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Mustafa Durmaz[a]; Selahattin Bozkurt[a]; Abdulkadir Sirit[a]; Mustafa Yilmaz[a]
[a] Department of Chemistry, Selçuk University, Konya, Turkey

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Synthesis of 1,3-(distal) Diamide Substituted Calix[4]arene Based Receptors for Extraction of Chromium (VI)

MUSTAFA DURMAZ, SELAHATTIN BOZKURT, ABDULKADIR SIRIT and MUSTAFA YILMAZ*

Department of Chemistry, Selçuk University, 42031 Konya, Turkey

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The synthesis of novel diamide derivatives of calix[4]-arene by aminolysis of calix[4]arene diesters was reported. The ^{1}H and ^{13}C NMR, data showed that the synthesized compounds exist in the cone conformation. The complexation properties of these calix[4]arenes have been studied towards $Cr_2O_7^{=}/HCr_2O_7^{-}$ anions and it has been found that the protonated alkyl ammonium forms of calix[4]arene diamide derivatives (5,11,17,23-tetra-tert-butyl-25,27-(diethylpiperidineacetamido)26,28-dihydroxy-calix[4]arene 3 and 25,27-(diethyl-piperidine-acetamido)26,28-dihydroxycalix[4]arene 4) are effective extractants for transferring $HCr_2O_7^{-}/Cr_2O_7^{=}$ anions.

Keywords: Calix[4]arene; Diamide; Dichromate anions; Solvent extraction

INTRODUCTION

Chromium is a considerable environmental concern as it is used in numerous commercial applications including corrosion inhibition, leather tanning, metallurgy, electroplating, petroleum refining, textile manufacturing, and pulp production [1]. At many industrial and waste disposal locations, chromium has been released to the environment via leakage and poor storage during manufacturing or improper disposal practices. In the natural environment, chromium is found in Cr(III) and Cr(VI) forms. Cr(III) has relatively low toxicity and tends to form insoluble complexes with hydroxides at neutral pH [2,3]. On the other hand, Cr(VI) is highly soluble and, therefore, mobile and bioavailable in aquatic systems [4]. At relatively high concentrations, Cr(VI) compounds are potent irritants whose acute effects include ulceration of skin, eyes, mucous membranes, and the gastrointestinal tract. At low concentrations, typical of those found in the environment, Cr(VI) has mutagenic and carcinogenic effects [5,6].

Development of efficient separation processes for Cr(VI) as either $Cr_2O_7^{2-}$ or CrO_4^{2-} from soils and waters is one of the most important areas in the field of supramolecular chemistry. Several strategies have been adopted for the environmental removal of Cr(VI). These approaches involve precipitation after its reduction to Cr(III), electrochemical separation or extraction methods. Among them, solvent extraction is one of the most commonly used treatment methods and employs a selective complexant especially for ions in aqueous solution. Although there are numerous examples of molecules that act as hosts and complexants for cations, relatively few molecules have been reported as hosts for anions [7–10]. Thus, the development of an efficient extractant for anions has received considerable attention in recent years [11].

Calixarenes, cyclic oligomers of phenolic units linked through the ortho positions, are a fascinating class of macrocycles. Chemical modification from the upper or lower rims have made this class of synthetic ionophores effective extractants for transferring anionic and cationic ions or neutral molecules from aqueous solution into an organic layer. The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms and also upon the conformation of the calix[4]arene moiety [12–15]. Therefore, a variety of sophisticated anion complexing ligands containing calix[4]arene backbone have been designed and synthesized for use as selective anion extractants [16–19]. These molecules are generally calix[4]arene derivatives bearing amine or amide functions and

*Corresponding author. E-mail: myilmaz@selcuk.edu.tr

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capable of interacting with anions by hydrogen bonds [20]. In recent years, we have reported the calix[4]arene based receptors that effectively bind anions and can be useful for multiple applications such as laboratory, clinical, environmental, and industrial process analysis [21–23]. Herein we report the syntheses and ion binding properties of new ionophores bearing diamide functions which have often been claimed to act as binding sites in the complexation of dichromate anions.

