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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Tabakci, Mustafa , Ersoz, Mustafa and Yilmaz, Mustafa(2006) 'A Calix[4]arene-Containing Polysiloxane Resin for Removal of Heavy Metals and Dichromate Anion', Journal of Macromolecular Science, Part A, 43: 1, 57 – 69

To link to this Article: DOI: 10.1080/10601320500405901

URL: <http://dx.doi.org/10.1080/10601320500405901>

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A Calix[4]arene-Containing Polysiloxane Resin for Removal of Heavy Metals and Dichromate Anion

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A new calix[4]arene-based polysiloxane resin (CBPSR) was prepared from 5,11,17,23-tert-butyl-25,27-bis(cyanomethoxy)-26-(chloroformyl)-28-hydroxy-calix[4]arene via nucleophilic substitution reaction with 3-aminopropyltriethoxysilane and followed by copolymerization with octyltriethoxysilane. Batchwise extraction studies have revealed a high adsorption ability of the calix[4]arene-nitrile derivatives loaded resin toward heavy metals (Cu^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Hg^{2+} and Pb^{2+}) and dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$). Liquid–liquid extraction studies show that the monomeric analogs (2, 3 and 4) do not exhibit a good affinity toward these ions.

Keywords calixarene, polysiloxane resin, metal, dichromate anion, extraction, adsorption

Introduction

Calixarenes, which are considered the third-generation of supramolecules (1, 2), have a molecular framework with ‘upper rim’ and ‘lower rim’ that can be separately and selectively modified with different functionalities to achieve metal complexing properties and the desired solubility characteristics (3, 4). A number of polymeric calixarenes, for removal of toxic metal ions and dichromate anion from aqueous media, have been reported in the literature (5–15). Generally, two strategies have been adopted in order to enhance the affinity of calixarenes toward metal ions and anions; either there have been incorporated different ionophoric groups, such as carbonyl, amide, nitrile and other suitable functionalities, onto the calix-platform or the calixarene units were fixed in a polymeric matrix. In this regard, various studies have been carried out, for instance, calix[4]arene tetraethyl ester and calix[6]arene hexaethyl ester were incorporated onto the surface of silica particles after hydrosilylation of the *p*-allyl calixarenes for selective adsorbents of Na^+ ions (16, 17). Chelating calix[4]arene hydroxamates supported onto silica particles have been studied for their uptake of different transition metal ions (18). Silica-bonded tetrameric calixarene tetra-diethylamide was evaluated for its chromatographic selectivity (19). Li et al. reported the preparation of polysiloxane resins by the cohydrolysis and the polycondensation of calix[4]arene-containing organo-siloxane monomers and tetraethyloxysilane (20). In 1995, Zhong et al. reported the first

Received May 2005; Accepted July 2005.

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efforts in synthesizing such polymers (21). As a result, the modified polysiloxanes were widely used as stationary phases or adsorbents in analytical chemistry and separation technology, as catalyst supports in catalysis and organic synthesis (22–32).

From an environmental and economic viewpoint, there remains a need to discover more selective and effective extractants for anions particularly chromate/dichromate from waters and soils. 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 expression (33–36). Although chromium(VI) can be removed after 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 or solid–liquid extraction of chromium(VI) from aqueous solution has some advantages. Since chromium(VI) is an anion, occurring either as HCr_2O_7^- or CrO_4^{2-} , in order to remove it by extraction in which necessary to use an anion host (37–44). In our previous work, we have also synthesized a few polymeric calixarenes and were investigated in details their cation and anion extraction properties (7–11).

The increase in industrial activity over the years has resulted in the contamination of ground and surface water by toxic metal ions (45). In developing countries, water pollution generated by industrial effluents has been a serious issue (46). In order to have ecologically sustainable growth, time-to-time analysis of metal ions, such as Cr^{6+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Co^{2+} , Ni^{2+} etc. in natural waters, as well as in bio-fluid samples, is required. Toxic heavy metals are dangerous because of their accumulative and persistent character in the environment. Some of these metals such as cadmium, mercury, copper and lead are toxic and pose a threat to human health (47). The importance of controlling the levels of environmental pollutants has generated an increasing interest in the development of novel sensors such as, calixarene-based ion selective electrodes or chemically modified field effect transistors for the detection of the heavy metals (48–51).

