Synthesis of Calix-Styrene Copolymer Carrying Thioether Groups and Examination of the Cation-Anion Extraction Properties

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Summary This study comprises the synthesis of new calix [4] arene thioether derivative (3), its corresponding oligomer (**5**) and copolymers (**6**), which are a selective extractant for toxic metal cations and anions and liquid-liquid and solid-liquid extractions of these compounds. Structures of these compounds were described by elemental anaysis, FT-IR, ^1H NMR and ^{13}C NMR. To determine the ion transport properties of the synthesized compounds, transition metal picrate and dichromate liquid-liquid extraction studies were carried out. It is seen from the extraction results that the calix-styrene copolymer (**6**) has a good selectivity for the Pb^{2+} and Hg^{2+} cation from the selected metal cations, but it shows poor extraction behavior towards dichromate anion.

Keywords: Calixarene, Metal cations, Copolymer, Chromium(VI), Toxicity, Thioether.

Introduction

Toxic heavy metals are among the most detrimental environmental pollutants today. They spread through the environment indirectly via natural resources and human factors, as well as directly due to their utilization, causing pollution. Various methods were developed for the removal from the environment of these toxic heavy metals that result in the deterioration of the natural structure and composition of the environment, affecting alive life negatively. Most frequently used methods are adsorption and nanofiltration-complexation methods [1-8]. Cyclodextrins and crown ethers are widely used as adsorbent or ligands in these methods. Recently, calixarenes, known extensively in supramolecular chemistry with their increasing significance have joined these agents. Calixarenes are macrocyclic oligomers synthesized from the condensation of phenol and formaldehyde in basic environment [9]. Characteristics such as their ringed structure, easy functionalization and ability to create different sizes of molecular gaps enable them as great carriers for cations, anions and neutral molecules [10-13]. Due to these characteristics, they have a rather wide application area. Recently, use of calixarenes functionalized by different functional groups in liquid-liquid, solid-liquid extraction and membrane studies of certain cations and anions increasingly found their way into the literature [14-20].

Oxyanions are known as chemicals that pose significant problems in terms of environmental pollution. Due to their toxicity these anions are significant pollutants of soil and water. Among these pollutants chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), phosphate (PO_4^{3-}), nitrite (NO_2^-) and selenate (SeO_4^{2-}) are the most common ones [21]. Chromium is widely used in industries, especially in steel welding, chromate production and chromium plating, oxidation processes, etc. Many of the industries that use chromium compounds leaves a high amount of chromium-containing waste which poses a serious threat to microorganisms in aquatic systems and human life [22]. In aqueous medium Cr(VI) mostly found in two ways in alkaline medium chromate (CrO_4^{2-}) and in acidic medium dichromate ($Cr_2O_7^{2-}$) [23]. Thus, today the removal of these anions is rather significant for the environmental health issues. Therefore, it is necessary that treatment of dichromate containing wastewater using efficient methods with low cost materials having efficient extraction ability. Therefore, waste water containing dichromate should be efficiently extracted with low cost materials [24].

The objective of this study is to synthesize certain macrocyclic compounds that could form selective complexes with toxic heavy metals, especially mercury and lead. Furthermore, synthesis of a suitable compound that could be utilized in the liquid-liquid extraction of the dichromate anion, in addition to metal cations was aimed.

Experimental

Instrumentation

Melting points were determined using Barnstead/electrothermal brand melting point

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determination equipment. IR spectra were obtained from Perkin Elmer 1605 Fourier transform infrared (FTIR) System Spectrum BX spectrophotometer in KBr disks. ^{1}H NMR and ^{13}C NMR spectra were taken with Varian 400 MHz spectrophotometers in $CDCl_3$ and TMS was used as a standard. In NMR spectrum, chemical shift values were indicated in (δ) ppm. Shimadzu UV-1700 Pharma UV-Visible spectrophotometer was used in UV-visible measurements. Molecular weight readings were conducted using an Agilent (HP) gel permeability chromatography (GPC) equipment supported by refractive index detector with a solvent flow rate of 0.6 mL/min and sample concentration of 2.0 mg/mL, in THF at 30 °C. The micro columns were calibrated with polystyrene standards. The thermal stability of the copolymer was examined by a Shimadzu TG 60 H Thermogravimetric analyzer at a heating rate of 20 ºC/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min. Elemental analysis determinations were made using Elementar CHNS analyser.

