Synthesis, evaluation and theoretical studies of calix-crown based ligands for cesium recovery from acidic media

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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 eralier as a whole or in part for a degree / diploma at this or any other Institution / University.

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LIST OF PUBLICATIONS

Publications in refereed Journals

1. An amide functionalized calix-benzocrown-6 ionophore for the selective extraction of cesium from highly concentrated nitric acid: the effect of intramolecular buffering,
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Dedicated to
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SYNOPSIS

In the middle of the last century the discovery of nuclear fission by Otto Hahn opened up a new abundant and concentrated energy resource to meet the challenges of modern day industrialization and human life style. The nuclear fission of a few grams of ^{235}U by thermal neutrons produce energy equivalent to the burning of tonnes of coal and that too without any significant discharge of pollutants like CO_2, SO_2 etc. to atmosphere. Dwindling natural resources of conventional fuels are inadequate to support the ever increasing demand of energy, especially in developing countries. Hence from the middle of the last century, a number of reactor concepts were developed for utilization of fission energy and different types of reactors were designed and operated for power production. Currently around 430 reactors are operating all over the world and near about 15-20% of the total energy is produced through nuclear fission [1].

Today nuclear energy has matured into a technically viable alternate to fossil fuel energy and is a clean source capable of reducing the carbon footprint in the wake of global warming. Based on resource position, two different fuel cycles are in vogue in nuclear industry. A once through cycle, where the fuel is irradiated once in reactor and at the end of the irradiation, the spent fuel is discarded as waste. This option utilizes only a small fraction of the fuel, usually <1%. In the closed fuel cycle, the fuel is irradiated in reactor and after its life time in reactor, is reprocessed to recover the fuel values for further recycle in reactors. The closed fuel cycle approach allows optimum resource utilization by multiple recycling. In both the fuel cycles, the spent fuel as such or the fission product waste separated from the spent fuel will have high radiation levels and will have to be isolated from the biosphere for thousands of years to bring down its radiotoxicity. This has resulted in lack of public acceptance of nuclear energy. But, the alternate clean nonconventional energy sources like wind energy, solar energy, geothermal energy etc. are playing only a supporting role and are yet to be developed to meet the base load requirements. Hence, nuclear energy developed and matured over for more than half a century is the only alternate available to stand in as a source to meet the immediate demands till an alternate stable source with lesser impact is developed.

The apathy of the public stems from the dangers of radioactive waste generated by the spent fuel and the calamities associated with the nuclear power generation in almost every decade since the Three Mile Island accident. Hence the reliability of nuclear reactors and associated fuel cycles along with the long term issues of radiotoxicity of waste have to be resolved technologically to convince the general public prior to stepping up the pace on nuclear power generation. Steps have been already initiated in this direction and the global collaborative efforts in the last two decades are towards improving the design safety of nuclear reactors and associated fuel cycles. Leaving the spent fuel as a waste as practiced in open fuel cycle will not allow efficient utilization of resources and will not provide any reduction in toxicity. Whereas the closed fuel cycle with recycling will allow the use of full potential of fuel and also will offer treatment options to bring down the surveillance time to acceptable levels by reducing the toxicity or by improving confinement techniques for the separated individual fractions.

Nuclear fuel, usually a combination of fissile and fertile elements (^{235}U & ^{238}U or ^{239}Pu & ^{238}U), undergoes irradiation in reactor. Fissile nuclides undergo fission and fertile nuclides capture neutrons to get transformed into heavier nuclides which undergo radioactive decay to produce fissile or fertile nuclides. Due to fission, a number of fission products are generated. Many of them are in their excited state and undergo radioactive decay till they attain stability. Accumulated fission products due to their strong neutron capture limit the useful life of the fuel in the reactor and finally gets discharged as spent fuel. This spent fuel will still have more 95% of the fuel value as an admixture with fission products. Minor actinides like Np, Am and Cm will also be generated in grams per ton of spent fuel. Separating the fuel values from fission products for recycle in reactor is known as reprocessing. World over PUREX process is used for the separation of U and Pu from each other and also from fission products. This process leaves behind a high level liquid waste containing more than 99% of the fission products, residual uranium, plutonium and the minor actinides for management. Currently, this waste is vitrified in borosilicate glass and is waiting for final disposal in geological repository after achieving the target decay heat values. As on today this is the best option, as the accelerated leaching rates of radioactivity are the lowest and engineering design of the repository can take care of the foreseeable accident scenarios. This concept of high level waste management has met with many hurdles from general public globally and a consensus on disposal sites could not be achieved yet.

Research and development on partitioning of potential radionuclides from the high level waste is in progress for more than two decades globally to isolate toxic nuclides into a small volume either to transmute them into short lived fission products or to condition them in special matrices to isolate them away from the biosphere in a more secured way. The radio activity of high level liquid waste generated during the reprocessing of 5-10 years cooled spent fuel by PUREX process is mainly due to $^{90}\mathrm{Sr}-{}^{90}\mathrm{Y}$ and $^{137}\mathrm{Cs}$. In the initial years the contribution from other fission products and actinides are not significant. Currently vitrification in glass matrix is adopted for the isolation of this waste from biosphere. Since $^{137}\mathrm{Cs}$ and $^{90}\mathrm{Sr}$ have half lives of around 30 years they significantly contribute to the decay heat of the waste product for around first 300 years. Thus, the intense gamma radiation of $^{137}\mathrm{Cs}$ and the combined decay heat of $^{90}\mathrm{Sr}$-$^{90}\mathrm{Y}$ and $^{137}\mathrm{Cs}$ necessitate near surface cooling of the high level vitrified product for the initial few decades prior to moving to the final geological repository. During partitioning, removal of radio strontium and Cs are also planned along with toxic actinides to reduce the decay heat of the waste product. The bulk of the remaining waste containing trace quantities of toxic nuclides can be vitrified and disposed off in engineered barriers without the fear of breach in containment and spread of toxicity as these wastes will decay to natural activity levels in a few hundreds of years. This approach will eliminate or bring down the footprint of the geological repository drastically. A number of tailor made reagents are designed and synthesized to address this difficult task of separating a few actinides and selected fission products from a host of impurities covering almost the entire periodic table with mass numbers ranging from 60 to 170. Our laboratory is involved in the indigenous design and synthesis of novel solvents for accomplishing this task on an industrial scale.

Cs-137, a major radionuclide present in the spent fuel is a β, γ $-$emitters and can be used as an alternate source for cobalt-60 for medical and industrial applications like preservation of foodstuffs by killing bacterial growth, blood irradiation and medical accessories sterilization, cancer treatment by brachytherapy and scintillation cameras. This makes the separation and recovery of cesium economically viable. Among the alkali metal ions, cesium ion is weekly coordinated and resists the formation of organic adducts easily for its separation. This makes the effective partitioning of cesium from HLW most challenging [2].

There are a number of methods developed for the separation of cesium from acidic as well as alkaline medium depending upon the waste composition. These methods include precipitation, ion exchange and solvent extraction. For precipitation, the most commonly used reagents are alums, lime, iron salt, organic polymers, sodium tetraphenylborate (NaTPB) and sodium phosophotungstic acid ($Na_3[PW_3O_{10}].4H_2O$) . In ion exchange separation, inorganic ion exchangers (Zeolites) were the first compounds used for treatment of radioactive waste solutions. This was used for large scale decontamination of reactor containment building and primary reactor coolant after the Three Mile Island accident [4]. When polybasic acids and certain hydrolysable cations like zirconium, thorium and titanium are suitably combined with anions like phosphate, vanadate, tungustante and molybdate, it produces better ion exchangers over zeolites. The general formula for these are as $M(IV)(HXO_4)_2.nH_2O$ where M= Zr, Ti, Th and X= P, V, W, Mo etc. Zirconium phosphate was studied extensively and it was found that the exchange behaviour was unaffected over a range of temperatures, pH and in presence of various anions like EDTA, phosphate etc. in the feed solution[5]. Ammonium molybdophasphate (AMP) is the more promising ion exchanger for selective cesium recovery over large amounts of other metal ions like Rb^+, K^+ ,Na^+ present in the high level liquid waste solution [6]. In the solvent extraction field, number of novel solvents like crown ethers and hydrophobic anions like chlorinated cobalt dicarbollide were found to be suitable for cesium complexation.

For the separation of cesium form high level liquid waste, specific ionophore have been developed, based on the molecular platform of crown ethers. Calixarene when suitably condensed with crown ethers results in calix-crown. This particular class of cation ligand based on calixarene framework has received more attention in recent years. The ion binding properties of this class of ligand can be tuned by varying the size of crown ring, substitution of upper rim and selecting diluents-extractant mixture for complexation. Out of many conformation possible, calix[4]arene-crown-6 ethers seems to have relatively well optimized structural properties especially, when fixed in 1,3-alternate conformation for cesium ions extraction over large amount of sodium ions [7]. On the other hand, 1,3- alternate calix-bis-crown (BOBCalix6 and BEHBCalix6) has been found to serve as a potential selective ionophore for cesium from alkaline waste solutions. FPEX (fission product extraction) process was based on simultaneous extraction of cesium and strontium from acidic waste solutions, using solvent combination containing two extractants, DtBu18C6 for strontium and BOBCalixC6 for cesium, dissolved in Isopar L and modified with Cs-7SB [8]. The presence of four benzene rings and 6-12 oxygen in calix-crown make it highly polar, therefore it requires highly polar diluents like, florosulphone (FS-13), nitrobenzene, CS-7SB, o-NPHE and o-NPOE for its dissolution before carrying out the extraction studies. These diluents are toxic/corrosive and not compatible with PUREX type diluents like dodecane for plant scale operation. The major hurdle is the difficulty in synthesis of calix-crown extractants on a larger scale.

In view of this, the main objective of the present work is to synthesize indigenously a suitable calix-crown molecule and develop an alternate diluent system for the selective removal of cesium from high level liquid waste. This report presents the synthesis routes followed for 1,3-dioctyloxy calix[4]arene-crown-6 (CC-6) and 1,3-dioctyloxy calix[4]arene-benzocrown-6 (CBC) on a larger scale indigenously and the development of a diluent system based on n-dodecane and isodecyl alcohol, already in use in the on-going program on separation of minor actinides and strontium from HLLW.

The analysis of solvent extraction results by theoretical methods are much more difficult due to involvement of various species like metal cations, counter ions, solvent and extracted species. Based on Molecular Dynamics (MD) and Free Energy Perturbation simulations (FEP) on extraction of alkali metal ions with calix-crowns by employing thermodynamical cycle are reported. The extraction of Na^+, K^+, Rb^+ and Cs^+ complexes in four different solvents (water, methanol, acetonitrile and chloroform) and in the gas phase were analysed by MD simulations and it was observed that Cs^+ is complexed by calix[4]-bis-crown-6 better than Na^+ in water and methanol, whereas in chloroform and in the gas phase, Na^+ is preferred [9]. Recently Density Functional Theory (DFT) calculations have received much attention in elucidating the complexing ability of a ligand towards a particular ion by predicting the structure, free energy of complexation and various bonding analysis [10]. Hence, in addition to the experimental studies, DFT based calculations were also performed to obtain molecular level insights which includes the structure of the free calix-crown ether and its complex with Cs^+ and Na^+ ions and their free energy of extraction in aqueous-organic biphasic system.

Chapter 1 This Chapter covers the overview of Indian three stage nuclear power program formulated by Dr. Homi Bhabha based on the limited uranium resource and vast thorium reserve in the monazite sand with reprocessing and recycle of spent fuel for closing the fuel cycle [11]. Categorization of nuclear wastes generated during the reprocessing and their impact on the environment have been discussed [12]. The cesium fission yield, hazards, potential applications as an alternate source in place of ^{60}Co is included. This Chapter also summarize various separation techniques viz., precipitation, ion-exchange and solvent extraction for the recovery of cesium from different waste solutions. The challenges in the recovery of cesium from HLLW originating from PUREX process is described. In the solvent extraction technique, the substituted crown ethers like, Dibenzo18-crown-6, Dicyclohexano-18-crown-6 and Dibenzo-21-crown-7 for cesium extraction has been summarized. The major bottleneck of these crown ethers is due to the poor solvation of counter anion during the extraction process. Methods like substitution on crown ether by hydrocarbon chain, proton-ionisable group and use of polar phase modifiers for overcoming this limitation is discussed. The dicarbollides (DC) and hexachlorinated cobalt dicarbollide derivatives (CCD) for extraction of cesium from aqueous solutions to nitro-based organic diluents have been summarized. The advantage of CCD over DC in terms of high stability towards acid and the recent development on the use of diluent system like phenyltrifluoromethylsulfone (FS-13) has been discussed. The extractant composition with 0.08M CCD, 0.6 vol % PEG-400 in phenyl trifluoromethyl sulfone (FS-13) diluents for the recovery of cesium and strontium has been included. In the light of the available literature, the synthesis of calixarene and conformation analysis by ^{1}H, ^{13}C NMR has been presented. The reaction with crown ether to produce calix-crown in different conformations and their solvent extraction evaluations has been explained elaborately. A brief comparison on solvent extraction evaluation has been included for different types of calix-crowns available in literature. Different diluent systems for solubility enhancement in PUREX type diluents have been summarized. The process developed at Oak Ridge National Laboratory using 0.01 M calyx [4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6), 0.50 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphen oxy)-2-propanol (Cs-7SBT) as a modifier, 0.001 M trioctylamine (TOA) in an aliphatic diluent Isopar L (mixture of branched chain hydrocarbon C_{10}-C_{12}) is discussed in detail in this chapter. A brief review of the available reports of the computational calculations of calix-crown molecules are also outlined in this chapter.

Chapter 2 elaborates the synthesis, characterization and solvent extraction evaluation of calix-benzo-crown (CBC) and calix-crown-6 (CC6) for cesium and other metal ions from nitric acid medium. The calix-crowns were synthesized indigenously starting from its intermediates in good yield and purity. Various spectroscopic techniques viz. ^{1}H, ^{1}C NMR spectroscopy, and gas chromatograph-mass spectrometry (GC-MS) were used to elucidate the structure and conformation of these molecules. The purities of the compounds were confirmed by melting points and elemental analyses. To investigate the basic complexion process of Cs by Calix-benzo-crown (CBC) and calix-crown-6(CC6), solvent extraction studies were carried out and the effect of various factors like, concentration of phase modifier, aqueous phase acidity, ligand concentration, nitrate ion concentration and temperature on extraction of cesium is described in this chapter. In addition to this, a process was developed using 0.01 M calix-crown in dodecane modified with 30 % o-Nitrophenyl hexyl ether (o-NPHE) and 30 % isodecyl alcohol (IDA) separately. In the quantum chemical calculation study, the structures of metal hydrates and their complexes with CBC and CC6 were optimized at hybrid B3LYP level using SVP basis set deployed in TURBOMOLE 7 package. The gas phase binding energy and free energy indicate selectivity order: $Na^+ > Cs^+$ whereas after suitable hydration of metal ions and nitrate ions, the order becomes reverse as obtained in the solvent extraction results. In order to study the selective extraction of cesium with respect to other metal ions, the extraction of cesium was carried out from simulated high level liquid waste solution using 0.01 M calix-crown /30 % phase modifiers/n-dodecane. The results showed that D_{Cs} is much higher compared to other elements, thus indicating the solvent had a very high selectivity for cesium over other elements.

Chapter 3 This chapter elaborates the synthesis of novel amide substituted calix-crowns (CBCAs) for the selective extraction of cesium at high nitric acid concentration. As the amide groups are known to provide intramolecular buffering effects to the extractants from nitric acid, these substituted amides are expected to extract Cs even from high acid. The synthesis of three novel amide substituted calix [4] arene benzocrown-6 (CBCAs) with amide substitution on the benzo group of crown-ether ring has been carried out. The techniques of ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis were used to elucidate the complete structure of molecules.The extraction studies of CBCAs were carried out in n-dodecane modified with isodecyl alcohol (IDA) and o-nitrophenylhexyl ether (o-NPHE) and the results were compared with its non-amide analogues viz. calix-benzo-crown (CBC). Two different diluent systems were used to study the extraction process viz. 30 % IDA/n-dodecane and 30 % o-NPHE /n-dodecane separately. It was observed that in case of 0.01 M /30 % IDA/ n-dodecane the extraction maxima was seen at 8 M HNO_3 while in the case of 0.01 M /CBC/n-dodecane it was observed at 4.5 M nitric acid concentration. For verifying the results, nitric acid uptake was studied and it was found that the difference of uptake by solvent and blank was more in case of CBCAs than for CBC. Higher nitric acid uptake in CBCAs as compared to CBC for all the concentration range of nitric acid, without a fall in D_{Cs}, confirms the intramolecular buffering by amide group. Similar pattern was observed in o-NPHE diluents system also. In order to study the selective extraction of cesium with respect to other metal ions, the extraction of cesium was carried out from simulated PUREX raffinate solution using 0.01M CBCA/30 % IDA/n-dodecane. The property of extracting Cs at higher acidities by the ligand has been successfully utilized for selective separation of Cs from raffinate solution and it was found that CBCA was more effective compared to CBC at higher concentration of nitric acid. In the quantum chemical calculation study, structures of CBCA and its complexes with cesium and cesium nitrate were optimized with at hybrid B3LYP level using SVP basis set in TURBOMOLE 7 package. The gas phase binding energy without ZPE correction were calculated and compared with its non-amide analogue viz. CBC, it was found that the binding energy of CBCA is always higher (∼5 kcal/mol) than the CBC in all three different models, which is in good agreement with the experimentally determined D_{Cs} values. This chapter also includes the radiolytic studies of CBC and CBCA and possible identification of degradation products. The hydrolytic and radiolytic study of both the CBCA-6 and CBC ligands were carried out and the probable degradation pathways were demonstrated which were based tentatively on the mass peak observed in the mass spectrum. From the degradation spectras it was observed that the reaction pathways includes the cleavage of octyl group (C_8H_{17}), crown moiety, $CONR_2$, from calixarene backbone which undergoes further reaction like oxidation and nitration.

Chapter 4 covers the synthesis, characterization and solvent extraction evaluations of novel calix-benzo-crown-6 bisglycolamide (CBCBGA) ionophore in 1, 3-alternate conformation. The techniques of ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis were used for elucidation of structure of molecule. Detailed investigations on the effect of various parameters like, diluents, extraction of alkali metal ions, aqueous phase acidity, ligand concentration and nitrate ion concentration on extraction of cesium are carried out. Stoichiometry of the extracted complex determined by slope analysis method which revealed a molar ratio 1:1 for $CsNO_3$:CBCBGA. The solvent composition of 0.01 M CBCBGA in o-Nitro phenyl hexyl ether (o-NPHE) showed D_{Cs} of 12.5 from 3.2 M nitric acid feed solution. This ionophore is found to be a highly selective ionophore for cesium over other metal ions present in the simulated high level liquid waste solution. DFT studies predict the exothermic nature of complexation in the gas phase as well as solution phase for complexation of Cs^+ and Na^+ ions with CBCBGA as observed in the experiments. The calculated value of difference in free energy, $\Delta\Delta G$ (ΔGext, Cs^+ - ΔGext, Na^+) is found to be -9.49 kcal/mol, which is in good agreement with the experimentally determined value of -5.59 kcal/mol. The extraction free energy was found to be highest with nitrobenzene and lowest with chloroform for both the Cs^+ and Na^+ ions as observed in the solvent extraction experiments. The free energy of extraction was seen to be increased with increase dielectric constant of the organic solvents as observed in the solvent extraction experiments.

Chapter 5 includes the development of a process for selective separation of cesium from acidic nuclear waste solution using 1,3-dioctyloxycalix[4]arene-crown-6 (CC6)/n-dodecane modified with isodecyl alcohol. In order to get complete recovery of cesium from HLLW, it is necessary to develop a process which can be utilized for plant scale application. By varying the parameters like concentration of phase modifier (IDA), aqueous phase acidity, ligand concentration, nitrate ion concentration etc. it was observed that the solvent with 0.03 M CC6 / 30% isodecyl alcohol/n-dodecane is efficient for quantitative recovery of cesium. Counter-current mixer-settler experiments was performed with four stages of extraction, two scrubbing stages and four stripping stages which gave about 99% recovery of cesium with very high selectivity from simulated high level waste solution. Mixer-settler runs were smooth without any hydrodynamic problems, the extraction and stripping efficiencies were high and about 99% recovery of cesium was obtained using SHLW solution. The experimental results obtained in this work would help to freeze flow sheet design for efficient recovery of cesium from actual HLW.

Chapter 6 Summarises and concludes the important results of the research work presented in this thesis along with a direction for future research.

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1. Introduction

1.1 Introduction

India is the seventh largest country and the second largest population (~ 1.3 billion) of the world. With rapid economic growth expected in the coming decades, conventional energy resources will not be adequate to guarantee energy sustainability. Moreover, the impact of green house gases from conventional sources will also put a cap on generation rate using conventional fuels. Moreover, coal and other natural resources in India would be insufficient to meet even today's world average per capita consumption, both quantitatively and qualitatively. However, to meet the increasing energy demands of a developing country like India, the only sustainable energy resource available on a near-term time frame is nuclear energy. Nuclear energy has proven as an alternate source of sustainable energy for almost half a century and is a "green energy" source with practically no carbon emission. The cost of production is comparable with available low grade fossil fuels and other renewable energy sources. Till now only about 2.77% of country energy requirement is fulfilled by nuclear sources while oil and coal continue to be the major sources of energy production as shown in Fig. 1.1 [1].

A three stage nuclear power programme was evolved by Dr. Homi Bhabha to secure the countrys long term energy independence, through the use of limited uranium resources and the vast reserves of thorium in the monazite sand. In the first stage of the programme, natural uranium fuelled pressurized heavy water reactors (PHWR) produce electricity while generating plutonium-239 as a by-product. In the second stage, fast breeder reactors (FBRs) would be deployed to use a mixed oxide (MOX) fuel made from plutonium-239 and uranium, recovered by reprocessing spent fuel from the first stage PHWRs. In FBRs, plutonium-239 undergoes fission to produce energy, while the uranium-238 present in the mixed oxide fuel breeds additional plutonium-239. Thus, the Stage II FBRs are designed to "breed" more fuel

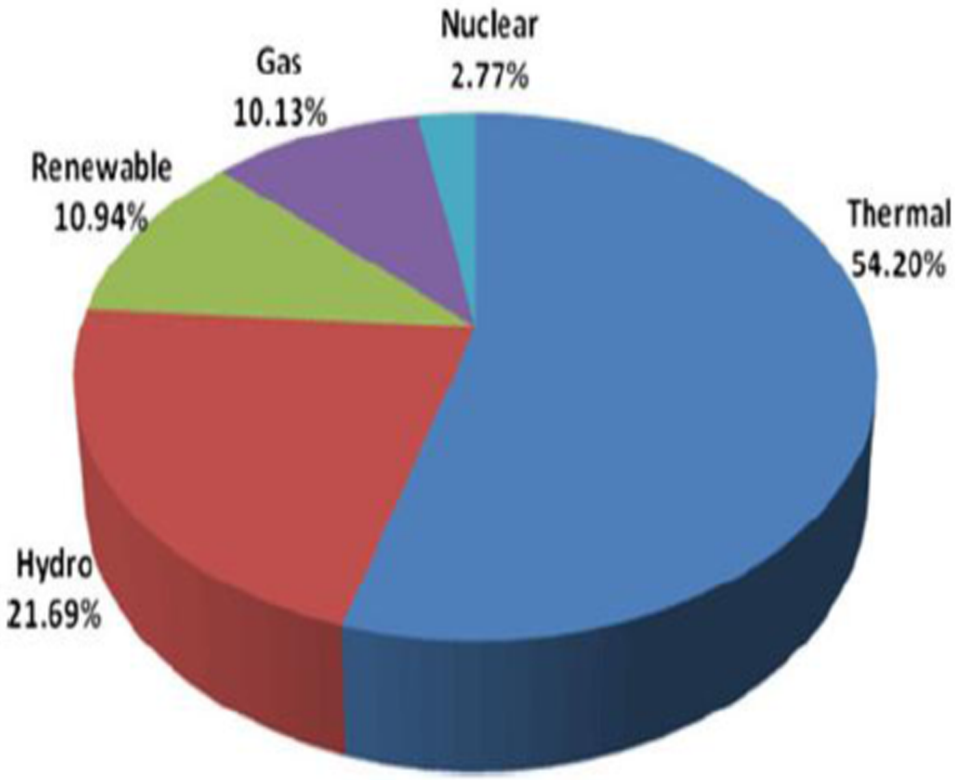


Figure 1.1: *Break–up of installed power capacity in India as on January 31, 2011*

than they consume. Once the conversion of all the available uranium to plutonium is achieved, thorium will be introduced as blanket material in the fast reactor and will be converted to uranium-233 for use in third stage ^{232}Th -^{233}U based reactors [2]. Fig 1.2 shows the three stage Indian nuclear energy programme as envisaged by Dr. Bhabha. Reprocessing and recycling of both fissile and fertile components into appropriate reactor systems is the salient feature of this programme.

1.1.1 Nuclear fission

Nuclear fission was discovered as a chance finding during the production of transuranium elements with atomic number greater than 92 by means of (n, γ) reactions followed by β-decay of the product nucleus. The product formed could not be explained by the above mechanism [3]. But in 1939, Hahn and Strassmann performed a beautiful and thorough set of experiments which proved beyond doubt the phe-

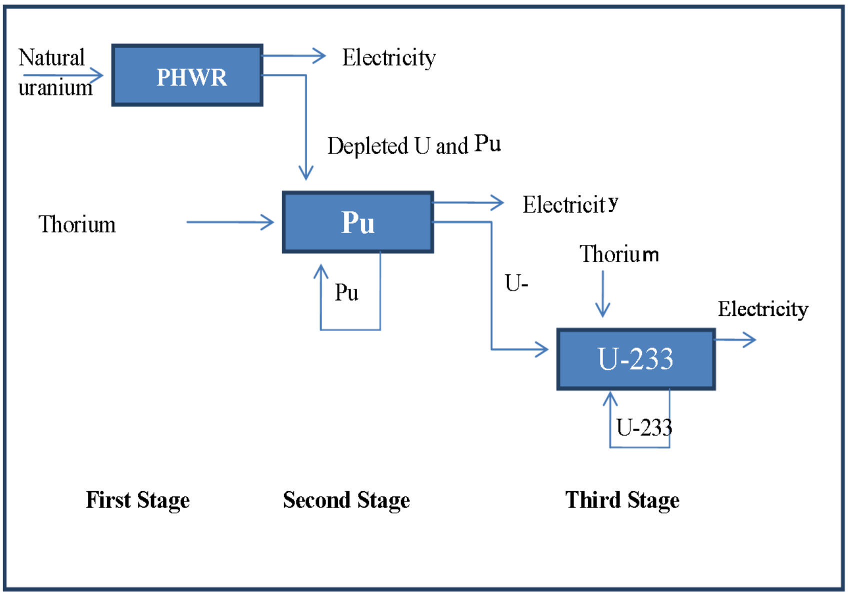


Figure 1.2: *Three-stage Indian Nuclear Program*

nomena of nuclear fission.

This discovery had laid a milestone in the history of science. When U-235 undergoes fission in a nuclear reactor by slow neutron (E∼0.025 eV), it splits into fission products of lighter masses along with release of neutrons and extra binding energy of the nucleons. According to Einsteins mass-energy relation, the binding energy corresponds to ∼ 200 MeV per fission. This large energy is utilized for production of electricity in nuclear reactor. The following equation shows the nuclear fission process.

$$^{238}U +^{1} n \rightarrow A + B + 2 - 3^{1}n + Energy \tag{1.1}$$

The fission products include every element from zinc through lanthanides as a result of unsymmetrical fragmentation of fission nuclides. The majority of mass yield falls under the two maxima around mass number 95 and 140 as given in the mass-yield curve of thermal neutron fission of ^{235}U in Fig. 1.3 below. The absorption of slow neutron by U-235 rendering it unstable leading to nuclear fission yielding an average of 2.5 neutrons per fission. The fast neurons released have little capture probability in U-235, hence to increase the capture probability these neutrons are slowed down by moderation. These slow neutrons are now able to sustain further

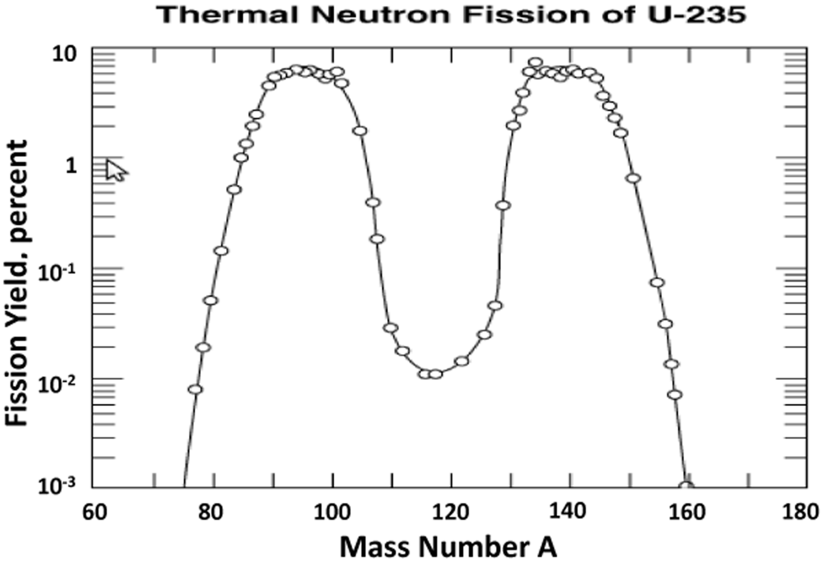


Figure 1.3: *Fission yield curve of U-235 by thermal neurons*

nuclear chain reactions, the process might be self-perpetuating, but this will end up with an uncontrolled enormous amount of energy release leading to explosion. Hence, in a nuclear reactor the net availability of neutron is just maintained to sustain the chain reaction. This is possible by using proper fuel composition and control mechanism. The energy released during fission is converted to heat energy using a suitable coolant. The heat produced is finally converted to electricity using steam turbines. This elemental idea was used for electricity production from controlled fission reaction by designing a nuclear reactor. There are three more fissile nuclides viz. U-233, Pu-239 and Pu-241 which can undergo nuclear fission with thermal neutrons. Only U-235 is naturally existing and the other are manmade.

Nuclear fuel used in a reactor usually is a mixture of fissile and fertile nuclides. U-238 and Th-232, the two naturally existing fertile nuclides, are used in combination with fissile nuclides which on irradiation with neutron yield fissile nuclides.

$$^{238}U \overset{1n}{\rightarrow} {}^{239}U \overset{-\beta}{\rightarrow} {}^{239}Np \overset{-\beta}{\rightarrow} {}^{239}Pu \tag{1.2}$$

$$^{232}Th \overset{1n}{\rightarrow} {}^{233}Th \overset{-\beta}{\rightarrow} {}^{233}Pa \overset{-\beta}{\rightarrow} {}^{233}U \tag{1.3}$$

1.1.2 Nuclear reactors

There are more than 438 commercial nuclear reactors presently operating in over 30 countries, accounting for about 14 percent of world electricity production. The most widely used reactor type is Light Water Reactor (LWR) both in number and total power generation [4]. There are mainly two types of LWRs. One is Boiling Water Reactor (BWR) in which coolant water in reactor core is allowed to boil and resulting steam is directly send to turbine. The second one is pressurized water reactor (PWR) where coolant water in reactor core is kept under sufficiently high pressure to suppress boiling of coolant, steam is generated in heat exchanger and sent to turbine for the electricity generation. In India, a number of pressurized Heavy Water Reactors (PHWR) with natural uranium as fuel (0.7 % U-235, 99.3 % U-238) and heavy water as moderator to thermalize the fast neutrons are deployed for power generation. Two BWRs and a PWR are also inducted into the fleet of reactors to augment the growing energy need. India has an installed nuclear energy capacity of 4,391 MWe and has five more units under construction. The installed nuclear capacity will reach 9,580 MWe by 2016 and may reach 20,000 MWe by 2020 with the induction of a few more LWRs, AHWRs and FBRs.

1.1.3 Nuclear Fuel Cycle

There are two matured fuel cycles in vogue globally. The open fuel cycle and the closed fuel cycle. In the open fuel cycle, the fuel after irradiation is treated as a waste and is discarded as such without any attempt to recover the fuel values. This concept is followed in countries like USA, Germany, Sweden etc. Some other countries like France, UK, Japan, India etc. follow a closed fuel cycle approach and adopt reprocessing and recycle policy to maximise the utilisation of fuel resources. The process of recovering fissile and fertile components from the highly active fission products and converting the fission product waste into an amenable form for waste management is known as reprocessing. In the closed fuel cycle, the fuel value can be extracted to the optimum and generate maximum energy from the mined uranium.

Closed fuel cycle also provides a path for the advanced management of the reprocessed waste and is considered as a better option capable of providing solutions to the long term hazards of nuclear waste.

The combined process of mining, milling, crushing and grinding of ore, followed by enrichment of fissile element in fuel, fabrication into fuel rods, burning in reactor and management of nuclear waste is known as the complete nuclear fuel cycle. The schematic of the complete nuclear fuel cycle is shown in Fig.1.4. The fuel cycle is divided into two parts, processes prior to irradiation in reactors are known as the front-end of the fuel cycle while the processes after irradiation are termed as the back-end of the nuclear fuel cycle.

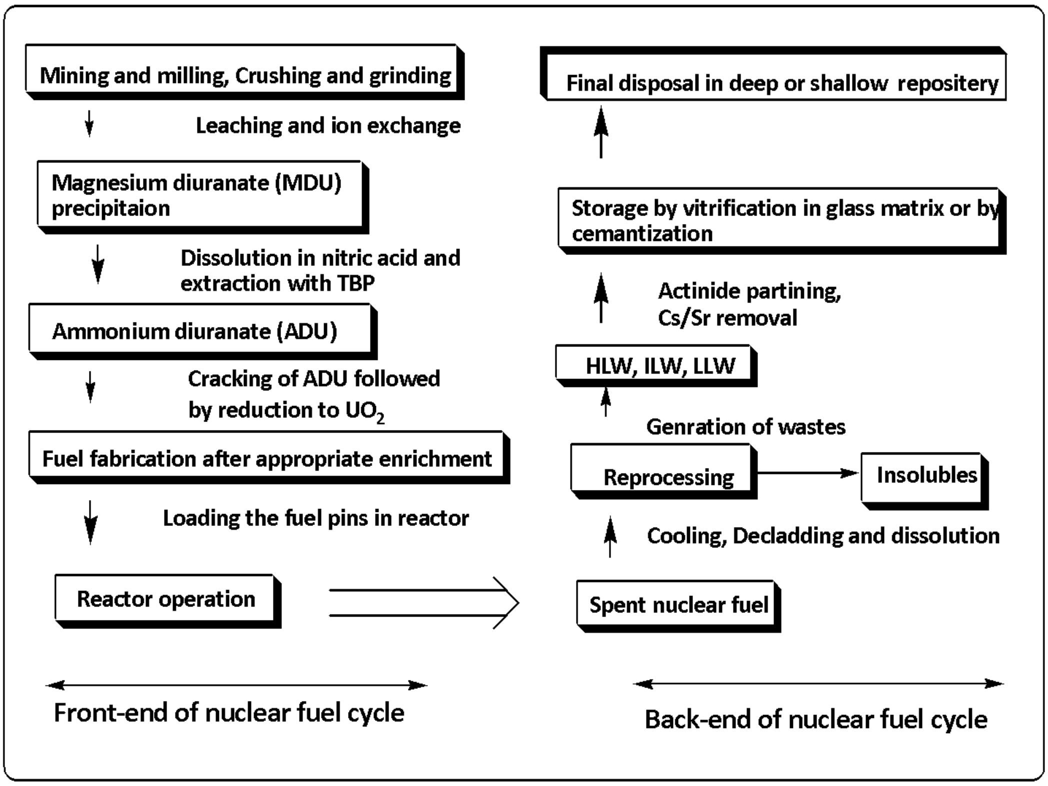


Figure 1.4: *Complete nuclear fuel cycle*

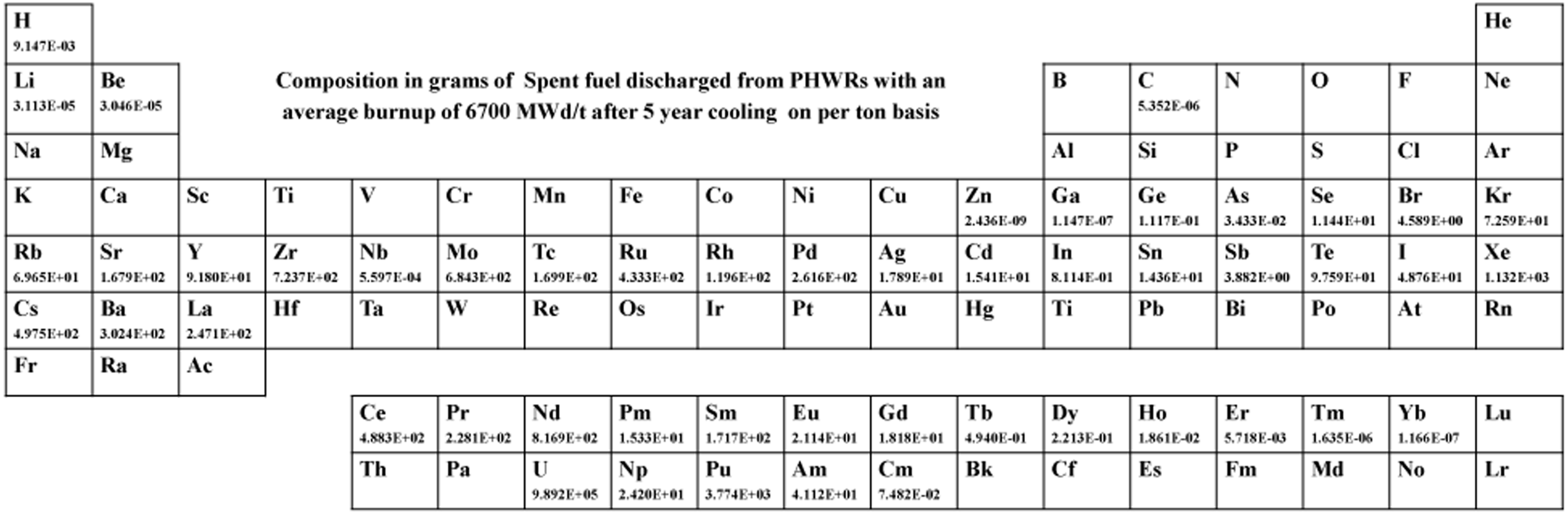
1.1.4 Reprocessing

The spent fuel contains both fissile and fertile components with significant energy value along with radioactive fission products. The spent fuels from the reactors are stored for 5-10 years prior to reprocessing. The composition of the spent fuel is dependent on the initial fuel composition, burn up and the type of reactors from which they originate. Fig. 1.5 gives the typical fission product composition of one ton of spent fuel from PHWRs with an average burn up of 6700 MWd/t after a cooling period of 5 years.

Reprocessing started way back in the middle of the last century and a number of processes were developed especially for military purpose. Decades after the second war saw significant development in this technology into industrial scale. The process evolved, PUREX, is synonymous to reprocessing. Today world over only PUREX process and its variations are in use all over the world wherever reprocessing is adopted. In the generic scheme of PUREX process, the fuel assemblies are routed through a shearing and dissolution unit before extraction of uranium and plutonium by Tributyl phosphate from fission products. The uranium and plutonium are further separated from each other using a selective reductive stripping of Pu from U-Pu loaded organic phase. Purification of uranium and plutonium is further achieved by one or more supplementary solvent extraction cycles and are recycled back in appropriate reactors after fabrication into fuels. The acidic waste originating from the PUREX process contains residual U and Pu, long-lived minor actinides such as Np, Am, Cm and radioactive fission products, mainly rare earths,Sr-90, Cs-137 and Tc-99. The present strategy is to vitrify the waste in glass matrix for disposal in geological repositories after cooling in surface facilities. The generic Purex flow sheet is given in Fig.1.6.

1.1.5 Nuclear Waste

During the entire fuel cycle from mining to reprocessing radioactive wastes are generated differing in constituents and composition. These wastes are handled in a safe manner as per the national and international guide lines. But, among these wastes, the spent fuel in the open cycle and the high level waste generated during the reprocessing of spent fuel contain toxic nuclides which need isolation of about a million years prior to losing its toxicity. This issue is in the fore front and is



Composition in grams of Spent fuel discharged from PHWRs with an average burnup of 6700 MWd/t after 5 year cooling on per ton basis

H 9.147E-03																	He
Li 3.113E-05	Be 3.046E-05											B	C 5.352E-06	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn 2.436E-09	Ga 1.147E-07	Ge 1.117E-01	As 3.433E-02	Se 1.144E+01	Br 4.589E+00	Kr 7.259E+01
Rb 6.965E+01	Sr 1.679E+02	Y 9.180E+01	Zr 7.237E+02	Nb 5.597E-04	Mo 6.843E+02	Tc 1.699E+02	Ru 4.333E+02	Rh 1.196E+02	Pd 2.616E+02	Ag 1.789E+01	Cd 1.541E+01	In 8.114E-01	Sn 1.436E+01	Sb 3.882E+00	Te 9.759E+01	I 4.876E+01	Xe 1.132E+03
Cs 4.975E+02	Ba 3.024E+02	La 2.471E+02	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce 4.883E+02	Pr 2.281E+02	Nd 8.169E+02	Pm 1.533E+01	Sm 1.717E+02	Eu 2.114E+01	Gd 1.818E+01	Tb 4.940E-01	Dy 2.213E-01	Ho 1.861E-02	Er 5.718E-03	Tm 1.635E-06	Yb 1.166E-07	Lu
				Th	Pa	U 9.892E+05	Np 2.420E+01	Pu 3.774E+03	Am 4.112E+01	Cm 7.482E-02	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.5: *Typical PHWR Spent Fuel Composition (Origen code calculated values)*

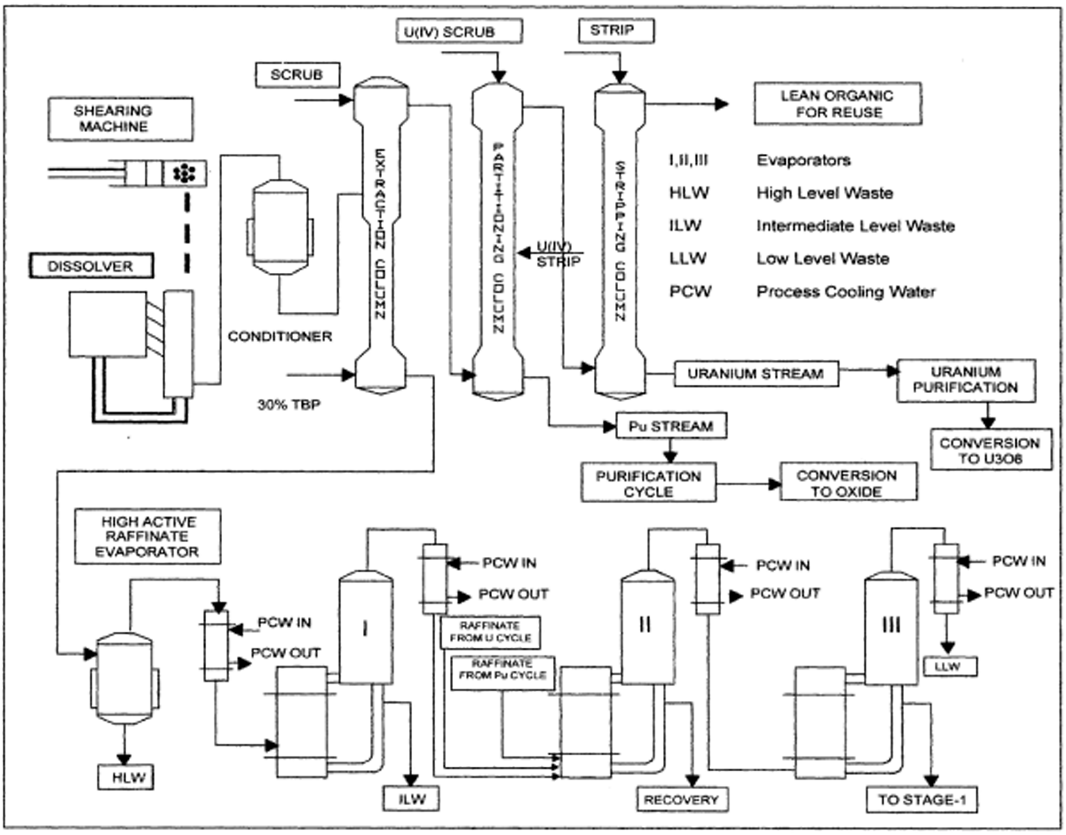


Figure 1.6: *Generic PUREX Flow sheet*

the major reason for the apathy of general public towards acceptance of nuclear energy as a sustainable source of energy. An strategy to reduce the long term radiotoxicity of the waste is being developed in countries like US, France, Japan, India and Russia, aims to separate minor actinides and long lived fission products from high level waste and transmute them into short lived products. This strategy will leave a waste containing mainly Cs and Sr which contribute to more than 90 percent of decay heat. They can also be further separated to reduce the decay heat of the vitrified waste and will result in a much reduced waste volume. Further the surveillance requirement of the repository also will be greatly reduced. Countries like USA, not interested in civilian reprocessing earlier, are currently considering reprocessing as a means of reducing the toxicity based on the above strategy. It is necessary to eliminate harmful radiotoxic elements from the large volume of high level radioactive waste which pose a high risk to public and environment when exposed. The annual spent fuel generated by nuclear plants is approximately 10,500 tonnes of heavy metal per year, with roughly 8,500 tonnes of heavy metal going into long-term storage and about 2,000 tonnes of heavy metal going for reprocessing, but much of it is in interim storage. Safe management of this radioactive waste by efficient separation processes is key to the success and public acceptance of nuclear energy [5, 6]. To achieve the objectives discussed above different countries have embarked on various partitioning and transmutation strategies to deal with the threat posed by the long lived radioactive nuclides. This has resulted in the development of processes in aqueous and non aqueous routes. Even though the non aqueous routes may have many advantageous over the aqueous routes, the level of maturity needed for an industrial process will be eluding at least for a few decades. Whereas aqueous routes are more easily adaptable, scalable and endowed with large scale expertise. Given below is a brief discussion on radioactive waste classification followed in the nuclear fuel cycle.

1.1.6 Categorization of Nuclear waste

Several methods are used to categorize radioactive waste; like waste origin (front end or back end), physical properties (solid or liquid), type of radiation emitters (alpha, beta or gamma radiation), dose rate at the surface of the waste package etc. These systems will be difficult to use as the waste streams differ on a case to case basis. A system of classification depending upon the final safe disposal of conditioned waste is preferable as outlined in the waste category classification defined by IAEA[7]. Worldwide, the nuclear waste is categorized depending on the radioactivity level of the wastes as described under:

1.1.6.1 Low level liquid waste

Any solid waste with a dose rate greater than or equal to 30 mrad/Hour gamma radiation on the surface is called LLW. The liquid waste having activity greater than or equal to 1mCi/L is called LLW. It is generated in various streams in nuclear reprocessing operations, laboratories and hospitals etc. It contains mainly the short lived radioactive elements associated with paper, bags, filter and lean waste solutions. The LLW is dumped in the surface sites after reducing the waste volumes.

1.1.6.2 Intermediate Level Waste (ILW)

Any solid waste with a dose rate less than one Rad/hour and greater than 30 mrad/hour on the surface of waste package is called ILW. The liquid waste ranges from millicurie to curie per litre called ILW. Usually, ILW composed of materials originating from the management of high active wastes, resins, chemical sludge, nuclear fuel cladding, contaminated materials from reactor decommissioning etc. used for concentration of activity, components of nuclear reactor etc. This waste requires more attention compared to low level liquid waste due to large radioactivity associated with it. It needs to be buried in shallow repository after solidification in concrete. This needs constant surveillance and monitoring.

1.1.6.3 High-level waste (HLW)

Any solid waste with a dose rate greater than or equal to 1 Rad/Hour by gamma radiation on the surface of waste package is called HLW. The liquid waste having activity greater than or equal to 1 Ci/Lt is called HLW. Any other waste with the radioactivity level enough to generate heat more than 2 KW/m^3 by radioactive decay process is defined as HLW. Because of the high activity HLW is handled by remote handling facilities in properly shielded hot cells. High-level waste originates from spent nuclear fuel (SNF) reprocessing and contains large concentrations of both short and long lived radionuclides. The concentration and containment (CC) approach is planned for the safe management of HLW. In this process, the HLW is disposed off in deep geological repositories after immobilization of waste in glass matrices followed by containment in stainless steel canisters. Constant surveillance is required for any kind of radioactivity escape into the environment. Due to various heat emitting radioisotopes (e.g. Cs-137, Sr-90 etc.) present in the HLW, there is a considerable risk of deformation of glass matrices and leaching out of radionuclides causing adverse effect on environment. Hence surface storage with proper cooling is adopted prior to disposing of the vitrified waste as a part of the management for disposal of HLW. After treatment of the spent fuel by PUREX process, the HLW contains mainly unrecovered U and Pu, long-lived minor actinides such as Np, Am, Cm and radioactive fission products, mainly rare earths, Tc-99, Sr-90 and Cs-137. Partitioning of minor actinides and their transmutation, removal of Sr-90, Cs-135 and Tc-99, will considerably reduce the radiological hazard associated with this waste, thereby making the waste more amenable for management[8–10].

1.1.7 Advanced PUREX process and Actinide Partitioning

Currently Purex processes is aiming quantitative recovery of uranium and plutonium from the associated fission products and also from each other. Hence this process leaves behind a few potentially toxic actinides like Np, Am and Cm in the high level waste along with trace amounts of residual U and Pu. These nuclides along with some long lived fission products like Tc-99, I-129, Cs-135 etc., make nuclear energy unfriendly to the environment from public perspective. Some of the by-products from this waste has commercial application and their separation from the waste will make the disposal period very short with minimum surveillance. Almost three decades of research has gone into the field of separation of minor actinides from the Purex HLW. Feasibility of separating Tc-99, I-129 and Np by an advanced PUREX process along with residual U and Pu has been demonstrated. Minor actinide group separation has been demonstrated on an engineering scale along with trivalent fission products conclusively using a number of potential tailor made solvents from actual Purex HLW. Further separation of actinides from trivalent fission products is at demonstration stage and the potential ligands are under various trial runs. Tailor made reagents for separation of ^{137}Cs and ^{90}Sr are also on trials in different laboratories and pilot plants. Pyrochemical methods parallel to the aqueous routes are also being pursued in many laboratories globally. Fig. 1.7 gives the advanced spent fuel treatment and waste management strategies for closing the fuel cycle for an environmentally friendly future for nuclear energy through aqueous processing.

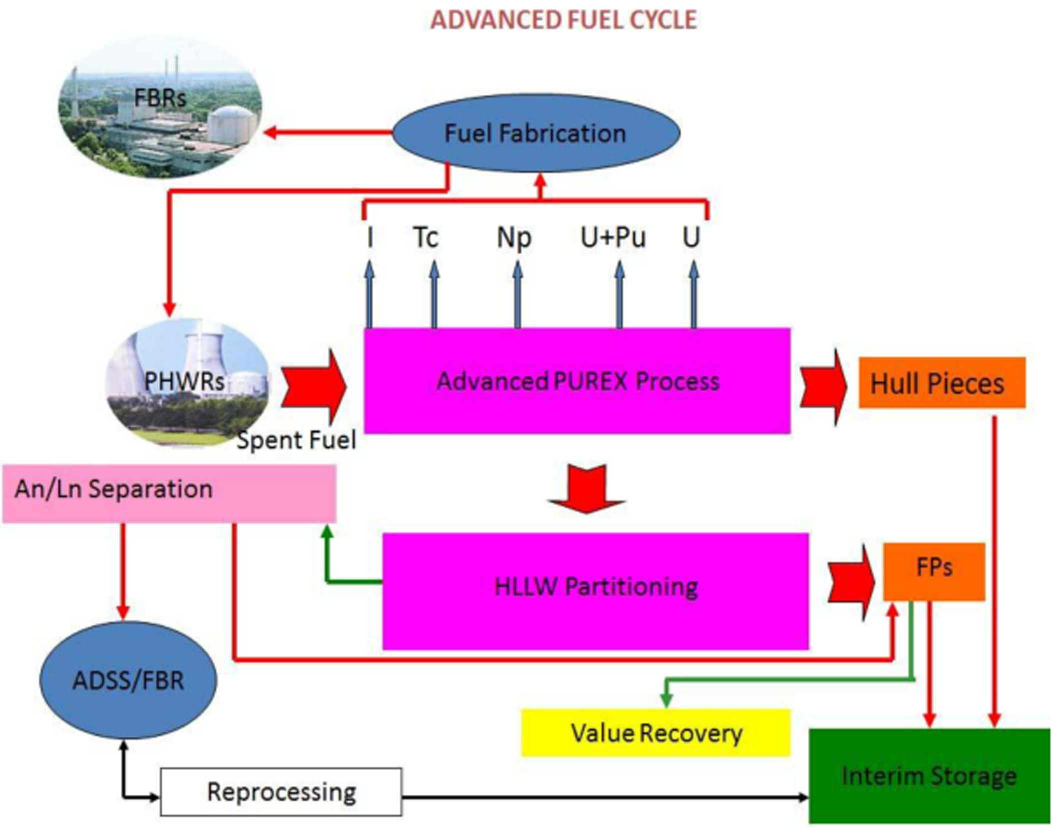


Figure 1.7: *Advanced Spent fuel Treatment and Waste management*

1.2 Motivation for the present work

Considerable work has been done in the field of minor actinide separation as a part of the development studies on actinide partitioning and transmutation. Several reagents are currently available commercially at reasonable purity and at economical rates. Whereas, the solvent design for separation of alkali metal ions are often intricate and the costs are often prohibitive for commercial applications. In the present context, the targeted nuclide was Cs-137 as it has many potential applications and also available in plenty in Purex HLW. Hence the goal of the present work is to indigenously synthesise Cs specific molecules from commercially available reagents with good yield and purity at economical rates for use with PUREX HLW. Characterisation and testing of these molecules for their efficacy in separation of Cs from Purex HLW is planned. Literature survey was carried out to explore the status of various reagents and techniques used for the separation of Cs and to identify potential ligands for the task in hand. The following section will briefly cover the potential applications of Cs-137 in the Indian context and also the design, synthesis and the processes reported in literature on the separation of Cs using different reagents.

1.3 Radiocesium: Occurrence, hazards and benefits of separation from nuclear waste

Cesium and strontium are the major fission products formed during fission reaction as can be observed from Fig 1.3, the maxima occurs at mass numbers 90-100 and 135-145 for the fission of U-235. The major isotopes of cesium, Cs-135 and Cs-137 are released to the environment by nuclear plant accident, nuclear weapons testing and reprocessing of nuclear waste. During the reprocessing, the raffinate of PUREX process (HLW) mainly contains long lived minor Actinide, Cesium, Strontium and other F.Ps. Among the various isotopes of cesium, the two major radioisotopes Cs-135 ($t_{1/2} \sim 10^6$yrs) and Cs-137 ($t_{1/2} \sim 30$ yrs) are present in the High level liquid waste solution in significant concentration. The removal of these radionuclides will result in following advantages[11]:

- Cs-137 is one of the major heat emitting radionuclides and its removal leads to reduction in heat load hence, less volume of repository will be required for final vitrification. While doing so the surveillance period above ground also will be reduced.

- It also reduces the risk of leaching out of other radioactive elements from the repository along with.

- Cs-135 is long lived ($t_{1/2} \sim 10^6$yrs) and one of the most mobile ones in the repository and can cause adverse effect on environment after leaching out from repository along with Cs-137 and other radionuclides.

- Cs-137 is a β, $\gamma -$ emitter and can be used as alternate source for cobalt-60 for medical and industrial applications like, preservation of foodstuffs by killing bacterial growth, blood irradiation and medical accessories sterilization, cancer treatment by brachytherapy and scintillation cameras.

- Cs-137 ($t_{1/2} \sim 30$ yrs) have half life of almost 6 time higher than Co-60 ($t_{1/2} = 5.2$ yrs), so need not to be replaced frequently as Co-60. Also Cs-137 with $E_\gamma = 0.661$ MeV makes it easier to shield as compared to Co-60, $E_\gamma = 1.173$, 1.332 MeV.

This makes the separation and recovery of cesium valuable. Among the alkali metal ions the cesium ion is weekly coordinated and offers resistance to formation of coordination complexes for separation. This makes the effective partitioning of cesium radionuclides from HLW, most challenging.

1.4 Cesium recovery processes

There are number of methods developed for separation of cesium from acidic as well as alkaline medium depending on the requirement. These methods include techniques like precipitation, ion exchange and solvent extraction. The next part describes the various method developed.

1.4.1 Precipitation

Precipitation is a method for separation of metal ion from a concentrated solution with the help of suitable reagent called coagulant. The most commonly used reagents are alums, Lime, iron salt and organic polymers. The alums were used at Oak Ridge National Laboratory (ORNL) for separation of cesium at commercial scale [12]. Since their target was to use it at large scale, so the yield and purity of precipitate was not looked into. Another coagulant sodium tetraphenylborate (NaTPB) has been used for precipitation of cesium and potassium form radioactive waste solution. The sodium of NaTPB was replaced with cesium in precipitation reaction and settles down in bottom as slurry. This slurry after removal was vitrified in borosilicate glass for final disposal. The poor stability of NaTPB in acidic as well as alkaline medium was its disadvantage [13]. The next reagent Sodium phosophotungstic acid$Na_3[P(W_3O_{10}).4H_2O$,has been used at Hanford Site, USA to precipitate the cesium from acidic waste solution (0.5 to 2M)[14].

