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### Ester and Ketone Groups Substituted Mono- and Di- Azo-coupled Azocalix[4]arenes as Extractant for Hg<sup>+</sup> and Hg<sup>2+</sup>, or Cr<sup>3+</sup>Cations

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# Ester and Ketone Groups Substituted Mono- and Di-Azo-coupled Azocalix[4]arenes as Extractant for Hg<sup>+</sup> and Hg<sup>2+</sup>, or Cr<sup>3+</sup> Cations

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This article describes extraction properties of *mono-* (**A1–A8**) and *di-* (**B1–B8**) substituted azocalix[4]arene analogues. The ionophore solvent extractions of alkaline-earth (Sr<sup>2+</sup>), basic metal (Pb<sup>2+</sup>) and transition metal cations (Ag<sup>+</sup>, Hg<sup>+</sup>, Hg<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>) from aqueous phase to organic phase were carried out by azocalix[4]arene derivatives. It has been observed that they show a good extraction behavior toward selected heavy metal (Hg) and toxic metal (Cr), while **A4** and **B4** prefer Hg<sup>+</sup>, Hg<sup>2+</sup> and Cr<sup>3+</sup> among transition metal cations, respectively. The azocalix[4]arenes (**A1–A8**) and (**B1–B8**) are not efficient extractants for all of the selected metal cations, whereas **A4** and **B4** are selective only for Hg metal cation.

**Keywords:** Calix[n]arene, azocalix[4]arenes, solvent extraction, metal cations, mercury, chromium

## 1 Introduction

Calixarene family is one of the most important molecular building platforms in host-guest chemistry (1). Potential applications of azocalix(n)arene, a new member of the calix(n)arene family are based on replacing traditional methyl bridges with azo groups (2). Up to now, some of diazo coupling calixarenes, such as azocalix(n)arenes, and their binding properties were studied by Chawla (3), Kim (4), Renault (5) and Lu (6), etc.

Calix[4]arene derivatives with a linkage in *mono-* and *di-* position, which are consist of double and triple calixarenes with various connecting chains have been reported (7). The interesting properties shown by these cyclic oligomeric molecules stimulated the exploitation of useful methods towards their incorporation into polymeric matrices, which are important for the development of ion selective electrodes and membranes, chemical and biochemical sensors and selective extraction of ions and neutral molecules (8,9).

Various studies have been carried out to synthesize new complexants for charged and neutral molecules. Among

all kinds of azocalix[n]arene derivatives, substituted azocalix[4]arenes play a much more important role with respect to unsubstituted azocalix[4]arenes. Because they do not inhibit the flexibility of azocalix[4]arene conformation whereas unsubstituted ones do contrarily (10).

During the past decades, scientists have tried to insert several groups on calix[n]arene skeleton(s) to combine the unique properties of both species in one molecule. Thus, parent calix[n]arenes and their substituted derivatives are combined through the bridging of phenolic oxygen atoms of the calixarene moiety by functional groups. The design of macromolecules with high ionic affinities is important for numerous applications in chromatography, catalysis and separation studies (11,12). Immobilization of ion selective ligands to form azocalixarene reagents results in an extended set of applications ((13,14).

Previously, our group has synthesized functionalized calix[n]arene derivatives and their selective extraction of transition metals (15–19). In the course of synthesis studies of new chromogenic azocalix[4]arene derivatives containing phenolic neighboring groups at *lower rim* (20), we have extended our research into transition metal cations.

Conformational flexibilities of azo groups of calix[4]arene and those of azocalix[4]arene derivatives (ester and ketone) are compared. In this study, we have investigated binding properties of a series of novel azocalix[4]arenes by using *mono-* and *di-* azo-coupling derivatives as building blocks in details.

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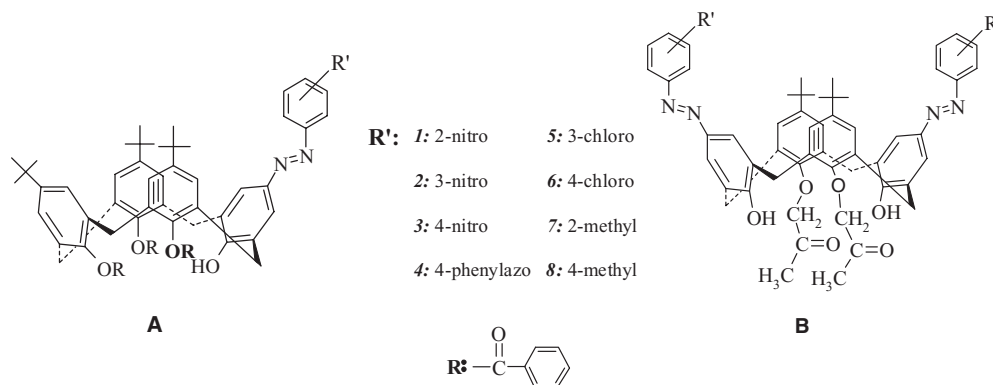


Fig. 1. Extractants used in this work.

