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ORIGINAL PAPER

Chromate-selective electrodes prepared by using calix[4]arenes for the speciation of Cr(VI) and Cr(III)

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Abstract The calix[4]arene and its mono-, di-, tri-, and tetra-acryloyl esters were used as suitable ionophores for Cr(VI) species to develop poly(vinyl chloride) (PVC) membrane electrodes. The influence of membrane contents and pH on the potentiometric response of the electrodes was described. Five novel chromate-selective PVC membrane electrodes displayed close to Nernstian behavior with slopes of 53–62 mV/decade of hydrogen chromate ion concentration in the dynamic range of 1.0×10^{-6} and 1.0×10^{-2} M at pH 1.0. Other response characteristics of these electrodes such as response time (~10 s), lifetime (>12 months), and detection limit (6.2×10^{-7} M) were identified, and the selectivity coefficients towards various anions were determined by using fixed interference method. Moreover, the proposed electrodes were successfully used for speciation of Cr(VI) and Cr(III) and for the potentiometric titration of Cr(VI) species with standard Fe(II) solution as an indicator electrode.

Keywords Chromate-selective electrode · Potentiometry · Calix[4]arenes · Sensors · Cr(VI) and Cr(III) speciation

Introduction

In general, most of the metals affect the health of living organisms due to the contamination of the surface of the earth by metallic pollutants. Chromium is considered as a priority pollutant mainly coming from industrial process including metal planting, leather tanning, textile manufacturing industries, wood preservation, electricity generation, paint production, and galvanizing [1, 2]. It could be spread out in a noteworthy quantity into the environment resulting with an adverse ecological effect. Among the species of chromium, Cr(III) and Cr(VI) are commonly found in water; however, Cr(VI) species are toxic to humans and animals in comparison with Cr(III) acting as an essential micronutrient to our bodies. Cr(VI) species cause serious problems because of mutagenic, genotoxic, and carcinogenic effects [3–5]. This fact leads to put excessive emphasize on the monitoring of Cr(VI) content in the environmental samples [6]. Total chromium contamination in environmental samples does not provide information of toxicity and bioavailability of chromium species. Therefore, a separately and accurate determination of chromium species is necessary to evaluate these effects. However, various analytical techniques were used to determine the total chromium quantity in literature. Among these, chromatographic techniques such as HPLC [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], atomic absorption and atomic emission spectrometry (AAS, GFAAS and AES) [9, 10], X-ray spectroscopy [11], neutron activation analysis [12], and electrochemical methods [13, 14] have been reported. Although these types of methods suffer from drawbacks mostly involving complex procedures for separation and determination steps, they are also performed for speciation analysis. For this reason, they are not utilized as routine speciation techniques and for monitoring the hazardous metal species. Furthermore, capillary electrophoresis (CE) allows the simultaneous determination of these species [15]. All the methods mentioned above have long analysis time, tedious and time-consuming pretreatment, and need highly sophisticated instrumentation and expertise.

To avoid these drawbacks, potentiometric methods especially based on ion-selective electrodes (ISEs) can be suggested as a suitable choice if the concentration of chromium

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in the sample is sufficiently high for speciation analysis, owing to reasonable selectivity, relative simplicity, low cost, and portable options. Because, direct quantitative analysis of the species and indirect analysis of other related ones can be provided by using ISEs. Also, they could be proposed due to the high applicability of monitoring in routine analysis and ease of preparation for specific ions.

Chromium speciation has been an important task being still underdeveloped due to overutilization of this metal in various industries resulting with the release of different forms of chromium wastes into the environment. Literature survey revealed that there are some Cr(VI)-selective electrodes based on several ionophores [6, 16–21]; however, to the best of our knowledge, these ISEs have not been employed for chromium speciation in aqueous media up to now.

In this study, we aimed to develop new chromate-selective PVC membrane electrodes based upon calix[4]arene derivatives (Fig. 1). For this purpose, the effect of membrane components were investigated by changing the ratio of calix[4]arene derivative, plasticizer, poly(vinyl chloride), and lipophilic salt in order to prepare membranes with optimum composition. Their performance characteristics such as slope, linear working range, lifetime, response time, and selectivity against some ions were identified. Finally, the electrodes were manipulated for the speciation analysis of chromium species in aqueous media including both Cr(VI) and Cr(III).

Experimental

Reagents and solutions

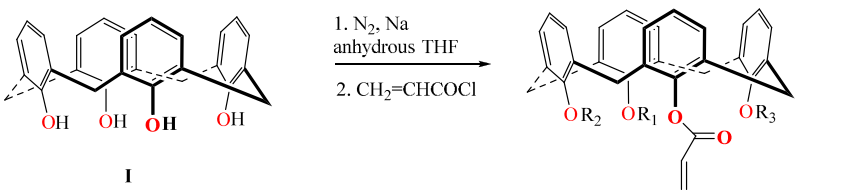
For membrane construction, high-molecular-weight poly(vinyl chloride) (PVC), *o*-nitrophenyl octylether (*o*-NPOE), dibutyl phthalate (DBP), bis(2-ethylhexyl) sebacate (BEHS), tetrahydrofuran (THF), and tetraheptylammonium tetraphenylborate (THATPB) were purchased from Sigma-Aldrich (St. Louis, MO, USA). To prepare standard Fe(II) solution as a titrant for potentiometric titrations, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ was provided by Merck (Darmstadt, Germany). Reagent-grade $K_2Cr_2O_7$ (The science company, Lakewood, OC, USA) was used to prepare standard solution after drying at 150–200 °C before being weighed. Cr(III) solution was prepared from $Cr(NO_3)_3$ (Fluka, Buchs, Switzerland) and standardized gravimetrically. All chemicals used without further purification were of analytical grade. Britton-Robinson (BR) buffer solution was prepared by mixing boric acid (Merck, Darmstadt, Germany), acetic acid (Merck, Darmstadt, Germany), and phosphoric acid (Aldrich, St. Louis, MO, USA), and the pH of this solution was adjusted with sodium hydroxide (Riedel–deHaën, Seelze, Germany), according to the procedure in literature [22]. Stock solutions of dichromate and the tested interfering anions were prepared from their sodium or potassium salts (Fluka, Buchs, Switzerland) using deionized water. The working solutions were obtained by successive dilutions of the stock solutions with deionized water, and their pH was adjusted to 1.0 by 1.0 M HCl solution (Sigma-Aldrich, St. Louis, MO, USA). Calcium chloride (Riedel–deHaën, Seelze, Germany) was used to prepare inner filling solution. HNO_3 and H_2O_2 were purchased from Merck (Darmstadt, Germany). ELGA Purelab Option ultrapure water system was used to supply deionized water.