1.4.2 Inorganic Ion exchangers: Zeolites

These were the first compounds for treatment of radioactive waste solutions. The zeolites are only used for recovery of caesium from neutral and alkaline medium. This was used for large scale decontamination of reactor containment building and primary reactor coolant after the Three Mile Island accident [15–17]. These have advantages like radiation stability, good selectivity and easy implantation during the separation process. On the other hand its efficiency largely depends on presence of competitive ions and its inherent instability in mild acid condition.

1.4.3 Metal phosphates of Polybasic acids (III) and (IV) metals

Polybasic acids and certain hydrolysable cations like zirconium, Thorium and Titanium when suitably combined with anions like phosphate, vanadates, tungustante and molybdate were known to produce better ion exchangers over zeolites. The general formula for these are as $M(IV)(HXO_4)_2.nH_2O$ where M= Zr, Ti, Th and X= P, V, W, Mo etc. The zirconium phosphate was studied extensively and it was found that exchange behaviour was unaffected for a narrow temperature change, pH and presence of various type of anions present like EDTA, phosphate etc. in the feed solution. This was synthesised by reacting zirconyl chloride with phosphoric acid and obtained as gelatinous precipitates. This contains a number of exchangeable sits H, -OH etc. for the exchange of various cations. This material is amorphous and tends to hydrolyse in alkaline and hot water. Due to amorphous behaviour it was difficult to get structural information of zirconium phosphate [18–21] .The zirconium phosphate shows better exchange for caesium but after making crystalline, the caesium exchange ceased due to structural changes. These zirconium and titanium phosphate after modification with ferrocyanide and molybdate are found to be highly selective for caesium [22].

1.4.4 Ammonium MolybdoPhasphate (AMP's)

The "Baxer and Griffin" discovered the phenomenon of exchange of potassium ion by ammonium ion during the washing of ammonium molybdophoasphate precipitate with potassium nitrate solution. They found this exchange to be reversible as the replaced molybdate when treated back with ammonium nitrate they obtained the ammonium molybdate again. Further research by many researchers led to the fact that exchange is also possible in acidic solution of various metal nitrates [23, 24]. This Ammonium molybdophosphate with an chemical formula $(NH_4)_3PMo_{12}O_{40}.3H_2O$ have dark yellow appearance and its structure consists of a polyhedran with 12 MoO_3 making a porous polyhedron sphere and phosphate group sitting in the centre of this polyhedron [25].

This AMP was seemed to be the more promising ion exchangers for selective cesium recovery from the acidic waste solution. The affinity of AMP for cesium is quite high over large amounts of other metal ions like Rb^+, K^+ present in the waste solution with almost quantitative recovery. Also the separation factor for Cs^+/Na^+ is quite high and thus utilized for separation of cesium from high level liquid waste solution. The merits of AMP include the high radiation stability, easy to synthesize with cheaper chemicals, high cesium loading and the faster sorption rate [26]. The disadvantage of AMP arises due to its microcrystalline structure making it difficult to handle during the column operation. This was overcome by using the various reagents like alumina, poly-acrylonitrile etc., which act as binder and also provides solid support for better usability without affecting the cesium uptake behavior. Ammonium molybdophosphate-alumina (AMP-A1203) and Polyacrylo nitrile (PAN) has been studied by various researchers for recovery of cesium from simulated high level liquid waste solution having $\sim$ 3 M nitric acid [27–30]. Another drawback arises from its high distribution ratio of cesium making it very difficult to elute with de-ionised water. The sorption is found to be hardly reversible and this cesium loaded AMP needs large volume of alkaline solution for dissolution. After dissolution in sodium hydroxide this will no longer be available for reuse and thus it is kept as such after concentrating to small volumes.

1.4.5 Metal hexacyanoferrates (MHCFs)

The studies on these MHCFs established that these can be utilized for selective cesium extraction at high nitric acid medium. In general, these have been represented by a structural formula $A_mB_n[Fe(CN)_6]xH_2O$, where A is transition metal ions like Cu , Ni etc and B is alkali metal ions. These exhibits a face-centered cubic lattice with an average inner diameter of $\sim$ 320 pm. The inner diameter is mainly governed the cyanide ions. The alkali metal ions which are present on the surface of lattice are being exchanged by cesium ions [31, 32]. These can be synthesized by the reaction of transition metal salt with alkali metal hexacyanoferrates salt at a particular reaction condition. The product obtained as a powder and therefore difficulty arises during practical operations. In order to obviate the difficulties, these were blended with polymer supports like polyacronitrile, silica, zeolites etc. The advantage of these includes the fast-binding kinetics and high loading capacity through rigidly open porous structure and extremely high surface area of the support [33]. The disadvantage of these HCFs is its instability in highly alkaline medium and it cannot be incorporated into classical embedding matrixes for final vitrification [34].

1.4.6 Organic ion exchangers:Phenol formaldehyde resin

Miller and Kline first introduced the phenolsulfonic acid based cation exchange resin named, IR-100 and IR-120 for removal of cesium from alkaline medium [35]. The Resorcinol-formaldehyde (RF resin) resin was first used for removal of cesium from Hanford Tank waste. Since then, it was assumed as a satisfactory solution for removal of Cesium form alkaline medium. This has been used worldwide due to its low cost of production, easy operation and good selectivity of cesium over large amount of sodium ion present in alkaline waste solution [36].

The Resorcinol-formaldehyde polycondensate (RF-resin) was synthesized by condensation of Resorcinol with formaldehyde in presence of an inorganic base like sodium carbonate. The mechanism of synthesis includes three steps. In the first step called addition step, the phenoxide ion (electrophile) formed in alkaline medium attack on carbonyl group (electrophilic) of formaldehydeto give methylolphenols. In the second step called condensation, formation of the methylene (-CH_2-) and methylene ether (-CH_2O-) bridged structures takesplace. In the third step, disproportionation of methylene ether occurs as shown in Fig. 1.8 resulting in phenol formaldehyde resin. [37, 38]. The phenolic -OH groups present in resin ionizes under alkaline environment thereby, providing the cation exchange sites to separate cesium with very high efficiency from the alkaline solution. The instability of re-

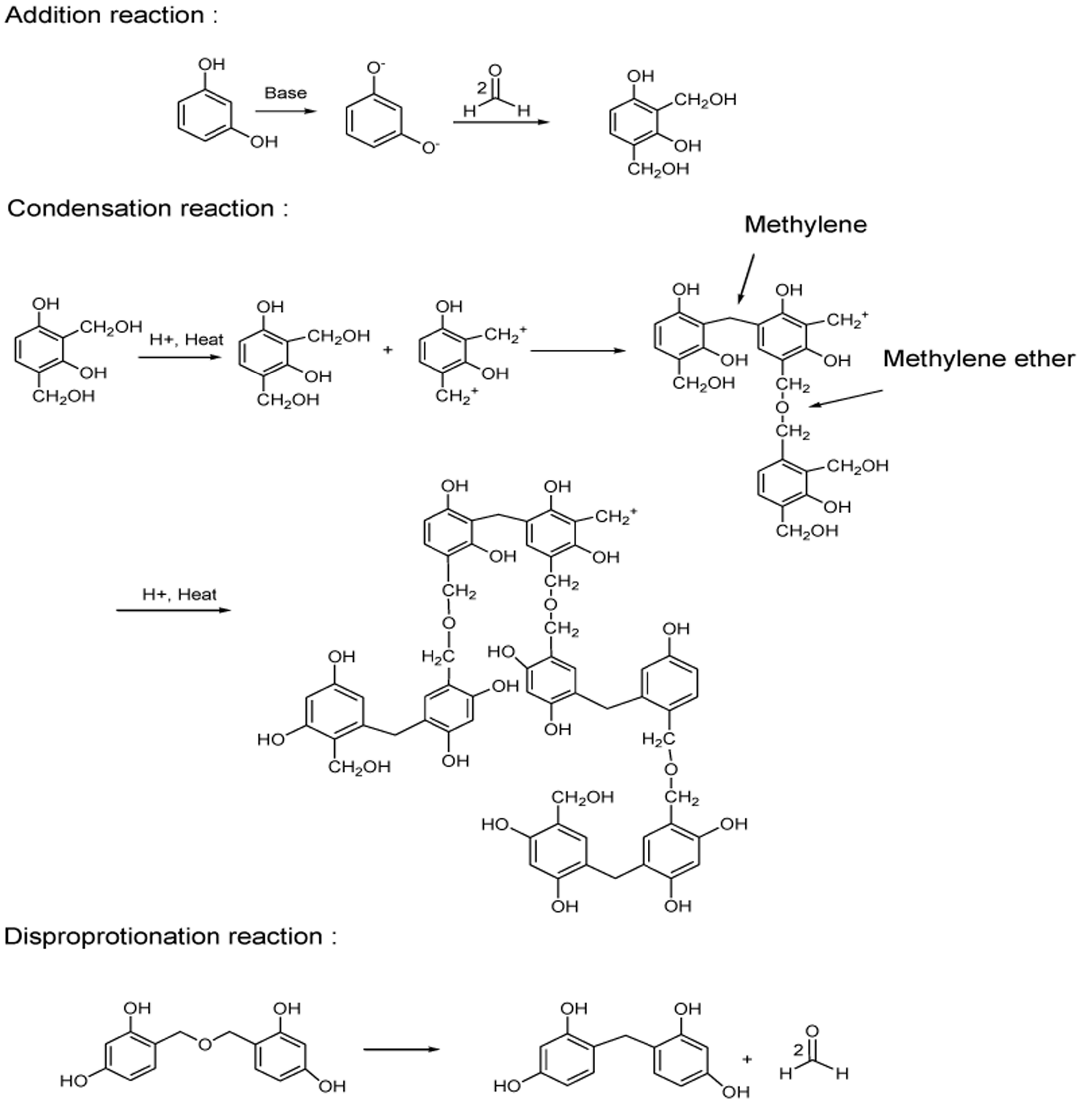


Figure 1.8: *Reaction mechanism for Resorcinol-formaldehyde synthesis*

sorcinolformaldehyde in alkaline solutions arises mainly due cleavage of the bridge methylene bonds. This deploymerization of polymer leads to the loss of selectivity for cesium over other cations. In acidic medium nitration occurs on benzene and alters the structure leads the variation in distribution ratio of cesium. Degradation in acidic medium leading to partial dissolution of polymer in acid after nitration of aromatic rings and cannot be of further use. Being used at higher pH, the need large volume of acid for elution is one of its disadvantage [39]. Similar compounds with the common phenol group Duolite ARC-9359 (phenolic-methylenesulfonic), Duolite S-30 (phenolic), Duolite S-761 (phenolic), etc. exibits the same characteristics towards cesium extraction from alkaline solution. These were tested on both type of waste low level liquid waste (LLW) and high level liquid waste (HLW) solution for cesium removal [40, 41].

1.4.7 Solvent Extraction

Solvent extraction is a method for separation of one or more solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid. It is an extraction of a metal ion of interest from one liquid into another liquid phase. Due to its various advantages like high throughput, good selectivity and easy operation makes it attractive for separation chemists. The cationic cesium have large size, therefore, least hydrated among other alkali metal ions placed above in the periodic table. The size selective crown ethers like 21-crown-6 are suitable for cesium complexion and solvent extraction can be utilized for selective cesium separation. The hydrophobic anions like chlorinated cobalt dicarbollide is also found for selective cesium separation by solvent extraction. There are various calix-crown-6 available having cavity of similar size as that of hydrated cesium for selective cesium extraction.

1.4.7.1 Crown ethers

In 1967, Charles Pedersen discovered the crown ethers while synthesizing a complexing agent named bis[2-(o-hydroxyphenoxy)ethyl] ether for divalent cations. Pedeson et. al. obtained a white crystalline by-product arising from the small impurity of catechol. After characterization it was found to be 2, 3, 11, 12-dibenzo-1, 4,7, 10, 13, 16-hexaoxacyclo-octadeca-2, 11-diene (DB18-crown-6) a cyclic polyether capable of forming stable complexes with potassium ions and many salts of other alkali and alkaline earth metals shown in Fig. 1.9. After this they realized that these types of cyclic polyethers can represent the new class of molecules which will be capable of binding alkali metal ions. Many other similar compounds along with their binding properties were explored in his seminal series of papers. He had synthesized over 50 crown polyether, characterized and extensively studied their complexiation nature with alkali and alkaline metal ions. He found that the compound formed with 1:1 ratios of Crown: cation salt with many alkali and alkaline metal ions but in case of cations too large to fit in the hole, the 2:1 & 3:2 ratios of Crown: cation is predominated and is postulated the“sandwich structure” type A. This cyclic polyethers forming a cavity which is quite similar to shape of crown hence named as crown ethers to this class of molecules. The crown ethers were named according to the total number of atoms and number of oxygen atoms in the cyclic ring. For example 18-Crown-6 means the 18 atoms (carbon plus oxygen) and 6 oxygen in the cyclic ring of crown ether. A number of crown ethers synthesized and found that the cavity size plays an important role during the complexation of alkali metal which in turn depends upon the number of oxygen atoms in the ring. Another factor which governs the size selection is the hydration of metal ion and different substituents

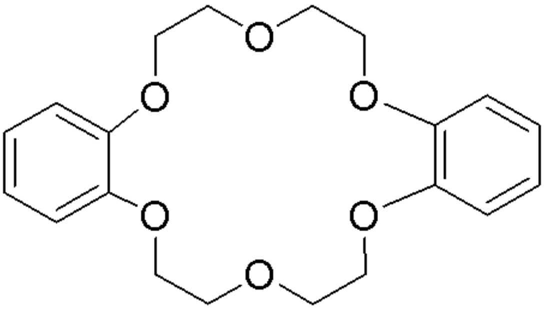
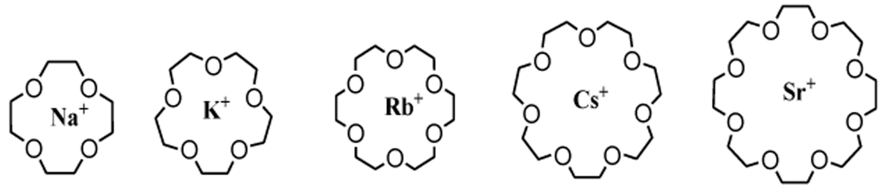


Figure 1.9: *2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16-hexaoxacyclo-octadeca-2, 11-diene (Dibenzo18-crown-6)*

on the crown ring. The stability of complex formed also depends upon ion-dipole interaction between the metal ion and coordinating oxygen atom present in crown ring [42–44] Based upon these observations various crown ethers were synthesized and were found to be suitable for binding different metal ions as shown in Fig. 1.10. The crown ethers such as 15-crown-5, 18-Crown-6 are too hydrophilic to use them for solvent extraction. To increase the lipophilicity, the alkyl or aryl groups must be added like Dicyclohexano-18-crown-6 and Dibenzo-21-crown-7 implying enhancement in the distribution ratio for alkali metal ions. Furthermore the solvent extraction of alkali metal ion using crown ethers is limited due to poor solvation of counter anion in organic phase. This can be eliminated by using various approaches like the use of polar phase modifiers such as 2-ethylhexanol or nonyl phenol and some modifications as discussed below.

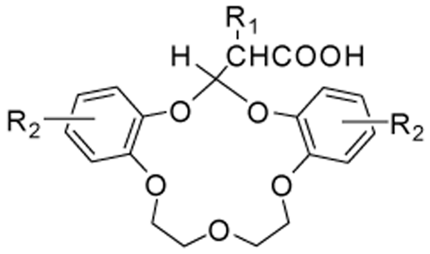


Name:	12-Crown-4	15-Crown-5	18-Crown-6	21-Crown-7	24-Crown-8
Cation Size (A°):	0.95	1.33	1.48	1.69	1.13
Cavity Size(A°):	0.67 ± 0.07	0.97 ± 0.12	1.45 ± 0.15	1.92 ± 0.23	2.25 ± 0.28

Figure 1.10: *Ionic size of alkali/alkaline metal ions and their corresponding specific crown cavity size*

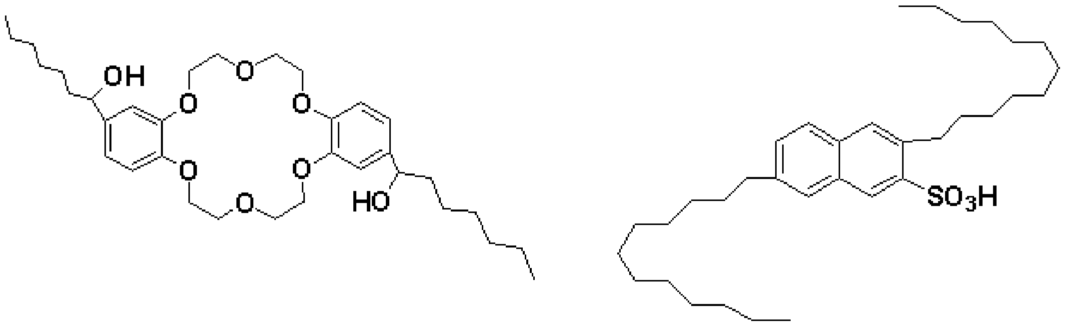
The addition of certain cation exchangers like versatic acid, didodecylnaptalene-sulponic (HDDNS) acid or di(2-ethylhexyl) phosphoric acid(D2EHPA) played an important role in extraction of alkali metal ions. The mechanism proposed by McDowel et. al. [45, 46] says that the cation exchanger exchanges the cation at the interface and forms organic phase soluble salt which can easily make adduct with crown ether thus eliminates the necessity of transferring the counter anion to organic phase. With this approach the selectivity of crown ether relative to size was found to be unaffected.

In another approach the crown ether condensed with a proton-ionisable group were used in which the crown-ether as a whole molecule behaves as both the cation exchanger and the coordinator as shown in Fig. 1.11. This compound includes the acyclic carboxylic acid group which when ionizes at certain pH can effectively transport the cation. This was found superior than the above discussed cation exchangers mixed with crown ether in terms of both selectivity and extractability. On the other hand its expensive synthesis discourages further studies like radiation stability etc. which were not studied [47–49]. Gerow et. al [50, 51] studied the various benzo substituted crown ethers by considering the effect of various parameters like alkyl substitution - branched or straight, size of crown cavity, solubility in organic and aqueous phase, cation exchanger, hydrogenation of benzene ring, effect of cation exchanger etc. They developed a solvent extraction process for the first time and used 0.02 M Bis-(4,4(5)-[1-hydroxyheptyl]-benzo)-18-crown-6 (Fig. 1.12) along with 5 % didodecylnaphthalene sulfonic acid (DNS) and 27 % Tributyl phosphate(TBP) in kerosene for cesium ion extraction. The highest distribution coefficient value of 2 was achieved by above solvent system where DNS acts as cation exchanger and the process runes nicely by extracting cesium from 3 M nitric acid at Savannah River plant leaving Sr and La behind. The system is also found to be compatible with the PUREX type of diluents like kerosene or dodecane. Among the various crown ethers, Blasius et. al chooses dibenzo-21-crown-7 (DB 21-crown-7) for selective ex-



R_1= H, C_2H_5, C_4H_9,C_6H_{13}, C_8H_{17} etc.
R_2 =H, tert. butyl(C_4H_9)

Figure 1.11: *Crown ether condensed with a proton ionisable group*



Bis-(4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6

Didodecylnaphthalene sulfonic acid (DNS)

Figure 1.12: *Reagents constituting the process for recovery of cesium*

traction of cesium from nitric acid and sodium nitrate solution by using the high polarity diluents like nitrobenzene, nitro-methane. The distribution ratio was too low to be of any practical use and so, in order to increase the distribution ratio, a voluminous and polarisable anion such as molybdophosphate, tetra phenylborate (TPB) or hexachloroantimonate was added. The hydrolysis of TPB and precipitation of molybdophosphate were major issue for their use. The crown ether modified with hexachloroantimonate diluted in nitrobenzene shows good results for cesium extraction [52, 53]. Dietz et al. studied a variety of crown ethers for cesium extraction from nitric acid medium. The derivatives of DB18-crown-6 displayed higher distribution ratios and selectivity.

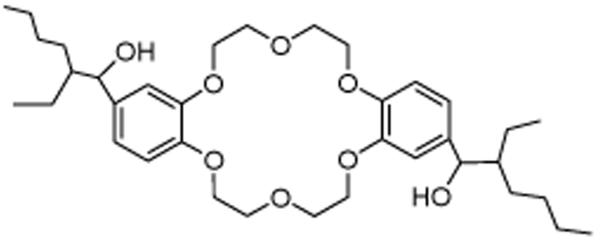


Figure 1.13: *Structural formula of 4,4'(5)-di-[(1-hydroxy-2-ethylhexyl) benzo]-18-crown-6*

The compound especially 4,4(5)-di-[(1-hydroxy-2-ethylhexyl) benzo]-18-crown-6 (Fig. 1.13) exhibited better results comparable with the system where lipophilic organic cation exchanger were used for synergistic extraction of cesium. Its modest solubility in paraffinic diluents along with phase modifier provoked the thought of it to be a suitable cesium recovery process [54, 55].

1.4.7.2 Cobalt dicarbollides (CD)

Polyhedron of borane with "closo" structure are found to have interesting properties when carbon becomes the part of framework $B_nH_n^{-2}$. This polyhedral carborane theoretically can be considered as derived from $B_nH_n^{-2}$ 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 $B_nH_n^{-2}$ ($C_2B_{10}H_{12}$) due to greater stability than others [56]. 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 [57–59]. One compound synthesized by Hawthrone M.F where the cobalt is sandwiched between open faces of two $C_2B_9H_{11}^{2-}$ ion is shown in Fig.1.14. The Dicarbollylcobaltate (III) (DCC) or Dicarbollides (DC) properties are:

- This is considered to be an ideal hydrophobic anion with no free electron pair for binding with proton and thereby is difficult to protonate with strong acid.
- The compound $H^+(\Pi-(3)-1,2-C_2B_9H_{11})_2Co$ is fully dissociated in aqueous as well as in nitrobenzene based diluents, thus behaving as a super acid.
- Its closed structure with the maximum delocalized electron density provides various advantages like high stability against radiation, heat, strong acids and oxidation-reduction agents [60].

These properties of the dicarbollylcobaltate(III) anion along with its low specific charge density, make this anion a wonderful agents for the extraction of cations

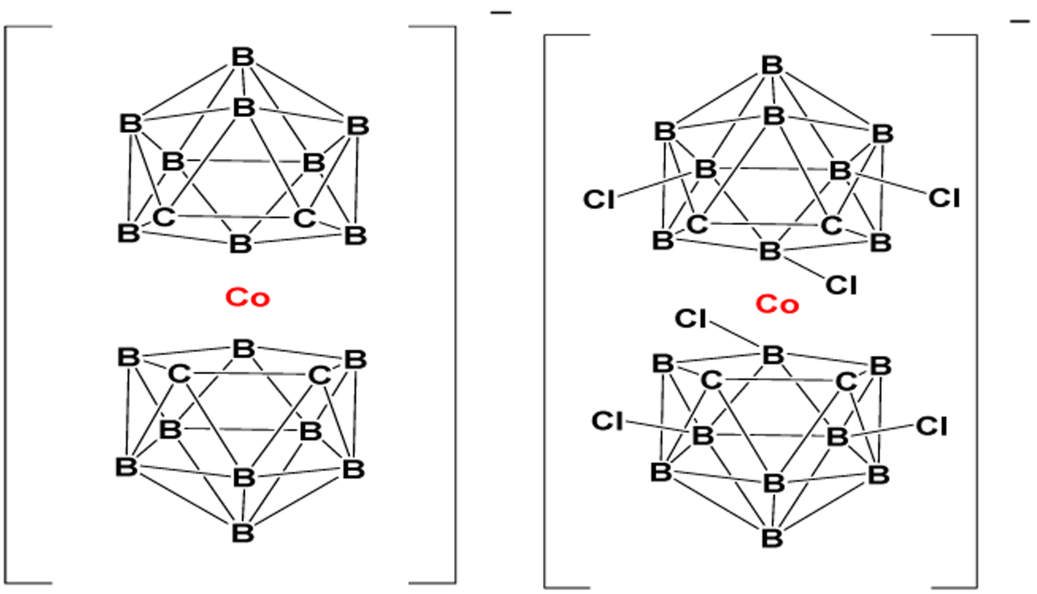


Figure 1.14: *Structures of Bisdicarollylcobaltate (dicarbollide) anion and Hexachlorinated cobalt dicarbollide (CCD)*

from aqueous solutions into some organic solvents like nitrobenzene etc. Rais et.al first utilized this dicarbollides for extraction of cesium or other large cations from water into nitro-based organic diluents [61]. In this particular system the strongly hydrated multivalent elements were least extracted. This cobalt dicarbollide anion can be chemically modified by substitution with chlorine resulting in hexachlorinated cobalt dicarbollide derivative (CCD) as shown in Fig. 1.14. This CCD compound has even more advantageous over DC in terms of high stability towards acid and can be used in nitrobenzene as well as fluorinated diluents. The one such diluents is phenyltrifluoromethylsulfone (FS-13) which is being used by Czech scientists for cesium extraction. This CCD anion discriminates the cations according to their Gibbs free energy of transfer. The cesium shows the lowest Gibbs free energy of transfer to polar organic solvents as compared with other metal ion present in solution [62]. The mechanism of transfer can be written as:

$$M_{aq}^{n+} + nH_{org}^{+} + nCoB_2 \rightarrow nH_{aq}^{+} + M_{org} + nCoB_{2org} \tag{1.4}$$

In early 1980s the removal of cesium alone has been performed well with 47 stage mixer-settlers at Gatchina. They use 0.06 M CCD in 60:40 v/v, nitrobenzene:CCl4, without the Polyethylene glycol. One more process with 0.15 CCD in a fluoropol diluent, a 40:60 v/v mixture of di(tetrafluoropropyl) ethers of diethylene glycol and ethylene glycol was developed at INEEL. They achieved a cesium removal efficiency of >99.998 % from acidic tank waste with co-extraction of 50 % and 34 % of the K^+ and Hg^{2+} in the feed, respectively[63]. The other ions like Sr^{2+} and actinides do not bind because of their high hydration number therefore, in order to extract strontium, the polyethylene glycols (PEG: $HO(C_2H_4O)_nH$) and particularly, nonylphenyl nonaethylene glycol (Slovafol 909 $HO(C_2H_4O)_9$ was added to the dicarbollide. The purpose of adding PEG was to dehydrate the strontium ion thereby facilitating to transfer in organic phase. In fact this results in slight sacrifice of Cs/Na selectivity. The extractant composition with 0.08 M CCD, 0.6 vol% PEG-400 in a phenyl trifluoromethyl sulfone (FS-13) diluents provides excellent recovery of cesium and strontium.[64]

In addition to this an extraction mixture containing chlorinated cobalt dicarbollide (CCD), N, N-dibutyl carbamoyl methyl phosphine oxide (CMPO), and polyethylene glycol (PEG) has been used for recovery of cesium, strontium, lanthanides, and actinides from highly acidic media. The solvent composition was 0.08 M chlorinated cobalt dicarbollide, 0.5 vol.% polyethylene glycol-400 (PEG-400), and 0.02 M diphenyl- N,N-dibutylcarbamoyl phosphine oxide (Ph_2Bu_2CMPO) in a diluent consisting of phenyltrifluoromethyl sulfone (FS-13). This process was found suitable for recovery of all major radionuclides and the process was named as universal extraction (UNEX) process. The striping of Cs and Sr has been done by using HNO_3 solutions containing bases like guanidine, methylamine which transfer proton into organic phase thus displacing Cs and Sr in organic phase. The actinides and lanthanides was stripped by a buffer solution of $pH > 3$ along with a complexing molecule. Uranium can be stripped by sodium or ammonium carbonate solution [65, 66].

The major drawbacks of these systems are

- The use of harmful nitrobenzene or fluorinated diluents which are highly toxic and corrosive.
- Efficiency decreases as the acidity/salinity of solution increase.
- Extraction at 0.5 M nitric acid and stripping at higher than 5 M nitric acid thus, before extraction, the feed needs to undergo the denitrification process.

1.4.7.3 Calixarenes

Calixarenes are the cyclic compounds where numbers of substituted phenol units are attached via. methylene bridge. These are characterized by a narrow ring (or lower rim, phenolic hydroxyl group) and wide rim (or upper rim, aromatic position para to phenolic hydroxyl group) with a central annulus. The typical calix[4]arene are characterized as three dimensional basket shape with a volume of around 10 nm^3 as shown in Fig.1.15. There are various reactive sites available like phenolic group, para position after dealkylation and methylene bridge which results in large number of functionalized calixarenes. In the recant years calixarenes have been used in different fields like sensors, ion transport, enzyme mimics etc. Calixarene was first seen in the lab of Adolf Von Bayer while doing reaction of p-substituted phenols

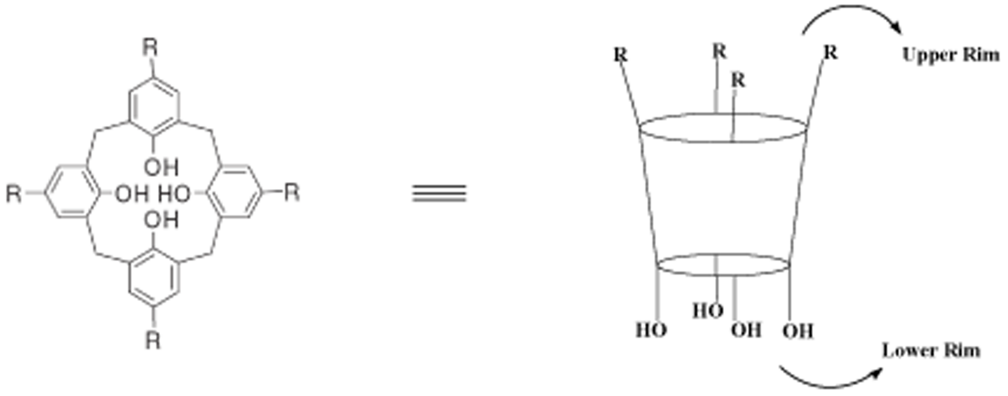


Figure 1.15: *Structural representation of Calix[4]arene*

with formaldehyde in presence of acid or base. He obtained a viscous cement-like substance which was difficult to identify. Also due to lack of analytical tools it was not possible to characterize these viscous materials. However, Bayer provides some structural insight by carrying the reaction of mesitylene with formaldehyde and he proposed a dimesitylene structure as shown in Fig. 1.16. Although, Bayer was unable to characterize the phenol formaldehyde product but he had given birth to phenol formaldehyde chemistry. In early 1940s Alois Zinke suggested that they possess a cyclic tetramer structure but there was no direct evidence for the same due to inadequate analytical tools. This was first recognized by Cornforth in 1950s that it was actually an oligomeric mixture of macrocycle compounds. This was further described in 1970s by C.David Gutsche. He had developed the one step method for synthesis of cyclic tetramer, cyclic hexamer and cyclic octamer from the reaction of p-tertbutylphenol and formaldehyde. By this time techniques like chromatography, X-ray facility, NMR spectroscopy etc. have underwent great transformations and the chemical analysis could reliably establish the structure of the calixarenes obtained by these one step procedure. He gave the compounds the name“calix[n]arenes”, which derives from Latin “calix” meaning vase, like the shape of a Greek vase (cup-like structure) of these macrocycles and arene indicate the presence of aryl residue in the macrocyclic array. A bracketed number between calix and arene [n] refers the size of the macrocycle and the name of the p-substituent is added to indicate from which phenol the calixarene is derived. For example if a cyclic tetramer is

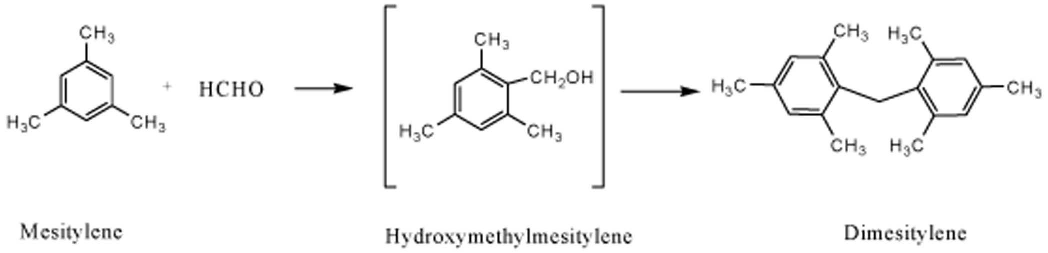
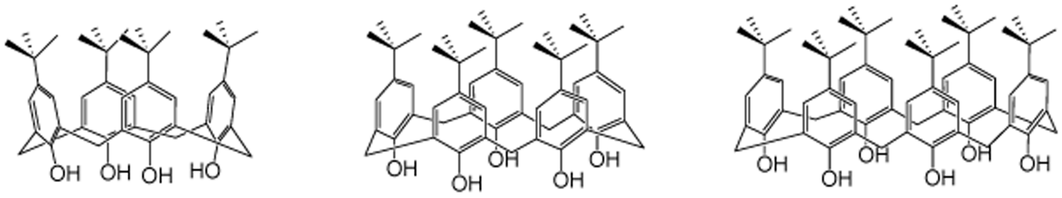


Figure 1.16: *The structure of calixarene with different sizes*

derived from p-tert-butyl phenol than it will be called as p-tert-butyl calix[4]arene. The structures of various p-tert-butyl substituted calixarenes with different sizes are shown in Fig.1.17.



p-tert-butylcalix[4]arene p-tert-butylcalix[5]arene p-tert-butylcalix[6]arene

Figure 1.17: *The structure of calixarene with different sizes*

Synthesis of Calixarenes Calix[4]arene can be synthesized with good yield by modified Zinke procedure through the condensation of p-alkyl phenol and formaldehyde with small amount of sodium hydroxide in presence of diphenyl ether (high boiling) as solvent. Calix[8]arene can be synthesised by the petrolite procedure which uses xylene as solvent instead of diphenyl ether. These reactions proceed via thermodynamic control and kinetic control respectively. Another modified Zinke procedure with larger amounts of potassium hydroxide produces cyclic haxamer i.e. Calix[6]arene ,where template effect of K^+ is assumed [67].

Conformations of Calix[4]arenes Among all the calixarenes the Calix[4]arene is one of the most extensively studied one. The ^{1}H NMR spectra of calixarene shows a pair of doublet at low temperature and a singlet at high temperature for the bridge methylene protons. This behavior can be accredited to interconversion of two mirror image cone conformation as shown in Fig.1.18. which is slow (on the NMR time scale) at low temperature and fast at higher temperature.

The low temperature spectrum corresponds to the cone conformation where the axial protons Ha doublet appears at low field and the equatorial protons He doublet appears at high field. This interconversion depends upon the p-substituents

Figure 1.18: *Ring inversion of calixarene*

on phenyl ring and the solvent used for spectra. The substitution of alkyl group larger than ethyl block, the ring inversion thus produces the compound with different conformation depending upon the orientation of each aryl group. There are four conformation of calix[4]arene possible as shown in Fig. 1.19. These were first recognized by Cornforth with various numbers of aryl groups projecting upward ("u") or downward ("d") relative to the plane of bridgemethylene groups.These conformations were further named by D. Gutsche as "cone" (u,u,u,u), "partial cone" (u,u,u,d), "1,2-alternate" (u,u,d,d) and "1,3-alternate" (u,d,u,d). In the cone conformation all phenol rings projects in one direction whereas in partial cone one phenol ring is inverted with respect to average methylene bridge plane. In 1, 2-alternate two adjacent phenol rings are inverted while in the 1,3-alternate the opposite phenol rings are inverted. These four conformations can be easily differentiated by ^{1}H NMR and ^{13}C NMR spectroscopy by capturing the patterns of bridging methylene group [68]. 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.1.20.

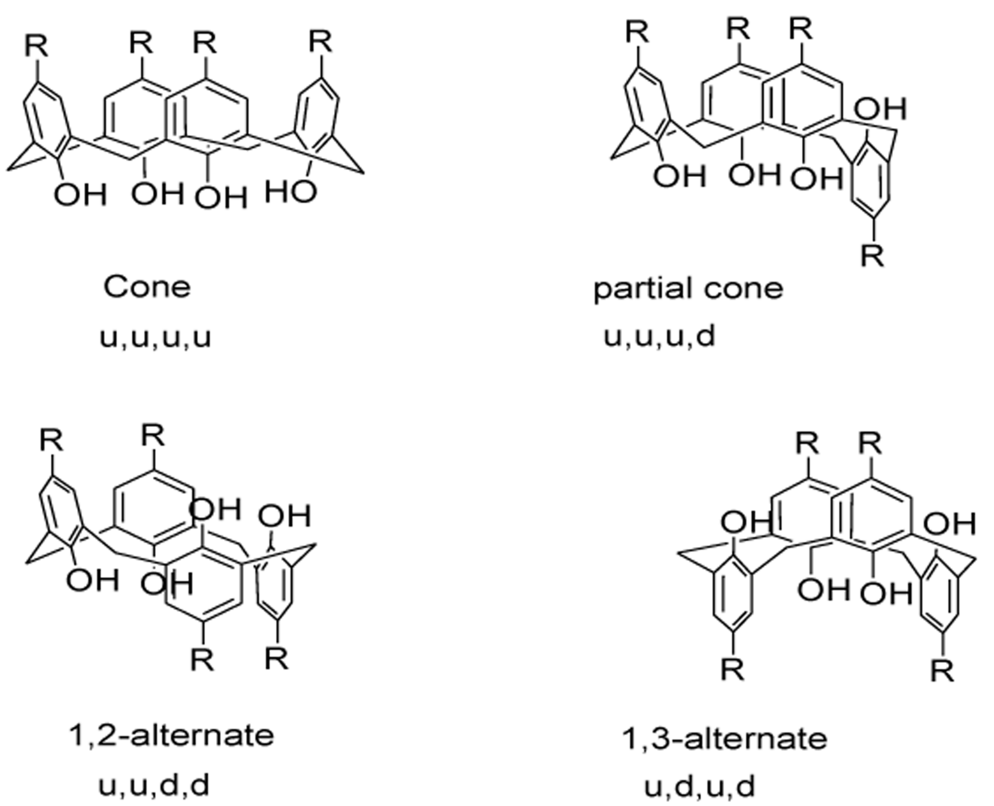


Figure 1.19: *Different conformation of Calix[4]arene*

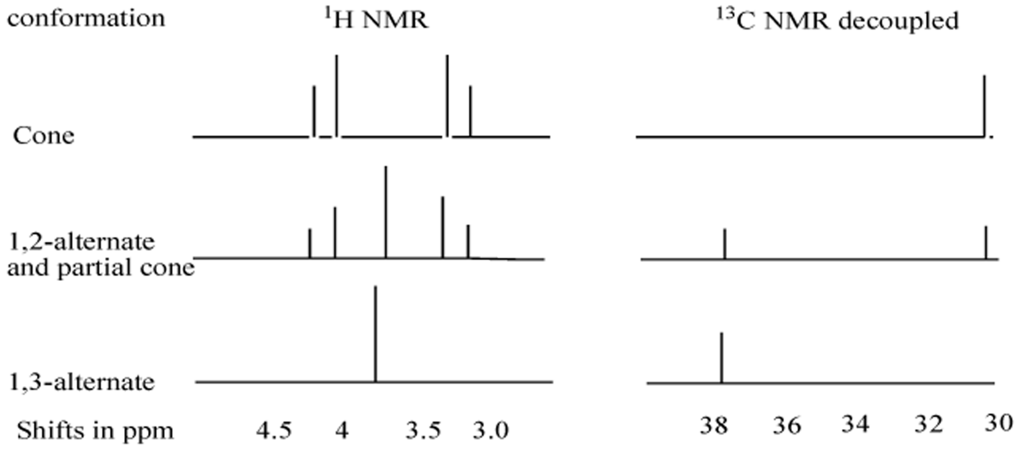


Figure 1.20: ^{1}*H NMR and* ^{13}*C NMR patterns of different conformations for calix[4]arene*

Applications in separations The calixarenes display novel ion-binding properties like crown ethers and cryptands. In 1979 , Ungaro et.al. demonstrated for the first time the binding properties of t-butyl-calix[4]arene with toluene in solid state by using X-ray crystallography where they showed that the toluene was tightly bound with calixarene molecule. In solution phase oxyallyl ether of p-tert-butylcalixarene binding with guanidinium ion was also demonstrated by the same group. Izatt et. al. used calixarenes for selective transport of cesium through SLM from alkaline medium. The transport rate rise, small below pH 12, rose suddenly beyond this value confirmingthe deprotonation of phenol units of calixarene during complexation. It was also observed that the rate of transport increases with the reduction in size of calixarene [69].

1.4.7.4 Calix-crown

Calixarene when suitably condensed with crown ethers results in calix-crown. This particular class of cation ligand based on calixarene framework has been received more attention in recent years. The ion binding properties of this class of ligand can be tuned by varying the size of crown ring, substitution of upper rim and changing the solvent used for complexation. The first calix-crowns synthesized were l,3-dihydroxycalix[4]-crowns which were derived from p-tert-butylcalix[4]arene by condensing with their corresponding polyethylene diols and have structures as shown in Fig.1.21. The ligand 1 acts as an ionisable ligand with the loss of the protons in basic conditions and thus form neutral complexes with monovalent or divalent cations. The second ligand 2 was found to serve as an efficient carrier for the transport of alkali metal ions through the membrane from an alkaline phase to receiving acidic phase. This compound acts as “neutral” ligand for extraction of metal and ammonium picrates from aqueous feed solution to organic dichlorometane solution. Neither the parent calyx(4)arene nor dibenzo- 18-crown-6 alone was able to transfer Na^+ and K^+ from basic medium to acid aqueous solutions with such efficiency. It was observed that the introduction of crown ring moiety in calixarene network leads to

- Increase in binding ability as compared to parent calixarene molecule
- Increase in selectivity for a particular metal ion by altering the crown ring size.

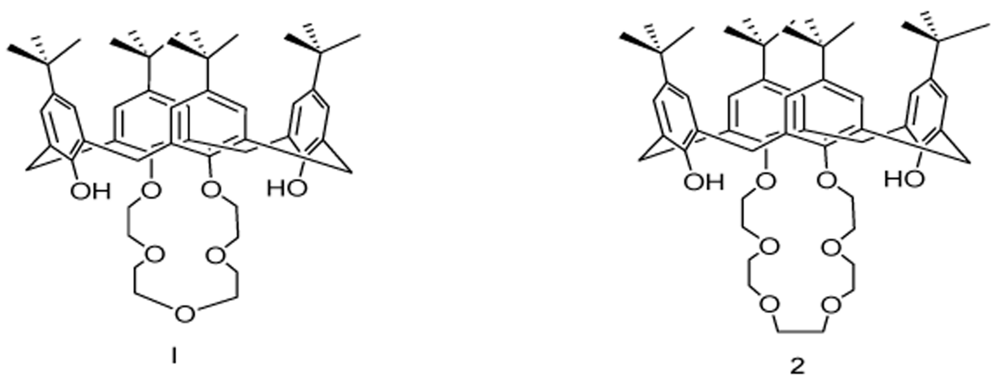


Figure 1.21: *Structures of l,3-dihydroxycalix[4]-crown-5 and l,3-dihydroxycalix[4]-crown-6*

This is due to presence of two ionisable phenolic -OH group and a hydrophilic crown ring which greatly enhance the transport ability of ligand under these conditions. The 1,3-dihydroxycalix[4]arenecrown-5 (1) and 1,3-dihydroxycalix[4]arene crown-6 (2) were found to be selective for K^+ and Cs^+ ion transport respectively through the membrane [70–72].

Conformational changes after complex formation The 1,3-dimethoxy p-tert-butylcalix[4]arene crown-5 and 1,3-dimethoxy calix[4]arene crown-5 having structure as shown in Fig.1.22 , exhibits a flattened cone conformation in solid as well as in solution phase. It was observed that when 1,3-dimethoxy p-tert-butylcalix[4]arene crown-5 was complexed with potassium picrate in chloroform, it induces a partial cone conformation. This partial cone conformation is achieved by flipping the methoxy group through central annulus of calixarene. Similarly when the 1,3-dimethoxy calix[4]arene crown-5 is complexed with potassium picrate in chloroform it flips into 1,3-alternate conformation. Evidences for conformation change was clearly observed in ^{1}H NMR spectrum of 1:1 complex of K^+pic^- : calix-crown in $CDCl_3$ medium. On the basis of above it was established that the most preferable conformation for K^+ binding is 1,3-alternate followed by partial cone in case of unsubstituted calixarene. In the second set of experiments where the cone 1,3-dimethoxy calix-crown-6 complexes with cesium picrate, it lead to 1,3-alternate

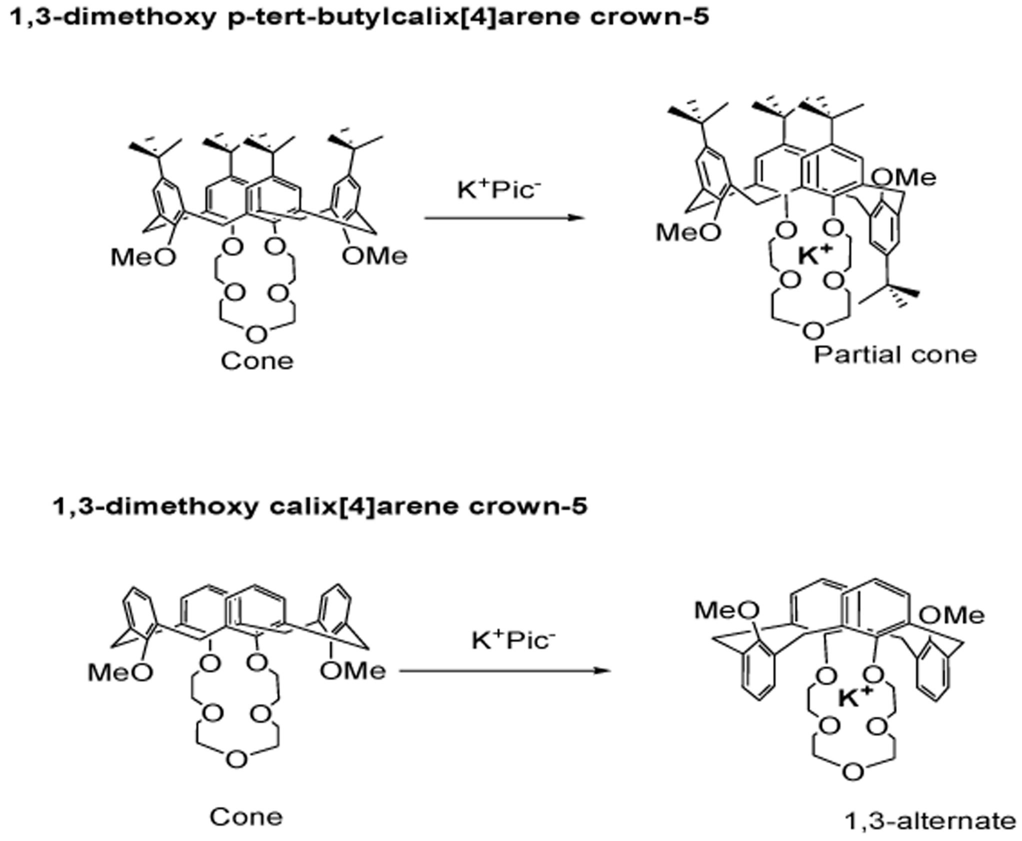


Figure 1.22: *Conformational change observed after complexiation with potassium picrate*

conformation while with sodium picrate it remains intact as shown in Fig. 1.25. This difference can be observed in the ^{1}H NMR spectra of methylene bridge protons. The sodium complex exhibits a AX type of NMR spectra with a J = 14 for axial and equatorial protons whereas a singlet for these axial and equatorial proton

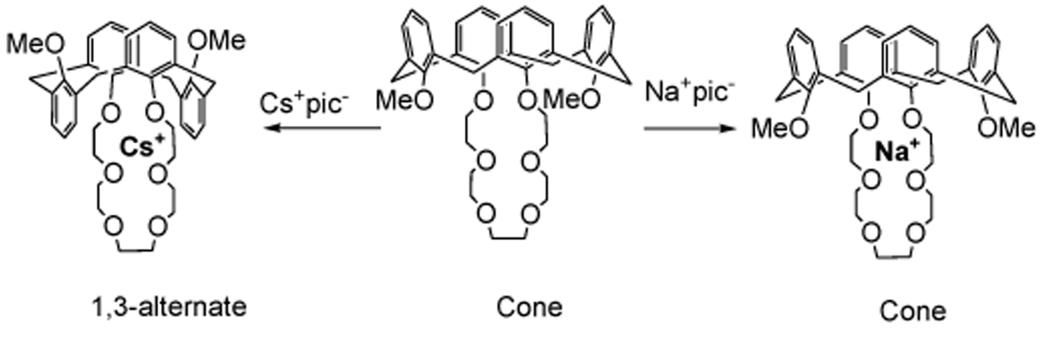


Figure 1.23: *Change in conformation of 1,3-dimethoxy calix-crown-6 after complexiation with sodium and cesium picrate*

has been observed for cesium complex because of similar environment of these two set of protons in 1,3-alternate conformation. More interestingly this cesium complex structure shows that the cesium is not only bound with the oxygen of crown ring but also with the opposite aromatic ring of phenolic group (cation-pi interaction) which was further supported by NMR results. This conformational change (cone to 1,3-alternate) for cesium was further established with X-ray crystal structure data [73]. Depending upon above observation it was concluded that the conformational outcome after complexation will depend upon various factors like,

- Nature of complexing cation.
- Different types of substituents attached on calixarene ring.
- Size of crown ether ring.

Concept of preorganization This information based upon conformation of 1,3-dimethoxy calix-crown-6 complexes has been used for the synthesis of preorganized receptors in a particular locked conformation. This was easily done by introducing alkyl groups larger than methyl at 1,3-positions. The various substitutions like ethyl, isopropyl have been done for selective encapsulation of metal ions. The synthesis of l,3-diethoxycalix[4]crown-5 and l,3-diisopropyloxycalix[4]crown-5 were carried out and the different stereoisomers viz. cone, partial cone and 1,3-alternate were isolated and fully characterized. Out of these the 1,3-alternate conformers were showing the highest efficiency and selectivity for complexaition of K^+ over Na^+, especially the isopropyl one [74].

Similarly the 1,3-alternate conformation of l,3-diisopropyloxycalix[4]crown-6 shows a very high efficiency for the complexation Cs^+ over Na^+ ions. It was also observed from the thermodynamic calculations that the conformationaly mobile ligands are less selective and less effective than their corresponding locked conformation. The thermodynamic experiments carried out on 1,3-alternate diisopropyl calix-crown-6 for cesium complexation studies in methanol reveals that the enthalpy term plays important role in the complexation and is the highest among other cyclic liagands such as 18-crown-6 as shown in table 3.3.

The entropy of complexation (ΔS) comes less negative in the conformationally locked calix-crown as compared to other crown ether which can be explained in terms of preorganization where only a small part of crown ether moiety is flexible. Thus flexibility is lost with the large cesium cation, which fits well into the cavity created by aromatic nuclei and polyether ring. This locked conformation provides the "preorganised" binding site for better complexation of a metal ion [75]. Therefore, it important to note that the "preorganization" is one of the major factors for controlling the binding strength of metal ions.

Table 1.1: *Thermodynamic parameters of the complexiation of alkali cations in methanol at 25^{o}C.*

Ligands	**1,3-alternate diisopropyl calix-crown-6**			**18-crown-6**
Cations	**K**	**Rb**	**Cs**	**Cs**
LogK(KJmol^{-1})	4.5	5.93	6.1	4.8
-ΔG$_c$(KJ mol^{-1})	25.6	33.8	35	27.4
-ΔH$_c$(KJ mol^{-1})	18.1	40	50.2	47.2
TΔS(JK^{-1})	7.5	-6	-15	-19.8

General method of synthesis of 1,3-alternate calix-crowns

Mono crown The initial precursor calix[4]arene is selectively alkylated at 1,3 position by reacting the calixarene with corresponding alkyl iodide/ tosylate/ bromide in presence of week base like potassium carbonate in acetone/acetonitrile. This 1,3 dialkyloxy calixarene was further condensed with the polyether ditosylate in presence of Cs_2CO_3 where cesium has being used to provide the"template effect" for 1,3-alternate conformation. This results in 60-65 % yield with respect to initial calix[4]arene. Generally high dilution is required for cyclization to take place and the scheme is as shown in Fig.1.24.

Bis crown Similarly when the calix[4]arene is condensed with two equivalents of polyether ditosylates in presence of cesium carbonate resulted in Bis crowns as shown below [76].

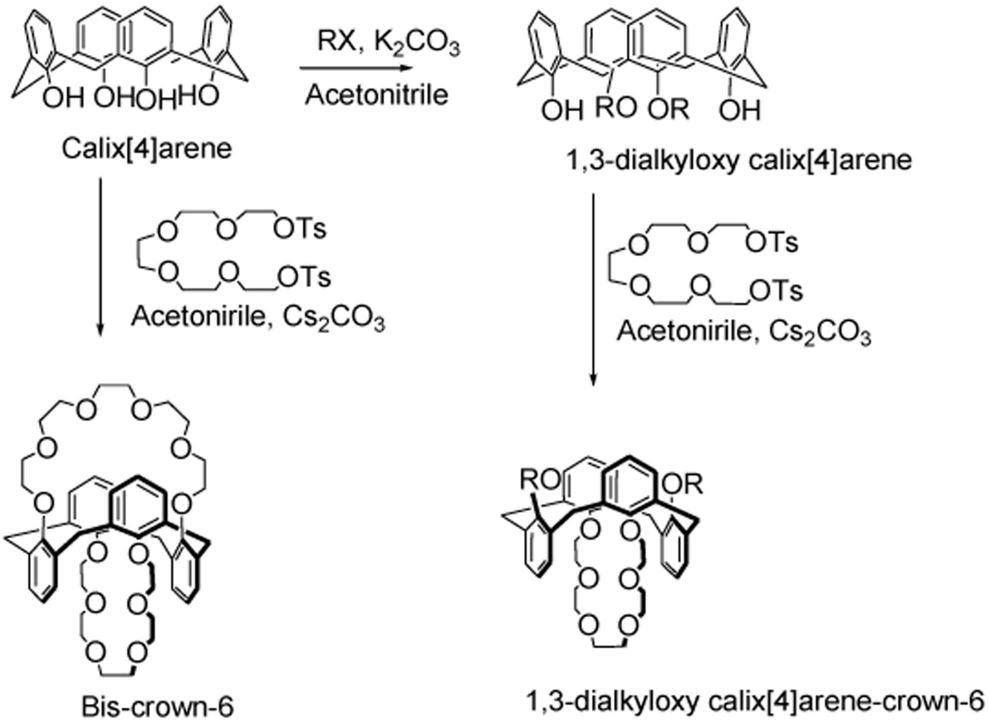


Figure 1.24: *General method for synthesis of Mono and Bis calix-crowns*

Complexion studies The complexiation studies of different sized polyether ring calix-crown were carried out for the extraction of alkali metal ion and it was observed that selectivity is shifted towards the larger alkali metal ions as the number of oxygen atoms increases. For example,Calix[4]arene-crown-4 ligands are selective for Na^+ ion and calix[4]arene-crown-5 for K^+ ion while calix[4]arene-crown-6 and calix[5]arene-crown-x (x = 4, 5, 6) are selective for Cs^+ ions [77].

Extraction studies of cesium using mono crowns

Supported liquid membrane studies: The diisopropyloxycalix[4]arene-crown-6 was used for carrying the extraction studies through supported liquid membranes (SLMs) of radioactive waste solution where the amount of sodium ions present was much higher as compared to cesium ions. The exact complementary size between crown ring and cesium cation makes this ligand highly selective over large amount of sodium ions present. The recovery of more than 98 % of the cesium from the waste solution, make this ligand exceptionally smart for the "declassification" of nuclear waste [78].The complex formed is stabilized with the oxygen atoms of the crown and the benzene units. From the above discussions it seems that the efficiency and selectivity of a calixarene-mono-crowns depend on factors such as crown ring size and calixarene conformation and stiffness of crown ring which will be discussed later.

Solvent Extraction Studies of Calix-Mono-Crown: The distribution coefficients of cesium and sodium were determined by contacting the acidic solution (1 M HNO_3, $5X10^{-4}$ M MNO_3) with different calix-crowns in o-NPHE (ortho nitrophenyl ether)[79]. o-NPHE is chosen as it can dissolve the calix-crown in high concentration, also being a diluent with high dielectric constant, it can improve the extraction by solvating the counter anion. The results of extraction showed that the fixed 1,3-alternate conformation exhibit a higher value of D_{Cs} and lower D_{Na} and hence a high Cs/Na selectivity can be achieved. But when the conformationally mobile dimethoxy calix-crown-6 was used it resulted in large decrease in selectivity as it is not preorganised for cesium binding. The Calix[4]arene-dimethoxy-crown-7 having non perfect matching cavity of complementary size leads to improper fitting of cesium cation, hence resulting in decreasing distribution coefficient and separation factor. The structure of few calix-crowns are shown in Fig.1.25. The results are summarized in Table 1.2.

