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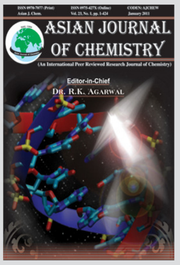

REVIEW

Binding Abilities and Extractive Applications of Nano-baskets of Calixarenes

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Because of the recent rapid growth in the publications about applications of nano-baskets of calixarene in extraction of ionic and molecular species, this review paper has focused on different extractive applications of calixarene derivatives. The objectives and the results of about 140 references that were published in recent 6 years with emphasis on the binding ability and extractive applications were reviewed. A tutorial algorithm was designed to explain the recent advances in binding ability of calixarene and their applications in extractions of analytical chemistry. The applications of calixarene derivatives to bind and extract the seven following fields were reviewed, including alkali and alkaline earth metals, *p*-block cations, transition metals, actinides and lanthanides, molecular species, organic cations and anions.

Key Words: Nano-basket, Calixarene, Complexation, Separation, Solvent Extraction, Transport.

INTRODUCTION

Ganjali *et al.*[1], reported that evolution of macrocycles field comes back to 1987 when Lehn, Cram and Pedersen won the Nobel Prize in chemistry for synthesizing compounds with cavities within which metal ions and other molecules could be bound. Supramolecular chemistry is a field of chemistry that studies the multimolecular species formed from complexation of molecular components with relatively similar structures. These systems are bound together reversibly by intermolecular forces, rather than by covalent bonds and shared electrons.

Calixarenes, were introduced in 1870 for the first time but were ignored until 1940. In 1970s, calixarenes were studied with uncertainty. During 1990, calixarenes were presented in brief out line with emphasize on the use of these molecules for chemical separations. Finally, the discovery of calixarenes was attributed to Zinke (1940) and fully interpreted by Gutsche in 1970. Gutsche was also the first to draw attention to the potential use of them as molecular receptors or enzyme mimics. He proposed that these cyclic oligomers, known as collectively calixarenes in 1978, having recognized in space-filling models of the tetramer a chalice or cup-like shape reminiscent of a Greek crater vase.

According to Baldini *et al.*[2], the concept of valency as the number of ligating functionalities of the same or similar types in a supramolecule and connected to each of the guest entities. Calixarenes were obtained by the oligomerization of phenol and formaldehyde and their valency can be easily varied at least from 1-8, while the stereochemical orientation of the ligating arms can be properly tuned by shaping.

Depending upon the relative orientation of the *para* and phenolic sites, the tetramer (calix[4]arene) can adopt four different conformations[3]. Baldini *et al.*[2] in their review paper, illustrated these conformations of calixarenes including: cone, partial cone, 1,2-alternate and 1,3-alternate. Various methods for functionalizing calixarenes have been developed and numerous calixarene derivatives have been synthesized during the past two decades. Uysal-Akkus *et al.*[4] have referred to Tabakci's paper and reported that the binding properties of calixarenes appear to be highly dependent upon the nature and the number of donor atoms of the calix[4]arene moiety.

Various applications of calixarenes are used in purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels and self-assembling monolayers[5]. Different complexing groups at the upper rim of calixarenes are able to attract desirable molecules with pre-defined selectivity. The lower rim functional groups of calixarenes are usually responsible for physical properties of calixarene molecules[6].

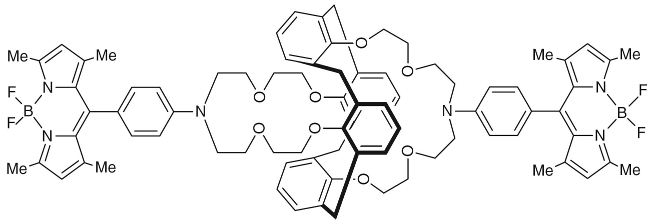
Calixarenes have demonstrated outstanding complex ability towards ions, neutral molecules, *etc.* and are considered as the third best host molecules after cyclodextrins and crown ethers[7]. During the last three decades calixarene chromoionophores have long been studied as specific metal ion indicators. Various types of chromogenic calix[4]arene derivatives have recently been synthesized which have shown selective recognition and complexation with metal ions[8]. The analysis without first requiring physical separation is a major driving force for separation techniques, which calixarenes have been used for this purpose[9]. Although several ligands have been well studied in terms of chemical stability in acid conditions, their behavior under irradiation condition has been less explored[10].

Some of those researches are including: complexation of alkali metal cations by calix[4]arene-*bis*-crown-6 in methanol, acetonitrile and propylene carbonate[11], induced aggregation of calix[4]arene ethers[12], determination of ionicity and electronic structures for the non-covalent complexes of calix[4]resorcinarene[13], thermodynamics of complexation of alkali metal cations by *tert*-butyl-26,28,25,27-*tetrakis* (O-methyl-d-α-phenylglycylcarbonylmethoxy)calix[4]arene, a lower-rim calix[4]arene amino acid derivative[14], transfer of calix[4]resorcinarene derivative from water to aqueous dipeptide solutions[15] and *bis*(crown-6)calix[4]arene/Cs^+ coordination chemistry[16].

In this review article, a tutorial algorithm was designed to explain the recent advances in binding ability of calixarene and their applications in extractions of analytical chemistry. The applications of calixarene derivatives to bind and extract the seven following fields were reviewed, including of alkali and alkaline earth metals, *p*-block cations, transition metals, actinides and lanthanides, molecular spices, organic cations and anions.

Complexation studies: Calixarenes accommodate neutral and ionic species and complexation is their important feature. Complexation studies are reviewed in this section, followed by the abstracted tables, which listed the research works on calixarenes complexation. Diamond in 1986 published the first calixarene-sodium complex, which were useful in the estimation of sodium cation in blood. After that, many researches were conducted on the alkali and alkaline earth cations. Table-1 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and s-block cations.

Iranian researchers[3] evaluated the complexation abilities of 26,28-*bis*-benzyloxy-25,27-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene and 25,26,27,28-tetra-benzyloxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene towards alkali metal ions Li^+, Na^+, K^+, Rb^+ and Cs^+ in methanol-chloroform mixture. Yaftian *et al.*[17], evaluated the complexation ability of a phosphinoymethoxy calix[4]arene towards alkaline earth cations. The stability constants of complexes of boron-dipyrromethene dye 1,3-alt calix[4]bisazacrown-5 (**01**) with Na^+, K^+, Cs^+, Ca^{2+} and Ba^{2+} ions were determined by Sliwa and Girek[18]. Two azacrown-5 ether binding sites well fitted the K^+ and showed a high K^+/Na^+ selectivity in acetonitrile, ethanol and ethanol/water mixtures.



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Finlander chemists reviewed the synthesis and properties of calix[4-8]crowns, calix[4-8]biscrowns and resorcinarenecrowns and concluded that these macrocycles exhibit remarkable ionophoric properties towards alkali and alkaline earth metal cations. Their selectivity has been attributed to their structural features (size of the crown ether moiety) and conformation of the parent calixarene[19]. Kim and Vicens[20] reviewed the complexing properties of calixcrowns, calixbiscrowns and related compounds such as resorcinarene crowns and they reported that calixcrowns exhibit remarkable ionophoric properties towards alkali and alkaline earth metal cations.

TABLE-1
LIST OF CALIXARENES USED IN COMPLEXATION STUDIES WITH *s*-BLOCK CATIONS

Type of calixarene	Analytes were used	References
Benzyloxy-hydroxycalix[4]arene	Li^+, Na^+, K^+, Rb^+ and Cs^+	[3]
Phosphinoymethoxy calix[4]arene	Li^+, Na^+, K^+, Rb^+ and Cs^+	[17]
1,3-Altcalix[4]bisazacrown-5	K^+	[18]
Calix[4–8]crowns and calix[4–8]biscrowns	Alkali and alkaline earth metal cations	[19]
Calixcrowns, calixbiscrowns	Alkali and alkaline earth metal cations	[20]
C_3-Symmetrical *p*-*tert*-butylhexahomotrithiacalix[3]arene	Alkali metal cations	[21]
Azocalixarenes	Alkali and alkaline earth metal cations	[22]
p-Tetraphenyl tetrahomodioxacalix[4]arene ethylester	Alkali and alkaline earth metal cations	[23]
p-Tetraphenyl tetrahomodioxacalix[4]arene amide	Alkali and alkaline earth metal cations	[24]
Calix[4]arenes bearing hydroxystyryl cyanine dyes	Li^+	[25]
1,3-Alternate thiacalix[4]arene	Li^+	[26]
Tetra-*tert*-butyl-tetrakis(methyl-α-Phenylglycylcarbonylmethoxy)calix[4]arene	Alkali metal cations	[27]
Calix[4]arene bearing two ester, polyether, urea, and bipyridine units	Na^+	[28]
Cone and 1,3-alternate tetrakis[(N,N-diethylaminocarbonyl)methoxy] Thiacalix[4]arene	Na^+ and K^+	[29]
Calix[4]pyrroles	Cs_2CO_3	[30]
Calix[4]arene bearing azopyridyl moieties	Radioactive Cs^+	[9]
A cone-shaped calixarene	Mg^{2+} and Ca^{2+}	[31]
1,3-Alternate calix-biscrowns	Cs^+	[18]

Ashram in Jordan synthesized C_3-symmetrical *p-tert*-butylhexahomotrithiacalix[3]arene and studied its binding properties with alkali cations using biphasic picrate extraction method. The results showed only weak abilities to bind the alkali cations examined[21]. In Turkey, complexation of azocalixarenes towards alkali and alkaline earth metal cations and their applications were reviewed[22]. In Tunisia, the complexation and binding properties of *p*-tetraphenyl tetrahomodioxacalix[4]arene ethylester[23] and *p*-tetraphenyl tetrahomodioxacalix[4]arene amide[24] derivatives towards alkali and alkaline earth metal cations was studied using UV-absorption spectrophotometry and ^{1}H NMR spectroscopy. Fig. 1 presents ^{1}H NMR spectra of first macrocycle and related complexes.

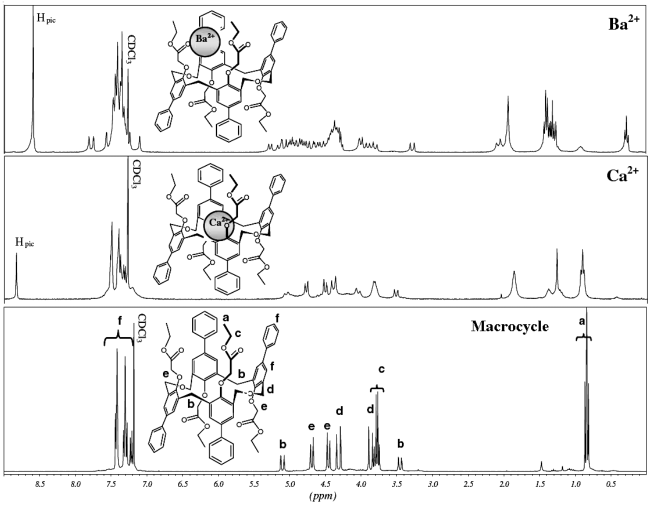


Fig. 1. ^{1}H NMR spectra of *p*-tetraphenyl tetrahomodioxacalix[4]arene macrocycle and its complexes towards two alkaline earth metal cations

Calix[4]arene derivatives bearing one or two hydroxystyryl cyanine dyes at the wide rim were synthesized and the influence of Li^+ on its UV-VIS spectra was investigated[25]. Perez-Casas *et al.*[26] examined the binding behaviors of 1,3-alternate thiacalix[4]arene with Li^+ by ^{1}H NMR titration experiment. The exclusive formation of mononuclear complexes of was observed even though the formation of the heterogeneous binuclear complexes was expected. In Croatia[27], the solvent effect on the binding ability of alkali metal cations with 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-*tetrakis*(O-methyl-D-α-phenylglycylcarbonylmethoxy) calix[4]arene was examined in methanol and acetonitrile solutions with different affinities for hydrogen bonding by means of spectrophotometric, conductometric and potentiometric titrations. The intramolecular (NH···O=C) hydrogen bonds in macrocycle need to be disrupted to allow metal ion binding, but it was shown to be an efficient binder for Li^+ and Na^+ cations in acetonitrile and moderately efficient for K^+; whereas, Rb^+ and Cs^+ did not fit in its cavity. The complex stabilities in methanol were measured to be significantly lower.

