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A useful approach toward the synthesis and metal extractions with polymer appended thioalkyl calix[4]arenes

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Abstract

This article describes a convenient method for the synthesis of two new polymeric resins via nucleophilic substitution reactions involving 5,11,17,23-tetrakis[(propylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene **4**, and 5,11,17,23-tetrakis[(methylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene **6**, as precursors with Merrifield's resin. The extraction studies were made using both liquid–liquid extraction and solid–liquid batchwise sorption procedures. The calix[4]arene based polymeric resins have high extraction ability toward metal cations and $Na_2Cr_2O_7$ as compared to their monomeric precursors.

Keywords: Polymeric calixarenes; Metal cations and oxoanions; Chromium(VI) toxicity

1. Introduction

The design of molecules with high ionic affinities is important for numerous applications in chromatography, catalysis and separations [1–3]. Immobilization of ion selective ligands to form polymer-supported reagents results in an extended set of applications [4–16]. Several studies have been carried out to synthesize new complexants for charged and neutral molecules. Among these, 'Calixarenes' after crown ethers and cyclodextrins are an important class of macrocycles widely used in supramolecular chemistry as useful basic skeleton and an excellent 'platform' for the design of receptor sites for the specific recognition of guests. They have two well-defined 'rims', an upper rim defined by the *para* substituents of the phenolic rings and a lower rim defined by the phenolic hydroxy groups. Between these two regions lies a hydrophobic cavity of aromatic rings. This excellent skeleton makes calixarenes to be able to function as molecular baskets to complex ionic and neutral guests in supramolecular cavities [17–19]. Since calixarenes have both an upper and a lower rim, attention has been focused primarily on attachments to the *p*-carbons at the upper rim and the phenolic oxygens at the lower rim. Relatively few attempts have been reported concerning the replacement of the OH groups with other groups, which often makes calixarenes high-performance receptors [20–22].

From an environmental and economic view point there remains a need to discover more selective and effective extractants for toxic heavy metals and anions (chromate/-dichromate) from waters and soils. The challenge is to find complexants that selectively extract those ions from a mixture, and allow them to be readily released in pure form. During the past three decades much research effort has been expended in embellishing calixarene frameworks with functional groups for the recognition of cations and anions. In general, oxygen containing macrocycles are effective extractants for alkali and alkaline earth metals [23–30]. By contrast, sulfur containing calixarenes are an important class of compounds because they can be used for the selective extraction of soft heavy metal ions against alkali, alkaline earth, or other hard metal ions [31–40]. Furthermore, in acidic conditions sulfur atom may be protonated and hydrogen bond to chromate/dichromate anions [41]. As a result, calixarenes with sulfur-derivatized functionalities potentially meet the requirements as extractants because

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they are multidentate preorganized macrocyclic type ligands with appended functionalities. As one of the applications of chemically modified calixarenes, an attempt can be made to prepare selective chelating adsorbents by immobilizing them onto solid support materials. Several studies on cation and anion recognition have been reported using calixarene based chelating resins [42–46].

In view of the above considerations, during the course of our continuing study we have chosen calix[4]arene as a building block. The calix[4]arene has therefore been derivatized with different thioether groups appended to the upper rim, and these ion-selective ligands (**4** and **6**) then immobilized onto Merrifield's resin (Schemes 1 and 2) to form polymer-supported reagents (**5** and **7**). These functionalized resins have been used for the extraction of heavy metal cations and dichromate anions.

2. Experimental

2.1. Apparatus

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as 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.