EXPERIMENTAL

General

Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were obtained on a Perkin Elmer 1605 FTIR spectrometer using KBr pellets. UV–Visible spectra were obtained on a Shimadzu 160A UV–Visible spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. A Crison MicropH 2002 digital pH meter was used for the pH measurements.

Analytical TLC was performed using Merck prepared plates (silica gel 60 F_{254} on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 Mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Toluene was distilled from CaH_2 and stored over sodium wire. Other commercial grade solvents were distilled, and then stored over molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous $MgSO_4$. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system.

SYNTHESIS

Compounds **1**, **2** and **7–8** were synthesized according to previously described methods [24,25].

General Procedure for the Synthesis of Compounds 3–6

Appropriate primary amine (20.0 mmol) was dissolved in 1:2 toluene/MeOH mixture (60 mL) and added dropwise into a solution of 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonyl-methoxy-26,28-dihydroxycalix[4]arene **1** or 25,27-diethoxycarbonyl-methoxy-26,28-dihydroxycalix[4]arene **2** (4.0 mmol) in 20 mL toluene with continuous stirring at room temperature for about 30 min. Then the reaction mixture was refluxed and the reactions were monitored by TLC. After the substrate had been consumed the solvent was evaporated under reduced pressure and the residue was triturated with MeOH to give a crude product.

5,11,17,23-Tetra-tert-butyl-25,27-(diethylpiperidine acetamido)26,28-dihydroxy-calix[4]arene (3)

The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2/Hexane 2:1) and recrystallized from CH_2Cl_2/MeOH. White crystals; yield 78%; mp 237–240°C; IR (KBr): 3365 (OH), 1672 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.72 (t, 2H, N*H*), 7.64 (s, 2H, O*H*), 6.98 (s, 4H, Ar*H*), 6.82 (s, 4H, Ar*H*), 4.48 (s, 4H, OCH_2CO), 4.10 (d, 4H, $J = 13.3$, ArCH_2-Ar), 3.46 (q, 4H, NHCH_2CH$_2$N), 3.33 (d, 4H, $J = 13.4$, ArCH_2Ar), 2.43 (t, 4H, NHCH$_2$CH_2N), 2.25 (m, 8H, NCH_2), 1.28 (m, 12H, NCH$_2$CH_2CH_2), 1.20 (s, 18H, C(CH_3)$_3$), 0.96 (s, 18H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$): δ 167.92 (*C*═O), 149.59, 148.88, 148.28, 142.95, 132.36, 127.27, 126.16, 125.49, (Ar*C*), 74.79 (O*C*H$_2$CO), 57.83, 54.54 (NH*C*H$_2$*C*H$_2$N), 36.65, 34.10, 33.90, 32.17, 31.64, 30.99 (Ar*C*H$_2$Ar, *C*(*C*H$_3$)$_3$), 25.72, 24.38, 22,65 (*C*H$_2$); FAB-MS *m/z*: (1008.5) $[M + Na]^+$. Anal. Calcd for $C_{62}H_{88}N_4O_6$ (985.4): C, 75.57%; H, 9.00%; N, 5.69%. Found: C, 75.68%; H, 8.87%; N, 5.80%.

25,27-(Diethylpiperidineacetamido)26,28-dihydroxy calix[4]arene (4)

The crude product was purified in a similar manner as described for compound **3**. White crystals; yield 75%; mp 241–244°C; IR (KBr): 3357 (OH), 1680 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.65 (t, 2H, N*H*), 7.98 (d, 2H, O*H*), 7.00 (d, 4H, Ar*H*), 6.85 (d, 4H, Ar*H*), 6.72 (t, 2H, Ar*H*), 6.63 (t, 2H, Ar*H*), 4.50 (s, 4H, OCH_2CO), 4.15 (d, 4H, $J = 13.4$, ArCH_2Ar), 3.48 (q, 4H, NHCH_2CH$_2$N), 3.40 (d, 4H, $J = 13.4$, ArCH_2Ar), 2.45 (t, 4H, NHCH$_2$CH_2N), 2.23 (m, 8H, NCH_2), 1.25 (m, 12H, NCH$_2$CH_2CH_2); ^{13}C NMR ($CDCl_3$): δ 167.87 (*C*═O), 149.50, 148.78, 148.15, 142.57, 132.24, 127.15, 126.08, 125.34 (Ar*C*), 75.20 (O*C*H$_2$), 58.16, 55.24 (NH*C*H$_2$*C*H$_2$N), 31.44, 30.83 (Ar*C*H$_2$Ar). FAB-MS *m/z*: (783.8) $[M + Na]^+$. Anal. Calcd for $C_{46}H_{56}N_4O_6$ (760.9): C, 72.60%; H, 7.42%; N, 7.36%. Found: C, 72.48%; H, 7.61%; N, 7.24%.

