

## A Study on The Usability of Some Phthalonitrile and Diiminoisoindoline Substituted Calixarenes as Liquid-Phase Extraction Agents for Some Toxic Ions

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**ABSTRACT:** The liquid-phase extraction performance of phthalonitrile (**3** and **4**) and isoindoline (**5** and **6**) substituted calix[4]aren derivatives was studied towards (i) some selected divalent heavy metal cations (i.e Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup>), (ii) dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/HCr<sub>2</sub>O<sub>7</sub><sup>-</sup>), and (iii) arsenate (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>/HAsO<sub>4</sub><sup>2-</sup>). In general, extraction yield was observed to be higher in the case of compounds **3** and **5** (cone conformation) when compared to **4** and **6** (1,3-alternate conformation). This indicated a somehow positive effect of cone conformation on the extraction performance rather than 1,3-alternate conformation. The stoichiometric ratio between the compound **3** and **4** with mercury picrate was estimated through job's plot analysis method.

**Keywords:** Heavy metal, liquid-liquid extraction, dichromate, arsenate, calixarenes.

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## INTRODUCTION

Calixarenes are known as the third generation of subramolecular chemistry after crown ethers and cyclodextrin. They have cylindrical shapes with various cavity sizes due to the presence of different numbers of phenols (Neri et al., 2016). The cavity of calixaren skeleton of calix[4]arenes offers an appropriate binding structure for the complexation of ionic and molecular species. Owing to their flexible chemistry, calixarenes can exhibit different conformations when they are in unsubstituted forms, and this property is valuable when relatively small substituents are on the structure (Roundhill, 1995.; Asfari et al., 2007).

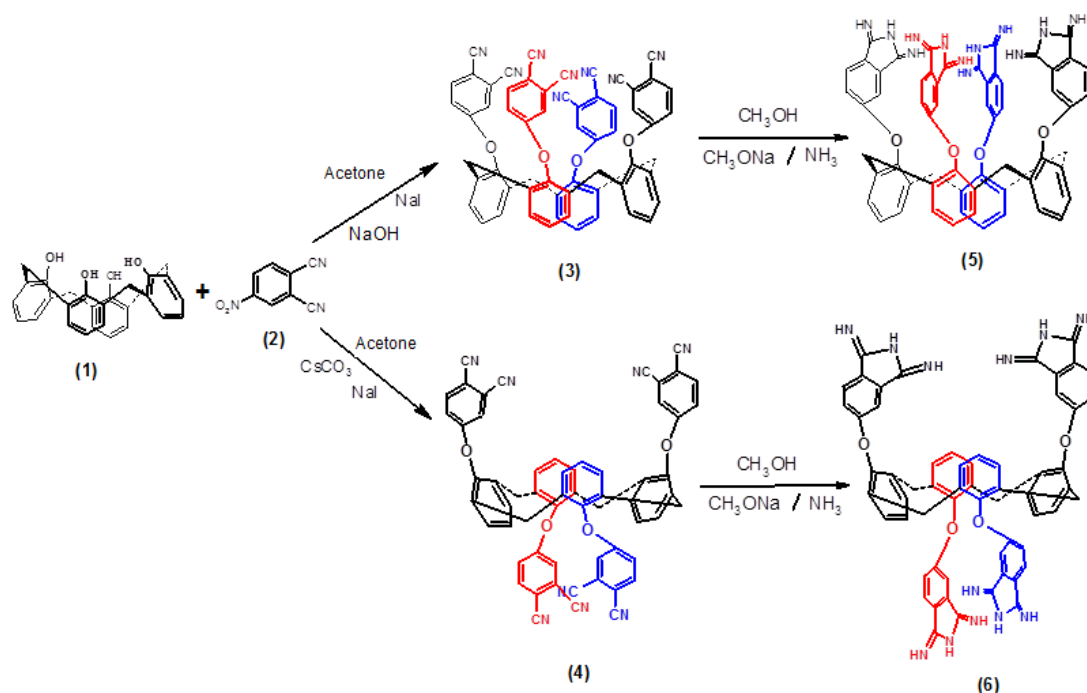
One of the serious environmental problems today is heavy metal pollution. Due to the rapid development of industry, direct or indirect discharge of waste heavy metals to nature leads to serious environmental problems (Yordanov et al., 1999.; Talanov et al., 2002). Mercury and its compounds are the most toxic contaminants even in small quantities, and they can damage the nervous system (Roundhill et al., 2009.; Talanova et al., 1999.; Lidsky and Schneider 2003.; Antonio et al., 2003). Some neurological symptoms, such as nervousness, memory loss, insomnia, and depression, are related to mercury exposure (Mishra et al., 1998.; Samanta and Bandyopadhyay, 2007.; Qian and Dong-su, 2007). Mineral deposits and industrial wastes are the major mercury contamination sources. The removal and control of potentially hazardous heavy metals are unavoidable to prevent contamination of aquatic and continental ecosystems (Förstner and Wittmann, 2012). Moreover, recovery of mercury is economically important because mercury has widespread applied such as electrodes for some types of electrolysis, catalysts, fluorescent lamps, batteries (Mendonça Fábrega and BorgesMansur, 2007). In recent years, various techniques have been developed for removal of mercury such as liquid-liquid extraction, ion exchange, electrolysis, and precipitation.