2.2. Materials

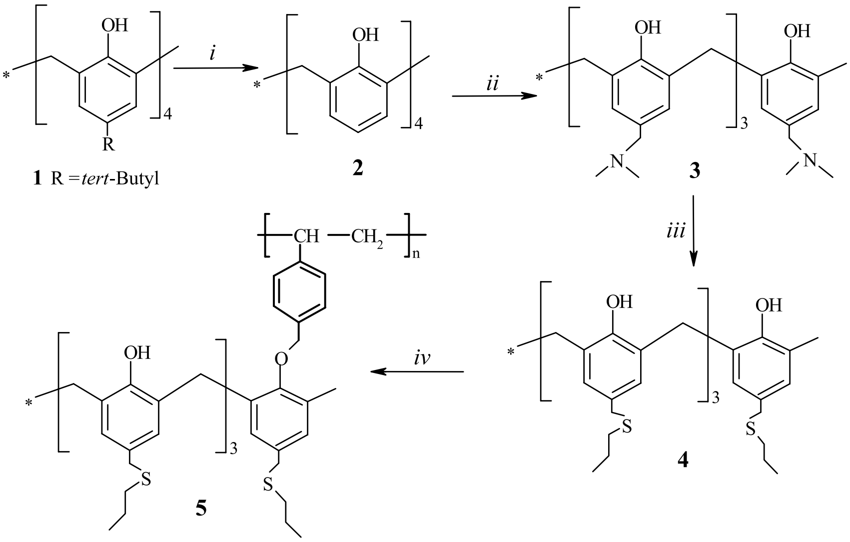
Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Merrifield's resin was purchased from Fluka (No. 63865). NaH was used as an 60% dispersion in oil and washed twice with *n*-hexane before use. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Toluene/tetrahydrofuran (BDH) were dried by refluxing over sodium/benzophenone, fractionally distilled, and then stored over molecular sieves. CH_2Cl_2 was distilled from $CaCl_2$. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.3. Synthesis

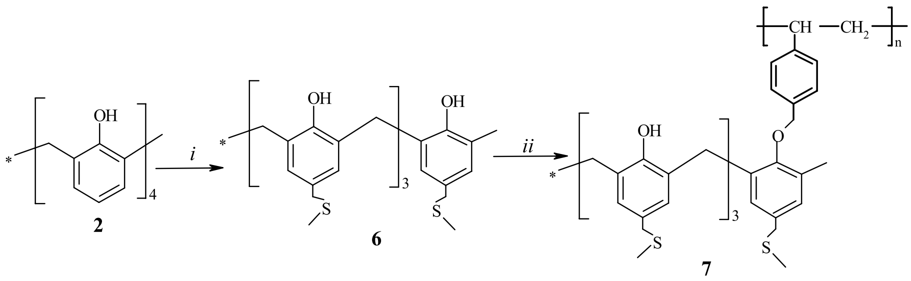
Compounds **1**, **2**, **3**, and **6** (Schemes 1 and 2) were synthesized according to the literature procedures [47–50], whereas, the compound **4** and calixarene-based polymers **5** and **7** employed in this work (Schemes 1 and 2) were synthesized as follows.

2.3.1. 5,11,17,23-Tetrakis[(propylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (*4*)

To a solution (3.0 g, 4.6 mmol) of *p*-(*N*,*N*-dimethylaminomethy)-25,26,27,28-tetrahydroxycalix[4]arene (**3**) in 50 mL of DMSO was slowly added with continuous stirring 2.5 mL (5.7 g, 40.14 mmol) of CH_3I. In another flask, to a solution of 1-propanthiol 8 mL (6.72 g, 88.3 mmol) in 50 mL of DMSO was added 25 mL (18.2 g, 180 mmol) of triethyl amine (99%). Both the solutions were stirred separately for 2 h at room temperature in N_2 atmosphere. Then, the solution of calixarene was added slowly with the help of dropping funnel to the solution of propanethiol with continuous stirring at the room temperature. The contents of the flask were heated for one week at 50–60 °C in an



Scheme 1. (i) Toluene, phenol, $AlCl_3$ (ii) THF, CH_3COOH, HCHO, $NH(CH_3)_2$ (iii) DMSO, CH_3I, 1-propanthiol, $N(C_2H_5)_3$ (iv) DMF, Merrifield's resin, NaI, NaH.