Reagents

Analytical TLC's were conducted using aluminum plates covered with silica gel coating (SiO_2, Merck 60 F_{254}). Silica gel 60 (Merck, particle size 0.040-0.063mm, 230-240 mesh) was used in column chromatography studies. All of the starting materials and reagents were standard analytical grade, purchased from Merck or Fluka, and used without further purification. Commercial grade solvents such as acetone, acetonitrile, chloroform, methanol, ethyl acetate, and n-hexane were distilled and stored over molecular sieves (Aldrich; 4Å, 8–12 mesh). Acetonitrile and toluene (BDH) were boiled over CaH_2 and tetrahydrofuran sodium-benzophenone under condenser and dried and distilled with fractional distillation. CH_2Cl_2 was used after it was distilled over $CaCl_2$ and MeOH over Mg and stored over molecular sieves.

All aqueous solutions were prepared with deionized water that had been distilled by Millipore Milli-Q Plus water purifying equipment.

Synthesis

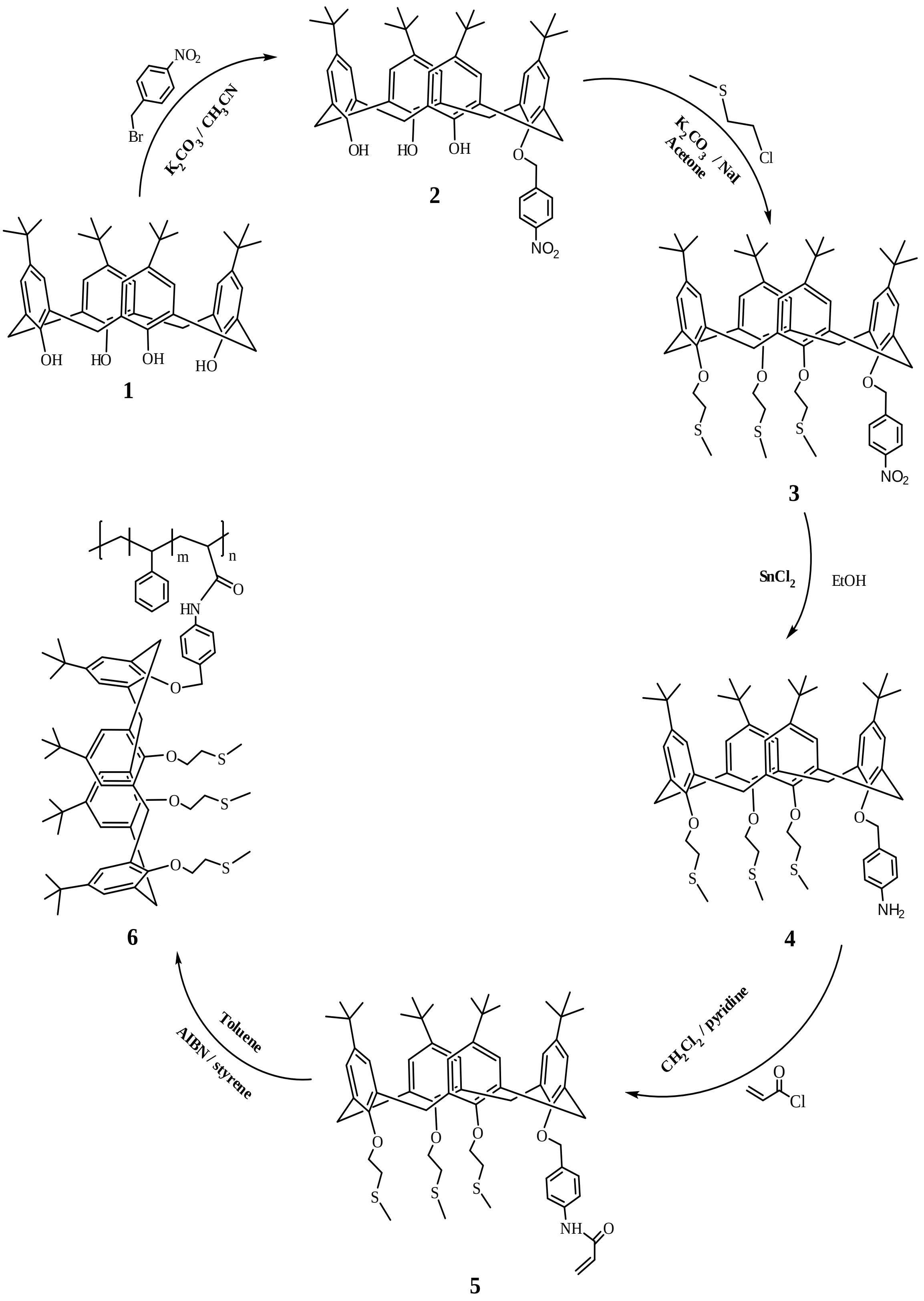
The compounds **1** and **2** were prepared according to the literature [25, 26] and the other compounds (**3-6**) employed in this work as illustrated in Scheme-1 have been synthesized according to the methods given next:

