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Ezgi Akceylan[a]; Mustafa Yilmaz[a]; Richard A. Bartsch[b]
[a] Department of Chemistry, Selçuk University, Konya, Turkey [b] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA

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Immobilization of Cyclic Alkylamine Calix[4]arene Derivatives on Merrifield Resin: Evaluation of Extraction Ability Toward Dichromate

EZGI AKCEYLAN,[1] MUSTAFA YILMAZ,[1]
AND RICHARD A. BARTSCH[2]

[1]Department of Chemistry, Selçuk University, Konya, Turkey
[2]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA

*Two new calix[4]arene-based polymeric resins were synthesized via nucleophilic substitution reactions involving 5,11,17,23-tetrakis(N-piperidinomethyl)-25,26,27,28-tetrahydroxycalix[4]arene (**2**) and 5,11,17,23-tetrakis[4-carboethoxy-N-piperidino]-25,26,27,28-tetrahydroxycalix[4]arene (**4**) as precursors with Merrifield resin. Extraction studies were performed by liquid–liquid extraction and solid–liquid adsorption procedures. The monomeric compounds showed excellent extraction ability toward dichromate in liquid–liquid extraction systems. Polymeric resin **3** with calixarene moieties exhibited high adsorption properties, while resin **5** showed lower adsorption of dichromate in solid–liquid extractions.*

Keywords calixarenes, polymers, liquid–liquid extraction, adsorption, dichromate

Introduction

In the field of supramolecular chemistry, the calix[4]arene platform displays interesting organizing properties for the construction of ligating sites to recognize various species, including cations, anions and neutral molecules. A variety of calix[4]arene-based receptors that possess unusually-shaped cavities have been prepared via "upper" and "lower" rim functionalization. Complexation properties of these molecules are highly dependent upon the nature and number of donor groups and the conformation of the calix[4]arene moiety. It is known that calix[4]arenes can exist in the conformations cone, partial cone, 1,2-alternate, and 1,3-alternate (1–3). The available sites on these macrocyclic compounds can be easily modified to tailor them for many applications, such as ionophores in catalysis, heavy metal adsorption agents, alkali metal complexation agents and chemical sensors (4–7). Among the functional groups that have been appended are ethers, esters, amides, ketones, alkenes, ammonium species, phosphines and heterocycles (8–18).

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Address correspondence to Mustafa Yilmaz, Department of Chemistry, Selçuk University, Konya 42031, Turkey. E-mail: myilnaz@selcuk.edu.tr

Although cation complexation has been extensively studied, the recognition of anions by synthetic receptors based on calixarenes remains relatively unexplored. Molecular recognition of anionic guest species by positively charged π electron-deficient neutral abiotic receptor molecules is an area of intense current interest. In designing complexants for particular guest anions, a number of structural features can be incorporated into the host molecule that may be important in achieving selective binding. The importance of favorable amine, amide or protonated imine ($-NH_2/OC-NH/OC{=}N$) hydrogen bonding interactions for anion binding has recently been exploited in the design of calix[4]arene-based receptors (19–31).

In previous work, we have designed different calix[4]arene-based receptors for the extraction of dichromate from aqueous solution into an organic phase (32–40). Chromate and dichromate anions are important due to their high toxicity and contamination in soils and waters (41–43). Following previous studies, we have extended the field of research to design structures based on the calix[4]arene platform for extraction of dichromate. Moreover, in our previous work (35–37), we reported a few polymeric calixarenes with different functionalities and have investigated their ionophoric properties towards dichromate. Herein, we report the synthesis and extraction studies of novel polymers based on a calix[4]arene platform with cyclic amino groups on their lower rim.

Experimental

Melting points were determined on a Gallenkamp apparatus in sealed capillaries and are uncorrected. ^1H NMR spectra were recorded on a Bruker 400 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 spectrophotometer. Elemental analyses were performed with a Leco CHNS-932 analyzer.

Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}). NaH was used as a 60% dispersion in oil and washed twice with hexane before use. Generally, solvents were dried by storage over molecular sieves (Aldrich; 4Å, 8–12 mesh). Dichloromethane was distilled from $CaCl_2$. MeOH was distilled over Mg and stored over molecular sieves. Merrifield resin was purchased from Fluka (No. 63865). All other chemicals were purchased from Merck. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Synthesis

Calix[4]arene (**1**) was synthesized according to the literature procedures (44, 45). The calixarenes **2** and **4** and polymers **3** and **5** employed in this work (Figure 1) were synthesized as follows.

The following general procedure (46) was adopted to transform calix[4]arene (**1**) into the corresponding cyclic amine derivatives **2** and **4**.

General Procedure (Mannich Reactions)

To a solution of calix[4]arene (**1**) (10 mmol) in 90 mL of THF were added 11 mL of acetic acid, the secondary amine (piperidine or ethyl-4-piperidincarboxylate) (50 mmol), and 37% aqueous formaldehyde (50 mmol) and the reaction mixture was stirred for 24 h at

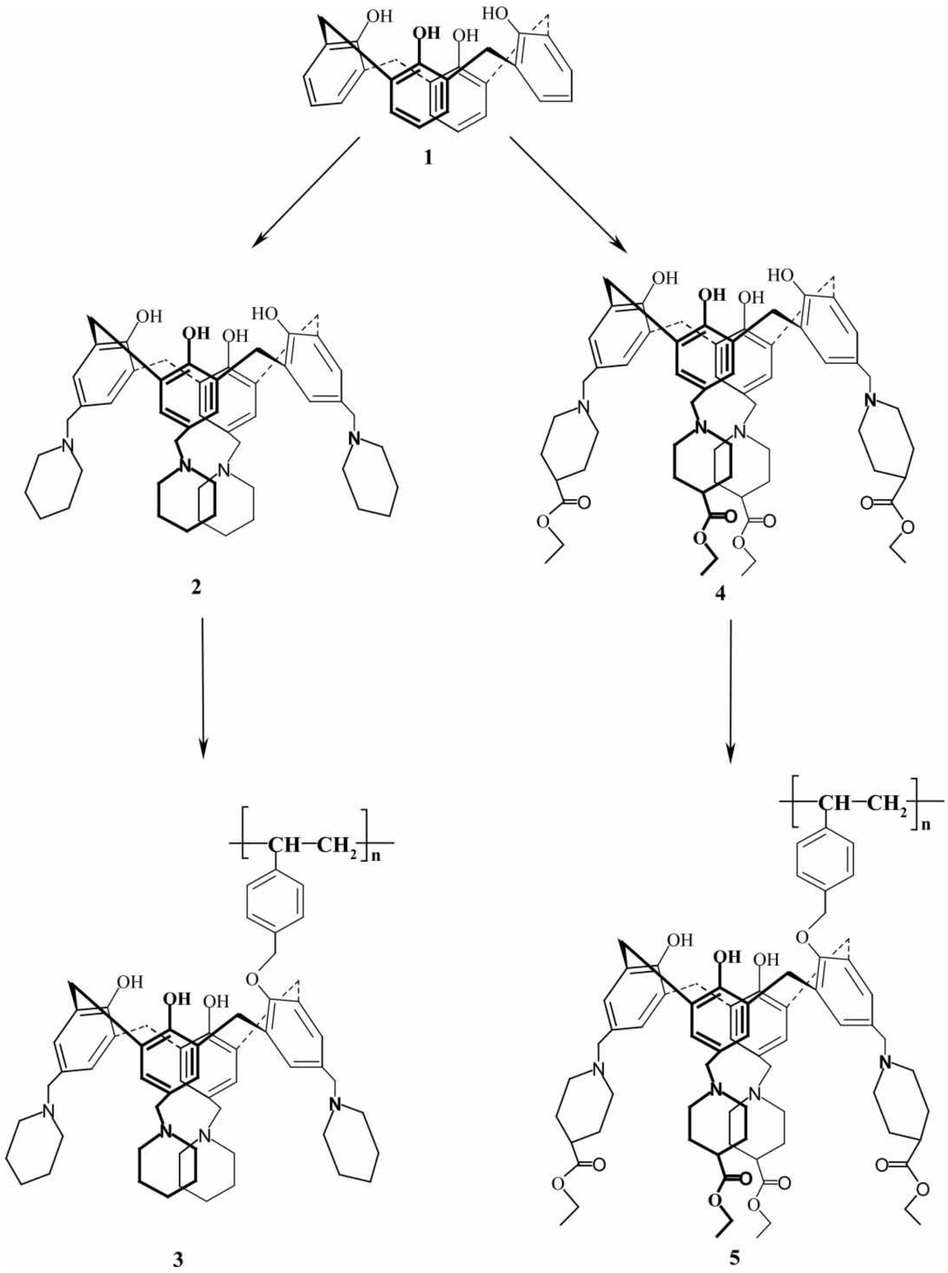

Figure 1. Schematic representation of the synthesis of calix[4]arene derivatives **2** and **4** and their corresponding polymeric resins **3** and **5**.

room temperature. The solvent was removed *in vacuo* and the residue was dissolved in 75 mL of water. The aqueous solution was extracted twice with 50 mL of diethyl ether and then neutralized with 10% aqueous K_2CO_3 solution. The precipitate that formed was removed by suction filtration. The product was dried *in vacuo* and recrystallized from chloroform.

5,11,17,23-Tetrakis(N-piperidinomethyl)-25,26,27,28-tetrahydroxycalix[4]arene (2)