Scheme 2. (i) CH_2Cl_2, DMSO, $SOCl_2$, $N(C_2H_5)_3$ (ii) DMF, Merrifield's resin, NaI, NaH.

atmosphere of N_2. The solution was cooled, treated with 1 L ice water, and then taken in dichloromethane, neutralized with 2 N HCl, washed with water, and dried with Na_2SO_4. The crude product comes out 3.1 g (98%), which was purified by column chromatography (acetone/*n*-hexane, 1:2) followed by recrystallization to give **4** in 68% (2.14 g) yield; m.p. 128–130 °C. IR (KBr): 3164 cm^{-1} (OH), 666 cm^{-1} (C-S), ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 12H, $J=7.5$ Hz, CH_3), 1.53–1.61 (m, 8H, CH_2), 2.36 (t, 8H, $J=7.5$ Hz, SCH_2), 3.47–3.52 (m, 12H, SCH_2Ar, $ArCH_2Ar$), 4.27 (d, 4H, $J=$ 14 Hz, $ArCH_2Ar$), 6.99 (s, 8H, ArH), 10.15 (s, 4H, ArOH). Anal. Calc. for $C_{44}H_{56}O_4S_4$: C, 67.99%; H, 7.26%; S, 16.50%. Found: C, 68.01%; H, 7.27%; S, 16.53%.

2.3.1.1. Synthesis of polymer appended thioalkyl calix[4]-arenes. The following general procedure was adopted to transform **4** and **6** into the corresponding polymer appended thioalkyl calix[4]arenes (**5** and **7**). A 2 mmol amount of **4/6** was dissolved in THF (50 ml). To this solution 10 mmol NaH (60%) was added. In another flask 1.0 g of Merrifield's resin (0.8 mmol Cl/1 g resin) was dissolved in DMF (50 ml). To this solution NaI (2 mmol) was added. Both the mixtures were stirred for half an hour at room temperature separately. After that, the contents of both the flasks were mixed together and heated at 60 °C in an inert atmosphere with continuous stirring for 48 h. The cooled contents were filtered through a bed of celite, and the filtrate and dichloromethane washings were combined and concentrated at reduced pressure. Crude product was washed several times with with ether to ensure removal of unreacted calixarene derivative **4/6**, and then taken in dichloromethane, neutralized with dilute HCl, washed with water and dried in Na_2SO_4. Finally, after the work up the product was dried in vacuo.

2.3.2. Polymer appended thioalkyl calix[4]arene 5 from 5,11,17,23-tetrakis-[(propylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (4) and Merrifield's resin

The loading shows the range of calixarene moieties between 19–20% for the given weight of the polymer. According to the elemental analysis, the resulting polymer contains 1.94% sulfur corresponding to 0.151 mmol of **4**/g of polymer, s.p. >268 °C (decomp.). IR (KBr): 3458 cm^{-1} (OH), 694 cm^{-1} (C–O and C–S). Anal. Calc. for **5**, Found: C, 85.73; H, 6.59; S, 1.94%.

2.3.3. Polymer appended thioalkyl calix[4]arene 7 from 5,11,17,23-tetrakis-[(methylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (6) and Merrifield's resin

The loading shows the range of calixarene moieties between 17–18% for the given weight of the polymer. According to the elemental analysis, the resulting polymer contains 1.73% sulfur corresponding to 0.135 mmol of **6**/g of polymer, s.p. >230 °C (decomp.). IR (KBr): 3424 cm^{-1} (OH), 694 cm^{-1} (C–O and C–S). Anal. Calc. for **7**, Found: C, 86.24; H, 6.78; S, 1.73%.

