DEVELOPMENT OF MACROCYCLIC EXTRACTANTS FOR SELECTIVE SEPARATION OF CESIUM, STRONTIUM AND TECHNETIUM FROM RADIOACTIVE WASTE SOLUTIONS

By

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DECLARATION

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

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CONTRIBUTIONS OF THE PRESENT WORK AND FUTURE PERSPECTIVES

Following are the major contributions of the present work:

1. Process for bulk synthesis of high purity CC6 and BCC6 is established.
2. Diluent system, a mixture of IDA and *n*-dodecane has been tested for the first time and found to be very effective for separation of radionuclides without any hydrodynamic problems from nuclear waste solutions containing high salt.
3. The process for separation of Cs from HLLW with CC6 is deployed at engineering scale for production of ^{137}Cs glass pencils as γ source.
4. Branched CC6 (BCC6) is tested for selective separation of Cs^+ from HLLW.
5. Hydrogenation of DtBuDCH18C6 in the presence of reaction accelerator-isovaleric has resulted in reproducible formation of *cis-syn-cis*-DtBuDCH18C6 with high yield.
6. Selective separation of ^{90}Sr from HLLW was successfully carried out by 0.1 M DtBuDCH18C6 + 50% IDA/*n*-dodecane solvent in presence of high concentration of interfering divalent group like calcium and barium. This has lead to its use in separation of ^{90}Sr from high salt content HLLW where salt content was as high as 300 g/L. 1Ci of pure ^{90}Sr is separated from high salt content HLLW using 0.1 M DtBuDCH18C6 + 50% IDA/*n*-dodecane solvent. Carrier free ^{90}Y was generated from recovered ^{90}Sr for medical use.
7. ^{99}Tc removal from alkaline LLW was efficiently carried out with DtBuDB18C6 dissolved in a mixture of IDA + *n*-dodecane diluent. This process was successfully demonstrated with 100 mL LLW of Waste Management Facility (WMF) of Tarapur and Kalpakkam, in a five stage cross-current extraction mode with fresh solvent in

each stage. The results have shown more than 99.5% removal of ^{99}Tc and the depleted waste is found to qualify for direct disposal to environment. With the use of this solvent, ^{99}Tc can be selectively removed from the LLW which will pave the way for development of a suitable waste form for further management of recovered ^{99}Tc. Counter-current mixer-settler experiments are being planned at WMF, Tarapur to generate engineering scale process parameters for separation of ^{99}Tc from LLW.

SUMMARY

Reprocessing of spent nuclear fuels for the recovery of Pu and U using solvent extraction process called PUREX (Plutonium Uranium Reductive EXtraction), generates considerable volume of acidic high level liquid waste (HLLW). This HLLW consists most of the metallic elements in the periodic table both radioactive & non-radioactive and retains majority of radio-toxicity of the original spent fuel. The toxicity of the waste is due to the presence of long-lived minor actinides (MA) such as ^{237}Np ($t_{1/2}$ = 2.16 x 10^6 y), ^{241}Am ($t_{1/2}$ = 432.7 y) and ^{245}Cm ($t_{1/2}$ = 8.5 x 10^3 y) and radioactive fission products, mainly rare earths, ^{99}Tc, ^{90}Sr and isotopes of Cs (^{135}Cs, ^{134}Cs and ^{137}Cs). Development of efficient separation processes for removal of harmful radiotoxic elements from waste solutions is vital for the success of the nuclear energy program. ^{137}Cs ($t_{1/2}$ = 30.1 y) and ^{90}Sr ($t_{1/2}$ = 28.9 y) are major heat emitting nuclides contributing largely on heat and radiation load of HLLW and ^{135}Cs ($t_{1/2}$ = 2.3 x 10^6 y) has a long term adverse impact on ecology due to its mobility in repository. Separation of these elements is necessary for safe waste management and also for their uses in societal applications. ^{99}Tc, a beta emitting radionuclide ($t_{1/2}$ = 2.11x10^5 y) is primarily exists as $HTcO_4$ or $NaTcO_4$ in highly oxidising HNO_3 medium or in alkaline solution. Management of HLLW leads to generation of intermediate waste (ILW) and low level waste (LLW) streams which are made alkaline for further separation processes and for intermittent storage in carbon steel tanks. LLW generated from power reactor contains about 0.3 mCi/L of ^{99}Tc, the β-load of which makes the waste unsuitable for direct discharge to environment, this necessitates separation of ^{99}Tc to bring down the activity level of waste below discharge limits (0.01mCi/L). Selective separation of these fission products from radioactive waste streams containing large concentrations of active/inactive interfering elements has been one of the most challenging goals. Macrocyclic extractants like calix-crown-6 and crown ethers

when fixed in a particular isomeric form possesses a cavity which is highly complementary to some of the alkali/earth alkali metal ions and serve as potential extractants for selective separation of Cs^+, Sr^{2+} and $Na^+ TcO_4^-$. Complementarity is due to close size fit of cavity to metal ion, dipole-dipole and cation-π-electron cloud interactions. Owing to high polarities of these extractants, they are mostly insoluble in *n*-dodecane; a PUREX-type industrial diluent. The current study is thus focused on developing the calix-crown-6 and crown ethers having less polar substituents in order to enable their solubility and effective use in *n*-dodecane based diluent. The extractants developed are 1,3-dioctyloxycalix[4]arene-crown-6 and 1,3-bis(2-ethylhexyloxy)calix[4]arene-crown-6 for selective separation of Cs^+ from HLLW, 4,4′(5′)-[di-*tert*-butyldicyclohexano]-18-crown-6 for selective separation of Sr^{2+} from HLLW and 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 for selective separation of $Na^+TcO_4^-$ from LLW. The work presents, modification in their reported synthesis procedures to obtain high yield and purity, solvent extraction investigations to determine process solvent compositions, extraction mechanism, stoichiometry of metal-extractant complex, selectivity of extraction from actual nuclear waste solutions having high salt content, degradation behaviour under hydrolytic & radiolytic conditions and regeneration of degraded solvent. All these extractants have shown insufficient solubility and extraction properties with *n*-dodecane. Therefore, a new diluent, a polar paraffinic alcohol namely isodecyl alcohol (IDA) having a dielectric constant of 8.1 is added to *n*-dodecane to improve their solubility and extraction behaviour. The extraction mechanism determined for Cs^+ and Sr^{2+} displays solvation and $Na^+TcO_4^-$ as ion-pair association. The combining ratio of extractant to metal ion is 1:1 in all the cases. Radiolytic and hydrolytic degradation studies have indicated fairly high stability of solvents towards degradation. Identification of degradation products and regeneration of spent solvent are established.

CHAPTER 1

Introduction

Nuclear power plays an important role to meet the world's energy demand with the diminishing sources of fossil fuel. To increase nuclear power generation capacity in the county, consistent with available resources in a safe, economical and rapid manner in keeping with the growth of energy demand in the country, a massive nuclear power programme is committed by our government. Nuclear Power Corporation of India Limited (NPCIL) is presently operating 22 commercial nuclear power reactors with an installed capacity of 6780MW. The reactor fleet comprises two Boiling Water Reactors (BWRs) and 18 Pressurized Heavy Water Reactor (PHWRs) and two 1000MW Voda Voda Energo Reactor (VVER) reactors. Currently NPCIL has eight reactors under various stages of construction totaling 6300 MW capacity. PHWR uses natural U as its fuel and heavy water as coolant and moderator. Energy released from continuous neutron induced fission of the fuel atom is harnessed as heat and is used to produce steam. The steam is used to drive the turbine which produces electricity [1,2]. Formation of fission products in the fuel depends on the quantity of U burned in the reactor. Beyond a certain burn up, the accumulation of the fission products in the fuel hinders the operation of the reactor in terms of neutron economy and radiation and the fuel is discharged as spent fuel. In addition to the fissile and fertile heavy nuclides- ^{235}U, ^{239}Pu and ^{238}U, a considerable amount of fission fragments do exist in the spent fuel along with some minor actinide elements due to nuclear reactions.

All the activities associated with the production of electricity from nuclear reactors are collectively referred as the nuclear fuel cycle. The cycle starts with the mining of U and ends with disposal of highly active nuclear waste. Front end of the fuel cycle includes mining, milling and fuel fabrication. Back end of the fuel cycle deals with the management of the spent fuel. The management of spent nuclear fuel and radioactive waste from nuclear energy production is a major challenge and possible obstruction for the countries wishing to start a nuclear power programme. Legacy of Fukushima Daiichi will be a sharper focus on nuclear safety everywhere. Development of efficient separation techniques for removal of radiotoxic elements from nuclear waste will be the key for success and public acceptance of nuclear energy program [3,4].

Spent fuel is managed either by closed or open fuel cycle option. In closed fuel cycle, emphasis is given on the recycling of useful nuclear elements whereas spent fuel is directly disposed into the deep geological repositories in remote area in open/once through fuel cycle. To sustain our nuclear energy program, India has adopted closed fuel cycle by recovering fissile and fertile nuclear materials from the spent fuel and recycling these materials into the reactors [5,6]. Schematic of fuel cycle operations is given in **Fig.1.1**. Indigenous technology for reprocessing spent fuel as well as waste management programme has been developed in our country through comprehensive R&D efforts. Reprocessing plants were set up and are in operation attaining self-reliance.

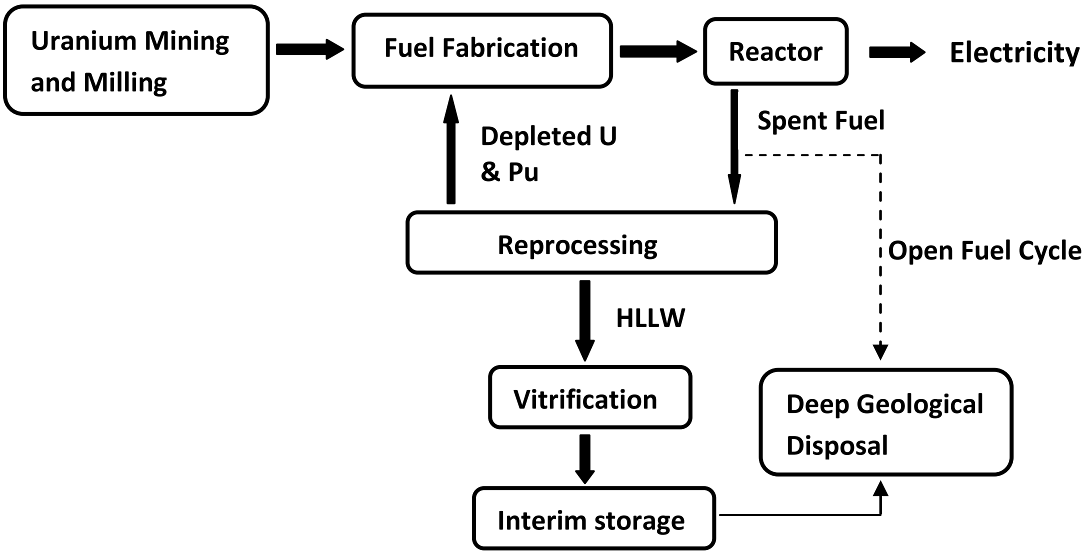


Fig.1.1: Fuel cycle operations

1.1 Reprocessing of spent fuel by PUREX process

After withdrawing the spent fuel from reactor, it is cooled for the decay of short lived fission products. Then it is subjected to reprocessing. Reprocessing refers to the processing of the spent fuel to separate the fissile and fertile materials from fission products. This is conventionally carried out by a liquid-liquid extraction process called PUREX [7,8]. Prior to this solvent extraction process, pretreatment steps are adopted to remove the cladding from the spent fuel so that the fuel is exposed to processing. Depending upon the cladding material, chemical or mechanical decladding operations are followed. The spent fuel which is in the form of solid is dissolved in nitric acid to be amenable for extraction. A feed conditioning step is followed to attain the feed at the desired solvent extraction conditions. During feed conditioning, free acidity and U concentration are maintained at optimum values to obtain high decontamination factors for the nuclear materials from fission products and to achieve minimum losses in the waste streams. 4th valancy of Pu is maintained by the addition of nitrogen dioxide gas to convert Pu(III) and Pu(VI) to Pu(IV) for attaining highest extraction by tri-*n*-butyl phosphate (TBP) [9]. U and Pu are together extracted according to the following equilibrium reactions.

$$UO_2(NO_3)_{2(a)} + 2\ TBP_{(o)} \rightleftharpoons UO_2(NO_3)_2.2TBP_{(o)} \qquad 1.1$$

$$Pu(NO_3)_{4\ (a)} + 2\ TBP_{(o)} \rightleftharpoons Pu(NO_3)_4.2TBP_{(o)} \qquad 1.2$$

Where, “a” and “o” stands for aqueous and organic phases respectively.

Pu is partitioned from U with the addition of reducing agent by changing the valancy of Pu from IV to III. Then the loaded U is stripped with low concentrated nitric acid. The entire cycle consisting of co-extraction, scrubbing, partitioning and stripping with the decontamination from fission products is known as Co-decontamination cum partitioning cycle. The raffinate of extraction column in this cycle contains most of the activity associated with the spent fuel. The waste containing traces of nuclear materials, minor actinides along with highly radioactive fission products is the source for acidic high level liquid waste (HLLW). U stream obtained after this cycle is subjected to two more cycles of solvent extraction in order to achieve higher decontamination factors and finally converted to oxide by ammonium diuranate route. Pu stream is also subjected to two more cycles of solvent extraction in order to achieve higher decontamination factors and finally converted to oxide.

1.2 Generation of radioactive waste

Operation of front end, reactor and back end in nuclear fuel cycle generates various forms of waste like solid, liquid and gaseous. The concentration of radioactivity depends on the source of generation. Depending upon the radioactivity content, liquid and gaseous wastes are classified whereas solid waste classification is based on the surface dose. Radioactive waste management policy is based on the universally adopted philosophy of (i) delay & decays of short-lived radionuclides (ii) concentrate and contain the activity as much as practicable and (iii) dilute and disperse of very low activity to the environment well below the nationally accepted levels which are in line with the international practices.

Nuclear waste is treated to achieve high volume reduction and high decontamination factors. Liquid waste is classified into low level waste (LLW) with activity level $\leq 10^{-3}$ Ci/L; intermediate level waste (ILW) with activity level 10^{-3} to 1 Ci/L and HLLW with activity level ≥ 1 Ci/L [10]. LLW is generated from radioactive laboratories, hospitals and industries in addition to the fuel cycle operations. Depending on the nature of waste, radionuclide present and level of contamination, processes based on chemical precipitation, ion exchange evaporation and reverse osmosis are employed for the treatment of LLW and ILW. After processing, bulk of the activity is concentrated and the supernatant is discharged to water bodies as per national standards. The radioactive concentrate is conditioned in highly durable matrices like cement, polymer etc.

HLLW generated during reprocessing of spent fuel will vary in composition depending on several factors like type of the reactor, nature of the fuel, burn-up, cooling period, reagents added during reprocessing, efficiency of the reprocessing plant, etc. It contains useful and stable radionuclides such as Np, Am & Cm and small amounts of unrecovered U and Pu along with highly radioactive fission products such as ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{147}Pm, $^{152-154}$Eu, ^{99}Tc etc. The toxicity of the waste is mainly due to the presence of unrecovered U and Pu, long-lived minor actinides, ^{237}Np, ^{241}Am, ^{245}Cm radioactive fission products ^{99}Tc, ^{90}Sr and ^{137}Cs [11,12].

For the management of HLLW, a three step strategy involving i) immobilization of waste oxides in glass matrix ii) interim retrievable storage of the conditioned waste under surveillance and continuous cooling. iii) Disposal in deep geological formations (repositories) is being adopted. However, this approach does not entail for reduction in radio-toxicity of the vitrified waste, which is a concern for their long-term storage in deep geological repositories. In order to reduce the burden on the geological storage system by minimising the nuclear waste mass, reducing the heat load and ultimately the quantity of potential radiotoxic isotopes, separation of all the valuable and hazardous radionuclides such as long-lived fission products and minor actinides will be necessary. Removal of unrecovered U and Pu of the waste can be done by employing TBP as a solvent. P&T is the proposed strategy for safe management of minor actinides, where they will be separated from the waste and converted to short-lived or stable nuclides in a high energy flux reactors. It is known that, ^{137}Cs and ^{90}Sr are major short term heat source in the vitrified waste [13]. Removal of ^{137}Cs and ^{90}Sr from HLLW provides significant reduction in the cooling requirement and the storage span prior to its disposal. It also facilitates the handling and transport of waste. In addition, ^{137}Cs and ^{90}Sr find numerous applications in medical and industrial as irradiators [14], compact power sources [15] etc.

1.3 Motivation for the present work

^{137}Cs and ^{90}Sr are produced in high yield (^{137}Cs: 6.332% and ^{90}Sr: 4.505%) during thermal fission of ^{235}U in nuclear reactors. Both these radio-nuclides posses long half lives (^{137}Cs: 30.1 y, ^{90}Sr: 28.5 y). ^{137}Cs emits gamma radiation of 661 keV while ^{90}Sr emits pure beta particles converts to ^{90}Y which is also a pure beta emitting radionuclide with E_{β} = 2.28 MeV. ^{137}Cs is not the only Cs isotope present in the spent fuel or in the waste solution. The other isotopes are ^{133}Cs (stable), ^{135}Cs ($t_{1/2}$: 2.3x10^{6}y) and ^{134}Cs ($t_{1/2}$: 2.06y). ^{133}Cs and ^{135}Cs are fission products while ^{134}Cs is generated from stable ^{133}Cs. High heat output and relatively long half life, make ^{137}Cs a suitable source in gamma irradiators. Due to favourable half life, high heat output, and pure beta-emitting property of ^{90}Sr, it is used in the treatment of bone cancer, ^{90}Y is used in radiopharmaceuticals for treatment of certain types of cancers due to its suitable radiological half life of 64.1 h. ^{90}Sr is a viable candidate as fuel for thermoelectric and thermo-mechanical power generators.

The major heat output of HLLW is contributed by ^{137}Cs and ^{90}Sr. Large scale utilisation of these isotopes as radiation source requires the selective separation from HLLW. A variety of processes have been used/being developed for the recovery of Cs from nuclear waste solutions. Precipitation of Cs was attempted using phosphotungstic acid at Hanford site, USA [16]. This process suffers with lack of selectivity due to co-precipitation of divalent/trivalent radionuclides and generation of large amount of liquid radioactive waste. One of the extensively studied processes is use of ion-exchange resin, ammonium molybdophosphate (AMP) for separation of Cs from HLLW, the resin is highly selective for Cs but suffers with lack of recyclability, the entire resin need to be dissolved in NaOH to recover Cs, resulting in generation of huge amount of liquid waste [17]. The use of lead sulphate as a precipitating agent followed by ion exchange was implemented at the Hanford for the recovery of ^{90}Sr. However, the process was discontinued due to relatively low ^{90}Sr yield along with the numerous chemical addition steps and the toxicity of lead [18]. Solvent extraction process using highly selective extractants such as crown ethers, calix-crowns, cobalt dicarbollides were extensively studied for removal of Cs and Sr from acidic solutions [19]. Separation by solvent extraction is preferred over other separation techniques because of its continuous operation mode, high throughput, simultaneous operation of extraction, stripping and regeneration of solvent.

^{99}Tc is a long lived beta emitting radionuclide ($E_{\beta\text{-max}} = 295.5$ keV, $^{99}Tc_{43}(\beta)^{99}Ru_{44}$) having a half life of $2.11\text{x}10^{5}$ year produced with a high fission yield of 6.13% during fission of ^{235}U. It imparts long-term radiotoxicity to the waste stream. Tc exists as $HTcO_4$ in HLLW and being acidic in nature, its separation is extremely difficult from acidic HLLW. Tc existing as TcO_4^- in alkaline LLW is highly mobile under environmental conditions and thus not advisable for direct discharge to environment [20,21]. Several bench scale column test with SuperLig$^{®}$639 ion-exchange resin were carried out with simulated Hanford waste for removal of TcO_4^-. High competition with KNO_3 and $KReO_4$ for the sorption sites on the resin made it unsuitable for trial with actual waste [22]. A crown ether, 4,4′(5′)-[di-*tert*-butyldicyclohexano]-18-crown-6, was investigated for separation of TcO_4^- from alkaline waste [23], but the process could not be deployed due to its difficulties in bulk synthesis.

In our country, there is no industrially viable solvent system developed for separation of fission products from various nuclear waste streams. This provides the motivation for studying the selective solvent extraction separation of Cs and Sr from HLLW and Tc from LLW by employing metal-specific macrocyclic extractants dissolved in PUREX-type diluent suitable for large scale operations.

1.4 Problem definition

Progressively stepping up of reprocessing capacity has increased the concern for safe handling of HLLW. Remediation schemes are focussed on reduction in radioactivity and volume of the waste with generation of minimum secondary waste. Selective separation of Cs^+, Sr^{2+} and TcO_4^- from radioactive waste streams containing large concentrations of Na^+, Ca^{2+}, HNO_3, NO_3^-, and OH^- has been one of the most challenging goals. Macrocyclic extractants of the class crown ethers and calix-crown-6 are capable of selectively binding with these fission metals due to their better conformity between ligand and the metal ion properties. The architectures, shape, size, and coordination patterns of this class of extractant can be more exactly adjusted for a particular metal ion leading to development of metal-specific extractants. These extractants are usually polar due to presence of etheric linkage in the molecule, which makes them almost insoluble in PUREX-type paraffinic diluents like *n*-dodecane. The current study is thus focused on developing the calix-crown-6 and crown ethers having less polar substituents in order to enable their solubility in a modified industrial paraffinic diluents mixture for selective separation of Cs^+, Sr^{2+} and TcO_4^- from nuclear waste solution.

1.5 Scope of the work

The present study aims on the synthesis of the following calix-crown-6 and crown ethers with high yield and purity, their characterisation and experimental investigation for selective separations of Cs^+, Sr^{2+} and TcO_4^- from actual nuclear waste solutions including their degradation behaviour under hydrolytic & radiolytic conditions and regeneration.

i. 1,3-dioctyloxycalix[4]arene-crown-6 & 1,3-bis(2-ethylhexyloxy)calix[4]arene-crown-6 for selective separation of Cs^+ from HLLW
ii. 4,4′(5′)-[di-*tert*-butyldicyclohexano]-18-crown-6 for selective separation of Sr^{2+} from HLLW
iii. 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 for selective separation of TcO_4^- from LLW

The thesis starts with a general introduction of nuclear fuel cycle, reprocessing of spent fuel, generation of radioactive waste and their management. **Chapter 2** gives a detailed review on solvent extraction process with an emphasis on separation of Cs, Sr and Tc from nuclear waste solutions using different macrocyclic extractants. **Chapter 3** covers the experimental setup and analytical procedures involved in this work. **Chapter 4** gives the synthesis and characterization of calix-crown-6 extractants used for separation of Cs from HLLW, determination of process solvent composition, mechanism of Cs extraction, stoichiometry of extracted species, selectivity studies of calix-crown-6, batch and counter-current extraction of Cs from HLLW, degradation studies and regeneration of degraded solvent. **Chapter 5** and **6** describe the synthesis and characterization of crown ethers used for separation of Sr from HLLW and Tc from LLW, determination of process solvent composition, mechanism of extraction, stoichiometry of extracted species, selectivity studies, batch extraction of Sr and Tc from respective waste solutions, degradation studies and regeneration of degraded solvent. The results of this thesis will be a benchmark for development of process for separation of Cs, Sr from HLLW and Tc from LLW using calix[4]arene-crown-6 and crown ethers based solvents.

CHAPTER 2

Review on Separation of Cs, Sr and Tc from Nuclear Waste Solutions using Macrocyclic Extractants

This chapter presents a review on solvent extraction process, mechanism of extraction, contacting devices being used in nuclear industries and macrocyclic extractants used for separation of Cs, Sr and Tc from nuclear waste solutions.

2.1 Solvent extraction process

Solvent or liquid-liquid extraction is based on the mass transfer of one or more components between aqueous and organic phases due to the existence of a driving force arising from differences in chemical potentials. In practice, this requires intimate mixing of both the phases for some period of time, during which equilibrium is approached as mass transfer proceeds. An extractant is an organic substance primarily responsible for the transfer of a metal solute species from aqueous phase to organic phase.

Solvent is an organic solution obtained on dissolving extractant in a suitable diluent or in a mixture of diluents. The organic phase after extraction is called ‘extract’ containing the required solute and aqueous phase is called ‘raffinate’ which is the depleted feed with a certain amount of solute. The two phases are chemically different and separation of the components takes place according to their distribution ratio. The distribution ratio D can be defined as the ratio of total concentration of solute in the extract phase to the concentration of solute in the raffinate phase at equilibrium. There are several factors which affect the distribution of metal ions. Some of the prominent are: nature and concentration of solute (metal ions), extractant, diluent, complexing agent present in the aqueous phase, acidity of the aqueous phase, salting agent presence in the aqueous phase, and temperature. Distribution ratio almost remains constant with variation in concentration of metal species for dilute solutions.

When the two phases are vigorously shaken, these are intimately dispersed in each other which help the solute to migrate from one phase to another. The dispersal is in the form of droplets. More vigorous the contact, smaller are the droplets formed and more surface area is available for the mass transfer between the two liquid phases. Thus, the linear distance that molecules will have to travel to reach the other phase and migrate into it becomes smaller and more rapid will be the extraction. . Similarly, the solvent loaded with solute is regenerated by contacting it with another aqueous phase having more affinity for the solute at a given condition than the solvent. This process of back-extraction is called stripping. The disengagement of two phases largely depends on differences in their densities and interfacial tension [24]. Solvent washing or scrubbing is sometime required if the solvent extracts undesirable impurities. Selective removal of the impurities is achieved by contacting the extract phase with new immiscible aqueous phase normally by water, dilute acid/base or by an aqueous solution of a salt of the metal solute of interest in the solvent phase. The scrub raffinate may contain some amount of desired metal solute, thus, it is usually mixed with feed stream so that the desired solute is not lost.

A large number of extractants are being used in front end and back end of nuclear technology. In front end, Alamine 336, D2EHPA and TOPO are being used for separation of U from ore leach liquor and phosphoric acid [25,26], reactor materials like rare earth, zirconium, niobium and tantalum are purified by TBP and D2EHPA [27,28]. In back end, TBP is being used for separation and purification of thorium, uranium, plutonium [29] and tetra(2-ethylhexyl)diglycolamide (TEHDGA) for minor actinide partitioning of HLLW [30]. Extractants are also used in purification of radionuclides artificially produced by nuclear reactions for their applications in agriculture, industry, medicine and science research. Some of the extractants used for the separation of certain radionuclides is listed in **Table 2.1**.

Table 2.1: Extractants for separation of radionuclides

Isotopes	Extractants	References
$^{6}Li/^{7}Li$	Crown ethers	[31]
^{48}Ca	Crown ether	[32]
^{90}Sr	Crown ether	[33]
^{90}Y	PC88A	[34]
^{137}Cs	Calix-crown-6	[35]
^{64}Cu	Dithizone in CCl_4	[36]
^{198}Au	Ethyl acetate	[37]
^{106}Ru	CCl_4	[38]

2.2 Mechanism of extraction

The extractant are classified on the basis of their extraction mechanism. Various mechanisms are described below.

- Solvation: The extraction of metal species by neutral extractants is followed by solvation mechanism. The extraction process proceeds via replacement of water molecules from the co-ordination sphere of metal ions by basic donor atoms such as ‘O’ or ‘N’ of the extractant molecules [39]. The well known example is the extraction of UO_2^{2+} by TBP from nitric acid medium in the form of $UO_2(NO_3)_2.2TBP$ [40].
- Chelation: The extraction of metal ions proceeds via the formation of metal chelates with chelating extractants. The example of this type is the extraction of Pu(IV) by thenoyltrifluoroacetone (HTTA) in benzene [41].

- Ion exchange/ion pair extraction: Cation exchangers or acidic extractants provide anions by liberating protons which then complexed with the metal cation to form neutral ion-pair examples are organophosphorous acids (D2EHPA, PC88A, etc) sulphonic acids, carboxylic acids. Cobalt dicarbollides is a macrocyclic cation exchange used for extraction of Cs from nitric acid medium. Liquid anion exchangers or basic extractants provide cations which complex with aqueous anion metal complex to form neutral ion-pair, examples are Aliquat 336 (quaternary ammonium salts), Alamine 336 etc.
- Ion-pair: Extraction of ion pair without ion-exchange takes place with macrocyclic extractants like crown ether and calix-crown. These compounds extract metal ions by trapping in their cavity followed by extraction of counter anion for charge neutrality resulting in formation of ion-pair. In general, metal ion extraction by calix-crown and crown ether takes place in polar diluents where the extracted ions are stabilized by solvation by diluent.
- Synergistic extraction: Extraction of metal ions take place in the presence of two or more extractants preferably one acidic extractant and other neutral extractant which results in more distribution ratio than that expected from the sum of distribution ratios employing individual extractants. Extraction of Pu(IV) from nitric acid medium by a mixture of HTTA and tri-*n*-octylphosphine oxide (TOPO) in benzene, extraction of UO_2^{2+} from phosphoric acid medium using a mixture of D2EHPA and TOPO are some of the well known examples of synergistic extraction [42].

2.3 Selection of solvents

Proper solvent selection is important in extraction process because the efficiency and cost of overall operation depends on the type of solvent. The following properties of a potential solvent should be considered before use in a solvent extraction process.

- Distribution ratio: Measures the extractability of a metal species in the organic phase, it should be large enough for sufficient extraction.
- Separation and selectivity factor: When more than one metal species e.g. A and B, are extracted then selectivity of the solvent for A against B is given as the ratio of D_A to D_B. This ratio is known as separation factor and denoted as β. More is the β, more efficiently A is separated from B. β should not be equal to 1, in that case there will be no separation.
- Insolubility of solvent: Solvent must be immiscible with aqueous phase to obtain clear and fast phase disengagement.
- Stripping: It regenerates the solvent for re-use. Stripping agents are chosen based on the type of extraction mechanism.
- Density: Appreciable difference in densities of both the phases is needed for clear and fast separation between the phases. It is one of the important parameters for design of liquid-liquid contactors.
- Interfacial tension: During mixing of the phases, coalescence of emulsion and dispersion of one phase to other depends largely on interfacial tension. More is the interfacial tension better is the coalescence of emulsion and poor will be the dispersion of the phases. High interfacial tension is favoured as it enhances the phase separation kinetics and leads to clear phase disengagement.
- Stability: Stability of the solvent (i.e. resistance to break down), with respect to hydrolysis and radiolysis is important as the breakdown products decreases the extractability and selectivity of extraction and also leads to impure product formation. Solvent should also be stable during storage and should have high shelf-life. Finally, solvent should be chemically compatible with the metal ions to be separated, particularly in multi-stage processes where high purity product is desired.

- Vapour pressure and viscosity: Viscosity of the solvent can be suitably adjusted by the content of diluents present in it. Vapour pressure should be low for ease in handling, storage and operation; high volatile solvents are fire hazard and results in loss of mass during operation.
- Commercially available and cost: The solvent should be cheap and commercially available.
- Other criteria: Toxicity and flammability of the solvent should be as low as possible.

2.4 Stages in solvent extraction

A stage is a unit in which the contacting occurs and where the phases are separated physically. **Fig.2.1** shows a single stage extraction process. While in a single stage limited extraction of a metal species is achieved, hypothetically, maximum extraction is possible by using infinitely large organic to aqueous volume. However, multistage counter-current extraction permits maximum extraction using limited volume of solvent. In counter current process aqueous feed and organic phase flows in opposite directions by repeating single stage contacts. **Fig.2.2** shows a three stage counter current extraction process, where fresh solvent contacts nearly barren raffinate (stage 1), while the nearly saturated solvent contacts with fresh aqueous feed (stage 3) [43].

