

Review Article

Azocalixarenes: Synthesis, Characterization, Complexation, Extraction, Absorption Properties and Thermal Behaviours

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Abstract

Azocalixarenes, which have a conjugated chromophore azo ($-N=N-$) group in *p*-positions, are synthesized in “one-pot” procedures in satisfactory yields. Their structures in the solid and solution are elucidated by UV–vis, FT-IR, 1H and ^{13}C NMR spectroscopic methods as well as elemental analysis techniques. Some of them are complexed with metal ions (alkali, alkaline-earth and transition metal ions) under neutral conditions. A wide variety of applications is expected by the functionalization of the side arms. The selective liquid–liquid extraction of various alkali, alkaline-earth and transition metal cations from the aqueous phase to the organic phase is carried out by using azocalixarenes. Furthermore, the synthesized azocalixarenes are utilized for selective extraction of Fe^{3+} cations from the aqueous phase to the organic phase. The effects of varying pH and solvent upon the absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*-positions are examined. The thermal behaviours of azocalixarenes containing *upper rim* functionalized groups are investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG).

Introduction

Calixarenes, which are accessible by the base-catalyzed condensation of *para*-substituted phenols with formaldehyde, are ideal frameworks for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest since the incorporation of a suitable sensory group into the calixarene result in a tailored chromogenic receptor. These compounds have lately attracted considerable attention because of their potential as enzyme mimics. The chemistry of calix[*n*]arenes [*n* = 4–8] is well represented in the literature due to the easeness of their synthesis [1–3]. Extraction, transport, stability constant and colorimetric measurements, augmented by NMR, X-ray and computer simulation studies provide evidence that many of these *lower rim* derivatives have very significant ionophoric properties for cations, several with good selectivity within groups of metals [4].

Calix[*n*]arenes, which are appropriately designed, exhibit a large variety of functions; e.g., as inclusion

compounds [5], selective complexing agents for metal ions [6, 7], and catalysts [8, 9].

Calix[*n*]arenes are readily converted into a wide range of derivatives by the alkylation of the phenolic groups at the *lower rim* [10]. This type of chemical modification is first introduced by Gutsche as part of conformational studies in calix[*n*]arenes [11], since then this has been widely used by several research groups to produce pendant ether [12], carboxylate [13], ester [14, 15], amide [16], phosphine [17, 18], *vic*-dioxime [19–21], and keto [22] derivatives. Azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibre and the colouring of differing materials, and for plastics, biomedical studies, and advanced applications in organic synthesis [23–26]. Moreover, azo groups bring to calixarenes a chromogenic activity. These compounds are an important class of organic colorants and consist of at least a conjugated chromophore azo ($-N=N-$) group and two or more aromatic rings. The color properties of organic dyes depend on both the presence of the chromophore groups and the crystallographic arrangement of molecules in the solid state [27].

With these subjects in mind, we have synthesized several azocalix[*n*]arene derivatives [28–31]. We have

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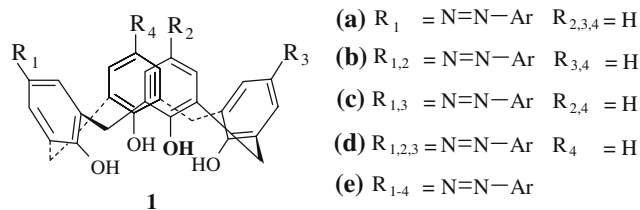


Figure 1. Structures of mono-, di-, tri- and tetra-azocalix[4]arenes.

found that these azocalixarenes act as excellent host molecules for the selective binding of metal ions [32–34]. They also act as excellent enol–keto tautomers and as thermal decomposition behaviour [35]. This review article briefly discusses various molecular designs of azocalixarene-type macrocycles for metal ions, and gives examples on the relationship among the structure, complexing, metal selectivity and thermal behaviours.

Formation of azocalixarene structures

Azocalixarenes, which are generated by the insertion of nitrogen atoms into the *p*-position unit of the calixarene structure, have several isomers based on the position of the nitrogen atoms and the ring size. The first reported calixarene diazo coupling involved the reaction of *p*-nitrobenzenediazonium tetrafluoroborate with calix[4]arene [36]. Unexpectedly, it proceeded in an autocatalytic fashion to give **1e** as the almost exclusive product with only small amounts of **1a–d**. Benzenediazonium, *p*-methylbenzenediazonium, *p*-methoxybenzene diazonium, and *p*-carboxybenzenediazonium chlorides react in comparable fashion to give the corresponding tetra-substituted compounds **1e** [37]. However, the monosubstituted **1a**, A,B-disubstituted **1b**, A,C-disubstituted **1c** and trisubstituted **1d** [38] have been isolated and characterized by limiting the amount of the diazonium salt prepared from 6-amino-1,3-benzodioxin and by adding the calixarene to the diazonium solution. Calix[4]arenes carrying fewer than four arylazo groups (e.g. allyl [39]) at one or more of the *p*-positions (Figure 1) [1].

Nomura and his coworkers describe azo group containing compounds which are of interest because of their properties as binding sites for complexation or as chromophores of dyes [40]. They report the synthesis of a calix[6]arene derivative containing azo groups and its binding properties for metal ions. They observe that

although the *p*-phenylazocalix[6]arene is much less effective than the 4-phenylazo-2,4-dimethylphenol for the extraction of transition metal ions it is more selective for Ag^+ , Hg^+ , Hg^{2+} cations.

In the laboratory Shimizu synthesized a chromogenic calix[4]arene which has within the molecule a calix[4]aryl triester moiety as a metal binding site and an azophenol moiety as a coloration site [41]. Diazo-coupling reactions of calix[6]arene are studied by Morita and Shinkai and their coworkers. In the resulting NMR spectra, they have found that the diazo coupling reactions are the most convenient method which gives the best yield [36, 37].

In our previous work, we have synthesized a *vic*-dioxime derivative of calix[6]arene and its complexes [42–45], polymeric calix[*n*]arene derivatives and have performed selective extraction of transition metal cations [46–49]. Because of the first our paper on azocalix[*n*]arenes is issued, the synthesis of various calix[*n*]arenes and their characteristics are studied by us [28, 29, 32]. On the other hand, the amphiphilic host calixarenes developed with azo-linkages are functionalized by Collard and his coworkers. These macrocycles possess a large hydrophobic cavity suitable for binding of organic guests and chromophoric linkages which can be monitored for responses to host-guest interactions. In this point, we report the synthesis of five substituted calix[4]arenes (**2a–d**, **3**) (Figure 2). These are synthesized from calix[4]arene with 4-*n*-butylaniline, 4-(phenylazo)aniline, 4-aminoacetanilide, *N'*-2-thiazol-2-ylsulfanylamine and 2-amino thiazole by diazo coupling reactions [32, 50].

As a general procedure, *p*-substituted azocalix[*n*]arenes are obtained by the diazo-coupling reaction in the following manner. At first, the calix[*n*]arene is prepared by the debutylation of *p*-*tert*-butylcalix[*n*]arene [51]. Furthermore, a solution of diazonium chloride, which was prepared from carbocyclic and heterocyclic amines, water and concentrated hydrochloric acid is heated to 40–45 °C while being stirred until a clear solution is obtained. This solution is cooled down to 0–5 °C, and a solution of sodium nitrite in water is then added dropwise, maintaining the temperature below 5 °C. The resulting solution is stirred for an additional 30 min. in an ice bath, before an excess nitrite is destroyed by addition of urea. This solution is buffered with solid sodium acetate [52].

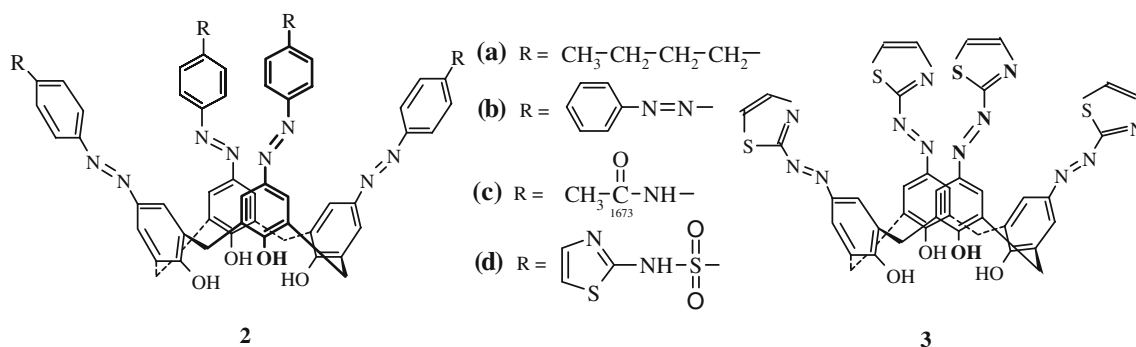


Figure 2. Structures of five substituted azocalix[4]arenes.

The coupling reaction of calix[*n*]arene with diazonium chloride in aqueous THF gave azocalix[*n*]arene. The reactions proceeded smoothly to produce the corresponding azo compounds in good yields.

In the context of the host–guest complexing properties of cyclophanes and calixarenes based on cyclic oligomers of phenol derivatives [3], Shinkai *et al.* [53] synthesize arylazo derivatives of a resorcinol-based cyclophane (**4**) and calix[4]arenes (**5**) (Figure 3) [40, 54, 55].

The cyclophane reacts with 4.8 equivalents of benzenediazonium-4-sulfonate to give the tetraarylozo derivative **4** in good yield. In contrast to the starting material the product is water-soluble. Without going into details, the authors mention a spectrophotometrically determined pK_a -value of 10 which is attributed to the dissociation of four protons (Figure 4). (From the plot of absorbance given in their publication, the present author has the impression that the four protons are not dissociated at exactly the same pH value).

The azo coupling reaction of the calix[4]arene shows an unexpected auto-catalytic effect. If the molar ratio of the diazonium ion ($X = \text{NO}_2$) to the calix[4]arene is 4:1, the yield of the tetra(arylozo)calix[4]arene is 99%, but with ratios 3:1, 2:1, and 1:1 the tetra(arylozo) compound is also a major product (70%, 45%, and 22%, respectively). If ratios 3:1, 2:1, and 1:1 are used the yields of the tris- and bis(arylozo) products are in the range of only 1.2–3.4%, and the mono(arylozo) compounds are formed with a yield of 5.3–6.0%. Using the ratio 4:1 the bis- and mono(arylozo) products are not found at all, and the tris(arylozo) compound is found only in 1% yield. These results clearly indicate that each of the consecutive azo coupling steps is significantly faster than the proceeding step. This autocatalytic effect is probably related to the acidity constants K_{a1} to K_{a4} of the four hydroxy groups in the tetra(arylozo)calix[4]arene. From the changes in the UV–vis spectra, pK_{a1} , pK_{a2} , pK_{a3} , and pK_{a4} for **5a** are calculated such as 0.5, 2.0, 10.0, and about 13, respectively. By potentiometric titration a similar large spread of pK_a values is found for **5b**, which is related to the strong hydrogen-bonding interaction in calix[4]arenes [2, 56]. Therefore, at a given pH each addition of an arylazo residue increases the equilibrium concentrations of the phenoxide groups, and consequently the next azo coupling reaction proceeds faster.

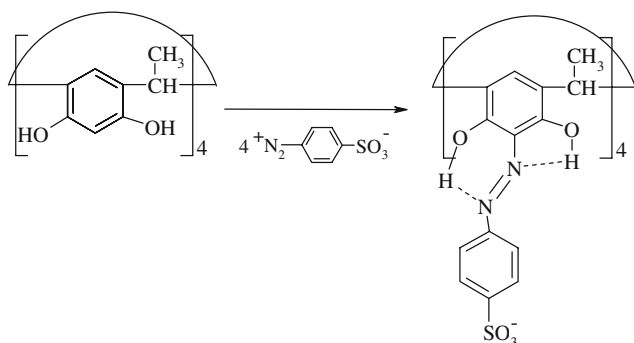


Figure 3. Structure of a resorcinol-based cyclophane (**4**).

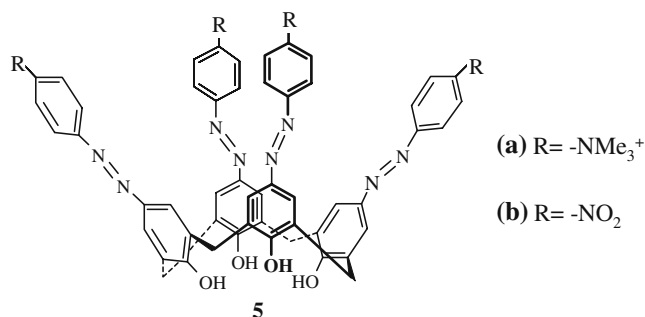


Figure 4. Structures of substituted azocalix[4]arenes.

In laboratory of Dumazet–Bonnamour, they are interested in the development of a new class of chromoionophore sensors. Thus, they are build molecular design constituted of calix[4]arene which contains both 2,2′-bithiazole (*btz*) moiety as a metal-binding site and azophenol moiety as coloration site. The incorporation of *btz* subunit has been chosen here due to its potential double-site complexation abilities, completed by its fluorescence properties. This had led to the preparation of three diazo coupling calix[4]arenes substituted by thiazole subunits **6a, b**, **7a, b** and **8a, b** (Figure 5) [57].

In another study of Dumazet–Bonnamour in this field, they have developed three steps strategy which permits incorporation of the ligands **9a, b**, **10a, b** and **11a, b** two azo groups on the *upper rim* and both amide and ester functions on the *lower rim* of calix[*n*]arene with a retention of the *cone* conformation (Figure 6) [58].

In recent study of Dumazet–Bonnamour, the incorporation of only two phenylazo groups on the *lower rim* of calix[4]arene requires to graft the biheterocyclic moieties for the first time. Then, bipyridyl and bithiazol derivatives of calix[4]arene are synthesized and chosen in order to block the two distal hydroxy groups of calix[4]arene. Thus using conventional procedure with substituted diazonium BF_4^- , disubstituted derivatives are obtained in *cone* conformation with 66% and 61% yields, respectively [59].

