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Fabrication and Comparison of Three Chromium(III) Selective Electrodes Prepared using N-(Imidazol-2-ylcarbamothioyl) Benzamide

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Abstract- In the present work, N-(imidazol-2-ylcarbamothioyl)benzamide was developed and employed as an ionophore for preparing three kinds of membrane chromium(III) selective electrode including electrode with liquid internal electrolyte (LIE), solid-state electrode (SSE) and coated wire electrode (CWE). Optimal membrane composition was determined to be 2% sodium tetraphenylborate, 58% dibutyl phthalate, 10% ionophore, and 30% polyvinyl chloride, resulting in Nernstian slope behavior. Linear concentration range was 1×10^{-3}-7×10^{-6} mol L^{-1}, 1×10^{-3}-3×10^{-7} mol L^{-1}, and 7×10^{-3}-3×10^{-9} mol L^{-1} of chromium(III) with Nernstian slope 20.76, 21.79 and 19.05 mV/decade for LIE, CWE and SSE, respectively. An improvement was note in detection limit for SSE (3×10^{-9} M) and CWE (2×10^{-7} M) in comparison with LIE (7×10^{-6} M). Response times were approximately 5 seconds for LIE and CWE, and 4-6 seconds for SSE. The applicable pH range for the electrodes was 3.0-5.0. SSE and CWE demonstrated longer lifetimes of about 13 and 12 weeks, respectively, compared to LIE (11 weeks). These electrodes were utilized as indicator electrodes in the chromium(III) potentiometric titration with ethylenediaminetetraacetic acid.

Keywords- Chromium determination; Coated wire; Liquid membrane; Potentiometry; Solid-state electrode

1. INTRODUCTION

The precise measurement of chromium(III) is crucial due to its significance in numerous biological systems and industrial samples. Chromium(III) serves as an essential nutrient for humans, playing a role in glucose metabolism and lipid regulation, particularly cholesterol [1]. However, excessive intake of chromium(III) can lead to adverse health effects, such as skin rashes, and in vitro studies have indicated potential DNA damage from high cellular concentrations of chromium(III) [1]. Various analytical approaches, including X-ray fluorescence, spectrophotometry, atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, voltammetry [2–8], as well as potentiometric methods employing ion-selective electrodes [9,10,11–20], have been developed for detecting chromium. Despite their sensitivity, these methods often involve costly and laborious sample preparation procedures. Potentiometric measurements using ion-selective electrodes offer several advantages, including easy sampling conditions, equipment simplicity, cost-effectiveness, relatively low detection limits, and wide linear concentration ranges [10,21]. Potentiometric membrane electrodes are particularly suitable for chromium(III) analysis. Depending on the method of membrane immobilization, various types of ion-selective electrodes can be created, like solid-state electrodes (SSE), coated wire electrodes (CWE), and electrodes with liquid internal electrolytes (LIE). LIE requires a filling solution and an internal reference electrode, whereas CWE, without the need for a solution and an internal reference electrode exhibits lower detection limits and higher mechanical stability than LIE. However, water penetration through the sensitive membrane in CWE can lead to unstable metal ion concentrations, causing potential instability [22]. SSE, utilizing a graphite-epoxy resin mixture, offers improved sensing membrane adherence to a solid surface.

This study aims to develop new membrane electrodes for the rapid, selective, and precise potentiometric evaluation of chromium(III). The selection of the sensing constituent is critical to construct electrode membrane. Various inorganic and organic substances, including rhodamine-B chromate [9], nano-chitosan [10], oxalic acid bis (cyclohexylidene hydrazide) [18], 4-dimethylaminoazo-benzene [19], and 4-(5-bromothiophen-2-carboxylidene amino)-3-methyl-5-mercapto-s-triazole [20], have been suggested as sensing agents for chromium(III) selective electrodes, each with its advantages and limitations. However, many existing potentiometric electrodes suffer from drawbacks such as elevated detection limit, extended response durations, cationic interference, and abbreviated longevity. Therefore, this work focuses on synthesizing N-(imidazol-2-ylcarbamothioyl)benzamide as a novel sensing substance in the liquid membrane of three chromium(III) selective electrode types: LIE, CWE, and SSE. Multi-walled carbon nanotubes are employed in SSE preparation to enhance electrode performance. They are used as electron-ion exchanger of electrodes because of acceptable hydrophobicity and conductivity [22]. After evaluating various liquid membrane compositions, the optimal composition is determined. A comprehensive comparison is conducted on detection

limits, Nernstian slopes, dynamic response time, lifespan, pH dependence, and selectivity of the electrodes in chromium(III) concentration measurement. To the best of our knowledge, this study represents the first synthesis of N-(imidazol-2-ylcarbamothioyl)benzamide, and these novel membrane electrodes serve as the first to utilize this ionophore.

