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Synthesis of Thiol Amine Surfactant for Sensor Fabrication to Determine Chromium(III) Ions in Different Water Samples

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Abstract

A thiol amine surfactant, poly-3-(dodecylthio)-N-hexadecylacrylamide (iphI) was prepared and characterized using spectral methods of analyses. The proposed potentiometric method was based on the fabrication of iphI-modified carbon paste (iphI-MCPE; electrode IV) sensor. Fast, highly sensitive and wide dynamic range potentiometric sensor was constructed using the prepared ionophore to quantify Cr(III) ions in spiked water sample under optimum conditions. The electrode (IV) exhibited an excellent Nernstian response to Cr(III) ion ranging from 4.8×10^{-7} to 1.0×10^{-2} mol L-1 with a detection limit of 4.8×10^{-7} mol L^{-1} and a slope of 19.59±0.45 mV decade-1 over a wide pH range (2.0-8.0) with a fast response time (7 s) at 25 oC. The proposed sensor showed fairly good discriminating ability towards Cr(III) ion in comparison with many hard and soft metal ions. The developed electrode has been successfully applied for the Cr(III) ions potentiometric determination in different water samples. The results obtained compared well with those obtained using atomic absorption spectrometry.

Keywords: Thiol amine ionophore; Modified carbon paste sensor; Cr(III) determination; real water samples.

1. Introduction

Heavy metals are more attractive in toxicological, pharmaceutical, environmental and biomedical analysis [1, 2]. Among those, the detection of chromium had more attention due to the high toxicity of Cr(VI), while Cr(III) is considered less toxic and unexpectedly necessary to human health in trace concentration. The reverse effects of higher concentration of Cr(III) comes from its high coordination ability with different organic compounds, resulting in inhibiting some metallic-enzyme systems [3, 4]. The allowed limit for aqueous effluent discharged into inland waters is 1.0 mg L^{-1} for total chromium (Cr(III) and Cr(VI)) and 0.10 mg L^{-1} for Cr(VI) [5, 6].

Generally, complicated analytical techniques like high performance liquid chromategraphy (HPLC) [7], atomic absorption spectroscopy (AAS) [8], X-ray fluorescence (XRF) [9], and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [10, 11] are used for the trace level determination of metals. The disadvantages of these techniques can summarized as the cost of routine analysis, time consuming and uninteresting procedure of sample preparation. On the other side, the advantages of chemical sensors comes from their simple instrumentation, speed and easy preparation of the sample, cheap instrument as well as analysis, online monitoring, broad dynamic range, good selectivity and nondestructive analysis [12-16]. Recently ion-selective electrodes proved promising alternative as these provide linear dynamic range, fast response time, non-destructive analysis and online analysis. To develop a good sensitive sensor for chromium ion determination [17-24], many efforts were done using various neutral ionophores. However, reported sensors showed narrow working concentration range, non-Nernstian response and high response time [25-28] and significant interference from foreign ions

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were appeared [29-33]. To achieve wider applicability, these limitations need to be removed. To prepare the selective ion sensor, the electroactive materials used in the membranes is the important requirement where it should display high lipophilicity and strong affinity for a particular metal ion to be determined and poor affinity for others. Sensors include Schiff bases as electroactive ingredient has been reported to appear excellent selectivity for specific metal ions [34-37]. Schiff base ligands were widely studied mainly because their facile syntheses, electronic properties, easily tunable steric and good solubility in common solvents. They are stable under a diversity of oxidative and reductive conditions, and these imine ligands are border line between hard and soft Lewis bases. They are more important as biochemical, analytical and antimicrobial reagents. The use of Schiff bases as neutral carriers have been displayed as ion selective electrodes to determine cations such as copper(II) [38-40], mercury(II) [41], nickel(II) [42], silver(I) [43], lead(II) [44] and cobalt(II) [13] .