2.3.4. Analytical procedure

Picrate/dichromate extraction experiments were performed following Pedersen's procedure [51]. 10 mL of a 2.5×10^{-5} M aqueous picrate, or a 1.0×10^{-4} M dichromate solution and 10 mL of 1×10^{-3} M solution of calixarene (**4/6**), or a 1.0×10^{-3} M solution of calix[4]arene unit/g oligomer (**5/7**), in $CHCl_3$ were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. The solutions were then magnetically stirred in a thermostated water-bath at 25 °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 [52]. Blank experiments showed that no picrate/dichromate extraction occurred in the absence of calixarene. The percent extraction ($E\%$) has been calculated as:

$$(E\%) = (A_o - A)/A_o \times 100 \tag{1}$$

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

Alkali picrates were prepared by the following method. A saturated solution of picric acid was prepared by dissolving the acid in hot (near boiling) water. Alkali carbonate (Na_2CO_3, K_2CO_3 and Cs_2CO_3) was then added to the solution until no more carbon dioxide was evolved, and the solution pH tested as neutral. The color changed from yellow to orange and some precipitate started to form. As the solution was cooled gradually to 0 °C, the alkali picrate forms a mass of crystals. The yield can be maximized by evaporating the solvent to half of its original volume and then cooled it to 0 °C, at which temperature additional crystals form. After washing with a small amount of cold water the pure alkali picrates were dried under vacuum for 24 h and protected from moisture and light before use.

Lithium picrate was prepared by adding stepwise a saturated aqueous picric acid solution to LiOH until neutralization is reached. After evaporation of water, the residue was crystallized from ethyl acetate. The pure crystals were obtained by washing with a small amount of ethyl acetate, followed by drying under vacuum for 24 h and protection from moisture and light before use.

Ni^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+} picrates were prepared from the respective metal carbonate [53]. Lead picrate was prepared by dissolving picric acid in methanol and heated until no solid remained. This procedure yielded a yellow solution to which an equal amount of lead monoxide was added. The methanol was heated further until boiling commenced and stirring was maintained. After the mixture began to boil lead picrate formed. Boiling was continued until the solution became a thick emulsion. This was then filtered and washed with methanol. The filtrate was then allowed to dry. Heating at 100 °C for 2 h gave pure lead picrate.

Hg^{2+} picrate was prepared in situ by dissolving excess of freshly prepared metal oxide or hydroxide, respectively in a hot aqueous solution of picric acid. The mixture was stirred for 2–3 days and then filtered. After standing at room temperature for 24 h, the solution pH was measured, being in agreement with theoretical value.

2.3.5. Batchwise sorption of selected transition and post transition metal ions, and dichromate anions

About 25 mg of the resin was shaken with a 10–mL of aqueous solution containing 2.5×10^{-5} M metal picrate, and/or 10 mL of aqueous solution containing 1×10^{-4} M sodium dichromate, in a 50 mL stoppered glass flask at 25 °C for 1 h and filtered off. The concentration of the metal ion remaining in aqueous phase after the sorption was then determined by spectrophotometrically. The sorption percentage was calculated by the Eq. (1).

