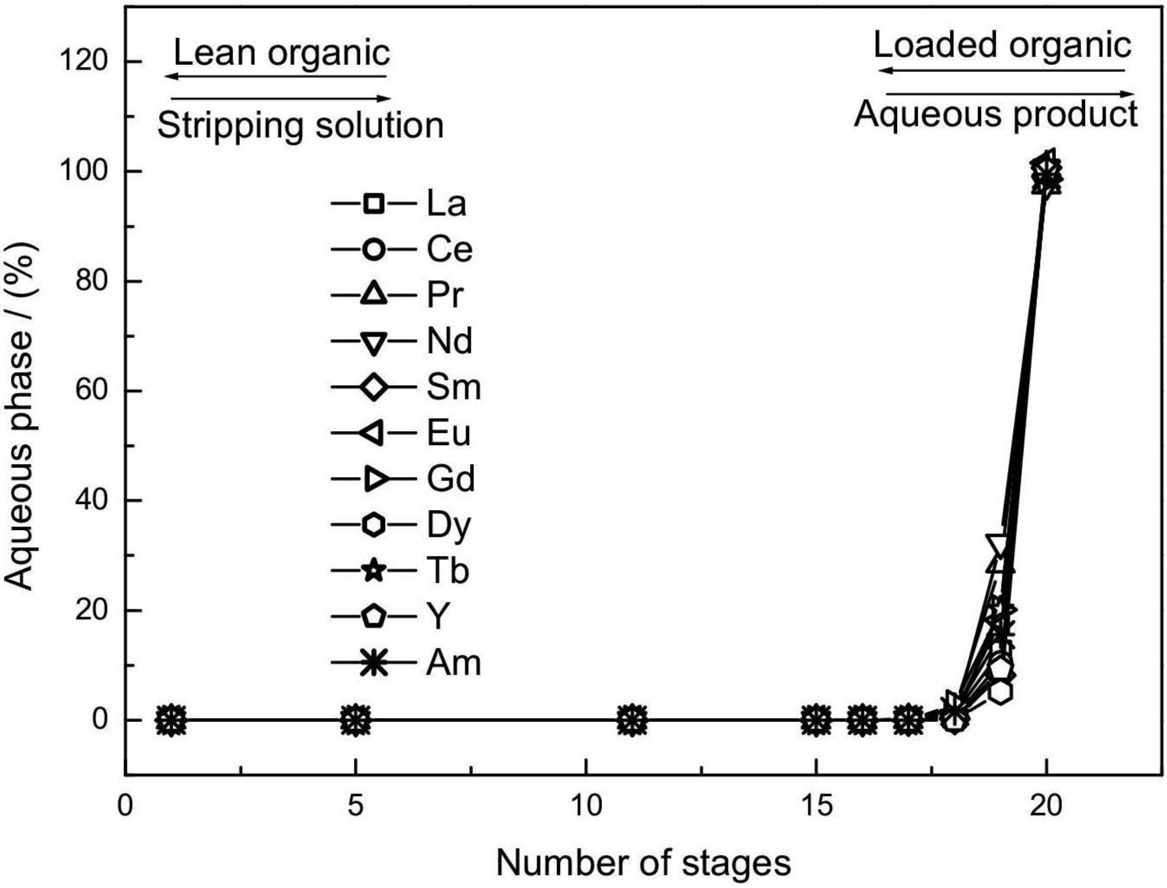

Figure 6.3: Counter-current stripping profiles for lanthanides, Y(III) and Am(III) using 20-stage mixer-settler. Organic phase: 0.4 M DOHyA in *n*-dodecane loaded with metal ions from FR-SHLLW. Aqueous phase: 0.5 M HNO_3 .Organic to aqueous phase ratio 1:1 Temperature 298 K