2. EXPERIMENTAL SECTION

2.1. Reagents and materials

Acetonitrile, 1H-imidazol-2-amine, potassium thiocyanate, and benzoyl chloride were prepared by Sigma-Aldrich. Nitrobenzene (NB), dibutyl phthalate (DBP), reagent-grade sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), high relative molecular weight polyvinyl chloride (PVC), and benzyl acetate (BA) were obtained from Merck Co. and these materials were employed as the way they were prepared. Multiwalled carbon nanotubes were purchased from Sigma-Aldrich. Graphite powder (particle size< 20 μm) was obtained from Fluka. Hardener (desmodur RFE) and epoxy were prepared by Bayer and Henkel (Germany). The cations' nitrate salts, obtained from Merck and Sigma-Aldrich, were of the maximum purity. Deionized double-distilled water was utilized consistently throughout the tests. Iodine vapor served as the detection method in thin-layer chromatography (TLC).

2.2. Apparatus

FT-IR spectra were acquired using a Bruker Tensor 27 with KBr disks. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using an Ultra shield Bruker 400 tool with $CDCl_3$ as the deuterated solvent. Melting point determination was carried out using a Bransetead Electro Thermal B1 gadget. Potential tests were done by a multi-meter equipped with a volt-meter with a precision of ±0.1 mV (Japan) at a temperature of 25.0 (±0.1) °C. Ag/AgCl reference electrodes (Azar-Electrode, Iran) were employed as the external reference electrode, while internal reference electrodes with liquid membrane were employed. The electrochemical cells are as follows:

LIE: Ag-AgCl ‖ internal solution, 0.01 M chromium(III) | PVC membrane | sample solution ‖ Ag-AgCl, saturated KCl

CWE or SSE: SS or CW membrane | sample solution ‖ Ag-AgCl, saturated KCl

The SSE and CWE did not contain an internal solution. Calibration curves were generated using standard solutions, and the Debye-Hückel method was utilized to ascertain the activity values.

2.3. Ionophore synthesis

Acetonitrile was used to reflux potassium thiocyanate and benzoyl chloride. The resulting reaction mix was stirred for 30 min at ambient temperature. Following separation and filtration, a mix of benzoyl isothiocyanate (2 mmol) and 1H-imidazol-2-amine (2 mmol) was refluxed for 12 h at 60 °C in acetonitrile solvent (10 mL) (Figure 1). The reaction's conclusion was verified through thin-layer chromatography (TLC). Following the reaction's completion, the solvent was vaporized under decreased pressure. The crude yellowish product (N-(imidazol-2-ylcarbamothioyl)benzamide) underwent purification via crystallization from a mixture of n-hexane and ethyl acetate. This purified product was subsequently incorporated into an electrochemical membrane composite. The ligand's structure was confirmed through measurements of melting point and ^{1}H-NMR, FT-IR, and ^{13}C-NMR spectroscopy.

