Chapter 1

Introduction
1.1 Introduction

Supramolecular chemistry focuses on the noncovalent bonding of the molecules having weaker and reversible interactions. These interactions are due to hydrogen bonding, metal coordination, hydrophobic forces, Van der Waals forces, pi-pi interactions and electrostatic effects. Supramolecular chemistry provides molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically interlocked molecular architectures and dynamic covalent chemistry. Macrocycles having the cavities can completely surround guest molecules and may be chemically modified to desired application.\(^1\) Calixarene appeared as the third generation of supramolecular host compound after crown ether, cyclodextrins.\(^2\)–\(^3\) Calixarenes have been proved to the important building blocks in supramolecular chemistry. Calixarene have received special attention because their easy large scale preparation and ability to undergo further synthetic elaboration. The easy chemical transformability of this molecule together with its "tunable" structure make calixarene an attractive candidate for molecular design strategies.\(^4\)–\(^9\) Calixarenes derived from the Greek calix meaning vase or chalice and arene, which indicate the presence of aryl residues in macrocyclic array. The calixarene exist in a ‘cup’ like shape with a defined upper-rim, lower-rim and central annulus (Fig. 1).

Historically, calixarene can be depended on discovery of phenol-formaldehyde resins investigated by Von Bayer in the 1970s. The polycondensation of phenol and formaldehyde in acid or base proceeds through the ortho and para positions, leading ultimately to the highly cross-linked matrix, such as bakelite. When para position is blocked with alkyl substituents, condensation is restricted to a liner progression and this aspect of phenol-formaldehyde chemistry, led in the 1940s to the discovery of calixarene. Gutsche\(^10\) was the first to draw the attention to their potentiality as molecular receptor or enzyme mimics which are known collectively as "Calixarenes". The calixarenes are synthesized by acid catalyzed condensation of a variety of aromatic compounds. Among these the aldehydes viz. formaldehyde, acetaldehyde, propionaldehyde etc. have been reported extensively. Calixarene contains four, six and eight aryl units can easily be prepared in good to excellent yields. Calix(4)arenes are macrocyclic molecules with unique
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Figure 1.1: Representation of calixarene and designation of the faces

three dimensional structures. Functionalisation of the calix(4)arene is referred to either narrow rim (previously called lower rim) if it occurs at the phenolic oxygen or wide rim (previously called upper rim) if it occurs at the para position after the removal of p-tert-butyl groups. Their controlled synthetic functionalisation and versatile complexation properties allow the use of these compounds in supramolecular chemistry as molecular scaffolds for the construction of various receptors. They are frequently employed as platforms that permit functional groups to be orientated well organised cavities. The great interest in compounds of this type is primarily motivated by the ionophoric property of the narrow rim which leads to applications in the area of cation binding and transport as well as highly selective receptors and novel sensors for polyanionic species. This polyfunctional property stems from the fact that the narrow rim is relatively easy to chemically modify via well established acid-base and nucleophilic reactions. Calixarenes made up of phenol and methylene units have many conformational isomers because of two possible rotational modes of the phenol unit: the oxygen through the annulus rotation and the para substituent through the annulus rotation. By rotation of phenolic units, calixarene molecules may adopt different conformations
for examples, calix(4)arene compounds have four limiting conformations are cone, partial cone, 1,2-alternate and 1,3-alternate. Calix(6)arene is constructed by six phenolic units, which results not only in more kinds of derivatives, but also in more conformation mobility than that of calix(4)arene. The conformational interconversion in calix(6)arene can occur not only via the oxygen through the annulus but also by the para substituent through the annulus pathway, even in the case of p-tert-butyl derivatives. Thus, it is difficult to immobilize the conformation of calix(6)arene by introducing bulky substituents onto the lower-rim simply, even if the substituent is as bulky as cholesteryl group. Considering only the relative orientations (syn or anti) of the aromatic nuclei there are eight possible conformations for calix(6)arene i.e., cone, partial cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate and 1,3,5-alternate the number increases dramatically if the value of the angles that each aromatic nucleus makes with the average plane of the molecule is taken into account. Recently calixarene family has been extended to the compounds with similar aromatic units due to its conformational flexibility, diverse binding affinity and easiness for the applications.

1.1.1 Biscalixarenes

Biscalixarenes have attracted great interest because of their peculiar multicavity structure and molecular recognition abilities. In the case of tail-to-tail linkage, the biscalixarenes, providing two diverging cavities have been used as tectons for poly-cap self-assemblies. The detailed synthesis methodologies with various types of spacers of biscalixarene depending upon the nature of the base, stochiometry of the reactant, complexation and extraction behaviour of these calixarenes are summarised by Agrawal et al. Shinkai et al. reported the synthesis of a series of bis[calix(4)arenes] possessing two metal binding sites, each containing four ester or four ether groups. Double and triple calix(4)arenes connected through the oxygen atoms were described, produced by reactions between calix(4)arenes 1,3-difunctionalized at the smaller (lower) rim and difunctional reagents such as diacid dichlorides or diamines. Double calixarenes linked through one bridge at the smaller (lower) rim and bearing urea groups on the larger (upper) rims
have also been reported.\textsuperscript{20−21} Rebek et al. described\textsuperscript{22} the synthesis and the encapsulation behaviour of bis[calix(4)arenes] linked by one bridge at the larger (upper) rims and bearing urea groups in the same rims. The complexation behaviour of bis(calixarenes) towards fullerenes $C_{60}$ and $C_{70}$ was studied.\textsuperscript{23} A series of bis[calix(4)arenes] derivatives linked through their phenolic oxygens with the aid of a single aliphatic or aromatic chain (tail-to-tail) were obtained by alkylation of 28-hydroxy-25,26,27-tripropoxy calix(4)arenes with a,u-dibromoalkanes in the presence of NaH\textsuperscript{24} and by condensation of p-tert-butylcalix(4)arene with methyl 2,6-bis(bromomethyl)benzoate,\textsuperscript{25} 2,6-bis(bromomethyl)-4-methylanisole\textsuperscript{26} or with 5,5'-bis(bromomethyl)-2,2'-bipyridine N,N-dioxide.\textsuperscript{27} The symmetrical quadruply-linked bis-tBu-calix(4)arene with ethylene linkers has been synthesized, which shows remarkable affinity for potassium ion. The aryl groups radiating from the central core in these tubular receptors are also of importance in the control of metal ion selectivity, behaving as filtering gates by way of cation-$\pi$ interactions.\textsuperscript{28} A series of new biscalixarenes consisting of two p-tert-butyl thiacalix(4)arene units linked through lower rims with bridging moieties containing diimine units of different aromatic or heteroaromatic dialdehydes were reported by Kumar et al.\textsuperscript{29} Their complexation behavior was studied towards different metal ions. (Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Pb\textsuperscript{2+} and Ag\textsuperscript{+}) Bhalla et al. replaced the conventional calix(4)arene unit of biscalixarenes with thiacalixarenes which is an attractive host for soft metal ions.\textsuperscript{30} To evaluate the binding ability of bisthiacalixarenes toward different metal ions, two-phase solvent extraction of metal picrates (Na\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{2+} and Ag\textsuperscript{+}) was carried out. Biscalixarene derivatives have been studied for cation complexation, anion recognition, organic, neutral and charged molecular recognition, redox active ionophore, ion selective electrodes and ditopic receptors.\textsuperscript{31−39}

