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“Studies on the transport behavior of actinides and lanthanides across supported liquid membranes containing di-glycolamide as carriers”

In the ever growing demand of energy with minimal impact on environment, ‘nuclear power’ has been projected as one of the potential alternatives to fossil fuel. The basis of nuclear energy is the neutron induced controlled fission of various fissile materials like, $^{235}$U, $^{239}$Pu, $^{233}$U etc. However due to limited resources of naturally occurring fissile element ($^{235}$U), closed nuclear fuel cycle is the option to sustain the nuclear power programme. Closed fuel cycle has been adopted by various countries like India, and emphasizes on the reprocessing of the spent fuel. During reprocessing of spent nuclear fuel, the recyclable fissile elements (Plutonium and Uranium) are recovered using solvent extraction process leaving behind very highly radioactive liquid waste solution which is subsequently concentrated to yield the High Level Waste (HLW). The HLW solution consists of long lived alpha emitting radio-nuclides such as $^{241}$Am, $^{243}$Am, $^{245}$Cm and $^{237}$Np (referred to as minor actinides) apart from small amount of unrecovered plutonium and uranium as well as beta / gamma emitting fission products and significant concentrations of structural materials and process chemicals. HLW poses a long term radiological risk to the environment due to very long half lives of the minor actinides [1]. Efficient management of the HLW for minimizing the long term radiotoxic effect is essential for sustainability of nuclear power.

Minor actinides having half lives of several million years are the major concern for the safe disposal of HLW. The most accepted strategy for the safe management of HLW is to vitrify it in glass matrix. However due to the long half lives of the minor actinides, surveillance of the vitrified matrix is required which makes it economically as well as environmentally a daunting task. Partitioning and Transmutation (P&T) is an alternative / complimentary concept for the management of HLW [2]. This process
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involves selective removal of minor actinides from HLW by a process called ‘actinide partitioning’ followed by their subsequent and burning in reactors as mixed oxide fuels. Apart from alleviating the need for long term surveillance of the geological repositories, the P&T process would also lead to the generation of extra energy. After partitioning of the actinides along with the long lived fission products, the residual waste can be vitrified and buried in subsurface repositories at a much reduced risk and cost. Concerted efforts are being made by separation scientists to develop efficient and environmentally benign processes for the separation of long-lived radionuclides from HLW solution.

Various ‘actinide partitioning’ processes have been proposed by different laboratories viz. TRUEX, DIAMEX, DIDPA and TRPO which employ octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO), N,N’-dimethyl-N,N’-dibutyl tetradecyl malonamide (DMDBTDMA), diisodecyl phosphoric acid (DIDPA) and trialkyl phosphate oxide (TRPO) as the extractants, respectively [3]. All these reagents have their advantages and drawbacks. This led to the search for alternative and efficient reagents for actinide partitioning purpose. It has been observed that the introduction of etherial oxygen atom between the two amide groups of diamides (diglycolamide) causes significant enhancement in the extraction of trivalent actinides / lanthanides. Amongst the several derivatives of diglycolamide studied, N,N,N’,N’-tetraoctyl diglycolamide (TODGA) has been identified as one of the most promising extractants for the partitioning of trivalent actinides and lanthanides from HLW solutions [4]. Some of the salient features of TODGA include; (i) high distribution co-efficient values of trivalent actinides from moderate acidic aqueous solutions, (ii) possibility of complete incineration as the constituent elements are C, H, N and O, (iii) good radiolytic and hydrolytic stability, and (iv) the ease of synthesis. In view of these favorable properties TODGA was evaluated for the partitioning of actinides from HLW solution by a series of mixer-settler runs [5]. Recently, a branched chain homolog of TODGA has also been synthesized and evaluated for actinide partitioning [6]. This reagent has been reported to have similar extraction properties as TODGA though somewhat reduced extraction of
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fission products due to stereo chemical hindrance from branched chain.

The main objective of the present work is to evaluate TODGA and TEHDGA as the carrier molecule and to study the transport behavior of actinides, lanthanides and fission products across supported liquid membranes. The present research work includes transport behavior of actinides in various oxidation states using TODGA and TEHDGA as carrier extractants. Effect of diluents and irradiation dose on the extraction and transport behavior of actinides was also carried out. Effect of structure variation of diglycolamides on the extraction and transport of actinides and lanthanides have also been evaluated in the present study.

