Synthesis of Novel Silica Gel Immobilized-Calix[4]Arene Amide Ionophores and Their Anion Binding Abilities Toward Phosphate and Chromate Anions

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ABSTRACT: This article describes the synthesis and characterization of four new calix[4]arene ionophores **5–7** and **9** and corresponding two new silica gel-immobilized calix[4]arene ionophores containing pyridine **10** and **11** via modification of calix[4]arene monoamide derivatives **5** and **6** with aminopropyl silica gel, respectively. The extraction studies have been performed using liquid–liquid extraction for receptors **5–7** and **9** and solid–liquid batchwise sorption procedures for receptors **10** and **11**. Obtained extraction results showed that the immobilized-calix[4] arene ionophores **10** and **11** have high extraction ability toward chromate and phosphate anions as compared to their corresponding monomeric precursors **5** and **6**. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3831–3839, 2012

Key words: dichromate; phosphate; calix[4]arene; sorption; immobilized calixarene

INTRODUCTION

Immobilization of ion selective ligands to form polymer-supported reagents results in an extended set of applications.[1] Silica materials with functional groups have been widely used as solid phase in high performance liquid chromatography (HPLC) and solid phase extraction (SPE).[2] In this field, silica gel-immobilized calix[4]arene derivatives as extractants have received considerable interests due to increasing importance of anions in many fields.[3] Calix[4]arenes belong to a larger family of calix[*n*]arene molecules that are prepared from formaldehyde and *para*-substituted phenols via cyclic condensation under alkaline conditions.[4–8] They are extensively used as effective and selective receptors of ions and molecules due to their unique vase-shaped structure.[5,6] It is well known that calix[4]arene derivatives can adopt four conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate and their complexing behaviors have been proved to depend on the conformation of the calixarene moiety. Much attention has been paid to calix[4]arenes in the cone conformation, *O*-substituted with amide, ester, and their complexing properties towards some anions.[9] The rapid growth in this area is due to the realization of the many roles that anions play in many areas of research and everyday life. In addition, their utilization is also oriented to nuclear medicine and nuclear waste reprocessing biochemical research and environmental area (binding of anionic pollutant—nitrate, phosphate, chromate, etc.) The most utilized groups for the purpose of anion binding by hydrogen bonds are amide, thioamide, and amine functions.[10,11] Phosphate levels having a negative effect on aquatic ecology and water quality in freshwaters have increased in the past 50 years.[12] With increasing use of phosphate fertilizers in agricultural industries, monitoring of phosphate ions becomes very important. Many phosphorus compounds cause serious health problems. On the other hand, it plays an important role in biochemical processes and it is a key factor in the eutrophication of surface water.[13,14] Phosphorus exists in a wide variety of physicochemical parameters forms in natural waters, and they are highly mobile in aquatic ecosystem.[15] Efficient receptors of phosphate anions may afford new methods for their detection, separation, quantification, or transportation. However, most receptors devised for phosphate anions are organic molecules that work only in nonaqueous media via hydrogen bonding interaction.[16] On the other hand, chromium has been extensively detected in soil and groundwater, particularly at sites associated with wood processing, leather tanning, metal plating, and metal corrosion inhibition.[17] Chromate, which is the most prevalent form of Cr(VI) present in several industrial solid/liquid waste products, is one of the most dangerous

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pollutants. Because, it is a strong oxidant irritating plant and animal tissues and is also carcinogenic and mutagenic.[18] Chromium can be in several oxidation states, of which the most stable and common forms in the environment are trivalent [Cr(III)] and hexavalent [Cr(VI)] species. The hazard of chromium is dependent on its oxidation state.[19] Compared to Cr(VI), which is soluble, mutagenic, oncogenic, and highly toxic to all organism, Cr(III) is water-insoluble and the much less toxic than Cr(VI).[20] Conventionally, Cr(VI) is removed from water through reduction of Cr(VI) to Cr(III) using reducing agents such as ferrous sulfate, sulfur dioxide, or sodium bisulfite, followed by precipitation as Cr(III).[21] In addition, hexavalent chromium can also be extracted directly from soils by the use of a mixture of NaOH and Na_2CO_3 at 90–95°C.[22]

Although several works regarding the synthesis and complexation of metal cations and toxic anions with macrocyclic ligands as calixarenes have been reported,[23–25] there is no more published studies about complexion of both silica gel-immobilized and precursor type calix[4]arene ionophores containing pyridine with phosphate anion. Until now, we have not explored the ligating behavior of silica gel-immobilized calix[4]arene receptors toward phosphate anions. Therefore, the purpose of the present work was to explore the ligating behavior of calix[4]arene ionophores based silica gel immobilized and their corresponding precursors containing pyridinium units towards phosphate and chromate anions by means of liquid–liquid and/or solid–liquid extraction experiments.

EXPERIMENTAL

Materials

All of the reagents used in this study were obtained from Merck (Darmstadt, Germany) or Fluka (Milwaukee, USA) and used without further purification. Dry tetrahydrofuran (THF) was distilled from the ketyl prepared from sodium and benzophenone. CH_2Cl_2 was distilled from $CaCl_2$, MeOH over Mg, and stored over molecular sieves. Toluene was distilled from CaH_2 and sodium wire. Acetonitrile was dried from CaH_2 and stored under N_2 over molecular sieves (4 Å). Other commercial grade solvents were distilled, and then stored over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Anions were used as their sodium salts. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Column chromatographic separations were performed on Merck Silica gel-60 (230–400 mesh).

