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Construction of a new Cu^{2+} coated wire ion selective electrode based on 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylidene amino)phenyl)disufanyl)phenylimino)methyl)-4-methoxyphenol Schiff base

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ABSTRACT

In this article a new coated platinum Cu^{2+} ion selective electrode based on 2-((2-(2-(2-(2-hydroxy-5-methoxybenzylideneamino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol Schiff base (L_1) as a new ionophore is described. This sensor has a wide linear range of concentration (1.2×10^{-7}–1.0×10^{-1} mol L^{-1}) and a low detection limit of 9.8×10^{-8} mol L^{-1} of $Cu(NO_3)_2$. It has a Nernstian response with slope of 29.54 ± 1.62 mV $decade^{-1}$ and it is applicable in the pH range of 4.0–6.0 without any divergence in potentioal. The coated electrode has a short response time of approximately 9 s and is stable at least for 3.5 months. The electrode shows a good selectivity for Cu^{2+} ion toward a wide variety of metal ions. The proposed sensor was successfully applied for the determination of Cu^{2+} ion in different real and environmental samples and as indicator electrode for potentiometric titration of Cu^{2+} ion with EDTA.

1. Introduction

Copper is an essential element in human body and plays an important role in various biological processes and has widespread occurrence in environmental samples. Large amount of Cu^{2+} ion can be tolerated by human beings, however, excessive dosage and long term exposure may cause irritation of the nose, mouth and eyes and it causes headache, stomach ache, dizziness, vomiting and diarrhea. Copper deficiency results in anemia while its accumulation resulting in Wilson disease [1]. Copper also has vital importance in biological [2,3], geochemical [4] and industrial systems [5]. In this regard various methods including flame atomic absorption spectroscopy (FAAS), inductively coupled plasma (ICP), voltammetry, coupling of these techniques with preconcentration methods [6–10] and ion selective electrode have been used for trace determination of Cu^{2+} ion. Among these methods ion selective electrodes have a wide spread use for the direct determination of ionic species in complex systems and direct potentiometric measurement of various ionic species in environmental, industrial and clinical samples [11–21]. In recent decades, many intensive studies have been reported on the design and synthesis of highly selective ionophores as sensory molecules for ISEs [22,23]. The development of miniaturized and micro sized ISE probes continues to be a "hot" area of research, because most commercial ISEs, with tip diameters of the order of 3–15 mm, are regarded as macro in size. One way to reduce the size of conventional ISEs is to remove the internal reference solution [24,25]. Coated wire ion selective electrodes (CWEs) using solid metals such as platinum, copper, or silver as the internal contact wires [26] have been found to be quite useful for many direct determinations if the electrodes are calibrated often [24]. The first report on CWEs was published by Cattrall and Freiser [27], since then a variety have been reported [14,28]. In this procedure electroactive species directly incorporated into a thin polymeric film coated directly on a metallic or graphite conductor have been shown to be very effective for a wide variety of inorganic and organic ions [29–34]. Electrodes of this sort has unique advantages including simplicity, low cost, durability, capability of reliable response in a wide concentration range for a wide variety of both organic and inorganic ions and suitable for measurements in small volumes of sample or for the desired in vivo applications. In comparison with most commercially available electrodes, these electrodes were readily prepared and had high sensitivities with a low detection limits [26,35].

The purpose of this work is the development of Cu^{2+} ion selective electrode based on plasticized PVC membranes containing L_1 with high selectivity toward Cu^{2+} ion as the membrane active ingredients coated on the surface of platinum wire electrode. The selectivity for a variety of ions and the effect of the membrane

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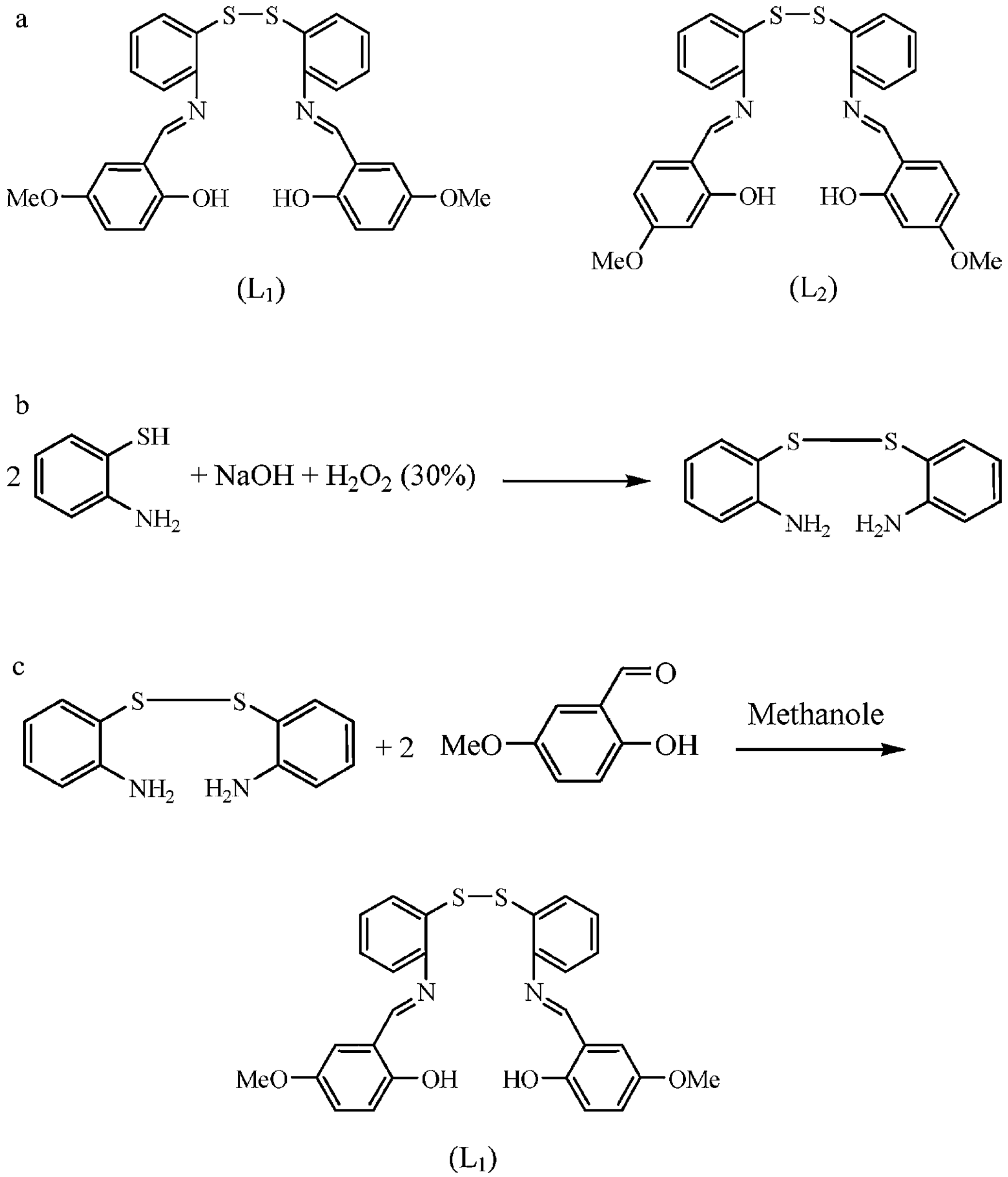