Compound **2** was obtained in 65% yield, m.p. 290°C (decomp.). ^{1}H NMR ($CHCl_3$): δ 1.40–1.60 (br m, 24H, CH_2), 2.65–2.85 (m, 16H, CH_2-N), 3.20 (s, 8H, CH_2-N), 3.55 (d, 4H, $J = 14$ Hz, Ar-CH_2-Ar), 4.38 (d, 4H, $J = 14$ Hz, Ar-CH_2-Ar), 6.85 (m, 4H, Ar-H-OH). Anal. Calcd. for $C_{52}H_{68}O_4N_4$: C, 76.81; H, 8.43; N, 6.89%. Found: C, 76.69; H, 8.35; N, 6.59%.

5,11,17,23-Tetrakis[4-carboethoxy-N-piperidino]-25,26,27,28-tetrahydroxycalix[4]arene (4)

Compound **4** was obtained in 77% yield, m.p. 18°C, ^{1}H NMR ($CHCl_3$): δ 1.25 (t, 12H, CH_3), 1.78 (t, 8H, N-CH_2), 1.87 (d, 8H, $J = 11$ Hz, CH_2), 1.96 (t, 8H, N-CH_2), 2.27 (m, 4H, CH), 2.81 (d, 8H, $J = 11$ Hz), 3.26 (d, 8H, Ar-CH_2-N), 3.52 (d, 4H, $J = 13$ Hz), 4.14 (q, 8H, CH_2-O), 4.23 (d, 4H, $J = 13$ Hz), 6.99 (s, 8H, Ar-H), 7.28 (s, 4H, Ar-OH). Anal. Calcd. for $C_{64}H_{84}O_{12}N_4$: C, 69.79; H, 7.69; N, 5.09%. Found: C, 69.70; H, 7.40; N, 5.02%.

The following general procedure was adopted to transform **2** and **4** into the corresponding polymers **3** and **5**.

General Procedure

A 2.0 mmol amount of **2** or **4** was dissolved in THF (50 mL). To this solution, 10 mmol of NaH (60%) was added. In another flask, 1.0 g of Merrifield resin (0.8 mmol Cl/g resin) was dissolved in DMF (50 mL). To this solution, NaI (2.0 mmol) was added. Both mixtures were stirred for 30 min at room temperature. The contents of the two flasks were mixed together and heated at 70°C under nitrogen with stirring for 2 days. The THF was removed *in vacuo* and the polymeric beads were filtered, rinsed with water, and 1 N HCl, and then repeatedly washed with $CHCl_3$ and MeOH to ensure removal of any unreacted Mannich base. Finally, the beads were dried in a vacuum oven. The amount of the calixarene amine derivative **2** or **4** bonded to the polymeric support was determined from the difference of mass taken before and after the coupling with the dry resin, and also from the results of elemental analysis.

