



## Azocalixarene. 5: *p*-Substituted Azocalix[4]arenes as Extractants for Dichromate Anions

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### Abstract

In this article, chromium(VI) extraction properties of two azocalix[4]arene based receptors (**L4** and **L6**) are reported. A preliminary evaluation of the binding efficiencies of *p*-substituted azocalix[4]arene derivatives **L4** and **L6** was carried out by solvent extraction of Na-dichromate from aqueous solution into dichloromethane at different pH. It was observed that the new compounds are effective extractants for transferring the  $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$  anions at low pH. The binding ability of these compounds toward  $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$  anions depends upon  $\text{Na}^+$  extraction.

**Keywords:** Calix[4]arene; azocalixarene; extractants; dichromate anions; phase transfer

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### Introduction

Understanding the nature of ion solvation is important to understand the relative inclination for a specific ion to cross an aqueous/non-aqueous phase barrier. More directly stated, the higher the energy of hydration for an ion, the more difficult it will be to move this ion into non-polar media where the solvation of ions is ordinarily much weaker. Generally, this trend follows the charge/size ratio; larger the ratio, more difficult it is to extract an ion from an aqueous solution [1,2].

The solvation of the host molecule and its complexes plays a similar role in terms of the phase barrier, but often neglected. The host molecule is solvated in the organic media (diluent), and this solvation is at least partially disrupted by the arrival and coordination of the guest species. This disruption represents an energy penalty that may be more or less compensated by subsequent solvation of the host-guest complex. What if the host molecule contained a volume of space that was inaccessible to solvent molecules, but would allow to guest species? This should enhance the extraction capability towards these guests, as there would be no desolvation required in the protected cavity [3].

Supramolecular chemistry has developed new synthetic methods directed to research areas such as host-guest chemistry, molecular and ionic recognition, supramolecular catalysis, self-organization, aggregation, signal transfer, allosteric effects, etc. Much attention has been paid to the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they delineate a suitable binding site. This was achieved with the development of macrocyclic molecules such as synthetic crown ethers, cryptands, spherands, cyclophanes, natural cyclodextrins and calixarenes [4-6].

Over the last decade, calixarenes are macrocycles with a high degree of preorganization. They consist of phenolic units linked by methylene bridges *ortho* to the OH functions. Calixarenes can be chemically modified by substitution of the phenolic hydrogens with various functionalities known for their affinity to cations of interest. Furthermore, phenolic groups can be functionalized on the *para* position to make the calixarene either lipophobic or lipophilic [4]. In this study, azo groups are assembled to provide the required structure (Fig.1)

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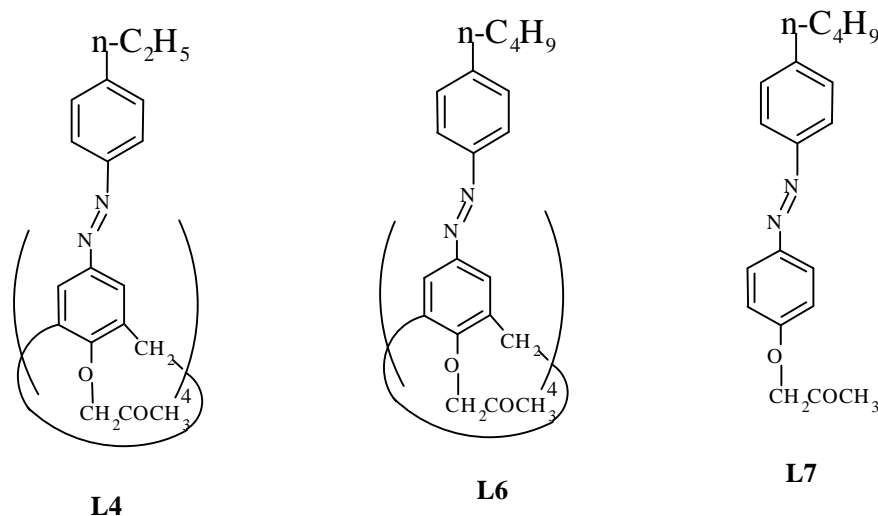


Figure 1. Structures of the extractants

The available sites on these macrocyclic compounds can be easily modified to tailor them for many applications, as carriers in liquid membrane technology, heavy metal adsorption agents, as alkali metal complexation agents, as extractants for chromium(VI) and as chemical sensors [7-9]. Thus, synthetic receptors (**L4** and **L6**) contain two individual recognition sites for cation and anion sensing devices. Chromate and dichromate ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) anions are important because of their high toxicity [10] and because of their presence in soils and waters [11].