Fig. 1. Structure of ionophores (a), synthesis of diamine (b), and synthesis of ionophore 1 (L_1) (c).

matrix, ionophore, additive amount and pH on the potentiometric response properties of the proposed electrodes are investigated.

2. Experimental

2.1. Materials

Analytical-reagent grade diethyl phthalate (DEP), dibutyl sebacate (DBS), diethyl sebacate (DES), and *o*-nitrophenyl octyl ether (*o*-NPOE) were supplied from Fluka Co. (Buchs, Switzerland). Poly(vinylchloride) (PVC), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) were purchased from Merck Co. (Darmstadt, Germany). The ionophores, L_1 (ionophore I) and L_2 Schiff bases (ionophore II) (Fig. 1a), were synthesized in our laboratory. Chloride and nitrate salts of metal ions were provided either from Merck or Fluka and were used without further purification. All solutions were prepared from analytical reagents and triply distilled water. Typical procedure for synthesis of ionophores is explained in Section 2.2.

2.2. Synthesis of ionophores

2.2.1. Synthesis of diamine

5 g of NaOH was dissolved in a minimum amount of distilled water. 15.5 g of 2-aminophenol was added to the NaOH solution and stirred in an ice bath. Then 20 mL of H_2O_2 (30%, W/W) was added to the solution while stirring it for 2 h. The obtained yellow precipitate was washed with distilled water and recrystallized it from ethanol (Fig. 1b).

2.2.2. Synthesis of $S_2N_2O_2$ Schiff base ligand

The tetradentate Schiff base ligand was prepared by dissolving the appropriate amount of diamine and 5-methoxy-2-hydroxybenzaldehyde (5-methoxysalicylaldehyde) in methanol for synthesis of ionophore 1 (L_1), (or 4-methoxy-2-hydroxybenzaldehyde (4-mesthoxysalicylaldehyde) for synthesis of ionophore 2 (L_2)). The solution was stirred for 2 h at room temperature to give a light orange (L_1) or yellow (L_2) precipitate. The precipitate was filtered and washed with methanol then recrystallized it from dichloromethane/methanol mixture (Fig. 1c). Analytical characteristics for L_1: ^{1}H NMR $\delta = 3.75$ (s, 6H, O$-$CH$_3$), $\delta = 6.92$–7.89 (m, 14H), $\delta = 8.98$ (s, 2H, HC=N), $\delta = 12.04$ (s, 2H, OH). FT-IR (KBr cm^{-1}) ν_{max} 1614.3 (C=N), 1273.4 (C–O). GC–Mass 516 (27, L_1), 258 (83, ph(MeO)(OH)(HC=N)phS), 136 (100, ph(MeO)(OH)CH), 369 (17, ph(MeO)(OH)(HC=N)phS-Sph). UV–vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (L_1): 385 (11,541), 285 (17,847).

For L_2: ^{1}H NMR $\delta = 3.82$ (s, 6H, O$-$CH$_3$), $\delta = 6.52$–7.61 (m, 14H), $\delta = 8.93$ (s, 2H, HC=N), $\delta = 13.04$ (s, 2H, OH). FT-IR (KBr cm^{-1}) ν_{max} 1607.6 (C=N), 1244.0 (C–O). GC–Mass 516 (25, L_2), 258 (100, ph(MeO)(OH)(HC=N)phS), 136 (23, ph(MeO)(OH)CH), 291 (29, ph(MeO)(OH)(HC=N)phS-S). UV–vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (L_2): 350 (36,620), 292 (24,406).

2.3. *Spectrophotometric titration*

Standard stock solutions of ligand L_1 (1.0×10^{-3} mol L^{-1}) and the Cu^{2+} ion (2.0×10^{-3} mol L^{-1}) were prepared by dissolving exactly weighted amount of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with DMF. Working solutions were prepared by dilution of the stock solutions. Titration of the 2.6 mL (3.8×10^{-5} mol L^{-1}) of ligand was carried out by the addition of Cu^{2+} ion using a pre-calibrated micro-syringe at 25.0 °C in 0.05 mol L^{-1} TEAP [36]. The spectrum was recorded after each addition (Fig. 2).