## 2 Experimental

### 2.1 Chemicals and Reagents

Figure 1 illustrates the formulae (**A1–A8**) and (**B1–B8**). 25,26,27-Tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(2-nitrophenylazo)calix[4]arene (**A1**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(3-nitrophenylazo)calix[4]arene (**A2**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(4-nitrophenylazo)calix[4]arene (**A3**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(4-phenylazo-phenylazo)calix[4]arene (**A4**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(3-chlorophenylazo)calix[4]arene (**A5**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(4-chlorophenylazo)calix[4]arene (**A6**), 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(2-methylphenylazo)calix[4]arene (**A7**) and 25,26,27-tribenzoyloxy-28-hydroxy-5,11,17-tri(*tert*-butyl)-23-(4-methylphenylazo)calix[4]arene (**A8**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(2-nitrophenylazo)calix[4]arene (**B1**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(3-nitrophenylazo)calix[4]arene (**B2**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(4-nitrophenylazo)calix[4]arene (**B3**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(4-phenylazophenylazo)calix[4]arene (**B4**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(3-chlorophenylazo)calix[4]arene (**B5**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(4-chlorophenylazo)calix[4]arene (**B6**), 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(2-methylphenylazo)calix[4]arene (**B7**) and 25,27-diacetonyloxy-26,28-dihydroxy-11,23-di(*tert*-butyl)-5,17-(4-methylphenylazo)calix[4]arene (**B8**) were synthesized according to the method described previously (21,22).

All of the chemical reagents used were of analytical grade purity and used without further purification. Some of the solvents used in crystallization were retained in the analytical samples, best fits between the analytical values and appropriate fractional increments of solvents were used.

All aqueous solutions were prepared with deionized water purified by a Human Power I Plus I+UV water purification system.

### 2.2 Apparatus

Melting points of the substances have been identified by using Electrothermal IA9100 digital melting point apparatus and they are noted without correction. UV-Vis spectral data are obtained by a Shimadzu 1601 UV-Visible recording spectrophotometer.

### 2.3 Solvent Extraction

A solution (10 mL) of ligand ( $1 \times 10^{-3}$  M) in chloroform and an aqueous solution (10 mL) containing  $2 \times 10^{-5}$  M picric acid and  $1 \times 10^{-2}$  M metal nitrate were shaken at 25°C for an hour. An aliquot of the aqueous solution withdrawn, and its UV spectrum was recorded. A similar extraction was performed in the absence of picrate ion in the aqueous solution. The extractability of the metal cations is expressed by means of the following equation:

$$\text{Extractability (\%)} = [(A_0 - A)/A_0] \times 100$$

where A and  $A_0$  are the absorbencies with and without ligand, respectively.

## 3 Results and Discussion

The binding ability of the azocalix[4]arenes depends on their macrocyclic ring sizes, conformations and the nature of the functional groups attached (1). All sixteen novel compounds which are prepared for extraction have taken *cone* conformation in solution. Azocalix[4]arenes **A1–A8** and **B1–B8** are synthesized with the methods used in our previous studies (21, 22). Their diazo couplings of benzoyl and methyl ketone are carried out according to published methods (23, 24).

Azocalix[4]arene with a linkage in *mono*- and *di*- position, and calix[4]arene derivatives with double methyl ketone and triple benzoyl ester calix[4]arenes with various connecting chains have been previously reported (21, 22). An alternative strategy has been developed for the synthesis of azocalix[4]arenes in which the distal position on the *lower rim* of calix[4]arenes were coupled with 1,3-diketone derivatives. The complexation properties of these molecules appear to be highly dependent on the nature, number of donor groups, and the conformation of the calix[4]arene moiety. The interesting properties shown by these cyclic oligomeric molecules stimulated the exploitation of useful methods towards their incorporation into azocalix[4]arenes, which may be interesting for the development of ion selective electrodes and membranes, chemical and biochemical sensors and selective extraction of ions and neutral molecules. Previously, to increase the affinity of azocalix[4]arenes toward metal ions and anions, two main strategies have been followed. Firstly, different ionophoric groups including esters and ketones have been incorporated onto the calixplatform. Secondly, the azocalix[4]arene units have been fixed in ester and ketonic groups.

