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ARTICLE



Comprehensive experimental and theoretical investigations on chromium (III) trace detection in biological and environmental samples using polymeric membrane sensor

Saeid Ahmadzadeh^{a,b}, Mehdi Yoosefian^c and Majid Rezayi^{d,e}

^aPharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran; ^bFood, Drug and Cosmetics Safety Research Center, Kerman University of Medical Sciences, Kerman, Iran; ^cDepartment of Chemistry, Graduate University of Advanced Technology, Kerman, Iran;

^dDepartment of Modern Sciences and Technologies, School of Medicine, Mashhad University of Medical Sciences, Mashhad, Iran; ^eStudent research committee, Kerman University of Medical Sciences, Kerman, Iran

ABSTRACT

In the current work, a new highly selective and sensitive sensor based on PVC membrane for accurate trace detection of chromium (III) ions as the environmental contaminant based on 4-Isopropylcalix[4]arene (4-IPC4) was developed. The electrode demonstrated a working range from 1.0×10^{-6} to 1.0×10^{-1} M with 19.45 ± 0.21 mV and 9.0×10^{-7} M of Nernstian slope and detection limit, respectively. The pH of the electrode was independent of the potential response over the range of 3.0 to 5.5. The developed sensor revealed acceptable repeatability for at least three months with fast response time (less than 15 seconds). The impedance changes of the solution/electrode interface were investigated using the EIS technique. The proposed sensor was used successfully for direct detection of Chromium (III) ions in biological and environmental samples and the obtained values validated by AAS and ICP techniques with the recovery values varied from 99.6 to 101.9% for the concentration range of 15.0 to 75.0 ppm. Moreover, the electrode was successfully applied as an indicator electrode for potentiometric titration of Cr^{3+} cation with standard EDTA solution. The characterisation of the proposed sensor and its selective membrane were carried out using FT-IR, UV-Vis, and SEM techniques. The adsorption energy as an important parameter of trapping has been calculated at B3LYP/3-21G (d) level via using the density functional theory (DFT). The strong interactions were resulted by natural bond orbital (NBO) calculations between lone pair of O with lone pair* of chromium (III) ions which revealed that the charge transfer plays important role in the formation of the complex.

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1. Introduction

In recent decades, the growing need of fast and accurate determination of ionic and neutral species in various matrixes such as clinical, industrial, environmental and agricultural samples extremely abetted the chemists to develop the new chemical sensors. Ion selective electrodes (ISEs) received extensive practical applicability as a novel potentiometric sensor

CONTACT Saeid Ahmadzadeh chem_ahmadzadeh@yahoo.com

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due to its ability to recognise the activity of particular ions effecting by various interfering ions [1–6]. It is noteworthy to mentioned that, various electrochemical techniques have been used by the current research group for quantitative determination of various species in environmental, biological and pharmaceutical samples, which among them potentiometric techniques received much more attention due to offering valuable opportunities such as simple preparation, wide linear working range with reasonable sensitivity and selectivity, and rapid detection procedure, portability and economical method [7–13].

Literature surveys revealed that, even though ISEs studies are developed field, still it is subjected to some active research investigations by utilising new membrane materials and synthesising novel ionophores to improve its upper and lower detection limit [14]. Moreover, various theoretical works have been developed to clarify the response mechanism of ISEs and it is still continued to be argued [15]. The two most noticeable theories are the phase boundary model [16] and the ion transport model [17]. Although both of the mentioned models have proved their ability to explain the mechanism of ISEs response, but there are some inconsistent between their assumptions and approximations. Obviously, all the mentioned parameters are highly interdependent to each other. A comprehensive understanding of the response mechanism of ISEs may result in the synthesis of appropriate ionophores that provide a stable complex with high selectivity and efficient binding properties towards the target ion. Consequently, it has also helped to improve the detecting limit of the ISEs.

Chromium is used extensively in industrial fields such as chrome plating, pigment manufacturing, leather tanning, refractory industries, and wood treatment. The high toxicity of chromates has caused serious environmental pollution and severe health hazards. For instance, continuous exposure to concentrated chromic acid produced during the plating process, damage the nasal tissues of the workers. Besides, chromates may also cause skin irritation, kidney injuries and intestinal inflammation. Obviously, there is just a narrow line between essentiality and toxicity of the chromium samples concentration. Chromium as a trace element essential for animals and humans has an important role in carbohydrate and lipid metabolism. Hence, insufficient intakes of chromium can cause diabetes melituria and cardiovascular disease. However, excess intake of chromium also will result in health risk [18].

This is, to the best of our knowledge, the first work of ion elective electrode fabrication based on 4-IPC4. The significance of chromium in the biological and environmental field has prompted the development of a novel method for chromium (III) selective determination. A new selective and sensitive sensor for accurate trace detection of Chromium (III) ions contaminant in the biological samples such as synthetic urine and environmental sample such as industrial electroplating wastewater were developed in the current study.

2. Experimental

2.1. Reagents

Both membrane matrix and ionophore of High molecular weight polyvinyl chloride (PVC) and 4-Isopropylcalix[4]arene (4-IPC4) were supplied from Sigma-Aldrich, respectively. In this work, all reagents were in analytical grade and used directly after vacuum drying over P_2O_5 . All used plasticisers such as 2-nitrophenyl octyl ether (o-NPOE), dioctyl phthalate

(DOP), dibutyl phthalate (DBP) and benzyl acetate (BA) were purchased from Sigma-Aldrich. Sodium tetraphenylborate (NaTPB), potassium tetrakis(4-chlorophenyl)borate (KTPCIPB), tetradodecylammoniumtetrakis(4-chlorophenyl)-borate (TDATpCIPB) and sodium tetrakis [3,5-bis (trifluoromethyl) phenyl] borate (NaTFPB) as lipophilic salts were obtained from Fluka. All nitrate and chloride salts provided by Sigma-Aldrich, Merck, Fisher Scientific, and Fluka. Cationic salts of solutions were prepared in double distilled de-ionised water. Analytical reagent grade of tetrahydrofuran (THF) as a solvent, sodium hydroxide (NaOH), nitric acid (HNO_3) and hydrochloric acid (HCl) from Merck were used for pH adjustments.

