

Full Paper

Symmetric and Asymmetric Copper Selective Electrodes based on N-(benzothiazol-2-ylcarbamoithiyl)benzamide

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Abstract- The present work aimed at comparing the capabilities and efficiency of symmetric and asymmetric electrodes for potentiometric detection of Cu^{2+} . Initially, we synthesized N-(benzothiazol-2-ylcarbamoithiyl)benzamide, and $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR spectroscopy approaches were used for characterization. Subsequently, it was employed as an ionophore to fabricate asymmetric electrodes of coated wire (CWE) and solid-state (SSE) and symmetric electrodes with liquid internal electrolyte (LIE). The best liquid membrane was prepared with an Ionophore: DBP: PVC: NaTPB ratio of 12:56:30:2. All electrodes exhibited Nernstian responses. The detection limits for SSE (1×10^{-9} mol/L) and CWE (1×10^{-7} mol/L) were superior to LIE (2×10^{-6} mol/L). Moreover, all three electrodes demonstrated very short response times (approximately 6 seconds) and exhibited large selectivity coefficient values for different cations. Asymmetric electrodes displayed longer lifetimes (SSE: 13 weeks and CWE: 12 weeks) compared to the symmetric electrode (LIE: 10 weeks). Finally, the electrodes were utilized for potentiometric titration of Cu^{2+} with ethylenediaminetetraacetic acid.

Keywords- Coated wire electrode; Cu^{2+} ; Liquid membrane; N-(benzothiazol-2-ylcarbamoithiyl)benzamide; Potentiometry; Solid-state electrode

1. INTRODUCTION

Potentiometric membrane electrodes have emerged as valuable tools for analyzing various species due to their simplicity and speed of operation [1–3]. These electrodes can be

categorized into symmetric and asymmetric types based on the approach used for immobilizing polymeric membrane onto electrode surface. Conventional PVC membrane electrodes usually necessitate both an internal reference electrode and a filling solution, which can lead to the leaching of membrane components into the surrounding solutions and reduced mechanical stability. However, the use of coated wire electrodes eliminates the need for internal solutions and reference electrodes by directly coating the polymeric membrane onto the surface of a conducting wire [4,5]. This reduces the leaching process and enhances the detection limit [6]. Coated wire electrodes involve the coating of a thin polymeric film with an ionophore onto a metal wire [7], signifying the initial development of solid-state ion-selective electrodes. Despite their simplicity, coated wire electrodes may experience potential drift due to sensitivity to small charges and interface issues between the wire and membrane [8]. The permeation of water through the membrane can result in forming a thin water layer on the wire surface [9], causing instability in electrode potentials. To address this, carbon-based nanomaterials, such as MWCNTs are used as electron-ion exchangers due to their conductivity and hydrophobicity. Potentiometric sensors incorporating MWCNTs have shown improvements in performance and resistance to water film formation [10,11].

On the other hand, the discharge of toxic metals into the environment, such as copper, poses significant health concerns worldwide [12,13]. While copper is essential for enzyme function, excess copper can lead to toxicity, as seen in Wilson disease [14]. To facilitate the rapid and simple measurement of Cu^{2+} ions, we aimed to develop symmetric and asymmetric copper-selective electrodes and compare their efficiency. The selection of an appropriate ionophore is crucial as it affects the electrode's selectivity. Various ionophores have been explored for copper-selective electrodes such as Cefazoline [15], Schiff base [16], Salens [17], benzothiazole derivative [18], and hydroxybenzylidene thiosemicarbazide [19], 4-methylcoumarin-7-yloxy-N-phenyl acetamide [3] and 2-(2-((4-Methoxybenzoyl) imino)-4-(4-methoxyphenyl) thiazol-3(2H)-yl)-2-phenylacetic acid [20]. However, many of such electrodes have limitations, like elevated detection limits, limited working concentration scopes, interference from additional ions, and short lifespans.