### 1.1.2 Calixcrown

Calix(n)crown ethers compound are macrocycles characterized by possessing two kinds of receptor elements compose of calixarene and crown ether, joined via the phenolic oxygen of calix component. Calix(n)crown in which the calixarene is functionalized at the distal phenolic oxygen with a poly chain have been utilized
as the molecular scaffold. The reaction of calix(n)crown with different equivalents of various ditosylates (containing 2,3,4,5,6,7-oxygens) in the weak alkaline medium gives different calix(n)crown ethers. Different calix(n)crown ether and their analytical potentialities are summarised by Agrawal et al.\textsuperscript{40} Calix(n)crown compounds exhibit superior reorganization ability toward alkali, alkaline earth metal, ammonium and transition metal ions due to co-operative effect of the calixarene and crown ether moieties.\textsuperscript{41,43,44} Mori et al.\textsuperscript{45} have reported that structure features and presence of bulkier substituents also play a relevant role in determining the selectivity. Reinhoudt et al.\textsuperscript{42} have reported the substituent’s at the remaining -OH group for the first time. Study reveals that introduction of four ester, keto, amide or mixed type binding sites on the phenolic groups of the p-tert-butyl calix(4)arene fixes the macrocycle in non conformation giving a $Na^+$ selective cation receptor on the other hand the selective 1,3 dialkylation of the calix(n)crown followed by the polyether group attached at two remaining group results in $K^+$ selective ionophore. Reinhoudt et al.\textsuperscript{46} have reported that 1,3 dialkoxy calix(4)arene crown derivative were found to be exceptionally selective ionophore for cesium ion due to the complexation of the cesium ion not only with crown ether moiety but also two rotated aromatic nuclei when fixed in 1,3 alternate conformation. Kim et al. reported that the introduction of benzene rings in to the crown ether loop of calix(4)arene can improve the selectivity for cesium ion due the flattening effect. Kurita et al.\textsuperscript{47} have reported a platinum complex with calix(4)dithia crown. This platinum complex catalyzed hydroxylation of olefins with ($Eto$)$_3$SiH. Ungaro and coworkers\textsuperscript{48} have carried out an analytical study with a new class of calix(4)crown ether with one of two pyridine appended to the poly ether chain and studied the luminescence properties of europium and terbium. A novel dinuclear gold(I) calix(4)crown acetylide complex has been reported by Yam et al.\textsuperscript{49} showing a high $K^+/Na^+$ selectivity over other alkali cataion. Dodi\textsuperscript{50} reported the calix(4)crown displaying and exceptional selectivity towards cesium using high performance liquid chromatography with UV detection. Kim et al.\textsuperscript{51} reported a new fluorgenic benzothiazolyl ionophore based upon calix(4)crown ether co-determination in aqueous media. In the study, pronounced selective fluorgenic behaviour toward $K^+$, $Na^+$ and $Mg^{+2}$ has also been determined. The effect of crown ether units and $Na^+$ ion binding towards anion
binding ability have been studied by Tongraung et al.\textsuperscript{52} Calix(4)arene containing urea and crown /urea moieties formed complexes with $Cl^-$ and $Br^-$ to a different extent. Upon addition of $Na^+$ the binding ability is increased due to ion-pair enhancement.

