# Novel Copper(II)-Selective Membrane Electrode Based on a New Synthesized Schiff Base

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A PVC membrane electrode for copper(II) ion based on a recently synthesized Schiff base as a suitable ion carrier was constructed. The electrode exhibits a Nernstian slope of 28.3 ± 0.6 mV per decade of $Cu^{2+}$ over a wide concentration range of $7.0 \times 10^{-6}$-$2.6 \times 10^{-2}$ M with a detection limit of $5.0 \times 10^{-6}$ M in the pH range of 4.2-5.8. The response time is about 10s and it can be used for at least 1 month without any considerable divergence in potential. It was successfully applied as an indicator electrode in the potentiometric titration of copper ions.

**Keywords:** Copper(II) ion-selective electrode; PVC membrane; Potentiometry; 2-(2-Mercaptophenylnitrilomethylidyne)-phenol; Schiff Base.

## INTRODUCTION

Ion-selective electrodes (ISEs) are chemical sensors with the longest history and probably with the most frequent routine application. Polymeric membrane based ISEs are the most versatile ones and have been described for many different analytes.[1-2] Copper is an essential element and is also toxic at high concentration that its reactivity and biological uptake are strongly influenced by its free ion concentration. Potentiometric measurement with a copper selective electrode allows direct determination of free copper ion concentration in analytical samples. Due to the vital importance of copper in industry,[3] in many biological systems,[4] and in medicinal and environmental samples, researchers have attempted to develop sensors for copper determination with high selectivity and sensitivity.[5-10] For construction of these copper selective electrodes a variety of ion-carriers such as macrocyclic polyethers,[11] lariat crown ether,[12] acyclic neutral ionophores with dithiocarbamate groups,[13-14] dithioacetal,[15] and Schiff bases[16-17] have been used; however, most of these sensors suffer from the interfering effect of such cations as $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$, and $Ag^{+}$.

In this paper, 2-(2-mercaptophenylnitrilomethylidyne)-phenol, recently synthesized in our laboratories, was used as an ion carrier for construction of a copper(II)-poly(vinyl chloride) (PVC) membrane electrode. Optimal experimental conditions, selectivity over interferents, and sensing characteristics of poly(vinyl chloride) membranes are evaluated for potentiometric analysis toward copper ions.

## RESULTS AND DISCUSSION

Ionophores for use in sensors should have rapid exchange kinetics and adequate complex formation constants in the membrane. Also, they should be easily soluble in the membrane matrix and have a sufficient lipophilicity to prevent leaching from the membrane into the sample solution.[18] In preliminary experiments, 2-(2-mercaptophenylnitrilomethylidyne)-phenol was used as an ion carrier to prepare a PVC membrane ion selective electrode for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential responses of various ISEs based on 2-(2-mercaptophenylnitrilomethylidyne)-phenol were obtained separately for each ion and the results are shown in Fig. 1. As seen among the different cations, $Cu^{2+}$ had the most sensitive response and so seems to be suitably determined with the membrane electrode based on 2-(2-mercaptophenylnitrilomethylidyne)-phenol. It was reported that Schiff bases upon deprotonation form

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complex with $Cu^{2+}$, which act as charge carriers in the membrane matrix.[17] The existence of a donating sulfur atom as well as -N=C- group in this Schiff base was expected to both increase stability and selectivity of its copper complex over other metal ions, especially alkali, and alkaline earth cations.[17,19-20] The spectrophotometric studies in acetonitrile solution and mol ratio plot revealed that 2-(2-mercaptophenylnitrilomethylidyne)-phenol as a chelating agent can form a 1:2 (metal/ligand) complex with a $Cu^{2+}$ ion. Fig. 2 shows the absorption spectra of $Cu^{2+}$-2-(2-mercaptophenylnitrilomethylidyne)-phenol complex as a function of the ligand concentration. The spectrum reflects that the absorbance at about 410 nm increased, while the maximum at $\lambda = 347$ nm decreased slightly until a 1:2 metal/ligand mole ratio was reached.

It is well known that the sensitivity, linearity, and selectivity obtained for a given ionophore depends significantly on the membrane composition.[18] The optimization results of the membrane composition are shown in Table 1. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligands,[21] it was expected to play a key role in determining the ion-selective characteristics. It was found that o-NPOE acts superior with respect to other common plasticizers such as DBP, DMS, and BA in construction of proposed copper(II) ion-selective electrodes. The electrode based on o-NPOE as a plasticizer exhibits a nice Nernstian slope 28.3 mV per decade over a wide concentration range of $7.0 \times 10^{-6}$ - $2.6 \times 10^{-2}$ M.

