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Synthesis of Various Calix[4]arene Derivatives with Mercaptoalkyl Chains and Their Application in Removing Cr(VI) from Aqueous Solution

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ABSTRACT

Four different mercaptoalkyl-substituted calixarene derivatives (5,11,17, 23-tetra-*tert*-butyl-25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene, 25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene, 25,27-bis(5-mercaptopentanoxyl)-26,28-dihydroxycalix[4]arene and 5,17-di-*tert*-butyl-11,23-di-carboxyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene) were synthesized. Their structures were characterized by Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C NMR spectroscopy, and elemental analysis techniques. Moreover, their extraction capabilities at different parameters such as pH, shaking speed, and shaking time were examined toward dichromate ions. Results implied that all mercaptoalkyl-substituted calixarene derivatives showed an extraction capability toward dichromate anion while the carboxyl-functionalized calixarene-mercapto-alkyl derivative exhibited the highest extraction capability.

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Calixarene; Cr(VI) removal;
host-guest; solvent
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Introduction

In industries such as electroplating, leather tanning, dyeing, cement production, and photography that use significant amounts of chromium and its compounds (1, 2), effluents of chromium seep into nearby water or soil sources. In various ways, these contaminated sources then come into contact with humans and wildlife and cause considerable harm, including liver damage, pulmonary congestion, and severe diarrhea. The reason for such effects is that Cr(VI), the stable oxidized form of chromium in water, possesses mutagenic, toxic, and carcinogenic properties (3–6). However, the other stable oxidized form, Cr(III), is biologically essential to mammals, for it supports effective metabolic processes, involving glucose, lipid, and proteins. As such, ridding Cr(VI) of its contaminant nature is an important task for environmental protection, and researchers in the field have developed adsorption materials, such as activated carbon, coir pith, chitosan, and calixarene (7–13). Nevertheless, producing an effective and selective receptor to remove Cr(VI) remains an unfinished task.

In supramolecular chemistry, a major objective is to designate an artificial extractant that exhibits selectivity and a high affinity to toxic and hazardous ions (14–17). In that sense,

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calixarenes, characterized extensively as promising receptors for extracting anions, cations, and even neutral molecules from solution, are common in third-generation supramolecular chemistry (4–6, 10, 15–18). With a condensation reaction of *p*-substituted phenol and formaldehyde, calixarenes can be selectively functionalized at both their lower and upper rims (18–23). Moreover, the arms substituted at those rims accommodate versatile approaches, including cooperative and rigidity scaffolding, which can drastically improve calixarenes' extraction affinity and selectivity. To date, various calixarene ligands have excelled as extractants for removing dichromate ions from aqueous solutions, especially when appended with amino substitutions, given the easily obtained protonation in acidic media that exhibits strong electrostatic interactions with anions (2, 5, 6, 10, 15, 16, 24, 25). However, to our knowledge, mercaptoalkyl-functionalized calixarenes have never been tested as selective receptors for dichromate anions, despite their potential convenience. In response, we pioneered an investigation into the synthesis and dichromate anion extraction behaviors of four mercaptoalkyl derivatives of calixarene, with opposite arrangements of functional groups and mercaptoalkyl chains at the upper and lower rims of the calixarene scaffold. In this study, we also report how various pH levels, shaking durations, and shaking speeds affected the extraction capacities of calixarene-mercapto-alkyl derivatives with dichromate anions in aqueous solutions.

Materials and methods

Reagents and instrumentation

Merck plates (silica gel 60 F₂₅₄ on aluminum) were used for Analytical Thin Layer Chromatography (TLC). All reactions, unless otherwise noted, were conducted under nitrogen atmosphere. All starting materials and reagents were purchased from Fluka, Merck, and Aldrich companies, and used without further purification. All the solutions were prepared with ultra-pure water that had been passed through a Millipore milli-Q Plus water purification system. Leco CHNS-932 analyzer was used for Elemental analysis. NMR spectra and FT-IR spectra were recorded on a Varian 400 MHz spectrometer and a Perkin-Elmer 100 spectrometer, respectively. UV-vis spectra were recorded on a Shimadzu 160A UV-vis spectrophotometer.

Synthesis

p-*tert*-butylcalix[4]arene (**1**), calix[4]arene (**2**), 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (**4**), 25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (**5**), 5,11,17,23-tetra-*tert*-butyl-25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene (***t*-Bu-C[4]-C₃-SH**), 25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene (**C[4]-C₃-SH**), 5,17-di-*tert*-butyl-11,23-bis-methanoyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene (**6**) and 5,17-di-*tert*-butyl-11,23-di-carboxyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene (**Crx-C[4]-C₃-SH**), 25,27-bis(5-bromo-1-oxypentane)-26,28-dihydroxycalix[4]arene (**3**) and 25,27-bis(5-mercapto-pentanoxy)-26, 28-dihydroxycalix[4]arene (**C[4]-C₅-SH**) were synthesized according to the literature procedure (17, 26–30).