5,11,17,23-tert-butyl-25-(4-nitrobenzyloxy)-26,27,28-(2-metylthioethoxy)calix[4]arene **(3)**

The mixture of compound **2** (3.92 g, 5.00 mmol), potassium carbonate (2.87 g, 20.80 mmol), 2-chloroethyl methyl sulfide (3.76 g, 34.02 mmol) and sodium iodide (3.34 g, 22.30 mmol) in anhydrous acetone (200 mL) was boiled by mixing under condenser for 3 days in a nitrogen atmosphere. At the end of this period, the reaction mixture was cooled at room temperature, filtrated and washed with acetone. Then, the filtrate and acetone effluent were combined and most of the solvent is evaporated. The remaining portions was precipitated with distilled water and acidified with 2 M aqueous HCl. The precipitates was washed with distilled water and dried in vacuo. Compound **3** was obtained by crystallization of the crude product with dichloromethane-ethanol mixture. Yield: 52 %, mp: 123 ºC. IR (KBr) 1527 and 1370 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$), δ (ppm) 1.10 (s, 27 H, Bu^t), 1.22 (s, 9 H, Bu^t); 2.27 (s, 9 H, S-CH_3), 2.87 (t, 6 H, ^2J(H,H) =6.7 Hz, S-CH_2); 3.50 (d, 4H, ^2J(H,H) =13.5 Hz, ArCH_2Ar), 4.08 (t, 6 H, ^2J(H,H) =6.3 Hz, O-CH_2); 4.25 (d, 4H, ^2J(H,H) =13.5 Hz, ArCH_2Ar); 4.97 (s, 2H, OCH_2Ar); 7.18 (m, 6H, ArH); 7.61 (m, 2H, ArH); 7.82 (s, 2H, ArH, *4-nitrophenyl*); 7.98 (s, 2H, ArH, *4-nitrophenyl*). ^{13}C NMR ($CDCl_3$), δ (ppm): 15.4; 31.3; 33.0; 34.8; 74.6; 126.0; 127.1; 128.9; 133.4; 136.7; 156.8; 153.6. Calculated for: $C_{60}H_{79}NO_6S_3$: C, 71.60; H, 7.91; N, 1.39; S, 9.56. Found: C, 71.75; H, 7.84; N, 1.32; S, 9.47%.