Synthesis of calix[4]arenes

Calix[4]arene **I** was synthesized as explained in the literature [23, 24]. The mono-, di-, tri-, and tetra-acryloyl esters of calix[4]arene were synthesized by reacting calix[4]arene with metallic sodium and then with acryloyl chloride in N_2 atmosphere by using molar ratios of 1:1; 1:2; 1:3, and 1:4 (Fig. 1). All acryloyl ester derivatives **II-V** were synthesized in a manner similar to that described by Özkınalı and Kocaokutgen in literature [25].

Membrane preparation and construction of electrodes

The membrane of the electrodes without lipophilic additive was prepared by dissolving 12.8 mg ionophore, 285.1 mg plasticizer, and 127.6 mg PVC in 5 mL THF. By keeping these



I

II R_1, R_2, R_3= H

III R_1= COCH=CH_2, R_2, R_3= H

IV R_1, R_2= COCH=CH_2, R_3= H

V R_1, R_2, R_3= COCH=CH_2

Fig. 1 Structures of calix[4]arene and its mono-, di-, tri-, and tetra-acryloyl esters

amounts constant, lipophilic additive 60% mole ratio relative to the ionophore was added to this mixture to obtain membranes with lipophilic additives. The PVC membrane electrodes were fabricated as described in our previous study [26]. These electrodes were conditioned in deionized water for a day and stored in deionized water when not in use. The chromate-selective electrodes thus obtained were used as an indicator electrode.

Potential measurements

All potential measurements were performed with an Orion 720A Model pH-ion meter.

The electrode potentials of the cell below constructed with Double-junction (DJ) Ag/AgCl reference electrode (Orion 9002) and the proposed chromate-selective electrode were measured at 23 ± 1 °C:

DJ Ag | AgCl reference electrode | test solution | PVC membrane | inner filling solution $\left(1.0 \times 10^{-3}\ \mathrm{M\ CaCl_2}\right)$ | AgCl | Ag

The filling solutions of DJ Ag|AgCl electrode were Orion 900002 and 900003. The pH measurements of the solutions were monitored simultaneously with combined pH glass electrode (Orion 912600).

The potentiometric response of the electrode was evaluated by measuring the potentials within the range of 5.0×10^{-8}–5.0×10^{-3} M dichromate solutions at pH 1.0. The potentials were recorded after the equilibrium potentials had been reached when the experimental solution was stirred. The calibration graph was plotted as the measured potential value versus the negative logarithm of the ion concentration.

Electrochemical measurements

EIS experiments and *E-t* measurements were carried out with CHI660D Electrochemical Workstation (Austin, TX, USA) under open circuit potential by using three electrode cell in which Ag|AgCl|KCl, 3 M (as the reference electrode; BASi MF-2052), platinum wire (as the auxiliary electrode; BASi MW-1032), and proposed chromate-selective electrode as the working electrode. The impedance spectra of the membranes were recorded in different concentrations of dichromate solutions at pH 1.0 containing 0.1 M NaCl within the frequency range of 10^6–0.5 Hz, and the amplitude for the excitation signal was 25 mV.

Analytical application

Two different analytical applications of the proposed chromate-selective electrodes as an indicator electrode were demonstrated: (i) the potentiometric titration of standard Fe(II) solution with standard $K_2Cr_2O_7$ solution and (ii) the speciation of Cr(III) and Cr(VI) species by using synthetic mixtures of target ions. To determine Cr(III) in the absence and in the presence of Cr(VI), the sample solution was oxidized with excess hydrogen peroxide in alkaline solution to convert all the Cr(III) to Cr(VI). The excess hydrogen peroxide was destroyed by heating. Then, nitric acid was added in this solution to form an acidic media. All the potentiometric titrations were carried out using the proposed chromate-selective electrodes and Orion 940 expandable ion analyzer *S/N* 5816 automatic titrator.

Results and discussion

The determination of the membrane composition

It is noteworthy that, in most of the previously reported sensors, the membrane composition was found to affect the performance characteristics such as the sensitivity, working range, detection limit, and selectivity of an ion-selective electrode [16, 21]. For this purpose, 25 different membranes containing PVC, ionophore, plasticizer, and lipophilic additive were prepared by varying the concentration and/or the nature of the membrane components. Additionally, the contribution of the matrix to Cr(VI) species response was investigated by membranes without ionophore. The influence of these parameters on the potential response of the electrodes was investigated in potassium dichromate concentrations in the range of 5.0×10^{-8}–5.0×10^{-3} M.