3. Results and discussion

Generally it has been accepted that calixarene based ionophores frequently show ion selectivity superior to crown ether-based ionophores. In some cases this is enhanced by the use of appropriate functionalities. Our earlier work with polymeric calix[4]arenes was mostly focused on derivatives with functionalities appended to the lower rim [21,28,44–46]. The main focus of this work is the design of new polymeric calix[4]arene derivatives with functionalities appended to the upper rim. These compounds are easily synthesized, have effective binding character for a particular set of cation/anions, and can potentially be useful for multiple applications such as laboratory, clinical, environmental and industrial process analysis. To achieve the desired goal, we have synthesized *p-tert*-butylcalix[4]arene **1** as a starting material through the base catalyzed condensation reaction [47]. Two synthetic schemes have been developed to enable its derivatization. Such synthetic routes are depicted in Schemes 1 and 2. The syntheses for compounds **2**, **3**, and **6** are based on the previously published procedures [48–50], while the syntheses for **4** and calixarene based polymer resins **5** and **7** are reported for the first time. Therefore, following the strategies outlined in Schemes 1 and 2, compound **1** has been treated with anhydrous $AlCl_3$ in toluene in the presence of phenol to yield the calix[4]arene **2** [48]. The Mannich reaction is known to be a very effective derivatization tool at the *para* position (upper rim) of the calixarenes [49]. Therefore, calix[4]arene **2** has been treated with dimethylamine and fomaldehyde in the presence of acetic acid in THF to yield 5,11,17,23-tetrakis[(dimethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene **3**. 5,11,17,23-tetrakis[(propylthio)methyl]-25,26,27,28-tetrahydroxycalix[4]arene **4** has been obtained through the quinone methide route by treatment of **3** with CH_3I, 1-propanthiol and triethylamine in DMSO at 50–60 °C in an inert atmosphere. Compound **4** has been purified by column chromatography (acetone/*n*-hexane 1:2) and obtained in 68% yield. The ^1H NMR spectrum of **4** has a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 4.27 ppm ($J=14$ Hz), indicating that the compound **4** exists in cone conformation [54]. Although, **4** has also been prepared through the quinone methide route [49] using NaH as a strong base, **4** is obtained in only a trace amount. Therefore it has been decided to use triethylamine, a moderate base, which prevents the side reaction of excess CH_3I with phenolic oxygens, and as a result gives a higher yield. This is a convenient method that depends upon parameters such as reaction time and stoichiometry of the reagents. Compounds **4** and **6** have been used as precursors for the synthesis of polymer supported calixarene ionophores (**5** and **7**) by nucleophilic substitution reactions. Polymers **5** and **7** have been prepared by heating **4** and **6** with Merrifield's resin (0.8 mmol Cl/1 g) in the presence of NaI and NaH in DMF for 48 and 33.5 h, respectively in an inert atmosphere. The amount of the loaded calixarene derivative **4**/**6** on the polymeric support has been evaluated by the difference of mass taken before and after the coupling for the dry resin, and also from the results of elemental analysis.

3.1. Extraction studies

3.1.1. Metal cation extraction

The binding selectivity of the calix[4]arenes is related to the macrocycle ring sizes, their conformations, and the nature of the functional groups. Lower rim functionalized calix[4]arene derivatives can be effective extractants for metal cations [17–22]. This work is focused on identifying the strategic requirements for both the two-phase extraction and the binding abilities of the upper rim functionalized thioalkyl calix[4]arene derivatives **4** and **6** toward selected alkali, transition and post-transition metal ions such as Li^+, Na^+, K^+, Cs^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+} and Pb^{2+}.

These derivatives have been evaluated by solvent extraction of their metal picrates, and the results are summarized in Tables 1 and 2 (Figs. 1 and 2), and are also compared with those of their related calixarene based polymeric resins **5** and **7**. Comparison is also made with the unsubstituted Merrifield's resin. The data have been obtained by using chloroform solutions of the compounds to phase-transfer metal picrates from aqueous solution. The equilibrium concentration of the metal picrate in the aqueous phase is then determined spectrophotometrically.

From the results it is apparent that the precursor calix[4]arenes **4** and **6** are poor extractants for the metal cations used in the experiments (Tables 1 and 2/Figs. 1 and 2). It is in agreement with literature results [33,50,55]. Compounds **4** and **6** contain phenolic groups, and it has been demonstrated that unsubstituted calixarenes display little or no ionophoric activity toward metal ions in aqueous solution if the source phase is neutral. However, if the source phase is sufficiently basic to permit deprotonation of the phenolic groups, alkali metal cations can be transported as neutral phenoxide complexes through a chloroform liquid membrane [55]. The poor extraction ability of compound **6** for heavy metal cations has also been reported [33,50], but its extraction ability increases with increase in pH. It has also been shown that Cd^{2+} and Pb^{2+} are extracted completely at pH 8, while the other metals are not extracted completely up to pH 10 under the conditions used for extraction [50]. As a control we find that the Merrifield's resin itself does not extract any of the metal cation used in the two-phase extraction experiments significantly (Tables 1 and 2). Thus the Merrifield's resin backbone is not an extractant for these metal ions.