In another set of experiments, selectivity of these 1,3-alternate calix-crowns was verified by competitive extraction of cesium from nitric acid medium in presence of large amount of sodium nitrate 4 M $NaNO_3$. The result showed very high distribution coefficients especially for calix-mono-benzo-6 (BC6) and calix-dibenzo-crown-6 (B2C6). The distribution coefficient of 45 and 56 was obtained respectively. This modification by incorporating the benzene units on crown ether leads to "stiffening"

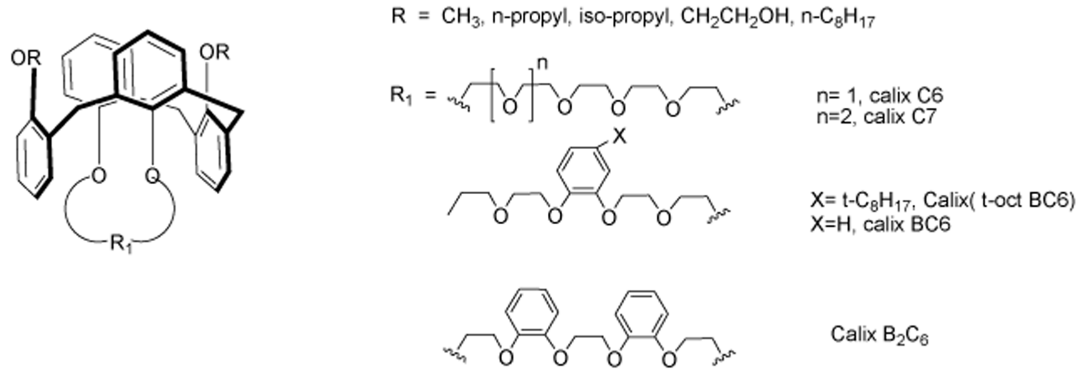


Figure 1.25: *Structures of few mono-crowns*

Table 1.2: *Distribution coefficients of cesium and sodium for various calix-crowns and their corresponding separation factor. Organic phase 0.01 M Calix-crown/o-NPHE and aqueous phase 1 M* HNO_3*,* $5X10^{-4}$ *M* MNO_3

Calix-crown	$\mathbf{D}_{Na}$	$\mathbf{D}_{Cs}$	**Separation factor** ($\beta_{Cs/Na}$)
Calix [4]arene-dimethoxy-crown-6 (C6)	3×10^{-3}	4×10^{-2}	13
Calix[4]arene-hydroxyethoxy-crown-6 (C6)	4×10^{-3}	4.2	>4200
Calix[4]arene-dipropoxy-crown-6(C6)	2×10^{-3}	19.5	>19500
Calix[4]arene-diisopropoxy-crown-6 (C6)	$<10^{-3}$	28.5	>28500
Calix [4]arene-di-n-octyloxy-crown6 (C6)	$<10^{-3}$	33	>33000
Calix[4]arene-di-n-octyloxy-dibenzo-crown6 (B2C6)	$<10^{-3}$	31	>31000
Calix[4]arene-dimethoxy-crown7 (C7)	4×10^{-3}	7×10^{-3}	>1.7

of polyether ring. Therefore, it is difficult to dehydrate the hydrated sodium (Na-H_2O) for complexation in more hydrophobic site resulting in enhancement of Cs/Na selectivity. These are found to be the most cesium selective ligands known so far [80, 81].

Solvent extraction Studies of Cesium extraction from radioactive waste: In 1994, real raffinate was treated to extract cesium by using calix-crown. After the successful batch extraction studies the experiments were carried out for cesium removal from high level liquid waste solution. Initially the experiment was done by using o-NPHE as diluent because of its good dielectric constant give good extraction of cesium. This was suitable mostly for supported liquid membrane transport studies on a small scale. On the other hand due to inappropriate hydraulic properties like density and viscosity (very high)it is not suitable for use at large scale. Therefore, a diluent along with a modifier compatible with the processes like PUREX is needed for spent fuel reprocessing and waste management applications with the following advantages:

- Good cesium extraction without third phase formation
- Good hydraulic properties for liquidliquid extraction like viscosity, density, phase separation and emulsion formation.
- Provide the appropriate extraction at 3-4 M nitric acid and stripping at $\sim$0.05 M nitric acid.
- Stability with respect to thermal, chemical and radiolytic interactions. Keeping these point in view two solvent systems were selected
- 0.05 M Calix [4]arene-di-n-octyloxy-crown6 /30 % o-NPHE/ TPH
- 0.065 M Calix [4]arene-di-n-octyloxy-crown6/ 1.5 M TBP /TPH

Keeping these point in view two solvent systems were selected

- 0.05 M Calix [4]arene-di-n-octyloxy-crown6 /30 % o-NPHE/ TPH
- 0.065 M Calix [4]arene-di-n-octyloxy-crown6/ 1.5 M TBP /TPH

Both the solvent systems resulted in interesting hydraulic properties comparable to PUREX process. Therefore, the same plant equipments could be used for cesium extraction without formation of a third phase.

Another modification on the calix-crown has been done for increasing the solubility in aliphatic diluents. This was achieved by increasing the alkyl chain length up to 14 carbon atoms at lower rim [82]. The structure of few such molecules are shown in Fig.1.26. This modification certainly increased the solubility in TPH (mixture of branched alkane) but it was not adequate to get sufficient cesium extraction. Different modifiers like, malonamides were also tried, as these had been used as an

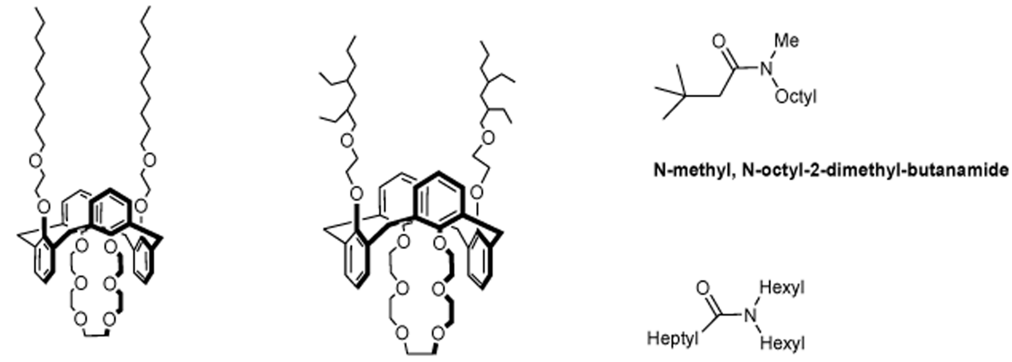


Figure 1.26: *Structure of calix-crowns and modifiers optimized for cesium recovery process from nitric acid medium*

alternate for TBP in many processes. Different calix-cown-6 molecule were tested with different malonamides phase modifiers and all of them gave a good hydraulic behavior without any third phase formation.

Tests were conducted at ATALANTE facility using genuine waste solution for recovery of cesium from4 M nitric acid-0.2 M oxalic acid. 0.01 % of ^{137}Cs was retained in organic phase with a recovery of 99.9 % Cs-137 [83]. This solvent system consisted of 0.1 M Calix-crown(R14)/1.0M N-methyl, N-octyl-2-dimethyl-butanamide (DOHA)/ TPH, structure as shown above. Another researcher proposed the solvent system based on Calix[4]arene-di-n-octyloxy-crown6 dissolved in 10 % dihexyloctanamide (DHOA) in 1-octanol [84]. Jianchen et. al. demonstrated the extraction performance of cesium by using 0.025 M Calix[4]arene-diisopropoxy-crown-6 in 1-octanol with 99.5% recovery of cesium from simulated high level liquid waste solution. Stripping was done by using 0.005 M nitric acid solution [85].

Extraction studies of cesium using calix-bis crown

Solvent Extraction - membrane transport studies of cesium There are various types of calix-bis-crowns formed by capping the lower rim of calixarene with suitable polyether network [86, 87]. Among them 1,3-alternate is one of the most studied for extraction of metal ions from acidic as well as alkaline medium. Asfari et. al. synthesized various calix-bis-crown in 1,3 alternate conformation and found that these can be used for selective extraction of cesium over other metal ions [88]. These results were further verified with membrane transport studies across the semi permeable membranes. The structure of calix-bis-crown is shown in Fig 1.27.

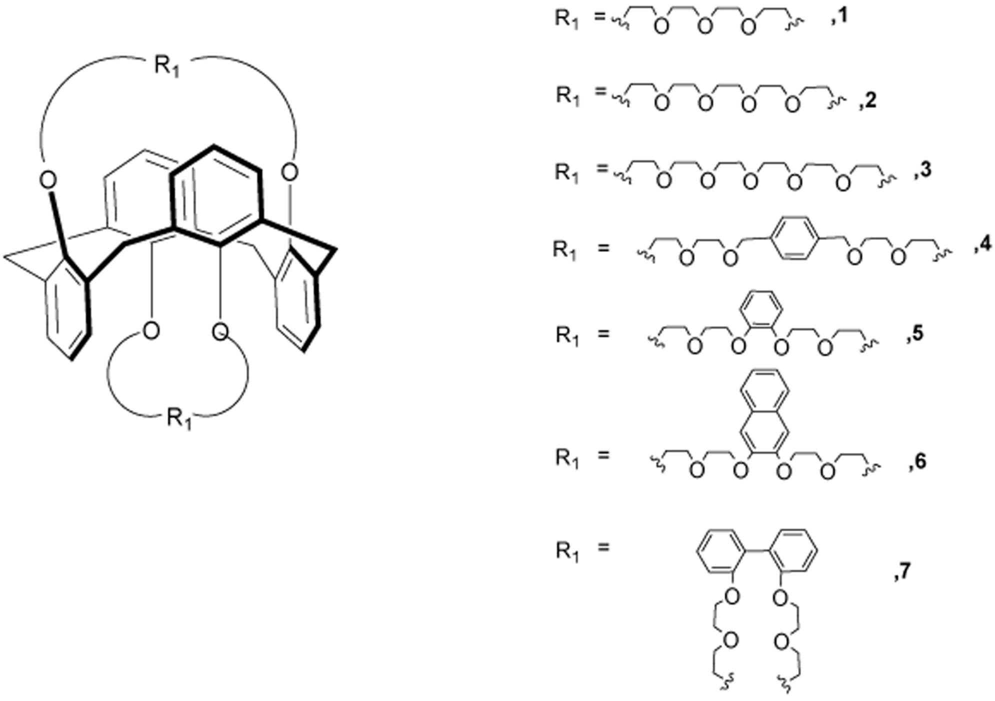


Figure 1.27: *Structure of bis-crown studied for extraction studies of cesium*

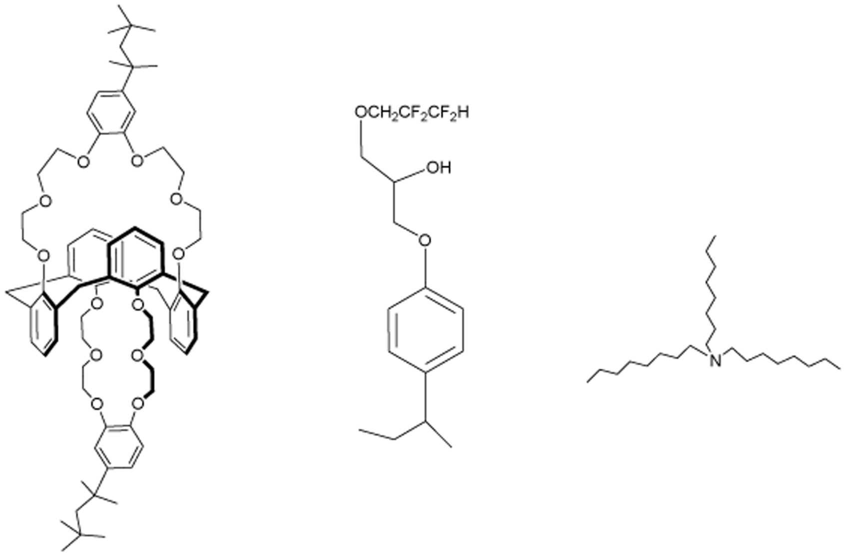
The distribution coefficients of cesium and sodium were determined by contacting the acidic solution (1 M HNO_3, 5X10^{-4} M MNO_3) with different calix-bis-crowns in o-NPHE. The bis-crown with 5 or 7 oxygen in crown ring is not selective for cesium over sodium. Also the increase in crown cavity size by biphenyl leads to reduction in Cs/Na selectivity due to imperfect matching of cation and cavity size. The results are displayed in Table 1.3.

Solvent extraction Studies of Cesium extraction from radioactive waste: Bis-crowns have been demonstrated for the treatment of alkaline waste like, high-level liquid waste stored at savannah river site (SRS) U.S, DOE by Oak Rigde National labora-

Table 1.3: *Distribution coefficients of cesium and sodium for various calix-bis-crowns and their corresponding separation factor. Organic phase 0.01 M Calix-crown/o-NPHE and aqueous phase 1 M HNO_3, $5X10^{-4}$ M MNO_3*

Calix-crown	$\mathbf{D}_{Na}$	$\mathbf{D}_{Cs}$	**Separation factor** ($\beta_{Cs/Na}$)
1,3-calix[4]biscrown-5 (1)	2×10^{-3}	0.4	-
1,3-calix[4] biscrown-6 (2)	1.2×10^{-2}	19.5	-
1,3-calix[4]biscrown-7 (3)	$<10^{-3}$	0.3	1500
1,3-calix[4] bis-p-benzo-crown-6(4)	$<10^{-3}$	2×10^{-2}	-
1,3-calix[4] bis-o-benzo-crown-6(5)	1.7×10^{-3}	32.5	19000
1,3-calix[4] bisnapthyl-crown- 6(6)	29.5	31	29000
1,3-calix[4] bisdiphenylcrown- 6(7)	$<10^{-3}$	7×10^{-2}	-

tory group. The solvent consisted of 0.01 M calix[4]arene-bis-(tert-octylbenzo-crown-6 (BOBCalixC6), 0.50M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butyIphenoxy)-2-propanol (Cs-7SBT) as a modifier, 0.001 M trioctylamine (TOA) in an aliphatic diluent IsoparL (mixture of branched chain hydrocarbon C_{10}-C_{12}) [89]. The structure of the constituents is shown in Fig.1.28. This process of Caustic-Side Solvent Extraction (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) leads to following advantages like,



BOBCalixC6 Cs-7SBT Trioctyl amine(TOA)

Figure 1.28: *: Structure of BOBCalix-6, Cs-7SBT and trioctyl amine*

- Increase in solubility of calix-crown and its extracted complex by solvating the counter anion.
- Resists the formation of third phase.
- Acts as synergistic agent and shows less degradation.

In addition to this, the low concentration of trioctyl amine (TOA) has been used. This waste contains the surfactant impurities like, dodecylsulphonate which hinders the back extraction with dilute nitric acid. In order to neutralize this effect, a hydrophobic base (TOA) has been added. This TOA acts as counter ion for dodecylsulphonate anion and makes complex with it hence renders cesium nitrate free in organic phase for effective stripping. This experimental demonstration of this process was done and found to work well. Later it was observed that the solvent is supersaturated with respect to calix-crown and hence more susceptible to precipitation, although this phenomenon was never observed in reality. Therefore, another modified solvent system was recommended which composed of 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar L. This change in composition removed the possibility of calix-crown precipitation in solvent. Both the processes CSSX and modified CSSX were found to be very effective for removing Cs from SRS high-level tank waste (Tank 37H=44F) when tested in a 33-stage, 2-cm contactor. The averaged decontamination factor of greater than 40000 was observed in both the solvent systems [90, 91]. Another modification for further improvement of solubility of calix-crown in modified aliphatic diluents was carried out. The tert.octylgroup was replaced by 2-ethylhexyl group just by observing that the 2-ethylhexyl group in many commercial solvents like D2EHPA etc has been used. Introduction of 2-ethylhexyl group results in at least eight times higher solubility in modified diluents as compared to t-octyl group, that too without the change in other properties like extraction strength, third phase formation etc. [92].

1.5 Computational simulations

Computational chemistry has broadly the following components: molecular dynamics simulation, ab initio and semi-empirical quantum mechanics, density functional methods[93, 94]. The brief description of topic are given below.

1.5.1 Molecular dynamics simulation (MD

This simulation describes the motions of the atoms within a molecule and in presence of surrounding molecules. It uses the Molecular mechanics or force field calculations which are based on a model that treats a molecule as a collection of atoms held together by bonds governed by a set of classical mechanical potential (ball and spring). This method relies on force-field with embedded empirical parameters obtained mainly from experiment and quantum mechanical calculations. These models simplify the systems to good extent for understanding of the molecular properties on the microscopic level. This simulation describes the motions of the atoms within a molecule and in presence of surrounding molecules. The major limitation of computations using classical force fields is the fact that electronic effects are not taken into account explicitly.

1.5.2 Ab initio and semi-empirical calculations

These calculations are based on the Schrodinger equation which describes the behavior of electrons in a molecule. This method solves Schrodinger equation for a molecule that provides electron distribution and energy of the system considering the values of the fundamental constants and the atomic numbers of the atoms present. However, the Schrodinger equation cannot be solved exactly for a system with more than one electron. Thus, several approximations are adopted for practical purposes. Ab inito calculations are computationally demanding; needs good computer resource and applicable for small size molecules. It is mathematically rigorous and useful for a broad range of systems with no input from experiment. On the other hand, semi-empirical calculations are based on Schrodinger equation but parameterized with experimental values. It is computationally less demanding than ab initio method and it can handle systems of 100 atoms easily.

1.5.3 Density functional theory (DFT)

These are quantum mechanical modelling method which uses electron density to calculate energy often fitting the functional with empirical data. DFT is computationally more demanding than semi-empirical methods but faster than ab initio correlated (post HF) methods. While electronic structure calculations (Ab initio, semi-empirical or DFT) describe the motions of electrons and generate energy surface.

1.5.4 Computational studies of Calixarenes

Molecular dynamic (MD) simulations provides the ligands and metal-ligands structures preciously which further explains the stability of metal-ligand complexs of the reactions. Reports on Molecular dynamics and free energy calculations for 13-dimethoxy-p-tert-butyl and the p-H-derivatives in the cone, I,3-alternute, and partial cone conformations, has been simulated in the gas phase and in solvent phase. The simulations on Li, Na, K, Cs complex with p-tert-butyl calix[4]arene were studied in three different diluents. It was observed that endo complexiation(anti-parallel butyl groups) was favored in less polar dilents like chloroform, but exo complexiation (parallel butyl groups) was favored in highly polar dilents like, acetonitrlie, acetone etc which were consistence with the experimental results[95, 96].

The tetrmethyoxy calix[4]arene (TMC) was theoretically studied by Nicholas et. ol with density functional theory (BLYP/6-31G**) second order perturbation (MP2/aVDZ) level of theory for Na^+ and Cs^+ complexiation. BLYP results were thought to be less authentic then MP2 as this DFT functional do not consider the repulsive non-bonded interaction, therefore, were not considered. By MP2 calculations authors observed the various binding modes for cesium and sodium. The more stable conformations from gas phase calculations observed for Na^+-TMC complex was partial cone (88 %) followed by cone (12 %). Similarly for Cs^+-TMC complex the more stable conformations was partial cone (99.99 %) rest of 1,3-alternate. In rigid calixarenes, additional binding modes appeared which were found to be selective for particular a metal ion, for example the 1,2-alternate and partial cone were an alternate binding mode to 1,3-alternate for cesium selective over sodium ions. These theoretical results were well within the solvent extraction results[97, 98].

Apart from Cs^+/Na^+ ion binding, the complexation of methyl-glycine-amide functionalized thiacalix[4]arene for Ag^+, K^+ ions were studied by using density functional theory (DFT) in the gas phase. According to observed structural and free energy calculations the silver cation preferred to coordinate with one sulfur bridge and three carbonyl groups, whereas potassium cation favored interaction with the four carbonyl oxygens of the amide arms[99]

1.5.5 Computational studies of Mono-crowns

1,3-alt-dimethoxy-calix[4]arene-crown-6 (DMC6) ligand was studied with B3LYP/6-31+ G* level of theory and the structure was made form X-Ray Crystallographic data of K^+-bis-crown complex. The major observations were that the optimized Cs^+-complex was having C2 symmetry while Na^+-Complex was highly distorted. The alkali metal cations, Na^+, K^+, Rb^+, and Cs^+ was found to be coordinated with 3, 4, 5, 6 crown oxygen respectively. In $NaNO_3$-complex the nitrate ion pulls the sodium ion outside to the plane of paper by opening the crown, which is due to repulsion of nitrate with the oxygens of crown moiety. The Na^+, K^+, Rb^+, and Cs^+ complexes were found to have the free energy of -73.1 kcal/mol, -64.1 kcal/mol, -57.2 kcal/mol, -63.4 kcal/mol respectively. After addition of nitrate ion in Na^+-Complex lowers the free energy value to 20 kcal/mol[100].

Iichenko et ol studied the cesium complexation by 25,27-dihydroxycalix[4]arene-crown-6 (DHC6) by using B3LYP functional with GAUSSIAN package. They observed that the central ion Cs^+ is coordinated with six crown oxygens. The addition of water molecule/molecules along with cesium in cavity leads to distortion of DHC6 geometry[**?**]. Molecular mechanics calculations performed on DHC6 predict that the 1,3-dihydro derivatives will exhibit greater complementarity for potassium and cesium ions than the parent 1,3-bis(alkyloxy) calixcrowns[102].

1.5.6 Computational studies of bis-crowns

1,3-alternate-bis-crown-6 (BC6) molecule having large number of atoms thus difficult to perform the DFT and ab-initio, therefore, semiemperical method (AM1) was used to simulate. The optimization and free energy calculation were made by taking the account of both the possibilities of mononuclear and bi nuclear complexes (Cs^+-BC6, $2Cs^+$-BC6). The solvent effects were introduced by using the continuum model which assumes an ellipsoid shape for molecular cavity. From the optimized structures of both the complexes it was observed that average Cs-O distance in mononuclear complex was 3.33 A^o which is well with the experimental X-Ray crystallography results. A similar value of Cs-O, 3.20 A^o was found for binuclear complex. The validation the AM1 calculation were made by carrying the similar studies on DMC6 and found that the free energy values obtained for DMC6 was same as in DFT calculations. Free energy calculations shows that the Cs^+-BC6 has more exothermic than DMC6 ($\sim$10 kcal/mol). The solvent contribution leads to a slight decrease in Cs-O distance ($\sim$0.026A^o)[103].

2. Synthesis, characterization, solvent extraction and theoretical studies using calix-crowns

2.1 Introduction

The major challenge for the nuclear community is the safe management of the spent fuel discharged from the nuclear reactor. Even though reprocessing is able to address this issue to a limited extent, the current technology addresses only the recovery of fissile and fertile components of the spent fuel. The spent fuel contains U and Pu, long-lived minor actinides such as Np, Am, Cm and other radioactive fission products, mainly rare earths and Sr-90, Cs-137, Tc-99 etc. Safe management of the radioactive waste by efficient separation and destruction/containment of radiotoxic nuclides is the key to success and public acceptance of nuclear energy program [104, 105]. PUREX process is employed worldwide for the treatment of spent fuel and selectively (nearly quantitatively) removes U and Pu from rest of fission and activation products [106, 107]. Actinide partitioning and transmutation (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 appropriate reactor or accelerator systems. Extractants like carbamoyl-phosphonate(CMP), carbamoyl methyl phosphine oxide(CMPO), Diglycolamides(DGA) etc. are tested and their utility have been demonstrated in the actinide partitioning from acidic high level liquid waste solutions[108, 109].

Two major radioisotope of cesium produced from fission of uranium from reactors are Cs-135 ($t_{1/2} \sim 10^6$yrs) and Cs-137 ($t_{1/2} \sim 30$ yrs). During reprocessing of spent nuclear fuel, these two radioisotopes formed in significant quantities are left out in the high level liquid waste solutions. The complete removal of these two radioisotopes is necessary as one of them is long lived (Cs-135) and other (Cs-137) has high decay heat and short lived. Both of them are potential mobile species in repository conditions capable of producing adverse effects if they are released in environment by some mechanism. Also Cs-137 is one of the major heat generating radionuclide and if removed can enhance the stability of vitrified waste. The removal of these two radionuclides from waste will lead to reduction in waste volume and cooling time for the final vitrified waste in glass matrix. Furthermore, Cs-137 is a β, $\gamma -$ emitter and can be used as an alternate source for cobalt- 60 for medical and industrial applications like, preservation of foodstuffs by killing bacterial growth, blood irradiation and medical accessories sterilization, cancer treatment by brachytherapy and in scintillation cameras [111, 112]. This makes cesium separation and recovery valuable. In fact, the effective separation of these radionuclides has been one of most challenging task.

Out of solvent extraction, ion exchange and precipitation, solvent extraction method is found to be most suitable for plant scale operation in nuclear fuel processing [113]. Solvent extraction using various crown ethers has been discussed in the previous chapters. It is well established that for the separation of cesium form high level liquid waste, many of the specific ionophore that has been developed is based on the molecular platform of crown ethers. Among them, calix[4]arene-crown-6 ethers seems to have relatively well optimized structural properties especially when fixed in 1,3-alternate conformation for cesium ions extraction over large amounts of sodium ions [114, 115]. Mono and bis crowns of calix[4]arene backbone were investigated for their potential use in the removal of radio cesium from alkaline and acidic nuclear waste. The bis-crown namely BOB-calix-6 was used along with Isopar L and trioctyl amine modified with Cs-7SB for cesium extraction from caustic side solvent extraction process (CSSX). In addition to CSSX process, FPEX (fission product extraction) process based on simultaneous extraction of Cs and Sr where DtBu18-C-6 was added for strontium extraction was also developed [116]. In Mono-crown, the extraction performance of 0.125M ipr-C[4]arene-crown-6 in ocatnol was tested on simulated and real high level liquid waste using centrifugal contractors [117, 118]. The major problems associated with the calix-crown are:

- These are very difficult to synthesized in large scale.
- The solubility in dodecane based diluents is very low. This has resulted in a search for new solvent combinations which are compatible with the existing diluent system for the on-going program of separation of minor actinides and strontium from HLW.

This chapter describes the work carried out in our laboratory on the synthesis of 1,3-dioctyloxy calix[4]arene-crown-6 (CC6) and Calix-benzo-crown (CBC) indigenously at larger scale by the procedure reported. In addition to this, development of a process based on dodecane modified with 30 % o-Nitrophenyl hexyl ether and 30 % isodecyl alcohol separately is also described. 30 % IDA/n-dodecane is already established as an alternate diluent for actinide partitioning demonstration studies on engineering scales [119].

2.1.1 Experimental

2.1.1.1 Chemical and solutions

Calix[4]arene was purchased from M/s. Numex Chemical Corporation, Mumbai, India and purified by recrystallization. o-NPHE was procured from M/s. Orion Chem. Pvt. Ltd, Mumbai, India and was used after distillation. n-dodecane (99.9%) and isodecyl alcohol (99.0%) were obtained locally and used as received. All other reagents were of Analytical-Reagent grade and purchased from Sigma-Aldrich and used as received. Acetonitrile was dried over calcium hydride and used after distillation. Demineralised water was used for preparation of all aqueous solutions. Composition of Simulated High Level Waste (SHLW) solution listed in Table 2.8 corresponds to the first cycle raffinate from reprocessing of long-cooled pressurized heavy water reactor spent fuel with an average burn up of $\sim$ 6500 MWd/ton. Cesium nitrate salts were used for inactive Cs in aqueous phase and analysis was done with AAS (GBC, Australia make). Radioactive Cs-137 analysis was carried on NaI (Tl) gamma scintillation detector. Other inactive metal ions of SHLW were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) of Horiba Jobin-Yvon make. Melting points were determined with a Mel-Temp melting point apparatus and GC-MS spectra were recorded on Shimadzu GC-2010 plus. NMR spectra were obtained with a Bruker 500 MHz FT-NMR spectrometer in $CDCl_3$ with TMS as internal standard. Elemental analysis was performed at CHNS-Thermo apparatus and ESI-MS spectra obtained by Q-TOF micro mass (YA-105) Bruker in positive ion mode.

2.1.2 Synthesis of calix-benzo-crown (CBC)

The synthesis of CBC has been done in parts. First the synthesis of crown part tosylate and then 1,3-Dioctyloxy-calix[4]arene was synthesized. Later both the compounds were condensed to obtain the resultant calix-crown.

2.1.2.1 Synthesis of polyether ditosylate

This also constitutes two steps- one for diol and second for their tosylate. In the first step the diol was synthesized by reacting catechol with 2-(2-chloroethoxy) ethanol in presence of base potassium carbonate. The second step for conversion of this diol into tosylate by reacting with tosyl chloride in presence of sodium hydroxide as shown in Fig. 2.1.

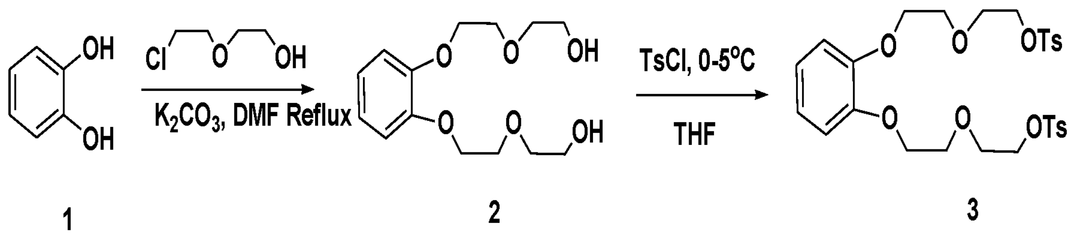


Figure 2.1: *Synthesis of polyether ditosylate*

Synthesis of Diol part The polyether diol was synthesized by refluxing catechol (25 gm, 0.227 mol) with 2-(2-chloroethoxy) ethanol (56.4 gm, 0.45 mol.) and K_2CO_3 (63 gm, 0.456 mol) in dry DMF (1000 ml) for 48 hours . After cooling the reaction mixture to room temperature, the reaction mixture was passed through silica pad to ensure complete salt removal. Column was eluted with 2X250 ml acetonitrile to get back the trapped product. This solution was dried over anhydrous sodium sulphate and concentrated by rotavapour by evaporating the solvent. The product was obtained as thick viscous oil (61.1 gm, Yield 94 %. GC-MS spectra showed a single peak at m/z 286 which clearly indicates the presence of diol.

Synthesis of polyether ditoisylate NaOH(40 gm, 1 mol) solution was prepared in distilled water (200 ml) and cooled to 0^{o}C under ice-water bath. The diol(55 gm, 0.19 mol) dissolved in 250 ml THF was added to above cooled sodium hydroxide solution. Tosyl chloride (36.6 gm, 0.19 mol) dissolved in 250 ml dry THF was added dropwise in the above reaction mixture by using a pressure equalizer dropping funnel. Temperature was maintained between 0-5^{o}C throughout the addition. The addition was completed in one hour and the reaction mixture was stirred at room temperature for three hours. The reaction mixture was poured into mixture of ice-

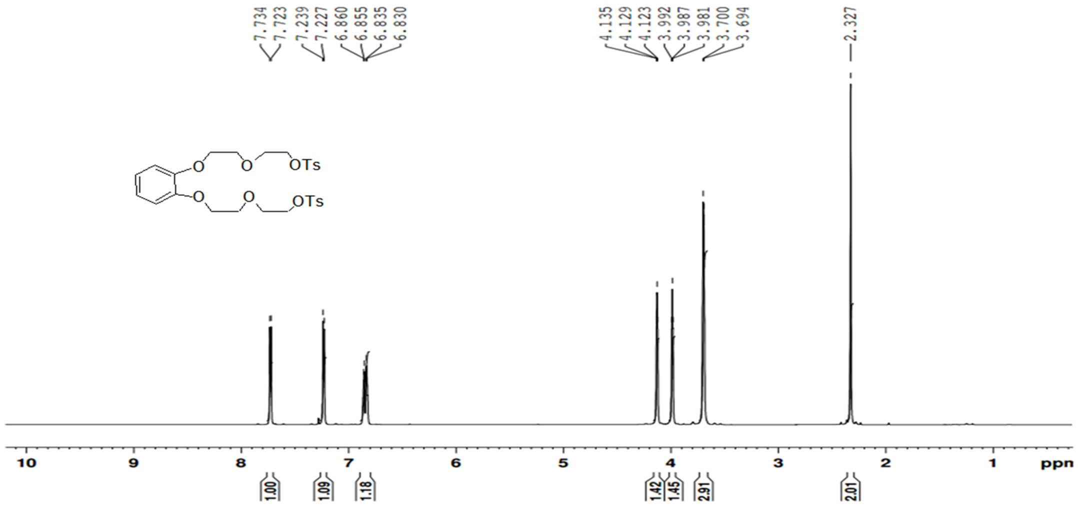


Figure 2.2: ^1H *NMR spectra of polyether ditosylate*

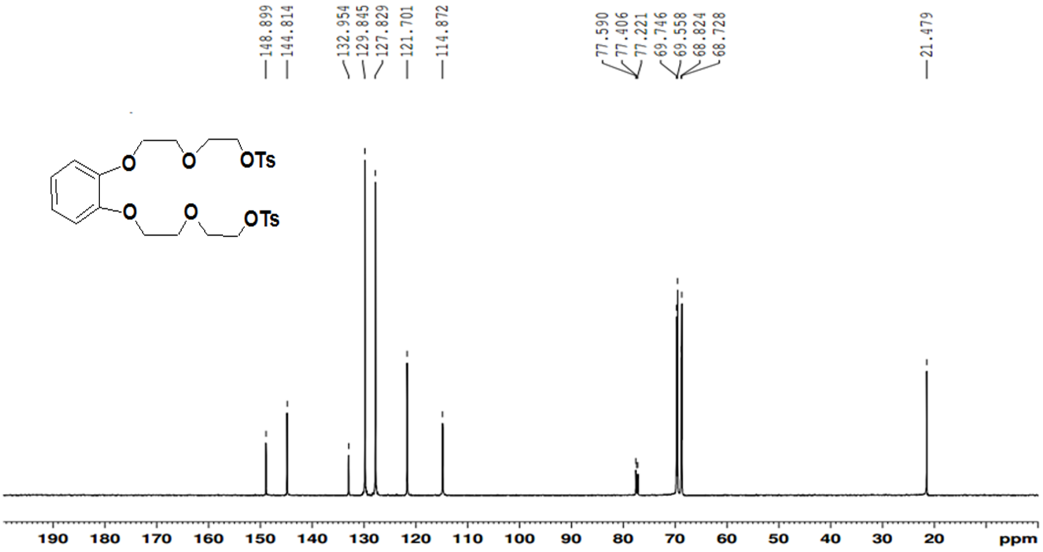


Figure 2.3: ^{13}*C NMR spectra of polyether ditosylate*

water (250gm/ 250gm). When ice melted down totally, THF was removed under reduced pressure and product was extracted in dichloromethane (2X250 ml). The organic was washed with 0.1 N HCl (2X250ml) and de-ionized water (3X250ml). The organic phase was dried over anhydrous sodium sulphate, filtered and concentrated by vacuum evaporation. Yield was found to be 98 %, 112 gm. The ^{1}H, ^{13}C NMR spectra of the compound 3 are shown in Fig.2.2 and Fig.2.3. These spectra clearly indicate the presence of polyether tosylate.

Synthesis of 1,3-dioctyloxy calix[4]arene The compound p-tert-buty phenol was reacted with formaldehyde in presence of base to obtain the p-tert-butyl calix[4]arene. This p-tert-butyl calix[4]arene was dealkylated in presense of anhydrous $AlCl_3$ and phenol to obtain the calix[4]arene. This calix[4]arene was further reacted with two moles of octyl iodide to obtain crude 1,3-dioctylaoxy calix[4]arene which was further purified by recrystalization in cold hexane as per reported procedure [120]. GC-MS spectra shows m/z 648 which clearly indicates the formation of dioctyloxycalix[4]arene.

Synthesis calix-benzo-crown (CBC) 1,3-Dioctyloxy calix[4]arene (20 gm, 30.8 mmol) dissolved in 4 liters of acetonitrile was reacted with polyether ditosylate (19 gm, 31.9 mmol) in presence of excess of cesium carbonate (29.3 gm, 90 mmol) under nitrogen atmosphere. The reaction mixture was refluxed for 48 hours. The acetonitrile was evaporated under reduced pressure and product was extracted in dichloromethane (500 ml). The organic phase was washed with 10 % HCl (2X300 ml) and distilled water (3X300ml). The organic phase was dried over anhydrous sodium sulphate, filtered and then the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (100-200 mesh size) with 1:3 ratio of ethylacetate: hexane as eluent to obtain 18.8 gram,(68 %) as white shiny crystals. The complete synthesis scheme is shown below in Fig.2.4. The ^{1}H NMR spectrum displayed in Fig.2.5 exhibits an expected resonance at δ 3.78, sharp singlet (8H), for bridged methylene protons. The ^{13}C spectra shown in Fig.2.6 exhibit a singlet at δ 37.77 which clearly indicates the presence of bridge methylene carbons. This compound was further characterized by ESI-MS (m/z 916.1, M$^+$ +NH$_4$ $^+$) and

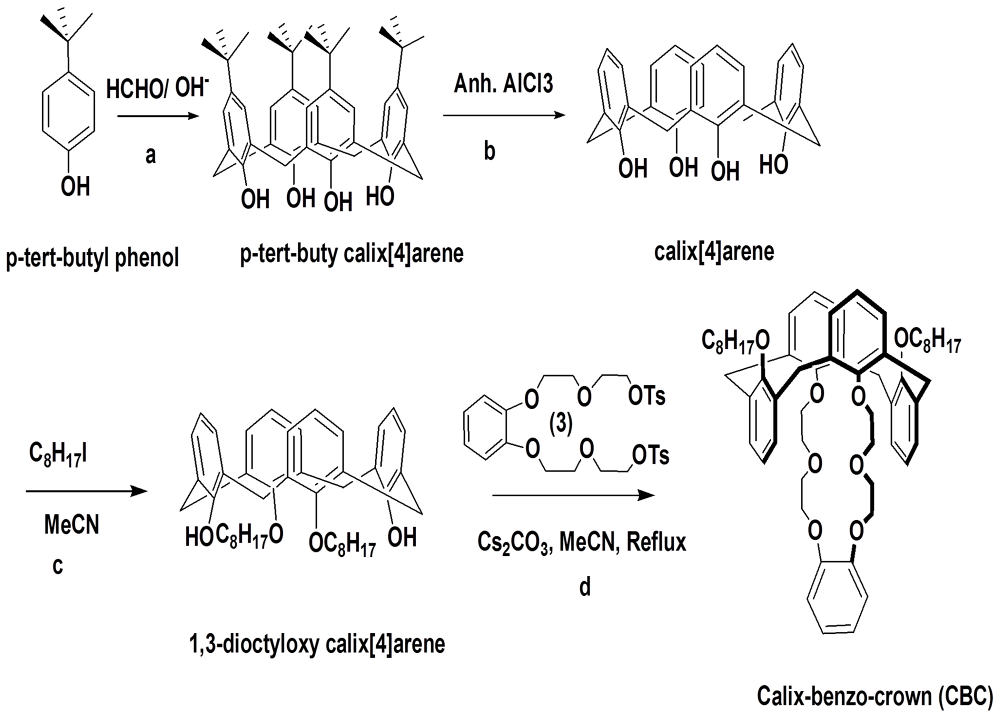
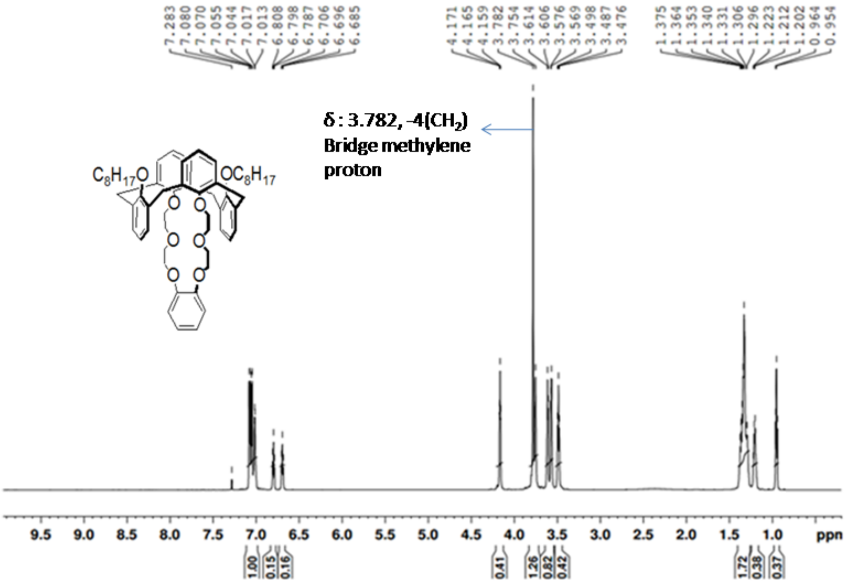
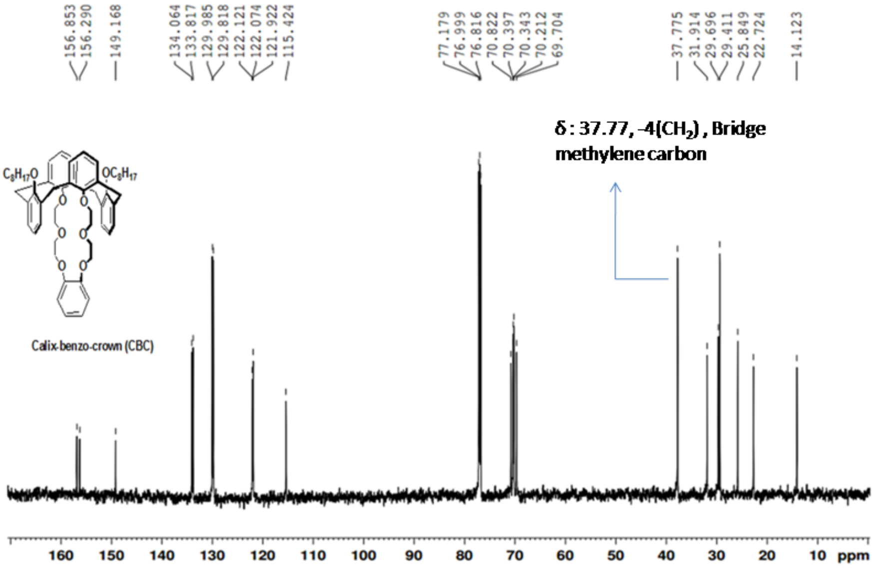


Figure 2.4: *Synthesis of Calix-benzo-crown: a) HCHO/OH$^-$, b) Anh. AlCl$_3$/Phenol c) K$_2$CO$_3$, C$_8$H$_{17}$I, MeCN, reflux; d) Cs$_2$CO$_3$, MeCN, reflux.*



δ : 3.782, -4(CH$_2$) Bridge methylene proton

Figure 2.5: ^{1}H *NMR spectra of Calix-benzo-crown (CBC)*



δ : 37.77, -4(CH$_2$), Bridge methylene carbon

Figure 2.6: ^{13}C *NMR spectra of Calix-benzo-crown (CBC)*

also the melting point (65-67^{o}C) matched with the standard value reported [121].

2.1.3 Synthesis of Calix-crown-6 (CC6)

1,3-dioctyloxy-calix[4]arene (25 gm, 38.5 mmol) dissolved in 5 liters acetonitrile was reacted with polyether tosylate (22 gm, 40.2 mmol) in presence of excess of cesium carbonate (39 gm, 120 mmol) under reflux for 48 hours as described in Fig.1.7. After evaporation of acetonitrile under reduced pressure the product was taken in

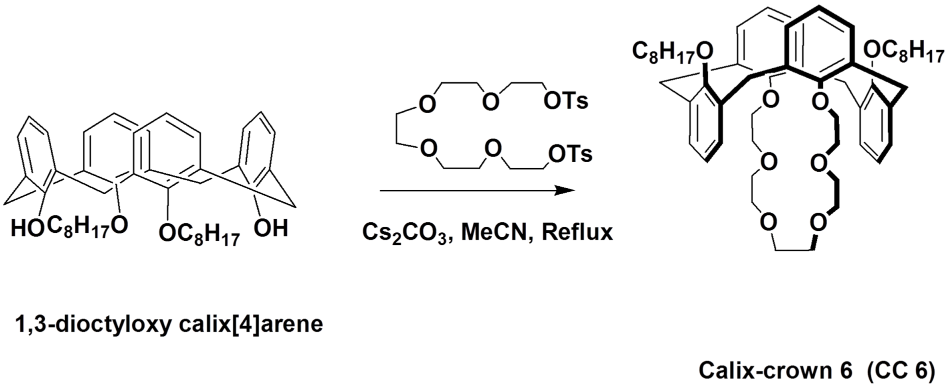


Figure 2.7: *Synthesis of 1,3-alternate di(octyloxy) calix[4]arene-crown-6 (CC6). Reagents and conditions:* Cs_2CO_3*, MeCN, reflux.*

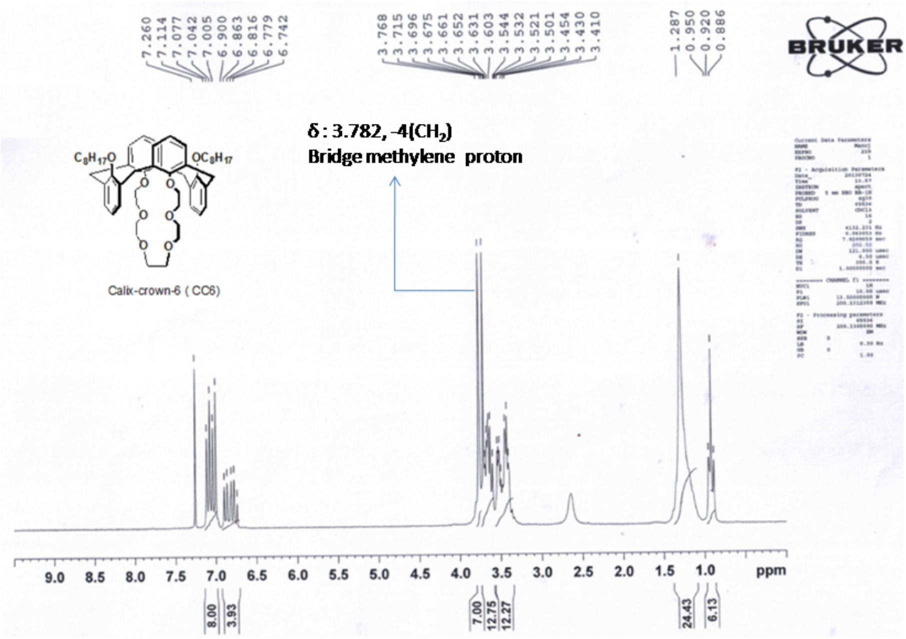


Figure 2.8: ^1H *NMR Spectra of calix-crown-6 (CC6)*

dichloromethane (500 ml). The organic phase was washed twice with 10% HCl (2X 300 ml) and thrice with distilled water (3X300ml). The organic phase was dried over anhydrous sodium sulphate. The dichloromethane was evaporated under reduced pressure. The crude product was crystallized in methanol. The product was obtained as white needle crystals with melting point of 94-96 ^{o}C. The ^{1}H NMR spectra shows (Fig.2.8) a singlet at Δ 3.78 for methylene protons (8H) and ^{13}C spectra Fig. 2.9 at Δ 37.8 clearly indicates the 8 equivalent hydrogen in bridge methylene groups of 1,3-alternate conformation.

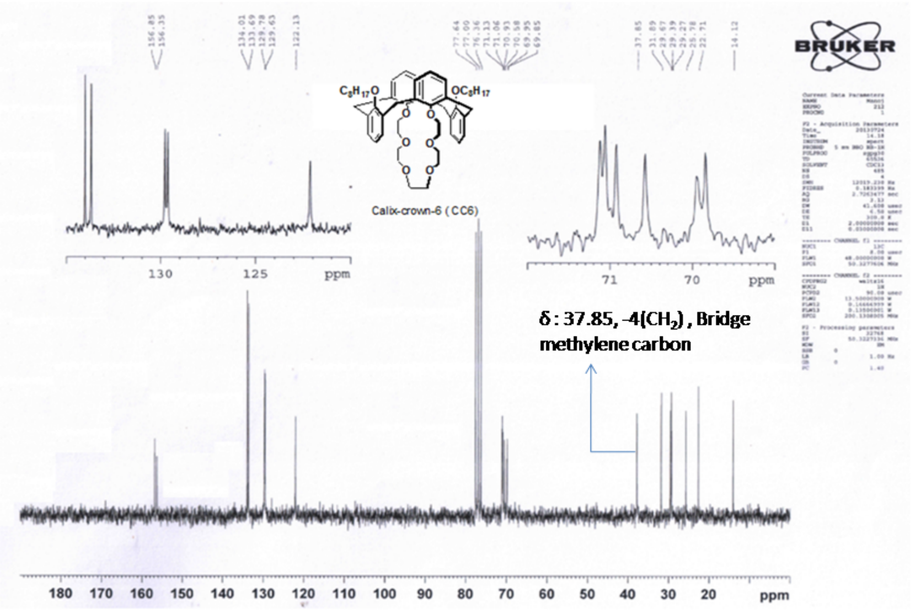


Figure 2.9: ^{13}C *NMR Spectra of calix-crown-6 (CC6)*

2.1.4 Extraction procedure

Distribution ratio measurements were performed by equilibrating 5 ml each of organic and aqueous phase for 15 minutes in 10 ml stopper glass vials. All the experiments were carried out in a thermostated bath at 25 ± 1^{o}C. After equilibrium, phases were separated by centrifugation and aqueous phase was analyzed with ICP-AES after suitable dilution. The concentrations of elements in organic phase were determined by taking the difference in concentration of feed and aqueous solution. Equilibrium was reached within 5 minutes and there was no considerable change in D_{Cs} for subsequent intervals of time. The reproducibility of results obtained was within ±5 %. Distribution ratio of metal ion was calculated by taking the ratio of metal ion concentration in organic phase to that of the metal ion concentration in aqueous phase.

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

Stripping studies were carried out with deionised water. For measuring the effect of temperature on distribution ratio, experiments were conducted in a thermostat ($\pm 0.5^o$ C) with mechanical shaking for 30 min. Temperature was varied in the range of 300−333 K. Agitated samples were then left in the thermostat for half an hour to allow complete separation of two phases. The aqueous phases were separated and analyzed for metal ions.

2.1.5 Computational methodology

Detailed DFT analysis for the calculation of binding energy and free energy of complexiation of both the ligands viz. Calix-benzo-crown (CBC) and Calix-Crown-6 (CC6) with cesium and sodium ion has been explored. The structure of free CBC CC6 and its complexes with Cs^+ and Na^+ ions with and without nitrate ion has been optimized using hybrid Becke-Lee-Young-Parr (B3LYP) density functional[122] approach employing split-valence plus polarization (SVP) basis set[123] as supplied in the TURBOMOLE suite of program[124]. The 46 core electron based effective core potentials (ECP) was used for Cs^+ ion [125]. The free energy was computed at 298.15 K using B3LYP functional approach. The hybrid B3LYP functional approach was shown to be quite successful in predicting the thermodynamic properties of Cs [126]. The solvent phase was accounted for using popular conductor like screening model (COSMO)[127].

2.2 Results and Discussion

2.2.1 Extraction equilibrium studies

The molecules under investigation in this study are already reported and the solvent extraction data in different diluents are available in literature. Hence prior to optimising the solvent extraction parameters, cesium distribution coefficients of these molecules were studied under the reported conditions to ascertain the quality of the synthesized product. The values are reported in Table 2.1. From the table, it can be seen that the D_{Cs} of indigenous products match very well with the values reported in literature and confirms the chemical characterization of the compound reported above. In order to optimise parameters for the development of a solvent extraction flow sheet for Cs extraction form HLLW, basic studies were carried out to establish the effects of various factors like, concentration of phase modifiers, aqueous phase acidity, ligand concentration, nitrate ion concentration and temperature on extraction.

Table 2.1: *Solvent extraction comparison data of reported and indigenous products*

Compounds	**Solvent System**	**D_{Cs} (Reported)**	**D_{Cs} Experimental**
Calix-benzo-crown (CBC)	0.01 M CC/o-NPHE	31	32
Calix-crown-6 (CC6)	0.01 M CC/o-NPHE	33	30

2.2.1.1 Effect of Isodecyl alcohol and o-NPHE

Initial experiments have shown that CBC has little solubility in n-dodecane and CBC/n-dodecane has almost no extraction of cesium from nitric acid medium. In order to enhance the solubility, polar phase modifiers such as isodecyl alcohol and o-NPHE were used. For optimization of modifier concentration, experiments were carried out by varying the percentage of modifier and measuring the distribution ratio of cesium at constant nitric acid concentration of 3.5 M while keeping other parameters fixed. 3.5 M HNO_3 was chosen based on the acidity level of high level liquid waste in general. A polar phase modifier enhances the solubility of the extractant in organic phase and its extraction efficiency by solvating the counter anion.

From the results as shown in Fig.2.10, Fig. 2.11 it was also observed that the extraction of cesium increased with increasing concentration of phase modifiers and this effect was less pronounced in case of isodecyl alcohol as compared to o-NPHE. Moreover D_{Cs} values sharply increased with the increase in phase o-NPHE for both the molecules, but CBC gave higher values. Use of 30 % (v/v) IDA as phase modifier with n-dodecane as diluent, resulted in a very stable solution and didnot gave rise to third phase even at higher metal and nitric acid loading. Also, n-dodecane modified with 30% IDA system has been used in TEHDGA-actinide partitioning process, thus IDA concentration was limited to 30% in our experiments. Finally 30 % NPHE in n-dodcane was also tested since this composition had also shown good behaviour in terms of hydraulic properties, chemical criteria and diluent compatibility during cesium extraction.

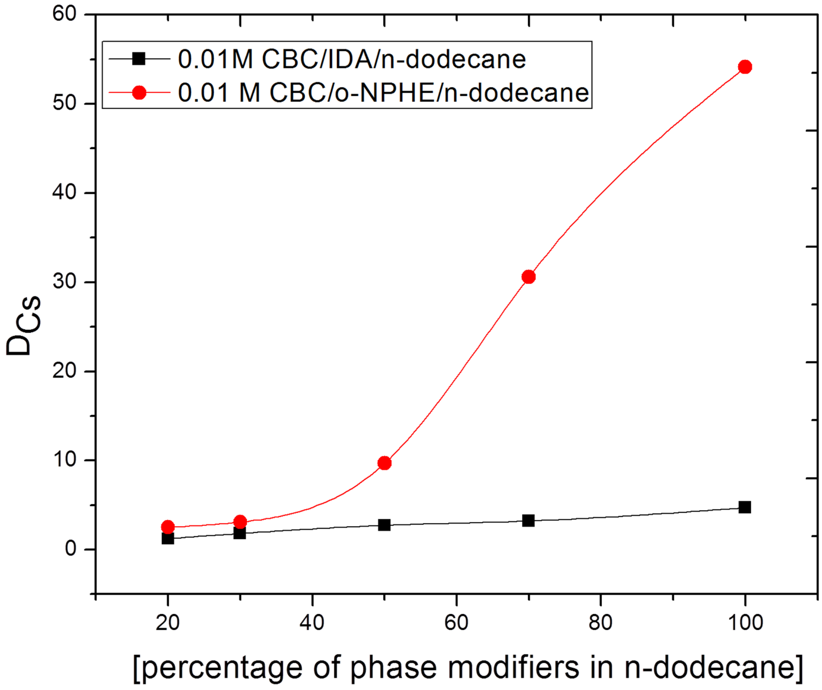


Figure 2.10: *Effect of phase modifiers on extraction of cesium. Organic phase: 0.01 M CBC/phase modifiers/n-dodcane; Aqueous phase ∼ 300 ppm cesium in 3.5 M nitric acid*

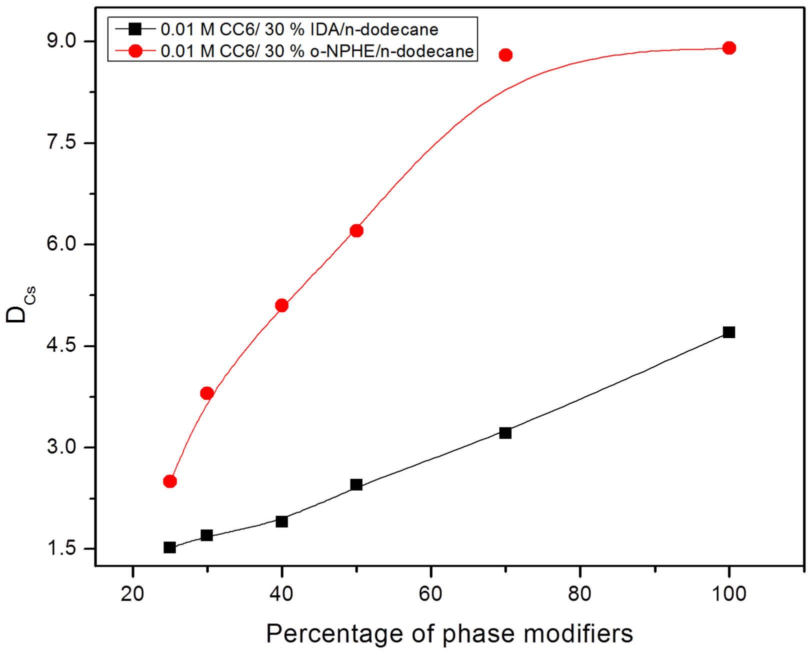


Figure 2.11: *Effect of phase modifiers on extraction of cesium. Organic phase: 0.01 M CC-6/phase modifiers/n-dodcane; Aqueous phase ∼ 100 ppm cesium in 3.5 M nitric acid.*

2.2.1.2 Effect of nitric acid concentration

The relation between D_{Cs} and HNO_3 (initial) concentration for 0.01 M CBC + 30% phase modifier/n-dodecane is shown in Fig.2.12. Aqueous phase consisted of ∼ 300 ppm of cesium as cesium nitrate.A very small increase in D_{Cs} was observed in lower region of nitric acid, up to 1 M nitric acid concentration D_{Cs} was 0.32, 0.49 for IDA and o-NPHE respectively, There was continuous increase of D_{Cs} for both the solvent systems with increasing nitric acid concentration. It was observed that D_{Cs} maxima was obtained at 4.5 M acid for o-NPHE and 5 M acid for IDA and beyond these the distribution ratio decreased.

Similar studies on the nitric acid influence on D_{Cs} with 0.01 M CC-6 in 30 % phase modifier/ n-dodecaneis shown in Fig.2.13. It can be observed that D_{Cs} increases with increase in nitric acid concentration for both the phase modifier solvent systems. For Isodecyl alcohol modified solvent system this increase is upto ∼6 M acid and for o-NPHE system the increase is upto ∼4 M nitric acid concentration.