In the field of our previous work, two monomeric (**12**, **13**) and two calix[*n*]arene (**14**, **15**) derivatives containing azo groups is synthesized and characterized. First, *p*-nitroaniline was diazotized by sodium nitrite in conc. HCl. Resulting *p*-nitrobenzene diazonium chloride is coupled to *p*-*tert*-butylphenol. Coupled product is secondly reduced by SnCl_2 . After then, prepared amino azo compound was rediazotized. Lastly, novel azobenzenediazonium chloride solution is coupled to phenol, *p*-*tert*-butylphenol, calix[4]arene, and calix[6]arene (Figure 7) [28].

In recent study of us [30], we have carried out similar studies. Seven substituted calix[6]arenes (**16a–f**, **17**) is prepared by us (Figure 8). The same azocalix[6]arene compound **17** is synthesized by Lu and He [60]. We have found that the diazo coupling reactions are the most convenient method which gives the best yield. The molecular design of chromogenic calix[*n*]arenes has

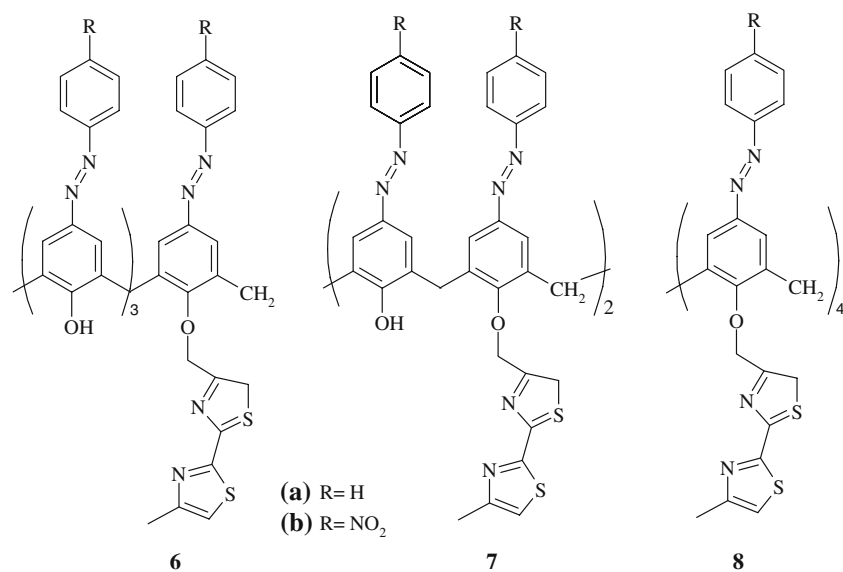


Figure 5. Structures of *O*-thiazole substituted azocalix[4]arenes.

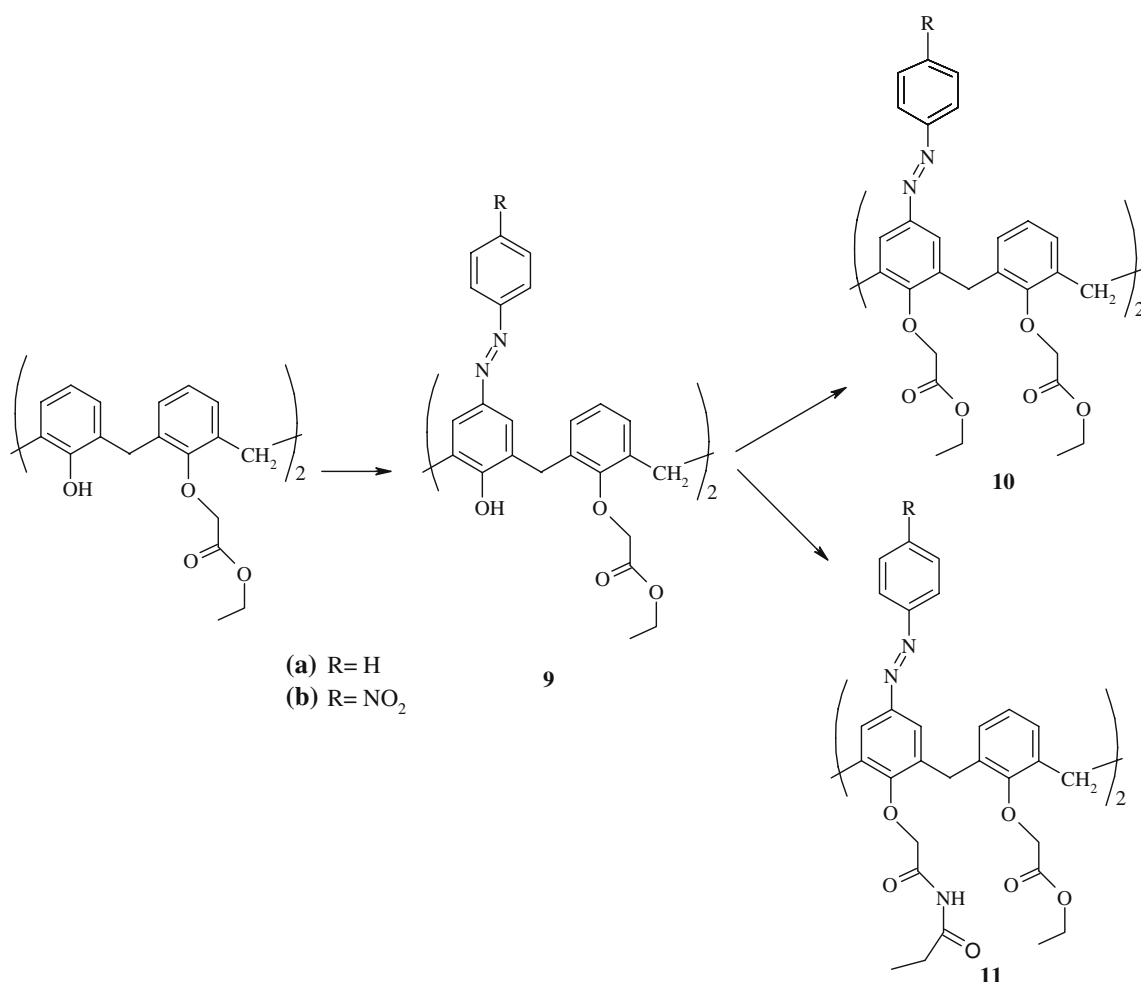


Figure 6. Structures of ester and amide substituted azocalix[4]arenes.

attracted much attention in the past years. These azocalixarenes change their absorption (or fluorescence) spectra upon the binding of metal cations similar to chromogenic azo groups. The color formation resulting upon complexing serves as a transducer of chemical

signals to physical. Recently a number of chromogenic azocalix[6]arene derivatives have been synthesized to obtain highly selective ligands which may have great potential in the development of new metal ion sensors.

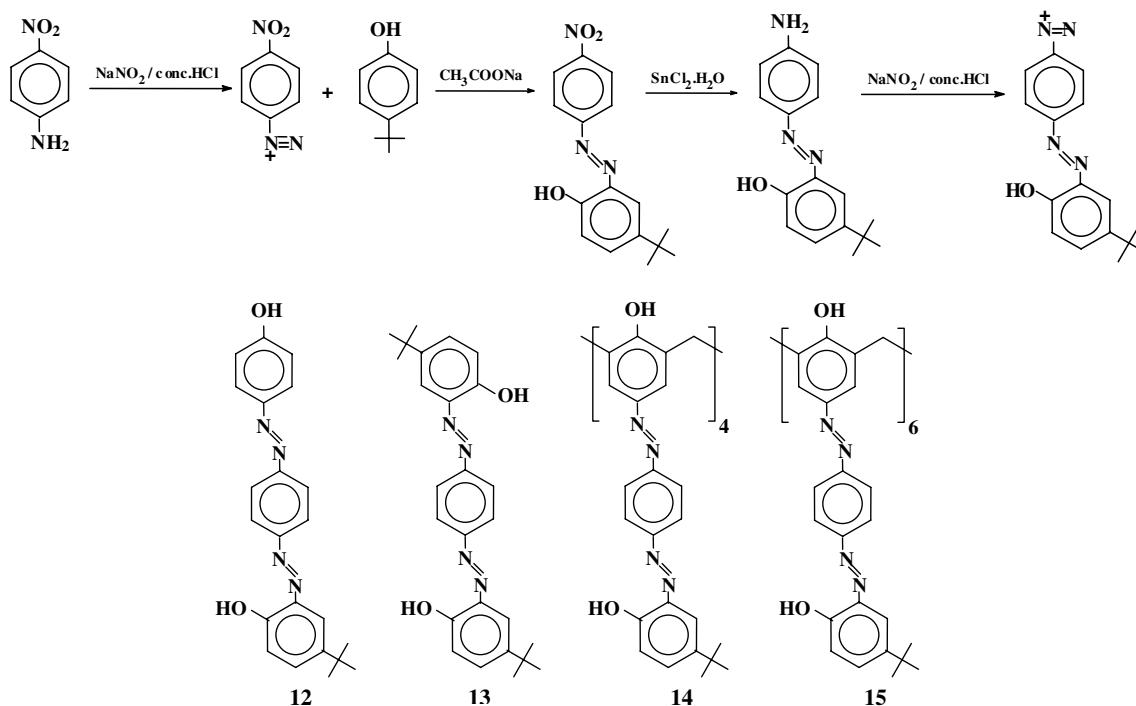


Figure 7. Structures of two monomeric and two calix[*n*]arene derivatives.

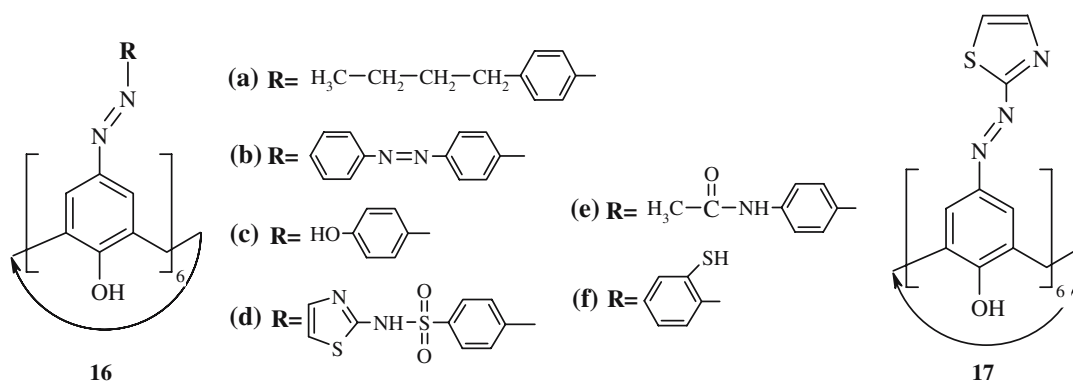


Figure 8. Structures of various substituted calix[6]arenes.

According to Zollinger in the *Diazo Chemistry I*, the major problem of these diazotizations is the oxidation of the initial aminophenols by nitrous acid to the corresponding quinones, for example **16c**. Easily oxidized amines, in particular aminonaphthols, are therefore commonly diazotized in a weakly acidic medium ($\text{pH} \sim 3$, so-called neutral diazotization) [61].

There is a large number of heteroaromatic compounds of very different structural types. Pyrazolones have been widely used for yellow and orange monoazo dyes since the end of 9th century. Other types have become important as a source of new industrial aspects. These coupling components are not classified on the basis of their structures, but from the viewpoint of what is important for tinctorial properties of the dyes obtained with these types of coupling components.

The first group consists of monocyclic heteroaromatic compounds with one heteroatom and without strongly electron-donating substituents ($-\text{OH}$, $-\text{NH}_2$). Pyrrole, furan, and thiophene are better electron donors

than benzene. Descending other of their reactivities in azo coupling is thiophene > pyrrole > furan > benzene.

Another recent work in this field, the synthetic route to bisazocalix[4]arenes is illustrated in Figure 9. In order to introduce functional groups into each azo group one must choose a reaction with a quantitatively high yield, because the isolation of a fully-substituted product from lower-substituted by products is fairly difficult. In Figure 9 the key step to synthesize bisazocalix[4]arene is the diazo coupling step which proceeds quantitatively under optimized conditions. The azo groups are coupled to the amino groups to afford tribenzoyl calix[4]arene. Final products, **18**, **19** and **20** have obtained by diazo coupling with the corresponding aromatic diamines *p*-phenylenediamine, 4,4'-diaminobiphenyl and 4,4'-diamino-2,2'-dinitrobiphenyl, consecutively. Extraction studies of these bisazocalix[4]arenes show no difference in their extraction behaviour and selectivity, whereas azocalix[4]arenes are poor extractants for heavy metal cations. The absorption spectra of the prepared