2.4. *Apparatus and emf measurement*

All measurements of emf were made at 25 °C by a Metrohm pH/Ion meter, model 780 (Metrohm Co., Herisau, Switzerland) with a double junction Ag/AgCl, KCl (saturated) electrode as reference electrode in the cell assembly as follows:

Ag/AgCl||Cu^{2+}soln.|membrane|Ptwire

Activities were calculated in accordance with the Debye–Huckel procedure [37].

pH was measured by use of Metrohm pH lab. Absorbance measurements were carried out with a Jasco model V-570 spetrophotometer (Jasco Co., Hachioji, Tokiyo, Japan) and atomic absorption measurements were carried out by use of Varian SpectrAA model 220 (Varian Co., Walnut Creek, CA). ^{1}H NMR, FT-IR and GC–Mass spectroscopies were, respectively carried out with Bruker 250 MHz (Bruker Co., Ettlingen, Germany), Shimadzu FTIR-8300 and Shimadzu GCMS-QP1000EX spectrophotometers (Shimadzu Co., Tokiyo, Japan).

2.5. *Membrane preparation*

The schematic setup and general protocol for preparation of this sensing electrode used in this work was similar to our and some others previous studies [38–51] except that this electrode was a wire electrode coated with a composite of PVC and a suitable Cu^{2+} selective ionophore. The optimum composition was ionophore (6 mg), DES (61.1 mg), additive (2.4 mg) and PVC (30.5 mg). A total weight of 100 mg of these reagents was mixed and dissolved in a freshly dried distilled THF (1.0 mL) and the mixture was homogenized by use of ultrasound. Platinum wire was coated with this composite by dipping the wire five times into the mixture. After coating the membrane was air-dried for 24 h until a thin film was formed by using the technique as our previous works [24,26,51]. The electrode was finally conditioned for 60 min in 10^{-3} mol L^{-1} $Cu(NO_3)_2$ solution.

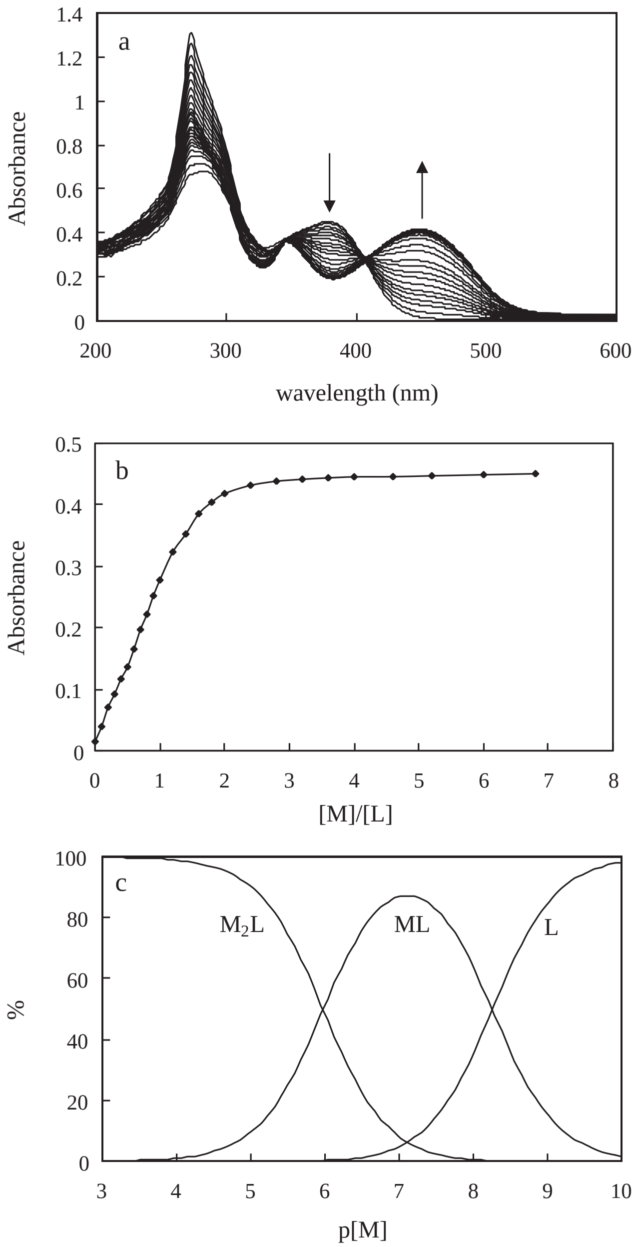

Fig. 2. UV–visible spectra for titration of L_1 (3.8×10^{-5} mol L^{-1}) with Cu^{2+} (2.00×10^{-3} mol L^{-1}) in DMF ($T = 25$ °C and $I = 0.05$ mol L^{-1}) (a), the molar ratio plot in λ_{max} of 450 nm (b) and the corresponding distribution curve (c).

2.6. *Preparation of real samples*

The applied procedure for the extraction of Cu^{2+} ion from tea and coffee samples is similar to that reported in the literature [52]. One gram of the dry tea or coffee sample (dried at 110 °C) was placed in a 50 mL beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a glass watch. The beaker was allowed to stand overnight, and the contents were heated on a hot plate (150 °C for 15 min). After cooling the sample, 8 mL of perchloric acid was added, and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was then removed and the acid was evaporated to dryness at 150 °C. The white residue was completely dissolved in 5 mL of 1 mol L^{-1} nitric acid and the solution was transferred to a 100 mL calibrated flask and neutralized with NaOH solution. Finally, 10 mL of a 0.1 mol L^{-1} lithium acetate/acetic acid buffer solution of pH

Table 1
Results obtained from Cu^{2+} ion selective electrodes of various membrane composition.