N-(imidazol-2-ylcarbamothioyl)benzamide: Pale yellow crystals, m.p. 140-141°C; yield: 90%. IR (KBr): 3367, 3170, 1660, 1622, 1575, 1401, 1254, 1120, 792, 770 cm-1. 1H NMR (300 MHz, CDCl3): δ = 7.26 (2 H, s, 2 CHim), 7.46 (2 H, t, 3J = 7.2, 2 CH), 7.55 (1 H, t, 3J = 7.2, CH), 7.83 (2 H, d, 3J = 7.2, 2 CH), 8.90 (1 H, s, NH), 11.13 (1 H, s, NH) ppm. 13C NMR (300 MHz, CDCl3): δ 127.2 (2 CHim), 128.4 (2 CH), 131.9 (2 CH), 132.3 (CH), 133.5 (C), 158.0 (C), 169.5 (C=O), 177.3 (C=S) ppm. Anal. Calcd for C11H9N4OS (263.3): C, 53.87; H, 3.30; N, 22.84; S, 13.07. Found: C, 53.96; H, 3.45; N, 23.02; S, 12.87.
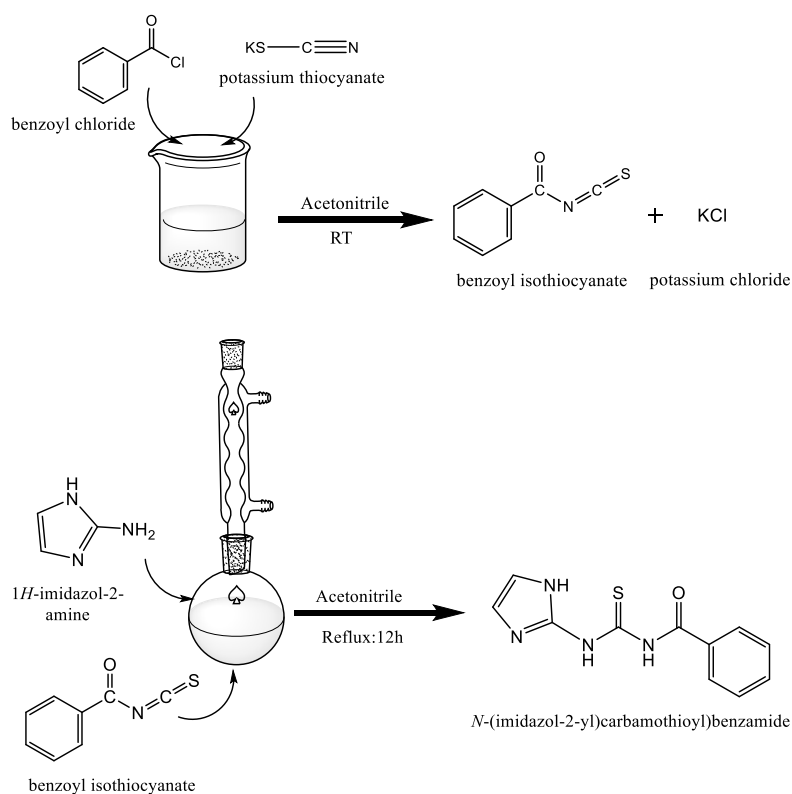

Figure 1. N-(imidazol-2-ylcarbamothioyl)benzamide synthesis

2.4. Electrode Preparation

LIE- Different formulations of PVC membranes were created by dissolving varying proportions of plasticizer, ionophore, PVC, and ionic additive in THF (refer to Table 1). The THF solvent was gradually removed to yield a concentrated viscous solution. Plastic tubes with outer diameters ranging about 3 to 5 mm were individually immersed in these mixtures for about 5 seconds to generate transparent membranes with an approximate thickness of 0.3 mm. These membranes were then allowed to air-dry for approximately 24 hours. Subsequently, an internal filling solution containing 0.01 M $Cr(NO_3)_3$ was instilled in the samplers. After a 24-hour hydration period, the membrane electrode was conditioned by immersing it in a 1.0 mM $Cr(NO_3)_3$ solution. The response characteristics of each membrane-based ion-selective electrode were assessed separately for chromium(III).

CWE- A viscous solution containing the optimal membrane components (10% ionophore, 2% NaTPB, 30% PVC, and 58% DBP) was developed for coating the wire electrode. On the end surface, a transparent membrane was created by immersing a copper wire (length: 10 cm, diameter: 0.5 mm) into the mix three times. Subsequently, the electrode was allowed to dry for at least 12 hours at room temperature. Afterward, it was immersed for 24 h in a solution of 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$.