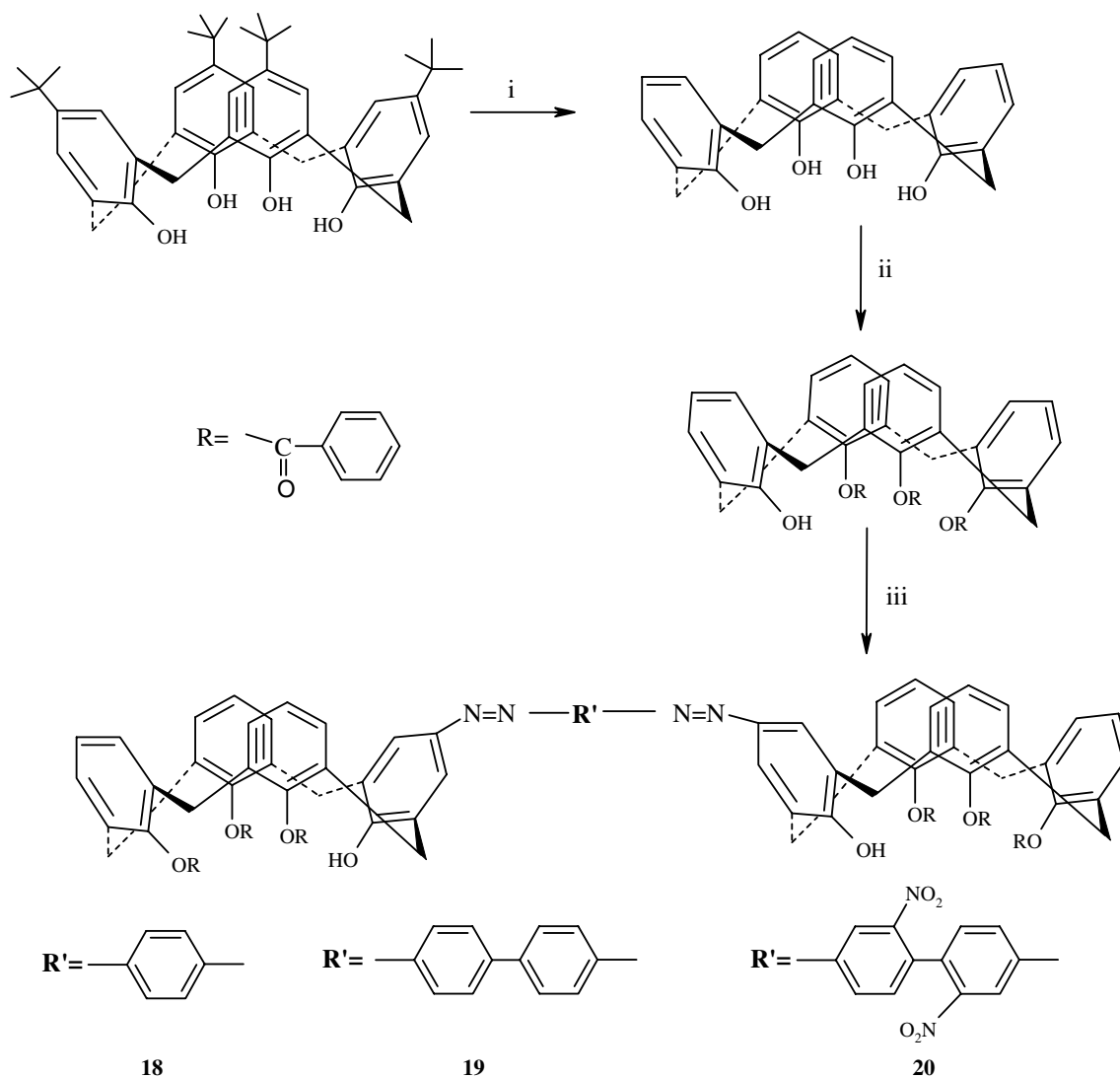


Figure 9. The synthetic route for three novel bisazocalix[4]arene derivatives (i) $\text{AlCl}_3/\text{toluene}$, (ii) PhCOCl , Pyridine, (iii) $\text{NaNO}_2/\text{conc.HCl}$, $\text{NH}_2\text{-R'-NH}_2$.

bisazocalix[4]arenes are discussed under both varying pH and solvent [31].

Synthesis, structures, and characterization

Calixarenes are often described as “macrocycles with unlimited possibility” because of their versatility and utility as host molecules, which mostly come from the ease in the synthesis of the basic platform and ready functionalization at *lower* and *upper rims* to construct variously modified three-dimensional structures [1].

Considerable attention was devoted in the 1990-mid, and this has continued unabated in the 2000s. This comes as no surprise, because the utility of the azocalixarenes for the majority of potential applications, depend upon suitable modification of the parent azocalix[*n*]arene compounds. Many papers describe the synthesis and dyeing properties of *p*-phenylazocalix[*n*]arene, and several studies have been published with respect to *p*-hetaryl azocalix[*n*]arene. Especially, azoca-

lix[*n*]arenes based on heterocyclic amines have been developed, and the resultant azocalixarene have been higher tinctorial strength and give brighter dyeing than those derived from aniline-based diazo components [2].

Synthesis of azocalixarenes with various carbocyclic amines

Because functional groups can be introduced into two sites and calix[*n*]arenes (aromatic ring and phenolic oxygen atom), further functionalization and application can be expected. Firstly, we have tried the development of a new class of chromoionophore dyes. The aim of the present work is to design calix[4]arenes which contain both an aniline moiety as an electron-donating or electron-withdrawing group and an azophenol moiety to provide color. The prepared azocalix[4]arenes are summarized in Figure 10. The incorporation of an aniline subunit is chosen because of its potential double-site wavelength shift abilities. This led to the preparation of 12 diazo-coupled calix[4]arenes substituted aniline

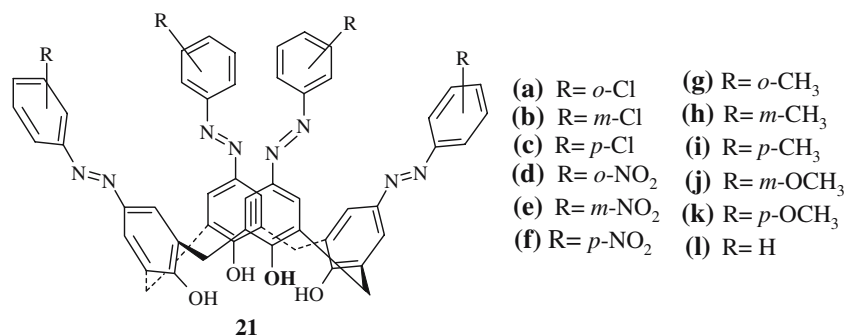


Figure 10. Structures of *o*-, *m*-, *p*-substituted azocalix[4]arene derivatives.

derivative subunits **21a–l**. On the other hand, very high yields are obtained in the case of the reactions with electron-withdrawing groups such as $-\text{NO}_2$ group [62].

In the following study it was found that calixarene is composed of a ring of six phenolic units used as molecular substructures, on which preorganized ligands, such as the six azo groups in C_6 symmetry are assembled to provide the required structure. In this review, the application of amphiphilic calix[6]arenes (**22a–l**) are reported for the effect of varying pH and solvent upon the absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*-positions (Figure 11) [63].

Synthesis of azocalixarenes with various heterocyclic amines

In the field of our investigations, we were interested in the development of a new class of chromogenic dyes. Azocalixarenes containing calix[*n*]arene as coupling components have also been described as having blue to violet colors in various publications. As a continuation of our previous work in this area, we report molecules **23a–f** having calix[4]arene as the coupling component in synthesis of the calix[4]arenes (Figure 12) [64].

Recently, our previous experience has been forwarded us to synthesize azocalix[6]arenes (**24a–g**) and their hetarylazo derivatives by substituting different rings on *lower rim* and to investigated both the effect of varying pH and solvent upon the absorption ability of hetarylazo calix[6]arenes [65] (Figure 13).

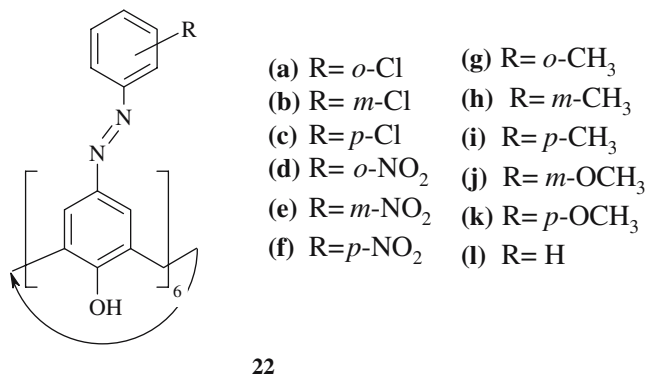


Figure 11. Structures of *o*-, *m*-, *p*-substituted azocalix[6]arene derivatives.

Structures of azocalixarenes

It is well known that most of the functional groups are not able to be incorporated into calixarene by a direct condensation process. Therefore, the functional groups are introduced into the existing calixarene framework by a functionalized method either in the “*lower rim*” (the oxygen-position of the phenolic moieties) or in the “*upper rim*” (the *p*-position of the aromatic nuclei).

Diazotized calixarene derivatives, “*azocalixarenes*”, have recently attracted great interest in a number of fields. The extensive organic and organometallic chemistry of calixarene certain isolated azocalixarenes have been shown to have interesting layered solid state structures. Also, the discovery that the parent azocalix[*n*]arenes effect the transport of transition metal ions in water/organic solvent systems which led to particular interests in *mono*- and *di*-azocalix[*n*]arenes.

The ultraviolet spectral behaviours of the azocalix[4]arenes are investigated in chloroform and other solvents. In comparison of UV spectra, it is found that all of the spectra show a strong absorption maximum in the 285–298 nm range with high extinction coefficients. It can be seen that azocalix[4]arene gives two absorption bands ($\pi-\pi^*$ and $n-\pi^*$ transitions).

In the IR spectra, the stretching vibrations of the azocalix[4]arenes appear at $3300-3200\text{ cm}^{-1}$ ($-\text{OH}$), $3100-3000\text{ cm}^{-1}$ (arom. $-\text{C}-\text{C}-$), $2950-2900\text{ cm}^{-1}$ (aliph. $-\text{C}-\text{H}$), $1700-1650\text{ cm}^{-1}$ (arom. $-\text{C}=\text{C}-$) and $1600-1500\text{ cm}^{-1}$ ($-\text{N}=\text{N}-$) for azocalix[*n*]arene **21–24**, approximately.

^1H NMR spectroscopy is a versatile tool for the identification of calixarene conformations. The ^1H NMR data showed that all azocalix[4]arenes **21**, **23** exist in a *cone* conformation due to the appearance of ArCH_2Ar as a typical AB protons signal at 3.2–4.8 ppm. The lower field signals of the hydroxyl group of the azocalix[4]arenes, which substituent weakens hydrogen bonds of OH-groups, resonate at ca. 9.0–11.0 ppm, approximately and these are typical for intramolecular hydrogen bonding protons (Figure 14).

The azocalix[4]arenes (**21a–l**) may exist in two possible tautomeric forms, azo-enol and keto-hydrazo (Figure 15). Deprotonation of two tautomers leads to a common anion. The infrared spectra of all compounds (in KBr) has showed broad $-\text{OH}$ bands at

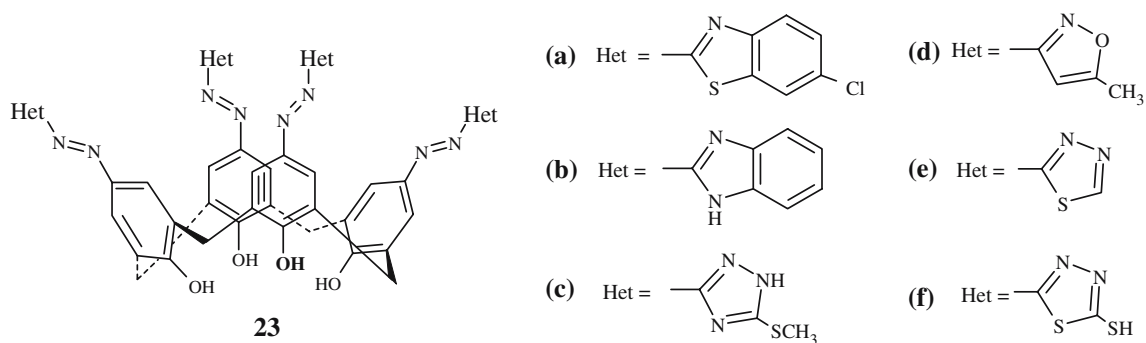


Figure 12. Structures of hetarylazocalix[4]arene derivatives.

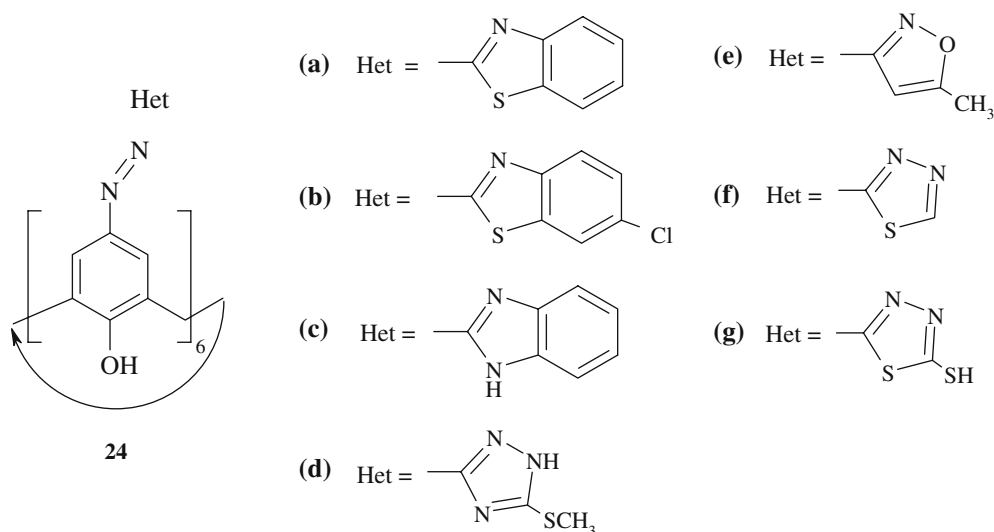


Figure 13. Structures of hetarylazocalix[6]arene derivatives.

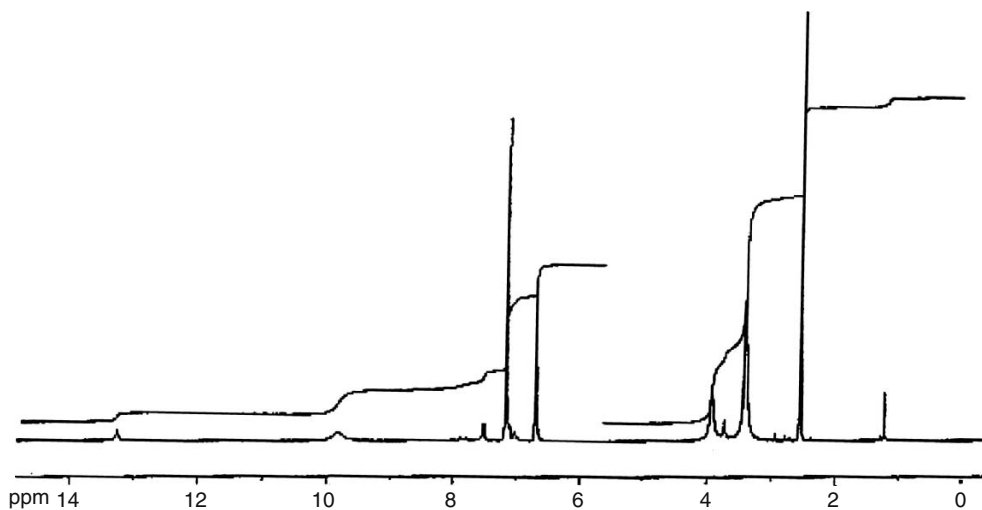


Figure 14. ^1H -NMR spectrum of 6-(chlorobenzothiazolylazo)calix[4]arene (**23a**).