Oxyanions are known to be hazardous chemicals for the environment, and among them, chromate, dichromate, phosphate, arsenate, and nitrite are the most common (Tabakçı et al., 2003). These anions are pollutants that cause significant problems in soils and waters due to their toxicity. Cr(III) is naturally found in rocks, soils, plants, volcanic emissions and animals and it is a beneficial element for the human. However, Cr(VI) has a wide application range such as stainless steel welding, chromium plating, chromate production, and chrome pigment industries despite its high toxicity (Shahabuddin et al., 2004). Arsenate is a carcinogenic and toxic compound (Habuda-Stanic et al., 2008). The World Health Organization (WHO) recommends the arsenate limit in drinking water to be  $10 \mu\text{g L}^{-1}$ . (WHO 2001). When arsenate is found in drinking water, it causes pigmentation change, skin thickening, neurological disorder, muscle weakness as well as skin, bladder, kidney and lung cancer (Yolcubal and Akyol, 2008.; Hering et al., 1997.; Viraraghavan et al., 1999.; IPCS, 2001). Acute toxicity symptoms in case of oral exposure to inorganic arsenate poisoning are muscle cramps, nausea, hepatotoxicity, vomiting abdominal pain, cardiac abnormalities, dermatitis, anorexia and epigastric (Hall, 2002; Valenzuela et al., 2007.; Bayrakçı et al., 2009).

In this study, calixarene derivatives were used as the carrier in liquid-liquid extraction of some divalent heavy metal cations and oxyanions (dichromate and arsenate). This is the first report focuses on the interaction of compounds **3**, **4**, **5**, and **6** with some chemical species under liquid-phase extraction conditions. The results are believed to have an important contribution to building new concepts for the removal of chemical species from aqueous media.

## MATERIALS AND METHODS

The carriers used throughout the study (**3**, **4**, **5** and **6**) were synthesized according to the literature method (Güngör, 2018), and their molecular structures were shown in Figure 1. Analytical reagent-grade chemicals were used to prepare solutions. Organic solutions were prepared by dissolving carriers in dichloromethane. Metal picrate solutions were prepared with ultrapure water (Visser et al., 2001).



**Figure 1.** Synthesis procedure of calix[4]aren derivatives

### Liquid-liquid extraction

In this study, dichromate/Arsenic/picrate extraction experiments were performed by using Pederson's procedure (Pedersen 1968). Furthermore, other techniques for the determination of arsenate are available in the literature (Bayrakçı and Yiğiter, 2013). A 10 mL of  $2 \times 10^{-5}$  M aqueous picrate (for metal ions) or a  $1 \times 10^{-4}$  M oxyanion solution were vigorously agitated with 10 mL of  $1 \times 10^{-3}$  M calixarene derivatives in  $\text{CH}_2\text{Cl}_2$  at room temperature. pH of oxyanion solution has been adjusted by using dilute NaOH and HCl solutions. The remaining metal or oxyanion species concentration in the aqueous phase was determined by using a UV-Vis spectrometer (at 610 nm for chromate, at 346 nm for arsenate and at 354 nm for metal picrate). The percentage of extraction was calculated by the following formula.

$$E\% = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

In this formula,  $C_0$  and  $C$  are the initial and final concentrations of ligand in aqueous solution before and after particular extraction process, respectively.