5,11,17,23-tert-butyl-25-(4-aminobenzyloxy)-26,27,28-(2-metylthioethoxy) calix[4] arene **(4)**

A suspension of the compound **3** (2.0 mmol, 2.011 g) and $SnCl_2 \cdot 2H_2O$ (10.0 mmol) in EtOH (25 ml) was refluxed under nitrogen until no starting material was detected by TLC. After cooling to room temperature, the mixture was poured into ice-water and the pH was adjusted to 9–10 using 5 M KOH solution. After extraction with CH_2Cl_2 the combined organic layers were washed with brine (25 ml) and dried over $MgSO_4$. After filtration, the evaporation of the solvent under reduced pressure the compound **4** was obtained and used without further purification. Yield 90 %. Mp: 123 ºC. IR (KBr) 3397 cm^{-1} (NH_2); δ (ppm) 0.97 (s, 27 H, Bu^t), 1.12 (s, 9 H, Bu^t); 2.14 (s, 9 H, S-CH_3), 3.15 (t, 6 H, ^2J(H,H) =6.2 Hz, S-CH_2); 3.23 (d, 4H, ^2J(H,H) =13.1 Hz, ArCH_2Ar), 3.60 (brs, 2H, NH_2) 3.98 (t, 6 H, ^2J(H,H) =6.8 Hz, O-CH_2); 4.28 (d, 4H, ^2J(H,H) =12.0 Hz, ArCH_2Ar); 4.55 (s, 2H, OCH_2Ar); 6.98-7.12 (brm, 6H, ArH); 7.31 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$), δ (ppm): 15.7; 32.0; 33.7; 34.8; 74.3; 106.1; 130.5; 125.9; 135.4; 141.0; 150.6. Calculated for: $C_{60}H_{81}NO_4S_3$: C, 73.80; H, 8.36; N, 1.43; S, 9.85. Found: C, 73.55; H, 8.61; N, 1.30; S, 9.37%.



Scheme-1: A schematic representation of the synthesis of copolymer **6.**

Treatment of Compound 4 with Acryloyl Chloride **(5)**

In a 250 mL flask with two necks with a dropping funnel on one, compound **4** (0.98 g, 1.00 mmol), pyridine (0.5 mL), and $CHCl_3$ (50mL) were added. To the mixture at 0 °C, the solution of acryloyl chloride (0.10 mL, 1.20 mmol) in $CHCl_3$ (5 mL) was added by drops with continuous stirring. When the process of dropping was over, it was stirred for one hour at 0 ºC and for one day at room temperature. After completion of the reaction, the reaction mixture was extracted with $CHCl_3$. The Organic phase was washed with cold diluted NaOH and then with distilled water several times. Combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. After the crude product was purified with column chromatography with $CHCl_3$ and n-hexane mixture the compound **5** was obtained in 85 % yield. Mp: 109 ºC. IR (KBr) 3421 cm^{-1} (NH); 1682 (CONH). ^{1}H-NMR ($CDCl_3$), δ (ppm) 0.98 (s, 27 H, Bu^t), 1.21 (s, 9 H, Bu^t); 2.87 (s, 9 H, S-CH_3), 3.25 (t, 6 H, ^2J(H,H) =6.2 Hz, S-CH_2); 3.42 (d, 4H, ^2J(H,H) =12.1 Hz, $ArCH_2Ar$), 4.31 (t, 6 H, ^2J(H,H) =6.7 Hz, O-CH_2); 4.25 (d, 4H, ^2J(H,H) =13.0 Hz, $ArCH_2Ar$); 4.71 (s, 2H, OCH_2Ar); 6.68-6.90 (m, 11 H, HC=CH_2, ArH); 7.01-7.12 (m, 4H, ArH); 7.20 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ (ppm): 15.4; 31.1; 33.7; 74.6; 121.8; 125.6; 126.9; 128.7; 131.4; 133.5; 143.7; 152.3; 166:4. Calculated for: $C_{63}H_{83}NO_5S_3$: C, 73.43; H, 8.12; N, 1.36; S, 9.33. Found: C, 73.75; H, 7.94; N, 1.28; S, 9.17%.