2. Experimental

Materials and methods:

Analytical grade reagents were used. Throughout all experiments bidistilled water was used. Chromium chloride [$CrCl_3.6H_2O$] and graphite powder (synthetic 1–2 μm) were supplied from Aldrich. *o*-Nitrophenyloctylether (*o*-NPOE) was supplied from Fluka, poly-3-(dodecylthio)-N-hexadecylacrylamide (iphI) was prepared according to the previous reported method [45]. Interfering materials such as chloride salts of copper, magnesium, potassium, cobalt, sodium, ferric and aluminum, cadmium, nickel, calcium, in addition to bromide, iodide, chloride and sulphate anions were used. Potassium chromate and potassium dichromate were used as source for Cr(VI). 1-Dodecylamine (98%), n-hexadecylmercaptan (90%) and 1-dodecanethiol (98%) were purchased from (Acros, USA). Acrylic acid, azoisobutyronitrile and tetrahydrofuran were purchased from El-Gomhouria Company, Egypt.

Water Samples

Real water samples included formation water (sample 1; Qarun Petroleum Company, Agiba Petroleum Company, Egypt), tab water (samples 2; Cairo university, Giza, Egypt), river water (samples 3; Cairo, Egypt) and cooling tower water (sample 4; EMISAL, Egyptian Mineral and Salts Company, Fayoum, Egypt).

Potentiometric measurements

Laboratory potential measurements were carried out by using Jenway 3505 pH-meter. Reference electrode Silver-silver chloride double-junction was used (Metrohm 6.0726.100). Using Thermo-Orion, model Orion 3 stars, USA for pH measurements. Prior to analysis, all glassware used were washed very well with bidistilled water and dried in the oven before use.

Preparation of ionophore:

a- Condensation reaction between 1-dodecanethiol with acrylic acid:

The condensation reaction was carried out in three-neck glass flask equipped with magnetic stirrer, thermometer, nitrogen gas inlet and a reflux condenser. The reaction was carried out using 100 ml of tetrahydrofuran (THF) as a solvent; in which 1 mole of 1-dodecanethiol were dissolved. Using azoisobutyronitrile [AIBN] as an initiator (0.1% from the total weight of 1-dodecanethiol) was dissolved in a suitable amount of THF. During the first two hours of the reaction the AIBN was added into four proportions. In the beginning of the reaction, the reaction flask was swept with nitrogen gas, then the temperature of the mixture was raised up to 80 °C and 1 mole of acrylic acid was continuously introduced during the reaction progress. After six hours the product poly-3-(dodecylthio) acrylic acid (I) was precipitated. The precipitated product was collected and washed with water and then dried in vacuum oven at 60 °C.

b- Amidation reaction between product I with hexadecan-1-amine:

The reaction was carried out using 30 ml of THF as a solvent; in which 1 mole of poly-3-(dodecylthio)acrylic acid (I) was dissolved in three-neck glass flask equipped with reflux condenser. In the beginning of the reaction, the reaction flask was swept with nitrogen gas, then the temperature of the mixture was raised up to 80 °C and 4.5 mole of hexadecan-1-amine was continuously introduced during the reaction progress. After eight hours the product poly-3-(dodecylthio)-N-hexadecylacrylamide (iphI) was precipitated. The scheme of the prepared compound was shown in scheme 1.

Preparation of modified carbon paste electrode

A 500 mg pure graphite powder and 5-15 mg of (iphI) ionophore were transferred to mortar and mixed well with plasticizer (0.2 mL of *o*-NPOE). The modified paste is filled in electrode and kept in distillated water for 24 h before use [35, 41, 46]. A fresh surface was formed by gently pushing the stainless-steel screw forward and by filter paper polishing the new carbon-paste surface to form a shiny new surface.

Calibration of the new MCPEs

A calibration graphs were constructing by plotting the recorded potentials of the MCPEs (against Ag/AgCl reference electrode) as a function of -log [Cr(III)] within the concentration range from 1×10^{-6} to 1×10^{-2} mol L^{-1} at pH 6 (using acetate buffer). This graph was used for determination of unknown Cr(III) concentration [17].