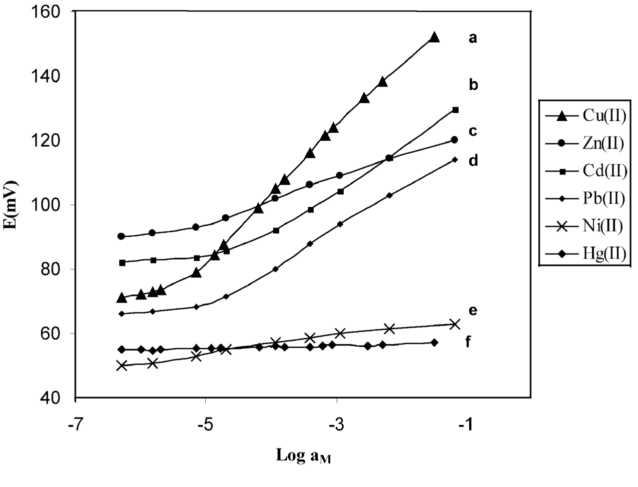


Fig. 1. Potential response of various ion-selective electrodes based on 2-(2-mercaptophenylnitrilomethylidyne)-phenol: (a) $Cu^{2+}$, (b) $Zn^{2+}$, (c) $Cd^{2+}$, (d) $Pb^{2+}$, (e) $Ni^{2+}$, (f) $Hg^{2+}$.

In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improve the potentiometric behavior of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity,[22] inducing permselectivity to some PVC membrane selective electrodes[23] and in some cases by catalyzing the kinetics at the sample-membrane interface.[24-25] The use of ionic additives such as different tetraphenylborate salts and their more lipophilic derivative, tetrakis(p-chlorophenyl)borate (K-TCPB) and also fatty acids such as oleic acid as lipophilic additives, have been widely reported in the preparation of different ion selective electrodes.[26-28]

The data given in Table 1 reveal that the nature and amount of additive influences the performance characteristics of the membrane sensor significantly. Addition of 8.3% NaTPB will increase the sensitivity of the electrode response considerably so that the selective electrode demonstrates a Nernstian behavior (No. 10 of Table 1). The effect of OA as an additive was examined on the potentiometric response of the copper electrode. The results show that OA is not a suitable lipophilic additive, in contrast to NaTPB. Therefore, NaTPB was used as an additive for further studies.

In general, the thickness and hardness of the membrane depend upon the amount of PVC used. At higher

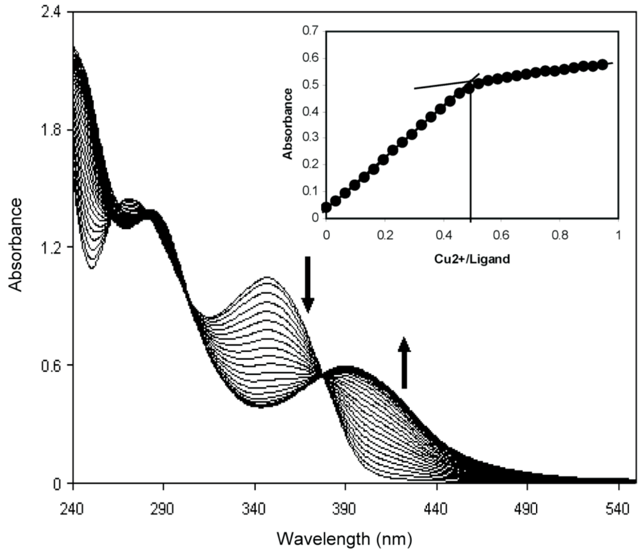


Fig. 2. UV-visible spectra of $1 \times 10^{-4}$ mol/L of 2-(2-mercaptophenylnitrilomethylidyne)-phenol in acetonitrile in the presence of various concentrations of $Cu^{2+}$ $1 \times 10^{-3}$ mol/L, Inset: mol ratio plot.