Effect of ionophore

The electrode prepared with ionophore free membrane showed very low sensitivity to chromate in the narrow linear range. The complex stoichiometry between the ionophore and the target ion is of major importance upon the performance of the electrode in the literature [27, 28]. As a result, chromate sensitivity was supplied by the introduction of the calix[4]arenes as ionophore to the membrane. Five different recently synthesized calix[4]arenes given in Fig. 1 were used as ionophores (**I-V**) in this study [25]. Therefore, Table 1 lists the compositions of different membranes with ionophores, along with their other characteristics. A 1.0×10^{-3} M $CaCl_2$ as filling solution was used in all experiments performed with

Table 1 Composition of membranes and potentiometric response characteristics of chromate-selective electrodes based on calix[4]arene derivatives at pH 1.0

Electrode no.	Ionophore no.	Membrane composition, mg				Slope ± $ts/\sqrt{N}$, mV per decade[b]	Linear working range, M
		Ionophore	PVC	Plasticizer	Liphophilic additive[a]		
E1	I	8.5	126.4	290.6 *o*-NPOE	–	35.8 ± 1.7	1.0×10^{-6}–1.0×10^{-2}
E2	II	8.5	126.4	290.6 *o*-NPOE	–	37.7 ± 0.8	1.0×10^{-6}–1.0×10^{-2}
E3	III	8.5	126.4	290.6 *o*-NPOE	–	36.6 ± 0.2	1.0×10^{-6}–1.0×10^{-2}
E4	IV	8.5	126.4	290.6 *o*-NPOE	–	34.1 ± 0.5	1.0×10^{-6}–1.0×10^{-2}
E5	V	8.5	126.4	290.6 *o*-NPOE	–	33.4 ± 0.6	1.0×10^{-6}–1.0×10^{-2}
E6	I	12.8	127.6	285.1 *o*-NPOE	–	38.6 ± 1.7	1.0×10^{-6}–1.0×10^{-2}
E7	II	12.8	127.6	285.1 *o*-NPOE	–	37.7 ± 1.9	1.0×10^{-6}–1.0×10^{-2}
E8	III	12.8	127.6	285.1 *o*-NPOE	–	37.6 ± 1.5	1.0×10^{-6}–1.0×10^{-2}
E9	IV	12.8	127.6	285.1 *o*-NPOE	–	38.8 ± 1.4	1.0×10^{-6}–1.0×10^{-2}
E10	V	12.8	127.6	285.1 *o*-NPOE	–	37.7 ± 1.9	1.0×10^{-6}–1.0×10^{-2}
E11	I	12.8	127.6	285.1 DBP	–	22.6 ± 3.0	1.0×10^{-6}–1.0×10^{-2}
E12	II	12.8	127.6	285.1 DBP	–	34.6 ± 1.5	1.0×10^{-6}–1.0×10^{-2}
E13	III	12.8	127.6	285.1 DBP	–	27.2 ± 1.7	1.0×10^{-6}–1.0×10^{-2}
E14	IV	12.8	127.6	285.1 DBP	–	29.9 ± 0.9	1.0×10^{-6}–1.0×10^{-3}
E15	V	12.8	127.6	285.1 DBP	–	31.0 ± 1.8	1.0×10^{-6}–1.0×10^{-2}
E16	I	12.8	127.6	285.1 BEHS	–	17.0 ± 1.1	1.0×10^{-6}–1.0×10^{-3}
E17	II	12.8	127.6	285.1 BEHS	–	14.3 ± 1.3	1.0×10^{-6}–1.0×10^{-2}
E18	III	12.8	127.6	285.1 BEHS	–	31.5 ± 1.3	1.0×10^{-5}–1.0×10^{-2}
E19	IV	12.8	127.6	285.1 BEHS	–	22.4 ± 0.7	1.0×10^{-6}–1.0×10^{-3}
E20	V	12.8	127.6	285.1 BEHS	–	25.1 ± 0.3	1.0×10^{-6}–1.0×10^{-2}
E21	I	12.8	127.6	285.1 *o*-NPOE	13.22	62.1 ± 0.2	1.0×10^{-6}–1.0×10^{-2}
E22	**II**	**12.8**	**127.6**	**285.1 *o*-NPOE**	**11.51**	**60.8 ± 0.4**	**1.0×10^{-6}–1.0×10^{-2}**
E23	III	12.8	127.6	285.1 *o*-NPOE	10.54	60.6 ± 0.2	1.0×10^{-6}–1.0×10^{-2}
E24	IV	12.8	127.6	285.1 *o*-NPOE	9.56	58.0 ± 1.7	1.0×10^{-6}–1.0×10^{-2}
E25	V	12.8	127.6	285.1 *o*-NPOE	8.17	53.4 ± 0.2	1.0×10^{-6}–1.0×10^{-2}

[a] Lipophilic additive 60% mole ratio to ionophore

[b] $t_{crit} = 3.18$ for $N = 4$ at 95% CL

these electrodes conditioned in deionized water. Ionophore ratio of the membrane was differentiated within the range of 1–3% in the preliminary studies. Due to the insignificant sensitivity (18–21 mV per decade) of the electrodes with polymeric membrane containing 1% of all ionophores towards chromate, the percentage of the ionophores in the membrane was changed as 2 and 3%. As it is seen in Table 1, the sensitivities of the electrodes with 2% ionophores (E1–E5) were found very close to those of the electrodes with 3% ionophores (E6–E10) in the linear working range of 1.0×10^{-6}–1.0×10^{-2} M. The optimum ionophore ratio was preferred as 3% since the sensitivity of the electrodes with 3% ionophores was in some degree higher than the electrodes with 2% ionophores.