In our study, we developed N-(benzothiazol-2-ylcarbamothioyl)benzamide and used it as a novel ionophore due to its ability to form strong complexes with Cu^{2+} ions. Three types of liquid membrane copper-selective electrodes were prepared: solid-state electrodes (SSE) incorporating a conductive polymer composite with MWCNTs, coated wire electrodes (CWE), and electrodes with liquid internal electrolyte (LIE). The performance of these electrodes was compared in measuring Cu^{2+} concentration. These novel membrane electrodes represent the first utilization of N-(benzothiazol-2-ylcarbamothioyl)benzamide as the recognition component.

2. EXPERIMENTAL SECTION

2.1. Materials and apparatus

Sodium tetrphenylborate (NaTPB), high molecular weight poly(vinyl chloride) (PVC), nitrobenzene (NB), tetrahydrofuran (THF), and dibutyl phthalate (DBP) were procured from Merck Co. and employed without further purification. Multiwalled carbon nanotubes were prepared by Sigma-Aldrich, while graphite powder (particle size < 20 μm) was obtained from Fluka. Bayer and Henkel provided hardener (desmodur RFE) and epoxy, respectively. The cations' nitrate salts were obtained from Sigma-Aldrich and Merck with the greatest purity. Potassium thiocyanate, 2-aminobenzothiazol, benzoyl chloride and acetonitrile were acquired from Sigma-Aldrich. Deionized double-distilled water was employed in the experiments. Iodine vapor served as the detection method in thin-layer chromatography (TLC).

A Bransetead Electro Thermal B1 apparatus was employed for specifying the melting point. A Bruker Tensor 27 instrument with KBr disks was utilized for recording Fourier transform infrared (FT-IR) spectra. Ultra shield Bruker 400 equipment with CDCl_3 as the deuterated solvent was employed for recording ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra. The potentiometric examination was done at $25.0(\pm 0.1)$ $^\circ\text{C}$ by the use of a multi-meter with a voltage measurement precision of ± 0.1 mV (Japan). The reference electrodes used were internal and external (with Liquid membrane electrode) reference electrodes (Azar-Electrode, Iran).

Potentiometric measurements were conducted at room temperature by specifying the potential difference between ISE and reference electrode by a multi-meter. These electrochemical cells were utilized:

LIE:

$\text{Ag-AgCl} \parallel \text{internal solution, } 0.001 \text{ mol/L } \text{Cu}^{2+} \mid \text{liquid membrane} \mid \text{Cu}^{2+} \text{ test solution} \parallel \text{Ag-AgCl, KCl (satd.)}$

SSE or CWE:

$\text{solid-state-membrane or coated wire membrane} \mid \text{Cu}^{2+} \text{ test solution} \parallel \text{Ag-AgCl, KCl (satd.)}$

A small amount of KCl was added to the internal solution of LIE. Both the SSE and CWE were devoid of an internal solution. Standard solutions were employed to establish the calibration curve, and activity values were determined using the Debye-Hückel method.

2.2. N-(benzothiazol-2-ylcarbamoithioyl)benzamide synthesis

After dissolving potassium thiocyanate and benzoyl chloride in acetonitrile, the mix was blended for 30 minutes at ambient temperature. Following filtration and separation, the solid residues were used without additional refinement. A mixture of 2-aminobenzothiazol (2 mmol) and benzoyl isothiocyanate (2 mmol) in 10 mL acetonitrile was combined, refluxing for 12 hours at 60°C (Figure 1). TLC was utilized for confirming formation of the product. At the end

of the reaction, the solvent was vaporized under reduced pressure. The resulting yellow crude yield (N-(benzothiazol-2-ylcarbamoithioyl)benzamide) was purified by crystallizing from n-hexane/ethyl acetate and subsequently employed in the membrane composite. Structural validation was achieved by calculating the melting point and utilizing $^1\text{H-NMR}$, FT-IR, and $^{13}\text{C-NMR}$ spectroscopy methods.