5,11,17,23-Tetra-tert-butyl-25,27-(dipropyl imidazoleacetamido)26,28-dihydroxy-calix[4]arene (5)

The crude product was purified by washing with H_2O and recrystallized from CH_2Cl_2/MeOH. White crystals; yield 74%; mp 153–156°C; IR (KBr): 3352

(OH), 1678 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$): 8.69 (t, 2H, NH), 8.23 (s, 2H, OH), 7.45 (b, 2H, NCH═N), 7.05 (d, 4H, ArH), 6.98 (s and b, 6H, ArH and NCH═CHN), 6.82 (b, 2H, NCH═CHN), 4.45 (s, 4H, OCH_2CO), 4.15 (d, 4H, $J = 13.0$, $ArCH_2Ar$), 3.96 (t, 4H, $NHCH_2CH_2CH_2N$), 3.38 (d, 4H, $J = 13.0$, $ArCH_2Ar$), 3.28 (q, 4H, $NHCH_2CH_2CH_2NH$), 1.98 (p, 4H, $NHCH_2CH_2CH_2N$), 1.17 (s, 18H, $C(CH_3)_3$), 1.06 (s, 18H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 168.25 (C═O), 149.91, 149.75, 148.45, 142.82, 137.31, 132.96, 129.15, 127.36, 126.25, 125.91, 122.53 (ArC), 74.66 (OCH_2CO), 44.39, 40.14, 36.15 ($NHCH_2CH_2CH_2N$), 34.37, 34.00, 32.11, 31.86, 31.74, 31.18 ($ArCH_2Ar$, $C(CH_3)_3$); FAB-MS m/z: (979.3) $[M + Na]^+$. Anal. Calcd for $C_{60}H_{78}N_6O_6$ (1002.3): C, 73.59%; H, 8.03%; N, 8.58%. Found: C, 73.84%; H, 8.21%; N, 8.93%.

25,27-(Dipropylimidazoleacetamido)26,28-dihydroxycalix[4]arene (6)

The crude product was purified in a similar manner as described for compound **5**. White crystals; yield 71%; mp 210–213°C; IR (KBr): 3331 (OH), 1675 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.54 (t, 2H, NH), 8.22 (s, 2H, OH), 7.45 (s, 2H, NCH═N), 7.08 (d, 4H, ArH), 6.97 (d, 6H, ArH and NCH═CHN), 6.82 (s, 2H, NCH═CHN), 6.78 (t, 2H, ArH), 6.55 (t, 2H, ArH), 4.48 (s, 4H, OCH_2CO), 4.18 (d, 4H, $J = 13.0$, $ArCH_2Ar$), 3.95 (t, 4H, $NHCH_2CH_2CH_2N$), 3.38 (d, 4H, $J = 13.0$, $ArCH_2Ar$), 3.28 (q, 4H, $NHCH_2CH_2CH_2NH$), 1.95 (p, 4H, $NHCH_2CH_2CH_2N$); ^{13}C NMR ($CDCl_3$): δ 168.26 (C═O), 152.54, 152.23, 137.46, 133.85, 129.53, 129.15, 128.83, 127.80, 126.23, 120.08, 119.44 (ArC), 74.61 (OCH_2CO), 44.30, 40.11, 36.21 ($NHCH_2CH_2CH_2N$), 31.73, 31.18 ($ArCH_2Ar$). FAB-MS m/z: (754.87) $[M + Na]^+$. Anal. Calcd for $C_{44}H_{46}N_6O_6$ (777.7): C, 70.01%; H, 6.14%; N, 11.13%. Found: C, 70.38%; H, 5.84%; N, 10.94%.