2.2. Instruments

The membrane morphology of each fabricated electrode was performed by Jeol scanning electron microscope (Model JSM 6400 SEM). Membrane samples for SEM observation were mounted on the aluminium pin stubs which has been covered with double-sided carbon tape and coated in a vacuum with a gold thin layer using Baltec sputter coater (Model SCD005) for better visibility of the surface and to eliminate the possible interference and charging effect. The images were captured at various magnifications and saved in the computer, which was attached to the SEM machine. Furthermore, Atomic Absorption Spectrometer (Thermo Scientific, model S Series, S_4), Fourier Transform Infrared Spectrophotometer (Perkin-Elmer, model 1725X), Lambda Spectrophotometer (Perkin-Elmer, model 1650PC SHIMADZU) and inductively coupled plasma sequenced with atomic emission spectrometer (ICP-AES) (Perkin-Elmer Emission Spectrometers, model Optima 2000DV) were used. electrochemical impedance spectroscopy investigations carried out by Autolab PGSTAT204-Metrohm potentiostat/galvanostat programmed and controlled by NOVA 1.11 software and equipped with FRA module.

2.3. Membrane preparation and potentiometric measurements

The PVC based membrane was prepared by dissolving 33.0, 5.0, 61.5 and 0.5 mg of PVC, 4-IPC4, o-NPOE and NaTPB, respectively in 3 ml THF-fresh solvent to acquire a homogenous solution. Then, THF was allowed to evaporate at room temperature which was resulted in a viscous oily solution. For preparing the PVC membrane sensor based on the dip coating method, a Pyrex tube (3 mm o.d) was dipped for about 5 seconds into the oily solution and then kept at room temperature overnight to prepare a non-transparent thin membrane layer. The internal solution of 1.0×10^{-3} M $\text{Cr}(\text{NO}_3)_3$ and Ag/AgCl internal reference electrode was placed in the tube. The electrode set was finally soaked for a night in the equal concentration of $\text{Cr}(\text{NO}_3)_3$.

All EMF measurements were performed using presented cell-assembly:

$\text{Ag}/\text{AgCl} | 3\text{M KCl} | \text{salt bridge} | \text{test solution (xM)} | \text{PVC membrane} | 10^{-3}\text{M Cr}(\text{NO}_3)_3 | 3\text{M KCl} | \text{AgCl}/\text{Ag}$.

The potential and pH measurements versus Metrohm Ag/AgCl double junction reference electrodes and Mettler Toledo pH electrode, respectively, were carried out by using a seven multi-Ion Metre (Mettler Toledo, Ion pH/mV/ORP) at room temperature.

3. Results and discussion

3.1. Molecular modelling

In the present section, the adsorption of Cr^{+3} in the 4-IPC4 ligand was theoretically investigated. All the computational data were obtained from the Gaussian 09 program package [19] using B3LYP/3-21G (d) method. Structure and electronic properties of 4-IPC4 during and after the adsorption of Cr^{+3} were studied. The adsorption energy, E_{ads} , is calculated according to expression (1):

$$E_{\text{ads}} = E_{4\text{-IPC4-Cr}^{+3}} - (E_{\text{Cr}^{+3}} + E_{4\text{-IPC4}}) \quad (1)$$

where $E_{4\text{-IPC4-Cr}^{+3}}$ is the total energy of 4-IPC4 with Cr^{+3} and $E_{\text{Cr}^{+3}}$ and $E_{4\text{-IPC4}}$ are the total energy of Cr^{+3} ion and 4-IPC4 ligand respectively. The optimised geometries were verified to be local minima since no imaginary frequencies were found in frequency calculations. Figure 1(a) displays the optimised structures of 4-IPC4 and 4-IPC4- Cr^{+3} . Slight deformation has been occurred due to the Cr^{+3} adsorption. The high value of chemisorptions adsorption energy of complexes (-40.8 eV) especially demonstrates that 4-IPC4 is extremely sensitive to Cr^{+3} .

After the chemical adsorption of Cr^{+3} on the 4-IPC4, the electrical properties of the ligand significantly change. The evaluation of the energetic behaviour of these complexes was carried out through the frontier molecular orbital energy calculations. The green and red colours represented the negative and positive phase respectively. The HOMO-LUMO energy gap is expressed to exist the difference in the lowest unoccupied molecular orbital (LUMO) with the highest occupied molecular orbital (HOMO). The HOMO-LUMO orbitals computed at B3LYP level with 3-21G (d) basis set and generated via Gauss view 5.0. The