Table 1. Optimization of the membrane ingredients

| No. | PVC (mg) | o-NPOE (mg) | Ionophore (mg) | Additive (mg) | Slope (mV/decade) |
|---|---|---|---|---|---|
| 1 | 33.0 | 66.0 | 1.0 | -------- | 10.0 |
| 2 | 32.2 | 64.4 | 3.4 | -------- | 13.3 |
| 3 | 32.1 | 64.1 | 3.8 | -------- | 11.0 |
| 4 | 29.8 | 59.6 | 3.4 | 7.2 OA | 20.0 |
| 5 | 29.3 | 58.7 | 3.4 | 8.6 OA | 23.0 |
| 6 | 28.9 | 57.7 | 3.4 | 10.0 OA | 22.0 |
| 7 | 30.2 | 60.5 | 1.0 | 8.3 NaTPB | 19.5 |
| 8 | 30.0 | 59.9 | 1.8 | 8.3 NaTPB | 21.9 |
| 9 | 29.7 | 59.6 | 2.4 | 8.3 NaTPB | 23.1 |
| 10 | 29.4 | 58.9 | 3.4 | 8.3 NaTPB | 28.3 |
| 11 | 31.5 | 63.0 | 3.4 | 2.2 NaTPB | 14.2 |
| 12 | 30.8 | 61.5 | 3.4 | 4.3 NaTPB | 16.4 |
| 13 | 29.6 | 59.2 | 3.4 | 7.8 NaTPB | 23.2 |
| 14 | 29.3 | 58.7 | 3.4 | 8.6 NaTPB | 22.0 |
| 15 | 29.3 | 58.7 | 3.4 | 6.0 NaTPB + 2.6 OA | 18.0 |
| 16 | 30.5 | 61.2 | -------- | 8.3 NaTPB | 4.0 |
| 17 | 30.5 | 60.9 | -------- | 8.6 OA | ~0 |

PVC content, the membrane becomes too dense and results in increased resistance. At lower PVC content, the membrane becomes mechanically weak and swells up easily in aqueous solution. The o-NPOE/PVC ratios of 1.5-2.5 were examined. The membrane prepared with a o-NPOE/PVC ratio of ~2 was found to have the highest sensitivity and the widest linear range.

The effect of amount of ionophore was investigated, and 3.4 mg of ionophore was chosen as the optimum amount of ionophore in the PVC membrane. It was reported that the high amount of ionophore, however, resulted in some decreases in the response of the electrode, most probably due to some inhomogeneities and possible saturation of the membrane.[29] The results that were obtained indicate that the best sensitivity and linear range obtained for a membrane (No. 10 of Table 1), with PVC/o-NPOE/Ionophore/NaTPB of 29.4 mg:58.9 mg:3.4 mg:8.3 mg.

The proposed sensor was examined at various concentrations of inner reference $Cu(NO_3)_2$ solution in the range of $1.0 \times 10^{-1}$-$1.0 \times 10^{-3}$ M. The results showed that variation of the concentration of the internal solution does not cause any significant difference in the corresponding potential response, except for an expected change in the intercept of the resulting Nernstian plots. A $1.0 \times 10^{-3}$ M concentration of the reference solution was found quite appropriate for smooth functioning of the electrode membrane. The optimum conditioning time of the membrane electrode is 20 h. Afterward it then generates stable potentials when placed in contact with $Cu^{2+}$ solutions.

For analytical applications, the response time of a membrane sensor is an important factor. The static response time of the electrode, tested by measuring the average required to achieve a potential within ± 1 mV of the final steady-state potential upon successive immersion of a series of $Cu^{2+}$ ion, each having a tenfold difference in concentration, was within 10s for $Cu^{2+}$ concentrations $< 1.0 \times 10^{-3}$ M. The potential stayed constant for about 3 min, after which a very low divergence within the resolution of the mV was observed. Reproducibility of the electrode was examined by using six similarly constructed electrodes under the optimum conditions. The results showed good reproducibility for the proposed electrode. For instance, the slopes observed were 28.3 ± 0.6 mV per decade. The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions and calculating the response slope. The slope of the electrode responses was reproducible over a period of at least 1 month. Therefore the proposed electrode can be used for 1 month without a considerable change in its response characteristics towards $Cu^{2+}$.

The influence of pH for $1.0 \times 10^{-4}$ M $Cu^{2+}$ on the potential response of the membrane sensor was tested in the pH range 1-9, and the results are shown in Fig. 3. As seen, the potential remained constant from pH 4.2-5.8. A substantial increasing trend in the potential at low pH may be due to the interference from the hydrogen ions, which are greater at low pH in comparison to the $Cu^{2+}$ ion. At higher pH, turbidity was observed and activity of the $Cu^{2+}$ ion was decreased due to the formation of some hydroxyl complexes of $Cu^{2+}$ ion in solution.

