ANALYTICAL APPLICATIONS OF CALIXARENES

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ABSTRACT

Calixarene chemistry is developing fast; in the present decade its status in supramolecular chemistry gives the scientific community a springboard to expand the applications of these cyclic oligomers into other areas of science. Though calixarenes have shown more of their molecular ability as ionophores, still a large part of their utility remains unexplored. In the present review we try to present the history of calixarenes by tracing the various stages of their development and their applications.

INTRODUCTION

Calixarenes, a family of vase-like cyclic macrocycles, have been under development in the research laboratories for just over 50 years, with the first paper on calixarenes having appeared in 1944 /1/. In the half century since their inception, calixarenes have evolved from a scientific curiosity to a topic truly useful in the utilitarian sense or just intriguing in the intellectual sense, obviously complemented by a group of versatile techniques capable of characterizing these macromolecules and assessing their potentiality. In the present decade emphasis was placed on their supramolecular properties because of their flexibility towards structural-molecular modifications which account for a hydrophobic cavity and the use of second sphere coordinations to assemble large aggregates.

The origin of calixarenes, however, can be traced back to Baeyer's discovery of phenol formaldehyde resins in the 1870s /2/. Baeyer, best known for his work on saturated carbocyclic ring compounds and synthesis and structural elucidation of naturally occurring dye indigo, examined compounds obtained by mixing aldehydes and phenols in the presence of strong acids /3,4/. Though failing to characterize the cement-like condensed product, Baeyer nevertheless gave to the chemical world "phenol-formaldehyde chemistry". Investigation of these compounds was actively pursued by researchers like Lederer /5/, Manasse /6/, Blumer /7/ Storey /8/ and Luft /9/, who all tried to subdue these resinous tars and find their commercial applications but were unable to produce materials of marketable quality.

These compounds crossed the academic-industrial dividing line in 1907 when Baekeland /10-13/ filed a patent on his process to make Bakelite /14/. Both Baeyer and Baekeland /2-4, 10,11/ as well as Gills /13/, realized that CH_2 and CH_2OCH_2 groups are the most likely type of linkages between a pair of aromatic rings in a phenol-formaldehyde condensation product. Zinke and coworkers /1,15-18/ simplified the problem by looking at p-substituted phenols instead of phenols because, unlike phenol which itself reacts at the ortho and para positions to form a highly cross-linked polymer, a para alkyl phenol on the contrary can react only at the two ortho positions, denying

cross-linking possibilities. The product that Zinke *et al.* obtained in their first experiment /17/ was a crystalline acetate (m.p. 314°C) and it had a surprisingly high molecular weight of 1725. Zinke /16/ proposed a cyclic tetrameric structure for his product in accordance with Niederl and Vogel /19/, who had also proposed a cyclic structure for compounds obtained by acid-catalysed treatment of aldehydes and phenols. In contrast to Zinke tetrols, wherein the four OH groups were intrannular, the Niederl octols had eight extrannular OH groups /20/.

Abundant 'new evidence accumulated to substantiate the structure and synthesis of these compounds when the further four papers published by Zinke /15-18/ described cyclic tetramer prepared from p-methyl-, p-tert butyl-, p-tert pentyl-, p-(1,1,3,3-tetra methyl)-, p-cyclo hexyl-, p-phenyl- and p-benzyl phenol. Zinke /16/ assigned tetrameric structure to these macro-cycles and called them "mehrkernmethylenephenolverbindungen" (poly-nuclear methylenephenol compounds) /15/.

The other method, first worked out by Hayes and Hunter /21/ in 1952 and exploited and improved a few years later by Kämmerer *et al.* /22-29/ involves the sequential addition of methylene groups and aryl functions to a p-substituted phenol blocked at one of the ortho positions by a halogen. A linear oligomer can be elaborated, which carries a hydroxymethyl group at one end and the halogen blocking group at the other end. Removal of the halogen by hydrogenolysis, followed by acid-catalyzed high dilution cyclization, gives the cyclic oligomer. This method demonstrated its potential in the preparation of a series of methyl 4-tert butyl substituted calixarenes, including cyclic tetramers, pentamers, hexamers and heptamers. Molecular weight determination, melting point, elemental analysis and ultraviolet spectra were consistent with a cyclic tetramer.

Cornforth /30/ ventured into the Zinke procedure and negated the tacit assumption that a single product is formed in every instance. He used p-tert butyl phenol as the starting material and isolated two materials, both crystalline, having high but non-identical melting points. When p-(1,1,3,3-tetra methyl butyl) phenol was used as the starting material, again two compounds were isolated. Cornforth inferred that both compounds were diastereoisomers arising from hindered rotation. However, this interpretation was disproved

when Kämmerer *et al.* /22/ and John Munch /31/ of the Petrolite Corporation (St. Louis) produced data on ^1H NMR studies which showed rapid conformational interconversion occurring at room temperature. Buriks *et al.* /32,33/ investigated the petrolite demulsifier made by oxyalkylating p-tert butyl phenol and formaldehyde and concluded that, although the synthetic route followed was different from the one described by Zinke, the material they isolated must be Zinke's cyclic tetramer.

Gutsche /34-38/, a pioneer in calixarene chemistry, explored Zinke's compounds and accredited them as potential candidates for enzyme mimic building. He coined the word "calixarenes" in 1975 /35/, with 'calix' meaning vase or chalice and 'arene' indicating the number of aryl moieties in the macrocyclic array. He further used different substituted phenols, viz., p-methyl-, p-tert butyl-, p-phenyl-, p-methoxy- and p-carboxy methoxy phenol and elucidated the condensation products as cyclic tetramers /34/. However, Gutsche demonstrated that the outcome of the reactions can be strongly influenced by reaction conditions, thereby showing the synthesis of calixarenes with $n = 4-8$. All structures are in complete agreement with chemical, spectral and analytical data, further definitely destablished by single crystal X-ray crystallography by Andreetti, Ungaro and Pochini /39-41/.

During the decade that followed, calixarene chemistry progressed steadily in the academic laboratories, ultimately becoming accessible to a wider community of research. Attention is presently focused on ways in which the baskets have been or might be put to use with change in structural-molecular properties, and their promise as selective and useful complexation agents.

Several methods are in practice for attaching the calixarenes with functional groups. These involve:

reactions at the lower rim of the calix:

viz., ester formation with monofunctional reagents, ether formation with monofunctional reagents and esterification/etherification with polyfunctional reagents.

reactions at the upper rim of the calix:

viz., dealkylation of p-substituted calixarenes, functionalization via p-Claisen rearrangement route, p-quinonemethide route and p-chloromethylation route.

oxidation reaction of calixarenes:

viz., oxidation of the methylene bridges and oxidation of the aryl rings.

The phenol derived calixarenes carry hydroxyl groups at their lower rim and they provide sites for attaching other functional groups. When an excess of acylating agent is used, generally all the hydroxyl groups are converted into ester groups /42/. Partial acylation /43,44/ occurs under certain conditions, for example a pair of acetates that are not conformational isomers can be isolated from the sulfuric acid catalysed reaction of acetic anhydride and tert-butyl calix(4)arene. Calix(6)arene and calix(8)arene on acid catalysed acylations yield hexaacetoxy and octaacetoxy compounds respectively /36/. Benzoylation /45/ of calix(6)arene has been reported to yield the hexabenzoate as a solid melting above 400°C.

By etherification methyl, ethyl, allyl and benzyl ethers have all been prepared with high yields /44/. Treatment of calixarene with an alkyl halide in THF-DMF solution in the presence of sodium hydride is reported. Cornforth *et al.* /30/ have synthesized a series of polyalkoxy ethers by using tosylate of the alkylating agent in the presence of potassium tert-butoxide /46/. Other reagents like diazomethane /47/, benzyl tosylate, dimethyl sulfate /44/, hexamethyl disilazene, N,O-bis (trimethylsilyl) acetamide and chloromethyl silane effect etherification.