N-(benzothiazol-2-ylcarbamoithioyl)benzamide: Yellow crystals, m.p. 137-139 °C; yield: 95%. IR (KBr): 3332, 3320, 1674, 1597, 1543, 1449, 1276, 1243, 1169, 933, 755, 704 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 7.50 (1 H, t, 3J = 7.1, CH), 7.60 (2 H, t, 3J = 7.8, 2 CH), 7.69 (1 H, t, 3J = 7.8, CH), 7.84 (1 H, t, 3J = 7.1, CH), 7.90 (2 H, d, 3J = 7.8, 2 CH), 7.94 (1 H, t, 3J = 7.1, CH), 8.27 (1 H, d, 3J = 7.1, CH), 9.20 (1 H, s, NH), 13.50 (1 H, s, NH) ppm. ^{13}C NMR (300 MHz, CDCl_3): δ 121.2 (C), 121.6 (CH), 124.6 (2 CH), 126.4 (CH), 127.6 (CH), 129.3 (2 CH), 131.0 (CH), 131.9 (CH), 134.1 (C), 148.3 (C), 158.6 (C), 166.6 (C=O), 176.0 (C=S) ppm. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{OS}_2$ (313.0): C, 57.49; H, 3.54; N, 13.41; S, 20.46. Found: C, 58.02; H, 4.15; N, 13.72; S, 21.19.

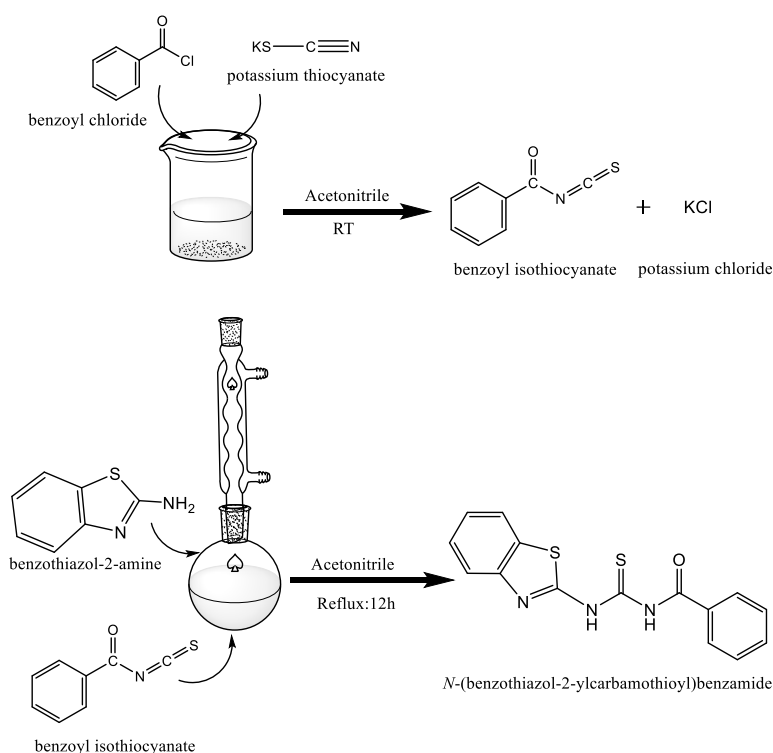


Figure 1. N-(benzothiazol-2-ylcarbamoithioyl)benzamide synthesis

2.3. Preparation of the copper-selective electrodes

2.3.1. Symmetric copper-selective electrode

N-(benzothiazol-2-ylcarbamoithioyl)benzamide, ionic additive, plasticizer, and PVC were solved in THF as per the ratio in Table 1 to fabricate LIE. The solution was mixed in a beaker,

and THF was slowly vaporized to yield a viscous solution. Plastic tubes with diameters ranging from 3 to 5 mm were plunged individually into the mixes for about 5 seconds, forming transparent membranes about 0.3 mm thick. The tubes were left at room temperature for approximately 12 hours. Subsequently, they were filled with a 0.001 mol/L $\text{Cu}(\text{NO}_3)_2$ solution as the internal filling and conditioned in a 1.0 mmol/L $\text{Cu}(\text{NO}_3)_2$ solution for 24 hours.