No	PVC[a]	Plasticizer[a]				Ligand[a]		Additive[a] (NaTPB)	Slope[c]	L.R.[b]	R^2	D.L.[d]
		DMS	DES	DBP	o-NPOE	L_1	L_2					
1	32.5	64.9	–	–	–	–	2.0	0.6	37.85	50–0.1	0.995	39
2	32.0	64.0	–	–	–	–	3.0	0.9	34.18	100–0.1	0.992	81
3	31.5	63.1	–	–	–	–	4.0	1.3	32.57	50–0.1	0.997	40
4	31.1	62.2	–	–	–	–	5.0	1.7	33.49	100–0.1	0.993	89
5	30.7	61.3	–	–	–	–	6.0	2.0	29.28	500–0.1	0.999	290
6	30.2	60.4	–	–	–	–	7.0	2.3	37.31	50–0.01	0.991	35
7	29.8	59.6	–	–	–	–	8.0	2.6	39.42	500–0.1	0.998	290
8	29.3	58.7	–	–	–	–	9.0	3.0	14.23	50–0.001	0.998	38
9	29.0	57.8	–	–	–	–	10.0	3.2	45.53	50–0.1	0.999	30
10	32.5	64.9	–	–	–	2.0	–	0.6	35.55	0.12–0.1	0.992	0.12
11	32.0	64.0	–	–	–	3.0	–	0.9	52.60	0.12–0.1	0.993	0.021
12	31.5	63.1	–	–	–	4.0	–	1.3	47.98	0.52–0.1	0.993	0.42
13	31.1	62.2	–	–	–	5.0	–	1.7	24.51	0.12–0.1	0.996	0.12
14	30.7	61.3	–	–	–	6.0	–	2.0	30.10	0.12–0.1	0.995	0.12
15	30.2	60.4	–	–	–	7.0	–	2.3	26.63	0.12–0.1	0.994	0.11
16	29.8	59.6	–	–	–	8.0	–	2.6	38.80	0.12–0.1	0.994	0.10
17	29.3	58.7	–	–	–	9.0	–	3.0	30.41	0.52–0.1	0.998	0.52
18	29.0	57.8	–	–	–	10.0	–	3.2	40.22	0.52–0.52	0.996	0.52
19	30.7	61.3	–	–	–	6.0	–	2.0	30.10	0.12–0.1	0.995	0.12
20	30.7	–	61.3	–	–	6.0	–	2.0	40.64	0.52–0.1	0.992	0.39
21	30.7	–	–	61.3	–	6.0	–	2.0	29.93	0.12–0.1	0.998	0.10
22	30.7	–	–		61.3	6.0	–	2.0	14.50	0.12–0.1	0.990	0.12
23	31.2	–	–	62.4	–	6.0	–	0.4	24.04	1.0–0.1	0.995	1.0
24	31.1	–	–	62.1	–	6.0	–	0.8	40.70	0.12–0.1	0.996	0.12
25	30.9	–	–	61.9	–	6.0	–	1.2	25.26	1.0–0.5	0.998	0.75
26	30.8	–	–	61.6	–	6.0	–	1.6	25.96	0.12–0.1	0.995	0.12
27	30.7	–	–	61.3	–	6.0	–	2.0	29.93	0.12–0.1	0.998	0.10
28	**30.5**	–	–	**61.1**	–	**6.0**	–	**2.4**	**29.54**	**0.12–0.1**	**0.999**	**0.098**
29	30.3	–	–	60.5	–	6.0	–	3.2	34.86	0.12–0.1	0.993	0.12
30	30.1	–	–	60.3	–	6.0	–	3.6	37.33	0.52–0.001	0.996	0.52
31	30.0	–	–	60.0	–	6.0	–	4.0	38.62	0.12–0.1	0.990	0.042
32	32.5	–	–	65.1	–	–	–	2.4	39.93	5000–0.1	0.994	2600
33	31.3	–	–	62.7	–	6.0	–	–	30.91	5.0–0.05	0.990	1.9
34	30.5	–	–	–	–	6.0	–	2.4	24.88	5.0–0.1	0.985	5.0

[a] mg.
[b] Linear range ($\mu mol\ L^{-1}$–$mol\ L^{-1}$)
[c] Slope (mV $decade^{-1}$ concentration)
[d] DL ($\mu mol\ L^{-1}$).

5.5 were added and the solution was diluted to the mark. Analysis of all water samples for determination of its Cu^{2+} ion content was carried out as follows: known amounts of concentrated HNO_3 was added to all water samples. After adjustment of pH to 2, the samples were allowed to stand for 1 h. Then appropriate volumes of samples were neutralized by addition of appropriative amounts of NaOH. Solutions were finally filtered and the content of Cu^{2+} ion was estimated by proposed electrode using standard addition method.

3. Results and discussion

3.1. Study of complexation between ionophore and analyte

It is known that the Schiff base ligands form very stable complexes with transition metal ions. The unique nature of *N*-donor Schiff bases is enhanced by the existence of a widely spread π-conjugation system [53]. In this context, the complexation of Cu^{2+} ion with L_1 in DMF solvent was investigated and the titration spectra, corresponding to mole ratio plot and fitted curve are depicted in Fig. 2 at 450 nm as λ_{max}. Observing this figure, the significant apparent changes in the spectrum of ligand, after addition of Cu^{2+} ion is due to that, the ligand has strong interaction with Cu^{2+} ion and is an efficient ionophore for construction of a sensor for this ion. Further more the spectrum data in 400–500 nm range was used for obtaining stoichiometry and stability constant of L_1 complexes with Cu^{2+} ion using HypSpec program as a new version of PHab program [54,55]. The best fitting was obtained for ML ($\varepsilon = 7.405 \times 10^3\ mol\ L^{-1}\ cm^{-1}$), M_2L ($\varepsilon = 1.162 \times 10^4\ mol\ L^{-1}\ cm^{-1}$) model. The obtained stability constants for ML and M_2L are 8.25 ± 0.10 and 5.97 ± 0.12, respectively. This result seems to be not originated from the backbone structure of ligands but mainly is from the use of ligand-*N*-donors upon the complexation.