The theme of using ether/ester formation to introduce functionalization has been exploited by Arduini *et al.* /48/. They prepared the first water soluble calixarenes (soluble to the extent of ca. 10^{-4} M) by preparing a tetra-acid from tetraester by base induced hydrolysis. A diacid was also obtained from diester using potassium tert-butoxide rather than NaH in the former reaction /49/. Ungaro *et al.* carried out this same procedure on a lower rim bridged calixarene to produce the crown 5-diacetic acid. Later on Ungaro,

Mckerverey *et al.* and others /41-54/ reported various structural combinations. Several patents were filed because of the commercial interest in these compounds.

The selective removal of the tert-butyl groups from dimethyl di tert-butyl calix(4)arene is adequately described by Böhmer *et al.* /55/. The procedure is now extensively used as a means for obtaining calixarenes containing unsubstituted p-positions, thereafter making the amenable to functionalization, for example calix(4)arene /56,57/ (yield: 65-70%), calix(6)arene /45/ (yield: 89%), and calix(8)arene /45/ (yield: 93%) were synthesized following this procedure.

p-sulfonato calix(6)arene /58,59/ and p-nitro calix(6)arene /60,61/ can be prepared by functionalization via electrophilic substitution or direct nitration to get nitrocalix(6)arenes /62,63/.

One of the most productive reactions involves the p-Claisen rearrangement in which calix(4)arene is readily converted into tetra allyl ether, which on refluxing with N,N'-diethyl aniline produces p-allyl calix(4)arene, which is further converted to p-toluene sulfonate that can give a variety of functionalized calix(4)arenes. Another procedure for direct electrophilic substitution takes into account the nucleophilic character of the para positions of the phenolates /62/. When calix(4)arene is mixed with formaldehyde along with the secondary amines, a Mannich type reaction occurs to produce alkyl amino methyl calix(4)arenes.

Another procedure for dealkylation via the p-quinone methide route provides a particularly short pathway to a variety of functionalized calixarenes, its importance being the introduction of carboxyl groups into the calixarene framework /63/. Functionalization of calixarenes has been further expanded by the p-chloromethylation route /64/, introduced by Arduini *et al.* to produce a number of p-chloromethyl compounds.

Oxidation reactions of calixarenes include oxidation of the methylene bridges and oxidation of the aryl rings. Moshfegh *et al.* /65-67/ and Ninagawa *et al.* /68/ have reported the action of chromic acid on ester of cyclic tetramers, cyclic hexamers and cyclic octamers with methylene groups converted to keto groups. Oxidation of aryl rings by Fremy's salt has been reported by Rosyk /69/.

Various functionalization possibilities give calixarenes good recognition in the list of complex forming macrocycles, with facets in both state and solution state complexation. Solution state complexation involves both aqueous and non-aqueous solvents. Calixarenes form endocalixarene complexes with aromatic molecules, viz. pyridine /70/, chloroform /36,71,72/, benzene /41,73,74/, xylene /41/, anisole /41/, toluene /39,75-78/; non-aromatic guest molecules /51,79/, viz., acetonitrile /80/, cyclohexane /81/, isopropyl alcohol /82/, acetic acid /83/, acetone /84/, sodium bromide /80/, carbon disulfide /85,86/, methanol /36,87/, methylene chloride /88/, methyl cyanide /89/; metal cation complexes /43,49,53,90-99/; organic cations viz., amines /100,101/ and neutral organic molecules /102,103/, viz., glycerol, D-ribose, riboflavin, D-glucose, Vitamin B₁₂, hemin and sugars. Attractive CH₃... π interactions contribute to the binding which occurs between the protons of the tert-butyl groups and the aromatic ring of the guest molecule /70,88/. Atwood /104/ has reported an example of inclusion complexation of water by a calix(4)arene sulphonate. The tenacity with which the guest molecule is held varies widely within the series. The structures of complexed calixarenes and those of parent calixarenes are most effectively revealed by X-ray crystallography /105/. Another analytical technique that has been infrequently applied to molecular complexes is that of ¹³C cross polarisation magic angle spinning NMR /106/. Elements like S, Cl, Cs, As and N are captured in the cavities by joining a pair of cavitands, viz., upper rim to upper rim.

Calixarenes, as ionizable receptors, were first exploited by Izatt *et al.* /91,92/, who achieved selective transport of alkali cations from one aqueous phase to a chloroform membrane containing the p-tert butyl tetramer, hexamer or octamer. The octamer showed the fastest rate, with a cation selectivity order Cs > Rb > K > Na > Li.

The p-tert butyl calix(8)arene can be deprotonated and this feature can be used for converting the lanthanides into complexes that are soluble in organic solvents /107/, suggesting that it may be used in solvent extraction and purification of these elements. The complexation of alkali and alkaline earth cations by neutral ligands has been examined extensively by using phase transfer from water into an organic solvent, ion transport through liquid

membranes and stability constant measurements. The ratio of the stability constants adequately expresses the selectivity of one cation relative to another. These values are important when behaviour of calixarenes is compared with crown ethers, cryptands and natural ionophores such as valinomycin and monensin. Shinkai *et al.* /108/ have found stability constants for UO_2^{+2} with calixarene derivatives up to 10^{19} mol^{-1} and selectivity factors of $10^{11} - 10^{19}$ with respect to other divalent cations, viz., Hg^{2+} , Zn^{2+} , Ni^{2+} and Cu^{2+} .

Crystal structures are now available for various complexes of calixarenes with metals including Co^{2+} , Fe^{2+} , Ni^{2+} and Cu^{2+} . Calix(4)arene diquinone crown ether shows strong complexation and electrochemical recognition for Na^+ , K^+ , Ba^{2+} , NH_4^+ and BuNH_3^+ guests. The structures of three chromium complexes prepared from cone and 1,3-alternative 25,26,27,28-tetra propoxy calix(4)arene and $\text{Cr}(\text{CO})_3$ were determined by single crystal X-ray studies /109/.

Recent developments involve studies on solid co-ordination compounds of calcium and cadmium with a p-tert butyl hydroxy calix(8)arene, extraction and solution thermodynamics of complexation of alkali and alkaline earth cations by calix(4)arene amides, conformational and binding properties of calix(6)arene based ester ligands, calixarene derivatives and their rare earth metal complexation, spectroscopic characterization of the interactions between calixarene ionophores and metal ion solutions, and so on.

With the horizon of complexation abilities and salient properties of calixarenes increasing, there is an increase in the number of reports, monographs and patents. Most of the patents feature calixarenes as an item of commerce. However, its varied applications and molecular structural properties shows calixarene chemistry as a subset of supramolecular chemistry /110/. One of the first applications was that of the Petrolite company in the US, who in 1950 marketed the product of o-alkylation of p-tert butyl phenol formaldehyde oligomers as a surfactant with excellent demulsifying properties. Most of the recent applications are associated with their properties as molecular receptors /91-92/. Izatt has used calixarenes for the recovery of cesium from nuclear waste. Calix(6)arene hexa acid "Super Uranophile" attached to polystyrene is applied for the recovery of uranium from sea

water. A polymethacrylate with calix(4)arene esters spaced regularly about the backbone is capable of sequestering Na^+ selectively and may be useful in trans-membrane channels /110/.