1.1.3 Calixresorcinarenes

Resorcinarenes are the analogous of calixarenes with two hydroxyls groups in benzene rings forming a macrocycle. Calixresorcinarenes have been revived considerable attention for the synthesis of the cavitands and (hemi)carcerands etc. Such molecules contain an enforced cavity with the shape of an american football, sufficiently large to accommodate small organic molecules. Calixresorcinarenes play an important role in the field of host molecule, metal ion extraction agents, selective membrane, molecular inclusion and recognition.\textsuperscript{53–57} Resorcinarenes have been synthesized from acid-catalysed condensation reaction of resorcinol and aliphatic aldehyde or aromatic aldehyde. The synthesis, complexation and analytical application are well documented by Agrawal et al.\textsuperscript{58} The large number of calixresorcinarenes have formed the complexes with iron, gold, copper, silver, mercury, platinum, lanthanides.\textsuperscript{59–63} Calixresorcinarenes also have shown the complexing behavior with a variety of guest molecules such as sugars, steroids, amino acids, triethyl amine and [2.2.2] cryptand.\textsuperscript{64–68} The extraction properties of the calix(4)resorcinarene resins have been evaluated in competitive extraction and show a selectivity in favour of cesium(I).\textsuperscript{69} The extraction of cesium by resorcinol based resin was investigated.\textsuperscript{70} The iono selective properties of these new ion-exchange resins are stongly influenced by the nature of the cross linker. The presence of macrocycle lead to an improvement of selectivity towards cesium in the relation with the size of the macrocycles introduced. Binding study of new amino pyridinyl resocene receptors for the recongitions of alkali metal ions have been reported.\textsuperscript{71} A new calix(4)resorcinarene bearing eight hydroxamic acid groups has been synthesized and its analytcs properties were investigated and showed high affinity and selectivity toward thorium(IV) and uranium(VI) in the presence of large quantities of associated metal ions.\textsuperscript{72–73} A new method for liquid-liquid extraction, separation and preconcentration of cerium(IV) with
a calix(4)resercinerene hydroxamic acid derivative is reported, that was applied for the determination of cerium in standard geological samples, monazite sand and sea water samples. Aminophosphonate calix(4)resorcinarene derivatives extract lanthanum(III) and lutetium(III) ions from aqueous solutions to chloroform much more efficiently than diethyl [(4-nitrophenyl)aminobenzyl]phosphonate does. The alkyl amino menthylated calix(4)resorcinarene derivatives, modified by dimethyl amino-piperidyl and trimethylammonium moieties have been synthesized to investigate their extractability towards lanthanide(III) ions and to compare with the extractability of calix(4)resorcinarene. Spectrophotometry and pH measurements were used to study the non-substituted and ortho-substituted calix(4)resorcinarene mediated transport of copper(II) and cobalt(III) complexes with diamine and amino acids from an aqueous source phase to an aqueous receiving phase throug a bulky chloroform membrane. Extraction ability of water soluble calix(4)resorcinarene octacarboxylate toward phenol by the assistance of iron(II) ions was investigated in aqueous solutions by photoluminescence (PL) and quantum-chemical methods (QCM). The results showed that water soluble calix(4)resorcinarene octacarboxylate forms stable sandwich type complexes with phenols by 1:2 stoichiometry. Binding properties of resorcinarene-based cavitands functionalized with N-acylimidourea moieties towards different cations are described. Extraction studies with metal (Pb$^{2+}$, Cu$^{2+}$, Ag$^{+}$, Hg$^{2+}$, Eu$^{3+}$, Fe$^{3+}$, K$^{+}$, Na$^{+}$ and Ca$^{2+}$) picrates and the incorporation in the ions selective electrodes (ISEs) show that there is more than a 40% increase of the silver(I) extraction. Tetrathiophosphonate calix(4)resorcinarene shows excellent extraction properties towards soft metal ions with a better affinity for silver(I) (91%) than thallium(I) (38%) and mercury(II)(16%). The extraction of other picrate salts (Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Pb$^{2+}$) was not detected. Aminomethylated calix(4)resorcinarene forms the 2:1 complex with copper(II) ions. Resorcinarenes of C$_2$V symmetry tetrasulfonates are useful as molecular platforms of the design of cation receptor for alkali metals and ammonium(I) ions, containing binding units in the molecule.
1.1.4 Calixnaphalene

Calix(4)naphthalenes are a class of molecules which possess deeper cavities than those of the analogous calix(4)arenes. Over the last several years, Georghiou has pioneered and substantially developed the chemistry of calixarenes derived from naphthalene subunits. The term calix(4)naphthalene was coined to describe these structures, typically prepared from 1 or 2-naphthol or their derivatives. Condensation of 1-naphthol with formaldehyde produces a mixture of regioisomeric calix(4)naphthalenes. Moreover, each isomer can be individually prepared by a convergent method because the naphthalene units are linked at the $C_2$ and $C_4$ positions; this class of calixarenes has the same connectivity as a typical calixarene, yet with a deepened pocket owing to the naphthalene core. The deep binding pocket and the pendant functionality conspire to produce a versatile host that has been used to recognize a range of guests from metal ions to [60] fullerene. Despite the ample precedent for preparation of the 2,4-linked calix(4)naphthalenes, the analogous 3,6-linked isomer cannot be approached in a similar manner. It has been shown that 2,7-dihydroxynaphthalene reacts with electrophiles including formaldehyde, exclusively at the $C_1$ position thwarting a simple condensation strategy toward its derivatives. Thus, a properly functionalized derivative would be required in order to obtain the desired substitution pattern. The complexation of [60] fullerene (“$C_{60}$”) with the $C_4$-symmetrical endo-calix(4)naphthalene and its tert-butyl-substituted derivative show that they form supramolecular 1:1 complexes with $C_{60}$ in benzene, toluene or $CS_2$ solution with relatively high association equilibrium constants.

1.1.5 Calixfullerene

Fullerene is a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid or tube. Because of their unique physical and chemical properties, such as efficient singlet oxygen sensitizing ability, strong electron accepting character, photoinduced charged separation ability and superconductivity upon binding with metals fullerene have attracted intense research interest in various field. In parallel, calixarene may be regarded as third generation of potent host molecule. Since fullerene has globular structure
with external-electron surfaces and calixarene have cavity structure with internal-electron surfaces, a marriage of the two third generations by guest host complexation e.g., through $\pi-\pi$ interaction is an obvious possibility. The ready availability of fullerene has increasingly invited exploration of its outstanding physical and chemical properties of these the superconductivity observed for certain endohedral metallofullerenes has proved a most attractive subject for research. The synthesis of ionophoric fullerene derivatives in which a metal-binding site is closely situated near the fullerene surface is necessary. Such fullerene derivatives with ionophoric functional groups have been reported by several groups but spectroscopic evidence for the direct fullerene-metal interaction was obtained only in a few systems. It is considered that this working hypothesis would be realized most conveniently and most efficiently by using ionophoric calixarenes since they not only provide strong and well characterized ionophoric cavities but also interact with fullerene in the solid state and in solutions. It is known that the highly ion-selective and highly ionophoric cavities can be created by the appropriate modification of the lower rim OH groups while the upper rim p-basic cavities of certain calixarenes can accept fullerene even in solution. If fullerene is used as a 'lid' for the ionophoric cavity, a metal cation bound therein would inevitably interact with the fullerene surface. Fullerene which were discovered in 1985 and isolated in microscopic quantities in 1990 can be regarded as the third carbon allotropies after graphite and diamond. Calix(8)arene selectively included $C_{60}$ from carbon soot and forms precipitate with 1:1 stoichiometry and provides novel and very useful method to obtain $C_{60}$ in very large quantity and high purity. This finding greatly stimulated research into the host guest chemistry of fullerenes. It was found that variety of microcyclic host molecules, such as calixarenes or calixarene analogues form complexes with fullerenes. Williams et al. reported that water soluble calix(8)arene derivatives extract $C_{60}$ fullerenes from an organic into an aqueous phase. Atwood et al. shown that p-benzylcalix(5)arene and p-benzyl-homo-oxacalix(3)arene form 1:2 complex with $C_{60}$ from fullerene solution in toluene. Shinkai et al. reported that p-tertbutylcalix(8)arene can be used to selectively sequester fullerene ($C_{60}$) from a mixture containing $C_{60}$ and fullerene($C_{70}$). This is accomplished by the formation of a 1:1 clathrate in which a $C_{60}$ guest molecule is bound within the cavity of the host molecule.
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NH NH
NH NH
O O
O O

Figure 1.2: Heterocalixarenes.

p-tertbutyl calix(6)arene and calix(6)arene form fullerene rich 1:2 complex with $C_{60}$ or $C_{70}$. The structure of complexes was determined by X-ray diffraction studies.