Instrumentation

^{1}H NMR spectra were obtained at room temperature using a Varian 400 MHz spectrometer in $CDCl_3$ operating at 400 MHz. IR spectra was recorded on a Perkin–Elmer spectrum 100 FTIR spectrometer (ATR). UV–visible spectra were on Jen way 6105 and Shimadzu 160 A UV–visible recording spectrophotometers. Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. Elemental analyses were performed by a Leco CHNS-932 analyzer. An Orion 410 A + pH meter was used for the pH measurements.

Synthesis

Compounds **1** and **2** were synthesized according to the previous described methods.[4,5] The synthesis of **3** and **4** has been carried out according to literature[26,27] and compound **8** was synthesized according to published literature procedure.[23]

Synthesis of calix[4]arene compound (5)

4-(Aminomethyl)pyridine (10.0 mmol) was dissolved in toluene/methanol 1 : 2 mixture (30 mL) and added dropwise to a solution of 25,27-dimethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **3** (2.0 mmol) in toluene (10 mL) with continuous stirring at room temperature for an hour. Then the reaction mixture was refluxed under a nitrogen atmosphere and the reactions were monitored by TLC. After the substrate had been consumed the solvent was evaporated under reduced pressure and recrystallized (CH_2Cl_2-MeOH) to give the white crystalline product. Yield = 0.65 g (46%); m.p. 248–250°C. IR (KBr): 3362 (OH), 1745 (CO), 1689 (CONH) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.26 (t, 1H, NH), 8.42 (d, 2H, J = 8.0, Py-H), 7.98 (s, 2H, OH), 7.40 (d, 2H, J = 7.6, Py-H), 7.14 (m, 4H, ArH), 6.93 (m, 4H, ArH), 6.80–6.82 (m, 2H, ArH), 6.72–6.75 (m, 2H, ArH), 4.84 (d, J = 6.2, 2H, $NHCH_2$), 4.60 (s, 2H, OCH_2CO), 4.46 (s, 2H, OCH_2CO), 4.26 (d, 2H, J= 13.3 Hz, $ArCH_2Ar$), 4.17 (d, 2H, J = 13.2 Hz, $ArCH_2Ar$), 3.62 (s, 3H, OCH_3), 3.48 (d, 4H, J= 13.2 Hz, $ArCH_2Ar$); Anal. Calc.: $C_{39}H_{36}N_2O_7$. C, 72.66; H, 5.63; N, 4.35%. Found: C, 72.69; H, 5.67; N, 4.30%.

Synthesis of calix[4]arene compound (6)

Monoamide compound **6** was synthesized employing the same procedure as the one used for the synthesis of compound **5** by the reaction of 5,11,17,23-tetra-*tert-butyl*-25,27-dimethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **4** and 4-(aminomethyl)-pyridine. Yield = 0.71 g (45%); m.p.: 222°C. IR (KBr): 3399 (OH), 1750 (CO), 1687 (CONH) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.28 (t, 1H, NH), 8.48 (d, 2H, J = 8.0, Py-H), 7.49 (s, 2H, OH), 7.39 (d, 2H, J = 7.6, Py-H), 7.06

(s, 4H, ArH), 6.83–6.87 (m, 4H, ArH), 4.78 (d, J = 6.0, 2H, $NHCH_2$), 4.57 (s, 2H, OCH_2CO), 4.47 (s, 2H, OCH_2CO), 4.24 (d, 2H, J = 13.3 Hz, $ArCH_2Ar$), 4.16 (d, 2H, J = 13.2 Hz, $ArCH_2Ar$), 3.55 (s, 3H, OCH_3), 3.39 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 1.27 (s, 18H, $C(CH_3)_3$), 0.99 (s, 9H, $C(CH_3)_3$), 0.96 (s, 9H, $C(CH_3)_3$); Anal. Calc.: $C_{55}H_{68}N_2O_7$. C, 76.01; H, 7.89; N, 3.22%. Found: C, 76.08; H, 7.83; N, 3.14%.

Synthesis of calix[4]arene compound (7)

Diamide compound **7** was synthesized employing the same procedure as the one used for the synthesis of compound **6** by the reaction of 5,11,17,23-tetra-*tert-butyl*-25,27-dimethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **4** and 5-methylfurfuryl amine. Yield = 0.90 g (57%); m.p.: 249–252°C. IR (KBr): 3330 (OH), 1741 (CO), 1680 (CONH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.19 (t, 2H, NH), 7.43 (s, 2H, OH), 7.17 (s, 4H, ArH), 6.87 (s, 4H, ArH), 6.26 (d, J = 3.0, 2H, ArH, ph), 5.84 (d, 2H, J = 3.0, ArH, ph), 4.48–4.55 (m, 8H, $NHCH_2$, OCH_2CO), 3.91 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 3.36 (d, 4H, J = 13.1 Hz, $ArCH_2Ar$), 1.63 (s, 6H, CH_3, ph), 3.26 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 1.22 (s, 18H, $C(CH_3)_3$), 0.93 (s, 18H, $C(CH_3)_3$; Anal. Calc.: $C_{60}H_{74}N_2O_8$. C, 75.76; H, 7.84; N, 2.94%. Found: C, 73.71; H, 7.77; N, 2.93%.

