

REMEDICATION AND LIQUID-LIQUID PHASE TRANSFER EXTRACTION OF CHROMIUM(VI). A REVIEWShahabuddin MEMON^{a1}, D. Max ROUNDHILL^{a2,*} and Mustafa YILMAZ^b^a Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, U.S.A.; e-mail: ¹ shahabuddinmemon@yahoo.com, ² david.m.roundhill@ttu.edu^b Department of Chemistry, Selçuk University, 42031 Konya, Turkey; e-mail: myilmaz@selcuk.edu.tr

Received January 26, 2004

Accepted April 26, 2004

Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to the area of supramolecular chemistry.

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Chromium(VI) is a widely used industrial chemical, and is generally considered to pose a greatest human health risk because it is more toxic, more soluble, and more mobile than chromium(III). Workers in industries that use chromium, in particular stainless steel welding, chromate production, chromium plating, and chrome pigment industries, where exposure via inhalation of aerosols is primarily to hexavalent chromium, are at increased risk of chromium effects. In this article we demonstrate various studies regarding remediation methods in particular liquid-liquid extraction of chromate and dichromate anions with various functionalized calixarenes. This review article briefly discusses various molecular designs of calixarene-type macrocycles for chromium(VI) oxoanion recognition, and gives examples on the relationship between structure and selectivity. The article does not, however, attempt to cover all of the different approaches to chromium(VI) extraction. A review with 73 references.

Keywords: Calixarenes; Liquid-Liquid extraction; Ion recognition; Chromium(VI) toxicity; Oxoanions; Supramolecular chemistry; Remediation; Chromates.

1. INTRODUCTION

Chromium(VI) is a problematic contaminant of soils and waters because of its toxicity. Although its occurrence as a pollutant is not widespread, there are numerous sites where it is present. These sites often result from industrial activities such as leather tanning, textile dyeing, wood preserving, plating operations, oil drilling, or locations where large tanks have been cleaned with chromium(VI) solutions. The manufacture of inks, pigments, glass, ceramics and glues can also be problematic¹⁻³. Chromium has been released into the environment and has become one of the most frequently detected ground water and soil contaminants at hazardous waste sites. A series of *in vitro* and *in vivo* studies have demonstrated that chromium(VI) induces an oxidative stress through enhanced production of reactive oxygen species (ROS) leading to genomic DNA damage and oxidative deterioration of lipids and proteins. A cascade of cellular events occur following chromium(VI)-induced oxidative stress including enhanced production of superoxide anion and hydroxyl radicals, increased lipid preoxidation and genomic DNA fragmentation, modulation of intracellular oxidized states, activation of protein kinase C, apoptotic cell death and altered gene expression⁴⁻⁷.

Although chromium(VI) can be removed by several methods, one of the major methods employed is its reduction to chromium(III). This method often results in the formation of insoluble oxides and hydroxides, which require undesirable filtration methods for their removal. As a result, the direct liquid-liquid extraction of chromium(VI) from aqueous solution has some advantages. Since chromium(VI) is an anion either as HCr_2O_7^- or CrO_4^{2-} , in order to remove it by liquid-liquid extraction it is necessary to use an anion host⁸⁻¹⁵.

The liquid-liquid extraction of chromium(VI) presents several challenges. One challenge is that it occurs as an oxoanion and there is no way to directly bind a complexant to the chromium(VI) center. A second problem is that chromium(VI) is a good oxidizing agent, therefore any compounds used in the process must be resistant to oxidation. A third problem is that the structure of the oxoanion is dependent on the solution acidity. As the pH of the aqueous solution is lowered ($\text{pH} < 6$), the oxoanion structure changes from the monomeric CrO_4^{2-} to the dimeric HCr_2O_7^- . The design of an extractant for chromium(VI) must involve consideration of all three of these factors. Three important aspects of liquid-liquid extraction of an oxoanion from an aqueous into an organic phase are the association between the oxoanion and the extractant, the concurrent phase transfer of

the cation, and the loss of hydration energy of both the anion and cation as they are transferred to the organic phase. However, in this study an attempt has been made to elaborate the general remediation methods employed by various researcher groups.

2. REMEDIATION METHODS

Chromium(VI) remediation can involve vegetation to enhance in situ bioremediation, reduction to chromium(III) or liquid-liquid phase transfer of the chromium(VI) oxoanion with a host. The reduction can be carried out with chemical reagents, but this approach often leads to other chemical contaminants being added to the polluted site. As a result, the reduction is frequently carried out in a biological rather than in a chemical process. If a reduction strategy is adopted, there still remains the need to selectively remove the chromium(III) product. One approach is to remove the chromium(III) by precipitation, but this is best avoided because of the engineering problems involved in separating solids. The direct liquid-liquid extraction of the chromium(VI) oxoanion eliminates both the reduction step and the need to separate insoluble chromium(III) salts. The concept of utilizing plants as bioindicators is a practical possibility for monitoring water and wetland environments. There is, therefore, a need for identifying plants that can be used for biomonitoring in the polluted environments. Below is given an elaborated outlook about some reliable remediation methods generally adopted.