3.2. Electrode response characteristics

Before any optimization the potential responses of platinum CWEs for individual solutions containing a selected cation were obtained and the results are shown in Fig. 3. As this figure exhibits this sensor has a better response to the Cu^{2+} ion than to the other cations. The Cu^{2+} ion coated platinum electrode with optimum composition showed a linear Nernstian response with a slope of 29.52 ± 0.25 mV $decade^{-1}$ over the range of 1.2×10^{-7}–$1.0 \times 10^{-2}\ mol\ L^{-1}$ for $Cu(NO_3)_2$ and a correlation coefficient of 0.998 ($n = 13$).

3.3. Optimization of membrane composition

Studies on the response characteristics of Cu^{2+} ISEs based on ionophores L_1 and L_2, show that ionophore L_1 has a better characteristics than the other with a good Nernstian response over a wide linear range (1.2×10^{-7}–$1.0 \times 10^{-1}\ mol\ L^{-1}$). The results are shown in Table 1. So L_1 was used to fabricate Cu^{2+} ion selective electrode.

Some important features of PVC composite such as the properties and amounts of the plasticizer are investigated as one of significant influence on sensitivity and selectivity of pro-

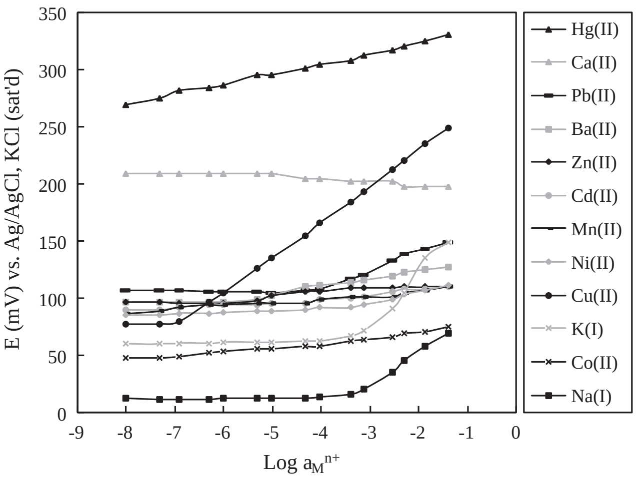

Fig. 3. The potential response of various cations at optimum conditions.

posed membrane. For this purpose several solvent mediators such as *o*-NPOE, DES, DMS, DBP and additive were tested and respective results are presented in Table 1. As it can be seen, among applied plasticizers DBP exhibits a better Nernstian slope (30.50 ± 0.25 mV decade^{-1}) than *o*-NPOE, DMS and DES (with slopes of 14.50, 31.14 and 39.78 mV decade^{-1}, respectively) therefore, DBP has been selected for the rest of experiments.

There are several reports on the effect of ionic additives in ISEs [13,42,43]. In this case, we examined the effect of NaTPB or anionic additive on the response of the Cu^{2+} ion selective electrode. As Table 1 shows, the obtained optimum amount of NaTPB was 2.40 mg and the experimental slope for this CWE at optimum condition of ligand became 29.54 ± 1.62 mV decade^{-1} with a correlation coefficient of 0.999 (No. 28).

The best selectivity and sensitivity depends significantly on the membrane compositions, in this report the proposed sensor was examined by different compositions and the effect of these membrane compositions are given in Table 1. It is apparent from the table that the response of the electrode coated with the composite containing no ligand (No. 32) has a super Nernstian slope of 39.93 mV decade^{-1} over a short range of concentration whereas at the optimum composition of ionophore (6.0 mg), DBP (61.1 mg), NaTPB (2.4 mg) and PVC (30.5 mg) the slope obtained was 29.54 ± 0.25 mV decade^{-1} in the concentration range of 1.2×10^{-7}–1.0×10^{-1} mol L^{-1} (No. 28). The electrode response in the absence of additive (No. 33) and/or plasticizer (No. 34) are far from Nernstian slope (super and near Nernstian, respectively). From this table it is clear that the detection limits and dynamic ranges for this CWE are not only influenced by additives, but also depend on the amount of the ionophore. The results obtained in this study indicated that the electrodes based on the L_1 and NaTPB show a high selectivity and sensitivity for Cu^{2+} ions.

3.4. Effect of pH

The pH response profile of the proposed electrode for 1.0×10^{-7}, 1.0×10^{-5}, 1.0×10^{-3} and 1.0×10^{-2} mol L^{-1} Cu^{2+} ion solutions was investigated over the pH range of 1.5–10.0, while each pH was adjusted by addition of HNO_3 and/or NaOH solutions. The obtained results are given in Fig. 4. As this figure shows the potential remains constant in the pH range of 4.0–6.0 that is chosen as the working pH range for the electrode. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Cu^{2+} ion in solution [56–58]. While, the increased potential observed at lower pH values either could be due to the response of the electrode to H^+ ions or may be is due to the protonation of ligand.