Synthesis of 25,27-bis(5-bromo-1-oxypentane)-26,28-dihydroxycalix[4]arene (**3**)

White color solid was obtained in 29% yield. ¹H NMR (400 MHz CDCl₃): δ 1.86–1.93 (m, 8H, –CH₂–), 2.06–2.12 (m, 4H, –CH₂–), 3.42 (d, 4H, *J* = 13.2 Hz, Ar–CH₂–Ar), 3.52 (t, 4H, *J* = 6.8 Hz, –CH₂–Br), 4.02 (t, 4H, *J* = 6.8 Hz, –CH₂–O), 4.29 (d, 4H, *J* = 13.2 Hz, Ar–CH₂–Ar),

128.51, 129.04, 133.29, 134.29, 151.42, 153.14. Anal. Calcd. For $C_{34}H_{36}O_4S_2$: C, 71.30; H, 6.34. Found (%); C, 71.28; H, 6.46.

Synthesis of 25,27-bis(5-mercaptopentanoxy)-26,28-dihydroxycalix[4]arene (C[4]-C₅-SH)

A mixture of 25,27-bis(5-bromo-1-oxyptane)-26,28-dihydroxycalix[4]arene (**3**) (1.07 g, 1.48 mmol) and thiourea (0.37 g, 4.97 mmol) in 40 mL of CH_3CN was refluxed. The reaction was monitored by using TLC (CH_2Cl_2 :hexane (1:1)). After 30 h, the solvent was evaporated to dryness, and a solution of 0.51 g of KOH (6.41 mmol) in 21 mL of deionized water was added to the residue. The mixture was refluxed for 2 h. Then, 1 M HCl was added to the mixture, and extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$, filtered off, and evaporated. The resultant was recrystallized from MeOH to produce white-colored **C[4]-C₅-SH** in 55% yield, m.p. 110–112 °C. 1H NMR (400 MHz $CDCl_3$): δ 1.51 (brs, 2H, -SH), 1.87 (brs, 8H, - CH_2 -), 2.12 (brs, 4H, - CH_2 -), 2.68 (brs, 4H, - CH_2 -S), 3.44 (d, 4H, $J = 12.8$ Hz, Ar- CH_2 -Ar), 4.06 (brs, 4H, - CH_2 -O), 4.35 (d, 4H, $J = 12.8$ Hz, Ar- CH_2 -Ar), 6.72–6.77 (m, 4H, ArH), 6.95 (d, 4H, $J = 7.6$ Hz, ArH), 7.11 (brs, 4H, ArH), 8.21 (s, 2H, -OH). Anal. Calcd. For $C_{38}H_{44}O_4S_2$: C, 72.57; H, 7.05. Found (%); C, 72.48; H, 6.96.

Synthesis of 5,17-di-tert-butyl-11,23-bis-methanoyl-26,28-bis(3-mercaptopropoxy)-25,27-dihydroxycalix[4]arene (6)

Yellow-colored powder was produced in 55.6% yield, m.p.: 262–264 °C. FTIR (ATR): 1681 cm^{-1} (C=O). 1H NMR (400 MHz $CDCl_3$): δ 1.19 (s, 18H, Bu^t), 2.42–2.48 (m, 2H, -SH), 3.44–3.45 (m, 4H, - CH_2 -), 3.44–3.46 (m, 4H, - CH_2 -S), 3.53 (d, 4H, $J = 12.8$ Hz, Ar- CH_2 -Ar), 4.06 (t, 4H, $J = 4.8$ Hz, O- CH_2 -), 4.22 (d, 4H, $J = 12.8$ Hz, Ar- CH_2 -Ar), 7.14 (s, 4H, ArH), 7.59 (s, 4H, ArH), 9.71 (s, 2H, -CHO), 10.14 (s, 2H, -OH). ^{13}C NMR (400 MHz $CDCl_3$): δ 28.22 (S- CH_2), 31.29 (CH_3), 32.10 (Ar- CH_2 -Ar), 33.82 (- CH_2), 34.43 (C), 75.16 (O- CH_2), 126.53 (ArC), 128.68 (ArC), 129.15 (ArC), 130.97 (ArC), 132.61 (ArC), 148.81 (ArC), 148.95 (ArO-C), 159.40 (ArO-C) 190.79 (C=O). Anal. Calcd. For $C_{44}H_{52}O_6S_2$: C, 71.32; H, 7.07; S, 8.65. Found (%); C, 71.29; H, 7.17; S, 8.56.

