

Full Paper

Rapid Measuring of Cu²⁺ ions by Selective Potentiometric Sensor based on a New Ion Carrier

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Abstract- In this paper, 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone was synthesized and used as an ion carrier in Cu²⁺ ion selective sensor. The potentiometric sensor was worked well in a concentration range of 1.0×10⁻² to 1.0×10⁻⁶ M of Cu²⁺ ions with Nernstian slope of 30.7±0.6 mV/decade. Workable pH range of the sensor was 3.5-8.5 and the response time of the electrode was about 10 s. Detection limit of the electrode was obtained 1.0×10⁻⁶ M. The sensor has a relatively fast response time (~10 s) and a useful working pH range of 3.5-8.5. The proposed electrode responded to copper ions selectively respect to other common metal cations. Performance of the copper electrode as an indicator electrode was checked in a potentiometric titration of Cu²⁺ ions with EDTA as titrant which confirmed the monitoring ability of the copper selective sensor. Finally, direct determination of Cu²⁺ ions in some river water samples was done to show the analytical ability of the designed sensor.

Keywords- Cu²⁺ selective electrode, Liquid membrane, 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone, Potentiometric sensors

1. INTRODUCTION

Ion-selective electrodes (ISE) are an important analytical tool designed to measuring of ion in solution. Superiorities of ISEs respect to other analytical methods are low cost, sensitivity, selectivity, non-destructivity of analyte, online monitoring ability, simple operation and

portability. These features led to the development and application of many ISEs based on the various ion carrier called ionophores. Ionophore is the most important part of an ISE which provides the electrode selectivity. Hence, many researches were focused on synthesis and/or introducing new organic molecules as suitable ionophore for the ions during the years [1-18].

On the other hands, copper is one of the most widespread heavy metals in the industrialized countries [10]. It is extensively used in numerous industries, such as electroplating, electrical, fertilizer, painting, wood manufacturing and pigment industries [19,20]. Also, it is an essential element at low concentration and toxic at high concentration in many biological systems [21]. Toxic copper species are generally $\text{Cu}(\text{OH})^+$, $\text{Cu}_2(\text{OH})_2^{2+}$, and CuCO_3 [22]. It is well known that Cu^{2+} ion can catalysis lipid peroxidation, and lead to form free radicals. Due to the widespread of copper species in environment and considering their toxicities, their monitoring is of great important.

During the years, many copper selective electrodes have been introduced using various organic molecules including Cefazoline [23], Schiff base [24], salens [25], benzothiazol derivative [26], hydroxybenzylide thiosemicarbazide [27]. Still, synthesis and finding new ionophore possessing proper selectivity seems to be interesting in the field of ion selective electrodes.

Therefore, in this study, 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone (Fig. 1) was synthesized and a selective liquid membrane electrode was introduced for potentiometric measuring of Cu^{2+} in environmental samples by using it as a new ionophore.

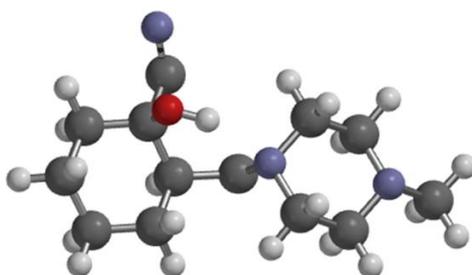


Fig. 1. The structure of 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone

2. EXPERIMENTAL SECTION

2.1. Reagents and Materials

Plasticizer used in this work were benzyl acetate (BA), dibutyl phthalate (DBP), nitrobenzene (NB), and the ionic additive was sodium tetraphenyl borate (NaTPB), as well as high relative molecular weight polyvinyl chloride (PVC) and tetrahydrofurane (THF) were all from Merck Chemical Company. Nitrate or chloride salts of the cations used were also from Merck. Doubly distilled deionized water was used throughout.

