COPPER (II)-SELECTIVE MEMBRANE ELECTRODES BASED ON Cu (II)-SCHIFF BASE COMPLEXES AS AN IONOPHORE

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ABSTRACT

A new PVC membrane electrode for copper (II) ion based on the mixture of mononuclear aqua-[N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II) (I) and dinuclear dioxane-[N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride (II) is developed. The electrode exhibits a Nernstian response for copper (II) ion over a wide concentration range, $1.0 \times 10^{-1} - 3.2 \times 10^{-5}$ M with a slope of 28.3 mV per decade. It has a relatively fast response time, 20 – 30 s, and can be used for at least four months without any considerable divergence in potential. The proposed electrode shows a high selectivity against Ca (II), Co (II), Zn (II), Ni (II), Mg (II), Sr (II), Ba (II), Cd (II), Al (III), Na (I), Hg (II) and Mn (II) and can be used in a pH range 4.5-6.5. Only Ag (I) ion was observed to have a significant interference. It is successfully used as an indicator electrode in potentiometric titration of copper (II) with EDTA and direct potentiometric determination of copper.

Key words: Potentiometry, Copper (II)-selective electrode, Schiff base-copper complexes, PVC membrane, determination of copper, alloys.

1. INTRODUCTION

As is known, Schiff bases are reagents, which are becoming increasingly

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important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology in addition to their uses in analytical chemistry /1/. However, the latest research has revealed that Schiff bases and/or their metal complexes can be employed as ionophores in the construction of many anion or cation-selective electrodes /2-6/.

It is known that copper ion forms stable complexes with Schiff bases /7, 8/. It was reported that the mononuclear aqua [N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II) complex could be used as a titrant in the titrimetric determination of copper /9/. There are also several other studies related to the preparation of copper (II)-selective electrodes by the use of other Schiff bases and their complexes /10-14/.

In this study an attempt was made to prepare a Cu (II)-selective electrode using Cu (II)-Schiff base complexes in PVC based membranes. For this purpose a mixture of mononuclear aqua [N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II) (I) and dinuclear dioxane [N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride (II) was used as an ionophore. The structures of Schiff base-copper (II) complexes are given in Fig. 1.

Fig. 1: The structures of mono and dinuclear Cu (II)-Schiff base complexes used as ionophore. (I) Aqua [N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II). (II) Dioxane [N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride.

The structure of the mononuclear complex given in Fig. 1 was elucidated with x-ray crystallography /15/. The structure of the dinuclear complex was proposed as depicted in Fig. 1 based upon elemental analysis data and a

structure given for a similar compound in the literature /16/.

In this study the pH range, selectivity against other ions, response time and lifetime of the Cu (II)-selective electrode were determined. The practical aspects of using the electrode for the determination of copper in real samples were also investigated.

2. EXPERIMENTAL

2.1 Reagent and solutions

All chemical substances used were of reagent grade and were used without further purification. The stock solutions of metal ions were 0.1 M. Working solutions were obtained by proper dilution of the stock solutions with deionized water.

Mononuclear aqua [N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II) (**I**) and dinuclear dioxane [N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride (**II**) complexes were synthesized at the Department of Analytical Chemistry, Ankara University by Atakol *et al* /15/.

High molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyloctylether (2-NPOE) and tetrahydrofuran (THF) were obtained from Fluka in selectophore purity. Sodium tetraphenylborate (STPB) was purchased from Aldrich.

Standard reference materials (Messing XV: Cu 63.76 %, Pb 1.90%, Sn 0.08%, Fe 0.14%, Ni 0.14%, Zn 34.06%; Messing VII: Cu 84.96%, Pb 0.15%, Sn 0.02%, Fe 0.01%, Ni (spuren), Zn 14.86%) were obtained from Dr Hoefner's Subztanz Company. Suitable amounts taken from these standard materials were dissolved using nitric acid and diluted to a certain volume.

pHs of test solutions were adjusted to about 5.6 using acetic acid/acetate buffer. The ionic strength of the solution was maintained at 0.25 M potassium nitrate.

The studies were carried out by the use of deionized water obtained from Barnstead Nanopure Infinity Ultra Pure Water System.