Synthesis of 5,17-di-tert-butyl-11,23-di-carboxyl-26,28-bis(3-mercaptopropoxy)-25,27-dihydroxycalix[4]arene (Crx-C[4]-C₃-SH)

Yellow-colored product was obtained in 43% yield, m.p.: 160–162 °C. FTIR (ATR): 1681 cm^{-1} (C=O). 1H NMR (400 MHz DMSO): δ 1.11 (s, 18H, Bu^t), 1.99 (brs, 2H, -SH), 2.27–2.47 (m, 4H, - CH_2 -), 3.48–3.68 (m, 8H, Ar- CH_2 -Ar and CH_2 -S), 4.08–4.22 (m, 8H, Ar- CH_2 -Ar and O- CH_2 -), 7.16 (s, 4H, ArH), 7.82 (s, 4H, ArH), 9.47 (s, 2H, -OH). ^{13}C NMR (400 MHz DMSO): δ 26.52 (S- CH_2), 31.38 (CH_3), 31.53 (Ar- CH_2 -Ar), 34.11 (- CH_2), 34.54 (C), 76.20 (O- CH_2), 121.98 (ArC), 126.51 (ArC), 128.45 (ArC), 130.81 (ArC), 132.77 (ArC), 147.86 (ArC), 149.95 (ArO-C), 157.56 (ArO-C) 167.66 (C=O). Anal. Calcd. For $C_{44}H_{52}O_8S_2$: C, 68.37; H, 6.78; S, 8.30. Found (%); C, 68.31; H, 6.67; S, 8.48.

Extraction procedure

We assessed the sorption capacities of four different calixarene derivatives substituted with mercapto-alkyl moieties at lower rim of calixarene toward dichromate anion by using an extraction technique relying on liquid–liquid extraction of a 1.0×10^{-3} M solution of each derivative in CH_2Cl_2 and an aqueous solution of $Na_2Cr_2O_7$ (1.0×10^{-4} M). Typically, an

aqueous solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ (10 mL, 1.0×10^{-4} M) was added to a solution of calixarene-mercapto-alkyl derivatives (10 mL, 1.0×10^{-3} M) in CH_2Cl_2 . The resulting mixture was shaken at 25°C . The residual Cr(VI) concentration was determined at 346 nm using an ultraviolet-visible spectrophotometer, as previously reported in the literatures (2, 31). To investigate pH effects on the extraction capability of the calixarene-mercapto-alkyl derivatives, we prepared various pHs (1.5–4.5) of the dichromate solutions using diluted HCl and an aqueous solution of KOH at 25°C . We calculated the extraction percent (E%) according to Eq. (1).

$$(E\%) = \frac{(A_0 - A) \times 100}{A_0}, \quad (1)$$

where A_0 and A are the initial and final concentrations of Cr(VI) before and after the extraction, respectively.