2.3.2. Asymmetric copper-selective electrodes

To prepare a CWE, a 10 cm long copper wire (d: 0.5 mm) was refined and dipped three times in a viscous solution achieved from 12% N-(benzothiazol-2-ylcarbamoethyl)benzamide, 2% NaTPB, 30% PVC, and 56% DBP. Afterward, it was allowed to air dry for 12 hours and then immersed in a 1.0 mmol/L $\text{Cu}(\text{NO}_3)_2$ solution for 24 h for conditioning.

The solid-state electrode (SSE) comprised three components: Part A consisted of an unshielded copper wire (d: 0.5 mm, L: 10 cm), Part B was a conductive composite acting as both an internal and transducer contact, and Part C was the PVC liquid membrane. To prepare the conductive composite, hardener (15%), carbon nanotubes (3%), epoxy resin (35%), and powdered graphite (47%) were combined in tetrahydrofuran (THF). The mix was allowed to stand for 30 minutes in the air, after which a combination of epoxy resin and hardener was employed for binding the graphite. The copper wire was then immersed into the resulting product 10 times and left to dry for 12 hours. The use of carbon nanotubes in this composition enhanced the transducer's performance. Next, resulting product was submerged three times in the liquid membrane cocktail (Part C), comprising 30% PVC, 56% DBP, 2% NaTPB, and 12% N-(benzothiazol-2-ylcarbamoethyl)benzamide. It was air-dried for 12 hours and then submerged in a 1.0 mmol/L $\text{Cu}(\text{NO}_3)_2$ solution for 24 hours for conditioning.

3. RESULTS AND DISCUSSION

We first determined the optimal composition of the polymeric membrane as a sensing layer. Subsequently, we prepared symmetric and asymmetric electrodes using this membrane and compared their efficiency in potentiometric Cu^{2+} measurement.

3.1. Polymeric membrane composition

To evaluate the composition, several LIE based on N-(benzothiazol-2-ylcarbamoethyl)benzamide as the ionophore with varying membrane compositions were developed, followed by an assessment of their response characteristics (Table 1).

Elevating the ionophore concentration in the membrane up to 12% wt. (no. 5) resulted in an increase in the slope of the electrode, indicating N-(benzothiazol-2-ylcarbamoethyl)benzamide affinity to Cu^{2+} . However, further addition of the ionophore led to a reduction in the electrode's response (no. 6), possibly due to membrane saturation and

inhomogeneity [21]. It is noteworthy that the ionophore absence in the membrane (no. 1 and 2), the response can be neglected.

The plasticizer amount and nature had a significant impact on the response features of ion-selective electrodes. Plasticizers affect the mobility of ionophore molecules and dielectric constant of the membrane phase [22-25]. Two plasticizers, namely DBP with a small dielectric constant and NB with a large dielectric constant, were employed (no. 5 and 10). DBP showed better performance compared to NB, possibly due to the higher affinity of N-(benzothiazol-2-ylcarbamothioyl)benzamide to Cu^{2+} , compensating for its lower extraction by DBP-containing membrane.