2.1. Phytoremediation

Phytoremediation is an innovative technology that utilizes the natural properties of plants in engineered systems to remediate hazardous waste sites¹⁶. A number of vascular plants have been successfully used¹⁷. The use of rooted plants appears to be particularly promising as they can accumulate metals from soil, sediments and water. The plants act as diffuse samplers, accumulating pollutants to a higher concentration than their surroundings. Because they absorb minerals continuously over time, they also integrate pollution peaks, such as wastewater discharges, and can therefore be used for monitoring surges of heavy metals in water. Recent reports have demonstrated the success of this approach in monitoring the status of heavy metal contamination in rivers and wetlands¹⁸⁻²². Plant species vary in their capacity to remove and accumulate heavy metals. There are reports indicating that some species may accumulate specific heavy metals^{23,24} and

other species are reported to be unspecific accumulators of various heavy metals^{25,26}. Differences also exist among plants as to whether the removed metal is accumulated in the root or translocated to the shoot^{27,28}. Hydrophytes show similar metal-removing characteristics to terrestrial plant species. They may, however, be more useful for monitoring environmental pollution at the interface between aquatic and terrestrial ecosystems.

The adsorption of metals by living plants and trees, is of rather limited use for chromium(VI) because it is a strong oxidant that is often toxic to such species. A few examples regarding the ability of hydrophytes to remove and accumulate trace metals including Cr have been demonstrated. *Salvinia molesta* (Mitch) removed Cr and Ni more effectively²⁹ than *Spirodela polyrhiza* (Schleid) when grown in a solution culture containing up to 8 ppm Cr and Ni. *Lemna minor* was also shown³⁰ to be a good accumulator of Cd, Se and Cu, a moderate accumulator of Cr and a poor accumulator of Ni and Pb. Water hyacinth (*Eichhornia crassipes* L.) has been intensively studied^{21,31} as a bioindicator, and is reported to effectively concentrate a number of contaminants within a broad concentration range such as Sr, V, As, Sb, P, B, I, Cd, Pb, Cr, and Zn. Physiological responses of *Salvinia* to Cr(VI) and its potential use in phytoremediation as well as selected physiological responses of kudzu to different chromium concentrations^{32a,b}, uptake of chromium by sunflower plants^{33a}, trees^{33b} and a review article on phytoremediation of heavy metal-contaminated land by trees^{33c} have also been reported.

2.2. Bioremediation and Biosorption

The ability of some micro-organisms to reduce Cr(VI) to Cr(III) has led to the suggestion that Cr(VI)-reducing micro-organisms might be useful agents for the remediation of Cr(VI)-contaminated waters and soils³⁴. Sulfate-reducing bacteria (SRB) are good candidates for industrial metal removal³⁵⁻³⁸. In addition to the chemical indirect reduction due to the production of H₂S, these bacteria can also reduce metals directly by an enzymatic way. SRB are anaerobic bacteria that all have in common the presence of polyheme c-type cytochromes in their electron-transfer chains. Most of these cytochromes have been well characterized at a molecular level³⁹. A specific feature for these metalloproteins is their low redox potential (from -200 to -400 mV). Cytochromes c₃ have been proposed as useful agents for the bioremediation of metals^{37,38} in contrast to mitochondrial c-type cytochromes⁴⁰. *Microbacterium* sp. NCIMB 13776 and *Desulfovibrio vulgaris* NCIMB 8303 reduced Cr(VI) to Cr(III) anoxically using 25 mM so-

dium citrate buffer (pH 7), with 25 mM sodium acetate and 25 mM sodium formate as electron donors at 30 °C⁴¹. When *Pseudomonas mendocina* is added to soil microcosm, chromium(VI) is immobilized by its conversion into the trivalent form⁴². Various sulfate-reducing bacteria have been compared for the enzymatic reduction of chromium(VI), with the best reductase activity being obtained with *Desulfomicrobium norvegicum*. Several metalloenzymes such as cytochromes c_3 and hydrogenases also reduce chromium(VI)⁴³. A poly(vinyl alcohol)-based immobilization technique has been used to entrap the chromium(VI) reducing bacterium, *Microbacterium liquefaciens* MP30. Cell activity is maintained during immobilization, but the rate of Cr(VI) removal by immobilized cells was only half that of an equivalent mass of free cells⁴⁴. The microbial reduction of chromium(VI) can be coupled with the anaerobic degradation of benzoate⁴⁵. Earlier research on the removal of chromium by microbial reduction has already been reviewed⁴⁶. Bioreduction is not the only pathway for the removal of chromium(VI), since biosorption can also be effective⁴⁷. A representative example involves the use of biomass of the filamentous algae *Spirogyra* species. Since the adsorption capacity of this biomass is strongly pH-dependent, it can be used for the reversible extraction of chromium(VI).