European and U.S. patents /111-114/ from Loctite Corporation contain claims on instant adhesive composition utilizing calixarene accelerators. Compositions for cyanoacrylate adhesives use calixarenes as additives which lead to an important decrease of fixture times and cure on deactivating substrations such as wood and leather. One of these patents /111/ claims calixarenes to be useful not only as ion-exchangers but also as phase transfer catalysts, coatings, adhesives and potting compounds. Ion selective field effect transistors (ISFET) containing a calixspherand as the ionophore enable the quantitative determination of K^+ in the presence of a large excess of Na^+ . Calix(6)arene bound to an ISE is used to determine Pb^{2+} , Ag^+ and Cr^{2+} ions simultaneously by using differential pulse anodic stripping voltammetry. Bridged calixarenes are also possible, in which the structural features of calixarenes and spherands are combined to make receptors fixed in a very rigid binding conformation /109,115/.

Chromatographic applications include using calixarenes as a stationary phase in gas chromatography for separating alcohols, chlorinated hydrocarbons and aromatic compounds /116/. Some calixspherand complexes exhibiting high thermodynamic and kinetic stability, suggesting possible applications, are beginning to emerge in medical diagnostics, sensors and chromatography /117/. A recent approach is to include the calixarene based sensor with several others in an array of sensors. Ion selective electrodes for K^+ and Cs^+ have been made using dioxocalix(4)arene and calix(6)arene respectively as ionophore /118/. PVC membranes along with calix(4)arene show remarkable selectivity. This material has been used to make bench and miniaturised Na selective electrodes /119a/ and a Na electrode for flow injection analysis (FIA) /119b/. This approach gives very accurate assays for sodium and other ions in blood and mineral water /120/.

Table 1 presents an updated summary of complexometric studies on the various calixarenes.

TABLE 1Host-guest complexometric studies of various substituted/unsubstituted calixarenes

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene R = CMe ₂ CH ₂ CMe ₃ R' = OH	4	toluene	X-Ray	forms 1:1 complex with toluene, the guest molecule occupies channel type intermol. cavities in the host lattice.	75

Calix(n)arene (macrocyclic polyphenol)	-----	Cs ⁺ , heavier nonvalent alkali metal cations	AAS	used for recovering cesium from radioactive waste solution by establishing a separate basic source phase, a separate recipient phase and a liquid membrane phase contg. calixarene.	115
Calix(n)arene R = H, NH ₄ , alkyl ammonium R' = H, C ₁₋₈ n-alkyl	6	Na ⁺	UV	λ_{max} of aq. phenol blue (10 ⁻⁵ mol.) shifted from 668nm to 685nm in the presence of calixarene containing Na.	121
Tetra-ethyl p-tert butyl calix(n)arene tetra carbonate	4	MeCN	X-Ray & Mol. studies	shows increased intramol. tert butyl -tert butyl seps., MeCN mol. lies along the 4-fold axis with Me grp oriented towards the inside of the cavity.	51
Calix(n)arene R=SO ₃ Na, R'=OCH ₂ COOH	6	UO ₂ ²⁺	Stability studies	log k = 18.7±0.1 at pH 10.4 and 25° C	60

Table 1. Continued 2

Host	n	Guest	Method	Remarks	Ref. No.
Hexa sulfonated calix(n)arene $R=SO_3M^+(M=Na, H, NH_4)$ $R'=OR (R=H, MeCH_2CO_2H, hexyl, dodecyl)$	6	pyrene, 2-aminonaphthalene & orange OT	light scattering, surface tension & conductance fluor. and absorption spectra	forms 1:1 complexes, accelerates acid catalysed hydration of 1-benzyl 1,4-nicotinamide, rate consts. were greater by 426-1220 fold than those for noncyclic analogs.	122
p-tert butyl/methoxy calix(n)arene	4	$Me_2Al, PhMe, Na^+$	X-Ray	inclusion of both anion and cation, first solid state evidence for the coordination of an alkali metal by a calixarene.	78
Lipophilic p-tert butyl calix(n)arene $R=CM_e_3$ $R'=OH/CH_2COOH/O(CH_2CH_2O)_4$	4	divalent metal cations	solvent extn.	extn. from water to CH_2Cl_2	49

p-tert butyl calix(n)arene	4	Ti^{4+} , Fe^{3+} , Co^{2+}	X-Ray	first 3-sigma bonded transition metal derivs. of a calixarene.	123
p-tert butyl calix(n)arene	8	Eu^{3+} , DMF	X-Ray	bimetallic lanthanide complexes of calixarenes.	124
Amide calix(n)arenes $R=CM_e$, $R'=CH_2CONHBu$	2,4,6	Group IIA cations	solvent extn.	selective towards group IIA compared to group IA cations.	53
Calix(n)arene $R=SO_3Na$, $R'=H, CH_2COOH$, $(CH_2)_4Me$	6	phenol blue, Orange OT, UO_2^{2+}	-----	used as catalyst in the hydration of 1-benzyl-1,4-dihydronicotinamide.	125
p-alkyl calix(n)arene	4	Me_3CNH_2	UV, 1H NMR	Me groups of the amine and the alkyl groups of the calixarene are proximate in agreement with endo calix structure of the complex.	101
Calix(n)arene methyl ether	8	$CDCl_3$	X-Ray	resides two mols. of the solvent per mol. of host.	71

Table 1. Continued 3

Host	n	Guest	Method	Remarks	Ref. No.
Polymeric calix(n)arenes $R=H$, hydrocarbyl, CH_2COR , $CONHR^*$ $(R^*=hydrocarbyl)/$ unsaturated group $R^*=H, Hydrocarbyl/$ unsaturated grp	4-8	Na picrate	solvent ex'n.	polymer prep'd in CH_2Cl_2 extracted 32% Na picrate.	126
Ethoxycarbonyl methyl/carboxymethyl/methyl/ethoxy ethyl derivative of calix(n)arene	4, 6, 8	Na^+, Cs^+, K^+	solvent ex'n.	extn. of metal ions(as picrate salts) from the aq. phase to CH_2Cl_2 , strong participation of O atom of ester $C=O$ group.	98
Calix(n)arene $R=CMes$, $R^*=CH_2CONEt_2$	4	KSCN, methanol	X-Ray	forms 1:1 complex with KSCN, hydrophobic cavity contains a methanol molecule.	95

Calix(n)arene (RESINS) R=SO ₃ M, NO ₂ , NH ₂ , CO ₂ M, OM ₂ , OR ⁺ (M ⁺), M ₂ , M=H, NH ₄ , low alkyl ammonium, inetal ions, A, B=H, alkyl, arom. hydrocarbons. R ⁺ =H, R ⁺ OH, R ⁺ COOH, R ⁺ NO ₂ , R ⁺ NH ₂ , R ⁺ SO ₃ M (R ⁺ =low hydrocarbons. R ⁺ =H, low alkyl, low alkyl carboxylic acids or salts, unsat alkyl groups or arom. hydrocarbons.	2-10	U(IV)	ion exchange column	absorbed 108mg U/0.1g in 7 days on passing of sea water at 30ml/min.	127
p-alkyl calix(n)arene R=(CH ₂) _m Me(m=0-17), R'=lower carboxyalkyl/ thiocarboxyalkyl/ aminoalkyl; A, B=H, alkyl, aryl	4-10	UO ₂ ²⁺	solvent extn.	extn. rate was 99.8% compared to 18% of p-tert butyl calix(6)arene.	128