ANALYTICAL PROCEDURE

The dichromate anion extraction experiments of calix[4]arene diamide derivatives **3–8** were performed following Pedersen's procedure [26]. Ten mL of 1×10^{-4} M an aqueous solution of sodium dichromate (0.01 M KOH/HCl solution was used in order to obtain the desired pH at equilibrium) and 10 mL of 1×10^{-3} M calixarene ligand in CH_2Cl_2 were 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. The concentration of dichromate ion remaining in the aqueous phase was then determined spectrophotometrically as described previously [27]. Blank experiments showed that no dichromate extraction occurred in the absence of calix[4]arene. The percent extraction ($E\%$) was calculated from the absorbance A of the aqueous phase measured at 346 nm (for pH 1.5–4.5) using the following expression:

$$(E\%) = A_o - A_o/A_o\, x\, 100$$

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

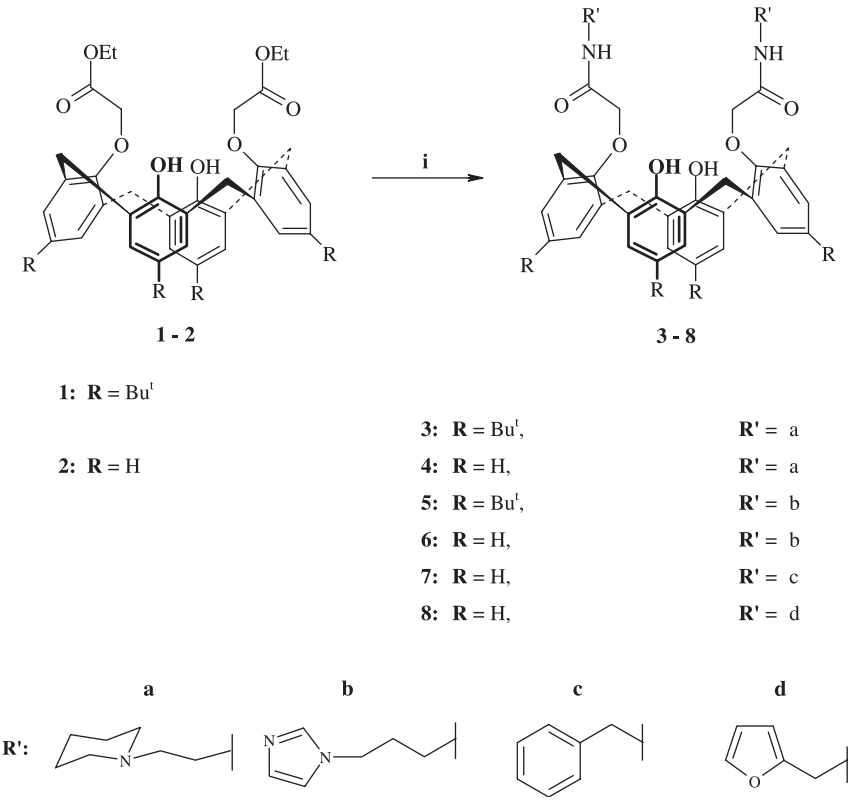
RESULTS AND DISCUSSION

Design and Synthesis of the New Hosts

In this work, we extend our previous studies and explore the binding properties of calix[4]arene diamide derivatives **3–8** towards dichromate anions. The synthetic route for the preparation of calix[4]arene diamide derivatives is described in Scheme 1; 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]-arene **1** or 25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene **2** was refluxed with 1-(2-aminoethyl) piperidine and 1-(3-aminopropyl)-imidazole respectively to give corresponding diamide derivatives of calix[4]arene **3–6** in 71–78% yields. A mixture of toluene-methanol (1:1) was employed as toluene facilitates the dissolution of diester while methanol is beneficial to transforming the ethyl ester to the more reactive methyl ester prior to aminolysis [28].

The new compounds **3–6** were characterized by a combination of IR, ^1H NMR, ^{13}C NMR, FAB MS, and elemental analysis. The formation of diamide derivatives of calix[4]arene **3–6** was confirmed by the appearance of the characteristic amide bands at about 1680 cm^{-1} and by the disappearance of ester carbonyl band at 1755 cm^{-1} in the IR spectra. The conformational characteristics of calix[4]arenes were conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^1H and ^{13}C NMR spectroscopy [29,30].