In this paper, the synthesis of a new calix[4]arene-containing polysiloxane copolymer (CBPSR) with octyltriethoxysilane and its adsorption properties for some heavy metals and dichromate anion have been reported in details.

Experimental

Materials

Analytical TLC was performed on precoated silica gel plates (SiO_2 , Merck PF₂₅₄), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 Mesh). Acetone, CH_2Cl_2 and MeOH was distilled from CaSO_4 , CaCl_2 and over Mg, respectively. Tetrahydrofuran (BDH) and toluene were dried by refluxing over sodium/benzophenone and CaH_2 , fractionally distilled, respectively and then stored over molecular sieves. All the chemicals were purchased from Merck or Aldrich. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Co^{2+} ,

Ni²⁺, Cu²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ picrates were prepared according to previously studies (10, 11).

Measurements

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃ with TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-VIS spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. Sodium determinations were made on a JENWAY PFP7 flame photometer.

Synthesis

Compounds **1** and **2** were prepared according to known procedures (52, 53), and the other compounds employed in this work, as illustrated in Scheme 1, have been synthesized as follows.

Synthesis of 5,11,17,23-*tert*-butyl-25,27-bis(cyanomethoxy)-26-(ethoxyformyl)-28-hydroxy-calix[4]arene (**3**)

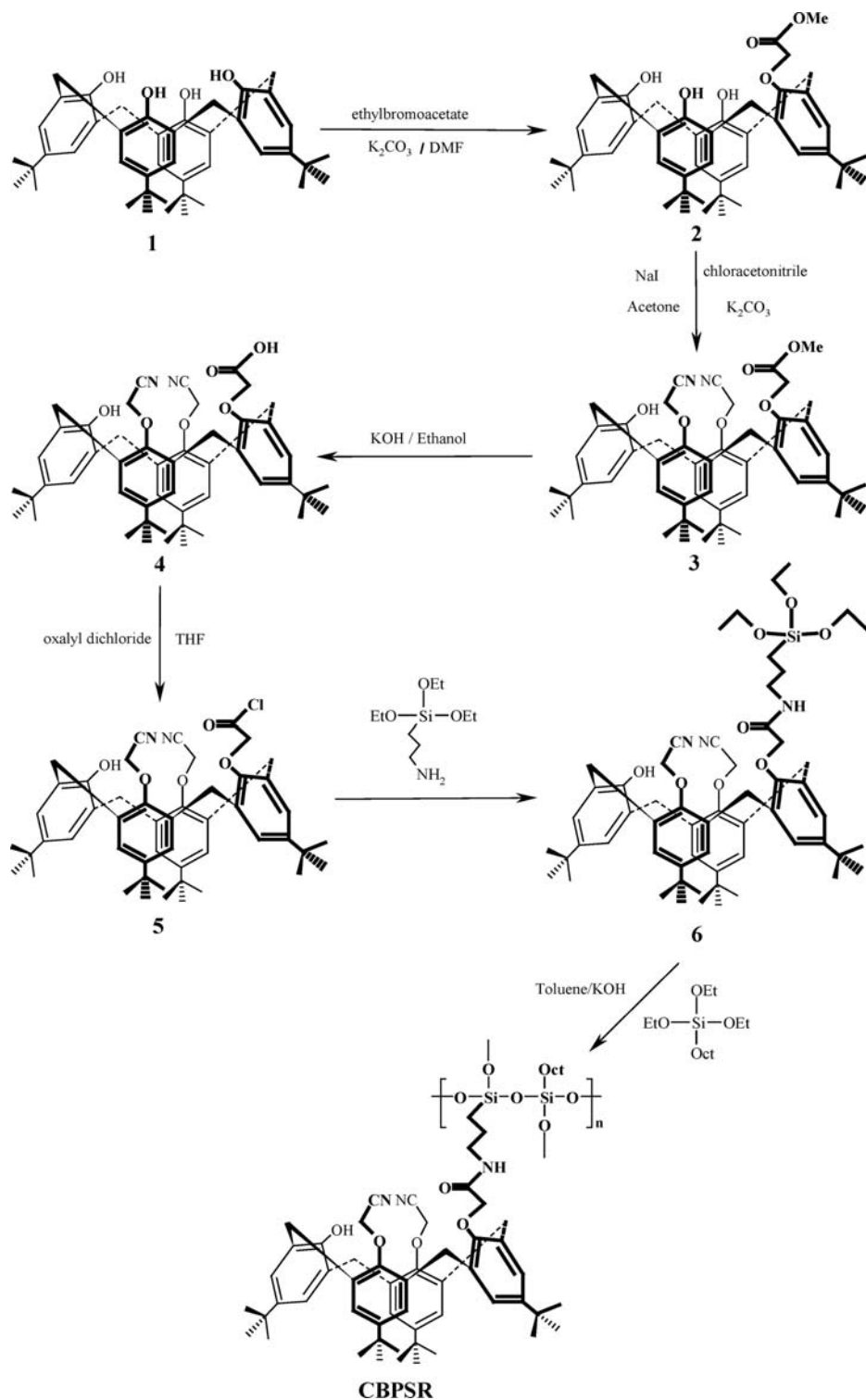
A mixture of **2** (3.00 g; 4.08 mmol), K₂CO₃ (2.32 g; 16.81 mmol), chloroacetonitrile (0.77 mL; 12.24 mmol), and sodium iodide (3.67 g; 24.48 mmol) in dry acetone was stirred and heated under reflux for 8 h. The cooled mixture was filtered, and then washed with dichloromethane. The filtrate was evaporated under reduced pressure, and 40 mL anhydrous ethanol was added to produce a light yellow precipitate. The light yellow precipitate was removed by filtration and recrystallized from anhydrous acetone to give pure crystals of 2.8 g of compound **3**. Yield 87%; m.p. 135°C.