An investigation of the ionic recognition properties of synthesized chromoionophores with alkaline-earth ( $\text{Sr}^{2+}$ ), basic metal ( $\text{Pb}^{2+}$ ) and transition metal cations ( $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ) was also conducted, but surprisingly, significant interaction has not been observed due to the fact that azo groups ( $-\text{N}=\text{N}-$ ) containing molecular receptors should be expected to exhibit pronounced changes on interaction with transition metal ions.

The present study is focused on identifying the strategic requirements for the estimation of ionophoric properties of the *upper rim* functionalized azocalix[4]arene derivatives **A1–A8** and **B1–B8** toward selected alkaline-earth, basic and transition metal ions such as  $\text{Sr}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$ . The extraction properties of azocalix[4]arene derivatives **A1–A8** and **B1–B8** have

**Table 1.** Extraction of metal picrates with *Mono*-Azocalix[4]arenes<sup>a</sup>

Ligand	Picrate Salt Extracted (%)								
	$\text{Sr}^{2+}$	$\text{Ag}^+$	$\text{Hg}^+$	$\text{Hg}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Cr}^{3+}$
<b>A1</b>	—	—	15.3	6.3	—	—	—	—	6.0
<b>A2</b>	—	—	14.3	12.3	—	—	—	1.2	7.3
<b>A3</b>	—	—	11.3	6.9	—	—	—	—	5.8
<b>A4</b>	—	8.5	47.8	43.1	—	—	—	3.0	19.0
<b>A5</b>	0.9	2.0	18.9	16.4	1.5	4.4	2.8	1.7	5.0
<b>A6</b>	—	—	18.6	11.7	—	—	—	0.3	6.3
<b>A7</b>	1.8	2.0	20.1	16.0	1.2	4.4	2.8	1.5	4.8
<b>A8</b>	1.2	1.8	19.0	15.6	1.5	4.4	2.8	0.9	5.8

<sup>a</sup> $\text{H}_2\text{O}/\text{CHCl}_3 = 10/10$  mL (v/v); [picric acid] =  $2 \times 10^{-5}$  M, [ligand] =  $1 \times 10^{-3}$  M, [metal nitrate] =  $1 \times 10^{-2}$  M; 298 K, 1 h contact time.  $\alpha \leq \pm 2\%$ .

**Table 2.** Extraction of metal picrates with *Di*-Azocalix[4]arenes<sup>a</sup>

Ligand	Picrate Salt Extracted (%)								
	$\text{Sr}^{2+}$	$\text{Ag}^+$	$\text{Hg}^+$	$\text{Hg}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Cr}^{3+}$
<b>B1</b>	—	2.3	22.8	22.0	3.0	4.2	1.0	5.7	11.4
<b>B2</b>	4.0	—	28.0	22.0	2.7	3.6	—	6.7	8.7
<b>B3</b>	—	—	15.6	15.3	0.3	0.6	—	5.4	7.0
<b>B4</b>	1.0	28.0	89.6	89.0	4.0	5.5	12.8	17.0	66.0
<b>B5</b>	2.3	3.6	27.0	23.0	4.6	5.8	—	8.0	8.7
<b>B6</b>	—	4.3	22.0	19.3	5.0	5.5	1.3	4.7	9.0
<b>B7</b>	—	4.6	20.0	19.7	3.7	3.3	—	3.3	7.2
<b>B8</b>	1.0	5.0	40.0	28.6	6.0	4.2	2.0	11.0	9.3