2.2. Apparatus

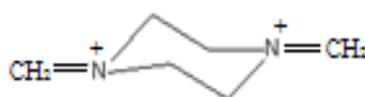
The potential was recorded by an ion analyzer 250 pH/mV meters (Corning) at 25.0 ± 0.1 °C. Internal and external reference electrodes were Ag/AgCl reference electrodes from Azar-Electrode, Iran. Melting point was determined with Bransstead Electro Thermal B. IR spectra were obtained using a Bruker, Tensor 27 instrument by KBr disks. ^1H and ^{13}C NMR spectra were gotten with a Bruker Avance BRX-250 MHz. FT-NMR Spectrometer using $(\text{CD}_3)_2\text{SO}$ as the deuterated solvent containing tetramethylsilane as internal standard. Mass spectra were recorded with a Ferigan-MAT Electron impact ionization-mass spectrometer (70 eV) (in m/z).

2.3. Synthesis of Ionophore

The 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone was prepared in two steps, as follows:

Step 1. The 2-(4-methyl piperazine-1-yl methyl) cyclohexanone was synthesized as follows: This compound was prepared by Mannich reaction [28-30]. 17.68 g (180 mmol) cyclohexanone, 10.94 g (90 mmol) 4-methyl piperidinium chloride, 2.7 g (90 mmol) paraformaldehyde and 20 ml acetic acid was poured in a 250 ml flask. The reaction mixture was stirred and refluxed for 2 h at 120 °C and homogenous solution was achieved. The acetic acid was removed at 90-95 °C. The flask contents precipitated after 1 h at ambient temperature. The resultant precipitate was refluxed with 20 ml acetone at 45 °C for 30 minutes. Then, the solid was recrystallized with ethanol 96% and faint yellow crystals were obtained. The melting point of product was 103-107 °C.

This precipitate was dissolved in distilled water and under continues stirring in ice mixture, NaOH 30% was added until pH reached to 14. The product was extracted three times by diethylether and dried over dehydrated sodium sulfate. After evaporation of ether, 5.723 g yellow viscose product was obtained. (Yield 25.5%) (Fig.2.a). RF=0.29 (Normal Hexane; Ethyl acetate, 1:3). IR(CHCl_3): 2937.04; 2858.30; 1711.46; 1579.50; 1454.05; 1288.11; 1162.69; 1009.58; 814.52 cm^{-1} . MS: Molecular weight (M^+)=210, m/e =212



Step 2: The 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone was synthesized as follows [31-33]:

0.735 g (3.5 mmol) 2-(4-methyl piperazine-1-yl methyl) cyclohexanone was poured in a 250 ml flask and 4 mmol sodium metabisolphite and a little distilled water were added. Then, 1.01 g (15.5 mmol) KCN which dissolved in 8 mL distilled water, was added too. The solution was acidified with hydrochloride acid 10%. The mixture was well stirred for 72 h at ambient temperature. End of the reaction was recognized through thin layer chromatography (TLC)

method. When three times extraction by diethylether was done, it was dried over dehydrated sodium sulfate, the product was filtered and its solvent was evaporated. Finally, 0.649 g (yield 75%) solid compound was obtained (Fig. 2.b). The schematic representation of reaction is shown in Fig. 1. (m.p.156-158°C). IR (KBr cm^{-1}): 3386.99; 2943.32; 2858.87; 2252.23; 1433.87; 1353.48; 1271.16; 1195.14; 1115.25; 876.08; 638.51. ^1H NMR: (CDCl_3) δ ppm, 1.17-1.25 (1H, m); 1.25-1.32 (1H, m); 1.43-1.50 (5H, m); 1.52-1.59 (6H, m); 1.64-1.66 (2H, d); 1.71-1.84 (6H, m); 1.90-2.15 (2H, q). ^{13}C NMR: (CDCl_3), δ (ppm, TMS), 21.05, 22.74, 23.67, 25.16, 25.40, 30.65, 32.11, 32.82, 35.68, 39.67, 40.50, 103.11, 107.23. MS: m/e(relative intensity): 41.2(34.44); 55.2(40.0); 69.2(30.37); 83.2(22.05); 91.2(100); 11.2(85.88); 135.2(14.81); 151.2(51.85); 283(61.48).