1.1.6 Heterocalixarene

Heterocalixarene$^{109-112}$ constituted by replacement of arylene units of calixarene with heterocyclic moiety and/or attachments of heterocyclic moieties, depending on the electron-rich$^{109}$ and electron deficient$^{110}$ nature by heterocyclic unit(s), encompass numerous new opportunities for interaction with electron rich and electron deficient systems. The protonizable hydrogen and hetero atom of the heterocyclic constituent could also induce H-bonding interaction with anionic and acidic "H" substrates. Heterocalix(n)arenes possessing varied heterocycles viz. furan, thiophene, pyridine, imidazole, benzimidazole, indole, benzofuran, benz-1,3-oxazine, pyrimidine-2,4-dione, benzimidazol-2(1H)-one, quinazoline-1,4(1H,3H)-dione etc.$^{113}$

Calixpyrrole belongs to the family of heterocalixarene macrocycles, which has four pyrrole units instead of phenolic units. Calixpyrrole, as the name implies,
offer a cup-shaped skeleton, in which four pyrrole hydrogen bond donors are ideally pre-organized for anions and ion pair binding. This heterocalixarene possesses unique supramolecular characteristics and presents remarkable chemical and physicochemical properties as well as wide application possibilities. The host properties of calixpyrroles continue to draw research interests due to their potential application as neutral substrates optical sensors and anion transporting agents. Moreover, they have been applied in many aspects, such as biologically active species, electroanalytical chemistry, colorimetry as well as they have found novel application as cobalt(II)calix(4)pyrroles complex which was screened for its capability to be used as a catalyst in the epoxidation reaction. The hybrid calixpyrroles are being used for biological applications such as anion sensing and antiviral drug delivery due to their amphiphilic binding characteristics. A hybrid calixpyrrole chelating resin has been used for sorption studies of some noble metals like Au(III), Ag(I), Pt(IV), Pd(II) and other metal cations including Cu(II), Pb(II) and Cd(II). Functionalized calix(4)pyrroles are also distinguished as solid supports for the separation of anionic substrates. They also show promising quality as calix(4)pyrroles modified silica gels for separation of inorganic anions, amino acids, phenols, benzene, carboxylic acids, some medicines and for selective separation and preconcentration of Ag⁺ and Tl⁺ by liquid liquid extraction. Calix(4)pyrrole receptor used for uncharged guests species such as simple alcohols, amines and amides. Colorimetric and electrochemical sensor for anion, in addition to new support capable of separating mixture of anion. Octa-alkyl porphyrinogens which was renaming as octa-alkyl calix(4)pyrrole by sessler and co-worker adopted four extreme conformation like cone, partial cone, 1,2-alternate and 1,3-alternate like calix(4)arene used for binding neutral substrates like methanol, ethanol benzyl alcohol, DMF, isopropyl alcohol, sec-butanol, N, N-dimethylacetamide and N-formylglycine ethyl ester. Selective anion complexation with octamethyl calix(4)pyrrole and 2,5-dimethylpyrrole has been investigated by Monte Carlo (MC) simulations in \(CH_2Cl_2\) and their gas-phase calculation shown that they adopt the 1,3-alternate conformation in the absence of halide-anions and cone conformers was not stable in the presence of halide-anions due to the formation of four NH-halidehydrogen bonds and octa-methyl calix(4)pyrrole-anion complexes with colored species such as
4-nitrophenolate anion would perturb the electronic properties of the anion sufficiently to produce color change and calorimetric properties studied using UV/VIS spectroscopic techniques in $CH_2Cl_2$ at 25°C. $^{134}$ Dansyl, Lissamine-rhodamine B and Fluorescien use as fluorescent labels with spacer elements contain sulfonamide or thiourea moieties provided additional H-bonding donor sites in calix(4)pyrrole which was tested as potential receptor for $F^-$ and $Cl^-$. These anion studied in the form of their tetrabutyl ammonium ($TBA^+$) salts were chosen because of their biological importance.$^{135}$

1.1.7 Calixfurans

Calixfurans are the earliest entries amongst heterocalixarenes. Calixfurans appear to be a tactful supporting actor in the chemistry of calixarenes. Regardless of their rather modest intrinsic binding abilities, the weak coordination by the furan units of calixfurans or hybrid systems plays a crucial role in certain cases. More importantly, calixfurans can be converted into a wide variety of macrocycles including those otherwise difficult to access since the furan unit serves as a versatile functional group. Further development of the synthetic strategy of calixfurans as well as the novel methods for their transformation to other functional molecules is highly anticipated. Since the conformational behavior of calixfurans has not been sufficiently clarified yet, the more sophisticated strategy for regulation of their conformational dynamics should be explored for the ready construction of the desired molecular framework. Calix(4)furan, methylene bridged cyclic oligomer of furan was first taken as the product of furan condensation reaction in the presence of ketones and HCl catalysis.$^{136}$ After the first synthesis, many other methods to make calix(4)furan and extended calix(n)furan ($n = 6, 8$ and $10$) have been reported.$^{137-143}$ Calix(4)furan also allows four main conformations and the predominant conformer is the 1,3-alternate determined by X-ray$^{139}$ and theoretical methods. Since the oxygen atom in a furan ring provides the electron abundant nature, calix(4)furan is expected to bind cationic guest molecules.$^{140-141}$ As receptors, calix(n)furans and hybrid $C_4$ systems reveal some unique metal cation binding modes. As compared with calix(n)furans, calix(n)tetrahydrofurans, show better cation binding abilities which are influenced by the cavity size and bridge sub-
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stituents. Calix(n)furans constitute precursors for many otherwise inaccessible cyclic entities including heterocalix(n)arenes. The reactions of calix(4)furan (n = 1, R = Me) with $H_2S$ and $H_2Se$ constitute the only synthesis of calix(4)thiophene and its selena analog.