Copolymerization of Compound 5 **(6)**

In a polymerization tube, monomer **5** (0.79 g, 0.77 mmol) was dissolved in toluene (1 mL). Then, styrene (0.44 mL, 3.85 mmol) and AIBN (12.5 mg; 0.076 mmol) were added on. To remove the oxygen and other gases in polymerization tube, nitrogen gas was flushed to the solution for 30 min. Then the tube was heated at 80 ºC for 12 h. Reaction was precipitated in methanol afterwards and the resulting precipitate was filtered. The crude product was purified by several precipitations from chloroform solution in methanol. Then it was filtered and dried in vacuum. s.p > 235 ºC. Yield: 73 % . IR (KBr): 1670 cm^{-1} (CONH), ^{1}H NMR ($CDCl_3$), δ (ppm) 0.94-1.12 (brs, 36 H, Bu^t), 1.55-1.73 (s, 44 H, CH_2 ve CH); 2.28 (s, 9 H, S-CH_3), 3.25-4.39 (brm, 22 H, S-CH_2, O-CH_2, $ArCH_2Ar$, $ArCH_2O$), 6.81-7.02 (brs, 16 H, ArH); 7.20-7.35 (brs, 34 H, ArH), 7.48-7.67 (brs, 33 H, ArH ve NH).

Extraction Procedures

Liquid-Liquid Extraction

Picrate and/or dichromate extraction experiments were carried out according to the literature [27]. 10 mL of 2.5x10^{-5} M aqueous metal picrate or 1x10^{-4} M aqueous dichromate solution (pH of dichromate solution has been maintained by 0.01 M NaOH/HCl solution) and 10 mL of a 1x10^{-3} M solution of (**3- 5**) and/or 10 mL of a 1x 10^{-3} M solution of calix[4]arene unit/g oligomer (**6**) in CH_2Cl_2 were powerfully shaken in a stoppered glass tube with a mechanical shaker for 2 min; then magnetically stirred in a thermostated water bath at 25 ºC for 1 h. After left standing for an additional 30 min, the concentration of picrate/ dichromate ion remaining in the aqueous phase was measured spectrophotometrically. Blank experiments showed that in the absence of calixarene no picrate/ dichromate extraction have occurred. The percent extraction (E%) was calculated as:

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

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

Solid–Liquid Extraction

The copolymer **6** (25 mg) was shaken with a 10 mL of aqueous solution containing 2.5x10^{-5} M metal picrate in a stoppered glass flask plunged in a thermostated water bath kept up at 25 ºC for 1 h and finally filtered off. The concentration of metal picrate remaining in the aqueous phase was then measured spectrophotometrically [28].

Results and Discussion

Synthesis

Synthesis of calix[4]arene monomer 5 and copolymer 6 are given in Schemes 1 and 2 respectively. The synthesis of tetra-p-*tert*-butylcalix[4]arene **1** and 5,11,17,23-Tetra-*tert*-butyl-25-(4-nitrobenzyloxy)-26,27,28-trihydroxycalix[4]arene **2** were synthesized according to the literature [25, 26]. The compound **2** was refluxed with 2-chloroethyl methyl sulfide (5 equiv.) using anhydrous acetone as the solvent in K_2CO_3 and NaI medium to produce the compound **3** with 52% yield. ^{1}H NMR analysis confirms that the appearance of two pairs of AB type dublets at δ 3.50 and 4.25 ppm (J = 13.5 Hz) for $ArCH_2Ar$ protons is in cone conformation of compound 3.

The nitro group of the compound **3** was then reduced to the amino group. For this, the compound 3 was reacted with $SnCl_2$ in ethanol solvent medium to give the compound **4** with 90% yield. The reaction was followed by ITK and it was understood that the reaction was carried out by the disappearance of the peak of NO_2 at 1527 cm^{-1} and the formation of the peak of NH_2 at 3397 cm^{-1} in IR.

The monomer **5** was obtained in 85% yield by purification of the crude product by column chromatography of the product obtained by the reaction of compound **4** with acryloyl chloride in the presence of pyridine. It was understood that the reaction was carried out by observing a peak at 1680 cm^{-1} of the amidine carbonyl group in the FT IR spectrum.

Copolymer 6 was obtained in 73% yield by the reacting of monomer 5 with styrene (1: 5 ratio) in toluene as solvent and using AIBN as a radical initiator in the capped glass bottles. The ^1H NMR spectrum of the copolymer (**6**) demonstrated that both styrene and calix monomers were joined into the repeating unit, because the signals of both monomers are observed in the copolymer 6.