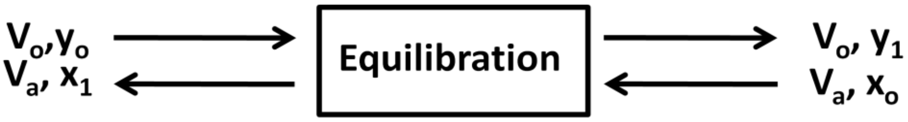


Fig.2.1: Equilibrium contact of aqueous and organic phases

Here, $\mathbf{x_o}$ = Concentration of metal ion in aqueous feed solution

$\mathbf{y_o}$ = Concentration of metal ion in organic feed solution

$\mathbf{x_1}$ = Concentration of metal ion in raffinate at equilibrium

$\mathbf{y_1}$ = Concentration of metal ion in organic product at equilibrium

$\mathbf{V_o}$ = Vol. of organic phase

$\mathbf{V_a}$ = Vol. of aqueous phase

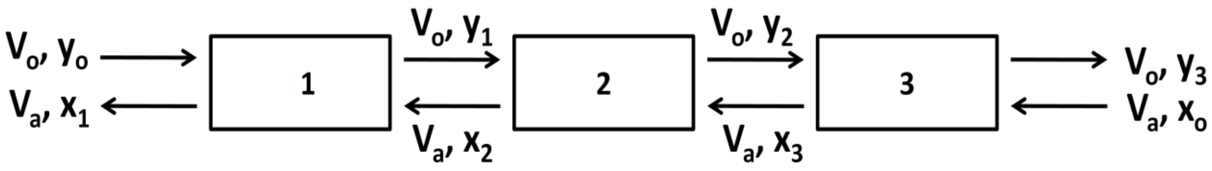


Fig.2.2: Counter current three stage extraction process flow diagram

In the above diagram, the aqueous volumetric flow rate is denoted as V_a and corresponding organic as V_o and the concentration of extractable species as x and y in aqueous and organic phases respectively. Here, the fresh solvent (V_o, y_o) enters from one end of the stage 1, while the feed (V_a, x_o) containing the extractable species as x_o enters from the other end of stage 3. The aqueous and organic phases flows in opposite directions to each other and the final products are solvent loaded with the solute (V_o, y_3), leaving stage 3 and the aqueous raffinate (V_a, x_1), depleted in solute leaving stage 1. The streams V_o,y_1, V_o,y_2 and V_a,x_2, V_a,x_3 contain intermediate concentrations of the metal ion. The rough estimate of the concentration of solute in a counter current process is shown graphically in **Fig.2.3**, where the orange colour shows the relative concentration of the solute in the process.

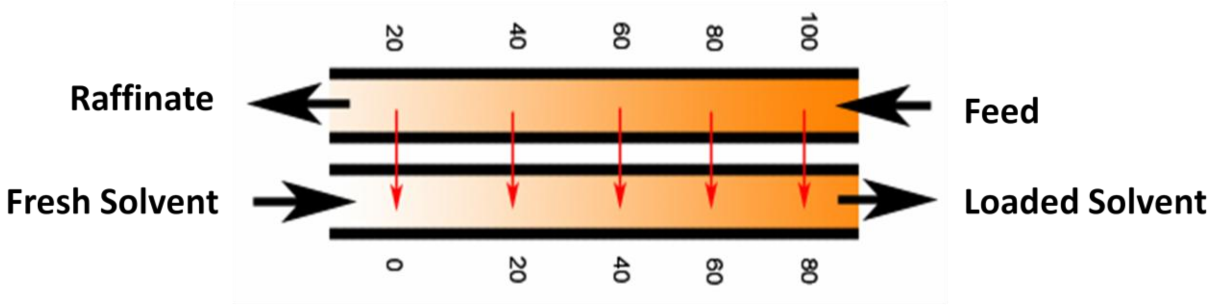


Fig.2.3: Counter current process concentration profile of solute

2.5 Contacting devices

There are number of contacting devices by which counter current solvent extraction can be carried out. One scheme divides contactors into two groups, stagewise (discrete-stages) and differential (continuous) [44]. In stagewise contactors the components are mixed, extracted and then separated in discrete stages after reaching equilibrium. In differential contactors the immiscible phases are contacted counter-currently and mass transfer takes place throughout the length of contactor under the influence of a continuous concentration gradient aiming to work at near equilibrium unlike discontinuities in solute concentration gradient that would occur in a series of discrete well-mixed stages. Differential contactors can provide a degree of separation equivalent to more than one theoretical stage, the key parameter determining the degree of separation being the length.

Some of the most important considerations in selecting a contactor for a specific duty are the number of stages or transfer units required, the volumetric throughput, the residence time, process foot print and head room availability, solvent inventory, stability of the solvent, time to reach steady state, process chemistry and kinetics and the economic factor. Solvent extraction contactors employed in nuclear industries are mainly of three basic types: mixer-settlers, pulse columns and centrifugal contactors. Among these mixer-settler and centrifugal contactor are stage-wise discrete contactors while pulse columns are continuous contactor.

2.5.1 Mixer settlers

Mixer-settler composed of a small mixing chamber where the aqueous and organic phases are mixed together by a rotating impeller, and a large gravity settling chamber where the mixed phases are given enough time to separate from each other. Cross-sectional image of a typical single stage mixer-settler is shown in **Fig. 2.4**. Each such unit composes a stage. Mixing time of a mixture is just more the equilibration time required to reach the mass transfer equilibrium and the settling times is kept nearly 4 to 5 times of the mixing time. From the settling section the organic phase exit by flowing over a weir and aqueous phase through an underflow then over a weir. The height of the weirs on the outlets of the settler section controls the separation interface. Only minimal instrumentation is required and mechanical maintenance is limited to occasional mixing motor replacement. A multiple stage mixer settlers working in counter current mode are composed of mixing and settling chambers located at alternating ends for each stage as the outlet of the settling sections feed the inlets of the adjacent stage's mixing sections. Mixer-settlers are preferred for the processes having longer residence (equilibration) times and when the mixed phases are easily separated by gravity. The apparatus is very efficient, minimal instrumentation is required and mechanical maintenance is limited to occasional mixing motor replacement, do not require much headspace however, requires a large facility footprint. A multistage unit is built as one box with partition to create different stages with suitable exit points for interstage mixing. Diagram of a typical three stage mixer-settler is shown in **Fig.2.5**.

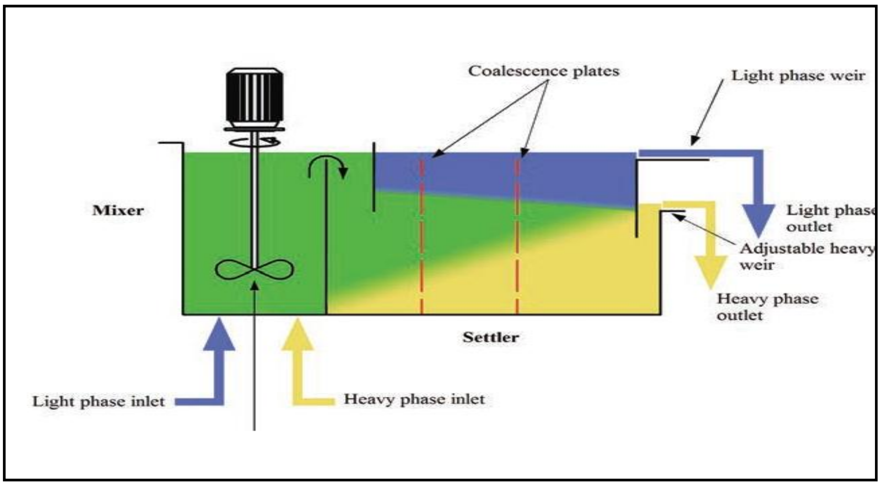


Fig.2.4: Diagram of a mixer-settler

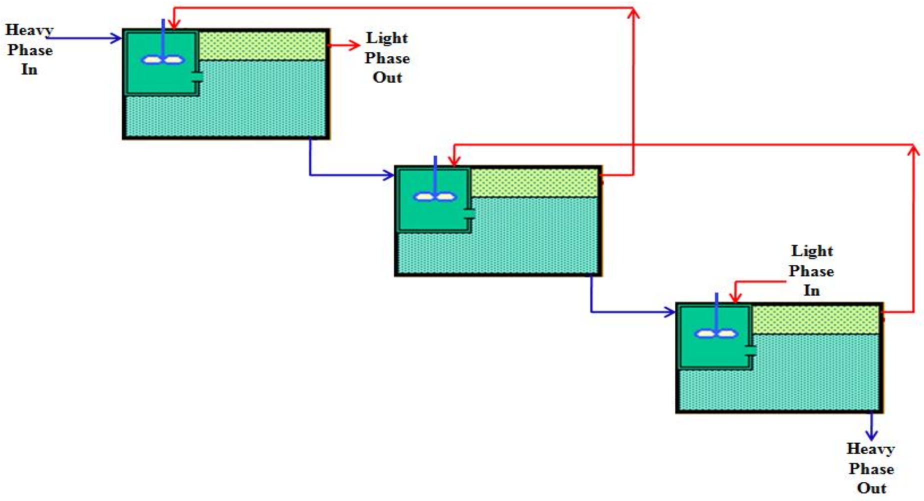


Fig.2.5: A three stage mixer-settler

2.5.2 Centrifugal contactors

Working principle of centrifugal contactors and mixer-settlers are similar, like mixer-settlers, centrifugal contactors are also having discrete-stage units providing one stage of extraction per unit. Centrifugal contactor differs from a mixer-setter in mixing and separation of the two-phase mixture. A spinning rotor intensely mixes the two phases in centrifugal contactors and separates the phases inside the rotor with high centrifugal forces of about 300 G, to result in fast and efficient phase separation. Similar to a mixer-settler, the separated phases exit the contactor by overflow and underflow weirs. A cross-sectional view of an operating centrifugal contactor is shown in **Fig.2.6**. The two liquids (typically an aqueous phase (heavy) and an organic phase (light)) enter the annular mixing zone where liquid-liquid dispersion is formed and extraction occurs as solutes are transferred from one phase into the other. Inside the rotor, the liquids will be separated into a heavy (blue) and a light (yellow) phase by their respective densities. This proportion of each phase (phase ratio), total flow rate, rotor speed, and weir sizes are varied to optimize separation efficiency. The separated liquids are discharged without pressure and flow by gravity to exit the stage. Centrifugal contactors are employed to processes which require short separation time, on the order of several seconds, mainly in high radioactive field where longer duration of contacts results in degradation of solvent. Centrifugal contactors are compact require small facility footprint, and minimum headspace, but do require maintenance for periodic removal of the motor and/or rotor.

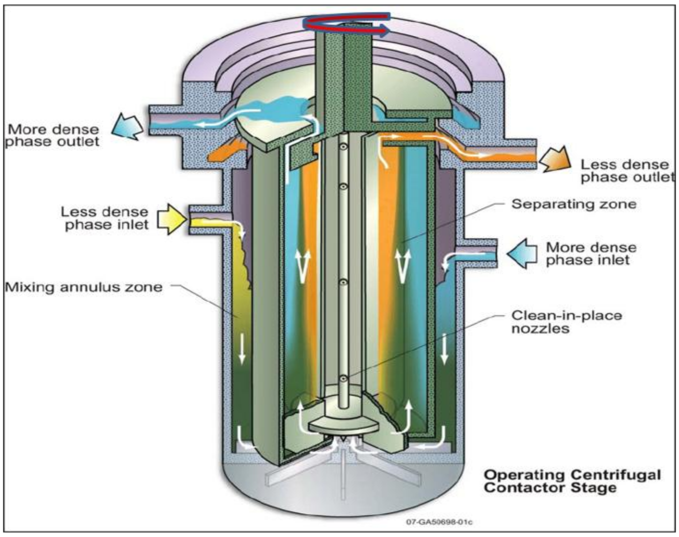


Fig.2.6: A cross-sectional view of a single stage operating centrifugal contactor

2.5.3 Continuous contactors (Columns)

Columns are example of continuous contactors, unlike mixer-settlers or centrifugal contactors they do not have discrete stages, the number of stages are determined by the height of a theoretical stage. The height of one theoretical stage is usually several feet, meaning that a very tall columns is required to achieve a given separation factor in a counter current extraction process. The height of a theoretical stage is reduced by improving the mass transfer kinetics by employing packing (trays or perforated plates) and mechanical energy in the form of pulse to convert the dispersed phase into smaller droplets. A suitable packing reduces the continuous phase back mixing and increases the extraction efficiency. The packing is preferentially wetted by continuous phase to minimise coalescence and increase the interfacial area per unit volume. Pulse columns are the most common type of columns used in the nuclear industry. Here, organic and aqueous phases are continuously fed to the column in counter-current mode and pulse is applied to push the liquids in the column.

Pulsation is created by introducing pressurized air into a pulse leg that pushes liquid into the column, then venting the pulse leg to fill the pulse leg with solution back from the column. In this way the pulse action lifts and lowers the solution in the column, usually only a few inches. Perforated plates are fitted in the column (or other plates) to promote droplet formation of the dispersed phase as it pushes through the plates and improves the mass transfer. A cross-section view of perforated plate pulse column is shown in **Fig.2.7**. Pulse columns are used when the process requires longer residence time and solutions are easily separated by gravity. Since there is no moving part inside, it does not require any remote maintenance. However, it requires a large facility footprint and headspace.

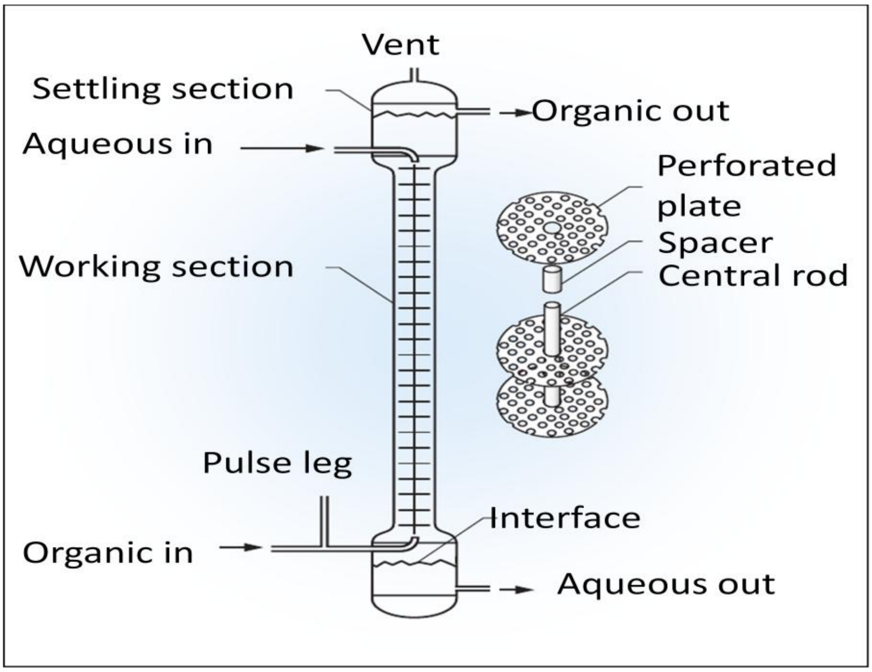


Fig.2.7: A perforated plate pulse column

For laboratory scale counter-current experiments, mixer-settler is preferred as it can be operated with relatively low phase ratio with flexibility in changing flow rates and mixing speed. In addition, study of concentration gradient of solute is simple and easy to generate data for process optimization [45].

2.6 Macrocyclic extractants for separation of Cs, Sr and Tc

Selective separation of Cs^+, Sr^{2+} and TcO_4^- from nuclear waste solution is difficult and challenging due to the presence of excessive competing species. The search for more effective and selective cation-binding compounds has resulted in the development of novel macrocyclic reagents (ring structure with more than 15 atoms) capable of selectively binding with very low concentration of fission metal from large concentration of interfering elements. This is achieved by better conformity between ligand and the metal ion properties. The well-known examples for macrocyclic structures are calix-crowns and crown ethers, which have already been extensively investigated. In this case an extended metal ion-ligand complementarity is achieved by the correspondence of size and donor sites of the ligand with the corresponding properties of the cation. Here the architectures, shape, size, and coordination patterns of the ligand can be more exactly adjusted for a particular metal ion [46]. Since the mid-1990s, macrocyclic polyethers, or crown ether containing compounds have been regarded as promising extractants for the utilization in radioactive waste clean-up. This fact was supported by the Nobel Prize for Chemistry in 1987 being awarded jointly to Cram, Lehn and Pedersen for their development and use of molecules with structure-specific interactions of high selectivity [47]. Their feature of high selectivity of complexation with cations of similar class of metal ions possessing similar chemical properties is characterized by the ratio of the size of the macrocyclic cavity to the cation radius. In this way, the selectivity of metal extraction can be controlled and ligands are tailored for the specific binding of a metal ion in a much better way compared to their linear counterpart. Macrocyclic polyethers are chemically very stable and can be easily regenerated. These properties of polyethers encouraged studies on the possibilities of their use as extractants in solvent extraction processes in nuclear waste clean-up and management. Also, the introduction of lipophilic substituents and their effect on binding modes, weak or strong, allows a further modification in view of an effective extractant. The most effective macrocyclic compounds used for separation of Cs^+, Sr^{2+} and TcO_4^- from nuclear waste solutions are calix-crown-6 and 18-crown-6 ethers. Here, crown ethers and calix-crown-6 ethers are reviewed in detail; also a carbon-boron framework macrocyclic extractant "Chlorinated cobalt dicarbollides" used for separation of Cs^+, Sr^{2+} from acidic nuclear waste solution is also discussed.

2.6.1 Crown ethers

Crown ethers are macrocyclic polyethers forming a cavity having crown like shape; hence, the name crown ether is given to this class of molecules [48]. The most common crown ethers are cyclic oligomers of ethylene oxide with a repeating unit of ethyleneoxy, $-CH_2-CH_2-O-$, group. Various crown ethers were synthesized and named according to the number of total atoms and number of oxygen atoms in the cyclic ring e.g. 15-crown-5 stands for a crown ether having 15 atoms (carbon and oxygen) and 5 oxygen atom in the cyclic ring of crown ether **Fig.2.8** shows structures of various crown ether molecules.

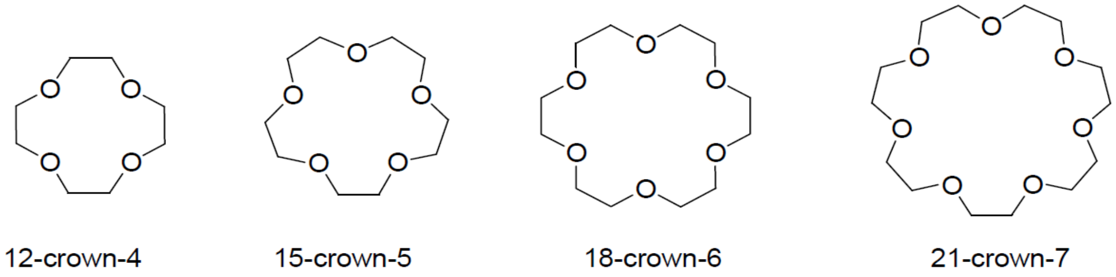


Fig. 2.8: Structural formulae of various crown ethers

The major factors governing the binding of metal ion with the crown ether are:

- The relative sizes of the crown ether cavity and the metal ion.
- The number of oxygen atoms in the crown ether ring (the more the better).
- Dipole-dipole interaction of oxygen atom and metal ion.
- The co-planarity of the crown ether ring.
- The symmetrical placement of the oxygen atoms.

- The basicity of the oxygen donor atoms (the stability of the complex increases with increasing basicity).
- Substituents on crown ether ring
- Steric hindrance in the crown ether ring (the less steric hindrance, the more stable is the complex formed).
- The tendency of the ion to associate with the solvent (complexation of the metal ion requires desolvation).
- The electrical charge on the cation.

Cavity size of the crown ether plays an important role in the binding of the metal ion. It was observed that metal ions having good size compatibility with the cavity of crown ether, bind more strongly with the particular crown ether. Dipole-dipole interactions with metal ion and oxygen atom of crown ether are responsible for the metal ion complexation with crown ethers (**Fig.2.9**).

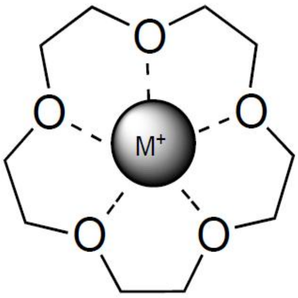


Fig.2.9: Dipole-dipole interactions between metal ion and oxygen atoms of crown ether

The cavity sizes of different crown ethers had been calculated by various groups using the Corey-Pauling-Koltun (CPK) model. The cavity size of different crown ethers and ionic size of various ions are given in **Table 2.2** [48]. Crown ethers are stereo specific extractants as they have a cavity structure that can be highly selective for the alkali and alkaline earth metal ions such as Na^+, K^+, Rb^+, Cs^+ or Sr^{2+}. A major aspect of the “size fit” of the metal ion with respect to the size of the crown ether cavity can therefore be related to the ratio of the ionic diameter of the metal ion to the effective diameter of the crown ether. It is reported that, for the alkali metals, ratios of 0.75 to 0.90:1 is favourable for direct ion-crown ether binding [49].

Table 2.2: Ionic radius of various alkali / alkaline earth metal ions and cavity size of different crown ethers

Metal ion	Ionic radius (Å)	Crown ether	Cavity radius (Å)
Li^+	1.2	12-crown-4	1.2
Na^+	1.90	14-crown-4	1.2-1.5
K^+	2.66	15-crown-5	1.7-2.2
Rb^+	2.96	18-crown-6	2.6-3.2
Cs^+	3.38	21-crown-7	3.4-4.3
Mg^{2+}	1.3	24-crown-8	~4.5
Ca^{2+}	1.98		
Sr^{2+}	2.26		
Ba^{2+}	2.70		

For, 18-crown-6 ratios of 0.61 to 0.75, 0.83 to 1.02, 0.61 to 0.76, 0.7 to 0.86, 0.84 to 1.04 and 1.03 to 1.27 : 1 are obtained for Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and Cs^+ respectively, thus selective binding for 18-crown-6 takes place for K^+, Sr^{2+} and Ba^{2+} over Na^+, Ca^{2+} and Cs^+. Likewise, for 15-crown-5 a ratio of 0.89 to 1.11: 1 is obtained for Na^+ indicating exact size match for Na^+.

It was found that the substituents on the crown ether ring highly influence the extraction chemistry of metal ions. The substituent groups make the geometry of the crown ether molecule rigid and thereby making it more selective for a particular metal ion.

Early work on crown ethers as extractants for Cs^+ and Sr^{2+} was performed by Gerow et al. [50] at the University of South Carolina and also by Kinard et al. [51] at the Oak Ridge national Laboratory. Researchers at the Argonne National Laboratory developed dibenzo-18-crown-6 ether for the selective recovery of Cs^+. The interaction between the π-electron cloud of benzo group and the Cs ion is considered to be one of the reasons for the higher selectivity of dibenzo-18-crown-6 for Cs ion over other alkali metal ion. Since the size of Cs^+ ion is bigger than the cavity size of this crown ether, it was observed that the Cs ion sits above the cavity of molecule and coordinate with two crown rings in a sandwich type structure. More size matching dibenzo-21-crown-7 was also tested for extraction of Cs from acidic and alkaline medium [52]. McDowell et al. suggested 4,4'(5')-[di-*tert*-butyldibenzo]-21-crown-7 to be a better extractant for Cs as compared to its unsubstituted homologues. Their studies using 0.5 M of this reagent with di-*n*-dodecylnaphthalene sulphonic acid (HDDNS) in toluene, indicated the possibility of Cs extraction from 0.1 M acidity [53]. But due to its low extraction ability and use of toluene as a diluent, could not be implemented at plant scale. A solvent comprising of 0.05 M of bis-4,4'(5')-[1-hydroxy-2ethylhexyl]-benzo)-18-crown-6 in 5% nonylnaphthalenesulphonic acid (HNNS) with 27% TBP + 68% kerosene was used by Shuler et al. [54] for Cs recovery (D_{Cs} = 1.6). But low D_{Cs} and the contamination of Zr was observed and attributed to the well known affinity of TBP for Zr. **Fig.2.10** shows the structural formula of bis-(4,4'(5')-[1-hydroxy-2ethylhexyl]-benzo)-18-crown-6.

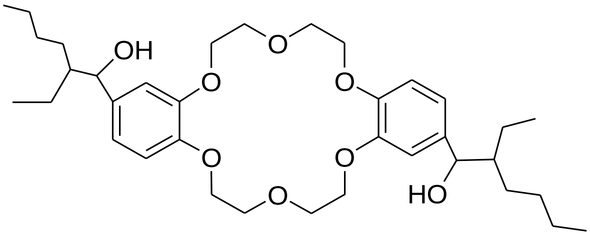


Fig.2.10: Structure of bis(4,4'(5')[1-hydroxy-2-ethylhexyl]benzo)-18-crown-6

The nature of the diluent also affects the extraction ability of crown ether significantly. Crown ethers are least soluble in non-polar diluents and hence, polar diluents are used to prepare their solutions. The polarity is introduced in the molecule due to the presence of large number of oxygen atoms in the molecule. In addition to this, the polar diluents also stabilize the ion-pair formed and increase the extraction ability of the crown ether.

More recently, a variety of alcohols, ketones, and carboxylic acids were investigated as potential diluents for extraction of Sr from 18-crown-6 extraction systems [55]. In this study, alcohols and ketones were found to be most effective as diluents. It was also observed that the extraction of Sr was increased with decrease in number of carbon atoms. However, from a practical standpoint, there is a lower limit on the size of an alcohol or ketone (i.e., due to flashpoint, aqueous phase solubility, etc.). In a follow-up study, Horwitz et al. [56] tested a variety of diluents and concluded that 1-octanol was the preferred diluent when considering characteristics such as the ability to extract Sr^{2+}, flash point, density etc. and proposed a process for Sr^{2+} recovery using dicyclohexano-18-crown-6 (DCH18C6) in 1-octanol. DCH18C6 is produced by hydrogenation of its precursor, dibenzo-18-crown-6 (DB18C6). Addition of hydrogen to four phenoxy bonds of DB18C6 leads to formation of various isomers of DCH18C6 like *cis-syn-cis*, *cis-anti-cis*, *trans-syn-trans*, *trans-anti-trans* and *cis-anti-trans*, which are expected to have different affinities for Sr^{2+}. Yakshin et al. [57] observed that *cis-syn-cis* isomer of DCH18C6 is the most effective in extracting Sr^{2+}. A report on hydrolytic and radiolytic stability studies of dicyclohexano-18-crown-6 ether (DCH18C6) [58], showed that under continuous extraction condition, the DCH18C6 radiolytic products cannot perturb a reprocessing using DCH18C6 as selective extractant. In another report, radiolytic stability of DCH18C6, dissolved in chloroform, 1-octanol, toluene and cyclohexane, was measured by ^{60}Co γ-rays irradiation. Stability was more in case of aromatic diluent due to stabilization of free radical by arene rings. Radiolytic destruction of

DC18C6, as measured by gas chromatography, was found to decrease in the order: chloroform > cyclohexane > 1-octanol > toluene. *D* of Sr^{2+} showed minimum effect by γ-irradiation in toluene solution, but decreased with the absorbed dose in chloroform solution. It was suggested that the D_{Sr} for the extraction system was influenced by radiolytic products. D_{Sr} of organic phase with radiolytic products was higher than that without radiolytic products due to synergistic effect of degradation products. The radiolytic products were thus shown to contribute to the increase in the extraction of Sr^{2+} [59].

The utilization of dicyclohexano-18-crown-6 is deterrent due to its high aqueous solubility. Modifications were made to reduce the solubility of DCH18C6 in aqueous phase by using its dimethyl or di-*tert*-butyl derivatives. Subsequently, Horwitz et al. **[**60**]** proposed a process called SREX (Strontium EXtraction) for Sr^{2+} recovery by using 4,4'(5')-[di-*tert*-butyldicyclo hexano]-18-crown-6 (DtBuCH18C6) (**Fig.2.11**) in 1-octanol as the diluent. In this process, Sr^{2+} is extracted from acidic (≥ 1 M HNO_3) solution using a 0.2 M solution of DtBuCH18C6 in 1-octanol. The extracted Sr^{2+} was readily stripped from the organic phase using either water or dilute (~0.05 M) HNO_3. Sr^{2+} was extracted effectively from the simulated dissolved sludge waste solution. However, extraction of Ba^{2+} and TcO_4^- was also observed to some extent. The solvent exhibited good radiolytic stability on prolonged exposure to γ-radiation of 50 Wh/L from a ^{60}Co source. It was noted that Sr^{2+} extraction is highly dependent on the nitric acid concentration in the feed, typically requiring 3-6 M acidity for efficient extraction. However, a significant amount of acid uptake was observed by the use of 1-octanol as the diluent. SREX solvent composition was later changed to incorporate a mixture of TBP and an iso-paraffinic hydrocarbon, Isopar L® as a diluent [61]. But extraction of metal ions like, U, Pu and Zr by TBP restricts the use of SREX solvent for selective separation of Sr from HLLW.

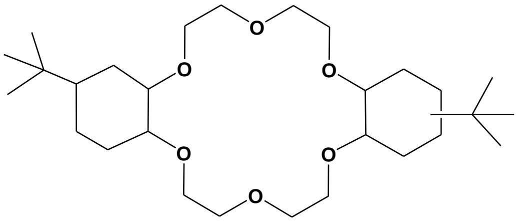


Fig.2.11: Structure of 4,4'(5')-[di-*tert*-butyldicyclohexano]-18-crown-6

Korpusov et al. [62] described the use of DCH18C6 dissolved in trichlorobenzene for extraction of $KTcO_4$ ion from KOH solution. It was shown that the compound of composition $[K^+DCH18C6].TcO_4^-$ was extracted in organic phase. Jalhoom [63] studied the effect of crown ether cavity size, substitution, organic diluent and type of base on the extraction of TcO_4^-. The crown ethers, 12-crown-4, 15-crown-5, 18-crown-6, DB18C6 and DCH18C6 dissolved in diluents, benzene, chloroform, 1,2-dichlorobenzene, o-chlorobenzene, 1,2-dichloroethene and nitrobenzene having different dielectric constants were studied in NaOH and KOH medium. The extraction of $NaTcO_4$ was found to increase with increase in dielectric constant of the diluent. Nitrobenzene having highest dielectric constant of 34.82 among all the studied diluent showed maximum D_{Tc} of 10 for 0.01 M DB18C6 from 4 M NaOH solution. It suggests that polarity of the solvent is important when the counter ions of the ion pair are loosely bonded and separated by the solvent molecules. The high selectivity of DCH18C6 towards K^+ ion gave the best extraction of TcO_4^- ion. DCH18C6 competes with 12-crown-4 which is more selective towards Na^+ ion. Dibutyl-24-crown-8 showed precipitation due to low solubility of complex ion in the organic phase.

Effective separation of TcO_4^- from Hanford tank-LLW simulants was demonstrated by Bonnesen et al. of Oak Ridge National Laboratory (ORNL) by using DtBuCH18C6 dissolved in a mixture of TBP and Isopar® M [64]. Presence of high Na^+ ion in the alkaline LLW drives the equilibrium toward the formation of the crown ether-Na^+ ion complex during extraction. An anion is necessary to conserve charge neutrality, and in this way, TcO_4^- is also extracted and a neutral complex of Na^+-crown ether-TcO_4^- is formed in the organic phase.

2.6.2 Calixarenes and calix-crown ethers

Calixarenes as a molecular receptor (host) was introduced by Gutsche for the cyclic oligomers which are obtained from the condensation of formaldehyde with *p*-alkylphenols in alkaline conditions [65]. **Fig.2.12** shows the formation of calix[n]arenes having four, six or eight phenol units by reaction of *p-tert*-butylphenol with formaldehyde in alkaline medium. Derived from the Greek word calix meaning vase, and arene indicating the presence of aromatic rings, calixarenes exist in a ‘cup’ like shape with a defined upper-rim, lower-rim and central annulus (**Fig.2.13**). Calixarenes are found in various conformations *viz.*, cone, partial cone, 1,2-alternate and 1,3-alternate conformations as shown in **Fig.2.14**. These four conformations can be easily differentiated by ^1H NMR and ^{13}C NMR spectroscopy by capturing the patterns of bridging methylene group [66]. The cone conformation shows a pair of doublet between δ 3.1-4.5 while the partial cone and 1,2-alternate behave identically and shows a multiplet at δ 3.5-4. The 1,3-alternate conformation exhibits a singlet at δ 3.7-3.8. The less common partial cone and 1,2-alternate can be distinguished in the aromatic part of spectrum. The peaks in ^{13}C NMR spectra for methylene carbon in cone conformation appears as singlet at δ 31-32 whereas in 1,3-alternate it appears as singlet at δ 37-38. The two singlets in partial cone and 1,2-alternate appears at δ 31-32 and δ 37-38 as shown in **Fig.2.15**. Among the several classes of synthetic macrocyclic compounds currently used as receptors in host-guest chemistry, calix[n]arenes have assumed a key role in metal extraction due to their synthetic accessibility and versatility.