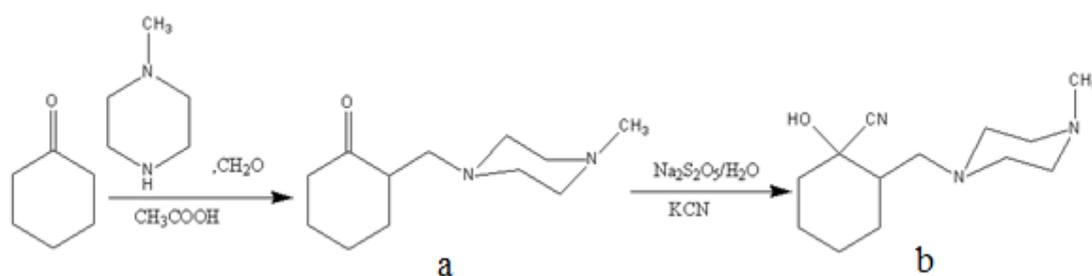


Fig. 2. The Schematic illustration of synthesis of 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone

2.4. Preparation of the Electrode

Since the used ISEs in this work were a kind of liquid membrane electrodes, following procedure was used for their preparation. Altered amounts of the ionophore (2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone) was mixed well with suitable amounts of an ionic additive (NaTPB) and a plasticizer (DBP or BA or NB) and PVC in 2 mL of tetrahydrofuran (THF). The solvent of the mixture was evaporated slowly until an oily concentrated residue was found. Then, a plastic tube (3-5 mm o.d.) was dipped into the mixture for some seconds till a transparent membrane of about 0.3 mm thickness was formed at the end. Next, the tube was kept at room temperature for about 24 h to be dried. The tube was then filled with an internal filling solution of 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$. The electrode was lastly conditioned in a 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ solution for 24 h.

2.5. Emf Measurements

The electromotive force (emf) measurements was done according to the below cell assembly;

$\text{Ag}-\text{AgCl}, \text{KCl (satd.)} \mid \text{internal solution, } 1.0 \times 10^{-3} \text{ M Cu (NO}_3)_2 \mid \text{PVC membrane} \mid \text{sample solution} \mid \text{Ag}-\text{AgCl}, \text{KCl (satd.)}$

These measurements were followed by calibration of the electrodes with several standard solutions. Activities were calculated according to the Debye- Huckel procedure.

3. RESULTS AND DISCUSSION

3.1. Optimization of the electrode ingredients

In ISEs, selectivity is one of the essential factor in performance of the electrode. Selectivity generally creates from nature and amount of the membrane components especially the used ionophore [34-38]. Table 1 shows some of the important composition which were tested in this work to achieve the best electrode performance. Potentials corresponded to the various membranes were recorded in a standard series solutions of Cu^{2+} ion. The slope of the calibration curve was considered as each electrode response.

Table 1. Optimization of the membrane elements

Membrane No.	Composition (%)				Slope (mV per decade)
	PVC (%wt.)	Plastisizer (%wt.)	Ionophore (%wt.)	NaTPB (%wt.)	
1	33	(DBP)60	5	2	5.6 ±0.4
2	30	(DBP)60	8	2	16.7±0.4
3	30	(DBP)58	10	2	17.3±0.5
4	29	(DBP)59	10	2	14.8±0.3
5	29	(NB)59	10	2	20.3±0.5
6	29	(BA)59	10	2	30.7±0.6
7	28	(BA)58	12	2	26.2±0.5
8	33	(BA)60	5	2	24.5±0.4
9	35	(BA)65	0	0	1.2±0.3
10	35	(BA)63	0	2	2.7±0.5
11	31	(BA)59	10	0	25.2±0.4

The extraction of Cu^{2+} ion from aqueous solution into the organic layer of the membrane is mostly because of strong and selective interaction between the organic ligand as ionophore and the copper ions. Accordance to Table 1, it can be seen that in the lack of ionophore (no. 9, 10), the sensors poorly respond (slope of 1.2±0.3 and 2.7±0.5 mV per decade). Furthermore,

sensitivity of the electrode response increases by increasing the ionophore amount up to 10% (no. 6). This behavior can confirm high affinity of the 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone toward Cu^{2+} ion.