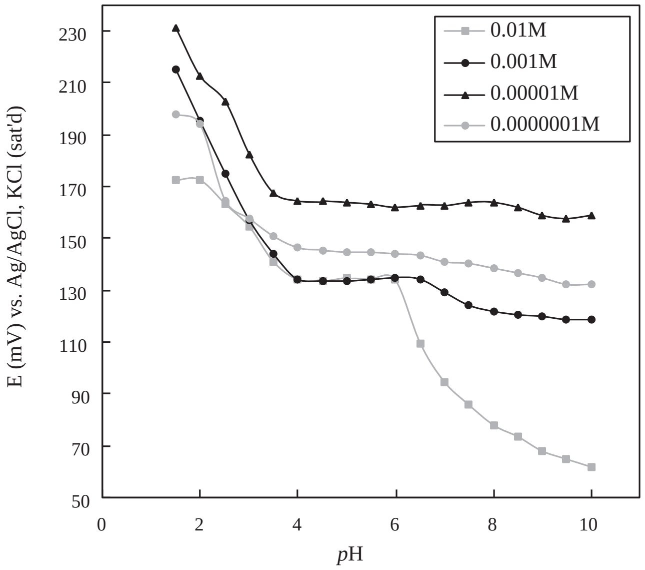

Fig. 4. Effect of pH on the response of the proposed electrode.

3.5. Effect of water miscible solvent on electrode potential

Ionophores in the membrane composition may be soluble in non-aqueous solvents, and reduce the stability (life time) and reproducibility of the electrode by leaching out of the membrane. Therefore investigation of the applicability of this membrane composition electrode in mixed (water/organic) solutions is necessary sometime. If the potential of the proposed CWE remains constant in such a solution therefore this electrode can be applied in the partially nonaqueous solutions for this purpose. For this reason the functioning of the sensor was also tested in partially non-aqueous media using a 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, and 100% ethanol–water mixture (v/v). It was observed that the membranes work satisfactorily up to a maximum of 20% ethanol content. It appears that 20% (v/v) of ethanol to water does not affect the characteristics of the membrane significantly. That is in this mixture, the working concentration range and the Nerstian slope remained unaltered. Above 20% ethanol mixture, the media properties affected the performance of the electrode, and results a non-Nernstian slope and affects working concentration range. Also, the membranes were destroyed by leaching of the ionophore from the PVC matrix. Hence, the electrode assembly can only be used in non-aqueous medium when its ethanol content is not more than 20% (Table 2).

Table 2
Effect of water miscible solvent on electrode potential.

Ethanol/water (%V/V)	Slope (mV decade^{-1} concentration)	R^2	L.R. (μmol L^{-1}–mol L^{-1})
5	31.02	0.997	0.12–0.1
10	30.73	0.992	0.12–0.1
15	29.78	0.992	0.12–0.1
20	29.40	0.993	0.12–0.1
25	24.21	0.990	1.0–0.1
30	22.76	0.992	1.0–0.1

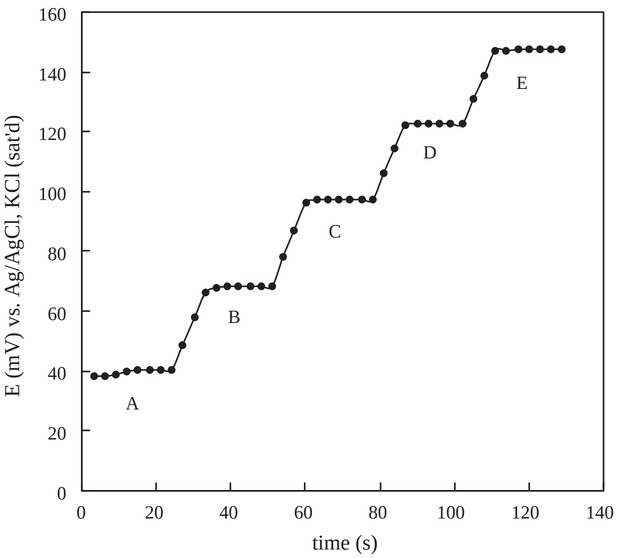

Fig. 5. Dynamic response time of platinum CWE based on L_1 at different concentration of Cu^{2+} ion: (A) 1.0×10^{-5} mol L^{-1}; (B) 1.0×10^{-4} mol L^{-1}; (C) 1.0×10^{-3} mol L^{-1}; (D) 1.0×10^{-2} mol L^{-1}; (E) 1.0×10^{-1} mol L^{-1}.

3.6. Detection limit, reproducibility and repeatability of the Cu^{2+} ion selective electrode

According to the IUPAC recommendation of 1976, the detection limit is defined by the cross-section of two extrapolated linear calibration curves [13]. The evaluated detection limit of the proposed electrode with respect to this recommendation was 9.8×10^{-8} mol L^{-1} of $Cu(NO_3)_2$. The reproducibility was investigated by preparing nine similar electrodes at optimum membrane composition then the slope of each electrode was determined and the average slope with standard deviation was 29.54 ± 1.62 mV decade^{-1}. This result shows that this electrode is sufficiently reproducible. In the repeatability study, the calibration curves of one electrode in five times were obtained during ten days, the calibration curves had been taken every other day. The average slope with standard deviation was 29.16 ± 0.79 mV decade^{-1}.

3.7. Response time and life time of the Cu^{2+} ion selective electrode

Dynamic response time is an important factor for an ion sensitive electrode. The response time of the Cu^{2+} ion selective electrode was evaluated by measuring the time required to achieve 90% of the steady potential for a Cu^{2+} ion solution. In this study, the practical response time was recorded by changing solutions with different low-to-high Cu^{2+} ion concentrations. The actual potential vs. time traces is shown in Fig. 5. As can be seen, in the whole concentration range, the electrode reaches the equilibrium response in a very short time (approx. 9 s). The measurement sequence was from the lower (1.0×10^{-5} mol L^{-1}) to the higher (1.0×10^{-1} mol L^{-1}) concentration.