2.3. Chemical and Electrolytic Methods

Chemical methods involve the direct extraction of chromium(VI) with a mixture of sodium carbonate and sodium hydroxide, the precipitation of chromium(III) from a solution at pH 8–10 as the hydroxide $\text{Cr}(\text{OH})_3$ ⁴⁸, or the coprecipitation of copper(II) and chromium(VI) as copper chromate⁴⁹. Minerals are also used to extract chromium(VI). Among those used are goethite, hydrocaluminite and ettringite^{50–52}. An advantage of minerals is that they are usually resistant to oxidation.

Electrolytic methods involve electrokinetic extraction, a technique where electrodes are placed in the ground and the metal ions migrate under the influence of a DC current¹, and electrochemical oxidation where any recovered chromium(III) can be converted back to the chromium(VI) form⁵³. In the electrokinetic extraction of chromium(VI) from glacial till soils, alkaline conditions exist throughout the soil because of its high carbonate buffering capacity. The migration of CrO_4^{2-} toward the anode is efficient. By contrast, in kaolin soils a pH gradient ranging from ≈ 2 near the anode to 12 near the cathode develops because of the electrolysis of water. Adsorption of chromium(VI) and its conversion to the large monoanionic HCr_2O_7^- in the vicinity of the anode results in low chromium(VI) removal⁵⁴.

2.4. Liquid-Liquid Extraction with Amines

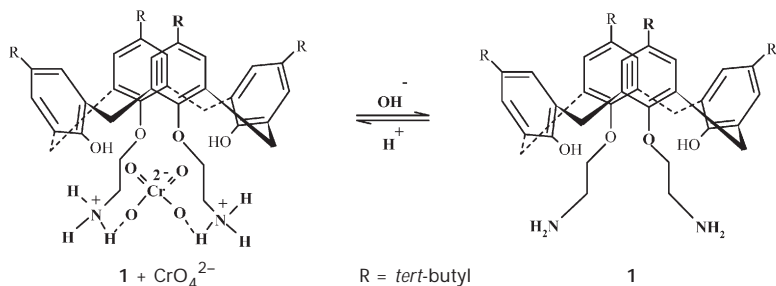
Chromium(VI) has been extracted from aqueous solution by phase transfer into an organic liquid. The phase transfer is assisted by the addition of an amine. In acid solution the nitrogen on the amine is protonated, and the resulting alkylammonium cation forms a salt with HCr_2O_7^- . Simple short chain amines do not extract chromium(VI), but trioctylamine is effective⁵⁵. The *bis*-ammonium salt $\text{Oct}_3^+\text{NCH}_2\text{CH}_2\text{N}^+\text{Oct}_3$ also shows good extraction properties for both dichromate and chromate anions⁵⁶.

2.5. Liquid-Liquid Extraction with Calixarenes

Calixarenes⁵⁷⁻⁵⁹ have several advantages for use as extractants for chromium(VI). One advantage is that their aromatic core structure is stable to oxidation. Other advantages are that multiple functionalities can be appended both for associating with the oxoanion and for binding to the cation. This association can be in the form of hydrogen bonding between substituents on the calixarene and one or more of the oxygen atoms on the periphery of the oxoanion. Herein the present approach highlights a series of examples for chromium(VI) oxoanion recognition with functionalized calixarenes.

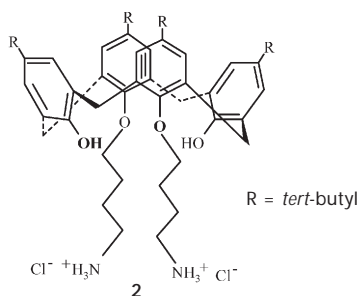
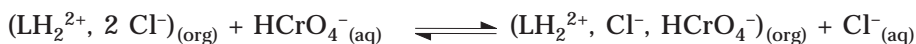
2.6. Calixarenes with Aminoalkyl Functionalities

An early use of a calixarene for the extraction of chromium(VI) employed amine substituents on the narrow rim of the calix[4]arene which can hydrogen-bond with the oxoanion⁶⁰. In this system a calix[4]arene diamine **1** extracted chromium(VI) from an acidified aqueous phase into a chloroform phase, but not from a neutral aqueous phase (Scheme 1).