SSE- The SSE was assembled in three sections: Part A consisted of an exposed copper wire, Part B was comprised of a conductive composite, and Part C involved a PVC membrane. To prepare the conductive composite, epoxy resin (35%), powdered graphite (47%), hardener (15%), and carbon nanotubes (3%) were combined in tetrahydrofuran (THF). After thorough mixing, the solution was allowed to settle for 20-30 minutes, during which the graphite became bound with the hardener and epoxy resin mix. The exposed copper wire was then immersed into the composite approximately 10 times to ensure complete coverage, followed by drying for 12 hours. The inclusion of carbon nanotubes in the conductive solid-state composition enhanced the performance of the transducer. Subsequently, the solid-state contact material was dipped into Part C, which comprised a liquid membrane cocktail containing 10% ionophore, 2% NaTPB, 30% PVC, and 58% DBP, three times, and left to dry for 12 hours in the air. Notably, the sensor did not contain an internal solution. Lastly, it was plunged for 24 h in a 1.0 mM $Cr(NO_3)_3$ solution.

3. RESULTS AND DISCUSSION

The constitution of polymer membrane serving as the sensing component and the transducer responsible for converting the chemical signal into an electrical one are pivotal factors influencing the potentiometric membrane electrodes' responsiveness. Therefore, in this study, three types of liquid membrane ion-selective electrodes were prepared, and after optimizing the membrane composition, the impact of different transducers was investigated.

3.1. Membrane composition optimization

The ionophore quantity is a crucial factor in composition of membrane, significantly influencing the sensor's potential response. Therefore, several LIEs were prepared using different amounts of N-(imidazol-2-ylcarbamothioyl)benzamide to evaluate their response characteristics (Table 1). Analysis of Table 1 reveals that when the membrane lacks ionophore (no. 1 and 2), the response is negligible. Furthermore, even with the addition of an additive, the absence of the ligand prevents the attainment of a Nernstian slope (no. 2). Increasing the ionophore content in the membrane beyond 10% weight enhances the electrode's response, indicating the ionophore's affinity for chromium(III) (no. 3-5). However, a reduced sensor response (no. 6 and 7) is observed upon further addition of the ionophore, likely due to potential saturation and membrane inhomogeneity [23].

Table 1. Optimizing membrane constituents

NO.	% Plasticizer	% Ionophore	% PVC	% NaTPB	Slope, mV/decade
1	DBP (70)	0	30	0	1.5
2	DBP (68)	0	30	2	3.2
3	DBP (60)	5	33	2	11.3
4	DBP (60)	8	30	2	14.1
5	DBP (58)	10	30	2	20.7
6	DBP (56)	12	30	2	18.5
7	DBP (54)	13	30	3	16.5
8	NB (58)	10	30	2	6.3
9	NB (56)	12	30	2	9.7
10	NB (54)	13	30	3	11.4
11	BA (58)	10	30	2	11.4
12	BA (56)	12	30	2	15.3
13	DBP (58)	10	32	0	15.6
14	DBP (58)	10	31	1	17.8

The plasticizer's quantity and type significantly impact the response characteristics of ion-selective electrodes. In general, Plasticizers act as solvent facilitators, ensuring consistent dispersion and aiding the movement of ionophores within the membrane. Thus, careful control of plasticizer's quantity and type is essential. Three plasticizers, namely nitrobenzene (NB), benzyl acetate (BA), and dibutyl phthalate (DBP), were evaluated (Table 1). DBP with a dielectric constant (DC) of 6.4 (no. 5) exhibited superior plasticizing properties in comparison to NB with DC=34.8 (no. 8) and BA with DC=5.1 (no. 11). The lower dielectric constant of DBP and BA results in weaker extraction of chromium(III) ions, with a large charge density. However, this is seemingly compensated by the selective complexation of the ionophore with chromium(III) ions [23]. Additionally, reduced extraction of polar interfering ions has a beneficial effect on the sensor's selectivity characteristics.

Furthermore, the addition of NaTPB enhances the electrode response sensitivity (no. 13, 14, and 5). Particularly, the utilization of 2% NaTPB (no. 5) induced a Nernstian behavior in the electrode response. Research has shown that the potentiometric functioning of cation-selective electrodes improves with the inclusion of lipophilic additives with negative charge. These additives reduce ohmic resistance, thereby improving response and selectivity characteristics. Furthermore, when the ionophore's extraction capacity is insufficient, the membrane electrode sensitivity is bolstered by the suitable additive. Additionally, additives may accelerate exchange kinetics at the interface between the sample and the membrane.