Herein, we report the chromium(VI) extraction properties of two azocalix[4]arene based receptors (**L4** and **L6**). Both compounds provide specific information about guest-size host cavity interactions and have ability to extract dichromate anions at different pH.

### Experimental Section

All reagents used in this study were purchased from Merck or Carlo-Erba and they were chemically pure. Melting points of them were determined on an Electrothermal IA9100 digital melting point apparatus and were uncorrected. UV-Vis. spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer.  $\text{Na}^+$  metal determinations were made on a JENWAY PFP7 flame photometer. All aqueous solutions were prepared with deionized water that had been passed a Millipore mili-Q Plus water purification system.

### Preparation of the Ligands

*p*-*tert*-Butylcalix[4]arene, [12] calix[4]arene, [13] *p*-(4-*n*-ethylphenylazo)calix[4]arene [14] (**L3**) 25,26,27,28-tetramethyl-*p*-(4-ethylphenylazo) calix[4]arene tetraketone [14] (**L4**), *p*-(4-*n*-butylphenylazo)calix[4]arene [15] (**L5**), and 25,26,27,28-tetramethyl-*p*-(4-*n*-butylphenylazo)calix[4]arene tetraketone [14] (**L6**), 4-ethylphenylazophenylacetone (**L7**) were synthesized as described previously.

### Dichromate Extraction Procedure [16]

To a vial were pipetted, an aqueous solution (10 mL) containing sodium dichromate at a concentration of  $1 \cdot 10^{-4}$  M, a few drops of 0.01 M KOH/HCl solution in order to obtain the desired pH at equilibrium and maintain the ionic strength, and 10 mL of a  $1 \cdot 10^{-3}$  M solution of the calixarene in  $\text{CH}_2\text{Cl}_2$ . The mixture was shaken for 2 min, then magnetically stirred in a thermostated water-bath at 25 °C for 1 h contact time and, finally, this was left standing for an additional 30 min. The concentration of dichromate ion remaining in the aqueous phase was determined spectrophotometrically. Blank experiments showed that no dichromate extraction occurred in the absence of calixarene. Each extraction experiment was repeated three times. The percent extraction (*E*%) was calculated as:

$$(E\%) = A_0 - A / A_0 \times 100$$

Where  $A_0$  and  $A$  are the initial and final concentrations of the metal dichromate before and after the extraction, respectively.

## Results and Discussion

Recently a number of chemically modified calixarenes have been synthesized and they can be used as hosts for simple anions [17-27]. Thus we have targeted the synthesis of an extractant based on the calix[4]arene framework for the dichromate anion. For this purpose, we have designed extractants (**L4** and **L6**) having a proton-switchable binding moiety for anions. A preliminary evaluation of the binding efficiencies of the extractants **L4** and **L6** was carried out by solvent extraction of  $\text{Na}_2\text{Cr}_2\text{O}_7$  from aqueous solution into dichloromethane at different pH.