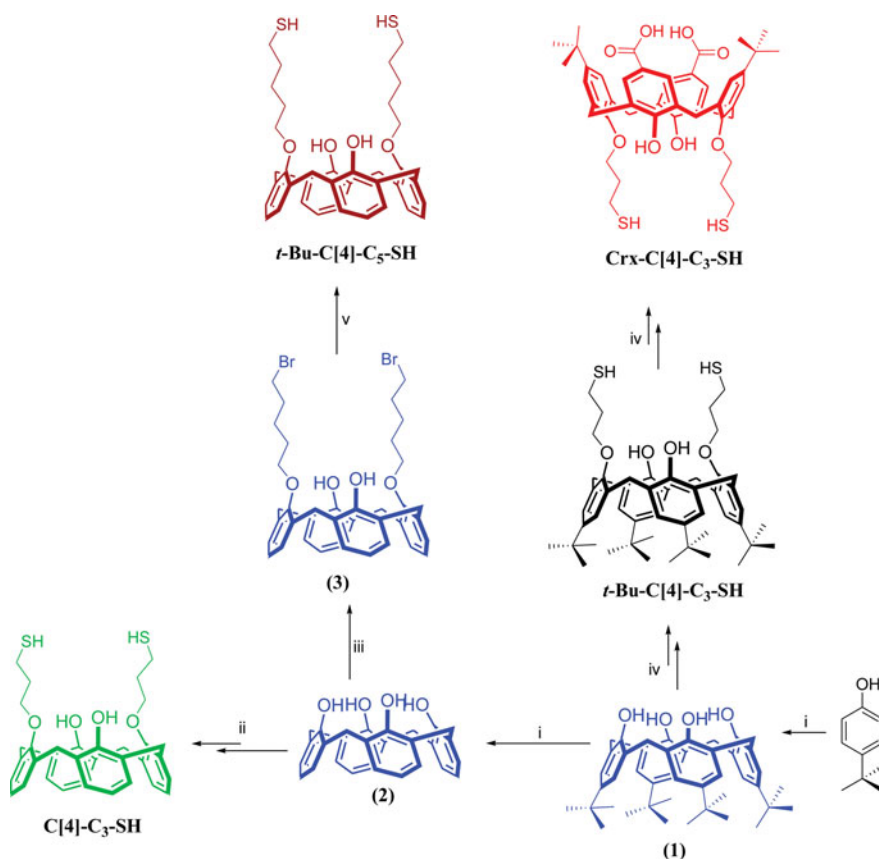
Results and discussion

Synthesis and characterization of the calixarene-mercapto-alkyl derivatives

Scheme 1 illustrates the synthesis routes of mercapto-alkyl chain-appended calixarenes at the lower rim of calix[4]arene, all of which informed our examination of the dichromate extraction efficiencies of four calixarene-mercapto-alkyl derivatives. *p*-*tert*-Butylcalix[4]arene (1), calix[4]arene (2), 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (4), 25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (5), 5,11,17,23-tetra-*tert*-butyl-25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene (*t*-Bu-C[4]-C₃-SH), 25,27-bis(3-mercaptopropoxyl)-26,28-dihydroxycalix[4]arene (C[4]-C₃-SH), 5,17-di-*tert*-butyl-11,23-bis-methanoyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene (6) and 5,17-di-*tert*-butyl-11,23-di-carboxyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene (Crx-C[4]-C₃-SH) were synthesized, as reported previously in the literatures (17, 26–29). Structures of all calixarene derivatives were determined by Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C NMR spectroscopy, and elemental analysis techniques.

The reaction of 5,11,17,23-tetra-*tert*-butyl-25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (4), 25,27-bis-(bromopropoxy)-26,28-dihydroxycalix[4]arene (5), and 25,27-bis(5-bromo-1-oxypentane)-26,28-dihydroxycalix[4]arene (3) with thiourea was yielded with *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH and C[4]-C₅-SH, respectively. The ¹H NMR spectra of *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, and C[4]-C₅-SH exhibit that these derivatives state in cone conformer; they possess a typical AX pattern for the protons of their Ar-CH₂-Ar groups at 3.35 and 4.27 ppm ($J = 12.8$ Hz), 3.41 and 4.29 ppm ($J = 12.8$ Hz), and 3.44 and 4.35 ppm ($J = 12.8$ Hz), respectively. Moreover, appearing at the additional peak for the protons of their -SH groups at about of δ 1.5 ppm (2H) in the ¹H NMR spectrum confirms structures of *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH and C[4]-C₅-SH (Figure 1). ¹³C NMR spectra of *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, and C[4]-C₅-SH reveal also the existence of S-CH₂ groups at approximately 21.42 ppm.

Regioselective substitution of *t*-Bu-C[4]-C₃-SH at the upper rim (i.e., Duff reaction) was conducted in the presence of hexamethylenetetramine in TFA to produce the cone conformer 5,17-di-*tert*-butyl-11,23-bis-methanoyl-26,28-bis(3-mercaptopropoxyl)-25,27-dihydroxycalix[4]arene (6) at a yield of 55.6%. In that product, the FTIR spectra of 6 signified its structure by characteristically peaking at 1681 cm^{-1} , which represented the vibration



Scheme 1. The synthetic route for preparation of the mercapto-alkyl-functionalized calix[4]arene derivatives. Reaction conditions: (i) lit. (26); (ii) lit. (29); (iii) 1,5-dibromopentane, K_2CO_3 ; (iv) lit. (27); (v) thiourea, KOH.

stretch of the aldehyde $\text{C}=\text{O}$ bond. At the same time, the ^1H NMR spectrum of **6** confirmed the formation of the aldehyde derivative **6**, not only with the disappearance of protons of one *tert*-butyl group of $t\text{-C[4]-C}_3\text{-SH}$, but also with the characteristic peak of the aldehyde proton (CHO) at 9.71 ppm. Along with indicating the characteristic peak of aldehyde carbonyl ($\text{C}=\text{O}$) at 190.79 ppm in the ^{13}C NMR, this arrangement provided complementary information about the structure of aldehyde derivative **6**.

Next, selectively oxidizing aldehyde derivative **6** using sodium chlorite in the presence of sulfamic acid in acetone yielded $\text{Crx-C[4]-C}_3\text{-SH}$. The FTIR spectra of the carboxylic-acid-appended $\text{Crx-C[4]-C}_3\text{-SH}$ confirmed its structure with a vibration band at 1681 cm^{-1} , which represented the carbonyl moiety of the carboxyl derivative ($\text{Crx-C[4]-C}_3\text{-SH}$). ^1H and ^{13}C NMR spectra of $\text{Crx-C[4]-C}_3\text{-SH}$, moreover, provided complementary information concerning the carboxyl group of $\text{Crx-C[4]-C}_3\text{-SH}$. Ultimately, the disappearance of both peaks for **6** at 9.71 ppm and 190.79 ppm on the ^1H NMR and ^{13}C NMR spectrum, respectively, indicated the structure of $\text{Crx-C[4]-C}_3\text{-SH}$.