The molecular weight (M_n) of the copolymer **6** was measured against the polystyrene standard in THF with GPC as roughly 5640 g/mol. The percent composition of the copolymer **6** in ^1H NMR was calculated as the integration result of the peaks of each monomer (monomer 5 and styrene monomer). The *n/m* value for copolymer composition from the integration of *p-tert*-butyl proton signals (0.94-1.12) of calixarene and methylene proton signals (1.55-1.73) of styrene was found as 1/12. This value of *n/m* demonstrated that styrene monomer in copolymer **6** was dominant and calixarene unit barely and randomly bonded along the chain. This was the result of the steric hindrance induced by bulky structure of the calixarene unit [29].

The thermal stability of copolymer **6** was measured with thermogravimetric analysis (TGA) method under nitrogen atmosphere and its TGA curve presented in Fig 1. As seen in Fig. 1, the weight-loss of **6** occurred in three stages explained in Table-1. The first stage observed at 243-280 ºC shows decomposition of ethyl methyl thioether at the lower rim of the calix unit. The second stage observed at 402-422 ºC shows decomposition of calix unit, and the last stage observed at 422-448 ºC shows decomposition of almost the entire copolymer [30].

Table-1. Thermogravimetric analysis results of copolymer **6** [a, b]

Stage (ºC)	The temperature (ºC) for a weight loss (%)	Assignment
243-280	**9.5**	**Ethyl methyl thioether**
402-422	**46.4**	**Calix unit**
422-448	**93.4**	**Decomposed copolymer**

[a] The sample weight was almost 10 mg

[b] Analysis was performed from 0-600 ºC at a heating rate of 20 ºC/min. In a nitrogen atmosphere with a glass flow rate of 40 mL/min.

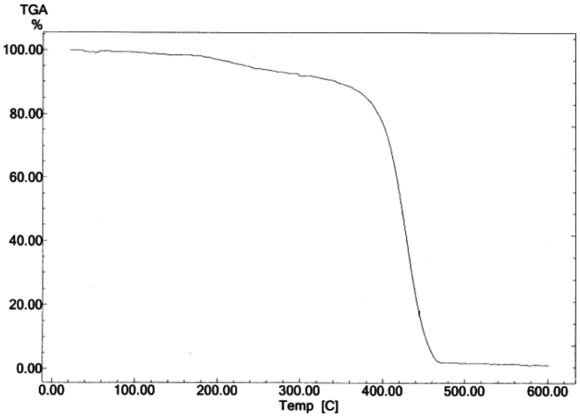


Fig. 1: The thermal degradation curves of copolymer **6.**

Extraction Studies

Metal Cation Extraction

When compared to crown ethers and cryptants, calixarenes carry metal cations from one phase to the other more selectively. These selectivity of the calixarenes are further increased as the various groups attach to the calix skeleton [28, 29]. In this study, liquid-liquid extraction studies were performed to see if the compounds synthesized were selective towards metal cations, and the results are given in Table-2.

Table-2: Extraction of metal picrates with ligands[a.]

Ligand	**Picrate salt extracted [a] (%)**				
	Cu^{2+}	**Co^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**Hg^{2+}**
2[b]	**12.2**	**19.7**	**21.6**	**23.6**	**40.0**
3	**31.5**	**13.1**	**22.3**	**19.0**	**78.6**
6	**62.0**	**66.6**	**69.5**	**81.4**	**86.8**
6[c]	**48.1**	**-**	**-**	**52.6**	**63.0**
Polystyrene	**<1.0**	**<1.0**	**<1.0**	**<1.0**	**17.1**

a) [a] Aqueous phase [metal picrate]= 2x 10^{-5} M; organic phase, dichloromethane [ligand]= 1x 10^{-3} M or 1x10^{-3} M solution of calix[4]arene unit/g resin for copolymer **6** 25 °C for 1h.

b) [b] Lit [38]

c) [c] Solid–solid batchwise adsorption extraction experiments

For this purpose, aqueous solutions of the picrate salts of some transition metals (Cu^{+2}, Co^{+2}, Cd^{+2} , Ni^{+2} ve Hg^{+2}) and CH_2Cl_2 solution of the compound **3** and copolymer **6** were activated in equal volumes [31]. At the end of the extraction, the picrate equilibrium concentration in the aqueous phase was determined by spectrophotometric method (UV-visible). Extraction results of the compound **2** were used for comparison [28].