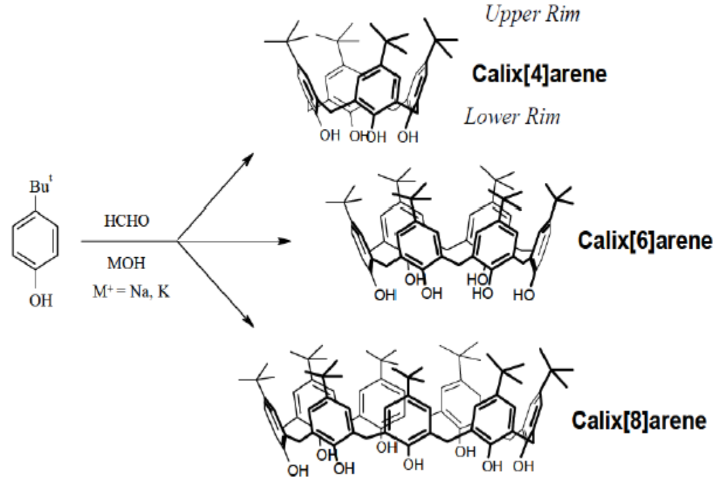


Fig.2.12: Some typical calix[n]arene structures and their formations

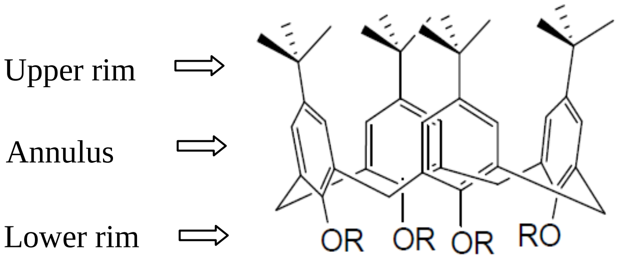


Fig.2.13: Division of calix[4]arene (applicable to all calix[n]arenes)

Indeed, the insertion of new functional groups onto both the “rims” (upper and lower) of the macrocycles can be easily accomplished using common reactions typical of the organic chemistry. Such functionalization reactions allow either the insertions of ancillary binding sites or the extension of the host aromatic cavity.

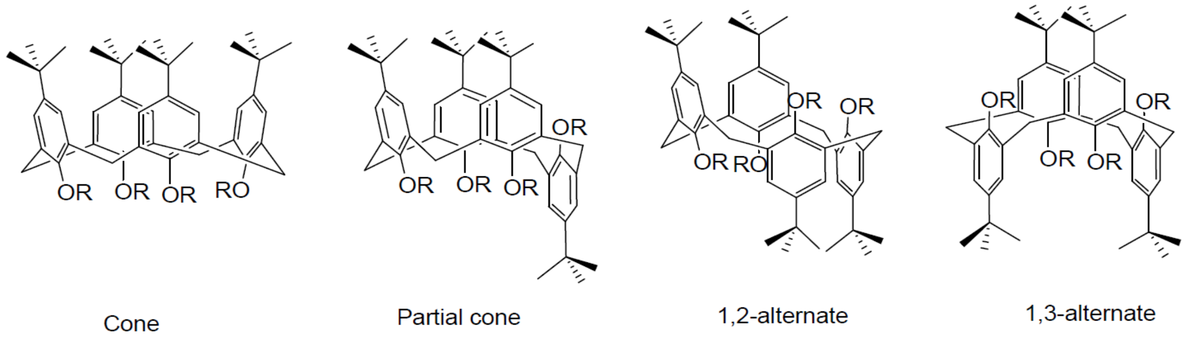


Fig.2.14: Different conformations of calix[4]arenes

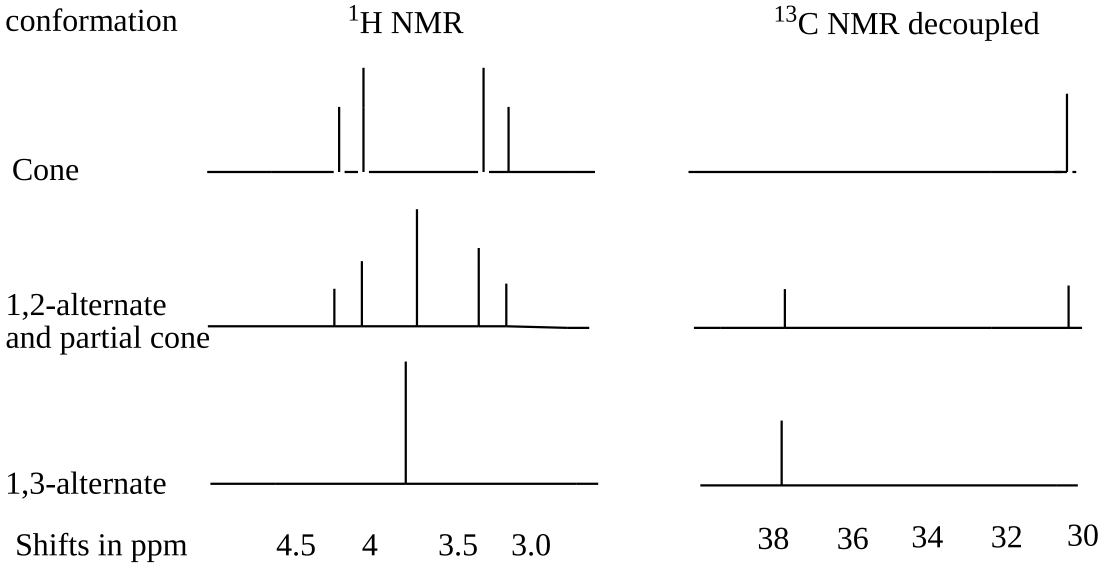
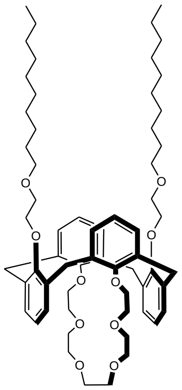


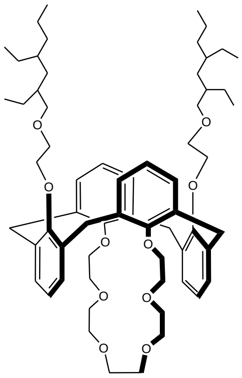
Fig.2.15: ^{1}H and ^{13}C NMR patterns of different conformations for calix[4]arene

Also, cyclic annulus of calix[n]arene behaves similar to crown ether-like cavity size selectivity in complex formation with metal ions. Earlier studies of Zinke et al. **[**67**]**, suggested that the calixarenes are capable of extracting alkali or alkaline earth metal ions. The substituents on calixarene framework are responsible for the extraction of different metal ions. Introduction of *p*-*tert*-butyl group on the molecule increases the Cs extraction by the calixarene. The substitution by ketone/ester group on calix[4]arene makes it susceptible for alkali metal ion extraction. In the mid-1980's, Izatt et al. [68] first investigated utilization of *p*-*tert*-butylcalix[4]arenes a cyclic compounds constituted by four phenolic units linked by methylene groups, for selectively separating Cs^+ from other alkali cations. Measurements on CPK model gives the dimension of elliptical 'lower rim' annuli of calix[4]arene of about 3Å which is very close to the ionic radius of Cs^+ ion, indicating a high specificity of calix[4]arene for Cs ion [69]. Studies performed by Commission of the European Communities at Cadarache, France, found that functionalized calix[4]arenes, particularly 1,3-dialkyoxycalix[4]arene-crowns are better extractants for Cs. This leads to synthesis, lab scale testing and development of numerous calixarene-crown extractants to meet the criteria of high extractability and selectivity of Cs extraction from its monovalent competitive elements. It was determined that compounds with a polyethylene glycol chain containing six oxygen atoms (crown-6) were more efficient for Cs extraction and more selective for Cs^+ over Na^+ than compounds containing five or seven oxygen atoms. Calix[4]arene in 1,3-alternate conformation coupled with one or two crown-6 rings (calix-mono and bis-crown ethers) has been found to be highly selective for Cs ion **[**70-72**]**. This is attributed to the favourable cavity size of crown ring & annulus as complexation with Cs^+ ion takes place by six oxygen atoms of the ring and also by a strong cation-π-interaction (pπ-dπ back-bonding) with the two rotated aromatic nucleus of the 1,3-alternate-calix[4]arene annulus. Ungaro et al. demonstrated the use of 1,3-dialkyloxycalix[4]arene for selective separation of Cs from picrate medium and shown that these types of ionophores are highly attractive for treatment of radioactive waste [73]. Casnati et al. [74] reported synthesis of different alternate 1,3-dialkyloxycalix[4]arene with a yield of 63-85%. Extraction experiments with 1,3-di(2-propyloxy)calix[4]arene-crown-6 and 1,3-dioctyloxycalix[4]arene-crown-6 dissolved in *o*-nitrophenylhexyl ether (NPHE) revealed high preference of Cs^+ from alkali picrates salt solution. It was found that the entropy of complexation ($T\Delta S = -15\ \mathrm{kJmol^{-1}}$) was less negative than other crown ethers and explained in term of pre-organization of 1,3-dialkyloxycalix[4]arene [75,76]. The X-ray structure of the Cs picrate-calixcrown-6 complex showed clearly that the Cs^+ is positioned between the two aromatic rings with short Cs-C distances of 3.49 and 3.69 °A, respectively. These ligands were incorporated in supported liquid membrane and shown high preference of Cs^+ extraction over Na^+ from 1 M HNO_3 and 4 M $NaNO_3$ solution. More than 99.8% Cs^+ was removed from this solution by maintaining anion gradient across the membrane. The diluent used in above studies was NPHE. This diluent was found incompatible in large scale extraction process, due to its toxicity, low flash point, poor hydrodynamic properties and less stability in radioactive environment.

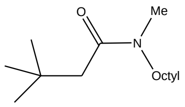
ATALANTE facility (CEA-Valrhó) demonstrated a complete flow sheet for Cs separation from acidic DIAMEX raffinate using 1,3-dioctyloxycalix[4]arene-crown-6 with TBP modifier in Tetra Propylene Hydrogenated (TPH) diluent and established scientific feasibility of Cs selective extraction by calix[4]arenes using actual acidic waste solution. In another test conducted at ATALANTE facility for recovery of Cs$^+$ from genuine waste solution of 4 M HNO$_3$ and 0.2 M oxalic acid, the solvent used was 0.1 M 1,3-[(decylethoxy)oxy]calix-crown-6 modified with 1.0 M N-methyl, N-octyl-2-dimethyl-butanamide in TPH. Dihexyloctanamide (DHOA) as phase modifier, to mitigate third phase formation, along with 1-octanol as diluent was also used with 1,3-[(2,4-diethyl-heptylethoxy)oxycalix-crown-6 extractants (**Fig.2.16**) [77]. Jianchen et al. **[**78**]** demonstrated an extraction process for Cs$^+$ from simulated HLLW by using 0.025 M 1,3-di(isopropyloxy) calix[4]arene-crown-6 in 1-octanol with 99.5% recovery of Cs. Stripping was done by contacting the loaded organic with 0.005 M nitric acid solution.



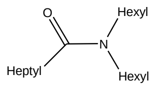
1,3-[(decylethoxy)oxy]
-calix-crown-6



1,3-[(2,4-diethyl-heptylethoxy)oxy]
-calix-crown-6



N-methyl, N-octyl-2-dimethyl-butanamide



N,N-Dihexyloctanamide)(DHOA)

Fig.2.16: Structures of calix-mono-crown-6 and modifiers used at ATLANTE facility

There are various types of calix[4]arene-bis-crowns formed by capping the lower and upper rim of calixarene with suitable polyethylene glycol network **[**79,80**].** Among them 1,3-alternate calix[4]arene-bis-crowns are most studied for extraction of metal ions from acidic as well as alkaline medium. Asfari et al. [81] synthesized various calix[4]arene-bis-crown in 1,3-alternate conformation and found that they can be used for selective separation of Cs over other metal ions. These results were further verified with membrane transport studies across the semi permeable membranes. Various structures of calix[4]arene-bis-crown are shown in **Fig.2.17**.

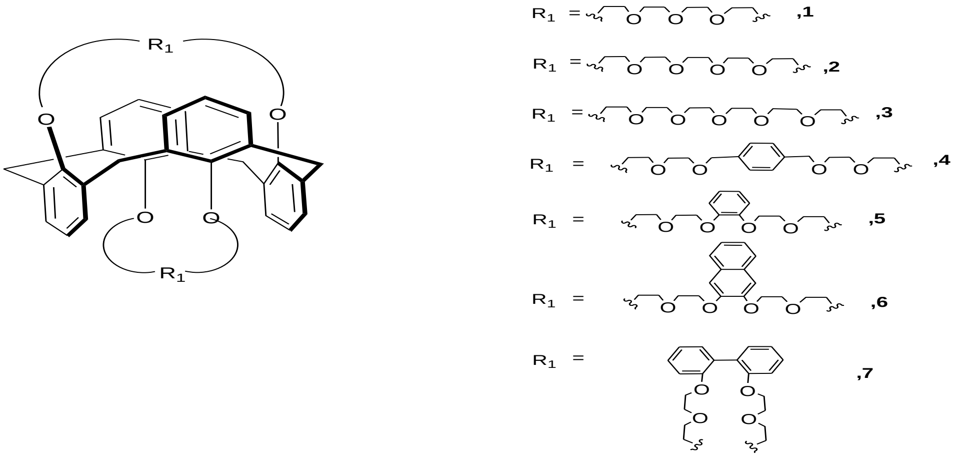
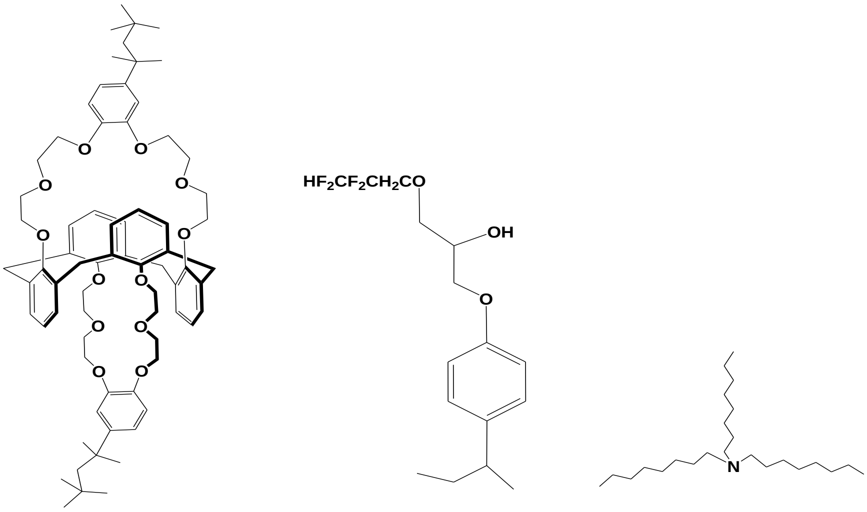


Fig.2.17: Structures of various calix[4]arene-bis-crown studied for Cs extraction

The *D*s' of Cs^+ and Na^+ were determined by contacting the acidic solution (1 M HNO_3, 5x10^{-4} M $NaNO_3$) with different 0.01 M calix[4]arene-bis-crowns in *o*-NPHE. The bis-crown with 5 or 7 oxygen in crown ring are not the efficient extractant for Cs^+ and also not selective for Cs^+ over Na^+. Also, the increase in crown cavity size by biphenyl leads to reduction in D_{Cs} and D_{Na} due to imperfect matching of cation and cavity size [81]. The results are shown in **Table 2.3**. ORNL successfully developed a Caustic-Side Solvent Extraction (CSSX) process to separate Cs^+ from alkaline waste. This process was demonstrated on actual alkaline waste solutions using small-scale centrifugal contactors at the Savannah River Site. The solvent consisted of 0.01 M calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOBCalixC6), 0.50 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7S BT) as a modifier, 0.001 M trioctyl amine (TOA) in an aliphatic diluent Isopar L (mixture of branched chain hydrocarbon C_{10}-C_{12}) **[**82**]**. The structures of the constituents are shown in **Fig.2.18**.

Table 2.3: D_{Cs} **and** D_{Na} **and separation factor (**D_{Cs}/D_{Na}**) for various calix[4]arene-bis-crowns**.

Calix-bis-crown	D_{Cs}	D_{Na}	Separation factor
1,3-calix[4]arene-bis-crown-5 (1)	0.4	$2x10^{-3}$	200
1,3-calix[4]arene-bis-crown-6 (2)	19.5	$1.3x10^{-2}$	1500
1,3-calix[4]arene-bis-crown-7 (3)	0.3	$<10^{-3}$	> 300
1,3-calix[4]arene-bis-*p*-benzo-crown-6 (4)	$2x10^{-2}$	$<10^{-3}$	> 20
1,3-calix[4]arene-bis-*o*-benzo-crown-6 (5)	32.5	$1.7x10^{-3}$	1911
1,3-calix[4]arene-bis-napthyl-crown-6 (6)	31.0	29.5	1.05
1,3-calix[4]arene-bis-biphenylcrown-6 (7)	$7x10^{-2}$	$<10^{-3}$	> 70



BOBCalixC6 Cs-7SBT Trioctyl amine(TOA)

Fig.2.18: Structures of constituents of CSSX solvent

This process of CSSX worked very satisfactorily under various stages of extraction, stripping with dilute nitric acid and excessive loading. The use of polar phase modifier (Cs-7SBT) showed advantages like, increase in solubility of BOBCalixC6 and its extracted complex by solvating the counter anion, mitigation in the formation of third phase. In addition, it acts as a synergistic agent and shows stability towards degradation. A combining ratio of 1 Cs^{+}: 1

BOBCalixC6 was obtained with this solvent system and the structure of the complex is shown in **Fig.2.19**.

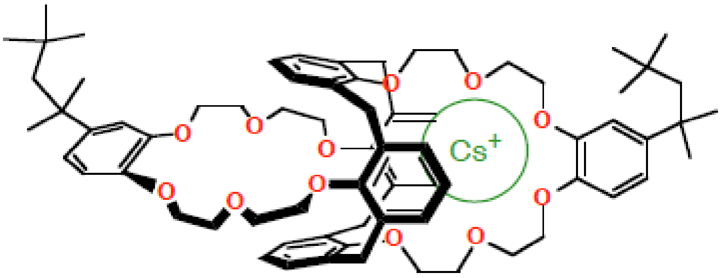


Fig.2.19: Cs$^+$- BOBCalixC6 structure

The waste contained surfactant impurities like, dodecylsulphonate which hinders the back extraction with dilute nitric acid. In order to neutralize this effect, a hydrophobic base, TOA was added. TOA acts as counter ion for dodecylsulphonate anion and makes complex with it and hence renders cesium nitrate free in organic phase for effective stripping. This experimental demonstration of this process was found to work well. However, it was observed that the solvent was susceptible to precipitation due to supersaturation with respect to calix-crown. Therefore, composition of the solvent was modified to 0.007 M BOBCalixC6, 0.75 M Cs-7SBT, and 0.003 M TOA in Isopar L. This change in composition removed the possibility of calix-crown precipitation in solvent phase. Both the processes CSSX and modified CSSX were found to be very effective for removing Cs from Savannah River Site high-level tank waste when tested in a 33-stage, 2-cm centrifugal contactor. The averaged decontamination factor was found to be greater than 40,000 for both the solvent systems **[**83**]**. Another modification for further improvement of solubility of BOBCalixC6 in aliphatic diluents was carried out. The *tert*-octyl group of BOBCalixC6 was replaced with 2-ethyl hexyl group (BEHBCalixC6, **Fig.2.20**) just by observing that the 2-ethylhexyl group in many commercial solvents like D2EHPA, PC88A has been used. Introduction of 2-ethylhexyl group resulted in at least eight times higher solubility in aliphatic diluents as compared to *tert*-octyl group, and also shown better extraction properties and least susceptible to third phase formation **[**84,85**]**.

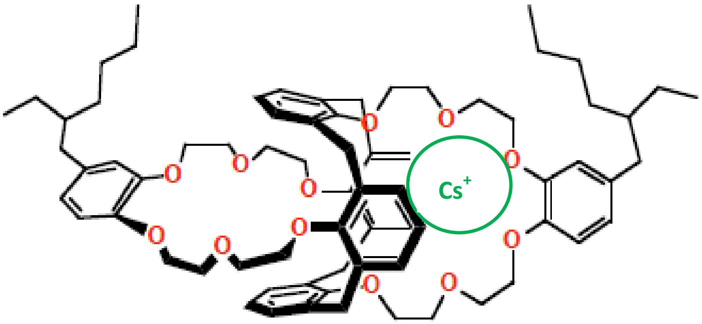


Fig.2.20: Structure of calix[4]arene-bis-(2-ethylhexylbenzo-crown-6); BEHBCalixC6

Jankowski et al. investigated the radiolytic stability of mono and bis-calix-crown-6 by irradiating diisopropoxy-18-crown-6-calix[4]arene and bis-18-crown-6-calix[4]arene diluted in *o*-nitrophenyloctyl ether (NPOE) with ^{60}Co γ-source up to a dose of 3 MGy (considered equivalent to 10 years of continuous contact with HLLW) [86]. The behaviour of degradation in the absence and presence of 3 M HNO_3 was examined by ESI-MS. Calix-crowns irradiated in the absence of HNO_3 showed fragmentation in crown ether ring while irradiation in the presence of HNO_3 undergoes nitration and oxidation. Oxidation produces hydroxylation and ketonization, as well as loss of methyl and isopropoxide substituents, whereas nitration leads to mono- and di-nitro substitution on phenoxy moity of calix ring structure. A total of 90% mono-crown and 75% bis-crown were degraded under this condition. Radiolytic degradation mechanism of 1,3-di(isopropyloxy)calix[4]arene-crown-6 (abbreviated as BPC6) was reported by AO YinYong et al. at different absorbed dose [87]. It was found that BPC6 exhibited excellent radiation stability at dose less than 100 kGy. However, the isopropyl groups in BPC6 underwent oxidation and de-alkylation to form carbonyl groups and phenolic hydroxyl groups at dose above 300 kGy, respectively. When the dose was more than 1000 kGy, the ring opening of crown ether structure of BPC6 resulted in the formation of phenolic hydroxyl groups as well. The formation of radiolytic products containing phenolic hydroxyl groups during the irradiation of BPC6 was confirmed by using $FeCl_3$ as a probe.

2.6.3 Chlorinated cobalt(III)dicarbollides (CCD)

CCD is a polyhedral carborane, theoretically can be considered as derived from $B_nH_n^{2-}$ framework on the basis that CH group is isoelectronic and isostructural with BH^- group. Thus, the two replacements lead to a neutral compound with general formula $C_2B_{n-2}H_n$. All such carborane with n = 5 to 12 are known and the most extensively studied compound is $B_{12}H_{12}^{2-}$ (closo-$C_2B_{10}H_{12}$) due to greater stability compared to others [88]. This carborane can be synthesized by reacting the $B_{10}H_{12}$-ligand and acetylene at proper reaction conditions. The abstraction of one boron with methanolic potassium hydroxide resulted in $C_2B_9H_{12}^-$anion. This anion can be readily converted into its dianion $C_2B_9H_{12}^{2-}$ by sodium or sodium hydride. These dicarbollide ions serve as ligands for transition metal complexes which often look like the well-known metallocenes [89-91]. Cobalt diarbollides anion (dicarbollidecobaltate (III)) and chlorinated cobalt(III)dicarbollides anion synthesized by Hawthrone M.F where the cobalt(III) is sandwiched between open faces of two $C_2B_9H_{11}^{2-}$ ion are shown in **Fig. 2.21**.

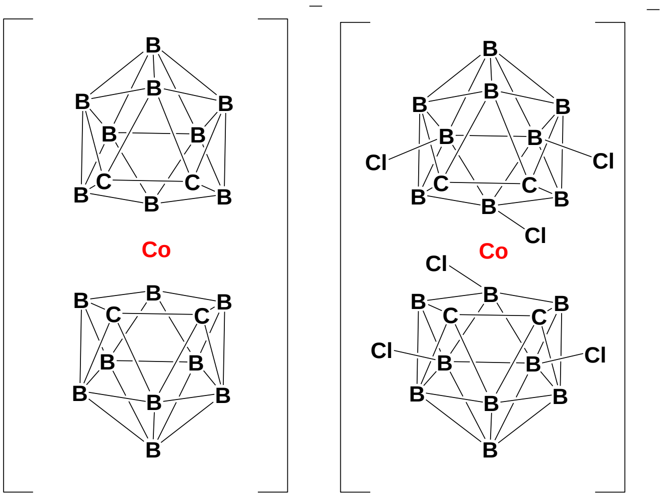


Fig.2.21: Structure of cobalt(III)dicarbollide and CCD anion

Important properties of these ligands for cation exchange are:

1. The compound $[Co(III)(C_2B_9H_{11})_2]^-$ is a hydrophobic anion fully dissociated in highly polar aprotic diluent like nitrobenzene, fluorosulfones etc.

2. These ligands have closed structure with the maximum delocalized electron density (low specific charge density) which makes them soft base having more affinity for softer acid like Cs^+ compared to harder acid like H^+ [92].

3. Least extraction of strongly hydrated multivalent elements.

Rais et. al [93] first utilized these dicarbollides for extraction of Cs and other larger cations from aqueous medium into nitro-based organic diluents. Cobalt dicarbollide anion can be chemically modified by substitution with chlorine resulting in hexachlorinated cobalt dicarbollide, $[Co(III)(C_2B_9H_8Cl_3)_2]^-$, (CCD) derivative as shown in Fig.2.21. This CCD compound has shown more stability towards acidic environment compared to cobalt dicarbollide and can be used in nitrobenzene as well as fluorinated diluents like phenyltrifluoromethylsulfone (FS-13). CCD anion discriminates the cations according to their Gibb's free energy of transfer. Cs shows the lowest Gibb's free energy of transfer to polar organic solvents as compared with other metal ion present in solution [93-96].

The extraction equation can be written as:

$$Cs^+_{aq.} + H^+.[Co(III)C_2B_9H_8Cl_3)_2]^-_{org.} \rightleftharpoons H^+_{aq.} + Cs^+.[Co(III)C_2B_9H_8Cl_3)_2]^-_{org.}$$

Where, $H^+.[Co(III)C_2B_9H_8Cl_3]^-$ is protonated form of CCD.

CCD is found to be a highly selective extractant for Cs from acidic medium. The Czech researchers reported that Sr could also be extracted along with Cs by adding polyethylene glycol (PEG) to the CCD dissolved in nitrobenzene. Cs^+ is the least hydrated ion in aqueous solutions compared to other metal ions and combines to the poorly hydrated CCD anion and gets transferred to the organic phase. Addition of PEG is considered to dehydrate the Sr ion and thereby facilitating the extraction of Sr along with Cs. In the UNiversal solvent

EXtraction (UNEX) process, Cs and Sr are extracted along with all lanthanides and actinides from nuclear waste solution at 1.6 M nitric acid by using a mixture of 0.08 M CCD + 0.4 % (v/v) polyethylene glycol-400 + 0.02 M diphenyl-N,N-dibutylcarbamoyl phosphine oxide (Ph_2Bu_2CMPO) dissolved in FS-13 diluent. Striping was done by 1 M sodium carbonate solution containing 20 g/L DTPA or guanidine carbonate as complexing agent for actinides. CCD has main advantage of being highly radiation resistant which makes it a viable candidate for its use in the treatment of nuclear waste [97-98]. The major limitation of the UNEX process is the use of toxic / corrosive diluents and low extraction efficiency at higher acidity (>2 M nitric acid). CCD dissolved in FS-13 has been used to separate mega-curie of ^{137}Cs from HLLW at Russia.

Remarks: The reported work shows that 1,3-dialkyloxycalix[4]arene-crown-6 derivatives and crown ethers are the most potent synthetic macrocyclic extractants for selective binding with Cs, Sr and Na ions. Owing to their high polarities, these extractants are mostly studied in polar diluents like NPHE, NPOE, TBP and 1-octanol. However, these diluents are not suitable for their use in large scale separation processes with actual HLLW. Thus, despite these studies quest for suitable diluent system still continues.

CHAPTER 3

Experimental Setup and Analytical Procedures

This chapter covers the chemicals and radiotracers used in the studies, radiometry, analytical methods, instruments for analysis of active/inactive metal ions, experimental setup for carrying synthesis of extractants, instruments for characterization of extractants and metal-organic complex, solvent extraction procedures and details of irradiation experiments.

3.1 Chemicals

3.1.1 Chemicals for synthesis

The extractants synthesised in this work are (i) 1,3-dioctyloxycalix[4]arene-crown-6 (ii) 1,3-bis(2-ethylhexyloxy)calix[4]arene (iii) 4,4'(5')-[di-*tert*-butyldibenzo]-18-crown-6 and (iv) 4,4' (5')-[di-*tert*-butyldicyclohexano]-18-crown-6. Chemicals used in their synthesis, grade and name of suppliers are given in **Table 3.1**.

Table 3.1: List of chemicals used in synthesis

Chemicals	Purity/Grade	Name of supplier
p-*tert*-butyphenol	Crystallized, AR grade	Spectrochem Pvt. Ltd., Mumbai
Formaldehyde	37% in water	Spectrochem Pvt. Ltd., Mumbai
Diphenyl ether	98%	Spectrochem Pvt. Ltd., Mumbai
Ethyl acetate	AR grade	Spectrochem Pvt. Ltd., Mumbai
Acetic acid glacial	AR grade	Spectrochem Pvt. Ltd., Mumbai
Toluene	AR grade	Spectrochem Pvt. Ltd., Mumbai
Phenol	AR grade	Spectrochem Pvt. Ltd., Mumbai
$AlCl_3$ anhydrous	AR grade	Spectrochem Pvt. Ltd., Mumbai
HCl	35-36%, LR grade	S.D. Fine Chemicals, Mumbai

NaOH	Pallets, LR grade	S.D.Fine Chemicals, Mumbai
Methanol	GR grade	Spectrochem Pvt. Ltd., Mumbai
Chloroform	GR grade	Spectrochem Pvt. Ltd., Mumbai
Octanol	98%, LR grade	Spectrochem Pvt. Ltd., Mumbai
Pentaethylene glycol	98%	Orion chem. Pvt. Ltd.
Toluene sulphonyl chloride	AR grade	Spectrochem Pvt. Ltd., Mumbai
THF	LR grade	Spectrochem Pvt. Ltd., Mumbai
Dichloromethane	LR grade	Spectrochem Pvt. Ltd., Mumbai
Acetonitrile	Anhydrous grade	Spectrochem Pvt. Ltd., Mumbai
$MgSO_4$	AR grade	S.D. Fine chemicals, Mumbai
Cs_2CO_3	98%	Orion Chem Pvt. Ltd.
Basic alumina	Activated Brockman I grade, particle size ~ 150 meshes.	Orion Chem Pvt. Ltd.
2-Ethylhexanol	99%	Spectrochem Pvt. Ltd., Mumbai
p-*tert*-butylcatechol	Crystallized, AR grade	Spectrochem Pvt. Ltd., Mumbai
Diethyleneglycol ditosylate	98%	Orion Chem Pvt. Ltd.
Hexane	LR grade	Spectrochem Pvt. Ltd., Mumbai
5% Rh on activated γ-alumina	Activated catalyst	Sigma Aldrich, Bangalore
Isovaleric acid	99%	Spectrochem Pvt. Ltd., Mumbai
1-Butanol	98%	Spectrochem Pvt. Ltd., Mumbai
H_2 gas	High purity gas cylinder	BOC India Limited

3.1.2 Diluent

Diluent used in this study is a mixture of *n*-dodecane and IDA, both are of commercial grade having purity more than 99% pure and used as received.