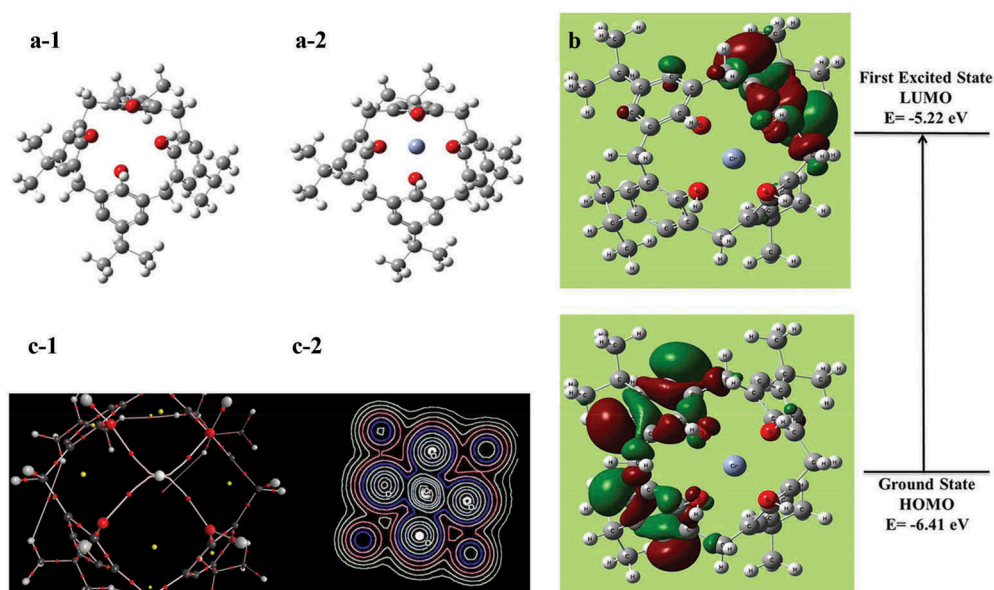


Figure 1. (a) Full optimised geometry of (A-1) 4-IPC4 ligand and (A-2) $[4\text{-Isopropylcalix[4]arene-Cr}]^{+3}$ complex. (b) The HOMO-LUMO iso-surfaces of with the corresponding HOMO-LUMO energy gap. (c) Molecular graph (C-1) and the contour map (C-2) of the $[4\text{-Isopropylcalix[4]arene-Cr}]^{+3}$ complex.

HOMO-LUMO energy value of molecular orbitals including their energy gap is shown in Figure 1(b). According to data presented in Table 1, the HOMO-LUMO gap of 4-IPC4 noticeably decreases after the Cr^{+3} adsorption.

DFT-based reactivity descriptors have been calculated to predict reactivity and stability of the complex according to Koopman's theorem equations [20]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V(r),T} \quad (2)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(r),T} \quad (3)$$

where μ is the chemical potential and η is chemical hardness. Parr introduced the global electrophilicity index using the chemical potential and chemical hardness:

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

Higher energy gap and chemical potential of 4-IPC4 ligand present higher kinetic stability. Electrophilicity, the electron flow between HOMO and LUMO, have been computed for the ligand and the 4-IPC4- Cr^{+3} complex to describe higher global chemical reactivity. The resistance towards the deformation of the electron was signified with higher hardness cloud under small perturbations. The lower bond gap for 4-IPC4- Cr^{+3} complex represents the softer system with higher electrophilicity index. Results are presented in Table 1.

Quantum theory atom in molecule (QTAIM) analysis was performed employing the AIM2000 package to get detailed information about the inter and intramolecular interactions [21]. According to the results listed in the table of the supplementary 1, larger electronic density at Cr^{+3} -O bond critical points with smaller path length could be attributed to a stronger interaction. The sign of Laplacian of electron density has been used to distinguish the closed-shell (non-covalent such as ionic and van der Waals) and open shell (covalent) interactions. The positive values of Laplacian $\nabla^2 \rho(r)$ confirm the domination of kinetic energy and closed shell (non-covalent) interactions between Cr^{+3} and oxygen atoms. Figure 1(c) shows the molecular graph and the contour map of the 4-IPC4- Cr^{+3} complex. Blue lines in the contour map diagram show the isodensity around the Cr^{+3} and oxygen atoms that illustrate the strong interactions.

The electron density delocalisation effects in the 4-IPC4- Cr^{+3} complex over the occupied Lewis-type (donor) NBOs and unoccupied non-Lewis type (acceptor) NBOs have been investigated. The NBO 3.1 program in the Gaussian 09 package at the same level of theory was performed for the natural bond orbital (NBO) calculations [22]. The second order perturbation theory analysis of the Fock matrix in NBO basis for the most important interactions in 4-IPC4- Cr^{+3} complex are listed in Table 2. The interaction between LP(O) as

Table 1. DFT-based reactivity descriptors for the ligand and the 4-IPC4- Cr^{+3} complex.

Complex	E_{HOMO}	E_{LUMO}	E_g	η	μ	ω
4-IPC4	-7.38	0.22	7.6	3.8	-3.58	1.69
4-IPC4- Cr^{3+}	-6.41	-5.22	1.19	0.595	-5.815	28.42

Table 2. The donor-acceptor interactions evaluated from the second order perturbation energies, by the energy threshold equal to 2 kcal/mol.

NBO donor	NBO acceptor	$E^{(2)}$
LP (2)O 25	LP*(4)Cr 85	19.26
LP (2)O 31	LP*(3)Cr 85	18.59
LP (2)O 25	LP*(3)Cr 85	18.08
LP (2)O 27	LP*(3)Cr 85	17.4
LP (2)O 31	LP*(5)Cr 85	15.01
LP (2)O 29	LP*(3)Cr 85	14.78
LP (2)O 27	LP*(5)Cr 85	12.15
LP (2)O 29	LP*(6)Cr 85	10.33
LP (2)O 29	LP*(4)Cr 85	7.74
LP (2)O 27	LP*(6)Cr 85	5.86
σ O 31–H 32	LP*(5)Cr 85	3.44
σ O 27–H 28	LP*(5)Cr 85	3.27
σ O 29–H 30	LP*(4)Cr 85	3.08
σ C 4–O 27	LP*(5)Cr 85	2.93
σ C 22–O 31	LP*(5)Cr 85	2.61
σ C 18–O 29	LP*(4)Cr 85	2.42
σ C 11–O 25	LP*(4)Cr 85	2.38
σ O 25–H 26	LP*(4)Cr 85	2.60
LP (2)O 31	LP*(6)Cr 85	2.11
LP (1)O 31	LP*(4)Cr 85	2.10

an effective donor and the LP*(Cr³⁺) as acceptor have strongest stabilisation energy by means of higher second-order perturbation interaction energies $E^{(2)}$.