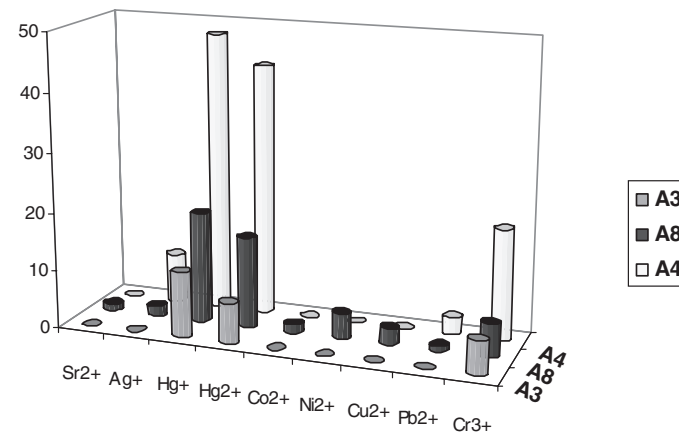
<sup>a</sup> $\text{H}_2\text{O}/\text{CHCl}_3 = 10/10$  mL (v/v); [picric acid] =  $2 \times 10^{-5}$  M, [ligand] =  $1 \times 10^{-3}$  M, [metal nitrate] =  $1 \times 10^{-2}$  M; 298 K, 1 h contact time.  $\alpha \leq \pm 2\%$ .

been evaluated by solvent extraction of selected metal picrates (Tables 1 and 2).

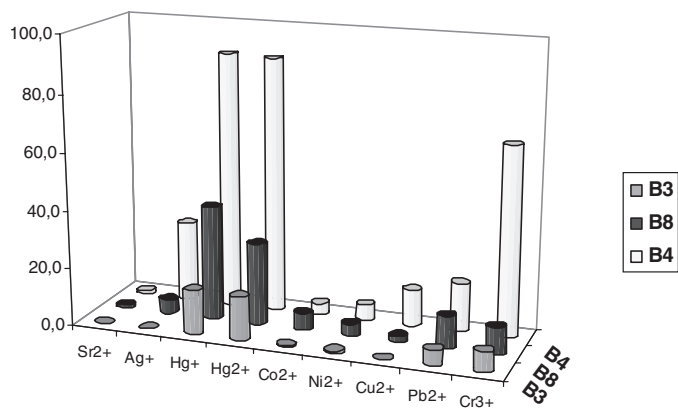
These data were obtained by using chloroform solutions of the ligands in extracting metal picrates from aqueous solution. Equal volumes (10 mL) of aqueous solutions of metal picrates ( $2 \times 10^{-5}$  M) and solutions of azocalix[4]arene derivatives ( $1 \times 10^{-3}$  M) in chloroform were vigorously shaken at 25°C for an hour. After the completion of phase separation, absorbance values have been measured three times. The equilibrium concentration of picrate in aqueous phase has been determined as 354 nm ( $\lambda_{\text{max}}$ ) spectrophotometrically.

The ionophoric properties of azocalix[4]arene derivatives **A1–A8** and **B1–B8** towards the alkaline-earth, basic and transition metal cations were initially investigated by the picrate extraction method (19). The results, expressed as percentage of cation extracted (E%) are used to graph Figures 2 and 3.

The extractions of these cations ( $\text{Sr}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$ ) with ligands **A1–A8**



**Fig. 2.** Extraction percentages of tribenzoyl derivatives of *mono*-azocalix[4]arene.



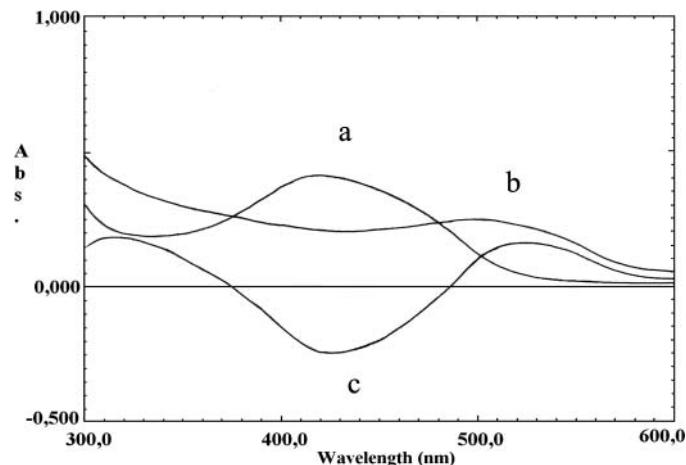
**Fig. 3.** Extraction percentages of dimethyl ketone derivatives of *di*-azocalix[4]arene.

and **B1–B8** have previously been reported under the same experimental conditions (19). Unlike the formerly used azocalix[4]arene derivatives, containing  $-OH$  functional groups, the azocalix[4]arene derivatives used in this present study contain benzoyl and ketone derivatives. This is mainly due to the positive effect of these functional groups on solubility leading to higher extraction efficiency. While the extraction levels of **B4** for  $Hg^+$  (89,6%) and  $Hg^{2+}$  (89,0%) appear to be superior, the extraction levels of **A4** and **B4** for  $Cr^{3+}$  (19,0% and 66,0% respectively) are found to be inferior.