$3339\text{--}3200\text{ cm}^{-1}$ and $\text{C}\text{--}\text{O}$ bands at $1196\text{--}1063\text{ cm}^{-1}$. It can be suggested that these compounds do not exist as the keto-hydrazo form in the solid state.

The structures of azocalix[4]arenes **21a**–**l** are examined in solution by high-resolution NMR. The ^1H -NMR spectrum measured in DMSO-d_6 at $25\text{ }^\circ\text{C}$ showed broad bands of hydroxy and imine protons ($\delta = 10.82\text{--}11.67$ (OH) and $\delta = 13.56\text{--}14.57$ (NH), respectively). Also,

the ^1H -NMR spectra of these compounds in DMSO-d_6 showed single bands at $\delta = 2.09\text{--}2.24$ ($-\text{CH}_2-$) and $\delta = 4.08\text{--}4.23$ ($-\text{CH}_2-$). These findings suggest that the compounds may exist as a mixture of the two tautomeric forms in DMSO-d_6 .

The structures of azocalix[4]arenes **23a**–**f** are examined in solution using NMR. The ^1H -NMR spectra measured in DMSO-d_6 at $25\text{ }^\circ\text{C}$ has showed singlet

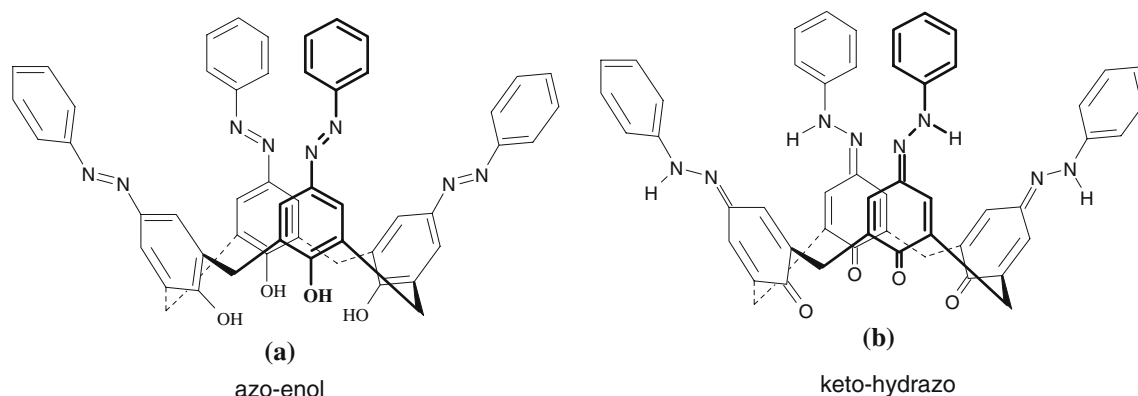


Figure 15. The tautomeric forms of 4-(phenylazo)calix[4]arene (**21**).

peaks for methylene protons ($-\text{CH}_2-$) at δ 2.09–2.25 and 4.17–4.20, a singlet at 2.90 ($-\text{SCH}_3$), a singlet at 2.45 ($-\text{CH}_3$), a multiplet at 6.10–9.69 for aromatic protons (Ar-H), a broad peak at 10.37–11.81 ($-\text{OH}$), a broad peak at 13.68–14.82 ($-\text{NH}$) for tautomer and a broad peak at 2.37 ($-\text{SH}$). At room temperature the singlets at 10.37–11.81 and 13.68–14.82 indicate that the compounds may exist as a mixture of several tautomeric forms in $\text{DMSO}-d_6$ (Figure 16).

Conformational study has been realized by ^1H -NMR spectra at room temperature. Thus, at 25 °C hydroxy and imine ($\delta = 10.82$ – 12.30 and 13.75 – 14.75) protons display two broad singlets for azocalix[6]arene **22a–I**. At room temperature the singlets indicate that the calix[6]arenes are conformationally mobile. In the case of azocalix[6]arene the phenomenon is the same, but at

room temperature, there is only one broad singlet showing a better mobility than in azocalix[4]arene. Indeed, in an azocalix[6]arene mobility is more easy than in azocalix[4]arene related to site difference of size and less strong hydrogen bond stabilization (Figure 17).

The structures of azocalix[6]arene **24a–g** are examined in solution using high-resolution NMR. The ^1H -NMR spectrum measured in $\text{DMSO}-d_6$ at 25 °C has showed singlet peaks for methylene protons ($-\text{CH}_2-$) at δ 2.09–2.25 and 4.12–4.21, a singlet at 2.85 ($-\text{SCH}_3$), a singlet at 2.45 ($-\text{CH}_3$), a multiplet from 6.10–9.69 for aromatic protons (Ar-H), a broad peak at 10.75–11.87 ($-\text{OH}$), a broad peak at 13.80–14.54 ($-\text{NH}$), a broad peak at 7.02 and 9.61 ($-\text{NH}$) a broad peak at 6.17 and 12.17 ($-\text{NH}$) and a broad peak at 2.37 ($-\text{SH}$). At room temperature the broad peaks at 10.75–11.87 and 13.80–14.54 indicate that the dyes may exist as a mixture of tautomeric forms in $\text{DMSO}-d_6$ (Figure 18).

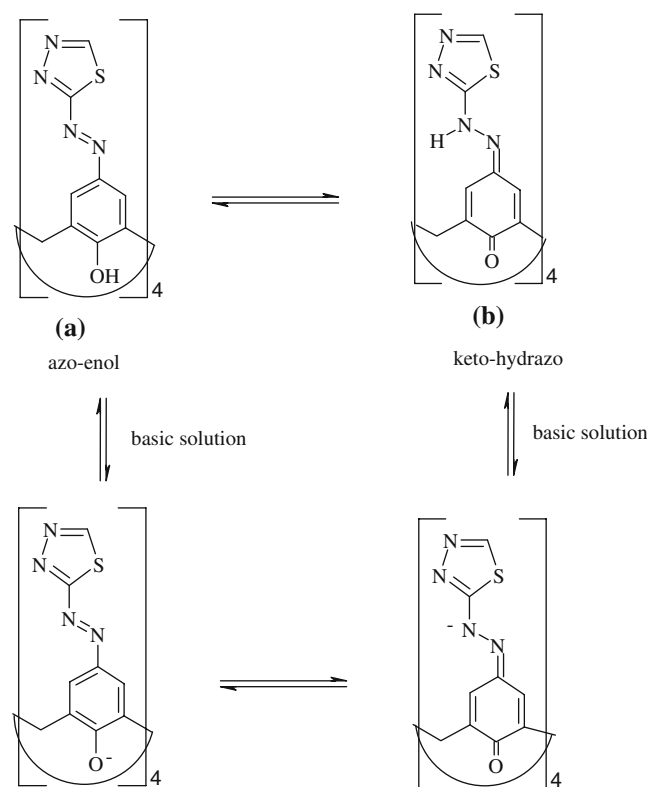


Figure 16. The tautomeric and anionic forms of 4-(thiadiazolyl)calix[4]arene (**23e**).

Complexation of azocalixarenes with metals

The coordination chemistry of the simplest azocalix[n]arene is now relatively well developed as highlighted by a number of recent paper [1]. The vast majority of these metalloazocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligand [66]. By contrast, metal compounds containing the larger ring systems ($n \geq 5$) are still quite rare despite the conformational variations offered by the increased flexibility of the larger number of carboxylic and heterocyclic rings. An additional attractive feature of the later is their ability coordinate more than one metal centre simultaneously [67]. Another study, complexation of diazonium ions with a calixarene-type coupling compound has been also observed by Shinkai *et al.* [68]. In this chapter, we herein review the coordination chemistry for azocalix[n]arene complexes paying particular attention to the degree of “metallation” of both the ring and the conformations adopted.

5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxycalix[4]arene through a diazo-coupling reaction by Ma and his

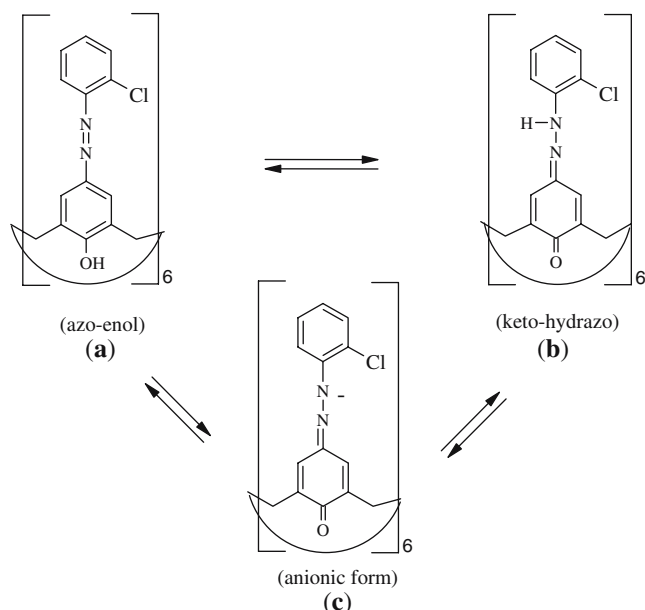


Figure 17. The tautomeric and anionic forms of 4-(2-chlorophenylazo)calix[6]arene (22a).

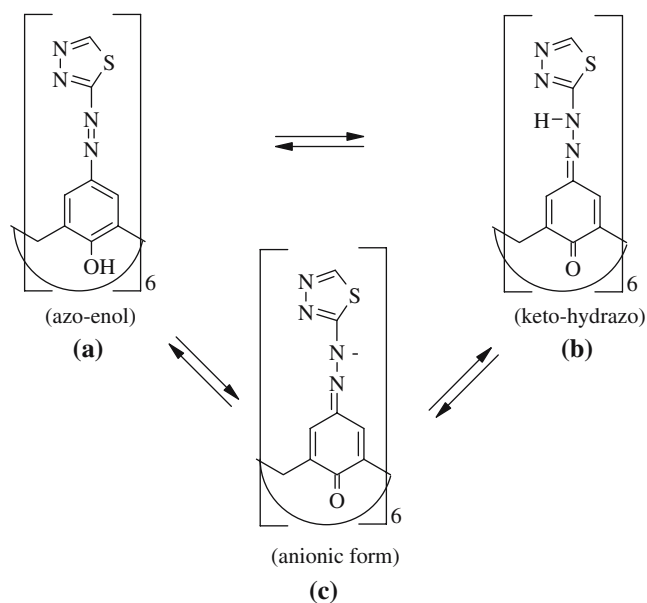


Figure 18. The tautomeric and anionic forms of 4-(thiadiazolylazo)calix[6]arene (24f).

coworkers. Based on that a simple, sensitive and selective spectrophotometric method has been developed for the determination of Ni^{2+} . In basic media, Ni^{2+} formed a 1:1 complex with **27** [69].

The 8-aminoquinoline is chosen as an optical moiety due to the fact that quinolylazo group shows a high selectivity towards Ni^{2+} [70]. The specific skeleton structure of azocalixarene might also play a role in improving analytical properties, one can therefore expect that such a coupling azocalix[4]arene **27** would have a unique property of sensing Ni^{2+} . Their experimental results did show that the reagent exhibits excellent selectivity for Ni^{2+} , and a sensitive and selective spectrophotometric method was developed for the

determination of Ni^{2+} with the help of that selectivity (Figure 19).

Using conductometric and potentiometric techniques, Ma [69] and Lu [71] and their coworkers have made careful studies of complexation of the calixarenes with metal cations, and have provided thermodynamic parameters for these processes.

Generally, the most chromogenic reagents based on the supramolecular calixarene have been prepared by attaching a chromogenic moiety for the optical reading-out to the platform of calixarene. Their ability to recognize and discriminate metal ions is one of the most remarkable features in previous reports, which makes them suitable as specific receptors. Similarly the target reagents, a new water-soluble chromium-selective chromogenic azocalix[4]arene (**28a, b**) (Figure 20) had been gathered from diazo coupling reaction between calix[4]arene and diazonium salts, and they both displayed excellent chromogenic behaviour towards chromium (III). It possesses an absorbance maximum at 365 nm in aqueous environment, but addition of chromium (III) ion induced a weak blue shift to 350 nm, and a new absorption peak at 520 nm (bathochromic shift of 155 nm), exhibited an *isosbestic* point at 470 nm [71].

In our laboratory, an extra survey has been carried out for phenolic azo compounds. These compounds (**29a–c**) which are synthesized by diazo-coupling reaction have been defined as molecular design of

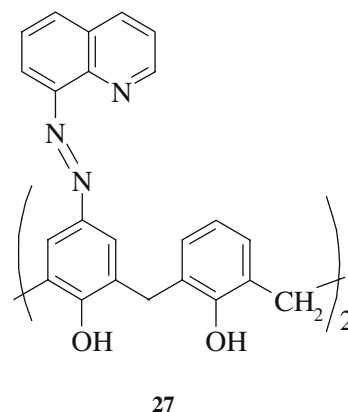


Figure 19. Structure of 5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxycalix[4]arene.

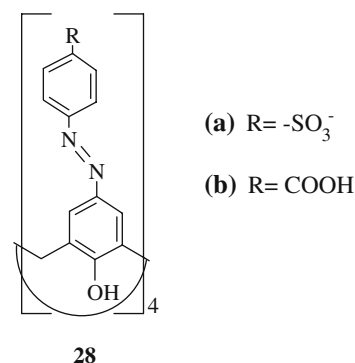


Figure 20. Structure of two water-soluble azocalix[4]arenes.

chromogenic phenolic compounds in the literature [72] (Figure 21).

The azocalix[4]arenes which are synthesized by diazo-coupling reactions have been defined as molecular design of chromogenic phenolic compounds in the literature. The metal–ligand ratio in all complexes is 1:2. The presence of coordinated or lattice water in the Cu(II) and Ni(II) complexes is indicated by the presence of broad bands in the 3420–3430 cm^{-1} region of the IR spectra of these complexes and ascribed to O–H of water. The band in the IR spectra of the Cu(II) and Ni(II) complexes disappear after heating at 100 °C for 6 h. This shows that water molecules are held in the crystal lattice of these complexes.