Synthesis of calix[4]arene compound (9)

25,27-Bis(3-bromopropoxy)-26,28-dihydroxycalix[4]-arene **8** (0.328 mmol) was dissolved in dry THF (16.4 mL) and NaI (1.64 mmol) was added. After the solution was mixed for an hour, 4-(aminomethyl)pyridine (0.765 mmol) was added. Then the reaction mixture was refluxed under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After complete disappearance of the starting material the remaining NaI was filtered off. The solvent was evaporated and the residue was recrystallized from CH_2Cl_2 : MeOH to get dark yellow crystalline product. Yield = 0.87 g (57%); m.p. >300. ^1H NMR ($CDCl_3$): δ 8.66 (br s, 2H, Py-H), 8.61 (d, 2H, Py-H), 8.31 (m, 2H, Py-H), 7.91 (m, 2H, Py-H), 7.42 (s, 2H, OH), 7.2 (m, 4H, ArH), 6.96–6.80 (m, 8H, ArH), 4.27–4.20 (overlapped, 8H, OCH_2 and $ArCH_2Ar$), 4.09 (br s, 4H, $NHCH_2Ar$), 3.58–3.51 (overlapped, 6H, NH and $ArCH_2Ar$), 3.10–3.08 (m, 4H, $NHCH_2$), 2.30–2.26 (m, 4H, $CH_2CH_2CH_2$); Anal. Calc.: $C_{46}H_{48}N_4O_4$. C, 76.64; H, 6.71; N, 7.77%. Found: C, 76.63; H, 6.77; N, 7.82%.

Immobilization of calix[4]arene ionophores (10 and 11)

3-Aminopropyl silica gel (1.5 g) was stirred in dry toluene (25 mL) and added dropwise into a solution of compound **5** or **6** (1.12 mmol) in 5 mL toluene with continuous stirring at room temperature for about 30 min. Then the reaction mixture was refluxed under nitrogen atmosphere for two days. The cooled mixture was filtered and washed in sequence three times with warm toluene, methanol, acetone, and distilled water. The product was dried under vacuum at 120°C for 3 h to give 1.5 g of immobilized calix[4]arene receptors **10** and **11** and kept in a desiccator before use.

Receptor 10

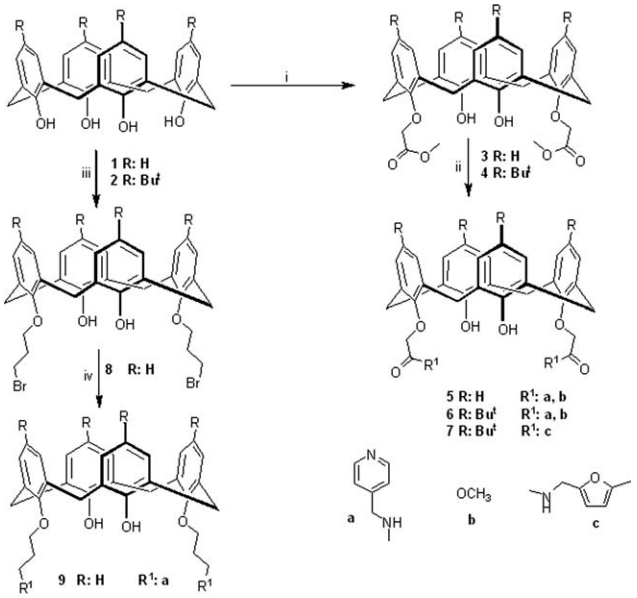
According to the elemental analysis, the bonded calixarene amount onto APS was found to be approximately 0.30 mmol of **5**/g of polymer. IR ν_{max} (KBr)/cm^{-1}: 3329; 1564; 1461; 1193; 863; elemental analysis for **10**, found: C, 19.27; H, 2.12; N, 1.26%.

Receptor 11

According to the elemental analysis, the bonded calixarene amount onto APS was found to be approximately 0.22 mmol of **6**/g of polymer. IR ν_{max} (KBr)/cm^{-1}: 3270; 1583; 1524; 1481; 1432, 1393, 1048; 862; elemental analysis for 11, found: C, 19.81; H, 2.21; N, 1.23%. Elemental analysis for APS, found: C, 5.21; H, 1.18, N, 1.09%.

Analytical procedure

The liquid–liquid or solid–liquid extraction experiments of phosphate or chromate anion were performed using amide-based receptors **5–7** and **9**, silica gel immobilized receptors **10** and **11** following the literature procedures.[23,27] An aqueous solution (10 mL) containing disodium hydrogen phosphate or dichromate at a concentration of $1 \times 10^{-4}M$ was pipetted into a vial, and a few drops of 0.01M KOH/HCl solution were added in order to obtain the desired pH equilibrium. The organic phase consisted of macrocyclic ligands 5–7 and 9 or calix[4]arene unit/g polymer 10 and 11 and CH_2Cl_2 (10 mL) at a concentration of $1 \times 10^{-3}M$. The mixture was shaken vigorously in a stoppered glass tube with a mechanical shaker for 2 min, and then magnetically stirred in a thermostated water bath at 25°C for 1 h, and finally left standing for an additional 30 min. Then, the concentration of dichromate or phosphate ion remaining in the aqueous phase was determined spectrophotometrically as described previously.[22,28] Blank experiments showed that no dichromate or phosphate extraction occurred in the absence of the receptors **5–7** and **9**, immobilized receptors **10** and **11**. The percent extraction (E%) was calculated through the absorbance of the aqueous phase measured at 346 nm for dichromate and 830 nm for