The potential response of the optimized electrode to varying concentrations of $Cu^{2+}$ ions was examined. The calibration plot is shown in Fig. 4, which indicates a linear range of $7.0 \times 10^{-6}$-$2.6 \times 10^{-2}$ M with a Nernstian slope of $28.3 \pm 0.6$ mV per decade of $Cu^{2+}$ activity. The practical limit of detection was $5.0 \times 10^{-6}$ M as determined from the intersection of the two extrapolated segments of the calibration graph based on the recommended procedure by IUPAC.[30]

The most important characteristics of any ion sensitive sensor is its response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficient. Potentiometric selectivity coefficients ($K_{Cu^{2+},M}$), describing the preference by the membrane for an interfering ion $M^{n+}$ relative to $Cu^{2+}$, were determined by the matched potential method (MPM).[31] In this method, the selectivity coefficient is defined by the ratio of the activity of primary ion relative to an interfering ion when they generate identical potentials in the same reference solution. The characteristics of the matched potential method are: (1) The charge number of the primary and interfering ions does not need to be taken into consideration, and (2) Nernstian responses are not assumed either to the primary or interfering ions. The characteristics lead to the following advantages: (1) The power-term problem for ions of unequal charge disappears, and (2) This method is widely applicable, even to non-Nernstian interfering ions.[32] The resulting values are summarized in Table 2. As can be seen, for most of the diverse ions used, the selectivity coefficients are in the order of $10^{-3}$ or smaller, which seems to indicate that these metal ions show negligible interference with this sensor and will not disturb the functioning of the $Cu^{2+}$ ion-selective membrane electrode significantly. Moreover a comparison between the selectivity coefficients of the proposed electrode with those previously reported for the copper reveals that the proposed electrode shows somewhat similar in some cases, and superior in most cases, selectivity behavior to foreign ions.

The applicability of the proposed sensor was checked by its use as an indicator electrode for the titration of 20 mL $5.0 \times 10^{-3}$ M $Cu^{2+}$ solution with 0.01 M EDTA and the result is shown in Fig. 5. A very good inflection point, showing perfect stoichiometry, is observed in the titration plot. As seen, the amount of copper ion in solution can be accurately determined with the electrode. Also the performance of the sensor system was investigated in partially non-aqueous medium. The membrane was tested in 25% (V/V) content of ethanol. In this condition the slope and working concen-

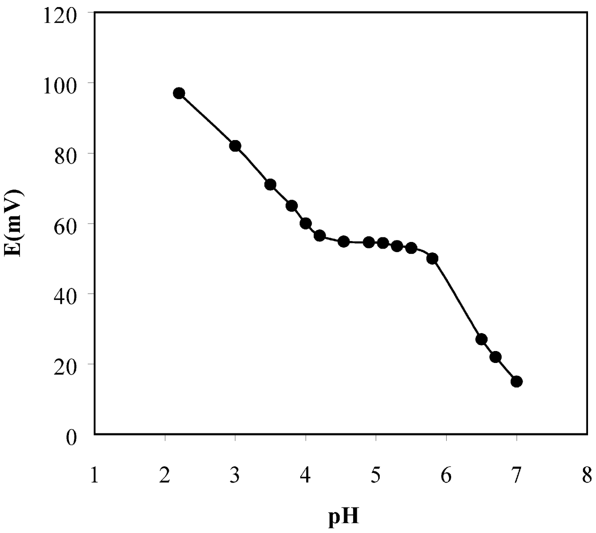


Fig. 3. The effect of pH on the response of the proposed $Cu^{2+}$-selective membrane electrode.

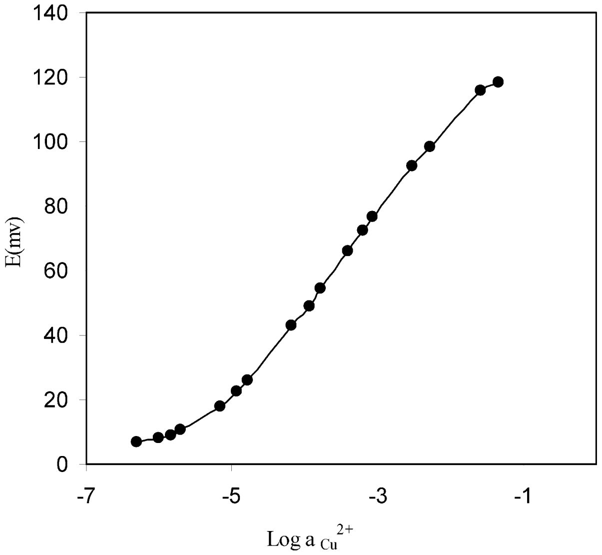


Fig. 4. Calibration plot for the proposed $Cu^{2+}$-selective electrode. Membrane ingredients: 29.4% PVC, 58.9% o-NPOE, and 3.4% ionophore and 8.3 NaTPB.