Nabeshima *et al.*[28] synthesized a calix[4]arene framework bearing two ester units, two polyether units, two urea units and two bipyridine units and used it to recognize Na^+. Casas and Yamato[29] assessed the complexation behaviors of both cone and 1,3-alternate *tetrakis*[(N,N-diethylaminocarbonyl) methoxy]thiacalix[4]arene by ^{1}H NMR titration experiments. They obtained the evidence of 1:2 (homo- and hetero-binuclear) complexes formation of 1,3-alternate derivative with K^+ and Na^+ cations. Custelcean *et al.*[30] studied the complexation of calix[4]pyrrole with cesium carbonate. A single anion bridged two calix[4]pyrroles-cesium complexes and formed a crystal structure of Cs_2CO_3 complex. Arora *et al.*[9] reported that calix[4]arene bearing azopyridyl moieties at the upper rim can be used as a selective filter for radioactive wastes containing Cs^+. A cone-shaped calixarene that influenced the Mg^{2+}, ATP-dependent Ca^{2+} accumulation in mitochondria and sarcoplasmatic reticulum of the smooth muscle cells was synthesized and investigated by Klyachina *et al.*[31]. Sliva and Girek[18] presented the complexation of 1,3-alt calix-biscrowns with hard cations like Cs^+ *via* π interaction. They reported that 1,3-alternate derivatives have oxygen atoms able to bind hard cations and they have *p*-basic aromatic cavity which may bind soft electron acceptors.

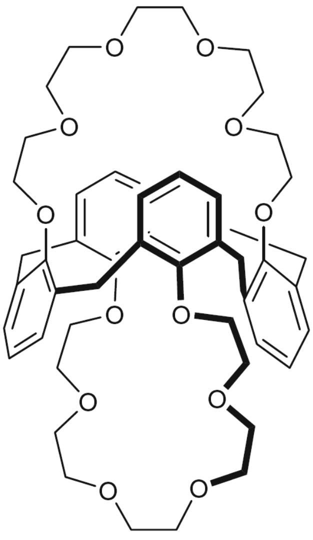
One of the most interesting properties of the macrocyclic calixarenes is their capacity to recognize *p*-block cations because of their ability to form compounds of high stability with these chemical species. Table-2 presents the complexation studies conducted on calixarene derivatives and *p*-block cations.

TABLE-2
LIST OF CALIXARENES USED IN COMPLEXATION STUDIES WITH *p*-BLOCK CATIONS

Type of calixarene	Analytes were used	Ref.
p-tert-Butylcalix[4]arene thioamides	$Pb(ClO_4)_2$	[32]
1,3-Alt-calixbiscrowns	Tl^+	[18]
Calix[4]arene derivatives	Tl^+	[33]
p-Sulfonatothiacalix[4]arene	Tl^+	[34]
Calix[4]arene diethers	Ge^{4+} and Sn^{4+}	[35]
Calix[4]arene-1,3-di-acid derivative	Sn^{4+}	[36]

Bochenska *et al.*[32] synthesized a number of *p-tert*-butylcalix[4]arene thioamides and presented the X-ray structures of the macrocycle towards $Pb(ClO_4)_2$. Its slightly distorted cone conformation was established. Sliwa and Girek[18] reported that the 1,3-alt-calixbiscrowns are able to coordinate metal ions *via* π interaction. They contain π-basic aromatic cavity that may bind soft electron acceptors and they have oxygen atoms able to bind hard cations. Therefore **02** may serve as a receptor for Tl^+.

Konishi *et al.*[33] used electrospray-ionization mass spectrometry to study the complexation of π-coordinate calix[4]arene derivatives toward Tl^+. Competitive complexation of three calix[4]arene derivatives demonstrated no effect of olefinic substituents and their location on the Tl^+ complexation. They also determined the stability constants for the complexes in methanol using 18-crown-6 as the reference ligand. Guo *et al.*[34] reported that Tl^+ is particularly favorable to be included into the cavity of *p*-sulfonatothiacalix[4]arene due to the cation polarizability. Hascall *et al.*[35] prepared germanium and tin complexes of calix[4]arene diethers and demonstrated that the produced complex exist as exo and endo isomers in which the metal is located either outside or inside the calixarene cavity. The exo isomer was considered to be



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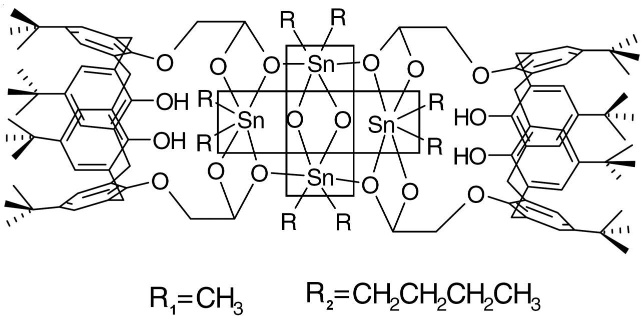
the kinetic product, whereas the endo isomer was thermodynamically more stable. Amjad *et al.*[36] synthesized Sn^{4+} complexes (**03** and **04**) with a calix[4]arene-1,3-di-acid derivative to investigate the ability of Sn^{4+} complexes in preventing absorption of lead.



03 and **04**

The selective interaction process between calixarenes and transition metal ions requires among other conditions, structural characteristics and dimensions of the cavity formed by the calixarene ring so that it can be capable to fit suitably to a specific cation. The efficiency of interaction may also be affected by the nature of the metal ion and by the number, distance and orientation of the donor atoms of calixarene that are structurally accessible to the complexed cation. The ability of the solvent molecules to compete with the donor atoms of the calixarene towards the coordination sites of the cation, is another factor that can thermodynamically influence the complexation process. Table-3 presented the content of this sub-section including the complexation studies conducted on calixarene derivatives and *d*-block cations.

Mewis and Archibald[37] outlined recent advances towards biomedical applications of calixarene complexes with transition metals. Seigle-Ferrand *et al.*[38] synthesized a calixarenic ditopic podand incorporating at the lower and upper rims two bipyridine and two dipyrrolyl groups, respectively. This calixarene fixed in cone conformation formed complexes with Cu^+ but with different stoichiometries. Qureshi *et al.*[8] studied complexation behavior of *p*-morpholinomethylcalix[4]arene (**05**) toward Cu^{2+}, Co^{2+} and Ni^{2+} by UV-VIS and fluorescence techniques.

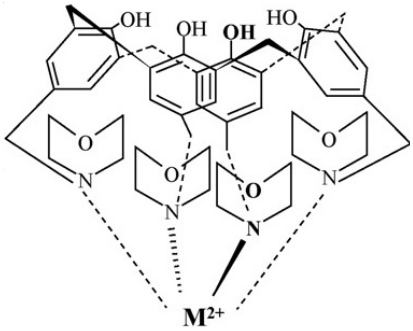


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TABLE-3
LIST OF CALIXARENES USED IN COMPLEXATION STUDIES WITH *d*-BLOCK CATIONS

Type of calixarene	Analytes were used	References
–	Transition metals	[37]
Bipyridine-dipyrrolyl calixarene	Cu^+	[38]
p-Morpholinomethylcalix[4]arene	Cu^{2+}, Co^{2+} and Ni^{2+}	[8]
Bipyridyl-amino calixarene	Cu^+ and Zn^{2+}	[39]
Sulfonato dipyridylcalixarene	Cu^{2+} and Co^{2+}	[40]
Aldimines calix[4]arene-Schiff base	$AgClO_4$	[41]
Alkyl thiol calix[4]arene	Ag^+	[42]
O,O''-*bis*[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene	Ag^+	[43]
Calix[4]pyrrole Schiff base	Cu^+ and Cu^{2+}	[44]
Tetraalkyl(tolyl)thiomethylcalix[4]arenes	Pd^{2+} and Ag^+	[45]
1,3-Alternate thiacalix[4]arene bearing two rhodamine B lactams	Cr^{3+} and Fe^{3+}	[46]
1,3-Alternate thiacalix[4]arene	Ag^+	[26]
Tetramethyl-tetra(4-hydroxy phenyl) calix[4]pyrrole and tetramethyl-tetra(dihydroxy phenyl) calix[4]pyrrole	Cu^{2+}	[47]
Azocalix[4]arenes	Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^+, Hg^+ and Hg^{2+}	[48]
Azocalixarenes	Transition metal cations	[22]
Tetraphosphineoxide calix[4]arene	Co^{2+} and Ni^{2+}	[49]
Thiacalix[4]arene	Ag^+	[50]
p-*t*-Butyl-thiacalix[4]arenes and *p*-*t*-butylcalix[4]arenes	Transition metal cations	[51]
Calix[4]arenas	Ag^+	[33]
Calixarenes bearing β-ketoimine groups	Cu^{2+}, Ag^+ and Hg^{2+}	[52]

Gaetano *et al.*[39] synthesized a calix[4]arene derivative incorporating two bipyridyl groups and one primary amino attachment function at the lower rim. They coupled it to Wang benzaldehyde resin and displayed its complexation abilities towards Cu^+ and Zn^{2+} cations. Arena *et al.*[40] introduced sulfonato groups into the backbone of a bipyridyl-based calixarene to obtain a novel water-soluble compound able to complex Cu^{2+} and Co^{2+} and showed the different stoichiometries and stabilities of new complexes from the analogous water insoluble calixarene by spectrophotometric titration. Creaven *et al.*[41] synthesized two novel calix[4]arene:Schiff base receptors, one had prepared by two pendant aldimines, while the other had two-point attachment of a calixarene:dialdehyde onto a calixarene:diamine to form a calix-tube. Its binding with $AgClO_4$ showed large complexation-induced shifts in H NMR positions.