Consequently, a square-planar structure for the Cu(II) and Ni(II) complexes is proposed as shown in Figure 22.

The electronic spectra of the complexes exhibits intense charge-transfer bands around 409–488 nm, but weak d–d transitions are observed only for the Cu(II) and Ni(II) complexes with **29b** at 542, 521 nm and with **29c** at 568, 551 nm, respectively.

On the other hand, recent research in this field has been synthesized by Deligöz *et al.* [73]. Four azocalix[4]arenes (**30a–d**) have been synthesized from *p*-*tert*-butylphenol, *p*-nitrophenol, *p*-aminobenzoic acid and 1-amino-2-hydroxy-4-naphthalenesulphonic acid by diazo coupling reactions with *p*-aminocalix[4]arene (Figure 23). The resulting ligands are treated as three transition metal salts (e.g., $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). Cu(II), Ni(II) and Co(II) complexes of the azocalix[4]arene derivatives were obtained and characterized. All the complexes have a metal:ligand ratio of 2:1. The Cu(II) and Ni(II) complexes of azocalix[4]arenes are square-planar, while the Co(II) complexes of azocalix[4]arenes are octahedral with water molecules as axial ligands.

The electronic spectra of the complexes exhibits intense charge-transfer bands around 314–394 nm, but weak d–d transitions are observed only for the Cu(II), Ni(II) and Co(II) complexes with **30a** at 538, 527, 529 nm, with **30b** at 550, 417, 407 nm, with **30c** at 438, 606, 608 nm and with **30d** at 450, 517, 603 nm, respectively (Figure 24).

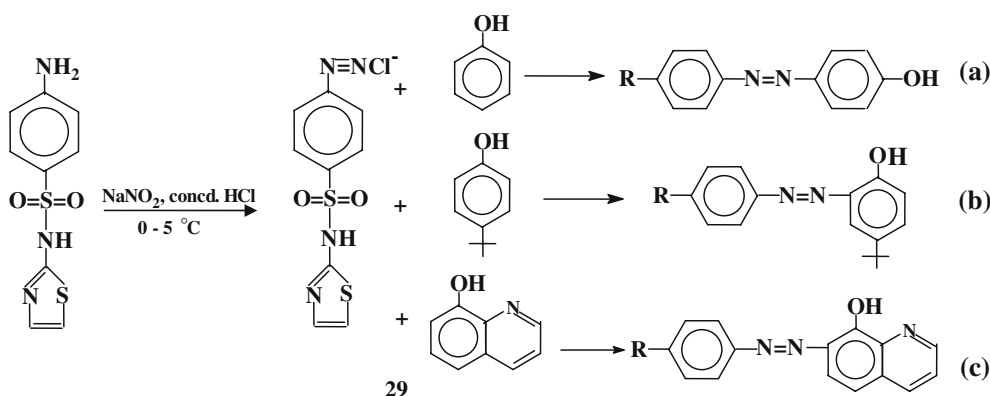


Figure 21. Structure of phenolic azo compounds.

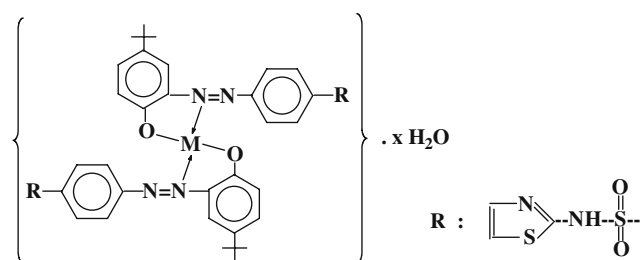


Figure 22. Square-planar structure Cu(II) and Ni(II) Complexes of **29b**. For M = Cu, $x = 2$; for M = Ni, $x = 1$.

Consequently, both a square-planar structure for the Cu(II) and Ni(II) complexes of azocalix[4]arenes and an octahedral structure with water molecules as axial ligands for the Co(II) complexes of azocalix[4]arenes is identified as shown in Figure 25.

The resulting ligands (**30a–d**) are synthesized the chelation between different metal ions (Cu^{2+} , Ni^{2+} and Co^{2+}). In the FT-IR spectra of all these complexes, there are new bands observed in the region 650–420 cm^{-1} , which were absent in the spectrum of the free ligand. The bands observed at 649–603 cm^{-1} (M–O) and 487–425 cm^{-1} (M–N) provided conclusive evidence concerning the bonding of oxygen and nitrogen to the metal ions. Azo groups bands of azocalix[4]arenes exhibits at 1483–1473 cm^{-1} , which disappears on complexations. The appearance of these bands gives the evidence that azo groups were involved in chelation with Cu^{2+} , Ni^{2+} and Co^{2+} . The free **30d** ligand exhibits bands at 3340, 3160, 2970, 1620, 1473, 1186 and 1034 cm^{-1} due to different modes of vibrations of –NH₂ group. On complexations, these bands are also absent.

Extraction of metals with azocalixarenes

The interaction between a host and guest to form a complex can involve one or more of the following features: hydrogen bonding, electrostatic attraction, π – π stacking, van der Waals attraction and charge-transfer interactions. The experimental measure of the collective magnitude of such interactions can be expressed in a variety of ways, including the rate of transport through

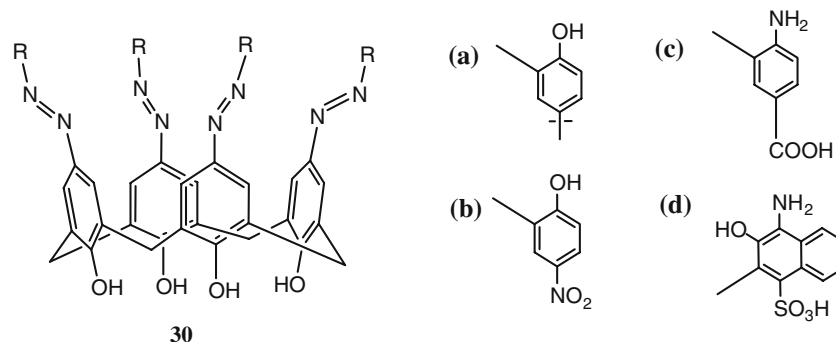


Figure 23. Structures of substituted azocalix[4]arenes.

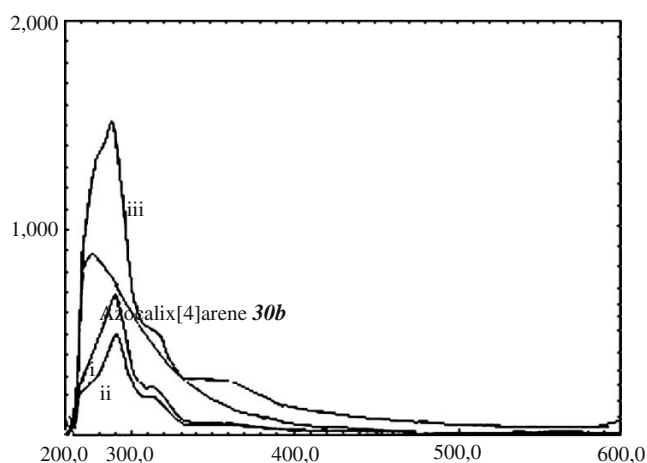


Figure 24. Absorption spectra of azocalix[4]arene **30b** and their complexes in CHCl_3 . [(i) Cu^{2+} , (ii) Ni^{2+} and (iii) Co^{2+}].

a membrane (liquid or supported liquid), stability constants determined by spectroscopy or potentiometry, or the percentage of extraction in phase transfer processes from water into an immiscible solvent. It should be realized, however, that there is not necessarily exact parallelism in the values produced by these various measurements. For example, the rate of transport through a membrane is influenced by features those are not operative in other types of measurements, including

the rate of complexation, the rate of transport within the membrane, and the rate of decomplexation.

The actual acquisition of the data of determining complexation capabilities similarly employs a variety of experimental techniques. In addition to the powerful spectrophotometric methods available, most often NMR and/or UV-vis spectrometry (picrate salts are frequently used in complexation measurements because of the advantage provided by the color of the picrate anion), various other techniques are also being used [1].

Liquid-liquid extraction of transition metal cations

A variety of compounds based upon calixarene having nitrophenylazophenol [74–77], nitrophenol [78], indoaniline [79], indophenol [80], and azophenol [81] functional groups have been successfully designed and exhibited a pronounced chromogenic behaviour towards Na^+ , K^+ , Cs^+ , Ca^{2+} , UO_2^{2+} , and even chiral amines. Shinkai et al. has synthesized calix[4]arene with a 4-(4-nitrophenyl)azophenol unit and three ethyl ester residues on the lower rim and observed the lithium sensitivity of the ionophore. Toth *et al.* also reports the sodium selectivity of related azophenol derivatives [82].

An extensive survey has been pointed out that while extraction behaviour for transition metal ions were also

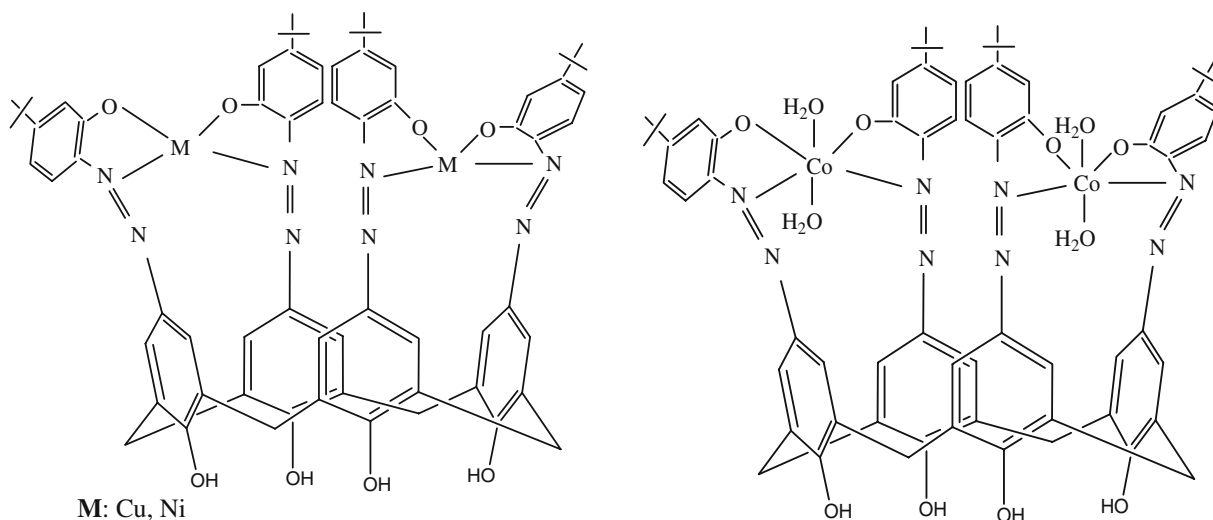


Figure 25. Structures of azocalix[4]arene-metal complexes.

studied for calix[4]arenes. Extraction efficiencies of the azocalix[4]arenes **30a–d** have been carried out by the two-phase solvent extraction of transition metal picrates (Ag^+ , Hg^+ , Hg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+} , Cr^{3+} and La^{3+}) into chloroform under neutral conditions. The results are summarized in Table 1 [73].

From the data in Table 1 it can be seen that, azocalix[4]arenes **30a–c** are very selective for transition metal cations such as Ag^+ , Hg^+ and Hg^{2+} . Those azocalix[4]arenes show higher selectivity toward Hg^+ and Hg^{2+} than the azocalix[4]arene **30d**. The above phenomena can be explained by the (hard–soft) acid–base (HSAB) principle as follows: the azocalix[4]arenes **30a, b** contain electron-donating and electron-withdrawing groups, respectively. Azocalix[4]arene **30a** containing electron-donating groups (*tert*-butyl) is a harder base and prefers the Hg^{2+} cation (91.0%). Azocalix[4]arene **30b** containing electron-withdrawing groups ($-\text{NO}_2$) is a softer base and prefers the Hg^+ cation (68.5%) (Figure 26).

Interestingly, it is observed that azocalix[4]arene **30c** shows remarkable change in the extraction of transition metals, especially in the case of Co^{2+} (23.4%), Zn^{2+} (38.7%) and Cr^{3+} (21.8%) due to the presence of neighbouring $-\text{NH}_2$ group sites in the $-\text{N}=\text{N}-$ groups. The effectiveness of azocalix[4]arene **30c** in transferring transition metals rather than others indicates that, in this case, bridging amine ($-\text{NH}_2$) groups appeared to be operative and play an important role at water–chloroform interphase, since the metal ions could possibly be interacted with these soft ligating sites. This is in agreement with our previous results [34]. The other reason for this high binding ability displayed by azocalix[4]arene **30c** may be due to the preorganization and fine tuning of the cation binding sites in the *lower rim* of calixarene moiety, which is immobilized in *cone* conformation possibly because of such an environment for the complexation of metal cations.

Under the light of our previous experience [34], the metal binding properties of azocalix[4]arenes are investigated and showed high selectivity for Ag^+ , Hg^+ and Hg^{2+} ions, promoting us to elaborate on its structure so that it could be incorporated into different types of azocalix[*n*]arenes. Thus azocalix[4]arenes **30a–d** are diazotized on the $\text{NaNO}_2/\text{H}_2\text{SO}_4$ to yield the azo derivatives. The aim was to synthesize neighbour groups ($-\text{OH}$ and $-\text{NH}_2$) to diazo ($-\text{N}=\text{N}-$), which may help in most of the solvent extraction.

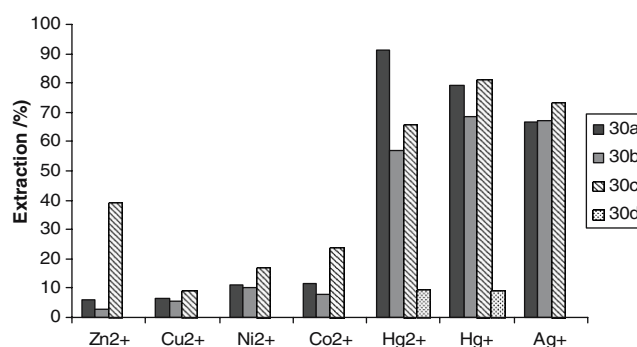


Figure 26. Extraction percentage of the metal picrates with azocalix[4]arenes. Aqueous phase, [metal nitrate] = 10^{-2} M; [picric acid] = 2×10^{-5} M; organic phase, chloroform [ligand] = 1×10^{-3} M; 25 °C for 1 h.