Effect of plasticizer

Plasticizer is one of the important constituents of PVC membrane electrodes as its nature affects the dielectric constant of the membrane phase, decreases the glass transition temperature of PVC, serves as solvents for membrane component, and increases the diffusion coefficients of the species in the membrane [29]. Various types of plasticizers such as *o*-NPOE, DBP, BEHS, dioctyl sebacate (DOS), and dioctyl phthalate (DOP) have been used to fabricate many ion-selective electrodes [6, 19]. The effect of plasticizer type on the potentiometric response of the chromate-selective PVC membrane electrodes was studied by using three different plasticizers as *o*-NPOE (E6–E10), DBP (E11–E15), and BEHS (E16–E20). Among the several membranes tested for each of the calix[4]arenes, the incorporation of *o*-NPOE to the membranes displayed better potentiometric responses due to the interaction between the membrane and test solution dominated by ion-exchange process. This plasticizer has been selected for subsequent work.

Effect of lipophilic additive

The addition of lipophilic salts to ISE membranes improved the electrode performance, since they stabilize the membrane operating conditions, decrease the membrane resistance, and significantly reduce the response times. The influence of the lipophilic additive was examined by the addition of THATPB for each electrode based on five different calix[4]arenes and prepared with optimum membrane composition. For this purpose, the electrodes (E21–E25) were constructed by using

lipophilic additive 60% mole ratio to ionophore as shown in Table 1. The electrodes without calix[4]arenes prepared by the incorporation of THATPB as additive displayed smaller slopes and narrower working ranges when compared with both E21–E25 and E6–E10. On the other hand, addition of THATPB to the calix[4]arene-based membranes caused an increase in the slopes of calibration plots (E21–E25), which approached the close to Nernstian behavior (about 60 mV/decade). It was thought that calix[4]arenes in the membranes acting as positively charged ionophores in acidic solution studied (pH 1.0) together with the use of same charge signed additive (THA^+) might be the reason for better sensitivity due to the increase of THA^+ by the higher polarity of *o*-NPOE and serving of these cations as anion-exchanger sites for target ions as it was previously stated in the literature related to a salicylate-selective electrode [27, 30–33].

As a consequence, the electrodes with lipophilic additive 60% mole ratio to calix[4]arenes (**I-V**) (E21–E25) in Table 1 demonstrated the best chromate response in consideration of both the linear range and the slopes of the electrodes.

Response characteristics of the electrode

To determine the response mechanism of the electrode, the predominant Cr(VI) species should be known at the working pH. It is emphasized in the literature that the mole fraction of Cr(VI) species was related to both the working pH and the analytical concentration of them [34]. Generally, it is claimed that the possible Cr(VI) species could be such as H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}. The chemical equilibria consisting of these species and the related equilibrium constants are given below:

$$H_2CrO_4 \rightleftarrows H^+ + HCrO_4^- \; K_1 : 0.18$$

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-} \; K_2 : 3.2 \times 10^{-7}$$

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O \; K_3 : 98$$

Considering the calculations using these equilibrium constants and analytical concentrations of the Cr(VI), the dominant species with a ratio of >90% was found to be $HCrO_4^-$ at pH 1.0 in all concentrations lower than 10^{-2} M $Na_2Cr_2O_7$. However, the composition of 10^{-2} M $Na_2Cr_2O_7$ is approximately as 48% $Cr_2O_7^{2-}$, 51% $HCrO_4^-$, and 1% H_2CrO_4 [34]. As a result, we can conclude that the proposed electrode could be sensitive to $HCrO_4^-$ species at pH 1.0, and therefore, the calibration plots were drawn versus $pHCrO_4$.

In addition, the potentiometric response of the electrodes in the range of pH 2–11 was evaluated to understand whether the calix[4]arenes used in this study were sensitive to hydrogen ions or not. It was previously reported that some calix[4]arenes were used as ionophores to be promising H^+ receptors employed in hydrogen ion-selective electrodes [33, 35, 36]. For this purpose,

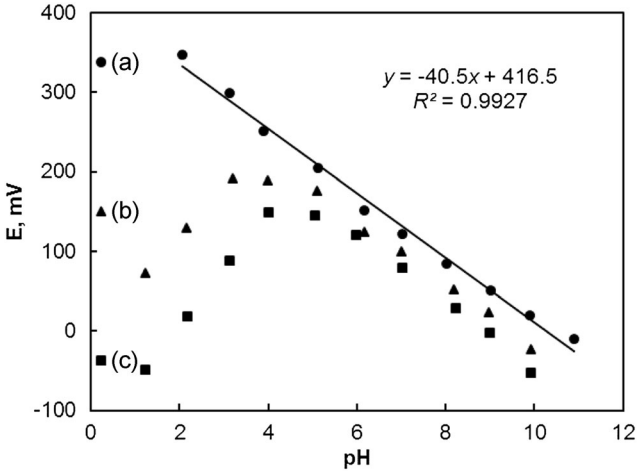


Fig. 2 Effect of pH of test solutions on the response of the proposed electrode (E22) 0 M (*a*), 1.0×10^{-3} M (*b*), and 1.0×10^{-4} M (*c*) sodium dichromate by using BR buffer solution

hydrogen ion sensitivities of the proposed electrodes were examined in BR buffer solutions containing with or without sodium dichromate solution, and typical pH response graph for ionophore II was given in Fig. 2 as an example. In Fig. 2a, it was obvious that the electrode showed H^+-sensitivity within the range of pH 2–11 with a slope of about 40 mV/pH. The response of this electrode was obtained in two different BR buffer series containing 1.0×10^{-3} (Fig. 2b) and 1.0×10^{-4} M (Fig. 2c) dichromate solutions. From the related calibration graphs, the potentiometric response was increased by pH until 4.0, was almost remained constant in approximately 2 pH units, and then was diminished by a slope of about 40 mV. This change of behavior can be explained in terms of the sensitivity of the electrode to $HCrO_4^-$ predominantly until pH 4.0 and to hydrogen ion after pH 6.0.