Determination of Cr(III) in spiked real water samples

About 5 ml of spiked real water samples were carried to a 25 ml beaker and pH 6 was adjusted then content was estimated via potentiometric calibration using MCPE as sensing electrodes. The method was repeated many times to make sure about the accuracy and reproducibility of the proposed method [17, 47].

Surface tension measurements (γ)

Surface tension was measured by using De-Noüy Tensiometer (Kruss-K6 type, Germany) and applying a platinum ring technique. A freshly prepared aqueous solution of the synthesized surfactants in distillated water was formed with a different molar concentration range from 1×10^{-2} to 1×10^{-6} mol L^{-1} at room temperature (25 °C). The ring was washed twice after each reading first by ethanol and then distilled water. The surface tension was measured five times for each sample within a 2 minute interval between each reading.

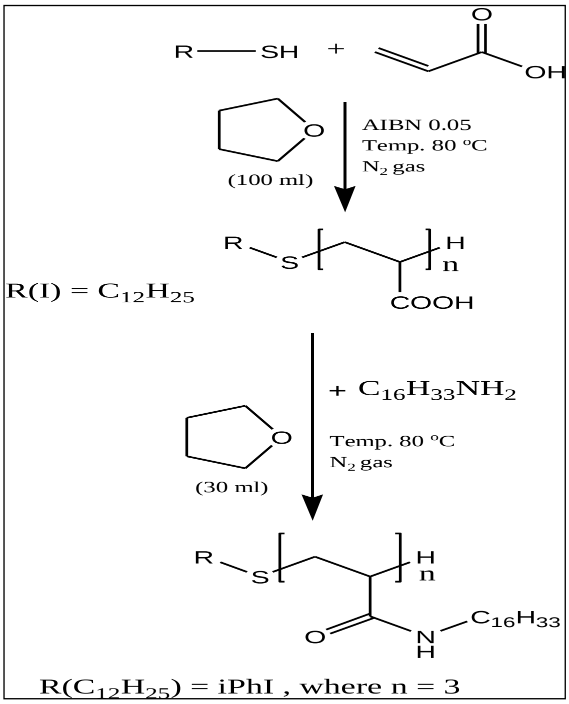
Results and Discussion

Chemical Structure Confirmation

The characterization of the prepared ionophore was carried out using FTIR spectra as shown in Figure 1 and GPC analysis**.**

FTIR:

The FTIR spectrum for compound iphI (Figure 1) showed NH peak at 3306 cm^{-1} and the presence of CONH peak at 1661 cm^{-1}. The absence of C=C peak at 1620 cm^{-1}, absence of SH peak at 2400 cm^{-1} and absence of OH peak at 3200 cm^{-1} proved that the amidation process took place.



Scheme 1: Synthesis of iphI (poly-3-(dodecylthio)-N-hexadecylacrylamide) ionophore.

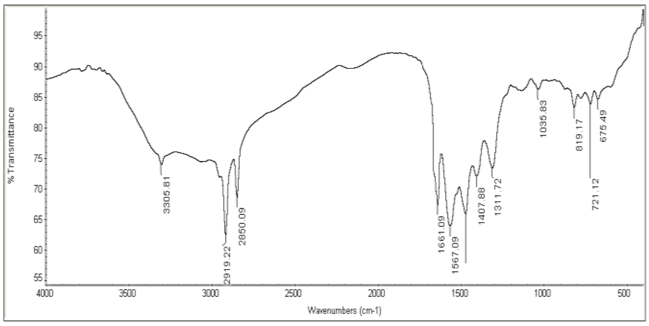


Figure 1. FTIR spectra of iphI (poly-3-(dodecylthio)-N-hexadecylacrylamide) ionophores.

Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC; model waters 515/2410) was used to determine the molecular weight and poly dispersity (Mw, Mn and Mw/Mn) of iphI ionophore. The dissolved sample in THF is passed across filter paper (pore size of 0.45 µm) and column (stryragel) calibrated using standard (poly styrene; shodex) at constant temperature (40 °C) and flow rate (1 ml min^{-1}). The MW of iphI compound was 922 g/mol.