^1H NMR data showed that compounds **3–6** are in the cone conformation. A typical AX pattern was observed for the methylene bridge $ArCH_2Ar$ protons at 3.33 ppm and 4.10 ppm ($J = 13.3$ Hz) for **3**, 3.40 ppm and 4.15 ppm ($J = 13.4$ Hz) for **4**, 3.38 ppm and 4.15 ppm ($J = 13.0$ Hz) for **5** and 3.38 ppm and 4.18 ppm ($J = 13.0$ Hz) for **6** in ^1H NMR. The high field doublets at 3.33 ppm for **3**, 3.40 ppm for **4**, 3.38 ppm for **5** and **6** were assigned to the equatorial protons of methylene groups, whereas the low field signals at 4.10 ppm for **3**, 4.15 ppm for **4**, 4.15 ppm for **5** and 4.18 ppm for **6** were assigned to the axial protons in the ^1H NMR.



SCHEME 1 (i) Primary amine, MeOH/Toluene (1:1), reflux.

Extraction Studies

Chromate and dichromate anions are important because of their high toxicity and presence in soils and waters [31–34]. 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 chromate and dichromate ($Cr_2O_7^{2-}/HCr_2O_7^-$) ions are dianions where the periphery of the anions have oxide moieties. These oxides are potential sites for hydrogen bonding to the host molecule. It is known that calix[4]arenes with amino functionalities on their lower rim are efficient extractants for oxoanions [35–38].

We were interested in synthesizing new calix[4] arene diamide derivatives in the cone conformation and examining their extraction properties for dichromate ions. The present work determines the strategic requirements for two-phase extraction measurements. A preliminary evaluation of the extraction efficiencies of **3–8** has been carried out by solvent extraction of $Na_2Cr_2O_7$ from water into dichloromethane at different pH values. The results are summarized in Table I.

The extraction data (Figs. 1 and 2) showed that the extractants **3** and **4** are more effective for the extraction of dichromate anions at low pH. The percentage of dichromate ions extracted was 89.1 for **3** and 82.5 for **4** when the pH of the aqueous solution was 1.5 and they attained minimum 11.6 for **3** and 1.8 for **4** when pH of the aqueous solution increased to 4.5. Calix[4]arene derivatives **3** and **4** provide suitable binding sites for dichromate anions at low pH due to containing protonable amine moieties. Therefore, an anion switchable complex is formed in the two phase extraction system (Scheme 2) because of the proton transfer to the nitrogen atom of the amine unit in **3** and **4**. This reflects the fact that the complex with dichromate ions is more stable in low pH medium.

However, it was observed that $HCr_2O_7^-/Cr_2O_7^{2-}$ ions were highly extracted by **3** and **5**. They were

TABLE I Percentage extraction of dichromate by extractants **3–8** at different pH values[†]

	Dichromate anion extracted (%)[‡]			
	pH			
Compound	1.5	2.5	3.5	4.5
3	89.1 ± 0.4	85.4 ± 0.3	82.8 ± 0.3	11.6 ± 0.4
4	82.5 ± 0.5	78.2 ± 0.6	68.0 ± 0.4	1.8 ± 0.5
5	¶	25.4 ± 0.3	13.3 ± 0.5	11.7 ± 0.4
6	¶	18.5 ± 0.6	10.4 ± 0.4	10.0 ± 0.4
7	6.1 ± 0.5	2.0 ± 0.4	3.3 ± 0.4	2.6 ± 0.3
8	6.8 ± 0.4	2.7 ± 0.4	3.5 ± 0.5	3.0 ± 0.5

[†] Aqueous phase, [metal dichromate] $= 1 \times 10^{-4}$ M; organic phase, dichloromethane, [ligand] $= 1 \times 10^{-3}$ M or solid phase [ligand] $= 1 \times 10^{-3}$ M at 25°C, for 1 h. The percentage extraction is given by [initial aqueous anion] − [final aqueous anion]/[initial aqueous anion] × 100.
[‡] Averages and standard deviations calculated for data obtained from three independent extraction experiments. ¶ Partly Soluble at this pH.