Based on the results, a membrane composed of 10% ionophore, 2% NaTPB, 58% DBP and 30% PVC exhibited the greatest performance, displaying a Nernstian slope of 20.7 mV/decade. As a result, this formulation was identified as the optimal configuration, which was subsequently employed in the fabrication of the LIE, SSE, and CWE.

3.2. pH study

For assessing the influence of pH on responses of three electrode types, the potential was evaluated at a specific chromium(III) concentration (0.1 mM) across a pH range of 2.0 to 8.0 (pH adjusted by the use of concentrated NaOH or HCl solutions). Given the findings, in the pH range of 3-5, the potential did not alter, suggesting consistent electrode performance within this pH range (Figure 2). However, at pH levels above or below this range, the potentials noticeably changed because of chromium(III) ion hydrolysis or incomplete complexation reactions. This pattern was noted across all three sensor varieties.
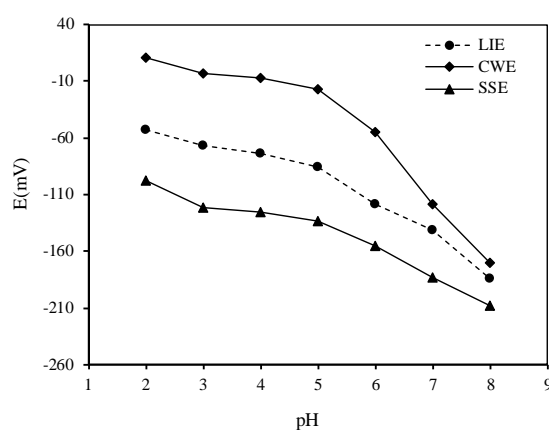

Figure 2. Impact of pH on three electrodes' responses

3.3. Calibration curves and detection Limit

To extend the linear range of the LIE, the optimized membrane composition was applied onto both shielded copper wires (for preparing SSE) and unshielded copper wires (for preparing CWE). The electrode exhibited a potential response range of 1×10^{-3}-7×10^{-6} mol L^{-1}, 1×10^{-3}-

3×10^{-7} mol L^{-1}, and 7×10^{-3}-3×10^{-9} mol L^{-1} of chromium(III) ions in the calibration solution, with 20.76, 21.79, and 19.05 mV/decade Nernstian slopes for LIE, CWE, and SSE, respectively (Figure 3). While the mechanical stability of CWE and SSE electrodes surpasses that of LIE, their measurable linear concentration range is also improved.

Detection limits are obtained by replacing the potential value, corresponding to the cutoff point, into the appropriate equation. The electrodes exhibited detection limits of 2×10^{-7} mol/L, 3×10^{-9} mol/L, and 7×10^{-6} mol/L for CWE, SSE, and LIE.
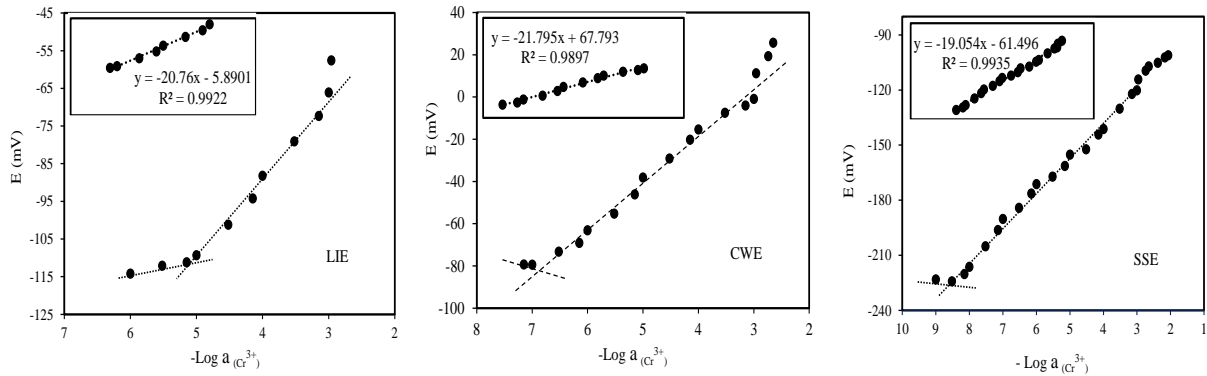