Liquid–liquid extraction

Although many ionophores such as calixarene derivatives have been developed to remove dichromate anion from contaminants, it remains a challenge to design a molecule that

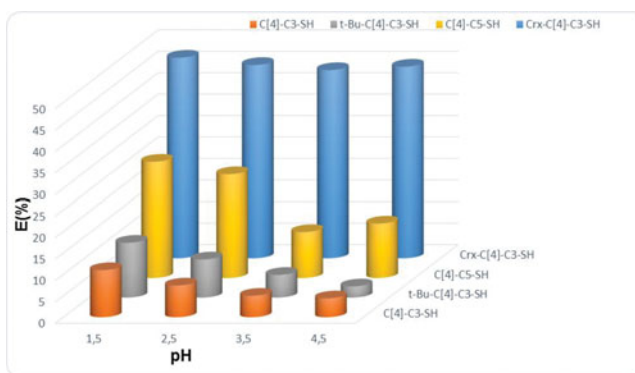


Figure 2. Extraction percentages of dichromate anion with *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH and Crx-C[4]-C₃-SH at pH 1.5–4.5. Aqueous phase, H₂O/CH₂Cl₂, 10:10 v/v; Na₂Cr₂O₇ (1×10^{-4} M), ligand (1×10^{-3} M), 1 h, 155 rpm, 25°C, $\lambda_{\text{max}} = 346$ nm.

effectively hosts dichromate anions, due to their high toxicity and presence in soils and water. However, given their enormously rigid, bowl-shaped scaffold, as well as accommodation of significant chemical modification at both the upper and lower rims, calixarenes have been extensively used to that end. With that in mind, we used four different calixarene derivatives substituted with mercapto-alkyl moieties as ionophores in this study to investigate their extraction properties regarding dichromate anions at various pHs (1.5–4.5) as part of a liquid–liquid extraction system.

The extraction results shown in Figure 2 indicate that the carboxyl-appended receptor (Crx-C[4]-C₃-SH) exhibits the highest extraction efficiency for dichromate anions among other mercapto-alkyl derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, and C[4]-C₅-SH). The maximum extraction percentage of Crx-C[4]-C₃-SH in terms of HCr₂O₇[−] was approximately 47%, whereas the minimum percentage of extracted HCr₂O₇[−] ion by C[4]-C₃-SH was only roughly 6%. As a result, due to both carboxyl and mercapto moieties, the receptor Crx-C[4]-C₃-SH provided a convenient binding site for dichromate anions.

To investigate how pH affected the extraction capacities of the mercapto-alkyl derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH, and Crx-C[4]-C₃-SH), we applied different pHs. However, since no notable differences in their extraction capacities were observed (Figure 2), the mercapto groups of mercapto-alkyl derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH, and Crx-C[4]-C₃-SH) likely play a key role in constructing dichromate-calixarene complexes by hydrogen bonding. By adding the carboxyl group to the mercapto-alkyl-functionalized calixarene, the scaffold became more rigid, as did the cooperatives of the functionalities that contributed to the high extraction percentages.

To investigate how shaking speed and shaking time affected the extraction capacity of the mercapto-functionalized calix[4]arene derivative, various shaking speeds and durations were used during dichromate anion extraction. Results showed that the maximum dichromate ion extraction percentage occurred when the shaking speed and shaking time were 170 rpm and 1 h, respectively (Figures 3 and 4). As Figure 4 shows, dichromate ion extraction amid strong shaking yielded lower extraction efficacy by reducing the possibility of complex formation with calixarene derivatives.

We performed a classical slope analysis method (10) to assess dichromate anion extraction performance of the mercapto-alkyl derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH and Crx-C[4]-C₃-SH). The equilibrium given below was introduced to describe dichromate

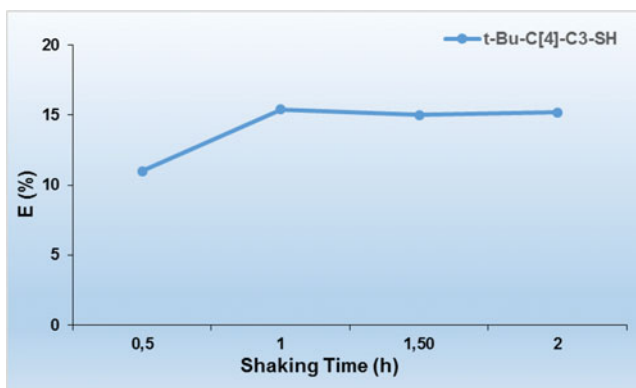
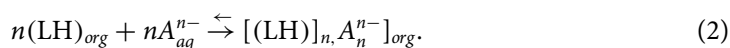


Figure 3. Different shaking time influences on extraction percentages of dichromate anion with *t*-Bu-C[4]-C₃-SH at pH 1.5. Aqueous phase, H₂O/CH₂Cl₂, 10:10 v/v; Na₂Cr₂O₇ (1 × 10⁻⁴ M), ligand (1 × 10⁻³ M), 170 rpm, 25°C, λ_{max} = 346 nm.

extraction (A^{n-}) by the receptor (LH).