Surface active properties:

Micelles of surfactants are prepared in the bulk aqueous solution above a given concentration for each surfactant and this concentration known as the critical micelle concentration (CMC). The CMC of the surfactants at room temperature (25 °C) was determined by plotting the surface tension (c) versus -ln concentration of the surfactant, as shown in Figure 2 for iphI as a representative example. The CMC values of the iphI was calculated from the abrupt change in the slope of (γ) against (-ln C). The surface tension of surfactant solutions decreased with increasing concentration of the aqueous solutions, reaching clear break points, which were taken as the CMC. Table 1 lists the CMC, the surface tension at the CMC (γ_{CMC}), the maximum surface excess concentration (Γ), and the area occupied per molecule (A_{min}). It is noteworthy that the thiol amine surfactant had small CMCs. This suggests that the thiol amine surfactant easily form aggregates in solution.

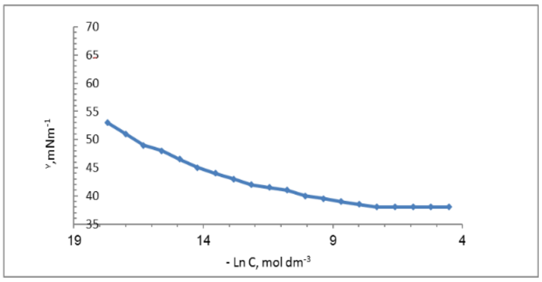


Figure 2. Surface tension versus -ln C of the iphI ionophore at room temperature

Effectiveness of Surface Tension Reduction (π_{cmc}) [48].

The effectiveness of surface tension reduction (π_{cmc}) was calculated according to the equation:

$\pi_{cmc} = \gamma_o - \gamma_{cmc}$

Where γ_o is the surface tension measured for pure water at the suitable temperature and γ_{cmc} is the surface tension at CMC.

Surface Excess Concentration (Γ_{max})

Applying the equation $\Gamma_{max} = -10^{-7}$ [1/RT] [dγ/dlnC]γ, the surface excess concentration can be calculated where (Γ): surface excess concentration of surfactant (mol/cm^3), R: gas constant (8.314 J/ mol.K), T: temperature in K, **γ:** surface or interfacial tension (mN/m) and **C**: concentration of surfactant (mol/L) [49].

Minimum Surface Area per Molecule (A_{min})

The minimum surface area was calculated applying the equation: $A_{min} = 10^{16} / [\Gamma_{max} . N_A]$

Where A_{min}: surface area per molecule of solute in square nanometers (nm^2), **Γ**: surface excess in mol/m^2 and N_A is Avogadro's number [49]

Gibbs Free Energy of Micellization (ΔG_{mic}) [50]

The Gibbs free energy of micellization was calculated from the relation:

$\Delta G_{mic} = R\ T\ (1+\alpha) \ln CMC$

Where R: gas constant, T: absolute temperature, α: fraction of counter ions bound by the micelle

Gibbs Free Energy of Adsorption (ΔG_{ads}) [51]

According to the relation: $\Delta G_{ads} = \Delta G_{mic}$ - [0:6022 x π_{CMC} x A_{min}], the Gibbs free energy of adsorption can be evaluated. The data of surface active parameters and thermodynamic parameters of the prepared surfactants are listed in Table 1. It was clear that, the CMC values decrease in case of iphI

Table 1: Surface active and thermodynamic parameters of iphI at room temperature.