The above observations suggest that nitric acid plays a very important role in

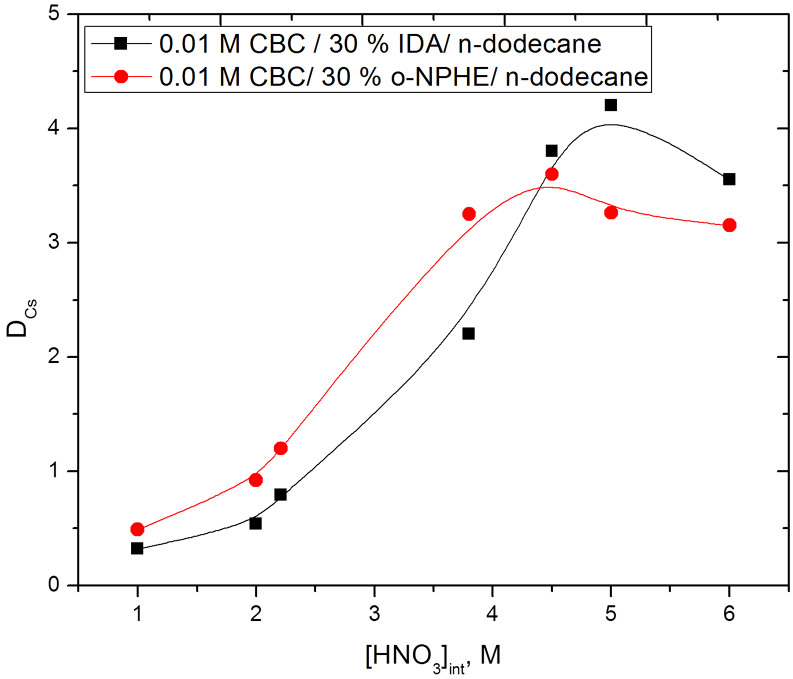


Figure 2.12: *Extraction dependency of cesium on initial nitric acid concentration. Organic phase : 0.01 M CBC/30 % phase modifier/n-dodecane; Aqueous phase containing ∼ 300 ppm cesium at varying nitric acid concentration.*

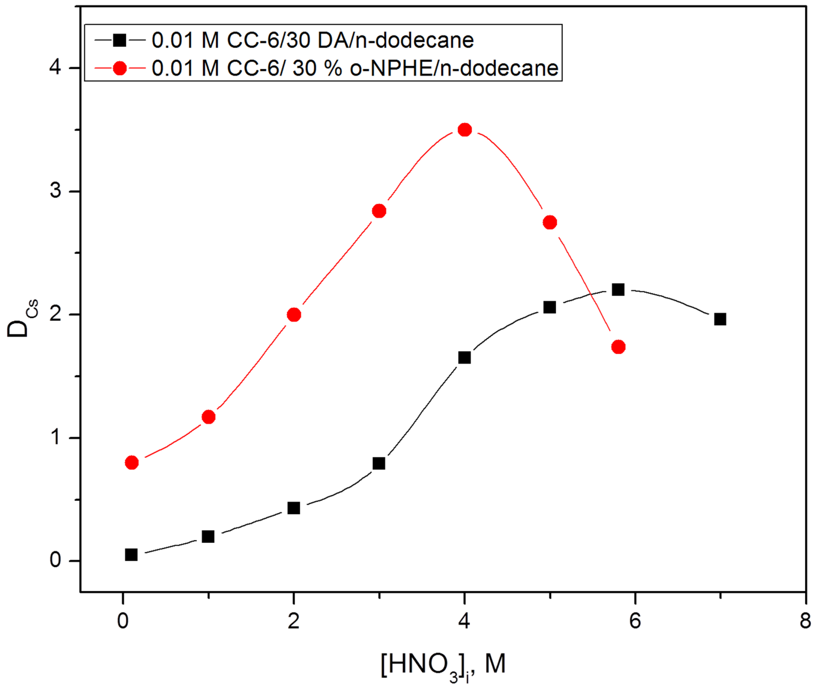


Figure 2.13: *Extraction dependency of cesium on initial nitric acid concentration. Organic phase : 0.01 M CC6/30 % phase modifier/n-dodecane; Aqueous phase containing ∼ 100 ppm cesium at varying nitric acid concentration)*

extraction of cesium. It was therefore of interest to investigate the participation of nitric acid in the extraction reaction. $D_{Cs}$was determined from nitric acid solutions of fixed ionic strength of 4.0 M using mixtures of HNO_3 and $NaNO_3$ and the results obtained were identical with the results of D_{Cs} vs. $[HNO_3]_i$. Fig 2.14and Fig.2.15 show that D_{Cs} increases with the nitric acid concentration at fixed ionic strength. This suggests that there is no significant effect of nitrate ion present in other forms ($NaNO_3$) on extraction of cesium at these extraction conditions. It is interesting to note that extraction of cesium is almost negligible at lower nitric acid concentrations < 0.1 M), therefore this important property is used for stripping cesium with deionized water.

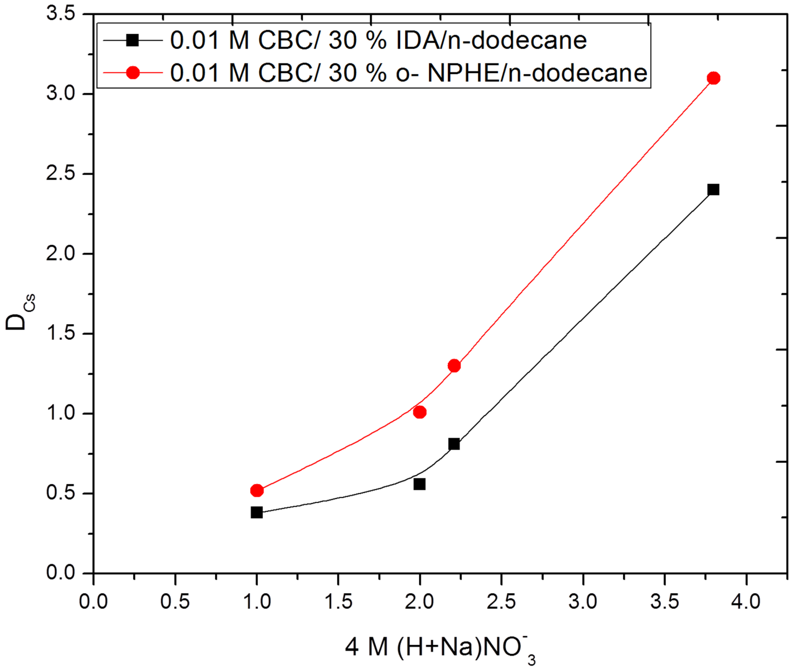


Figure 2.14: *Extraction dependency of cesium on nitric acid concentration under the constant ionic strength. Organic phase: 0.01 M CBC/ 30%phase modifier/n-dodecane: Aqueous phase: ∼ 300 ppm cesium in 4M (H + Na)* NO_3

2.2.1.3 Effect of ligand concentration

In order to study the effect of ligand concentration on D_{Cs}, the ligand concentration was varied while keeping other parameters fixed. Plot of log D_{Cs} vs. log [CBC] at constant nitric acid concentration (Fig.2.16) shows a slope (n) of 0.87 and 1.1 in IDA

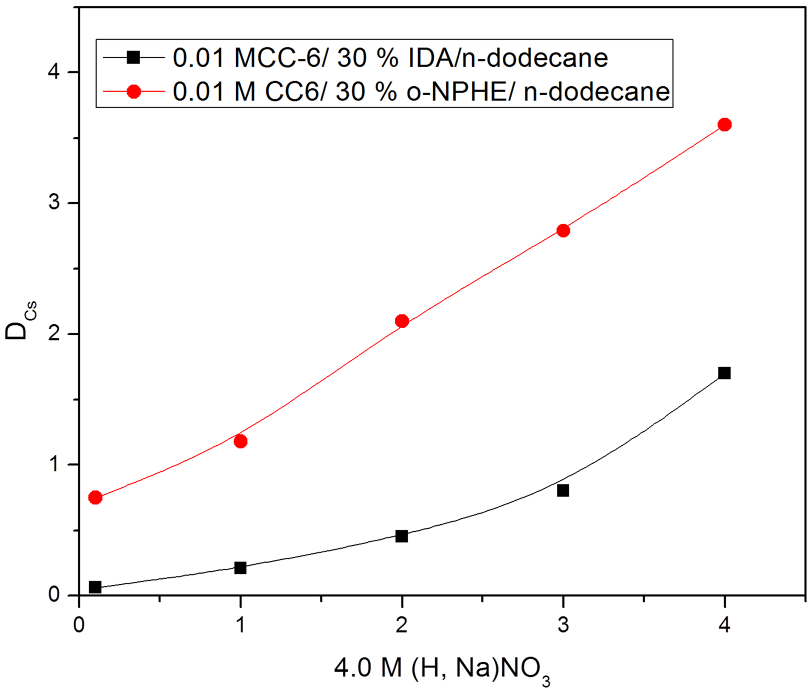


Figure 2.15: *Extraction dependency of cesium on nitric acid concentration under the constant ionic strength. Organic phase: 0.01 M CC-6/ 30%phase modifier/n-dodecane: Aqueous phase: ∼ 100 ppm cesium in 4M (H + Na) NO_3*

and o-NPHE respectively, suggesting a 1:1 stoichiometry of Cs with Ligand. The solvent composition was optimized as 0.01M Calix-crowns + 30% phase modifiers/n-dodecane, as this concentration of CBC in 30 % phase modifiers/n-dodecane has given workable distribution ratio of 1.8 and 2.87 for IDA and o-NPHE respectively for extraction of Cs from aqueous solutions of 3.5 M nitric acid. Similar studies on the effect of ligand concentration on extraction of cesium from 3.5 M nitric acid concentration at constant 30 % phase modifier concentrations in n-dodecane using CC-6 have been studied. The log D_{Cs} v/s. log[CC6] plot as shown in Fig.2.17 indicates a slope of 0.99 and 0.95 for IDA and o-NPHE respectively.

2.2.1.4 Effect of nitrate ion concentration

In order to investigate the effect of counter ion during cesium extraction, graphs between D_{Cs} and $[NO_3]^-_{ini}$ were plotted (Figs. 2.18, 2.19). The initial content of feed solution was kept at 1M nitric acid to ensure significant distribution ratio for Cs and then D_{Cs} was obtained as a function of sodium nitrate concentration. It was

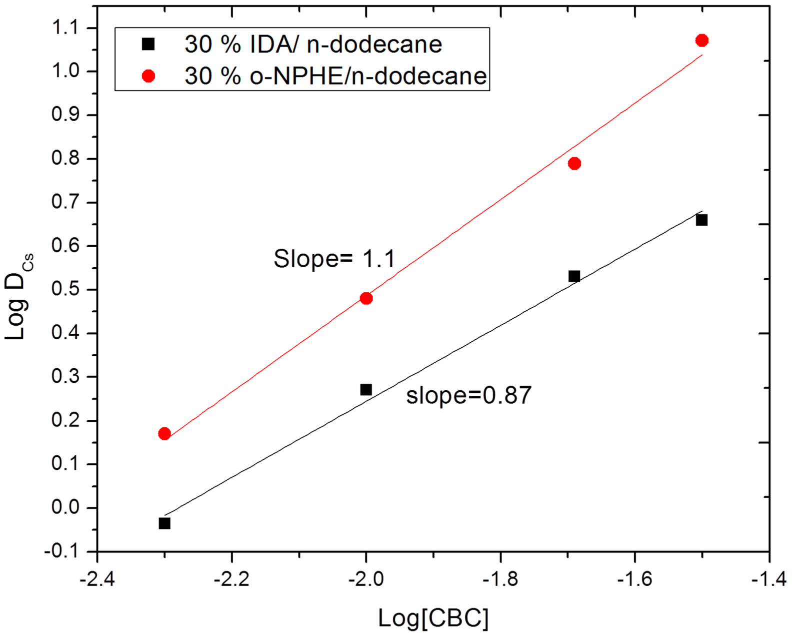


Figure 2.16: *Dependency of log D_{Cs} on log [CBC]. Organic phase: 0.005–0.02 M CBC/30 % phase modifier/n-dodecane; Aqueous phase: ∼ 300 ppm cesium at 3.5 M HNO_3*

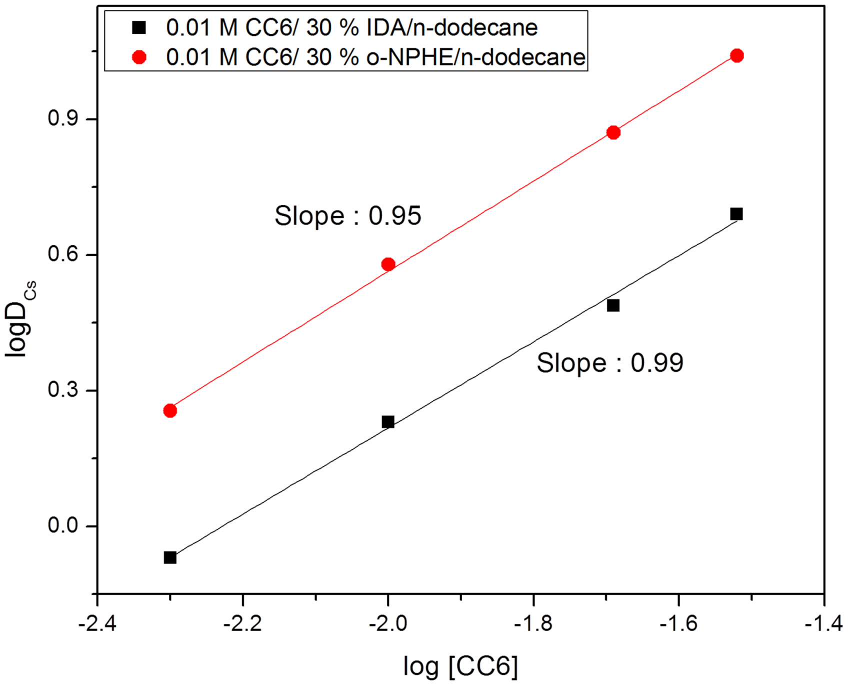


Figure 2.17: *Dependency of log D_{Cs} on log [CC6]. Organic phase: 0.005–0.02 M CC6/30 % phase modifier/n-dodecane; Aqueous phase: ∼ 100 ppm cesium at 3.5 M HNO_3*

observed from Fig.2.18, that there is no significant effect of counter ion on extraction of cesium in both the solvent systems, contrary to the behaviour of other neutral extractants where a considerable effect of nitrate ions on the distribution ratios of metal ions are observed. Similar studies (Fig. 2.19) on the effect of nitrate ion during cesium extraction on CC-6 also show constant D_{Cs} with the increase of nitrate ion concentration. This suggests that the nitrate ion required for maintaining charge neutrality in the complex.

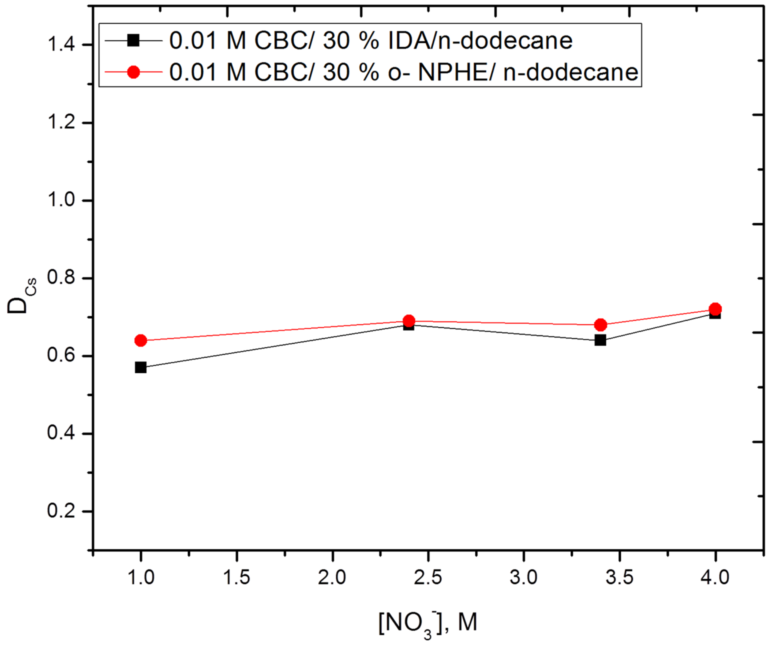


Figure 2.18: *Extraction dependency of cesium on initial nitrate ion concentration. Organic phase: 0.01 M CBC and 30 % phase modifier in n-dodecane ; Aqueous phase: ~ 300 ppm cesium in 1 M HNO_3 (fixed) + $NaNO_3$*

Nitrate effect has been masked due to high nitrate ion concentration present in aqueous solution resulting in reduced activity coefficient cesium ion. After required correction on activity coefficient of cesium in presence of large nitrate ion concentration Eve Bazelaire et.al have obtained the slope of 0.70 for the graph D_{Cs} v/s NO_3^- indicating the stoichiometry close to 1:1 for CBC.Cs to NO_3^- ion [128]. However in our studies, we have not carried out the necessary activity correction for cesium in the presence of excess nitrate ions therefore, similar behaviour was not observed by us, but to maintain the charge neutrality the extracted species can be written as

CBC.$Cs^+.NO_3^-$.

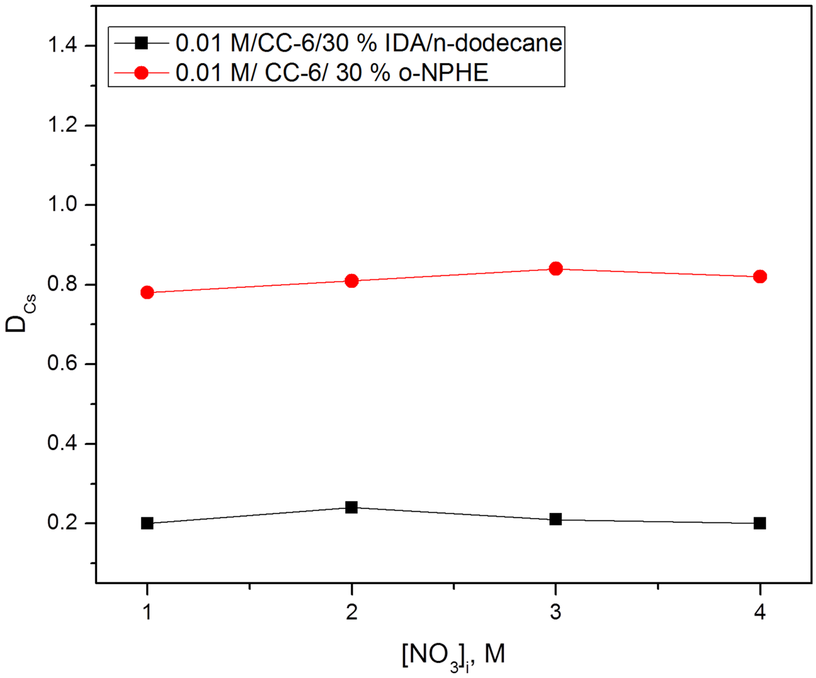


Figure 2.19: *Extraction dependency of cesium on initial nitrate ion concentration. Organic phase: 0.01 M CC6 and 30 % phase modifier in n-dodecane ; Aqueous phase: ~ 100 ppm cesium in 1 M HNO_3 (fixed) + $NaNO_3$*

2.3 Probable Mechanism of Extraction of Cesium by Calix-Crownethers

Based on the experimental data and that reported on extraction mechanism by crown ethers, uptake of Cs from nitric acid medium can be treated as follows taking CBA as an example:

$$CBA + H^+ + NO_3^- \overset{K_H}{\leftrightarrow} CBA.HNO_3 \tag{2.1}$$

$$CBA.HNO_3 + Cs^+ \leftrightarrow CBA.Cs.NO_3 + H^+ \tag{2.2}$$

$$CBA + Cs^+ + NO_3^- \overset{K_{ex}}{\leftrightarrow} CBA.Cs.NO_3 \tag{2.3}$$

$$K_{ex} = \frac{CBA.CsNO_3}{[CBA][Cs^+][NO_3^-]} \tag{2.4}$$

Where the quantities inside the square bracket denote the activities of the respective species. The organic phase activities will probably vary as the aqueous phase concentration especially of acid increases and more acid is transferred to organic phase. Since there is lack of information on organic phase activity coefficients, it is assumed that the ratio of organic phase coefficients remain constant. Assuming the activity coefficient of organic phases as constant , equation 4 can be rewritten as

$$K'_{ex} = \frac{D_{Cs}}{C_{CBA}C_{HNO_3}\gamma_{Cs^+}\gamma_{NO_3^-}} = \frac{D_{Cs}}{C_{CBA}C_{HNO_3}\gamma^2_{\pm CsNO_3}} \tag{2.5}$$

Where K'$_{ex}$ is the conditional equilibrium constant and $\gamma_\pm$ indicate the mean ionic activity coefficient. As

$$D_{Cs} = \frac{C_{CBA.CsNO_3}}{C_{Cs^+}} \tag{2.6}$$

Where the molar concentrations are denoted by C Since all the Cs is present as Cs$^+$ in the nitrate medium

$$D_{Cs} = \frac{C_{CBA.CsNO_3}}{C_{(Cs)_T}} \tag{2.7}$$

where C$_{(Cs)T}$ indicate total Cs Activity of CBA, [CBA]$_i$, at equilibrium can be obtained from the following relation

$$[CBA]_i = [CBA] + [CBA.HNO_3] + [CBA.CsNO_3] \tag{2.8}$$

Where [CBA]$_i$ = initial CBA activity Since Cs loading in CBA is at tracer levels.This equation reduces to

$$[CBA]_i = [CBA] + [CBA.HNO_3] \tag{2.9}$$

[CBA.HNO$_3$] can be obtained from equation 2.1 as follows

$$K_H = \frac{[CBC.HNO_3}{[CBA][H^+][NO_3^-]} \tag{2.10}$$

Where K$_H$ is equilibrium acid uptake constant

$$[CBC.HNO_3] = K_H[CBA][H^+][NO_3^-] \tag{2.11}$$

Substituting in equation 9 gives

$$[CBC]_i = [CBA] + K_H[CBA][H^+][NO_3^-] \tag{2.12}$$

$$[CBC]_i = [CBA](1 + K_H[H^+][NO_3^-]) \tag{2.13}$$

$$[CBC]_i] = [CBA]A where A = (1+K_H[H^+][NO_3^-]) = 1+K'_H C^2_{HNO_3}\gamma^2_{\pm HNO_3} \tag{2.14}$$

Where [K'$_H$] is the conditional equilibrium acid uptake constant

$$[CBA] = [CBC]_i/A \tag{2.15}$$

Hence equation 5 can be modified by assuming activity coefficient in organic phase as constant

$$K'_{ex} = \frac{D_{Cs}A}{C_{CBA}C_{HNO_3}\gamma^2_{\pm CsNO_3}} \tag{2.16}$$

$$D_{Cs} = \frac{K'_{ex}C_{CBA_i}C_{HNO_3}\gamma^2_{\pm CsNO_3}}{A} \tag{2.17}$$

$$logD_{Cs} = logK'_{ex} + logC_{(CBA)_i} + logC_{HNO_3} + log\gamma^2_{\pm CsNO_3} - logA \tag{2.18}$$

The effect of nitrate on the extraction of Cs is more complex as can be seen from equation 2.18. With increase in nitrate concentration log D$_{Cs}$ has an increasing log C$_{HNO3}$ term, varying mean ionic activity term and a decreasing log A term. These terms seems to be mutually neutralizing, giving a flat response to the plots shown in Figs. 2.18 and 2.19.

2.3.1 Effect of temperature on extraction

The effect of temperature on extraction of cesium was studied in the temperature range of 300 -323 K for both the solvent system. According to equation 2.5 and 2.18

the logK$_{ex}$ can be written as

$$logK'_{ex} = logD_{Cs} - logC_{(CBA)_i} - logC_{HNO_3} - log\gamma^2_{\pm CsNO_3} + logA \tag{2.19}$$

The activity coefficient of nitric acid at 3.5 M was taken as 0.912 from literature [129] and the values of log$\gamma^2_{\pm CsNO_3}$ obtained by the procedure reported in literature [130]. The values of D$_{Cs}$ and ligand concentration obtained from the experiments were used for the calculation of log K$_{ex}$ using equation 18 assuming the values of close to 1. The values of K$_{ex}$. are listed in Table 2.2.

Table 2.2: *Extraction equilibrium constant at 300 K.*

30% IDA/n-dodecane			**30 % o-NPHE/ n-dodecane**	
[CBC]M	**Log K$_{ex}$**	**Average**	**Log K$_{ex}$**	**Average**
0.005	1.761	1.746	1.949	1.960
0.01	1.751		1.949	
0.015	1.750		1.949	
0.02	1.725		1.949	

Similarly logK$_{ex}$ at different temperature were calculated and the average value of log K$_{ex}$ were listed in Table 2.3 log K$_{ex}$ vs. 1/T (K^{-1}) was plotted for both the systems as shown in Fig.2.20. Enthalpy and entropy of the extraction were calculated from slope (ΔH^o/2.303R) and intercept (ΔS^o/2.303R) respectively from the Vant Hoff equation.

Table 2.3: *Effect of temperature on equilibrium constant*

Temp.(K)	**log K$_{ex}$(IDA)**	**log K$_{ex}$(o-NPHE)**
300	1.75	1.96
313	1.35	1.75
323	1.12	1.36

log K$_{ex}$ = - △H^o/2.303RT + △S^o/2.303R

Slope and intercept for IDA system were 2.47 and -6.50. The values for enthalpy and entropy were -47.29 kJmol^{-1} and -124.45 JK^{-1}mol^{-1} respectively. On the other hand, for NPHE system, the slope and intercept were 2.41 and -6.10 and their

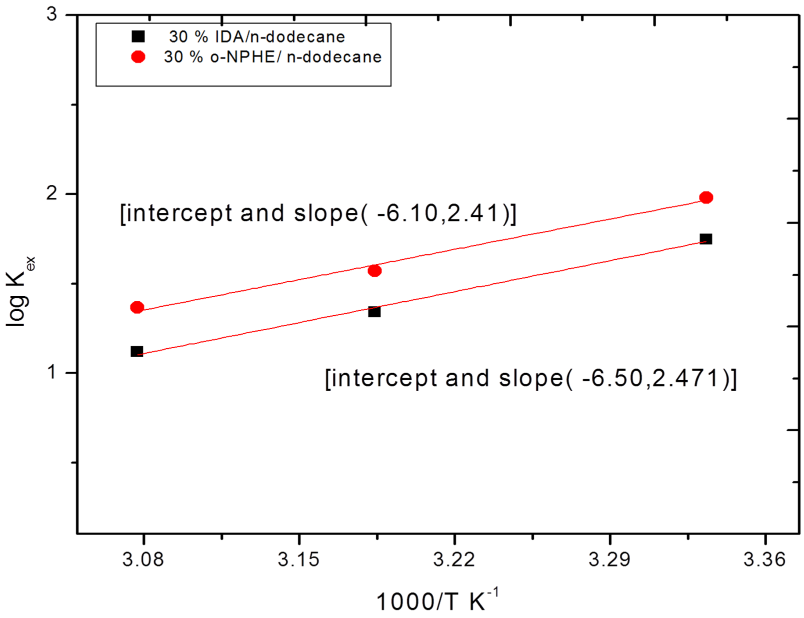


Figure 2.20: *Effect of temperature on equilibrium constant of cesium. Organic phase: 0.01 M CBC/30 % modifiers/n-dodecane ; Aqueous phase: ∼ 300 ppm cesium in 3.5 M nitric acid.*

corresponding values for enthalpy and entropy were -46.14 $kJmol^{-1}$ and -116.79 $JK^{-1}mol^{-1}$ respectively.

Negative enthalpy for both the systems indicates that the extraction process is exothermic in nature. This enthalpy term contributes to change in dehydration enthalpy of metal ion and change in enthalpy during complex formation. The dehydration enthalpy terms in both the solvent system are same as it is dependent on type of metal ion. So the overall contribution is from extraction reaction enthalpy. The negative value for entropy change indicates that the chelation of metal ion with calix-crown resulting in formation of more organized metal-ligand complex. In both the solvent systems, thermodynamic parameters were found to be almost identical thus indicating the similar mechanism for extraction of metal ion.

2.4 Structural parameters by Computational results

Generally the extraction of metal ions is carried out in aqueous nitric acid solution. In this experimental condition, the metal ions might coordinate with the nitrate ions or aqua molecules in its first sphere of coordination. The nitric acid concentration is small as compared to water therefore, the first coordination sphere is considered to fulfill by aqua molecules alone. In view of above experimental condition, the first sphere coordination of metal ion was optimized with aqua molecules. The cesium ion being a large ionic size is considered to have coordination number of eight while sodium was provided a coordination number of six. The optimized minimum energy structures of various species: $(H_2O)_6$, $(H_2O)_8$, $NO_3^-(H_2O)_6$, Na-$(H_2O)_6{}^+$, Cs-$(H_2O)_8{}^+$, ions are presented in fig 2.21. The minimum energy structures of free

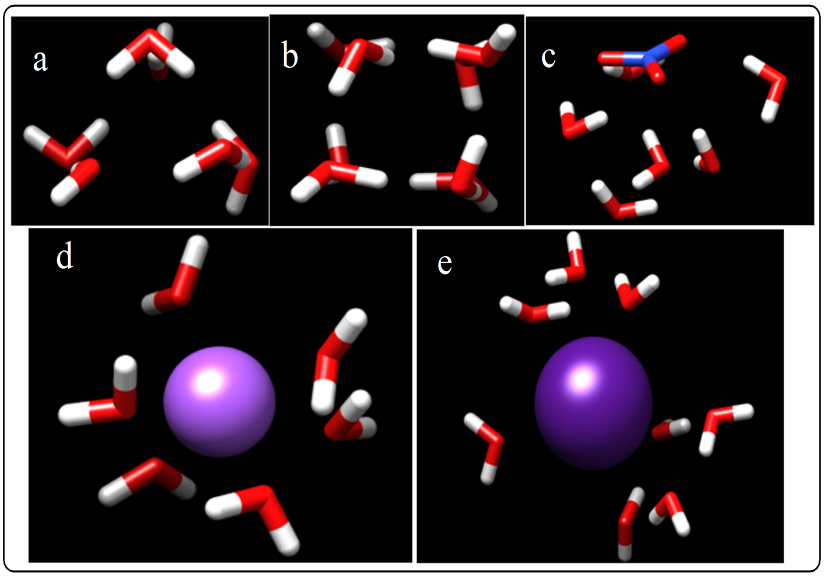


Figure 2.21: *optimized Structures of a) $(H_2O)_6$, b) $(H_2O)_8$, c) $NO_3^-(H_2O)_6$, d) Na-$(H_2O)_6{}^+$, e) Cs-$(H_2O)_8{}^+$ with B3LYP/SVP level of theory.*

CBC & CC6 are displayed in Figure 2.22 and figure 2.23. From the figures it is seen that both the calix-crowns offers a fine cavity to trap the metal ions inside it.

2.4.1 Structure of Ligand and Metal IonLigand

The optimized structure of ligands and complexes has been displayed in fig 2.22 and fig 2.23.The CBC, complexed with Metal (Cs & Na) and metal nitrates (Cs & Na NO_3) has been displayed in fig 2.22.The average cavity size of CBC after subtracting the diameter of oxygen (diameter of O atom of 2.644 A^o and average O-O distance in

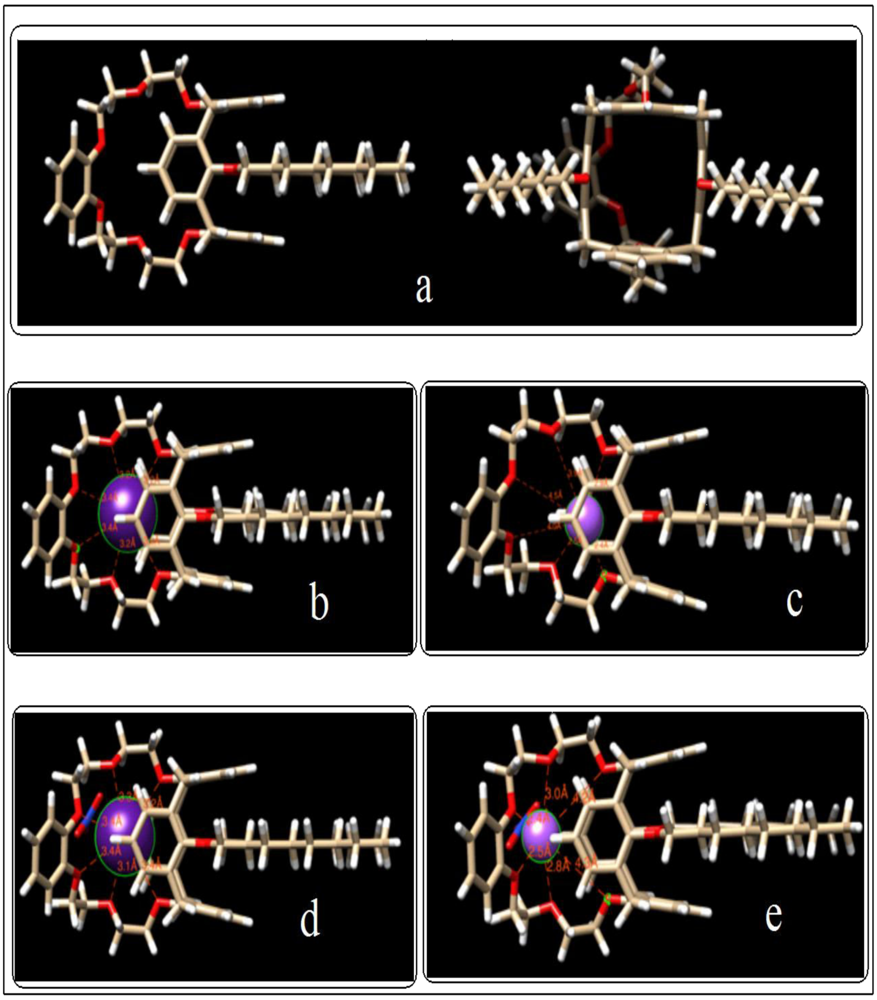


Figure 2.22: *a) Optimized structure of free CBC at B3LYP/SVP level of theory. Side view and top view, b) Optimized structure of CBC-Cs^+, c) Optimized structure of CBC-Na^+, d) Optimized structure of CBC-$CsNO_3$, e) Optimized structure of CBC-$NaNO_3$*

CBC, 6.427 A^o) was observed to be 3.783 A^o which is quite complementary to Cesium ion (3.38 A^o). The calculated value of structural parameters at the B3LYP/SVP level of theory is displayed in Table 2.4.

The CBC-Cs^+ complex was found to be hexa coordinated (four from crown and two from phenolic) with average Cs-O distance of 3.289 A^o. In CBC-$CsNO_3$ complex the average Cs-O distance is 3.285 A^o with an octa coordinated complex (four from crown, two from phenolic and two from nitrate ion) observed where NO_3 is behaving as bi-dentate ligand. On the other hand the CBC complex with Na^+, the sodium is found to be coordinated with three O atom (two phenolic one crown) with an

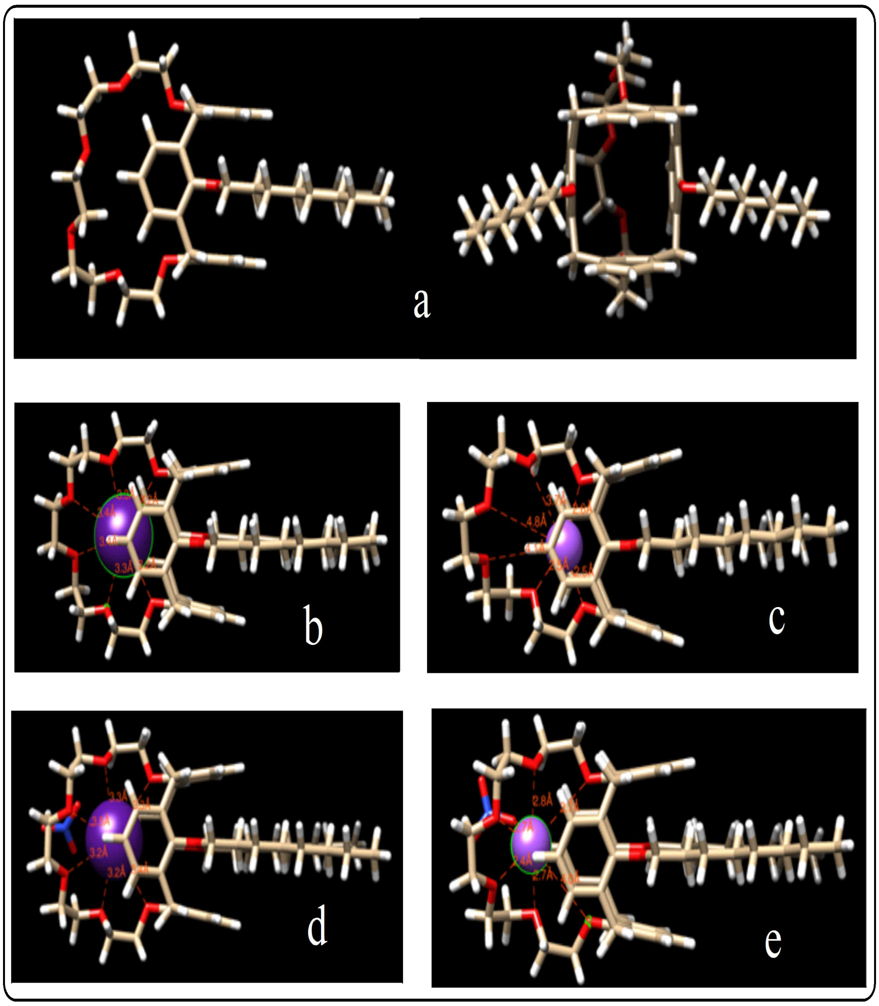


Figure 2.23: *a) Optimized structure of the free CC6 at the B3LYP/SVP level of theory. Side view and top view, b) Optimized structure of CC6-Cs^+, c) Optimized structure of CC6-Na^+, d) Optimized structure of CC6-$CsNO_3$, e) Optimized structure of CC6-$NaNO_3$*

average distance of 2.604 A^o. The other crown oxygens are quite far away from the Na ion with an average distance of 4.140 A^o. In CBC-$NaNO_3$ complex the sodium ion is shifted toward the outer crown oxygen with an increased coordination of four (two from crown oxygen two from nitrate ion) with an average distance of 2.410 A^o. From the figures it was also observed that the nitrate ion pulled the sodium ion towards itself while the in CBC-$CsNO_3$ complex the position of cesium ion is almost unchanged.

On a similar track the CC6-Cs^+ and CC6-$CsNO_3$ were found to be hexa and octa co-ordinated with an average Cs-O distance of 3.299 A^o and 3.326 A^o respectively

Table 2.4: *Calculated Structural Parameters of Metal Ion−CBC Complexes at the B3LYP/SVP Level of Theory*

Complex	**M-O(A^o)crown oxygen**	**M-O (A^o)phenolic oxygen**	**M-O(A^o)(nitrate ion oxygen)**
Na^+-CBC	3.934, 4.482, 4.004, 2.519	2.884, 2.409	-
Cs^+-CBC	3.450, 3.167, 3.418, 3.250	3.235, 3.189	-
$NaNO_3$-CBC	2.460, 2.448, 2.826, 3.011	4.190, 4.228	2.385, 2.349
$CsNO_3$-CBC	3.256, 3.352, 3.387, 3.105	3.404, 3.209	3.248, 3.179

as shown in Table 2.5. It was also observed that in CC6-$CsNO_3$ complex one nitrate oxygen is shifted slightly away from the cesium ion. The CC6-Na^+ complex is found to be the tri-coordinated (two from phenolic one from crown oxygen) with an average distance of 2.604 A^o where one of the phenolic oxygen is slightly away from sodium ion. In CC6-$NaNO_3$ complex the nitrate ion pulls out the sodium ion towards itself and it was found to bi-coordinated (one from nitrate and one from crown oxygen).

Table 2.5: *Calculated Structural Parameters of Metal Ion−CC6 Complexes at the B3LYP/SVP Level of Theory*

Complex	**M-O(A^o)crown oxygen**	**M-O (A^o)phenolic oxygen**	**M-O(A^o)(nitrate ion oxygen)**
Na^+-CC6	2.461, 4.13, 4.779, 3.654	2.570, 2.451	-
Cs^+-CC6	3.291, 3.425, 3.41, 3.268	3.207, 3.196	-
$NaNO_3$-CC6	2.426, 2.692,2.701, 2.844	3.723, 4.024	2.223, 3.649
$CsNO_3$-CC6	3.184, 3.197, 3.494, 3.31	3.282, 3.381	3.064, 3.700

2.4.2 Binding and free energy of complexation

The biding energy (BE, $\triangle$E) which basically measures the interaction of metal ions towards ligands. It is a very important parameters for predicting the preferential selectivity among competitive metal ions and can be expressed by following reaction

$$M_g^+ + L_g \rightarrow M^+L_g \tag{2.20}$$

$$B.E = E_{M^+L} - E_{M^+} - E_L \tag{2.21}$$

Where E_{M+L}, E_M, E_L represents the total energy of the metal ionligand complex, metal ion, and the ligand, respectively. Three different models was chosen for studying the binding energies as shown below. First is purely the gas phase reaction of Metal ions (Cs, Na) and calix-crown, In the second model, the hydration of metal ion is taken into account by providing a coordination of eight to cesium and six to sodium by providing the water molecules. In the third modal the hydration of both the cation (Cs, Na) and anion (nitrate) is being considered.

$$M^+_{(g)} + CC_{(g)} \rightarrow M^+CC_{(g)} \tag{2.22}$$

$$M(H_2O)^+_n + CC_{(g)} \rightarrow M^+CC_{(g)} + (H_2O)_n \tag{2.23}$$

$$M(H_2O)^+_n + NO_3(H_2O)^-_6 + CC_{(g)} \rightarrow MNO_3.CC_{(g)} + (H_2O)_n \tag{2.24}$$

Where n = 6 for Sodium and n = 8 for cesium, CC = CBC, CC6 From the table 2.6, it has been observed that for model 1 the binding energy and free energy of CC6 with Na^+ ion is more (-76.04 kcal/mole, -85.26 kcal/mole) as compared to CC6 complex with Cs^+ ion (-45.68 kcal/mole, -57.44 kcal/mole), which is contrary to experimental results in solution phase. Similar trend was observed for CBC where the binding energy and free energy for Cesium (-56.25 kcal/mol, -66.62 kcal/mol) complex was lower than the sodium complex (-87.11 kcal/mol, -89.73 kcal/mol).

Table 2.6: *Calculated value of binding energy with ZPE correction (B.E w ZPE Corr.) and free energy ($\triangle G$) of Complexes of calix-crown in gas phase at the B3LYP level of theory using SVP basis set.*

	Calix-Crown	**Cesium**		**Sodium**	
		B.E with ZPE Corr.(kcal/mol)	**$\triangle$G (kcal/mol)**	**B.E with ZPE Corr.(kcal/mol)**	**$\triangle$G (kcal/mol)**
1	CC6	-45.68	-57.44	-76.04	-85.26
	CBC	-56.25	-66.62	-87.11	-89.73
2	CC6	-26.62	-38.84	-10.06	-10.43
	CBC	-26.65	-37.49	-9.656	-3.98
3	CC6	-88.02	-91.14	-79.23	-70.50
	CBC	-85.60	-87.32	-78.33	-63.55

It is interesting to note that in model 2, where hydration of metal ion were taken into account, the binding energy and free energy of CC6 complexed with cesium is found to be -26.62 kcal/mole, -38.84 kcal/mole respectively. Whereas for CC6-Na complex the binding energy and free energy obtained were -10.06 kcal/mol, -10.43 kcal/mol respectively. This is in accordance with the experimental results obtained by solvent extraction studies. This finding was supported by the fact that sodium, being a smaller cation is more hydrated as compared to cesium ion, therefore requires more energy to dehydrate than caesium cation. Similarly, for CBC complex with cesium the binding energy and free energy was obtained to be -26.65 kcal/mol, -37.49 kcal/mol respectively. Whereas the CBC complex with sodium the binding energy and free energy obtained were -9.65 kcal/mol, -3.98 kcal/mol respectively.

Similar trend was observed in model 3 where hydration of nitrate ion was also considered. Here the binding energy and free energy values were found to be much higher than model 1 and model 2. The binding energy and free energy values for CC6 complex with caesium was obtained as -88.02 kcal/mol, -91.14 kcal/mol, whereas as the CC6-sodium complex was having the binding energy and free energy of -79.23 kcal/mol, -70.50 kcal/mol respectively. On the other hand the CBC was behaving almost equally and identically with CC6 and the binding energy and free energy values for cesium-CBC complex was obtained as -85.60 kcal/mol, -87.32 kcal/mol respectively. Which is higher than CBC-sodium complex (-78.33 kcal/mol, -63.55 kcal/mol).

2.5 Selectivity towards various metal ions

In order to study the selective extraction of cesium with respect to other metal ions, the extraction of cesium was carried out from simulated high level liquid waste solution (Table 2.7) using 0.01M calix-crown /30 % phase modifiers/n-dodecane.Calix-benzo-crown (CBC) the D_{Cs} for 0.01 M CBC in 30 % IDA/n-dodecane and o-NPHE/ n-dodecane comes out to 1.9 and 3.04 respectively. Only Molybdenum has shown a D of 0.012 and 0.011 in IDA and o-NPHE respectively. Rest of metal ions like

Sr, Na , Ba, Ln, U, Zr, Ru, K present in waste have D_M less than 0.001. On the other side for Calix-crown-6 (CC6), 0.01 M CC6 in 30 % IDA/n-dodecane and o-NPHE/n-dodecane exhibits D_{Cs} value of 1.2 and 2.8 respectively. Molybdenum has shown a D of 0.015 in 0.01 M CC6/30 % IDA/n-dodecane and 0.012 in 0.01 M CC6/ 30 % o-NPHE/ n-dodecane solvent systems. The rest of metal ions have D_M value less than 0.01 in both the solvent systems.

Table 2.7: *Extraction of metal ions from simulated high level liquid waste solution Organic phase: 0.01M Calix-crown/ 30 % phase modifiers/n-dodecane. Aqueous phase: Simulated high level liquid waste solution, HNO_3= 3.5 M*

Element	**Conc.(ppm)**	**D_M(IDA) [CBC]**	**D_M(o-NPHE)[CBC]**	**D_M(IDA) [CC6]**	**D_M(o-NPHE)[CC6]**
Cs	**300**	**1.9**	**3.04**	**1.2**	**2.8**
Sr	**70**	**1.0E-03**	**1.2E-03**	**1.0E-03**	**1.4E-03**
Mo	**160**	**1.2E-02**	**1.1E-03**	**1.5E-02**	**1.2E-02**
Zr	**80**	**1.0E-03**	**1.0E-03**	**4.0E-02**	**4.0E-02**
Ru	**60**	**1.4E-03**	**1.6E-03**	**4.0E-02**	**2.0E-03**
Ba	**350**	**1.2E-03**	**1.3E-03**	**2.0E-03**	**3.1E-03**
Na	**5600**	**1.0E-03**	**1.1E-03**	**3.0E-03**	**4.2E-03**
Ce	**250**	**4.0E-03**	**2.0E-03**	**1.8E-03**	**3.1E-03**
Nd	**120**	**1.0E-03**	**4.0E-03**	**3.0E-03**	**7.1E-03**
Y	**60**	**1.0E-03**	**1.0E-03**	**5.2E-03**	**2.3E-03**
K	**210**	**1.0E-03**	**1.3E-03**	**4.0E-03**	**4.7E-03**
U	**8000**	**1.0E-03**	**1.2E-03**	**2.0E-03**	**8.1E-03**

2.6 Conclusions

It is observed from table 2.3 that CBC and CC6 are found to be effective in both the solvent systems viz. IDA and o-NPHE. The results showed that D_{Cs} is much larger compared to other elements, thus, indicating a very high selectivity for cesium extraction over otherelements. In case of Calix-benzo-crown (CBC) the D_{Cs} for 0.01 M CBC in 30 % IDA/n-dodecane and o-NPHE/ n-dodecane comes out to 1.9 and 3.04 respectively. Only Molybdenum has shown a D of 0.012 and 0.011 in IDA and o-NPHE respectively. And rest of metal ions like Sr, Na , Ba, Ln's, U, Zr, Ru, K present in waste have D_M less than 0.001. On the other side for Calix-crown-6

(CC6), 0.01 M CC6 in 30 % IDA/n-dodecane and o-NPHE/n-dodecane exhibits D_{Cs} value of 1.2 and 2.8 respectively. Molybdenum has shown a D of 0.015 in 0.01 M CC6/30 % IDA/n-dodecane and 0.012 in 0.01 M CC6/ 30 % o-NPHE/ n-dodecane solvent systems. The rest of metal ions have D_M less than 0.01 in both the solvent systems. The structure of metal hydrates and their complexes with CBC and CC6 were optimized at hybrid B3LYP level using SVP basis set. The gas phase binding energy and free energy indicates the selectivity order: $Na^+ > Cs^+$ whereas after suitable hydration of metal and nitrate the order becomes reverse as obtained in the solvent extraction results.

3. Synthesis, extraction, theoretical studies and radilolytic studies of new calix-crown benzo-amides

3.1 Introduction

Out of the multiple conformations of calix-crown-6 derivatives, the 1,3-alternate conformation has been found to be most selective for cesium extraction from acidic and alkaline aqueous solutions having excess of other alkali metal ions [131, 132]. There are many variations possible in calix[4]arene-benzocrown-6 by substitution of different groups on the benzene of polyether ring. Reports are there for alkyl amine, water soluble and mono-ionizable group, substituted on benzene ring for their uses in pH switchable cesium nitrate extractants, nanofiltration and as cation exchanger for extraction of Ag^+ ion, respectively[133–135].

Our interest in radioactive cesium ion separation from acidic nuclear waste solutions has led to the search for a suitable calix-crown-6 which can withstand high nitric acid concentration without loss of cesium uptake. As cesium is one of the major heat generating radionuclide, its removal before PUREX process will certainly minimize the degradation of TBP and other extractants during further reprocessing. In most of calix-crowns studied for cesium uptake, a fall in the distribution ratio of cesium was observed beyond 2-3 M nitric acid concentration [136]. Extraction of cesium ion at high nitric acid concentration decreases due to competitive extraction of nitric acid at higher concentrations. Amide groups are known to buffer extractants against nitric acid effects by intramolecular acid buffering, thus, protecting donor-metal bond from attack by hydrogen ions [137]. Therefore, calix-crown-6 with an amide group, possibly away from the crown ether cavity can be an effective ligand for cesium extraction from strong nitric acid medium. This type of calix-crown-amide will be a potential extractant for cesium separation from solutions with high nitric acid concentration (>3 M) [138]. Hence synthesis of three different amide substituted calix [4]arene benzocrown-6 (CBCA) with amide on the benzo group of crown-ether ring was taken up.

It is well known fact that during the process of solvent extraction involving HLLW the extractant will be exposed to high radiation dose in contact with nitric acid. Since the nuclear radiation energies are higher by several orders than the chemical bond energies, extractant in due course will experience radiolytic degradation. The radiolysis will result in loss of active sites of extractant and degradation products which will have harmful effects on the extractant performance. The radiolytic degradation is further enhanced due to formation of large number of radicals and ionized species (H OH., solvated electrons etc.) in the HLLW solution. These can lead to alteration of physico-chemical properties, distribution ratio and extraction kinetics [139–141]. The calix-crown are formed by the combination of calix[4]arene and crown ethers. Large numbers of reports are there for radiolysis & hydrolytic stabilities of calixarenes and crown ethers separately.

In the calix[4]arene, it was found that the calixarenes are highly stable under hydrolytic and radiolytic environments because of aromatic backbone. Further, the stability depends upon the nature of substituents on calixarens. In the crown ethers, these effects were extensively studied in nuclear application like removal of caesium and strontium from nuclear waste streams. These extractants are found to have good radiation resistance and following order of stability was observed: benzocrown¿ dicyclohexanocrown¿ crown [142–144].

The dicyclo-hexano-18-cron-6 (DCH18C6), a highly selective extractant for strontium was found to undergoes various changes like cleavage (ring opening), evolution of volatile products (hydrogen and ethylene) depending upon the irradiation conditions[145]. The diluents also play an important role on the radiolytic degradation, for example the degradation follows the order: chloroform > 1-octanol > toluene. This behavior can be explained on the basis of ionization potential difference of diluents and crown-ether. Toluene having the low ionization potential than the crown-ether, thus prevents the crown-ether degradation. On the other hand extensive degradation was observed in chloroform/C_2Cl_6 diluents as these diluents have high ionization potential. The degradation certainly leads to variation in extraction behavior. In spite of degradation, the distribution ratio was found to be always higher, indicating the contribution from degradation products. For example, in case of DCH18C6/ chloroform system with a dose of 0.84 MGy led to 70% degradation of crown while the distribution ratio (D_{Sr}) exhibited only a 30 % decrease [146].

Reports are there on radiolytic stability studies for calix-crown (mono & bis), where mono-calix-crown and bis-crown representatives were ipr-MC-6 (1,3-alt-diisopropyloxy-calix-crown-6 and rBC-6 (1,3-alt-calix[4]arene-bis-crown-6) respectively. The irradiated solutions were examined by ESI-MS, LC-MS techniques rather than conventional GC-MS because of high mass range (m/z $sim1000$) of compounds[147, 148]. The present study aims at the synthesis of a few amide substituted CBCAs and their chemical and physical characterization. Solvent extraction evaluation for the extraction of cesium at varying concentrations of aqueous nitric acid will be carried out in n-dodecane modified with isodecyl alcohol (IDA) and o-nitrophenylhexyl ether (o-NPHE). The results will be compared with its non-amide analog viz. calix-benzo-crown (CBC). DFT based calculation will be performed to obtain molecular level insights which includes the structure of the free calix-crown and its complex with Cs^+ and $CsNO_3$. For establishing a process for the selective removal of cesium from high level liquid waste solutions, the radiolytic and hydrolytic stability will also be investigated.

3.2 Synthesis

The synthetic route for the preparation of Calix-benzo-crown (CBC) is already reported in the last chapter. The synthetic route for the preparation of Calix-benzo-crown-amide (CBCAs) (5-7) is presented in scheme 3.1. Compounds (2-4) were

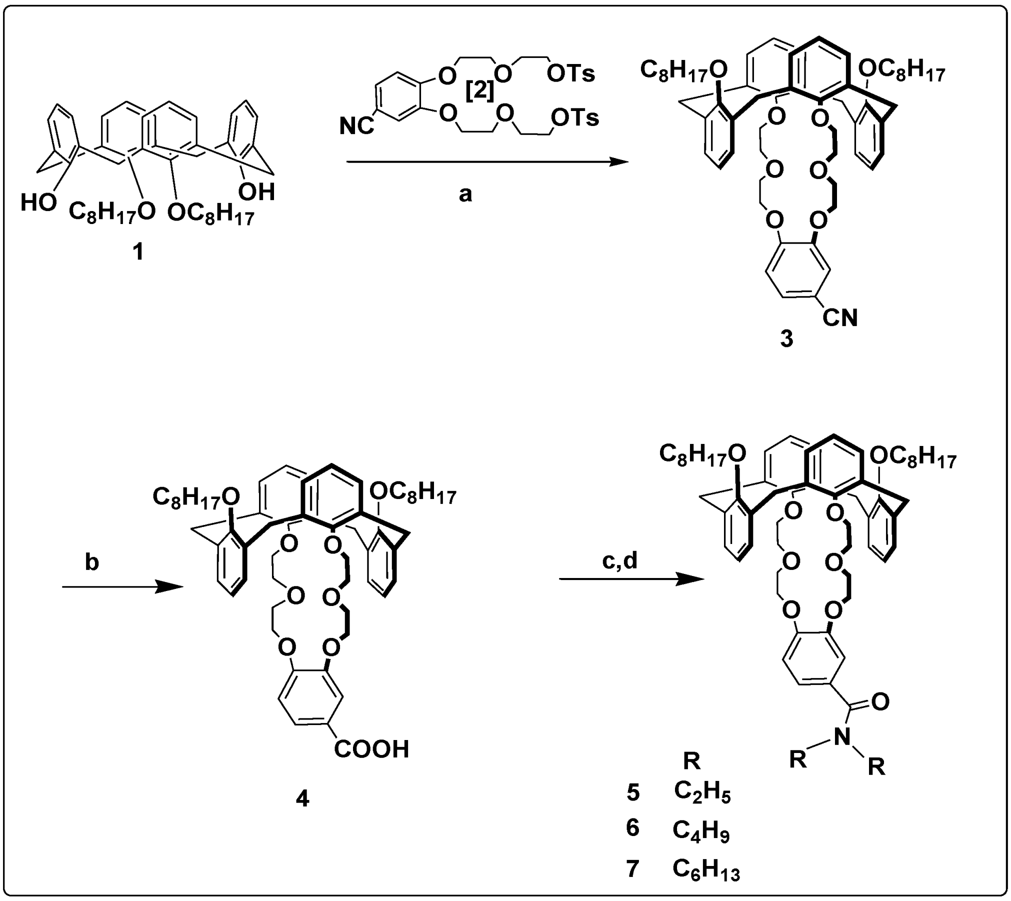


Figure 3.1: *Synthesis of 1,3-alternate calix benzo crown amide. Reagents and conditions: a) Cs_2CO_3, MeCN, reflux; b) KOH, aq. EtOH, reflux; c) $(COCl)_2$, C_6H_6, reflux; d) R_2NH, THF, heat*

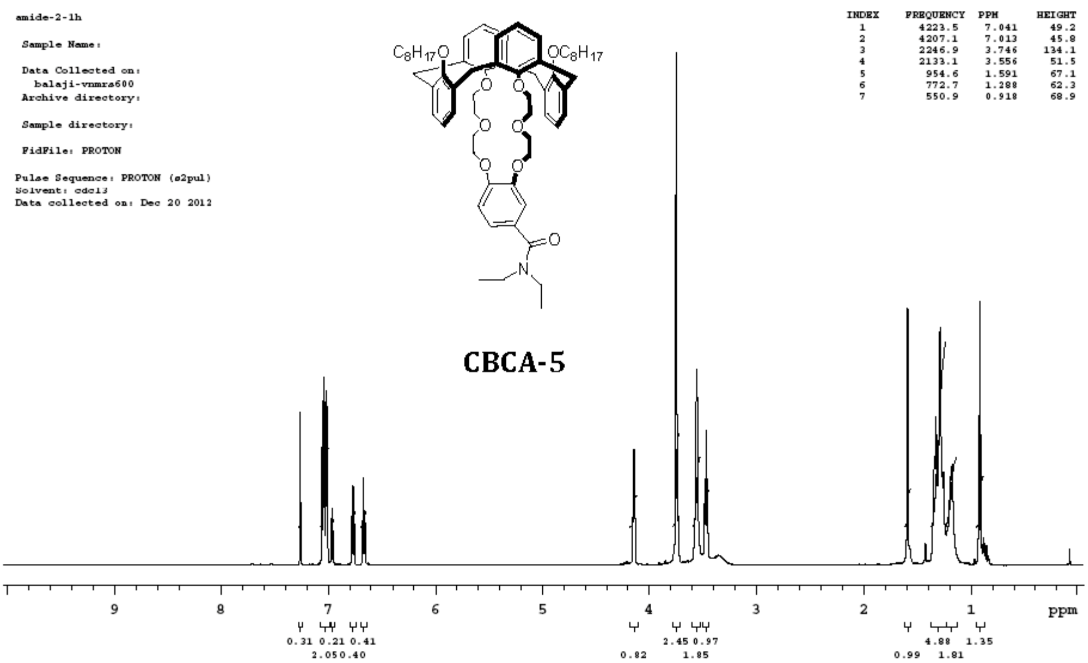
synthesized as per procedure reported elsewhere [136]. The crown part (2) was synthesized by reaction of 4-cyanocatechol with 2-(2-chloroethoxy) ethanol and K_2CO_3 in DMF and subsequent conversion of the resultant diol into ditosylate. Further condensation of di(octyloxy)calix[4]arene [1] and ditosylate (2) with Cs_2CO_3 in MeCN at reflux, produced 4-cyano-25,27-di(octyloxy)-26,28-calix[4]arene-benzocrown-6 (3) in the 1,3-alternate conformation. Hydrolysis of nitrile (4)was carried out by refluxing with 10% KOH in aqueous EtOH (1:1, v/v) which gave a quantitative yield of 4-(carboxy)-25,27- di(octyloxy)-26,28-calix[4]arene-benzocrown-6 (5). It was converted to acid chloride and product was further reacted with secondary amines to get the desired products as per the following procedure.