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

$$K_{ex} = \frac{[(\text{LH})_n A_n^{n-}]_{org}}{[A_n^-]_{aq}^n [\text{LH}]_{org}^n} \quad (3)$$

$$\log D_A = \log K_{ex} + n \log [\text{LH}]_{org}, \quad (4)$$

where D_A is defined as the ratio of the analytical concentration of dichromate anion A^{n-} in aqueous and organic phases.

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

To determine the stoichiometry of the extracted species stated as the analytical concentration of the receptor, we plotted the log D_A versus log $[L]$ (Figure 5).

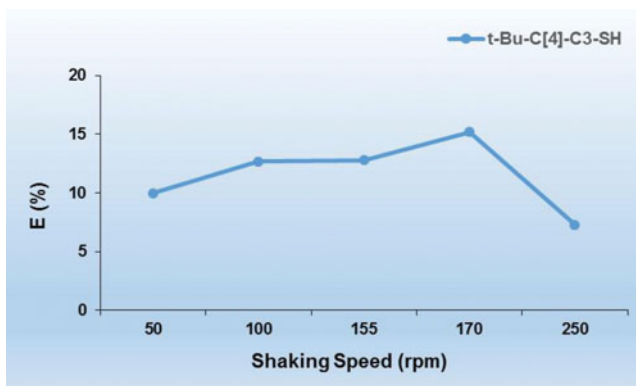


Figure 4. Various shaking speed influences on extraction percentages of dichromate anion with *t*-Bu-C[4]-C₃-SH at pH 1.5. Aqueous phase, H₂O/CH₂Cl₂, 10:10 v/v; Na₂Cr₂O₇ (1 × 10⁻⁴ M), ligand (1 × 10⁻³ M), 1 h, 25°C, λ_{max} = 346 nm.

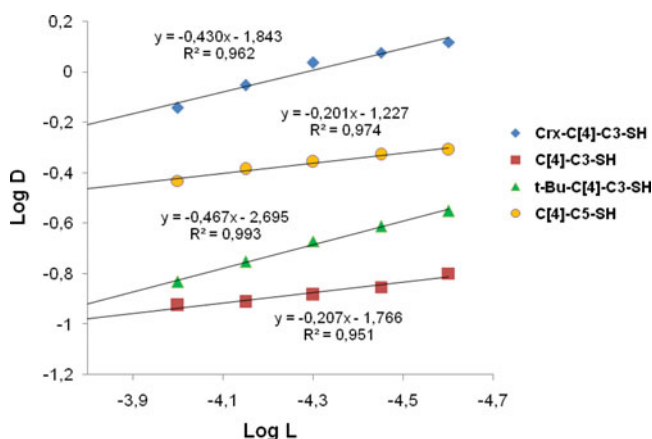


Figure 5. Plot of log D versus log[L] for the extraction of dichromate and its anions by four different substituted mercapto-alkyl calixarene derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH and Crx-C[4]-C₃-SH) from an aqueous phase into dichloromethane at 25°C and pH 1.5.

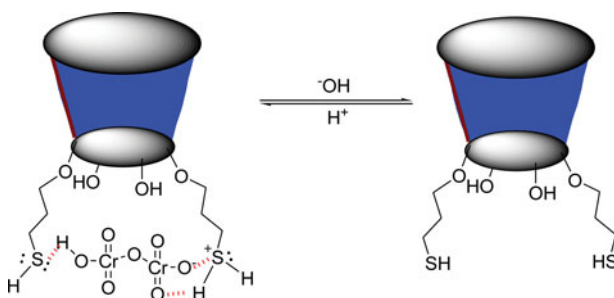
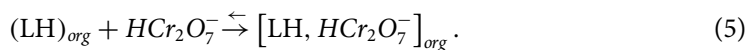


Figure 6. The suggested interactions of the mercapto-alkyl-functionalized calix[4]arene derivative with dichromate ion.

A linear relationship between log DA versus log[L] is found with the slope of the line for extraction of dichromate anion by the mercapto-alkyl derivatives (*t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH, and Crx-C[4]-C₃-SH) and is about equal to 1 (at pH 1.5), attributing that all mercapto-alkyl derivatives form a 1:1 complex with the HCr_2O_7^- anion (Figure 6). Therefore, following equilibrium, Eq. 5 provides the experimental data with similar K_{ex} values using Eq. 4. By using these constant values, log K_{ex} for *t*-Bu-C[4]-C₃-SH, C[4]-C₃-SH, C[4]-C₅-SH, and Crx-C[4]-C₃-SH is calculated as 5.15 ± 0.2 , 3.2 ± 0.2 , 4.91 ± 0.2 , and 4.48 ± 0.2 , respectively.