Surfactants	CMC mole/dm^3	γ_{cmc}m N/m	Γ_{max}, mol/m^2.10^{10}	A_{min}, nm^2.100	Π_{CMC}	ΔG_{mic}Kj/mol^{-1}	ΔG_{ads}Kj/mol^{-1}
iphI	6.82×10^{-4}	38	0.57	2.90	7	-23.6	-24.8

compound. This may be explained based on decreasing the internal alkyl chain and molecular weight leads to an increase of the mobility of the iphI that might be adsorbed on the water surface. The values of Γ_{max} and A_{min} are listed in Table 1. The results of the thermodynamic parameters of micellization expressed by the standard Gibbs free energy, ΔG_{mic} (micellization) and ΔG_{ads} (adsorption), of the surfactant are listed in Table 1. Since (ΔG_{mic}<0) which means that the micellization is a spontaneous process, in addition, ΔG_{mic} becomes less negative with the decrease of the internal alkyl chain, which leads to the steric inhibition of micellization. The ΔG_{ads} (negative values) is greater than ΔG_{mic}, indicating that the surfactant preferred to adsorb on the interface than to form micelles. Since the adsorption on the interface is associated with a decrease in the free energy of the system then there is a direct relationship between the efficiency of surfactant and the values of ΔG_{ads}. In this respect, the maximum negative value of ΔG_{ads} (-24.803 kJ/mol^{-1}) was obtained by iphI compound which exhibited the highest detection for the Cr(III) in the samples (accuracy 99.95%, precision 0.194).

As shown in Table 1, the area occupied per molecule for the prepared thiol amine surfactant increases by increasing the alkyl chain length because the surfactant molecules adsorb at the air/water interface to orient themselves, so as the hydrophobes are directed away from water. But it is obvious that A_{min} decreases by increasing the hydrophilic chain length within the group.

Calibration Curve

Poly-3-(dodecylthio)-N-hexadecylacrylamide (iphI) compound was used as ionophore for the construction of Cr(III) selective modified carbon paste electrodes. The effect of paste composition, selectivity, working range, pH of the media and the life time of electrodes were examined. The sensors plasticized with *o*-NPOE were calibrated against a double junction Ag/AgCl reference electrode, at 25±1°C, using the direct calibration technique.

The potential response of the electrodes was determined and they found to have a linear response over wide concentration range from 4.8×10^{-7} to 1.0×10^{-2} mol L^{-1} of Cr(III) with a divalent cationic slope of 19.59±0.45 mV decade^{-1} and exhibit detection limit of 4.8×10^{-7} mol L^{-1} for electrode (IV) (Table 2).

Table 2: Response characteristics of modified CPE sensor (electrode IV) with poly-3-(dodecylthio)-N-

Parameter	CPE
Slope (mV decade^{-1}) ±SD	19.59±0.45
Concentration range (mol L^{-1})	4.8×10^{-7} - 1×10^{-2}
Correlation coefficient, r	0.998
Lower detection limit (mol L^{-1})	4.8×10^{-7}
Upper detection limit (mol L^{-1})	1×10^{-2}
Working pH range	2.0 – 8.0
Intercept (mV)	245.34±0.82
Life time (days)	166
Response time (s)	7
Standard deviation (SD)*	0.078
Relative standard deviation (RSD%)*	0.795
Accuracy (%)	99.95
Precision (%)	0.194

Composition and characteristics of the sensors

Previous experiments showed that chemically modified carbon paste sensors which do not contain ionophores have no response or low response towards Cr(III) ion. For this purpose, new ionophore as (iphI) was investigated as modifier for the present electrodes. It was known that obtaining the sensitivity and linearity with a given electrode depend on the amount of ionophore in the electrode composition. Thus, five modified carbon paste electrodes (MCPEs) were prepared to determine the best electrode. The proportion of (iphI) ionophore was varied as 5, 7.5, 10, 12.5 and 15 mg (w/w) %. The results (Table 3) showed that on using paste of optimum compositions (electrodes IV), a slope of 19.59±0.45 mV decade^{-1} over a relatively wide range of Cr(III) concentration from 4.8×10^{-7} to -1×10^{-2} mol L^{-1} was obtained. In all subsequent studies, electrode (IV) made of paste consisting of 12.5 mg ionophore was used. A calibration plot for the electrode is shown in Figure 3. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.8×10^{-7} mol L^{-1}.

Effect of plasticizer

The impact of solvent mediator (plasticizer) type and its concentration on the characteristics of the Cr(III) modified carbon paste sensors (Cr(III)-MCPEs) were investigated using five solvents with different polarities namely o-NPOE, TCP, DBP, DOP and DOS.