To a solution of (4)(2gm, 2.12 mmol) in dry benzene (40 ml), oxalyl chloride

(1 gm, 7.8 mmol) was added with stirring. The reaction mixture was kept under reflux for 5 hours in nitrogen atmosphere. Excess of oxalyl chloride was removed by coevoporation with benzene under reduced pressure to give the corresponding acid chloride. To this dialkylamine (3.8 mmol) was added in 30 ml dry toluene, drop wise for 15 minutes. After addition, the reaction mixture was heated upto 70^o C and heating was continued for one hour. Solvent and excess amine were evaporated in rotary evaporator. The product was dissolved in dichlromethane and washed with 1N HCl (3 X 50mL) and distilled water (3 X 50mL). This was finally dried over anhydrous magnesium sulphate and the solvent was removed on rotavapour. The residue was passed through silica gel column in ethyl acetate/hexane to get the amide substituted products.

3.2.1 1,3-Alternate-4-(N,N-diethylamidyl)-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6:(CBCA-5)

(5) was obtained as thick viscous liquid, Yield: 98%, ^{1}H NMR (600 MHz,CDCl$_3$, δ in ppm) : 0.9-1.0 (m, 6H, -2CH$_3$), 1.1-1.2 (m, 6H, -2CH$_3$), 1.22-1.38 (m, 24H, 12CH$_2$), 3.2-3.4 (br, s, 2H, -NCH$_2$), 3.4-3.5 (t, J=7Hz, 4H,, -2OCH$_2$), 3.5-3.55 (m, 8H, -4OCH$_2$), 3.56-3.6 (m, 2H,-NCH$_2$),3.78 (s, 8H, 4ArCH$_2$Ar), 3.78-3.9 (m, 4H, -2OCH$_2$), 4.1-4.2 (d, J=4.7Hz ,4H, -2OCH$_2$), 6.6-6.7 (t, J=7Hz, 2H, 2ArH), 6.7-6.8 (m, 2H, 2ArH), 6.95-7.0 (m, 1H, ArH), 7.0-7.1 (m, 10H, 10 ArH). ^{13}C NMR (150 MHz, CDCl$_3$, δ in ppm) : δ : 172.18, 156.82, 156.24, 149.85, 148.77, 134.06, 133.77, 130.53, 130.00, 129.84, 122.10, 121.95, 120.10, 114.23, 113.69,77.23, 77.02, 76.818, 70.041, 69.72, 69.62, 37.698, 31.90, 29.67, 29.40, 25.81, 22.71, 14.12. Anal.Calcd.for $C_{63}H_{83}O_9N$: C, 75.77; H, 8.37; N, 1.40. Found: C, 75.72; H, 8.31; N, 1.42. ES-MS (ES)$^+$1000.6: [MH$_2$]$^+$, 1037 .2: [M+K$^+$]. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig 3.23.33.4.



amide-2-1h

Sample Name:

Data Collected on:
balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 20 2012

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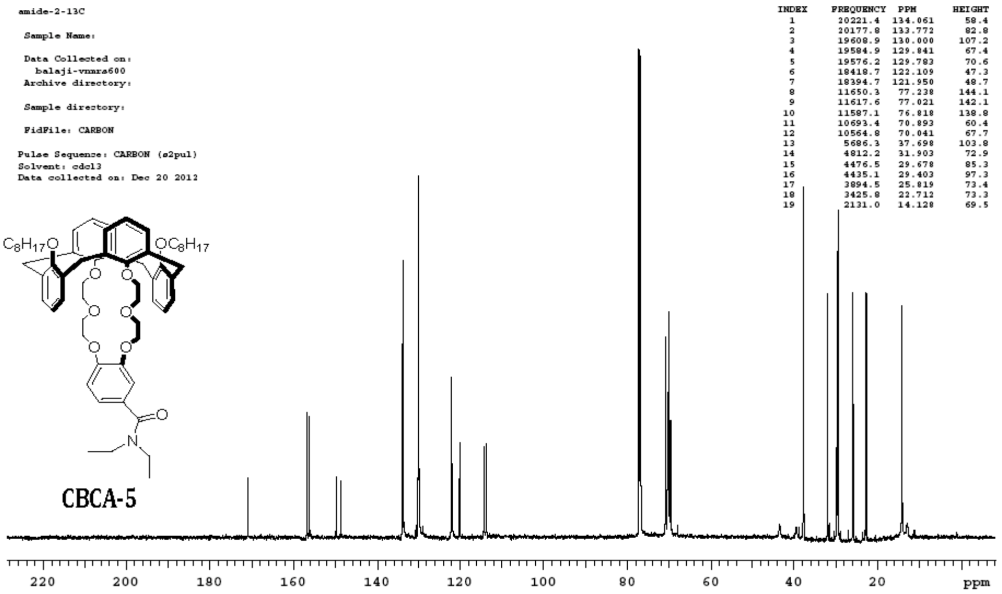
2	4207.1	7.013	45.8
3	2246.9	3.746	134.1
4	2133.1	3.556	51.5
5	954.6	1.591	67.1
6	772.7	1.288	62.3
7	550.9	0.918	68.9

Figure 3.2: ^1H *NMR of CBCA-5*



amide-2-13C

Sample Name:

Data Collected on:
balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 20 2012

INDEX	FREQUENCY	PPM	HEIGHT
1	20221.4	134.061	58.4
2	20177.8	133.772	82.8
3	19608.9	130.000	107.2
4	19584.9	129.841	67.4
5	19576.2	129.783	70.6
6	18418.7	122.109	47.3
7	18394.7	121.950	48.7
8	11650.3	77.238	144.1
9	11617.6	77.021	142.1
10	11587.1	76.818	138.8
11	10693.4	70.893	60.4
12	10564.8	70.041	67.7
13	5686.3	37.698	103.8
14	4812.2	31.903	72.9
15	4476.5	29.678	85.3
16	4435.1	29.403	97.3
17	3894.5	25.819	73.4
18	3425.8	22.712	73.3
19	2131.0	14.128	69.5

Figure 3.3: ^{13}C *NMR of CBCA-5*

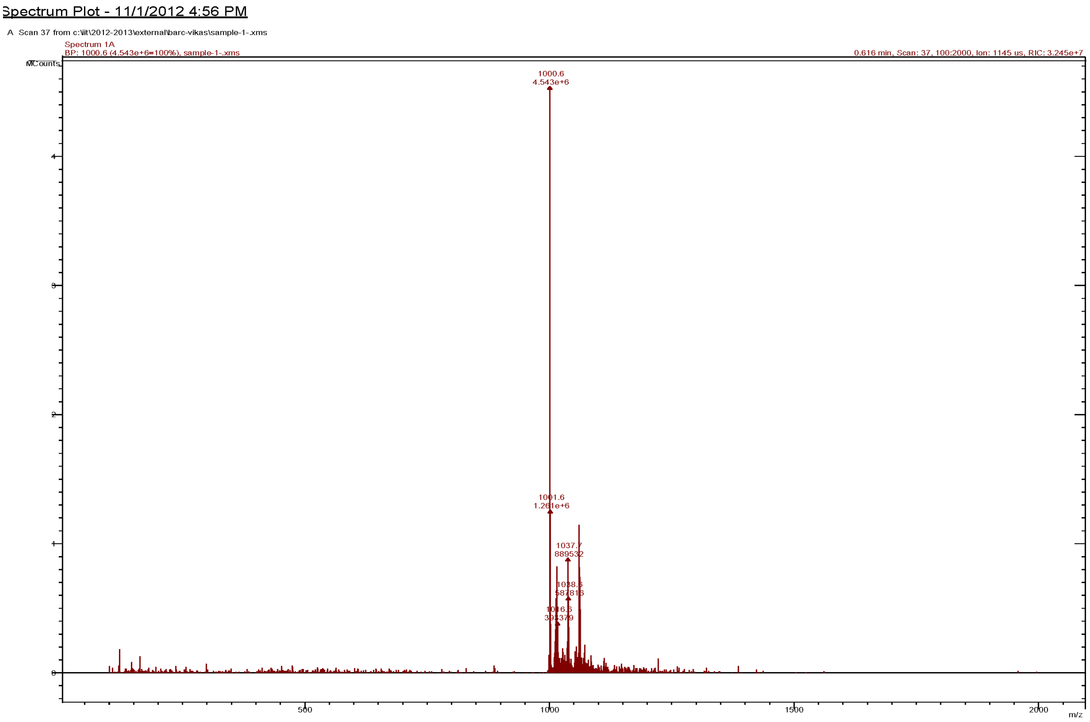
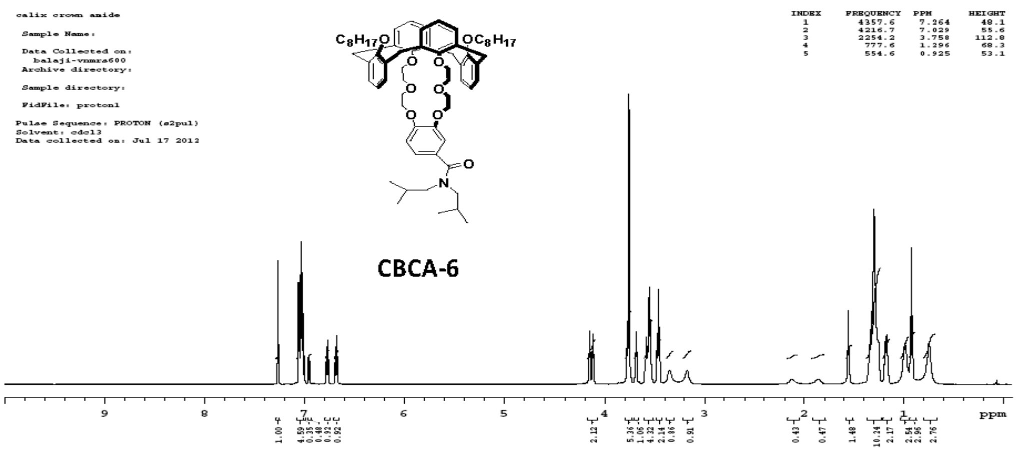


Figure 3.4: *ESI-MS spectra of CBCA-5*

3.2.2 1,3-̈Alternate-4-(N, N-diisobutylamidyl)-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6:(CBCA-6)

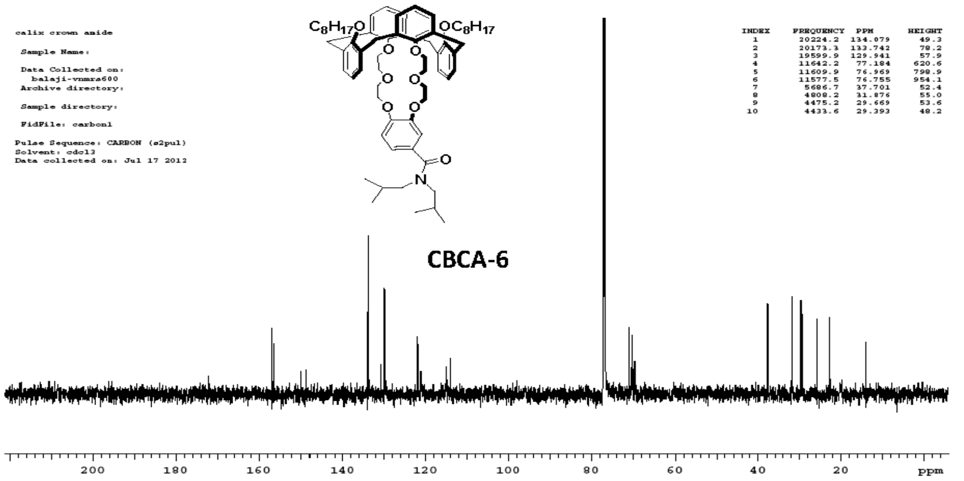
(6) was crystallized in hexane, white solid beads obtained, yield 96%, m.p 134-136^{o}C. ^{1}H NMR (600 MHz ,$CDCl_3$, δ in ppm) : 0.7-0.8 (bs, 6H, -$CH(CH_3)_2$), 0.9-0.95 (t, J=7Hz,6H, -CH_3), 1.0 (br, s, 6H,-$CH(CH_3)_2$), 1.15-1.19 (m, 4H, -2CH_2), 1.21-1.40 (m, 20H,10CH_2), 1.83 (br, s, 1H, -$CH(CH_3)_2$), 2.10 (br, s, 1H, -$CH(CH_3)_2$), 3.18 (br, s, 2H, -NCH_2), 3.33 (br, s, 2H, -NCH_2), 3.47 (t, J=2Hz ,4H, -OCH_2), 3.52-3.60 (m, 8H, 4-OCH_2), 3.66-3.70 (m, 2H, -OCH_2), 3.78 (s, 8H, 4ArCH_2Ar), 3.78-3.80 (m, 2H, O-CH_2), 4.10-4.12 (m, 2H, O-CH_2), 4.17-4.20 (m, 2H, -OCH_2), 6.66-6.69 (t, J=7.5Hz, 2H,Ar-H), 6.75-6.79 (t, J=7.5Hz, 2H, 2ArH), 6.93-6.96 (d, J=8.2Hz, 1H, ArH), 7.0-7.1 (m, 10H, ArH). ^{13}C NMR: (150 MHz, $CDCl_3$, δ in ppm): 172.36, 157.03, 156.46, 150.15, 148.80, 134.29, 134.27, 133.97, 130.92, 130.117, 130.02, 129.92, 122.31, 122.16, 121.33, 115.11, 114.21, 77.52, 77.20, 76.77, 71.03, 70.70, 70.60, 70.54, 70.39, 70.28, 70.13, 69.75, 37.93, 32.10, 29.88, 29.60, 26.02, 22.92, 14.33. Anal.Calcd. for $C_{67}H_{91}O_9N$: C, 76.31; H, 8.69; N, 1.32. Found: C,

76.28; H, 8.68; N, 1.31.. ES-MS (ES)$^+$ 1055: [MH]$^+$ 1093.7. [M+K$^+$]. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig. 3.53.63.7.



INDEX	FREQUENCY	PPM	HEIGHT
1	4357.6	7.264	48.1
2	4216.7	7.029	55.6
3	2254.2	3.758	112.8
4	777.6	1.296	68.3
5	554.6	0.925	53.1

Figure 3.5: ^{1}*H NMR of CBCA-6*



INDEX	FREQUENCY	PPM	HEIGHT
1	20224.2	134.079	49.3
2	20173.3	133.742	78.2
3	19599.9	129.941	57.9
4	11642.2	77.184	620.6
5	11609.9	76.969	798.9
6	11577.5	76.755	954.1
7	5686.7	37.701	52.4
8	4808.2	31.876	55.0
9	4475.2	29.669	53.6
10	4433.6	29.393	48.2

Figure 3.6: ^{13}*C NMR of CBCA-6*

3.2.3 1,3¨-Alternate-4-(N, N dihexylamidyl)-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6:(CBCA-7)

(7) crystallized in hexane/methanol, obtained as white solid, yield 97%, mp 94-96^{o}C, ^{1}H NMR (600 MHz, CDCl$_3$, δ in ppm) : 0.8-1.0 (m, 12H, 4-CH$_3$), 1.1-1.2 (m, 8H,

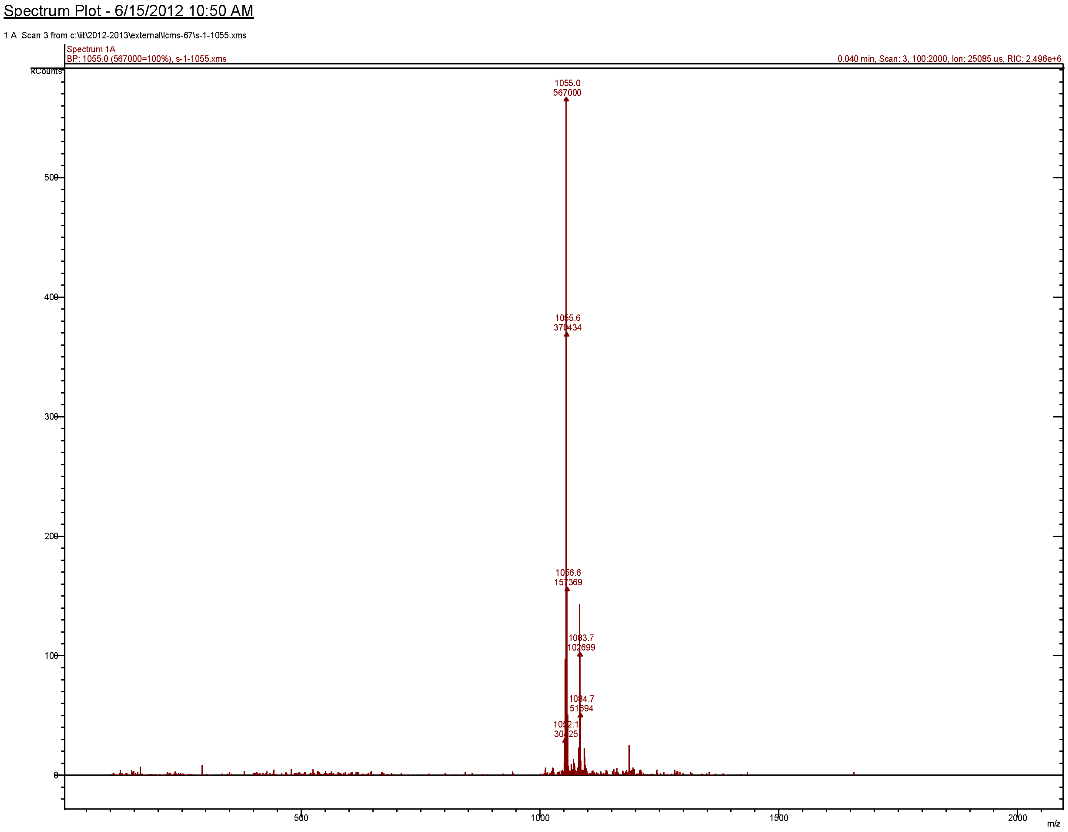
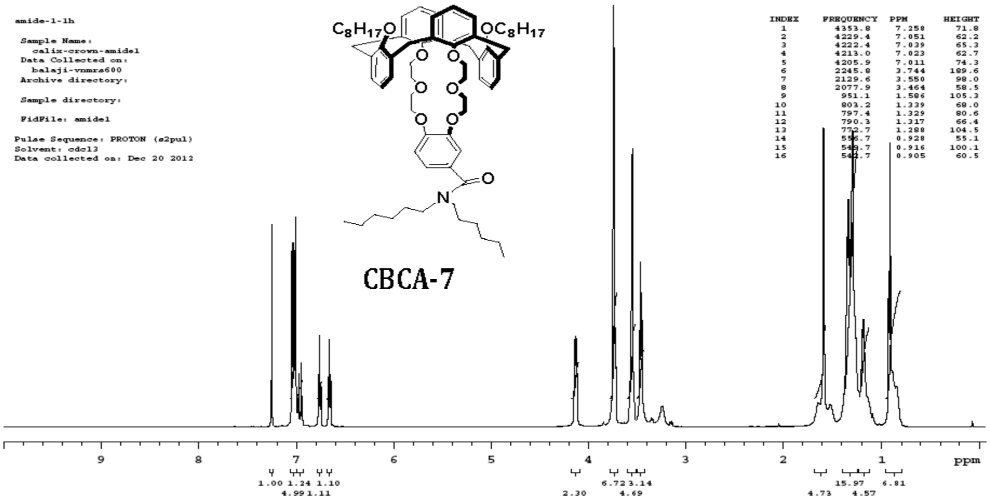


Figure 3.7: *ESI-MS spectra of CBCA-6*

4CH$_2$), 1.22-1.4 (m, 28H, 14CH$_2$), 1.5-1.7 (m, 8H, 4CH$_2$), 3.2 (br, s, 2H, -NCH$_2$), 3.4-3.45 (m, 4H, -2OCH$_2$), 3.45-3.5 (m, 2H,-NCH$_2$),3.5-3.6(m, 8H, -4OCH$_2$), 3.78 (s, 8H, ArCH$_2$Ar), 3.78-3.9 (m, 4H, -OCH$_2$), 4.1-4.2 (m, 4H, -OCH$_2$), 6.6-6.7 (t, J=7Hz, 2H, 2ArH), 6.7-6.8 (t, J=7Hz, 2H, 2ArH), 6.9-7.1 (m, 11H, 11ArH). ^{13}C NMR: (150 MHz,CDCl$_3$, δ in ppm): 172.25, 156.8, 156.25, 149.8, 147.7, 134.06, 133.77 130.67, 129.98, 129.84, 129.78, 122.09, 121.95, 120.33, 114.17, 113.9, 77.20, 77.006, 76.775, 70.87, 70.44, 70.35, 70.30, 70.04, 69.75, 69.60, 37.69, 31.88, 29.66, 29.403, 25.81, 22.69, 22.55, 14.11, 13.99.Anal. Calcd. for $C_{71}H_{99}O_9N$: C, 76.78; H, 8.98 ; N, 1.26. Found: C, 76.75; H, 8.96; N, 1.26.ES-MS (ES)$^+$, 1110.9: [MH]$^+$, 1148.9 : [M+K$^+$]. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig 3.83.93.10



amide-1-1h

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calix-crown-amide1
Data Collected on:
balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: amide1

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Solvent: cdcl3
Data collected on: Dec 20 2012

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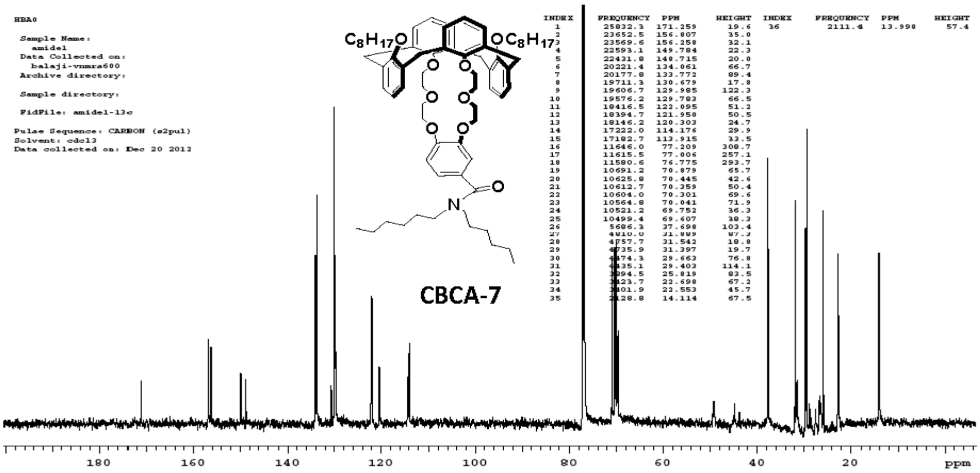
3	4222.4	7.039	65.3
4	4213.0	7.023	62.7
5	4205.9	7.011	74.3
6	2245.8	3.744	189.6
7	2129.6	3.550	98.0
8	2077.9	3.464	58.5
9	951.1	1.586	105.3
10	803.2	1.339	68.0
11	797.4	1.329	80.6
12	790.3	1.317	66.4
13	772.7	1.288	104.5
14	556.7	0.928	55.1
15	549.7	0.916	100.1
16	542.7	0.905	60.5

Figure 3.8: ^1H *NMR of CBCA-7*



HBA0

Sample Name:
amide1
Data Collected on:
balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: amide1-13c

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 20 2012

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1	25832.3	171.259	19.6
2	23652.5	156.807	35.0
3	23569.6	156.258	32.1
4	22593.1	149.784	22.3
5	22431.8	148.715	20.0
6	20221.4	134.061	66.7
7	20177.8	133.772	89.4
8	19711.3	130.679	17.8
9	19606.7	129.985	122.3
10	19576.2	129.783	66.5
11	18416.5	122.095	51.2
12	18394.7	121.950	50.5
13	18146.2	120.303	24.7
14	17222.0	114.176	29.9
15	17182.7	113.915	33.5
16	11646.0	77.209	308.7
17	11615.5	77.006	257.1
18	11580.6	76.775	293.7
19	10691.2	70.879	65.7
20	10625.8	70.445	42.6
21	10612.7	70.359	50.4
22	10604.0	70.301	69.6
23	10564.8	70.041	71.9
24	10521.2	69.752	36.3
25	10499.4	69.607	38.3
26	5686.3	37.698	103.4
27	4810.0	31.889	87.3
28	4757.7	31.542	18.8
29	4735.9	31.397	19.7
30	4474.3	29.663	76.8
31	4435.1	29.403	114.1
32	3894.5	25.819	83.5
33	3423.7	22.698	67.2
34	3401.9	22.553	45.7
35	2128.8	14.114	67.5
36	2111.4	13.998	57.4

Figure 3.9: ^{13}C *NMR of CBCA-7*

3.3 Solvent extraction studies

Distribution ratio measurements were performed by equilibrating 2mL each of organic and aqueous phase for 15 minutes in 10 mL stoppered glass vials. All the experiments were carried out in a thermostated bath at a temperature 25±1^{o}C. Distribution ratio D_{Cs} was calculated by taking the ratio of metal ion concentration in organic phase to the metal ion concentration in aqueous phase. After equilib-

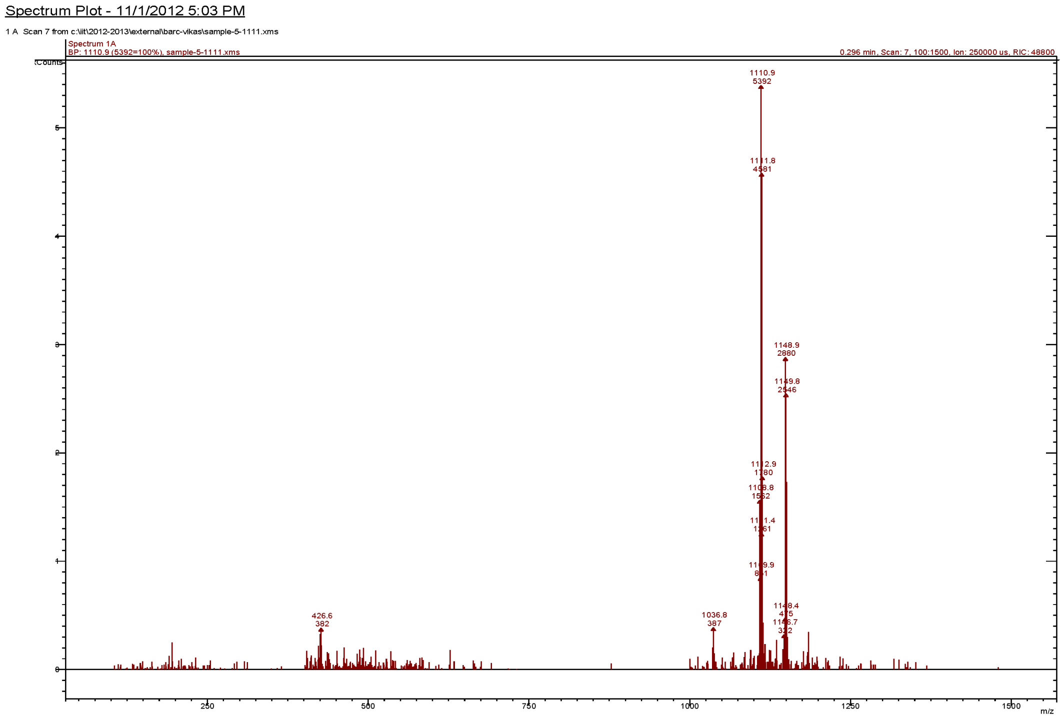


Figure 3.10: *ESI-MS spectra of CBCA-7*

rium, phases were separated by centrifugation and aqueous phase was analyzed by ICP-AES.

3.3.1 Effect of Ligand concentration

In order to study the effect of ligand concentration on D$_{Cs}$ value, the ligand conc. was varied while keeping other parameters fixed. Extraction of cesium from nitric acid medium can be represented as equation (3.1). In order to study the effect of ligand concentration on D$_{Cs}$ value, the ligand conc. was varied while keeping other parameters fixed. Extraction of cesium from nitric acid medium can be represented as equation 3.1

$$Cs^+_{aq} + nL_{org} + mH^+ + (m+1)NO_3^- aq \rightleftharpoons Cs^+.nL.NO_3^-.mHNO_{3org} \tag{3.1}$$

The conditional extraction equilibrium constant, K$_{ex}$ in reaction (3.1) can be written as:

$$K_{ex} = \frac{[Cs^{+}.nL.NO_3^{-}.mHNO_3]_{org}}{[Cs][NO_3]_{aq}^{m+1}[L]_{org}^{n}[H^{+}]_{aq}^{m}} \tag{3.2}$$

D, distribution coefficient and defined as:

$$D = \frac{[Cs^{+}.nL.NO_3^{-}.mHNO_3]_{org}}{[Cs^{+}]_{aq}} \tag{3.3}$$

By substituting Eq. (3.3) into Eq. (3.2) and converting into logarithmic form the following equations are obtained

$$K_{ex} = \frac{D}{[L]_{org}^{n}[HNO_3]_{aq}^{m}} \tag{3.4}$$

$$logK_{ex} = logD - nlog[L]_{org} - mlog[HNO_3]_{aq} \tag{3.5}$$

The plot of log D$_{Cs}$ vs. log[ligand] at constant nitric acid concentration 3.11 shows a slope (n) $\sim$ 1 in both CBC(3) and CBCA(6), thus, suggesting 1:1 stoichiometry of Cs and Ligand. The D$_{Cs}$ value for CBCA(6) was always higher than CBC due to presence of lipophilic amide group in the calix-crown. The solvent concentration was optimized as 0.01M Calix-crown + 30% IDA/n-dodecane. As this concentration of CBC and CBCA(6) in 30 % IDA/n-dodecane have given workable distribution ratio of 1.8 and 2.7 respectively.

3.3.2 Effect of nitric acid concentration and nitric acid uptake studies

For investigating the effect of the amide substituent on polyether ring of calix-benzo-crown, solvent extraction studies were carried out by varying nitric acid concentrations. Results were compared with its non-amide analog Fig. 3.12.

Aqueous phase consisted of 300 ppm of Cs(I) as cesium nitrate. At lower nitric acid concentration D$_{Cs}$ is low, with increase in nitric acid the enhanced nitrate ion favors extraction of cesium is seen in Fig. 3.12. It was observed that in case of

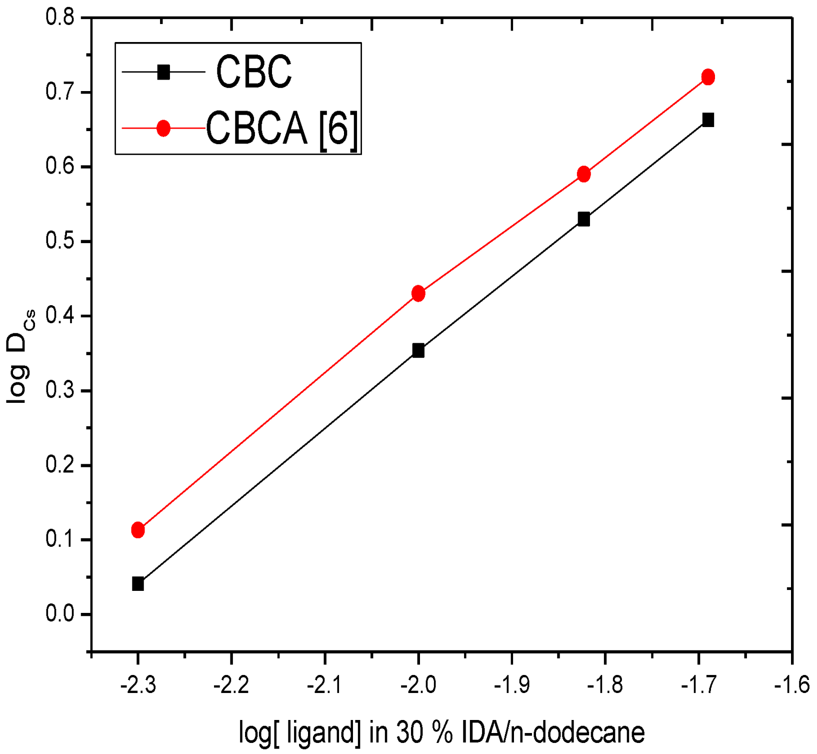


Figure 3.11: *Distribution coefficients of cesium as a function of initial ligand concentration (Aqueous phase ∼ 300 ppm cesium at 3.6 M nitric acid concentration and organic phase as 0.01 M ligand in 30 % IDA/n-dodecane)*

CBC/IDA system the increase in D_{Cs} was up to ∼ 5 M nitric acid and beyond this acidity the distribution ratio decreased due to competitive extraction of H^+ ions. D_{Cs} obtained at 4.5 M nitric acid was 3.8.

However, in case of CBCAs these extraction maxima shifted to ∼ 8 M nitric acid concentration (Fig.3.12). D_{Cs} obtained at 8 M nitric acid was 4.6. After 8 M HNO_3 the distribution ratio started falling due to competitive extraction of H^+ ion. All the three amides behaved identically, and were independent of alkyl chain length with practically no change in their corresponding D_{Cs}. This may be explained by attributing the complexion of cesium mainly by calix-crown cavity and not by amide group present on crown part as cavity is same for all CBCAs. This shift in extraction maxima of CBCAs is attributed to intra molecular buffering effect by amide groups, thereby, protecting the cavity of calix-crown from H^+ ions uptake.

Nitric acid uptake in organic phase was also determined to verify these results. Nitric acid uptake of 0.01 M ligand/30 % IDA/n-dodecane and 30 % IDA/n-

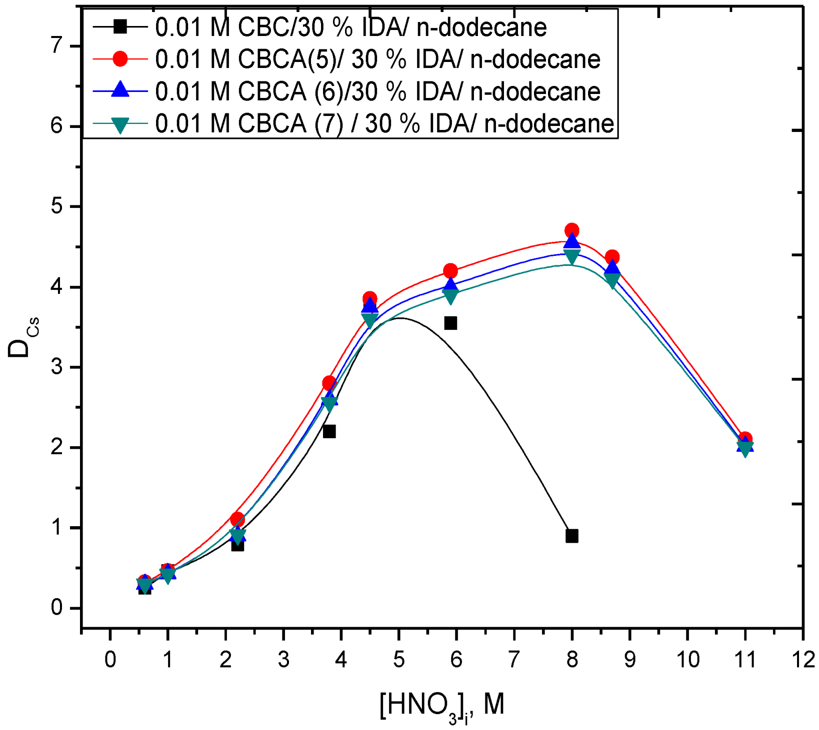


Figure 3.12: *Distribution coefficients of cesium as a function of initial nitric acid. (organic phase 0.01 M ligand/30 % IDA/n-dodecane and aqueous phase ~ 300 ppm cesium with varying aqueous acidity)*

dodecane (blank) were determined separately. It was observed that the nitric acid uptake by the ligands, obtained by difference of uptake by solvent and blank, was more in case of CBCAs than for CBC. The CBCAs have shown higher nitric acid uptake as compared to CBC for all nitric acid concentrations (Fig.3.13).

The ratio of nitric acid uptake to ligand in moles was less than or equal to one for CBC in the nitric acid concentration range of 2 to 8 M, and for CBCAs this ratio was more than one in the same nitric acid range of 2-8 M. Higher nitric acid uptake in CBCAs as compared to CBC for all concentration range of nitric acid without fall in D_{Cs}, conforms the intramolecular buffering by amide group.

With the above estimates, the extraction reaction of cesium with CBC and CBCA in the nitric acid range of 2 to 8 M can be written as the following equations:

$$Cs^+_{aq} + L_{org} + NO_3^- aq \rightleftharpoons (Cs^+.L).NO_3^-{}_{org} \qquad (3.6)$$

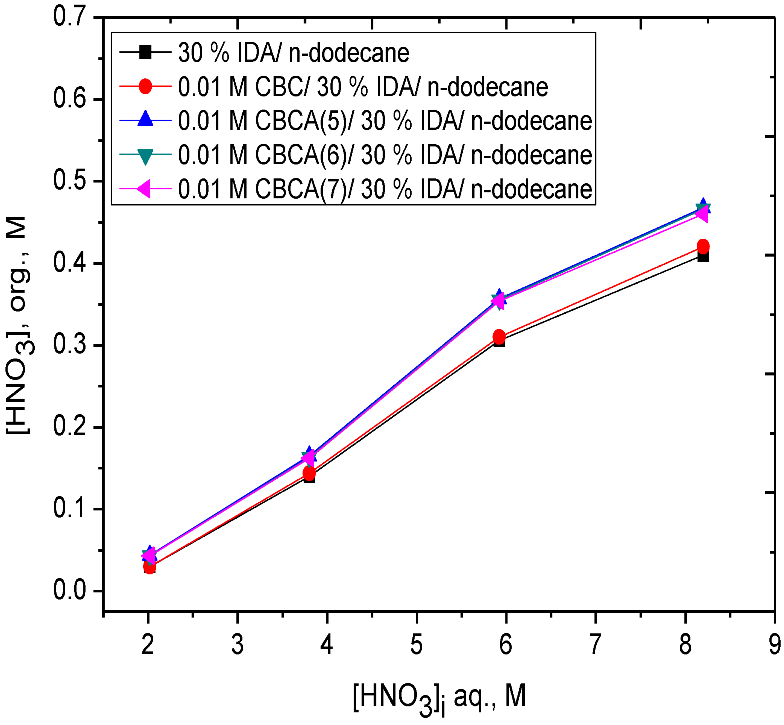


Figure 3.13: *Nitric acid uptake at varying nitric acid concentrations by diluent and solvents.*

$$L_{org} + nH^{+}_{aq} + NO_3^{-}aq \rightleftharpoons L.nHNO_{3org} \tag{3.7}$$

For CBC, n = 0 to 1 for 2-8 M nitric acid For CBCAs n =1 upto 3 M Nitric acid, n >1 from 4 to 8 M nitric acid.

The results obtained with IDA systems were further verified by using 30 % o-NPHE as phase modifier in n-dodecane. The results obtained have the same trend as the previous solvent system and no significant effect of alkyl chain were observed in the distribution ratio of cesium as shown Fig. 3.14. From this plot was also observed that extraction maxima shift slightly towards lower acidity as compared to previous solvent system. For CBC it is at ∼ 4.5 M and in case of CBCAs this is at ∼ 7 M. This shift towards lower nitric acid concentrations may be due to the lower uptake of 30 % NPHE/n-dodecane as compared to 30 % IDA/n-dodecane as shown in Fig 3.15.

This again proves that amide substitution has substantial effect on the extraction of Cs over a wide range of nitric acid concentration by protecting the inner cavity

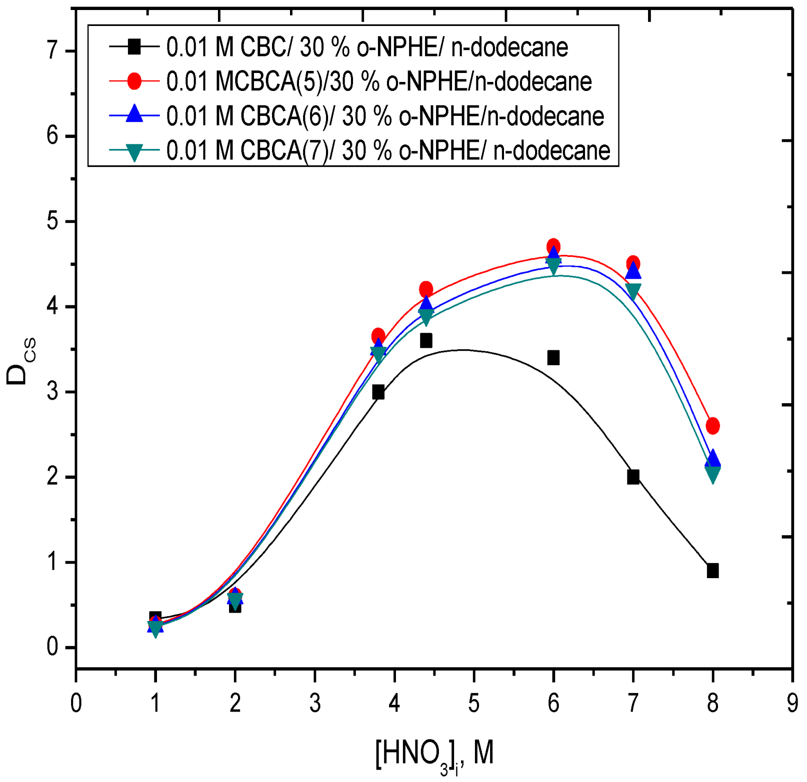


Figure 3.14: *Distribution coefficients of cesium as a function of initial nitric acid concentration. (organic phase 0.01 M ligand /30 % o-NPHE/n-dodecane and aqueous phase ~ 300 ppm Cs at varying nitric acid concentration*

from nitric acid uptake.

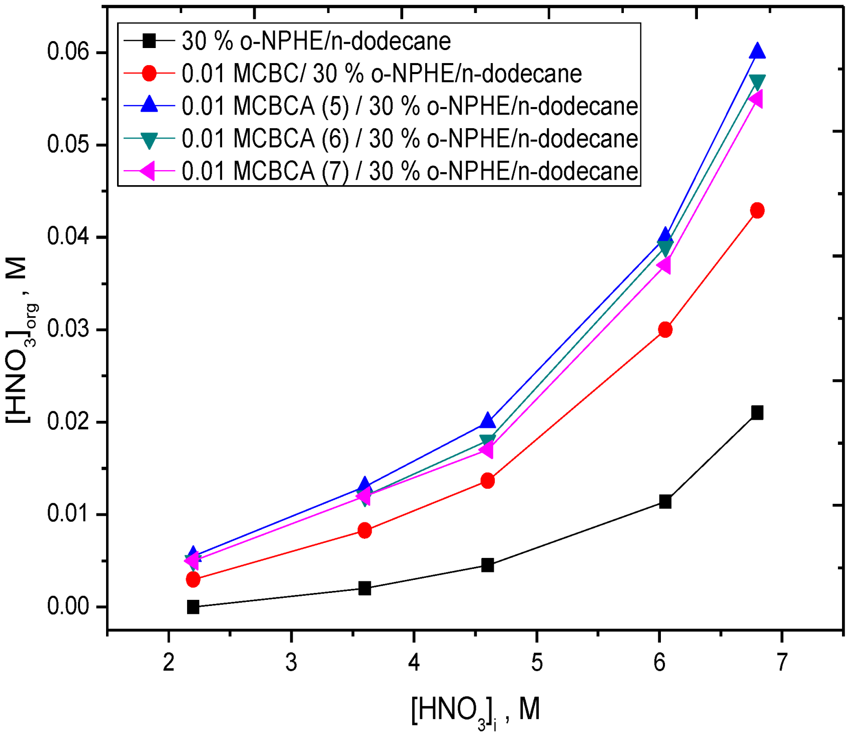


Figure 3.15: *Extraction of nitric acid at different nitric acid concentrations with and without ligand in 30 % o-NPHE solvent system*

3.4 Computational results

Minimum energy structures of free CBCA and its complexes with Cs and $CsNO_3$ have been calculated with B3LYP hybrid density functional approach using split-valence plus polarization (SVP) basis set as available in the TURBOMOLE. The water and dodecane phase was taken care by the use of conductor like screening model (COSMO) as discussed in previous chapter. For comparison of CBCA with CBC, the optimized parameters for CBC are taken from the precious chapters.

3.4.1 Structural parameters

The minimum energy structures of free CBCA(6) and its complex with cesium and cesium nitrate are displayed in Fig. 3.16. From these figure it is seen that the CBCA offers a fine cavity to trap the metal ions inside it. The CBCA, complexed with cesium ion (Cs^+) and cesium nitrates ($CsNO_3$) has been displayed in Fig. 3.16. The average cavity size of CBCA after subtracting the diameter of oxygen (diameter

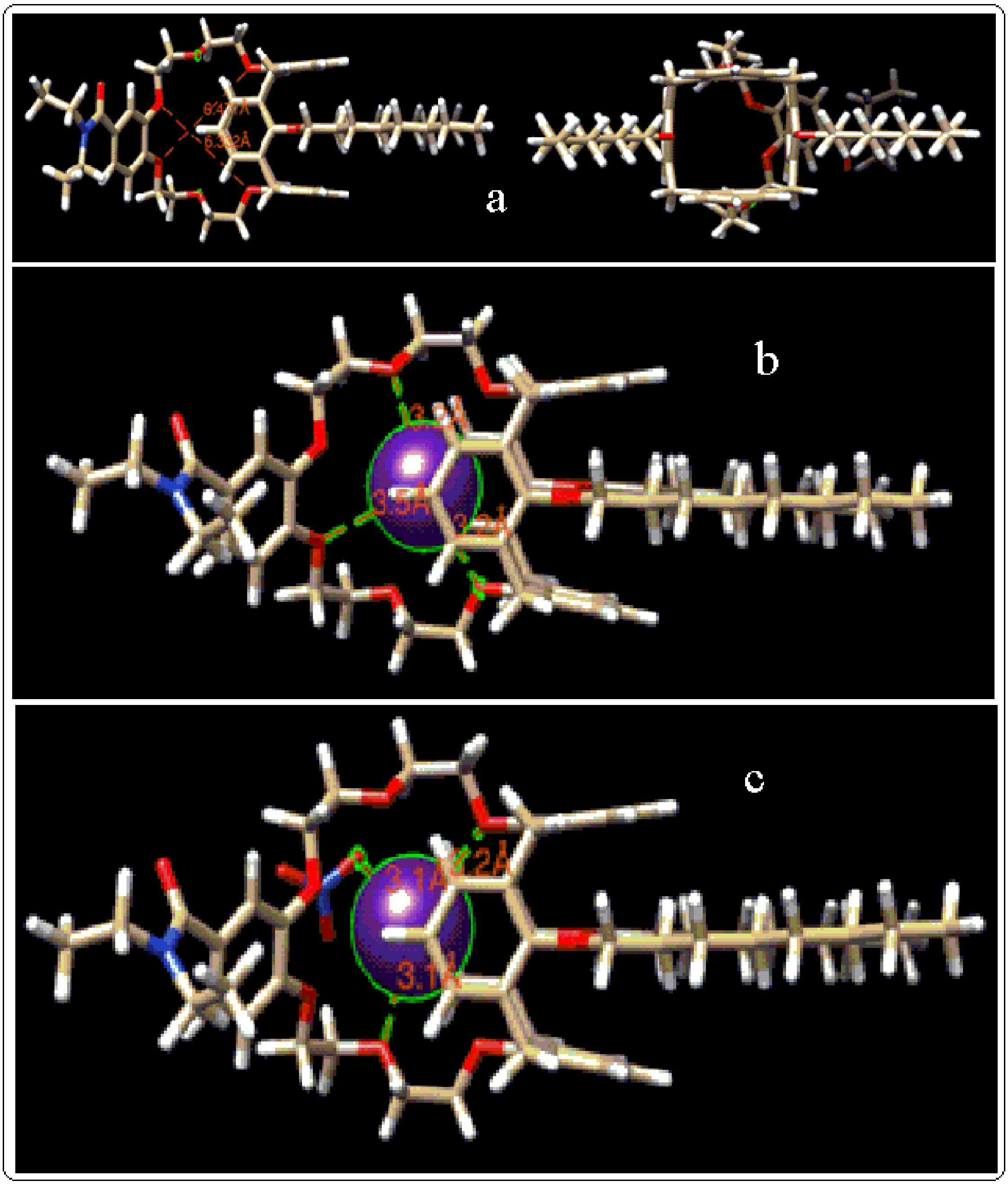


Figure 3.16: *a) Optimized structure of the free CBCA at the B3LYP/SVP level of theory.Side view and top view b) Optimized structure of CBCA-Cs*$^+$ *c) Optimized structure of CBCA- CsNO*$_3$

of O atom of 2.644 A^o and average O-O distance in CBC, 6.388 A^o) was observed to be 3.744 A^o which is quite complementary to cesium ion (3.38 A^o). On the other hand the CBC is also having the same cavity dimensions as CBCA. The CBCA-Cs$^+$ complex was found to be hexa coordinated (four from crown and two from phenolic) with average Cs-O distance of 3.279 A^o. In CBCA-CsNO$_3$ complex the average Cs-O distance is 3.419 A^o with an octa coordinated complex (four from crown, two from phenolic and two from nitrate ion) observed where NO_3^- is behaving as bi-dentate ligand. The same set observations was found in case of CBC as discussed in previous chapters also shown in Table 3.2.

Table 3.1: *Calculated Structural Parameters of Metal Ion−CBCA Complexes at the B3LYP/SVP Level of Theory*

Complex	**M-O(A^o)crown oxygen**	**M-O (A^o)phenolic oxygen**	**M-O(A^o)(nitrate ion oxygen)**
Cs^+-CBCA	3.230, 3.377, 3.491, 3.19	3.202, 3.188	-
$CsNO_3$-CBCA	3.368, 3.266, 4.323, 3.094	3.195, 3.417	3.080, 3.613
Cs^+-CBC	3.450, 3.167, 3.418, 3.250	3.235, 3.189	-
$CsNO_3$-CBC	3.256, 3.352, 3.387, 3.105	3.404, 3.209	3.248, 3.179

3.4.2 Complexes, Binding of complexation

The biding energy (BE, △E) which basically measures the interaction of metal ions towards ligands. It is very important parameters for predicting the preferential selectivity among competitive metal ions and is described in previous chapters. Three different models were chosen for studying the binding energies as shown below. First is purely the gas phase reaction of cesium and calix-crown, in the second model, the hydration of cesium is taken into account by providing a coordination of eight to cesium by water molecule. In the third model the hydration of both cesium and nitrate are being considered.

$$M^+_{(g)} + CC_{(g)} \rightarrow M^+CC_{(g)} \tag{3.8}$$

$$M(H_2O)^+_n + CC_{(g)} \rightarrow M^+CC_{(g)} + (H_2O)_n \tag{3.9}$$

$$M(H_2O)^+_n + NO_3(H_2O)^-_6 + CC_{(g)} \rightarrow MNO_3.CC_{(g)} + (H_2O)_n \tag{3.10}$$

Where n = 6 for Sodium and n = 8 for cesium, CC = CBC , CBCA

From the table 3.3, it is observed that the binding energies of cesium for CBCA(6) is -61.09 kcal/mole, -45.99 kcal/mole, -94.00 kcal/mole the three different models. It is interesting to note that the binding energy of CBCA(6) is always higher (∼

Table 3.2: *Calculated values of binding energies (B.E in kcal/mol) without ZPE correction for three different models.*

Calix-Crown	**B.E[1]**	**B.E[2]**	**B.E[3]**
CBC	-56.2534	-41.1573	-89.122
CBCA(6)	-61.0909	-45.9948	-94.0065

5 kcal/mol) than the CBC which is in good agreement with the experimentally determined D_{Cs} values.

3.5 Selectivity

In order to study the selective extraction of cesium with respect to other metal ions, the extraction of cesium was carried out from simulated dissolver solution (Table 3.1) using 0.01M /30 % IDA/n-dodecane. Since our existing process for actinide partitioning have been tested with 30 % isodecyl alcohol/n-dodecane diluents, to maintain compatibility of process solvents, same diluent system was decided for cesium extraction process from SHLW solution and it was found that CBCA(6) was more effective as compared to CBC even at higher concentration of nitric acid. The distribution ratios for cesium were obtained as 4.0 and 3.0 for CBCA (6) and CBC

Table 3.3: *Extraction of Metal ion from simulated dissolver solution, Organic phase: 0.01 M Calix-crown/30 % IDA/n-dodecane. Aqueous phase: Simulated dissolver solution, HNO_3 = 6.2 M*

Element	**Conc.(ppm)**	**D_M CBC**	**D_MCBCA-6**
Cs	**315**	**3**	**4.02**
Sr	**60**	**0.001**	**0.0015**
Mo	**150**	**0.012**	**0.013**
Zr	**90**	**0.001**	**0.001**
Ru	**60**	**0.00015**	**0.002**
Ba	**375**	**0.0013**	**0.0012**
Na	**5602**	**0.001**	**0.001**
Ce	**210**	**0.004**	**0.005**
Nd	**130**	**0.001**	**0.002**
Y	**60**	**0.001**	**0.002**
K	**215**	**0.001**	**0.007**
U	**8000**	**0.01**	**0.0014**

respectively. Only Molybdenum has shown a D of 0.013 for CBCA (6) and 0.012 for CBC , rest of metal ions have D_M value less than 0.01.

3.6 Radiolytic and hydrolysis stability of CBC and CBCA-6

To establish the process for the selective removal of cesium from high level liquid waste solutions the radiolytic and hydrolytic stability of CBC/isodecyl alcohol/n-dodecane and CBCA/ isodecyl alcohol/n-dodecane were studied.

3.6.1 Hydrolysis studies of CBC and CBCA-6

Both the calix-crowns with solvent composition, 0.01 M Ligand/30 % IDA/n-dodecane were kept in contact with 3.5 M nitric acid with continues stirring for two weeks. It was observed that the colour of solution turned to pale yellow with no considerable change in distribution ratio of cesium. This implies that 0.01 M ligand/30 % IDA/n-dodecane solvent system is hydrolytically stable at room temperature.

3.6.2 Radiolytic stability of CBC and CBCA-6

In the result section we deliberated on a process for separation of cesium using, the solvent system of 0.01 M CBC/30 % IDA/n-dodecane and 0.01 M CBCA/30 % IDA/n-dodecane from HLW. In order to check the robustness of solvent systems for actual process a systematic study on the degradation of the solvent systems were carried out. Irradiation was carried out under representative conditions of the actual feed acidity and dose factors.

3.6.2.1 Irradiation with gamma ray

Three types of samples were prepared in glass test tubes for irradiation, they are as follows:

- 0.01 M calix-crown+ 30 % IDA/n-dodecane.
- 0.01 M calix-crown+ 30 % IDA/n-dodecane in contact with 3.2 M nitric acid

- 0.01 M calix-crown+ 30 % IDA/n-dodecane saturated with 3.2 M nitric acid.

These were irradiated by ^{60}Co source with a dose rate of 20 Gy/minute in air at room temperature. After irradiation samples were withdrawn on 3_{rd}, 7_{th}, 14_{th}, 21_{th} and 29_{th} day and analyzed for distribution ratios. The qualitative degradation product analysis was performed using ESI-MS.