Scheme 1 Synthetic route of preparation of calix[4]arene derivatives **5–7** and **9**. (i) Brommethylacetate, CH_3CN, reflux, 48 h, (ii) 4-(aminomethyl)pyridine or 5-methylfurfurylamine, toluene : methanol (1 : 2) reflux, (iii) 1,3-dibromopropane, CH_3CN, reflux, 48 h, (iv) THF, NaI, 4-(aminomethyl)pyridine.

phosphate anions (for pH 1.5–4.5) using the following expression:

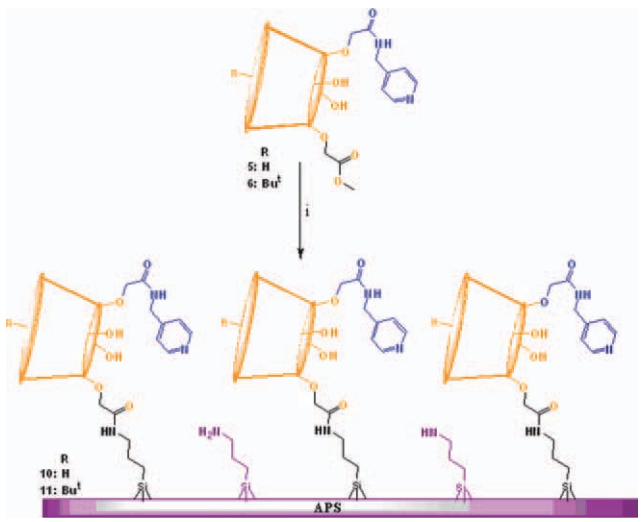
$$\text{Extraction } \% = (A_0 - A/A_0) \times 100$$

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

RESULTS AND DISCUSSION

Synthesis and characterizations

In this work, a set of new calix[4]arene ionophores **5–7** and **9** bearing pyridine or furan units on their lower rim and two new corresponding immobilized calix[4]arene ionophores **10** and **11** with pyridine amide function that have an effective binding character for chromate and phosphate anions were prepared. The anion binding properties of calix[4]arene derivatives **5–7** and **9** by two-phase solvent extraction and corresponding immobilized derivatives **10** and **11** by solid–liquid extraction towards dichromate and phosphate were explored. The synthetic route is given in Scheme 1. Compounds **1–4** were synthesized according to published procedures.[4,5,26,27] Calix[4]arene derivatives **5–7** have been prepared in two steps as shown in Scheme 1. Firstly, *p-tert-butyl*calix[4]arene was dealkylated and then functionalized with bromomethylacetate in presence of K_2CO_3 in dry acetonitrile to obtain the disubstituted methylester derivatives of **3** or **4** by *O*-substitution on the lower rim of calix[4]arene in 1,3-(distal) position. The last step, the diester calix[4]arene derivatives were treated with suitable amine compounds such as 4-(aminomethyl)pyridine or 5-methylfurfurlyamine to synthesize corresponding calix[4]-arene amide derivatives (**5–7**) in a mixture of toluene–methanol solvent system. Compound **1** was functionalized with 1,3-dibromopropane in the presence of K_2CO_3 to obtain compound **8**.[23] In the following step, compound **8** was treated with 4-aminomethylpyridine to synthesize calix ionophore **9** based pridinium unit. Immobilized calix ionophores **10** and **11** were obtained from the reaction of calix monoamide ionophores **5** or **6** with aminopropyl silica gel as shown in Scheme 2. The new calix[4] arene ionophores **5–7** and **9** and immobilized derivatives **10** and **11** were characterized by a combination of IR, ^{1}H NMR, and elemental analysis. ^{1}H NMR data showed that calix[4]arene ionophores **5–7** and **9** are in the cone conformation. A typical AX pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 4.26, 4.17, and 3.48 ppm (J = 13.2 Hz) for **5**, 3.91 ppm and 3.36 ppm (J = 13.1 Hz) for **7**, 4.27 ppm and 3.58 ppm for **9** in the ^{1}H NMR. Furthermore, the pyridinium units for calixarene ionophores **5**, **6**, and **9** or furan units for calixarene ionophores **7** on lower rim of calixarene skeleton are characterized by the presence of singlet peaks at 4.84, 4.78, 4.48, and 4.09 ppm ($NHCH_2Ar$) for **5–7** and **9**, respectively. Overlapping peaks in the range of 3.58–3.51 ppm (NH and $ArCH_2Ar$) for **9** and 2.30–2.26 ppm ($OCH_2CH_2CH_2$ and NH) for **9** were also observed. ^{1}H NMR spectra of the monoamide calix[4]arenes



Scheme 2 Synthetic route for preparation of immobilized calix[4]arene ionophores (**10** and **11**). (i) Aminopropyl silica gel, toluene, reflux, 48 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