At the steady state, the gamma activities of both ^{241}Am and $^{(152+154)}$Eu was negligible in both aqueous and organic phases from stages 17 to 1. At the 20th stage, where the loaded organic phase meets the aqueous phase initially, nearly 87% of the total Am(III) activity and 93% of the total Eu(III) activity was back extracted into the aqueous phase. The remaining gamma activity of ^{241}Am and $^{(152+154)}$Eu in the organic phase was recovered in 19th and 18th stages leaving negligible radioactivity in other stages. A similar stripping profile was obtained for all the extracted lanthanides and Y(III) based on the analysis of aqueous samples from stages 20 to 1 by ICP-AES. It was noted that the recovery of Zr(IV) and Pd(II) was far less compared to the lanthanides and Am(III). Based on the elemental analysis of Zr(IV) and Pd(II) in the aqueous phase after 20 stages, the recovery of Zr(IV) and Pd(II) in the product was determined to be 0.55% and 0.87% respectively. In the first five stages of stripping, the recovery of these elements was negligibly small. Therefore, the results revealed that less than five stages are enough for the quantitative recovery of trivalent metal ions from the loaded DOHyA/*n*-dodecane phase using 0.5 M nitric acid. It should be noted that the concentration of Mo(VI) in the aqueous product was below the detection limits of ICP-AES after 20 stages. This indicates that all the extracted Mo(VI) was retained in the lean organic phase.

6.6 Comparison with other extractants

Table 6.4 shows the results of the counter-current run obtained in the present study, with the results of two counter-current runs reported in the literature. The two literature process methods used genuine PUREX raffinate and its reported composition was reasonably comparable with the FR-HLLW [78]. It should be noted that the extraction and recovery of americium and all the lanthanides was above 99.9% in all the three process methods. In the DIAMEX (DIAmide EXtraction) process, the concentration of DMDBTDMA employed for extraction was 0.5 M in TPH. The extraction was complete in seven stages and the recovery of the loaded metal ions was carried out by a solution of 0.1 M nitric acid [63]. For the other counter-current run, 0.2 M TODGA + 0.5 M TBP in TPH was employed for extraction. The results revealed that four stages were sufficient for quantitative extraction of Am(III) and lanthanides; however stripping was possible only with 0.01 M nitric acid. For the present study using

0.4 M DOHyA in *n*-dodecane, the number of stages required for extraction of Am(III) was three and efficient recovery was possible even with 0.5 M nitric acid. The concentrations of extractants used in both the DIAMEX process and TODGA process were far higher as compared to the DOHyA method.

Table 6.4 Comparison of the results of counter-current extraction studies of various extractants. The retention in the raffinate and recovery in the product are expressed in percentage compared to the feed.

	Extractant	
0.5 M DMDBTDMA in TPH [63]	0.2 M TODGA + 0.5 M TBP in TPH [78]	0.4 M DOHyA in *n*-dodecane
	Feed	
Genuine PUREX raffinate of UO_2 fuel (45 GWd/Te) at 3.5 M HNO_3 + 0.1 M $H_2C_2O_4$	Genuine PUREX raffinate of UO_2 fuel (60 GWd/Te) at 4.4 M HNO_3 + 0.2 M $H_2C_2O_4$ + 0.05 M HEDTA	FR-SHLLW (80 GWd/Te) at 4 M HNO_3 spiked with ^{241}Am and $^{(152+154)}$Eu tracers + 0.05 M CyDTA
	Raffinate	
< 0.01% Am < 0.01% Ln 99.9% Mo 99.9% Zr < 0.01% Pd	< 0.01% Am < 0.01% Ln 99.9% Mo 99.9% Zr 99.9% Pd	< 0.01% Am < 0.01% Ln < 0.01% Mo 73% Zr 94% Pd
	Stripping solution	
0.1 M HNO_3	0.01 M HNO_3	0.5 M HNO_3
	Product	
>99.9% Am >99.9% Ln < 0.1% Mo < 0.1% Zr 94% Pd	>99.9% Am >99.9% Ln < 0.1% Mo < 0.1% Zr < 0.1% Pd	>99.9% Am >99.9% Ln < 0.01% Mo < 1% Zr < 1% Pd

It should be noted that in the DIAMEX process, the extraction of Mo(VI) and Zr(IV) was masked by the employment of oxalic acid in the feed. However, Pd(II) was extracted and recovered along with Am(III) and lanthanides in the product. In the counter-current studies using TODGA-TBP system, extraction of Pd(II) also was efficiently masked by the use of HEDTA in the feed. For DOHyA, the use of oxalic acid and HEDTA in the feed was not very effective as discussed above. However, using CyDTA in FR-SHLLW phase, the extraction of Pd(II) and Zr(IV) were 5% and 27% respectively in 20 stages. The product was free from contamination of Mo(VI) and the amount of Zr(IV) and Pd(II) in the product was less than 1% after 20 stages of stripping.