3.1.3 Radiotracers for extraction studies

Extraction evaluation of Cs was carried out by spiking radiotracers ^{137}Cs in the respective aqueous solutions. 0.1 mCi ^{137}Cs in 0.1 M HCl was procured from Board of Radiation and Isotope Technology (BRIT), Mumbai. For extraction studies involving Sr, radiotracer ^{85,89}Sr was used; it was also added to HLLW as a surrogate for ^{90}Sr. Radiometry of ^{90}Sr is difficult due to interference from its daughter product ^{90}Y as both are pure β-emitters, while ^{85,89}Sr is a γ-emitter and there is no interference from other γ-emitters. 0.1 mCi ^{85,89}Sr in 0.1 M HNO_3 was procured from BRIT, Mumbai. The radiochemical purity of both the isotopes was checked by gamma ray spectrometry using a high purity germanium (HPGe) detector. ^{99}Tc used for extraction studies was separated from LLW using tetraphenyl arsonium chloride (TPAC)-chloroform reagent as described by Sonar et al. [99]. Concentration of it was estimated by measurement of β-activity by Geiger-Müller (GM) counter.

3.2 Analytical techniques used

Radionuclides in the samples were analyzed by radiometry. Activities of ^{137}Cs and ^{85,89}Sr were counted using a NaI(Tl) scintillation counter (Para Electronics) coupled to a multi-channel analyzer. The efficiency of the counter was ~10% as standardized against ^{137}Cs standard source. Individual fission products in HLLW as well as in product samples were assayed using gamma spectrometry employing HPGe detector (Baltic Scientific Instruments) coupled to a 4K multi-channel analyzer. List of radionuclides assessed by radiometry is given in **Table 3.2**. Uranium estimation was done by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) as well as by spectrophotometry using 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol (Br-PADAP) as a chromogenic agent [100]. Other active/inactive elements were analyzed by ICP-AES. Details of the instruments and their operative specifications are described below.

Table 3.2: Nuclear data of radionuclides

Elements	Decay mode	Half Life	Energy	Counting mode
^{137}Cs	β, γ	30.2 years	661 keV	γ
^{85}Sr	EC, γ	64.85 days	514 keV	γ
^{89}Sr	γ	50.57 days	909 keV	γ
^{90}Sr	β	28.5 years	546 keV (β_{max})	Liquid scintillation
^{22}Na	β, γ	373 days	511 keV	γ
^{99}Tc	β, γ	2.1 x 10^5 years	300 keV	β
^{95}Zr	β, γ	64 days	724, 756	γ
^{239}Pu	α	24360 years	5.15, 5.14	Liquid scintillation
^{241}Am	α, γ	432 years	60	γ

3.2.1 NaI(Tl) Scintillation counter

Sodium iodide activated with 0.1-0.2 % of thallium, NaI(Tl), is a widely used inorganic scintillator for the assay of gamma emitting radionuclides. Salient features of the detector are low cost, ease of operation, and ruggedness. The band gap in NaI crystal is of the order of 5-6 eV. When a gamma ray falls on the detector, its energy is used up either for excitation of the electrons from the valence band to conduction band or for the ionization of atom. De-excitation of the electrons from conduction band to the valance band leads to the emission of photons in the UV region as the band gap is large. To shift the energy of the emitted photons to the visible region, which is required for the detection by photomultiplier tube (PMT), NaI crystal is doped with an activator impurity like thallium (Tl) which forms the intermediate level conduction band. The resolution of NaI(Tl) detector is about 7% at 662 keV. In the present work, a 3” x 3” well type NaI(Tl) detector coupled with a multichannel analyzer (**Fig. 3.1**) has been used for gamma counting. Nearly 100% detection efficiency for moderate energy photons in a well type NaI(Tl) detector offers great advantages for counting of low activity samples [101]. A suitable aliquot (usually 0.1 mL) of the desired analyte solution is taken in glass counting tubes which is then placed in the well of the detector. Each sample is counted for sufficient time so as to get more than 10,000 counts to restrict the counting statistics error to <1 %.

Fig.3.1: NaI(Tl) detector for γ-counting

3.2.2 Geiger-Müller counter

Geiger-Müller (GM) counter is a widely used detector for α, β and γ counting and common survey meter for radiation measurements in various areas of research [102]. GM counter consists of a copper cylinder closed with thin mica window at one end. The cylinder is filled with helium or argon gas and alcohol vapour at a pressure of about 10 mm of Hg. A tungsten wire, which acts as anode is placed in the middle of the cylinder and kept at a potential of 1500 volts. The inner wall of the copper cylinder acts as a cathode. During the radioactivity measurement, the radioactive particles enter the cylinder and cause ionization of gaseous molecules. Gas multiplication is very high in the order of 10^8-10^{10} and, therefore, large pulses are produced. The positive ions slowly drift away from the anode wire and reach to cathode and are neutralised by combining with electrons from the cathode surface. During the process, an amount of energy equal to the ionisation energy of the gas minus the energy required to eject the electron from the cathode surface is liberated. This liberated energy if exceeds the effective energy required to produce an electron at cathode surface (cathode work function), then another electron is ejected out. This electron will then drifts towards the anode and trigger another avalanche of electron and produce a continuous output of current which is amplified. The efficiency of measurement is 100%, however, for γ-ray counting, efficiency depends on the probability of interaction of γ-rays with fill gas, normally efficiency for γ-counting is low. An image of GM counter is shown in **Fig.3.2**. Statistical error is minimized to less than 1% by taking large number of counts.

Fig.3.2: An image of GM counter

3.2.3 High purity germanium detector

High purity germanium (HPGe) detector measures γ-ray emitted from a radioactive material. [103]. High purity germanium with impurity level less than 10^{10} atoms/cc is employed to make this detector. The use of high purity germanium semiconductor has enabled high resolution γ-ray measurement over NaI (Tl) based detectors. Germanium semiconductor diode is having *p*-type, intrinsic layer (depleted zone) and *n*-type (*p*-*i*-*n*) structure, in which intrinsic layer of the detector is sensitive to γ-rays. When photons interact with the depleted zone of the detector, holes and electrons are produced which results in generation of electricity at *p* and *n*-zones. The energy deposited by the charge transfer is proportional to the intensity of the incoming photon which is then converted into a voltage pulse by an amplifier.

The band gap of germanium is relatively low, 0.7 eV, therefore, germanium detectors need to be cooled by liquid nitrogen up to a temperature of 77 K to reduce the heat generated by reverse leakage current to an acceptable level. The HPGe detectors can be either *p*-type or *n*-type depending on the concentration of donor or acceptor atoms in the crystal lattice. In *p*-type detectors, the *n*-type impurities are heavily doped as a result detection sensitivity is low below 100 keV. While, *n*-type of detectors are doped with *p*-type of impurities, compared to a *p*-type detector, these detectors are more resistant to radiation damage in a neutron field because the damage sites preferentially trap holes rather than electrons. The *n*-type detector is therefore preferred as compared to the *p*-type detectors. In the present study, an *n*-type HPGe detector of M/s. Baltic Scientific Instrument make has been employed. Analyses of samples generated during extraction and stripping studies from diluted and actual HLLW have been carried out using HPGe detector coupled to a multi-channel analyzer as shown in **Fig.3.3** after appropriately diluting the sample with 1 M HNO_3. Each sample is counted for sufficient time so as to get more than 10,000 counts to restrict the statistical counting error to within ±1%.

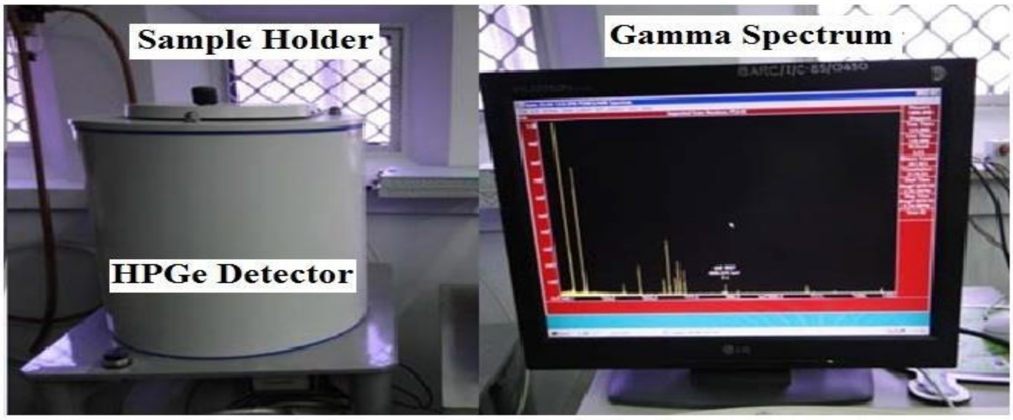


Fig.3.3: HPGe detector used for γ-spectrometry

3.2.4 Liquid scintillation counter

Liquid scintillation counter is the most widely used detector for quantitative analysis of alpha or beta emitters. Detection efficiency of this detector is nearly 100 %, which is a great advantage as a few Becquerel (Bq) of alpha activity can be assayed with good precision. A scintillator shows luminescence due to interaction with the ionizing photon at a suitable wavelength region. Interaction of charged particles (α or β particles) with the scintillator results in emission of photons and the intensity of the emitted light is a quantitative measure of the incident radiation. The light emitted from scintillator is then collected at the PMT which produces signal representative of the primary radiation. When scintillator emits photons in the UV region, a wavelength shifter is added to the scintillator which has intermediate energy levels. In such cases, the de-excitation takes place via these intermediate energy levels and hence the wavelength of the emitted photons is shifted from UV to the visible region which is subsequently recorded in the PMT as photocathode of most PMTs is compatible with visible light. The liquid scintillation counter is used to monitor gross alpha activity as it cannot distinguish between alpha energies and thus cannot be used for alpha spectrometry. The liquid scintillation cocktail comprises of a solvent like dioxane or toluene, a scintillator like 2,5-diphenyl oxazole (PPO) and a wavelength shifter such as 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) [104]. In case of toluene based scintillator, a suitable extractant such as D2EHPA is also added which facilitates estimation of alpha activity in the aqueous samples by transferring the fission-radionuclides from the aqueous phase to the organic phase. Dioxane based liquid scintillator consist of 0.1 % (v/v) PPO, 0.025 % (w/v) POPOP and 10 % (w/w) naphthalene. Here, naphthalene increases the stability of the mixture. In addition, TOPO is also added as an anti-quenching agent to suppress the effect of acid. On the other hand, the toluene based liquid scintillator consists of 10 % (v/v) D2EHPA, 0.7 % (w/v) PPO and 0.03 % (w/v) POPOP. Suitable aliquots (25-100μL) of solutions containing alpha activity are taken in glass vials containing about 5 mL of the liquid scintillator solution. Two phases are mixed vigorously for ~2 min using an ultrasonic agitator to transfer the radionuclides into the organic phase. Each sample is counted for sufficient time so that the counting statistics is less than ±1%.

3.2.5 Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

Plasma is a common source of atomization in emission spectroscopy. In ICP-AES, argon is ionized by the influence of a strong electric field generated by radio-frequency. Plasma source operates at high temperature in the range of 7000 to 15000 K. The argon stream carries the sample in the form of an aerosol passes through the plasma and produces a large number of excited atoms and ions that emits electromagnetic radiations at specific wavelength characteristics of a particular element and intensity proportional to the concentration of the element [105]. Plasma source is able to produce atomization conditions with high degree of precision; as a result spectra are produces for a large number of elements simultaneously. A given element emits radiation at multiple wavelengths, therefore, during analysis a single wavelength (or very few) is selected and intensity of emitted radiation at that wavelength is measured. Thus, by selecting the wavelengths and by determining their intensities, quantitatively estimation of the elements from the given sample relative to a reference standard is achieved. Block diagram of the instrument is given in **Fig.3.4**. The radiation emitted from the plasma enters through a single slit and then reflected from a concave grating and reaches a series of exit slits which isolates the selected emission lines for specific elements. The photons from each slits, as isolated spectral line, fall on the cathode of a photomultiplier tube to give an output which is integrated on a capacitor. The resulting output voltages of capacitor are proportional to the concentrations of the elements in the sample.

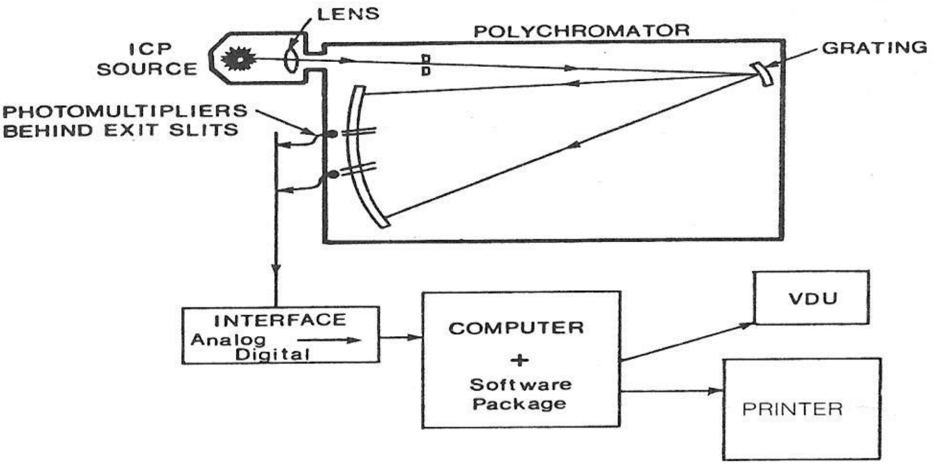


Fig.3.4: Block diagram of ICP-AES

ICP-AES of M/s. Jobin Yvon make comprising of multi-channel (JY- 48) and high resolution scanning monochromator (JY-38) was used in this work. A low resolution monochromator, JY-H20 with 0.2 m focal length and a spectral range of 400-800 nm was also used. The error percent in analysis is within ±5%.

3.3 Estimation of uranium

Uranium estimation was also done by spectrophotometry using 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol (Br-PADAP) as a chromogenic reagent. This method is valid both in aqueous phase as well as in the organic phase. An alcoholic solution of Br-PADAP forms a stable intense violet coloured complex with UO_2^{2+} at pH 7-8 buffered with triethanolamine. The complex shows a very high molar extinction coefficient of ~70,000 at absorption maxima at 578. To a known volume of uranium solution in standard flask (10 mL), 1 mL of complexing solution (1.25 g *trans*-1,2-cyclohexanediaminetetraacetic acid + 0.25 g NaF + 3.25 g sulphosalicylic acid dissolved in 100 mL water adjusted to pH 7.8 with concentrated NaOH), 1mL buffer solution (14 g TEA dissolved in 100 mL water adjusted to pH 7.8 with perchloric acid) and 0.8 mL Br-PADAP solution (50 mg Br-PADAP dissolved in 100 mL ethanol) are added. Ethanol was added to make organic volume to 10 mL, while to aqueous samples 4 mL of ethanol was added and adjusted the final volume to 10 mL by adding distilled water. The final absorption measurements are performed after 30 minute of colour development at 578 nm. This method is found to be very sensitive and no interference of Pu, Th, Al and Fe is observed. Standard uranium solution in the concentration range of 1×10^{-6} M to 1×10^{-4} M is used to plot the calibration curve. The concentrations of unknown samples are determined from the calibration plot. The estimated error of measurement is within ±1%. A double beam JascoV-530 UV-Spectrometer was employed for UV-Visible spectrophotometry analysis.

3.4 Estimation of ^{99}Tc in LLW and in other aqueous streams

One mL of the LLW containing ^{99}Tc is taken in 50 mL capacity conical flask. To this solution, 4 mL of distilled water is added followed by 1 mL of 30% H_2O_2. This is followed by addition of 0.1 mL of 0.02 M $HClO_4$. Addition of H_2O_2 and $HClO_4$ is done to ensure the +7 oxidation state of Tc. Distilled water is added to make the total volume to 10 mL. Into this, 5 mL of TPAC in chloroform (0.019 M) is added. The solution was equilibrated using magnetic stirrer. Chloroform being heavier forms the bottom layer which avoids the losses of chloroform due to volatilization. After equilibration, the organic layer is separated and 0.1 mL of the chloroform layer is placed on a planchet. The chloroform is then allowed to evaporate at room temperature. Beta activity counting is done using GM counter. Counting is repeated after placing Al absorber of 100 mg/cm^2 thickness over the planchet. On the basis of the ^{99}Tc concentration in the solution, the sample volume for extraction as well as the volume of chloroform layer for plancheting is varied. The percentage extraction is calculated using the equation:

% Extraction = $[Tc]_{org}/[Tc]_{initial} \times 100$

Where, $[Tc]_{org}$ = concentration of ^{99}Tc extracted in organic phase and

$[Tc]_{initial}$ = concentration of ^{99}Tc present in LLW

Similar procedure is followed for estimation of ^{99}Tc present in other aqueous streams like stock solution, strip solution etc.

3.5 Experimental setup for synthesis of extractants

Synthesis of (i) 1,3-dioctyloxycalix[4]arene-crown-6 (ii) 1,3-bis(2-ethylhexyloxy)calix[4] arene-crown-6 and (iii) 4,4'(5')-[di-*tert*-butyldibenzo]-18-crown-6 are carried out at atmospheric pressure. Conventional glass distillation setup consisting of heater, reflux column, condenser, addition flask, motor stirrer, nitrogen purging and vacuum line used for the synthesis of above extractants is shown in **Fig. 3.5**. Synthesis of 4,4' (5')-[di-*tert*-butyldicyclohexano]-18-crown-6, is done by hydrogenation of 4,4'(5')-[di-*tert*-butyldibenzo]-18-crown-6 at high pressure and temperature, therefore, a gas induction autoclave as shown in **Fig. 3.6** supplied by M/s. Amar Equipments Pvt. Ltd. is employed. The specifications of autoclave are summarized in **Table 3.3**.

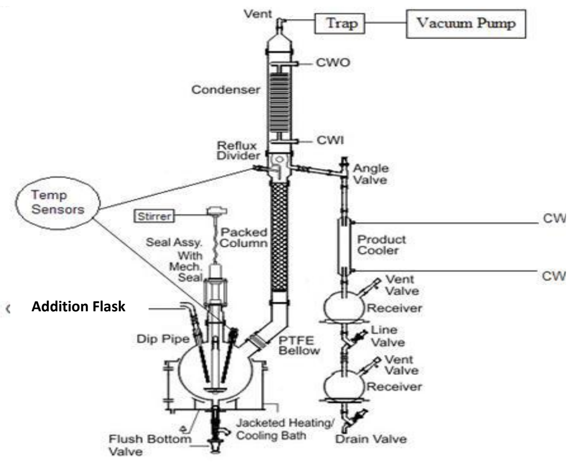


Fig.3.5: Glass reactor-distillation assembly

Fig.3.6: Trolley mounted autoclave

Table 3.3: Specifications of autoclave

Items/parts	Specifications
Volume	2L
Material of Construction	Wetted parts: SS 316
Design pressure	100 bar
Maximum working temperature	250°C
Head mounting style	Removable head and vessel design

Items/parts	Specifications
Heating	External electrical ceramic band heater with insulation & high temperature steel cladding. It shall have insulated heater plate to prevent thermal shock to operator and cascade temperature controller to prevent temperature over shoot.
Auto-cooling system	With water pump, for forced cooling SS tank & hose pipes for exothermic reaction & faster cooling.
Motor & drive	¼ HP AC Motor with 100-1450 RPM
Shaft sealing	Zero leakage Magnetic drive coupling, Note: Material of construction of bush- carbon filled PTFE
Stirrer	Hollow shaft with gas induction impeller (for gas-liquid reaction).
Standard fittings	External valves & fittings: Pressure gauge with vacuum protection, SS-316 pressure transmitter, Gas inlet-valve & liquid sampling valve mounted on common dip tube Vent needle valve Ball valve with funnel (PEEK Seat) for powder/liquid inlet with funnel at atmospheric pressure Flush bottom valve of SS-316 Needle valves of ¼” end connections
	Internal Fittings: Helical cooling coil Thermowell (with RTD Pt-100 temperature sensor)
Gasket	PTFE Gasket with split clamp type quick opening system with clamp bolts.
Closure type	Split clamp with clamp bolts
Pressure regulator	With self-venting for releasing the pressure, pressure gauge & 4m long flexible hose pipe with NRV for 0-140 bar O/P pressure for H_2 gas & adaptor for N_2 cylinder.
Control Panel	SS control panel with programmable P.I.D temperature controller, parameter to control overshoot with standby mode to cut off heating & cooling with high temperature alarm system, digital pressure indicator in bar or psi & motor speed controller.
Power Supply	1φ, 220VAC, 50 Hz
Mounting	SS Trolley with lockable wheels.
Safety features	Safety rupture disc (Inconel) with vacuum protection Pressure relief valve of SS- 316

3.6 Characterisation of organic intermediates and extractants

3.6.1 Gas chromatograph-Mass spectrometer (GC-MS)

Identification and quantification of organic molecules were carried out using Shimadzu make GC-MS model QP2010 Ultra having mass range of 1.5-1090 m/z and unit mass resolution [106]. The operating parameters of GC-MS are described in **Table 3.4**.

Table 3.4: Operating parameters of GC-MS

Carrier gas and column flow	He, 10 mL/min
Injector temperature	300°C
Split ratio	40:1
Oven temperature	60 to 300°C, hold for 30 min at 300°C
Temperature program	10°C/min
Capillary column	Rxi^{TM}-5MS, length: 30 m, id: 0.25 mm, df: 0.25 µm
Mass analyzer	Single quadrupole mass filter with pre-rod
Interface temperature	300°C
Ion source mode	Electron ionization
Direct injection (DI) port temperature	100 to 300°C
Vacuum	~10^{-4} Pa

3.6.2 Nuclear magnetic resonance spectrometer (NMR)

NMR is a powerful analytical tool in determination of molecular structure as well as content and purity of a compound. It is one of the best tools to provide information on conformational geometry of calix-crown-6 molecule. It works on the interaction of magnetic moment of a spinning charged particle with the applied external magnetic field. The atomic nucleus is a spinning charged particle, and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random and spin in random directions. By keeping the nuclei in a magnetic field of appropriate radio frequency, two different energy states are produced due to the alignment of the nuclear magnetic moments relative to the applied field and a transition between these energy states takes place. The energy absorbed in this process produces signal at the detector and the signal is amplified and recorded as a band in the spectrum. A plot of the absorption frequency expressed as chemical shift given in parts per million (ppm) verses the intensity of the absorption constitutes the NMR spectra. In this work, ^{1}H &^{13}C-NMR spectra were recorded with a Bruker 500 MHz FT-NMR spectrometer in $CDCl_3$ with tetramethyl silane (TMS) as internal standard. Frequency for ^{13}C-NMR was kept at 125 MHz [107].

3.6.3 Elemental analyzer

Thermo Scientific^{TM} FlashEA1112 elemental analyzer equipped with thermal conductivity detector (TCD) was used for simultaneous determination of percentage composition of C, H, N and O in the calix-crown-6 and crown ether samples. It comprises of left and right furnaces (temperature up to 1100°C), left furnace is a combustion chamber for CHNS determination and right furnace is pyrolysis chamber for determination of O percentage in the sample. High purity He is used as carrier gas and high purity oxygen gas is used for combustion [108]. For CHNS determination, sample weighted in mg in a tin capsule, is dropped into the left furnace for a complete combustion and the combustion mixture will flow into the GC column for separation and detected by TCD in the sequence of N_2, CO_2, H_2O and SO_2. For O determination, sample weighted in mg in a silver capsule, is dropped into the right furnace where it undergoes instant pyrolysis, the gas mixture will cross the adsorption filter and flow into the GC column and the eluted gases are detected by TCD.

3.6.4 Electrospray ionization-Mass spectrometry (ESI-MS)

ESI-MS, a soft-ionization desorption technique was used for direct measurement of cations in the extract phase [109]. The spectra are recorded by Triple-Quadrupole Quattro II instrument

(Micromass, Manchester, UK) in positive ionization mode with the electrospray needle voltage at 3.5 kV, cone voltage at 20 V and skimmer voltage at 1.9 V. The sample solution on injection converts to an aerosol of highly charged electrospray (ES) droplets due to the presence of strong electric field. The injection rate of sample is maintained at 10 μL/min and source temperature is adjusted to 80°C. Flow of dry nitrogen, a coaxial sheath gas, is kept around the capillary for better nebulization. This gas flow guides the spray emerging from the capillary tip towards the mass spectrometer and also assists in solvent evaporation to result in size reduction of the charged droplet and release of charged analyte. This then passes through the conical orifice of a heated capillary of 0.2 mm ID and 60 mm length kept in the interface of atmospheric pressure and the high vacuum at 200°C for complete desolvation of the ions and to the analyser of the mass spectrometer held under high vacuum. Ions are detected by scanning the *m/z* over the range 10-2200 in 10 s. At least 50 scans are averaged to obtain representative spectra. A schematic representation of ESI-MS is shown in **Fig. 3.7**.

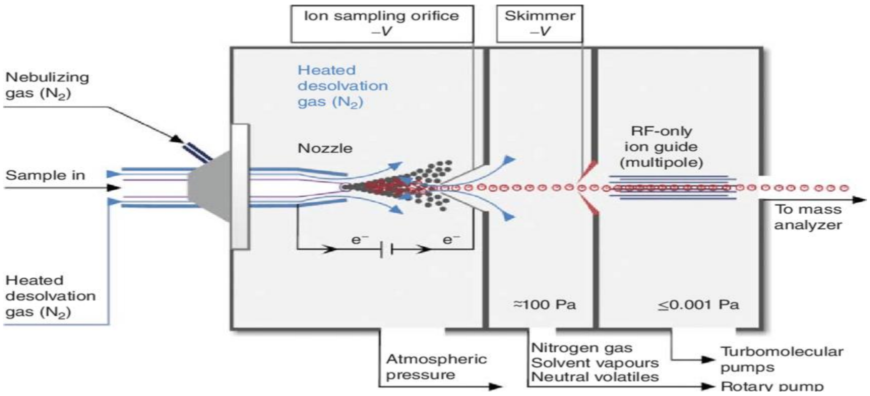


Fig.3.7: A schematic representation of ESI-MS

3.6.5 Melting point measurements

Physical form of most of the intermediates and product of calix-crown-6 and crown ether are solid in nature, therefore, their melting points (MP) are determined to ascertain the purity.

MPs are determined with an Electrothermal melting point apparatus in a capillary and are uncorrected.

3.7 Solvent extraction experiments

3.7.1 Extraction procedures

For the distribution studies, suitable volume (0.5-5 mL) of the aqueous phase of the desired acidity containing the required radio tracer/metal ion is equilibrated in stoppered Pyrex glass tubes with equal volume of the organic phase. For all solvent extraction studies, except stated otherwise, the organic phases are pre-equilibrated with the respective acid solutions to eliminate the effect of acid uptake. The agitation of the two phases is carried out by rotating the sealed tubes in a thermostated water bath maintained at 25 ± 0.1°C. After equilibration, the phases are centrifuged and assayed for the desired constituents by removing suitable volumes (20-50µL) from both the phases. The distribution ratios (D_M) of the metal ions are calculated as the ratio of concentration (or radioactivity) of metal ion in the organic phase to that in the aqueous phase at equilibrium (expressed in the same unit). Error in the measurement of D_M is within ±5%. All the extraction experiments are carried at an O/A ratio of 1, except stated otherwise. Percentage extraction is calculated as:

$$\%\ \text{Extraction} = \frac{\boldsymbol{E}}{\boldsymbol{E+1}} \times 100$$

Where, $E = \frac{Vo}{Va} \times D_M$

V_o is volume of organic and V_a is volume of aqueous.

Selectivity of extraction of a metal ion M over another metal ion M′ is measured by calculating separation factor (SF), which is the ratio of D_M to $D_{M'}$ determined under same condition.

The hydrogen ion concentrations in the aqueous and organic phases are determined by titration with standard alkali solution using phenolphthalein as the indicator. Different solvent extraction studies are carried out to understand the extraction kinetics, effect of diluent composition, nitric acid concentration, nitrate ion concentration, extractant concentration, and interfering elements on the extraction behaviour of desired radionuclides. With help of these studies, extraction & stripping mechanism and stoichiometry of the extracted complex are determined. Studies on extraction of Cs^+, Sr^{2+} from actual HLLW and TcO_4^- from actual LLW are carried out to establish the selectivity of extractant molecules. Counter-current mixer-settler run including extraction, scrubbing and stripping for separation and recovery of ^{137}Cs from HLLW is also carried out.

3.7.2 Determination of solubility of extractants

Solubility of an extractant in a diluent is determined by taking a known weight of extractant in a 10 mL volumetric flask and then mixing well with a diluent for 30 minutes. Final volume is made to 10 mL by adding diluent. Then the mixture is left undisturbed for 24 h. Visual observation for formation of any precipitate or cloudiness is done to decide the solubility of the extractant. If the solution is clear and shows no sign of cloudiness or precipitation, the extractant is considered to be soluble.

3.7.3 Constitution of solvent

Solvent solution is prepared in a volumetric flask by dissolving known weight of extractant in required quantity of IDA and then making up to the mark on flask by adding *n*-dodecane.

3.7.4 Counter-current mixer-settler studies

Mixer settler unit made up of acrylic polymer having a mixer volume of 80 mL and settler volume of 300 mL is used for counter-current extraction, scrubbing and stripping studies in a continuous mode. The agitator is turbine-type and made up of stainless steel. Peristaltic pumps (PP 20) with a flow accuracy of ± 5 %, procured from M/s. Miclins, Chennai, India, are used for adjusting the flow rate of aqueous/organic solutions while flexible polypropylene tubing are used for the transportation of the solutions. Stage wise analysis of ^{137}Cs activity in both the phases is carried out periodically to ascertain the mass balance. At the end of runs, exit samples of aqueous and organic phases are drawn for analysis of ^{137}Cs and other radionuclides/metal ions.

3.8 Solvent irradiation studies

In order to study the stability of the solvent towards gamma radiation, 10 mL of the solvent is kept in contact with 10 mL of 4.0 M HNO_3 in stoppered glass vials for irradiation in a gamma chamber. The dose rate is kept at 56 Gy/min and maintained for the predefined time to acquire the desired radiation dose. Irradiation experiments are carried out up to 0.6 MGy absorbed dose to simulate the more realistic conditions. After irradiation, the organic samples are separated from nitric acid phase and subjected to GC-MS analysis and extraction studies to know the nature of degraded products formed and the extent of degradation of irradiated solvent.

CHAPTER 4

Process for Separation of Cs from HLLW using 1,3-Dioctyloxycalix[4]arene-crown-6 and 1,3-Bis(2-ethylhexyloxy)calix[4]arene-crown-6

Calix-crown-6 ethers, when fixed in 1,3-alternated conformation posses a cavity which is highly complementary to Cs^+ and serve as potential extractants for selective separation of Cs^+ from solution containing large amount of Na^+, H^+ and other metal ions [74]. This property has enabled their exploitation in selective separation of radioactive Cs from acidic solutions. However, difficulty in synthesis of calix-crown-6 molecules at larger scale and their incompatibility with paraffinic diluents like *n*-dodecane complicates the attempt to develop a process for separation of Cs from HLLW at industrial scale. In this work, a less polar calix-crown-6 with two *n*-octyl group attached to two rotated aromatic nucleus of the 1,3-alternate-calix[4]arene annulus, namely, 1,3-dioctyloxycalix[4]arene-crown-6 (CC6) has been selected and a new synthesis route is devised to obtain the product in high yield. Selection of this calix-crown-6 is also done on the basis of its ease of synthesis at larger scale and compatibility to paraffinic diluents. Effect of nitric acid, nitrate ion and extractant concentration on Cs extraction is discussed. Nature of the extracted species, mechanism of extraction, selectivity of Cs extraction in the presence of high concentration of interfering elements and stripping conditions have been studied. Results of the batch and continuous counter-current extraction of Cs from HLLW with high salt content have been shown. Degradation of the solvent with γ-ray irradiation using ^{60}Co source and under actual conditions of extraction with HLLW was studied and recovery and recyclability of the solvent also established. In order to further enhance the selectivity for extraction of Cs from

HLLW, a more sterically hindered branched isomer of 1,3-dioctyloxycalix[4]arene-crown-6 namely 1,3-bis(2-ethylhexyloxy)calix[4] arene-crown-6 (BCC6) has been developed where the crown ether moiety is kept intact to retain the extraction power for Cs and the hydrophobic part i.e. octyloxy group has been changed to a more sterically hindered branched 2-ethylhexyl group to impart an additional steric hindrance to further reduce the extraction of undesirable metal species.