Another aspect which can cause the extraction of Cu^{2+} ion into the membrane is solvent mediator called plasticizer. In fact, it is the membrane solvent allowing homogeneous dissolution and diffusional mobility of ions inside the membrane. It is a water-immiscible organic solvent possessing low vapor-pressure, compatible with PVC without any functional groups competing with ionophore. Nature of the plasticizer has a noticeable effect on the electrode responses e.g. slope, linear domain and selectivity of PVC membrane electrodes [33-40]. After the evaluation of DBP, NB and BA as solvent mediators, it was observed that BA display the better sensitivity (no. 6). Therefore, benzyl acetate (BA) was chosen to be employed in the sensor construction. It should be noted that copper ions is a rather polar ions and seems NB with higher dielectric constant (DC) would be better plasticizer, however, DBP or BA with lower DC than NB (with DC of 64 and 5 respectively) was used not to compete the selective complexation of 2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone with the Cu^{2+} ions.

Using ionic additive in liquid membrane sensors decreases the Ohmic resistance and increases the response behavior of the sensors. Also, when the solvation of the ions are high, and extraction capability is poor, it can help the membrane to extract the ionic species in to the hydrophobe layer [40-42]. Table 1 also showed that NaTPB addition of 2% as an anionic additive led to the slope increase from the sub-Nernstian value of 25.2 ± 0.4 mV per decade (no. 11) to the Nernstian value of 30.7 ± 0.6 mV per decade (no. 6).

To conclude, membrane with composition of 29% PVC, 10% ionophore, 2% NaTPB and 59 % BA (no. 6) which shows the best Nernstian slope (30.7 ± 0.6 mV/decade) was selected as the optimum one for next experiments.

3.2. Effect of Filling Solution

Three concentration of CuCl_2 (1.0×10^{-2} , 1.0×10^{-3} and 1.0×10^{-4} M) was used as filling solution of the electrode and the potential response of the Cu^{2+} ion selective electrode was recorded. As can be seen in Fig. 3, the variation of the concentrations of the internal solution does not cause any significant changes in potential response of the electrodes, except small changes in the intercept of the resulting Nernstian plot. Therefore, 1.0×10^{-3} M CuCl_2 solution was selected as appropriate filling solution.

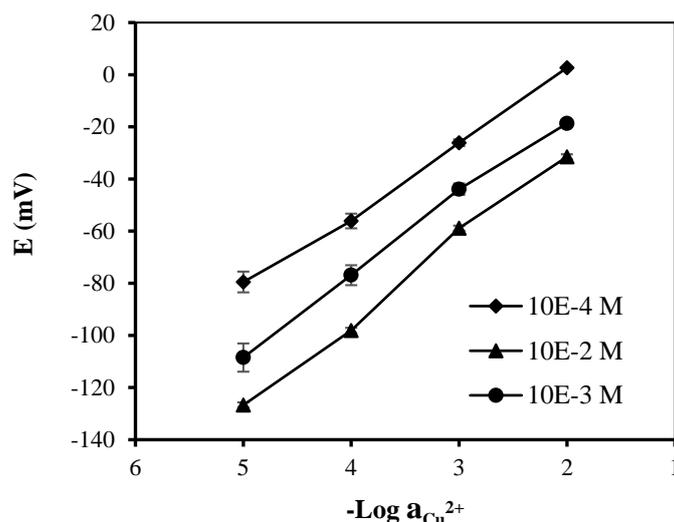


Fig. 3. Various filling solution and their effect on the sensor response

3.3. pH study

pH of the working solution on the potential response of ISE was studied at 1.0×10^{-3} M Cu^{2+} solution in the range of 2.0 to 11. pH adjustment was done by addition of HCl or NaOH. As it can be seen from Fig. 4, the potential has no changes in the pH range of 3.5 to 8. Below and above this range, potential changes drastically.