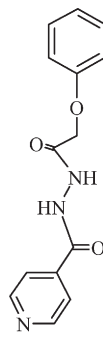
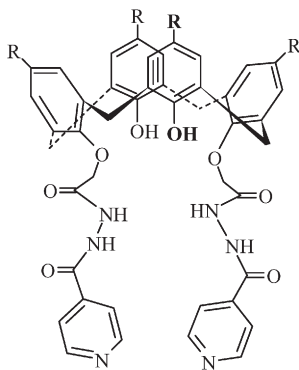
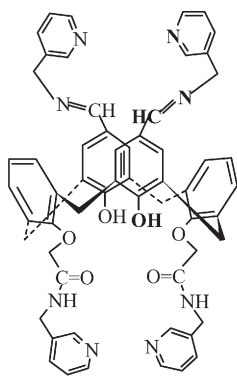
SCHEME 1

Longer alkyl chain homolog **2** extracts Cr(VI) as the protonated diamino-calix[4]arene derivative⁶¹. A study of parameters such as ligand concentration, pH or diluent was carried out and allowed to specify the stoichiometry of the extracted species. At pH 2.6 chromium(VI) was shown to be extracted by the diprotonated diamino-calix[4]arene and at higher pH by the monoprotinated diamino-calix[4]arene. It seems that the following two equilibria coexist:



2.7. Calixarenes with Pyridine Functionalities

Pyridine is another substituent that is more oxidatively stable than an amine, and two derivatives **3** and **4** have been used to synthesize pH-reversible chromium(VI) extractants^{62,63}.



Aqueous solutions of $\text{Na}_2\text{Cr}_2\text{O}_7$ show no extraction into an organic phase in absence of extractant. From the extraction data in Table I, **3** is effective for the phase transfer of dichromate at pH 3.5, and **4** is effective at lower pH. The extraction with **3** at pH 1.5–2.5 cannot be carried out. It is clear that **3** does not extract HCr_2O_7^- significantly at pH 4.5 because **3** contains proton-switchable binding sites appropriate for the aggregation of anions at low pH (i.e. pH 3.5). Liquid–liquid experiments were also performed with the non-cyclic monomeric analog **5**, to understand the chelating effect of both pyridine fragments in the anion binding. It was observed that the dichromate anion was extracted only in trace amounts. Based on the results it has been concluded that calix[4]arene unit plays a very important role in confirming the cooperative participation of the both peripheral pyridine groups⁶³.

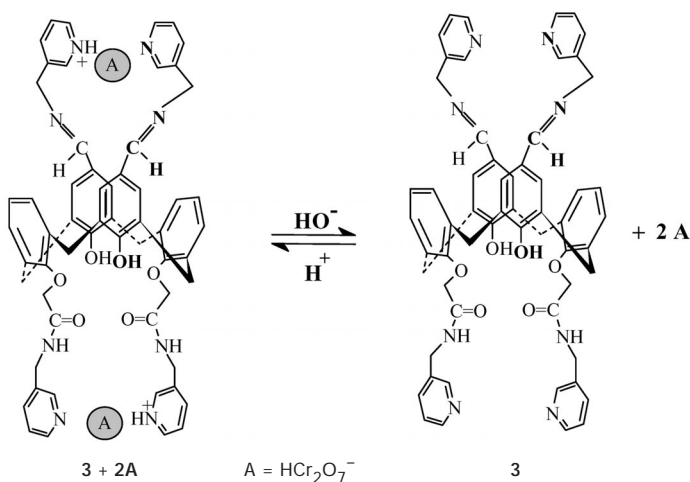
TABLE I
Percentage extraction of dichromate with ionophores **3**–**5**

Compound	Dichromate anion extracted, %			
	pH			
	1.5	2.5	3.5	4.5
3	n.d.	n.d.	40.0	5.0
4	60.8	25.2	–	–
5	<1.0	<1.0	<1.0	<1.0

Observations show that the extraction ratio decreases as the pH of the solution increases, showing that the partially protonated form of **3** is the effective host for the dichromate anions. Upon addition of NaOH to the aqueous layer, the deprotonated calixarene **3** in the dichloromethane is no longer an effective host molecule for HCr_2O_7^- , and the monoanion migrates back into the aqueous layer in a reversible process⁶² (Scheme 2).

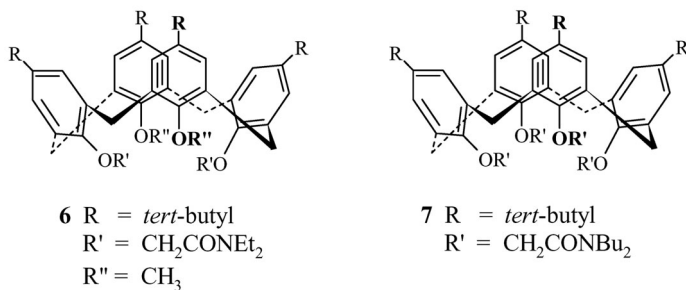
2.8. Calixarenes with Amide Functionalities

Subsequently amide substituents have been used because these functionalities are more resistant to oxidation, and also because amide **6** has both nitrogen and oxygen atoms available for hydrogen bonding with the oxoanion⁶⁴.