1.1.8 Calixthiophene

Calixthiophene can be obtained by introducing a sulfur atom instead of an O or NH in a heterocycle. Calix(4)thiophene, constituting four thiophene rings in the macrocycle has been scarcely synthesized compared to the other members in the family due to its synthetic difficulty. The first synthesis was reported from calix(4)furan in the presence of $H_2S$ and HCl. Among various conformations of calix(4)thiophene, 1,3-alternate was found to be the most stable conformer by theoretical method. It was suggested that the sulfur atom in a thiophene ring acts as a soft donor and consequently interacts with soft metal cations. Thiophene bearing substituents at the bridged carbon, due to steric strain, undergo facile acid catalysed condensations with carbonyl compounds to form calix(4)thiophenes. The chemical transformation mode involving sodium sulphide induced conversion of 1,4-butadyne chromophores provides a structurally intriguing category of calix(4)thiophenes possessing cyclopropylidene bridges.

1.1.9 Heteracalixarenes

Heteracalixarenes i.e., thia calixarene, azacalixarene and oxacalixarene, in which bridges between phenol unit contain hetero atoms S, N or O.

1.1.9.1 Thiacalixarenes

Thiacalixarenes, the calixarene analogs having sulfide bridges instead of methylene bridges, are recent members of the calixarene family. Analytical application of various thia calixarene with their derivatives have been discussed and their metal binding affinities have been summarized by Agrawal et al., Miyano et al. reported a facile procedure which involved heating a mixture of p-tert-butylphenol, elemental sulfur ($S_8$) and NaOH in tetraethylene glycol dimethyl
ether to afford p-tert-butylthiacalix(4)arene, accompanied by traces of p-tert-butylthiacalix(5)arene and p-tert-butylthiacalix(6)arene. The latter have also reported a high yield synthetic procedure starting from the sulfur-bridged dimer of p-tert-butylphenol, yielding predominantly p-tert-butylthiacalix(4)arene with p-tert-butylthiacalix(6)arene and p-tert-butylthiacalix(8)arene in synthetically useful yields. Thiacalix(4)arene prepared from p-tert-octylphenol, padmantylphenol and biphenyl-4-ol have also been reported. Thiacalixarene chemistry dates back to 1997, with the first report of p-tert-butylthiacalix(4)arene, achieved through a stepwise procedure in 4% yield by Sone et al. further, an intuitive strategy has been put forward for synthesis of p-tert-butylthiacalix(8)arene by terephthalate induced cyclization of a mixture of acyclic oligomers obtained by reacting a mixture of p-tert-butylphenol and sulfur in ethylene glycol/diphenyl ether in the presence of CaO. Recently, the same strategy has been extended to improve the yields of p-tert-butylthiacalix(4)arene, p-tert-butylthiacalix(6)arene and p-tert-butylthiacalix(4)arene using different organic acids as templates. Thiacalixarenes have three intrinsic properties, viz. larger cavity, oxidizability of bridging sulfur and coordination to transition metal ions. Their ability to bind metal ions has been investigated by solvent extraction method in several studies. Study of its binding ability toward first transition metal ions (Cu$^{+2}$, Co$^{+2}$, Ni$^{+2}$, Zn$^{+2}$) and Mg$^{+2}$ ion by solvent extraction has been carried out by the dimer method. This thiacalixarene shows a high selectivity towards Cu$^{+2}$ at pH 5.5 by coordination of the O and S donor sets. Polymeric thiacalix(4)arene derived from terephthaloyldichloride (Merrifield) resin is better at removing alkali (Li$^+$, Na$^+$, K$^+$, Cs$^+$) and heavy metal (Cu$^{+2}$, Cd$^{+2}$, Hg$^{+2}$, Pb$^{+2}$, Co$^{+2}$ and Ni$^{+2}$) cations than the precursor thiacalix(4)arenes. Heteroditopic receptors were synthesized by introducing amide functions at the lower rim of the thiacalix(4)arene as efficient extractants for both cations and anions due to their high stability and hydrophobicity. The presence of acetate functions in the opposite side and the sulphur atoms in the calix framework leads to high affinity towards K$^+$ and Ag$^+$ ions respectively. The ability of tetra(diethyl)-amide-p-tert-butylthiacalix(4)arene to bind with alkali and alkaline earth metal ions and some heavy and transition metal ions (Ag$^+$, Cd$^{+2}$, Pb$^{+2}$, Cu$^{+2}$ and Zn$^{+2}$) have been assessed through liquid-liquid extraction of the corresponding picrate salts.
Results show that replacement of the bridging $-CH_2$ units by sulphur atoms in thiacalixarenes led to a loss of selectivity within the alkali and the alkaline earth series. The thiacalixarene became selective for $Pb^{+2}$ ion among heavy and transition metal ions. The reaction of $Ag^+$ with thiacalixarene was proved by extraction of the picrate complexes of transitory metals in the organic phase. Cesium ion-selective electrodes have been fabricated from thiacalix(4)arene mono and bis(crown-6) ether derivatives which show excellent potentiometric performances with $Cs^+/K^+$ and $Cs^+/Na^+$ selectivities comparable with those of the calixcrown-based sensors. Among the thiacalix(4)bis (crown-6) ethers studied, the tert-butyl derivative has better selectivity for cesium than for the other alkali cations. The effective separation of americium from radioactive waste by a chelating ion-exchange method has been carried out using an octylphenyl-N, N-diisobutylcarbomoyl phosphate oxide (CMPO) or thiacalix(4)arene compound impregnated silica ion-exchanger. Thiacalixarene derivatives bearing amide groups effectively extract gold, palladium and platinum from chloride aqueous media via an ion-exchange mechanism. With the thiacalixarene amide, the efficiency for gold separation was much higher than for the other two metal species and the recovery was almost complete. Moreover, thiacalixarene allows the selective extraction of Pd(II) via the formation of a $PdCl_2I_2$ complex, where the metal is coordinated through S atoms. These ligands have also shown their effectiveness as carriers to transport gold and palladium from HCl solutions. Gold was selectively recovered from a mixture of Au, Pd and Pt in a supported liquid membrane system containing macrocycle thiacalix(4)arene, while palladium was transported through a plasticized polymeric membrane containing thiacalix(4)arene. Solid phase extraction systems prepared by adsorption of these ligands on activated polymeric cartridges have shown good results. Thiacalix(4)arene functionalized gold electrodes have also been used as sensors, since these materials present a strong affinity against sulphur derivatives and thiol groups which has an inert nature. Some thiacalixarences which are soluble in water having sulfonato groups like p-sulfonato thiacalixarene and tetrasulfonylarylated calix(4)resorcinarene been used as chelating agents in cloud point extraction of La(III), Gd(III) and Yb(III) ions with Triton X-100 as non ionic surfactant.
1.1 Introduction