3.2. Response characteristics of the electrode

In the preliminary experiments, the potential fabricated PVC sensor responses over a wide concentration range of 1.0×10^{-6} M to 1.0×10^{-1} M for variety of metal ions (heavy, transition, alkali and alkaline earth metal ions) were investigated (see Figure 2(a)).

In accordance with the literature surveys, it was found that both selectivity and sensitivity parameters in the current work significantly affected by the polymeric membrane composition which is the signal generated source of the Cr³⁺- selective electrode. Since, the amount and nature of ionophore, plasticiser and lipophilic additive have a considerable influence on the characteristics performance of the fabricated electrodes, comprehensive studies have been carried out to optimise the membrane composition to generate reproducible noiseless and stable potentials and the obtained results were summarised in the table of the supplementary 2.

As it is shown in Figure 2(b), the nature of plasticisers significantly affected the selectivity and measuring the range of Cr³⁺- selective electrode. It is known that the presence of o-NPOE as a polar plasticiser in a non-polar membrane improves the membrane's dielectric constant and consequently prevents the formation of ion pair between complexed Cr³⁺ cations and lipophilic counter ions within a PVC membrane [23]. Moreover, plasticisers play an important role to improve the membrane physical properties by reducing the high glass transition temperature of PVC, as well as increasing the mobility of the active species and enhancing the flexibility of the polymer chain. It is known that the addition of a proper lipophilic additive to membrane demonstrates a significant improvement in the characteristic performance of an ion selective electrode

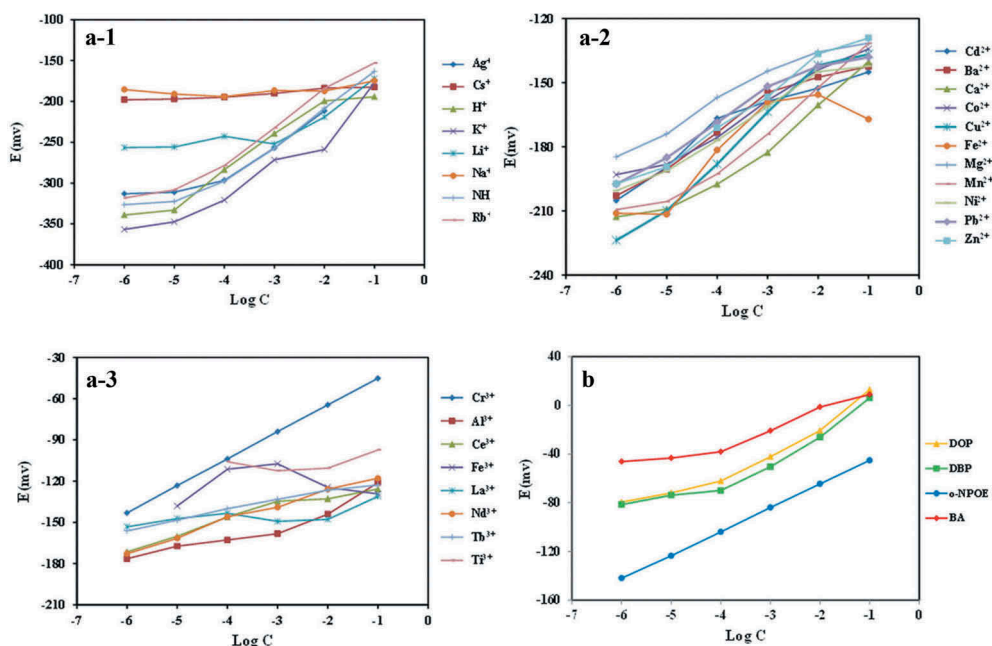


Figure 2. (a) The potential responses of PVC membrane sensor based on 4-IPC4 towards (A-1) monovalent, (A-2) bivalent and (A-3) trivalent cations. (b) Effect of different plasticisers in membrane composition, on the potential responses of Cr^{3+} -selective electrode at 25°C.

such as selectivity, stability and response time. Besides, it reduces the membrane impedance. It can be concluded from the table of the supplementary 2, even though the presence of NaTPB as an ion exchanger in the membrane provides beneficial effects, but the excess amount of it declines the electrode performance [24].

Further to improve the response characteristics of the fabricated Cr^{3+} -ISE, the concentration effect of internal solution from 1.0×10^{-3} M to 1.0×10^{-1} M of $\text{Cr}(\text{NO}_3)_3$ was investigated. The internal solution with optimum concentration of 1.0×10^{-3} M was found to have the best performance in different terms such as of Nernstian slope, response time and dynamic concentration range of the proposed ISE, hence, this concentration was used for further studies.

3.3. Characterisation of the polymeric membrane

3.3.1. Qualitative UV-Vis spectroscopic studies

Qualitative UV-Vis spectroscopic studies were conducted to investigate the preferential response of the membrane based on 4-IPC4 towards Cr^{3+} cation which is believed that associated with the coordination bonds between donor atoms and aromatic rings of 4-IPC4 with the target cation. The UV spectra absorption of the 4-IPC4, Cr^{3+} cation and their mixture with the ration of 1:1 was recorded over the wavelength range of 250–400 nm. As it is illustrated in Figure 3(a), chromium (III) shows significant absorption maximum at 262 nm and 4-IPC4 displays distinct absorption maximum at 282 nm, however, it was found that in the case of their mixture, a noticeable shift for both