Consequently, taking into consideration the effect of pH on the distrubition of Cr(VI) species and the potentiometric response, the electrodes were thought to be used as chromate-selective electrodes due to the presence of predominant $HCrO_4^-$ species in the highly acidic media (pH 1.0).

The working range, the detection limit, and the slope of the electrode were assessed according to IUPAC by using two types of calibration graphs plotted for each of the electrodes (E21–E25) conditioned in deionized water. Figure 3a belongs to potential-time (*E-t*) graph obtained chronopotentiometrically. Figure 3b, c shows the calibration plots of E22 with error bars ($N = 5$) drawn by using the data related to pH-ion meter and *E-t* graph, respectively. All of the calibration plots also demonstrated linearity in the range of 1.0×10^{-6}–1.0×10^{-2} M with slopes changing between 53 and 62 mV/$pHCrO_4$ for five electrodes conditioned in deionized water (Table 1). The limit of detection was found as 6.3×10^{-7} M which was much lower than the detection limits obtained in previously reported electrodes [6, 17, 37–41] and was comparable to the values shown in literature [16, 19, 42]. As a result, the electrodes prepared using calix[4]arenes as ionophore

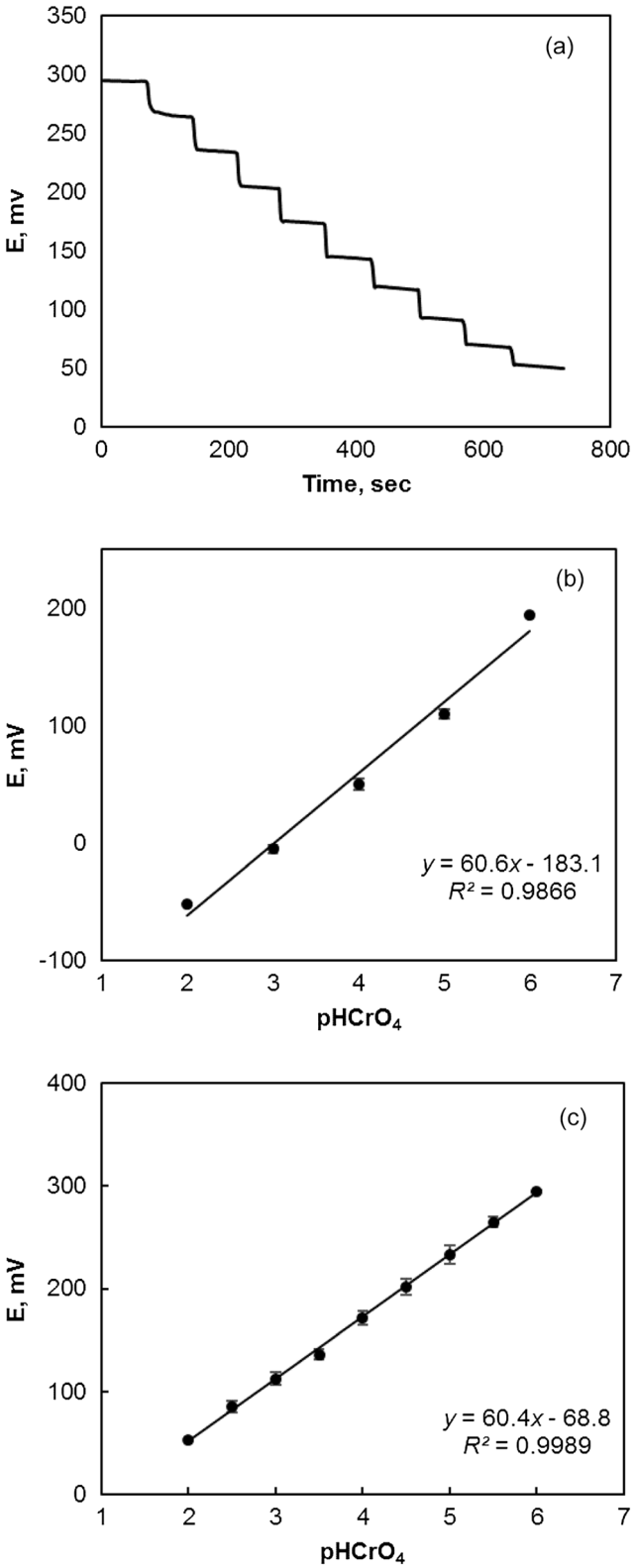


Fig. 3 **a** Potential-time graph of the chromate-selective electrode (E22) for step changes in dichromate concentration. Typical calibration graphs plotted by the data obtained from **b** pH-ion meter and **c** potential-time graph at pH 1.0 for E22

have exhibited close to Nernstian responses competitive with electrodes in literature [6, 17, 19, 38], and the small error bars in calibration plots have shown the good repeatability of them. When 1.0×10^{-3} M sodium dichromate solution was used as conditioning solution instead of deionized water, the electrodes displayed narrower working ranges (1.0×10^{-4}–1.0×10^{-2} M) and lower slopes. This situation can be attributed to leaching of hydrogen chromate ions to the analyte solution from the membrane and then changing the concentration of the hydrogen chromate on the membrane surface. Repeatable membrane surface can be formed by using deionized water as conditioning solution and easy reversible transfer of hydrogen chromate ions in a short time to/from membrane phase can be achieved. This situation also confirms the short response time of the electrode.

The response times of the electrodes were measured to reach 95% of equilibrium mV values after successive addition of the dichromate ion to obtain a tenfold change in the buffer solution. The static response time thus obtained was around 10 s over the entire working range. A very short dynamic response time for the electrodes is observed in Fig. 3a as an example. When compared with the electrodes having the same or narrower working ranges reported in literature, the response time of the proposed electrodes was found to be comparable, or even shorter than those [6, 17, 19, 38–40].