1.1.9.2 Oxacalixarene

Homooxacalixarenes represent a new class of macrocyclic receptors analogous to calixarenes\textsuperscript{167–169} where some or all methylene bridges between the aromatic rings are replaced by $\text{CH}_2\text{OCH}_2$ moieties. The oxygen atoms in the ring are potential binding sites and this prompted study of complexation and liquid-liquid extraction of metal ions. The parent compound hexa homo tri oxacalix(3)arene does not bind alkali metal ions\textsuperscript{170}, while tri o-sustituted derivatives hexa homo tri oxacalix(3)arene are effective but do not show marked selectivity in the extraction of $\text{Na}^+$, $\text{K}^+$ and $\text{Cs}^+$ ions\textsuperscript{171}. Among the o-sustituted derivatives with additional binding sites on the lower rim in the fixed cone conformation appears to be particularly strong and selective ligand with association constants in THF/$\text{CHCl}_3$ 1:1 at 25$^\circ$C larger than $10^7 \text{ M}^{-1}$ for $\text{Na}^+$, $\text{Ca}^{+2}$ and $\text{Ba}^{+2}$ ions. Inclusion in the cage, with four cation and several cation oxygen dipole interactions, probably occurs in the complex with $\text{Cs}^+$ ion for which a high extraction from water into dichloromethane and a high selectivity are observed\textsuperscript{172}. The shallow nest of hexa homo tri oxacalix(3)arene, both as the simple ligand and sub units in capsular hosts has proved to be particularly effective in complexation of fullerenes. The $C_3$ symmetry of the oxygen atoms array in the derivatives of hexa homo tri oxacalix(3)arene is suitable for complexation of primary ammonium ions. The cone form tri butyl ether of hexa homo tri oxacalix(3)arene showed a high affinity for Bu-$\text{NH}_3^+$ ions\textsuperscript{173–176}. Homo oxacalixarene strongly binds quaternary ammonium ions in lipophilic in the absence of such relatively strong interaction as hydrophobic forces, hydrogen bonding and ion pairing with the ligand, this binding essentially relies on the cation-$\pi$ interaction\textsuperscript{177}. Homooxacalix(3)arene forms 1:1 complex with $\text{C}_60$ in the solid state having ball and socket structure in which host molecule are perfect in the cone conformation with $C_3V$ symmetry. The study of complexing ability of oxacalix(3)arenes by extraction from water solution of Li, Na or K picrates into $\text{CH}_2\text{Cl}_2$ and by $^1\text{H}$ NMR spectroscopic membrane showed that oxacalixarene selectively measurements during titration with metal triflates.
1.1.9.3 Azacalixarene

Azacalixarenes, which are generated by the insertion of nitrogen atoms into the bridging methylene unit of the calixarene structure, have several isomers based on the position of the nitrogen atoms and the ring size. Azacalixarenes can be easily synthesized by heating bis(hydroxymethyl)phenol derivatives and benzylaminoles in refluxing toluene or xylene for 3 days. The desired cyclic compounds are obtained selectively in moderate to high yields. The choice of non-polar solvents is essential in this reaction because the template effect by OH-OH, OH-N hydrogen bonds play an important role in the cyclization. Thus, the high dilution technique is not required in this reaction. Several reports support this phenomenon i.e., a phenol cyclic trimer was observed in supersonic jets. Generally, condensation reactions between alcohol and amines require drastic reaction conditions and catalysts. However, in the case of hydroxyl methylphenols, C-N bond formation occurs under relatively mild conditions. In particular, in spite of their potential richness and versatility as ligands, the structural studies of their complexes are scarce compared to those of calixarenes and even oxacalixarenes, which are another closely related family of expanded calixarenes. The presence of a soft nitrogen atom in azacalixarenes is envisioned to bind soft cations like ion metals according to hard soft acid and base principle (HSAB) as well as other specific features such as building sophisticated receptors, metal ligand systems etc. The triaza[3.3.3] N-benzyl-triaza[3.3.3] extracted $UO_2^{2+}$ efficiently even in the presence of a high concentration of NaCl. The extraction ability has a high pH dependency; uranyl ion is most effectively extracted in the neutral region. Since azacalixarenes have nitrogen atoms as a base, they form metal complexes under neutral conditions. Lanthanide extraction experiments were carried out by using N-(2-picoly)-triaza[3.3.3] derivatives as a ligand in order to investigate the metal selectivities among lanthanide ions. It was showed that triaza[3.3.3] derivatives as a ligand extracted alkali metal ions efficiently, but the selectivity was very poor because of the flexibility of the picolyl side arms. In the case of lanthanide ions, extraction occurred very efficiently, however, the extraction is very sensitive to the pH of the aqueous phase. Thury et al. prepared $UO_2^{2+}$, $Nd^{3+}$ and $Yb^{3+}$ complexes of azacalixarenes without using any bases and succeeded in obtaining
1.2 Chemical modification of calixarene

1.2.1 Nitrocalixarenes

p-Nitrocalixarenes are a class of useful intermediates for the introduction of other functional groups to obtain N containing substituted calixarenes. A number of researchers have carried out the nitration of calixarenes and some direct (the parent p-tert-butylcalixarenes as the starting materials) or indirect methods have been developed. Shinkai et al. have examined the reaction of calix(6)arene with nitric acid to give a very low yield of the hexa nitro product, ostensibly because of oxidation of the phenolic ring present in the reactants. The one step direct synthesis of nitrocalixarene was reported by reacting p-nitrophenol with formaldehyde in the presence of conc. HCl as catalyst. Nitration of sulphonated calixarenes by nitric acid has also been determined to give low yields of desired nitro substituted calixarenes. Reinhoudt et al. have examined ipsonitration
1.2 Chemical modification of calixarene