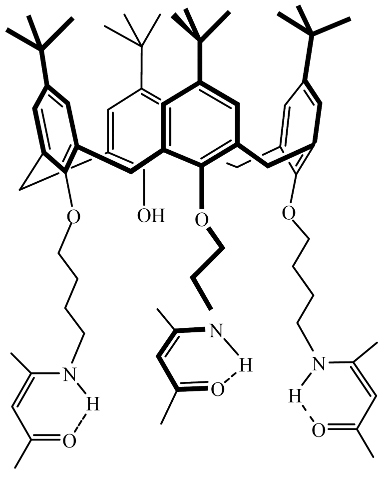
Shin *et al.*[42] synthesized two calix[4]arene derivatives containing four alkyl thiol linkages, which allow the calixarenes to attach on to the gold surface. The silver ion had affinity only to one of the monolayers, which had hydrophobic polarity. O'Dwyer and Cunnane[43] investigated the stoichiometry of O,O"-*bis*[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene-silver complex in water|1,2-dichloroethane interface and they found that the stoichiometry was shifted from 1:1 to 1:2 (metal:ligand) with increasing ionophore concentration. Veauthier *et al.*[44] used a calix[4]pyrrole Schiff base as binucleating ligand for Cu^+ and Cu^{2+}. In Cu^+ complexes, the metal centers were found to have a distorted tetrahedral geometry, while with Cu^{2+} the metal centers assumed distorted square planar geometry.

Torgov *et al.*[45] studied Pd^{2+} and Ag^+ complexation by tetraalkyl(tolyl)thiomethylcalix[4]arenes from main fission products. The stoichiometry and structural features of the complexes were studied by extraction, IR and mass spectroscopy methods and quantum mechanical calculations. Chinese and Japanese chemists synthesized 1,3-alternate thiacalix[4]arene bearing two rhodamine β-lactams to capture Cr^{3+} and Fe^{3+} in a fluorescent sensor. The association constants and stoichiometric ratios of the complexes were determined and they showed that the presence of Fe^{3+} or Cr^{3+} induced the sensor to form a stable 1:1 complex[46]. The complexation and binding behaviors of 1,3-alternate thiacalix[4]arene with Ag^+ were examined by ^1H NMR titration experiments[26]. Jain and Mandalia[47] synthesized the *meso*-tetra(methyl) *meso*-tetra(4-hydroxy phenyl) calix[4]pyrrole, *meso*-tetra(methyl) *meso*-tetra(3,5-dihydroxy phenyl) calix[4]pyrrole and their azo dyes and studied their efficiency towards Cu^{2+} using UV-VIS spectrophotometry. The experimental results showed a distinct colour change from yellow to red upon complexation.

Ak and Deligoz[48] synthesized four azocalix[4]arenes and investigated their complexes with Cu^{2+}, Ni^{2+} and Co^{2+} by means of UV-VIS, IR and ^1H NMR spectroscopic techniques. They reported that all the complexes have a metal:ligand ratio of 2:1 and the azocalix[4]arenes complexes with Cu^{2+}, Ni^{2+} are square-planar, while the Co^{2+} complexes are octahedral with water molecules as axial ligands. the thermal stability of metal:azocalix[4]arene complexes with Ag^+, Hg^+ and Hg^{2+} were also reported. Deligöz[22] reviewed azocalixarenes complexation for transition metal cations and reported a wide variety of their applications by the functionalization of the side arms.

Kostin *et al.*[49] synthesized the monomeric and the polymeric 1:2 complexes of a tetraphosphine oxide calix[4]arene with Co^{2+} and Ni^{2+} nitrates. Base upon their results, in the monomeric complexes each metal cation was coordinated by two bidentate NO_3-ligands and two proximal P=O groups at the calixarene skeleton. Tanaka *et al.*[50] studied the complexation of thiacalix[4]arene with Ag^+. Bouhroum *et al.*[51] reported the synthesis and crystal structure of *p*-*t*-butylthiacalix[4]arene and *p*-*t*-butylcalix[4]arene derivatives. They established their cation-binding properties by liquid-liquid extraction of metal picrates from water into dichloromethane. The stability constants were determination in acetonitrile using UV-absorption spectrophotometry. They found the stoichiometry of complexes to be 1:1 and the location of the metal cations was shown by ^1H NMR to be nearby the sulfur atoms.

Konishi *et al.*[33] investigated the complexation of π-coordinate calix[4]arene derivatives toward Ag^+. Competitive complexation of three calix[4]arene derivatives demonstrated a significant effect of olefinic substituents and their location on Ag^+ complexation. They determined the stability constants for Ag^+:calix[4]arene derivative complexes in methanol using a reference ligand (18-crown-6). Sliwa and Deska[52] reviewed the calixarene complexes with soft metal ions including copper, silver, gold, zinc, cadmium and mercury cations. They introduced the calixarenes bearing β-ketoimine groups (**06**) enable to complex with Cu^{2+}, Ag^+ and Hg^{2+} in a cone conformation.



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The complexation selectivity of calixarenes with *f*-block cations has often been explained in terms of the size-fit concept that the calixarene forms a more stable complex with the cation which is more suitable in size for the calixarene cavity. Table-4 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and *f*-block cations.

Mariani *et al.*[10] selected calixarene-based picolinamide ligands and determined the distribution coefficients for actinides and lanthanides. Leydier *et al.*[53] synthesized

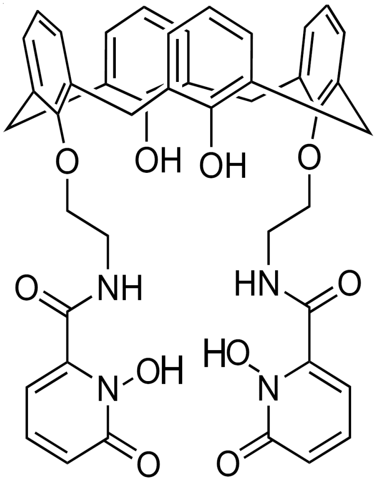
TABLE-4
LIST OF CALIXARENES USED IN COMPLEXATION STUDIES WITH *f*-BLOCK CATIONS

Type of calixarene	Analytes were used	Ref.
Calixarene-based picolinamide	Actinides and lanthanides	[10]
Hydroxypyridinone and sulfocatecholamide calixarene	Uranyl	[53]
–	Gd^{3+}	[37]
Phosphorylated calixarenes	Europium, americium, thorium and uranyl cations	[50]
Thiacalix[4]arene complex	Tb^{3+}	[54]

hydroxypyridinone (**07** and **08**) and sulfocatecholamide (**09**) calixarene ligands and determined their binding abilities for uranyl cation. They exhibited significant affinity towards uranyl ion at acidic and basic pHs, respectively.

Mewis and Archibald[37] reviewed some biomedical applications of macrocyclic ligand complexes like functionalized a calixarene to give four Gd^{3+}-DOTA (1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid) units attached on the upper rim. Karavan *et al.*[50] used phosphorylated calixarenes for recognition of europium, americium, thorium and uranyl ions and studding their complexes in single media (methanol and acetonitrile) followed by UV-spectrophotometric and isoperibolic calorimetric titrations. Tanaka *et al.*[54] studied the structure of thiacalix[4]arene complex with Tb^{3+} and discussed how the donor atoms (sulfur and oxygen) showed high selectivity toward Tb^{3+}. Table-5 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and molecular species.

Heparin recognition of calix[8]arene polycations (**10-13**) was compared with two other heparin antagonists: protamine and polylysine. Experiments confirmed that calixarene derivatives have a very high specificity and affinity than other antagonists towards heparin neutralization as in aqueous solution as in blood[55].



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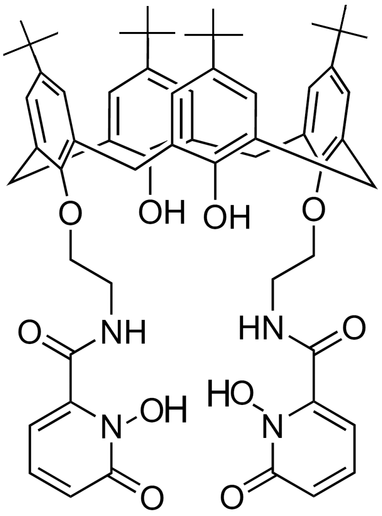

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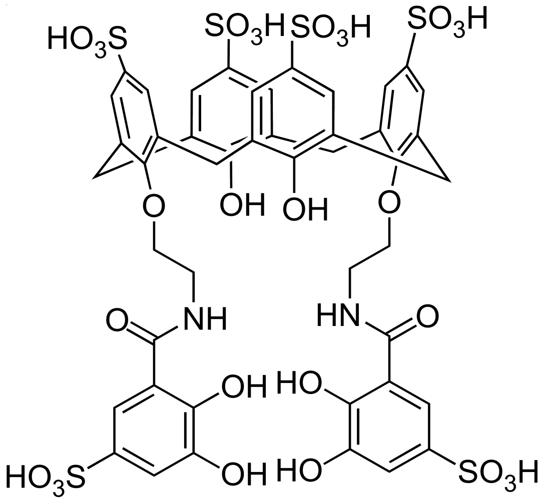
TABLE-5
LIST OF CALIXARENES USED IN COMPLEXATION STUDIES WITH MOLECULAR SPECIES

Type of calixarene	Analytes were used	References
Calix[8]arene polycations	Heparin	[55]
–	Lectin, proteins, DNA and cells	[2]
Double calix[5]arene	Fullerenes	[56]
p-Sulfonic acid calix[6]arene	Pyrrolizidine	[57]
Sulfonatocalixarene	Topotecan	[58]
p-Sulfonatocalix[6]arene	Phenothiazine dyes	[59]
p-Sulfonatocalix[4,6,8]arenes	NADPH oxidase	[60]
p-Sulfonatocalix[n]arenes	Heparin	[61]
Calix[4]arene phosphonic acids	Methyl esters of amino acids	[62]
p-Octanoylcalix[4]arene	Tetrahydrofuran	[63]
Calixarenes, thiacalix[4]arene-tetrasulfonate and calix[6]arene-Hexasulfonate	Fullerenes	[64]
p-Sulfonatocalix[8]arene	Phenothiazine dyes	[65]
1,2,3-Alternate calix[6]arene	Piperidine and triethylamines	[66]
Octaethyl-*p*-*tert*-butylcalix[8]arene	Methylene blue	[67]
Tetrabromocalix[4]arenes	Nitrile	[68]
p-Sulphonic acid calix[6]arene	Anesthetic tetracaine	[69]
p-Sulfonatocalix[*n*]arenes	Bovine serum albumin (BSA)	[70]
bis-1,3-Urea calix[4]arenes	α-Amino acids	[71]
4-Sulphonato-calix[*n*]arenas	Niclosamide	[72]
p-Sulfonated calix[4,6]arenes	Carbamazepine	[73]
Calix[4]resorcinarene	2-Naphthol and 1,5-naphthalenediamine	[74]
Calix[4]arene *bis*-hydroxymethylphosphous acid	Glycine, L-leucine, L-alanine, L-valine, and L-isoleucine	[75]



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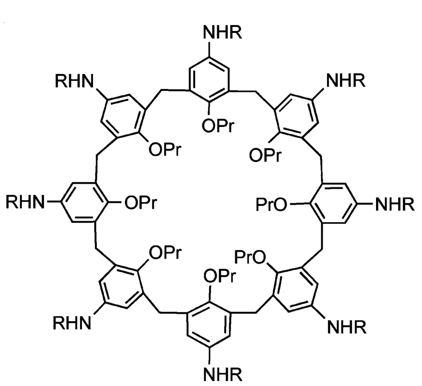


R = L- Lys
R = $CO(CH_2)_6NH_2$
R = L- Lys
R = $CO(CH_2)_6NH_2$

10-13

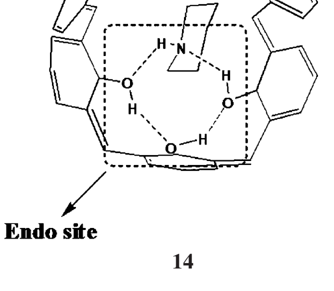
Baldini *et al.*[2] reviewed the fundamental aspects of multivalency and the properties of calixarene-based multivalent ligands in lectin binding and inhibition, protein surface recognition, DNA condensation and cell transfection, crystal engineering, self-assembly and nanofabrication. Haino *et al.*[56] revealed that *syn* isomer of a double calix[5]arene selectively captured higher fullerenes from fullerene mixtures and by elevation of the temperature more than 100 °C, its conformational was changed to the antiisomer and liberated the captured fullerenes. Drug toxicity in humans and animals is a major concern. Hence, Silva *et al.*[57] investigated the complexation properties of detoxificant agents. They investigated the inclusion complexation of a toxic alkaloid (pyrrolizidine) and *p*-sulfonic acid calix[6]arene by NMR techniques.