The azocalixarene compounds are effective extractants of towards transition metal cations. In our previous study, we have observed that compounds with phenolic $-\text{OH}$ groups are also effective in the extraction of Fe^{3+} at low pH values. However, this conclusion is not new, and has been previously reported in the literature [47]. Those azocalix[4]arenes, which are very effective in extracting the transition metal cations, particularly Ag^+ , Hg^+ and Hg^{2+} , do not extract the alkali metal cations to any significant extent, as reported by Nomura *et al.* [40], who used *p*-phenylazocalix[6]arene as the ligand.

Deligöz *et al.* [32] have also reported that the selective liquid–liquid extraction of various alkali, alkaline-earth and transition metal cations from the aqueous phase to the organic phase is carried out by using azocalix[4]arenes (**2a–d**) and the phenol derivatives (**31, 32**) (Figure 27). It is found that compounds **2a–d, 31, 32** show some selectivity towards Ag^+ , Hg^+ and Hg^{2+} , while extractability of all cations is observed with compound **2b** containing double diazo groups, unlike their azo compounds.

From the data given in Table 2, it can be seen that compounds with diazo groups are not effective at extracting Na^+ and K^+ ions. This result is derived from using 1A metal cations in the hydroxide form. Sr^{2+} cation exhibits 50.3% extraction by compound **2b** when the metal nitrate is used. Using metal cations in the hydroxide form causes a decline of metal cation extraction for pH values higher than 10. Ludwig [83] has

Table 1. Extractions of metal picrates with ligands^a

Ligands	Picrate salt extracted (%)										
	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}	Al^{3+}	Cr^{3+}	La^{3+}
30a	66.7	79.0	91.0	11.7	10.9	6.5	9.0	6.0	4.0	11.2	6.0
30b	67.0	68.5	57.1	7.7	10.1	5.7	6.9	2.6	1.2	17.8	5.3
30c	73.0	81.2	65.7	23.4	16.7	8.9	11.4	38.7	3.2	21.8	7.9
30d	–	8.6	9.3	–	–	–	–	–	–	–	–

^a $\text{H}_2\text{O}/\text{CHCl}_3 = 10/10$ (v/v): Aqueous phase, [metal nitrate] = 10^{-2} M; [picric acid] = 2×10^{-5} M; organic phase, chloroform [ligand] = 1×10^{-3} M; 25 °C for 1 h.

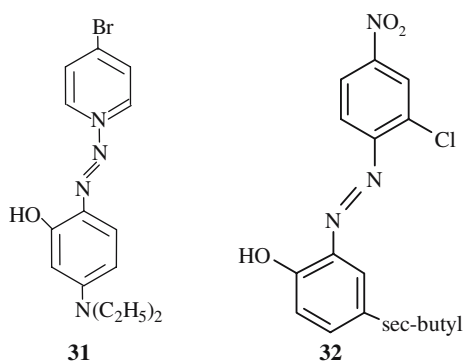


Figure 27. Phenol derivative extractants used in this work.

observed that the solvent extraction of lanthanides is more effective in the 2.0–3.5 pH range.

The compounds **2c** and **2d** show higher selectivity toward Hg^{2+} and Hg^+ than the other compounds do. Diazo group ($-\text{N}=\text{N}-$) is a soft base, hence has stronger affinity towards soft basic metal cations than hard metal cations. The strong participation of the compounds **2c** and **2d** containing electron-donating and electron-withdrawing groups in complex formation was further confirmed by the results shown for extraction experiments. Compound **2c** is a harder base and prefers Hg^{2+} cation, compound **2d** is a softer base and prefers Hg^+ cation.

The fact that all ligands failed to transfer Fe^{3+} ion from aqueous to organic phase which are not unexpected, since this ion prefers to bind with picric acid more than the other ligands. This property is typical for the Fe^{3+} ion only [84]. Yet, our previous observations [85] indicated that, when $\text{Fe}(\text{NO}_3)_3$ was used instead of metal picrate, it was possible to extract Fe^{3+} into the organic phase by utilizing ligands **2a–d**, **31**, **32** in an efficient way.

In a recent study of us [34], comparably lower extractabilities observed with ligands **12–15** were attributed to the formation of strong hydrogen bonds between $-\text{OH}$ and $-\text{N}=\text{N}-$ groups concealing metals for complexation. Little bit higher extractions observed with ligand **12** with respect to ligand **13**. This could support our suggestion because only one possible H-bond could form in ligand while two for **13**. Thus intramolecular H-bonding may be one of the effective

parameters in determining the extraction of metals with diazo group containing ligands.

The compounds **16a, b** have the highest extraction yield with Ag^+ , Hg^+ , Hg^{2+} , Sr^{2+} , Al^{3+} and Cr^{3+} metal cations of all compounds. It is found that compounds **16a, b** show some selectivity towards Ag^+ , Hg^+ , Hg^{2+} , Sr^{2+} . The affinities of metals for ligand **16a, b** in decreasing order is $\text{Hg}^{2+} > \text{Hg}^+ > \text{Ag}^+ > \text{Sr}^{2+}$, and $\text{Hg}^+ = \text{Sr}^{2+} > \text{Al}^{3+} > \text{Hg}^{2+} > \text{Cr}^{3+}$, respectively.

The compounds **16a, b** show higher selectivity toward Hg^{2+} and Hg^+ than the others compounds do. Compound **16a** containing electron-donating group is a harder base and prefers the Hg^{2+} cation. Compound **16b** containing electron-withdrawing group is a softer base and prefers the Hg^+ cation. The hard-base properties of ligands for Hg^+ , Hg^{2+} and Cr^{3+} cations are as follows: for Hg^+ **16b** > **16c** > **16a** > **17** > **16f**, for Hg^{2+} **16a** = **17** = **16c** > **16f** > **16b** and for Cr^{3+} **16f** > **16b**.

Selective extraction of Fe^{3+} cation

The most important contributions in this field are made by our first work [47]. We have embarked on an ambitious program that focuses on the uses to which calixarenes and azocalixarenes can be put. A good example, and one that represents an especially interesting study of cation complexation by calixarenes, deals with the extraction of Fe^{3+} from Cu^{2+} , Ni^{2+} , Co^{2+} and Fe^{3+} analytical mixture. Thus, the extraction of Fe^{3+} from analytical mixture poses a tantalizing challenge, which has been addressed by a number of chemists during the years.

Deligöz *et al.* [86] have theorized that azocalixarenes might be utilized as selective ionophores for Fe^{3+} . Thus, they are studied that Figure 2 illustrates the formulas of the extractants used, **2a–d**, **3**. In order to compare the complexation characteristics of the calix[4]arenes [*p-tert*-butylcalix[4]arene (**34a**), calix[4]arene (**34b**)], the azocalix[4]arenes (**2a–d**, **3**) and two phenol derivatives [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (**31**) (Bromo-PADAP) and 2-hydroxy-5-methylphenylazonaphthol (**33**) (HMPAN)], the solvent extraction of the Fe^{3+} cation with these ligands is carried out in a water/chloroform system at pH 2.2, 3.8, 4.5 and 5.4 (Figure 28).

Table 3 and Figure 27 illustrate the effect of pH and ligand type on the extraction of Fe^{3+} cation. The lower

Table 2. Extraction of metal picrates with ligands

Ligand	Picrate salt extracted (%)														
	Na^+	K^+	Sr^+	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	La^{3+}
2a	5.8	1.7	–	16.9	51.4	60.2	18.2	1.3	–	5.9	7.1	29.3	–	–	–
2b	–	–	50.3	74.6	72.7	58.6	83.3	81.8	78.9	84.0	84.0	79.1	–	44.7	80.0
2c	–	–	–	–	18.8	51.6	18.4	14.9	12.3	15.4	11.2	19.3	–	–	–
2d	–	–	–	31.0	56.8	35.9	14.3	–	1.3	4.3	–	6.9	–	–	–
3	–	–	–	78.7	76.4	78.0	15.5	–	16.6	–	5.0	–	–	–	–
31	–	3.5	6.2	89.1	72.2	84.2	42.6	6.0	77.3	59.6	5.9	11.8	–	14.1	–
32	–	–	–	10.9	16.0	25.6	8.0	–	2.6	4.3	8.1	–	–	7.1	–

extraction recovery of compound **34a** containing electron-donating *tert*-butyl groups than that of compound **34b** lacking this group can be explained by difficulty in removing the *tert*-butyl groups of compound **34a**. Compounds **2a–d** and **3** include both coupled diazo ($-\text{N}=\text{N}-$) groups and calix[4]arene. Due to the positive effect of this group on complex formation, higher extraction yields are observed especially at lower pH values. Compounds **31** and **33** are structurally similar to each other. The higher extraction yields have obtained with compound **33** than with compound **31**, though, because of the presence of two $-\text{OH}$ groups in ortho position. The decrease in extraction yield can be explained by presence of resonance among the three nitrogen atoms in compound **31** thus lowering the electron-donating capacity of diazo groups. It can be concluded that the extraction yields of azocalix[4]arenes are higher with respect to their monomers.

The extraction of Fe^{3+} ions is increased with increasing pH but exhibited a decrease at pH 2.2. The maximum extraction is observed at pH 5.4 for all compounds (64.5–92.4). Extraction recoveries of **34a, b** (lacking nitrogen) were much lower than those of others at pH 2.2. This is presumably due to the fact that diazo groups increase the complexation of Fe^{3+} cations. The extraction yields of the compounds (**2a–d, 3, 31, 33**) containing nitrogen at pH 2.2 are similar to those reported in our previous work [e.g., recovery of *p*-(diethyl amino)methylcalix[4]arene and *p*-nitrocalix[4]arene, 22.0 and 27.1, respectively] [47].

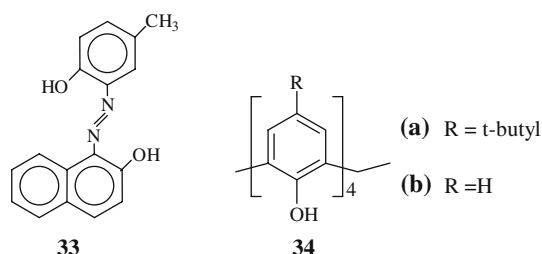


Figure 28. Extractants used in this work.

Table 3. Extraction of Fe^{3+} metal cation with ligands*

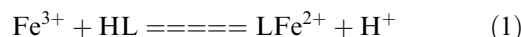
Ligand	pH 2.2	pH 3.8	pH 4.5	pH 5.4
<i>Percent recovery</i>				
34a	7	22.4	46.5	66
34b	8.4	56	57.5	90
2a	21.7	38.8	40.9	76.1
2b	31.1	36.9	41.7	78.6
2c	28.3	31.3	36.9	92.4
2d	22.8	35.9	52.5	77.5
3	22.4	28.9	36.6	66.9
31	28.2	30.4	36.5	56.8
33	34.1	44.6	46	64.5

*Aqueous phase [metal nitrate = 1.06×10^{-4} M]. Organic phase [chloroform (ligand) = 5.3×10^{-4} M]. pH: 2.2 (0.01 M $\text{NaNO}_3/\text{HNO}_3$, $\mu = 0.1$ with KCl), pH: 3.8; 4.5, and 5.4 (0.01 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$, $\mu = 0.1$ with KCl), at 25 °C for 12 h.

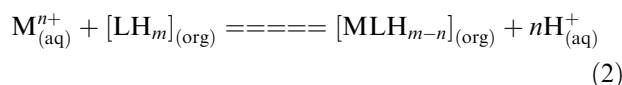
The UV spectra of compound **2c** and Fe^{3+} at the same concentrations (1×10^{-3} M) are taken in DMF individually or together. The formation of a complex is evident when the color of the mixture solution changed from light brown to dark brown and an absorption inflection appeared at 586 nm. The molar ratio of **2c** to Fe^{3+} ion in the complex is determined by the continuous variation plots (Job's Method). The complex has its maximum absorbance at $(\text{FeCl}_3/\text{calix} + \text{FeCl}_3) = 0.50$. The results indicate that **2c** forms a 1:1 complex with Fe^{3+} in solution.

It is concluded that the solvent (DMF) has a very important role in the formation of the complex with Fe^{3+} , since **2c** cannot complex with Fe^{3+} in chloroform. This can be interpreted by the higher Lewis basicity of DMF, completing the octahedral coordination of iron(III) in the complex.

The pH of the 10^{-2} M *p*-(4-acetanilido)calix[4]arene in DMF is 3.95 and the pH of the 10^{-2} M Fe^{3+} in DMF is 2.65. After the complexation, the pH has decreased to 2.48. The decrease in pH is due to the H^+ liberated (Equation 1), after the complex is formed between **2c** and Fe^{3+} in DMF.



The extraction reaction of the present system can be expressed by Equation (2),



(where aq and org denote the species in the aqueous and the organic phase, respectively).

$$D = [\text{MLH}_{m-n}]_{(\text{org})} / [\text{M}^{n+}]_{\text{aq}} \quad (3)$$

The extraction equilibrium constant (K_{ex}) is given by,

$$K_{\text{ex}} = \frac{[\text{MLH}_{m-n}]_{(\text{org})} \cdot [\text{H}^+]_{(\text{aq})}^n}{[\text{M}^{n+}]_{(\text{aq})} \cdot [\text{LH}_m]_{\text{org}}} \quad (4)$$

$$\log D = n\text{pH} + \log K_{\text{ex}} + \log [\text{LH}_m]_{\text{org}} \quad (5)$$

Equation (5) indicates that the slope n for the $\log D$ versus pH plot corresponds to the number of protons released upon extraction.