CHAPTER 1: GENERAL INTRODUCTION

This Chapter gives an introduction to the research problem dealt with in this thesis. The importance of separation of minor actinides and long-lived fission products from radioactive waste is discussed in detail. It describes the source and type of radioactive waste along with the environmental impact of the radionuclides present in those wastes. Major aim of radioactive waste management is to separate long lived, alpha emitting elements which belong to the actinide series of the periodic table. Chemistry of the actinides which is important for separation of the elements has been discussed in brief. A brief description of the separation techniques which are used for actinide separation like solvent extraction, membrane technique etc. is also given in this Chapter. Literature reports on actinide separation using different class of extractants have also been summarized. A brief background of the development of diglycolamide extractants has been included in this chapter.

Membranes are barriers that separate two fluid phases and allow the mass transfer from one side of the barrier to the other. Advantages of membrane based separation techniques are low energy requirements, low capital and operating costs, the possibility of achieving high separation factors and simple modular design [7]. One of the important features of
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liquid membrane separations is simultaneous extraction and stripping unlike solvent extraction process.

This Chapter gives a brief description of the principles of various liquid membranes and theory of facilitated transport of metal ion across supported liquid membranes. Equations to calculate flux and permeability co-efficient of the transported species have been derived. A brief description of mathematical modeling of transport using MATLAB-6.5 software has also been presented in this Chapter. Finally the aims and objectives of the present work are entitled.

CHAPTER-2: EXPERIMENTAL

A general outline of different experimental techniques and instrumentation used in the present work is given in this Chapter. The synthesis, purification and characterization of TODGA and other synthesized DGA’s have been described. A brief mention about the various analytical techniques followed is also made in this Chapter. Liquid scintillation counter was employed for radiometric assay of alpha emitting radio nuclides such as Pu, and 233U while gamma counting using NaI(Tl) scintillator counter was followed for the assaying of 85,89Sr, 152,154Eu, 234Th and 241Am. The basic principles of these detectors are also described. Preparation and purification of various radiotracers are included in this Chapter. The UV-visible absorption spectrophotometry was followed for the analysis of Nd. Methods to adjust the oxidation state of Pu is described in this Chapter. Purity of the different oxidation states of Pu was checked by spectrophotometry. The complexometric titrations carried out for the analysis of various elements such as thorium and uranium is also described in this chapter.

CHAPTER-3: TRANSPORT OF ACTINIDES ACROSS SLM’s USING N,N,N’,N’-TETRAOCTYL DIGLYCOLAMIDE (TODGA) AS CARRIER.
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N,N,N',N'-tetraoctyl diglycolamide (TODGA) has been proposed as a promising reagent for ‘Actinide Partitioning’ [8]. This Chapter deals with solvent extraction as well as supported liquid membrane transport studies of various actinides in different oxidation states using TODGA as the carrier extractant. The actinide ions studied in this work are Pu(III),Pu(IV),Pu(VI),U(VI) and Th(IV) and the oxidation states of Pu were confirmed by spectrophotometry as well as by TTA extraction.

Solvent extraction studies of Pu(III) with TODGA suggested extraction of a tetrasolvate species which was similar to the species reported with Am(III). Membrane transport properties of Pu(III) using varying reductants, varying feed acidity, varying TODGA concentration, different types of strippant are described in detail in the present Chapter. Flux of Pu(III) transport with varying concentration of Pu and stability of the membrane is also discussed in the Chapter. Striking similarities between Am(III) and Pu(III) transport behavior is the highlight of this work.

Present Chapter also describes the extraction and transport behavior of Pu in its tetravalent oxidation state with TODGA as the extractant/carrier. Nature of the extracted species formed with TODGA was different than that of Pu(III). Role of feed acidity, TODGA concentration, membrane thickness on the transport of Pu(IV) is discussed in the Chapter. The membrane stability was limited up to 5 days as compared to 20 days of continuous operation reported earlier for Am\(^{3+}\) transport. Transport studies are also carried out using irradiated TODGA upto a maximum absorbed dose of 15 MRad.