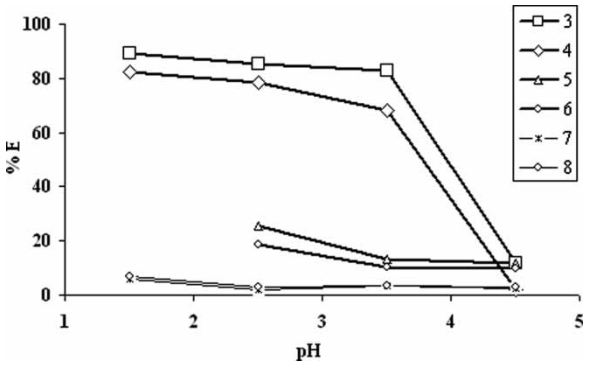


FIGURE 1 Plots of extraction (E %) vs. pH following the two phase solvent extraction of dichromate with compounds **3**–**8**.

extracted in less extraction ratios by **4** and **6** when compared with the parent p-*tert*-butylcalix[4]arenes (**3** and **5**). This implies the better preorganization of fixed **3** and **5** which have *tert*-butyl groups in the cone conformation in solution.

By contrast, **4** and **6** are significantly more flexible than **3** and **5** and they show less extraction ability toward $HCr_2O_7^-/Cr_2O_7^{2-}$. The conformations of **3** and **5** have significantly less flexibility because the *tert*-butyl groups lock it in the cone conformation in liquid phase. For the calix[4]arene diamides **3** and **4** we discount the possibility that increased extraction at lower pH values when compared to **7** and **8**, is due to protonation of the amine nitrogens.

Because the pK_a of protonated amides (R-C(OH^+)NH_2) is approximately -1, the protonated form of calix[4]arene amide derivatives **7**, **8** are not expected to be present in significant concentration in aqueous solutions having pH values in the 1.5–4.5 range.

All these data have been analyzed using the classical slope analysis method. Assuming that the extraction of an anion A^{n-} by the receptor

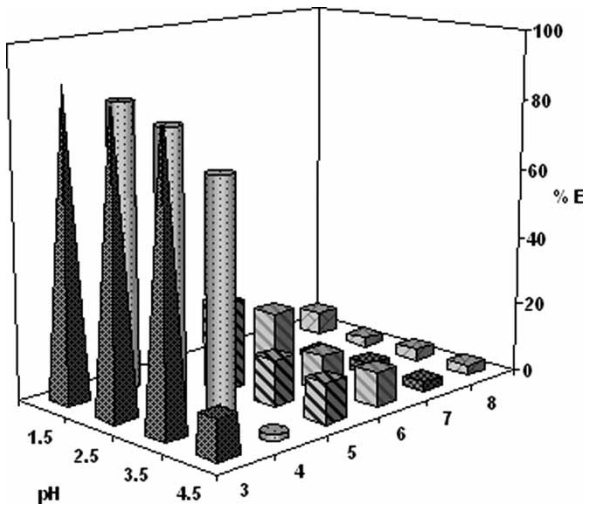


FIGURE 2 Extraction percentage of dichromate anions with **3**–**8** at pH 1.5–4.5.

LH^{n+} is according to following equilibrium:

$$n(\mathrm{LH}^{n+})_{\mathrm{org}} + n\mathrm{A}_{\mathrm{aq}}^{n-} \leftrightarrows ((\mathrm{LH}^{n+})_n, \mathrm{A}_n^{n-})_{\mathrm{org}} \quad (1)$$

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

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

Equation (2) can be re-written as;

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

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

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

Consequently a plot of the log D_A vs. log[L] may lead to a straight line with a slope that allows for the determination of the stoichiometry of the extracted species, where [L] is defined as the analytical concentration of the ligand in the organic phase. Figure 3 exhibits the extraction into dichloromethane at different concentrations of **3** and **4** with dichromate anions, respectively. A linear relationship between log D_A vs. log [L] is observed with the slope of the line for extraction of dichromate anion by ligands **3** and **4** being approximately equal to 1 (at pH 1.5), suggesting that these ligands form 1:1 complexes with the dichromate anion.