Figure 29 shows the pH versus $\log D$ plot of compound **2c** resulting in a slope of 0.89. The deviation from linearity observed especially at low pH values may be due to the different complexing effects of the side groups, e.g., $\text{H}_3\text{C}-\text{CO}-\text{NH}_2-$, $-\text{N}=\text{N}-$, resulting in different stoichiometries. The results indicate that in the two-phase solvent extraction with **2c** the dissociation of one proton (i.e., an exchange between Fe^{3+} and Na^+ or H^+) takes place at water–chloroform interface [43, 45, 49]. The logarithmic extraction constant, $\log K_{\text{ex}}$, for the Fe(III)-compound **2c** complex corresponding to Equation (5) is found to be

$$\log K_{\text{ex}} = 1.74 \pm 0.15$$

The solvent extraction processes with **30a**, **b**, **2a–d**, **3**, **31**, **33** are similar. In our recent work [43], it was shown that the solvent extraction mechanism is the same when calixarenes was used, containing different functional groups. The solvent extraction mechanism with the calixarenes and the phenols are shown in Figure 30.

In conclusion, the new diazo coupling calix[4]arene compounds can be successfully used for the extraction of the Fe^{3+} cation. The percent recovery of Fe^{3+} is increased with increasing pH, and the highest recovery of Fe^{3+} is observed at pH 5.4 within the range studied for all the ligands.

Absorption properties of azocalixarenes

The construction of ion selective molecular sensors continues to attract attention due to potential applications and as a testing ground for molecular recognition and signal transduction schemes. Progress in the field has been reviewed in recent years [87, 88]. In conjugated donor–acceptor chromophores or fluorophores (internal charge transfer–ICT sensors), if the receptor is a part of the donor moiety, cation binding induces a blue-shift (hypsochromic effect) with a decrease in the extinction coefficient (anti-auxochromic effect); however, if the acceptor group is part of the receptor then there is a red-shift (bathochromic effect) with an increase in extinction coefficient results (auxo-chromic effect) on cation binding [89].

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fiber, the coloring of different materials, coloured plastics, biological-medical studies and ad-

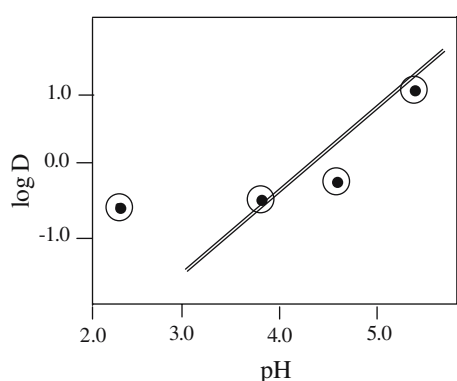


Figure 29. Relation between pH and Log D for **2c**.

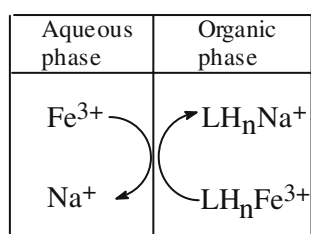


Figure 30. Extraction mechanism proposed for **2c**.

vanced applications in organic synthesis. Many patents and publications describe the synthesis and dyeing properties of azo compounds [90–93].

Azo compounds are an important class of organic colorants and consist of at least a conjugated chromophore azo ($-\text{N}=\text{N}-$) group and two or more aromatic rings. The coloring properties of organic dyes depend on both the presence of the chromophore groups and the crystallographic arrangement of molecules in the solid state [27].

Solvent effects

The absorption spectra of azocalix[4]arenes **21a–l** are recorded in various solvents at a concentration of $\sim 10^{-6}$ to 10^{-8} M. The visible absorption spectra of the compounds are found to exhibit strong solvent dependency, which do not show regular variation with the polarity of the solvents [62].

Strong evidence for the existence of these compounds in an equilibrium is provided by the isosbestic points in the visible spectra of compound **21j** in different solvents (Figure 31). This equilibrium may exist between tautomeric forms. The equilibrium depends on the basicity of the solvents used.

The λ_{max} of the compounds has showed large bathochromic shifts when a small amount of piperidine is added to each of the compound solutions in chloroform, DMSO or DMF; a typical example is shown in Figure 32. The λ_{max} of the compounds in methanol also show bathochromic shifts when 0.1 M KOH is added. These findings indicate that compounds **21a–l** exist in the anion form in chloroform + piperidine, DMSO + piperidine, DMF + piperidine and methanol + KOH.

The effect of concentration of the compound on absorption maxima is examined. The λ_{max} of all compounds do not change with compound concentration which also indicates that azocalix[4]arenes exist in their tautomeric form in all solvents used.

Absorption spectra of hetarylazocalix[4]arene dyes **23a–f** are measured in various solvents at a concentration of $\sim 10^{-6}$ – 10^{-8} M. They are run at different concentrations. The pH value of all solutions is in the range between acidic and basic. The choice of solvent is based on their polarity. The visible absorption spectra of the dyes are found to exhibit a strong solvent dependency which do not show regular variation with the polarity of solvents [64].

This equilibrium may exist between tautomeric forms. But, compound **23a** shows three absorption peaks in DMF and compound **23e** shows three absorption peaks in chloroform + piperidine. The equilibrium of compound **23a** in DMF and compound **23e** in chloroform + piperidine may exist between tautomeric forms and anionic forms (Figure 16). Absorption peaks at the longest wavelength of compound **23a** and compound **23e** may a peak of anionic forms. This indicates that compound **23a** dissociates in DMF and compound **23e** dissociates in chloroform + piperidine. The

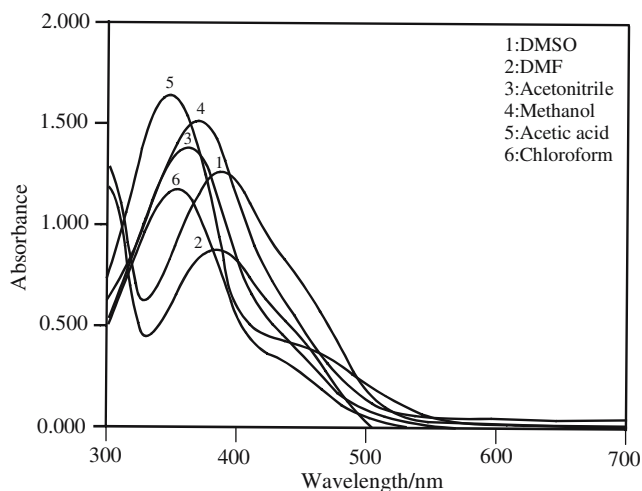


Figure 31. Absorption spectra of azocalixarene **21j** in various solvents.

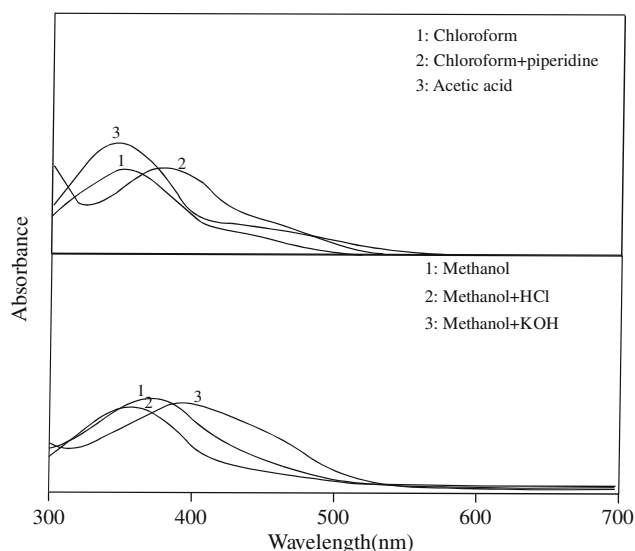


Figure 32. Absorption spectra of azocalixarene **21j** in acidic and basic solutions.

equilibrium depends on the basicity of the solvent used. In proton accepting solvents such as DMSO, DMF, chloroform + piperidine, acetonitrile and methanol, displayed a red shift of the λ_{\max} respect to the absorption spectra in acetic acid.

Heterocyclic-based azo dyes tends to show larger solvatochromic effects than azobenzenes because of the increased polarity of the dye system, especially of the excited state. Similar effects for dyes containing a benzothiazolyl, thiazolyl thienyl moieties have been reported for some derivatives of *N*- β -cyanoethyl-*N*- β -hydroxyethyl aniline [94].

Substituent effects

As it is appeared in our recent paper [62], the incorporation of electron-withdrawing nitro and chloro groups and electron-donating methoxy and methyl (*p*-) groups to the benzene rings led to bathochromic shifts in all solvents. However the introduction of electron-donating

methyl (*o*-, *m*-) groups to the benzene rings gave hypsochromic shifts in DMSO and DMF but produced bathochromic shifts in acetonitrile, methanol, acetic acid and chloroform. The introduction of nitro groups to the benzene rings imparted the greatest bathochromic shift of all groups. The position of all groups do not show a regular variation in all solvents.

The azocalix[4]arene derived from chloro- and nitro-anilines containing electron-withdrawing chloro- and nitro- groups and the azocalix[4]arenes (**21a–l**) do not give uniform bathochromic shifts of about 9–48 nm relative to the corresponding the azocalix[4]arene derivatives from methyl- and methoxy-anilines containing one electron-donating methyl- and methoxy-groups. Thus azocalix[4]arenes **21a** and **21c** with an *o*- and *p*-chloro substituent in the diazo component, absorbed at 407 and 415 nm. When the chloro group was in the *m*-position (**21b**), the absorption shifted to 386 nm in DMSO.

Azocalixarenes generally shows two absorption bands in the region 300–700 nm. The relatively small difference in the λ_{\max} may be related to the polarity change of the absorbing system caused by solvent interactions due to the general solvent effect. However, azocalixarenes show three absorption bands in DMSO and chloroform + piperidine, respectively. These results indicate that azocalixarenes are found as states of common anions forms in DMSO and chloroform + piperidine, respectively. Similar effects are apparent in substituted phenylazocalix[6]arenes.

The introduction of electron-donating thiol group into the thiadiazole ring resulted in bathochromic shifts in DMF, chloroform + piperidine, acetic acid, acetonitrile and methanol (for azocalixarene **21f** $\Delta\lambda = 29$ nm relative to azocalixarene **21e** for spectra in DMF).

Thermal behaviours of azocalixarenes

Thermogravimetric analysis is a valuable tool for the analysis of inclusion compounds of calixarenes, providing also a comprehensive method to analyze trends of molecular forces involved in the complexation, quantitatively. The azocalix[*n*]arene molecular complexes form small molecules with a variable stoichiometry in solid state. The increase of temperature promotes a reverse acid base reaction, with the loss of small molecule of the solid, and the temperature of leaving of the small molecule decreases for longest chain small molecules.

Thermal behaviours of two parents calix[4]arene (**3a**, **b**) and three azocalix[4]arene derivatives (**2a**, **b**, **d**) containing upper rim functionalized groups such as *n*-butyl, phenylazo and heterocyclic thiazol are investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG). The thermal decomposition points and the amounts of volatile pyrolysis products were determined in nitrogen and air atmosphere using TG, DTA and DTG curves. In the present study, the thermal analysis

of azocalix[4]arenes demonstrated that the stability of the calix[4]arene depends on substituted groups and their position in the calix[4]arene structure [35].

The TG and DTA curves of parent calix[4]arenes (**34a**, **b**) and azocalix[4]arenes (**2a**, **b**, **d**) in flowing nitrogen and air atmosphere are illustrated in Figures 33–36. The amount of volatile pyrolysis products for calix[4]arenes and the thermoanalytical results obtained from TG, DTA curves.

The thermal analysis curves for the different samples (parent calix[4]arenes and azocalix[4]arenes) do not show any marked differences of similar experimental conditions but indicated that the samples are not simply calix[4]arene.

The effect of the degradation, due to the oxidation process, on the thermal stability of complex has been revealed with the shift of the derivative curve maximum to lower temperature, in comparison with the one of parent calix[*n*]arene. Decomposition of these compounds have three steps. Firstly, H₂O was released from the lattice compounds. The first peak was occurred endothermic. This step is assigned to the decomposition of complex and it shifts to higher temperature in comparison with parent calix[*n*]arene. Secondly, DMF was released from the lattice compounds and this step was occurred endothermic too; in order to confirm this result, the complexes have been analysed by TGA analysis. In DTG curve the decomposition of complex is evident at about 420 °C. Lastly, the biggest decomposition were occurred. For complexes residues products are Fe₂O₃ but ligands did not any residue product, all of them decomposed. For complexes this step was occurred

exothermic due to calix[4]arene·Fe which is intermediate product is not stable [95].

From the TG–DTA curves of complex **34a**, it was found that it closes two DMF molecules (17.2%) in the range 132–279 °C, accompanied by a weak endothermic reaction; it then begins to decompose. In the decomposition process, a strong exothermic peak was seen at 285–554 °C. In the case of complex **34b**, dehydration occurred between 48 and 114 °C and two DMF molecules (22.0%) were lost in the range 118–270 °C. The decomposition process ends at 588.8 °C.