## RESULTS AND DISCUSSION

### Liquid phase extraction of metals ion

The cavity size, conformation and the type of functional groups within the structure are some parameters which influence the binding performance of calixarenes for chemical species. Owing to the absorbance of metal-picrates at around 270-300 nm, the concentration of metal ions can easily be

determined by using a UV-Vis Spectrophotometer (Yordanov et al., 1995.; Tabakçı et al., 2004.; Akkuş and Korcan, 2005.; Sayın et al., 2018). This is the reason why we preferred metal-picrates over respective nitrates, sulfates, and chlorides in the present study. In this study, firstly, control studies were performed. In order to examine the effect of picric acid on extraction, metal picrate extraction was performed in the absence of calixarene derivatives. In this control study, it was observed that no metal picrate passed from aqueous phase to organic phase. This study was performed separately for all metal picrates. Later, In order to examine the effect of picric acid, extraction was performed in the absence of metal (10 mL of  $2 \times 10^{-5}$  M aqueous picrate acid with 10 mL of  $1 \times 10^{-3}$  M calixarene derivatives in  $\text{CH}_2\text{Cl}_2$ ). It was observed that picrate acid not passed from aqueous phase to organic phase. This study was performed separately for all calixarene derivatives. This result shows that calixarene derivatives complex with metal cations.

The ion recognition properties of calixarene derivatives (**3**, **4**, **5** and **6**) were studied by liquid-liquid extraction experiments with the picrates of selected metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ ). The results are summarized in Table 1. Generally, receptor interactions with cations are based on noncovalent interactions, such as hard-soft acid base interaction, ion-pairs, coulomb forces or through coordinative interactions with metal ions included in the ligand (Ersoz, 2007.; Elçin and Deligöz, 2015). According to the extraction results, it was observed that compound **1** does not extract any metal ion into the organic phase from the aqueous phase. This result implies that metal ions are captured by the functional groups rather than by phenolic oxygen atoms. While compound **5** and **6** did not display any selectivity towards the studied metal cations, compound **3** and **4** showed an excellent selectivity and affinity toward Hg ions. Moreover, these compounds exhibited little affinity toward  $\text{Cd}^{2+}$ . Obtained results are thought to be in concordance to the hard-soft acid-base principle (Pearson's classification): Nitrile group is softer than diiminoisoindoline group and  $\text{Hg}^{2+}$  has a softer nature compared to other metals studied. The results are also in agreement with the previous reports (Gungor et al., 2005.; Tabakci et al., 2013). Besides, extraction results indicated that compound **3** has higher extraction capacities than compound **4** for  $\text{Hg}^{2+}$ . This result probably due to the rigidity of cone conformation (as in the case of compound **3**) compared to other conformations. In other words, in 1,3-alternate conformation, the benzene rings of calix[4]arene are perpendicular (or almost perpendicular) to the main plane of the molecule defined by the four methylene bridges. As a result, the inclusion of guest molecules into the host cavity is much more difficult compared to the cone conformation (Kinga 2016), resulting in less extraction yield.

**Table 1.** Extraction yields obtained for metal picrates <sup>a</sup>

Ligand	Picrate salt extracted (%)					
	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Hg}^{2+}$	$\text{Pb}^{2+}$
<b>3</b>	<1.0	<1.0	<1.0	12.3	96.4	<1.0
<b>4</b>	<1.0	<1.0	<1.0	9.1	75.7	<1.0
<b>5</b>	35.1	30.3	40.4	34.2	60.7	53.1
<b>6</b>	28.7	21.2	31.5	22.4	48.1	40.9

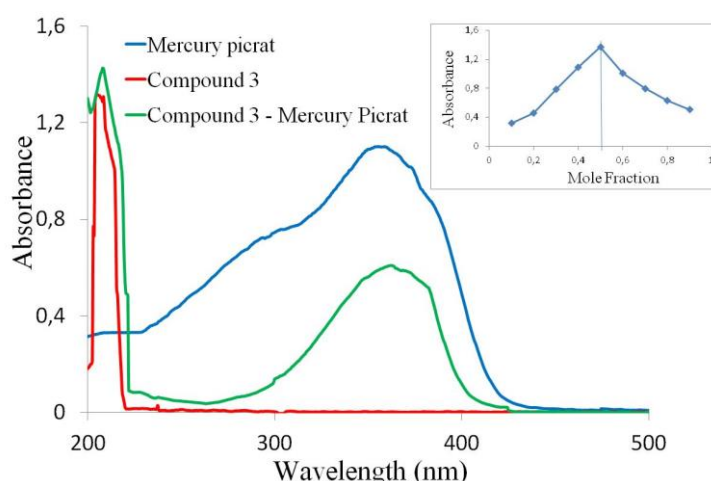
<sup>a</sup> Organic phase,  $\text{CH}_2\text{Cl}_2$  [ligand] =  $1 \times 10^{-3}$  M; at 25 °C, for 1 h.