IR(KBr): 3483 cm⁻¹ (OH) and 1754 cm⁻¹ (C=O). ¹H NMR (CDCl₃), δ 0.76 (s, 9H, *tert*-butyl), 0.89 (s, 9H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl), 1.29 (s, 3H, OCH₃), 3.31 (d, *J* = 13 Hz, 4H, ArCH₂Ar), 3.35 (s, 2H, OCH₂CN), 4.19 (d, *J* = 13 Hz, 2H, ArCH₂Ar), 4.29 (d, *J* = 13 Hz, 2H, ArCH₂Ar), 4.57 (s, 2H, OCH₂CN), 4.76 (s, 2H, OCH₂CO), 6.27 (s, 1H, ArOH), 6.60 (s, 2H, ArH), 6.73 (s, 2H, ArH), 7.01 (m, 4H, ArH). Calculated for C₅₁H₆₂N₂O₆: C, 76.66; H, 7.82; N, 3.51. Found: C, 76.69; H, 7.80; N, 3.54.

Synthesis of 5,11,17,23-*tert*-butyl-25,27-bis(cyanomethoxy)-26-(hydroxyformyl)-28-hydroxy-calix[4]arene (**4**)

Potassium hydroxide (0.10 g; 1.85 mmol) was added to a solution of monoester derivative **3** (1.50 g; 1.85 mmol) in ethanol and the solution was heated under reflux for 2 h, cooled and poured into distilled water and acidified with 0.1 N HCl. Then, the suspension mixture was filtered and washed with distilled water until free from acid and dried to give compound **4**. Yield (1.37 g; 95%); m.p. 272°C.

IR (KBr) 3438 cm⁻¹ (OH) and 1742 cm⁻¹ (C=O). ¹H NMR (CDCl₃), δ 0.80 (s, 9H, *tert*-butyl), 0.95 (s, 9H, *tert*-butyl), 1.18 (s, 18H, *tert*-butyl), 3.22–3.38 (m, 6H, ArCH₂Ar and OCH₂CN), 4.10 (d, *J* = 13 Hz, 2H, ArCH₂Ar), 4.15 (d, *J* = 13 Hz, 2H, ArCH₂Ar), 4.48 (s, 2H, OCH₂CN), 4.59 (s, 2H, OCH₂CO), 6.68 (s, 1H, COOH), 6.79 (s, 1H,



Scheme 1. Schematic representation of synthesis of CBPSR.