SCHEME 2

The introduction of the more hydrophobic butyl groups allows for the extraction into a less polar organic phase⁶⁵. The resulting compounds (**7** and its isomers) are effective extractants for chromium(VI) from an aqueous phase into a toluene phase, but ineffective for extraction into an isoctane phase.



Subsequent studies on these systems have resulted in the monomeric calix[4]arene amide **8**, which effectively extracts chromium(VI) being incorporated into a polymer⁶⁶. Merrifield resin having polystyrene backbone, which is generally insoluble in most of the organic solvents has been chosen for modification with **8**. The resulting polymer **9** is soluble in organic solvents, and can therefore be used as liquid-liquid extractant. The polymer **9** is a better extractant for chromium(VI) than is its parent monomer **8** (Fig. 1). It is possible that the polymer plays a role whereby it folds into conformations that place functional groups on several of the calix[4]arene moieties in the polymer in a preferred conformation where they can associate with the oxoanion.

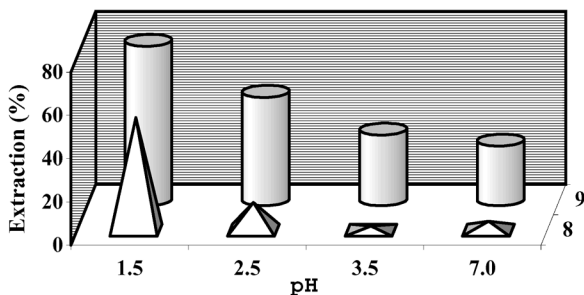
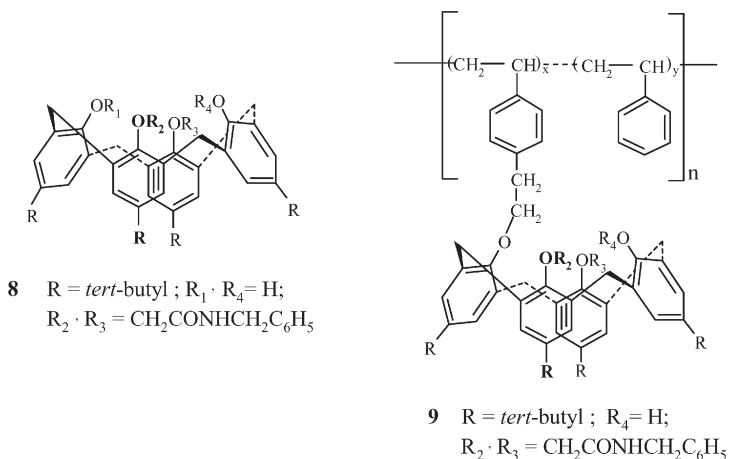


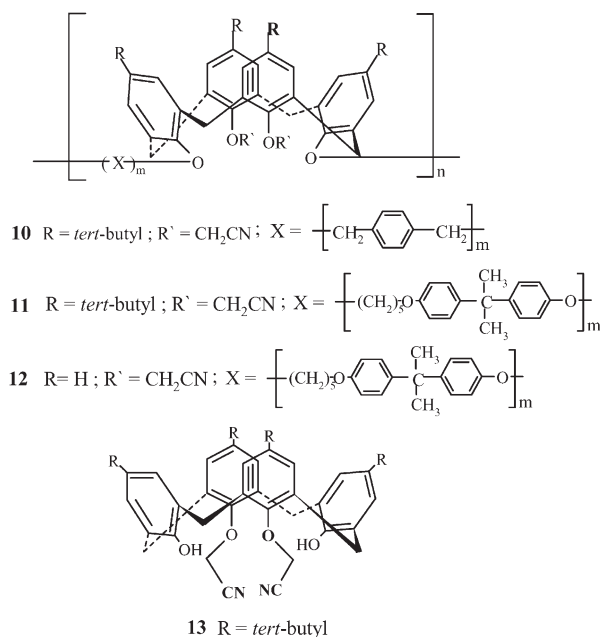
FIG. 1

Plots of extraction percentage versus pH following the two-phase solvent extraction of Cr(VI) with **8** and **9**

2.9. Calixarenes with Nitrile Functionalities

A recent development is the discovery that calix[4]arenes with nitrile substituents act as phase transfer extractants for chromium(VI), and that their effectiveness is higher with aqueous solutions that are acidic⁶⁷.