From the data given in Table 2, it is seen that compound **2** has no effect on the metal cations used. While compound **3** shows a considerable selectivity towards Hg^{2+} cation compared to other cations used in the extraction. This can be explained by the sulfur atom entering the structure. Because the sulfur atom is a soft donor group, soft acid makes soft base interaction with Hg cation, which is a soft metal [32, 33].

Connecting to a polymeric chain, the extraction capabilities of the compound have been varied. As can be seen from Table-2, the selectivity of the copolymer **6** to metal cations is increasing in the following order: $Co^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+} < Hg^{2+}$. This is due to the fact that monomer 5 changes conformation when it enters the polymeric bacbone. This is in agreement with the literature [28, 29].

In addition to liquid-liquid extraction studies, solid-liquid extraction studies of copolymer **6** with some metal cations (Cu^{2+}, Pb^{2+} and Hg^{2+}) were also carried out. This was performed exactly the same way as in the liquid-liquid extraction studies. It was fulfilled by stirring solid state copolymer with the metal picrate solutions for one hour at 25°C. The results are given in Table-2. A comparison of these results with the liquid-liquid extraction shows a significant reduction in the solid-liquid extraction abilities of copolymer. This shows that the solid phase has a lesser binding capacity [29].

Dichromate Anion Extraction

A literature review would demonstrate that chromate and dichromate anions have high toxicity and they are mutagenic and carcinogenic. It is known that Cr^{6+} could penetrate living cell membranes [34, 35]. Thus, it is essential to remove Cr^{6+} from the waters. Various methods have developed for this purpose. One of these is the liquid-liquid extraction technique. Thus, a Na-dichromate extraction study was also conducted to scrutinize the anion transfer properties of the synthesized compounds, in addition to metal picrate extraction studies. Liquid-liquid extraction studies were conducted by preparing Na-dichromate aqueous solutions in different pH values with **3, 4** and copolymer **6** dichloromethane solutions and by using same volumes from each solution. % Extraction values are given in Table-3 and plotted in Fig. 2.

Table 3. Percentage extraction of dichromate by extractant **3, 4** and copolymer **6** (%)

	Dichromate Anion Extracted (%)^a			
Compound	**pH 1.5**	**pH 2.5**	**pH 3.5**	**pH 5.0**
3	**9.1**	**7.2**	**2.5**	**<1.0**
4	**72.5**	**60.1**	**47.3**	**5.1**
6	**11.3**	**9.4**	**5.8**	**<1.0**

^{a} Aqueous phase, [metal dichromate]= 1x 10^{-4} M; Organic phase, dichloromethane, [ligand] = 1 x10^{-3} M or 1 x10^{-3} M Solution of calix[4]arene unit/g resin for oligomer (copolymer **6**) 25 ºC for 1h.

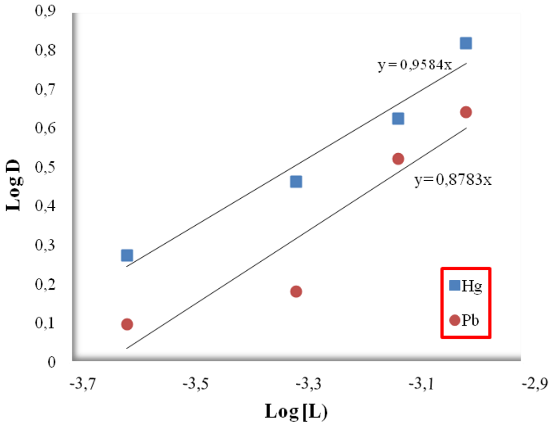


Fig. 2: Log D versus Log[L] for the extraction Hg^{2+} (■) and Pb^{2+} (●) picrates by copolymer **6** from an aqueous phase into dichloromethane at 25 °C.