2.2. Preparation of the electrode

10.0 mL of stock solution containing 0.5 mg mononuclear, 0.5 mg dinuclear and 8.0 mg sodium tetraphenylborate (STPB) per 1.0 mL

tetrahydrofuran was prepared (solution A). 90.0 mg 2-nitrophenoctylether and 40.0 mg poly(vinyl chloride) were dissolved in 2.0 mL of THF (solution B). 1.0 mL of solution A was added to solution B. The homogenous mixture formed was poured onto a glass disc with a diameter of 2.6 cm attached to a glass plate and kept at room temperature for 24 h for the evaporation of tetrahydrofuran. The 0.7 cm diameter disc of the polymer membrane was cut and fixed to the end of a glass tube with a diameter of 0.5 cm and a length of 10 cm.

An internal filling solution containing 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ and saturated KCl was put into this glass tube and a AgCl-coated silver wire was inserted into it. The prepared PVC electrode was conditioned in 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ solution for 12 h. The copper (II) ion-selective electrode obtained was also used as an indicator electrode.

2.3. Potential measurements

Using the single-junction Ag/AgCl reference and the copper (II)-ion selective electrodes the following electrochemical cells were prepared.

Reference electrode | analyte solution | membrane | 1.0×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ saturated KCl | AgCl | Ag.

The potential measurements were made by the use of Jenway 3040 Ion Analyser Model pH ion meter. The reference electrode was a single-junction Ag/AgCl electrode and a filling solution employed for this electrode was that of Orion's with catalogue number 900001. The pH measurements were performed with Ingold (10.402.3311) combined glass electrode. The combined glass electrode was kept in water when it was not in use. The experimental solution was stirred with a magnetic stirrer and the potentials were recorded after the equilibrium potentials had been reached.

3. RESULTS AND DISCUSSION

3.1. The determination of the composition of the membrane

The literature survey showed that the usual range of composition in the preparation of PVC matrix membrane electrodes was 1-7% ionophore, 28-33% PVC (internal matrix), 60-69% plasticizer (solvent) and 0.03-2%

lipophilic anion /16/. Therefore, the optimum membrane composition was sought within this composition range.

Using these values, the optimum membrane composition was defined by changing the ratio of Schiff base-copper complex, PVC, plasticizer and lipophilic anion and the membrane compositions used for five electrodes are given in Table 1. As can be seen from the table, the membranes contain only mononuclear or dinuclear Cu (II) complexes and their 1:1(m/m) mixture. Furthermore each membrane includes STPB as lipophilic anion.

Table 1. The compositions of Cu (II)-sensitive membranes

Electrode No	PVC (mg)	Mononuclear	Dinuclear	NPOE, mg	STPB, mg	THF, mL	Slope, mV/pCu
		Cu (II) complex, mg	Cu (II) complex, mg				
1	50.9	-	1.0	91.1	7.5	2.5	10.2
2	45.0	0.375	0.375	90.0	5.0	3.4	20.1
3	40.0	0.35	0.35	100.1	4.0	3.6	24.1
4	40.0	0.5	0.5	90.0	8.0	2.8	28.3
5	40.1	1.0	-	90.2	8.0	2.8	23.5

The five electrodes were prepared by the use of membranes listed in Table 1. The calibration graphs were plotted and the slope and the linear working range of each electrode were determined. The electrode constructed by the use of the membrane 4 showed a near Nernstian response with a slope of 28.3 mV/pCu over a Cu (II) concentration range of $1.0 \times 10^{-1} - 3.2 \times 10^{-5}$ M.

That the response of electrode 1 against Cu (II) is weak is attributed to the fact that the dinuclear complex is weak; easily splits into CuCl_2 and the mononuclear species in aqueous media; and thereby, we must have obtained a polymer membrane with a homogenous distribution of Cu^{2+} ions. With such a membrane, reaching a Cu (II) ion concentration gradient could only be possible through a leaching process of Cu (II) from the membrane to the solution and this would take a long time

On the other hand, with electrode 5, all the Cu (II) ions in the membrane are strongly held by the ligand and the Cu (II) concentration gradient is expected to be established through diffusion of the Cu (II) ions from the solution into the membrane; thereby a quicker and more intense potential difference across the faces.

With a mixture of (I) and (II) (electrode 4), the leaching and diffusion processes would be in action simultaneously, and the setting of a Cu (II) concentration gradient would take least time, which is the case. Indeed, electrode 4 appears to be virtually of Nernstian behavior.

It is known that the addition of a lipophilic anion to the medium changes the specific features of the electrodes with ionophore membranes /17, 18/. In our study, the data listed in Table 1 reveal that the sensitivities of the membranes against Cu (II) ions prepared without the use of sodium tetraphenylborate (STPB) as lipophilic salt is low. The addition of the lipophilic reagent improved the sensitivity of the electrode in accordance with the literature /17/.

