

Full Paper

Copper(II)–Selective potentiometric sensor based on *Bis*(2-chlorobenzaldehyde)phenyl disulphide diimine in PVC Matrix

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Abstract- An attempt has been made to develop a highly selective copper ion selective electrode based on a PVC based sensor using Bis(2-chlorobenzaldehyde)phenyl disulphide diimine as ionophore with 61% NPOE in presence of 33.5% PVC, 0.5% dithio ligand and 5% STPB as an anion excluder. The sensor exhibits a near Nernstian potential response of 29 ± 1 mV/decade. Over a wide concentration range of (5.0×10^{-6} to 5.0×10^{-2} mol/L) with a detection limit of 3.1×10^{-6} M between pH=4-7 with a fast response time of 5s. The selectivity coefficient values, as determined by matched potential method indicate excellent selectivity for Cu^{2+} over a large number of ions. The proposed sensor exhibit an adequate shelf time (3 months) with good reproducibility. The quantification of Cu^{2+} in waste water of copper wire manufacturing factory was successfully achieved using the proposed sensor.

Keywords: Schiff's base, PVC based Ionophore, copper(II), sensor

1. INTRODUCTION

Amongst the various analytical techniques available, use of ion selective membrane electrode is well establish routine analytical techniques. Good ion selective electrode possesses many advantages over the traditional method of analysis as they provide accurate, reproducible, fast and often selective determination of various ionic species. Because of these merits, the use of ISE's is increasing day by day in medicinal, environmental, agricultural and industrial field. Due to the vital importance of copper in industry [1] and in many biological system [2-3], there is still an urgent need for a better copper selective sensor for potentiometric monitoring of copper in different industrial, medicinal and environmental sample. Thus many cyclic and cyclic macromolecule have been suggested as electro active ionophores e.g. non-macrocyclic compounds [4-9], macrocyclic molecule compounds [10], polyamine [11] and metalloporphyrin [12]. In present study, we report Cu^{2+} ISE based on Bis(2-chlorobenzaldehyde)phenyl disulphide diimine as an ionophore ,which has been proved to be a superior electrode compared to some of the electrode reported earlier in terms of wide concentration range , better response time and longer life span. The Schiff base containing S-S (dithio moiety) ligand was used as a potential neutral carrier for the preparation of PVC membrane ion selective electrode for a variety of metal ion, including alkali, alkaline earth metal, transition and heavy metal ions.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

All the reagents and chemicals used were of analytical grade. High molecular PVC powder diamines were purchased from Sigma Aldrich. STPB and NPOE were used from Merck. Triply distilled water was used throughout. Ethanol was refluxed and distilled over lime before use

2.2. Synthesis of Electroactive Material

Electroactive material was synthesized by the method as reported earlier [13]. To a vigorously stirred solution of Bis(2-aminophenyl)disulphide in a dried ethanol (40mL), 2-chlorobenzaldehyde (1.9mmol) was added. The yellow mixture was stirred at room temperature for 1-4h. The precipitated product was collected by filtration, washed thoroughly with ethanol (10mL) and dried in vacuo over P_4O_{10} (Figure 1).

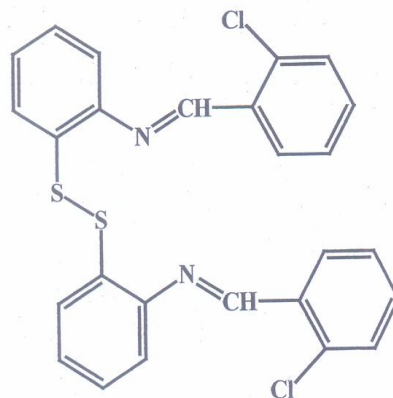


Figure 1. Structure of the ionophore

2.3. Electrode preparation

The solution of PVC membrane was prepared by thorough mixing of ionophore (Schiff base ligand) (0.5%), NPOE (66%) and PVC (33.5%) and STPB (5%) in THF. The resulting solution was poured into a glass mould and THF was allowed to evaporate off at room temperature for 24 h. A flexible membrane of the thickness of 0.2-0.4 mm was obtained. The disc of 6 mm diameter was cut and pasted onto the glass tube with PVC glue and conditioned with AgNO_3 solution of 0.01M for 2-3 days. The ratio of member constituents, time of contact and concentration of equilibrating solution were properly adjusted to obtain the best potential response.