4.1 Synthesis of CC6 and BCC6

4.1.1 Synthesis of CC6

The reported synthesis procedure described by Casnati et al. [74] for CC6 involves four major steps; (a) synthesis of *tert*-butylcalix[4]arene from *p*-*tert*-butylphenol (b) synthesis of calix[4]arene by Friedel-Crafts de-alkylation of *tert*-butylcalix[4]arene (c) synthesis of 1,3-dioctyloxycalix[4]arene by reaction of *n*-octylbromide with calix[4]arene in the presence of K_2CO_3 (d) and synthesis of CC6 by the reaction of pentaethyleneglycol ditosylate (PEG-diTs) with 1,3-dioctyloxycalix[4]arene in the presence of Cs_2CO_3. Step (c) is highly time consuming and takes almost 5 days for completion of the reaction and suffers from a lower yield of 52%. In the present work, a new synthesis route was devised by using *n*-octyltosylate instead of *n*-octylbromide, by considering tosylate as a better leaving group compared to bromide. Process scheme for synthesis of CC6 is shown in **Fig. 4.1**.

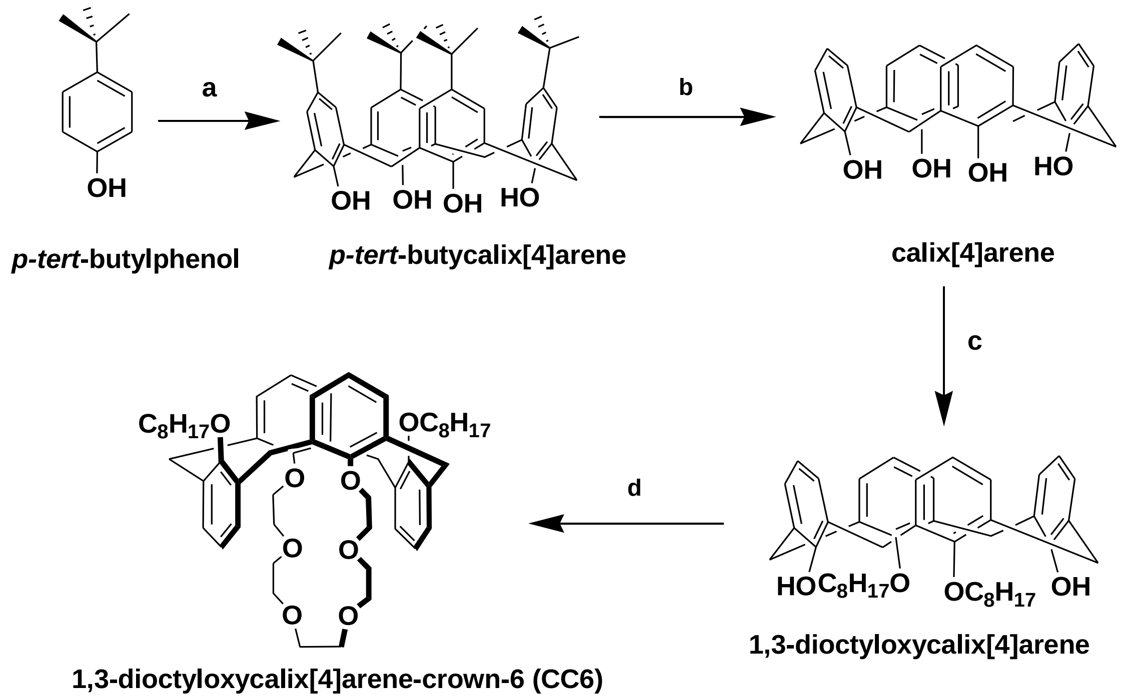


Fig.4.1: Synthesis scheme of CC6

Reagent and conditions: (a) HCHO, NaOH, 120°C (b) $AlCl_3$, Phenol, Toluene, 45°C (c) K_2CO_3, C_8H_{17}-OTs, CH_3CN, 85°C, 48 h (d) PEG-diTs, Cs_2CO_3, CH_3CN, 85°C, 24 h

Step a: Synthesis of *p-tert*-butylcalix[4]arene

Chemical reaction:

p-tert-Butylphenol (s) + HCHO (l) → *p-tert*-Butylcalix[4]arene (s) + H_2O (l)

Procedure: A mixture of 150 g (1mol) of *p-t*-butylphenol, 93 mL (1.2 mol) of HCHO and 2 g (0.05 mol) of NaOH in 5 ml of water is taken in a 3 L round bottom flask. The temperature of the reaction mixture is maintained at 120 °C for cyclization under vigorous nitrogen purging for 3-4 h. 1200 mL of diphenyl ether is added and refluxed at 260 °C for 4-5 h. Then the reaction mixture is cooled and 2 L ethyl acetate is added to precipitate the product. It is then filtered and washed with acetic acid and crystallized in toluene. The crystal is vacuum dried at 140°C for 48 h.

Yield: 94 g (58%)

Purity: 99.5% (GCMS)

MP: 343-345°C

GCMS: *m/z* 649 (M^+ calculated 649)

Step b: Synthesis of calix[4]arene

Chemical reaction:

p-*tert*-Butylcalix[4]arene(s) + Phenol(s) → Calix[4]arene(s) + *tert*-Butylphenol (s)

Procedure: A slurry of 649 g (1mol) of *p*-*t*-butylcalix[4]arene and 475 g of phenol in 7000 mL of toluene is taken in a round bottom flask. 703 g of anhydrous $AlCl_3$ (5.25mol) is added and stirred under stream of nitrogen gas for 5-6 h at 45°C. Then the mixture is neutralized by 0.5 M HCl. The organic phase is separated discarding third phase if any and concentrated in vacuum. Then CH_3OH is added to form the crystals of calix[4]arene. Repeated crystallization is done by 1:1 proportion of methanol and chloroform.

Yield: 288 g (68%).

Purity: 99.9% (GCMS).

MP: 313-315°C

GCMS: *m/z* 424 (M^+ calculated 424)

Synthesis of *n*-octyl tosylate and pentaethylene ditosylate (PEG-diTs)

Chemical reaction:

n-Octanol(l) + Toluene sulphonyl chloride(s) + NaOH(l) → *n*-Octyl Tosylate + NaCl (s) + H_2O,

Procedure: To a solution of 72 g (1.8 mol) NaOH + 250 ml water + 250 mL THF, 130 g (1 mol) of *n*-octanol is added and mixed well. Temperature of the flask is then reduced to 0°C. Addition flask is charged with a solution of 210 g (1.1 mol) toluene sulphonyl chloride in 350 mL THF maintained at 0°C. Drop wise addition is done to maintain the temperature between 0 to 5 °C for 4 h. After addition, mixture is stirred for one more hour at 5°C. The reaction mixture is then poured on 500 g of ice/water and stirred for ½ an hour. THF is removed by distillation at reduced pressure. Remaining aqueous layer is then extracted with 250 mL of dichloromethane (DCM) in 3 portions. Combined DCM layer is dried with $MgSO_4$ and concentrated to obtain *n*-octyltosylate as a colourless viscous liquid.

Yield: 218 g (77%)

Purity: 99.5 % (GCMS)

For synthesis of PEG-diTs, similar reaction was carried out by taking pentaethylene glycol instead of *n*-octanol.

Step c: Synthesis of 1, 3-dioctyloxycalix[4]arene

Chemical reaction:

Calix[4]arene(s) + *n*-Octyltosylate(l) + K_2CO_3(s) → 1,3-Dioctyloxycalix[4]arene(s) + Potassium tosylate (s) + CO_2 (g)

Procedure: Suspension of calix[4]arene (424 g, 1mol), K_2CO_3 (210g , 1.52 mol) and *n*-octyltosylate (853 g, 3 mol) in CH_3CN (7 L) is taken in a reaction vessel and refluxed at 85^{o}C for two days in N_2 atmosphere. CH_3CN is then removed under reduced pressure. 10 L of DCM is added to it and washed with 10 L of 10 % HCl. The organic phase is separated, washed twice with distilled water and dried over $MgSO_4$. It is then concentrated. To the residue, ethanol is added to precipitate the product. Crystallization in hexane is done to obtain the product as white crystals.

Yield: 480 g (74%)

MP: 117°C

Purity: 99.5% by GCMS

MS (DI): *m/z* 649 $(M+H)^+$

Elemental analysis: Calculated for $C_{44}H_{56}O_4$, C: 81.40%, H: 8.65 %; Found: C: 81.38%, H: 8.79%.

^{1}H NMR ($CDCl_3$): δ 8.25 (s,2H, OH), 7.1 (d, 4H, ArH meta), 7.077 (d, 4H, ArH meta), 6.83 (t, 7.5 Hz, 2H, ArH para), 6.77 (t, 7.5 Hz, 2H, ArH para), 4.33 (d, 4H, $ArCH_2Ar$), 4.00 (t, 4H, OCH_2R), 3.38 (d, 4H, $ArCH_2Ar$), 1.287 (m, 24H, $OCH_2(CH_2)_6CH_3$), 0.92 (t, 6H, $OCH_2(CH_2)_6CH_3$).

^{13}C NMR ($CDCl_3$): δ 154.85, 153.35 (s, Ar ipso), 133.01, 132.69 (s, Ar ortho), 129.18, 128.63 (d, Ar meta), 122.10 (s, Ar para), 77.64-69.85 (t, OCH_2R), 31.89-22.71(t, $ArOCH_2$ $(CH_2)_6CH_3$) and $ArCH_2Ar$), 14.12 (q, $-CH_3$).

Step d: Synthesis of CC6

Chemical reaction:

1, 3-Dioctyloxycalix[4]arene + PEG-diTs + Cs_2CO_3 → 1, 3-Dioctyloxycalix[4]arene-crown-6 + Cesium tosylate (s) + CO_2(g)

Procedure: 1,3-Dioctyloxycalix[4]arene (648 g,1 mol) is dissolved in 175 L CH_3CN and added to excess of Cs_2CO_3 (1300 g, 4 mol) and PEG-diTs (600 g, 1.1 mol) and refluxed at 85°C for 24 h under N_2 atmosphere. CH_3CN is then removed under reduced pressure and the residue is dissolved in 40 L of DCM and washed with 10 L of 10% HCl. The organic phase is separated and dried with $MgSO_4$ and concentrated. To the residue, methanol is added to precipitate the product. Crystallization is done in methanol to obtained white shinning crystals.

Yield: 588 g (69%)

MP: 94-95°C

Purity: 99.5% (GCMS)

MS (DI): *m/z* 851 $(M+H)^+$

Elemental analysis: Calculated for $C_{54}H_{74}O_8$, C: 76.20%, H: 8.76%; Found: C: 76.09%, H: 8.81%.

^{1}H NMR ($CDCl_3$): δ 7.114 (d, 4H, ArH meta), 7.077 (d, 4H, ArH meta), 6.83 (t, 7.5 Hz, 2H, ArH para), 6.77 (t, 7.5 Hz, 2H, ArH para), 3.78 (s, 8H, $ArCH_2Ar$), 3.71 (s, 4H, ArO $(CH_2CH_2O)CH_2$, 3.66 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 3.60 (t, 4H, $OCH_2(CH_2)_6CH_3$), 3.52 (t, 4H, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 3.41 (m, 8H, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 1.287 (m, 24H, $OCH_2(CH_2)_6CH_3$), 0.92 (t, 6H, $OCH_2(CH_2)_6CH_3$). ^{1}H NMR spectra are shown in **Fig.4.2**.

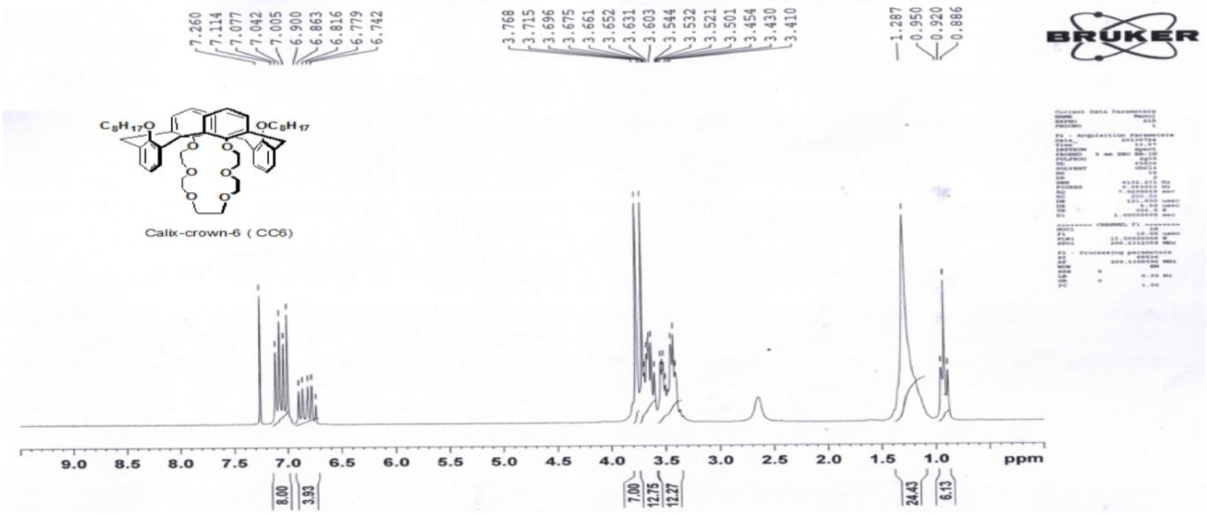


Fig.4.2: ^{1}H NMR spectra of CC6

^{13}C NMR ($CDCl_3$): δ 156.85, 156.35 (s, Ar ipso), 134.01, 133.69 (s, Ar ortho), 129.78, 129.63 (d, Ar meta), 122.13 (s, Ar para), 77.64-69.85 (t, OCH_2), 37.85 (t, $ArCH_2Ar$), 31.89-22.71(t, $ArOCH_2(CH_2)_6CH_3$), 14.12 (q, CH_3). ^{13}C NMR spectra are shown in **Fig.4.3**.

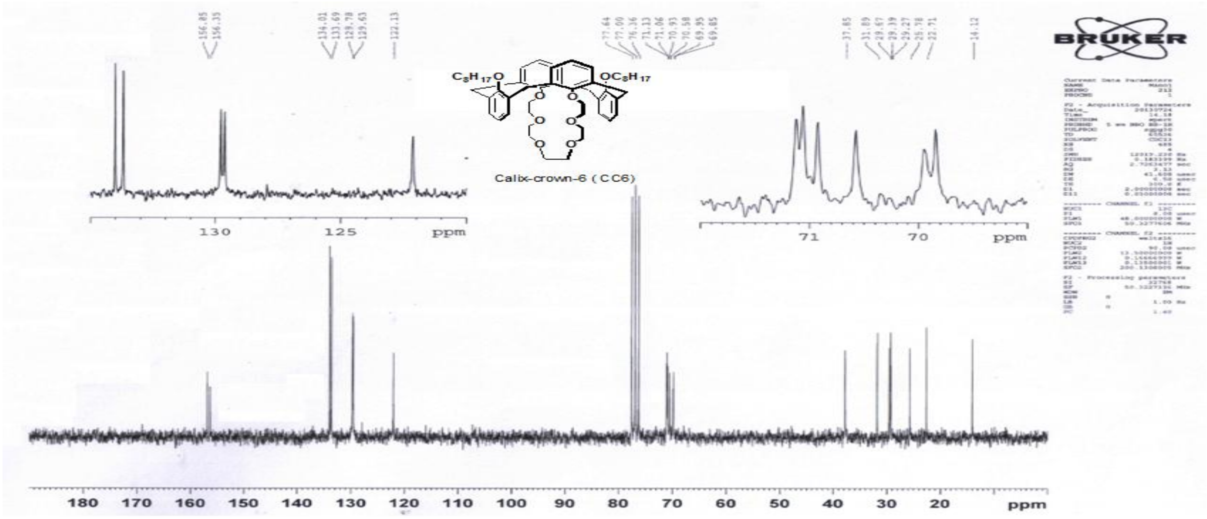


Fig.4.3: ^{13}C NMR spectra of CC6

Synthesis of 1,3-dioctyloxycalix[4]arene by using *n*-octyltosylate has resulted in reduction in reaction time to 2 days and an improved yield of 74%, instead of 5 days with a yield of 52% as obtained by Casnati el al. by using *n*-octylbromide. With this modification the overall yield of CC6 is increased from 14 to 20%.

4.1.2 Synthesis of BCC6

Synthesis of BCC6 is carried in two steps, (a) synthesis of 1,3-di(2-ethylhexyloxy) calix[4]arene and (b) synthesis of BCC6.

Step a: Synthesis of 1,3-di(2-ethylhexyloxy)calix[4]arene

Calix[4]arene(s) + 2-Ethylhexyltosylate(l) + K_2CO_3(s) → 1,3-Di(2-ethylhexyloxy)calix[4] arene(s) + Potassium tosylate (s) + CO_2 (g)

Procedure: Suspension of calix[4]arene (424 g, 1mol), K_2CO_3 (210g , 1.52 mol) and 2-ethylhexyltosylate (853 g, 3 mol) in CH_3CN (7 L) is taken in a reaction vessel and refluxed at 85°C for two days in N_2 atmosphere. CH_3CN is then removed under reduced pressure. 10 L of DCM is added to it and washed with 10 L of 10% HCl. The organic phase is separated, washed twice with distilled water and dried over $MgSO_4$. It is then concentrated. Ethanol is added to the residue to precipitate the product. Crystallization in hexane is done to obtain the product as white crystals.

Yield: 467 g (72%)

MP: 176°C

Purity: 99.5% by GCMS

MS (DI): *m/z* 649 $(M+H)^+$

Elemental analysis: Calculated for $C_{44}H_{56}O_4$, C: 81.45%, H: 8.69 %; Found: C: 81.34%, H: 8.80%.

^{1}H NMR ($CDCl_3$): δ 7.91 (s, 2H, OH), 7.07 (d, 7.4 Hz, 4H, Ar-H meta), 6.83 (d, 7.6 Hz, 4H, Ar-H meta), 6.69 (t, 7.6 Hz, 2H, Ar-H para), 6.65 (t, 7.4 Hz, 2H, Ar-H para), 4.36 (d, 13.4 Hz, 2H, $ArCH_2Ar$), 4.29 (d, 13.4 Hz, 2H, $ArCH_2Ar$), 3.86 (d, 4.75 Hz, 4H, OCH_2), 3.37 (d, 12.8 Hz, 1H, $ArCH_2Ar$), 3.36 (d, 12.8 Hz, 1H, $ArCH_2Ar$), 3.35 (d, 12.8 Hz, 1H, $ArCH_2Ar$), 3.34 (d, 12.8 Hz, 1H, $ArCH_2Ar$), 1.87 (m, 4H, $CHCH_2$), 1.73 (m, 6H, CH_2), 1.40 (m, 8H, CH_2), 1.06 (t, 7.2 Hz, 6H, CH_3), 0.92 (t, 6.9 Hz, 6H, CH_3).

^{13}C NMR (CDCl3): δ 153.5 (Ar ipso), 152.4 (Ar ipso), 133.0 (Ar ortho), 129.4 (Ar ortho), 128.6 (Ar meta), 128.3 (Ar meta), 125.4 (Ar para), 118.9 (Ar para), 79.2 (OCH_2), 40.9, 31.5, 29.8, 29.4, 23.9, 23.3 (CH_2), 14.4 (CH_3), 11.5 (CH_3).

Step b: Synthesis of BCC6

Chemical reaction:

1, 3-Di(2-ethylhexyloxy)calix[4]arene + PEG-diTs + Cs_2CO_3 → 1, 3-Di(2-ethylhexyloxy calix[4]arene -crown-6 + Cesium tosylate (s) + CO_2(g)

Procedure: 1,3-Di(2-ethylhexyloxy)calix[4]arene (648 g,1 mol) is dissolved in 175 L of CH_3CN and added to excess of Cs_2CO_3 (1300 g, 4 mol) and PEG-diTs (600 g, 1.1 mol) and refluxed at 85°C for 24 h under nitrogen atmosphere. CH_3CN is then removed under reduced pressure and the residue is dissolved in 40 L of DCM and washed with 10 L of 10% HCl. The organic phase is separated and dried with $MgSO_4$ and concentrated. To the residue, methanol is added to precipitate the product. Crystallization is done in methanol to obtained white shinning crystals

Yield: 579 g (68%)

MP: 102°C

Purity: 99.5% (GCMS)

MS (DI): *m/z* 851 $(M+H)^+$

Elemental analysis: Calculated for $C_{54}H_{74}O_8$, C: 76.20%, H: 8.76%; Found: C: 76.15%, H: 8.82%.

^{1}H NMR (CDCl3): δ 7.13 (d, 7.4 Hz, 4H, Ar-H meta), 7.02 (d, 7.4 Hz, 4H, Ar-H meta), 6.79 (t, 7.4 Hz, 2H, Ar-H para), 6.68 (t, 7.4 Hz, 2H, Ar-H para), 3.75 (s, 8H, ArCH2Ar), 3.72 (m, 8H, OCH_2), 3.61 (m, 8H, OCH_2), 3.62 (m, 4H, OCH_2), 3.56 (m, 2H, OCH_2), 3.50 (m, 2H, OCH_2), 1.79 (m, 2H, OCH_2CH), 1.39-1.21 (m, 16H, CH_2), 0.95 (t, 6.8 Hz, 6H, CH_3), 0.87 (t, 7.4 Hz, 6H, CH_3).

^{13}C NMR (CDCl3): δ 157.9 (Ar ipso), 156.6 (Ar ipso), 133.9 (Ar ortho), 133.6 (Ar ortho), 130.8 (Ar meta), 130.6 (Ar meta), 121.8 (Ar para), 75.8, 71.6, 71.2, 70.7, 70.6 (OCH_2), 40.8 (OCH_2CH), 37.4 ($ArCH_2Ar$), 30.6, 29.4, 23.3, 23.5 (CH_2), 14.3 (CH_3), 11.35 (CH_3).

Structure of BCC6 is shown in **Fig.4.4.**

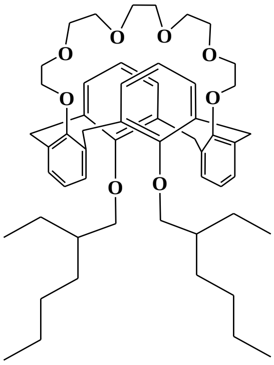


Fig.4.4: Structure of BCC6

4.2 Determination of solvent composition

CC6 is found to be insoluble in *n*-dodecane at room temperature. CC6 is polar in nature due to presence of etheric group of crown ether, therefore, to dissolve CC6, *n*-dodecane is made polar by adding IDA. CC6 is found to have good solubility in a mixture of IDA + *n*-dodecane. The solubility increases with increase in IDA content in the mixture. Extraction of Cs^+ with CC6 + IDA/*n*-dodecane solvent is carried out by contacting a ^{137}Cs tracer solution in 3.5 M nitric acid with varying concentration of solvent for 30 minutes. The variation of D_{Cs} as a function of IDA concentration at different CC6 molarities (0.01-0.03 M) is shown in **Fig.4.5.** Extraction of Cs^+ is found to increase with increase in concentration of IDA for all the concentrations of CC6. IDA, being a polar molecule helps in solvating the polar calix-crown-Cs^+ complex. Therefore, with increase in IDA concentration, D_{Cs} increases. From the results, it is clear that a higher concentration of IDA is more suitable for effective extraction of Cs. However, the extraction aspect of IDA with nitric acid needs to be considered while optimizing the concentration of IDA, as high nitric acid extraction by solvent is undesirable for stripping processes.

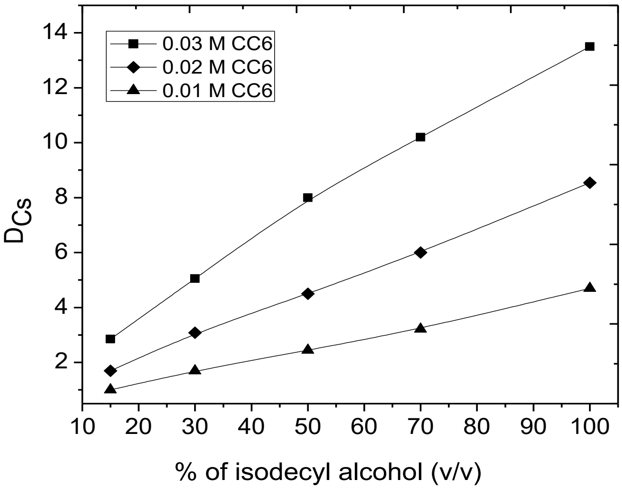


Fig.4.5: Variation in D_{Cs} with IDA concentration

Fig.4.6 shows the acid uptake by IDA/*n*-dodecane from 3.5 M HNO_3 solution at varying concentrations of IDA in the absence and presence of CC6 (0.3 M). As seen from the plot, both IDA and CC6 have finite extraction of nitric acid. Though, the acid uptake increases with increase in IDA concentration, but it does not contribute significantly to the acidity of the solvent. From Fig. 4.5, D_{Cs} of 5.3 is obtained for a solvent composition of 0.03 M CC6 dissolved in 30% IDA/*n*-dodecane, which is about 84% extraction of Cs^+ in a single contact. This is an adequate extraction in a single contact to obtain quantitative extraction in a multistage contactor. Thus, 0.03 M CC6 + 30% IDA/*n*-dodecane is considered as an appropriate solvent composition for extraction studies. This solvent has not shown any third phase formation on saturation with HLLW solution.

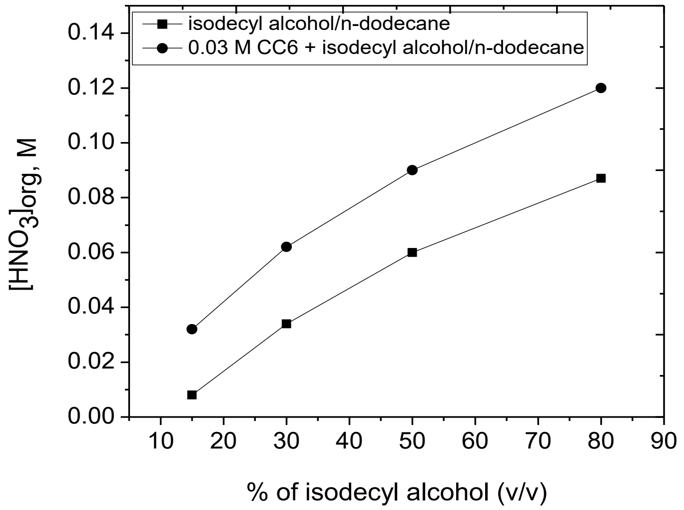


Fig.4.6: Extraction of HNO_3 at different concentrations of IDA

4.3 Extraction of Cs

Prior to evaluating the D_{Cs} with respect to various parameters, extraction equilibrium studies at various contact time were carried out. It showed that extraction equilibrium is attained within 5 minutes, thereafter, D_{Cs} remains constant for a given condition. Hence, for all the experiments contact time was kept as 10 minutes to ensure complete attainment of equilibrium. To determine the composition of extracted species, the dependence of D_{Cs} on initial concentrations of HNO_3, NO_3^- and CC6 has been studied. The relation between D_{Cs} and $HNO_{3\ (initial)}$ concentration for 0.03 M CC6 + 30% IDA/*n*-dodecane is shown in **Fig.4.7**. In lower region of nitric acid concentration up to 1 M, a very small increase in D_{Cs} is observed (D_{Cs} ~ 0.58). Afterwards, the increase is significant up to 6 M nitric acid (D_{Cs} ~ 6.6). With further increase in HNO_3 concentration, D_{Cs} is reduced (D_{Cs} ~ 6.2 at 6.5 M HNO_3). This indicates that nitric acid has a significant role during extraction. It is interesting to note that extraction of Cs is almost negligible at lower nitric acid concentrations (≤ 0.1 M). This property of very low extraction at lower acidity is used during stripping Cs with deionized water.

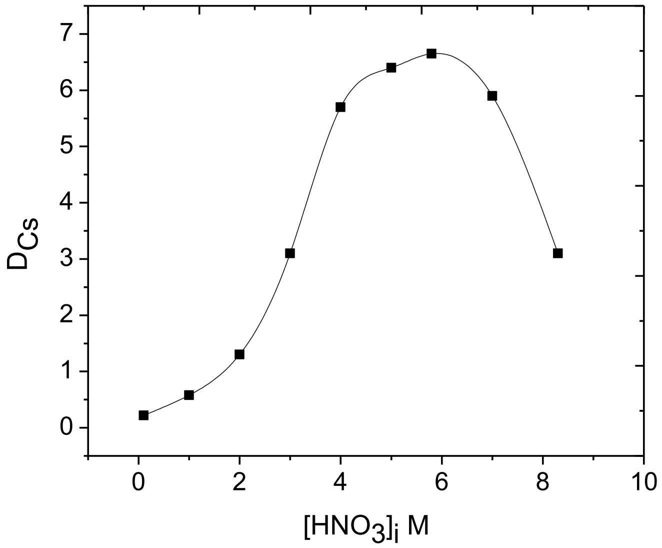


Fig.4.7: Extraction dependency of Cs on initial nitric acid concentration

The acid dependency on the extraction of Cs was determined from nitric acid solutions of constant nitrate concentrations or at fixed ionic strength of 4.0 M (H^+, Na^+) NO_3^- and shown in **Fig.4.8**. The observed slope of 0.976 ± 0.035 suggests the presence of one molecule of HNO_3 in the extracted complex. The increase in nitric acid concentration helps in the formation of organic soluble adduct, $Cs^+.CC6.HNO_3$, thus favouring Cs extraction. However, beyond 6 M nitric acid, decrease in D_{Cs} is observed. It could be attributed to the competitive extraction of nitric acid by CC6. The existence of nitric acid in the complex is likely due to hydrogen bonding between HNO_3 and etheric group of crown ether moiety of CC6.

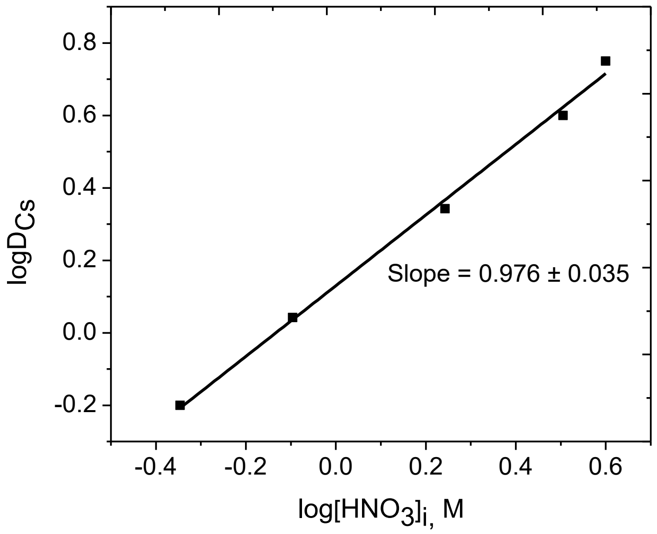


Fig.4.8: Extraction dependency of Cs on initial nitric acid concentration in a fixed ionic strength medium

It is also proved by measuring *D*(HNO_3) with increase in Cs concentration at a fixed HNO_3 concentration of 4 M. *D*(HNO_3) is found to increase with increase in Cs concentration, as given in **Table 4.1**, thus, conforming to the presence of HNO_3 in extracted metal complex.