Table 1. Continued 4

Host	n	Guest	Method	Remarks	Ref. No.
p-hexyl calix(n)arene	6	UO ₂ ²⁺	solvent extn.	aqueous soln (pH 10) contg. calixarene and UO ₂ (OAc) ₂ was extd. with O-C ₆ H ₄ Cl ₂ to show extn. rate of UO ₂ ²⁺ in the organic layer 28% vs 2.1% for dicyclohexyl 18-crown-6.	129
Calix(n)arene (1) R=H, alkyl, aralkyl, alkoxy, aryl, alkanoyl; R'=OCH ₂ COOH/OCH ₂ COOR ₁ (R ₁ =(un)substituted aliph. or arom. hydrocarbyl, carboxyl or aryl) (2.) R=NR ₃ R ₂ (R ₂ , R ₃ =H, (un)substituted hydrocarbyl) (3) R=CM ₃ ; R'=OCH ₂ COOH	4,6,8	transition metals (precious metals)	solvent extn.	calixarene in CH ₂ Cl ₂ extd. 77, 11.4, 44.7 and 0% from aq 2.5x10 ⁻⁴ solns. of silver, cupric, ferric and sodium picrate solns. resp, whereas 18-crown 6 gave 2.7, 1.3 and 13.5% extns. res:p.	130

Lipophilic calix(n)arene ester and amide deriv.	4	Na ⁺	ISE	the resultant PVC membrane - based electrodes were found to be highly selective for Na ⁺ .	131
p-sulfonato calix(n)arene	4,6,8	triethylammonium chloride	¹ H NMR	forms 1:2 complex, K values are 550-5600 m ⁻¹ .	132
Calix(n)arene(opp. para positions connected) R=Me, octyl, dodecyl, octadecyl, OMe ₃ C, cyclohexyl, Ph, Cl CH ₂) _n (n=5-10, 12, 14, 16) R'=OH	4	Cs ⁺	¹ H NMR, X-Ray	cone conformation is confirmed in this compds. by X-Ray studies.	133
Hexa sulfonated calix(n)arenes	6	arene diazonium ions	UV	$\lambda_{\max}$ of phenol blue undergoes an unusual blue shift owing to the electrostatic stabilization of protonated phenol blue.	134
Calix(n)arene ester	4,6,8	alkali picrates	UV	forms 1:1 complexes with alkali metal cations, K _a values smaller than crown ethers.	135

Table I. Continued 5

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene methyl ether	4	AlMe ₃	X-Ray, ¹ HNMR	the Al-O lengths in all the complexes are normal for donor-acceptor interactions.	136
Calix(n)arene R=SO ₂ ; R'=OR ₁ (R ₁ =H, lower alkyl, alkanol, thiol, amine, carboxylic acid, unsatd alkyl, arom. hydrocarbyl); A,B=H, alkyl, arom. hydrocarbyl	4-10	U	liquid-solid extn.	80g of calixarene powder added to an aq. soln. contg. 31.5ppm uranyl nitrate showed uranium adsorption 5100mg/0.1g after 4 days.	137
Carboxy calix(n)arene	5,6	U	CD spectra	exhibited record breaking uranyl affinity K=1018.4~19.2 M ⁻¹ and uranyl selectivity(1010.6~17).	63
Calix(n)arene R=CM ₂ ; R'=OR ¹ (R ¹ =N, CH ₂ CHCH ₂) ₂ , CH ₂ COOH	4-8	arom. hydrocarbons (durene to deacylene)	X-Ray	corelation between dimensions of the hydrocarbons and the lower rim of the calixarene contg. the array of OH groups have been made.	138

p-isopropyl calix(n)arene/p-tert butyl calix(n)arene	6	benzene	X-Ray	the Me ₃ C grps and the benzene mols. are disordered but the Me ₃ CH grps are not.	139
Calix(n)arene R=CM ₂ ; R'=OR ¹ (R ¹ =CH ₂ COOH, CH ₂ COSH or CH ₂ NH ₂), A,B=H, lower hydrocaryl	6	UO ₂ ²⁺	resin column	an aq soln contg 10ppm UO ₂ ²⁺ was extd in a resin column treated with 2.1x10 ⁻³ mol. calixarene deriv. at 30 for 24 h resulting in UO ₂ ²⁺ recovery of 99.8% vs 2.1% for a conventional adsorbent.	140
Calix(n)arene esters	6	arenediazonium ions	-----	strongly binds arenediazonium ions as do crown ethers but does not inhibit dediazonation.	141
(2-pyridyl methoxy) calix(n)arenes	6,8	alkali metal cations, Cu ²⁺ , Ag ²⁺ & UO ₂ ²⁺	solvent extrn.	complexes are stable even at high pH.	142

Table I.. Continued 6

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)aryl ester/amide deriv.	6	Na ⁺	ISE	excellent Na ⁺ neutral carriers, proper selection of electrode membrane solvent and lipophilic salts allowed high Na ⁺ selectivities against K ⁺ (selectivity coefficient 3.8×10^{-3}), applied successfully to Na ⁺ detn. in human blood sera.	143
Mono/Bis metallocene calix(n)arene	4	Fe & Co	X-Ray, ¹ HNMR & coulometric studies	redox active hydrophobic receptors.	144
p-tert butyl calix(n)arene	4	Nb, Ta	X-Ray	forms tetranuclear complex.	145
p-tert butyl calix(n)arene	4	Eu	X-Ray	forms binuclear complex, used in ligand purification.	146

Calix(n)arene	4	acetonitrile	^1H NMR, ^{13}C NMR, IR and elemental analysis	complex exists in an 'inside' partial cone conformation.	147
p-tert butyl calix(n)arene	4	Na^+	ISE	solvent mediator - 2-nitrophenyl octyl ether, ion exchanger - potassium tetrakis (p-chlorophenyl) borate, Nernstian slopes detection limits of ca. 10^{-5} for Na and excellent selectivity for a range of cations.	148
Hexameric calix(n)arene ester	6	Cs & Rb	phase transfer studies, pot. selectivity studies and ISE	solvent mediator - 2-mitrophenyl octyl ether, ion exchanger-potassium tetrakis(p-chlorophenyl) borate, selectivity coefficient of Cs with respect to Rb, K, Na, Li, Ca, Mg, H and NH_4 was detd.	149

Table 1. Continued 7

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene	4	alkali picrates	^1H NMR, solvent extn.	this is the first quantum est. of the ionophorecity of conformationally isomeric calixarenes.	150
p-aryl azo calix(n)arene $R=R'C_6H_5N=N-$	4	Ag^+	solvent extn.	22% Ag was extd. when chloroform soln. of calixarene (10^{-3}M) was shaken for 24h at 25°C with a soln. of $\text{AgNO}_3(10^{-2})$ in aq. picric acid ($2 \times 10^{-5}\text{M}$).	151
Ethoxy carbonyl methyl deriv. of calix(n)arene	4, 6, 8	Na^+	^1H NMR	relaxation times were estimated, benzene units feature a "se.1 saw" motion around the ArCH_2Ar circle and the motion is suppressed by Na serving as a template ion.	152

Calix(n)arene tetra ester (polymethylene chains at two opp. para positions)	6,7	alkali cations	X-Ray	no extn. of picrates is found in terms of compds with shorter chains.	153
Calix(n)arene (1) R=H, Me, (CH ₃) ₂ Me, CH ₃ COOH R'=C ₆ H ₄ CH ₂ COOH (2) R=CH ₂ COOH; R=H, CM ₂	6,8	aromatic hydrocarbons	X-Ray	strong complexes are formed with calixarene in which either the upper rim or the lower rim carries the carboxyl groups and the hydrophobic rim carries small substituents.	154
Hexamide deriv. of calix(n)arene	6	1-ethyl-4-methoxycarbonyl pyridinium iodide, formamide	UV	λ_{max} at 365nm indicates that the binding site is relatively polar. 1:1 host-guest complexation.	155
p-tert butyl calix(n)arene	6	Cu	solvent extn.	medium-alk NH ₃ to C ₆ H ₆ :CHCl ₃ , forms 1:1 Cu(II)-Calix(6) complex.	156