We have immobilized **4** and **6** onto a polymeric backbone and compared the extraction characteristics with those of the monomers. Therefore, comparable extractions have been performed between polymeric ionophores (**5** and **7**) and the monomers (**4** and **6**). We find that **5** and **7** show different extraction behavior toward all metal cations as compared to the monomers (Tables 1 and 2/Figs. 1 and 2). The selectivity pattern for **5** is $Ni^{2+} > Cu^{2+} > Hg^{2+} > Cd^{2+} > Pb^{2+} > Co^{2+}$, and that for **7** is $Cu^{2+} > Ni^{2+} > Hg^{2+} > Pb^{2+} > Cd^{2+} > Co^{2+}$. For alkali metals the selectivity pattern for **5** is $K^+ > Cs^+ > Na^+ > Li^+$, and for **7** is $K^+ > Li^+ > Cs^+ > Na^+$.

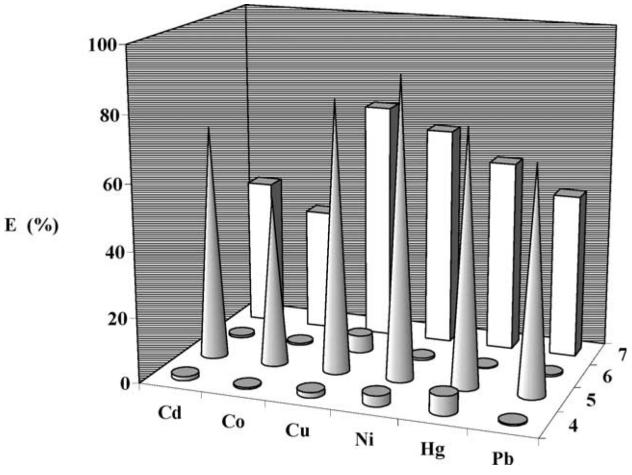


Fig. 1. Extraction percentage of the transition and post-transition metal picrates versus ligands **4**–**7**. Aqueous phase, [metal picrate] = 2.0×10^{-5} M; organic phase, chloroform, [ligand] = 1.0×10^{-3} M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

From these observations it can be concluded that the upper rim substituted calixarene monomers are poor extractants for metal cations at neutral conditions [17–19]. The presence of different terminal alkyl groups (propyl or methyl) in the thioether functionality does alter the selectivity of the ionophore. Furthermore, appending a polymeric skeleton favors complexation in the two-phase extraction systems. The immobilization of **4** and **6** onto a polymeric backbone may have changed their geometry into other conformations [56]. It is also possible that the polymer plays a role, whereby it folds into conformations that place functional groups on several of the calix[4]arene moieties bound to the polymer in preferred conformations where they can associate with the cation. This implies that better preorgnization of the immobilized calixarene ionophores **5** and **7** occurs whereby the cooperative effect of thioether groups is possible. This cooperative effect improves

Table 1
The Liquid–liquid extraction of transition metal cations with ligands

Extracted Metal Picrate (%)[a]						
Ligand	Cd^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Hg^{2+}	Pb^{2+}
4	1.3	1.0	1.6	3.3	5.9	<1.0
5	71.0	51.3	82.3	90.8	77.4	68.5
6	<1.0	<1.0	5.3	<1.0	<1.0	<1.0
7	45.1	37.5	72.7	66.9	58.4	50.0
Merrifield's resin[b]	<1.0	<1.0	2.0	2.0	<1.0	8.0

Aqueous phase, [metal picrate] = 2.0×10^{-5} M; organic phase, chloroform, [ligand] = 1.0×10^{-3} M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

[a] There may be ±5% error in the experimental measurements.