Table 4.1: Dependence of *D* (HNO_3) on Cs concentration

[Cs] mM	*D*(HNO_3)
0	0.02
1	0.02
10	0.024
100	0.032

4.4 Stoichiometry of the extracted Cs complex

The interpretation of the stoichiometry of the extracted metal complex in solvent extraction is fairly given by the slope analysis method. The extractant dependency data for extraction of Cs from 3.5 M nitric acid at constant IDA concentration of 30 % (v/v) is shown in **Fig. 4.9**.

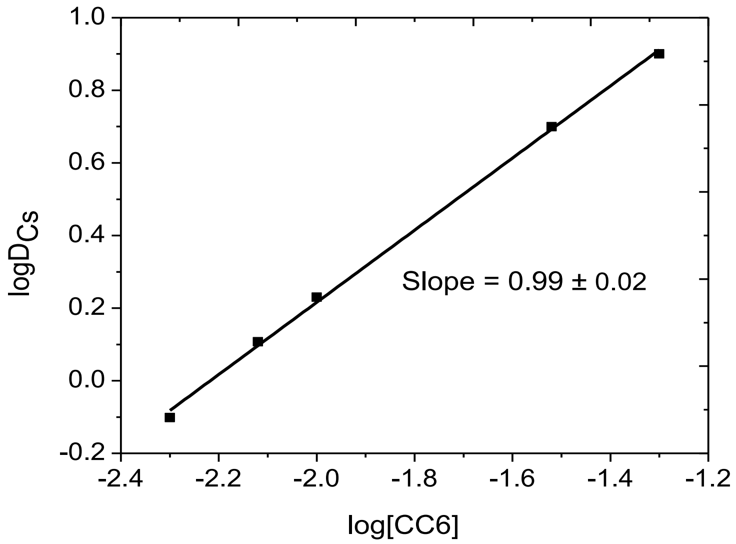


Fig.4.9: Extractant dependency of D_{Cs}

The plot is a straight line with a slope of 0.99 ± 0.02. This value indicates the participation of one molecule of CC6 in the extracted complex. Similar results are reported for calix-mono-crown by various authors [73,74]. Role of counter anion on the extraction mechanism is determined from the plots of D_{Cs} *vs.* $[NO_3^-]_{initi}$ at constant initial nitric acid concentration and is shown in **Fig.4.10**. No change is observed in D_{Cs} with increase in nitrate ion concentration. Contrary to extraction behaviour of most of the neutral extractants, this result suggests that nitrate ion doesn't participate in the Cs ion-CC6 complex.

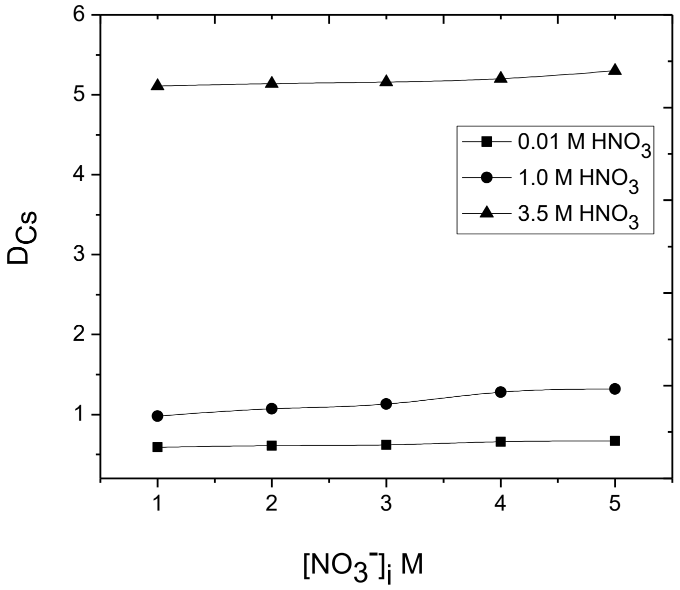


Fig.4.10: Extraction dependency of Cs on initial nitrate ion concentration at fixed nitric acid concentration

The stoichiometry of the complex indicated one Cs ion bonded with one molecule each of CC6 and HNO_3 to give a cationic complex of type $CsCC6^+.HNO_3$. This complex either remains ion paired with NO_3^- ion to give $CsCC6.HNO_3.NO_3$, or may remains dissociated from NO_3^- ion to give free ions $CsCC6^+.HNO_3$ and NO_3^-.

The mechanism of the extraction process may be thus represented as:

$$Cs^+_{aq} + NO_3^-{}_{aq} + CC6_{org} + HNO_3{}_{aq} \rightleftharpoons CsCC6.NO_3.HNO_3{}_{org} \qquad 4.1$$

$$Cs^+_{aq} + NO_3^-{}_{aq} + CC6_{org} + HNO_3{}_{aq} \rightleftharpoons CsCC6^+.HNO_3{}_{org} + NO_3^-{}_{org} \qquad 4.2$$

It is reported [110-111] that non-polar diluents with low dielectric constant such as paraffinic alkanes and aromatic hydrocarbons favour ion-pairing as shown in equation 4.1, whereas, in polar diluents like nitrobenzene, ion-pair dissociation is favourable following equation 4.2. The degree to which ion pair formed by Cs^+, BoB CalixC6 and NO_3^- dissociates to the free $CsBoBCalixC6^+$ and NO_3^- ions in the solvent on the basis of bulk dielectric constant and internuclear separation between the ionic centres was predicted by Bonnesen et al. [112]. It was also predicted that under ordinary conditions at constant temperature, the dissociation of ion pair increases with increase in bulk dielectric constant and internuclear distance. Since, in the present study the diluent used is *n*-dodecane with relatively high concentration (30% v/v) of polar IDA, it is expected that the diluent will have fairly high polarity to favour ion-dissociation mechanism as shown in equation 4.2. Also, due to hydrogen bonding and electron donating ability of IDA, it can stabilize the complex cation and anion by solvation, thereby, increasing internuclear separations and preventing their close contact. Thus, the anomalous behaviour of independency of D_{Cs} on NO_3^- ion concentration may be attributed to extraction mechanism following equation 4.2, where the ionic species are predominantly dissociated ions as $CsCC6^+.HNO_3$ and NO_3^- in the solvent. ESI-MS of the extract phase obtained on contacting with 0.1 M $CsNO_3$ dissolved in 3.5 M HNO_3, as shown in **Fig. 4.11,** confirms the presence of free solvated $CsCC6^+.HNO_3.IDA$ ion.

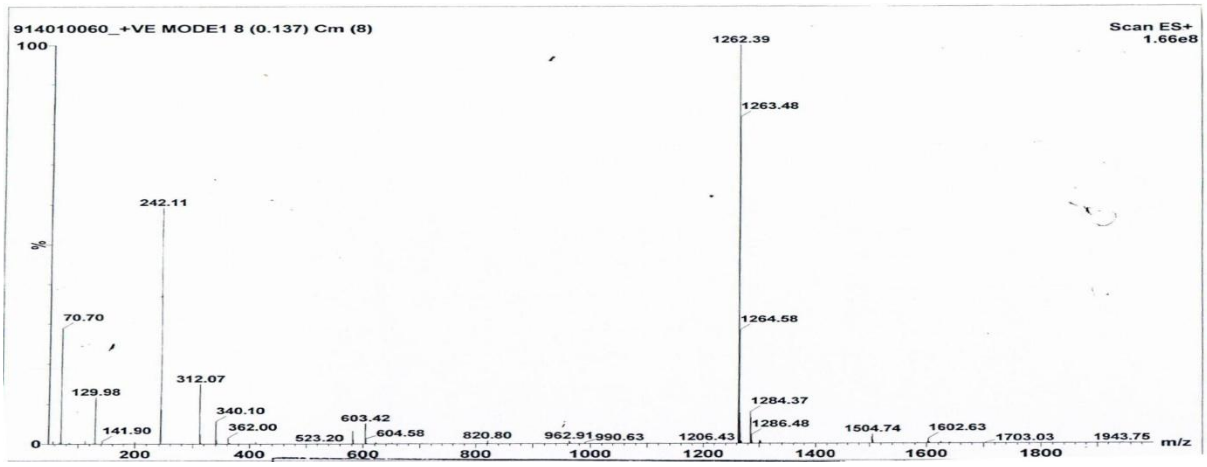


Fig.4.11: ESI-MS of extract phase, peak at *m/z* 1262 is assigned to [Cs.CC6.IDA.HNO_3. NO_2-H]$^+$

Extraction of Cs was estimated with increase in Cs ion concentration in the aqueous medium and the plot of D_{Cs} vs. Cs ion concentration is shown in **Fig.4.12**. D_{Cs} remains nearly constant up to 8 mM (1072 mg/L), thereafter, D_{Cs} decreases with increase in Cs ion concentration. Sharp decrease is observed when the Cs^+ in the aqueous phase was higher than 12 mM. At 90 mM Cs^+ concentration, D_{Cs} obtained is 0.55 which corresponds to extraction of about 0.032 M Cs^+ in the organic phase. This value remained unchanged even at higher concentration of

Cs^+ in the aqueous phase. The reason for this is the stoichiometry limit of 1:1 between Cs^+ and CC6.

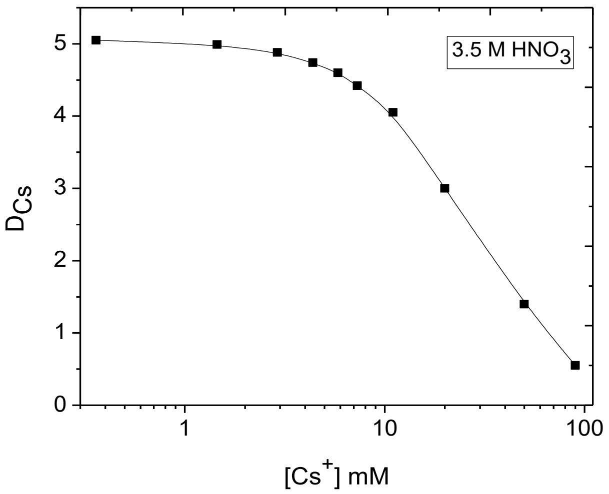


Fig.4.12: Effect of Cs^+ concentration in aqueous phase on D_{Cs}

4.5 Extraction of alkali metal ions

In HLLW, Cs^+ ion is present along with very high concentration of Na^+ and to a lesser concentration of K^+ and Rb^+ ions. Due to similarities in their chemical properties, these ions compete with Cs^+ and reduce the efficiency of Cs^+ extraction process. Therefore, the extraction of individual alkali metal ion dissolved in 3.5 M nitric acid has been tested with 0.03 M CC6 + 30% IDA/*n*-dodecane and the values are shown in **Table 4.2**. The results indicate very high selectivity for Cs extraction over Na and K ions and relatively low values for Rb ion ($SF_{Cs/Rb}$: 128).

Table 4.2: Extraction of alkali metal ions and selectivity of Cs extraction

Metal ions	D_M	SF (D_{Cs}/D_M)
Na	< 0.001	>5100
K	0.012	425
Rb	0.04	128
Cs	5.3	----

4.6 Batch extraction of Cs from HLLW

Radio-chemical composition of the HLLW used in this study is given in **Table 4.3**.

Table 4.3: Radio-chemical composition of HLLW

Gross β,γ = 5.4 Ci/L, Gross α = 3.66 mCi/L

^{137}Cs = 1.75 Ci/L (19.8 mg/L), ^{90}Sr = 1.5 Ci/L (9.8 mg/L), ^{106}Ru = 1.2 mCi/L, ^{125}Sb = 1.12 mCi/L, ^{144}Ce = 0.97 mCi/L, Sulphate = 10 g/L, TDS = 300 g/L, HNO_3 = 3.5 - 4.0 M.

Elements	Concentration (mg/L)	Elements	Concentration (mg/L)
Mo	130	Al	5750
Zr	86	La	300
Ca	1120	Nd	750
Ba	375	Y	60
Na	30,602	U	18
K	215	Pu	0.02
Cr	200	Am	0.9
Fe	7600		

The extraction behaviour of Cs and other metal ions present in HLLW solution was investigated using 0.03 M CC6 + 30% IDA/*n*-dodecane. The D of all the elements (D_M) and SF with respect to Cs^+ are tabulated in **Table 4.4**. The results show that D_{Cs} is much high compared to other elements, thus, indicating a very high selectivity for Cs^+ extraction over other elements. SF of > 1000 is obtained for Na, Sr, Ba, Al, Fe, Ln’s, U, Pu, Am and SF of >200 is obtained for other elements: Mo, Zr, Ru, K.

Stripping of the loaded organic was carried by deionized water at equal phase ratio. In first contact almost 85% of the Cs^+ is stripped. Total stripping is obtained in three more contacts with fresh deionized water.

Table 4.4: Extraction of metal ions from HLLW using 0.03 M CC6 + 30% IDA/*n*-dodecane

Elements	Concentration (mg/L)	D_M	SF (D_{Cs}/D_M)
Cs		5.2	---
Sr		1.0E-04	52000
Mo	130	2.0E-02	260
Zr	86	1.0E-02	520
Ru		2.0E-02	260
Sb		ND	very high
Ca	1120	1.0E-03	5200
Ba	375	5.0E-03	1040
Fe	7600	1.0E-03	5200
Na	30,602	1.0E-04	52000
K	215	1.0E-02	520
Al	5750	1.0E-04	52000
La	300	ND	very high
Ce		ND*	very high
Nd	750	ND	very high
Y	60	1.0E-03	5200
Cr	200	ND	
U	18	5.0E-03	1040
Pu	0.02	1.0E-03	5200
Am	0.9	1.0E-03	5200

*ND: Not detected

4.7 Stability test of 0.03 M CC6 + 30% IDA/*n*-dodecane solvent

The present studies have shown that CC6 dissolved in IDA and *n*-dodecane mixture is a promising extractant for Cs separation from HLLW. However, during the contact with HLLW, solvent will be exposed to high radiation and acidity for prolonged period. Therefore, it is of considerable interest to investigate the influence of these parameters on the performance of the solvent. This was assessed by measuring the extraction and stripping efficiencies of the process solvent obtained after hydrolysis and radiolysis. Hydrolysis was carried out by continuous stirring of equal volumes of solvent and 3.5 M nitric acid at room temperature for three months. After hydrolysis, the organic sample was tested for D_{Cs} at 3.5 M HNO_3 (extraction condition) and at 0.01 M HNO_3 (stripping condition). No change is observed in extraction behaviour with time at both the acidities, indicating that solvent is hydrolytically stable for a period equivalent to many cycles of continuous operation of the process in nitric acid. For radiolytic degradation studies, the solvent in contact with equal volume of 3.5 M nitric acid was irradiated with ^{60}Co source at a dose rate of 56 Gy/min up to cumulative dose of 0.6 MGy. The irradiated solvent after separating it from nitric acid was tested for extraction and stripping of Cs^+ and the results are presented in **Table 4.5**.

Table 4.5: Extraction and stripping behaviour of irradiated 0.03 M CC6 + 30% IDA/*n*-dodecane solvent

Absorbed dose (MGy)	% Extraction (D_{Cs})	% Stripping*
0	84 (5.25)	99.5
0.1	83 (4.88)	99.5
0.2	80 (4.0)	98
0.4	77.8 (3.5)	96
0.6	72 (2.57)	94.5

* Results after four contacts.

No appreciable change is noticed in the extraction of Cs^+, up to 0.2 MGy. Thereafter, there is a slight decline in the extraction. However, the solvent retains its high extraction property (from 84% to 72%) up to an absorbed dose of 0.6 MGy. At 72% extraction, D_{Cs} observed is 2.57. On the basis of 1:1 molar ratio of Cs and CC6 complex, corresponding concentration of CC6 at D_{Cs} of 2.57 is approximately 0.015 M, i.e. half of initial concentration of CC6 is remaining at absorbed dose of 0.6 MGy. Thus, indicating degradation of about 50% up to an absorbed dose of 0.6 MGy. Similar results were noticed for diisopropyloxycalix[4]arene-crown-6 dissolved NPOE [86]. The stripping of the loaded organic at different absorbed dose has been carried by giving four successive contacts with 0.01 M nitric acid solution. It is clear that radiolysis does not affect the stripping efficiency much. Stripping of 98% is obtained up to 0.2 MGy. Thereafter, 94.5% stripping is observed for 0.6 MGy irradiated solvent. It may be noted that the dose employed in the present study is much higher than the expected dose (few kGy/year) which would have been received by the solvent in contact with actual HLLW [113,114]. This shows that the solvent is sufficiently stable to radiolysis. Though, irradiation of the solvent up to 0.6 MGy resulted in a limited degradation, an attempt was also made to calculate the degree of degradation and radiation chemical yield of the solvent. Degree of degradation is calculated by using Mincher and Curry [115] equation.

$$\ln C_{irr} = \ln C_0 - k.d \qquad 4.3$$

Where C_{irr} is the molar concentration of extractant in the solvent after irradiation, C_0 is the initial concentration of extractant before irradiation. Dose absorbed by the sample is denoted by ‘d’ and *k* is the dose constant. The absolute value of dose constant indicates the degree of degradation by radiation and is obtained by slopes of the plots between ln C_{irr} *vs*. ln dose. Solvents with fixed concentration of CC6 and varying concentration of IDA & *n*-dodecane in contact with 3.5 M HNO_3 was irradiated with γ-ray. The decay curve obtained by plotting residual concentration of CC6 represented as $[CC6]_{irr}$ against the absorbed dose is given in

Fig.4.13. From the plot, it is evident that the degradation of CC6 due to irradiation occurs more when the IDA concentration in the solvent is less.

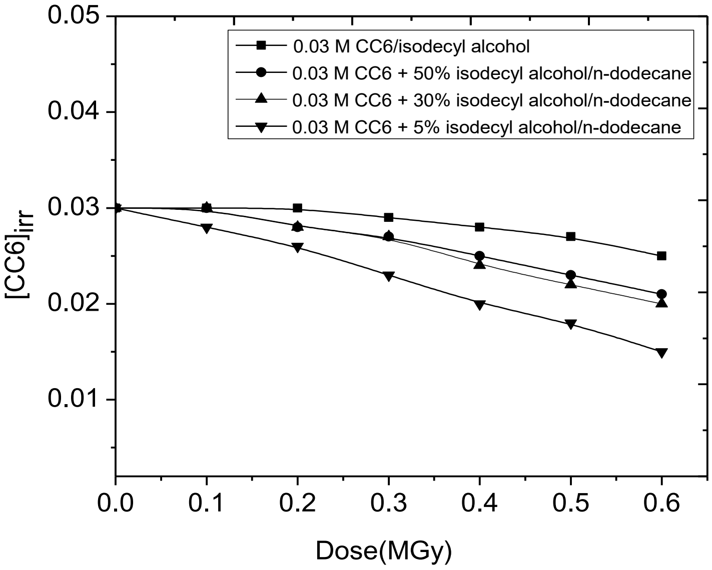


Fig.4.13: Degradation curve of CC6 as a function of absorbed dose

A similar pattern is observed in case of radiolysis of TEHDGA/IDA/*n*-dodecane solvent, where IDA has shown to shield TEHDGA from radiolytic degradation [116]. It is therefore, considered that IDA may shield CC6 from radiolysis while *n*-dodecane has a sensitization effect on the radiolysis of CC6. This effect may be attributed to the presence of hydroxyl group of IDA which helps to stabilize the reactive free radicals and thus making them less available for degradation of CC6. However, no such effect is seen with *n*-dodecane due to absence of any free radical stabilization group. Degradation of CC6 molecules can be quantified by calculating its radiation chemical yield ‘G’ which is defined as the number of molecules decreased by absorption of 100 eV energy and represented by the following equation:

$$C_{irr} = C_0 \exp(-1.04 \times 10^{-10} GMd) \qquad 4.4$$

Where, M is the molecular weight of CC6 and d is the dose (Gy) absorbed by CC6. The G value obtained from Fig. 4.13 is found to increase with increase in content of *n*-dodecane in the solvent, indicating more degradation of CC6 at higher *n*-dodecane content.

The G values obtained are 3.5, 6.8, 7.7 and 13 (error ±1) for CC6 dissolved in IDA, in 50% IDA/*n*-dodecane, in 30% IDA/*n*-dodecane and in 5% IDA/*n*-dodecane respectively. Under similar radiolysis conditions G value for CC6 is less than the reported value of TEHDGA (G value for neat TEHDGA is 8.65±1.0), indicating high stability of CC6 towards radiolysis compared to TEHDGA [116]. This is due to stabilization of reactive free radicals or electrons by arene moieties of CC6 which are absent in the non-aromatic TEHDGA molecule.

4.8 Laboratory scale counter-current mixer-settler studies

Counter-current mixer-settler runs were carried out to examine functional efficacy of the solvent and to optimize flow sheet parameters for maximum recovery of Cs at high purity from HLLW. Taking into account of reasonably high D_{Cs}, good stripping with deionized water, four stages each of extraction and stripping was considered for generating extraction and stripping data. Considering very low *D*s' of other elements, only two stage of scrubbing unit was employed. The extraction, scrubbing and stripping operations were carried out in continuous mode. Extraction was performed at an O/A ratio of 1:4. The residence time of 5 minutes was maintained in the mixer. Scrubbing of loaded organic phase was then carried out with 3.5 M nitric acid at an O/A ratio of 3:1. The scrub raffinate was mixed with feed stream in order to detain the loss of ^{137}Cs during scrubbing. Stripping of the extract phase was carried with deionized water at an O/A of 1:1. Stage wise analysis of ^{137}Cs activity in both the phases was carried out periodically to ascertain the mass balance. The steady state was achieved in 4 to 5 h. A complete cycle was lasted for about 12 h. No third phase formation was observed and exit streams had negligible amount of entrained phases. At the end of runs, exit samples of aqueous and organic phases of settler units were drawn for analysis.

Flowsheet of mixer-settler run is given in **Fig.4.14.** Concentration profile of ^{137}Cs in cpm/mL (counts per minute per mL after suitable dilution) across the extraction, scrubbing and stripping stages is shown in **Fig.4.15**. Since the extraction of other elements was very low, their concentrations were analyzed only in the final strip aqueous solution. The results show a good material balance with 99.5% extraction of ^{137}Cs from HLLW solution. Four stages of stripping is found adequate to strip Cs from loaded organic. The discharged solvent contained less than 0.5% Cs. The total concentration of impurities in the Cs strip solution is found to be less than 1.0 mg/L. The nitric acid concentration in the organic phase increased from 0.064 to 0.09 M in consecutive extraction stages and remained constant in the scrubbing stages. In the exit stage of stripping section, it is reduced to less than 0.01 M. The trial runs were repeated ten times with recycled solvent. The efficiency of the solvent is retained in all the runs.

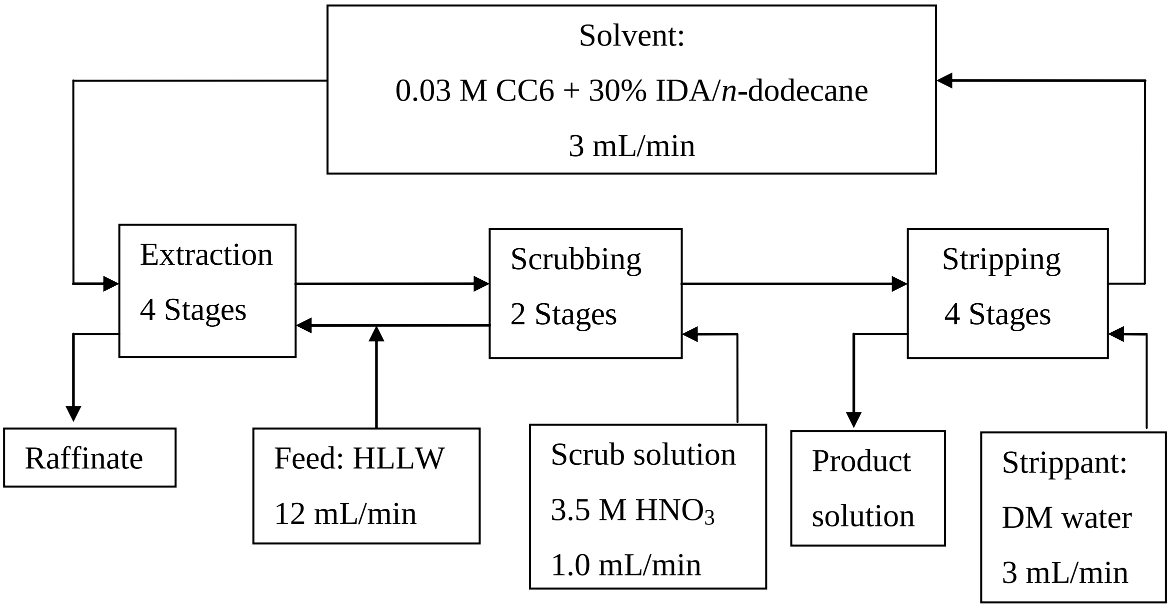


Fig.4.14: Flowsheet of mixer-settler run

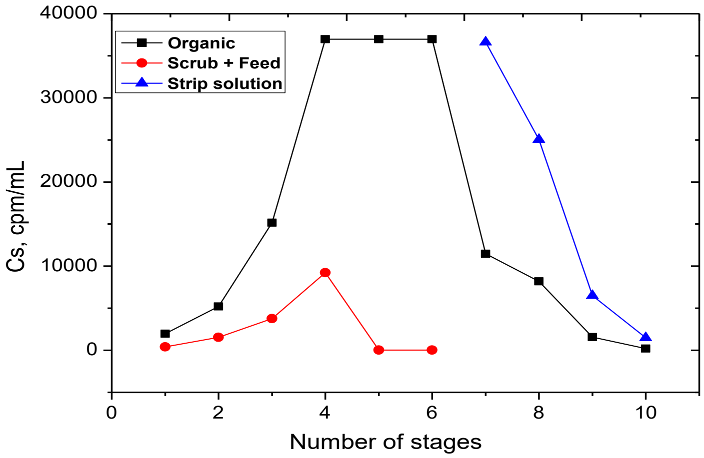


Fig.4.15: Concentration profile of ^{137}Cs during mixer-settler runs. Stages: 1-4 Extraction; 5-6 Scrubbing; 7-10 Stripping

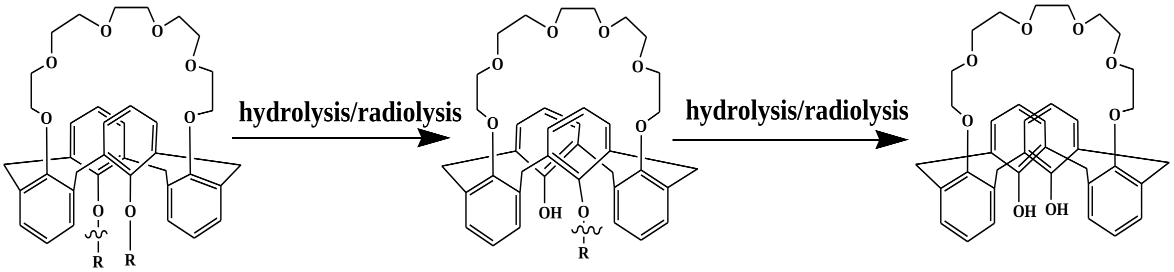
4.9 Degradation and regeneration of solvent

Hydrolysis and radiolysis carried out under standard/simulated conditions gives qualitative idea of stability of the solvent. However, a real situation is different from the simulated systems. When the solvent is exposed to HLLW having all α, β, γ emitting radionuclides and in hydrolytic medium of high nitric acid concentration, hydrolysis and radiolysis both simultaneously takes place. A test run at laboratory scale in counter-current mixer-settler for continuous 80 cycles of operation with HLLW was carried out to evaluate the degradation behaviour of the solvent. It is observed that after 60 continuous cycles, ^{137}Cs activity is retained by the solvent which could not be stripped. This activity is found to increase with further increase in number of cycles. The retention of ^{137}Cs is an indication of solvent degradation. The solvent was then separated and tested for its extraction of Cs at different acidity. No change is observed during extraction at higher acidities (> 2 M nitric acid), whereas, at stripping conditions i.e at lower acidities, the solvent shows good amount of extraction. D_{Cs} as shown in **Table 4.6**, is found to increase with increase in pH of the aqueous solution, thus, indicating formation of acidic phenolic impurities during degradation. The degradation scheme is shown in **Fig.4.16**.

Table 4.6: D_{Cs} of degraded solvent at different pH

Aqueous feed conditions	pH of solution	D_{Cs}
4 M HNO_3	----	4.5
0.01 HNO_3	2.1	1.6
1.0 M Na_2CO_3	12.2	2.86
1.0 M NaOH	13.8	5.65

Basic alumina is a known sorbent for these kinds of acidic impurities [116]. Therefore, the spent solvent was passed through a bed of basic alumina to regenerate the solvent. The bed volume capacity of basic alumina is found to be in the range of 50 to 100 depending on the extent of degradation. For the spent solvent obtained after 60 cycles of continuous operation, 100 mL (35 g) of basic alumina is able to regenerate 5 L of spent solvent to a level of recyclable purity thus giving a bed volume capacity of 50.



CC6

Phenolic degradation products

Fig.4.16: Schematic diagram for the gradation of CC6

4.10 Extraction studies with BCC6

BCC6 constituted as 0.03 M BCC6 + 30%IDA/*n*-dodecane was tested for extraction of metal ions from HLLW. The result shows that D_{Cs} for BCC6 remained same as that of CC6, while significant reduction is observed in the extraction of most of the other metal ions/fission products particularly Zr, Mo and U thus, giving the product solution more pure in Cs. As crown ether ring and size of the annulus kept unchanged, no change in the extraction of Cs is observed. While, branching in octyl chain prevents the approach of competitive ions by increasing the steric hindrance at complexation site. This has resulted in reduction in the extraction of undesirable elements leading to more selective extraction of Cs from HLLW. **Table 4.7** compares *D*s' for metal ions from HLLW elements for BCC6 and CC6.

Table 4.7: *D*s' and SF for HLLW metal ions for BCC6 and CC6

	BCC6		CC6	
	D_M	SF	D_M	SF
Cs	5.1		5.3	
Na	ND	---	ND	---
K	10^{-2}	510	10^{-2}	530
Ca	10^{-3}	5100	10^{-3}	5300
Sr	10^{-4}	51000	10^{-4}	53000
Ba	10^{-3}	5100	$5x10^{-3}$	1060
Mo	$2x10^{-3}$	2550	$2x10^{-2}$	265
Fe	10^{-3}	5100	10^{-3}	5300
Ru	10^{-2}	510	$2x10^{-2}$	265
Zr	10^{-3}	5100	10^{-2}	530
Ln's	ND	----	ND	----
U	10^{-3}	5100	$5x10^{-3}$	1060
Pu	10^{-3}	5100	10^{-3}	5300
Am	10^{-3}	5100	10^{-3}	5300

4.11 Conclusions

Modification in synthesis steps leads to an improvement in overall yield of CC6. A mixture of IDA and *n*-dodecane is found to be a suitable diluent for CC6 and BCC6. The process solvent is constituted as 0.03 M CC6 + 30% IDA/*n*-dodecane for efficient extraction of Cs^+. Stripping of the extracted Cs^+ is achieved by deionized water. Stoichiometry of the extracted complex determined by slope analysis method reveals 1:1:1 molar ratio for Cs^+, CC6 and HNO_3. The extraction mechanism shows that the extracted species are in dissociated form as $CsCC6^+.HNO_3$ and NO_3^- and are solvated by IDA. ESI-MS of the extract phase confirms the presence of free solvated $CsCC6^+.HNO_3.IDA$ ion. Extraction studies with HLLW show high selectivity for Cs over other elements. SF of more than 1000 is obtained for Na, Sr, Ba, Al, Fe, Ln's, U, Pu, Am and more than 200 for Mo, Zr, Ru, K.