Table 1. Continued 8

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene sulfonate	4	Na, K, Cs, Rb	X-Ray	exist in the solid state as bilayers of anionic calixarenes in the cone configuration. structure bear a close resemble to clay minerals.	104
Calix(n)arene esters	4-8	alkali metal ions	spec. studies	binding of alkali metal ions to the monolayer is specific.	157
Calix(n)arene R=N=NPh; R'=OH	6	Ag ²⁺ , Hg ²⁺ , Hg ²⁺	solvent extn.	-----	158
p-tert butyl calix(n)arene	4,8	Cu ₂ Cl ₂ , Cu, ClCuCl	X-Ray	forms octanuclear copper(I) complex.	159
Calix(n)arene (1) R=SO ₃ Na; R'=Me, Bu, (CH ₂) ₄ H (2) R=CMe ₃ , Bu; R'=O(CH ₂) ₃ SO ₂ Na	4,6,8	pyrene	¹ HNMR	relation btw shape and binding ability has been studied, (1) shows strong but non-selective binding site and (2) shows weak but selective binding site.	160

Calix(n)arene bearing hydroxamate groups	6	UO_2^{2+}	solvent extrn.	extracts from aqueous phase to organic phase, bears six hydroxamate groups.	161
Calix(n)arene bearing hydroxamic groups $\text{R} = \text{CMe}_3$; $\text{R}' = \text{OCH}_2\text{NHOH}$	4,6	UO_2^{2+}	solvent extrn.	two phase extrn. system : $\text{H}_2\text{O}-\text{CHCl}_3$, % extraction increases from pH 2 and saturates at about pH 5.	162
Calix(n)arene sulfonate	6	Na	X-Ray	has double partial cone conformation, strong coordination of the uranyl ion can be expected of this molecule because of metal ion induced calixarene reorganisation.	163
Ionophoric calix(n)arene	4	anthracene	photochem. studies	photochemically produced isomer showed much improved ion affinity and pronounced Na^+ selectivity.	164

Table 1. Continued 9

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene (1) R=H, allyl, SO ₃ M [M=H, monovalent cation]; R' = R'CONH(OH) (2) R = CMe ₃ ; R' = CH ₂ CONHOH	2-8	uranium ions	solvent extn.	aqueous UO ₂ (CHCO ₂) was extd. with a soln. of calixarene in O-Cl ₂ C ₆ H ₄ to give 100% recovery of UO ₂ ²⁺ in 1h.	165
Double cavity calix(n)arene	4	phenols, carboxylic acids, pyridines, imidazoles, aliph. amines, resorcinol	¹ HNMR	the K _{BSO₃} values range from 25 to 55 M ⁻¹ and are dependent both on the shape and acidity or basicity of the guest.	166
Calix(n)arene	4	pyrene, nitrobenzene	Fluoro.	new metal sensory system based on intramol. fluorescence quenching on the ionophoric calixarene cavity.	167

Calix(n)arene with anthracene moiety	4	Na picrate	photochem. studies	use of two anthracene moieties as a photochem lid for the ionophoric cavity was reported, extractibility of Na picrate is 40.8%.	168
Calix(n)arene R=A ⁺ ; R'=OR1(R1=OC ₄ H ₁₇)	4	Na & K picrate	solvent extn.	proved to be effective in exlg. behaviour than previously reported lower rim ester deriv.	169
Calix(n)arene p-hexasulfonate	6	UO ₂ (CO ₃) ₃ ⁴⁻ , UO ₂ (OH) ₃ ⁴⁻ , UO ₂ (CO ₃) ₃ ²⁻	solvent extn.	the presence of various uranyl species is calculated from a set of mass balances of participating ions and their stability consts.	170
Lipophilic calix(n)aryl ester deriv.	4	Na ⁺	ISE	the selectivity coefficient for Na ⁺ with respect to K ⁺ were nearly 2.5, this electrode is successfully applied to Na ⁺ assay in human blood sera.	171
Fluorescent calix(n)arene	4	metal ions	fluoro.	the ratio of the monomer vs excimer emission was sensitively affected by solvent polarity and added metal ions.	172

Table I. Continued 10

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene R=Bu; R'=OR ¹ (R ¹ =H, Me, Et)	4, 6	fluoroaroms., benzene or 2,2,2-trifluoro- ethanol	mass spec.	probed gas phase guest-host chem. between calixarenes and guest mols.	173
Calixspherands	4	radioactive alkali cations	kinetic studies	the spherands form very stable complexes with Li ⁺ and Na ⁺ but reject the larger cations like K ⁺ and Rb ⁺ .	174
Calix(n)arene 5,11,17,23-tetra sulfonate	4	Ce(III)	UV	forms colored complex with cerium in alkaline soln., $\lambda_{\text{max}} = 417\text{nm}$, $\epsilon = 1.09 \times 10^4 \text{ l. mol}^{-1} \text{ cm}^{-1}$	175
Tetra methyl ketone calix(n)arene	4	Na	ISE	plasticizing agent : 2-nitrophenyl octyl ether, ion exchanger : potassium tetakis(p-chlorophenyl)borate, electrode shows excellent discrimination for Na ⁺ against K ⁺ and Li ⁺ .	176

Calix(n)arene disulphonic acid	4	Cr, Yb, Cu	X-Ray	-----	177
p-tert butyl calix(n)arene	6	cyclic amines	spec. studies.	form exo complexes between the ammonium and phenolate groups.	178
Calix(n)arene	4	Na ⁺	ISE	the potentiometric selectivity coeffs. for Na ⁺ over K ⁺ and Li ⁺ are -1.9 and -2.5.	179
Chromogenic calix(n)arene	4	Li ⁺	solvent exn.	-----	180
Calix(n)arene (molecular capsule)	4	N-methyl formamide	-----	capsule is formed by equimolar reaction of 5,11,17,23,29,35- hexakis (chloromethyl)-37,38,39, 40,41,42-hexa methoxy calixarene and 5,11,17,23,29,35- hexakis (mercaptomethyl) - 37,38,39,40,41,42-hexamethoxy calixarene.	181
1,3-crowned calix(n)arene	4	transition metals	X-Ray , kinetic studies	ether oxygens contributed effectively to the binding of the metal ion in the transition state.	182

Table I. Continued 11

Host	n	Guest	Method	Remarks	Ref. No.
p-tert butyl calix(n)arene	8	La, Eu, Tm and Lu	X-Ray	bimetallic lanthanide complexes are isomorphous and orthorhombic and presents eight coordination geometry.	183
p-tert butyl calix(n)arene	8	actinide metals	X-Ray, ^1H NMR	-----	184
Calix(n)arene amides	4	Na^+	ISE	presence or absence of tetra phenyl borate ions in the membrane matrix showed remarkable difference in Na^+ Ca^+ selectivity.	185
Calix(n)arene with carboxyl groups at lower rim	4	alkali and alkaline earth metal cations	pH metry, stability studies	introduction of carboxylate groups enhances stability of the resulting complexes.	186

Calix(n)aryl esters	4	butyl ammonium cations	-----	recognized guest in the air-water interface through the change in the π -A isotherm which is induced by inclusion of guest cations.	187
Calix(n)arenes	4	Tb ³⁺	lumin. studies	complexed molecule shows strong fluorescent on the basis of energy transfer luminescence $\phi=0.02-0.20$.	188
Calix(n)arene	6	primary amine	ISE	at pH 3.2 the electrode exhibits a Nernstian response in the range of 1×10^{-3} to 3×10^{-4} with a slope of 57.5 ± 0.8 mV.	189
Butyl ester calix(n)arene	4	Na ⁺	ISE	electrode's behaviour towards Na ⁺ was tested in terms of detection limit, sensitivity and selectivity towards H ⁺ , alkali and alkaline earth metals.	190
p-tert butyl calix(n)arene tetramide	4	Li ⁺ to Cs ⁺ , Eu ³⁺	molecular dynamic stimulation	comparison of its dynamic behaviour in acetonitrile and in water demonstrates the dramatic solvent effect on the extent of ligand wrapping around the complexed ions.	191