Wang *et al.*[58] prepared inclusion complexes of topotecan with sulfonatocalixarene and investigated the stoichiometry, complex stability constants and inclusion mode by means of ^{2}D NMR and UV-VIS spectroscopy. They elucidated that the dimethylaminomethyl group of topotecan and the quinoline ring were encapsulated in sulfonatocalixarene and the complex was more soluble than free topotecan. Inazumi *et al.*[59] studied the inclusion complexation of *p*-sulfonatocalix[6]arene with three kinds of phenothiazine dyes spectrophotometrically in a mixture of ionic liquid and ethanol and determined their association constants under external static pressure up to 767 bar. The results of study revealed that with increasing external pressure, the inclusion equilibrium was shifted to the dissociation side in the alcohol-water mixtures; while, it was shifted to the association side in the ionic liquid mixture.

Paclet *et al.*[60] used three water soluble calix[*n*]arene derivatives including *para*-sulfonatocalix[4,6,8]arenes to investigate the effects of them on the activation of NADPH oxidase in neutrophils. They showed that all the three molecules do not induce NADPH oxidase activation and hence do not stimulate neutrophils and are not cytotoxic. Silva *et al.*[61] investigated the antithrombotic activity of water soluble *p*-sulfonato-calix[*n*]arenes and 6 O-monosubstituted derivatives (like heparin) and proposed a mechanism for the anticoagulant effect of those calixarenes. Dziemidowicz *et al.*[62] synthesized calix[4]arene phosphonic acids with various substituents at the lower rim and studied their complexing properties towards methyl esters of 6 amino acids using ^{1}H NMR spectroscopy. They observed mixed 2:1 and 1:2 (host-guest) complexes with all amino acids methyl esters.

Shahgaldian *et al.*[63] reported double inclusion of the guest molecules (tetrahydrofuran) in *para*-octanoylcalix[4]arene complex. One tetrahydrofuran molecule held in a four-fingered molecular hand formed by the aliphatic chains and the other deep in the aromatic cavity. Kunsagi-Mate *et al.*[64] used photoluminescence and quantum chemical methods to study the fullerenes encapsulation with water-soluble calixarenes, thiacalix[4]arene-tetrasulfonate and calix[6]arene-hexasulfonate. They reported that functionalization of calixarenes and fullerenes induced significant changes in the molecular encapsulation processes.

Sueishi and Asamo[65] examined the effects of solvent polarity and pressure on the inclusion complexation of *p*-sulfonatocalix[8]arene with phenothiazine dyes. They resulted that depending on the bulkiness of the guest dyes, solvent polarity and external pressures increase the inclusion equilibrium constants. They also established the structures of the inclusion complexes using ^{1}H NMR measurements. Kang *et al.*[66] investigated the hydrogen bonding networks by studying the binding nature of the 1,2,3-alternate calix[6]arene with piperidine (**14**) and triethylamines. They reported that calix[6]arene derivative strongly binds with triethylamines and piperidines at endo and exo binding sites. They discussed the proton transfer within the hydrogen bonding and the hydrogen bonding types, low barrier hydrogen bonding, normal hydrogen bonding and short strong hydrogen bonding.



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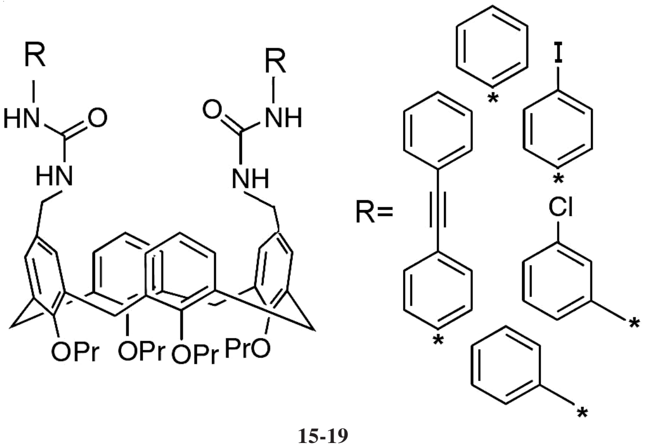
Inazumi and Sueishi[67] determined the equilibrium constants for the inclusion complexation of octaethyl-*p*-*tert*-butylcalix[8]-arene octaacetate with methylene blue and characterized the structure of the inclusion complex by 2D ROESY-NMR measurements. They found that calix[8]arene derivative forms a 1:1 inclusion complex with methylene blue in the upper main cavity. Maharaj *et al.*[68] synthesized tetrabromocalix[4]arene derivatives as inclusion hosts for nitrile guests and used X-ray to investigate the guests position inside and outside the calix[4]arene bowls. Calixarenes have also been used as pharmaceutical drug carriers to improve the bioavailability of medicines. The complexation of the local anesthetic tetracaine with *p*-sulphonic acid calix[6]arene was investigated using ^{1}H NMR experiments[69].

Binding stoichiometries and association constants for parent *para*-sulfonatocalix[*n*]arene derivatives with bovine serum albumin (BSA) were determined using electrospray ionization mass spectrometry. Silva *et al.*[70] concluded that the strength of the interactions between the bovine serum albumin and macrocycle is inversely proportional to the size of calix[*n*]arene ring: (4 > 6 >> 8). Bew *et al.*[71] reported the ability of five *bis*-1,3-urea calix[4]arene derivatives (**15-19**) to complex fourteen N-protected α-amino acids including N-Boc glycine, N-acetyl-(S)-phenylalanine, N-Cbz-proline, N-Fmoc-(S)-valine, N-Fmoc-glycine, N-Fmoc-(S)-proline, N-Fmoc-(S)-phenylalanine, N-Fmoc-(S)-tryptophan, N-Fmoc-(S)-arginine, N-Fmoc-(S)-histidine, N-Fmoc-(S)-histidine-Trt, N-Fmoc-(S)-phenylglycine, N-Fmoc-(S)-*t*-butoxityrosine, N-Fmoc-(S)-3,5-diiodotyrosine.



15-19

Yang and Villiers[72] investigated the complexation between the 4-sulphonato-calix[*n*]arene (water-soluble calixarenes) and niclosamide (a poorly water-soluble anthelmintic drug) by phase solubility studies. Carbamazepine is a poorly water soluble anticonvulsant drug. Panchal *et al.*[73] studied the effect of *para*-sulfonated calix[4]arene and *para*-sulfonated calix[6]arene on aqueous solubility of carbamazepine by means of HPLC, DSC, PXRD, FTIR, UV-VIS and FT-Raman spectroscopy. Their results were in good conformity to signify the formation of 1:1 calix[6]arene:drug and 2:1 calix[4]arene: drug complexes. Drug dissolution rate of inclusion complex was more than physical mixture and more than drug alone. Kharlamov *et al.*[74] investigated the association properties of water soluble calix[4]resorcinarene with 2-naphthol and 1,5-naphthalenediamine by NMR methods. They resulted that the pH dependency of those complexes makes them prime candidates for pH-responsive molecular machines applications.

Zielenkiewicz *et al.*[75] studied the host-guest complexes (1:1) of calix[4]arene *bis*-hydroxymethylphosphous acid with glycine, L-leucine, L-alanine, L-valine and L-isoleucine residues in methanol solution with the help of the titration experiments followed by ^{1}H NMR and UV spectroscopic methods. The stability constants for macrocycle and aliphatic L-amino acids were determined and the results indicated that the host-guest complexation was under control of the direct electrostatic interaction between amino acid residue NH_3^+ group and negatively charged calixarene phosphoryl group. They correlated the stability of the inclusion complexes with the size of the aliphatic amino acid's side-chain. Table-6 summarizes the recent studies conducted on the calixarene complexes with organic cations.

Fehlinger and Abraham[76] prepared calix[4]arenes bearing one cycloheptatrienyl and calix[4]arenes with one tropylium substituent and studied the complexation of them with organic cations such as quinolinium, ammonium and tropylium ions. Guo *et al.*[34] studied the complex structures, binding abilities and molecular selectivity of *p*-sulfonatocalixarenes and calculated the complex stability constants *via* calorimetric and spectroscopic methods. According to the results of their studies, in the cases of pyridinium guests, *p*-sulfonatocalixarenes also form stoichiometric 1:1 complexes with dipyridiniums and phenanthrolinium. The host-guest binding modes were determined by the ^{2}D NMR and they show that pyridinium guests are included into the cavity of *p*-sulfonatocalixarenes with the different patterns. Fig. 2 presents a graphical illustration for their interactions and steric conformations.

Kim and Vicens[20] reviewed the complexing properties of calixcrowns, calixbiscrowns and resorcinarenecrowns and reported their ionophoric properties towards amines and (alkyl) ammoniums. Salorinne and Nissinen[19] investigated the ionophoric properties of calix[4-8]crowns, calix[4-8]biscrowns and resorcinarenecrowns towards tertiary amines. They

TABLE-6
LIST OF CALIXARENE DERIVATIVES WERE USED IN COMPLEXATION STUDIES OF ORGANIC CATIONS

Type of calixarene	Analytes were used	References
Calix[4]arenes bearing cycloheptatrienyl and tropylium substituent	Quinolinium, ammonium and tropylium ions	[76]
p-Sulfonatocalixarenes	Pyridinium, dipyridiniums and phenanthrolinium	[34]
Calixcrowns, calixbiscrowns	Amines and alkyl ammoniums	[20]
Calix[4–8]crowns, calix[4–8]biscrowns	Tertiary amines	[19]
Calix[4,6]arenesulfonates and thiacalix[4]arene tetrasulfonate	Benzyltrimethylammonium	[77]
Calix[4,6]arenesulfonates and thiacalix[4]arene tetrasulfonate	Pyridinium	[78]

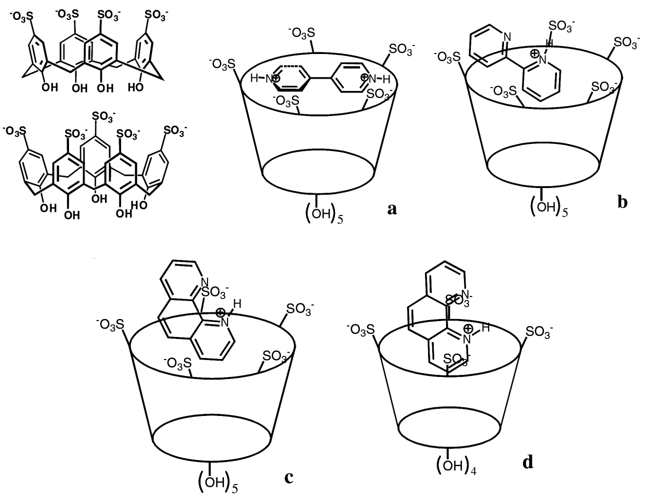


Fig. 2. Illustration of different patterns to include pyridinium guests into the cavity of *p*-sulfonatocalix[4-5]arenes

attributed the selectivity to the size of the crown ether moieties and the conformation of the parent calixarene. The complex stability constants, the binding mode and thermodynamics were determined for 1:1 inclusion complexation of calix[4,6]arenesulfonates and thiacalix[4]arene tetrasulfonate with benzyltrimethylammonium[77] and pyridinium guest ions[78]. The binding affinities from the viewpoint of π-π interactions, electrostatic interactions and size/shape relationship between host and guest were discussed. Table-7 shows recent complexation studies on anions recognition using calixarene derivatives.