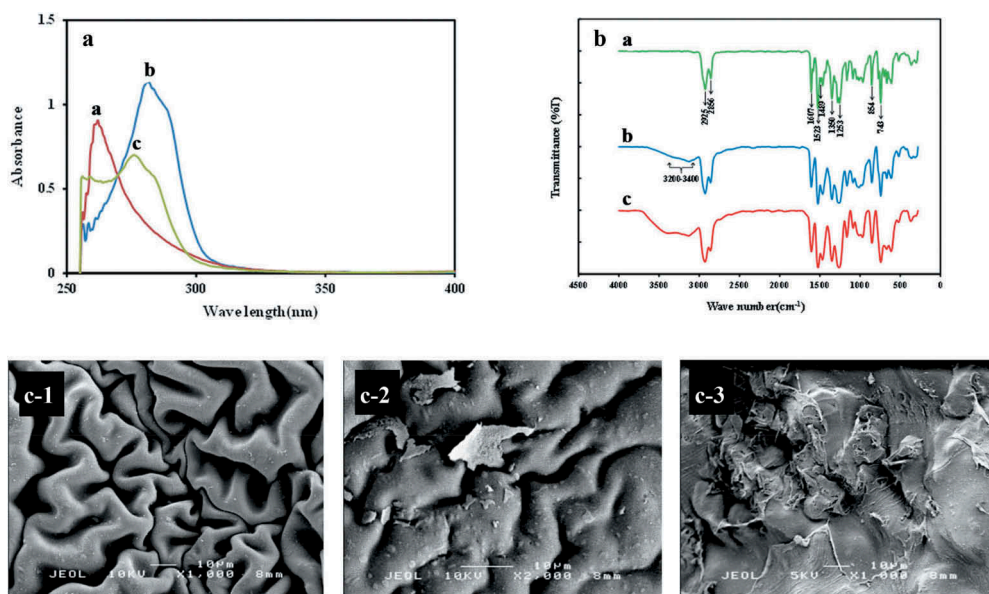


Figure 3. (a) UV-Vis absorption spectra of (a) 1.0×10^{-3} M Cr^{3+} , (b) 1.0×10^{-4} M 4-IPC4 and (c) mixture of ionophore and cation. (b) Comparison of FT-IR spectra for membrane ingredients under different conditions: (a) blank membrane without 4-IPC4 as an ionophore, (b) fabricated membrane with ionophore and (b) used membrane after 3 months. C: Scanning electron microphotographs (SEM) of Cr^{3+} -selective PVC membrane including (C-1) membrane that conditioned and used daily over one month, (C-2) membrane that conditioned and used daily over three months and (C-3) membrane morphology which was spoilt after six months.

absorption spectra was observed to 279 and 257 nm with decrease in their intensity that confirmed the selective interaction between 4-IPC4 and Cr^{3+} cations. It noteworthy to mention that several studies by the current research group have been carried out based on a conductometric method to investigate the complex reaction of macrocyclic ligands with metal cations including complex formation process between 4-IPC4 and Cr^{3+} cation [25].

3.3.2. Qualitative FT-IR spectroscopic studies

Due to the prediction leaching of membrane components during long-term usage of ISE, qualitative studies were carried out by analysing the fabricated membrane using FT-IR technique. The FT-IR spectra for blank membrane (no ionophore), optimised fresh membrane and after 3 months used membrane have been shown in Figure 3(b). The presence of 4-IPC4 in the membrane composition was confirmed with the characteristic absorption band observed in the range from 3200 to 3400 cm^{-1} associated with O-H stretching compared to the spectrum of the membrane without ionophore. Noticeably, reducing the o-NPOE amount in the membrane is results to the observed absorption bands in the regions of 1489 cm^{-1} and 1350 cm^{-1} due to NO_2 stretching, 740 to 743 cm^{-1} assigned to C-H out of plane bending and 2859 – 2856 cm^{-1} region associated to C-H sp^3 stretching. Moreover, the absorption band appears at 2925 cm^{-1} related to $=\text{C-H sp}^2$ stretching indicated the existence of lipophilic additive, NaTPB in the prepared membrane. As it is

obvious from Figure 3(b), there were no significant changes observed after daily usage of the electrode over a period of three months which confirmed the stability and long lifetime for the fabricated polymeric membranes. It is noteworthy to mention that, a slight variation on the characteristic performance of the proposed electrode was observed due to the slight leaching of membrane ingredients into the test solutions during daily usage.

3.3.3. Surface analysis of the fabricated membrane

In order to investigate the surface morphology of the fabricated membranes such as fouling, swelling and spoiling, scanning electron microscopy (SEM) technique were used [26]. As it can be seen from Figure 3(c), the membrane that conditioned and used daily over one month exhibited a smooth morphology without any surface fouling, whereas the membrane that used daily over three months illustrated some precipitates on its surface which affects the potential response and selectivity of the proposed electrode towards Cr^{3+} ions. However, the proposed membrane after six months demonstrated a much rougher surface with some pores, indicating that the membrane was spoilt completely. It is noteworthy to mention that, the acquired results are in satisfactory agreement with the characteristic performance of the proposed electrode in the current work.

3.4. Characterisation of the developed Cr^{3+} -selective electrode

The electrode exhibited a noticeable selectivity towards Cr^{3+} ion with the best Nernstian slope of 19.45 ± 0.21 (mV per decade of activity; with the correlation coefficient of 0.99). The obtained results revealed that Cr^{3+} ions could be rightfully determined with the optimised PVC membrane ISE based on 4-IPC4. It could be attributed to the high and selective affinity of the 4-IPC4 towards Cr^{3+} ion between chromium (III) cation and oxygen donor atoms through coordination bonds as well as its π -coordination with the aromatic rings [27]. Therefore, 4-IPC4 was employed as a new carrier (ionophore) in the fabrication of Cr^{3+} -selective electrode. As it is demonstrated in Figure 4(a), the value limit of detection (LOD) of the fabricated ISE as 9.0×10^{-7} M was obtained when the linear regions of the calibration curve extrapolated to the baseline potential.