2.4. Potential Measurements

The membrane was equilibrated with a 0.01M $\text{Cu}(\text{NO}_3)_2$ solution for 3 days and the potential across the membrane was measured by setting up the following cell assembly.

External 0.01 mol/L $\text{Cu}(\text{NO}_3)_2$ PVC Test Internal SCE Membrane Solution.

All the potential measurements were made by using a digital pH meter, potentiometer in conjunction with SCE as reference electrode.

2.5. Determination of Copper in Sample [15]

0.05-0.1 g of sample was dissolved in 20- 40 mL of HCl on a water bath and then 2-3 mL of 30% hydrogen peroxide was added. The excess of peroxide was decomposed by heating the solution on a water bath and mixture was cooled and filtered through the filter paper. The filtered mixture was diluted to 500 mL with distilled water in calibrated flask.

3. RESULTS AND DISCUSSION

The Schiff's bases derived from salicylaldehyde polydentate ligand are known to form very stable complex with transition metal ions [16-20]. Schiff base ligand should have highly selectivity for Cu^{2+} over other metal ions. They should have rapid exchange kinetics and sufficiently lipophilic to prevent the leaching of the ligand into the aqueous solution. The ligand is insoluble in water. Due to its similarity with biological systems [21-22], its complexation behavior with heavy transition metal ion such as Ag^+ , Hg^{2+} , and Cu^{2+} has been particularly investigated. The ionophore was used as neutral carrier to prepare membrane ISE for a wide variety of metal ions, including alkali, alkaline, heavy transition metal ions. The potential response of the resulting electrode is shown in Figure 2.

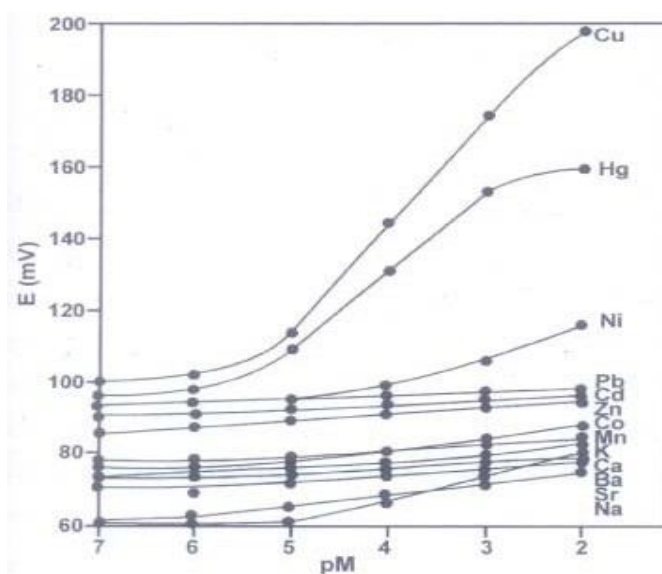


Figure 2 Potential response of various bivalent metal ion selective electrode based on dithio Schiff base ligands

(Membrane ingredients are 33.5% PVC, 66% NPOE, 5% STPB, 0.5% dithio ligands)

As can be observed, this ISE with such a good response can be suitable electrode for Cu^{2+} determination. Hg^{2+} and Ni^{2+} ions are expected to be the most interfering ions with this electrode

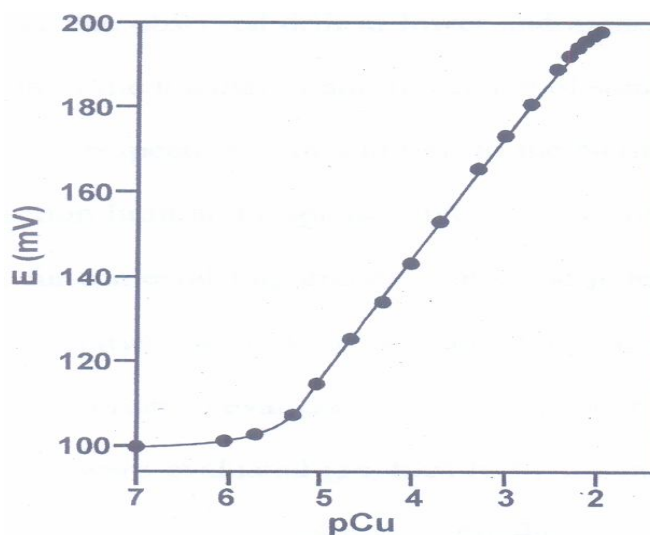


Figure 3 Calibration graph for the Cu^{2+} sensor

It is well known that electrode response for a specific metal ion depends on the amount and the nature of electrode components. Among the plasticizers commonly used in the preparation of ISE [23-30], NPOE was found to give the best selectivity and sensitivity of the membrane sensor. The optimum relative amount of PVC, NPOE, Schiff base, STPB as additive, for the construction of Cu^{2+} ISE was investigated and results are summarized in Table 1.