Table 2. Selectivity coefficients of various interfering ions for the proposed $Cu^{2+}$ selective electrode

| Cation | Log k | Ref. [11] | Ref. [15] | Ref. [17] |
|---|---|---|---|---|
| $Pb^{2+}$ | -2.2 | -2.69 | -3.28 | -------- |
| $Ce^{3+}$ | -2.5 | -2.44 | -------- | -1.08 |
| $Co^{2+}$ | < -4.0 | -3.42 | -2.52 | -1.10 |
| $Zn^{2+}$ | -2.1 | -2.85 | -2.88 | -1.09 |
| $Cd^{2+}$ | -2.4 | -3.39 | -3.04 | -1.09 |
| $Sr^{2+}$ | < -4.0 | -2.82 | --------- | -1.09 |
| $Hg^{2+}$ | -2.3 | -3.13 | -1.58 | -0.35 |
| $Mn^{2+}$ | < -4.0 | -------- | -2.87 | --------- |
| $Ni^{2+}$ | < -4.0 | -3.18 | -2.61 | -1.12 |
| $Ag^{+}$ | -2.0 | -2.13 | -0.10 | -0.27 |
| $Na^{+}$ | < -4.0 | -3.55 | -2.82 | -1.07 |
| $Fe^{3+}$ | -3.5 | -3.49 | -------- | -1.14 |
| $Al^{3+}$ | -3.7 | -3.74 | -------- | -------- |
| $NH_4^{+}$ | < -4.0 | -------- | -------- | -------- |
| $Ba^{2+}$ | -2.9 | -------- | -3.65 | -1.25 |
| $Mg^{2+}$ | < -4.0 | -3.53 | -3.10 | -1.21 |
| $La^{3+}$ | -3.0 | -1.62 | -------- | -------- |
| $Cs^{+}$ | < -4.0 | -------- | -2.41 | -1.22 |
| $Ca^{2+}$ | -3.0 | -------- | -3.25 | -1.20 |
| $K^{+}$ | < -4.0 | -------- | -1.97 | -1.22 |
| $Li^{+}$ | -2.7 | -------- | -3.10 | -2.35 |
| $Tl^{+}$ | -------- | -------- | -------- | -1.11 |

tration range of the electrode decreased and the results show that the electrode can't be used in a non-aqueous medium.

## EXPERIMENTAL

### Reagents

Sodium tetraphenylborate (NaTPB), high relative molecular weight poly(vinyl chloride) (PVC), tetrahydrofurane (THF), o-nitrophenyloctyl ether (o-NPOE), dibutyl phthalate (DBP), benzyl acetate (BA), dimethylsebacate (DMS), and oleic acid (OA), were purchased from Merck and used as received. The nitrate salts of all cations were used (all from Merck). Schiff base (Scheme I) was synthesized and purified as described elsewhere;[26] triply distilled deionized water was used throughout.

### Synthesis of ionophore

The 2-aminothiophenol was reacted with salicylaldehyde in methanol to give Schiff base as crystals in 85-99% yields (Scheme I). A solution of amine (0.01 mole) in methanol (15 mL) was added to a stirring solution of salicylaldehyde (0.01 mole) in methanol (10 mL). The reaction mixture was refluxed for about 1.5 hours. After the reaction was completed the mixture was cooled and the resulting precipitate was filtered off and washed with cold methanol. The product was recrystallized from an appropriate solvent for further purification. The structure of this compound was confirmed by spectroscopic data.

### 2-(2-Mercaptophenylnitrilomethylidyne)-phenol

Yellow solid; yield 90%, m.p = 123-125 °C, $R_f = 0.52$ (N-hexane-ethyl acetate/955); IR (KBr), 645 (m), 690 (m),