6.7 Summary

The extraction and stripping of americium and lanthanides from FR-SHLLW was successfully demonstrated using 0.4 M DOHyA in *n*-dodecane in a 20-stage ejector mixer-settler system. Co-current extraction and stripping of Am(III) in DOHyA/*n*-dodecane system was comparable to the results reported for diglycolamides such as TODGA and TEHDGA under similar conditions. Quantitative extraction of Am(III), Ln(III), Y(III), Mo(VI) was achieved in three stages of the counter current run. The co-extraction of Zr(IV) and Pd(II) was minimized by the addition of 0.05 M CyDTA to the feed. Nevertheless, about 25% or Zr(IV) and 5% of Pd(II) was loaded on to DOHyA phase during counter-current extraction. Quantitative stripping of Am(III), Ln(III), and Y(III) was achieved within three stages with the use of 0.5 M nitric acid. The amounts of Mo(VI), Zr(IV) and Pd(II) in the product were less than 1% compared to the initial feed solution. Compared to the TODGA system, the extraction of Fe(III) and Sr(II) was negligible in DOHyA system; however the extraction of Mo(VI) was significant. Since the stripping of unwanted metal ions in the product was negligible, it is necessary to clean-up the lean organic phase containing Mo(VI), Zr(IV) and Pd(II) before recycling. The results of the present study were comparable to the DIAMEX and TODGA processes reported in the literature. However, no phase modifier was required for extraction of trivalents from FR-SHLLW using DOHyA and efficient recovery of loaded metal ions was possible using 0.5 M nitric acid as stripping solution, which are considerable advantages in the actual solvent extraction process.

CONCLUSIONS AND FUTURE PERSPECTIVES 7

This chapter summarizes the conclusions of the work explained in the thesis. In this study, *N,N*-di-alkyl-2-hydroxyacetamides were identified as modifier-free extractants for minor actinide partitioning. These extractants showed structural similarity with the diglycolamide extractants, which have been widely studied for the same purpose. At the same time, they were found to have better back extraction properties and resistance to third phase formation, compared to the diglycolamides. The conclusions based on the various evaluation studies are elaborated in the following sections of this chapter.

7.1 Evaluation of extraction behaviour and radiation stability

Three *N,N*-di-alkyl-2-hydroxyacetamide derivatives, namely DHHyA, DOHyA and DDHyA were studied for their extraction of Am(III) and Nd(III) from nitric acid medium. The $D_{Am(III)}$ values gradually increased with increase in nitric acid concentration for all the three extractants. The results revealed the possibility of extraction of metal ions from 3- 4 M nitric acid solutions and back extraction of loaded metal ions using 0.5 -1 M nitric acid solutions. The efficient back extraction of loaded metal ions by other reported extractants required very low concentrations of nitric acid ($\leq$ 0.1 M). The extraction of nitric acid by these extractants was found to be lower than many other extractant systems studied so far. Although DHHyA showed early third phase formation similar to diglycolamide extractants, DOHyA and DDHyA were found to be stable towards third phase formation under higher loadings of nitric acid and Nd(III) ions. Thus the studies showed the possibility of modifier-free extraction using long chain DAHyA extractants. The $D_{Am(III)}$ values measured for all the three DAHyA derivatives were found to be satisfactory after irradiation with gamma rays up to an absorbed dose of 200 kGy. Irradiation in the presence of 4 M nitric acid did not bring about any further changes in

$D_{Am(III)}$ values, indicating hydrolytic stability of these extractants. Only minimal variation in hydrodynamic properties was recorded as a result of irradiation up to 500 kGy. The stripping behaviour of extractants did not change as a result of irradiation, indicating the absence of any acidic degradation products. There was only minimal variation in the aggregation behaviour of extractants as a result of irradiation, as indicated during the studies involving bulk extraction of Nd(III) by irradiated samples.