Table 1. Continued 12

Host	n	Guest	Method	Remarks	Ref. No.
25,26,27,28-tetakis (ethoxycarbonyl)methoxyp-t-octyl octyl calix(n)arene	4	Na^+	ISE	first example in which Na^+/K^+ selectivity exceeds a factor of 10^3 , highest log $K_{\text{pot}} \text{Na, M}$ value is -3.1.	192
Calix(n)arene bearing 3 carboxylate groups	6	UO_2^{2+}	solvent extn.	shows more selectivity than calixarene bearing six carboxylate groups, superamphiphilic is related to the molecular design of C_3 symmetry.	193
p-tert butyl calix(n)arene	8	lanthanides	photoph. properties	forms lanthanides dinuclear complexes.	194
p-tert butyl calix(n)arene methoxyethyl ester	4	Na^+	ISE	selective towards alkali and alkaline earth metals as well as towards hyd. and ammonium ions, best ionophore for the prepn. of Na selective electrodes.	195

Calix(n)arene	4	Ag ⁺ , alkali and alkaline earth and heavy metal cations	ISE	incorporation of metals like N and S in the calixarene moiety increases some selectivity towards heavy metal cations.	196
p-tert butyl calix(n)arene hexacarboxylic acid	6	trivalent lanthanides (La, Nd, Eu, Er and Yb)	solvent extn.	medium aqueous phase to CHCl ₃ , pH=2 to 3.5, extractability is Nd>Eu>La>Er>Yb, forms 1:2 metal ligand complexes	197
Bis(syn proximally) functionalized calix(n)arene	4	Na ⁺	picrate extn. method	suitable changes in regioselective functionalization influences the selectivity of guest mol.	198
37, 38, 39, 40, 41, 42-hexakis(decyloxy carbonyl) methyl-oxy calix(n)arene	6	primary amines (1-octylamine, 2-phenyl ethylamine & dopamine)	ISE	electrodes are capable of discriminating the steric shapes of non polar moieties of org. amines at neutral pH.	199

Table 1. Continued 13

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)resorcinarene (with four phosphonic groups)	4	Au, Cu	-----	forms tetranuclear complexes	200
Calix(n)arene p-tetrasulfonate	4	H ⁺	pot. and calorimetry studies	ΔH and ΔS values reveal that the pentaanion protonation is energetically costly.	201
Calix(n)arene cryptand/1,3-bispyridyl-/alkyl thioether calix(n)arene	4	transition metal ions	X-Ray, ¹³ C NMR	-----	202
Calix(n)arene	4	heavy metal ions viz., Ag, Cu, Cd, Pb	CHEMFET	the selective complexation of heavy metal ion by these calix(4)arene is transduced directly on a electric signal.	203

Calix(n)arene	3-8	Na, K, Cs	ISE	selectivity coefficients and slope measurements studies have been conducted.	204
Calix(n)arene based silica phase	4	Na, K, Cs, Li	HPLC	used for separation of alkali metals by HPLC and retention order is $\text{Na} > \text{K} > \text{Cs} > \text{Li}$	205
Bridged tetraester calix(n)arene	4	Na, K, Ag	spec., pot., ^1H NMR & X-Ray	conformational rearrangement of the calix part to fourfold symmetry to be necessary for the complexation.	206
p-tert butyl calix(n)arene ester deriv.	6	butyl ammonium picrates	solvent extrn.	selectivity of this deriv. is more than that of dibenzo-18 crown-6.	207
Calix(n)arene $\text{R} = \text{CMe}_3$; $\text{R}' = \text{O}(\text{CH}_2\text{CH}_2\text{O})\text{Me}$	6	alkali metals	solvent extrn.	extrn. from aqueous solns. to organic solvent's catalysis ester forming reactions of alkali metal carboxylates with alkyl halides.	208

Table 1. Continued 14

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene	4	Tb ³⁺ , Eu ³⁺	solvent extrn., lumin.	high lumin. quantum yield were attained by metal encapsulation, possible energy transfer mechanism from the sensitizer grp to the encapsulated metal ion are discussed.	209
Amino calix(n)arenes	4	transition metals	solvent extrn.	useful as ligands for transition metals in anal. and sepn. of metals.	210
Calix(n)arene tetra-ester	4	alkali metal	fluoro.	it gives fluorescent response to complexation with alkali metal.	211
1,3-bis(indole-3-yl)calix(n)arene	4	Ca ²⁺	UV	$\delta WL > 100\text{nm}$, shows a Ca ²⁺ induced pronounced colour change, association const. of the order of 10 ⁶ in 99% ethanol.	212
Schiff base calix(n)arene	4	Pb ²⁺ , Eu ³⁺	stability const studies	-----	213

Bis(cobalticenium) calix(n)arene	4	dicarboxylate anion adipate	¹ H NMR, cyclic voltametry	redox responsive.	214
Calix(n)arene	4	alkali cations	solvent extn.	extracts cations from aqueous soln. into inorg. solvents.	215
Tetra sodium calix(n)arene-p-tetrasulfonate	4	Tb ⁺³	fluoro.	Beer's law linear up to 3×10^{-7} detection limit was 2×10^{-9} , effect of foreign ions was studied.	216
p-tert butyl calix(n)arene	6	C ₆₀ and C ₇₀	solvent extn.	complexation of calixarene with a mixture of the toluene extract of crude fullerene soot, followed by recrystallisation affords >99.5% pure C ₆₀	217
p-tert butyl calix(n)arene	4,6,8	Cu	solvent extn.	the equilibrium consis and reaction mechanism for extn. of copper were discussed.	218
Asymmetric calix(n)arene	4	acetone	X-Ray	in spite of the mol. asym. the crystal structure shows high symmetry.	219

Table 1. Continued 15

Host	n	Guest	Method	Remarks	Ref. No.
Tetra sodium 25,26,27,28-tetra hydroxy calix(n)arene 5,11,17,23-tetra sulfonate	4	Mn ²⁺	UV spectra	forms 1:1 red purple complexes in aqueous alkaline soln., colour intensity increased with the increase in pH approaching a max. at pH 10.4-11.3, $\lambda_{\text{max}}=495\text{nm}$, molar absorptivity was $9.9 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$, interfering metals could be eliminated by removing them as their thiocyanate complexes by using a column packed with an anion exchanger	220
Calix(n)arene p-sulfonic acid	6	Fe(III)	near UV-Visible, spect. & pot. studies	violet coloured complex is formed, pH is between 2.5 and 5.5.	221

Calix(n)aryl acetates	4, 6, 8	Li, Na, K, Cs	mass spec.	new phenomenons were disclosed which cannot be found through conventional solvent extn.	222
Photoresponsive calix(n)arene	4	Li^+ , Cs^+ , Na^+	SISE's	new method to assign one electrode to detect two metal ions and showed affinity for ions in the presence of other alkali and alkaline earth metal ions in the dark.	223
25,27-dicarboxy 26,28-dimethoxy 5,11,17,23-tetra tert butyl calix(n)arene	4	Na^+ & K^+	solvent extn.	sensitivity of method suggests that dicarboxy calixarene grp. plays a role similar to that of the crown ether contg. 5 oxygen in ionizable crown ethers.	224
Calix(n)arene sulfonate	4	H_2O	-----	introduces new type of hydrogen bonds $\text{XH}-\pi$ bond ($\text{X}=\text{N}, \text{O}$).	225
Diazabenzocrown ether p-CMe ₃ calix(n)arene	4	Zn	¹ HNMR	forms 1:1 or 2:1 complex.	226