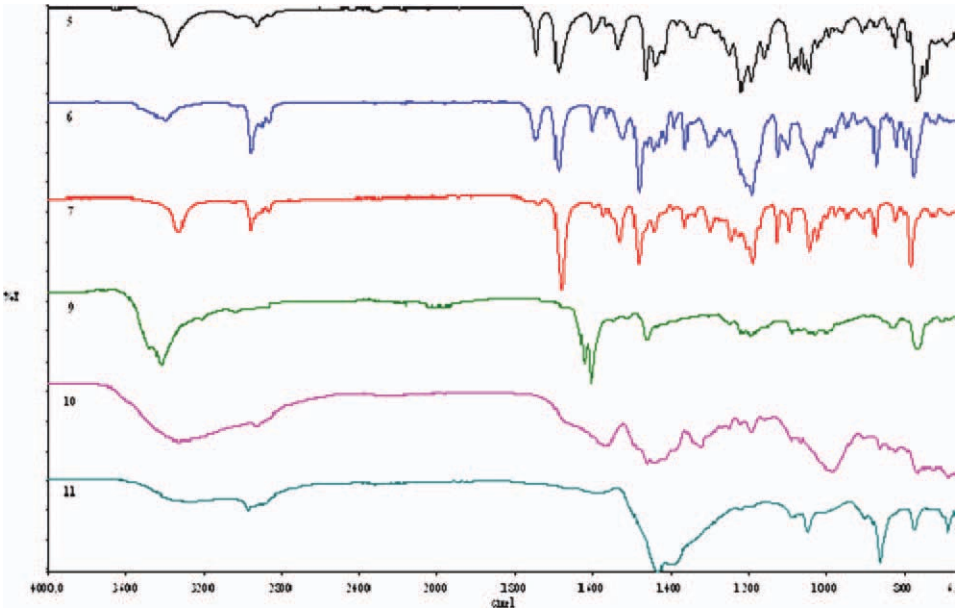


Figure 1 IR spectra of the newly synthesized compounds **5–7** and **9** and immobilized calix[4]arene based receptors **10** and **11.** [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showed a singlet for methoxy protons at 3.62–3.55 ppm for **5** and **6** while IR spectra showed both characteristic amide and ester carbonyl bands at around 1688 cm^{-1} and 1749 cm^{-1}, respectively. ^1H NMR spectra of the calix[4]arene diamide derivative **7** showed only the amide protons at 9.19 ppm, while IR spectra showed only characteristic amide bands at about 1680 cm^{-1} and the disappearance of ester carbonyl band at around 1741 cm^{-1}. All other data were in agreement with the proposed structures of calix[4]arene ionophores **5–7** and **9**. Immobilized calix[4]arene ionophores **10** and **11** were characterized by elemental analysis, UV spectra, and FTIR. Bounded amount of calixaren precursors **5** and **6** onto polymeric backbone was calculated according to literature procedure (mmol/g) = %C × 10/12*n*, where %C is the mass percentage of carbon in the product and *n* is the number of carbon in the ligand and found to be approximately 0.30 mmol of **5**/g of polymer and 0.22 mmol of **6**/g of polymer.[28] Furthermore, to support the obtained elemental analysis data for immobilized calix[4]arene ionophores **10** and **11**, the amount of remaining unreacted calixarene precursors **5** and **6** after immobilization reaction was also analyzed spectrophotometrically at 284 nm and calculated from the initial and final absorbance values of the compounds **5** and **6** before and after the immobilization reaction, respectively. Obtained results showed that the amount of unreacted calixarene was found around 0.81 and 0.88 mmol for compounds **5** and **6**, respectively. Also, the FTIR results of immobilized calix[4]arene ionophores **10** and **11** revealed that precursor **5** and **6** were immobilized onto polymeric backbone due to the bands appearing around 3300–3330 cm^{-1}, 2955–2970 cm^{-1}, 1600 cm^{-1}, and 1000 cm^{-1} bands in their FTIR spectra corresponding to Si—OH and/or calix O—H stretching, aliphatic C—H group, NH—C=O and —Si—O—Si, respectively. Furthermore, a strong band typical of ester carbonyl stretching band was not seen around 1700 cm^{-1} in the IR spectra of the immobilized calix[4]arene based receptors **10** and **11** (Fig. 1). The above results indicated that the calix[4]-arene monoamide derivatives **5** and **6** were successfully immobilized on the aminopropyl silica backbone.

Anion extraction studies

Chromate extraction

Several studies have reported the isolation and characterization of chromate and dichromate anions ($Cr_2O_7^{-2}$/ $HCr_2O_7^-$) from contaminated water but the toxic effect of chromate in water is not well documented despite its importance as an environmental pollutant. The synthesis of complexants and hosts for specific selective anions is an important goal for high value toxic anions. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anions. The dichromate ions are anions where the periphery of the anion has oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. Calix[4]arene derivatives bearing pyridine, amino, and imino on their lower rim are efficient extractant for oxoanions.[29,30] We have applied some preliminary evaluations to investigate

TABLE I
Percentage Extraction of Dichromate by Extractants 5–7 and 9, and Immobilized Extractants 10 and 11 at Different pH Values[a,b]

	pH				
Compounds	1.5	2.5	3.5	4.5	5.5
5	<0.1 ± 3	<0.1 ± 2	<0.1 ± 3	<0.1 ± 3	<0.1 ± 3
6	<0.1 ± 3	<0.1 ± 3	<0.1 ± 3	<0.1 ± 3	<0.1 ± 3
7	6.0 ± 2	<0.1 ± 2	<0.1 ± 3	<0.1 ± 3	<0.1 ± 3
9	80 ± 2	63 ± 2	47 ± 2	23 ± 2	10 ± 2
10	62 ± 3	50 ± 3	36 ± 3	30 ± 3	23 ± 3
11	70 ± 3	55 ± 3	50 ± 3	34 ± 3	27 ± 3

[a] Averages and standard deviations calculated for data obtained from two or three independent extraction experiments.