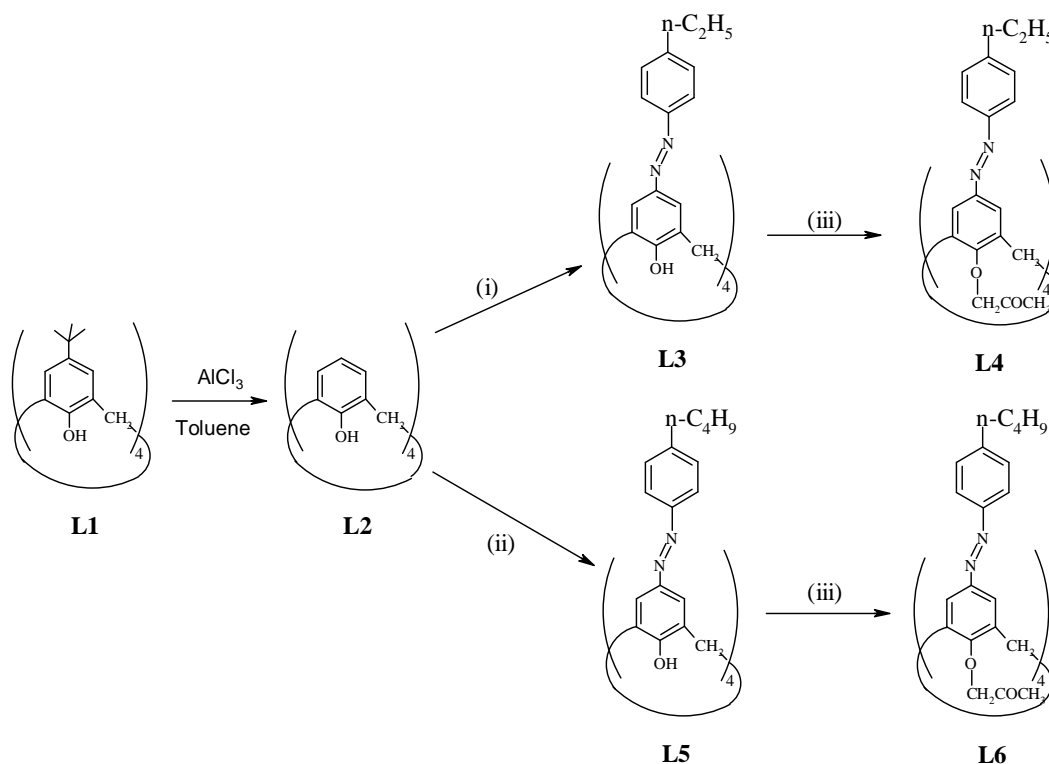
The present work determines strategic requirements for two-phase extraction measurements. The results are summarized in Table 1. From the extraction data, it seems clear that the tetra ketonic azo derivatives (**L4** and **L6**) show remarkable anion extraction ability at low pH. The pronounced increase may be due to the more rigid structural features and protonation of the azo groups of **L4** and **L6** helped in transferring anions.

Table 1. Percentage extraction of dichromate anion by ionophores

Compound	Dichromate anion extracted (%)				
	pH				
	1.5	2.5	3.5	5.5	7.0
<b>L4</b>	86.0	59.6	41.0	13.0	<1.0
<b>L6</b>	89.0	71.0	53.0	24.0	<1.0
<b>L7</b>	<1.0	<1.0	<1.0	<1.0	<1.0

- (1) Aqueous phase, [metal dichromate]= $1.10^{-4}$  M; organic phase, dichloromethane, [ligand] =  $1.10^{-3}$  M at 25 °C, for 1 h contact time.
- (2) The % extraction  $E$  is given by [initial aqueous anion - final aqueous anion] / [initial aqueous anion] x100.

Moreover, to understand the chelating effect of the azo fragment on the anion binding, the acyclic monomeric analog (**L7**) was used. It was observed that the  $\text{Cr}_2\text{O}_7^{2-}$  ions were extracted only in trace amounts. Based on these results it was concluded that the calix[4]arene unit plays an important role in confirming the cooperative participation of the azo groups.



Scheme 1. Synthesis of *p*-substituted azocalix[4]arenes and their ketone derivatives.

Reagents and conditions: (i) 4-ethyliline,  $\text{HNO}_2$ , conc.HCl, (ii) 4-*n*-butylaniline,  $\text{HNO}_2$ , conc.HCl (iii)  $\text{K}_2\text{CO}_3$ ,  $\text{ClCH}_2\text{COCH}_3$ , Acetone.

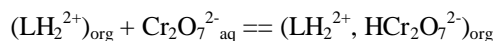
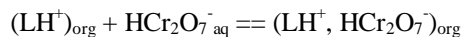
Table 2. Percentage extraction of sodium ions by ionophores [1,2]

Compound	Sodium ion extracted (%)				
	pH				
	1.5	2.5	3.5	5.5	7.0
<b>L4</b>	87.0	60.0	59.0	54.0	53.0
<b>L6</b>	82.0	75.0	97.0	93.0	87.0

- (1) Aqueous phase, [metal dichromate]= $1.10^{-4}$  M; organic phase, dichloromethane, [ligand] =  $1.10^{-3}$  M at 25 °C, for 1 h contact time.  
 (2) The % extraction  $E$  is given by [initial aqueous anion - final aqueous anion] / [initial aqueous anion] x 100.