Table 1. Continued 16

Host	n	Guest	Method	Remarks	Ref. No.
Ruthenium(II) bipyridyl calix(n)arene	4	halide, dihydrogen phosphate and hydrogen sulfate	^1H NMR	selectively amperometrically recognizes H_2PO_4^- in the presence of 10 fold excess anions of HSO_4^- and Cl^-	227
Calix salophen crown ethers	4	H_2O , MeOH & Me_2SO , Urea	^1H NMR, X-Ray	-----	228
Calix(n)arene ester	6	alkyl amines	^1H NMR	extn. efficiency is ammonium $\text{Me} > \text{Et} > \text{Pr} > \text{i-Pr} > \text{Bu} > \text{i-Bu} > \text{s-Bu} > \text{t-Bu}$ ammonium guests, ^1H NMR studies of complexation with cesium tetra phenylborate and butylammonium picrate guests suggest that the conformational recognition into a cone conformation has provoked complex formation.	229

p-perfluoroalkyl calix(n)arene	4	neutral n.c.s. and fluoro-carbons	-----	fluorine contg. calixarenes showed better solubilities in common organic solvents compared to their non-perfluoroalkylation analog.	230
Di/tetra amide calix(n)arene	4	Pb ²⁺	ISE	electrode shows greatly improved selectivity over Cu, Zn and Cd ions as compared with commercial solid state lead selective electrodes.	231
Calix(n)arene tetra amides	4	alkali and alkaline earth metals	solvent extrn., calorimetric measurements	the enthalpies and entropies of complexation of alkali and alk. earth cations by the di-Et and pyrrolidinyI tetraamide in acetonitrile have been detd. for the first time.	232
p-tert butyl hydroxy calix(n)arene	8	Ca ²⁺ & Cd ²⁺	elemental analysis, ¹ HNMR, IR and UV	forms solid coordination compounds and their forms are CaH ₆ L, 6DMF and CdH ₆ L, 6DMF	233

Table 1. Continued 17

Host	n	Guest	Method	Remarks	Ref. No.
1,3-Alternate 25,26,27,28-tetra propoxy calix(n)arene	4	$\text{Cr}(\text{CO})_6$	X-Ray	the single crystal included two similar but slightly different structures but the data were successfully refined to $R_w = 0.92$	234
p-tert butyl 1,3-dihydroxy-2,4-disulfanyl calix(n)arene	4	Hg(II)	X-Ray	forms mono nuclear complex in which Hg ion is co-ordinated linearly to two "arene thiolate" groups.	235
p-tert butyl calix(n)arene	6	Na, K, Cs, guanidinium thiocyanate	limiting area, compressibility modulus, dipole moment & CPK model studies	complexation and structural prop. were estd. for calixarene in monolayers at the air- water interface as functions of temp. and subphase compn.	236

Calix(n)arene	4-8	Cs, Rb, K, Na, Li	ISE	selection of suitable plasticizer for calix(n)arene based ISE are discussed, the polar soft membrane is favourable when the interfering metal ion is hard whereas the hard membrane is favourable when the interfering metal ion is soft.	237
p-tert butyl calix(n)esters and amides	4,5,6,8	Li, Na and K	solvent exln.	co-transport of alkali thiocyanates at 20°C from an aqueous source soln. into an aq. receiving soln thro' a bulk liq. dichloroethane soln.	238
Calix(n)arene dioxinone crown ether	4	Na, K, Ba NH ₄ and BuNH ₃	X-Ray	it strongly complexes and electrochem recognizes the metals.	239
Tetra cetyl calix(n)arene $R = OCH_2COOEt$, OCH_2COCH_3	8	I, F, Br, Cl, Cs, Rb, Na, K	XPS detn.	Langmuir-Blodgett films formed from calixarenes adsorb range of anion and cations, order of selectivity is $I > F > Br > Cl > Cs > Rb > Na > K$	240

Table I. Continued 18

Host	n	Guest	Method	Remarks	Ref. No.
Calix(n)arene	8	C ₆₀ & C ₇₀	spec. methods	calixarene and C ₆₀ /C ₇₀ were dissolved in dry benzene in a 1:1 stoichiometry and heated under reflux for 4h, calix(8)arene has some affinity for C ₆₀ as for C ₇₀ elemental analysis is found.	36 217 241 242 243
Non sym. carceplex	4	Au	XPS, ellipsometry, electrochem methods, contact angle measurement, grazing incidence FTIR	a non-sym. carceplex with DMF incarcerated(Cx.DMF) was synthesized by combination of calixarene and a resorcinarene deriv.	244

4-sulfonic calix(n)arene	6	U_2^{2+}	computer aided chem. speciation studies.	calixarene-uranyl ratio of 5:1 is sufficient to ensure optimum uranyl-4-sulfonic calix(6)arene complex formation.	243
25,26,27,28-tetrakis (acetoxymethoxy) 5,11,17,23-tetrakis (1,1,3,3-tetramethyl butyl) calix(n)arene	4	Ag(I), Pd(I)	solvent extrn., 1H NMR	medium-chloroform, pH - 12.5 or higher, calixarene is capable of highly selectively extg Ag over Pd from $1 \text{ mol. dm}^{-3} \text{ HNO}_3$ soln and effective in removing trace amts of Ag from a large excess of Pd.	245
5,11,17,23-tetrakis(N-p-chlorophenyl) hydroxamate-c-phenyl 25,26,27,28-tetrahydroxy calix(n)arene	4	Th(IV)	UV, ICPAES	medium-ethyl acetate, $\lambda_{\text{max}} 450 \text{ nm}$, $\epsilon = 2.2 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$, Beer's law limit = $1.3\text{--}13.2 \text{ ppn}$, the thorium calixarene hydroxamate EtOAc extract was directly subjected to ICPAES measurements which increases the sensitivity by 15 fold, thorium can be estimated at the 0.1 ppn level.	246

Table 1. Continued 19

Host	n	Guest	Method	Remarks	Ref. No.
5,11,17,23-tetrakis(N-p-chlorophenyl)hydroxamate-c-phenyl 25,26,27,28-tetrahydroxy calix(n)arene	4	U(IV)	UV	medium-ethyl acetate, λ_{max} 436nm, $\epsilon=9 \times 10^3 \text{ l. mol}^{-1} \text{ cm}^{-1}$, Beer's law limit=1.78-3.1ppm, the uranium hydroxamate ethyl acetate complex was directly aspirated for graphite furnace at. absorption spectrometry measurement.	247
Calix(n)arene diphosphite	4	Pd, Pt, Re	X-Ray	4-tert butyl calixarene reacts with two equivalents of PCl_3 to form a bidentate diphosphite ligand which co-ordinates to Pd, Pt and Re.	248
Calix(n)arene phosphine oxide	4	Eu	flow injection analysis, ISE	ionophore is selective for Eu in the presence of high background of Na and other common ions.	249