Lang and his team[79], investigated the stoichiometry of complexation of calix[4]arenes bearing two *p*-nitrophenyl-ureido functions at the upper rim. Substitution pattern and anion concentration factors were studied on distal and proximal isomers and showed that while the distally substituted receptor forms 1:1 complexes with anions, the corresponding proximal derivative prefers the 2:1 stoichiometry under identical conditions[70]. Nabeshima *et al.*[28] introduced a multi-responsive calix[4]arene macrocycle can recognize $CF_3SO_3^-$ and BF_4^-. Its recognize ability to those anions was increased in a stepwise manner using Na^+ and Ag^+ as effectors. The enhancement of the K_a reached factors of 1500 and 2000 for NO_3^- and $CF_3SO_3^-$, respectively, in the presence of both Na^+ with Ag^+, compared to the free.

As discussed, phenolic units bridged by methylene spacers in *meta*-position are called calixarenes, although in recent years macrocycles with related subunits such as resorcin or pyrrole and other spacers such as sulfur are also considered to belong to the same class. Calixpyridines and calixpyrroles belong to calixarenes and there are some analytical applications of them. In Korea[80] a calix[4]imidazolium[2]pyridine cation was synthesized and formed a complex with F^- anion in a 1:1 stoichiometry, which can be used as a macrocyclic ionophore for F^-. Custelcean *et al.*[30] illustrated the anion-recognition behavior of the calix[4]pyrrole for carbonate anion and Sessler *et al.*[81] studied the interaction of calixpyrrole with several chloride salts.

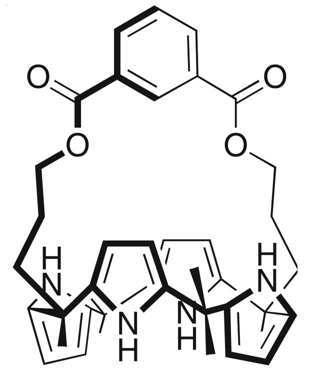
Yamato *et al.*[82] synthesized the cone-conformation of lower rim functionalized hexahomotrioxacalix[3]arene triamide and studied the anion complexation of triamide by ^{1}H NMR titration experiments. They reported that macrocycle: triamide binds halides through the intermolecular hydrogen bonding among the NH hydrogens in a 1:1 fashion in $CDCl_3$. They calculated the association constants from changes in chemical shifts of the amide protons to be Ka, Cl- = 223 M^{-1} and Ka, Br^- = 71.7 M^{-1}. Therefore, it revealed that macrocycle: triamide shows a preference for Cl^- complexation than Br^- complexation. Gross *et al.*[83] compared the binding properties of a series of phenyl (**20**), pyrrole (**21**) and furan (**22**) strapped calix[4]pyrroles towards fluoride, chloride, bromide and carboxylate anions. They showed that the pyrrole-strapped system of macrocycle displayed the highest affinity to anions.

Spherical halides, planar trigonal nitrate and tetrahedral hydrogen sulphate were subjected in some researches as their tetrabutylammonium salts. Hamdi *et al.*[84] studied the binding properties of 1,2,3,4-amido derivatives of *p-tert*-butyl calix[4]arene towards various anions by ^{1}H NMR. They determined the stability constants, varying from 0.76 ± 0.10 to 2.13 ± 0.04 for the mononuclear complexes. Othman *et al.*[85] prepared hyperbranched molecules based on multi-calixarenes and attached them to synthesized cores. Their complexation studies of prepared ligand with $Zn(Pic)_2$ showed that the ligand preferred to bind the picrate anions.

Solvent extraction: Calixarenes extract neutral and ionic species; hence, many studies have focused on this area. This section followed by the abstracted tables, which listed the research works on calixarenes ability to extract guest species. The solvation of alkali metal ions in the source phase, in the receiving phase and at the liquid-liquid interface demonstrates the active role of solvent on the structural features of the extracted complexes and on the effect of counter-ions. Solvent also markedly contributes to the thermodynamics of cation

TABLE-7
LIST OF CALIXARENES AND ANIONS USED IN EXTRACTION STUDIES

Type of calixarene	Analytes were used	References
Calix[4]arenes bearing *p*-nitrophenyl-ureido functions	Various anions	[79]
Multi-responsive calix[4]arene	$CF_3SO_3^-$ and BF_4^-	[28]
Calix[4]imidazolium[2]pyridine cation	F^-	[80]
Calix[4]pyrrole	Carbonate	[30]
Calixpyrrole	Several chloride salts	[81]
Hexahomotrioxacalix[3]arene triamide	Cl^- and Br^-	[82]
Phenyl, pyrrole, and furan strapped calix[4]pyrroles	F^-, Cl^-, Br^- and carboxylate	[83]
Amido *p-tert*-butyl calix[4]arene	Various anions	[84]
Multi-calixarenes	Picrate	[85]



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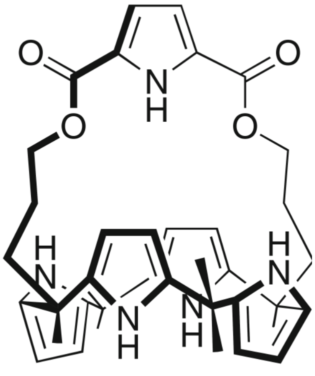

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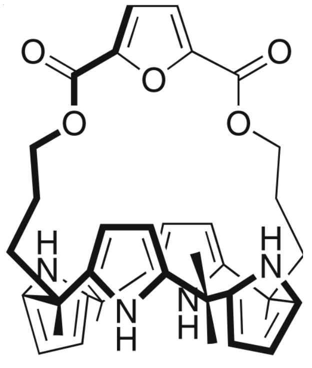

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complexation in homogeneous liquids and of transfer from one liquid phase to the other. Table-8 presents the content of this subsection including the solvent extraction studies using calixarene derivatives and *s*-block cations.

Mohapatra *et al.*[86] extracted radio ^{137}Cs using nitrobenzene solutions of calixcrowns from nitric acid solution of nuclear waste. They used calix[4]arene-bis(crown-6), calix[4]arene-*bis*(benzocrown-6) and calix[4]arene-*bis*(napthocrown-6) for that purpose. Tu *et al.*[87] synthesized di-ionizable calix[4]arene-1,2-crown-4 ethers that exhibited high Ba^{2+} selectivity ($Ba^{2+} >> Sr^{2+} > Ca^{2+} > Mg^{2+}$) in alkaline earth metal solutions into chloroform. Recently, Zhang and Hu[88] synthesized 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene and immobilized it into the pores of the SiO_2-P particles. It showed strong adsorption ability and excellent selectivity for Cs^+ over all the tested metals including Mo^{6+}, Pd^{2+}, La^{3+}, Y^{3+}, Ru^{3+}, Rh^{3+}, Cs^+ and Zr^{4+}.

Li *et al.*[89] synthesized triazole-modified calix[4]-diethylester and dimethylester and examined their selectivity towards alkali metal cations *via* two-phase extraction experiments. The cavity formed by two ester group is preferable for the complexing alkaline metal ions such as the Cs^+. Meanwhile, both modified calix[4]arenes displayed different selectivity towards alkali metal ions. Ohto *et al.*[90] investigated the solvent extraction of alkali metal ions with *p-t*-octylcalix-[4]arene tetracarboxylic acid and *p-t*-octylcalix[6]arene hexacarboxylic acid. The first one selectively extracted sodium ion among alkali ions at extremely low pH, while the other one exhibited only poor extraction ability for all alkali metals examined. They observed that two sodium ions were simultaneously extracted by a single molecule of calix[4]arene derivative and they found that the second sodium extraction was facilitated by the uptake of the first sodium. The authors proposed the self-coextraction mechanism of sodium ions. Vicens[91] described the development of calixbiscrowns for cesium removal in nuclear waste and related extraction methods.

Yang *et al.*[92] prepared *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 di(carboxylic acid) and evaluated its influence on competitive solvent extractions of alkali and alkaline earth metal cations. Park *et al.*[93] synthesized four calix[4]arene stereoisomers with two distal methoxycarboxy groups and two distal butoxy groups. They studied the influence of calix[4]arene conformation on metal ion complexation *via* extractions of alkali and alkaline earth cations from aqueous

TABLE-8
LIST OF CALIXARENES USED TO EXTRACT *s*-BLOCK CATIONS *VIA* SOLVENT EXTRACTION STUDIES

Type of calixarene	Analytes were used	References
Calixcrowns	Radio ^{137}Cs	[86]
Calixcrowns	Ba^{2+}	[87]
Calixcrowns	Cs^+	[88]
Triazole-modified calix[4]diethylester and dimethylester	Li^+, Na^+, K^+ and Cs^+	[89]
p-t-Octylcalix[4,6]arenes tetracarboxylic acid	Alkali metal cations	[90]
Calixbiscrowns	Cs^+	[91]
p-tert-Butylcalix[4]arene-1,3-thiacrown-5	Alkali and alkaline earth metal cations	[92]
Calyx[4]arene with two distal methoxycarboxy and butoxy groups	Alkali and alkaline earth metal cations	[93]
Hexahomotrioxacalix[3]arene triamide	Alkali metal cations	[82]
1,3-Alternate thiacalix[4]arene bearing carboxylic and aminopyridyl groups	Na^+, K^+ and Cs^+	[94]
1,2-Calix[4]crown-7,1,3-calix[4]crown-7,1,2-calix[4]crown-9 and 1,3-calix[4]crown-9	Sr^{2+}	[95]
p-tert-Butylcalix[4]arene-1,3-thiacrown-5 ether	Ba^{2+}	[96]
n-Homo calixnaphthalenes	K^+	[97]

solutions into 1,2-dichloroethane. Yamato *et al.*[82] synthesized the cone-conformation of lower rim functionalized hexahomotrioxacalix[3]arene triamide and discussed its extractability for alkali metal ions from water into dichloromethane.