7.2 Aggregation studies

The aggregation behaviour of DOHyA was studied in comparison with two TODGA-modifier systems at high loadings of nitric acid and Nd(III) ions in the aqueous phase. The average sizes of reverse micellar aggregates formed in the organic phases of these extractants were measured using dynamic light scattering. The observations on the variations in aggregate sizes of different extractants were co-related with the results of ATR-FTIR measurements. The objective of this study was to probe the modifier-free extraction of DOHyA compared to TODGA. The observations in this study have also been helpful in analysing the role of different phase modifiers in extraction systems.

The TODGA-DHOA system showed the formation of a third phase when the initial nitric acid concentration was above 8 M. However, TODGA-octanol system and DOHyA system did not show a third phase under these conditions. Both the extraction of nitric acid and sizes of reverse micellar aggregates were smaller in DOHyA compared to TODGA systems. It was inferred that the smaller aggregates of DOHyA having lesser number of polar functional groups in the polar cores were better stabilized in the organic phase compared to TODGA aggregates. The TODGA aggregates were found to be stabilized in the presence of phase modifiers. It was found that the aggregation in the organic phase of DOHyA increased with increase in extraction of nitric acid and/or metal ions. However, the aggregation in the organic phase of TODGA-modifier systems was reasonable even at very low concentrations of extracted nitric acid and/or metal ions. The average aggregate sizes of TODGA-octanol system were higher than TODGA-DHOA system, especially at high loadings of nitric acid and metal ions. Therefore, it was concluded that the reverse micelles formed in the presence of DHOA are more compact due to the interaction of DHOA molecules with the extracted species. The ATR-FTIR results also supported the increased interaction of extracted nitric acid and metal ions in TODGA-DHOA system compared to TODGA-octanol system. The minimal changes in the vibrational bands of DOHyA system compared to both the TODGA-modifier systems supported the better stabilization of DOHyA aggregates under high loadings. All the extractant systems in the present study did not show any third phase even when the concentration of Nd(III) ions in the aqueous phase was several times higher than the expected concentration of metal ions in HLLW. However, co-current studies with FR-SHLLW showed the formation of third phase in DOHyA system after 3 successive contacts. The TODGA-modifier systems showed no third phase, but crud formation was visible after 3-4 contacts in these systems also. Thus the study revealed that aggregation behaviour of extractants was different during extraction from FR-SHLLW.

7.3 Counter-current extraction and stripping studies using FR-SHLLW

The suitability of DOHyA for the counter-current extraction and stripping of trivalent americium and lanthanides from FR-SHLLW was successfully demonstrated using a 20-stage ejector mixer-settler system. Based on the results of batch studies using different complexing agents, the FR-SHLLW feed was charged with 0.05 M CyDTA for masking the extraction of Zr(IV) and Pd(II). Co-current extraction and stripping of Am(III) in DOHyA/*n*-dodecane system was comparable to the results reported for diglycolamides such as TODGA and TEHDGA under similar conditions. Quantitative extraction of Am(III), Ln(III), Y(III), Mo(VI) was achieved in three stages of the counter current run. Quantitative stripping of Am(III), Ln(III), and Y(III) was achieved within three stages with the use of 0.5 M nitric acid. Although co-extraction of the fission products, Mo(VI), Zr(IV) and Pd(II) was observed, the amounts of these metal ions in the product was less than 1% compared to the initial feed solution. Compared to the TODGA system, the extraction of Fe(III) and Sr(II) was negligible in DOHyA system; however the extraction of Mo(VI) was significant. Since the stripping of unwanted metal ions in the product was negligible, it is necessary to clean-up the lean organic phase containing Mo(VI), Zr(IV) and Pd(II) before recycling. The results of the present study were comparable with the DIAMEX and TODGA processes reported in the literature. The extraction efficiency of the DOHyA system without any phase modifiers was comparable with TODGA-modifier systems and efficient and easier back extraction of metal ions was feasible with DOHyA system using 0.5 M nitric acid.