3.6.2.2 Effect of radiation dose

After calculating the equivalent dose in RAD the distribution ratio V/s Dose was plotted. It was observed that after irradiation the distribution ratio decreased with increase in dose rate as shown in Fig. 3.17.

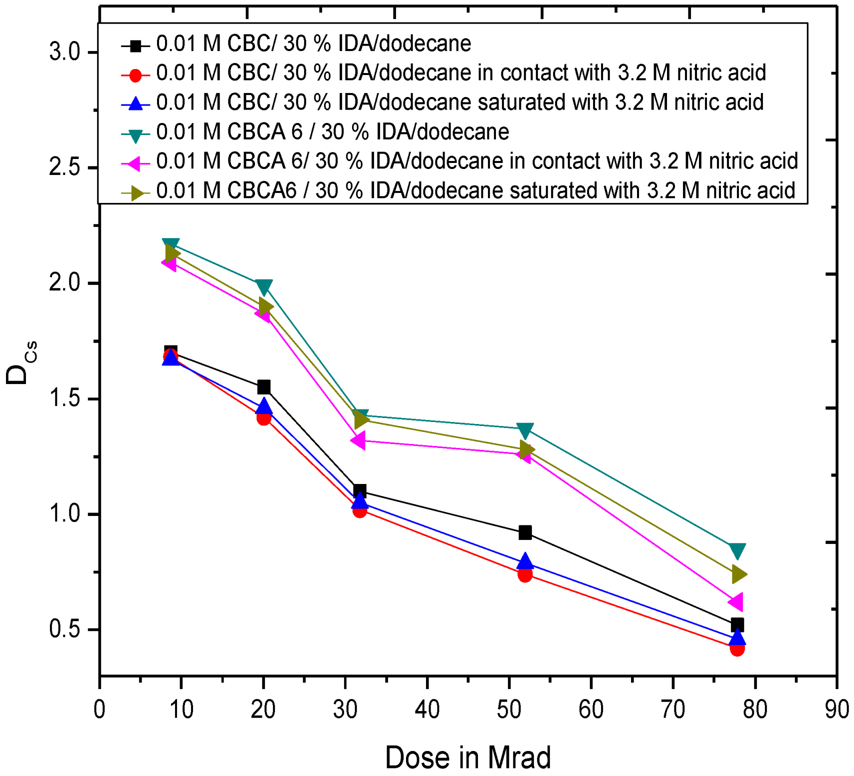


Figure 3.17: *Plot of D_{Cs} for CBC and CBCA(6) vs. radiation dose*

3.6.2.3 Qualitative analysis of radiolytic degradation products (CBC)

0.01 M CBC/30 % IDA/n-dodecane after 80 MRAD of irradiation dose was analysed for possible degradation products. The three ESI-MS spectrum as shown below corresponds to 0.01 M CBC/30 % IDA/n-dodecane, 0.01 M CBC/30 % IDA/n-dodecane contacted with 3.5 M nitric acid and 0.01 M CBC/30 % IDA/n-dodecane saturated with 3.5 M nitric acid solution.(Fig.3.183.19 3.20).

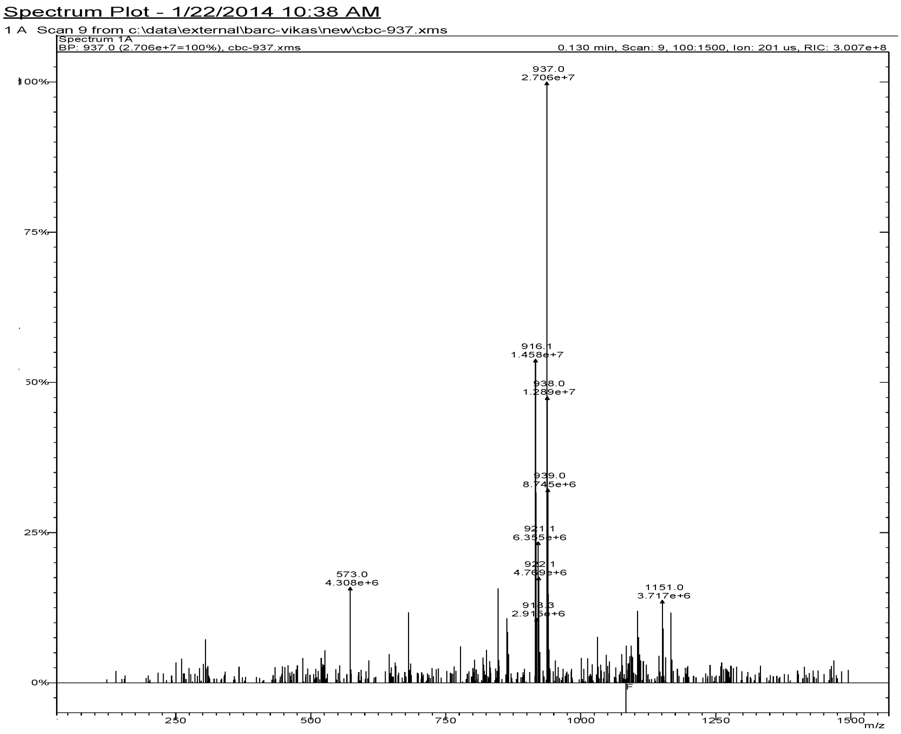


Figure 3.18: *ESI-MS spectra of 0.01 M CBC+ 30 % IDA/n-dodecane (80 MRad)*

The degraded products were analyzed with ESI-MS. The ESI-MS spectra shows large number of peaks which include great number of ions in the sample along with their Na^+ and K^+ and Cs^+ adducts. The major categories of product formed are tentatively based on nominal masses of isomeric molecule. The radiolytic studies of Dicyclohexano-18-crown-6 (DCH18C6) and DB18C6 crown ethers favors the formation of OH group at one end and ethylene group at other end. The cleavage continues through the loss of ethylene oxide (C_2H_4O) unit followed by recyclization [134]. But in the present case this loss has not been observed because of aromatic part which protects the ethyl methyl groups from radiolysis degradation presumably by minimizing the abstraction of hydrogen atom. Hence, instead of ethylene oxide unit loss a complete crown ($C_6H_4(OCH_2CH_2OCH_2CH_2)_2$) part has been observed in the spectrum. The other degradation pathways mainly include cleavage of

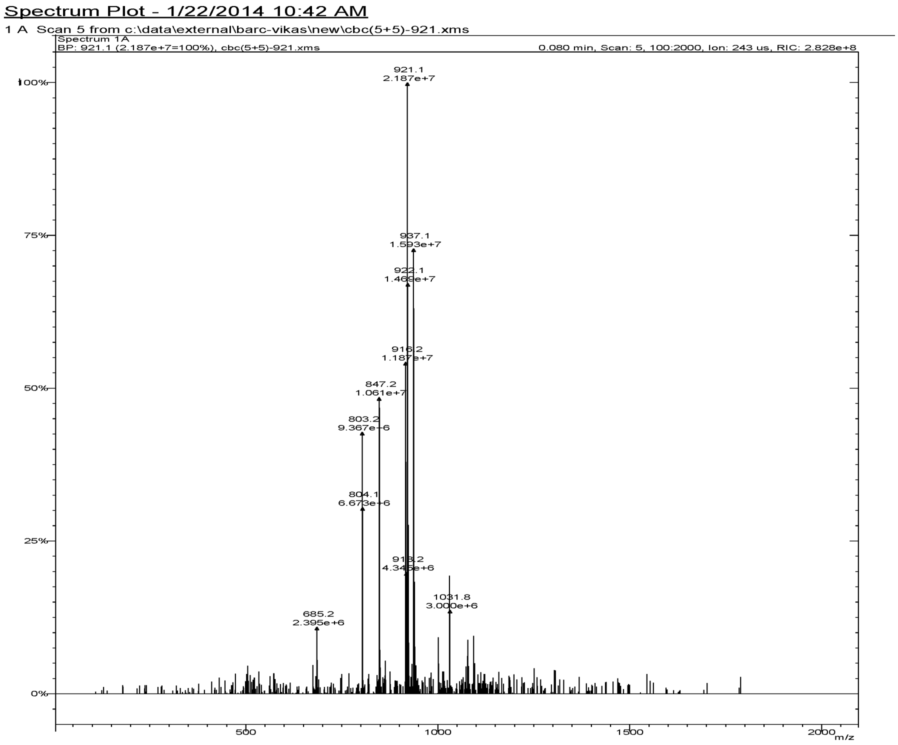


Figure 3.19: *ESI-MS spectra of 0.01 M CBC+ 30 % IDA/n-dodecane in contact with 3.2 M nitricacid(80 MRad)*

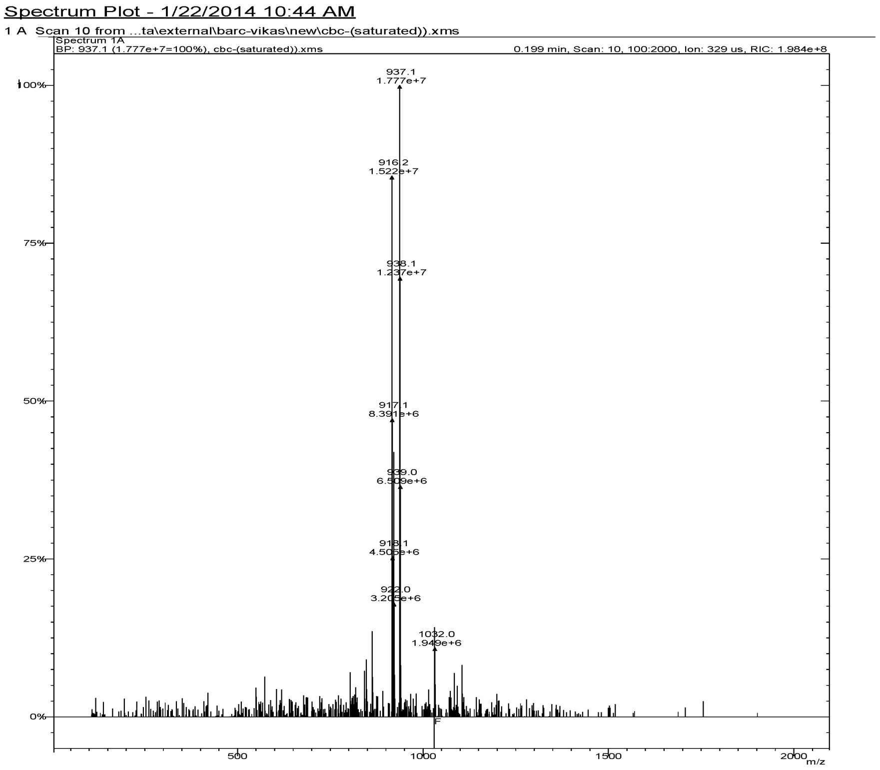


Figure 3.20: *ESI-MS spectra of 0.01 M CBC+ 30 % IDA/n-dodecane saturated with 3.2 M nitric acid(80 MRad)*

alkyl (octyl) and which were further followed by aromatic oxidation and nitration as shown in table 3.4. The modifier isodecyl alcohol forming an adduct which undergoes oxidation and nitration. The octyl part was cleaved from CBC.IDA adduct which subsequently undergoes oxidation, nitration etc.

3.6.2.4 Types of reaction undergoing radiolysis (CBC)

Based on the degradation products formed as shown in table 3.4, the reaction pathways can be summarized as follows in Fig.3.21. The major fragments proposed tentatively are based on nominal masses of isomeric molecule. Depending upon the molecular masses observed in the mass spectrum, the degraded products were designated based on probable oxidation, nitration, addition and degradation reactions as shown in Table.3.4.

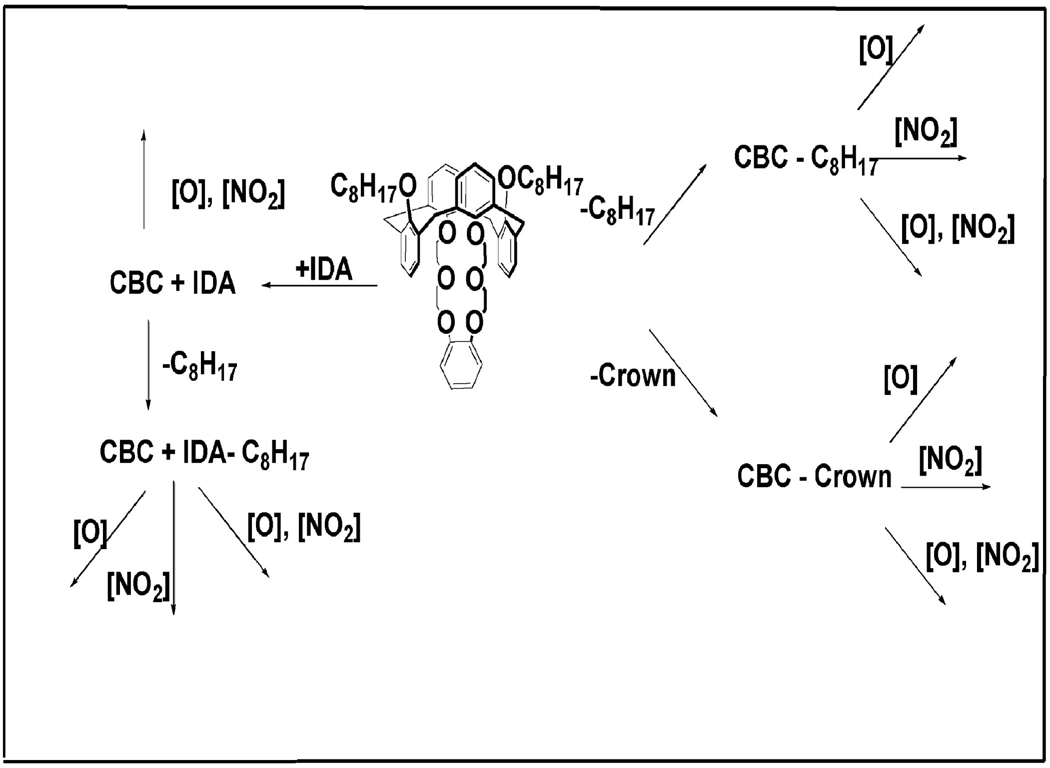


Figure 3.21: *Degradation pathways of CBC*

Table 3.4: *Assignments of ions observed in the ESI-MS of irradiated Calix-benzo-crown (CBC) M.W = 899 Crown Part :* $C_6H_4(OCH_2CH_2OCH_2CH_2)_2$

m/z.	CBC/ 30 % IDA/ n-dodecane irradiated to 80 Mrad	CBC/ 30 % IDA/ n-dodecane irradiated to 80 Mrad contacted with 3.2 M HNO_3	CBC/ 30 % IDA/ n-dodecane irradiated to 80 Mrad saturated with 3.2 M HNO_3
916.1	[CBC+NH_4 $^+$]	[CBC+NH_4 $^+$]	[CBC+NH_4 $^+$]
937	[CBC+K $^+$]	–	[CBC+K $^+$]
863.1	[CBC- C_8H_{17} + NO + 2O - H]	–	[CBC- C_8H_{17} + NO + 2O - H]
962.1	-	[CBC- C_8H_{17} + NO + 2O]	–
847.1	[CBC- C_8H_{17} + NO_2]	[CBC- C_8H_{17} + NO_2]	–
681.0	[CBC- Crown + OH + O]	–	–
573.0	[CBC- Crown - C_8H_{17} + K^+]	–	[CBC- Crown - C_8H_{17} + K^+]
1031.8	–	[CBC + Cs^+]	[CBC + Cs^+]
1039.9	–	–	–
1105.1	–	–	–
1151.0	[CBC +IDA + NO_3 + O + OH]	–	–
1167.0	[CBC +IDA + NO_3 + 2O + OH]	–	–
921.1	[CBC + Na^+]	[CBC + Na^+]	–
803.2	–	[CBC- C_8H_{17} + NH_4 $^+$]	–
847	[CBC- C_8H_{17} + NO_2 + O]	[CBC- C_8H_{17} + NO_2 + O]	[CBC- C_8H_{17} + NO_2 + O]
1001.2	–	[CBC + NO_2 + O + K^+ - H^+]	–
1030.9	-	–	–
1031.8	–	–	–
1251.0	–	[CBC + IDA + Cs^+ +NO_2 + O]	–
685.2	–	[CBC- Crown + NO_2 + O]	–
1095	–	[CBC + IDA +K^+]	–
1000.2	–	[CBC + NO_2 + O + K^+]	–
1078.2	–	[CBC + IDA + Na^+ - H^+]	–
1084.4	–	–	[CBC- C_8H_{17}+ IDA +2NO_2 + 3O]
1105.1	–	–	[CBC + IDA +3O]

3.6.3 Qualitative analysis of radiolytic degradation products of CBCA-6

Similarly the CBCA/30 % IDA/n-dodecane system was irradiated and their ESI-MS spectra were recorded as shown in Fig.3.22 3.23 3.24. The three type of samples were prepared similar to CBC as discussed in previous pages.

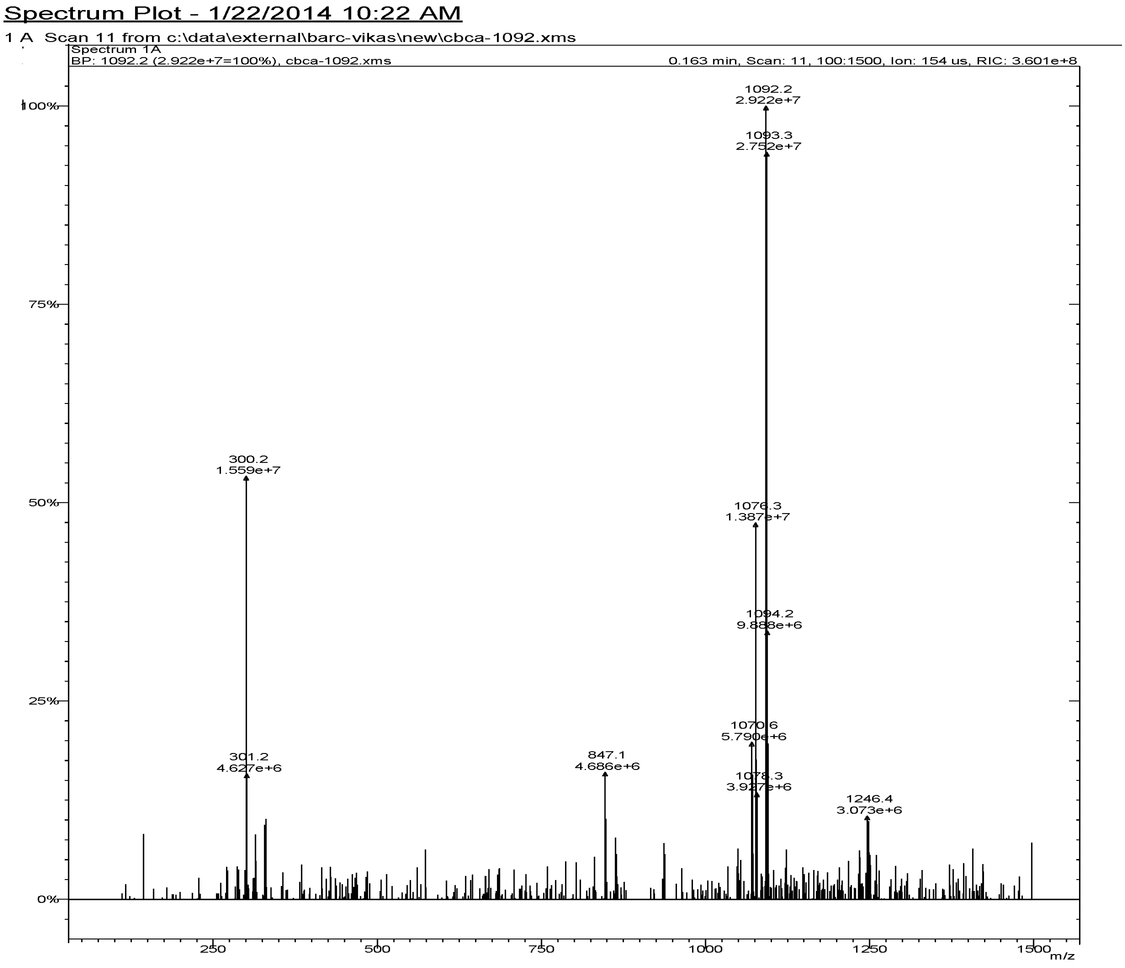


Figure 3.22: *ESI-MS spectra of 0.01 M CBCA+ 30 % IDA/n-dodecane(80 MRad)*

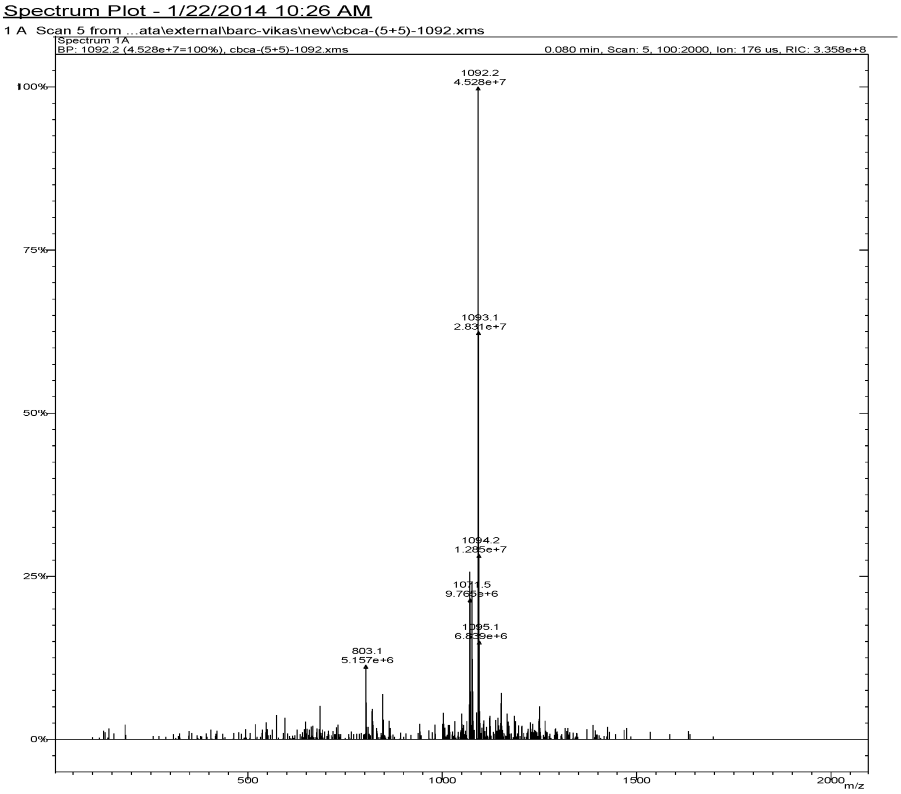


Figure 3.23: *ESI-MS spectra of 0.01 M CBCA+ 30 % IDA/n-dodecane in contact with 3.2 M nitric acid(80 MRad)*

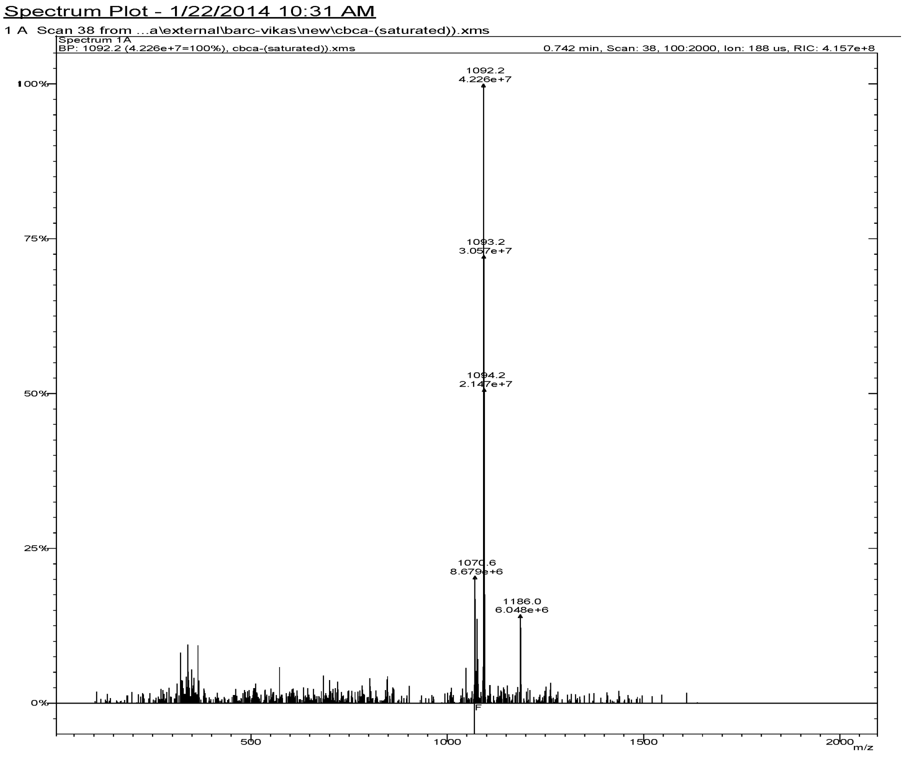


Figure 3.24: *ESI-MS spectra 0.01 M CBCA+ 30 % IDA/n-dodecane saturated with 3.2 M nitric acid (80 MRad)*

3.6.4 Types of reaction undergoing radiolysis (CBCA)

The possible formation mechanisms are tentatively proposed based on the nominal masses of the isomeric molecules which correspond to the simplest mechanism of formation. No accurate mass determinations were performed. All the reaction pathways include radical formation which further propagates the reaction. The reaction includes the cleavage of octyl group (C_8H_{17}) form the calixarene followed by $CONR_2$ cleavage from the benzene ring of crown moity. It is also observed that adduct of CBCA-IDA is formed during the irradiation subsequently undergo oxidation, nitration. The degradation scheme is presented below 3.24.

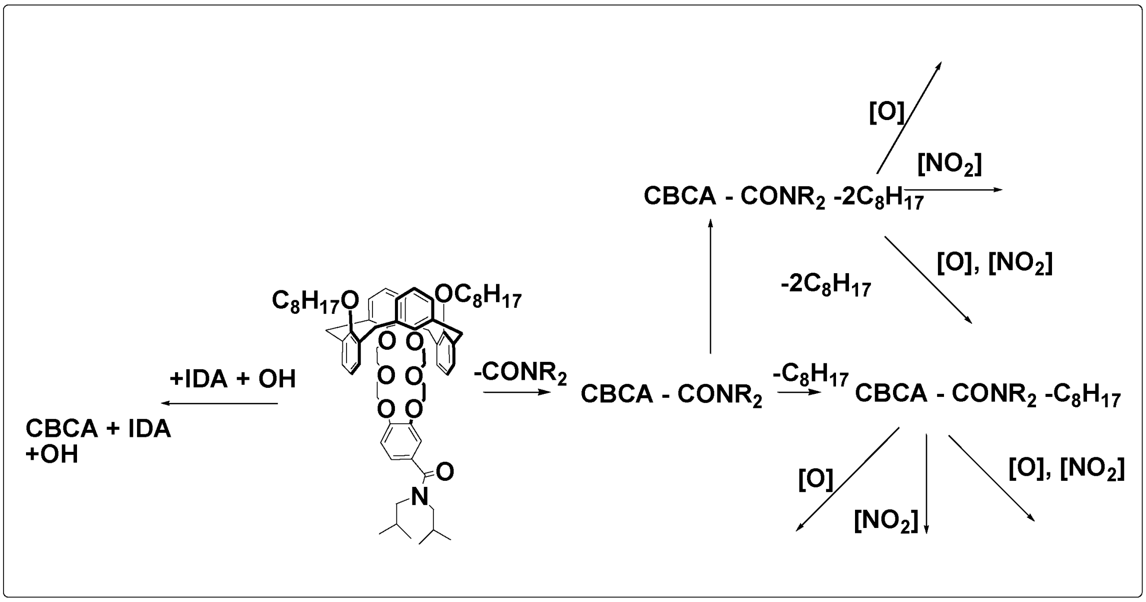


Figure 3.25: *Degradation pathways for CBCA*

This moity undergoes further reaction like oxidation and nitration. The remaining $CBCA-CONR_2$ moity undergoes further cleavage reaction which again undergo oxidation and nitration reaction. Depending upon the molecular masses observed in the mass spectrum, the degraded products were designated based on probable oxidation, nitration, addition and degradation reactions as shown in Table.3.5.

Table 3.5: *Assignments of ions observed in the ESI-MS of irradiated Calix-benzo-crown-amide (CBCA, M.W = 1054)*

m/z.	**CBCA/ 30 % IDA/ n-dodecane irradiated to 80 Mrad**	**CBCA/ 30 % IDA/ n-dodecane irradiated to 80 Mrad contacted with 3.2 M HNO_3**	**CBCA/ 30 % IDA/ n-dodecane irradiated to 80 Mrad saturated with 3.2 M HNO_3**
1093.2	**[CBCA+ K^+]**	**[CBCA+ K^+]**	**[CBCA+ K^+]**
1076.3	**[CBCA+Na^+]**	**[CBCA+Na^+]**	**[CBCA+Na^+]**
937	**[CBCA- $CONR_2$ + K^+]**	–	–
573.1	**[CBCA- $CONR_2$ - C_8H_{17} + K^+ - H^+]**	**[CBCA- $CONR_2$ - C_8H_{17} + K^+ - H^+]**	**[CBCA- $CONR_2$ - C_8H_{17} + K^+ - H^+]**
847.1	**[CBCA- $CONR_2$ - C_8H_{17} + NO_2 + O]**	**[CBCA- $CONR_2$ - C_8H_{17} + NO_2 + O]**	–
1246.14	**[CBCA + IDA + 2OH]**	–	–
1218.2	**[CBCA + NO_3 + NO_2 + OH + K^+]**	–	–
1371.5	**[CBCA + 2NO_3 + NO_2+ O + Cs^+]**	–	–
1007	–	**[CBCA- $CONR_2$ + 2NO_2 + OH]**	–
803	–	**[CBCA- $CONR_2$ -2C_8H_{17} + 2NO_2 + OH + Na^+]**	**[CBCA- $CONR_2$ -2C_8H_{17} + 2NO_2 + OH + Na^+]**
1250.2	–	**[CBCA +IDA + K^+ - H^+]**	–
848.1	–	–	**[CBCA- $CONR_2$ - C_8H_{17} + NO_2 + OH]**
1151.9	–	**[CBCA + NO_3 + $NH_4{}^+$]**	–
1263.2	–	–	**[CBCA +IDA +3OH]**
1186.0	–	–	**[CBCA+ Cs^+]**

3.6.5 Studies with simulated high level waste

In order to study the effect of degradation on the extraction of other metal ions the extraction from simulated HLW were carried out.

Table 3.6: *Distribution ratios (D_M) of various metal ions for irradiated CBC and CBCA(6) for simulated HLW*

Element	Conc.(ppm)	D_M CBC	D_MCBCA-6	D_M(CBC)/ saturated with 3.2 M nitric acid+ 80 MRAD	D_M(CBCA)/ saturated with 3.2 M nitric acid+ 80 MRAD
Cs	290	1.8	2.1	0.4	0.6
Sr	110	10^{-3}	1.5X10^{-3}	10^{-4}	3.2X10^{-4}
Mo	150	1.2X10^{-2}	1.3X10^{-2}	4.8X10^{-1}	6.7X10^{-2}
Zr	85	10^{-3}	10^{-3}	3.6X10^{-2}	1.2X10^{-2}
Ru	120	1.5X10^{-3}	2X10^{-3}	4.5X10^{-3}	3.5X10^{-2}
Ba	315	1.3X10^{-3}	1.2X10^{-3}	6.9X10^{-2}	3.7X10^{-2}
Na	6000	10^{-3}	10^{-3}	2X10^{-4}	3X10^{-4}
Ce	250	4X10^{-3}	5X10^{-3}	1.6X10^{-2}	7.4X10^{-3}
La	80	5X10^{-3}	2X10^{-3}	8.2X10^{-2}	1.2X10^{-2}
Y	68	10^{-3}	2X10^{-3}	1.7X10^{-2}	3.1X10^{-2}
K	250	10^{-3}	7X10^{-3}	1.3X10^{-2}	2.4X10^{-2}

The CBC and CBCA saturated with 3.2 M nitric acid prior to irradiation with a dose of ~ 80 MRAD were used in the experiments. Metal ion concentrations were determined by ICP-AES using suitable standards. From the Table 3.6, it was observed that the D_{Cs} value decreased substantially to 0.4, 0.6 from 1.8, 2.1 for CBC and CBCA respectively which indicate the loss of active crown cavity for cesium extraction. Also the distribution of other metal ions slightly increased which may be due to presence of phenolic moiety after degradation. In addition the phenolic moiety reduces the stripping to (90-95 %) with D_M water.

3.7 Conclusions

A new series of amide substituted calix-crown-benzo-amide (CBCAs) were synthesized and evaluated for the selective separation of cesium ion from dissolver solution. Compared to its non-amidic analogue, the amide has been found to extract cesium at higher nitric acid concentration without any decrease on its extraction ability. This may be attributed to intramolecular buffering effect of amide group, protecting the inner cavity of CBCA (calix-benzo-crown-amide) from counter ion. This property of ligand can be utilized for selective separation of Cs from feed solutions with higher acid concentration. In the quantum chemical calculation study the structures of CBCA(6) and its complexes with cesium and cesium nitrate were optimized with at hybrid B3LYP level using SVP basis set in TURBOMOLE 6.6 package. The gas phase binding energy without ZPE correction were calculated and compared with its non-amide analogue viz. CBC, it was found that binding energy of CBCA(6) is always higher ($\sim$ 5 kcal/mol) than the CBC in all three models, which is in good agreement with the experimentally determined D_{Cs} values. The hydrolytic and radiolytic study of both the ligand CBCA(6), CBC were carried out and the probable degradation pathways were demonstrated which were based tentatively on the mass peak observed in the mass spectrum. From the degradation spectras it was observed that the reaction pathways includes the cleavage of octyl group (C_8H_{17}), crown moiety, $CONR_2$, from calixarene backbone which undergoes further reaction like oxidation and nitration.

4. Synthesis, extraction and theoretical studies of a new biglycolamide substituted calix-benzo-crown-6

4.1 Introduction

During the spent fuel treatment and also during various decontamination activities, high active acid waste is generated in large volumes containing mainly fission products like ^{137}Cs, ^{90}Sr-^{90}Y etc. containing traces quantities of actinides. Extractant molecules are designed to separate and concentrate these nuclides almost quantitatively into smaller volumes so as to discharge bulk of the waste volume into the environment after appropriate treatment. Moreover this step will help in the subsequent handling of the radioactive waste and manrem budgeting [149, 150]. Large number of reports are available on the use various substituted calix-crown molecules and their modification to improve the solubility in nonpolar diluents and extraction efficiency [151]-[159].

In the present study, synthesis of a modified calix-benzocrown-6 is planned to explore the feasibility of coextracting actinides and lanthanides along with Cs. Last decade had seen the emergence of diglycolamide as a promising reagent for the bulk separation of actinides and lanthanides from acidic high level liquid waste from reprocessing. Two or more glycolamides molecules are found to solvate and transport actinide/lanthanide nitrates into the organic phase. The extraordinary affinity of these glycolamides for actinides from the acidic medium prompted the synthesis of a novel calix[4]arene-benzocrown-6 with two diglycolamide groups at 1,3 alternate side of the calix[4]arene ring spaced with three CH_2 groups.

4.2 Synthesis of CBCBGA

According to Fig.4.1, the compound (2) was synthesized by the reaction of calix[4]arene with allyl bromide in presence of base potassium carbonate as per the procedure reported in previous chapters.

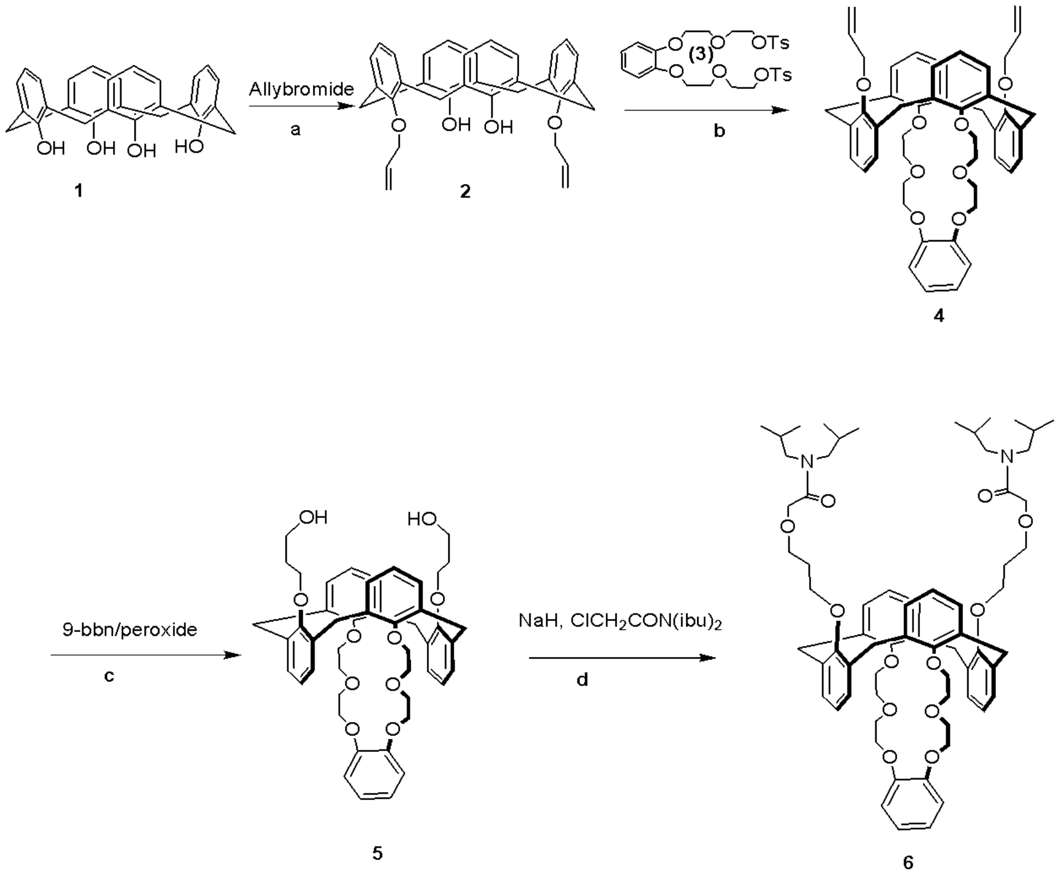


Figure 4.1: *Synthesis of 1,3-alternate Calix[4]arene-benzocrown-bis-glycolamide (CBCBGA) Reagents and conditions: a) Allylbromide, MeCN, K_2CO_3, reflux; b) Cs_2CO_3, MeCN, reflux ; c) 9-BBN, hydrogen peroxide, NaOH; d) NaH, THF, rt.*

This 1,3-dipropenyloxy calix[4]arene (2) was reacted with the compound (3) in presence of cesium carbonate by refluxing in acetonitrlie for 2 days to obtain the 1,3-dipropenyloxy calix-benzo-crown(4). The compound (3) ditosylate was synthesized by refluxing catechol with 2-(2-chloroethoxy) ethanol and K_2CO_3 in acetonitrile for 48 hours followed by conversion to ditosylate by reacting with tosylchloride reported in early chapters. 1,3-dipropyloxy calix[4]arene-benzocrown diol (5) was prepared by the reaction of 1,3-dipropenylyloxy calix[4]arene-benzocrown

(4) with 9-Borabicyclo[3.3.1]nonane (9-BBN) followed by hydrogen peroxide oxidation. Calix[4]arene-benzocrown-biglycolamide 6 was synthesized by the condensation of the 2-chloro-N,N diisobutylacetamide and 1,3-dipropyloxy calix[4]arene-benzocrown-6 diol(5) in presence of sodium hydride.

4.3 Experimental

4.3.1 Chemicals and solutions

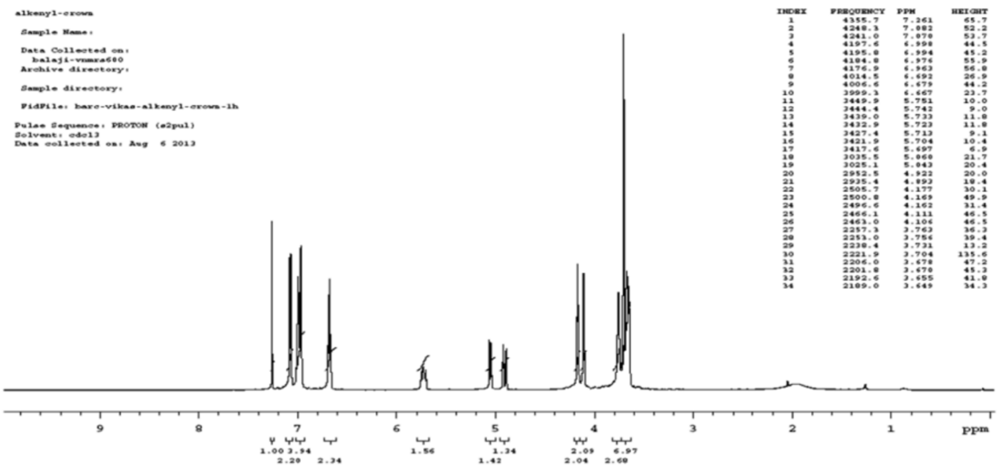
Calix[4]arene was purchased from M/s. Numex Chemical Corporation, Mumbai, India and purified by recrystallization. o-NPHE and 2-chloro-N,N-diisobutylacetamide was procured from M/s. Orion Chem. Pvt. Ltd, Mumbai, India and used after distillation. 9-BBN and allyl bromide were purchased from Sigma Aldrich. All the other reagents used were of Analytical-Reagent grade and purchased from Spectrochem Pvt. Ltd. Tarapur, Maharashtra, India. Solvents were further purified and dried by standard methods prior to use. The simulated waste solution was prepared by dissolving the chlorides of Na and Ba, nitrates of Cs and Sr, oxide of Ce, Nd, Zr, U and ammonium salts of Mo in nitric acid solutions. The Am-241 radiotracer was spiked in the above SHLW solution.

4.3.2 Physicochemical measurements

NMR spectras were obtained with a Bruker 500 MHz FT-NMR spectrometer in $CDCl_3$ with TMS as internal standard. Melting points were determined with a Mel-Temp melting point apparatus. Elemental analysis was performed at CHNS-Thermo apparatus and ESI-MS spectra obtained by Q-TOF micro mass (YA-105) Bruker in positive ion mode. Inactive Cs analysis in aqueous phase was done with AAS (GBC, Australia make). All the metal ions were analyzed by ICP-AES (Horiba Jobin-Yvon ultima 2 series) except, ^{241}Am analysis was carried on NaI(Tl) gamma scintillation detector. The nitric acid concentrations were measured by potentiometric titration, using Metrohm 905 Titrando device with 0.1 M NaOH solution.

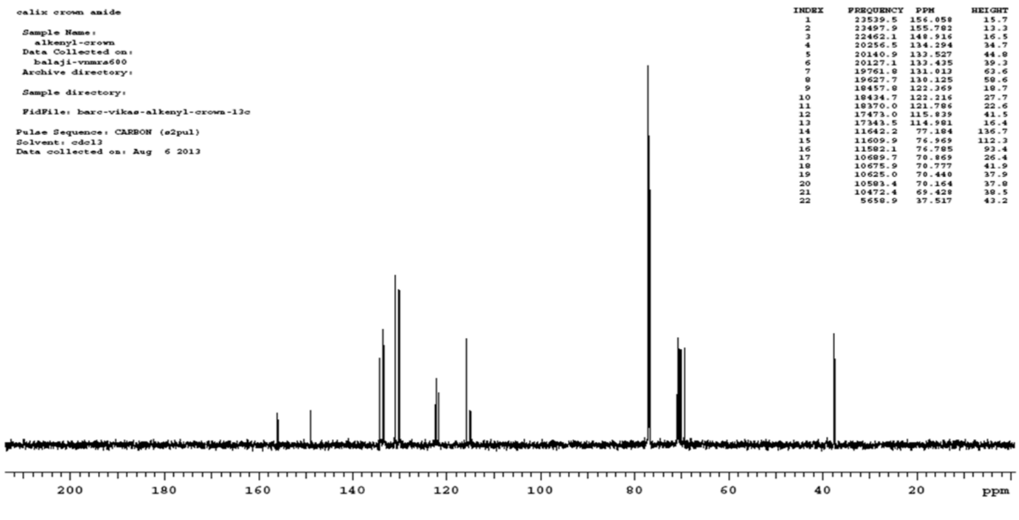
4.3.3 Synthesis of 1,3-dipropenyloxy calix-benzo-crown (4)

To the stirred solution of 2 (20 gm, 39.6mmol) in 4 lt., of dry acetonitrile 3 (12 gm, 20.2 mmol) and excess of cesium carbonate (39 gm, 120 mmol) were added. The reaction mixture was reflux for 24 hours and then the left over amount of 3 (12 gm, 20.2 mmol) was added in the reaction mixture and refluxing was continued further for 24 hours. The progress of reaction was monitored on TLC with 1:3, ethylacetate/hexane as the mobile phase. The solvent was evaporated by vacuum distillation on rotavapour.



INDEX	FREQUENCY	PPM	HEIGHT
1	4355.7	7.261	65.7
2	4248.3	7.082	52.2
3	4241.0	7.070	53.7
4	4197.6	6.998	44.5
5	4195.8	6.994	45.2
6	4184.8	6.976	55.9
7	4176.9	6.963	56.8
8	4014.5	6.692	26.9
9	4006.6	6.679	44.2
10	3999.3	6.667	23.7
11	3449.9	5.751	10.0
12	3444.4	5.742	9.0
13	3439.0	5.733	11.8
14	3432.9	5.723	11.8
15	3427.4	5.713	9.1
16	3421.9	5.704	10.4
17	3417.6	5.697	6.9
18	3035.5	5.060	21.7
19	3025.1	5.043	20.4
20	2952.5	4.922	20.0
21	2935.4	4.893	18.4
22	2505.7	4.177	30.1
23	2500.8	4.169	49.9
24	2496.6	4.162	31.4
25	2466.1	4.111	46.5
26	2463.0	4.106	46.5
27	2257.3	3.763	36.3
28	2253.0	3.756	39.4
29	2238.4	3.731	13.2
30	2221.9	3.704	135.6
31	2206.0	3.678	47.2
32	2201.8	3.670	45.3
33	2192.6	3.655	41.8
34	2189.0	3.649	34.3

Figure 4.2: ^{1}H *NMR of 1,3-dipropenyloxy calix-benzo-crown(4)*



INDEX	FREQUENCY	PPM	HEIGHT
1	23539.5	156.058	15.7
2	23497.9	155.782	13.3
3	22462.1	148.916	16.5
4	20256.5	134.294	34.7
5	20140.9	133.527	44.8
6	20127.1	133.435	39.3
7	19761.8	131.013	63.6
8	19627.7	130.125	58.6
9	18457.8	122.369	18.7
10	18434.7	122.216	27.7
11	18370.0	121.786	22.6
12	17473.0	115.839	41.5
13	17343.5	114.981	16.4
14	11642.2	77.184	136.7
15	11609.9	76.969	112.3
16	11582.1	76.785	93.4
17	10689.7	70.869	26.4
18	10675.9	70.777	41.9
19	10625.0	70.440	37.9
20	10583.4	70.164	37.8
21	10472.4	69.428	38.5
22	5658.9	37.517	43.2

Figure 4.3: ^{13}H *NMR of 1,3-dipropenyloxy calix-benzo-crown(4)*

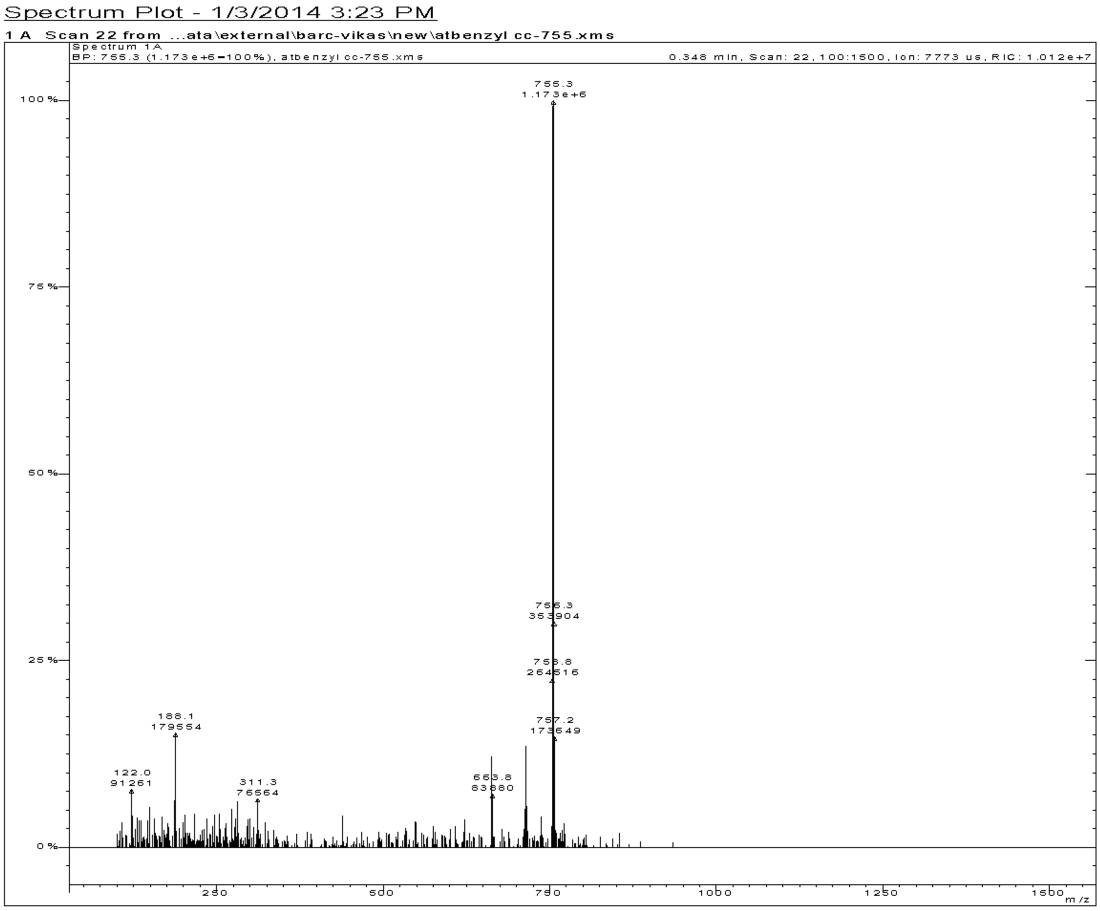


Figure 4.4: *ESI-MS spectra 1,3-dipropenyloxy calix-benzo-crown (4)*

The product was taken in dichlomethane (250 ml) and washed with 0.1 N HCl (3 X 250mL) and distil water (3 X 250mL). During washing the third phase formed in between the organic phase and aqueous phase was discarded. The organic phase was dried over anhydrous sodium sulphate, filtered and the solvent was removed under reduced pressure on rotary evaporator. The crude product was chromatographed on silica gel (100-200 mesh size) with 1:4, ethylacetate: hexane as eluent to obtain 21.5 gm, (72 %) of 4 with mp. 151-153^{o}C as the white shiny crystals. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig. 4.24.34.4.

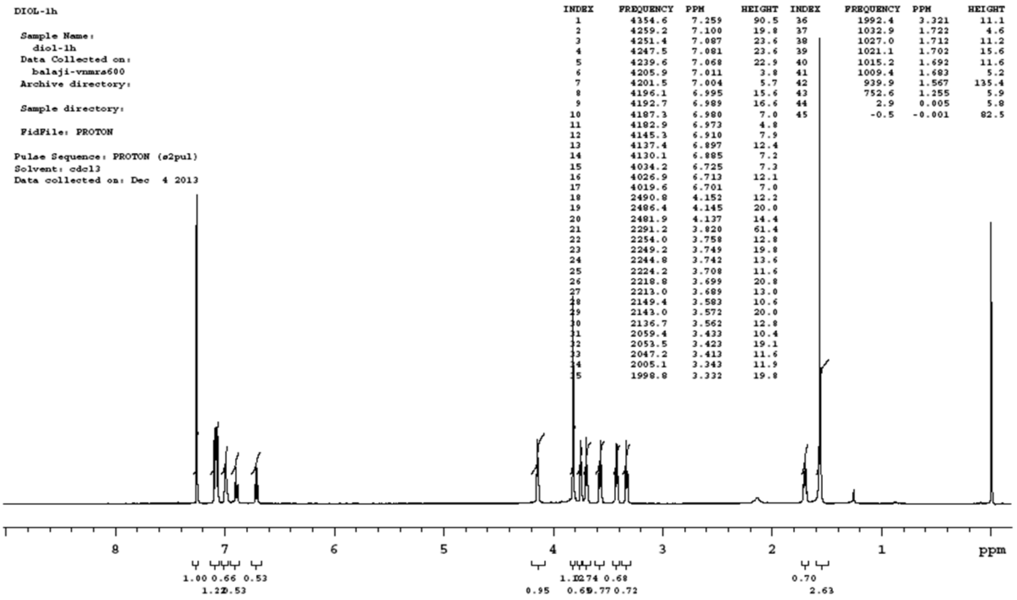
^{1}H NMR : ^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm) : 3.64-3.69 (m, 8H, 4-OCH_2), 3.70 (s, 8H, 4ArCH_2Ar), 3.71-3.76 (m, 4H, 2-OCH_2), 4.0-4.11 (m, 4H, -2OCH_2), 4.11-4.17 (m, 4H, -2OCH_2), 4.8-4.9 (m, 2H, -CH_2=CH-CH_2), 5.0-5.6(m, 2H, -CH_2=CH-CH_2),5.69-5.81(m, 2H,- 2CH_2=CH-CH_2), 6.66-6.69 (t, 4H, J=7.3 Hz, Ar-H), 6.96-

7.08 (m, 8H, ,Ar-H), 7.08-7.26 (d, 4H, J=7.4 Hz, Ar-H). ^{13}C NMR (150 MHz, $CDCl_3$, δ in ppm): 37.51, 69.42, 70.16, 70.44, 70.77, 70.86, 76.78, 76.96, 77.18, 114.98, 115.83, 121.78, 122.21, 122.36, 130.12, 131.01, 133.43, 133.52, 134.29, 148.91, 155.78, 156.05. Anal. Calcd. for $C_{48}H_{52}O_8$: C, 76.19; H, 6.87 ; O, 16.93. Found: C, 76.38; H, 6.62; O, 16.99. ES-MS $(ES)^+$, 755.3: $[M-H]^+$, 756.3 : $[M]^+$.

4.3.4 Synthesis of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5)

Compound 4 was dissolved (15 gm, 19.0 mmol) in 100 ml anhydrous THF and kept at 0-5^{o}C in ice water bath. To this 9-borabicyclo[3.3.1]nonane (17 gm, 0.15 mol) in 100 ml anhydrous THF was added drop wise for 30 min, maintaining the temperature at ∼0^{o}C. Reaction mixture was allowed to reach room temperature. The reaction mixture was refluxed for 24 hrs, then allowed to cool at room temperature. The resulting organoborane was oxidized by adding slowly 30 ml, 10 N NaOH and 100ml, 50 % v/v H_2O_2. The solution was stirred for 30 min then refluxed for 6 hrs to ensure the complete oxidation. The mixture was concentrated to remove the solvents by vacuum evaporation and extracted with dichloromethane (3X100 ml). The organic Phase was washed with 0.1 N HCl (2X250 ml) and de-ionized water (2X250 ml). The organic was dried over anhydrous sodium sulphate, filtered and concentrated by vacuum evaporation. Crude product was chromatographed on silica gel with 10:1, CH_2Cl_2-acetone as the mobile phase to yield 11 gm, 70 %. m.p 137-140^{o}C.

^{1}H NMR : ^{1}H NMR (600MHz, $CDCl_3$, δ in ppm) 1.52-1.60(s, 2H, 2-OH), 1.68-1.72 (t, 4H, J=5.9 Hz, -2OCH_2CH_2), 3.31-3.35 (t, 4H, J=6.4 Hz, 2-OCH_2), 3.42-3.44 (m, 4H, -2OCH_2), 3.56-3.58 (t, 4H, J=6.4 Hz, -2OCH_2), 3.69-3.71 (m, 4H, 2-OCH_2), 3.74-3.76(m, 4H, 2-OCH_2), 3.82(s, 8H, -4$ArCH_2Ar$), 4.13-4.16 (t, 4H, J=4.5 Hz, 2-OCH_2), 6.70-6.72 (t, 3H, J=7.3 Hz, Ar-H), 6.88-6.91 (t, 3H, J=7.3 Hz, Ar-H), 6.93-7.01 (m, 3H, Ar-H), 7.08-7.11 (m, 7H, Ar-H). ^{13}C NMR (150 MHz, $CDCl_3$, δ in ppm): 32.73, 38.00, 60.53, 69.24, 69.42, 69.70, 69.91, 70.22, 76.78, 76.96, 77.18, 94.38, 115.56, 122.00, 122.67, 122.79, 129.94, 133.68, 133.80, 149.22, 156.21, 156.94.