This research shows that due to the higher oxidative stability of nitrile groups, oligomers **10–12** have been developed as better extractants than is the monomer **13** for transferring the HCr_2O_7^- anion at pH 1.5–4.5 (Fig. 2). This implies that the better preorganization of the immobilized calix[4]arene receptors **10–12**, where the cooperative effect of both nitrile units is possible, improve extraction. By contrast, the monomer **13** is significantly more flexible than are the copolymers **10–12**, and it exhibits poor extraction ability towards dichromate anions. Besides this, the conforma-



tion of the immobilized calix[4]arene dinitrile derivative has significantly less flexibility because the dual xylene substitution locks it in the *cone* conformation in the liquid phase. It is observed that copolymer **10** does not exhibit enhanced ion-pair extraction of sodium salt at the water-dichloromethane interface.

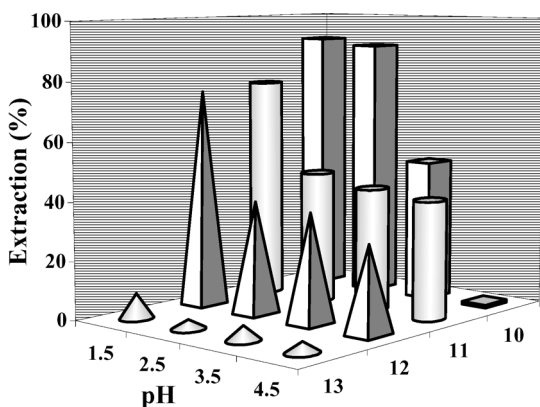
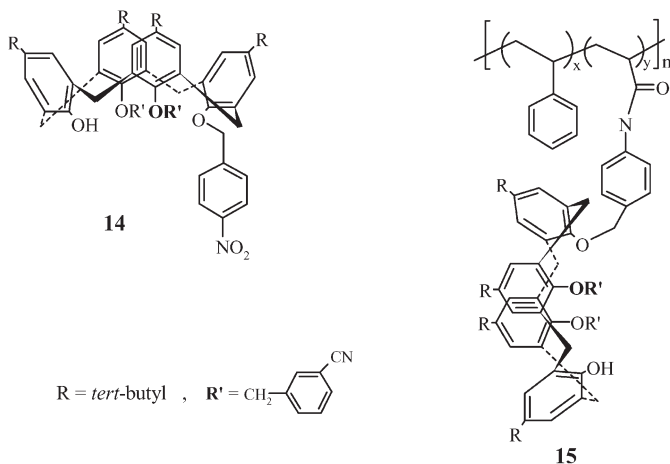


FIG. 2

Plots of extraction percentage versus pH following the two-phase solvent extraction of Cr(VI) with **10–13**

In this case, the alkylammonium cation functionalities can hydrogen-bond with HCr_2O_7^- .

Similar results are observed with the bis(benzonitrile) derivative **14** and its copolymer **15**⁷⁰.



A preliminary evaluation of the efficiency of the extractants **14** and **15** has been carried out by solvent extraction of sodium dichromate from water into dichloromethane at different pH values. The results are graphically summarized in Fig. 3. The monomer **14** exhibits a high extraction ability for dichromate at low pH, whereas the derivative **13** of *p*-*tert*-butylcalix[4]-arene shows poor extraction affinity toward dichromate. The increase in

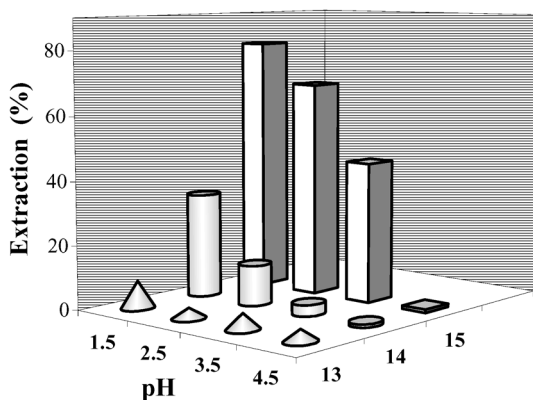


FIG. 3

Plots of extraction percentage versus pH following the two-phase solvent extraction of Cr(VI) with **13–15**

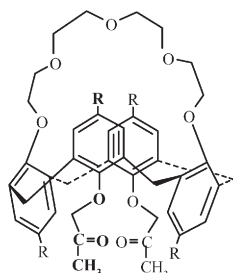
the extraction affinity of **14** over **13** may be due to the planar geometry of the aromatic rings with the nitrile groups, and its more rigid structural features as compared to **13**.