Conclusion

In sum, our study has contributed unprecedented data regarding the dichromate anion extraction affinities of four different mercapto-alkyl-substituted calix[4]arene derivatives in a liquid–liquid extraction system. Data show that Crx-C[4]-C₃-SH has the highest extraction capability of all mercapto-alkyl derivatives for the pHs tested, which demonstrates that structural properties, such as the ability to hydrogen bond and cooperate with functional groups of mercaptoalkyl derivatives, are considerably affected by HCr_2O_7^- anions. In short, dichromate anions have strong interactions with mercaptoalkyl derivatives. These insights into significant

formation complexes between dichromate anions and mercaptoalkyl derivatives of calixarene should open new routes in both anion-carrier and anion-recognition studies.

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References

1. Raji, C., and T. S. Anirudhan. “Batch Cr(VI) Removal by Polyacrylamide-grafted Sawdust: Kinetic and Thermodynamics.” *Water Res.* 32 (1998): 3772–80.
2. Sayin, S., F. Ozcan, and M. Yilmaz. “Synthesis and Evaluation of Chromate and Arsenate Anions Extraction Ability of a N-methylglucamine Derivative of Calix[4]arene Immobilized onto Magnetic Nanoparticles.” *J. Hazard. Mater.* 178 (2010): 312–9.
3. Wang, G., Q. Chan, X. Han, and M. Zhang. “Removal of Cr(VI) from Aqueous Solution by Flocculant with the Capacity of Reduction and Chelation.” *J. Hazard. Mater.* 248–249 (2013): 115–21.
4. Sayin, S., F. Ozcan, and M. Yilmaz. “Synthesis of Calix[4]arene Bearing Pyridinium Units Supported Silica gel for Sorption of Arsenate and Dichromate Anions.” *Desalination* 262 (2010): 99–105.
5. Bayrakci, M., S. Ertul, and M. Yilmaz. “Synthesis of Di-substituted Calix[4]arene-based Receptors for Extraction of Chromate and Arsenate Anions.” *Tetrahedron* 65 (2009): 796–8.
6. Akkuş, G. U., S. Memon, M. Sezgin, and M. Yilmaz. “Synthesis of Calix(aza)Crown and Its Oligomeric Analogue for the Extraction of Selected Metal Cations and Dichromate Anions.” *Clean-Soil, Air, Water* 37 (2009): 109–14.
7. Giri, A. K., R. Patel, and S. Mandal. “Removal of Cr(VI) from Aqueous Solution by *Eich-hornia crassipes* Root Biomass-derived Activated Carbon.” *Chem. Eng. J.* 15 (2012): 71–81.
8. Suksabye, P., and P. Thiravetyan. “Cr(VI) Adsorption from Electroplating Plating Wastewater by Chemically Modified Coir Pith.” *J. Environ. Manage.* 15 (2012): 1–8.
9. Yu, W., L. Zhang, H. Wang, and L. Chai. “Adsorption of Cr(VI) Using Synthetic poly(m-phenylenediamine).” *J. Hazard. Mater.* 260 (2013): 789–95.
10. Sayin, S., S. Eymur, and M. Yilmaz. “Anion Extraction Properties of a new “Proton-switchable” Terpyridin-conjugated Calix[4]arene.” *Ind. Eng. Chem. Res.* 53 (2014): 2396–938.
11. Kaya, A., C. Onac, H. K. Alpoguz, A. Yilmaz, and N. Atar. “Removal of Cr(VI) Through Calixarene Based Polymer Inclusion Membrane from Chrome Platingbath Water”, *Chem. Eng. J.* 283 (2016): 141–9.
12. Kaya, A., H. K. Alpoguz, and A. Yilmaz. “Application of Cr(VI) Transport Through the Polymer Inclusion Membrane with a New Synthesized Calix[4]arene Derivative” *Ind. Eng. Chem. Res.* 52 (2013): 5428–36.
13. Onac, C., H. K. Alpoguz, E. Akceylan, and M. Yilmaz. “Facilitated Transport of Cr(VI) Through Polymer Inclusion Membrane System Containing Calix[4]arene Derivative as Carrier Agent” *J. Macromol. Sci. Part A: Pure Appl. Chem.* 50 (2013): 1013–21.
14. Brunetti, E., A. Inthasot, F. Keymeulen, O. Renaud, I. Jabin, and K. Bartik. “Primary Amine Recognition in Water by a Calix[6]aza-cryptand Incorporated in Dodecylphosphocholine Micelles.” *Org. Biomol. Chem.* 13 (2015): 2931–8.
15. Bayrakci, M., Ş. Ertul, and M. Yilmaz. “Phase Solubility Studies of Poorly Soluble Drug Molecules by Using O-Phosphorylated Calixarenes as Drug-Solubilizing Agents.” *J. Chem. Eng. Data* 57 (2012): 233–9.
16. Memon, F. N., S. Memon, S. Memon, and N. Memon. “Synthesis and Application of a New Calix[4]arene Based Impregnated Resin for the Removal of Endosulfan from an Aqueous Environment.” *J. Chem. Eng. Data* 56 (2011): 3336–45.
17. Sayin, S., F. Ozcan, and M. Yilmaz. “Two Novel Calixarene Functionalized Iron Oxide Magnetite Nanoparticles as a Platform for Magnetic Separation in the Liquid-liquid/solid-liquid Extraction of Oxyanions.” *Mater. Sci. Eng. C* 33 (2013): 2433–9.