The dynamic response time of the fabricated electrode investigated by the IUPAC recommendation [28]. Herein, the practical response time of the sensor evaluated by changing the Cr^{3+} concentration from 1.0×10^{-6} to 1.0×10^{-1} M. The potential response of the electrode versus the time demonstrated in Figure 4(b). As seen, in whole concentrations (low-to-high), the sensor reached equilibrium in less than 15 s. To evaluate the reversibility of the sensor, a similar procedure by versus direction adopted. The response time of the proposed electrode evaluated by changing the sequence concentrations from the high-to-low of Cr^{3+} ions. As seen from Figure 4(b), the equilibrium time was less than 15 seconds which was probably attributed to the fast exchange kinetics of complexation-decomplexation of Cr^{3+} ions at the interface of the fabricated polymeric membrane and the examined solution.

The stability and lifetime of the fabricated Cr^{3+} -selective electrode were examined by performing quantitative and qualitative studies. Quantitative studies were carried out over a period of 15 weeks by measuring the potential responses of four electrodes. The

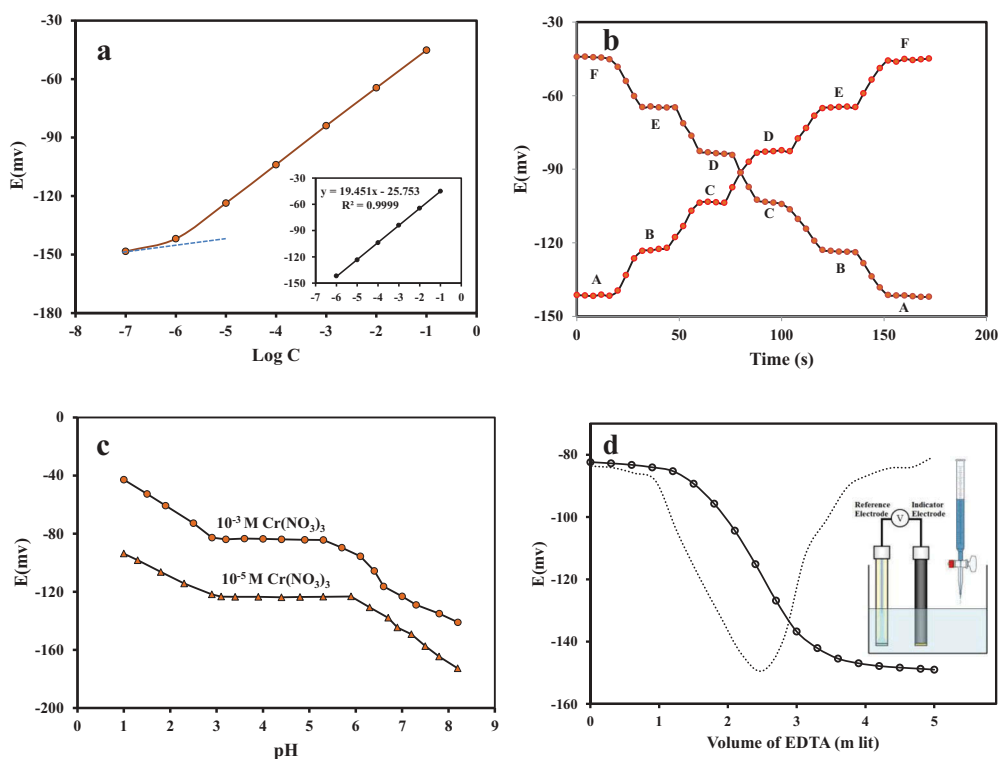


Figure 4. (a) Calibration plot of the Cr^{3+} -ion selective electrode. (b) The dynamic response time of the Cr^{3+} selective electrode for step changes in the concentration of chromium (III) solution: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M and (F) 1.0×10^{-1} M at 25°C . (c) pH effect of the sample solutions on the potential response of the proposed electrode. (d) Potentiometric titration curve of chromium (III) ion (1.0×10^{-3} M, 25 mL) with standard EDTA solution (1.0×10^{-2} M) using proposed electrode as an indicator electrode.

electrodes were employed for an hour each day and then, stored in 1.0×10^{-3} M $\text{Cr}(\text{NO}_3)_3$ solution to enhance their lifetime when they were not in use. The obtained results revealed that the proposed ISEs could be used without observing any significant drift in the Nernstian slope and detection limit over a period of 12 weeks. During the mentioned period of time, the fabricated electrodes revealed slight deviation in slope from 19.45 ± 0.21 mV per decade of activity to 18.50 ± 0.56 mV per decade of activity, and the detection limit changed from 9.0×10^{-7} M to 2.0×10^{-6} M which is probably owing to the membrane composition leaching into the solution. According to the obtained results, the proposed electrode revealed reasonable lifetime with satisfactory accuracy that nominated it as a practical sensor for monitoring the chromium (III) contaminant in various fields such as biological, industrial and environmental analysis over a period of 3 months without observing any divergence in potentiometric response.

The repeatability and reproducibility of the fabricated Cr^{3+} -ISE were investigated over a wide concentration range of 1.0×10^{-6} M to 1.0×10^{-1} M of Cr^{3+} cation standard solutions. Repeatability studies were conducted by using a single ISE for five times, while, reproducibility studies were done via applying five different ISEs, where each

electrode was used only once. The averages of Nernstian slopes were calculated as 19.45 ± 0.21 and 19.37 ± 0.25 mV per decade of activity, respectively. The relative standard deviations were obtained 1.08% and 1.29%, respectively, which consider as acceptable values for both studies. The observed discrepancy between electrodes responses could be probably attributed to the different morphology and thickness of the membranes at different sites, which resulted in variation in extraction equilibrium of Cr^{3+} ions at the proximity of the interface between the selective polymeric membrane and aqueous layer [18].