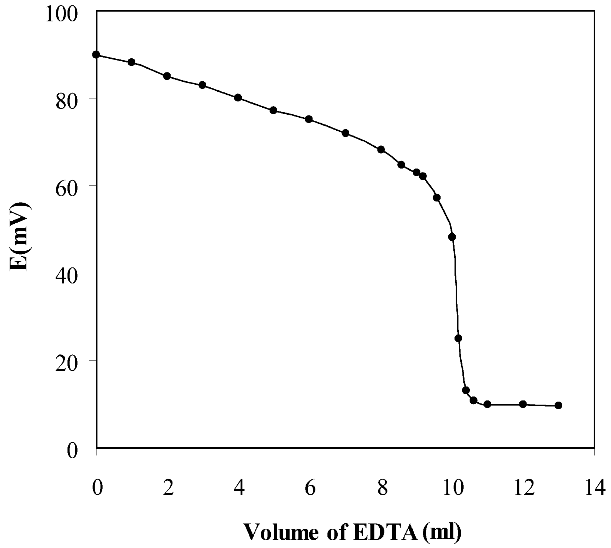
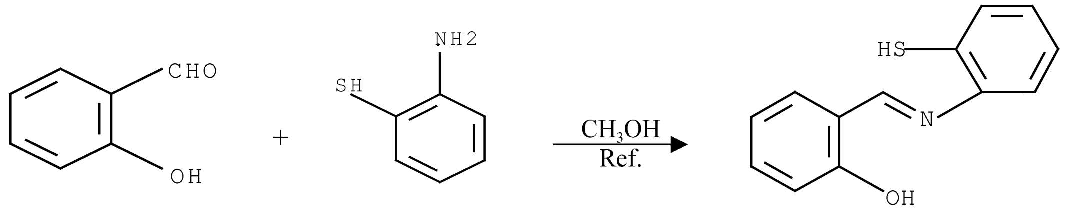


Fig. 5. Titration curve of 20 mL, 5.0 × $10^{-3}$ M of $Cu^{2+}$ solution with 0.01 M EDTA using the proposed sensor as an indicator electrode.

**Scheme I**



715 (s), 750 (vs), 780 (s), 818 (m), 845 (m), 910 (s), 975 (s), 1035 (s), 1050 (m), 1150 (s), 1180 (s), 1220 (s), 1280 (vs), 1365 (s), 1390 (br, m), 1460 (s), 1485 (s), 1560 (s), 1580 (m), 1615 (vs), 2990 (w), 3050 (m), 3410 (br, m) $cm^{-1}$, UV ($CHCl_3$); $\lambda_{max}$ ($\varepsilon$), 247 (22330), 271 (25600), 349 (20232) nm.

### Preparation of PVC membrane

The general procedure for preparing the PVC membrane was to mix 30.4 mg powdered PVC, 3.4 mg Schiff base, and 8.3 mg NaTPB with 58 mg o-NPOE as solvent mediator. The mixture was then thoroughly dissolved in 2 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was slowly evaporated until an oily concentrated mixture was obtained. A polyethylene tube of 5 mm i.d. was dipped into the mixture for about 5s so that a non-transparent membrane of about 0.3 mm thickness was formed. After removing the tube from the mixture it was kept at room temperature for about 3 h. Then it was filled with an internal filling solution of $1.0 \times 10^{-3}$ M $Cu(NO_3)_2$. The electrode was finally conditioned for 20 h by soaking in a $1.0 \times 10^{-3}$ M copper nitrate. A silver/silver chloride coated wire was used as an internal reference electrode.

### Electrode potential measurement

All emf measurements were carried out with the following cell assembly:

Ag, AgCl, | $1.0 \times 10^{-2}$ M KCl, $1.0 \times 10^{-3}$ M $Cu(NO_3)_2$ | PVC membrane |test solution | Hg, $Hg_2Cl_2$, KCl (saturated).

A HIOKI digital hitester (model 3256-01) as a potentiometer was used for potential measurement at 25 °C. The emf observations were made versus a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with a potassium nitrate solution. A Corning 130-pH meter was used for pH measurement at 25 °C.

## CONCLUSION

A new sensitive and selective membrane electrode for $Cu^{2+}$ ion based on a new synthesized Schiff base as a novel ionophore, o-NPOE as the plasticizer, and NaTPB as the anion excluder in a PVC matrix in the ratios 3.4:58.9: 8.3:29.4 (w/w%) can be used to determine $Cu^{2+}$ in the concentration range of $7.0 \times 10^{-6}$-$2.6 \times 10^{-2}$ M with a Nernstian slope of $28.3 \pm 0.6$ mV per decade. The functional pH range is 4.2-5.8. The selectivity coefficients for all cations are significantly low. The membrane showed poor response for all cations as often observed with copper electrodes. The proposed sensor exhibits a fast response time of 10s, and it is easy to prepare and use. It was successfully applied as a novel indicator electrode in potentiometric titration of copper ion.

## ACKNOWLEDGEMENT

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