7.4 Future perspectives

In the beginning of our studies, there were only few literature reports which dealt with the extraction properties of hydroxyacetamide extractants [111-113]. The results of our studies have thrown light over the promising nature of DOHyA for being used in process applications involving real radioactive waste solutions. However, it should be admitted that more studies are required before finalizing a flow-sheet for the process applications using DOHyA in the pilot scales. The following points may be considered as important in this regard:

i. Batch studies for extraction and stripping of other important metal ions in FR-SHLLW including uranium, plutonium, rhuthenium and technetium needs to be reported. Literature reports are available for individual extraction of these elements from nitric acid medium [113, 141]. These results need to be validated for extraction of these elements from FR-SHLLW medium.

ii. The results of the present study shows that the concentration of DOHyA extractant employed for counter-current studies can be reduced, as the extraction of metal ions was complete in three stages. Also, the number of stages in both extraction and stripping runs can be reduced from 20 to 10.

iii. The stripping of loaded metal ions using 0.5 M nitric acid was found to be complete in 3-4 stages during the present study. Further studies should make use of 1 M nitric acid solution for stripping.

iv. All the Mo(VI) extracted from FR-SHLLW was found to be retained in the lean organic phase after the stripping stages. Therefore, studies should be directed towards the clean-up of this lean organic phase. This problem can be solved by adding scrubbing stages for spent solvent using aqueous soluble hydroxyacetamide derivatives.

Dynamic light scattering technique was exclusively used for the aggregation studies in this work. The results of the studies have revealed some interesting facts, which need to be further probed by other techniques such as the SAXS (small angled X-ray scattering). Future studies planned in this direction shall involve tensiometry and viscometry for evaluation of basic parameters of reverse micellar systems. Also, comparison of aggregation behaviour of other available extractants such as the diamides and CMPO would help in a better understanding of third phase phenomena yielding valuable inputs for the design of better extractant systems.

Radiolytic stability of DAHyA extractants was studied under the irradiation of gamma rays in the present work. The radiolytic stability of these extractants needs to be confirmed under irradiation of alpha and beta sources also. Although gamma rays are responsible for a major fraction of radiolytic degradation of extractant systems, the assessment of radiolytic damage due to other radiations also needs to be performed as a part of evaluation of extractant systems. A detailed study of degradation products by mass spectroscopy and other suitable techniques is also essential for understanding the behaviour of extractant systems in contact with real waste solutions.

Among the three DAHyA derivatives studied, the hexyl derivative, DHHyA was found to form early third phase similar to diglycolamide extractants. However, DHHyA showed higher distribution values for extraction of Am(III) compared to other DAHyA derivatives studied. The efficient back extraction of loaded metal ions at relatively high nitric acid concentrations (0.5 M - 1 M) was common for all the DAHyA derivatives. These advantages of DHHyA can be explored in future studies. This extractant would be a better candidate for solid state extraction studies using inert polymer resin matrices as well as extraction studies in alternate diluents such as the ionic liquids. The extraction of Am(III) using DHHyA in ionic liquid medium was recently reported by Rout et al. [142].

The DAHyA derivatives were found to be selective for extraction of metal ions existing in oxidation states +3 or above in nitric acid medium. As it was demonstrated during our studies, they are useful for the group separation of trivalent actinides and lanthanides from high level liquid waste solutions. Therefore, selective partitioning of minor actinides would require one or more additional steps involving more selective extractants. Recently, extractant systems combining neutral and acidic extractants have been proposed for selective separation of trivalent actinides from HLLW in single extraction and stripping stages. There is scope for future studies in the development of combined extraction systems involving DOHyA by the selection of proper co-extractants. Swamy et al. [140] have reported studies on the synergistic extraction of Eu(III) and Am(III) in a combined system of DOHyA and bis-(2-ethylhexyl)phosphoric acid (HDEHP) in *n*-dodecane. Studies by Rama et al. [141] have shown unusually high extraction of Pu(IV) over U(VI) and Am(III) using DOHyA extractant in ionic liquid medium. Further studies aimed at development of better extraction systems incorporating hydroxyacetamides and basic studies involving this new class of extractants are expected to yield more promising results for selective separation of different metal ions from spent fuel solutions.