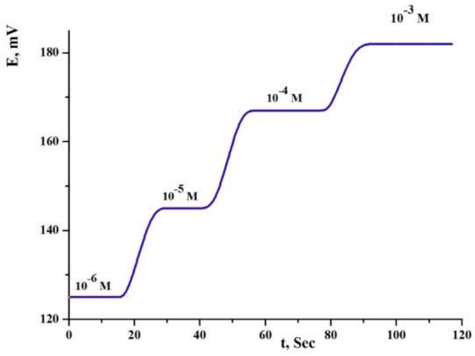


Figure 3. Calibration curve for Cr(III) ion using modified carbon paste electrode (electrode IV).

The plasticizers not only improve the workability of the sensor, but also participate in the improvement of the working concentration range, life span and stability of the electrode. The electrodes were found to have slope values of 19.59±0.45, 18.19±0.36, 14.37±1.45, 15.97±1.52 and 13.41±2.47 mV decade^{-1} for MCPEs plasticized with o-NPOE, TCP, DBP, DOP and DOS, respectively (Figure 4). The obtained calibration graphs shown in Figure (4) clarified that the MCPE electrode plasticized with *o*-NPOE showed the highest slope over the other studied plasticizers. This may be accounted to the fact that these plasticizers have different dielectric constant (ε = 24, 17.6, 3.8 and 4.7 for *o*-NPOE, TCP, DOS and DOP plasticizers, respectively).

Dynamic response time

The response time of MCPE is very important parameter and the average response time is the time required for the electrodes to reach a cell potential of 90% of the final equilibrium according to IUPAC

Table 3: Effect of ionophore content on the performance characteristics of modified CPE sensors.

No. of electrodes^{a}	Ionophore Content (mg)	Concentration rang (mol L^{-1})	Slope (mV decade^{-1}) ±SD	Recovery %
I	5	1×10^{-6}-1×10^{-2}	14.83±2.16	97.06
II	7.5	1×10^{-6}-1×10^{-2}	15.69±2.03	97.36
III	10	1×10^{-6}-1×10^{-2}	17.08±1.46	99.88
IV	12.5	4.8×10^{-7}-1×10^{-2}	19.59±0.45	99.99
V	15	1×10^{-6}-1×10^{-2}	18.27±0.92	99.92

^{a} Poly-3-(dodecylthio)-N-hexadecylacrylamide ionophore (iphI definition. A response time of 7s was obtained for this electrode (Figure 5).

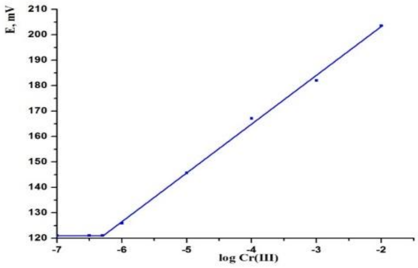


Fig. 4. Effect of plasticizer type on the performance characteristics of electrode IV.

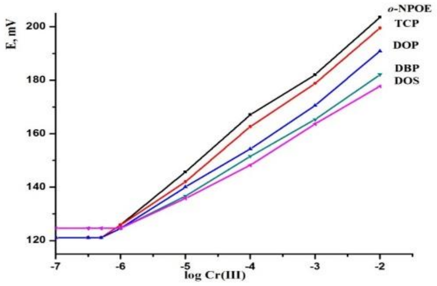


Figure 5. Dynamic response time of Cr(III) modified CPE sensor (electrode IV).

Effect of pH

The results showed the effect of the solution pH (pH = 1-10) on the potential response of the paste sensor (electrode IV) were shown in Figure 6. The potential does not change apparently at pH range 2.0–8.0, which can be used as the working pH range of the proposed electrode, as shown in Figure 6. While, outside this range, the potential changed. The increase of potential below pH 2.0 may be ascribed to the competitive binding of protons to the ligand on the electrode surface. The decrease of potential above pH 8.0 can be attributed to the formation of hydroxyl complexes of Cr(III) ions which diminished its ability to combine with the carrier [17].