of p-tert-butylcalix(4)arene methyl ether to yield nitromethoxy calix(4)arene by using fuming nitric acid, though they reported the failure of the method when attempted on the parent p-tert-butylcalix(4)arene.\textsuperscript{199} Nam and Kim have reported nitration of calix(4)arene through their di and tri-benzoyl derivatives which led to the introduction of nitro groups in positions para to the free hydroxyls.\textsuperscript{200} Huang et al. have nitrated calix(4)arene by reaction with $\text{AlCl}_3/\text{KNO}_3$ in $\text{CH}_3\text{CN}$ followed by treatment with an acid.\textsuperscript{201} All the methods known to date for obtaining p-nitrocalix(4)arenes suffer from one disadvantage or another. For example, while direct nitration leads to no product, nitration of debutylated calixarenes is accompanied by oxidized products and lesser yields besides involving additional debutylation step. Methods described by No and Noh, Nam and Kim also involve an additional step with eventual low overall yields. Additionally, the reported methods usually do not yield fully nitrated higher calix(n)arenes and the product is usually obtained as a complicated mixture. The amino calixarene derivatives and various acylated calixarenes were reported.\textsuperscript{202} Calix(5)arene containing a single p-nitrophenol unit as the most acidic phenolic units has been synthesised by [3+2] fragment condensation of trimer with p-nitrophenol in middle with various bishydroxymethylated alkanediyl diphenols.\textsuperscript{203}

1.2.2 Hydroxamic acid derivatives of calixarene

Hydroxamic acids are versatile metal extractants that have been the subjects of large number of physico chemical investigations because of their wide applications in analytical,\textsuperscript{204} agriculture\textsuperscript{205} and biological fields.\textsuperscript{206} The introduction of the hydroxamic acid group into macrocycle may enhance the complexing ability towards metal ions. A new calixarene hydroxamic acid, 25,26,27,28-tetrahydroxy 5,11,17,23-tetrakis(N-p-chlorophenyl)calix(4)arene hydroxamic acid is used for the extraction and spectrophotometric determination of thorium(IV).\textsuperscript{207} Agrawal and coworker have reported calixarene hydroxamic acid, 5,11,17,23-tetra-(N-p-chlorophenyl) hydroxamate c-phenyl-25,26,27,28-tetrahydroxy calix(4)arene and used for the extraction and spectrophotometric determination of uranium(VI).\textsuperscript{208} Agrawal et al. has synthesized calixarene hydroxamic acid, 25,26,27,28-tetrahydroxy-5,11,17,23-tetrakis (N-p-chlorophenyl) calix(4)arene hydroxamic acid (CPCHA)
1.2 Chemical modification of calixarene

and used for the extraction and graphite furnace atomic absorption determination of zirconium(IV).\textsuperscript{209} A calix(6)arene bearing three hydroxamic acid groups arranged in a $C_3$ symmetry has been synthesized by Asfari.\textsuperscript{210} Extraction properties towards transition metal ions are presented and compared with other proton-ionizable related calix(6)arene and monomeric hydroxamic acid analog. 4-tert-butylcalix(4)arene tetrahydroxamate chelators has been synthesized by Dasaradhi\textsuperscript{211} for selective solvent extraction of actinides(IV) ions. Shinkai\textsuperscript{212} synthesized calix(n)arene-based uranophiles bearing hydroxamic groups on the lower rim (n= 4 and 6). A p-t-butylcalix(6)arene derivative bearing six hydroxamate groups has been synthesized by Nagsaki\textsuperscript{213} and efficiently extracted $UO_2^{2+}$. Calix(6)arene hydroxamic acids are synthesised for the first time by reacting calix(6)arene acid chloride(II) with substituted hydroxylamines at low temperature in the presence of sodium bicarbonate. The thermodynamic ionization constants of calixarene hydroxamic acids have been determined by a pH titration technique in dioxane-water media.\textsuperscript{214} Poriel and co workers studied the affinity of calix(6)arenes bearing hydroxamic acid groups ($LH_3H_3$) towards americium by solvent extraction.\textsuperscript{215} The results showed that $LH_3H_3$ has a very good affinity for americium and enhance the possibility of separating Pu from U and Am. The affinity of calix(6)arene bearing hydroxamic acid molecule towards Pu(IV) and U(VI) has been studied and analyzing Pu traces from urine media and in the presence of uranium and the possibility to separate both elements has been shown. Arduini reported new synthetic methods for the monoalkylation of calix(4)arenes at the lower rim allows the synthesis of a new class of trihydroxamate siderophores. Three chelating hydroxamic acid units are introduced through a sequence of reactions which blocks the macrocycle in the cone conformation. The new ligands obtained form neutral 1:1 complexes (FeL) with iron(III). A selective and sensitive method for the extraction and microgram determination of molybdenum(VI) with hydroxamic acid as yellow molybdenum-hydroxamate complex from acidic medium is described. The molybdenum-PCPPSAHA complex has $\lambda_{max}$ 388 nm, molar absorptivity $5.0 \times 10^3$ $l \text{ mol}^{-1} \text{ cm}^{-1}$.\textsuperscript{217} The functionalisation of macrocyclic p-tertbutylcalix(4)arenes at the lower rim with hydroxamic acid and proline hydroxamic acid groups gives the calixarenes chelating properties similar to
1.2 Chemical modification of calixarene

siderophores. The $^1H$ NMR spectrum of p-tertbutylcalix(4)arene tetrahydroxameric acid shows a broad band at 10.8 ppm in DMSO-$d_6$ attributed to NHOH protons. Agrawal and Sharma\textsuperscript{218} have synthesized rotaxane with hydroxamic acid, and used for the liquid-liquid extraction, complexation, speciation and trace determination of vanadium(V). A biscalix(6)arene bearing two hydroxamic acid groups has been synthesized by Agrawal and Shripada.\textsuperscript{219} Agrawal et al.\textsuperscript{220} has synthesized calix crown hydroxamic acid, and used for the Speciation, liquid-liquid sequential separation preconcentration, transport and ICP-AES determination of Cr(III), Mo(VI) and W(VI). Calix(4)resorcinarene-hydroxamic acid, crown-calix(4)resorcinarene hydroxamic acid have been synthesized by Agrawal and Patadia\textsuperscript{221} and used for liquid-liquid extraction, separation and trace determination lanthanum(III), cerium(IV), neodymium(III) and gadolinium(III). A pyridinium bearing calix(4)arenehydroxamic acid, coumarin-calix(4)arenehydroxamic acid and tetracarboxycalix(6)crownhydroxamic acid have been synthesized by Agrawal and Thakkar\textsuperscript{222} and used for the liquid-liquid extraction, Preconcentration, Separation and trace determination of Niobium, Titanium, Zirconium, Hafnium and Tantalum. Thiacalix(4)arene hydroxamic acid, thiabiphenyl-calix(4)arene hydroxamic acid,thiabiphenylcalix(4)monocrow hydroxamic acid have been synthesized by Agrawal and Pancholi\textsuperscript{223} and used for the liquid-liquid extraction, complexation, speciation and trace determination of Ag(I), Cu(II), Zn(II) and Hg(II).
1.3 Aim and scope