99.5% recovery of ^{137}Cs from HLLW is obtained with laboratory scale mixer-settler unit having 4 stages of extraction, 2 stages of scrubbing and 4 stages of stripping. Radiolysis of the solvent up to an absorbed dose of 0.6 MGy produces essentially no deterioration in performance. Degradation products formed during continuous operation with HLLW are observed to be phenolic in nature. Regeneration of the degraded solvent is achieved by treatment with basic alumina. Branching in octyl groups of CC6 has resulted in more selective extraction of Cs compared to un-branched CC6. Branching has resulted in significant reduction in the extraction of Zr, Mo and U.

CHAPTER 5

Process for Separation of Sr from HLLW using 4,4´(5´)-[di-*tert*-butyldicyclohexano]-18-crown-6 + IDA/*n*-dodecane solvent

SREX [60] process employing DtBuCH18C6 dissolved in a mixture of 1.2 M TBP and iso-paraffinic hydrocarbon Isopar-L is one of the best known process for selective separation of Sr from HLLW. Use of TBP, however, results in significant extraction of U, Pu and Zr. This is undesirable while separating high purity ^{90}Sr from HLLW solution. In view of it, a new diluent, mixture of *n*-dodecane and IDA, a non-extracting diluent for DtBuCH18C6 is evaluated for extraction of Sr from HLLW.

Effect of nitric acid, nitrate ion and extractant concentration on Sr extraction is discussed. Nature of the extracted species, stoichiometry of extract, mechanism of extraction, selectivity of Sr extraction in the presence of high concentration of interfering elements and stripping conditions have been studied. Result of the batch extraction of Sr from HLLW with high salt content is discussed. Degradation of the solvent with γ-ray irradiation using ^{60}Co source has been studied. Recovery and recyclability of the solvent is also established.

5.1 Synthesis

Synthesis route of DtBuDB18C6 is also judiciously devised to obtain consistently improved yield of desired isomer. Synthesis of DtBuCH18C6 involves two steps (i) synthesis of precursor, 4,4´(5´)-[di-*tert*-butyldibenzo]-18-crown-6 (DtBuDB18C6) and (ii) synthesis of DtBuCH18C6 by catalytic hydrogenation of DtBuDB18C6.

5.1.1 Synthesis of DtBuDB18C6

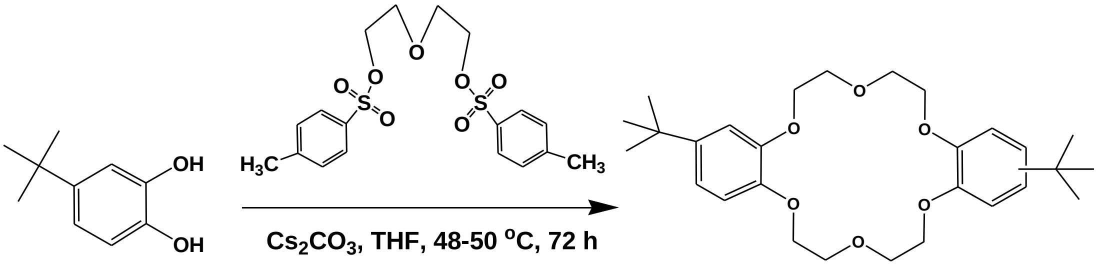
DtBuDB18C6 is synthesized according to reported method of Jun Fan et al. [117]. The reactants, *p*-*tert*-butylcatechol, diethylene glycol ditosylate and Cs_2CO_3 as template are taken in molar ratios of 1.0:1.1:3.0 in THF as reaction medium and stirred at 48-50°C for 72 h. The synthesis scheme is shown in **Fig. 5.1**. The crude product is then purified with basic alumina and crystallized in *n*-hexane. Repeated re-crystallization is done to ensure complete absence of any phenolic or acidic impurities.

Yield: 94 g (20%)

MP: 110-120°C

Purity: 99.5% by GCMS

MS (DI): *m/z* 472 $(M)^+$



tert-Butyl Catechol

DtBuDB18C6

Fig.5.1: Synthesis scheme of DtBuDB18C6

Elemental analysis: Calculated for $C_{28}H_{40}O_6$, C: 71.2%, H: 8.5%; Found: C, 71.15%, H, 8.81%.

^{1}H NMR ($CDCl_3$): δ 6.70–6.98 (6H, m, ArH), δ 3.82-4.26 (16H, m, CH_2OCH_2), δ 0.95-1.42 (18H, s, $C(CH_3)_3$).

5.1.2 Synthesis of DtBuCH18C6

The reported method for synthesis of DtBuCH18C6 is by catalytic hydrogenation of 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 in presence of 5% Rh on activated γ-alumina [118]. Hydrogenation results in formation of various isomers of DtBuCH18C6 having different affinity for Sr. The isomer *cis*-*syn*-*cis* is known to be most effective for extraction of Sr**.** In order to improve the yield of *cis*-*syn*-*cis* isomer in the product, synthesis route is carried out in the presence of the reaction accelerator-isovaleric acid at 65-70°C. Isovaleric acid is a weak (pK_a=4.77), hydrophobic carboxylic acid functions as an accelerator for the reaction by increasing the active sites on catalyst which favours isomeric distribution towards *cis-syn-cis* of the product [119]. As the reaction is catalytic hydrogenation, all the reactants/starting chemicals are made anhydrous prior to hydrogenation. The reaction mixture containing solution of DtBuDB18C6 (substrate) in minimum amount of toluene, reaction medium-butanol, catalyst-5% Rh on activated γ-alumina and reaction accelerator-isovelaric acid are taken in a weight ratio of 1:8:0.1:0.1. The content are hydrogenated in the temperature range of 65-70°C at a H_2 pressure of 500 psi. As the reaction proceeds, the pressure drops is observed. H_2 is added to maintain the pressure to about 500-600 psi for 24 hours to ensure complete hydrogenation of substrate. A typical batch consists of 50 g of substrate. Synthesis scheme of DtBuCH18C6 is shown in **Fig.5.2**. Determination of absolute purity of the *cis-syn-cis* isomer is found to be difficult by instrumental methods. The existing procedure to determine D_{Sr} under standard conditions of 1 M HNO_3 and 0.1 M DtBuCH18C6/1-octanol is reported by Horwitz et al. [55] and also mentioned that the value should be ≥ 2.5. The synthesised products were tested and the D_{Sr} is > 2.5 for all the batches.

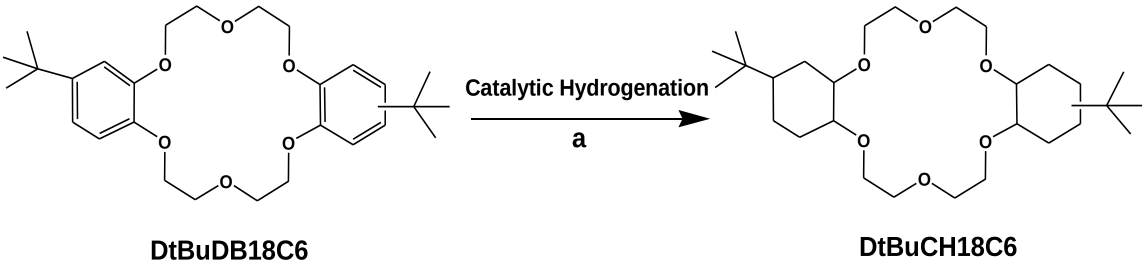


Fig.5.2: Synthesis scheme of DtBuCH18C6

Reagent and conditions: (a) Butanol, 5% Rh on activated γ-alumina, isovaleric acid, H_2 gas, 65-70°C, 500-600 psi, 24 h

5.2 Determination of solvent composition

DtBuCH18C6 dissolved in *n*-dodecane does not show appreciable extraction of Sr^{2+} from 4 M nitric acid. As reported by Horwitz et al. [55], extraction of hydrated nitrate ions and its solvation by the diluent is necessary for extraction of Sr^{2+} by DtBuCH18C6. Thus, in case of DtBuCH18C6 dissolved only in *n*-dodecane diluent, there is almost negligible extraction of hydrated nitrate ions is observed due to high hydrophobic nature of *n*-dodecane. Adding an oxygenated aliphatic polar diluent like alcohols along with *n*-dodecane facilitates the solubility of water in organic phase resulting in extraction of hydrated nitrate ions and Sr^{2+} by DtBuCH18C6. Here, IDA is added to DtBuCH18C6/*n*-dodecane to facilitate the extraction of Sr^{2+}. DtBuCH18C6 is found to have good solubility in IDA + *n*-dodecane mixture. With the increase in IDA content in the mixture the extraction of Sr^{2+} increases. Variation of D_{Sr} with IDA concentration at different DtBuCH18C6 molarities (0.05-0.15 M) is shown in **Fig.5.3**.

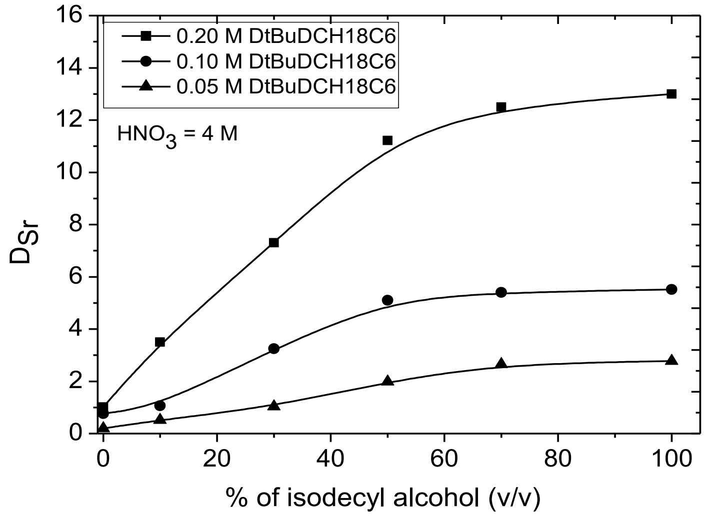


Fig.5.3: Variation of D_{Sr} with IDA concentration.

Extraction of Sr^{2+} was low when DtBuCH18C6 was dissolved only in *n*-dodecane. Extraction was found to increase with addition of IDA to the solvent for all the concentrations of DtBuCH18C6. From the results, it is clear that a higher concentration of IDA is more suitable for effective extraction of Sr^{2+}. However, at IDA content above 50 % (v/v), D_{Sr} remains unchanged. This may be due to increase in nitric acid uptake with increase in IDA content of the solvent [120] which in turn interacts with DtBuCH18C6 and results in saturating the extraction capacity for Sr^{2+}. As seen from Fig. 5.3, 0.1 M DtBuDCH18C6 + 50% IDA/*n*-dodecane gives a D_{Sr} of 5.1, which is about 84% extraction of Sr^{2+} in a single contact. This is an adequate extraction in a single contact to obtain quantitative extraction in a multistage contactor. Therefore, 0.1 M DtBuDCH18C6 + 50% IDA/*n*-dodecane is considered as appropriate process solvent for further studies. Kinetics of extraction shows that equilibrium is achieved in 5 minutes. Hence, for all the experiments contact time was kept as 10 minutes to ensure complete attainment of equilibrium.

5.3 Extraction of Sr

Extraction of Sr^{2+} with 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane was evaluated with respect to the initial concentrations of HNO_3, NO_3^- and DtBuCH18C6. The results of D_{Sr} dependency on HNO_3 (initial) concentration for 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane is shown in **Fig.5.4**.

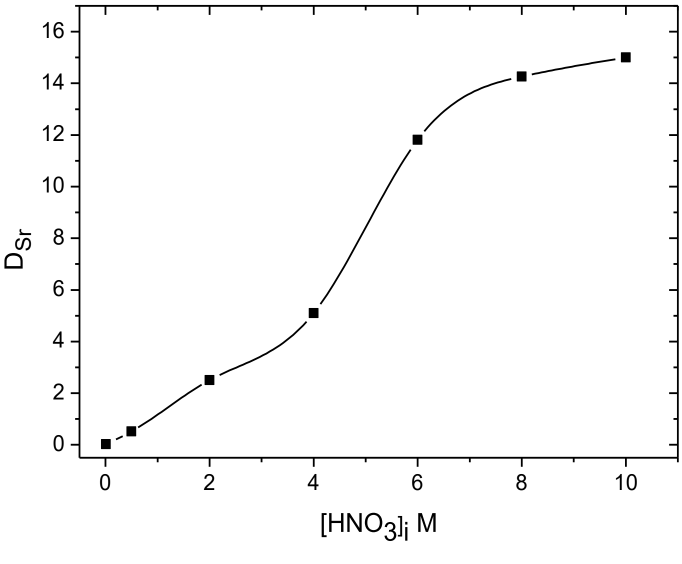


Fig.5.4: Extraction dependency of Sr on initial nitric acid concentration

A very small increase in D_{Sr} is observed when concentration of nitric acid is low. At 0.5 M nitric acid, D_{Sr} is 0.52. The steep increase is observed up to 8 M nitric acid (D_{Sr} = 14.26) and then remains constant with further increase in nitric acid concentration without any decline in

D$_{Sr}$. The absence of levelling-off of *D*$_{Sr}$ at higher acidities can be explained by solvation of extracted nitric acid by IDA and thus preventing its interaction with crown ether. Participation of nitric acid in extracted complex formation is determined by log-log plot of *D*$_{Sr}$ with initial HNO_3 concentration. As shown in **Fig.5.5,** at constant nitrate concentrations having fixed ionic strength of 4.0 M (H^+ + Na^+) NO_3^-, the observed slope of 0.947 ± 0.02 suggests the presence of one mole of HNO_3 in the extracted complex. The increase in nitric acid concentration favours the formation of organic soluble Sr^{2+}.DtBuCH18C6.HNO_3 adduct, thus, resulting in increase in *D*$_{Sr}$. Extraction of Sr^{2+} is almost negligible at lower nitric acid concentrations (≤ 0.1 M). Therefore, this important property is used for stripping Sr^{2+} from organic phase with deionized water.

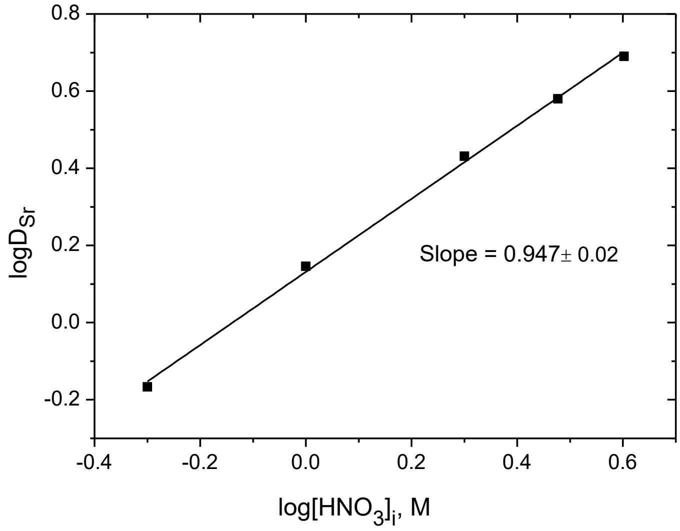


Fig.5.5: Extraction dependency of Sr on initial nitric acid concentration in a fixed ionic strength medium

Fig. 5.6 shows the extractant dependency on *D*$_{Sr}$ at 4.0 M nitric acid. The obtained slope of log-log plot is 1.21 ± 0.017. This value indicates 1:1 combining ratio of Sr^{2+} and crown ether. Similar results were also reported for DtBuCH18C6 dissolved in 1-octanol or 1.2 M TBP-Isopar L diluents [56,61]. Role of counter anion on the extraction mechanism at constant nitric acid concentration is determined from the plots of D_{Sr} vs. $[NO_3^-]_{initial}$ and shown in **Fig.5.7**.

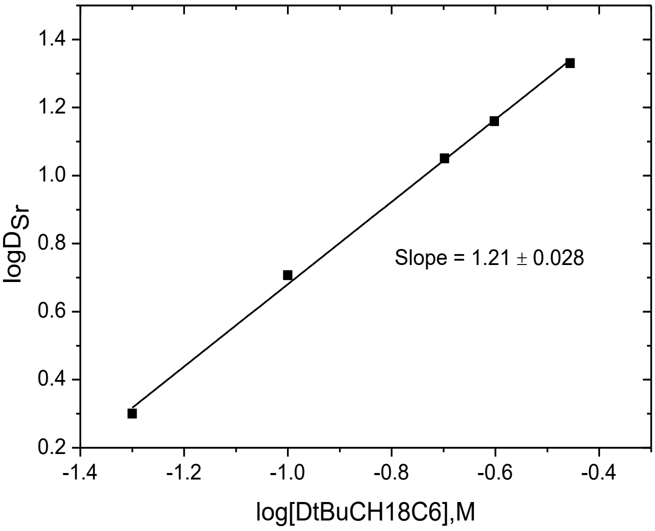


Fig.5.6: Extractant dependency on D_{Sr}

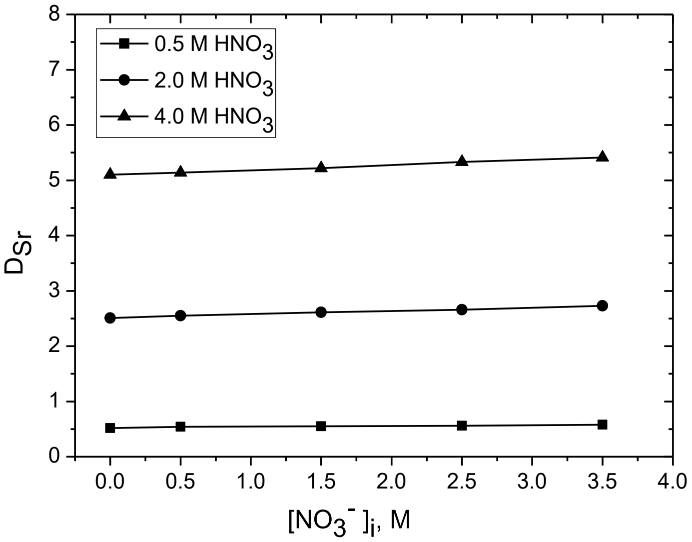


Fig.5.7: Extraction dependency of Sr on initial nitrate ion (contributed only from $NaNO_3$) concentration at fixed nitric acid concentration

Results show no change in D_{Sr} with increase in nitrate ion concentration. Contrary to extraction behaviour of most of the neutral extractants, this result also suggests that nitrate ion does not participate in the Sr^{2+}-crown ether complex formation. A quantitative explanation to this anomalous behaviour is quite difficult considering the complexity of the biphasic solution equilibrium in these kinds of systems. However, a reasonable explanation can be given by the nature of Sr^{2+}-crown ether complex formed and the polarity of organic medium. Slope analysis of the extractant and acid dependency plots indicates that one Sr^{2+} ion bonded with one molecule each of crown ether and HNO_3 forms a cationic complex of type Sr^{2+}.DtBuCH18C6.HNO_3. This complex either remains ion paired with NO_3^- ion to give Sr.DtBuCH18C6.HNO_3.2NO_3, or may remains dissociated from NO_3^- ion to generate free ions Sr^{2+}.DtBuCH18C6.HNO_3 and 2NO_3^-.

The extraction process may be thus represented as:

$$Sr^{2+}_{aq} + 2NO_{3\,aq}^{-} + DtBuCH18C6_{org} + HNO_{3\,aq} \rightleftharpoons Sr.DtBuCH18C6.HNO_3.2NO_{3org} \quad (5.1)$$

$$Sr^{2+}_{aq} + 2NO_{3\,aq}^{-} + DtBuCH18C6_{org} + HNO_{3aq} \rightleftharpoons Sr^{2+}.DtBuCH18C6.HNO_{3org} + 2NO_{3\,org}^{-} \quad (5.2)$$

Ion-pairing as shown in equation 5.1 is favoured by non-polar diluents with low dielectric constant such as paraffinic hydrocarbons, whereas, ion-pair dissociation (equation 5.2) is favoured in polar diluents like nitrobenzene. In the present case, the diluent used is 50% IDA + *n*-dodecane, the high concentration of polar IDA is expected to increase dielectric constant of the solvent which can predominantly support ion-dissociation extraction mechanism. Also, due to hydrogen bonding and electron pair donating ability of IDA, it can stabilize the cation and anion by solvation, thereby, increasing internuclear separations and preventing their close contact. Thus, the anomalous behaviour of D_{Sr} not depending on NO_3^- ion concentration may be attributed to extraction mechanism following equation 5.2, where NO_3^- ion is not a part of the Sr^{2+}-crown ether complex. Variation of D_{Sr} with concentration of Sr^{2+} ion present in 4 M nitric acid is shown in **Fig.5.8**.

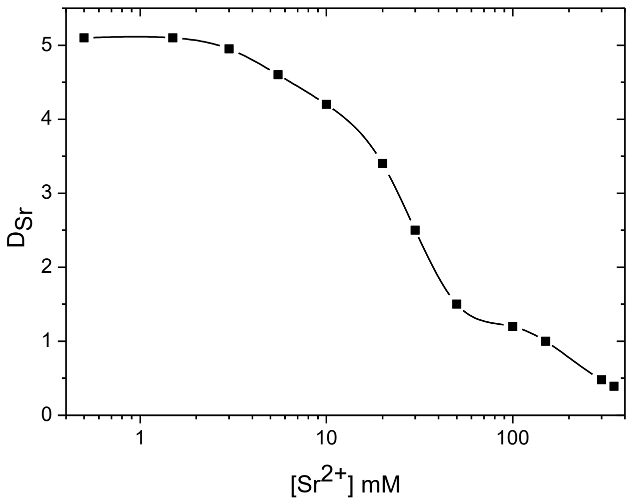


Fig.5.8: Dependency of D_{Sr} on Sr^{2+} concentration

D_{Sr} remains nearly constant up to 3.0 mM (270 mg/L) of Sr^{2+} concentration. Thereafter, D_{Sr} decreases with increase in Sr^{2+} concentration and sharp decrease is observed when the Sr^{2+} in the aqueous phase was higher than 30 mM. At 350 mM, D_{Sr} obtained is 0.39 which corresponds to extraction of about 0.098 M Sr^{2+} in the organic phase. This value of Sr^{2+} in the extract phase remains unchanged even at higher concentrations of Sr^{2+} in the aqueous phase. The reason for this is the stoichiometry limit of 1:1 between Sr and crown ether.

5.4 Extraction of group II elements

Selectivity of Sr extraction from other group II elements present in HLLW is important in view of recovery of ^{90}Sr in high purity. Ca^{2+} and Ba^{2+} are present in very high concentration compared to Sr^{2+} in the HLLW as indicated in Table 4.3 (1120 and 375 mg/L respectively). Their extraction in 4 M nitric acid was tested with 0.1 M DtBuCH18C6 + 50% isodecyl alcohol/*n*-dodecane and the *D* values obtained are 0.015 for Ca^{2+} and 0.2 for Ba^{2+}. A high selectivity of Sr extraction over Ca is observed but relatively lower for Ba. Extraction of Sr was measured with increase in concentration of Ca. Results indicate no change in D_{Sr} and high selectivity of Sr is retained over Ca extraction as given in **Table 5. 1**

Table 5.1: Extraction of Sr in the presence of Ca

$[Ca^{2+}]$ mg/L	D_{Ca}	D_{Sr}	SF (D_{Sr}/D_{Ca})
0	-----	5.1	-----
100	0.015	5.09	339
250	0.012	5.07	422
500	0.012	5.06	421.6
1500	0.01	5.06	506
2500	0.01	5.06	506

5.5 Batch extraction of Sr from HLLW

The results of D measurements of metal constituents of HLLW with 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane are summarized in **Table 5.2**. It is seen that D_{Sr} is much larger compared to other elements. However, Pu and Ba are also extracted to some extent. SF of more than 100 is obtained for Na, K, Ca, Al, Fe, Zr, Ln's, U, Am and more than 10 for Pu and Ba. Extraction of Pu is undesirable as it contaminate the ^{90}Sr - ^{90}Y recovery with alpha activity. Like trivalent Am, which is almost un-extractable, Pu extraction can also be minimized by reducing Pu (IV) (extractable species) to Pu (III) (non-extractable species) [121]. 0.5 M hydroxylammonium nitrate (HAN) as reducing agent in the feed solution containing 4 M nitric acid is found sufficient in converting Pu(IV) to Pu(III). The D_{Pu} obtained after reduction is 0.02. Stripping of the loaded organic is carried by deionized water at equal phase ratio. In first contact almost 85% of the Sr is stripped. Complete stripping is resulted in three consecutive contacts each with fresh deionized water.

Table 5.2: Extraction of HLLW metal ions

Elements	D_M	SF (D_{Sr}/D_M)
Sr	5.1	---
Cs	0.01	510
Mo	ND	very high
Zr	ND	very high
Ru	ND	very high
Ca	0.015	340
Ba	0.2	25.5
Fe	ND	very high
Na	0.01	510
K	0.03	170
Al	ND	very high
La	0.01	510
Ce	0.01	510
Nd	0.02	255
Y	0.03	170
U	0.01	510
Pu	0.3	17
Am	0.03	170

ND: Not detected

5.6 Stability test of 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane solvent

The present studies have shown that DtBuCH18C6 dissolved in a mixture of IDA and *n*-dodecane is a promising extractant for Sr separation from HLLW with high salt content. Moreover, it is necessary to investigate the influence of acidity and radiation on the stability of the solvent as it may affect the extraction performance, separation factors and solvent recycling properties. This was assessed by measuring the extraction and stripping efficiencies of the process solvent obtained after hydrolysis and radiolysis under controlled conditions. Hydrolysis was carried out by continuous stirring of equal volumes of solvent and 4 M nitric acid at 35-40°C for three months (HLLW is expected to have elevated temperature due to the presence of heat generating nuclides, ^{90}Sr and ^{137}Cs). After hydrolysis, the organic sample was tested for D_{Sr} at 4.0 M HNO_3 (extraction condition) and at 0.01 M HNO_3 (stripping condition). The solvent is found to retain its extraction and stripping properties at both the acidities indicating high hydrolytic stability of the solvent. Radiolytic degradation studies were carried out by irradiating the solvent in contact with equal volume of 4 M nitric acid by ^{60}Co γ-source at a dose rate of 56 Gy/min up to cumulative dose of 0.6 MGy. The irradiated solvent after separating it from nitric acid was tested for extraction and stripping of Sr and the results are presented in **Table 5.3**. The extraction of Sr, showed no appreciable change up to 0.2 MGy, however, beyond this, there is slight decline in the extraction. Still the solvent retains its high extraction property (84% to 72%) up to an absorbed dose of 0.6 MGy. The stripping of the loaded organic at different absorbed dose is performed by giving four successive contacts with 0.01 M nitric acid solution. No change is seen in the stripping behaviour of the irradiated solvent. GC-MS of the irradiated solvent depicted in **Fig.5.9** shows the presence of cyclohexanol groups, which are non-acidic and do not interact with Sr during stripping process. Schematic diagram of degradation of DtBuCH18C6 is shown in **Fig. 5.10**.

Table 5.3: Radiolysis of 0.03 M CC6 + 30%IDA/*n*-dodecane solvent

Absorbed dose MGy	% Extraction (D_{Sr})	% Stripping after four aqueous contacts
0	83.6 (5.1)	99.5
0.1	83.6 (5.1)	99.0
0.2	81.8 (4.5)	98.0
0.4	79.1 (3.8)	98.0
0.6	73.6 (2.8)	98.0

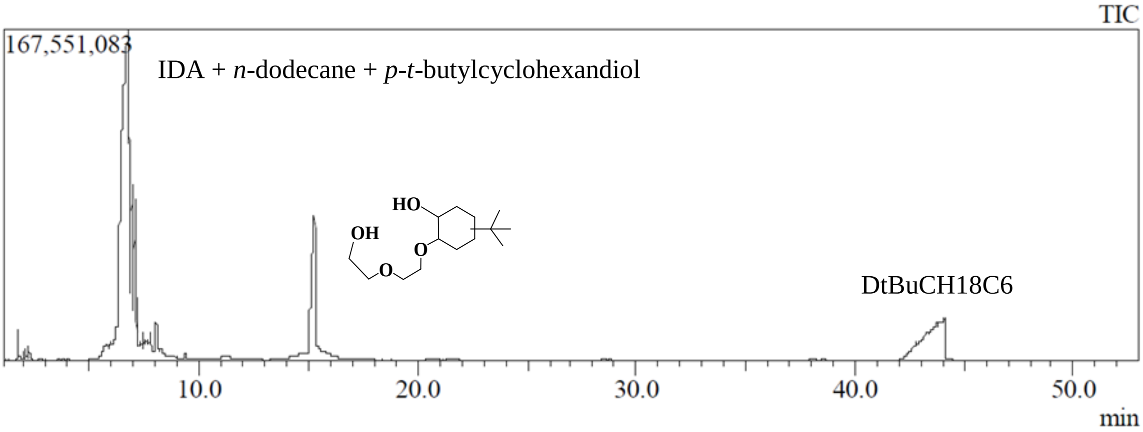


Fig. 5.9: GC-MS of irradiated 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane solvent

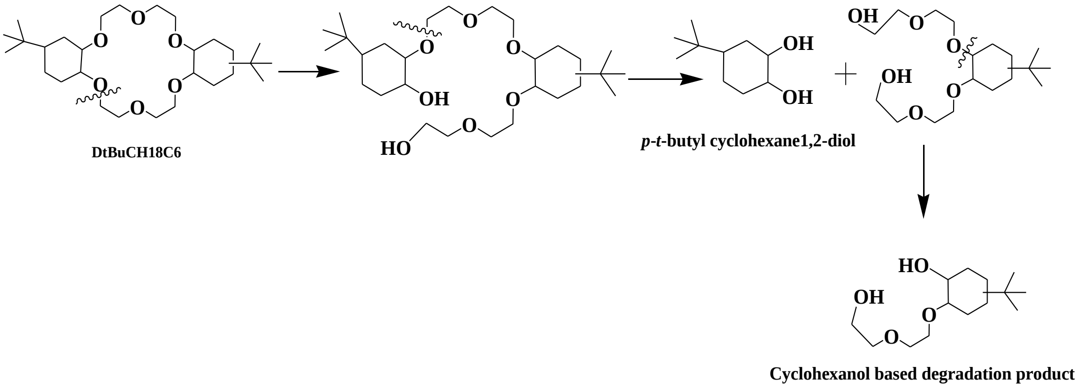


Fig. 5.10: Schematic diagram of degradation of DtBuCH18C6

5.7 Conclusions

Synthesis of DtBuCH18C6 by hydrogenation reaction of DtBuDB18C6 in the presence of reaction accelerator-isovelaric acid has ascertained the reproducible product quality. A mixture of IDA and *n*-dodecane is found to be suitable diluent, and the solvent is constituted as 0.1 M DtBuCH18C6 + 50% IDA/*n*-dodecane for efficient extraction of Sr^{2+}. The solvent showed increasing trend of D_{Sr} with nitric acid concentration. Suitable nitric acid concentration for extraction and stripping is found to be 4 M and 0.01 M respectively. D_{Sr} dependency on crown ether and nitric acid shows 1:1:1 complex formation of Sr^{2+} with crown ether and HNO_3. Extraction mechanism indicates that the extracted species, Sr^{2+}.DtBuCH18C6.HNO_3 and NO_3^- are solvated by IDA and remains in dissociated form. High selectivity for Sr^{2+} extraction is shown by the solvent from acidic HLLW containing high salt. SF of more than 100 is obtained for Na, K, Ca, Al, Fe, Zr, Ln’s, U, Am. Extraction of Pu is minimized by reductive extraction in the presence of 0.5 M HAN. Radiolysis of the solvent up to an absorbed dose of 0.6 MGy produces essentially no deterioration in its performance. Degradation products formed during radiolysis are neutral cyclohexanols derivatives which do not influence the stripping behaviour of the solvent.

CHAPTER 6

Process for Separation of Tc from Alkaline LLW using 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 + IDA/*n*-dodecane solvent

TcO_4^- removal from the LLW is difficult and challenging due to the presence of large excess of monoanions, NO_3^- and OH^- ions, which competes with TcO_4^- during separation processes. Bonnesen et al. of ORNL, have extensively studied the separation of $Na^+TcO_4^-$ from alkaline waste using various crown ethers and optimized the process with most suitable one, DtBuCH18C6 dissolved in a mixture of tributyl phosphate (TBP) and Isopar® M [64]. Using this solvent and water as stripping agent, more than 99% of Tc was removed from Hanford tank-waste simulants.