Polymer 3 from 5,11,17,23-Tetrakis(N-piperidinomethyl)-25,26,27,28-tetrahydroxycalix[4]arene (2) and Merrifield Resin

Loading showed a range of calixarene moieties between 15–17% from the weight increase of the resin. By elemental analysis, the polymer contained 0.72% nitrogen corresponding to 0.128 mmol of **2**/g of polymer, s.p. 250°C (decomp.). IR (KBr): 3420 cm^{-1} (OH). Elemental analysis for **3**, found: C, 86.01; H, 6.43; N, 0.72%.

Polymer 5 from 5,11,17,23-Tetrakis[4-carboethoxy-N-piperidino]-25,26,27,28-tetrahydroxycalix[4]arene (4) and Merrifield Resin

Loading showed a range of calixarene moieties between 25–27% from the weight increase of the resin. By elemental analysis, the polymer contained 1.02% nitrogen, corresponding to 0.182 mmol of **3**/g of polymer, s.p. 185°C (decomp.). IR (KBr): 3381 cm^{-1} (OH) and 1725 cm^{-1}(C=O). Elemental analysis for **5**, Found: C, 88.20; H, 7.92; N, 1.02%.

Liquid–Liquid Extraction

Dichromate extraction experiments were performed following Pedersen's procedure (47). A mixture of 10 mL of a 1×10^{-4} M aqueous dichromate solution at pH 4.5 and 10 mL of a 1×10^{-3} M solution of calixarene **2** or **4** in CH_2Cl_2 was vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at 25°C for 1 h, and finally left standing for an additional 30 min. Blank experiments showed that no dichromate extraction occurred in the absence of calixarene. The percent extraction (E%) of dichromate was calculated from the absorbance A of the aqueous phase measured at 346 nm using the following expression:

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

where A_o is the absorbance of the aqueous phase of a blank experiment carried out without calixarene.

Batch Adsorption Studies

Approximately 0.025 g (W) of resin was shaken with 10 mL of aqueous solution containing 10 mL (V) of aqueous sodium dichromate solution (1.0×10^{-4} M) at pH 1.5 (C_i) in a 50-mL, stoppered flask at 25°C for 1 h. The mixture was filtered. The concentration of dichromate remaining (C_e) in the aqueous phase after the adsorption was then determined spectrophotometrically. The adsorption capacity (q) was calculated as:

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

Results and Discussion

The main focus of our research program is the design of new calixarene-based ionophores that are easily accessible and have effective binding character for a particular set of cations or anions, which could be useful for a variety of applications, such as clinical laboratory, environmental and industrial process analysis. To achieve this goal, calix[4]arene (**1**) has been chosen as the precursor. The synthetic scheme for its elaboration is shown in Figure 1. The syntheses for compounds **1**, **2**, and **4** are based on previously published procedures (44–46). The substitution of calix[4]arene (**1**) at its upper rim (Mannich Reaction) was conducted in the presence of AcOH in THF with a cyclic secondary amine (piperidine or ethyl-4-piperidincarboxylate) and formaldehyde to afford the cone conformers **2** and **4** in 65 and 77% yields, respectively. The ^{1}H NMR spectra of **2** and **4** have a typical AB pattern for the methylene bridge protons ($ArCH_2Ar$) of the calixarene moiety at 3.55 and 4.38 ppm ($J = 14$ Hz) and at 3.52 and 4.23 ppm ($J = 13$ Hz) for **2** and **4**, respectively, which demonstrates that both the compounds exist in the cone conformation (48). Compounds **2** and **4** were used as precursors for the synthesis of polymer-supported calixarene ionophores **3** and **5**, respectively, by nucleophilic substitution reactions. Polymers **3** and **5** were prepared by heating **2** and **4**, respectively, with Merrifield resin in the presence of NaI and NaH in THF/DMF (1 : 1) for 24 h. The loading of **2** and **4** on the polymeric support was found to be 15–17% and 25–27%, respectively, based upon the weight increase of the polymers.