Table 1. Optimization of membrane ingredients

COMPOSITION						
No.	PVC	NPOE	Dithio Response	STPB	Slope (mV/Decade)	Interval of linear response (mol L^{-1})
1	34.6	64.4	1.0	-	6 ± 2	$1.0 \times 10^{-3} - 5.0 \times 10^{-3}$
2	34.5	60.8	1.0	1.7	12 ± 2	$1.0 \times 10^{-5} - 5.0 \times 10^{-3}$
3	34.0	61.8	1.0	3.2	23 ± 2	$5.0 \times 10^{-6} - 5.0 \times 10^{-3}$
4	33.4	60.6	1.0	5.0	27 ± 1	$1.0 \times 10^{-5} - 5.0 \times 10^{-3}$
5	31.0	62.5	1.0	5.0	25 ± 1	$1.0 \times 10^{-5} - 5.0 \times 10^{-3}$
6	33.5	61.0	0.5	5.0	29 ± 1	$5.0 \times 10^{-6} - 5.0 \times 10^{-2}$
7	35.1	58.5	1.0	5.3	21 ± 1	$1.0 \times 10^{-5} - 5.0 \times 10^{-3}$
8	31.7	57.7	1.0	9.6	19 ± 2	$1.0 \times 10^{-5} - 5.0 \times 10^{-3}$

It was found that use of 5% STPB resulted in a Nernstian behavior over a wide concentration range. The presence of such lipophilic ionic species, not only reduces ohmic resistance [31-32], but also catalyzes the exchange kinetics at the sample membrane interface. 0.5% of Schiff base containing S-S moiety was chosen as optimum amount of ionophore in the PVC membrane. The results indicate that best sensitivity and linear range is obtained for membrane - 6 with PVC/ NPOE/ Schiff base/ STPB of 33.5%, 61.0%, 0.5%, 5.0%.

The proposed membrane electrode was also examined with different concentration of inner reference solution from 1.0×10^{-2} to 1.0×10^{-4} mol/L. Functioning of the membrane sensor with reference solution of various $\text{Cu}(\text{NO}_3)_2$ concentration was found to cause no significant difference in the corresponding potential response. A 1.0×10^{-3} mol/L concentration of reference solution is quite appropriate for smooth functioning of the membrane electrode system. The optimum equilibration time for the membrane electrode is 24h after which a stable potential was generated in contact with the copper solution (Figure 3).

Electrode represented Nernstian slope of 29.8 ± 0.3 mV/decade over a wide concentration range with a detection limit, as determined from the intersection of the two extrapolated segment of the calibration curve, 3.1×10^{-6} mol/L. The membrane electrode was found to have a very fast potential response. The static response time is [33] is only about 5s over the entire concentration range. The potential stay constant for more than 5 min. and standard deviation of 10 replicate measurements was ± 0.3 mV. The membrane electrode could be used for at least 3 months without any measurable divergence.

The pH dependence of the potential of the electrode is shown in Figure 4. The pH adjustments in solution were made with nitric acid or sodium hydroxide solution. The response of the electrode is hardly affected by the change in pH in the range of 4.0–7.0. The observed drift at lower and higher pH value could be due the protonation of some hydroxyl complexes in Cu^{2+} solution.

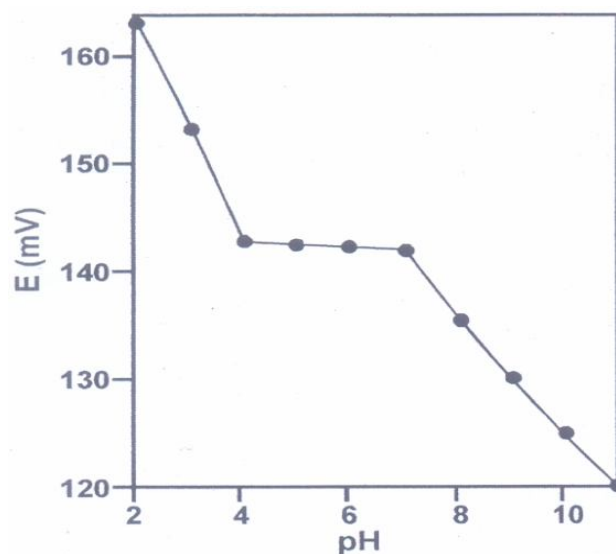


Figure 4 Effect of pH of the test solution on the potential response of Cu^{2+} ISE