3.2. Effect of pH

The influence of the pH of the test solution on the potential response of the proposed Cu (II)-selective electrode (electrode no 4) was tested at 1.0×10^{-3} M Cu (II) concentration by changing the pH between 2 and 7. As seen from Fig. 2, the response of the electrode remains nearly constant within the intervals of pH 2.0-3.5 and of 4.5-6.5. The calibration curves obtained at pH 4.3, 5.6 and 6.2 are shown in Figure 3. The slope was 17 mV/pCu at pH 4.3 and increased to 28.3 and 27.0 mV/pCu at pH 5.6 and 6.2 respectively. The electrode showed no selectivity against Cu (II) ions at pH values less than 3.5. The reason behind this is that in acidic media, the protons are attached to the suitable sites in the complexes, partially destroying the complex structure and competing with the Cu (II), thereby ions preventing their entrance to the membrane. The decrease in the response of the electrode around pH 7 may be due to the formation of some hydroxyl complexes of Cu (II) ions in the solution. The pH range where the complex formation is most favored was 4.5-6.5. It was also reported in the literature that this pH range is the most suitable range for the formation of (I) [10]. We have chosen the optimum working pH as 5.6.

Fig. 2: The effect of pH on the response of Cu (II)-selective electrode based on mononuclear aqua [N,N'-bis(salicylidene)-1,3-propanediaminato]copper (II) and dinuclear dioxane [N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride complexes (electrode 4)

Fig. 3: The calibration curves of the Cu (II)-selective electrode based on mononuclear aqua-[N,N'-bis(salicylidene)-1,3-propane-diaminato] copper (II) and dinuclear dioxane-[N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride complexes (electrode 4) at different pH values: (a) pH= 4.3, (b) pH= 6.2 and (c) pH= 5.6

3.3. Response time and life time of the electrode

The response time of the electrode depends slightly on the concentration change. The response time was about 30 s at Cu (II) concentrations between 10^{-5} to 10^{-3} M. However it was found to be shorter than 20 s at concentrations higher than 10^{-3} M. This value is comparable to, but is actually shorter than those electrodes reported in the literature, which gave linear response in the same working range /19-22/.

The lifetime of the electrode was determined by reading the potentials of a series of Cu (II) solutions and plotting the calibration curves for a period of 4 months. Fig. 4 illustrates the calibration graphs at different times. Even after 4 months, the slope of the electrode was observed to show no significant change. This shows that the lifetime of the electrode prepared by the use of (I) and (II) complexes was longer than 4 months. This is a longer lifetime than those reported in the literature for similar electrodes /10, 22/.

Fig. 4: The calibration curves of Cu (II)-selective electrodes plotted at different times: (a) 5 days (b) 30 days (c) 60 days and (d) 120 days

3.4. The selectivity of the electrode

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, as it often determines whether a

reliable measurement in the target sample is possible [23, 24]. In order to assess the selectivity of the proposed Cu (II)-selective electrode over other cations such as Ca (II), Co (II), Zn (II), Ni (II), Mg (II), Sr (II), Ba (II), Cd (II), Al (III), Na (I), Hg (II), Mn (II) and Ag(I), the mixed interference method was employed [25, 26] and the values of the selectivity coefficients are given in Table 2. As can be seen from the table the interference effect of Ag (I) ion was annoyingly high. This can be attributed to the fact that Ag (I) ions combine with the chloride ions in dinuclear Cu (II) complexes and clog the pores so as to obstruct the back and forth movement of Cu (II) ions. The interfering effects of other ions are ignorable.

Table 2

The selectivity coefficient values ($K_{Cu^{2+},B}^{Pot}$) for Cu(II)-selective electrode as calculated by mixed interference method

Interfering ion (B)	Selectivity coefficient values*
Ca^{2+}	$1.8 \times 10^{-2} \pm 3.0 \times 10^{-3}$
Co^{2+}	$7.1 \times 10^{-2} \pm 3.0 \times 10^{-3}$
Zn^{2+}	$2.2 \times 10^{-2} \pm 7.4 \times 10^{-3}$
Ni^{2+}	$7.6 \times 10^{-2} \pm 1.2 \times 10^{-3}$
Mg^{2+}	$5.5 \times 10^{-2} \pm 2.2 \times 10^{-3}$
Sr^{2+}	$5.6 \times 10^{-2} \pm 1.0 \times 10^{-3}$
Pb^{2+}	$5.2 \times 10^{-2} \pm 1.0 \times 10^{-3}$
Ba^{2+}	$6.1 \times 10^{-2} \pm 1.0 \times 10^{-3}$
Cd^{2+}	$6.1 \times 10^{-2} \pm 1.0 \times 10^{-3}$
Al^{3+}	$7.7 \times 10^{-2} \pm 2.5 \times 10^{-3}$
Na^+	$7.5 \times 10^{-2} \pm 4.0 \times 10^{-3}$
Hg^{2+}	$3.7 \times 10^{-2} \pm 5.0 \times 10^{-3}$
Mn^{2+}	$6.6 \times 10^{-2} \pm 7.0 \times 10^{-3}$
Ag^+	3.2 ± 0.02