3.8. Selectivity coefficients of Cu^{2+} ion selective electrode

Probably one of the most important characteristics of an ISE is its relative response to other ions present in solution, which expressed in terms of selectivity coefficients. The experimental selectivity coefficients depend on the activity and the method of their determination. Different methods of selectivity determination have found in the literature. In the present study, the selectivity coefficients were determined using three methods. Separate solution method (SSM) [13,59], mixed solution method (MSM) [60,46] and matched potential method (MPM) [44,45]. The Nicolskii coefficient is often determined by the so-called separate solution method by comparing two solutions, each containing a salt of the primary and interfering ion only. The selectivity coefficient, K_{IJ}^{SSM}, is determined by Eq. (1):

Table 3
Selectivity coefficient for Cu^{2+} ion in the presence of different ions, measured by SSM, FIM and MPM.

Interfering ion	Log K_{ij}		
	SSM	FIM	MPM
Cr^{3+}	−1.24	−1.35	−1.56
Fe^{3+}	−1.43	−1.50	−1.83
Ca^{2+}	−2.12	−2.13	−2.19
Co^{2+}	−1.40	−1.49	−1.55
Zn^{2+}	−3.20	−3.22	−3.25
Pb^{2+}	−3.16	−3.10	−3.18
Mn^{2+}	−2.92	−2.86	−3.02
Ba^{2+}	−1.06	−1.05	−1.20
Cd^{2+}	−2.32	−2.31	−2.46
Ni^{2+}	−1.23	−1.29	−1.61
Na^{+}	−1.21	−1.23	−1.23
K^{+}	−1.19	−1.21	−1.17

$$\ln K_{IJ}^{SSM} = \frac{Z_1 F\{E_2 - E_1\}}{RT} - \ln \alpha_I \left(1 - \frac{Z_I}{Z_J}\right) \qquad (1)$$

In Eq. (1) it is considered that $\alpha_I = \alpha_J$. E_1 and E_2 are the response of the electrode to main and interfering ion, respectively.

In the fixed interference method (FIM) which is a type of the mixed solution method (MSM), selectivity coefficients of the copper sensor were evaluated graphically with a fixed concentration of the interfering ions (M^{n+}) (1.0×10^{-3} mol L^{-1}) and different amounts of the Cu^{2+} ion; the results are shown in Table 3. The MSM based on the semi empirical Nikolskii–Eisenman equation is of questionable validity when ions of different charge are present; therefore the MPM was applied to these ions. The meaning of selectivity coefficients K_{IJ}^{FIM} determined with this method is intuitively convincing, because they clearly reflect what is observed with real-world sensors in relevant samples. The selectivity coefficient, K_{IJ}^{FIM}, is determined by Eq. (2):

$$K_{IJ}^{FIM} = \frac{\alpha_I(DL)}{\alpha_J(BG)^{Z_I/Z_J}} \qquad (2)$$

Matched potential method has two advantageous [46]. The first one is that when ions of unequal charges are involved, the MPM is recommended, as it gives practical K_{AB} values. Secondly, when interfering ions and/or the primary ion do not satisfy the Nernstian condition, the MPM is also recommended, even if the charges of the primary and interfering ions are equal. According to this method, the potentiometric selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution [45]. Thus, first the change in potential upon changing the primary ion activity is measured and then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, K_{AB}^{MPM}, is determined by Eq. (3):

$$\begin{gathered} K_{AB}^{MPM} = \frac{\Delta A}{\alpha_B} \\ \Delta A = \alpha'_A - \alpha_A \end{gathered} \qquad (3)$$

where α_A is initial primary ion activity and α'_A is the activity of A in the presence of interfering ion, α_B. It should be noted that the concentration of Cu^{2+} ion used as primary ion in this study was 1.0×10^{-5} mol L^{-1}. The resulting selectivity coefficient values thus obtained for the proposed Cu^{2+} ion sensor are given in Table 3.

Table 4
Results obtained by application of the Cu^{2+} ion selective electrode to real samples.

Sample	Proposed electrode	AAS method
Coffee	9.71 ± 0.08 μg/g	10.2 ± 0.03 μg/g
Black tea	46.70 ± 0.08 μg/g	47.3 ± 0.04 μg/g
Tap water	$1.19 \times 10^{-3} \pm 0.03 \times 10^{-3}$ mmol L^{-1}	$1.31 \times 10^{-3} \pm 0.01 \times 10^{-3}$ mmol L^{-1}
River water (Beshar)	$1.30 \times 10^{-3} \pm 0.05 \times 10^{-3}$ mmol L^{-1}	$1.34 \times 10^{-3} \pm 0.04 \times 10^{-3}$ mmol L^{-1}
Mineral water	$1.10 \times 10^{-3} \pm 0.04 \times 10^{-3}$ mmol L^{-1}	$1.09 \times 10^{-3} \pm 0.03 \times 10^{-3}$ mmol L^{-1}

Table 5
Comparing of various reported Cu^{2+} ISE with the present work.