ArOH), 6.85 (s, 2H, ArH), 6.92–7.12 (m, 6H, ArH). Calculated for $C_{50}H_{60}N_2O_6$: C, 76.50; H, 7.70; N, 3.57. Found: C, 76.55; H, 7.67; N, 3.59.

Synthesis of 5,11,17,23-tert-butyl-25,27-bis(cyanomethoxy)-26-(chloroformyl)-28-hydroxy-calix[4]arene (5)

Monoacid **4** (0.50 g; 0.64 mmol) was dissolved in 30 mL of dry THF, oxalyl dichloride (0.1 mL; 1.28 mmol) and two drops of Et_3N was added under N_2 atmosphere. The mixture was heated to reflux for 3 h and unreacted oxalyl dichloride and solvent were removed by distillation. The solid residue was diluted with 5 mL of dry THF and solvent was distilled off to remove traces of $(COCl)_2$. This procedure was repeated three times and the solid residue was then dried under vacuum at $80^\circ C$ to give 0.51 g of monoacid chloride **5** and used without purification for a further stage.

Preparation of Calix[4]arene-Based Polysiloxane Resin (CBPSR)

To a solution of compound **5** (1.3 g; 1.66 mmol) in dry THF (20 mL) 3-aminopropyltriethoxysilane (0.39 mL; 1.66 mmol) was added. The mixture was stirred at room temperature for 10 h under a nitrogen atmosphere and then octyltriethoxysilane (0.2 mL; 1.01 mmol), freshly distilled dry toluene (10 mL) and potassium hydroxide (0.1 mL; 1 M) were added, and stirred at room temperature for 5 h under nitrogen atmosphere. The mixture was stirred and boiled further at reflux under streaming dry nitrogen gas for 24 h. Finally, the solid product was filtered and washed in sequence with warm toluene, acetone, methanol, and distilled water three times. The product was dried at $120^\circ C$, under vacuum, for 3 h to give 0.8 g resin **7** in 73% yield and kept in a desiccator before use.

Liquid–Liquid Extraction Studies

Picrate/dichromate liquid–liquid extraction experiments were performed following Pedersen's procedure (54). A 10 mL of a $2.0 \times 10^{-5} M$ aqueous picrate/dichromate solution and 10 mL of $1.0 \times 10^{-3} M$ solution of calixarene (**3** and **4**) or a $1.0 \times 10^{-3} M$ solution of calix[4]arene unit/g oligomer (**5**) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at $25^\circ C$ for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described (33). Blank experiments showed that no picrate/dichromate extraction occurred in the absence of calixarene. The percent extraction (E%) has been calculated as:

$$(E\%) = A_0 - A/A_0 \times 100 \quad (1)$$

where A_0 and A are the initial and final concentrations of the metal picrate before and after the extraction, respectively.

Batchwise Adsorption Studies

About 0.025 g (W) of CBPSR was shaken with 10 mL of aqueous solution containing 10 mL (V) of a sodium dichromate ($1.0 \times 10^{-4} M$) or a metal picrate solution ($2.0 \times 10^{-5} M$) with known concentration (C_i) in a 50 mL-closed glass flask at $25^\circ C$ for 1 h and filtered off. The concentration of the dichromate ion remaining (C_e) in

Table 1
Elemental analysis results of CBPSR^a

Silanized calixarene	C (%)	H (%)	N (%)	Bonded-amount (mmol g ⁻¹)
CBPSR	71.61	8.12	4.11	0.978

^aCalculated according to the carbon, hydrogen and nitrogen content.

aqueous phase after the adsorption was then determined spectrophotometrically. The adsorption capacity (q) was calculated as:

$$q = [(C_i - C_e)V]/W(\text{mmol/g}) \quad (2)$$

Results and Discussion

The main focus of this work is the design of the new calixarene-based polymeric resin that is easily accessible, and effective binding character for a particular set of heavy metals and the dichromate anion. This resin could also be useful for multiple applications; such as laboratory, clinical, environmental, and industrial process analysis. To achieve the desired goal, we have prepared 5,11,17,23-*tert*-butylcalix[4]arene **1** as a starting material through the base catalyzed condensation reaction (52). A synthetic scheme has been developed to enable its derivatization. This synthetic route is depicted in