The effect of proton-ionizable group (carboxylic moiety) on the solvent extraction of some alkali metal (Na^+, K^+ and Cs^+) with 1,3-alternate thiacalix[4]arene bearing one carboxylic moiety and three aminopyridyl groups was investigated[94]. Xia *et al.*[95] synthesized cone conformers of 1,2-calix[4]crown-7, 1,3-calix[4]crown-7, 1,2-calix[4]crown-9 and 1,3-calix[4]-crown-9. Synthetic calixarenes showed average affinity for alkali and alkaline earth metal picrates in two-phase extraction experiments. They reported the selective extraction of Sr^{2+} by 1,2-calix[4]crown-9 among other alkaline earth metal cations. Tu *et al.*[96] synthesized the cone conformation of *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 ether and evaluated its complexing properties by solvent extractions of Ba^{2+} from aqueous solutions into chloroform and found that the macrocycle was efficient extractant with Ba^{2+} selectivity in competitive solvent extraction of alkaline earth metal cations. Tran *et al.*[97] synthesized two new large-ring *n*-homocalixnaphthalenes that demonstrated high extraction capability for K^+. In Texas, Tu *et al.*[87] used calix[4]arene-crowns to extract Pb^{2+} in single species extraction.

Ulewicz *et al.*[98] investigated Pb^{2+} transportation through a calix[4]crown-6 derivatives/membrane and studied the influence of attached group of calix[4]-crown-6 on the selectivity of Pb^{2+} transport. Tu *et al.*[96] examined the extraction ability of cone conformation of *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 ether towards Pb^{2+} and showed its high extraction ability in single species solvent extractions.

Most processes to separate transition metal ions from aqueous solutions depend on ion exchange processes, in which the desired metal cation replaces a different metal cation or protons from an anionic group in a complexing agent. Such complexing agents are deployed on solid supports in processes using ion exchange resins or in a water immiscible liquid in solvent extraction. Although toxic metal ions may be sequestered in this way, true purification of the aqueous stream is not achieved because: (a) in the case of proton exchange the pH of the stream may be significantly lowered; (b) the number of ions present in solution is, at best, unchanged and is often increased; and (c) the anion remains in the solution. The harmful effects of anionic species such as phosphate and sulfate have led to control of environmental discharge levels for these species. These considerations, combined with novel separation technologies to process leach solutions in primary metal recovery, had led the researchers to investigate a new class of extractant. These extractants simultaneously sequesters both a transition metal cation and its attendant anion such as calixarenes. There are few examples of ligands which simultaneously bind cations and anions. Table-9 shows recent extraction studies that carried out on *d*-block cations using calixarene derivatives.

Gong *et al.*[99] examined the extraction behavior of 1,3-dipropyn-2-yl-oxycalix[4]arene towards Hg^{2+}. With equal mole ratio of Hg^{2+} and calixarene, the extractive per cent reached to 99.1 %. Ersoz[5] reviewed mercury transport in liquid membranes by calixarene derivative carriers and demonstrated various

TABLE-9
LIST OF CALIXARENES AND *d*-BLOCK CATIONS USED IN EXTRACTION RESEARCHES

Type of calixarene	Analytes were used	References
1,3-Dipropyn-2-yl-oxycalix[4]arene	Hg^{2+}	[5, 99]
p-Morpholinomethylcalix[4]arene	Cu^{2+}, Co^{2+} and Ni^{2+}	[8]
Diazo-coupling calix[n]arenes	Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}	[100]
O,O''-*bis*[2-(Methylthio)-ethyl]-*tert*-butylcalix[4]arene	Ag^+	[43]
Calix[6]crown	Cr^{3+}, Mo^{6+} and W^{6+}	[101]
Tetraalkyl(tolyl)thiomethylcalix[4]arenes	Pd^{2+} and Ag^+	[45]
Tolylthiamethy calix[4,6]arenes	Au^{3+}	[102]
–	Hg^{2+}	[103]
Calix[4]crown-6	Cd^{2+} and Zn^{2+}	[98]
Di-ionizable calix[4]crowns	Hg^{2+}	[87]
Calix[4]pyrrole hydroxamic acid	Vanadium	[104]
Calix[4,6]arenes bearing phosphine oxide groups	Ru^{3+} and Zn^{2+}	[105]
Hexahomotrioxacalix[3]arene triamide	Transition metal cations	[82]
1,3-Alternate thiacalix[4]arene possessing aminopyridyl and carboxylic groups	Cu^{2+}, Zn^{2+}, and Ag^+	[94]
Azocalix[4]arenes	Ag^+, Hg^+ and Hg^{2+}	[48]
Azocalixarenes	Fe^{3+}	[22]
Calix[4,6]arenes bearing phosphine oxide	Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}	[106]
Thiacalixarenes	Cu^{2+} and Cd^{2+}	[107]
Distal-bis[(2-pyridylmethyl)oxy]thiacalix[4]arenes	Ag^+	[108]
p-t-Butyl-thiacalix[4]arene and p-t-butylcalix[4]arene derivatives	Ag^+	[51]
p-Azophenylazocalix[4]arene	Te^{4+}, Pd^{2+}, and Fe^{3+}	[109]
Tetrahydroxy-tetraphenylazocalix[4]arene	Cu^{2+}, Co^{2+}, Rh^{3+} and Ir^{3+}	[110]
p-tert-Butylcalix[4]thiacrown-5	Hg^{2+}	[96]
Calix[4,6,8]arene derivatives bearing pyridino groups	Tc^{7+}	[111]

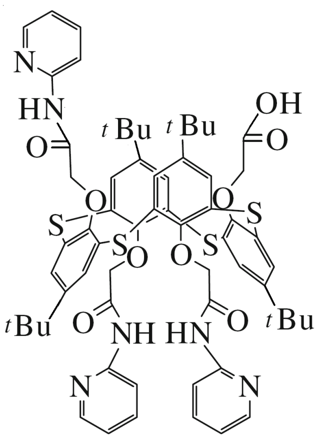
investigations up to 2007 regarding selective transport of Hg^{2+} in using calixarene derivatives as carrier. Qureshi *et al.*[8] applied Pederson method for the extraction of Cu^{2+}, Co^{2+} and Ni^{2+} *p*-bi morpholinomethylcalix[4]arene using their picrates in two-phase extraction experiments.

Deligoz and Erdem[100] used nine ligands including two diazo-coupling calix[*n*]arenes, four phenol derivatives and three ester derivatives to investigate ionophore solvent extraction of Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} and revealed that the best extraction efficiency was obtained with *p*-(4-phenylazophenylazo)calix[4]arene and 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol. Dwyer and Cunnane[43] used O,O"-*bis*[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene ionophore to facilitate Ag^+ transferring at the water|1,2-dichloroethane interface. Agrawal and Sharma[101] used 37,38,39,40,41,42-hexahydroxy-7,25,31-calix[6]crown hydroxamic acid to investigate extraction mechanism, kinetic of transport, speciation, liquid-liquid extraction, sequential separation and trace determination of Cr^{3+}, Mo^{6+} and W^{6+}. The maximum transport was observed at 35, 45 and 30 min for last cations, respectively.

Torgov *et al.*[45] used tetraalkyl(tolyl)thiomethylcalix[4] arenes to extract Pd^{2+} and Ag^+ from main fission products. He *et al.*[102] also studied Au^{3+} extraction from hydrochloric media by calix[4,6]arenes upper-rim functionalized with alkyl- or tolylthiamethyl groups. The most effective extractants were calixarenes with CH_2-S-CH_3 and CH_2-S-nC_4H_9 groups. Alpoguz *et al.*[103] made a flat-sheet-supported liquid membrane by calix[4]arene derivatives as carriers and Celgrad as solid support and investigated the transport behavior of Hg^{2+} into membrane from aqueous solution. Ulewicz *et al.*[98] investigated transport of Zn^{2+} and Cd^{2+} ions through a polymer inclusion membrane using calix[4]crown-6 derivatives and studied the influence of the group attached type to the calix[4]-crown-6 on the selectivity and efficiency of cations transport across polymer.

Tu *et al.*[87] synthesized di-ionizable calix[4]arene-1,2-crown-4 ethers, which exhibited high extraction ability for Hg^{2+} in single species extraction. The extraction of vanadium with the host calix[4]pyrrole hydroxamic acids were studied using examination of ICP-AES and UV-VIS spectroscopy by Jain *et al.*[104]. Torgov *et al.*[105] synthesized the calix[4,6]arenes grafted with different phosphine oxide groups and used them to extract Ru/Zn complexes. They investigated The Ru/Zn synergism and the calixarene macrocyclic effect in the extraction process and concluded that calixarene conformation, its size and electronic nature of substituents at phosphorus atom influence the extraction.

Yamato *et al.*[82] discussed the extractability of transition metal ions from water into dichloromethane by hexahomotrioxacalix[3]arene triamide. Li *et al.*[94] synthesized a 1,3-alternate thiacalix[4]arene possessing three aminopyridyl and one carboxylic group (**23**) and they studied it in the solvent extraction of some transition metal including Cu^{2+}, Zn^{2+} and Ag^+ from aqueous solutions into chloroform. They found that the introduction of carboxylic acid moiety (proton-ionizable group) into the macrocycle could further improve its Ag^+ extractability with high selectivity.



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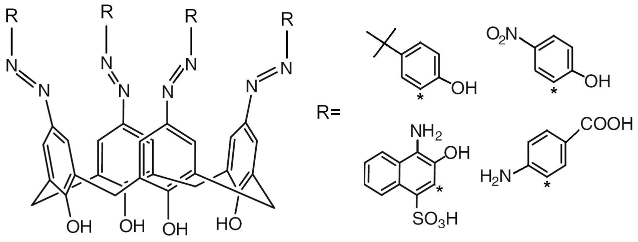
Ak *et al.*[48] synthesized azocalix[4]arenes and studied the solvent extraction of Ag^+, Hg^+ and Hg^{2+} from the aqueous phase to the organic phase. Deligöz[22] reported the use of azocalixarenes (**24-27**) in liquid-liquid extraction of various transition metal cations from the aqueous phase to the organic phase. In a part of his review paper, the complexation of four azocalixarenes with transition metal cations was discussed and the results is presented in Fig. 3. They also claimed that azocalixarenes were used for selective extraction of Fe^{3+} cations from the aqueous phase to the organic phase.



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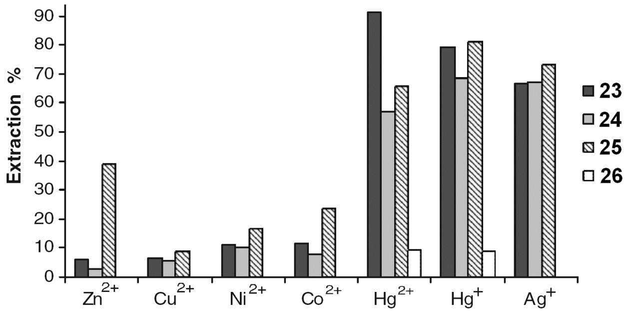


Fig. 3. Extraction efficiency of azocalixarenes towards transition metal cations

Kostin *et al.*[106] used calix[4,6]arenes bearing four or six phosphine oxide donor groups at the upper or at the lower rim to study the extraction of non-ferrous and two valence metal nitrates. The extraction constants for the both types of upper and lower rim were determined to be $Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. For the upper (wide) rim phosphorylated calix[4]arenes, M_2L and ML_2 complexes were more stable, while the lower (narrow) rim phosphorylated calix[4]arenes, provided better stability of ML complexes. Thiacalixarenes are a class of calixarenes in which the bridging methylene groups are replaced with sulfur. Fig. 4 illustrated that they are able to capture guest metal ions by coordinating with the bridging sulfur and adjacent phenol oxygen as well as *p*-substituent, aromatic ring and hydrophobic cavity. Iki[107] reviewed a 200-fold preconcentration of Cu^{2+} and Cd^{2+}.