The lifetime, stability, and reproducibility of the proposed electrodes were tested by drawing their calibration graphs each day during 12 months. In this period, it was observed that the dynamic range and the slope of the electrodes had not shown significant change. After that time, their slopes decreased about 5%. This shows that the lifetime of the electrodes was at least 1 year and was found longer than all the other PVC membrane chromate-selective electrodes reported in literature [6, 16, 17, 19, 38, 39].

The reason to have a longer lifetime for the proposed electrodes based on calix[4]arenes can be the result of the stability of these compounds and no leaching out of calix[4]arene from membrane at all in the acidic medium.

Response mechanism of the electrode

In order to demonstrate the uniform incorporation of calix[4]arene to the membrane and its interaction with the analyte ion, the surface morphology of PVC membranes was examined by SEM (Fig. 4). Figure 4 displays the typical SEM images of PVC membranes (Fig. 4a) without ionophore, (Fig. 4b) with ionophore, and (Fig. 4c) with ionophore conditioned in 1.0×10^{-3} M $Na_2Cr_2O_7$ solution, for E22. In Fig. 4a, the polymer matrix without ionophore was homogeneous. Figure 4b shows that the white spots and gray circular structures could be identified as calix[4]arene particles and THATPB as additive, respectively. Furthermore, Fig. 4c presents a specific change in morphology of the membrane with

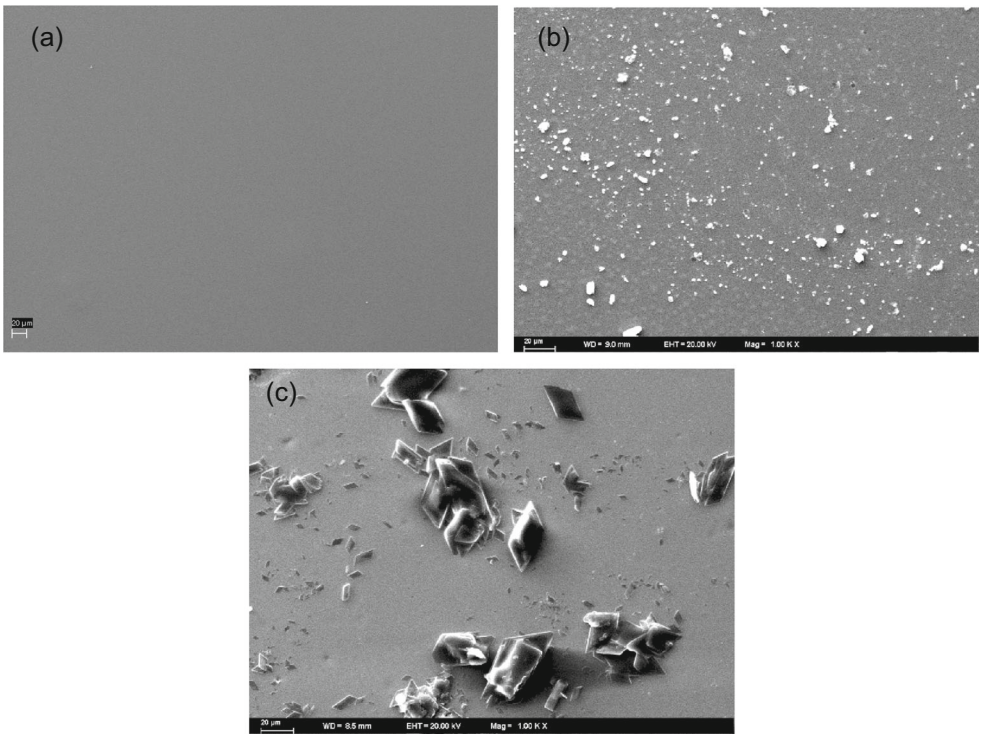


Fig. 4 SEM images of the PVC membranes **a** without ionophore, **b** with 3% ionophore, and **c** with 3% ionophore conditioned in 1.0×10^{-3} M $Na_2Cr_2O_7$ for E22

ionophore after conditioned in 1.0×10^{-3} M $Na_2Cr_2O_7$. This change could be attributed to the efficient interaction between calix[4]arene and chromate species in the solution.

It is known that EIS provided information on the impedance changes of the electrode surface during its construction and by varying the analyte concentration in the test solution. Figure 5 illustrates the Nyquist plots for electrode without ionophore containing same amount of additive (Fig. 5a (a)), electrode (E22) with ionophore II in 1.0×10^{-3} M sodium dichromate (Fig. 5a (b)), and (Fig. 5b) E22 in different concentrations of sodium dichromate at pH 1.0 containing 0.1 M NaCl. The Nyquist plots (the imaginary impedance (Z'') versus the real impedance (Z')) of impedance spectra include a semicircle portion at high frequencies and a linear portion at low frequencies which are related to the ion transfer limited process and the diffusion process, respectively [43, 44]. As it is obvious in Fig. 5, well-shaped semicircle plots were obtained. Comparing the semicircles in Fig. 5a revealed the electrical resistance for the ionophore-containing membrane (E22) was much lower than that of the ionophore-free membrane suggesting that the calix[4]arene derivative in the membrane can make the analyte ion transfer easier from the ions in solution. This observation could be explained by the increase of anion-exchange sites in the membrane for the analyte ions due to the positively charged ionophore in acidic solution and THA^+.