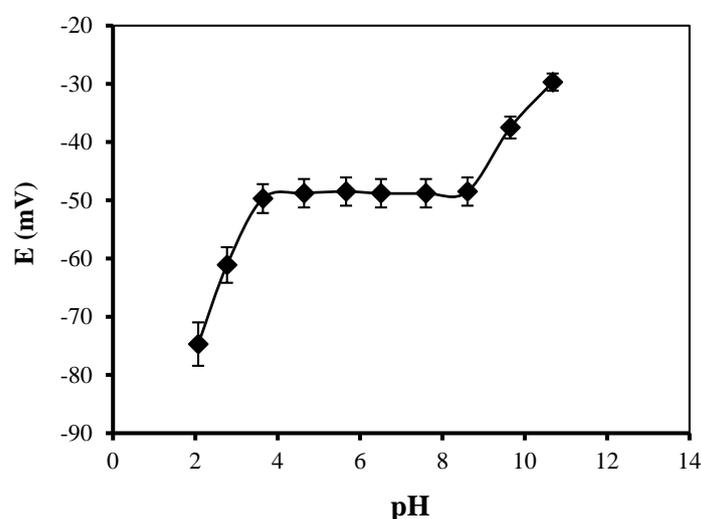


Fig. 4. Effect of pH on potential response of the Cu^{2+} ion electrode

These variations in potentials above the pH of 8.5 is due to the formation of the Cu^{2+} ion hydroxy complexes in the solution and below the pH value of 3.5 were attributed to the protonation of the ionophore [36]. The proposed ionophore has heteroatoms such as N and O atoms which are intermediate donor atoms. Therefore, charge-dipole interaction between Cu^{2+} ions and nitrogen atoms of ionophore is stronger than interaction between H^+ ions. In low pH,

H⁺ ions compete with Cu²⁺ ions in adsorption on ionophore. In below pH of 3.5, H⁺ concentration is enough to overcome such competition and protonates the ionophore.

3.4. Response Time of

Generally, response time of an ISE is estimated by measuring average time essential to achieve a potential within ± 0.1 mV of the final steady-state potential, while immerse the electrode in a standard calibration series of target ions (ten-fold difference in concentration of each solution). Some experimental conditions such as stirring, ionic concentration and composition of the test solution, in which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and temperature can affect the response time of a ISE [42]. Here, response time of 10 s was obtained by changing the Cu²⁺ concentration in solution, over a concentration range 1.0×10^{-5} to 1.0×10^{-2} M (Fig. 5).

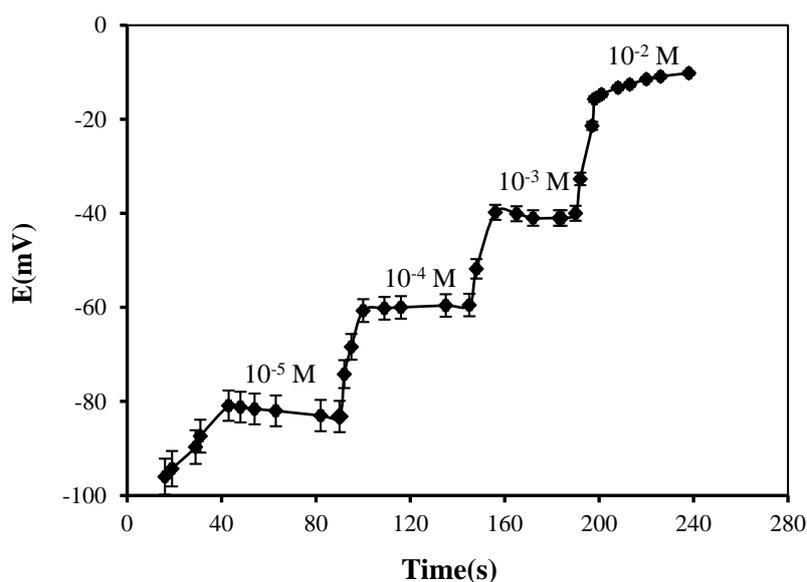


Fig. 5. Dynamic response of copper ion electrode for step changes in concentration of Cu²⁺

3.5. Analytical Characterization of the sensor

Analytical performance of the proposed sensors was presented in terms of linear range, detection limit, life time, and selectivity. Working range of an ion-selective electrode includes the linear part of the calibration curve as shown in Fig. 6. As can be seen, appropriate measuring range of the proposed sensor is between 1.0×10^{-6} and 1.0×10^{-2} M. In this work the detection limit of the proposed sensor was obtained 1.0×10^{-6} mol L⁻¹ which was calculated by extrapolating two segments of the calibration curve.