The influence of the pH on the characteristic performance of the proposed Cr^{3+} -selective electrode was studied over a wide pH range from 1.0 to 9.0 at concentrations of 1.0×10^{-3} M and 1.0×10^{-5} M $\text{Cr}(\text{NO}_3)_3$ solution. The pH was adjusted by adding small volumes of dilute nitric acid and sodium hydroxide solutions. As it can be seen from Figure 4(c), the potential response of the proposed electrode was stable over the pH range of 3.0–5.5 for both concentrations of $\text{Cr}(\text{NO}_3)_3$ solution which implied that the fabricated sensor could be applied for quantitative determination of chromium contaminant in various environmental and biological samples without pH adjustment. The observed drift in potential response at lower pH could be attributed to the simultaneous response of the proposed electrode to accessible positively charged of H_3O^+ and Cr^{3+} ions in the solution. On the other hand, at higher pH, the observed diminish in potential response could be ascribed to some Cr^{3+} hydroxide complexes formation in the solution.

3.5. Electrochemical impedance spectroscopic studies

In addition, the impedance changes of the solution/electrode interface were investigated by using the electrochemical impedance spectroscopy (EIS). Figure 5(a) shows the Nyquist plots of (a) optimised membrane without additive and ionophore, (b) optimised membrane without ionophore (electrode No. 1 in supplementary 2) and (c) optimised membrane (electrode No. 4 in supplementary 2) in the 1:1 mixture of potassium chloride (0.1 M) and $\text{Fe}[(\text{CN})_6]^{3-/4-}$ solution (0.1 mM). The potentiostat/galvanostat with a saturated calomel reference electrode (SCE) and platinum counter electrode was applied for EIS recording in the frequency range of 100 kHz to 0.1 Hz at open circuit potential (ocp) with an AC amplitude of 5 mV.

The impedance spectra for the membrane without additive and ionophore and blank membrane (no ionophore) recorded showed a charge-transfer which was obtained by fitting the equivalent circuit procedure presented at Figure 5(b). The electron transfer resistance (R_{ct}) can be evaluated by using the diameter of the semicircle. It is obvious that the R_{ct} can be significantly reduced due to the presence of NaTFB additive. Moreover, the enhancement in charge transfer resistance was observed due to the absence of the 4-IPC4 ionophore in the membrane which leads to a tight structure of PVC membrane. The observed EIS results prove that the exits of the 4-IPC4 ionophore in the membrane composition decrease the charge transfer resistance followed by an electrical conductivity enhancement. The Nyquist plots were applied for comparing the semicircle diameters of the modified

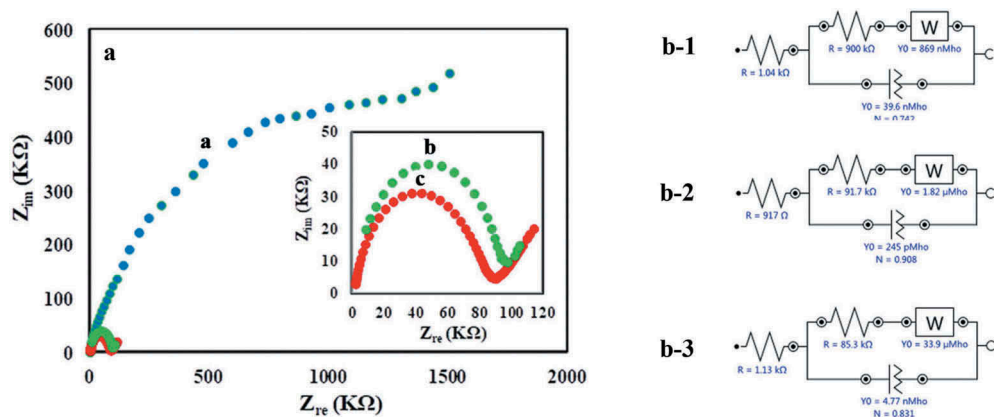


Figure 5. (a) Nyquist diagrams of (a) optimised membrane without additive and ionophore, (b) optimised membrane without ionophore and (c) optimised membrane in 0.1 M KCl solution containing 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ (1:1). (b) Equivalent circuit models and EIS obtained parameters for (B-1) optimised membrane without additive and ionophore, (B-2) optimised membrane without ionophore and (B-3) optimised membrane in 0.1 M KCl solution containing 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ (1:1).

ISEs by following the direction of R_{ct} : (R_{ct1}): PVC membrane (nil ionophore and additive) > PVC membrane (nil ionophore) > Optimised PVC membrane.

3.6. Selectivity coefficient

In accordance with the assumption of IUPAC technical report, the potential response of the proposed electrode for the same concentration of 1.0×10^{-1} M for both target and interfering ions were measured separately to determine the selectivity coefficient (K_{ij}^{Pot}) of the sensor based on separate solution method (SSM). Equation (5) was used to calculate the selectivity coefficients of the proposed electrode in the current work.

$$\log K_{ij}^{Pot} = \frac{E_j - E_i}{2.303 RT/z_i F} + \left(1 - \frac{z_i}{z_j}\right) \log(a) \quad (5)$$

As it is obvious from Table 3, the proposed electrode based on 4-IPC4 was highly selective and sensitive towards Cr^{3+} ions with respect to other common interfering cations and the typical selectivity pattern for the series of examined interfering cations based on 4-IPC4 is as follows:

$\text{Cr}^{3+} > \text{Rb}^+ > \text{Nd}^{3+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Mg}^{2+} \approx \text{Mn}^{2+} > \text{Co}^{2+} > \text{Ce}^{3+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Fe}^{3+} > \text{Ca}^{2+} > \text{La}^{3+} > \text{Ni}^{2+} > \text{Li}^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Cd}^{2+} > \text{K}^+ > \text{Cs}^+$.