* at 95% confidence level (N=3)

3.5. The analytical applications of the electrode

Standard Cu (II) solutions were titrated with standard EDTA solution in order to determine whether the proposed electrode could be used as an indicator electrode in the titration of Cu (II) ions. An example of a titration

curve thus obtained is given in Fig. 5. As it is seen, the amount of copper (II) ions in solution can be accurately determined with this electrode.

Whether the electrode prepared could actually be employed in real samples was also examined. Copper in various standard reference materials were titrated with EDTA by using the proposed electrode. The results obtained from two reference materials studied are given in Table 3. From the data given in Table 3, the following result from the determination of these standard reference materials with the proposed electrode at 95% confidence level have been obtained: $85.58 \pm 0.92\%$ for Messing VII and $63.26 \pm 0.57\%$ for Messing XV. The copper percentages on the labels of the above mentioned standard reference materials were 84.96% and 63.76%, respectively. The results obtained with the proposed electrode method show that the difference between the average copper percentage for each standard sample and the copper percentage on the labels, which is at 95% confidence level and with 5 degree of freedom, is smaller than $t.s/\sqrt{N}$ values. Therefore, it can be said that the proposed electrode is used for determinations of copper in alloys since the label percentage interval calculated for the average value.

Fig. 5: The potentiometric titration curve of Cu (II) with 0.0200 M EDTA by the use of the proposed Cu (II)-selective electrode.

Table 3
The data obtained from standard reference materials with the proposed Cu (II)-selective electrode method and iodimetric method *

Standard samples μ , Cu%	The proposed electrode method, $\bar{X}_1$, Cu%				Iodimetric method, $\bar{X}_2$, Cu%				Comparison of the method	
	$\bar{X}_1 \pm \frac{t.s.}{\sqrt{N}}$	S	N	$\mu - \bar{X}_1 < \frac{t.s.}{\sqrt{N}}$	$\bar{X}_2 \pm \frac{t.s.}{\sqrt{N}}$	S	N	$\mu - \bar{X}_2 < \frac{t.s.}{\sqrt{N}}$	$ \bar{X}_1 - \bar{X}_2 < t_{sb} \sqrt{\frac{N_1 + N_2}{N_1 \times N_2}}$	
84.96 (Messing VII)	85.58 ± 0.59	0.88	6	$0.62 < 0.92$	85.38 ± 0.39	0.40	6	$0.42 < 0.42$	$0.20 < 1.23$	
63.76 (Messing XV)	63.26 ± 0.50	0.54	6	$0.50 < 0.57$	63.93 ± 0.34	0.32	6	$0.17 < 0.34$	$0.67 < 0.80$	

* at 95% confidence level; $\bar{X}_1$ and $\bar{X}_2$ are the mean values; μ : nominal value.

Standard reference materials were also titrated iodometrically using the same conditions and the results are also given in Table 3. As can be seen from the data given in the table, there is no significant difference between the data obtained with these two different methods at a confidence level of 95 %.

4. CONCLUSION

A 1:1 (m/m) mixture of mononuclear aqua [N,N'-bis(salicylidene)-1,3-propane-diaminato]copper (II) (**I**) and dinuclear dioxane [N,N'-bis(salicylidene)-1,3-propane-diaminato]dicopper (II) dichloride (**II**) complexes could be used as an ionophore for the construction of a Cu (II)-selective electrode. The electrode is fairly selective against many metal ions. The working pH range is 4.5-6.5. It was observed that the electrode gave a linear response with a slope of 28.3 mV/pCu in a concentration range of 1.0×10^{-1} – 3.2×10^{-5} M.

The equilibrium time of the electrode to reach a stable potential was relatively short and it was observed that the electrode gave reproducible responses for four months with at least 15 measures per day without any appreciable change in its linearity and slope.

The proposed electrode may be a good alternative to many Cu (II)-selective electrodes reported in literature especially to those solid-state electrodes. The electrode can also be employed as an indicator electrode in the titration of copper with EDTA.

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