[c] Solid-liquid batchwise adsorption extraction experiments.

Table 2
The Liquid–liquid extraction of alkali metal cations with ligands

Extracted Metal Picrate (%)[a]				
Ligand	Li^+	Na^+	K^+	Cs^+
4	<1.0	<1.0	<1.0	<1.0
5	23.0	30.0	43.0	38.0
6	<1.0	<1.0	<1.0	<1.0
7	30.0	13.0	32.0	19.0
Merrifield's resin[b]	3.0	<1.0	2.0	5.0

Aqueous phase, [metal picrate] $= 2.0 \times 10^{-5}$ M; organic phase, chloroform, [ligand] $= 1.0 \times 10^{-3}$ M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

[a] There may be ±5% error in the experimental measurements.

[b] Solid-liquid batchwise adsorption extraction experiments.

extraction. By contrast, monomers **4** and **6** are significantly more flexible than are the polymeric ionophores **5** and **7**, and they exhibit poor extraction ability towards metal ions.

3.1.2. Dichromate anion extraction

Recently, we have synthesized a number of chemically modified calixarenes that can be used as host for dichromate anions [3,21,44–46]. This has occurred because the periphery of a chemically modified calixarene can be made structurally compatible with these ions. These sulfur containing extractants based on the calix[4]arene framework that can be immobilized into a polymeric matrix may also be extractants for both heavy metals and dichromate anion. Anion recognition and sensing is an increasingly important research topic in supramolecular chemistry due to the importance of various anions in biological and environmental locations. Dichromate anions are important because of their high toxicity and their presence in soils and waters [57–60]. For a compound to be effective as a host it is necessary that its structural features are compatible with those of the guest anions. The chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) ions are dianions where the periphery of the anions have oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. Therefore, calixarenes with sulfur-derivatized functionalities potentially meet the requirements as extractants for chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) ions because in acidic conditions sulfur atom may be protonated and hydrogen bond to chromate/dichromate anions [41]. A preliminary evaluation of the extractants **4**–**7** has been carried out by solvent extraction of $Na_2Cr_2O_7$ from aqueous solution into chloroform at different pH. The results are summarized in Table 3. From the extraction data given in Table 3 (Fig. 3) it is clear that the respective monomeric analogue **4** and **6** of polymers **5** and **7** have not significantly extracted dichromate anions. However, the conversion of **4** and **6** into immobilized polymeric structures (**5** and **7**) significantly increases the anion extraction ability. Again this 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 [56]. Again it is possible that the polymer plays a role, whereby it folds into conformations that place functional groups on

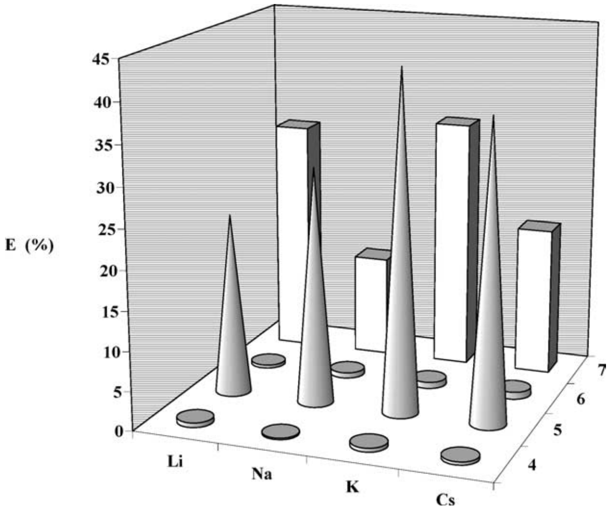


Fig. 2. Extraction percentage of the alkali metal picrates versus ligands **4**–**7**. Aqueous phase, [metal picrate] $= 2.0 \times 10^{-5}$ M; organic phase, chloroform, [ligand] $= 1.0 \times 10^{-3}$ M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