[b] Aqueous phase, [dichromate] = $1 \times 10^{-4}M$; organic phase, [ligand] = $1 \times 10^{-3}M$ for **5–7** and **9** at 25°C, for 1 h. Solid phase, sorbent = 25 mg immobilized derivatives **10** and **11**; aqueous phase, $Na_2Cr_2O_7$ = $1.0 \times 10^{-4}M$ at 25°C for 1 h.

binding efficiencies of the extractants **5–7** and **9** and immobilized receptors **10** and **11** for $Na_2Cr_2O_7$ by using solvent extraction. The results showed that $Na_2Cr_2O_7$ could be extracted from aqueous solution into dichloromethane at different pH values. The results are summarized in Table I and Figure 2. An aqueous solution of $Na_2Cr_2O_7$ showed no extraction into a phase in the absence of the extractant.

From the extraction data given in Table I, it was observed that the monomeric derivatives of calix[4]-arene **5** and **6** are poor extractants for chromate anions but ionophore **9** shows a significant extraction ability toward chromate anions at low pH. The percentage of dichromate ions extracted is 80% for **9** and 6.0% for **7** when the pH of the aqueous solution is 1.5 and they attain a minimum level of 10% for **9** and 1.0% for **7** when the pH of the aqueous solution is increased to 5.5. Furthermore, the percentage of extracted dichromate ions is very low for **5** and **6** when the pH of the aqueous solution is 1.5. Better extraction results were obtained with compound **9** which extracted the dichromate anions more efficiently as compared to compound **7** and monoamide derivatives **5** and **6**. This situation shows that calixarene derivatives containing protonable amine binding sites are more powerful extractants and this situation, which is in accordance with the literature.[29–31] Based on the results, it is concluded that calix[4]arene unit plays an important role in confirming the cooperative participation of the functional groups. Calix[4]arenes bearing monoamide-pridinium units **5** and **6** have exhibited lower extractability than the calix[4]arene derivative bearing amine-pyridinium units **9.** This reflects the fact that secondary amines of calix[4]arene **9** bind more strongly with dichromates in low pH medium. The p*K*a of protonated nitrogen of secondary amine groups is around 10 and 11, the protonated form of calix[4]arene monoamide derivatives **5** and **6** are expected to be present in significant concentration in aqueous solution (generally the p*K*a of protonated pyridines is around 5.25).[23] To compare the extraction properties of the immobilized calix[4]arene ionophores **10** and **11** with the precursors **5** and **6**, the same extraction experiments have been performed. The sorption data given in Table I indicate that the immobilized ionophores **10** and **11** show an increase in the extraction ability toward chromate anions as compared to the precursors **5** and **6**.

The higher complexation property of these ionophores **10** and **11** is due to hydrogen bonding between dichromate anion and the amide groups in the immobilized calix[4]arene.[27,32] Furthermore, this increase 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 when compared with monomers. 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 in the polymer in a preferred conformation where they can associate with the oxoanion. This pH dependence can be explained by anion hydration. In aqueous solutions having a lower Ph, the chromate 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

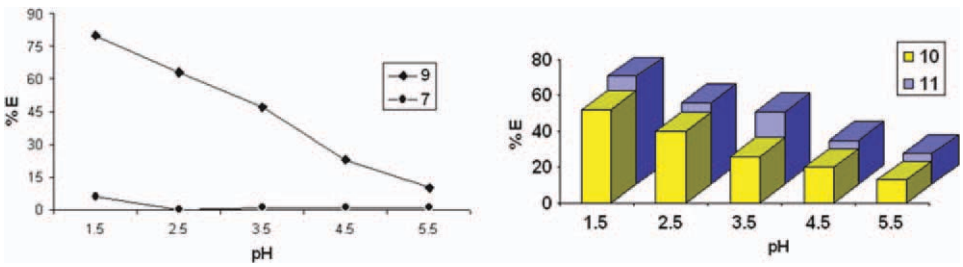


Figure 2 Extraction percentages (%*E*) versus pH following the two phase solvent extraction of dichromate anions with compounds **7** and **9** and immobilized receptors **10** and **11**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

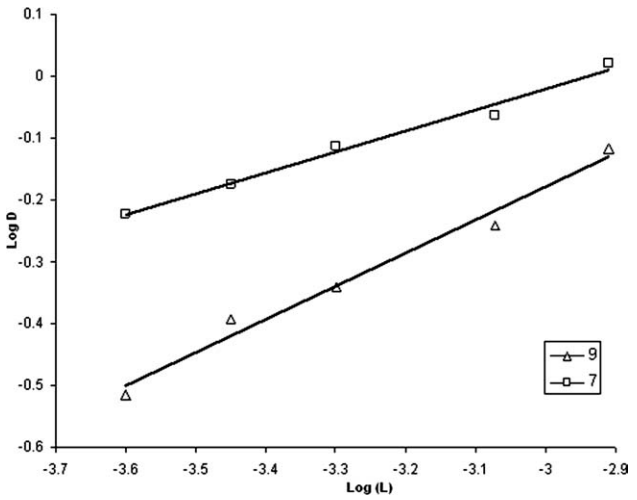


Figure 3 Log D versus log[L] for the extraction of chromate anions by the ligands **7** and **9** from an aqueous phase into dichloromethane at 25°C.