In order to indicate how the electrical resistance changes by varying the concentrations of dichromate solutions, impedance measurements were performed in five different concentrations (1.0×10^{-2}–1.0×10^{-5} M) at pH 1.0 containing 0.1 M NaCl and the impedance graphs were given in Fig. 5b. The electrode exhibited well-defined semi-cyclic impedances at high frequencies in all concentrations. However, the bulk resistance

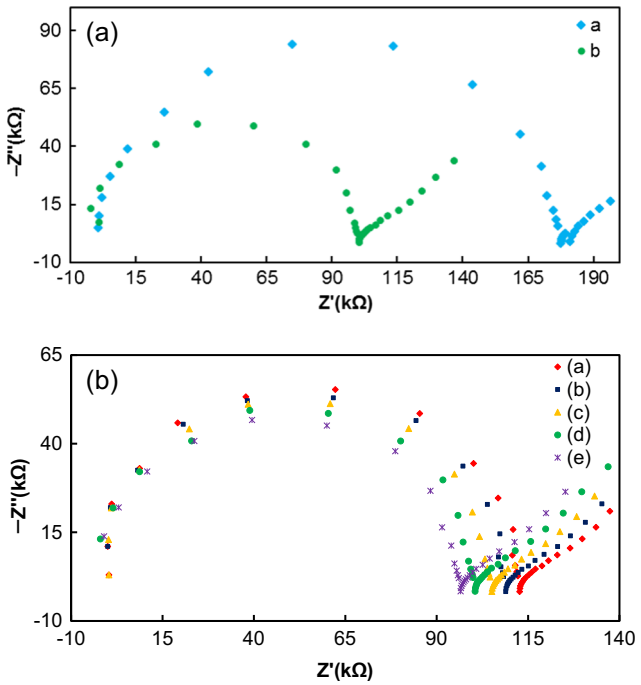


Fig. 5 Typical impedance plots of the membrane **a** without ionophore containing same amount of additive (*a*) and with 3% ionophore II in 1.0×10^{-3} M sodium dichromate for E22 (*b*), and **b** in containing different concentrations of sodium dichromate 0 M (*a*), 1.0×10^{-5} M (*b*), 1.0×10^{-4} M (*c*), 1.0×10^{-3} M (*d*), and 1.0×10^{-2} M (*e*) at pH 1.0 containing 0.1 M NaCl for E22

decreased as the dichromate concentration was increased, whereas that of the ionophore-free membrane remained almost constant. This phenomenon was related to the transfer of analyte ion across the membrane resulting from the increasing interaction between analyte ion and the calix[4]arene, while the solutions were concentrated. In conclusion, it can be said that the analyte ion transfer mechanism of the membrane of the presented electrodes was based on the introduction of Cr(VI) species into the cavity of calix[4]arene and/or the binding of $HCrO_4^-$ species with oxygen atoms in the calix[4]arene via possible hydrogen bonding. On the other hand, there are diffusional components at low frequencies which clearly indicate the reversible diffusion of the Cr(VI) species from the solution into the proposed electrode membrane [44, 45].

Table 2 The selectivity coefficients of the chromate-selective electrodes based on five different calix[4]arenes determined by FIM

Interfering ions	$\log K^{pot}_{HCrO4^-,j}$				
	E21	E22	E23	E24	E25
Citrate	−3.3	−3.9	−3.2	−3.2	−3.5
CH_3COO^-	−3.7	−3.8	−3.8	−3.4	−3.4
HSO_4^-	−3	−3.1	−3.2	−3.3	−3.0
$H_2PO_4^-$	−3.5	−3.7	−3.8	−3.4	−3.3
F^-	−3.4	−4	−3.2	−3.0	−3.0
Br^-	−0.8	−1	−2.0	−0.6	−1.6
ClO_4^-	−2.5	−1.7	−2.0	−1.1	−1.8
NO_3^-	−3.4	−3.7	−3.6	−3.3	−3.8
$HCOO^-$	−3.3	−3.2	−3.1	−3.1	−3.0
SCN^-	+1.1	+1.0	+1.2	+1.2	+1.1

The selectivity of the electrode

The selectivity coefficients ($K^{pot}_{HCrO4^-,j}$), defining the relative response for the analyte ion over other ions present in the solution, was investigated by using fixed interference method (FIM) [46]. In this study, the concentration of sodium dichromate was within the range from 1.0×10^{-6} to 1.0×10^{-2} M, while that of the interfering anion was 1.0×10^{-3} M. The selectivity coefficients of various anions for chromate-selective electrodes based on five different calix[4]arenes (E21-E25) were given in Table 2. According to the tabulated data, the interfering effects of the anions are in the following order:

$$SCN^- > HCrO_4^- > Br^- > ClO_4^- > HSO_4^- > HCOO^- \approx \text{Citrate} > F^- \approx NO_3 - > H_2PO_4^- > CH_3COO^- \quad (21)$$

$$SCN^- > HCrO_4^- > Br^- > ClO_4^- > HSO_4^- > HCOO^- > NO_3^- \approx H_2PO_4^- > CH_3COO^- > \text{Citrate} > F^- \quad (22)$$

$$SCN^- > HCrO_4^- > Br^- \approx ClO_4^- > HCOO^- > HSO_4^- \approx \text{Citrate} \approx F^- > NO_3^- > H2PO_4^- \approx CH_3COO^- \quad (23)$$

$$SCN^- > HCrO_4^- > Br^- > ClO_4^- > F^- > HCOO^- > \text{Citrate} > HSO_4^- \approx NO_3^- > H_2PO_4^- \approx CH_3COO^- \quad (24)$$

$$SCN^- > HCrO_4^- > Br^- \approx ClO_4^- > F^- \approx HCOO^- \approx HSO_4^- > H_2PO_4^- > CH_3COO^- > \text{Citrate} > NO_3^- \quad (25)$$

Having selectivity coefficients slightly different from each other for five electrodes based on different calix[4]arenes may be the result of changes in the required cavity size for the reversible transfer of anions from/to membrane due to the presence of different number of acryloyl groups (Fig. 1). Most of the ions, except thiocyanate and high concentrations of bromide and perchlorate ions, had low selectivity coefficients. This phenomenon indicated that there was no interference effect for the determination of dichromate ion by using the proposed electrodes in the presence of other ions tested. The reason that the selectivity coefficients of these electrodes do not comply with the Hofmeister series [47] could arise from the possible formation of new structures that depend upon the binding of anions via hydrogen bonding at pH 1.0, and strong and selective interaction of $HCrO_4^-$ with calix[4]arenes. However, the differences between the above-mentioned sequences related to the number of substituents could not be explained completely.