Figure 3. The calibration curves and detection limit of LIE, CWE, and SSE

3.4. Response time of membrane sensors

Response time refers to the duration necessary for the potential response to achieve values over ± 1 mV of the ultimate equilibrium potential, averaging around 5 seconds for LIE and CWE, while SSE exhibited an average response time of about 4-6 seconds across various concentrations (Figure 4). This is a crucial parameter for assessing the applicability of the presented technique in everyday practice.
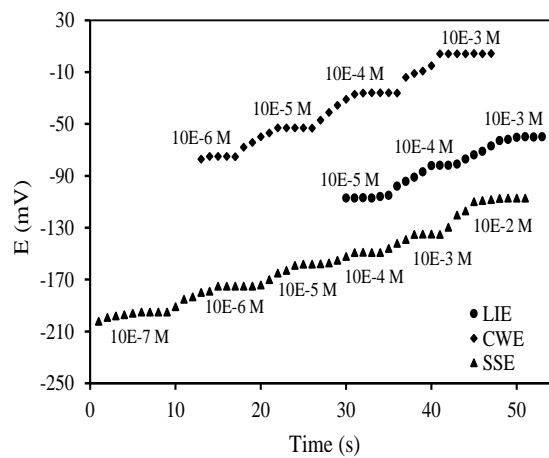

Figure 4. The response time of three electrodes in varying chromium(III) concentrations

3.5. Selectivity coefficients evaluation

The selectivity coefficients of the chromium(III) sensors were calculated utilizing the Matched Potential Method (MPM). This technique entailed measuring the potential variation upon modifying the primary ion's activity and introducing the interfering ion into an identical reference solution up to achieving the same potential change [24–26]. To derive the selectivity coefficient K_{MPM}, we conducted the following steps:

$$K_{MPM}= \Delta a_A/a_B$$

where a'_A indicates the activity of A, in the interfering ion presence, a_B and $\Delta a_A = a'_A - a_A$, a_A denotes the initial primary ion activity. The selectivity coefficient (K_{MPM}) values obtained were all significantly below 1.0, showing greater selectivity of the conventional sensor for chromium(III) ions (Table 2).

Table 2. The selectivity coefficients of interfering cations for three proposed sensors' stability and lifetime

Ion	K_{MPM}		
	LIE	**CWE**	**SSE**
Zn^{2+}	8.63×10^{-4}	6.22×10^{-2}	6.12×10^{-3}
Ag^+	1.67×10^{-4}	1.89×10^{-3}	4.27×10^{-3}
Pb^{2+}	5.64×10^{-3}	7.52×10^{-3}	5.44×10^{-3}
Ni^{2+}	4.88×10^{-3}	6.34×10^{-3}	9.25×10^{-3}
Mn^{2+}	3.25×10^{-3}	2.98×10^{-4}	3.50×10^{-3}
Co^{2+}	5.62×10^{-3}	1.54×10^{-3}	7.15×10^{-3}
Na^+	3.10×10^{-4}	4.55×10^{-4}	2.55×10^{-4}
Fe^{3+}	7.81×10^{-3}	8.20×10^{-3}	6.30×10^{-3}
Ca^{2+}	6.99×10^{-4}	4.12×10^{-4}	2.22×10^{-4}
Cd^{2+}	2.56×10^{-3}	9.54×10^{-3}	4.56×10^{-3}
Hg^{2+}	3.116×10^{-3}	4.57×10^{-3}	8.47×10^{-3}
Cu^{2+}	4.78×10^{-3}	2.67×10^{-3}	4.85×10^{-3}

3.6. Lifetime and stability of sensors

Three sensors of each type were selected, and their slopes were monitored over a 14-week period. The LIE exhibited stable performance for 11 weeks, without any significant changes in slope. In comparison, the SSE and CWE showed lifetimes of approximately 13 and 12 weeks, respectively, before experiencing a decrease in the Nernstian slope. The gradual leaching of the ionophore from the organic phase to the aqueous phase typically limits the lifetime of ion-selective electrodes [27-36]. However, the internal solution removal contributed to reducing the leaching process and extending the electrodes' lifetime.