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 $HCr_2O_7^-/Cr_2O_7^{2-}$ form. At higher acidic conditions $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr^{6+} form and pK_{a_1} and pK_{a_2} values of these equations are 0.74 and 6.49, respectively. It is apparent to us that the ligands **3** and **4** form complex mostly with $HCr_2O_7^-$ ion. This has allowed us to consider this simultaneous extraction of 1:1 complexes according to the following equilibria:

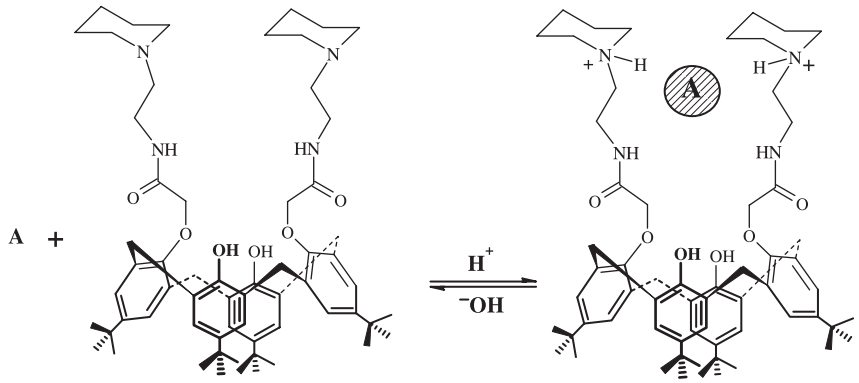
$$(\mathrm{LH}^+)_{\mathrm{org}} + \mathrm{HCr_2O_{7aq}^-} \overset{K_{ex}}{\leftrightarrows} \left(\mathrm{LH}^+, \mathrm{HCr_2O_7^-}\right)_{\mathrm{org}} \quad (4)$$

$$\left(\mathrm{LH_2^{2+}}\right)_{\mathrm{org}} + \mathrm{Cr_2O_{7aq}^{2-}} \overset{K'_{ex}}{\leftrightarrows} \left(\mathrm{LH_2^{2+}}, \mathrm{Cr_2O_7^{2-}}\right)_{\mathrm{org}} \quad (5)$$

According to these assumptions, the extraction constant has been calculated from the experimental data with similar K_{ex} and K'_{ex} values using Eq. (3). Calculations of these constant values lead to $\log K_{ex} = \log K'_{ex} = 4.38 \pm 0.2$ for **3** and $\log K_{ex} = \log K'_{ex} = 3.47 \pm 0.2$ for **4**.

CONCLUSIONS

In conclusion, the synthesis and complexation ability of calix[4]arene based receptors **3**–**8** were studied. The spectroscopic data indicated that the new compounds (**3**–**6**) are in the cone conformation.



SCHEME 2 The proposed interactions of compound **3** with $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ ions.

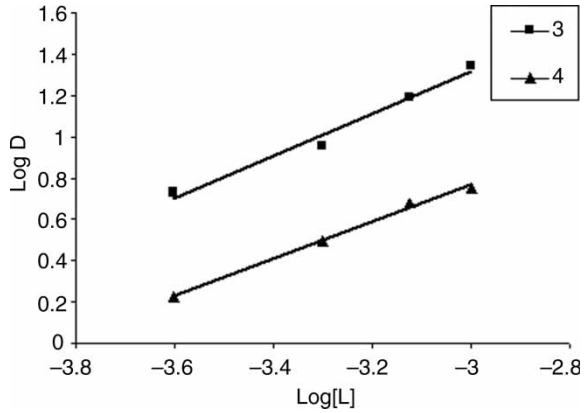


FIGURE 3 Log D vs. log [L] for the extraction of dichromate anions by the ligands **3** and **4** from an aqueous phase into dichloromethane at 25°C.

The complexation studies show that compounds **3** and **4** are better receptors for $Cr_2O_7^{2-}/HCr_2O_7^-$ anions compared with **5**–**8**. It could be concluded that the complexation of $Cr_2O_7^{2-}/HCr_2O_7^-$ depends on the nature and aggregation of the ions round the receptor. This is a particularly important feature if it is desirable to recover the particular metal in pure form and reuse the extractant. The calixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, using an electrochemical transduction/as conventional ion selective electrodes (ISE) and solid-state sensors (ISFETs).

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