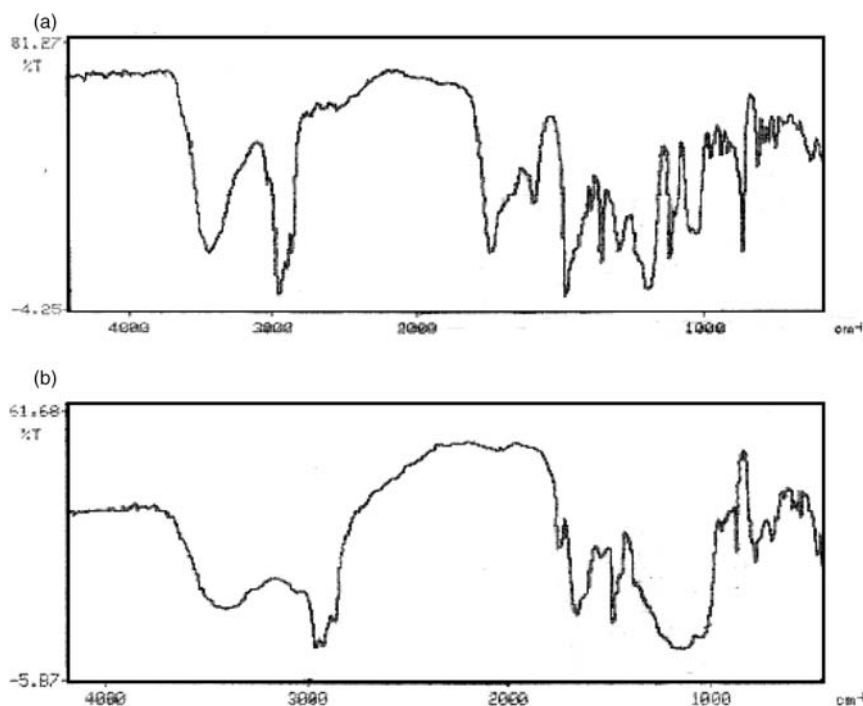


Figure 1. FTIR spectra of *p*-*tert*-butyl-calix[4]arene dinitril derivative **4** (a) and CBPSR (b).

Table 2
Extraction percentage of metal picrates with **2**, **3** and **4**^a

Ligand	Picrate salt extracted (%)					
	Co ²⁺	Ni ²⁺	Cu ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺
2	1.2	2.3	3.1	3.8	2.7	2.6
3	2.0	2.5	2.3	3.2	4.1	2.9
4	2.6	2.7	2.4	3.5	4.4	3.0

^aAqueous phase, [metal picrate] = 2.0×10^{-5} M; organic phase, chloroform, [ligand] = 1.0×10^{-3} M, at 25°C, for 1 h.

Scheme 1. The synthesis for compounds **1** and **2** are based on previously published procedures (52, 53), while the synthesis for the other compounds **3–6** and CBPSR are reported here for the first time. Therefore, the following strategy was outlined in Scheme 1, compound **1** has been treated with ethylbromoacetate in dry acetone in the presence of potassium carbonate to yield the calix[4]arene **2** (53). Refluxing a mixture of **2** with chloroacetonitrile in dry acetone in the presence of potassium carbonate and sodium iodide provide the cone conformer **3** in 81% yield. The ¹H NMR spectrum of **3** has a typical AB pattern for the methylene bridge protons (ArCH₂Ar) of the calixarene moiety at 3.31, 4.19 and 4.29 ppm ($J = 13$ Hz). The aliphatic protons at 3.35 and 4.57 ppm indicate that substitution of chloroacetonitrile groups has occurred. Subsequent hydrolysis of ester group of **3** by KOH in ethanol gives the acid derivative **4** in 95% yield. Completion of the reaction has been followed by IR spectroscopy, which shows the disappearance of the band is due to the ester carbonyl group at 1761 cm^{-1} , while the appearance of the band is due to the acid carbonyl group at 1742 cm^{-1} . The ¹H-NMR spectrum of **4** has typical protons of methylene bridges at 3.22–3.38 ppm (ArCH₂Ar and OCH₂CN), 4.10 ppm ($J = 13$ Hz, ArCH₂Ar), 4.15 ($J = 13$ Hz, ArCH₂Ar) and 4.48 (OCH₂CN), and at 6.68 ppm for COOH group. Then, **4** is treated with oxalyl dichloride in dry THF under reflux to yield the acid chloride in a quantitative yield. The acid chloride **5** is useful synthetically in a number of ways. Simple replacement of chlorine can lead directly to other modifications, but due to its high reactivity, no attempts were