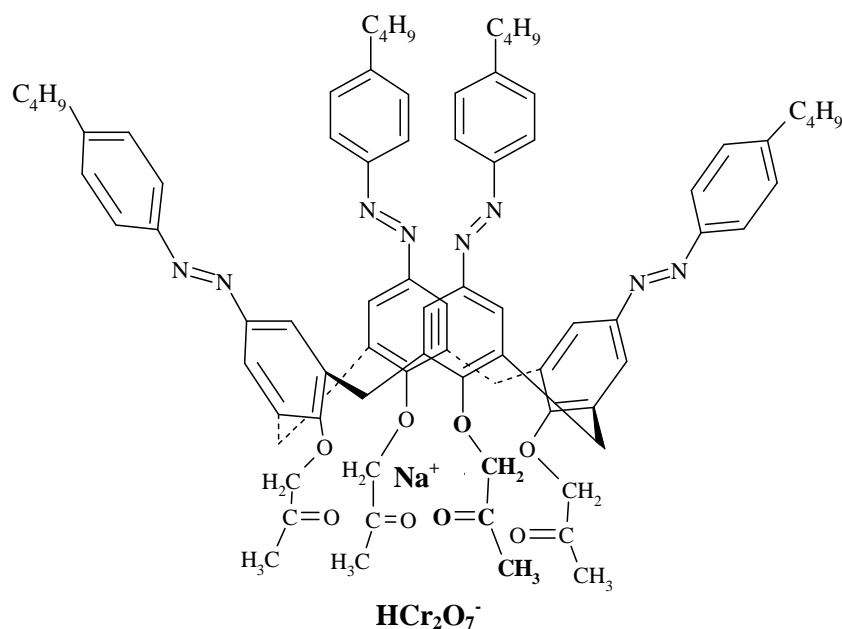
The extraction results (Table 1 and 2), suggests that significant extraction of  $\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$  ions occurs at pH 1.5-5.5, whereas the extraction of sodium ions is independent of pH. From these observations it has been revealed that both compounds (**L4** and **L6**) exhibit enhanced ion-pair extraction of sodium salt. It is not surprising because it has been reported that tetraketone derivative of calix[4]arene extracts sodium ion efficiently [17].

It is well known that at higher acidic conditions  $\text{Na}_2\text{Cr}_2\text{O}_7$  is converted into  $\text{H}_2\text{Cr}_2\text{O}_7$  and after ionization in aqueous solution it may exist in the  $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$  form. We therefore must consider this simultaneous extraction according to following equilibria:



These results can be explained by the fact that the azocalix[4]arene ketone derivatives may have gained a more rigid and appropriate structure, which assists the transfer of dichromate anions in a two-phase extraction systems. The role of azo functionalities has not been verified, but since diazo group has a large dielectric constant, thus it may involve in proton accepting process which in turn helps to form hydrogen bonding with oxoanions. The role of ketonic functionalities may be assumed that they help in coordination of  $\text{Na}^+$  cation as this environment is favorable for this process. (Scheme 2)

In summary, present work describes the excellent extraction behavior of **L4** and **L6** toward  $\text{HCr}_2\text{O}_7^-/\text{Cr}_2\text{O}_7^{2-}$  anions at low pH. The field of anion recognition and extraction is a relatively new one, where azocalix[4]arene has been shown to be a good extractant for dichromate anions. The variety of hydrogen bonding motifs that occur in the studied azocalix[4]arene derivatives may be of considerable importance for the future design of novel azocalix[4]arene-based receptors, carriers or supramolecular structures.



Scheme 2. Schematic representations of proposed interaction between ionophore &amp; ions

### Conclusion

- In conclusion, we can say that in these phase transfer experiments, the effectiveness of azocalixarenes for transferring the metal cations is reflected by the  $\pi$ -donor systems and intra cavity complexation.
- Conventional calix[4]arenes cannot extract them at all, the bridging azo groups play some important role in the recognition of oxoanions.
- The aim of this work was to design new chromogenic azocalix[4]arene molecules able to detect ionic pollutants and may be used in ion selective electrodes (ISE).

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