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, where as for $Cr_2O_7^{-2}$, two sodium ions are extracted with additional loss of hydration energy. All data have been analyzed by using the classical slope analysis method.[31] Assuming that the extraction of an anion A^{n-} by the receptor LH^{n+} is according to following equilibrium:

$$n(\mathrm{LH}^{n+})_{\mathrm{org}} + n\mathrm{A}^{n-}_{\mathrm{aq}} \longrightarrow \left[(\mathrm{LH}^{n+})_n, \mathrm{A}^{n-}_n\right]_{\mathrm{org}} \qquad (1)$$

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

$$K_{\mathrm{ex}} = \frac{\left[\left((\mathrm{LH}^{n+})_n, \mathrm{A}^{n}_{n-}\right)\right]_{\mathrm{org}}}{[\mathrm{A}_{n-}]^n_{\mathrm{aq}}[\mathrm{LH}^{n+}]^n_{\mathrm{org}}} \qquad (2)$$

Equation (2) can be re-written as;

$$\log D_{\mathrm{A}} = \log K_{\mathrm{ex}} + n\log[\mathrm{LH}^{n+}]_{\mathrm{org}} \qquad (3)$$

where D_A is defined as the ratio of the analytical concentration of the anion A^{n-} in both phases:

$$D_{\mathrm{A}} = [\mathrm{A}]_{\mathrm{org}}/[\mathrm{A}]_{\mathrm{aq}}$$

Consequently, a plot of the log D_A versus log [L] may lead to a straight line with a [L] slope that allows for the determination of the stoichiometry of the extracted species, where it is defined as the analytical concentration of the ligand in the organic phase. A linear relationship between log D_A versus log [L] is observed with the slope of the line for extraction of dichromate anion by ligands **7** and **9**, suggesting that these ligands **7** and **9** form 1 : 1 complexes with the dichromate anion (Fig. 3). However, it is well known that at more acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$ and after ionization in an aqueous solution it exists in the $HCr_2O_7^-$/ $Cr_2O_7^{-2}$ forms. At higher acidic conditions $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr^{6+} form and pK_{a1} and pK_{a2} values of these equations are 0.74 and 6.49, respectively. It is clear that the ligands **7** and **9** form complex mostly with $HCr_2O_7^-$ ion. This has allowed us to consider that [eq.(4)] this simultaneous extraction of 1 : 1 complexes according to the following equilibria:

$$(\mathrm{LH}^+)_{\mathrm{org}} + \mathrm{HCr_2O_{7\,aq}^-} \xrightarrow{K_{\mathrm{ex}}} \left(\mathrm{LH}^+, \mathrm{HCr_2O_7^-}\right)_{\mathrm{org}} \qquad (4)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} values using eq. (3).

Phosphate extraction

Phosphorus is the eleventh most abundant element on the surface of the earth and it is most commonly found as phosphate. Many phosphorus compounds cause serious health problems. So, several approaches have been used for the environmental removal of phosphate anion. Dihydrogen phosphate is one of the most basic anionic guest species, therefore it interacts strongly with the amide protons of the receptor.[3] Hence, binding efficiencies of newly synthesized calix[4]aren amide receptors **5–7** and **9** and immobilized derivatives **10** and **11** containing pyridine or furan moieties on phosphate anions recognition was performed by using solvent extraction or sorption studies.

The results were summarized in Table II and Figure 4. An aqueous solution of phosphate showed no extraction into a phase in the absence of the extractant. Calix[4]arene receptors **5–7** and **9** provide suitable binding sites for phosphate anions at low values of pH due to the presence of protonable amine moieties or hydrogen bonding sides. Better extraction results are obtained by compound **9** which extracted the phosphate anions more efficiently as compared to compound **7** and monoamide derivatives **5** and **6**. Because the higher extraction property of these ionophore **9** is due to the presence of the protonable secondary amine binding sites on lower rim of calixarene skeleton. At the lower pH values, both the formation of $H_2PO_4^-$ and the protonation of the amine nitrogens of calixarene ionophore **9** favor extraction into dichloromethane. Therefore, an anion-switchable complex is formed in the two-phase extraction system. The percentage of

TABLE II
Percentage Extraction of Phosphate by Extractants 5–7 and 9 and Immobilized Extractants 10 and 11 at Different pH Values[a,b]

	pH				
Compound	1.5	2.5	3.5	4.5	5.5
5	<0.1 ± 2	<0.1 ± 2	<0.1 ± 3	<0.1 ± 2	<0.1 ± 3
6	<0.1 ± 2	<0.1 ± 3	<0.1 ± 2	<0.1 ± 3	<0.1 ± 3
7	14 ± 3	4 ± 3	<0.1 ± 2	<0.1 ± 2	<0.1 ± 2
9	68 ± 2	51 ± 2	28 ± 2	7 ± 2	4 ± 2
10	63 ± 3	58 ± 3	33 ± 3	21 ± 3	14 ± 3
11	76 ± 3	55 ± 3	37 ± 3	19 ± 3	11 ± 3

[a] Averages and standard deviations calculated for data obtained from two or three independent extraction experiments.