DIOL-1h

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balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: PROTON

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Data collected on: Dec 4 2013

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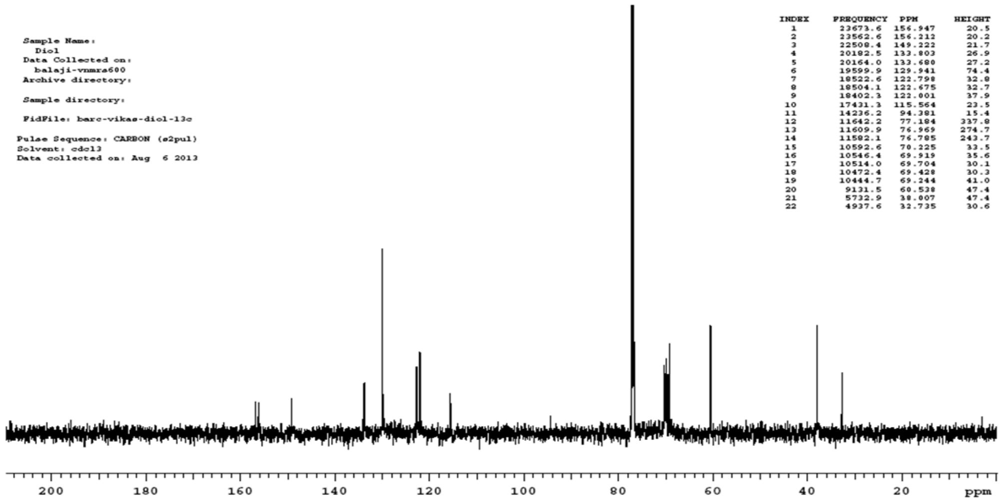
2	4259.2	7.100	19.8
3	4251.4	7.087	23.6
4	4247.5	7.081	23.6
5	4239.6	7.068	22.9
6	4205.9	7.011	3.8
7	4201.5	7.004	5.7
8	4196.1	6.995	15.6
9	4192.7	6.989	16.6
10	4187.3	6.980	7.0
11	4182.9	6.973	4.8
12	4145.3	6.910	7.9
13	4137.4	6.897	12.4
14	4130.1	6.885	7.2
15	4034.2	6.725	7.3
16	4026.9	6.713	12.1
17	4019.6	6.701	7.0
18	2490.8	4.152	12.2
19	2486.4	4.145	20.0
20	2481.9	4.137	14.4
21	2291.2	3.820	61.4
22	2254.0	3.758	12.8
23	2249.2	3.749	19.8
24	2244.8	3.742	13.6
25	2224.2	3.708	11.6
26	2218.8	3.699	20.8
27	2213.0	3.689	13.0
28	2149.4	3.583	10.6
29	2143.0	3.572	20.0
30	2136.7	3.562	12.8
31	2059.4	3.433	10.4
32	2053.5	3.423	19.1
33	2047.2	3.413	11.6
34	2005.1	3.343	11.9
35	1998.8	3.332	19.8
36	1992.4	3.321	11.1
37	1032.9	1.722	4.6
38	1027.0	1.712	11.2
39	1021.1	1.702	15.6
40	1015.2	1.692	11.6
41	1009.4	1.683	5.2
42	939.9	1.567	135.4
43	752.6	1.255	5.9
44	2.9	0.005	5.8
45	-0.5	-0.001	82.5

Figure 4.5: ^{1}*H NMR of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5)*



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Archive directory:

Sample directory:

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Solvent: cdcl3
Data collected on: Aug 6 2013

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1	23673.6	156.947	20.5
2	23562.6	156.212	20.2
3	22508.4	149.222	21.7
4	20182.5	133.803	26.9
5	20164.0	133.680	27.2
6	19599.9	129.941	74.4
7	18522.6	122.798	32.8
8	18504.1	122.675	32.7
9	18402.3	122.001	37.9
10	17431.3	115.564	23.5
11	14236.2	94.381	15.4
12	11642.2	77.184	337.8
13	11609.9	76.969	274.7
14	11582.1	76.785	243.7
15	10592.6	70.225	33.5
16	10546.4	69.919	35.6
17	10514.0	69.704	30.1
18	10472.4	69.428	30.3
19	10444.7	69.244	41.0
20	9131.5	60.538	47.4
21	5732.9	38.007	47.4
22	4937.6	32.735	30.6

Figure 4.6: ^{13}*H NMR of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5)*

Anal. Calcd. for $C_{48}H_{56}O_{10}$: C, 72.72; H, 7.07 ; O, 20.20. Found: C, 72.93; H, 6.82; O, 20.24. . ES-MS $(ES)^+$, 793.4.: $[M+H^+]$ 813.4 : $[M+Na^+-2H^+]$, 829.4 $[M+K^+-2H^+]$. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig 4.54.64.7.

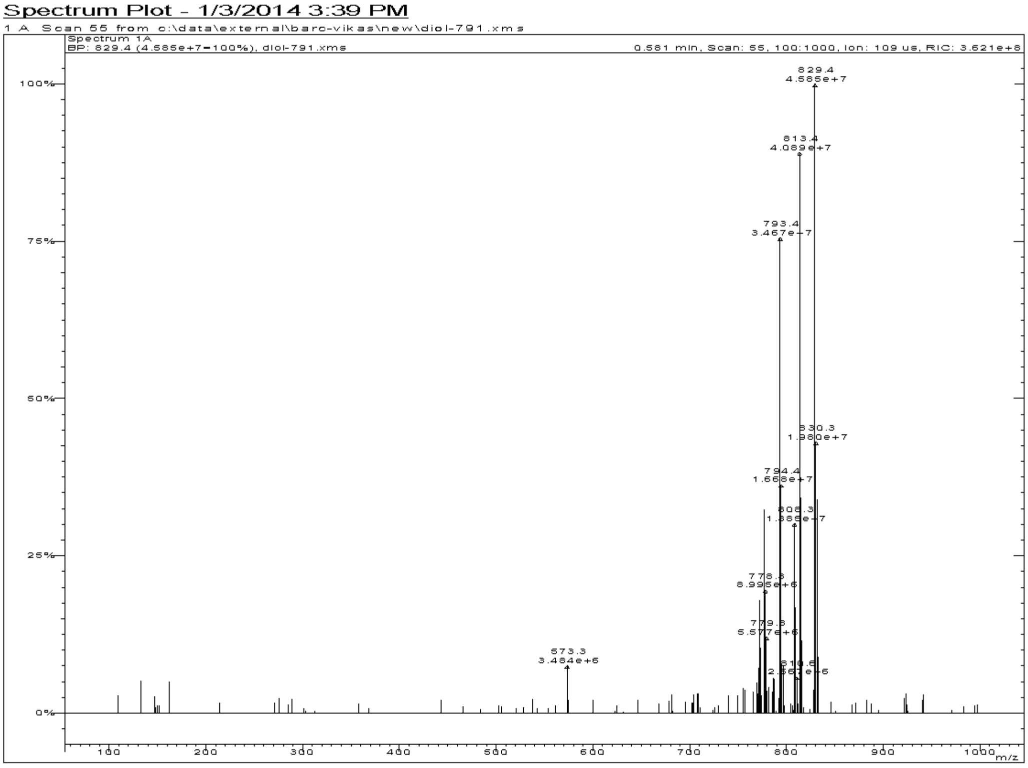
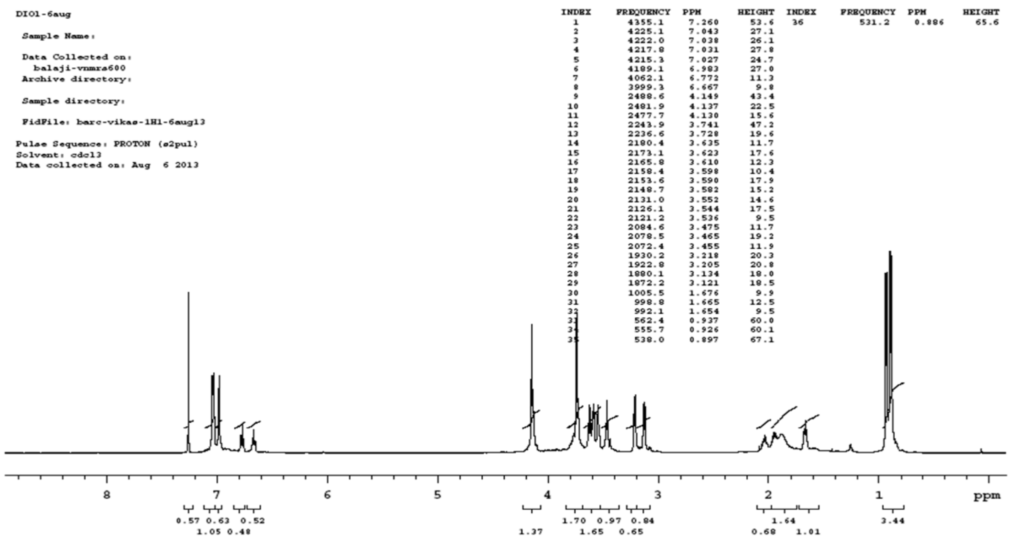


Figure 4.7: *ESI-MS spectra 1,3-dipropyloxy calix[4]arene-benzocrown diol(5)*

4.3.5 Synthesis of Calix[4]arene-benzocrown-biglycolamide (6)

Suspended NaH (7.6 gram, 60 mmol), 60 percent dispersion in mineral oil in the 100 ml of dry THF and cooled to 0-5^{o}C in ice/water bath. Dissolved 5 (9 gram, 11.3 mmol) in 100 ml dry THF and added slowly in the above cooled reaction mixture using pressure equalizer dropping funnel while maintaining the reaction temperature 0-5^{o}C. Ice bath was removed and the solution was warmed to 50^{o}C for one hour and after the solution became clear, 2-chloro-N,N diisobutylacetamide (2.47 gram, 12.0 mmol) dissolved in 50 ml dry THF, added drop wise for 30 min. Refluxed the reaction mixture for 16 hours and than allowed to reach room temperature. The reaction was stopped by adding slowly 75 ml of distilled water. The reaction mixture was concentrated under reduced pressure and product was extracted with CH_2Cl_2 (2X100 ml). Both the organic fractions combined and washed with 0.1 N HCl (3X150ml) and distilled water (3X150ml). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated by vacuum evaporation. After chromatography on silica gel with 1:4, ethylacetae/hexane, final product obtained was 8.7 gram, yield 68 %.viscous liquid.



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 Sample directory:

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Solvent: cdcl3
Data collected on: Aug  6 2013
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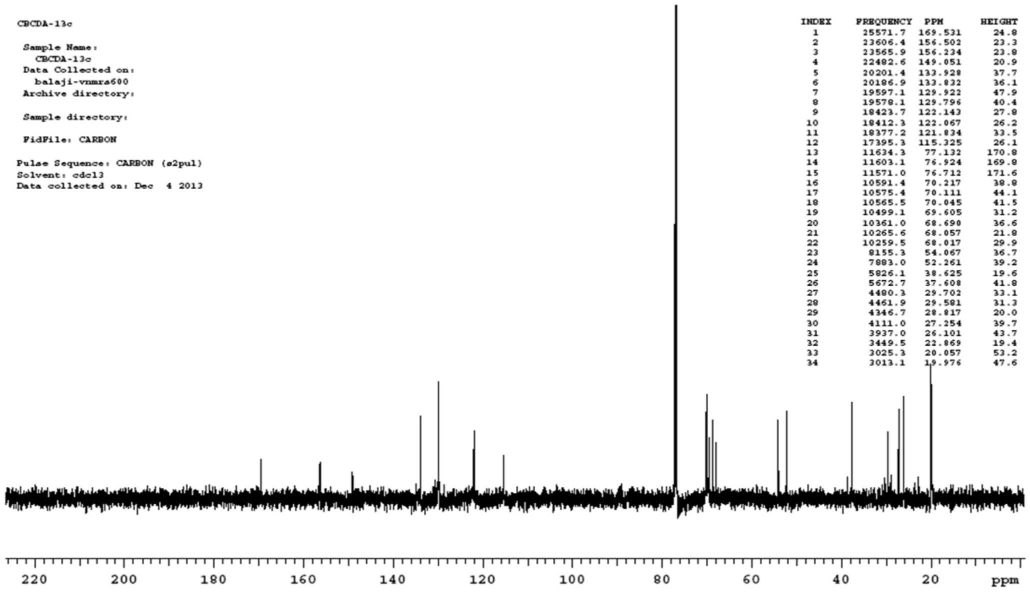
  1       4355.1   7.260    53.6   36        531.2   0.886    65.6
  2       4225.1   7.043    27.1
  3       4222.0   7.038    26.1
  4       4217.8   7.031    27.8
  5       4215.3   7.027    24.7
  6       4189.1   6.983    27.0
  7       4062.1   6.772    11.3
  8       3999.3   6.667     9.8
  9       2488.6   4.149    43.4
 10       2481.9   4.137    22.5
 11       2477.7   4.130    15.6
 12       2243.9   3.741    47.2
 13       2236.6   3.728    19.6
 14       2180.4   3.635    11.7
 15       2173.1   3.623    17.6
 16       2165.8   3.610    12.3
 17       2158.4   3.598    10.4
 18       2153.6   3.590    17.9
 19       2148.7   3.582    15.2
 20       2131.0   3.552    14.6
 21       2126.1   3.544    17.5
 22       2121.2   3.536     9.5
 23       2084.6   3.475    11.7
 24       2078.5   3.465    19.2
 25       2072.4   3.455    11.9
 26       1930.2   3.218    20.3
 27       1922.8   3.205    20.8
 28       1880.1   3.134    18.0
 29       1872.2   3.121    18.5
 30       1005.5   1.676     9.9
 31        998.8   1.665    12.5
 32        992.1   1.654     9.5
 33        562.4   0.937    60.0
 34        555.7   0.926    60.1
 35        538.0   0.897    67.1
```

Figure 4.8: ^{1}H *NMR of 1,3- alternate Calix[4]arene-benzocrown-biglycolamide (6)*



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CBCDA-13c

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 FidFile: CARBON

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Solvent: cdcl3
Data collected on: Dec  4 2013
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  1      25571.7  169.531    24.8
  2      23606.4  156.502    23.3
  3      23565.9  156.234    23.8
  4      22482.6  149.051    20.9
  5      20201.4  133.928    37.7
  6      20186.9  133.832    36.1
  7      19597.1  129.922    47.9
  8      19578.1  129.796    40.4
  9      18423.7  122.143    27.8
 10      18412.3  122.067    26.2
 11      18377.2  121.834    33.5
 12      17395.3  115.325    26.1
 13      11634.3   77.132   170.8
 14      11603.1   76.924   169.8
 15      11571.0   76.712   171.6
 16      10591.4   70.217    38.8
 17      10575.4   70.111    44.1
 18      10565.5   70.045    41.5
 19      10499.1   69.605    31.2
 20      10361.0   68.690    36.6
 21      10265.6   68.057    21.8
 22      10259.5   68.017    29.9
 23       8155.3   54.067    36.7
 24       7883.0   52.261    39.2
 25       5826.1   38.625    19.6
 26       5672.7   37.608    41.8
 27       4480.3   29.702    33.1
 28       4461.9   29.581    31.3
 29       4346.7   28.817    20.0
 30       4111.0   27.254    39.7
 31       3937.0   26.101    43.7
 32       3449.5   22.869    19.4
 33       3025.3   20.057    53.2
 34       3013.1   19.976    47.6
```

Figure 4.9: ^{13}H *NMR of 1,3- alternate Calix[4]arene-benzocrown-biglycolamide (6)*

^{1}H NMR : ^{1}H NMR (600MHz, $CDCl_3$, δ in ppm), 0.82-0.98 (m, 24H, -8CH_3), 1.62-1.72 (m, 4H, -4NCH$_2$CH), 1.81-2.12 (bs, 8H, -4NCH$_2$), 3.11-3.15 (d, 4H, J=7.9 Hz , -2OCH$_2$), 3.16-3.25 (d, 4H, J=7.4 Hz, -2OCH$_2$), 3.41-3.50 (m, 4H, 2-OCH$_2$), 3.51-3.68(m, 12H, 6-OCH$_2$), 3.74(s, 8H, - 4ArCH$_2$Ar), 4.12-4.18 (m, 8H, 2-ArOCH$_2$ + 2-OCH$_2$CO), 6.66-6.71 (t, 3H, J=7.3 Hz, Ar-H), 6.72-6.81 (t, 3H,J=7.3 Hz, Ar-H), 6.95-7.04 (m, 10H, Ar-H). ^{13}C NMR (150 MHz, CDCl$_3$, δ in ppm): 19.9, 22.86,26.10, 27.25, 28.8,29.58, 29.70, 37.6, 38.62, 52.26, 54.06, 68.01, 68.05,68.6, 70.11, 70.21, 76.71, 76.92, 77.13, 115.32, 121.83, 122.067, 122.06, 122.14, 129.79, 129.92, 133.83, 133.92, 149.05, 156.23, 156.50, 169.53. Anal. Calcd. for $C_{68}H_{94}O_{12}N_2$: C, 72.16; H, 8.31 ; O, 16.98 ; N, 2.47. Found: C, 72.31; H, 8.13; O, 17.05 ; N, 2.50 . ES-MS (ES)$^+$, 1151.7.: [M+Na$^+$-2H$^+$], 1152.6.:[M+Na$^+$-H$^+$], 1153.9.: [M+Na$^+$], 1168.7.:[M+K$^+$-H$^+$].1167.8 [M+K$^+$-2H$^+$]. The ^{1}H NMR, ^{13}C NMR and ESI-MS spectra are as shown in Fig. 4.84.94.10.

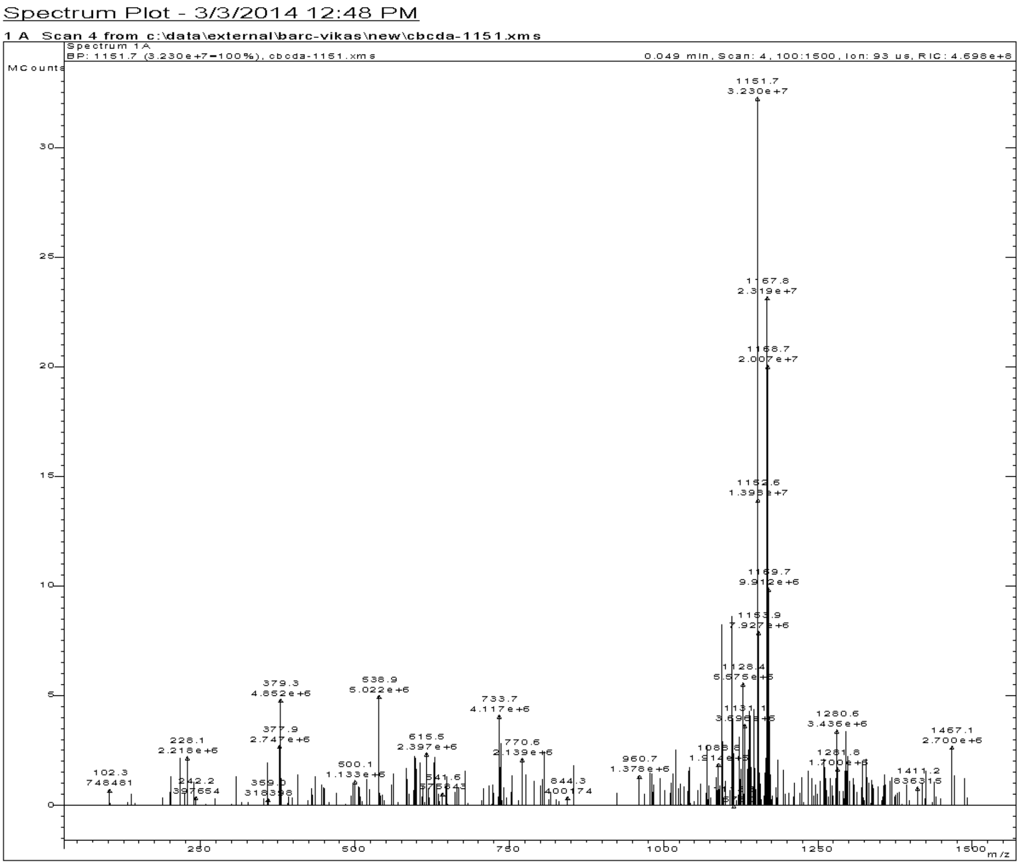

Figure 4.10: *ESI-MS spectra of 1,3- alternate Calix[4]arene-benzocrown-biglycolamide (6)*

4.4 Solvent extraction studies

4.4.1 Effect of ligand concentration on extraction of cesium

The CBCBGA has shown almost zero solubility in dodecane hence, in order to study the extraction behaviour a polar diluent o-NPHE (ortho nitrophenyl hexyl ether) was used. o-NPHE has been preferred as it can dissolve the calix-crown in high concentration, also having a high dielectric constant and can improve the extraction by solvating the counter anion.

$$Cs^+_{aq} + nCBCBGA_{org} + mH^+ + (m+1)NO_3^- aq \rightleftharpoons Cs^+.CBCBGA.NO_3^-.mHNO_{3org} \tag{4.1}$$

The conditional extraction equilibrium constant, K_{ex} in reaction (4.1) can be written as:

$$K_{ex} = \frac{[Cs^+.nCBCBGA.NO_3^-.mHNO_3]_{org}}{[Cs]_{aq}[NO_3]^{m+1}_{aq}[CBCBGA]^n_{org}[H^+]^m_{aq}} \tag{4.2}$$

D, distribution coefficient and defined as:

$$D = \frac{[Cs^+.nCBCBGA.NO_3^-.mHNO_3]_{org}}{[Cs^+]_{aq}} \tag{4.3}$$

By substituting Eq. (4.3) into Eq. (4.2) and converting into logarithmic form the following equations are obtained

$$K_{ex} = \frac{D}{[CBCBGA]^n_{org}[[H^+]^m_{aq}[NO_3]^{m+1}_{aq}} \tag{4.4}$$

$$logK_{ex} = logD - nlog[CBCBGA]_{org} - mlog[H^+]_{aq} - (m+1)log[NO_3^-]_{aq} \tag{4.5}$$

The species with the subscripts‘aq.’ and‘org.’ refer to those in the aqueous phase and in the organic phase. The aqueous phases were consisted of $\sim$ 100 ppm of Cs (I) as cesium nitrate and CBCBGA concentration was varied while keeping other parameters fixed. The D_{Cs} values were calculated by taking the ratio of cesium concentration in organic phase and aqueous phase. It was observed that the D_{Cs} value increases with the increase in ligand concentration. The graph between the

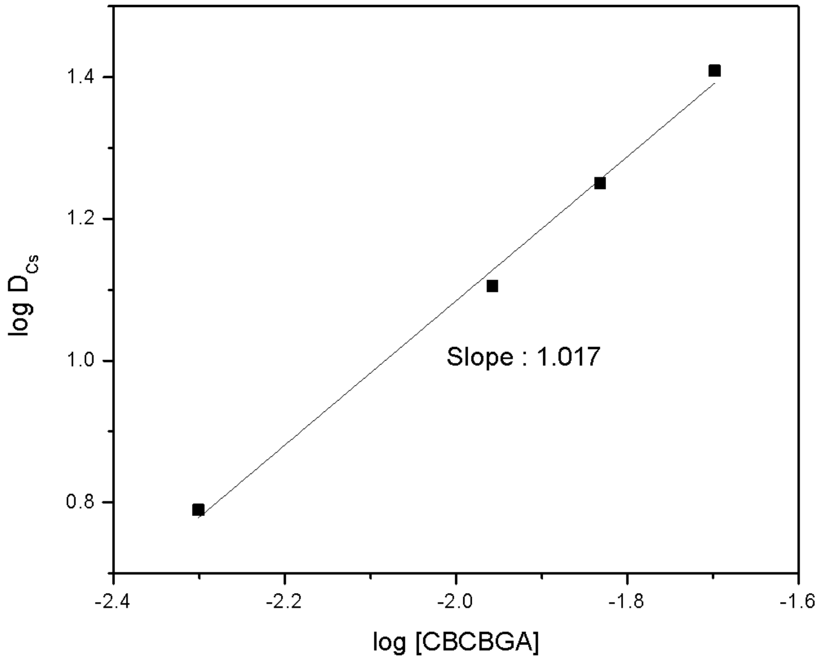

Figure 4.11: *Extraction dependency of cesium as a function of initial ligand concentration (Aqueous phase ∼ 100 ppm of cesium at 3.2 M nitric acid concentration and organic phase as 0.01 M CBCBGA in o-NPHE)*

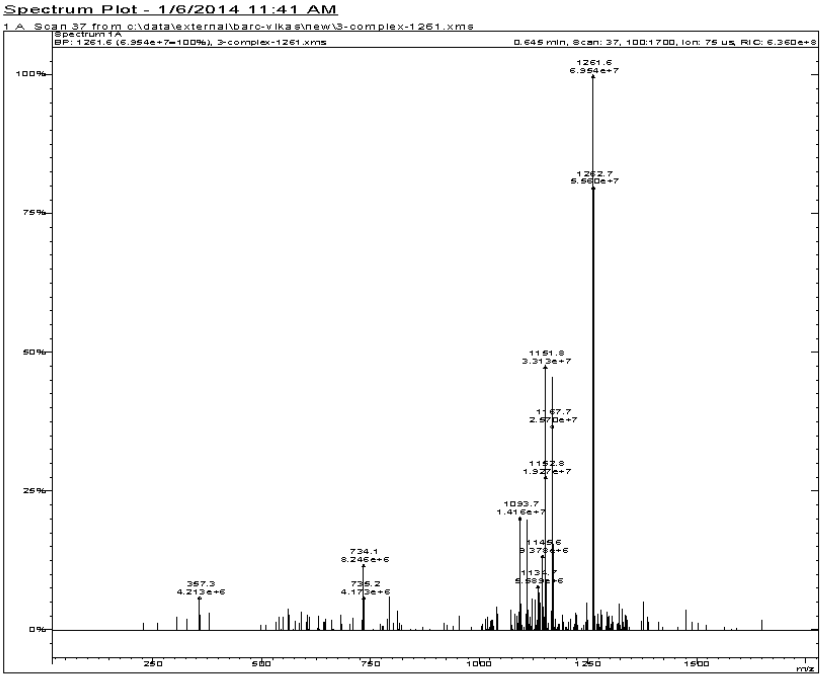

Figure 4.12: *ESI-MS spectra of 1,3- alternate Calix[4]arene-benzocrown-biglycolamide complexed with cesium*

logD_{Cs}, vs. log[CBCBGA] was plotted. From the Fig 4.11, Slope (n) of 1.017 suggests that one molecule of CBCBGA is participating in the extracted complex.

The same extracted complex was also analyzed with ESI-MS and the cesium binding at 1261.6, 1262.7 m/z were observed which further proves the 1:1 complex of Cs: CBCBGA in the extraction condition (Fig.4.12).

4.4.2 Effect of nitric acid concentration

The variation of the distribution ratio value with the feed acidity was studied using 0.01 M CBCBGA/o-NPHE as organic phase with the phase ratio 1:1 as shown in Fig.4.13. It was observed from Fig. 4.13 that at lower nitric acid concentration, increase in nitric acid favors extraction of cesium and this increase in D_{Cs} was up to ~ 3.2 M nitric acid and beyond this acidity the distribution ratio decresed, due to competitive extraction of H^+ ions. Dozol et. al. have reported D_{Cs} for different calix-crowns dissolved in o-NPHE, their values are comparable with our results [164]. It is important to note that in most of calix-crowns studied with o-NPHE diluent

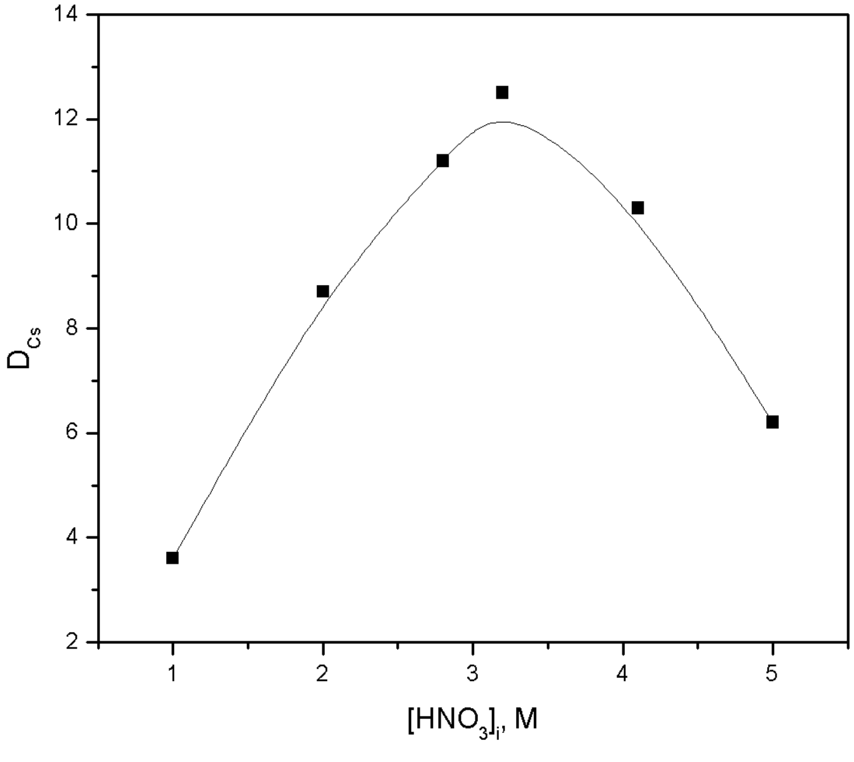

Figure 4.13: *Distribution coefficients of cesium as a function of initial nitric acid. (Organic phase 0.01 M CBCBGA in o-NPHE and aqueous phase ~ 100 ppm cesium with varying aqueous acidity)*

system the distribution ratios peak at 2 M nitric acid but in the present case this maxima is around 3 M nitric acid concentration with a D_{Cs} value of 12.5, due to presence of amidic groups in the molecule. These amidic provides intramolecular buffering effect to the molecule[165][166].

4.4.3 Effect of nitrate ion and extraction equation

In order to investigate the effect of counter ion during cesium extraction graph between D_{Cs} and $[NO3]^{-}_{ini.}$ was plotted. The initial concentration of feed solution was fixed to 1 M nitric acid to ensure a considerable distribution ratio (3.6) and then calculated the D_{Cs} with the increase of sodium nitrate concentration. It was observed from Fig 4.14, that there is no significant effect of nitrate ion on cesium extraction which is in contrary to other neutral extractants where a considerable effect of nitrate ion was present. This suggests that the nitrate ion is not participating in the complex formation. But for maintaining the charge neutrality the complex must contains the nitrate ion in the organic phase.

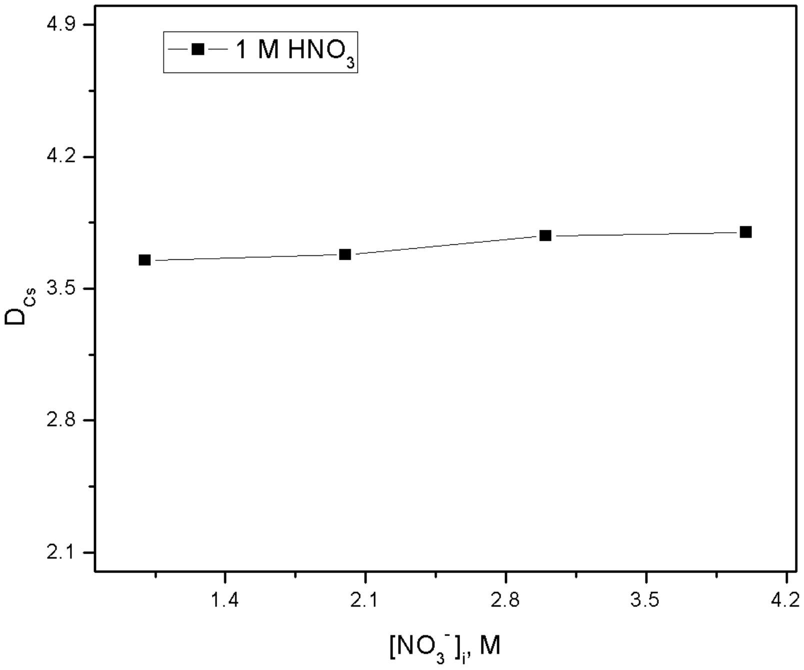

Figure 4.14: *Extraction dependency of cesium on initial nitrate ion concentration. Organic phase: 0.01 M CBCBGA and o-NPHE phase ; Aqueous phase : ∼ 100 ppm cesium in 1 M* HNO_3 *(fixed) +* $NaNO_3$.

4.4.4 Effect of diluents

The diluent plays an important role on extraction of metal ions. When an extractant molecule is dissolved in a particular diluent, the diluent molecule rearranges themselves around the extractant molecules by forming a solvation sphere. The CBCBGA being a polar molecule requires polar diluents for its dissolution prior to extraction process. These polar diluents like nitrobenzene, 1-octanol and o-NPHE etc. affect the extraction process by solvating the extracted complex in organic phase which depends on the their dielectric constant, dipole moment and H-bonding ability. The CBCBGA has limited solubility in aliphatic diluents like n-dodecane. Therefore, the role of diluents on extraction of cesium was investigated using different diluents. The distribution ratios of cesium were carried out with different diluents system at 3 M nitric acid concentration. The results are presented in table 4.1. The distribution constant was found to be highest with nitrobenzene and lowest with chloroform and follows the deceasing trend with decreasing dielectric constant of the diluents: nitrobenzene>o-NPHE>1-octanol>chloroform.

Table 4.1: *Effect of organic diluents on extraction of cesium. [CBCBGA]: 0.01 M.*

Diluent	**Dielectric Constant)**	**D_{Cs}(3 M HNO_3)**
Nitrobenzene	**34.8**	**15.7**
o-NPHE	**25.7**	**11.4**
1-octanol	**10.4**	**5.2**
Chloroform	**4.8**	**2.1**

4.4.5 Extraction of alkali metal ions

The amount of cesium present in HLW depends upon the burn-up of a nuclear reactor. In a typical high level waste from pressurized heavy water reactor (PHWR) with a burn-up of 6700 MWD/ton consists of 0.32 g/L of cesium. Generally, in HLW cesium is present along with very high concentration sodium with a lesser concentration of potassium and rubidium. Due to similarities in their chemical properties they compete with the extraction of cesium and thereby reduce the effectiveness of cesium extraction process. Therefore, the extraction of individual alkali metal ion dissolved in 3.0 M nitric acid was tested with 0.01 M CBCBGA/o-NPHE and the values are shown in Table 4.2. The results indicate very high selectivity of cesium extraction over sodium and potassium and relatively lesser for rubidium (S.F.Cs/Rb = 158).

Table 4.2: *Extraction of alkali metal ions, organic phase: 0.01 M CBCBGA/ o-NPHE: Aqueous phase: alkali metal ions (∼100 mg/L each) dissolved in 3.5 M HNO_3, O/A = 1).*

Metal ion	**D_M**	**Separation factor(S.F)**
Cs	**12.5**	–
Na	**< 0.005**	**> 3000**
K	**0.01**	**1250**
Rb	**0.08**	**158**

4.4.6 Selectivity

In order to study the extraction of cesium with respect to other metal ions, the extraction of cesium was carried out from simulated high level liquid waste solution (Table 4.3) using 0.01M CBCBGA /o-NPHE. The feed solution concentration of metal ions in Simulated High Level Waste (SHLW) is according to spent fuel of long-cooled pressurized heavy water reactor with a burn up of ∼ 6500 MWD/ton. Although CBCBGA contains two monoglycolamide units but its exhibits almost nil An/Ln extraction at this experimental conditions, this may be explained due to the large spacing between two monoglcolamide (MGA) units and non-fulfillment of the required An/Ln coordination numbers by a single bulky molecule. In general, 2-3 diglycolamides ligand are required to meet An/Ln coordination sphere. Here, it is difficult for three bulky ligands to come closer to participate in complex formation with An/Lns.

The results indicates that the cesium is having much higher distribution coefficient as compared to other metal ions present in simulated high level liquid waste, hence can be used a promising ligand for selective removal of cesium from the waste.

Table 4.3: *Distribution ratios of metal ions from simulated high level liquid waste solution.*

Element	**Conc.(ppm)**	$\mathbf{D}_M$
Cs	**100**	**12.5**
K	**220**	$\leqslant 10^{-2}$
Sr	**150**	$\leqslant 10^{-3}$
Am	**tracer**	$\leqslant 10^{-2}$
Mo	**250**	$\leqslant 10^{-2}$
Ce	**300**	$\leqslant 10^{-3}$
Nd	**60**	$\leqslant 10^{-3}$
Ba	**120**	$\leqslant 10^{-3}$
Na	**5000**	$\leqslant 10^{-2}$
Zr	**80**	$\leqslant 10^{-2}$

4.5 Computational Studies

The structure of free CBCBGA and its complexes with Cs^+ and Na^+ ions with nitrate ion has been optimized using hybrid Becke-Lee-Young-Parr (B3LYP) density functional[160][161] employing split-valence plus polarization (SVP) basis set as supplied in the TURBOMOLE suite of program[162][163]. The 46 core electron based effective core potentials (ECP) was used for Cs^+ ion. The free energy was computed at 298.15 K using B3LYP functional[167]. The hybrid B3LYP functional was shown to be quite successful in predicting the thermodynamic properties of Cs[168][169]. The solvent phase was accounted for using popular conductor like screening model (COSMO)[170]. The dielectric constant of water, nitrobenzene, NPHE, octanol and chloroform was taken to be 80, 34.81, 24.8, 11.8, and 4.81. The model complexation reaction was used as follows

$$M^+(H_2O)_{n(aq)} + NO_3^-{}_{aq} + CBCBGA_{org} \rightleftharpoons MNO_3.CBCBGA_{org} + nH_2O_{aq} \quad (4.6)$$

(M/n=Cs/8 and Na/6) The binding energy(B.E/ΔE_{ext})/ for the above complexation reaction can be evaluated as:

$$B.E = E_{MNO_3.CBCBGA(org)} + nE_{H_2O(aq)} - E_{M^+(H_2O)_{aq}} - E_{CBCBGA(org)} \tag{4.7}$$

where E is the total electronic energy of the respective chemical species in aqueous and organic phase.

4.5.1 Structural parameters

The minimum energy structure of free CBCBGA is displayed in Figure 4.15. From the figure it is seen that the CBCBGA offers a nice cavity to trap the metal ions inside it.

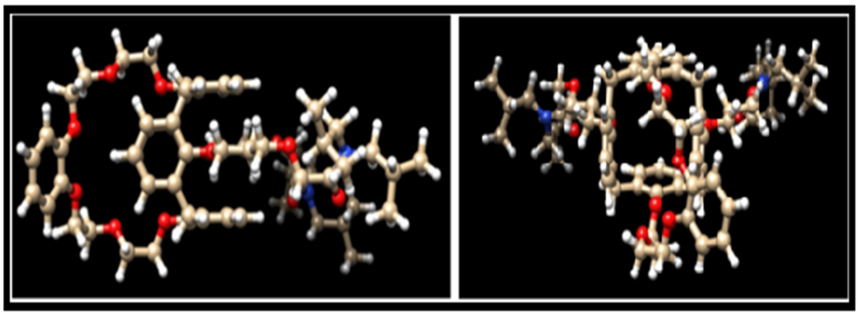

Figure 4.15: *Optimized structure of the free CBCBGA at the B3LYP/SVP level of theory. side view and top view.*

From the figure 4.16, it is seen that Cs^+ ion is coordinated to the 6 donor O atoms from the crown moiety and two donor atoms from one nitrate anion leading to 8-coordinated complex. The average Cs-O (O of crown moiety) bond distance is found to be 3.30 A^o which is longer than that of Cs-O (3.19 A^o) bond with nitrate O. Three donor O atoms of crown moiety was found to be coordinated from the top and three from the down as clearly shown in Figure 4.16. The optimized structure of complex of Na^+ with CBCBGA in the presence of nitrate ion is presented in Figure 4.17. From the figure 4.17 it is seen that Na^+ ion is coordinated to the 4 donor O atoms from the crown moiety and one donor atoms from one nitrate anion leading

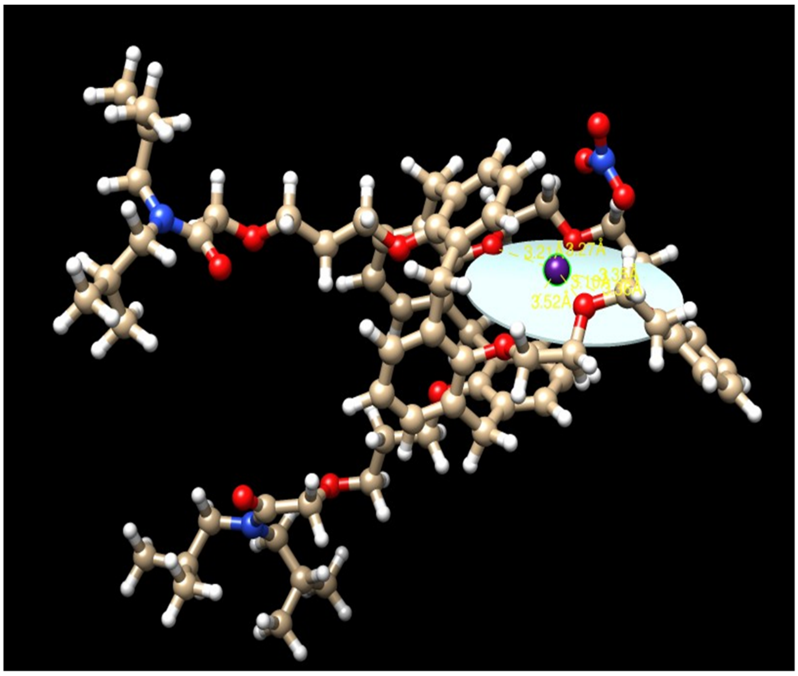

Figure 4.16: *Optimized structure of the complex of CBCBGA with Cs$^+$ at the B3LYP/SVP level of theory.*

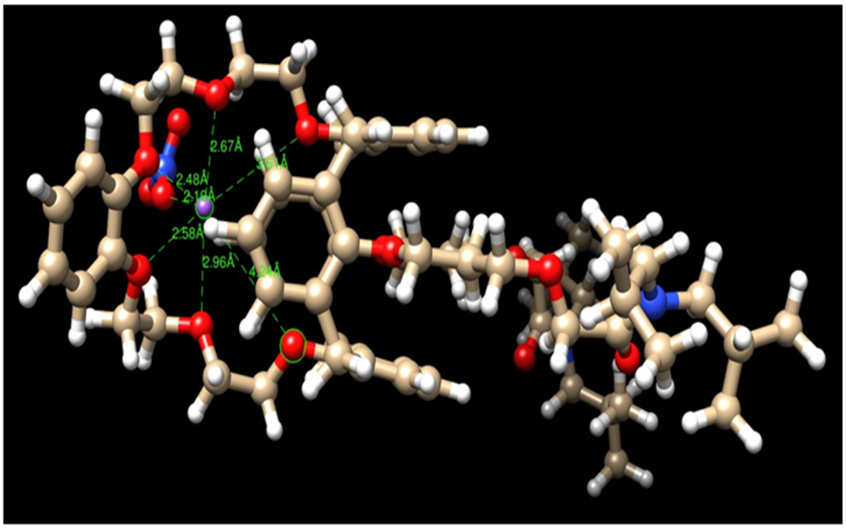

Figure 4.17: *Optimized structure of the complex of CBCBGA with Na$^+$ at the B3LYP/SVP level of theory*

to 5-coordinated complex. The average Na-O (O of crown moiety) bond distance is found to be 2.67 A^o which is longer than that of Na-O (2.19 A^o) bond with nitrate Oxygen.

4.5.2 Extraction energy during complexation

The free energy in the gas phase and solution phase was evaluated and are presented in Table 4.4. The coordination number for cesium and sodium was fixed to eight and six respectivelly as shown in equation 4.8 and equation 4.9.

$$Na^+(H_2O)_{6(aq)} + NO_3^-{}_{aq} + CBCBGA_{org} \rightleftharpoons NaNO_3.CBCBGA_{org} + 6H_2O_{aq} \quad (4.8)$$

$$Cs^+(H_2O)_{8(aq)} + NO_3^-{}_{aq} + CBCBGA_{org} \rightleftharpoons CsNO_3.CBCBGA_{org} + 8H_2O_{aq} \quad (4.9)$$

The free energy was found to be negative indicating highly exergonic nature of extraction complexation for both Cs^+ and Na^+ ions. The solution phase free energy of extraction was seen to be reduced considerably from their respective gas phase free energy due to the dielectric screening of the organic solvent. It is interesting to note that the gas phase free energy is seen to be higher with the Na^+ ion over Cs^+ ion as expected, because, the size of the Na^+ ion smaller than that of Cs^+ ion. Whereas the solution phase free energy for Cs^+ ion is found to be higher than that of Na^+ ion. The calculated value of difference in free energy, Δ ΔG (ΔGext, Cs^+ - ΔGext, Na^+) is found to be -9.49 kcal/mol, which is in good agreement with the experimentally determined value of -5.59 kcal/mol. The extraction free energy was found to be highest with nitrobenzene and lowest with chloroform for both the Cs^+ and Na^+ ions as observed in the solvent extraction experiments.

Table 4.4: *Calculated value of free energy in gas and solution phase at the B3LYP level of theory using SVP basis set*

Diluent	**Free energy (Na) Eq. 4.8**	**Free energy (Cs)Eq.4.9**
Gas	**-87.07**	**-81.52**
Nitrobenzene	**-16.68**	**-26.18**
o-Nitrophenyl hexyl ether	**-16.52**	**-25.98**
1-Octanol	**-15.64**	**-24.92**
Chloroform	**-14.11**	**-23.08**

In order to understand the type of interaction, the LUMO-HOMO energy gap for free ligand and metal ion was determined [171] and is given in Table4.5. The pictorial representation of HOMO and LUMO of CBCBGA ligand is displayed in Figure 4.18.

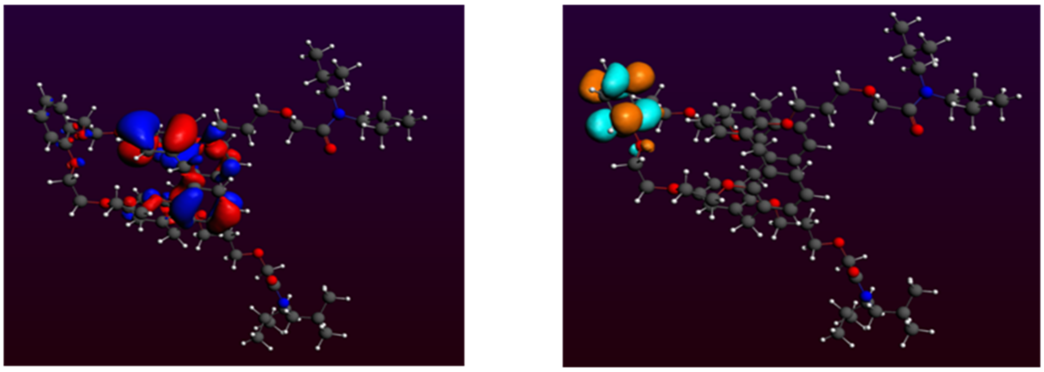

Figure 4.18: *Optimized structure of the complex of CBCBGA with* Na^+ *at the B3LYP/SVP level of theory.*

Table 4.5: *Calculated Quantum chemical descriptors in gas phase at the B3LYP/SVP level of theory.*

System	$\mathbf{E}_{LUMO-HOMO}$	η	χ	Δ**N**
Cs^+	**14.54**	**7.27**	**12.54**	**0.484**
Na^+	**32.26**	**16.13**	**23.02**	**0.536**
CBCBGA	**5.62**	**2.81**	**2.76**	–

The ionophore studied here represents the class of hard base because of hard O donor which is evident from the high value of $E_{LUMO-HOMO}$, χ and η. Further, the amount of charge transfer, ΔN ($\Delta N = (\chi_M - \chi_L) / 2(\eta_M + \eta_L)$, Here, M stands for metal ion, which acts as Lewis acid i.e. acceptor and L stands for the ionophore i.e. CBCBGA, which acts as Lewis base i.e. donor.)[172] was also calculated for the donor acceptor complexation and the values are listed in Table 4.5. The high metal-ionophore interaction can be correlated with the higher value of charge transfer, ΔN. Here, the value of ΔN was seen to be quite high indicating strong interaction. Furthermore, the value of ΔN is seen to be higher with the Na^+ ion over Cs^+ ion.which is well correlated with the gas phase free energy values. The calculated molecular electrostatic potential (Figure 4.19) clearly demonstrate the site for binding of the metal ions within the crown cavity.

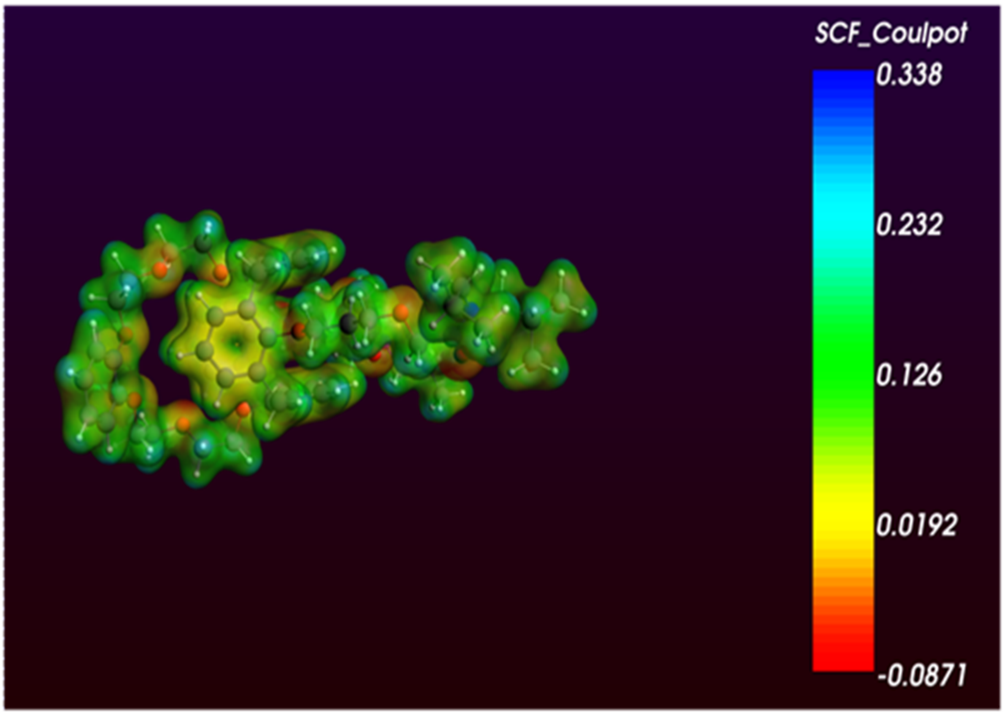

Figure 4.19: *Calculated molecular electrostatic potential of the CBCBGA ionophore at the B3LYP/DZP level of theory.*

The charge transfer was calculated using natural population analysis [173]. The residual charge on the Na^+ ion was found to be 0.900 whereas it was 0.906 for Cs^+ ion. The transfer of charge is found to be marginally higher for Na^+ compared to Cs^+ as evident from the value from Natural population analysis suggesting the higher binding energy for Na^+ ion compared to Cs^+ ion in gas phase.

4.5.3 Second Order Bonding Analysis

Natural bond order (NBO) analysis program NBO6.0 [174][175] was used to evaluate the second order stabilization energy to investigate the unusually high selectivity of Cs^+ over Na^+ ion towards CBCBGA at the B3LYP/DZP level of theory. The second-order interaction energies $E_{ij}^{(2)}$ indicate the strength of the metal ion-ionophore coordinated interactions. The second order stabilization energy $E_{ij}^{(2)}$ is defined as

$$E_{ij}^{(2)} = \frac{q_i.F_{ij}^2}{\varepsilon_i - \varepsilon_j} \tag{4.10}$$

where, q_i, $\varepsilon_{\ i}$, $\varepsilon_{\ j}$ and F_{ij}^2 represent the donor orbital occupancy, diagonal elements (orbital energies), and off-diagonal NBO Fock matrix element respectively. The strong donor-acceptor interaction is reflected in the large value of stabilization energy. The calculated value of $E_{ij}^{(2)}$ for Cs^+ ion was found to be 1.42 kcal/mol whereas for Na^+ ion it was 1.15 kcal/mol as shown in table 4.6. The stabilization energy for Cs^+ ion with CBCBGA was found to be higher compared to its corresponding Na^+ ion complex whereas, the gas phase free energy follows the reverse trend. For this reason, second order stabilization energy might not be helpful for the forecast of selectivity in the solution phase.

4.5.4 Bond Critical Points

The bond critical point (BCP) analysis are commonly used to measure the strength of the bond between the metal ion and the donor atom of the ionophore. Hence, the electron density at the BCP, ρ and the Laplacian of electron density, $\nabla^2\rho$ for metal ion-ionophore systems are evaluated using the atom in molecule methods [176]. The higher the value of ρ stronger is the bond, whereas, the negative value of $\nabla^2\rho$ points to covalent bond and positive value points to ionic, coordinated, hydrogen bond or Van der Waals type of interaction. The ellipticity (ε) parameter measures the cylindrical symmetry of the bond. The calculated values of ρ, $\nabla^2\rho$ and ε are presented in Table 4.7. The higher value of charge density for Na^+ ion over Cs^+ ion reflects the stronger interaction with the former than the later ion and is well correlated to the higher complexion free energy of Na^+ ion than Cs^+ ion in gas phase. The calculated positive values of $\nabla^2\rho$ demonstrate that the interaction of Na^+ and Cs^+ ions with O donor atoms of the ionophore are of closed-shell type. The small values of ρ, $\nabla^2\rho$ and ε, indicate little covalency in the bonding and the covalency is slightly higher for Cs^+ ion. The very low value of ε suggests that the deviation from cylindrical symmetry is not significant. Furthermore, the values of ρ,

Table 4.6: *Calculated Quantum chemical descriptors in gas phase at the B3LYP/SVP level of theory.*

Donar nbo (i)	**Accepter nbo (j)**	E(2) (kcal/mol)
LP(1)O1	**LV(1)Cs179**	**0.68**
LP(1)O3	**LV(1)Cs179**	**2.02**
LP(2)O3	**LV(1)Cs179**	**0.32**
LP(1)O5	**LV(1)Cs179**	**1.02**
LP(2)O5	**LV(1)Cs179**	**0.10**
LP(1)O6	**LV(1)Cs179**	**2.81**
LP(2)O6	**LV(1)Cs179**	**0.22**
LP(1)O7	**LV(1)Cs179**	**0.91**
LP(2)O7	**LV(1)Cs179**	**0.48**
LP(1)O8	**LV(1)Cs179**	**0.94**
LP(2)O8	**LV(1)Cs179**	**0.07**
LP(1)O13	**LV(1)Cs179**	**1.82**
LP(1)O14	**LV(1)Cs179**	**6.49**
LP(2)O14	**LV(1)Cs179**	**0.36**
LP(3)O14	**LV(1)Cs179**	**0.30**
LP(1)O15	**LV(1)Cs179**	**6.03**
LP(2)O15	**LV(1)Cs179**	**0.47**
LP(3)O15	**LV(1)Cs179**	**0.56**
Donar nbo (i)	**Accepter nbo (j)**	**E(2) (kcal/mol)**
LP(1)O69	(1)Na87	**1.00**
LP(2)O69	**LV(1)Na87**	**0.14**
LP(1)O70	**LV(1)Na87**	**2.27**
LP(1)O71	**LV(1)Na87**	**0.67**
LP(2)O71	**LV(1)Na87**	**0.23**
LP(1)O74	**LV(1)Na87**	**1.42**
LP(2)O74	**LV(1)Na87**	**0.07**
LP(1)O75	**LV(1)Na87**	**2.00**
LP(1)O76	**LV(1)Na87**	**0.84**
LP(1)O81	**LV(1)Na87**	**3.91**
LP(2)O81	**LV(1)Na87**	**0.12**
LP(1)O82	**LV(1)Na87**	**2.93**
LP(2)O82	**LV(1)Na87**	**0.09**
LP(1)O83	**LV(1)Na87**	**1.67**

Table 4.7: *Calculated values of the average electron density and Laplacian of electron density and ellipticity at B3LYP/DZP level of theory using Baders AIM calculation*

Complex	**BCP**	ρ	$\nabla^2\rho$	ε**=**λ**1/**λ**2-1**
Cs^+-CBCBGA	**Cs-O**	**0.008**	**0.039**	**0.069**
Na^+-CBCBGA	**Na-O**	**0.012**	**0.079**	**0.062**
Cs^+-$(H_2O)_8$	**Cs-O**	**0.008**	**0.031**	**0.078**
Na^+-$(H_2O)_6$	**Na-O**	**0.015**	**0.096**	**0.055**

$\nabla^2\rho$ and ε for the hydrated metal ion cluster are also evaluated to study the nature of bonding in hydrated cluster. The calculated electron density, ρ at the BCP for 8 Cs-O bonds and 6 Na-O bond are found to be almost equal, thought it is much higher for Na-O bond over Cs-O bond. Whereas, ρ at the BCP for 8 Cs-O bonds and 5 Na-O bond are found to be dissimilar. It is worthwhile to mention that the values of ρ and $\nabla^2\rho$ for hydrated Na^+ ion are reduced during complexation with CBCBGA, whereas for hydrated Cs^+ ion though ρ remains same, the value of $\nabla^2\rho$ is increased. Therefore, the increased bond strength might be responsible for the higher selectivity of Cs^+ ion over Na^+ ion towards novel CBCBGA ionophore.