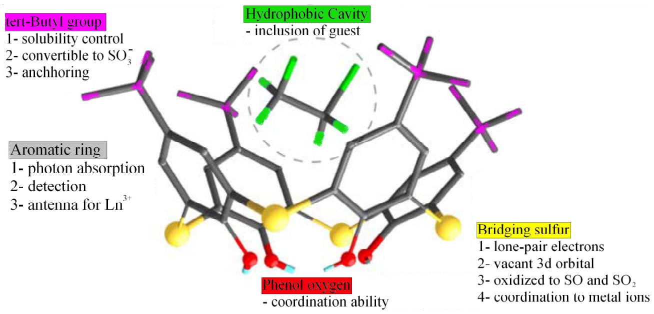


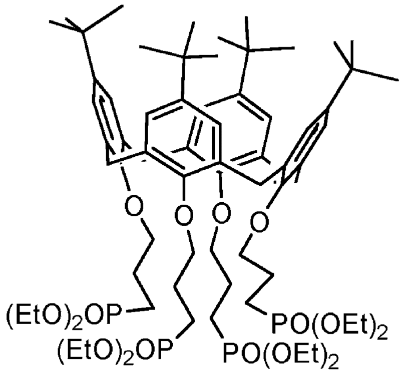
Fig. 4. Illustration of interaction sites in thiacalixarenes

Yamato *et al.*[108] synthesized distal-*bis*[(2-pyridylmethyl)-oxy]thiacalix[4]arenes and described its conformational studies. They used calix[4]arenes showed strong Ag^+ affinity in two-phase solvent extraction, which led to 97 % extraction, while no significant extraction was observed for K^+. Bouhroum *et al.*[51] synthesized *p*-*t*-butyl-thiacalix[4]arene and *p*-*t*-butylcalix[4]arene derivatives and used them in liquid-liquid extraction of metal picrates from water into dichloromethane. They reported 99 % extraction for Ag^+. Kumar *et al.*[109] used *p*-[4-(3,5-dimethylisoxazolyl) azophenylazo]calix[4]arene to extract tellurium, palladium and iron cations and determined them by spectrophotometric methods. The interference of various ions was studied and optimum conditions were developed for the extraction procedure of Te^{4+}, Pd^{2+} and Fe^{3+}.

As an extension, Kumar *et al.*[110] extracted copper, cobalt, rhodium and iridium cations from nitric acid by 25,26,27,28-tetrahydroxy-5,11,17,23-tetra-[4-(N-hydroxyl-3-phenylprop-2-enimidamido)phenylazo] calix[4]arene and determined the trace amounts of cations spectrophotometrically. The extraction of Hg^{2+} in single species solvent extractions by a *p-tert*-butylcalix[4]thiacrown-5 derivative was presented by Tu *et al.*[96]. Ludwig and Dzung[111] used calix[4,6,8]arene derivatives bearing pyridino groups at the lower rim for solvent extraction of Tc^{7+}.

The research and development activities for the partitioning and transmutation of long-lived actinide radionuclides are actively in progress in advanced nuclear countries. Long-lived actinide radionuclides contained in the spent nuclear fuel can be recovered by the separation processes using high temperature molten-salts and recycled to the reactor for transmutation. The resulting waste showed a remarkable reduction in the radiological toxicities and can be disposed of under milder conditions. At present, various concepts for the transmutation of long-lived actinide radionuclides are being studied in several countries. One of the concepts for the transmutation is the solvent extraction. This sub-section also reviewed the ability of calixarene derivatives for solvent extraction of actinide radionuclides. Table-10 presents the content of this subsection including the recent studies conducted on extraction of *f*-block cations using calixarene derivatives.

Mariani *et al.*[10] selected calixarene-based picolinamide ligands for liquid-liquid extraction of ^{241}Am and ^{152}Eu in high radioactive nitric solutions before and after γ-irradiation. Determination of the separation factors between elements of the two families was carried out by using γ-spectrometry and ICP-mass spectrometry. Matulkova and Rohovec[112] synthesized the calix[4]arenes (**28** and **29**) with four phosphonic acid groups on the lower rim and characterized their extraction behavior on certain lanthanide ions (La^{3+}, Eu^{3+} and Yb^{3+}). The extraction efficiencies of the prepared macrocycles were declined with decreasing radius of the lanthanide ions.



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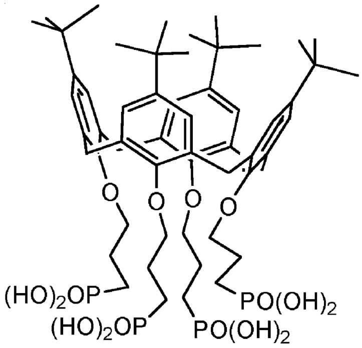

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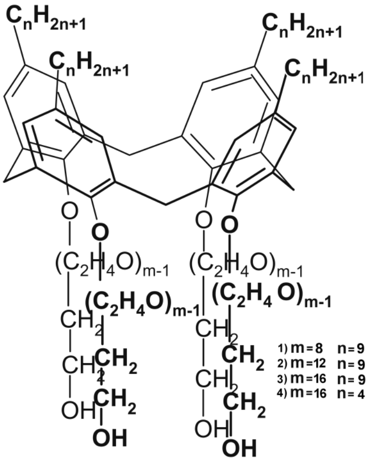
TABLE-10
LIST OF RESEARCHES ON THE EXTRACTION OF LANTHANIDES AND ACTINIDES USING CALIXARENES

Type of calixarene	Analytes were used	References
Calixarene-based picolinamide	Actinides and lanthanides	[10]
Propylene phosphonic acid calix[4]arene	La^{3+}, Eu^{3+} and Yb^{3+}	[112]
Cyclophanic calix[4]arene surfactants	La^{3+}, Gd^{3+} and Lu^{3+}	[113]
Calix[4]arene-*o*-vanillinsemicarbazone	U^{6+} and Th^{4+}	[114]
p-Octasulfonato-calix[8]arene	Permeable for NaCl, $MgCl_2$, $ZnCl_2$ and strongly rejected $LaCl_3$, $CeCl_3$, $PrCl_3$, $SmCl_3$	[115]
Phosphorylated calix[4]arene	Th^{4+} and Eu^{3+}	[116]
Caluix[6]arene derivative	Am^{3+} and Eu^{3+}	[117]
Calixarenes bearing phosphine oxide	Eu^{3+}, Am^{3+}, Th^{4+}, UO_2^{2+}	[50]

Conventional surfactants associate through closed model resulting in the formation of rather small micelle-like in cloud point extractions. Mustafina *et al.*[113] used non-ionic cyclophanic surfactants based on calix[4]arene platforms (**30-33**) with Triton X-100 to enhance the aggregation of La^{3+}, Gd^{3+} and Lu^{3+} in cloud point extractions.

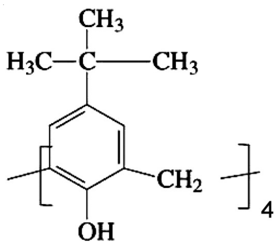


30-33

Jain *et al.*[114] developed a chelating polymeric sorbent using calix[4]arene-*o*-vanillinsemicarbazone for simultaneous preconcentration of U^{6+} and Th^{4+} from aqueous solutions with preconcentration factors of 143 and 153, respectively. Toutianoush *et al.*[115] built a layer-by-layer assembly of *p*-octasulfonato-calix[8]arene and polyvinylamine on porous polymer support. The membranes were permeable for NaCl, less permeable for divalent metal chlorides ($MgCl_2$ and $ZnCl_2$) and strongly rejected rare earth metal chlorides ($LaCl_3$, $CeCl_3$, $PrCl_3$ and $SmCl_3$). Yaftian *et al.*[116] studied the extraction of thorium(IV) and europium(III) by a phosphorylated calix[4]arene in dichloromethane and investigated the effects of ligand concentration, types of diluent and concentration of the salting-out agents.

Sansone *et al.*[117] synthesized five calix[6]arene derivatives and studied the liquid-liquid extraction for Eu^{3+} and Am^{3+} from aqueous nitric acid to *o*-nitrophenyl hexyl ether. Karavan *et al.*[50] evaluated the liquid-liquid extraction of europium, americium, thorium and uranyl ions from nitric acid solutions into two diluents dichloromethane and *m*-nitrobenzotrifluoride. They used three series of phosphorylated calixarene derivatives bearing phosphine oxide or phosphonate groups either at the wide or the narrow rims as extractants. Table-11 presented the content of this subsection including the extraction studies conducted on calixarene derivatives and molecular species.

Liu *et al.*[118,119] used poly-dimethylsiloxane (PDMS) membranes filled with calixarene and calixarene derivatives (**34** and **35**) for evaporative removal of benzene from dilute aqueous solution. They revealed that due to the higher hydrophobicity of calixarene derivative over calixarene, calixarene derivative-filled poly-dimethylsiloxane membranes exhibited higher separation factor than calixarene-filled poly-dimethylsiloxane membranes. In addition, both calixarene and calixarene derivative-filled poly-dimethylsiloxane membranes showed better selectivity than control poly-dimethylsiloxane membranes.



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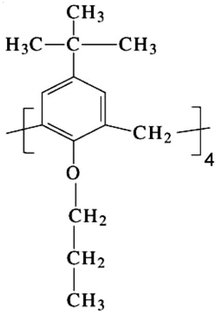

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TABLE-11
LIST OF CALIXARENES USED IN EXTRACTION STUDIES WITH MOLECULAR SPECIES

Type of calixarene	Analytes were used	References
–	Benzene	[118]
–	Benzene	[119]
Calix[6]arene and calix[8]arene carboxylic acid derivatives	Amino acids	[120]
Calix[6]arene carboxylic acid derivative	Adenine and cytosine	[121]
Sol-gel calix[4]arenes	Organochlorine pesticides	[122]
p-Sulfonato-calix[n]arenes	Neutral and charged aromatic compounds	[123]
Functionalized calix[n]arenes	Amines, amino acids and peptides	[124]
Sol-gel diglycidyloxy-calix[4]arene	Propranolol enantiomers	[125]
Calix[6]arene carboxylic acid derivatives	Cytochrome C and lysozyme	[126]
Chiral calix[4]arene diamide derivatives	α-Amino acid methylesters	[127]
p-tert-Butylcalix[4]arene bearing phenylethylamine	Chiral α-amines and α-amino acid methylesters	[128]
Calixarenes bearing acid or amido moieties	Native amino acid and amino acid esters	[129]
Calix[6,8]arenes bearing carboxylic acid	Catecholamines	[130]
p-tert-Butylcalix[6,8]arene	L-Tryptophan methylester and L-tyrosine methylester	[131]
1,3-*bis*-Arylformyl-hydrazone substituted thiacalix[4]arene and 1,3-bis-acyl hydrazone-bridged calix[4]arene derivatives	α-Amino acids	[132]

Oshima *et al.*[120] studied the calixarene carboxylic acid derivatives as powerful extractants for biologically important amino compounds. Based upon their work, the larger macrocycles calix[6]arene and calix[8]arene carboxylic acid derivatives were more effective for adsorption of amino acid derivatives on the impregnated resin than the calix[4]arene derivative[120]. Shimojo and Goto[121] used a calix[6]arene carboxylic acid derivative incorporating *tert*-octyl groups at the upper rim. In isooctane neither calix[6]arene nor D2EHPA were very effective at nucleobase extraction but addition of D2EHPA along with calix[6]arene drastically enhanced the efficiency of adenine and cytosine extraction and one nucleobases forms a stable complex with one calix[6]arene and two D2EHPA molecules.