ABBREVIATIONS

ADS	Accelerator Driven System
An(III)	Trivalent Actinides
ATR	Attenuated Total Reflectance
BRIT	Board of Radiation and Isotope Technology
CAC	Critical Aqueous Concentration
CE	Centrifugal Extractor
CHON	Carbon Hydrogen Oxygen Nitrogen
CMC	Critical Micellar Concentration
CMPO	*n*-Octyl(phenyl)-*N*,*N*-diisobutyl(carbamoylmethyl)phosphineoxide
CyDTA	Trans-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid
DAHyA	*N*,*N*-Di-alkyl-2-hydroxyacetamide
DDyA	*N*,*N*-Di-decyl-2-hydroxyacetamide
DHHyA	*N*,*N*-Di-hexyl-2-hydroxyacetamide
DOHyA	*N*,*N*-Di-octyl-2-hydroxyacetamide
DIAMEX	DIAMide EXtraction
DGAs	Diglycolamides
D^3DODGA	*N*,*N*- Di-(dodecyl)-di-(octyl)diglycolamide
DEHDODGA	*N*,*N*-Di-(ethylhexyl)-di-(octyl)diglycolamide
DHOA	*N*,*N* -Dihexyloctanamide
DLS	Dynamic Light Scattering
D_M	Distribution ratio of Metal ion, M
DMDBTDMA	*N,N'*-Dimethyl-*N,N'*-dibutyl(tetradecyl)malonamide

DMDOHEMA	*N,N’*-Dimethyl-*N,N’*-dioctyl-2-(hexylethoxy)malonamide
DMF	*N*,*N*-Dimethylformamide
ECIL	Electronic Corporation of India Limited
EDTA	Ethylenediaminetetraaceticacid
FBR	Fast Breeder Reactor
FR-SHLLW	Fast Reactor-Simulated High Level Liquid Waste
GWd/Te	Giga Watt day per Ton electrical
HAR	High Active Raffinate
HEDTA	*N*-(2-hydroxyethyl) ethylenediamine-N,N’,N’-triacetic acid
HLLW	High Level Liquid Waste
HMTA	Hexamethylene tetramine
HpGe	High pure Germanium
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
IEA	International Energy Agency
INEEL	Idaho National Engineering and Environmental Laboratory
ITU	Institute for Transuranium elements
JAERI	Japan Atomic Energy Research Institute
KHP	Potassium hydrogen phthalate
LET	Liner Energy Transfer
Ln(III)	Trivalent lanthanides
LOC	Limiting Organic Concentration
LPC	Liquid Pulsed Column
LWR	Light Water Reactor
MCA	Multi Channel Analyzer
MOX	Mixed OXide

MWe	Mega Watt electrical
MWd/t_{HM}	Mega Watt Days per ton of Heavy Metals
n-DD	*n*-Dodecane
NEI	Nuclear Energy Institute
NPH	Normal Paraffinic Hydrocarbon
ORNL	Oak Ridge National Laboratory
PDI	Polydispersity index
PDT	Phase Disengagement Time
PFBR	Prototype Fast Breeder Reactor
PHWR	Pressurized Heavy Water Reactor
PUREX	Plutonium and Uranium Recovery by EXtraction
P&T	Partitioning and Transmutation
TBP	Tri-*n*-butyl phosphate
TEA	Triethylamine
TEHDGA	*N,N,N'N'*-Tetra(ethylhexyl)diglycolamide
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
TODGA	*N,N,N'N'*-Tetra(octyl)diglycolamide
TRUEX	Trans Uranic EXtraction
UOX	Uranium OXide

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