Effect of temperature

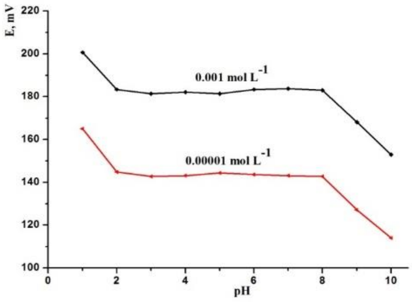


Figure 6. Effect of pH of the test solution on the potential readings of modified CPE sensor (electrode IV).

A change of electrode performance with temperature, at different test solution temperatures (10-65 ºC) for the Cr(III) electrode was examined.

The electrode IV exhibits good Nernstian behavior in the temperature range (20–60 ºC) as shown in Figure 7. The standard cell potentials (E^o_{cell}) which used to determine the isothermal temperature coefficient (dE^o/dt) of the cell, were determined as previously reported [52]. The isothermal coefficient of the electrode IV was found to be 0.000168 mV/ºC which pointed out that it had high thermal stability within the investigated temperature range and its ability to be usable up to 60 ºC without noticeable deviation from the Nernstian behavior.

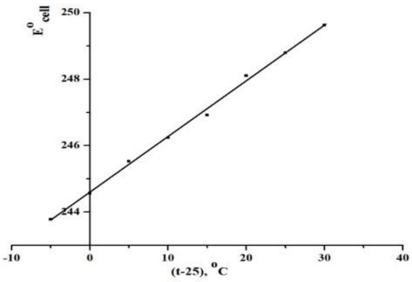


Figure 7. Variation of the cell e.m.f. with the temperature for the modified CPE sensor (electrode IV).

Potentiometric selectivity

The selectivity behavior was described in terms of selectivity coefficient which reflected the response of the modified sensor for the primary ion over the other ions present in the solution.

To examine the selectivity of Cr(III) selective electrode (electrode IV), the potential response was examined in the presence of different cations using the matched potential method (MPM) [37, 53]. The MPM was followed and the selectivity coefficient was calculated by:

$$K_{A,B}^{MPM} = \frac{a'_A - a_A}{a_B}$$

In the present study, a_A and a_A' were kept at 1.0× 10^{-3} and 5.0 × 10^{-5} mol L^{-1} Cr(III) and a_B was experimentally determined. Possible interferences from a number of cations were studied. Data listed in Table 4 reflected that most of the selectivity coefficients were very low, indicating that significant interference was not observed on the electrode IV performance for determination of Cr(III) ions in the presence of other interfering ions.

Table 4. Potentiometric selectivity coefficients of some interfering ions using the modified CPE sensor (electrode IV)

Interfering ions (B)	$-\log K_{A,B}^{MPM}$ (a)	Interfering ions (B)	$-\log K_{A,B}^{MPM}$ (a)
Na^+	3.90	Fe^{3+}	1.45
K^+	3.68	Ti^{3+}	4.25
Sr^{2+}	2.06	NH_4^+	4.33
Pb^{2+}	3.28	Al^{3+}	4.52
Ca^{2+}	4.16	Cl^-	3.14
Ni^{2+}	4.28	Br^-	3.42
Mn^{2+}	4.41	I^-	3.66
Mg^{2+}	3.96	SO_4^{2-}	2.47
Ba^{2+}	3.69	Cu^{2+}	4.07
Fe^{2+}	1.99	Cd^{2+}	3.93
Co^{2+}	3.70	-	-

Potentiometric determination of Cr(III) ion in different spiked water samples

The Cr(III)-MCPEs were used for determination of Cr(III) ions in various different water samples including formation water, tap, river Nile and cooling water samples. Determination of Cr(III) in these samples was performed using the standard addition method. The assay method for Cr(III) ions over the concentration range of 1 × 10^{-6} – 1 × 10^{-2} mol L^{-1} was accomplished using three batches (three determinations each) for the statistical treatment of the results. Water samples of very low concentration of Cr(III) (below the detection limit of the electrode) were spiked by adding aliquots of standard solution of Cr(III) ion to the samples. The samples were acidified with HNO_3 acid to dissociate the metal-complexes then adjusted to pH 4.0-6.0 using acetate buffers.