The rare earth elements are becoming increasingly more important for the production of modern technological materials. In addition to their use as neutron poisons in the nuclear industry, they find application in superconductors, optoelectronic materials, special alloys, catalysts, and radiotherapeutic reagents.\textsuperscript{224–225} Various classes of extractants ‘exhibit at least some utility in lanthanide separations [e.g., tertiary carboxylic acids\textsuperscript{226}, b-diketones\textsuperscript{227}, 4-acylpyrazolones\textsuperscript{228–229}, quaternary alkylammonium salts\textsuperscript{230}], mono and bifunctional neutral organophosphorus compounds.\textsuperscript{231–232} However, some of these are found toxic, costly and also the method of separation are time consuming, generate large volume of secondary waste as well as radiolytic and hydrolytic products. With this in view, it is required to develop a simple, cost effective technique for their separation and recovery. Review of literature reveals that the selectivity and extractability of an extractant employed for solvent extraction affect greatly the efficiency of the recovery process. Recently, cyclic host compounds i.e., calixarene derivatives, which are synthesized easily and functionalized in various ways, have been noted as useful extractants of metal ions.\textsuperscript{233–239} These novel compounds can recognize a target metal ion by the cavity size of the cyclic molecule together with the chelating effect of their functional groups. Therefore, functionalized calixarene is one of the most promising extractants for the innovative solvent extraction process and has been tried out for the separation of metal ions in recent years.\textsuperscript{240–243} Hydroxamic acids are versatile extractants and have achieved significant importance as analytical tools for separation and determination of a large number of metal ions. The macrocyclic platform among the derivatives of calixarenes, the hydroxamic acids functionalized calixarene are highly selective reagents for metal ions. However, very little work has been done in the field of separation and recovery of rare earth elements using calixarene substituted hydroxamic acid. With this in view, the aim of present work is to synthesize calixarene hydroxamic acid and developed the simple selective method for the kinetic extraction, separation, recovery, trace determination and sequential separation of rare earth.
1.4 Present investigation

The present work describes the synthesis of bis N-phenyl benzocalix(6)arenehydroxamic acid (NPCHA) by conventional as well as microwave assisted techniques. The conventional synthesis of NPCHA by reacting calix(6)arenehydroxylamine with acid chloride at low temperature in the presence of sodium bicarbonate. Microwave Assisted synthesis of NPCHA was developed. The comparison of conventional and microwave assisted synthesis have been discussed. The physico-chemical properties of NPCHA have been evaluated.

The kinetic extraction of vanadium with p-nitro calixarene hydroxamic acid (NPCHA) is reported. The vanadium is extracted from 6.5 M HCl and separated for commonly associated ions and determined in nutritional and biological substrates. The influence of NPCHA, molarity of HCl, diverse ions etc., on the extraction of vanadium have been examined. The system obeys Beer’s law in the range of 0.20-1.01 $\mu$g ml$^{-1}$ of vanadium. The molar absorptivity is found $4.54 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ at 517 nm. The NPCHA-vanadium(V) complex extract in dicholoromethane was directly inserted into plasma for ICP-MS measurement, which increases the sensitivity to several times and obeys Beer’s law in the range of 10-100 ng ml$^{-1}$ of vanadium(V).

The kinetic extraction, separation and trace determination of lanthanum(III) and cerium(IV) with p-nitro calixarene hydroxamic acid (NPCHA) is reported. Lanthanum and cerium are extracted at pH 8.5 and 9.5, respectively in dicholoromethane. The influence of NPCHA, pH and diverse ions of lanthanum and cerium was examined. Lanthanum(III) gives a colourless complex with NPCHA which is extracted into dicholoromethane having molar absorptivity $4.51 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ at 377 nm and obeys Beers law over the range of 0.5-2.77 $\mu$g ml$^{-1}$, while cerium(IV) forms pinkish red coloured complex, $\lambda_{max}$ 452 nm, molar absorptivity $4.53 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ and obeys Beers law over the range of 0.55-2.78 $\mu$g ml$^{-1}$. For trace determination the extract were directly inserted into plasma for inductively coupled plasma mass spectrometry (ICP-MS) measurement for lanthanum and cerium, which enhances the sensitivity to several times and obeys Beers law in the range of 25-140 ng ml$^{-1}$ for lanthanum and 30-160 ng ml$^{-1}$ for...
cerium. The method is applied for determination of lanthanum and cerium in real standard samples and environmental samples.

The kinetic extraction, sequential separation and trace determination of uranium(VI) and thorium(IV) with p-nitro calixarene hydroxamic acid (NPCHA) is reported. Uranium(VI) and thorium(IV) are extracted at pH 6.0 and 4.5, respectively in dichloromethane. The influence of NPCHA, pH and diverse ions of uranium(VI) and thorium(IV) was examined. The uranium(VI)-NPCHA complex has a maximum absorbance at 407 nm with molar absorptivity $3.69 \times 10^4 \, \text{mol}^{-1} \, \text{cm}^{-1}$. The system obeys Beer's law over the range of 0.94-4.74 $\mu g \, \text{ml}^{-1}$ of uranium(VI) at 407 nm. The thorium(IV)-NPCHA complex has a maximum absorbance at 372 nm with molar absorptivity $1.46 \times 10^4 \, \text{mol}^{-1} \, \text{cm}^{-1}$. The system obeys Beer's law over the range of 0.92-4.62 $\mu g \, \text{ml}^{-1}$ of thorium(IV) at 452 nm. For trace determination the extract were directly inserted into plasma for inductively coupled plasma mass spectrometry (ICP-MS) measurement for uranium(VI) and thorium(IV), which enhances the sensitivity to several times and obeys Beer's law in the range of 47-230 ng $ml^{-1}$ for uranium and 40-200 ng $ml^{-1}$ for thorium. The method is applied for determination of uranium(VI) and thorium(IV) in real standard samples and environmental samples.
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