The conversion of **14** into an immobilized polymeric structure **15** significantly increases the anion extraction ability at $\text{pH} < 4.0$. This result can be explained by the fact that the calixarene derivatives in the polymeric matrix may have gained a more rigid and appropriate structure, which assists the transfer of dichromate anions in a two-phase extraction systems. For ionophores **14** and **15**, lowering the pH of the aqueous phase increases the percentage of dichromate extracted. This pH dependence can again be explained by anion hydration. The importance of ion hydration in liquid-liquid phase extraction has been documented by Hofmeister⁶⁸. In aqueous solutions having a lower pH, the dichromate will be primarily in its protonated form HCr_2O_7^- . This monoanion has a smaller Gibbs energy of hydration than does the dianionic form $\text{Cr}_2\text{O}_7^{2-}$. As a result, there is a smaller loss in hydration energy as HCr_2O_7^- is transferred from the aqueous phase into the dichloromethane phase. An additional advantage of HCr_2O_7^- over $\text{Cr}_2\text{O}_7^{2-}$ is that for the former only one sodium ion needs to be coextracted to maintain charge balance, whereas for $\text{Cr}_2\text{O}_7^{2-}$ two sodium ions are extracted, with additional loss of hydration energy. For these compounds we discount the possibility that increased extraction at the lower pH values is due to protonation of the nitrile nitrogens to give a dication. Because the $\text{p}K_a$ of $\text{CH}_3\text{C}\equiv\text{NH}^+$ is -4.3 , the protonated form is not expected to be present in significant concentrations in aqueous solutions having pH values in the 1.5–4.5 range⁷¹. The extraction ratios decrease at higher pH. The most significant difference is observed for the case of copolymer **15**, which shows a high affinity toward HCr_2O_7^- . Due to the high oxidative stability of nitriles, copolymer **15** is a suitable candidate for the phase-transfer extraction of HCr_2O_7^- . Similar results have been found for polymeric calix[4]arene dinitriles and diamines. Both polystyrene and poly(oxyethylene) backbones have been used, but there is no evidence that the oxygen atom in the polymeric backbone is a binding site for the chromium(VI) anion⁶⁷.

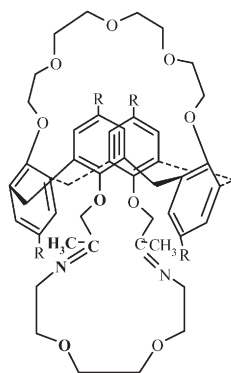
2.10. Calix[4]arenes Incorporated with a Crown Ether Moiety

A next generation of calix[4]arenes incorporate a crown ether moiety into the structure in addition to the functionalities that have previously resulted in them being extractants for chromium(VI). The crown ether moiety is used because it is a good complexant for Group 1 metal cations such as

sodium and potassium. These calix[4]arenes therefore have complementary binding sites for oxoanions and the widely occurring Group 1 cations. Examples of such calixcrowns are **16** and **17**⁷².