Table 1. Optimizing the membrane composition

NO.	% Plasticizer	% Ionophore	% PVC	% NaTPB	Slope, (mV/decade)
1	DBP (70)	0	30	0	7.8
2	DBP (68)	0	30	2	9.3
3	DBP (60)	5	33	2	11.4
4	DBP (58)	10	30	2	18.6
5	DBP (56)	12	30	2	28.6
6	DBP (55)	13	30	2	25.6
7	DBP (54)	13	30	3	23.5
8	DBP (56)	12	32	0	22.8
9	NB (60)	10	30	2	17
10	NB (56)	12	30	2	24.3
11	NB (54)	13	30	3	23.1

It was noted that incorporating lipophilic extracts with a negative charge is able to enhance the potentiometric functioning of cation-selective electrodes by diminishing ohmic resistance. Additionally, these materials might expedite exchange kinetics at the interface between the membrane and sample. Furthermore, additives have the potential to improve the inadequate extraction capability of certain ionophores. The addition of 2% NaTPB resulted in the electrode exhibiting Nernstian behavior (Table 1) (no. 5 and 8).

Ultimately, the membrane with an Ionophore: DBP: PVC: NaTPB ratio of 12:56:30:2 yielded a Nernstian slope of 28.6 mV/decade.

3.2. Impact of pH on copper- symmetric and asymmetric electrodes

We studied the impact of pH on response of three electrode types in a solution with 0.1 mmol/L Cu^{2+} over the pH range of 2.0 to 13.0. It was determined that the operational pH range for all three electrodes was pH 5 to 9.0, where the potential remained constant (Figure 2). The

alterations in potentials were attributed to the incomplete complexation reaction or hydrolysis of Cu^{2+} ions outside the specified pH range.

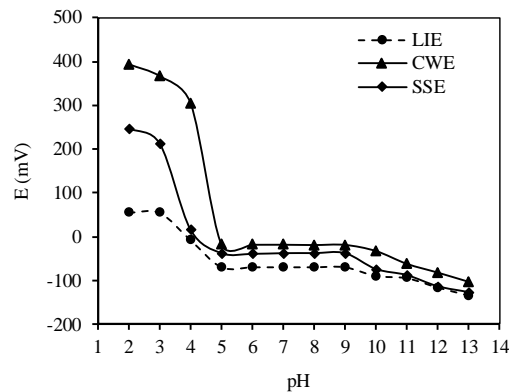


Figure 2. pH effects on the response of symmetric and asymmetric copper-selective electrodes

3.3. Calibration curves

For extending the linear concentration range of LIE, the optimal membrane composition was restrained on the conductive composite (for SSE) and unshielded copper wire (for CWE). The LIE exhibited a slope of 28.62 mV/decade in the range of concentrations as 1×10^{-2} - 3×10^{-6} mol/L of Cu^{2+} , while the SSE and CWE showed slopes of 28.93 mV/decade in the range of concentrations as 1×10^{-1} mol/L- 1×10^{-9} mol/L of Cu^{2+} and 29.18 mV/decade in the range of concentrations as 3×10^{-2} mol/L- 1×10^{-7} mol/L of Cu^{2+} (Figure 3).

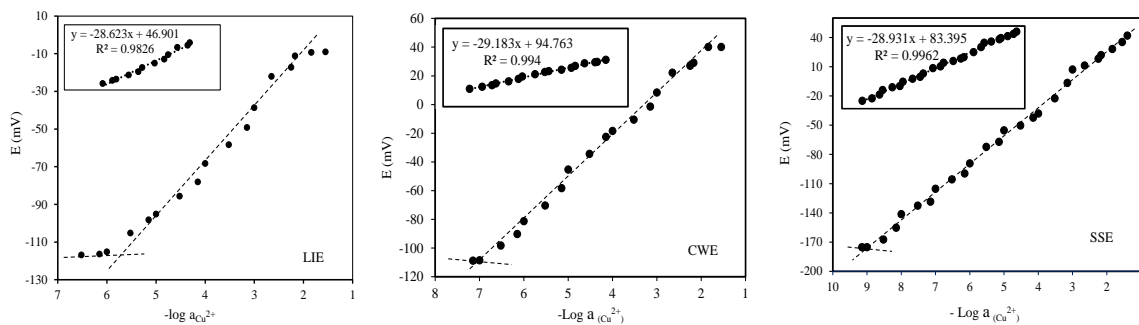


Figure 3. The calibration curves of CWE, SSE, and LIE

Since the optimal Nernstian slope value is $59.10/n$ (mV/decade), with (n) representing the valency [26], three electrodes exhibit the Nernstian slope for Cu^{2+} determination. Nevertheless, the solid-state electrode (SSE), being asymmetric, is capable of measuring a broader concentration range in comparison with symmetric electrodes like the liquid internal electrolyte (LIE). About CWE, although the linear range that can be measured with it is similar to that of the symmetric electrodes (LIE), but it can measure lower concentrations.