Table 3
Extraction percentage of dichromate anion with **2**, **3** and **4**^a

Ligand	pH			
	1.5	2.5	3.5	4.5
2	<1.0	<1.0	<1.0	<1.0
3	4.3	3.6	3.7	4.0
4	3.9	4.0	3.8	3.6

^aAqueous phase, [sodium dichromate] = 1.0×10^{-4} M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3} M, at 25°C, for 1 h.

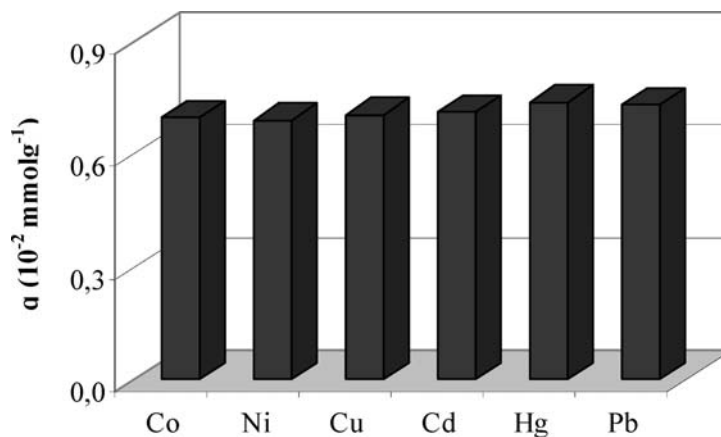


Figure 2. Adsorption capacity of heavy metals by CBPSR (25°C, 24 h, $C_i = 0.02 \text{ mmol} \cdot \text{L}^{-1}$).

made to purify the crude product; thus it was used in subsequent preparation without purification. Treatment of **5** with 3-aminopropyltriethoxysilane and then octyltriethoxysilane in dry toluene in the presence of KOH under nitrogen atmosphere gave polysiloxane resin **7**. Consequently, 0.8 g of an insoluble resin (CDBAPS) in organic solvents in 73% yield was obtained. It was characterized by elemental analysis and FTIR. According to the carbon, hydrogen and nitrogen content shown in Table 1, it was concluded that the bonded calixarene amount was found to be approximately $0.978 \text{ mmol g}^{-1}$. Also from the FTIR results shown in Figure 1, it was observed that compound **5** copolymerized with octyltriethoxysilane, due to 3398 cm^{-1} , 1664 cm^{-1} and 783 cm^{-1} bands in IR spectra corresponded to O–H, NH–C=O and Si–O, respectively.