Extraction results (Table-3) showed that the compound **3** had no effect on chromate anion. The reduced form of that compound, compound **4** was found to be quite effective on dichromate anions especially at low pH values such as 1.5-3.5. This was not an unexpected result. Because that compound carried an amino group and this functional group could provide a suitable environment for anion transfer by being protonated easily in acidic media. These results were in conformity with the literature [36-38]. This could be explained as follows: Compound **4** carries an amino group and this group plays an important role in the formation of intermolecular hydrogen bonds and thus an electrostatic interaction takes place between the protonated anilinium groups and the dichromate ions. Extraction results for the copolymer **6** demonstrated remarkably that this compound did not exhibit a significant effect on dichromate anion both under low and high pH values. These low extraction values were also expected. This structure did not carry an amino group, because amine group has turned into an amide group within the polymeric structure. Thus, this copolymer couldn't be protonated in acidic media and couldn't transfer the dichromate anion from aqueous phase to the organic phase.

It was observed in the extraction findings Fig. 3 that the amount of extracted dichromate increased with the decrease in pH value of the aqueous phase. In high acidic environments $Na_2Cr_2O_7$ turns into $H_2Cr_2O_7$ and the following equilibrium reaction takes place in the aqueous solution.

$$H_2Cr_2O_7 \rightleftharpoons H^+ + HCr_2O_7^-$$

$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}$$

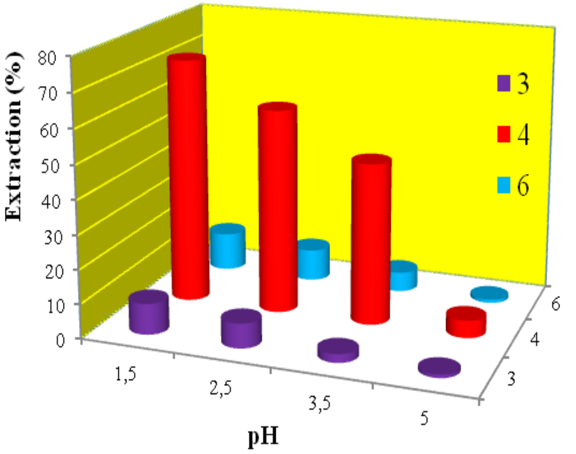


Fig. 3: Extraction percentage of dichromate with compounds **3, 4** and copolymer **6** at pH 1.5 – 5.0.

In higher pH media, the poor extraction of dichromate is due to not sufficient protonation of amino groups. The reason for the transport of chromate ion at lower pH is due to anion hydration and anion hydration is also very important in liquid liquid extraction [38]. Dichromate ions are found as protonated $HCr_2O_7^-$ at low pH. This mono anion has less hydration free energy than the dianionic form of $Cr_2O_7^{2-}$. Consequently dichromate ion in the form of $HCr_2O_7^-$ is extracted to the organic phase is higher. Another reason why the form of $HCr_2O_7^-$ is more advantageous than $Cr_2O_7^{2-}$ is while $HCr_2O_7^-$ is balanced with one sodium ion, $Cr_2O_7^{2-}$ is balanced with two sodium ions. These are the main reasons why dichromate is transported better to the organic phase at low pH [37,38].

Conclusion

In conclusion thioether functionalized calix[4]arene and its styrene copolymer were synthesized and they were found to be good extractants for metal cations and dichromate anion. Copolymer was synthesized from monomer **5** and styrene by radical initiated reactions. The extraction ability of the compounds **3, 4** and copolymer **6** were studied. Copolymer **6** has been observed to be a good extractant for all the metal picrate salts used. Anion extraction studies were carried out with $Na_2Cr_2O_7$ salt at different pH for **3**, **4** and **6**. While the styrene copolymer (**6**) is a weak extractant for the dichromate anion, compound (**5**) has a significant ability to extract it from aqueous phase to organic phases in acidic media.

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