Extraction Studies of Dichromate

Liquid–Liquid Extraction

Recently efforts have been made to synthesize modified calixarenes that can be used as hosts for simple anions. In this study, we targeted two new extractants based on a calixarene framework that can easily be immobilized onto a polymeric matrix and are suitable for anion extraction. Chromate and dichromate are important because of their high toxicity and their presence as contaminants in soils and waters ([39–42). For a compound to be effective as a host, it is necessary that its structural features be compatible with those of the guest anions. Chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$, respectively) are dianions in which the anionic periphery has oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule.

A preliminary evaluation of the phase transfer efficiency of extractants **2** and **4** was carried out by liquid–liquid extraction of $Na_2Cr_2O_7$ from aqueous solution at pH 4.5 water into CH_2Cl_2. This pH was chosen for the liquid-liquid extraction of **2** and **4** due to their water-solubility below pH 4.5. The results are summarized in Table 1. Aqueous solutions of $Na_2Cr_2O_7$ showed no extraction into CH_2Cl_2 in the absence of extractant.

The higher extraction affinity for **2** may be due to the planar geometry of the cyclic amine rings, and its more compatible structural features, compared to **4**.

The extraction data for varying concentration of **4** was analyzed by a classical slope analysis method. Assuming the extraction of an ion-pair [M^{n+}, A^{n-}] by the anion receptor [L] according to the following equilibrium:

$$m(L)_{org} + nA_{aq}^{n-} + nM^{n+} \rightleftharpoons [((L)_m, A_n^{n-}, M_n^{n+})]_{org} \tag{3}$$

The extraction constant K_{ex} is then defined by:

$$K_{ex} = \frac{[((L)_m, A_n^{n-}, M_n^{n+})]_{org}}{[M^{n+}]^n[A^{n-}]_{aq}^n[L]_{org}^m} \tag{4}$$

Equation 4 can be rewritten as:

$$\log D_A = \log K_{ex} + n \log[L]_{org} \tag{5}$$

where the distribution ratio D_A is defined as the ratio of concentrations of an ion-pair [M^{n+}, A^{n-}] in the two phases:

$$D_A = [M^{n+}, A^{n-}]_{org}/[M^{n+}, A^{n-}]_{aq}$$

Table 1
Liquid–liquid extraction of dichromate by calixarenes **2** and **4**

	Percent dichromate extracted (%)[a]
2	88.7
4	75.7

[a] Aqueous phase, [sodium dichromate] = 1.0×10^{-4} M, pH 4.5; organic phase, dichloromethane, [ligand] = 1.0×10^{-3} M at 25°C, for 1 h.

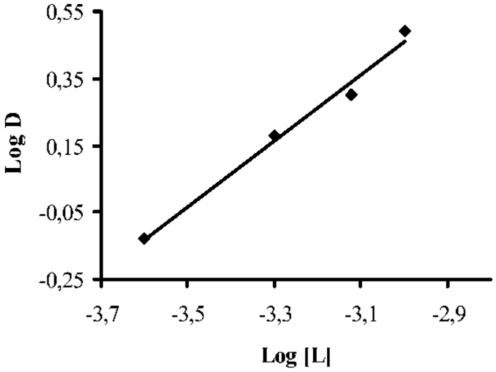

Figure 2. Log D vs. log [L] for extraction of dichromate by **4** from an aqueous phase at pH 4.5 into CH_2Cl_2 at 25°C.

Consequently a plot of log D_A vs. log [L] leads to a straight line whose slope allows the stoichiometry of the extracted species to be determined.

Figure 2 shows the extraction of dichromate into CH_2Cl_2 at different concentrations of **4**. A linear relationship between log D_A vs. log [L] is evident with a slope of 4.0, which equals 0.98 at pH 4.5, revealing that **4** forms a 1 : 1 complex with dichromate. Using equation (5), log K_{ex} is calculated to be 3.43 ± 0.20 at pH 4.5, $HCr_2O_7^-$ is the primary anionic form of Cr(VI) in aqueous solution. We propose that the extraction complex involves a two-site interaction of $HCr_2O_7^-$ with one protonated nitrogen to form an ion pair that is further stabilized by hydrogen bonding with an unprotonated nitrogen in **4** (Figure 3).