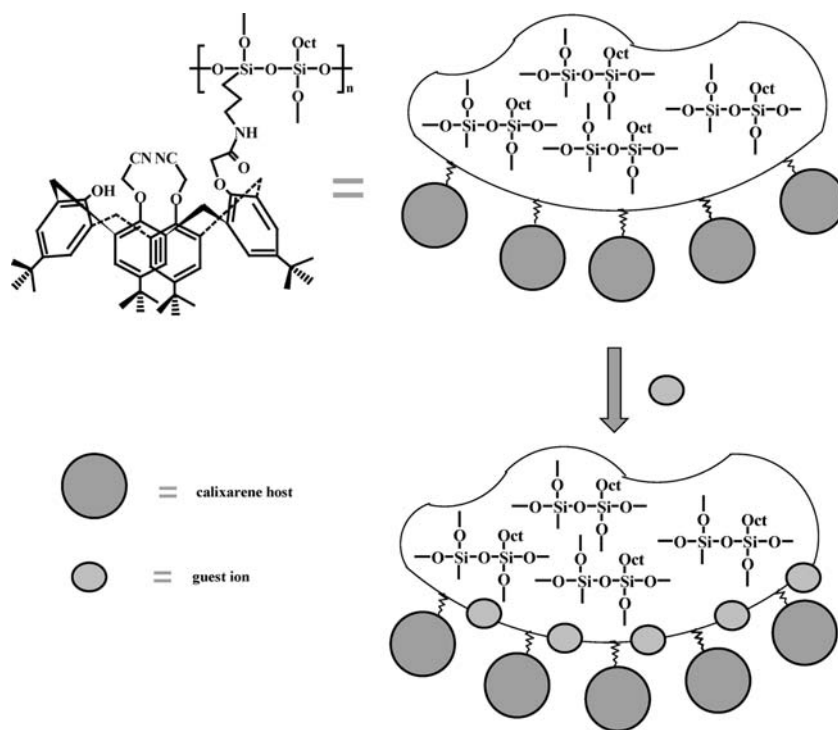
Liquid–Liquid Extraction Studies

We are interested in synthesizing a calix[4]arene-based polysiloxane resin, and to examine its extraction behavior for heavy metal cations and dichromate anion. Therefore, the

Table 4
Adsorption percentages of heavy metals by CBPSR^a

Selected heavy metals	
Co	87.4
Ni	86.4
Cu	88.1
Cd	89.3
Hg	92.4
Pb	91.4

^aSolid phase, adsorbent = 25 mg CBPSR; aqueous phase, metal picrate = $2.0 \times 10^{-5} \text{ M}$, 25°C, 1 h.



Scheme 2. Schematic representation of adsorption of CBPSR with guest ions.

evaluation of the extraction efficiencies of the compounds (**2**, **3** and **4**) has been carried out by the liquid–liquid extraction of heavy metal picrates (Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) under neutral conditions and dichromate anion ($\text{Cr}_2\text{O}_7^{2-}$) at different pH values (1.5, 2.5, 3.5 and 4.5) into chloroform. The results are summarized in

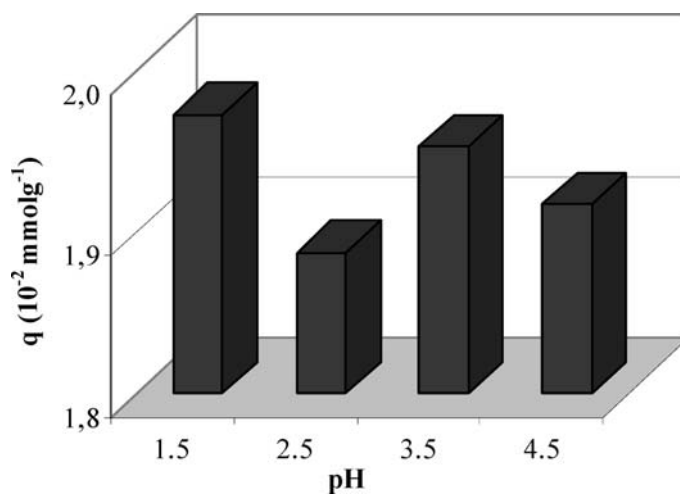


Figure 3. Adsorption capacity of dichromate anion capacity by CBPSR (25°C , 24 h, $C_i = 0.1 \text{ mmol} \cdot \text{L}^{-1}$) in different pHs.

Table 5
Adsorption percentages of dichromate anion by CBPSR^a

pH	
1.5	48.2
2.5	46.5
3.5	47.8
4.5	47.1

^aSolid phase, adsorbent = 25 mg CBPSR; aqueous phase, Na₂Cr₂O₇ = 1.0 × 10⁻⁴ M, at 25°C, 1 h.

Tables 2 and 3, and the data obtained with monomers are included for comparison purposes. These data have been obtained by using chloroform solutions of these compounds (**2**, **3** and **4**) to extract metal picrates and dichromate anion from an aqueous phase. The equilibrium concentration of picrate/dichromate in aqueous phase was then determined spectrophotometrically.