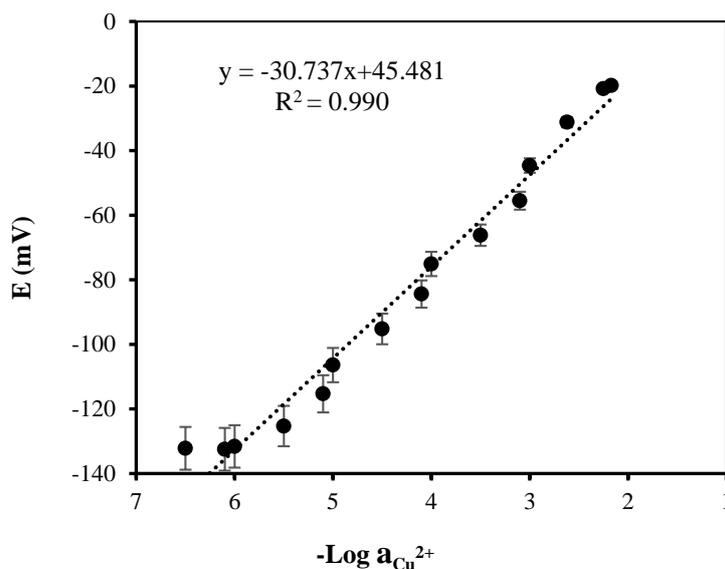


Fig. 6. Calibration curve of the Cu²⁺ selective electrode

Table 2. Selectivity coefficients of the proposed sensor calculated for various interfering cations

Ion	K _{MPM}
Zn ²⁺	9.5×10 ⁻³
Ag ⁺	1.0×10 ⁻¹
Hg ²⁺	8.9×10 ⁻²
Pb ²⁺	2.1×10 ⁻²
Mg ²⁺	3.7×10 ⁻²
Cd ²⁺	2.1×10 ⁻²
Cr ³⁺	9.3×10 ⁻³
Mn ²⁺	1.9×10 ⁻²
Co ²⁺	4.5×10 ⁻²
Na ⁺	1.5×10 ⁻²

Selectivity coefficients of the Cu²⁺ ion selective sensor were assessed by the matched potential method (MPM) [42-45]. The calculated selectivity coefficient (K_{MPM}) values are given in Table 2. K_{MPM}=1.0 designates equal response to both target and interfering ions.

Further, smaller values of selectivity coefficient, shows the selectivity of the sensor. As seen in Table 2, the selectivity coefficient values are almost smaller than 1.0, which signifying sufficient selectivity of the sensor towards Cu^{2+} respect to all the interfering ions tested.

Generally loss of plasticizer, ion carrier, or ionic additive from the polymeric membrane due to leaching into the sample solution during long time of usage, is a primary reason for the limited lifetime of the sensors [42]. Lifetime for this sensor was studied through monitoring the changes in slope of the sensor within a period of time. The sensors were tested for 17 weeks, during this period the electrodes were used continuously one hour per day. There was a slight gradual decreased in the slopes during 15 weeks (from 30.7 to 26.0 mV per decade). After that, a significant change in slope was observed (from 26.0 to 22.6 mV per decade). The proposed sensors can be used for about 15 weeks.

3.6. Analytical Performance

ISEs are low in cost, simple to be used, easily to be automated for rapid sampling, having low interferences from the matrix and can be applied to small volume of samples. These characteristics make them an ideal choice as an indicator electrodes for environmental pollutant monitoring.

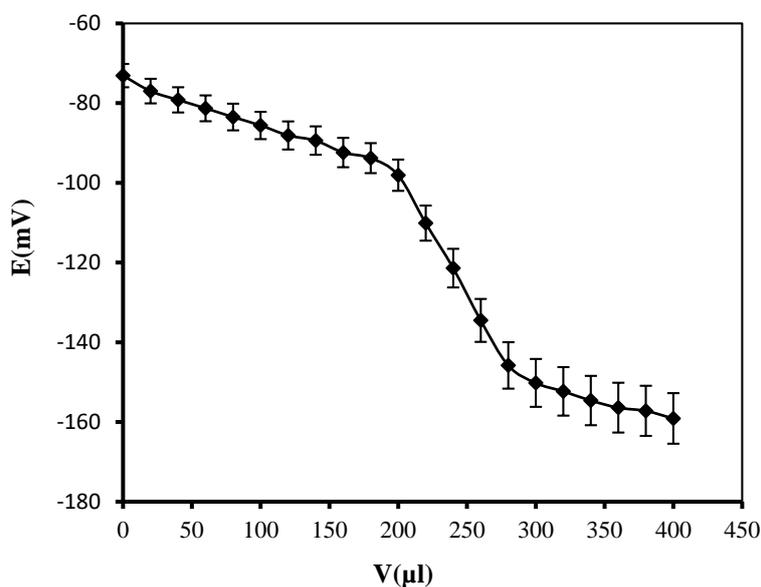


Fig. 7. Potentiometric titration curve of 1.0×10^{-4} M Cu^{2+} solution with 1.0×10^{-2} M EDTA using the proposed sensor as an indicator electrode