4.6 Conclusions

Combined experimental and density functional theoretical studies were conducted to understand the unusually high selectivity of the Cs^+ ion over Na^+ ion towards Calix-benzo-crown-6 bisglycolamide (CBCBGA) ionophore. The CBCBGA ionophore in 1, 3-alternate conformation has been synthesized and characterized by using ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis. The effect of various parameters like feed acidity, CBCBGA concentration and nitrate ion were studied to determine the stoichiometry of extracted complex. The slope analysis method reveals that 1:1:1 molar ratio for $CsNO_3$: CBCBGA: HNO_3 in the extracted complex. The CBCBGA molecule is found to serve a highly selective ionophore for cesium over other metal ions present in simulated high level liquid waste solution. The present DFT predicts the exergonic nature of complexation in the gas phase as well as solution phase for the complexation of Cs^+ and Na^+ ions with CBCBGA as observed in the experiments. The calculated value of difference in free energy, ΔΔG (ΔGext,Cs^+ - ΔGext,Na^+) is found to be -9.46 kcal/mol, which is in good agreement with the experimentally determined value of -5.59 kcal/mol. The extraction free energy was found to be highest with nitrobenzene and lowest with chloroform for both the Cs^+ and Na^+ ions as observed in the solvent extraction experiments. The free energy of extraction was seen to be increased with increase dielectric constant of the organic solvents as observed in the solvent extraction experiments. The calculated electron density, ρ at the BCP for 8 Cs-O bonds and 6 Na-O bonds are found to be almost equal, thought it is much higher for Na-O bond over Cs-O bond. Whereas, ρ at the BCP for 8 Cs-O bonds and 5 Na-O bonds are found to be dissimilar. It is worthwhile to mention that the values of ρ and $\nabla^2\rho$ for hydrated Na^+ ion are reduced during complexation with CBCBGA, whereas for hydrated Cs+ ion though remains same, the value of $\nabla^2\rho$ is increased. Therefore, the increased bond strength seems to play decisive role for the higher selectivity of Cs^+ ion over Na^+ ion towards CBCBGA ionophore. A corroborated experimental and theoretical studies were very helpful to understand the unusually high selectivity of Cs^+ ion over Na^+ ion towards the new CBCBGA ionophore which shows promise for the selective extraction of Cs^+ ion from the radioactive waste.

5. Process development for separation of cesium from acidic nuclear waste solution using CC-6

5.1 Introduction

Safe management of high level radioactive waste (HLW) solution is one of the most important technological challenges faced by the nuclear industries. Development of efficient separation processes for removal of harmful radiotoxic elements from waste solutions will be the key for success and public acceptance of nuclear energy program. The toxicity of the waste is mainly due to the presence of unrecovered U and Pu, long-lived minor actinides such as Np, Am, Cm and long lived radioactive fission products, mainly, ^{99}Tc, ^{129}I and an isotope of cesium (^{135}Cs). Removal of residual Uranium and Plutonium from the waste can be done by employing TBP solvent. Actinide partitioning and Transmutation (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 high energy flux reactors. It is known that, ^{137}Cs ($t_{1/2}$ = 30.1 years) and ^{90}Sr ($t_{1/2}$ = 28.9 years) are the major nuclides contributing largely to heat and radiation load of HLW in the near term and ^{135}Cs ($t_{1/2}$ = 2.3x10^6 years), ^{99}Tc and ^{129}I have a long term impact on environment due to their mobility in repository [177][178]. In the present HLW treatment strategy, it is planned to separate ^{137}Cs and ^{90}Sr from HLW prior to actinide partitioning in order to reduce radiation exposure to working personnel. Removal of ^{137}Cs and ^{90}Sr provides several advantages, like, significant reduction in cooling requirement of the waste solution, reduction in surveillance time of suface stored vitrified waste before disposal in geological formation, increases the stability of vitrified waste which results in increase in capacity of geological repository, facilitates the handling and transport of waste. The separated ^{137}Cs can be used as gamma source in medical and industrial applications. It is, therefore, imperative to develop an efficient separation process for recovery of cesium from HLW. In fact, its selective separation from HLW solution, containing large content of sodium and other competing ions, has long been one of the most challenging tasks [179] [180].

The calix [4] arene-crown-6 class of ethers are one of the most widely investigated class of calix-crown ring system for their application as host molecules for selective separation of cesium ion from acidic and alkaline nuclear waste solutions [181]. These calix-crown-6 ethers, when fixed in 1, 3 alternated conformation possess a cavity which is highly complementary to cesium ion and serve as potential extractants for selective separation of cesium ion in liquid-liquid extraction processes from solution containing large amounts of Na^+, H^+ and other metal ions. This property has enabled their exploitation in selective separation of radioactive cesium from acidic nuclear fuel reprocessing solutions containing much large amount of sodium compared to cesium. However, difficulty in synthesis of calix-crown-6 molecules at larger scale and their incompatibility with PUREX based diluents (n-dodecane) complicates the development of a process for separation of cesium from HLW on an industrial scale [182]. In an effort to recover cesium from HLW solution, we have successfully synthesized 1,3-dioctyloxy calix[4]arene-crown-6 at larger scale indigenously and also developed diluent system based on n-dodecane and isodecyl alcohol, which is existing tested diluent system employed in the on-going program on separation of minor actinides and strontium from HLW solution [184][185].

The multistage counter-current operation needed for solvent-extraction flowsheets requires the Mixer-Settlar device, which ordinarily consisted of two parts: a mixer for contacting the two liquid phases to bring about mass transfer, and a settler for their mechanical separation. The mixer and settler can be integral or separate and the operation may be continuous or batch wise. Mixer-settler can process hundreds of cubic meters of gallon per hour. The traditional mixer-settler has advantages in terms of high stage efficiency, can handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquid with high viscosity. Further improvements made at Savannah River Laboratory (SRL) results in a new contractor which is based upon the centrifugal force difference between two phases. This type of contractor has advantage like short contact time for unstable material, compact space required, handles systems with little liquid density difference, high throughput and high extraction efficiency [186][187]. The various processes for cesium recovery were developed which based on centrifugal contractor has been discussed below:

The caustic side extraction (CSEX) process developed at Oak Ridge National Laboratory for cesium recovery from of Savannah River Site high level tank solution. Three flow-sheet cases, corresponding to an 18-stage, a 20-stage, and a 22-stage (25-cm centrifugal contactor) process were evaluated. The final optimized process includes the ten stages extraction using 0.01 M BOBCalixC6/1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butyIphenoxy)-2-propanol (”Cs7SBT”), 0.50 M/ trioctylamine , 0.001 M, and the aliphatic diluents Isopar L (O/A of 0.5), two stages scrubbing (0.05 M $HN0_3$, O/A = 5), and ten stages stripping in (0.001 M HNO_3, O/A of 3) . The process exhibits a decontamination factor of 40,000 and a cesium concentration factor of 12 without affecting hydrodynamics and stage efficiency.[188]

In an another process for cesium recovery was developed which was based on 6 stages extraction, 2 stages scrubbing and 7 stages stripping in centrifugal contractors. The extraction was done using 0.025 mol/L iPr-C[4]C-6-n-octanol and strping 0.005 M nitric acid solution. The extraction and stripping percentage from simulated HLLW is 99.5 % , 99.2 % respectively [189].

This chapter presents the development of a new process for selective separation of cesium from acidic nuclear waste solution using 1,3-dioctyloxycalix[4]arene-crown-6 (CC6)/n-dodecane modified with isodecyl alcohol. The process solvent was optimized as 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane for efficient recovery of cesium. Extraction studies were corried out with the optimized solvent and the results were used to design a solvent extraction flow-sheet. Counter-current mixer-settler experiments with four extraction, two scrubbing and four stripping stages are reported.

5.2 Experimental

5.2.1 Chemicals, isotopes and solutions

CC6 was synthesized by the procedure discussed in chapter 1. n-dodecane (99.9%) and isodecyl alcohol (99.0%) were obtained locally and used as received. Stock solutions of radiotracers ^{134}Cs, ^{241}Am, Pu^{4+} (mainly ^{239}Pu), uranyl nitrate and inactive metal salts were used to prepare simulated waste solution. Basic Brockman I activated alumina of pore size 58 A^{o} and average mesh size of 150 was used for purification of irradiated solvent. The composition of simulated HLW (SHLW) solution as listed in Table 5.3 corresponds to first cycle raffinate from reprocessing of long-cooled pressurized heavy water reactor fuel with a burn up of $\sim$ 6500 MWD/tonne.

5.2.2 Mixer-settler configuration

Mixer-settler unit of rectangular shape were made up of acrylic polymer. The mixer volume and settler volume were of 30 ml and 130 ml respectively. Valve less metering pumps of adjustable flow rates were used with flow accuracy of ± 5 %. The turbine with six blades at bottom with the top shrouded has been used for stirring . To avoid vortex the mixer compartment is suitably deigned with baffle of proper dimensions.

5.2.3 Distribution ratio measurements

For the determination of distribution ratio (D$_{M}$), equal volume of organic phase constituted with CC6, isodecyl alcohol/n-dodecane and aqueous phase containing metal ions was equilibrated for 10 minutes in a 5 mL glass vial. After phase separation by centrifugation, the organic and aqueous phases were separated and analyzed for metal ions, the D$_{M}$ was calculated as the ratio of concentration (or radioactivity) of metal ion in the organic phase to that of the aqueous phase. All the extraction experiments were carried out in a thermostated water bath maintained at temperature 25±1^{o}C. Radiometricassay of ^{134}Cs, ^{85,} ^{89}Sr and ^{241}Am, was carried out by gamma counting employing an intrinsic Ge detector connected to 4K MCA at 604.7 keV, 511 keV and 60 keV respectively. Plutonium was analyzed by alpha counting using ZnS/Ag scintillation counter and uranium by spectrophotometry using bromo-PADAP as chromogenic agent [190]. Cesium in SHLW was analyzed by tracer technique[191] by using ^{134}Cs tracer and inactive metal ions of SHLW were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) of Horiba Jobin-Yvon make. Estimation of rubidium was carried out by ion chromatography, using Dionex ICS 1600 device. The nitric acid concentrations of aqueous and organic phases were determined by potentiometric titration, using a Metrohm 905 Titrandowith NaOH solution of 0.1 M concentration. It was ensured that the mass balance calculation has a maximum error of ± 5 % for all the techniques employed for analysis.

5.3 Results and discussion

5.3.1 Process solvent composition selection

Preliminary studies on dissolution of CC6 in n-dodecane at 25 ±1^{o}C has shown that a solution up to 0.03 M is stable for more than two months, above this concentration dissolution assisted by sonication was employed, however after standing for 48 hours, a powdery white solid precipitated out. CC6 was found to have good solubility in isodecyl alcohol + n-dodecane mixture, the solubility increases with increase in isodecyl alcohol content in the mixture. Extraction of cesium with CC6 + isodecyl alcohol/n-dodecane solutions was carried out and the results in variation of D_{Cs} as a function of isodecyl alcohol concentration at different CC6 molarities (0.01-0.03 M) were shown in Fig5.1

There was almost no extraction of cesium when CC6 was dissolved only in n-dodecane, extraction was observed only on addition of isodecyl alcohol to the solvent. Extraction of cesium increases with increase in concentration of isodecyl alcohol for all the concentrations of CC6. Isodecyl alcohol, being a polar molecule, helps in

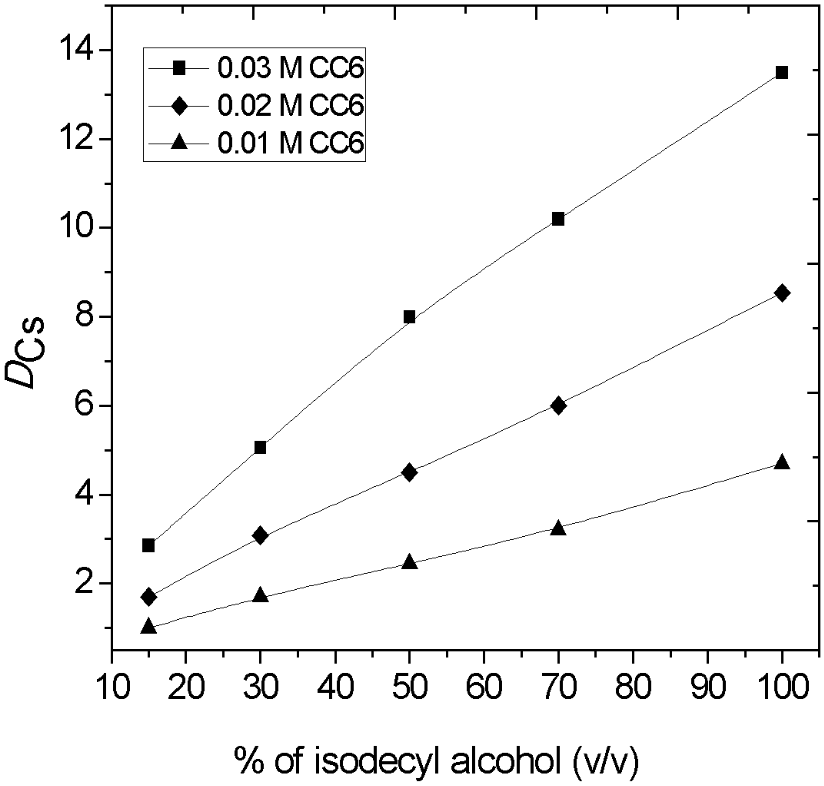

Figure 5.1: *Variation of D_{Cs} with isodecyl alcohol concentration (% v/v). Organic phase: CC6 + isodecyl alcohol/n-dodecane; aqueous phase: 3.5 M HNO_3.*

solvating the polar calix-crown-cesium complex, therefore, with increase in isodecyl alcohol concentration, D_{Cs} increases. From the results, it is clear that a higher concentration of isodecyl alcohol is more suitable for effective extraction of cesium. However, isodecyl alcohol, will itself has a finite extraction of nitric acid which is to be considered while optimizing the concentration of isodecyl alcohol, as high nitric acid extraction by solvent is undesirable for stripping processes. Fig 5.2 shows the acid uptake by isodecyl alcohol/n-dodecane at varying concentrations of isodecyl alcohol in the absence and presence of CC6 (0.3 M). As seen from the Fig. 5.2, both isodecyl alcohol and CC6 have finite extraction of nitric acid. Though, the acid uptake increases with increase in isodecyl alcohol concentration, but it did not contribute significantly to the acidity of the solvent so as to affect the stripping process. Therefore, concentration of isodecyl alcohol was chosen on the basis of our previous experience.A process developed in our laboratory for actinide partitioning

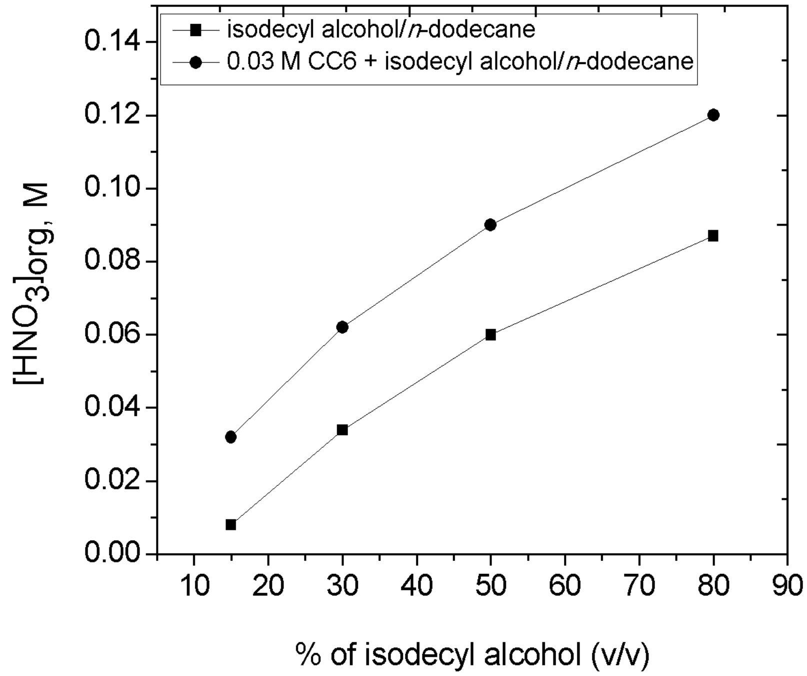

Figure 5.2: *Extraction of nitric acid at different concentrations of isodecyl alcohol. Organic phase: isodecyl alcohol/n-dodecane & 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane; aqueous phase: 3.5 M HNO_3.*

uses 30% isodecyl alcohol/n-dodecane diluent. Therefore, to maintain compatibility of process solvents, same diluent system was used in the present process. For efficient extraction and stripping at desired acidities, 0.03 M CC6 dissolved in 30 % isodecyl alcohol/n-dodecane was considered as appropriate process solvent. This solvent did not show any third phase formation on repeated contact with SHLW solution.

5.3.2 Extraction of cesium

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 was attained within 5 minutes, thereafter, D_{Cs} remains constant for a given condition. To determine the composition of extracted species, the dependence of D_{Cs} on the initial concentrations of HNO_3, NO_3^- and CC6 was studied. The relation between D_{Cs} and HNO_{3ini} concentration for 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane is shown in Fig.35.3. A very small increase in D_{Cs} was observed in lower region of nitric acid, up to 1 M nitric acid concentration D_{Cs} was 0.58, and above it the increase was significant up to 6 M nitric acid ($D_{Cs} \sim 6.6$) and then decreases with further increase in nitric acid concentration.

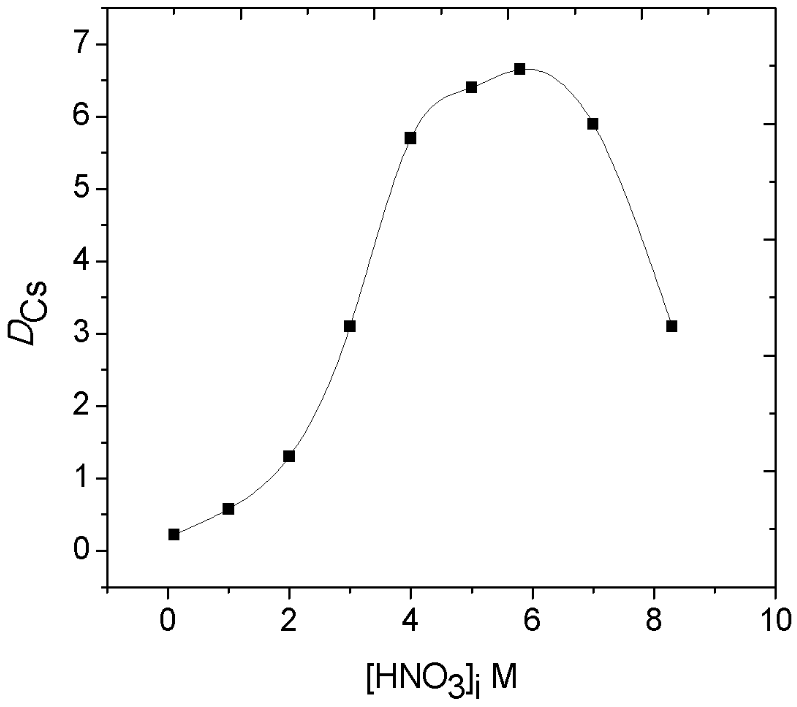

Figure 5.3: *Extraction dependency of cesium on initial nitric acid concentration. Organic phase: 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane; aqueous phase: 0.1 M–8.3 M* HNO_3

Thus, indicating a significant role of nitric acid in extraction process. The acid dependency on the extraction of cesium was determined from nitric acid solutions of constant nitrate concentrations or at fixed ionic strength of 4.0 M (H, Na) NO_3 (Fig.5.4).

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 favours the formation of organic soluble $Cs^+.CC6.HNO_3$ adduct, thus, resulting in increase in D_{Cs}. However, beyond 6 M nitric acid, the competitive extraction of nitric acid by CC6 is attributed to decrease in D_{Cs}. It was also proved by measuring $D(HNO_3)$ with increase in cesium concentration in aqueous medium. $D(HNO_3)$ was found to increase with increase in cesium concentration as shown in Table 5.1.

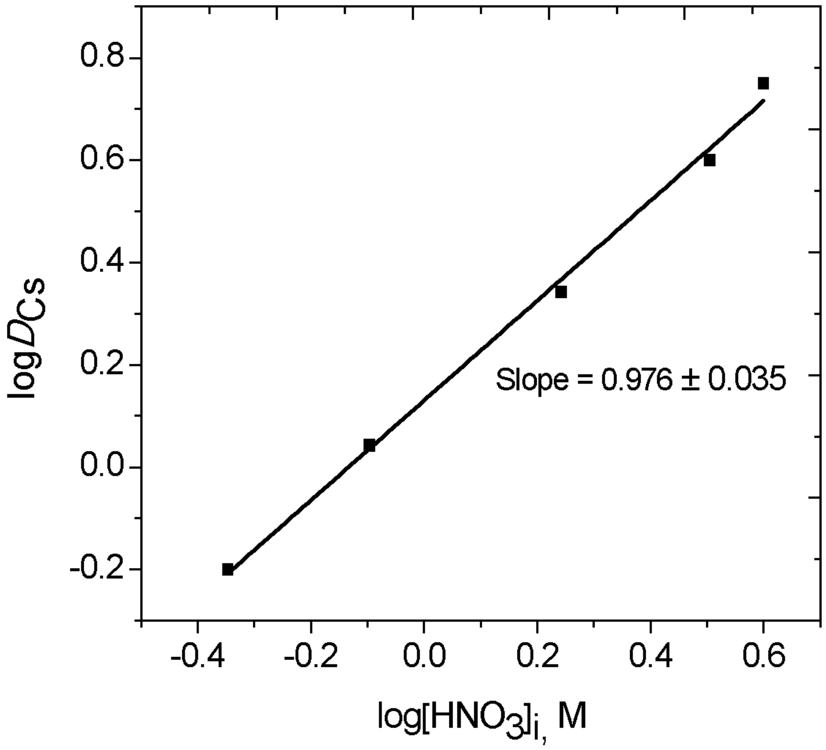

Figure 5.4: *Extraction dependency of cesium on initial nitric acid concentration in a fixed ionic strength medium. Organic phase: 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane; aqueous phase: 4.0 M (H+ Na) NO_3.*

It is interesting to note that extraction of cesium is almost negligible at lower nitric acid concentrations ($\leq$ 0.1 M), therefore this important property is used for stripping cesium with deionized water.

5.3.3 Stoichiometry of the extracted metal complex

The interpretation of the stoichiometry of the extracted metal complex in solvent extraction process is fairly given by the slope analysis method. The extractant

Table 5.1: *Dependence of D_{HNO_3} on cesium concentration Organic phase: 0.03 M CC6 + 30% isodecyl alcohol / n-dodecane, Aqueous phase: HNO_3 = 3.5 M, O/A = 1*

[Cs] mM in aqueous phase	**D (HNO_3**
0	**0.02**
1	**0.02**
10	**0.034**
100	**0.032**

dependency data for extraction of cesium from 3.5 M nitric acid at constant isodecyl alcohol concentration of 30 % (v/v) is shown in Fig.5.5.

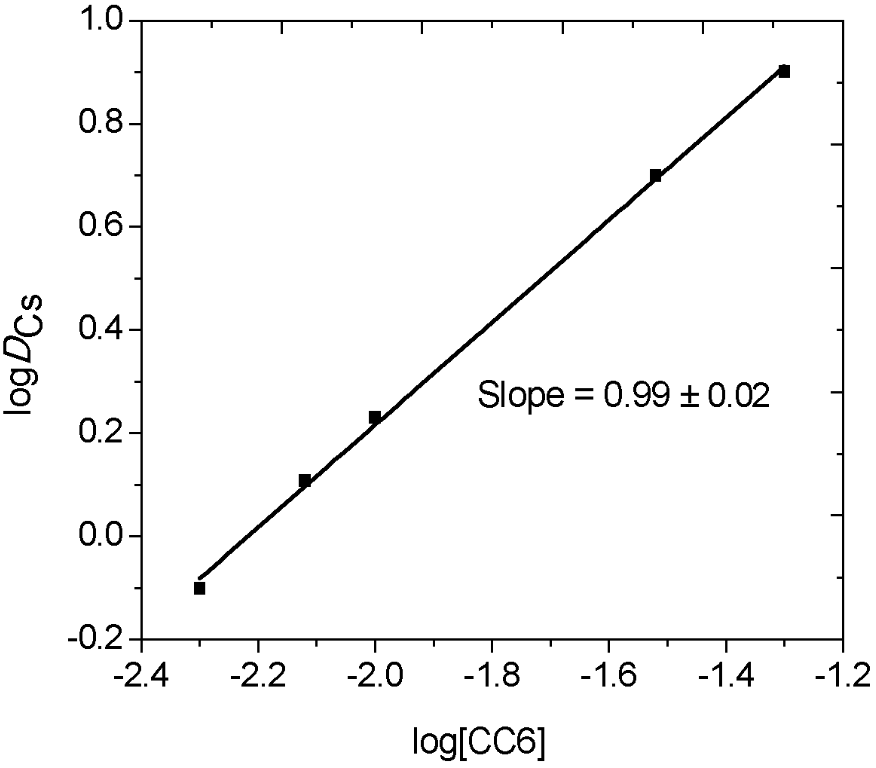

Figure 5.5: *Extractant dependency of D_{Cs}. Organic phase: (0.005–0.05 M) CC6 + 30 % isodecyl alcohol/n-dodecane; aqueous phase: 3.5 M Nitric acid*

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 as disscussed in previous chapters. Role of counter anion on the extraction mechanism was determined from the plots of D_{Cs} vs.$[NO3]_{initi}$ (Fig.5.6) at constant initial nitric acid concentrations. The results show no change in D_{Cs} with increase in nitrate ion concentration.

Variation of D_{Cs} with cesium concentration as shown in Fig.5.7 was studied for the solvent 0.03 M CC6 + 30 % isodecyl alcohol/n-dodecane. D_{Cs} remains nearly constant up to 8 mM (1072 mg/L) of cesium, thereafter, D_{Cs} decreases with increase in cesium concentration and sharp decrease was observed when the cesium in the aqueous phase was higher than 12 mM. At 90 mM cesium, D_{Cs} obtained was 0.55 which corresponds to extraction of about 0.032 M cesium in the organic phase, this

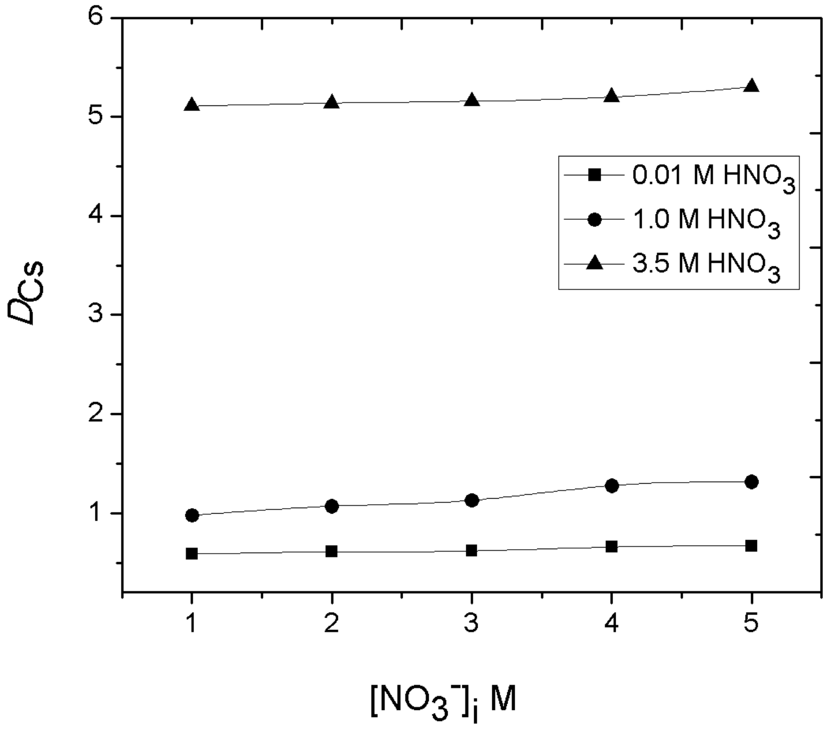

Figure 5.6: *Extraction dependency of cesium on initial nitrate ion concentration at fixed nitric acid concentration. Organic phase: 0.03 M CC6 + 30 % isodecyl alcohol/n-dodecane; aqueous phase: 1 M–5 M $NaNO_3$ at 0.01, 1.0, and 3.5 M HNO_3.*

value remained unchanged even at higher concentration of cesium in the aqueous phase. The reason for this is the stoichiometry limit of 1:1 between cesium and CC6.

5.4 Extraction of alkali metal ions

Usually in high level waste, cesium is present along with very high concentration of sodium and to a lesser concentration of potassium and rubidium. Due to similarities in their chemical properties they compete with the extraction of cesium and thereby reduce the efficiency of cesium extraction process. Therefore, the extraction of individual alkali metal ion dissolved in 3.5 M nitric acid was tested with 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane and the values are shown in Table 5.2. The results indicate very high selectivity of cesium extraction over sodium and potassium and relatively lesser for rubidium (S.FCs/Rb∼ 100).

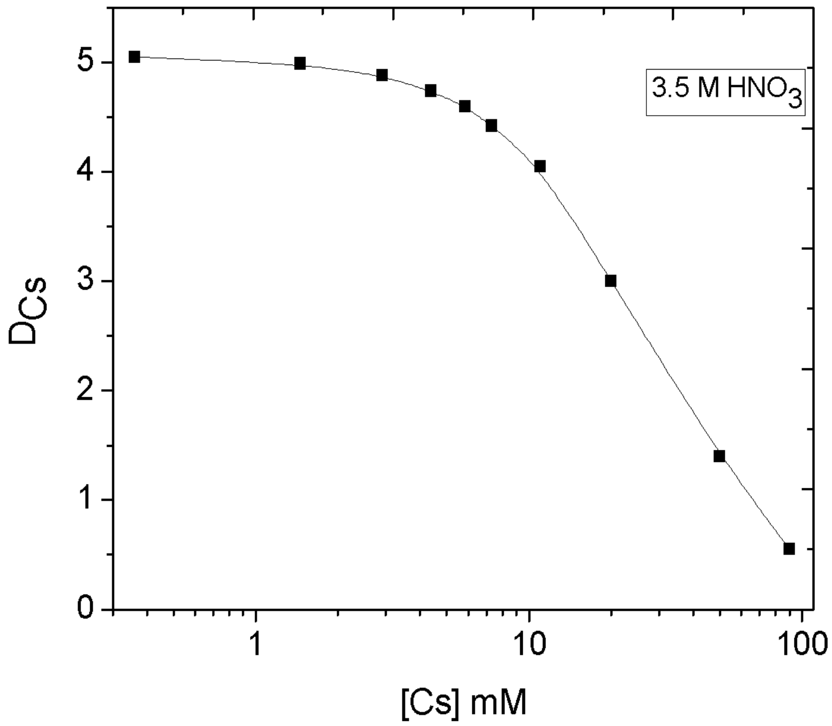

Figure 5.7: *Effect of cesium concentration of aqueous phase on D_{Cs}. Organic phase: 0.03 M CC6 + 30 % isodecyl alcohol/n-dodecane; aqueous phase: 0.3690 mM Csdissolved in 3.5 M nitric acid*

5.5 Batch extraction test of cesium from SHLW solution

The extraction behavior of cesium and other metal ions present in SHLW solution was investigated using 0.03 M CC6 + 30 % isodecyl alcohol/n-dodecane. Rubidium was not present in our actual waste, therefore, it was not added in the preparation of SHLW. The distribution ratios of all the elements (D_M) and separation factors with respect to cesium are tabulated in Table 5.3. The results showed that D_{Cs}

Table 5.2: *Extraction of alkali metal ions Organic phase: 0.03 M CC6 + 30% isodecyl alcohol/ n-dodecane, Aqueous phase: Alkali metal ions (~ 100 mg/L each) dissolved in 3.5 M HNO_3, O/A = 1*

Metal ions	**D_M**	**Separation factor**
Na	**< 0.001**	**> 5100**
K	**.012**	**425**
Rb	**0.04**	**128**
Cs	**5.3**	**–**

is much larger compared to other elements, thus, indicating a very high selectivity for cesium extraction over other elements. Separation factor of more than 500 was obtained for Na, K, Sr, Ba, Fe, Lns, U, Pu, Am, Al and other elements (Mo, Zr, Ru, K) showed S.F. of more than 200.

Table 5.3: *Extraction of metal ions from simulated high level liquid waste solution Organic phase: 0.01M Calix-crown/30 % phase modifiers/n-dodecane. Aqueous phase: Simulated high level liquid waste solution, $HNO_3 = 3.5$ M*

Element	**Conc.(ppm)**	**D_M**	**Separation factor(S.F)**
Cs	**310**	**5.2**	–
Sr	**60**	**1.0E-04**	**52000**
Mo	**130**	**2.0E-02**	**260**
Zr	**86**	**1.0E-02**	**520**
Ru	**55**	**2.0E-02**	**260**
Ba	**375**	**5.0E-03**	**1040**
Fe	**760**	**1.0E-03**	**5200**
Na	**5602**	**1.0E-04**	**52000**
K	**215**	**1.0E-02**	**520**
Al	**950**	**1.0E-04**	**52000**
La	**300**	**ND**	**very high**
Ce	**200**	**ND**	**very high**
Nd	**750**	**ND**	**very high**
Y	**60**	**1.0E-03**	**5200**
U	**8000**	**1.0E-04**	**52000**
Pu	**5**	**<1.0E-03**	**>5200**
Am	**tracer**	**<1.0E-03**	**>5200**

ND: Not detected

Nitric acid extracted in organic phase: 0.065 M. Stripping of the loaded organic was carried by deionized water at equal phase ratio. In first contact almost 85 % of the cesium was stripped, total stripping was obtained in three more contacts each time with fresh deionized water.

5.6 Stability test of 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane solvent

The present studies have shown that CC6 dissolved in isodecyl alcohol and n-dodecane mixture is a promising extractant for cesium separation from SHLW solution. However, for use with actual HLW, where the solvent will be exposed to high radiation and acidity, it is therefore 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). There was no change obtained in extraction behavior 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 ray from ^{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 cesium and the results are presented in Table 5.4. The extraction of cesium, showed no appreciable change up to 0.2 MGy, however, beyond this there was slight decline in the extraction, but still the solvent retains its high extraction property (from 84 % to 72 %) up to an absorbed dose of 0.6 MGy. Similar results have also been shown by Raut at al.[192] for the same extractant dissolved in 1:1 mixture of nitrobenzene and toluene. The stripping of the loaded organic phase at different absorbed dose was done by giving four successive contacts with 0.01 M nitric acid solution. Radiolysis does not affect the stripping efficiency much, stripping was 98 % up to 0.2 MGy, thereafter, 94.5 % stripping was observed for 0.6 MGy irradiated solvent. It may be noted that the dose employed in the present studies are in much excess of expected dose (few kGy/year) received by the solvent with actual high level waste. Thus, the solvent is considered to be sufficiently stable to radiolysis and will have no adverse effect on its performance for periods equivalent to many months of continuous operation with actual HLW [193][194].

Though, irradiation of the solvent up to 0.6 MGy resulted in a limited degradation, an attempt was made to recover the solvent to its original extraction properties. It was observed that on passing the irradiated solvent through basic alumina column results in complete regeneration of the solvent [195].

Table 5.4: *Radiolysis of process solvent*

Absorbed dose(MGy)	**% Extraction O/A=1,(D_{Cs})**	**% Stripping,O/A=1, After four aqueous contact**
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**

5.7 Counter-current mixer-settler studies

For efficient extraction and stripping properties at desired acidities, 0.03 M CC6 dissolved in 30 % isodecyl alcohol/n-dodecane was considered as appropriate process solvent. This solvent has not shown any third phase formation on multiple contacts with SHLW solution.

The main objective for counter-current mixer-settler runs was to optimize flow sheet for maximum recovery of cesium at high purity from HLW solution. Taking into account of reasonably high D_{Cs}, a four stage mixer-settler unit at aqueous to organic flow rate of 1:1 was thought suitable for extraction process. Considering very low distribution ratios of other elements, only two stage of scrubbing was employed. Stripping was carried with deionized water in four stages of mixer-settler.

The extraction, scrubbing and stripping operations were carried out separately, after the extraction runs, the loaded organic was collected in a container for settling of any entrained aqueous phase. Scrubbing of clear loaded organic phase was then carried out with 3.5 M nitric acid at O/A ratio of 2:1. Scrubbed organic phase was then collected and stripping was performed with deionized water at O/A of 1:1 as shown in Fig.5.8.

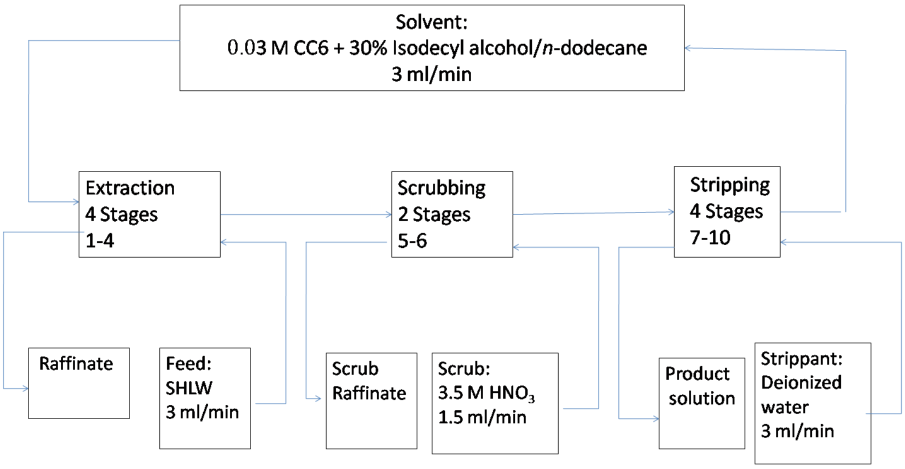

Figure 5.8: *Mixer-settler runs, Stages: 1-4 Extraction; 5-6 Scrubbing; 7-10 Stripping.*

Each independent run lasted for about 14 hours, no third phase formation was observed and exit streams had negligible amount of entrained phases. Stage wise analysis of ^{134}Cs activity in both the phases was carried out periodically to ascertain the mass balance. Steady state was achieved in 4 to 5 hours and at the end of runs, exit samples and samples of aqueous and organic phases of settlers were drawn for analysis.

The concentration profile of cesium in cpm/ml (counts per minute per ml) across the extraction, scrubbing and stripping stages are shown in Fig 5.9. The extraction of other elements were very low, therefore, their concentrations were only analyzed in the final strip aqueous solution.

The results showed good material balance with 99 % extraction of cesium from SHLW solution, four stages of stripping was found adequate to strip cesium from loaded organic, the discharged solvent contained less than 0.5 % cesium. The total concentration of impurities in the cesium strip solution was found to be less than 1mg/l. The nitric acid concentration in the organic phase increased from 0.064

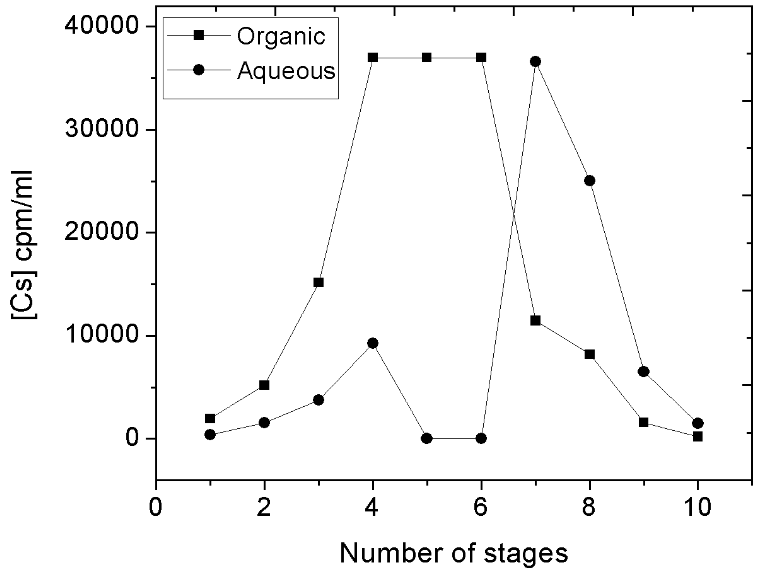

Figure 5.9: *Counter-current steady state concentration profile of cesium during mixer-settler runs.*

to 0.09 M in consecutive extraction stages, it remained constant in the scrubbing stages, and then reduced to less than 0.01 M in the exit stage of stripping section. The trials were repeated ten times with recycled solvent, the efficiency of the solvent remained practically same in all the runs.

Mixer-settler runs were smooth without any hydrodynamic problems, the extraction and stripping efficiencies were high and about 99 % recovery of cesium was obtained from SHLW solution. The flow sheet developed in this work will be validated with actual HLW.

5.8 Conclusions

0.03 M CC6 constituted with 30 % isodecyl alcohol/n-dodecane is found to be a suitable solvent for separation of cesium from acidic high level waste solution. The solvent showed reasonably high D_{Cs} at 4 M nitric acid and is highly selective for cesium extraction. Ease of stripping with deionized water is an advantage of this solvent. The solvent demonstrated fairly high stability towards hydrolysis and radiolysis. Mixer-settler runs were smooth without any hydrodynamic problems.Extraction and stripping efficiencies were high with 99 % recovery of cesium from SHLW solution. The experimental results obtained in this work would help to standardize a flow sheet for efficient recovery of cesium from actual HLW.

6. Summary and conclusions

Nuclear energy has proved its potential as an alternate and sustainable source of energy in the wake of the dwindling natural energy resources like coal, petroleum, natural gas etc. Moreover nuclear reactors are practically free from green house effects and have the potential to reduce the increasing carbon foot print. But, the major hurdle in its implementation as a primary resource is the fear of the long term effects of radiotoxicity of the spent fuel and the high level radioactivity waste left after reprocessing. Last few decades have seen hectic activities to improve the safety of the entire fuel cycle. Advanced rector systems capable of giving better safety, efficiency and economy, Generation IV systems, are identified for the future. Closed fuel cycle approach with separation and control in discharge of hazardous nuclides to geological repositories are envisaged in an effort to ensure integrity to engineered barriers at disposal sites. Both aqueous and nonaqueous processes are being developed to address the separation issue. Even though preliminary studies project nonaqueous processes are better suited to handle the spent fuel from future reactor systems, the maturity available with aqueous processes give an edge and definitely make it the first choice for immediate implementation.

Our laboratory, along with the laboratories in the rest of the world, are involved in the development of processes to separate specific radionuclides from the host of nuclides present in the high level acidic liquid waste generated during the processing of spent fuel by PUREX process, the only industrial process employed for the reprocessing of spent fuel from nuclear reactors. The potential nuclides from radiotoxcity view point left out in the high level liquid waste are residual uranium and plutonium, minor actinides and some long lived nuclides like Tc-99, I-129, Cs-135 etc. Advanced Purex process and newly developed aqueous processes employing tailor made reagents are able to address the separation of residual actinides, minor actinides along with Tc-99 and I-129. Engineering scale facilities are operated to demonstrate the application of these processes with actual wastes from reprocessing plants. These developments leave wastes containing mainly shorter lived nulcides like Cs-137, Sr-90, Y-90 etc. alongwith long lived Cs-135. From waste management point of view, the waste loading is mainly controlled by the decay heat load of the fission products in borosilicate glass matrix currently being employed in the fixation of high level waste.

Separation and recovery of cesium from high level waste originating from reprocessing of spent nuclear fuel can reduce many of the problems encountered in the handling during bulk radioactive waste management. Two major radioisotopes of Cs viz. Cs-135 and Cs-137 are produced in the nuclear reactor as a result of fission reaction of U-235 by thermal neutrons. Moderately long lived Cs-137 ($t_{1/2} = 30.1$ y) due to its large heat output of 0.42 W/g can cause degradation of the glass matrix thereby increasing the risk of leaching of radionuclides from the vitrified waste in case of a breach in the containment. Leaching of radioactive elements from the repositories can be extremely harmful for the environment especially when the nuclide is long lived and mobile like Cs-137. Therefore, the removal of both these radioactive Cs nuclides can increase the waste loading in glass and reduce the vitrified waste volume. Exposure to the operator can be considerably reduced during bulk volume vitrification if the shorter lived Cs-137 also can be separated along with Cs-135. Sr-90 and Y-90 are the other two nuclides which need separation from decay heat load perspective. Commercial application of these nuclides will make the separation economically viable. In the present work, efforts have been made to synthesise, characterise, evaluate experimentally and theoretically using computational techniques calix-crown based extractants for separation and recovery of cesium from Purex HLLW.

The work reported in this thesis can be summarized and concluded as follows:

Two macrocyclic calix-benzo-crown (CBC) and calix-crown-6 (CC6) extractants known to have good separation factors during extraction of Cs from Na were synthesized at large scale indigenously and characterized by the procedure reported. The synthesis of CBC and CC6 has been done in parts. First the synthesis of crown part tosylate and then 1,3-Dioctyloxy-calix[4]arene was synthesized. Later both the compounds were condensed to obtain the resultant calix-crown. The final product was characterized using melting points, NMR and GC-MS techniques and these results matched with the reference values reported.

In order to carry out the solvent extraction experiments, two different modifiers viz. IDA and o-NPHE has been selected. The concentration of phase modifiers was optimized to be 30% in n-dodecane to ensure optimum extraction of cesium. Detailed investigations on the effect of various parameters like, concentration of phase modifiers, aqueous phase acidity, ligand concentration, nitrate ion concentration and effect of temperature on extraction of cesium have been studied. With the increase in nitric acid concentration, increase in extraction of cesium was observed. Stoichiometry of the extracted complex determined by slope analysis method revealed 1:1 molar ratio for $CsNO_3$: Calix-crown.

The solvent extraction of Cs(I) and some typical metals Na(I), K(I), La(III), Y(III), Mo(VI), Zr(IV), Sr(II), Ba(II), Ru(III), and Pd(II) with both these ligands in nitric acid medium was carried out. In case of Calix-benzo-crown (CBC) the D_{Cs} for 0.01 M CBC in 30 % IDA/n-dodecane and o-NPHE/ n-dodecane came out to be 1.9 and 3.04 respectively. Only molybdenum has shown a D of 0.012 and 0.011 in IDA and o-NPHE respectively. On the other hand for Calix-crown-6 (CC6), 0.01 M CC6 in 30 % IDA/n-dodecane and o-NPHE/n-dodecane exhibits D_{Cs} value of 1.2 and 2.8 respectively. Molybdenum has shown a D of 0.015 in 0.01 M CC6/30 % IDA/n-dodecane and 0.012 in 0.01 M CC6/ 30 % o-NPHE/ n-dodecane solvent systems. The rest of metal ions have DM value less than 0.01 in both the solvent systems. Both the ligands exhibited strong extraction ability and selectivity for cesium(I) over all the metal ions present in simulated waste solution.

The effect of temperature on extraction of cesium was studied in the temperature range of 300-323 K for CBC in both the solvent systems. The values for enthalpy and entropy for IDA system were -47.29 kJmol-1 and -124.45 $JK^{-1}mol^{-1}$

respectively whereas for NPHE system the enthalpy and entropy were -46.14 kJmol $^{-1}$ and -116.79 JK^{-1}mol^{-1} respectively. Negative enthalpy for both the systems indicates that the extraction process is exothermic in nature. This enthalpy terms contributes to change in dehydration enthalpy of metal ion and change in enthalpy during complex formation.

High Cs/Na selectivity was also explained theoretically. Density functional theoretical studies were performed to investigate the better selectivity of Cs$^+$ion over Na$^+$ ion in gas as well as solvent phase. The structure of metal hydrates and their complexes with CBC and CC6 were optimized at hybrid B3LYP level using SVP basis set. The complexing ability of both the ligands towards cesium ion was calculated from free energy of reaction. Three different models were chosen for studying the binding energies, First is purely the gas phase reaction of metal ions (Cs, Na) and calix-crown, In the second model, the hydration of metal ion is taken into account by providing a coordination number of eight to cesium and six to sodium by providing water molecules around it. In the third model the hydration of both cation (Cs, Na) and anion (nitrate) is being considered. The binding energy and free energy values for CC6 complex with caesium was obtained as -88.02 kcal/mol, -91.14 kcal/mol, whereas as the CC6-sodium complex was having the binding energy and free energy of -79.23 kcal/mol, -70.50 kcal/mol respectively. On the other hand the CBC was behaving almost equally and identically with CC6 and the binding energy and free energy values for cesium-CBC complex was obtained as -85.60 kcal/mol, -87.32 kcal/mol respectively. Which is higher than CBC-sodium complex (-78.33 kcal/mol, -63.55 kcal/mol). The gas phase binding energy and free energy indicates the selectivity order: Na$^+$ $>$ Cs$^+$ whereas after suitable hydration of metal and nitrate the order becomes reverse as obtained in the solvent extraction results.

A number of variations are possible in calix[4]arene-crown moiety to bring about changes in the extraction property. Such a modification was planned to extend the useful range of Cs extraction to higher acidities. This resulted in the synthesis of another series of novel amide substituted calix-crown-benzo-amides (CBCAs). They were evaluated for the selective separation of cesium ion from solutions with higher initial acidity. The diluent composition developed for the earlier calix-crowns were found to be suitable for this amide substituted compound as well. Compared to its non-amidic analogue, these amides have been found to extract cesium at higher nitric acid concentration without any decrease on its extraction ability. This is attributed to intramolecular buffering effect of amide group, protecting the cavity of CBCA (calix-benzo-crown-amide) from counter ion. This property can be utilized for selective separation of Cs from feed solutions with higher acid concentration.

To establish the process for the selective removal of cesium from high level liquid waste solutions, the radiolytic and hydrolytic stability of CBC/isodecyl alcohol/n-dodecane and CBCA/ isodecyl alcohol/n-dodecane were studied. Both the calix-crowns with solvent composition, 0.01 M Ligand/ 30 % IDA/n-dodecane were kept in contact with 3.5 M nitric acid with continues stirring for two weeks. It was observed that the colour of solution turned to pale yellow with no considerable change in distribution ratio of cesium. This implies that 0.01 M ligand/30 % IDA/n-dodecane solvent system is hydrolytically stable at room temperature.

Three types of samples were prepared in glass test tubes for irradiation, as described below:

- 0.01 M calix-crown+ 30 % IDA/n-dodecane.
- 0.01 M calix-crown+ 30 % IDA/n-dodecane in contact with 3.2 M nitric acid
- 0.01 M calix-crown+ 30 % IDA/n-dodecane saturated with 3.2 M nitric acid.

These were irradiated by ^{60}Co source with a dose rate of 20 Gy/minute in air at room temperature. The qualitative degradation product analysis was performed using ESI-MS. The ESI-MS spectra shows large number of peaks which include great number of ions in the sample along with their Na^+ and K^+ and Cs^+ adducts. The major categories of product formed are assigned tentatively based on nominal masses of isomeric molecule. The degradation pathways mainly include cleavage of -alkyl (octyl), $CONR_2$, which were further followed by aromatic oxidation and nitration.

Both CBC and CBCA(6) saturated with 3.2 M nitric acid prior to irradiation with a dose of $\sim$ 80 MRAD were used for selectivity studies. It was observed that the D_{Cs} value decreased substantially to 0.4, 0.6 from 1.8, 2.1 for CBC and CBCA respectively which indicate loss of active crown cavity for cesium extraction. Also the distribution of other metal ions slightly increased which may be due to presence of phenolic moiety after degradation. In addition, the phenolic moiety reduces the stripping to (90-95 %) with D_M water.

In the quantum chemical calculation study the structures of CBCA(6) and its complexes with cesium and cesium nitrate were optimized with at hybrid B3LYP level using SVP basis set in TURBOMOLE 6.6 package. The gas phase binding energy without ZPE correction were calculated and compared with its non-amide analogue viz. CBC, it was found that binding energy of CBCA(6) is always higher ($\sim$ 5 kcal/mol) than CBC in all three models, which is in good agreement with the experimentally determined D_{Cs} values.

Yet another modification in the calix[4]arene was planned to synthesize a molecule which can co-extract several actinides and lantanides along with Cs. Two diglycolamides replaced the the octyloxy group in CBC. The novel ionophore, diglycolamide substituted calix [4]arene benzocrown-6 (CBCBGA) in 1,3-alternate conformation has been synthesized and characterized by using ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis. The glycolamide units attached on 1,3-alternate side of the calix[4]arene ring are spaced with three -CH_2 units. This calix-crown compound was found to be practically insoluble in the diluent compositions developed earlier. This molecule being more polar needed diluents like o-NPHE for solvent extraction studies. The effect of various parameters like feed acidity, CBCBGA concentration and nitrate ion were studied to determine the stoichiometry of extracted complex in o-NPHE. The slope analysis method reveals that 1:1 molar ratio for $CsNO_3$: CBCBGA in the extracted complex. The D_{Cs} in different diluents was calculated and it was found to be highest with nitrobenzene and lowest with chloroform and follows the deceasing trend with decreasing dielectric constant of the diluents: nitrobenzene > o-NPHE > 1-octanol > chloroform. This ionophore is found to be a highly selective for cesium over other metal ions present in simulated high level liquid waste solution.

The structure of free CBCBGA and its complexes with Cs^+ and Na^+ ions with nitrate ion has been optimized using hybrid Becke-Lee-Young-Parr (B3LYP) density functional employing split-valence plus polarization (SVP) basis set. The dielectric constant of water, nitrobenzene, NPHE, octanol and chloroform was taken to be 80, 34.81, 24.8, 11.8, and 4.81.

The optimized CBCBGA-$CsNO_3$ complex is found to be coordinated by 6 donor O atoms from the crown moiety and two donor atoms from one nitrate anion leading to 8-coordinated complex. The average Cs-O (O of crown moiety) bond distance is found to be 3.30 A^o which is longer than that of Cs-O (3.19 A^o) bond with nitrate O. From the optimized structure of complex of $NaNO_3$ with CBCBGA it was observed that Na^+ ion is coordinated to the 4 donor O atoms from the crown moiety and one donor atoms from one nitrate anion leading to 5-coordinated complex. The average Na-O (O of crown moiety) bond distance is found to be 2.67 A^o which is longer than that of Na-O (2.19 A^o) bond with nitrate Oxygen.

The free energy was found to be negative indicating highly exergonic nature of extraction complexion for both Cs^+ and Na^+ ions. The gas phase free energy is seen to be higher with the Na^+ ion over Cs^+ ion as expected, because, the size of the Na^+ ion smaller than that of Cs^+ ion. The solution phase free energy of extraction was seen to be reduced considerably from their respective gas phase free energy due to the dielectric screening of the organic solvent. Whereas the solution phase free energy for Cs^+ ion is found to be higher than that of Na^+ ion. The calculated value of difference in free energy, $\Delta\ \Delta G$ (ΔG_{ext}, Cs^+ - ΔG_{ext}, Na^+) is found to be -9.49 kcal/mol, which is in good agreement with the experimentally determined value of -5.59 kcal/mol. The extraction free energy was found to be highest with nitrobenzene and lowest with chloroform for both the Cs^+ and Na^+ ions as observed in the solvent extraction experiments.

Natural bond order (NBO) analysis program NBO6.0 was used to evaluate the second order stabilization energy to investigate the unusually high selectivity of Cs^+ over Na^+ ion towards CBCBGA at the B3LYP/DZP level of theory. The stabilization energy for Cs^+ ion with CBCBGA was found to be higher compared to its corresponding Na^+ ion complex whereas, the gas phase free energy follows the reverse trend. For this reason, second order stabilization energy might not be helpful for the forecast of selectivity in the solution phase.

The bond critical point (BCP) analysis are commonly used to measure the strength of the bond between the metal ion and the donor atom of the ionophore. Hence, the electron density at the BCP, ρ and the Laplacian of electron density, $\nabla^2\rho$ for metal ion-ionophore systems are evaluated using the atom in molecule methods. The values of ρ and $\nabla^2\rho$ for hydrated Na^+ ion are reduced during complexation with CBCBGA, whereas for hydrated Cs^+ ion though ρ remains same, the value of $\nabla^2\rho$ is increased. Therefore, the increased bond strength seems to play decisive role for the higher selectivity of Cs^+ ion over Na^+ ion towards CBCBGA ionophore.

In the final a complete process flow sheet was developed for selective separation of cesium from acidic nuclear waste solution using 1,3-dioctyloxycalix[4]arene-crown-6 (CC6)/n-dodecane modified with isodecyl alcohol. The process solvent was optimized as 0.03 M CC6 + 30% isodecyl alcohol/n-dodecane for efficient recovery of cesium. Extraction studies were carried out with the optimized solvent composition and the results were used to design a solvent extraction flow-sheet. The results showed good material balance with 99 % extraction of cesium from SHLW solution, four stages of stripping was found adequate to strip cesium from loaded organic, the discharged solvent contained less than 0.5 % cesium. The total concentration of impurities in the cesium strip solution was found to be less than 1 mg/lt. The nitric acid concentration in the organic phase increased from 0.064 to 0.09 M in consecutive extraction stages, it remained constant in the scrubbing stages, and then reduced to less than 0.01 M in the exit stage of stripping section. The trials were repeated ten times with recycled solvent, the efficiency of the solvent remained practically same in all the runs.

The solvent showed reasonably high D_{Cs} at 4 M nitric acid and is highly selective for cesium extraction. Ease of stripping with deionized water is an advantage of this solvent. The solvent demonstrated fairly high stability towards hydrolysis and radiolysis. Mixer-settler runs were smooth without any hydrodynamic problems.Extraction and stripping efficiencies were high with 99 % recovery of cesium from SHLW solution.

Testing of the proposed flow sheet with actual high level waste originated from the processing of low burnup spent fuel is the next step in the comprehensive ongoing programme of our group. This will necessitate the adaptation of the entire process in a hot cell where a few liters of the actual waste can be handled safely. The equipment and the sampling systems will have to be operated remotely and will necessitate elaborate arrangement. Planning and erection of the setup is currently in progress. After making the final adjustments in the flow sheet based on the actual HLLW experiments, it is planned to operate an engineering scale facility for the demonstration of this Cs separation process using 30,000 liters actual HLW containing about 45,000 Ci of ^{137}Cs. The separated cesium will be converted to vitrified radiation source (pencils) for supply to BRIT for commercial applications.

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