Since, the generation rate of LLW is large, correspondingly, more quantity of DtBuCH18C6 will be required for treatment of LLW. Bulk scale availability of DtBuCH18C6 is extremely difficult due to rigorous hydrogenation step involved in its synthesis. Therefore, crown ethers which are simple to make and have affinity for Na^+ ion are considered for this purpose. Dibenzo-18-crown-6 is also known to bind strongly with Na^+ ion due to strong interaction between the π-electron clouds of sp^2-hybridized dibenzo group with small sized Na^+ ion [48] and is easier to make at larger scale. Accordingly, *tert*-butyl derivative of dibenzo-18-crown-6 ether, 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 (DtBuDB18C6), is chosen in the present work for separation of $Na^+TcO_4^-$ from LLW. DtBuDB18C6 dissolved in a mixture of IDA and *n*-dodecane, has been studied for extraction of ^{99}Tc from actual LLW solution. Extraction parameters, mechanism of extraction, stoichiometry of extract and degradation behaviour of the solvent have been established to develop a process for ^{99}Tc separation from LLW.

6.1 Synthesis of DtBuDB18C6

The synthesis process scheme and characterization of DtBuDB18C6 is given in Section 5.1.1 of Chapter 5.

6.2 Radio-chemical composition of LLW

Radio-chemical composition of LLW is summarized in **Table 6.1**

Table 6.1: Composition of LLW

Species	Activity / Concentration
Gross α	10^{-5} mCi/L
Gross β	0.14 - 0.72 mCi/L
Gross γ	8×10^{-3} - 4×10^{-2} mCi/L
^{137}Cs	6×10^{-3} - 1×10^{-2} mCi/L
^{90}Sr	10^{-3} mCi/L
^{106}Ru	2×10^{-2} mCi/L
^{125}Sb	6×10^{-4} mCi/L
^{99}Tc	0.12 - 0.3 mCi/L (7.05-17.6 mg/L)
Na^+	3 - 3.5 M
NO_3^-	2 - 3 M
pH	12.7 – 13.2

6.3 Determination of solvent composition and extraction of Tc

Solubility studies of DtBuDB18C6 have shown that DtBuDB18C6 is insoluble in *n*-dodecane, while it has a fairly good solubility in a mixture of IDA and *n*-dodecane. Solubility of DtBuDB18C6 in a mixture of *n*-dodecane and IDA is shown in **Table 6.2**.

Table 6.2: Solubility of DtBuDB18C6 in *n*-dodecane, IDA mixture

Ratio of *n*-dodecane to IDA	Solubility of DtBuBB18C6 in M
4:1	0.05
3:1	0.10
2:1	0.15
1:1	0. 22
1:2	0.22
1:3	0.23

Solubility of DtBuDB18C6 is found to increase with increase in IDA content in the mixture. A mixture of 1:1IDA, *n*-dodeacne, having a solubility of 0.22 M DtBuDB18C6 is found to be most appropriate. DtBuDB18C6 obtained from different batches of synthesis have shown variation in their solubility. Up to 0.2 M, DtBuDB18C6 is freely soluble in 1:1 IDA, *n*-dodecane mixture for all batches. A slight inconsistency is observed above this concentration. DtBuDB18C6 exists in two isomeric forms i.e. 4',4''-DtBuDB18C6 (*cis*) and 4',5''-DtBuDB18C6 (*trans*). The product of synthesis, therefore, may have variation in isomeric composition from batch to batch. Probably these variations may result in solubility difference of DtBuDB18C6. Extraction of Tc from LLW at varying concentration of DtBuDB18C6 in a mixture of *n*-dodecane and IDA is shown **Fig. 6.1**. D_{Tc} is found to increase with increase in concentration of DtBuDB18C6. At 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane about 82% (D_{Tc} = 4.46) extraction of ^{99}Tc is observed. Increasing the content of IDA above 50% in 0.2 M DtBuDB18C6 + IDA/*n*-dodecane has not resulted in any significant increase in extraction of ^{99}Tc. Therefore, 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane is chosen as a process solvent for further studies.

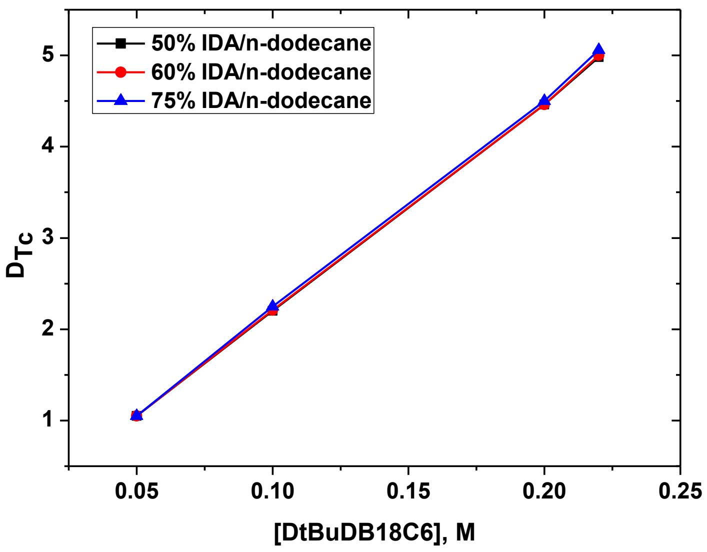


Fig.6.1: Variation in D_{Tc} with DtBuDB18C6 concentration at different IDA content

Kinetics of the extraction is also determined and shows attainment of equilibrium in 10 minutes, thus, for all the experiments contact time is kept at 15 minutes. The log-log plot of solvent dependency as shown in **Fig.6.2** is a straight line with a slope of 1.02 indicating 1:1 complex formation between DtBuDB18C6 and TcO_4^-.

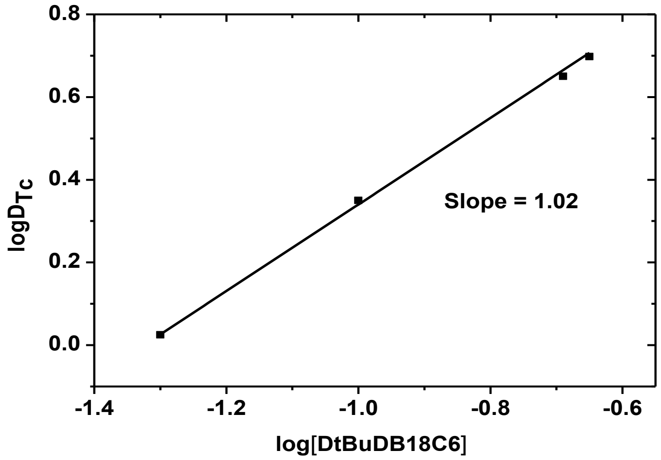


Fig.6.2: log-log plot of extraction dependency of TcO_4^- on DtBuDB18C6 concentrations

6.4 Effect of nitrate and hydroxide concentration

LLW contains large excess of $NaNO_3$ and NaOH compared to $NaTcO_4$. Due to similarities in their interaction with crown ether, they influence the extraction of $NaTcO_4$. Stock solution of

TcO_4^- prepared from LLW was added in the solutions of different concentrations of $NaNO_3$ and NaOH. The results of variation in D_{Tc} with $NaNO_3$ and NaOH concentrations are shown in **Fig. 6.3**.

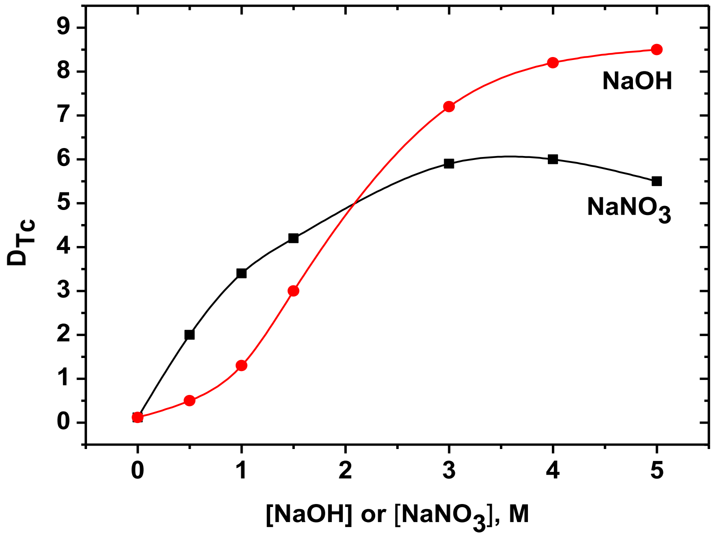


Fig.6.3: Extraction dependency of TcO_4^-on NaOH and $NaNO_3$ concentrations

D_{Tc} is observed to increases steadily with increase in $NaNO_3$ concentration. However, above 4 M $NaNO_3$, competitive extraction of NO_3^- over TcO_4^- results in decrease in TcO_4^-extraction. While, D_{Tc} increases with NaOH concentration up to 4 M, above it, D_{Tc} almost remains constant indicating weak competitive strength of OH^-. Extraction of TcO_4^- is preferred over $NO_3^-$and OH^- due to lower ionic hydration enthalpy of TcO_4^- (-251 kJ/mol) compared to NO_3^- (-289 kJ/mol) and OH^- (-410 kJ/mol) [122]. However, due to close difference between ΔH_h of TcO_4^- and NO_3^-, above 4 M NO_3^- ion concentration, a competitive extraction of NO_3^- takes place and decrease in extraction of TcO_4^- is observed. Similar effect is not seen with increase in NaOH concentration due to large difference between ΔH_h of TcO_4^- and OH^- ion. Since, in both the cases, D_{Tc} is observed to increase with increase in sodium (nitrate or hydroxide) concentration up to 4 M, implying that the loading of Na^+ increases with increase in $NaNO_3$ or NaOH concentration. At 4 M, crown ether is fully loaded with Na^+ ion. To study the role of $NO_3^-$and OH^- concentrations on D_{Tc} at saturation loading of Na^+ ion, D_{Tc} is plotted against 5 M $Na^+(NO_3^- + OH^-)$. Total Na^+ is kept at 5 M and concentrations of $NO_3^-$and OH^- are varied. The results, as shown in **Fig. 6.4** indicate a linear fall of D_{Tc} with increase in nitrate concentration, thus, confirming NO_3^- as a stronger competitor for TcO_4^- compared to OH^- ion.

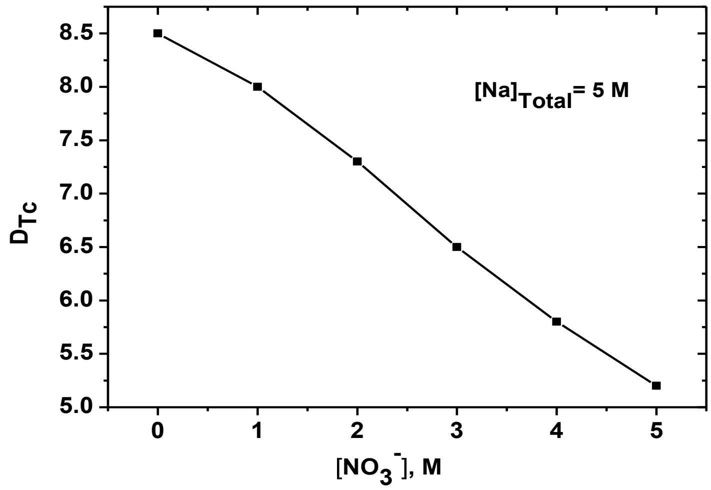


Fig.6.4: Extraction dependency of TcO_4^- on $NaNO_3$ concentration

6.5 Extraction mechanism

The results of extraction dependency of TcO_4^- on $NaNO_3$ and NaOH show that extraction of TcO_4^- increases with increase in concentration of Na ion. The higher Na ion concentration in the aqueous phase during extraction promotes the formation of cationic crown ether-sodium metal complex. Since, an anion is necessary to conserve the charge neutrality of the extracted species, preferential extraction of TcO_4^- occurs over $NO_3^-$and OH^-, and in this way TcO_4^- is also extracted. The extraction process, thus, follows ion-pair formation mechanism and is represented as the forward reaction of following equation:

$$Na^+ + TcO_4^- + DtBuDB18C6_{org} \rightleftharpoons Na^+\cdot DtBuDB18C6\cdot TcO_4^-{}_{org} \qquad 6.1$$

Pictorial representation of extraction is shown in **Fig.6.5**.

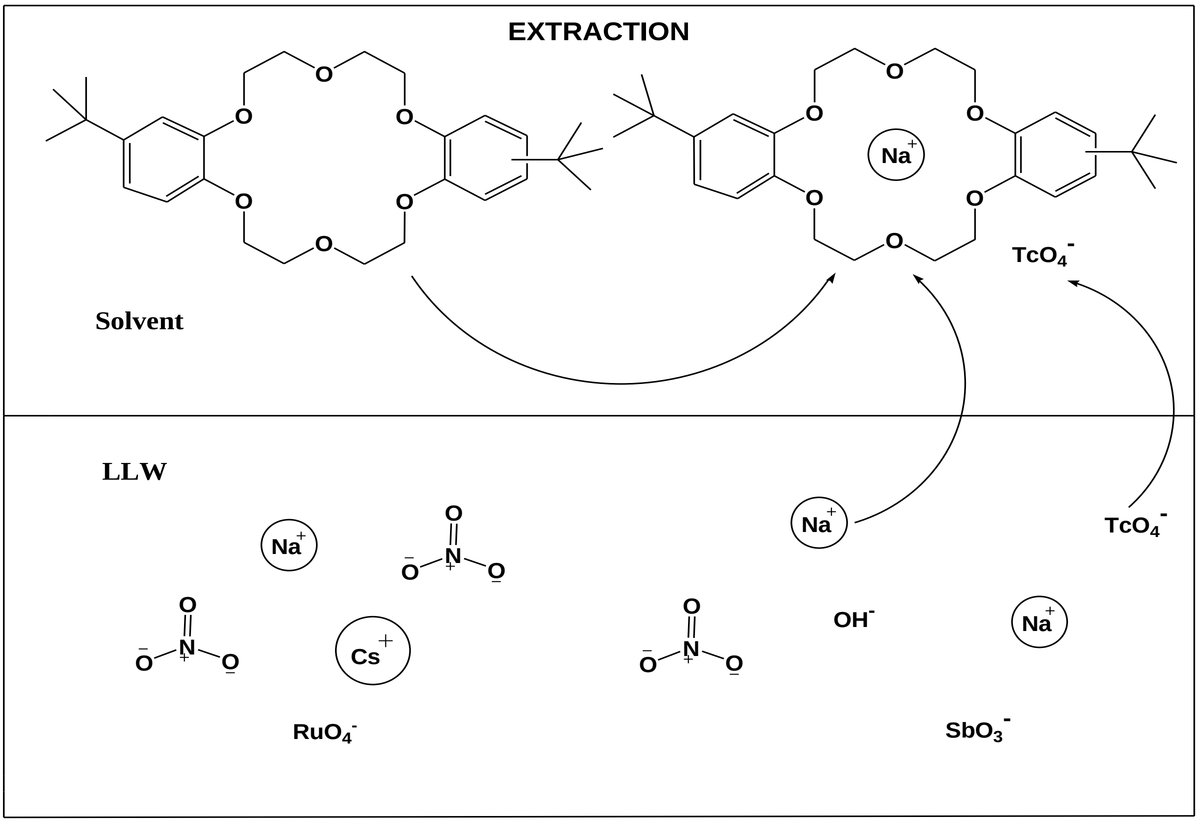


Fig.6.5: Pictorial representation of extraction of $Na^+ TcO_4^-$

6.6 Stripping studies

The reverse reaction of equation 6.1 is stripping, where the extracted species, $Na^+ \cdot DtBuDB18C6 \cdot TcO_4^-$, dissociates to free Na^+ and TcO_4^- in the aqueous phase and DtBuDB18C6 in organic phase. From Fig.6.3, it is evident that there is no extraction of TcO_4^- in absence of $NaNO_3$ and NaOH in the aqueous phase. Therefore, stripping of loaded organic was carried by deionized water. The schematic diagram of stripping is presented in **Fig.6.6.** Almost 95% of the loaded TcO_4^- is stripped in a single contact at 1:1 phase ratio. More than 99% stripping is obtained after providing two contacts for organic phase with deionized water.

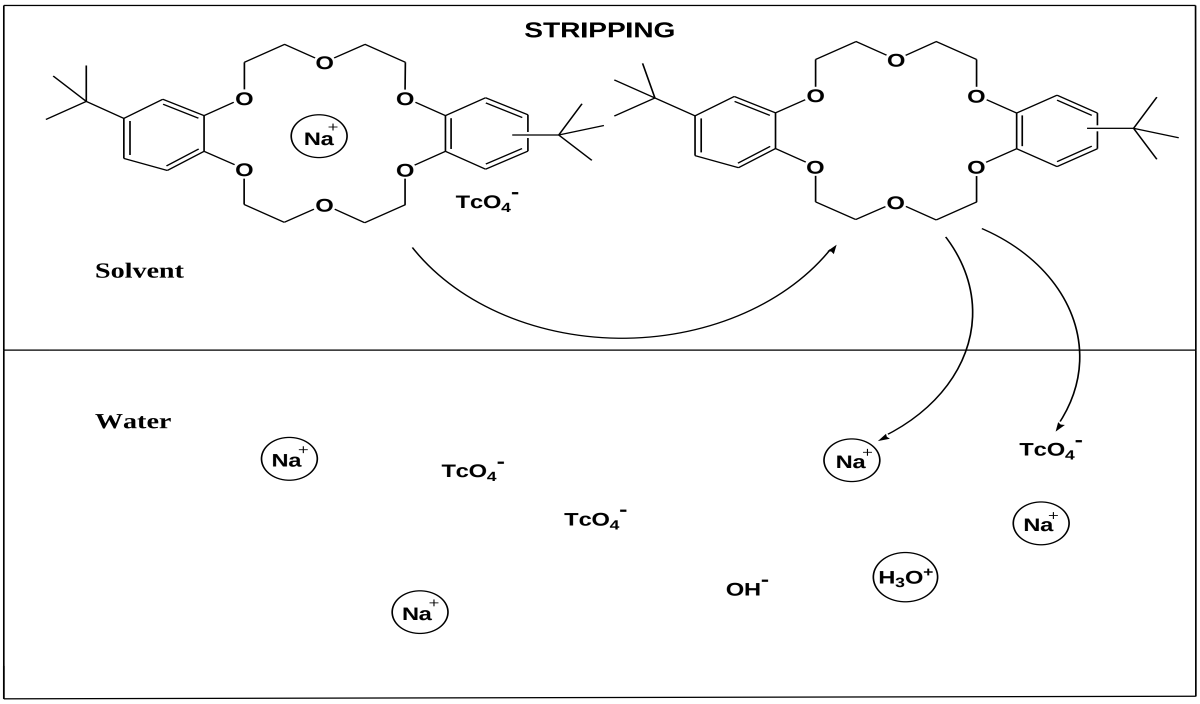


Fig.6.6: Pictorial representation of stripping of $Na^+ TcO_4^-$

6.7 Tc extraction from LLW

Extraction of Tc and other fission products present in LLW were evaluated using 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane. Their *D*s' and SFs' with respect to Tc are tabulated in **Table 6.3**. As can be seen, the extraction of Tc is much higher compared to other species. Extractant being crown ether, extraction of anionic species, RuO_4^- and cations like Cs^+ and Sr^{2+} are also observed following similar mechanism, although their extraction is low and not significant. The solvent, thus demonstrates high selectivity for Tc extraction over other fission products (SF > 22).

Table 6.3: Selectivity of ^{99}Tc extraction from other fission products of LLW

Species	D	SF (D_{Tc}/D_M)
TcO_4^-	4.5	
RuO_4^-	0.01	450
Sr	0.04	112.5
Cs	0.2	22.5

6.8 Stability test of 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane solvent

During the process of separating Tc, the solvent will be in continuous contact with LLW. Therefore, stability investigation of solvent towards alkalinity and radioactivity is very much required. This was assessed by measuring the extraction and stripping efficiency of the solvent after continuous stirring with equal volume of LLW at room temperature for six months. The solvent was then separated, washed with deionized water and tested for extraction with fresh LLW and stripping with deionized water. The solvent is found to retain its extraction and stripping properties, thus, indicating that the solvent is stable for a period equivalent to many cycles of continuous operation with LLW. Though, radioactivity associated with LLW is very low, the high alkalinity is bound to have detrimental effect on the stability of the solvent. Therefore, an experiment was carried out by providing continuous contact of solvent with 4 M NaOH solution at 60°C for 30 days to examine the nature of degradation products formed and recyclability of degraded solvent. The solvent after separating it from NaOH was analyzed by GC-MS and tested for extraction behaviour with LLW. Major degradation products of DtBuDB18C6, as shown in **Fig.6.7,** are identified as *t*-butylcatechol and di(*t*-butylphenol)-mono-18-crown-6. Schematic diagram of degradation path is shown in **Fig. 6.8**. Extraction of LLW elements with degraded solvent shows reduction in extraction of Tc due to degradation of the DtBuDB18C6 and loss of selectivity due to significantly high extraction of Cs and Sr. The results of extraction are summarised in **Table 6.4.** The extraction of Cs and Sr is due to presence of acidic phenolic degradation products which extracts metal ions by cation exchange mechanism under highly alkaline conditions. Since, the degradation products are acidic in nature, their removal by basic alumina treatment helps in completely regeneration of the degraded solvent to its reusable quality [116].

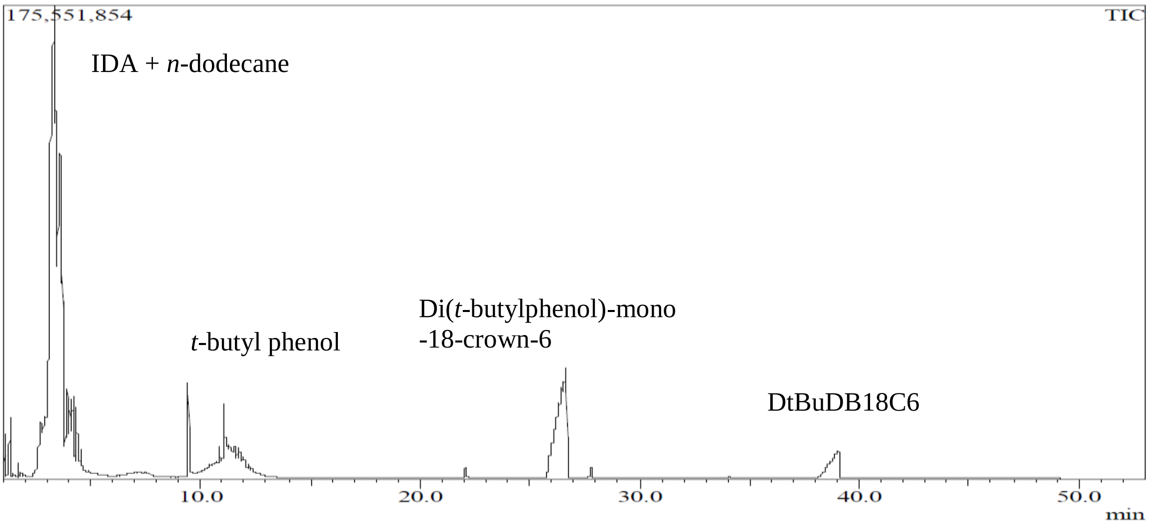


Fig.6.7: GC-MS of degraded 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane solvent

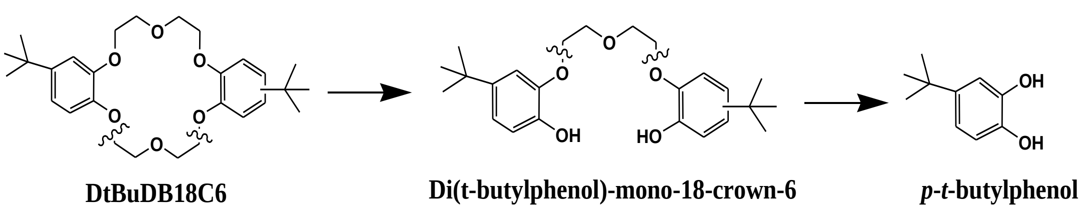


Fig.6.8: Schematic diagram of degradation of DtBuDB18C6

Table 6.4: Extraction of LLW elements with degraded solvent

Species	*D*
TcO_4^-	2.2
RuO_4^-	0.05
Sr	0.84
Cs	1.2

6.9 Conclusions

The present work demonstrates effective use of 0.2 M DtBuDB18C6 + 50% IDA/*n*-dodecane solvent for separation of ^{99}Tc from alkaline LLW. The important finding of this work is, direct extraction of TcO_4^- with high selectivity from high-nitrate-containing alkaline LLW without any adjustment of waste composition and stripping of the loaded solvent with only deionized water. Extraction of TcO_4^- increases with increase in $NaNO_3$ or NaOH concentration up to 4 M, thereafter, competitive extraction of NO_3^- over TcO_4^- takes place resulting in decrease in D_{Tc}. This phenomenon is not observed in case of NaOH, where above 4 M NaOH concentration, D_{Tc} remains unchanged. Stoichiometry of the complex determined by slope analysis method shows 1:1 complex formation between TcO_4^- and DtBuDB18C6. The mechanism of the extraction involves ion pair formation, where crown ether extracts sodium ion forming crown ether-sodium metal ion complex and simultaneous extraction of TcO_4^- to conserve charge neutrality. The solvent shows no sign of degradation when contacted continuously with LLW for six months, thus, exhibited very high stability towards use with LLW. Degradation of the solvent by contacting with 4 M NaOH at 60°C for 30 days indicated formation of phenolic impurities. These impurities extract Cs^+ and Sr^{2+} of LLW and decrease the selectivity of TcO_4^-extraction. The degraded solvent is regenerated and made to re-usable quality by treating it with basic alumina.

Name of the Student: JOTI NATH SHARMA

Name of the CI: BARC Enrolment No.: ENGG01201304031

Thesis Title: Development of Macrocyclic Extractants for Selective Separation of Cesium, Strontium and Technetium from Radioactive Waste Solutions

Discipline: Chemical Engineering Sciences

Abstract

High level liquid waste (HLLW) generated during reprocessing of spent fuel by PUREX (Plutonium Uranium Reductive EXtraction) process retains majority of radio-toxicity of the original spent fuel. ^{137}Cs ($t_{1/2}$ = 30.1 y) and ^{90}Sr ($t_{1/2}$ = 28.9 y) are major heat emitting nuclides contributing largely on heat and radiation load of HLLW. Separation of these elements is necessary for safe waste management and also for their societal applications. ^{99}Tc, a beta emitting radionuclide ($t_{1/2} = 2.11 \times 10^5$ y) present in alkaline low level waste (LLW) as $NaTcO_4$. It contributes largely to β-load of LLW. The thesis work is focused on development of macrocyclic extractants of the class calix-crown-6 and crown ethers for selective separation of Cs, Sr and Tc from radioactive waste solutions. Calix-crown-6 and crown ethers when fixed in a particular isomeric form possesses a cavity which is highly complementary to alkali metal ions like Cs^+, Sr^{2+}, Na^+ TcO_4^- and serve as potential extractants for their selective separation from waste solutions. The thesis is divided into six chapters; chapter 1 gives introduction to reprocessing, generation of radioactive waste, motivation and scope of the work. Review on solvent extraction processes with an emphasis of macrocyclic extractants for separations of Cs, Sr and Tc is given in Chapter 2. Chapter 3 covers experimental setup and analytical procedure involved in the work. Chapter 4 gives synthesis, characterization, solvent extraction evaluation, counter-current extraction, degradation and recyclability of 1,3-dioctyloxycalix[4]arene-crown-6 and branched calix[4]arene-crown-6. Chapter 5 and 6 describe the synthesis, characterization and extraction evaluation of 4,4′(5′)-[di-*tert*-butyldicyclohexano]-18-crown-6 for selective separation of Sr^{2+} from HLLW and 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 for selective separation of $Na^+TcO_4^-$ from LLW. A new diluents system, a mixture of isodecyl alcohol and *n*-dodecane is employed for extraction studies. The extraction mechanism determined for Cs^+ and Sr^{2+} displays solvation and $Na^+TcO_4^-$ as ion-pair association. The combining ratio of extractant to metal ion is 1:1 in all the cases. Radiolytic and hydrolytic degradation studies have indicated high stability of solvents. Recyclability of degraded solvent is also established.

Thesis Highlight

Name of the Student: JOTI NATH SHARMA

Name of the CI/OCC: BARC **Enrolment No.: ENGG01201304031**

Thesis Title: Development of Macrocyclic Extractants for Selective Separation of Cesium, Strontium and Technetium from Radioactive Waste Solutions

Discipline: Chemical Engineering Sciences **Sub-Area of Discipline: Separation Science**

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High level liquid waste (HLLW) generated during reprocessing of spent fuel by PUREX (Plutonium Uranium Reductive EXtraction) process retains majority of radio-toxicity of the original spent fuel. ^{137}Cs ($t_{1/2}$ = 30.1 y) and ^{90}Sr ($t_{1/2}$ = 28.9 y) are major heat emitting nuclides contributing largely on heat and radiation load of HLLW. ^{99}Tc, a beta emitting radionuclide ($t_{1/2} = 2.11 \times 10^5$ y) present in alkaline low level waste (LLW) as $NaTcO_4$. Separation of these elements is necessary for safe waste management and also for their uses in societal applications. The present studies are focused on development of macrocyclic extractants of the class calix-crown-6 and crown ethers for selective separation of Cs, Sr and Tc from high salt content radioactive waste solutions.

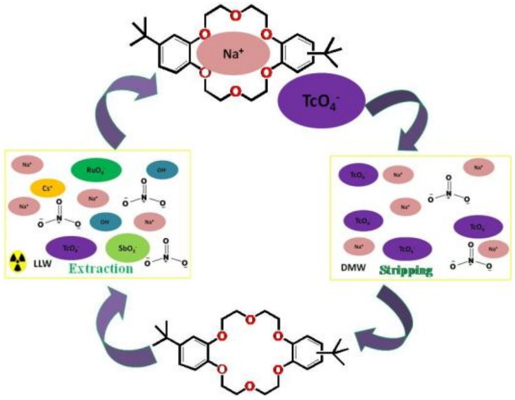

Figure1. Pictorial representation of extraction and stripping of $Na^+TcO_4^-$ from LLW

The extractants developed are 1,3-dioctyloxycalix[4]arene crown-6 (CC6) and 1,3-bis(2-ethylhexyloxy)calix[4] arene-crown-6 (branched calix-crown-6) for selective separation of Cs^+ from HLLW, 4,4′(5′)-[di-*tert*-butyldicyclohexano]-18-crown-6 (DtBuCH18C6) for selective separation of Sr^{2+} from HLLW and 4,4′(5′)-[di-*tert*-butyldibenzo]-18-crown-6 (DtBuDB18C6) for selective separation of $Na^+TcO_4^-$ from LLW and are dissolved in a new diluents system, a mixture of isodecyl alcohol and *n*-dodecane for extraction studies. ^{137}Cs removal from HLLW was more than 99.5% with impurity level <1 mg/L in 4 stage counter-current continuous extraction with 0.03 M CC6 +30% isodecyl alcohol/*n*-dodecane. The extraction mechanism determined for Cs^+ and Sr^{2+} displays solvation and $Na^+TcO_4^-$ as ion-pair association. The combining ratio of extractant to metal ion is 1:1 in all the cases. Fig. 1 shows pictorial representation of extraction of $Na^+TcO_4^-$ from LLW using 0.2 M DtBuDB18C6 +50% IDA/*n*-dodecane and stripping of $Na^+TcO_4^-$ from loaded solvent with DM water. Radiolytic and hydrolytic degradation studies have indicated high stability of solvents. Degradation mechanism and recycling of degraded solvent has also been established.