Solid–Liquid Extraction

In this study, another objective is to synthesize a conformationally stable form of calix[4]-arene amine covalently linked to Merrifield resin and examine its adsorption ability toward dichromate. We performed solid–liquid adsorption studies of dichromate with resins **3** and **5**. Aqueous solutions of $Na_2Cr_2O_7$ showed no extraction into a CH_2Cl_2 phase in the absence of the resin. From the results summarized in Table 2, it is seen that resin **3** possesses higher adsorption capability for dichromate than resin **5** and both polymeric

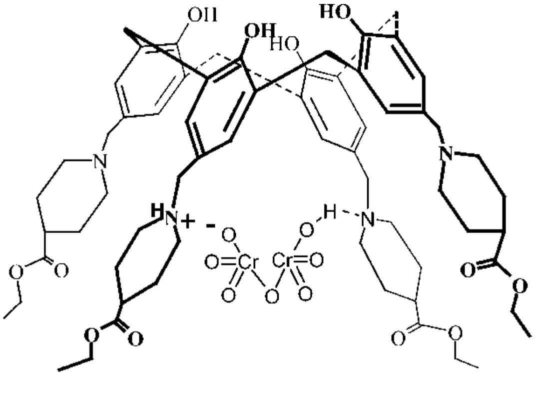

Figure 3. Proposed interactions of **4** with $HCr_2O_7^-$.

Table 2
Percentage adsorption of dichromate by resins **3** and **5** and Merrifield resin[a]

Ligand		
3	**5**	Merrifield resin
53	21	<1.0

[a] Solid phase, adsorbent = 25 mg of resin; aqueous phase, $Na_2Cr_2O_7 = 1.0 \times 10^{-4}$ M, pH 1.5, at 25°C, 1 h.

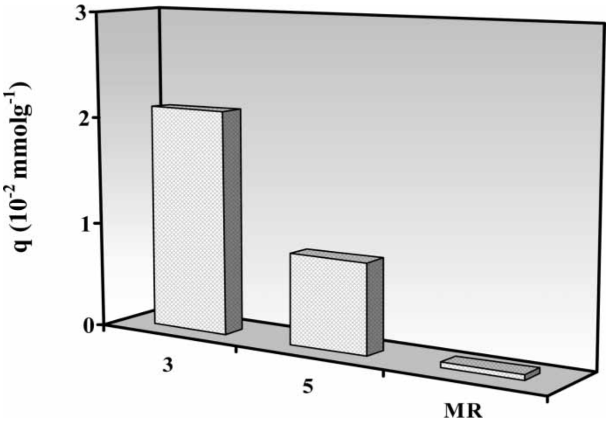

Figure 4. Adsorption capacity for dichromate of resins **3**, **5** and MR (25°C, 1 h, $C_i = 0.1$ mmol · L^{-1}) at pH 1.5 (MR: Merrifield resin).

calixarenes **3** and **5** show strong adsorptive behavior toward dichromate compared with Merrifield resin (Figure 4).

The decrease in absorption affinity of **5** may be due to a steric effect of its ester moieties compared to **3**. The conversion of Merrifield resin into immobilized polymeric calix[4]arene derivatives **3** and **5** significantly increases the anion extraction ability. 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 in two-phase extraction systems. It is possible that the polymer plays a role in which it folds into conformations that place functional groups from multiple calix[4]arene moieties in the polymer into a preferred conformation where they can associate with the oxoanion.

Conclusions

The research reported herein describes the sythesis of two new, wide rim-substituted calix[4]arene cyclic alkylamine derivatives. This work also demonstrates a convenient method for the synthesis of calixarene-based polymeric resins. Compounds **2** and **4** are versatile starting materials for the synthesis of polymerizable calixarene derivatives suitable for adsorption of anions. The extraction abilities of monomers **2** and **4** and their corresponding polymers **3** and **5**, respectively, was determined. It is observed that all ionophores are very good extractants or adsorbents for dichromate from aqueous solution. It is important to note that the conformation of the calix[4]arene unit and the cooperativity of the functionalities play important roles in the two-phase extraction systems.

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