Uranium is a major constituent of HLW and due to its presence in the +6 oxidation state, it is expected to behave differently than that of Pu or Am. Present Chapter gives a detailed description on the solvent extraction and transport properties of U(VI) using TODGA as the extractant/carrier. It was observed that the nature of species formed for U(VI) varied depending on the aqueous phase acidity. At 1 M HNO\(_3\), it formed a di-solvate whereas at 3 M HNO\(_3\) a mono-solvate was found to be formed. Membrane transport was described in detail with respect to variation of different parameters like feed acidity, carrier concentration, membrane pore size, feed U concentration etc.
In view of the importance of Th fuel cycle in Indian nuclear energy programme, separation of Th$^{4+}$ from acidic feed is also studied using TODGA using both SX as well as SLM methods. Conditions for quantitative Th$^{4+}$ transport has been arrived at by carrying out analogous transport studies.

Diluents play a major role in the extraction of metal ions for organic carriers. Solubility of the carriers in the diluents, polarity of the diluent, ability to form H-bonding, Hildebrand’s solubility parameter, Schmidt’s diluent parameter of the diluent are some of the parameters that determines the extraction performance and nature of species of the metal ion [9]. Present Chapter describes the role of diluents on the extractability and nature of species of Am(III) from nitric acid medium using TODGA as extractant. A series of diluents like kerosene, toluene, chloroform, methyl iso-butyl ketone, carbon tetra chloride, 1-octanol, tert butyl benzene etc. having widely different diluent properties have been used for Am(III) extraction in this study. Present Chapter also describes the transport property of Am(III) using TODGA in different diluents as the carrier solvents. Percentage transport of Am(III) with these diluents have been calculated and the effect of membrane pore size in these diluents have been investigated. Present Chapter also deals with the calculation of membrane diffusion parameters for different diluents.

Application of TODGA for actual process solution will lead to irradiation of the extractant by gamma radiation from the radio nuclides present in the HLLW solution. Gamma radiation leads to the degradation of TODGA with subsequent generation of degradation products which can affect the extraction/transport properties. Effect of radiolytic degradation on the solvent extraction of actinides and fission products have been reported [10]. But its effect on the membrane transport properties of various radio nuclides and fission products have not been reported in the literature. Present chapter describes the transport properties of actinides (+3,+4,+6 oxidation states) along with fission product (+2 oxidation state) using three chosen carrier concentrations with
varying irradiation dose. The transport rate variation for all the radio nuclides and its
effect on the decontamination factor of the actinides with respect to fission product have
also been discussed in detail in the Chapter.

CHAPTER-4: TRANSPORT OF ACTINIDES AND LANTHANIDES USING
N,N,N’,N’-TETRA (2-ETHYL HEXYL) DIGLYCOLAMIDE (T2EHDGA)

N,N,N’,N’-tetra (2-ethyl hexyl) diglycolamide (T2EHDGA) is a branched chain homolog of TODGA and has been evaluated for actinide partitioning purpose [6]. It is reported to favourably extract trivalent actinides similar to TODGA though higher decontamination factor values (with respect to the fission products) are expected due to stereo-chemical hindrance.

Present Chapter deals with the solvent extraction and the transport behavior of actinides in the trivalent (Am\(^{3+}\)) and hexavalent (UO\(_2^{2+}\)) state along with a trivalent lanthanide (Eu\(^{3+}\)) from nitric acid medium using TEHDGA as extractant/ carrier. Various parameters which effect the solvent extraction and transport behavior like feed nitric acid concentration/ nitrate concentration, carrier concentration, membrane pore size, nature of strippant, effect of phase modifier etc are described in this Chapter.

The Chapter gives a detailed description of the transport properties of trivalent actinide, Am(III) using T2EHDGA as carrier across a SLM. In contrary to TODGA which forms a tetra-solvate with Am(III), T2EHDGA was found to form a tri-solvate extractable complex. Membrane transport behavior was found to be comparable with that of TODGA. Effect of parameters such as feed acidity, T2EHDGA concentration, membrane pore size, nature of strippant etc on Am(III) transport have been investigated in detail in the present Chapter. Selectivity of Am(III) over other fission products was found to be quite high. Stability of the membrane was found to be quite satisfactory over a period of 15 days.
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Along with minor actinides, HLW consists of large concentrations of trivalent lanthanides whose behavior is similar to that of trivalent actinides. So it was necessary to understand the transport properties of trivalent lanthanides from nitric acid medium. This Chapter also describes the transport properties of a representative trivalent lanthanide (Eu(III)) with T2EHDGA as the carrier extractant. Similar to Am(III), Eu(III) was found to form a tri-solvate with T2EHDGA. In this Chapter, Eu(III) transport using T2EHDGA as the carrier has been described in detail with elaborate description on various factors which effect the transport rate. Role of phase modifier in solvent extraction and transport of Eu(III) has also been described in this current Chapter.