The potentiometric selectivity coefficients of the polymer membrane electrode, as one of the most important characteristic, are defined by its relative response for the primary ion over

the other ion present in the solution. In this work, potentiometric selectivity coefficients were determined graphically by MPM [34]. The resulting values are summarized in Table 2.

Table 2. Selectivity coefficients of various interfering ions

Interfering ions	Selectivity coefficients
Na ⁺	4.6×10^{-2}
K ⁺	1.3×10^{-4}
Mg ²⁺	9.3×10^{-4}
Ca ²⁺	1.0×10^{-3}
Sr ²⁺	8.1×10^{-4}
Ba ²⁺	7.2×10^{-4}
Mn ²⁺	5.1×10^{-3}
Co ²⁺	7.4×10^{-3}
Ni ²⁺	3.0×10^{-2}
Zn ²⁺	8.0×10^{-3}
Pb ²⁺	4.1×10^{-3}
Cd ²⁺	8.2×10^{-3}
Hg ²⁺	6.4×10^{-2}

As can be seen, for most of the diverse ion used selectivity coefficient are in the order of 10^{-3} or smaller, which seems the disturbance produced by these metal ions in the functioning of Cu²⁺ ion selective electrode is negligible. It is interesting to note that proposed selectivity electrode results in selectivity coefficient superior to those reported for other Cu²⁺ ion selective electrode including CuS-Ag₂S electrode especially for interfering ions [35-37] such as Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Hg²⁺.

The proposed electrode was found to work well under laboratory conditions. It was successfully applied to the determination of copper in the sample of local river canal taken from the nearby copper wire manufacturing factory. With the use of membrane sensor calibration curve, the copper contents in the sample solution obtained from the triplicate measurements with the electrode was found to be in satisfactory agreement with that determined by ICP emission spectrometry. It was successfully applied as an indicator electrode in the potentiometric titration of Cu(NO₃)₂ with EDTA and the resulting titration curve is shown in Figure 5.

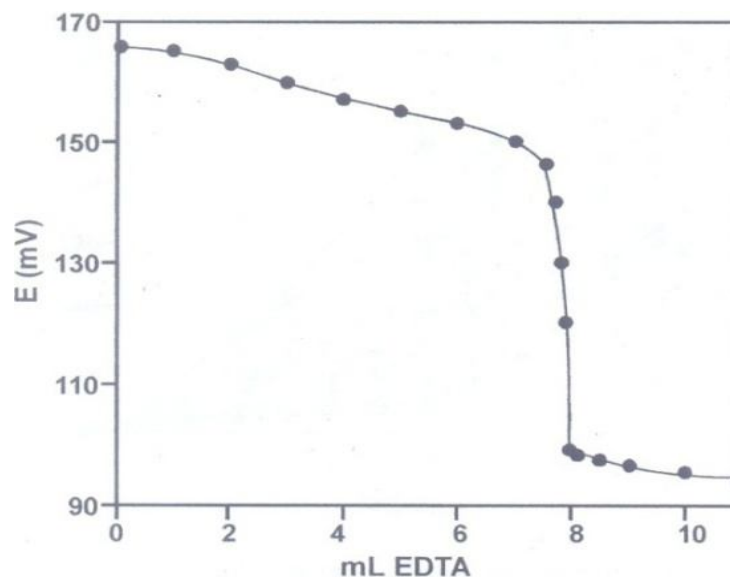


Figure 5. Potentiometric titration curve of 20.0 mL of 4.0×10^{-3} mol/L Cu^{2+} solution with 0.01 mol/L EDTA at pH 5, using the proposed sensor as an indicator electrode

4. CONCLUSION

The proposed sensors are very easy to prepare and show sensitivity and wide dynamic range. High selectivity, low detection limit and rapid response make these electrode suitable for measuring the concentration of copper ion in wide variety of sample, including biological and industrial sample without needing for preconcentration or pretreatment steps and without significant interaction from other cationic species present in the sample.

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