The amount of chromium was measured by the chromium selective electrode (electrode IV) and by atomic absorption spectrometry (AAS). It is clear from the results, given in Table 5, that there is good agreement between the results of the proposed sensor and those obtained from AAS method. The recovery ranges are between 98.20 and 99.20%.

Table 5. Potentiometric determination of Cr(III) in spiked water samples using modified CPE sensor (electrode IV).

Sample No.	$[Cr(III)]$ mg mL^{-1}			RSD (%)	
	Taken	Found		Sensor IV	AAS
		Sensor IV	AAS		
1	2.0	1.97	1.94	1.427	1.952
2	2.0	1.99	1.98	0.954	1.006
3	2.5	2.46	2.44	1.673	1.895
4	2.5	2.48	2.45	1.083	1.702
SD		0.095-0.263	0.152-0.371		

Comparison study

In Table 6, very important characteristics of the proposed electrode IV are compared with the corresponding values previously reported for Cr(III) selective electrodes based on various modifiers [17-24]. It is clear from this table that in many cases, the performances of the proposed electrode (electrode IV) showed good behavior if compared with the previously reported Cr(III) sensors.

CONCLUSION

The modified carbon paste electrode incorporating poly-3-(dodecylthio)-N-hexadecylacrylamide (iphI) ionophore as electroactive phase can be used in the development of chromium ion-selective electrodes. The electrode having the composition of 50.0% graphite, 45.0% TCP and 5.0% iphI ionophore (electrode IV) responds to Cr(III) ions in a Nernstian behaviour with slope of 19.59±0.45 mV $decade^{-1}$ and low detection limit of 4.8×10^{-7} mol L^{-1}. The electrode IV was characterized by a rapid response, responsive potential stability and reasonable long-term stability. Most of metal ions do not affect the selectivity of the chromium electrode. Table 6 showed the comparison study between the performance characteristics of the proposed sensor (electrode IV) with those of the previously prepared Cr(III) sensors. From the interference study it is obvious that the proposed sensor has no interference from many ions. Wider working concentration range and lower limit of detection were also offered by the proposed sensor (electrode IV) compared to some of those previously suggested [17-24]. The response time of the present sensor is smaller than many of the reported electrodes [17-24].

Table 6. Comparative study between the Cr(III)-MCPE (electrode IV).characteristics with some of the previously reported Cr(III)-ISEs.

References	Slope (mV $decade^{-1}$)	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode (IV)	19.59	7	2.0 – 8.0	<6	4.8×10^{-7} - 1.0×10^{-2}	4.8×10^{-7}
[17]	19.90	9	2.0 – 7.0	4	1.0×10^{-6} – 1.0×10^{-1}	2.8×10^{-7}
[18]	19.60	10	3.2 - 6.3	2	1.0×10^{-6} –1.0×10^{-1}	5.3×10^{-7}
[19]	20.00	15	4.5 - 6.5	5	4.0×10^{-6} –1.0×10^{-1}	2.0×10^{-7}
[20]	19.7	5	3.5-8.0	> 2	8.0×10^{-6} – 1.0×10^{-1}	7.0×10^{-6}
[21]	19.50	10	3.0 – 5.5	3	1.66×10^{-6} –1.0×10^{-2}	8.0×10^{-7}
[22]	19.88	< 13	3.0 - 10.0	< 3	1.0×10^{-7} – 1.0×10^{-2}	6.3×10^{-7}
[23]	19.00	10	3.5 – 6.5	5	7.0×10^{-6} –1.0×10^{-1}	1.0×10^{-6}
[24]	29.7	10	3.0-5.0	2	7.0×10^{-6} –1.0×10^{-1}	3.1×10^{-7}

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