Detection limits are determined by substituting the potential value, representing the cut-off point projection, into the appropriate equation. The electrodes exhibited low detection limits: 1×10^{-7} , 1×10^{-9} , and 2×10^{-6} mol/L for CWE, SSE, and LIE. These observations highlight that asymmetric electrode (SSE and CWE), besides offering higher mechanical stability, are capable of measuring lower concentrations compared to symmetric electrodes (LIE). In symmetric electrodes, where the membrane interfaces with the Cu^{2+} solution from both sides, the transmembrane ion fluxing from the inner filling solution into the sample solution is greater compared to asymmetric electrodes that lack an inner solution. This constraint affects the detection limit of symmetric electrodes [27]. Conversely, in the SSE design, the incorporation of carbon nanotubes (CNT) increases the surface area and promotes enhanced the target analyte's mass transport to the surface of the electrode. This improved mass transport results in lower detection limits and greater sensitivity, as a greater number of analyte molecules can attain the electrode.

3.4. Response time of copper selective electrodes

In potentiometric methods, electrode response time refers to the duration necessary for the potential response for reaching values over ± 1 mV of the final equilibrium potential [6]. To determine this value, the potential changes of the Cu^{2+} electrodes are monitored after successive immersion in various Cu^{2+} solutions, each with a 10-fold concentration difference. The response time for all three electrodes was approximately 6 seconds (Figure 4), indicating a rapid equilibrium response.

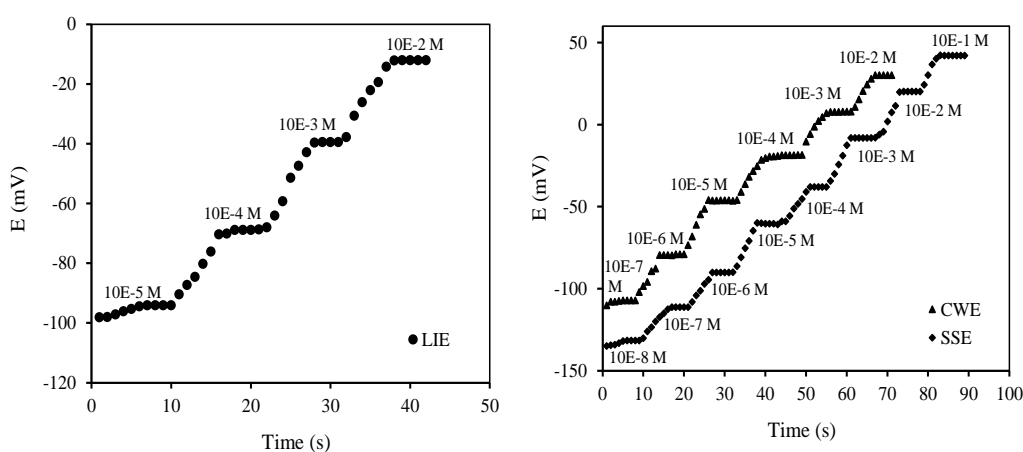


Figure 4. The response time of the presented symmetric LIE and asymmetric CWE and SSE

3.5. Lifetime of the asymmetric and symmetric electrodes

To examine the longevity of both asymmetric and symmetric electrodes, three electrodes of each type were chosen, and their slopes were measured over a period of 14 weeks.

Throughout this duration, the electrodes were operated for approximately one hour per day [28-33].