Type	Concentration range (mol L^{-1})	Slope (mV decade^{-1})	Detection limit (mol L^{-1})	Ionophore name	Response time (*S*)	Ref.
PME	1.0×10^{-5}–2.0×10^{-1}	29.4 ± 0.5	8.0×10^{-6}	1,10-Phenanthroline sub-unit	15	[62]
PME	3.0×10^{-6}–5.0×10^{-2}	29.0 ± 1.0	1.0×10^{-6}	1,3-Dithiane,2-(4-methoxy phenyl)	10	[39]
ISE	9.77×10^{-7}–7.6×10^{-2}	30.0 ± 2.0	7.0×10^{-7}	(3,4-Dihydro-4,4,6-trimethyl-2(1H)-pyrimidine thione)	45	[63]
PME	6.0×10^{-8}–1.0×10^{-1}	29.1 ± 0.1	3.0×10^{-8}	Bis-2-thiophenal propanediamine	5	[64]
CWE	1.0×10^{-6}–1.0×10^{-1}	28.0 ± 2.0	–	5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene	15	[65]
CWE	1.0×10^{-6}–1.0×10^{-1}	28.2	5.0×10^{-7}	2-Quinolyl-2-phenylglyoxal-2-oxime(phenylglyoxal-alphamonoxime)	10–50	[66]
CWE	4.0×10^{-6}–1.0×10^{-1}	29.5	1.5 × 10−6	N,N′-Ethylene bis(*p*-tert-butyl salicylaldiminato)	15	[67]
CWE	1.0×10^{-5}–1.0×10^{-1}	28.1	3.0×10^{-6}	Thiosemicarbazone	10–50	[68]
CWE	3.3×10^{-6}–1.0×10^{-1}	29.0	1.0×10^{-6}	1,8-Bis(2-hydroxynaphthaldiminato)-3,6-dioxaoctane	10–15	[69]
CWE	8.7×10^{-7}–1.0×10^{-1}	29.5 ± 0.17	1.1×10^{-7}	N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide	6	[70]
CWE	$1.2 \times 10^{-7} \pm 1.0 \times 10^{-1}$	29.5 ± 1.6	9.8×10^{-8}	(Bis(2-(2-hydroxyl-5-methoxy benzyliden)benzene)disulfide)	9	Proposed electrode

As it can be seen all cations investigated would not significantly influence the selectivity.

3.9. *Analytical applications*

3.9.1. *Potentiometric titration*

The proposed electrode was also successfully used as an indicator electrode in conjunction with a Ag/AgCl reference electrode for the potentiometric titration of 25.0 mL of a 1.0×10^{-2} mol L^{-1} Cu^{2+} ion solution with a 1.0×10^{-1} mol L^{-1} EDTA at pH 5.0 (acetate buffer) and results are shown in Fig. 6. As it is seen, the titration plot obtained has not a sigmoid shape which may be due to the response of the membrane toward Na^{+} ions as available from disodium salt of EDTA [61]. However, the sharp break point was observed which corresponds to the stoichiometry of Cu^{2+}–EDTA complex and therefore, the proposed sensor could be used as an indicator electrode for the potentiometric determination of Cu^{2+} ion.

3.9.2. *Determination of Cu^{2+} ion in coffee, black tea, river, mineral and tap water*

The proposed electrode was found to work well under laboratory conditions. To assess the applicability of the proposed electrode for evaluating the Cu^{2+} ion in real samples, an attempt was made to determine Cu^{2+} ion in coffee (Nescafe), black tea (Ahmad), river (Beshar), mineral (Mineral 360) and tap waters. The Cu^{2+} ion concentration of the samples was determined using the proposed electrode by standard addition method and the results are summarized in Table 4. The Cu^{2+} ion content in the black tea obtained from measurements with electrode (46.7 ± 3.9 μg/g) was found to be in satisfactory agreement with those obtained by atomic absorption spectrometry (47.3 ± 4.5 μg/g).

The Cu^{2+} ion content in the coffee obtained from measurements with electrode (10.0 ± 2.8 μg/g) was also found to be in satisfactory agreement with that determined by atomic absorption spectrometry (10.2 ± 2.5 μg/g) (Table 4).

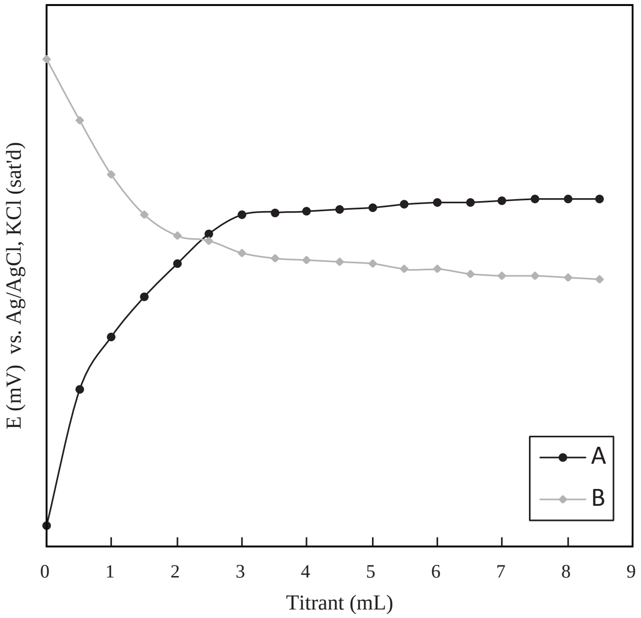

Fig. 6. Potentiometric titration curve of 25 mL of a (A) 1.0×10^{-2} mol L^{-1} Cu^{2+} ion solution with 1.0×10^{-1} mol L^{-1} EDTA and (B) 25 mL of a 1.0×10^{-2} mol L^{-1} EDTA solution with 1.0×10^{-1} mol L^{-1} Cu^{2+} ion, using the proposed sensor as an indicator electrode.

The electrode was successfully used for determination of Cu^{2+} ion in river (Beshar River in Yasuoj), mineral and tap water as matrixes. Use of the standard addition method for determination of Cu^{2+} ion by atomic-absorption spectroscopy again shows the applicability of the proposed electrode to water samples. Results are reported in Table 4.

3.10. Comparison of the proposed electrode with other Cu^{2+} ion selective electrodes

The characteristic responses of this and other-selective electrodes are listed in Table 5. From the results in this table, it can be concluded that, this electrode is comparable to previously reported electrodes in most cases. Furthermore in contrast to most of previous electrodes which are internal solution-ion selective electrodes (IS-ISEs) type, this one with miniaturized tip can easily be used in small sample volumes.

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