From the data in Table 2 and 3, it can be seen that all ligands are not effective in transferring heavy metal ions and dichromate anion into the organic phase. Herein, from our previous experience, it is important to clarify that dinitril-substituted *p*-tert-butylcalix[4]arene in cone conformation shows very low extraction ability toward Hg(II) and dichromate anion. From our previous studies (7, 8), it is apparent that nitrile functionalities containing calixarenes are selective extractants for Hg²⁺ due to the soft nature of Hg²⁺ as compared to competing cations (55). As we have noted, this may be related to the destabilization of the metal complex due to the steric effect of ester side arm that faces the dinitril groups.

Adsorption Studies

This study was also aimed to synthesize a conformationally stable form of *p*-tert-calix[4]-arene dinitril based polysiloxane resin, which may lead to the enhancement of heavy

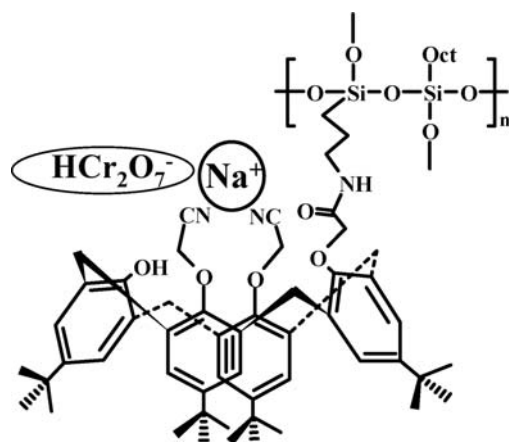


Figure 4. The proposed interactions of CBPSR with Na⁺ and HCr₂O₇⁻ ions.

Table 6
Adsorption percentages of
sodium anion by CBPSR^a

pH	
1.5	50.9
2.5	49.8
3.5	51.2
4.5	49.3

^aSolid phase, adsorbent = 25 mg
CBPSR; aqueous phase,
 $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4}$ M, at
25°C, 1 h.

metals and dichromate anion extraction by minimizing the side arm effect. To achieve this goal, we performed solid–liquid adsorption studies of heavy metals and dichromate anion with CBPSR.

Heavy Metals

From the data given in Figure 2 (Table 4), it was observed that CBPSR has excellent adsorption ability over 85% toward heavy metals. Consequently, the importance of polymeric structures in adsorption phenomena (Scheme 2), as explained in previous studies (7–11), has been seen.

Dichromate Anion

From the extraction and adsorption data given in Figure 3 (Tables 3 and 5), it is clear that the monomeric analogs (**2**, **3** and **4**) have not significantly extracted the dichromate anion. However, the conversion of **5** into the immobilized polymeric structure (CBPSR) has significantly increased the anion extraction ability of the compound. This increase may be due to the more rigid structural features of CBPSR, which could help in transferring anions when compared to **3**. For the CBPSR, this increasing of extraction at the pH 1.5–4.5 range is due to the protonation of the nitrile nitrogens to give a dication. Because the $\text{p}K_{\text{a}}$ of CH_3NH^+ is -4.3 , the protonated form is not expected to be present in significant concentrations in aqueous solutions.

The role of the nitrile functionalities has not been verified, but since by comparison with acetonitrile, the dielectric constant is expected to be high, the role of the calixarene nitrile may be to solvate the sodium cation (Figure 4). The better preorganization of the immobilized calix[4]arene resin (CBPSR), where the cooperative effect of both nitrile units is possible, this improves extraction. By contrast, the monomers (**2**, **3** and **4**) are significantly more flexible than the CBPSR and they exhibit poor extraction ability toward the dichromate anion. To examine this phenomenon, we carried out Na^+ ion analysis of aqueous phase by using flame photometer. The results (Table 6) showed that CBPSR was a good extractant for Na^+ ion and confirmed that phenomenon as explained in previous studies (7–11).

Acknowledgements

We thank the Technical Research Council of Turkey (TUBITAK-Grant Number 2302(103T029) and the Scientific Research Projects Foundation of Selcuk University (SUBAP-Grant Number 2003-187) for financial support of this work.

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