The lifetime of the LIE was at least 10 weeks, while it was 12 and 13 weeks for CWE and SSE, respectively. The extended lifespan of asymmetric electrodes in contrast to symmetric ones might stem from a decrease in leaching as a result of eliminating the internal solution.

3.6. Selectivity and Interference

The responsiveness of ion-selective electrodes to a certain ion stands out as a critical attribute, distinguishing it amidst various species and ions present in the solution. It is quantified as a selectivity coefficient. We assessed the selectivity coefficients of the newly devised electrodes by the matched potential method (MPM) [34-40] (Table 2). A selectivity coefficient (K_{MPM}) of 1.0 signifies that the sensor exhibits comparable reactions to the interfering and primary ions, but lower values indicate greater selectivity. Our findings consistently show values significantly below 1.0, underscoring the high selectivity of the presented electrodes for Cu^{2+} .

Table 2. The selectivity coefficients for LIE, SSE, and CWE

Ion	K_{MPM}		
	LIE	CWE	SSE
Zn^{2+}	3.22×10^{-3}	5.10×10^{-3}	5.24×10^{-2}
Ag^+	4.15×10^{-2}	2.50×10^{-3}	4.12×10^{-3}
Pb^{2+}	3.50×10^{-3}	2.45×10^{-4}	7.85×10^{-4}
Ni^{2+}	6.54×10^{-3}	6.51×10^{-3}	2.32×10^{-3}
Mn^{2+}	2.88×10^{-3}	3.45×10^{-2}	1.56×10^{-3}
Co^{2+}	9.12×10^{-3}	2.87×10^{-3}	4.26×10^{-3}
Na^+	3.50×10^{-3}	4.12×10^{-5}	7.26×10^{-5}
Fe^{3+}	7.74×10^{-4}	1.85×10^{-5}	3.20×10^{-5}
Ca^{2+}	6.55×10^{-3}	3.65×10^{-5}	8.52×10^{-5}
Cd^{2+}	5.50×10^{-3}	4.50×10^{-3}	4.65×10^{-3}
Hg^{2+}	1.22×10^{-2}	2.89×10^{-3}	5.58×10^{-3}
Cr^{3+}	4.25×10^{-3}	1.75×10^{-3}	1.63×10^{-3}

3.7. Analytical applications

A titration process was conducted using ethylenediaminetetraacetic acid (EDTA) solution at 1.0×10^{-2} mol/L concentration as the titrant, against Cu^{2+} (20 mL) solution at 1.0×10^{-4} mol/L concentration. Asymmetric and symmetric electrodes were employed as indicator electrodes in these potentiometric titrations. As depicted in Figure 5, the potential values decrease with increasing amounts of EDTA. Such decline is attributed to the development of a complex between Cu^{2+} and EDTA, resulting in a reduction in the Cu^{2+} ions' concentration within the solution. The titration curve endpoint indicates the successful utilization of copper-selective electrodes as indicator electrodes.

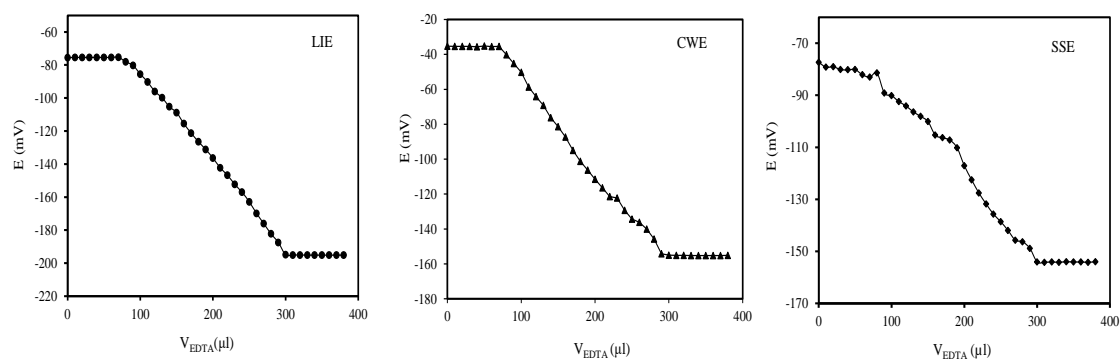


Figure 5. potentiometric titration of Cu^{2+} solution (20 mL) (1.0×10^{-4} mol/L) with EDTA (1.0×10^{-2} mol/L) by CWE, SSE, and LIE