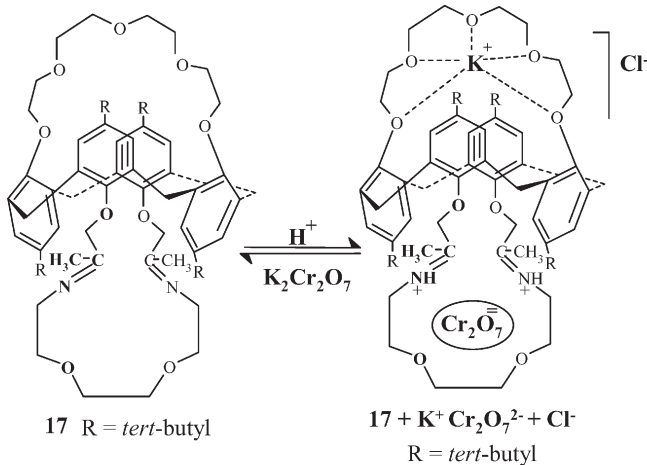


16 R = *tert*-butyl



17 R = *tert*-butyl

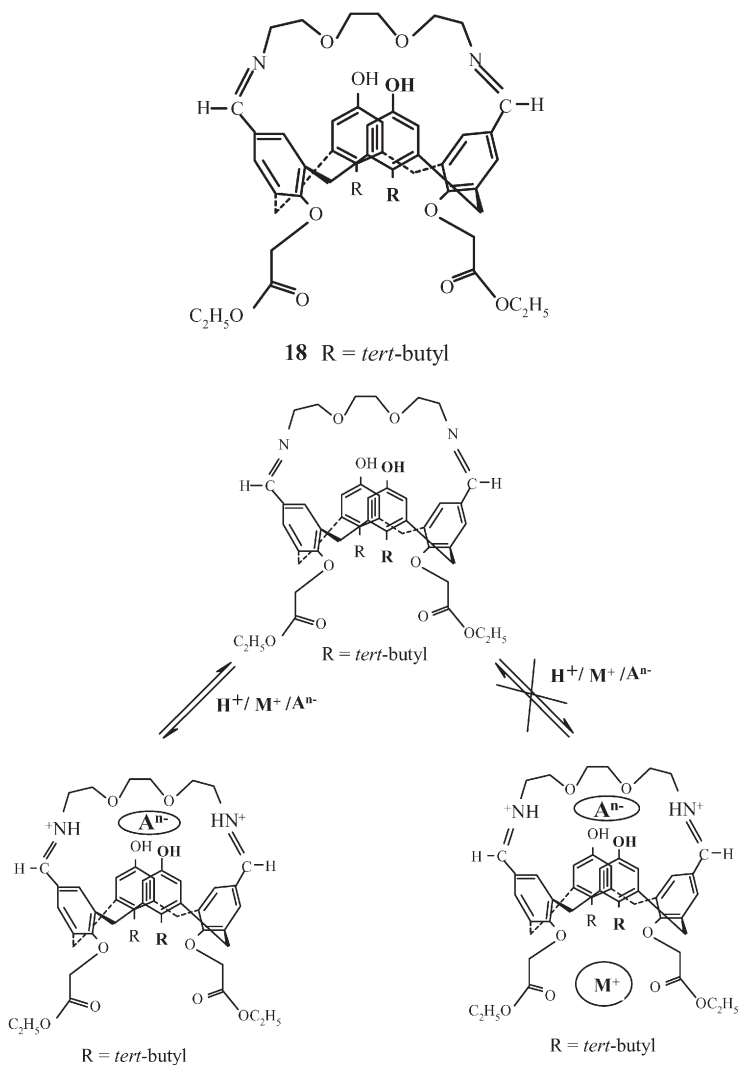
Calixcrown **17** is an effective extractant for transferring dichromate from an aqueous into a dichloromethane layer. The proposed interactions of **17** with the metal and dichromate ions are shown in Scheme 5.



SCHEME 5

Allosteric effects must, however, also be considered⁷³. The protonated form of **18** is an effective extractant for the dichromate anion, but not for the sodium cation.

A contribution to this observation is the allosteric effect of the crown part of the upper rim, which does not allow the ester groups on the lower rim to cooperatively complex with sodium (Scheme 6).



SCHEME 6

The data shown in Table II highlight the compound **18** as an excellent extractant toward dichromate anions at low pH and Table III shows the failure of **18** to extract Na^+ ions.

To clarify the phenomena, similar experiments were performed on compound **19** (Scheme 7). From the results it has been observed that the diester derivative of *p-tert*-butylcalix[4]arene (**19**), which has a cone conformation, is a good extractant for Na^+ ions even at low pH, but a poor extractant for

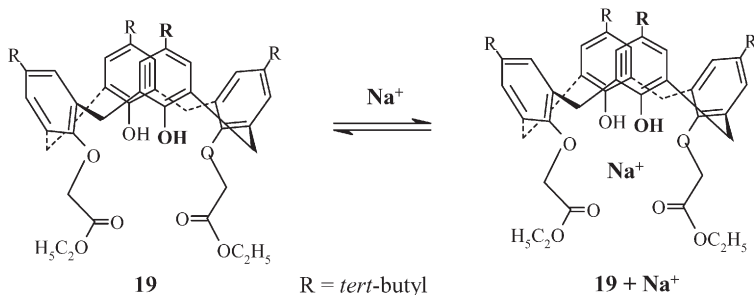
TABLE II
Percentage extraction of dichromate with ionophores **18** and **19**

Compound	Dichromate anion extracted, %		
	pH		
	1.5	2.5	4.5
18	73.7	78.8	7.9
19	3.8	3.1	3.4

TABLE III
Percentage extraction of sodium with ionophores **18** and **19**

Compound	Sodium ion extracted, %		
	pH		
	1.5	2.5	4.5
18	<1.0	<1.0	<1.0
19	43.4	52.5	53.7

dichromate ions (Tables II and III). From these observations it has been concluded that the conformation of the calix[4]arenes, the cooperativity and allosteric effects of the functionalities play important roles in two-phase extraction systems.



SCHEME 7

3. CONCLUSIONS

Although significant advances have been made in developing hosts that will extract chromium(VI) oxoanions, challenges still exist. One challenge is achieving selectivity against other oxoanions such as sulfate, phosphate and nitrate. Another is achieving resistance against oxidation by chromium(VI). The increased extraction of chromium(VI) at low pH has two consequences. The first is that at low pH the oxoanion is a dimeric monoanion with a low hydration enthalpy, therefore it aids selectivity against monomeric dianions. The second consequence, however, is that chromium(VI) is a better oxidizing agent in acidic solution, which increases the challenge to finding a stable extractant.

We thank the R. A. Welch Foundation (Grant No. D-1408), the US National Science Foundation (Grant No. INT-0111170), and the Scientific and Technical Research Council of Turkey (TUBITAK-Grant No. U/9-101T002) for financial support of this work.

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