Phenylazophenylazocalix[4]arene derivatives **A4** and **B4** displayed different extraction behaviors compared to the other substituted azocalix[4]arene moieties. Although they exhibited poor extraction abilities towards most of the metal cations, they appeared to be good extractants for  $Hg^+$  and  $Hg^{2+}$ . This phenomenon can be explained by the fact that, the conformation of azocalix[4]arenes with double azo groups may probably have been changed, which is well discussed in the literature (15,16).

In the case of azocalix[4]arenes with *cone* conformation, metal ion is in interaction with the phenol unit of the *upper rim* and azo group(s) in the medium cavity. However, due to the intramolecular hydrogen bonding of *lower rim*, metal ions may be accommodated within the region of the medium cavity of the azocalix[4]arene. This arrangement could simultaneously facilitate  $\pi - \pi$  interactions between metal ions and center of azocalix[4]arene derivatives charged negatively. In the case of azocalix[4]arene derivatives, alkaline-earth, basic and transition metal ions can be bound more strongly to the polar cavity defined by the ester or ketone and azo group(s) than monovalent mercury metal ion can bound, whereas the binding of azocalix[4]arenes with transition metal ions is weaker due to the lower polarity of in the substitute group of azocalix[4]arene.

The different detection limits observed for various basic ( $Pb^{2+}$ ) and transition metal ions ( $Ag^+$ ,  $Hg^+$ ,  $Hg^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Cr^{3+}$ ) can be explained by several pa-



**Fig. 4.** Absorption spectra of azocalix[4]arene **A4** and its mercury complex. (a)  $2.2 \times 10^{-5} molL^{-1}$  of **A4** solution against DMF blank; (b) the solution containing  $2.2 \times 10^{-5} molL^{-1}$  of **A4** and  $3.0 \times 10^{-3} molL^{-1}$  of  $Hg^+$  against water blank; (c) the solution containing  $2.2 \times 10^{-5} molL^{-1}$  of **A4** and  $3.0 \times 10^{-3} molL^{-1}$  of  $Hg^+$  against reagent **A4** blank.

rameters such as complexation constants and formation constants of metal picrates.

The UV absorption spectra of azocalix[4]arene **A4** and **A4**-mercury(I) complex in the wavelength range of 300–600 nm were measured in DMF solutions against DMF blank and shown in Figure 4. Due to  $n \rightarrow \pi^*$  transitions of the  $-N=N-$  bond, azocalix[4]arene **A4** (Fig. 4a) gave bimodal absorption maxima at 420 nm. This bimodal absorption has been replaced by a single absorption band around 501 nm with the addition of  $HgCl_2 \cdot 6H_2O$  to the solution of **A4** in DMF (Fig. 4b). The UV spectrum of **A4**-mercury(I) against the azocalix[4]arene **A4** DMF solution blank (Fig. 4c) exhibited the maximum absorption at 523 nm.

## 4 Conclusions

Solvent extraction study has shown that azocalix[4]arenes can extract transition metal ions. The goal of this work is to introduce a new chromogenic azocalix[n]arene molecule functioning as an ion selective electrode (ISE) for detection of heavy metal ion pollutants. The feasibility of extractants based on chromogenic azocalix[4]arene molecules has been shown.

Among these azocalix[4]arenes, **A4** and **B4** with the phenylazophenylazo groups in chloroform solution preferentially complexed heavy metal mercury ion, whereas no significant changes in absorption spectra are observed in the presence of transition metal ions. The conformation of the azocalix[4]arenes and cooperative behavior of the functionalities may play an important role in two-phase extraction systems.

A new chromium selective chromogenic azocalix[4]arene has been prepared by diazo coupling reaction between the

calix[4]arene and diazonium salts and their chromogenic behavior towards the important metal ion  $\text{Cr}^{3+}$  was also studied. The results of experiments displayed that the two chromogenic azocalix[4]arene derivatives exhibit remarkable selectivity towards  $\text{Cr}^{3+}$  ion.

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