3.8. Comparison with previous works

Comparisons were done between the linearity range, slope, appropriate pH range, detection limit, and response time of electrodes previously documented and the suggested solid-state electrode (Table 3) [20,41-43]. It is evident that the SSE exhibits satisfactory characteristics. There was an enhancement in the detection limit, working range, and applicable pH range for the presented SSE. Its response time is also comparable to the best-performing electrodes [42].

Table 3. Comparison between the presented SSE and several other copper selective electrodes

Ionophore	Slope (mV/decade)	Detection limit (mol/L)	Linear range (mol/L)	Response time (s)	pH	Ref.
2-(2-((4-Methoxybenzoyl) imino)-4-(4-methoxyphenyl) thiazol-3(2H)-yl)-2-phenylacetic acid	30.4	9.0×10^{-7}	1×10^{-6} - 1.5×10^{-1}	9-11	5.0-8.0	[20]
1,3-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]propane and 1,2'-bis[2-(1,3-benzothiazol-2-yl)-phenoxy]2-ethoxyethane	29.4	7.1×10^{-8}	1×10^{-7} - 1×10^{-1}	13	3-7.5	[41]
Etioporphyrin I dihydrobromide	30.3	8.9×10^{-7}	1.3×10^{-6} - 1.3×10^{-2}	5	4.5-8.5	[42]
1-phenyl-2-(2-hydroxyphenylhydrazo) butane-1,3-dione	28.8	6.3×10^{-7}	2×10^{-6} - 5×10^{-3}	10	3-8	[43]
N-(benzothiazol-2-yl)carbamothioyl)benzamide	28.9	1×10^{-9}	1×10^{-9} - 1×10^{-1}	6	5-9	This work

4. CONCLUSION

In present work, N-(benzothiazol-2-yl)carbamothioyl)benzamide was developed, purified, and its structure confirmed using ^{13}C -NMR, ^1H -NMR, and FT-IR spectroscopy. Subsequently,

it was employed as an ionophore for the development of three polymeric membrane copper-selective electrode types, comprising a SSE and a CWE as asymmetric electrodes, and a LIE as a symmetric electrode. The polymeric membrane compositions of the electrodes consisted of 12% N-(benzothiazol-2-ylcarbamothioyl)benzamide, 2% NaTPB, 30% PVC, and 56% DBP. Notably, the detection limit of asymmetric electrodes for Cu^{2+} (SSE: 1×10^{-9} mol/L and CWE: 1×10^{-7} mol/L) showed improvement compared to the symmetric electrode (LIE: 2×10^{-6} mol/L). Furthermore, all three electrode types exhibited very short response times, approximately 6 seconds. These electrodes demonstrated good selectivity coefficient values for different cations and were effectively employed in the determination of Cu^{2+} via potentiometric titration with EDTA. While all three electrodes performed acceptably in Cu^{2+} measurement, the solid-state electrode (SSE) emerged as the superior choice due to its broader working range, lower detection limit, and extended lifespan.

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Declarations of interest

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

Author contribution statement

Leila Hajiaghababaei and Mohammad Reza Allahgholi Ghasri: Supervision, designing experiments and writing the paper. Ashraf Sadat Shahvelayati: Consultant on ligand synthesis. Parviz Ebadi Vazifekhoran: Collecting data, Preparing figures. Khadijeh Kalateh: Preparing some figures and editing.

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