Aqueous phase [metal picrate] =  $2 \times 10^{-5}$  M.

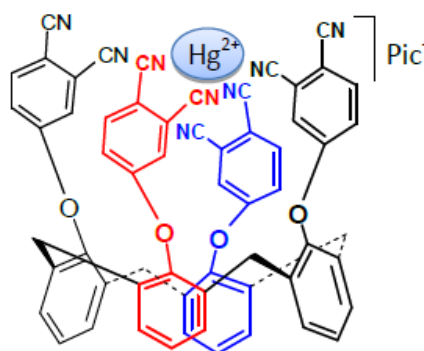
### Job's plot analysis (Complexation study)

Stoichiometric ratio between mercury picrate and the compounds **3** and **4** were examined by using Job's plot ratio to have some information about the nature of binding (Memon et al., 2016). The solutions were prepared by mixing different ratios (1:9–9:1) of equimolar concentrations ( $2.5 \times 10^{-5}$  M) of the

compounds and mercury(II) picrate in methanol. Complex formation can usually be understood by shifting the complex band to a longer or shorter wavelength or high intensity in UV-Vis. spectroscopy. Also, complex formation may arise new bands. UV-Vis spectra showed strong bands at 209 nm and 212 nm for the compound **3** and **4**, respectively. These bands are attributed to the interaction in calixarene derivatives. This confirm of the formation of endo-complex (Flor de Maria and Garcia-Sosa 2012). The sharp prominent peak at 354 is obvious for mercury picrate (Figure 2 for compound **3** as an example). In the spectrum of compound **3**-Mercury picrate complex, the intensity of calixarene band is augmented at 209 nm while the mercury picrate band at 354 nm decreased. These changes in the spectra of complexes are some pieces of evidence for the complexation between compound **3** and mercury picrate. For compound **3**-mercury picrate complex, the maximum mol-fraction value was found to be 0.50, which confirm the 1:1 ratio of a host-guest complex. The value of the maximum mol-fraction of compound **4**-mercury picrate complex was found to be 0.44 confirming a 1:1 ratio for a host-guest complex. Lower mol-fraction value observed for compound **4** (compared to compound **3**) was attributed to the conformational flexibility. Since the 1,3-alternate conformation is more flexible than the cone conformation, the complex formed between compound **3** and mercury picrate was thought to be less stable. The proposed complexation model between compound **3** and mercury picrate is given in Figure 3.



**Figure 2.** UV-Vis spectra for compound **3** before and after the addition of mercury picrate (inset:Respective Job's plot)



**Figure 3.** A proposed complexation model for the inclusion complexation of mercury(II) picrate with compound **3**

### Liquid phase extraction of oxyanions

Chromate, dichromate and arsenic anions constitute a series of important problems for living things. For this reason, it is necessary to control the concentration of these chemical species in water resources through suitable processes. Owing to the presence of oxygen atoms within the structure of oxoanions, a host molecule like calixarene can attract these species. It is well known that calixarenes having nitrile, amino, and amide functionalities are efficient extractants and/or host molecules for oxoanions (Yilmaz et al., 2007). A frontal evaluation of the phase transfer efficiency of the extractants **3**, **4**, **5** and **6** has been carried out by solvent extraction of  $\text{Na}_2\text{Cr}_2\text{O}_7$  or  $\text{Na}_2\text{HAsO}_4$  from water into dichloromethane at different pH values. The extraction results are summarized in Table 2 and Table 3. The results showed that the extraction yield of dichromate increased as the pH of the aqueous phase decreased. This can be explained by the phenomena called anion hydration (Yusof and Malek, 2009) so that dichromate anion is turned into its monoanionic form ( $\text{HCr}_2\text{O}_7^-$ ) upon its protonation in acidic solution. Since the monoanionic form ( $\text{HCr}_2\text{O}_7^-$ ) has less hydration free energy than dichromate anion ( $\text{Cr}_2\text{O}_7^{2-}$ ), the extraction of dichromate from the aqueous phase to the organic phase is thought to be much more efficiently performed at lower pH values.