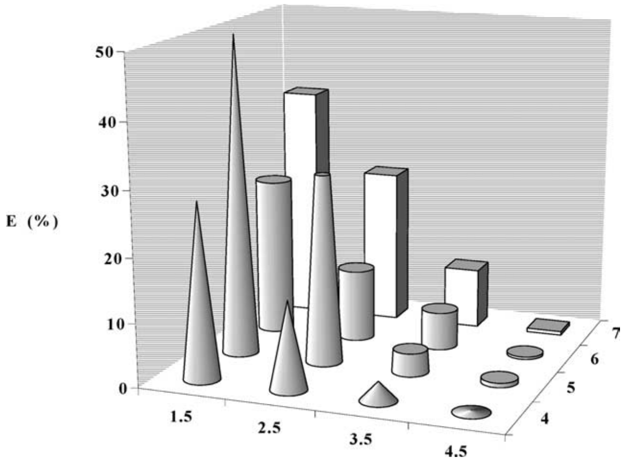


Fig. 3. Extraction percentage of sodium dichromate versus ligands **4**–**7**. Aqueous phase, [sodium dichromate] $= 1.0 \times 10^{-4}$ M; organic phase, chloroform, ligand] $= 1.0 \times 10^{-3}$ M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h.

Table 3
The Liquid–liquid extraction (*E%*) of dichromate anion with ligands

Ligand	pH			
	1.5	2.5	3.5	4.5
4	27.5	13.8	3.0	<1.0
5	50.0	29.6	3.6	<1.0
6	24.7	11.4	6.0	<1.0
7	36.7	24.2	9.5	<1.0
Merrifield's resin[a]	<1.0	<1.0	<1.0	<1.0

Aqueous phase, [sodium dichromate] $= 1.0\times10^{-4}$ M; organic phase, chloroform, ligand] $= 1.0\times10^{-3}$ M or a 1.0×10^{-3} M solution of calix[4]arene unit/g polymer resin at 25 °C, for 1 h. There may be ±5% error in the experimental measurements.

[a] Solid–liquid batchwise adsorption extraction experiments.

several of the calix[4]arene moieties in the polymer in a preferred conformation where they can associate with the oxoanion. Moreover, for polymers **5** and **7** the percentage of dichromate extracted is increased by lowering the pH of the aqueous phase. This pH dependence can be explained by anion hydration. The importance of ion hydration in liquid–liquid phase extraction has been documented by Hofmeister [61]. In aqueous solutions having a lower pH the dichromate will be primarily in its protonated form $HCr_2O_7^-$. This monoanion will have a smaller free energy of hydration than does the dianionic form $Cr_2O_7^{2-}$. 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 $Cr_2O_7^{2-}$ is that for the former only one sodium ion needs to be coextracted to maintain charge balance, whereas for $Cr_2O_7^{2-}$ two sodium ions are extracted, with additional loss of hydration energy. Two factors are now involved in the pH dependence of dichromate extraction. At the lower pH values both the formation of $NaHCr_2O_7$ and the protonation of the alkyl sulphides favors extraction into dichloromethane [21,46].

4. Conclusion

This work reports a convenient method for the synthesis of thioether functionalized calix[4]arene-based polymeric resins. Compounds **4** and **6** are versatile starting materials for the synthesis of polymerizable calixarene derivatives that are suitable for the extraction of toxic heavy metal cations as well as for dichromate anions. The extraction ability of **4** and **6**, and their corresponding polymers **5** and **7** has been studied. Polymeric ionophores are excellent extractants for both metal picrate and dichromate anions. The conformation of the calix[4]arenes and the nature and cooperativity of the functionalities may play important roles in the two-phase extraction systems.

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