The values of the calculated selectivity coefficients revealed that the developed electrode in the current work demonstrated considerable improvement in the term of selectivity behaviour compared to the previously reported Cr^{3+} -selective electrodes (see supplementary 3) [29–32].

Table 3. Determination of chromium (III) ion concentration in biological and industrial wastewater samples using AAS, ICP and developed Cr^{3+} -selective electrode.

Real Sample	Concentration of Cr ³⁺ ions (ppm)			Recovery (%)
	ISE method*	AAS method*	ICP method*	
Biological samples				
Amount added (ppm)				
15.00	15.23 ± 0.34	15.35 ± 0.21	15.31 ± 0.28	101.5
30.00	29.89 ± 0.23	29.71 ± 0.29	29.65 ± 0.31	99.6
45.00	45.24 ± 0.27	45.13 ± 0.24	45.08 ± 0.33	100.5
60.00	59.82 ± 0.20	59.65 ± 0.26	59.61 ± 0.27	99.7
75.00	76.41 ± 0.37	76.30 ± 0.32	76.26 ± 0.24	101.9
Industrial waste water				
Sample No.				
1	7.53 ± 0.28	7.41 ± 0.17	7.39 ± 0.24	101.9
2	9.35 ± 0.17	9.30 ± 0.15	9.26 ± 0.19	101.0
3	12.71 ± 0.38	12.36 ± 0.21	12.59 ± 0.36	100.9
4	5.19 ± 0.24	5.11 ± 0.16	5.13 ± 0.19	101.2

* Average and standard deviation for triplet measurements.

3.7. Analytical application and accuracy validation

The practical ability of the developed sensor was validated by direct quantitative determination of chromium (III) in several biological and environmental samples. The extraordinary sensitivity of the proposed sensor enabled us to determine the concentration of chromium (III) into synthetic urine samples using the standard addition method. Spiked samples were prepared and the potential of the solutions was measured by the proposed sensor. The obtained results compared with the data acquired from AAS and ICP and summarised in Table 4. The calculated recoveries for the spiked samples varied from 99.6 to 101.9% for the concentration range of 15.0 to 75.0 ppm.

Table 4. Selectivity coefficient of the developed Cr^{3+} -selective electrode based on Separate Solution Method (SSM) at 25°C.

Examined Cation	$\text{Log}K_{\text{Cr},M}^{\text{Pot}}$	$K_{\text{Cr},M}^{\text{Pot}}$
Cs^+	-4.54	2.88×10^{-5}
K^+	-4.29	5.12×10^{-5}
Na^+	-4.13	7.41×10^{-5}
Li^+	-4.03	9.33×10^{-5}
Rb^+	-3.07	8.51×10^{-4}
Zn^{2+}	-3.35	4.47×10^{-4}
Ni^{2+}	-4.01	9.77×10^{-5}
Ba^{2+}	-4.06	8.71×10^{-5}
Cd^{2+}	-4.16	6.92×10^{-5}
Co^{2+}	-3.61	2.45×10^{-4}
Cu^{2+}	-3.71	1.95×10^{-4}
Mn^{2+}	-3.51	3.09×10^{-4}
Pb^{2+}	-3.81	1.55×10^{-4}
Mg^{2+}	-3.51	3.09×10^{-4}
Ca^{2+}	-3.91	1.23×10^{-4}
La^{3+}	-3.95	1.12×10^{-3}
Ce^{3+}	-3.64	2.29×10^{-4}
Al^{3+}	-3.44	3.63×10^{-4}
Nd^{3+}	-3.30	5.01×10^{-4}
Fe^{3+}	-3.85	1.41×10^{-4}

On the other hand, five wastewater samples of electroplating industries were filtered to remove any turbidity or suspended matter and diluted using buffer acetic acid/sodium acetate ($\text{pH} = 4.5$) in a 50 mL volumetric flask. The proposed sensor was applied and the obtained results are presented in Table 4. As it is obvious the obtained values are in satisfactory agreement with those obtained from certified instrumental methods. It can be concluded that the developed Cr^{3+} -selective electrode in the current work was a promising approach for successful determination of chromium (III) trace amount in biological and environmental samples.

Moreover, Cr^{3+} -selective electrode was evaluated as an indicator electrode for potentiometric titration of 25 ml of 1.0×10^{-3} M Cr^{3+} cation with 1.0×10^{-2} M of standard EDTA solution. As it is demonstrated in Figure 4(d), the endpoint of the plot corresponds to 1:1 stoichiometry of EDTA- Cr^{3+} complex. Increasing the EDTA solution during the process resulted in a decrement in the potential owing to reducing the metal ion concentration. The standard sigmoidal shape of the titration plot indicates that the amount of chromium (III) cation could be accurately determined by the proposed sensor.

4. Conclusion

The fabricated potentiometric sensor based on the 4-IPC4 ionophore exhibited a good selectivity towards chromium (III) as the environmental contaminant including low interference from considerable concentrations of common monovalent, bivalent and trivalent cations. The optimised ISE showed a very short statistic response time of less than 15 seconds and its potential response was independent of pH levels in the range of 3–5.5. The fabricated chromium (III) sensor revealed a Nernstian slope of 19.45 ± 0.21 mV per decade of activity, a low detection limit of 9.0×10^{-7} M and a wide concentration range from 1×10^{-6} to 1×10^{-1} M. The proposed sensor validated by ICP and AAS techniques and the obtained results demonstrated satisfactory accuracy of the sensor for determining chromium (III) in biological and environmental samples. Results from the theoretical calculations demonstrate that the 4-IPC4 ligand could effectively determine the trace of Chromium (III) with respect to the high value of chemisorptions adsorption energy (40 eV) and confirmed the preferred coordination of Chromium (III) ions by 4-IPC4.

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Disclosure statement

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Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects

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