3.7. Analytical applications

The sensors effectiveness was showcased by utilizing them as indicator electrodes in the titration of a 20 mL 1.0×10^{-4} mol L^{-1} chromium(III) solution with 1.0×10^{-2} mol L^{-1} EDTA. The resulting curves (Figure 5) revealed that as the amount of EDTA increased, potential values decreased due to forming complexes between chromium(III) ions and EDTA, resulting in the concentration reduction in free chromium(III) ions in the solution.
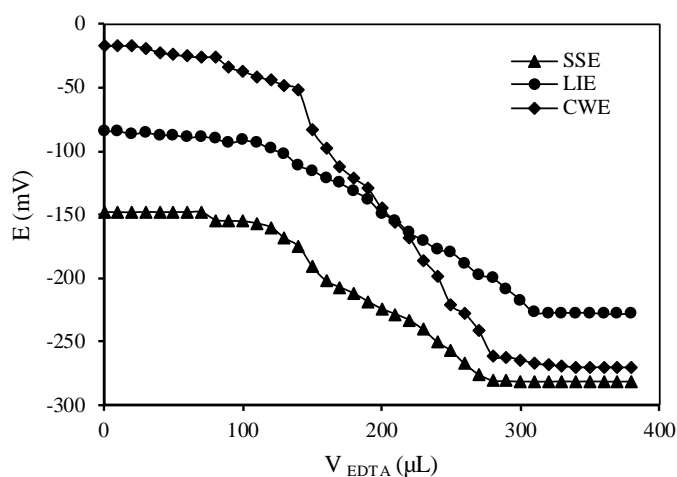

Figure 5. The potential titration curves of 20 mL 1.0×10^{-4} mol L^{-1} chromium(III) solution with 1.0×10^{-2} mol L^{-1} of EDTA by using LEE, CWE and SSE

Table 3. Comparison between the proposed solid-state electrode and some previously documented potentiometric chromium(III) selective electrodes

Ligand	Detection Limit (mol/L)	Slope (mV decade^{-1})	RT* (s)	pH	LT** (week)	Ref.
N, N-bis(salicylidene)-ophenylenediaminate chromium (III)	1.8×10^{-6}	20.1	8	4.5-7.7	--	[37]
1,3-bis[4-amino-5-benzyl-1,2,4-triazol-3-ylsulfanyl] propane	8×10^{-9}	20	<10	2.3-5.2	12	[38]
N-(1-(4-bromophenyl)-3-oxo-3-phenylpropyl) acetamide	3.1×10^{-7}	19.5	<15	4.0–6.5	8	[39]
N-(thiazol-2-yl carbamothioyl) benzamide	1×10^{-6}	21.8	5	4.0–6.0	12	[40]
N-(imidazol-2-ylcarbamothioyl) benzamide	3×10^{-9}	19.05	4-6	3.0-5.0	13	This work

* Response Time, ** Life Time

3.8. Critical comparison

A comparison of the presented SSE with other potentiometric chromium(III) electrodes [37–40] revealed improvements in response time, detection limit, and lifetime for SSE (Table 3). The SSE exhibited a significantly better detection limit compared to other electrodes, with response times and lifetimes of 4-6 seconds and 13 weeks, respectively, surpassing previous works.

4. CONCLUSION

In summary, N-(imidazol-2-ylcarbamothioyl)benzamide was developed for the first time and employed as an ionophore in the development of three varieties of liquid membrane electrodes. The LIE, CWE, and SSE according to this ionophore demonstrated promising performance as chromium(III) selective electrodes. The optimal membrane structure of 2% NaTPB, 30% PVC, 58% DBP, and 10% ionophore exhibited a Nernstian slope of 20.76 mV/decade and was selected for further use. The detection limits for SSE (3×10^{-9} M) and CWE (2×10^{-7} M) were improved compared to LIE (7×10^{-6} M). Each of the three electrodes displayed a response time of approximately 5 seconds. The removal of the internal solution led to an increase in the electrodes' lifespan. These designed electrodes were effectively utilized as indicator electrodes in the potentiometric titration of chromium(III) with EDTA.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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