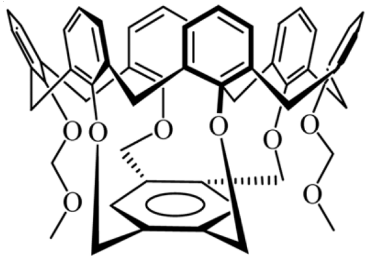
Dong *et al.*[122] used a sol-gel calix[4]arene/hydroxy-terminated silicone oil coated fiber for headspace solid-phase microextraction of 12 organochlorine pesticides and their metabolites in radish sample followed by gas chromatography determination. Tieke *et al.*[123] made a layer-by-layer assembled membrane containing polyelectrolytes, *p*-sulfonato-calix[*n*]-arenes and Prussian blue-type complex salts. Then they studied these membrane as molecular sieves and ion sieves for size-selective separation of neutral and charged aromatic compounds. The ability of functionalized calix[*n*]arenes to form complexes, to act as extractants in liquid-liquid extraction for ammonium ion, amines, amino acids and peptides has been the topics of recent papers. Mutihac *et al.*[124] investigated the effect of the factors that influence the separation of above biological amine compounds by liquid-liquid extraction using the calix[*n*]arenes.

Zhou *et al.*[125] made a new type of diglycidyloxy-calix-[4]arene coated fiber by sol-gel method. Using combination of headspace solid-phase microextraction and capillary zone electrophoresis, the simultaneous determination of propranolol enantiomers in human urine was achieved. Oshima *et al.*[126] described quantitative extraction and recovery of two proteins (with similar molecular weights), cytochrome C and lysozyme, using calix[6]arene carboxylic acid derivatives. Kocabas *et al.*[127], reported the extraction properties of chiral calix[4]arene diamide derivatives towards some selected α-amino acid methylesters. A chiral *p-tert*-butylcalix[4]arene bearing phenylethylamine was synthesized and its liquid phase extraction properties towards some chiral α-amines and α-amino acid methylesters was reported[128].

Hamdi *et al.*[129] synthesized cone calixarenes bearing acid or amido moieties and used them in the extraction of native amino acid and amino acid esters. Oshima *et al.*[130] investigated the extraction behaviours of catecholamines using calix[6,8]arene carboxylic acid derivatives. They reported that the calix[6]arene derivative selectively extracted dopamine with 1:1 complexation over other catecholamines, while calix[8]arene derivative extracted both dopamine and adrenaline due to the large cavity for induced-fit recognition. They stripped the dopamine extracted with the calixarene by contacting the organic solution with a fresh acidic solution.

Mutihac and Mutihac[131] studied the extractability of some amino acid methylesters (L-tryptophan methylester and L-tyrosine methylester) using *p-tert*-butylcalix[6,8]arene as extractant from the aqueous phase into chloroformic phase in the presence of a counter ion (tropaeolin 00) at pH ≈ 5.0. They concluded that the inclusion properties of the calixarenes are correlated with their structural properties and also they suggest further possibilities for optimal separation of amino acids. Yang *et al.*[132] synthesized 1,3-*bis*-arylformyl-hydrazone substituted thiacalix[4]arene derivatives and 1,3-*bis*-acyl hydrazone-bridged calix[4]arene derivatives to study their extraction ability towards α-amino acids. They showed similar binding properties with high extraction percentage but low extracting selectivities. hydrazone-bridged *bis*calixarene with calix[4]arene and thiacalix[4]arene subunits exhibited not only high extracting abilities but also good extracting selectivities towards α-amino acids.

Selective extraction of organic ammonium attracts an important research interest due to the application of biological systems. Calixarenes present attractive possibilities in the host-guest chemistry and their architecture is such that they also possess hydrophobic cavities generated by the aromatic walls of phenol residues, which are potentially useful for the inclusion of alkyl ammonium ions. Lee *et al.*[133] synthesized a quadruply bridged calix[6]arene derivative (**36**) and extracted alkylammonium cations with picrate anion into chloroform by two phase solvent extraction. They deduced the percentage extraction from the absorbance at 355 nm in the aqueous layer. The extraction efficiency for ammonium picrate, ethylammonium picrate, *n*-propyl ammonium picrate and *n*-butylammonium picrate, was 2.4, 3.7, 2.7 and 2.8 %, respectively.



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Wintergerst *et al.*[134] used *meso*-octamethylcalix[4]pyrrole as an ion-pair receptor for cesium chloride and cesium bromide. Their experiments were conducted in nitrobenzene solution *via* liquid-liquid extraction. Memon *et al.*[135] synthesized two polymer appended thioalkylcalix[4]arenes, which had high extraction ability toward $Na_2Cr_2O_7$ as compared to their monomeric precursors. They studied liquid-liquid extraction and solid-liquid batch wise sorption procedures on them and concluded that the calix[4]arene based polymeric resins have higher extraction ability than their monomeric precursors. He *et al.*[136] synthesized three amino/nitrile calix[4]arenes immobilized onto polymeric backbone and investigated its dichromate extraction.

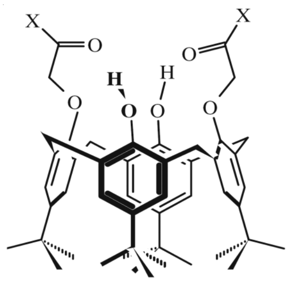
Transport phenomena: Solvent extraction, which is carried out by various organic liquid extractants, with or without diluents or modifiers, has been used for the recovery of metal cations and anions. Synthetic resins, which contain functional groups similar to those used in solvent extraction, are also widely used in hydrometallurgy for separation of metallic ions and in wastewater purification. The use of resins bearing active functional groups is a form of extraction that involves a solid substrate. Such a substrate may be active in the ion extraction process. The ability of calixarenes to form complexes as carriers in transport through liquid membranes has been the central topics of many researches. In this section, some recent studies are reviewed. Table-12 shows the topic of researches on the transport applications of calixarene derivatives.

TABLE-12
LIST OF TRANSPORT APPLICATIONS
OF CALIXARENE DERIVATIVES

Type of calixarene	Analytes were used	Ref.
p-*tert*-Butylcalix[4]arene-thioamides	Pb^{2+}	[137]
p-*tert*-Butylcalix[6,8]arene	L-Tryptophan methylester and L-tyrosine methylester	[131]
Functionalized calix[*n*]arenes	Ammonium ion, amines, amino acids, and peptides	[124]
Functionalized calix[*n*]arenes	Biological compounds	[138]
p-*tert*-Butylcalix[4]arene-crown-6	Alkali, alkaline earth and soft cations	[51]
Calix[4]arenes substituted by acid, amido, glycolic, and hydroxyl groups	Aromatic amino acid methylesters	[139]

A lead-ion selective membrane was made by Bochenska *et al.*[137] using *p*-*tert*-butylcalix[4]arene-thioamides as ionophores. Mutihac and Mutihac[131] investigated the transport through liquid membrane of L-tryptophan methylester and L-tyrosine methylester using *p*-*tert*-butylcalix-[6,8]arene as carrier. The transport depended on the pH, the structure of calixarenes, the structure of amino acids and the nature of anion used as ion pair for cation-receptor complexes. The properties of solvent involved in liquid membrane played an important role in selecting membrane systems and also in membrane stability. Mutihac *et al.*[124,138] studied the ability of functionalized calix[*n*]arenes as carriers in transport through liquid membranes of different biological amine compounds including ammonium ion, amines, amino acids and peptides. They presented the effect of the factors that influence the separation of above compounds by transport through liquid membranes using the calix[n]arenes.

Bochenska *et al.*[51] synthesized the cone and partial cone conformers of *p*-*tert*-butylcalix[4]arene-crown-6 derivatives and examined their ability to complex alkali, alkaline earth and soft cations as ionophores in ion-selective membrane electrodes. They used UV absorption spectrophotometry to compare complexing properties of two synthesized compounds in the PVC membrane with liquid-liquid extraction of alkali metal picrate in acetonitrile solution. Kim *et al.*[139] used a series of calix[4]arenes (**37-41**) substituted by acid and amido functions, glycolic chains and hydroxyl groups as carriers in liquid membranes. Transport of aromatic amino acid methylesters (**42-44**) through liquid membrane (from the aqueous source phase to the aqueous receiving phase) assisted by the pH gradient. They discussed the influence of calixarene and amino acid structures upon transport through liquid membranes.

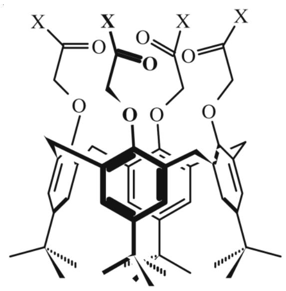


$X = OH$

$X = NHCH(CH_2OH)_2$

$X = NHC(CH_2OH)_3$

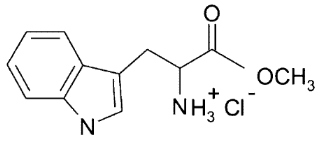
37-39



$X = OH$

$X = NH(CH_2)_2O(CH_2)_2OH$

40 and **41**



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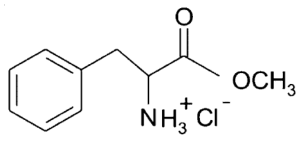

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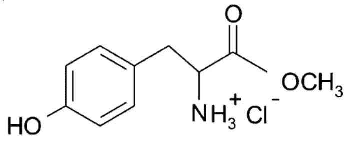

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Conclusion

This paper has focused on the recent researches in the binding ability and extractive applications of calixarenes as analytical tools. The examples described in this review illustrate the potential of them in the rapidly growing field of ion and molecular extraction. By searching in literatures, optimization of chelator design together with understanding of how to control the localization of ion complexes will be clarified. The objectives and the results of about 140 references that were published in last 7 years with emphasis on the binding ability and extractive applications were reviewed. A tutorial algorithm was designed to explain the recent advances in binding ability of calixarene and their applications in extractions of analytical chemistry. The applications of calixarene derivatives to bind and extract the seven following fields were reviewed, including of alkali and alkaline earth metals, *p*-block cations, transition metals, actinides and lanthanides, molecular species, organic cations and anions. The reader is introduced with frontiers in extractive application of calixarenes in terms of complexation and solvent extraction.

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