Therefore, these electrodes can satisfactorily be utilized for the determination of Cr(VI) species in the media that thiocyanate ions were not presented.

Analytical applications

The proposed electrodes in this study revealed good response characteristics for Cr(VI) species. In order to demonstrate their applicability as an indicator electrode, they were employed in the potentiometric titration of Fe(II) with standard $K_2Cr_2O_7$ solution. The titration plots with excellent inflection points in accordance with stoichiometric values were observed. The results showed that they could be satisfactorily used as an indicator electrode in

Table 3 Recovery results of Cr(VI) for speciation of Cr(VI) and Cr(III) in synthetic aqueous samples[a, b]

Electrode no.	Recovery $\pm ts/\sqrt{N}$, %		
	In the presence of Cr(III)	After the oxidation of Cr(III) to Cr(VI) in the absence of Cr(VI)	After the oxidation of Cr(III) to Cr(VI) in the presence of Cr(VI)
E21	103.4 ± 0.004	98.7 ± 0.03	103.0 ± 0.02
E22	103.0 ± 0.006	102.7 ± 0.04	102.0 ± 0.04
E23	104.2 ± 0.009	102.1 ± 0.04	102.0 ± 0.03
E24	96.0 ± 0.02	102.5 ± 0.09	102.0 ± 0.03
E25	97.0 ± 0.01	98.9 ± 0.06	102.0 ± 0.05

[a] t_{crit} = 3.18 for N = 4 at 95% CL. [b] Concentrations of Cr(III) and Cr(VI) are 1.0×10^{-4} M

the titration of Fe(II) with standard $K_2Cr_2O_7$ potentiometrically for some analytical purposes.

Furthermore, to present the speciation of Cr(III) and Cr(VI) species with the proposed electrode, standard Cr(III) and Cr(VI) solutions were prepared. For this purpose, three different titrations of Cr(VI) with standard Fe(II) solution were made separately, as follows: (i) in the presence of Cr(III), (ii) after the oxidation of Cr(III) to Cr(VI) in the absence of Cr(VI), and (iii) after the oxidation of Cr(III) to Cr(VI) in the presence of Cr(VI).

The results obtained by using five electrodes (E21–E25) based on different calix[4]arenes studied are summarized in Table 3. The critical value, t_{crit}, is 3.18 (N = 4) at the 95% confidence level. Since $t_{crit} > t_{exp}$, no remarkable differences were observed between the known concentrations of standard solutions and corresponding experimental results. As seen in the table, the recovery results obtained in the presence of Cr(III) were found satisfactory which lead us to conclude that the Cr(III) had no interference on the potentiometric titration of Cr(VI) by using the proposed electrodes. The results in second column of recovery data showed that Cr(III) could be successfully determined with these electrodes by the help of easy oxidation procedure given in the experimental section. Moreover, the mean recovery values of almost 100% in the last column indicated that total chromium content could be quantitatively determined in a solution containing Cr(III) and Cr(VI) after the oxidation of Cr(III) to Cr(VI) (Fig. 6 as an example). Consequently, achieving satisfactory recoveries resulted with effective tools for the speciation of Cr(III) and Cr(VI) by utilizing the developed calix[4]arene based PVC membrane electrodes.

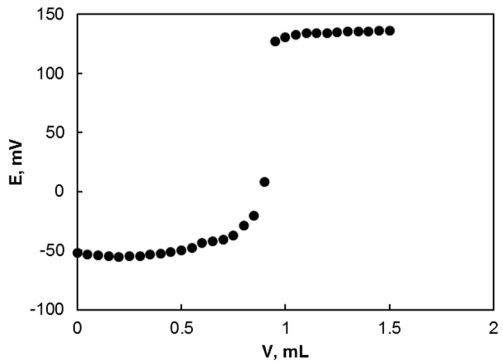


Fig. 6 Potentiometric titration plot of total chromium content in a solution containing Cr(III) and Cr(VI) with standard Fe(II) solution obtained after the oxidation of Cr(III) to Cr(VI) (for E22)

Conclusions

The results obtained showed that calix[4]arene and its mono-, di-, tri-, and tetra-acryloyl esters used in this study were found as suitable ionophores for the determination of Cr(VI) species. Only one study has been reported related to the use of calix[4]arenes as ionophores in the construction of chromate-selective electrodes. On the bases of the data in this article, it can be concluded that the proposed electrodes are very easy to prepare and have displayed good performance characteristics such as Nernstian response, feasible working range, low detection limit, and fast response. They had a lifetime of at least a year which was one of the longest among the PVC membrane chromate-selective electrodes reported in literature. Additionally, it was observed that the number of substituents bonded to the –OH groups in these calix[4]arenes affected the selectivity order for each electrode due to the change of the cavity size differentiated by the number of substituents. Good inflection points were obtained by using the proposed electrodes as an indicator electrode in the potentiometric titration of Fe(II) solution with standard dichromate solutions. These electrodes were successfully utilized for the Cr(VI) and Cr(III) speciation in aqueous medium for the first time. In conclusion, as a future process, various ion-selective electrodes could be developed for speciation analysis and monitoring for hazardous species.

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