**Table 2.** Extraction yields obtained for dichromate anion with calixarene derivatives<sup>a</sup>

Ligand	Dichromate anion extracted (%)			
	pH			
	1.5	2.5	3.5	4.5
<b>3</b>	21.4	9.3	<1.0	<1.0
<b>4</b>	11.3	5.8	<1.0	<1.0
<b>5</b>	95.8	81.4	72.1	50.5
<b>6</b>	82.3	67.5	58.1	42.9

<sup>a</sup> Organic phase,  $\text{CH}_2\text{Cl}_2$  [ligand] =  $1 \times 10^{-3}$  M; at 25 °C for 1 h.

Aqueous phase [sodium dichromate] =  $1 \times 10^{-4}$  M.

**Table 3.** Extraction yields obtained for arsenate anion with calixarene derivatives<sup>a</sup>

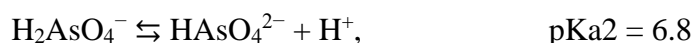
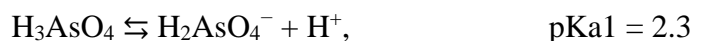
Ligand	Arsenate anion extracted (%)			
	pH			
	1.5	3.5	4.5	5.5
<b>3</b>	24.5	11.2	<1.0	<1.0
<b>4</b>	21.1	7.9	<1.0	<1.0
<b>5</b>	83.5	96.4	74.6	46.3
<b>6</b>	71.7	85.3	63.4	41.5

<sup>a</sup> Organic phase,  $\text{CH}_2\text{Cl}_2$  [ligand] =  $1 \times 10^{-3}$  M; at 25 °C for 1 h.

Aqueous phase [sodium arsenate] =  $1 \times 10^{-4}$  M.

Depending on the medium pH, arsenic species can be found in the forms (i) dianion ( $\text{HAsO}_4^{2-}$ ; at pH 8-11), (ii) monoanion ( $\text{H}_2\text{AsO}_4^-$ ; at pH 3-6), and (iii)  $\text{H}_3\text{AsO}_4$  (at pH 1-3). Furthermore, the dianionic form ( $\text{HAsO}_4^{2-}$ ) has a smaller free hydration energy compared to monoanion ( $\text{H}_2\text{AsO}_4^-$ ) (Qureshi and Memon, 2012). The arsenic extraction rate is increasing up to pH 3.5. Arsenic is present in the monoanionic form at this pH. Then the extraction rate at pH 1.5 decreases because it changes into  $\text{H}_3\text{AsO}_4$  form.





Diiminoisoindoline substituted calixarene derivatives (**5** and **6**) were found to be much better extractants than phthalonitrile substituted calixarene derivatives (**3** and **4**) for oxyanions. This is thought to be resulting from the protonation of nitrogen atom within the compounds **5** and **6** at lower pH values. Hence, the protonated forms of these compounds can attract oxyanions through electrostatic interactions, resulting in better oxyanions extraction efficiencies. Furthermore, the cooperative effect of hydrogen-bonding at lower pH values is thought to be contributing to the extraction yield. As a conclusion of this section, both medium pH and conformational effects were found to have an important role in dichromate extraction so that the best results were obtained with compounds **3** and **5** (which have a cone conformation) compared to other parent calix[4]arenes having a 1,3-alternate conformation (**4** and **6**).

## CONCLUSION

Liquid-phase extraction of some chemical species (i.e. picrates of  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$ , and oxyanions) was studied by using some calix[4]arene derivatives having different functionalities and conformations as the extractants. As a general trend, compounds **3** and **5** exhibited greater efficiency in the removal of metal picrates, dichromate, and arsenic compared to the other calix[4]arenes (**4** and **6**). This was explained on the basis of a conformational flexibility. Medium pH was also found to be influencing the extraction performance of some calixarene derivatives toward dichromate and arsenic. The extraction performance was observed to be increasing with decreasing medium pH. Hence, together with the chemistry of guest species, the type of functional groups on the host molecule, as well as its conformation, were understood to significantly influencing the extraction yield. Thus, the chemistry of functional group on the host molecule and the chemistry of the studied species were observed to be influencing the extraction performance, significantly.

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