5,11,17,23-tetra tert butyl 25,26,27,28-tetra (N,N-dimethyl dithiocarbamoyl ethoxy) calix(n)arene	4	Pd,Pt	solvent extn.	mercurium - chloroform. no extn of PtCl_4^{2-} is obsd under thermal condns., Under photochemical condns using a mixt. of PtCl_4^{2-} and PtCl_6^{2-} extn. of platinum into chloroform layer is obsd.	250
Resorcinol type calix(n)arene bearing four alkyl side chains	4	Cs^+	solvent extn.	Cs^+ in the outer aq. soln was transported thro' the liq. surfactant membrane of W/O/W emulsion into the inner HCl solution.	251
Calix(n)arene	4	W	X-Ray	functionalization of tungsten bonded over a calixarene oxomatrix with phenoxo groups leads to the self assembling of metal calixarenes into columnar structures.	252

Table 1. Continued 20

Host	n	Guest	Method	Remarks	Ref. No.
p-tert butyl calix(n)arene	4	Mo	^1H -NMR, UV, IR, raman spectra	each Mo-Mo unit weakly coordinated by an axial THF solvent mol. is included in the calixarene basket of neighbouring complex.	253
p-tert butyl calix(n)arene	4,5,8	C_{60}^+	voltametry	interaction strength follows the order of $\text{C}_{60}^+ > \text{C}_{60} > \text{C}_{60}^-$ and calix(8) > calix(5) > calix(4) bis ethyl ester.	254
Bis(N,N'-dimethyl 1,4,7-triazacyclononane) calix(n)arene	4	Ni(II)	X-Ray	forms a ferromagnetic dinuclear Ni(II) complex with three end on azide bridging ligands.	255
Diallyl sulfide substituted calix(n)arene	4	Au	IR, thickness, wettability	well ordered monolayer were formed.	256

Bridged Calix(n)arene R=CMMe ₃ R'=OY(Y=H, Me)	6	bromide	X-Ray	adopts the 1,2,3- alternate conformation with the central bromide functionality pointing towards the cavity.	257
Lower rim calix(n)arene amine	4	H/AuCl ₄ , Cd ²⁺ , Pb ²⁺ , Hg ²⁺ , Na ⁺ , K ⁺ , Ba ²⁺	¹ HNMR, UV, pH-metry	higher basic character of aliphatic and alicyclic p-tert butyl calix(4)arene amine relative to pyridino calix(4)arene is demonstrated, potential use of this ligands for the removal of toxic metal cations from contaminated sources is emphasized.	258
Calix(n)arene R = X ¹ X ² (X ¹ , X ² = C ₁₋₁₈ alkyl) OR' = OCH ₂ COOH/ OCH ₂ CONR ¹ R ² (R ¹ , R ² = alkyl, unsubstituted phenyl)	4	calcium and alkaline earth metals	solvent extn.	Ca ²⁺ was extd. From 1 x 10 ⁻⁴ M aq. Soln. into 5 x 10 ⁻⁴ M calixarene in CHCl ₃ with extn. Yield > 90% at pH > 6. Results of selective separation of Ca ²⁺ from Mg ²⁺ , Sr ²⁺ and Ba ²⁺ were also presented	259

Table 1. Continued 21

Host	n	Guest	Method	Remarks	Ref. No.
Chiral calix(n)resorcinarene	4	chiral methyl ammonium compd.	¹ HNMR	complexation behaviour of hepta hydroxy deriv. with chiral methyl ammonium compd. in methanol was investigated.	260
Calix(n)arene aryl ester appended bisfullerenes	4	-----	spec., light scattering	changed the absorption spectra upon changing the solvent from CHCl ₃ to chloroform:MeCN=1:1 vol./vol. or adding NaClO ₄ . unique characteristics can be rationalized in terms of aggregation-disaggregation equilibrium change.	261

p-tert butyl calix(n)arene	4	alkali cations	MD stimulation, FEP compu- tor investi- gation, pH-me-try	a theoretical study based on mol. dynamics and free energy stimulations in vacuo, in pure water, acetonitrile and chloroform on both endo and exo complexes, the role of the t-Bu"gate" and pH on the stability of endo complexes were investigated. -----	262
Calix(n)arene	4-8	metal and org. cations	spec, stability, association constants.	-----	263
Calix(n)arene	----	fullerenes	spec.	used for purification of fullerenes	264
Calixarene bearing phosphine oxide	4	Ca ²⁺	ISE	selective for Ca ²⁺ against other alkali metal ions and Mg ²⁺ ions, effective lifetime of 7 weeks.	265

Table 1. Continued 22

Host	n	Guest	Method	Remarks	Ref. No.
2,2'-Bipyridine grafted calix(n)arene quinones	4	K^+ , Ba^{2+}	cyclic voltametry	-----	266
p-tert butyl calix(n)arene	4	Na, K, Rb, Cs, Sr, Ba, benzyl ammonium cation	fourier transform ICR mass spectro-metry	complexes 2 metal cations at the same time with the accompanying large proton to yield species with +1 net charge, relative rate constants and reaction efficiencies for the formation of the 1:1 calixarene/alkali metal complexes vary inversely with cation size probably reflecting differences in the polarizing capabilities of the cations.	267

Calix(n)arene diamide	4	Fe, Er	X-Ray	forms 1:1 metal/calixarene complex, rigid nature of lower rim in the cone conformation ensures that four donor O atoms are approx. coplanar thus ruling out any possibility of orthogonal co-ordination and restricting the type of metals that form complexes.	268
Ketoxime deriv. of calix(n)arene	6	Cu, Ni, Co	X-Ray	metal/ligand ratio is 3:1. Cu and Ni complexes are square planar and Co complex is octahedral.	269
Calix(n)arene	---	iodine	solvent extrn.	passage of iodine through the org. bulk liq. membrane was governed by donor-acceptor interaction between n-donor atoms in the carrier and σ -acceptor (iodine atoms) by the diffusion of an n- σ -type charge transfer complex in the membrane followed by the release by the Lewis acid-base interaction in the aqueous phase.	270

Table 1. Continued 23

Host	n	Guest	Method	Remarks	Ref. No.
Monodisperse silica receptor colloids grafted with calixarene deriv.	4	Cs ⁺	¹ H-NMR, elemental analysis, light scattering, electrophoresis	calixarene-silica colloids indeed are receptors for Cs cations.	271
Calix(n)arene	-----	org. cations and anions, aromatic hydrocarbons	liquid chromat.	anion exchanger phases modified with calixarenes and porphine deriv. retained fullerenes, the stationary phase allowed sepn. of C ₆₀ and C ₇₀ by using PhMe.	272
Calix(n)arene tetramide	4	alkaline earth and uranyl cations	MD and FEP studies, X-Ray	computations show L.M ²⁺ complexes are of converging type in H ₂ O and in MeCN which contrasts with L.M ⁺ alkali cation complex which display conformational flexibility in solution.	273

Thioamide calix(n)arene deriv.	4	Pb ²⁺	ISE, pot.	proper choice of lipophilic salts, plasticizer for membrane preparation and membrane conditioning can alter and moderate ion selectivity.	274
1,3-Acid diethyl amide substituted calix(n)arene	4	Eu, Sm, Lu	X-Ray, solvent extn.	-----	275
Na-hydroxy calix(n)arene p-sulfonate	4,6,8	rare earth, alkali earth and Zr ⁴⁺ , Hf ⁴⁺ and Th ⁴⁺	X-Ray, elem-ntal analysis, IR	forms water soluble complexes.	276

AAS-atomic absorption spectroscopy, aq.-aqueous, asym.-asymmetric, ca.-calculated, contg.-containing, derivs.-derivatives, detd.-determined, extn.-extraction, extd.-extracted, FEP-field effect perturbation, fluor.-fluorescence, insol.-insoluble, intermol.-intermolecular, intramol.-intramolecular, IR-infrared spectra, lumin.-luminescence, MFD-molecular dynamics, mols.-molecules, pot.-potentiometric, prepd.-prepared, seps.-separations, spec.-spectroscopy.

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