Uranium is a major constituent of HLW. In order to assess the suitability of T2EHDGA as a carrier solvent, it was imperative to investigate the SX and SLM transport behavior of U(VI) using T2EHDGA as the extractant/carrier. The solvent extraction studies showed formation of mono-solvate of U(VI) with T2EHDGA at 3M HNO₃. The extraction was found to increase with increasing nitrate ion concentration in the feed and decrease with increasing phase modifier concentration in the extractant concentration. This Chapter also describes detailed membrane transport studies which were carried out to get the optimum transport rate as well as to understand the mechanism of transport. Some of the parameters described in the Chapter are: effect of phase modifier concentration, effect of feed acid concentration, effect of different acids and their corresponding salts, concentration of T2EHDGA, membrane pore size, concentration of U in the feed, effect of temperature etc.

CHAPTER-5: SOLVENT EXTRACTION AND MEMBRANE TRANSPORT BEHAVIOR OF TRIVALENT ACTINIDES AND LANTHANIDES USING SUBSTITUTED DI-GLYCOL AMIDES

Diglycolamide (RR-NCO-CH₂)₂-O, which is a kind of diamide derivative having two carbamoyl groups connected by the alkyl chain including an etherial oxygen, was
introduced initially by Stephan et al [11,12]. Diglycolamides contain three oxygen atoms that can form strong complexes with the metal ions, and act as tridentate ligands. Present Chapter describes the effect of alkyl chain length of the substituents in the diglycolamides on the extraction and transport behavior of trivalent actinides, lanthanides and fission products. Different di-glycolamides studied in this Chapter are N,N,N’,N’-tetraoctyl diglycolamide (TODGA), N,N,N’,N’-tetra (2-ethyl hexyl) diglycolamides (T2EHDGA), N,N,N’,N’-tetrahexyl diglycolamide (THDGA), N,N,N’,N’-tetrpentyl diglycolamide (TPDGA), N,N,N’,N’-tetradecyl diglycolamide (TDDGA).

A detailed description on the solvent extraction properties of the actinides, lanthanides and fission product elements such as Sr using the substituted diglycolamides from nitric acid medium form the first part of the present Chapter. Various parameters which affect the extraction properties of the radio nuclides like kinetics of extraction, effect of feed acidity, composition of phase modifier, effect of phase modifier on the extraction, LOC value of Nd, extraction from synthetic high level waste (SHLW) for different diglycolamides have also been described in detail.

In the second part of the Chapter SLM transport behavior of the radio-nuclides using the substituted DAG’s as the carrier have been described. Effects of feed nitric acid concentration, phase modifier concentration, membrane pore sizes etc have been described for the actinides, lanthanides and fission product elements

CHAPTER-6: SUMMARY AND CONCLUSIONS

In conclusion, the present thesis demonstrates the possible application of membrane based separation of actinides and lanthanides from nitric acid feeds using TODGA, T2EHDGA and several other substituted diglycolamides as the carriers. Transport properties of actinides were found to be dependent on their oxidation states for TODGA with the trend of transport rate being An(III)>An(IV)>AnO$_2^{2+}$. Various factors that affect the transport properties were evaluated in detail to get the optimum transport condition. Stability of the supported liquid membranes was found to be satisfactory over
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a period of 20 days making them promising alternatives to solvent extraction for actinide recovery from wastes. Diluents were found to play a major role in the extraction and transport of actinides for TODGA. Irradiation stability of TODGA with respect to transport of actinides and fission products was also evaluated. It was observed that the transport rate decreased with increasing irradiation dose for all the actinides and fission products. But the decontamination factor of the actinides with respect to fission product increased with increasing irradiation dose. T2EHDGA based supported liquid membrane was also found to be effective for the transport of actinides and lanthanides from nitric acid medium. The transport properties of the radio nuclides were described in terms of various diffusional parameters. Structural effects of diglycolamides with respect to solvent extraction and membrane transport were also evaluated. Large scale application of the technique needs further studies using Hollow Fiber Contactors.

REFERENCES

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