Thermal analysis results, suggest that the mechanism of decomposition of [calix[*n*]arene·Fe·2(DMF)]·H₂O occur in several steps before reaching stable intermediate species. Therefore, the mechanism of decomposition of the iron(III) complex can be proposed to occur as follows: the first stage is the formation of [calix[*n*]arene·Fe·*n*(DMF)] by the loss of H₂O groups, followed by complete loss of DMF, to form the intermediate [calix[*n*]arene·Fe]. Finally the formation of iron(III) oxide is reached by the elimination of calix[*n*]arene. The suggested mechanism for the thermal pyrolysis of calix[*n*]arene·Fe·2(DMF) complex can therefore be represented as follows:

For **34a** and **34b**:

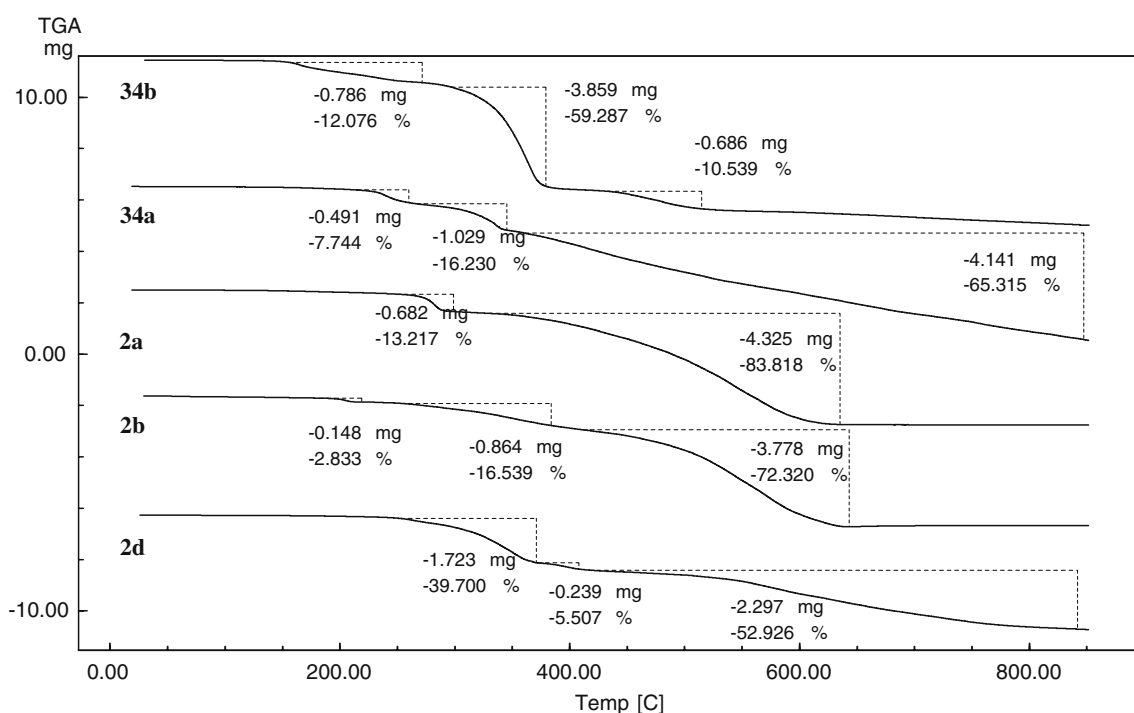
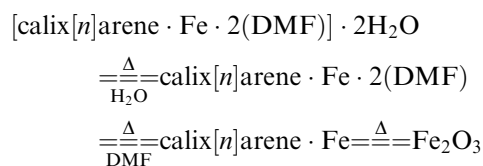


Figure 33. The TG curves of calix[4]arenes (**34a**, **b**) and azocalixarenes (**2a**, **b**, **d**) in air atmosphere.

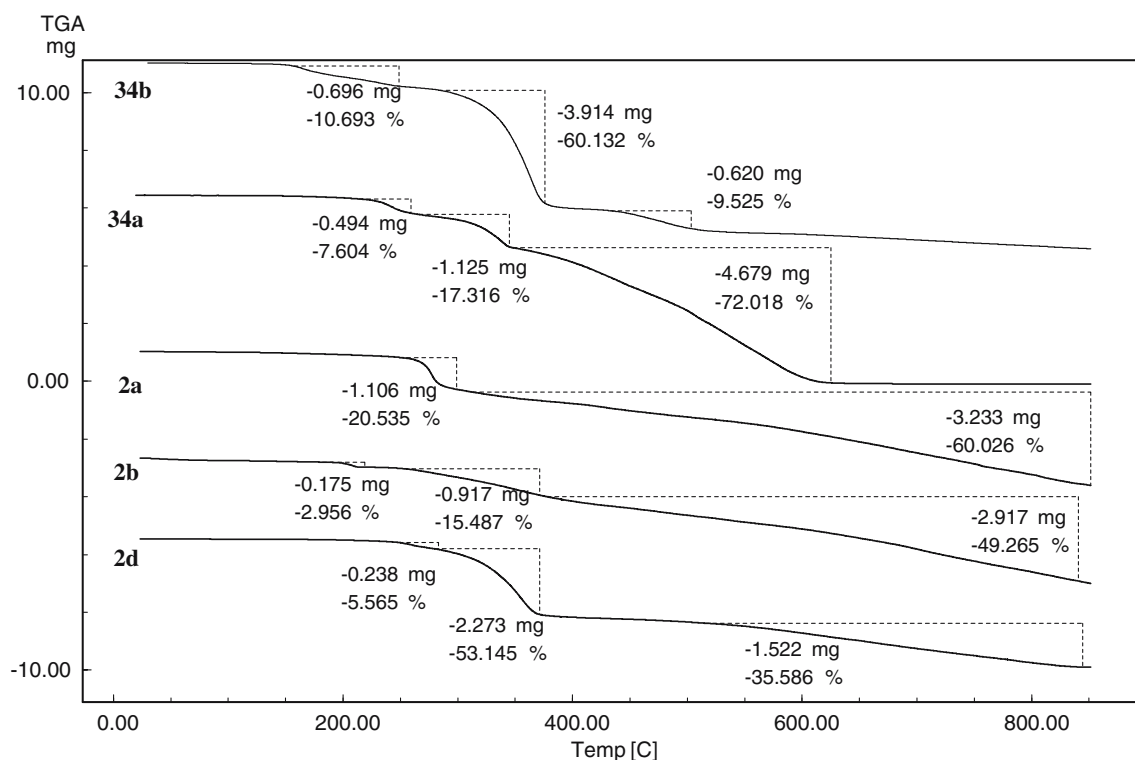


Figure 34. The TG curves of calix[4]arenes (**34a, b**) and azocalixarenes (**2a, b, d**) in N₂ atmosphere.

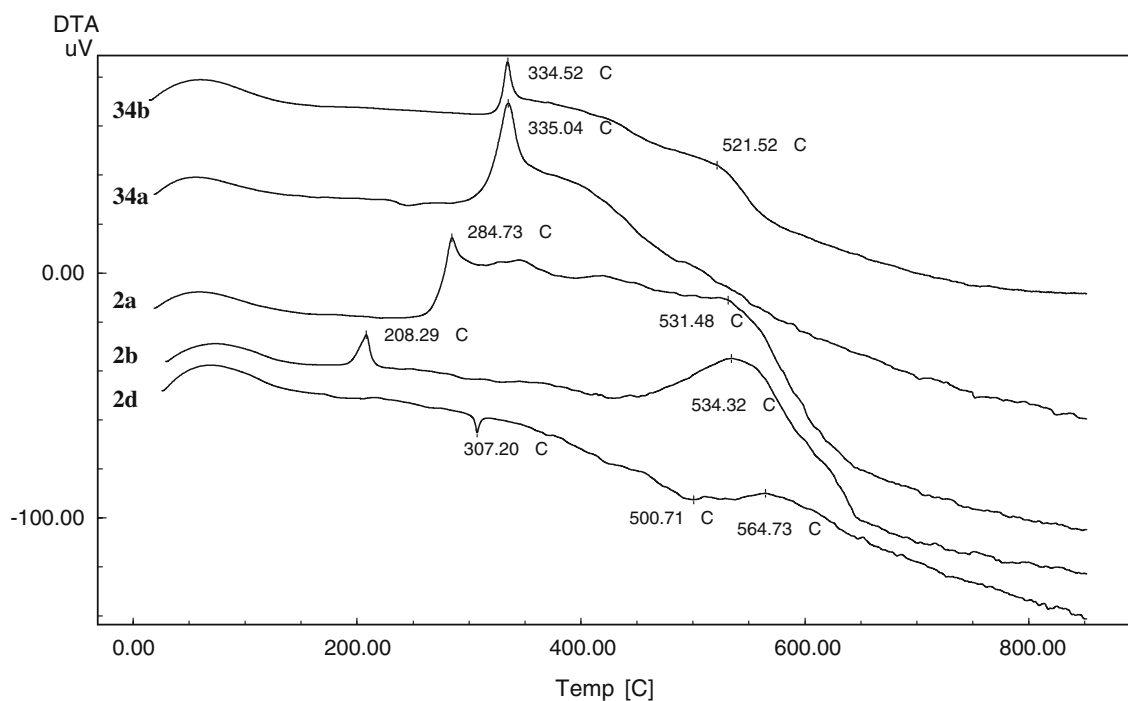


Figure 35. The DTA curves of calix[4]arenes (**34a, b**) and azocalixarenes (**2a, b, d**) in air atmosphere.

Conclusions

Diazo-coupling reactions are given in introduction as a general procedure [52]. This pathway is the most convenient one to give the best yield of azocalixarene compounds. We have studied the azo-coupling reactions of calix[*n*]arene with benzenediazonium chloride, *o*-, *m*-,

p-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-toluidine, *m*-, *p*-anisidine and aniline. Calixarene-based receptors with hydrogen-bonding groups immersed in a large cavity have been synthesized. The synthesis of all of the diazo-coupled compounds is achieved using the method of Morita [37]. These reactions produce the corresponding azocalixarenes in good yield.

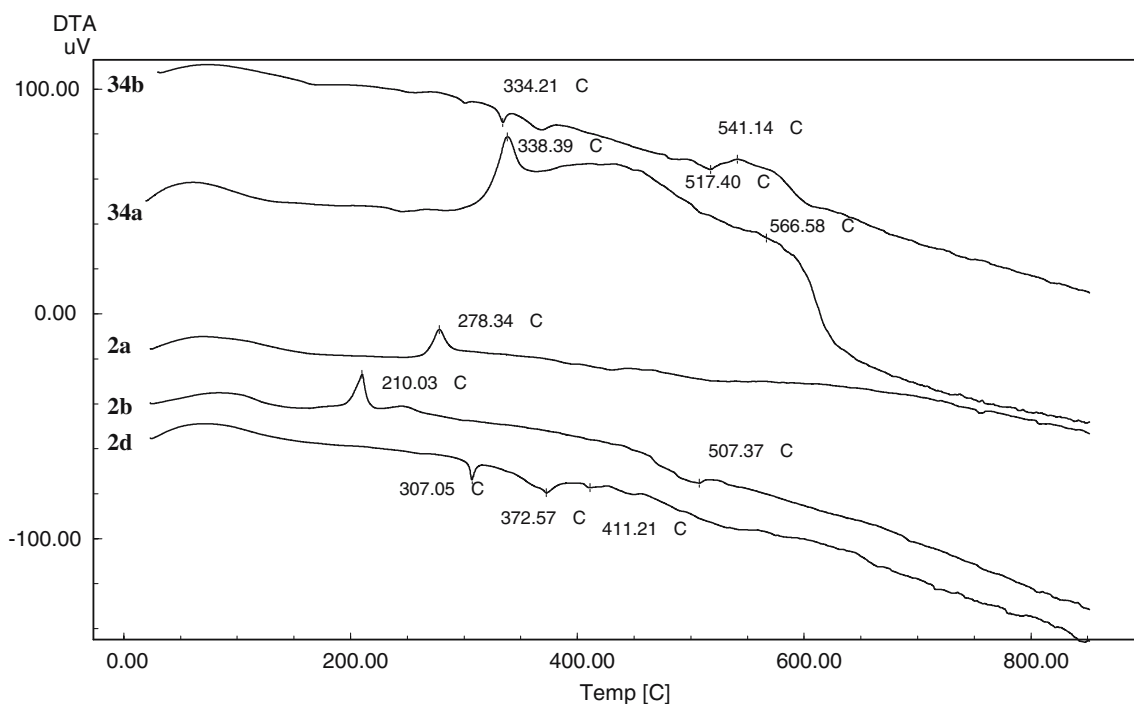


Figure 36. The DTA curves of calix[4]arenes (34a, b) and azocalixarenes (2a, b, d) in N_2 atmosphere.

The present review article reports on the synthesis, characterization, complexation, extraction, thermal behaviour and absorption spectra of a series of azocalix[n]arene. It was shown that bathochromic and hypsochromic effects produced are dependent on the *o*-, *m*-, *p*-substituted aniline derivatives of azocalix[6]arene. The effect of varying pH and solvent upon absorption ability of azocalixarenes substituted with electron-donating and electron-withdrawing groups at their *o*-, *m*-, *p*-positions is observed.

The *o*-, *m*-, *p*-substituted groups dissociate progressively in solution with increasing pH, forming azo-enol form and keto-hydrazo form species, with characteristic changes in the visible absorption spectra. The azocalix[4]arene derived from calix[4]arene and substituted aniline shows a pronounced color change from chloro-, nitro-, methyl- and methoxy- to an orange in dry $CHCl_3$ on addition of up to 0.5% water, due to the formation of the mono-anion, and can be used as analytical indicators for detecting low levels of water in solvents. Both neutral and mono-anionic forms of azocalix[n]arene derivatives are non-fluorescent, and they can be used as pH indicators.

Further study on the complexation properties of these new azocalixarenes is currently proceeding and will be presented in full in due course. It was shown that the mechanism of complexation is based on the interaction between metal cations and azo-groups. It is important to note that the conformation of the calix[n]arenes, and the cooperativity and allosteric effects of the functionalities play important roles in two-phase extraction systems. The variety of hydrogen bonding motifs that occur in the studied calix[n]arene derivatives may have considerable importance for the future design

of novel calix[n]arene based receptors, carriers or supramolecular structures. Azocalix[n]arenes can be excellent dyes for textile fiber.

In summary, the synthesis and complexation ability of azocalix[4]arenes based on neighbour receptors is studied. The spectroscopic results of all azocalix[4]arenes reveals that these compounds do exist in *cone* conformation. The complexation studies showed that azocalix[n]arenes are excellent receptors for Ag^+ , Hg^+ and Hg^{2+} metal cations. Based on the above results, we conclude that ligand groups circularly arranged on the *upper rim* of the calix[n]arene cavity construct, which is a novel cyclic metal receptor for selective extraction of transition metal cations.

It has been suggested that, by the introduction of appropriate functions and/or bridges or by choosing a particular conformation, the calixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, electrochemical transductions, conventional ion-selective electrodes (ISE), and solid-state sensors (ISFETs).

In contrast, the azo groups of these compounds are interesting because they act as microcontact printing sites as well as chromophores. The resistance to heat at elevated temperatures is one of the main properties required for azocalix[4]arene. Because it is used in high temperature processes such as the dyeing of textile fibers, ink-jet printing and photocopying and in high technology areas lasers and electro-optical devices. We are currently working on these azo group-containing calix[4]arene derivatives.

Conclusively, the specific feature of azocalixarenes arises from the presence of nitrogen atoms and side arms. Making further sophisticated molecules, metal

ligating system, chiral molecules, etc. will start from the manipulation of the side arms.

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