The practical usage of the proposed sensor as an indicator electrode was tested through titration of 25.0 mL of 1.0×10^{-4} M of Cu^{2+} solution with EDTA 1.0×10^{-2} M as titrant. The

resulting titration curve is shown in Fig. 7. As can be seen, the amount of Cu^{2+} ions in solution can be accurately monitored with the proposed electrode continuously.

To assess the applicability of proposed electrode in real samples, Cu^{2+} ions content of some water samples was tested. The electrode was applied to the direct measurement of Cu^{2+} ion in river water samples. All the samples were filtered using a 0.45- μm pore size membrane filter to remove suspended particulate matter. Some sample solutions were added the Cu^{2+} ions and some of the others were not. Potentials of the samples were then measured by direct potentiometry. As shown in Table 3, the proposed method could be applied successfully for the direct determination of Cu^{2+} ions in river water samples.

Table 3. Determination results of Cu^{2+} ions in various samples

Sample	Spiked amount	Measured with proposed sensor (M)
River water	0	$1.31 (\pm 0.06)^a \times 10^{-4}$
Spiked River water	2.0×10^{-4}	$3.28 (\pm 0.10) \times 10^{-4}$
Spiked River water	4.0×10^{-4}	$5.25 (\pm 0.13) \times 10^{-4}$

^a S_d based on three replicate analysis

Table 4. Comparison of the proposed Cu^{2+} ion electrode with some previously reports

Ionophore	Slope	Detection limit (M)	Linear range (M)	Response time (S)	pH	Ref.
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}	$1 \times 10^{-7} - 1 \times 10^{-1}$	13	3-7.5	[26]
4-(2-hydroxy-benzylideneamino)-5-phenyl-4H-1,2,4-triazole-3-thiol	28.7	1.0×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-2}$	25	4-8.5	[45]
N,N-(2,2-dimethylpropane-1,3-diyl)-bis(dihydroxyacetophenone)	30.0	2.5×10^{-7}	$3 \times 10^{-7} - 1 \times 10^{-2}$	<10	3-7.4	[46]
etioporphyrinI dihydrobromide	30.3	8.9×10^{-7}	$1.3 \times 10^{-6} - 1.3 \times 10^{-2}$	5	4.5-8.5	[47]
graphite oxide/imprinted polymer composite	26.1	4.0×10^{-7}	$1 \times 10^{-6} - 1.3 \times 10^{-1}$	3	4-8	[48]
(2,4-dihydroxybenzylidene)-1,6-diaminohexane	29.5	4.0×10^{-8}	$5 \times 10^{-8} - 1 \times 10^{-1}$	10	2.5-5.5	[49]
2-(4-methyl piperazine-1-yl methyl)-1-cyano cyclohexanone	30.7	1.0×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-2}$	10	3.5-8.5	This work

Nernstian slope, linearity range, detection limit, pH range and response time of the proposed Cu^{2+} ion sensor with some of the best previously reports are compared in Table 4 [26,45-49]. As it is obvious, the results clearly indicate that the proposed sensor is superior to the previously reported ones in the Nernstian slope and working pH range. In the detection limit and linearity range and response time, proposed sensor is not superior but is closed to the best previously reports.

4. CONCLUSION

In this work, 2-(4-methyl piperazine-1-yl methyl)-1-cyanocyclohexanone was synthesized and it was used in designing a potentiometric selective sensor for copper ions. The used ionophore can selectively complex with Cu^{2+} ions in the presence of considerable concentrations of common interfering ions. Applicable pH range from 3.5-8.0, fast response time about 10 s, low detection limit, and potentiometric selectivity coefficients of the proposed sensor make it a very good device to be used for the determinations of Cu^{2+} ions.

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