[b] Aqueous phase, $Na_2HPO_4 = 1 \times 10^{-4}M$; organic phase, [ligand] $= 1 \times 10^{-3}M$ for **5–7** and **9** at 25°C, for 1 h. Solid phase, sorbent = 25 mg immobilized derivatives **10** and **11**; aqueous phase, $Na_2HPO_4 = 1.0 \times 10^{-4}M$ at 25°C for 1 h.

phosphate anions extracted is 68% for **9** and 14.0% for **7** when the pH of the aqueous solution is 1.5. It is also observed that phosphate anion is only extracted in trace amounts by calix monoamide derivatives **5** and **6**. This interaction can be attributed to the hydrogen bonding and electrostatic interaction between pyridine or secondary amine groups of receptors and the oxygen of phosphate ions. The same extraction experiments have been performed to compare the phosphate extraction properties of the silica immobilized calix[4]arene ionophores **10** and **11** with the monomers **5** and **6**.

The sorption data given in Table II indicate that the ionophores **10** and **11** show considerably an increase in the extraction ability toward phosphate anions as compared to the monomers **5** and **6**. From Table II and Figure 4, it is clear that maximum extraction 63% for **10** and 76% **11** occur at pH 1.5, which shows the best interaction between the ligand **11** and the phosphate ions occurs at this pH. The higher complexation property of these ionophores **10** and **11** towards phosphate anions is thought to be similar to that in the case of chromate anions. All of the obtained data for phosphate anion extraction are not surprising results. Because, oxoanions, such as chromate and arsenate, are effectively transported from the aqueous phase to the organic phase by calixarene ionophores using solvent extraction process at low pH values.[23,30] Based on all of the above extraction results, calixarene based receptors in extraction processes are found to be very useful in extraction of toxic anions as chromate and phosphate in laboratory-scale applications. Comparing the solid-phase extraction with liquid-phase extraction process, large amount of calixarene compound and toxicity of organic solvent used in solvent extraction restricts its application for industrial-scale, due to the environmental and health considerations. But, the SPE technique reduces organic solvent and large amount of calixarene usage and exposure. Furthermore, immobilized calixarene derivatives can be recovered and/or reused in solid-phase extraction technique. It is well known that at more acidic conditions, Na_2HPO_4 is converted into H_3PO_4 and after ionization in an aqueous solution it exits in the $H_2PO_4^-/HPO_4^{2-}$ form. At higher acidic conditions pK_{a1} and pK_{a2} values of these equations $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} dimers are 2.1, 7.2, and 12.6, respectively. The P(V) species occur mainly in the form of $H_2PO_4^-$ in the pH range between 5 and 7, while a divalent anion HPO_4^{2-} dominates at higher pH values. The monoanion ($H_2PO_4^-$) has smaller free energy of hydration than that of the dianionic form HPO_4^{2-}. As a result, there is a smaller loss in hydration energy, as $H_2PO_4^-$ is transferred from the aqueous phase into the dichloromethane phase. An additional advantage of $H_2PO_4^-$ over HPO_4^{2-} is that for the former only one sodium ion needs to be co-extracted to maintain charge balance, whereas for HPO_4^{2-} two sodium ions are extracted, with additional loss of hydration energy.

CONCLUSIONS

As a summary in this study, the synthesis and complexation ability of new calix[4]arene based receptors

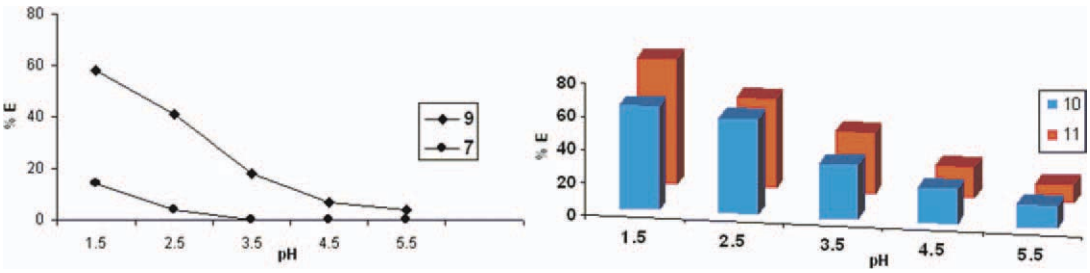


Figure 4 Extraction percentages (%*E*) versus pH following the two phase solvent extraction of phosphate anions with compounds **7** and **9** and immobilized receptors **10** and **11**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

5–7 and **9** and immobilized calixarene receptors **10** and **11** with amide functionality were successfully achieved. The extraction studies showed that compound **9** was better receptor for dichromate and phosphate anions compared with **5**, **6**, and **7**. The variety of hydrogen bonding sites that occur in these calix[4]arene derivatives may be of considerable importance for the future design of novel calix[4]arene-based receptors, carriers or supramolecular structures. The sorption studies of dichromate and phosphate were performed by using ionophores **10** and **11** as sorbent materials and the results were compared with their monomeric precursors **5** and **6**. The best sorption percentage and the highest distribution coefficient values were obtained with receptor **11**. It was observed that immobilized calixarene-based ionophores can be suitable sorbents for the removal of chromate and phosphate anions from aqueous solutions. The calixarene based pyridine or furan receptors could be proved to find remarkable applications in the design of chemical sensors, in anion-binding processes, especially phase transfer catalyses and solid-state sensors.

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