18. Stastny, V., P. Lhoták, V. Michlová, I. Stibor, and J. Sykora. "Novel Biscalix[4]arene-based Anion Receptors." *Tetrahedron* 58 (2002): 7207–11.
19. Bhatti, A. A., S. Memon, and N. Memon. "Dichromate Extraction by Calix[4]arene Appended Amberlite XAD-4 Resin." *Sep. Sci. Technol.* 49 (2014): 664–72.
20. Kim, S. K., V. M. Lynch, B. P. Hay, J. S. Kim, and J. L. "Sessler, Ion Pair-induced Conformational Motion in Calix[4]arene-strapped Calix[4]pyrroles." *Chem. Sci.* 6 (2015): 1404–13.
21. Zappacosta, R., A. Fontana, A. Credi, A. Arduini, and A. Secchi. "Incorporation of Calix[6]arene Macrocycles and (Pseudo)Rotaxanes in Bilayer Membranes: Towards Controllable Artificial Liposomal Channels." *Asian J. Org. Chem.* 4 (2015): 262–70.
22. Slavík, P., H. Dvořáková, V. Eigner, and P. Lhoták. "Regioselective Alkylation of a Methylene Group via meta-bridging of Calix[4]arenes." *Chem. Commun.* 50 (2014): 10112–4.
23. Elçin, S., G. K. Çilgi, A. Bayrakdar, and H. Deligöz. "The Synthesis and Characterization of Azocalix[4]arene Based Chemosensors and Investigation of their Properties." *Spectrochim. Acta Part A: Mol. Biomol. Spectro.* 142 (2015): 178–87.
24. Bhatti, A. A., S. Memon, N. Memon, A. A. Bhatti, and I. B. Solangi. "Evaluation of Chromium(VI) Sorption Efficiency of Modified Amberlite XAD-4 Resin." *Arabian J. Chem.* 7 (2014): 125–31.
25. Deligöz, H., and E. Erdem. "Comparative Studies on the Solvent Extraction of Transition Metal Cations by Calixarene, Phenol and Ester Derivatives." *J. Hazard. Mater.* 154 (2008): 29–32.
26. Gutsche, C. D., and K. C. Nam. "Calixarenes. 22. Synthesis, Properties, and Metal Complexation of Aminocalixarenes." *J. Am. Chem. Soc.* 110 (1988): 6153–62.
27. Demirkol, D. O., H. B. Yildiz, S. Sayin, and M. Yilmaz. "Enzyme Immobilization in Biosensor Constructions: Self-assembled Monolayers of Calixarenes Containing Thiols." *RSC Adv.* 4 (2014): 19900–7.
28. Gokoglan, T. C., S. Soylemez, M. Kesik, H. Unay, S. Sayin, H. B. Yildiz, A. Cirpan, and L. Toppare. "A Novel Architecture Based on a Conducting Polymer and Calixarene Derivative: its Synthesis and Biosensor Construction." *RSC Adv.* 5 (2015): 35940–7.
29. Kurzatowska, K., S. Sayin, M. Yilmaz, H. Radecka, and J. Radecki. "Calix[4]arene Derivatives as Dopamine Hosts in Electrochemical Sensors." *Sens. Actuators B* 218 (2015): 111–21.
30. Akin, S., M. Gülen, S. Sayin, H. Azak, H. B. Yildiz, and S. Sonmezoglu. "Modification of Photoelectrode with Thiol-functionalized Calix[4]arenes as Interface Energy Barrier for High Efficiency in Dye-sensitized Solar Cells." *J. Power Source.* 307 (2016): 796–805.
31. Tabakci, M., S. Memon, M. Yilmaz, and D. M. Roundhill. "Synthesis and Extraction Studies of a Versatile Calix[4]arene-based "Proton-switchable extractant" for Toxic Metals and Dichromate Anions." *J. Incl. Phenom. Macromol.* 45 (2003): 267–70.