Highly Copper(II)-selective PVC Membrane Based on a Schiff Base Complex of *N,N'*-Bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine as an Ionophore

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The polymeric membrane electrodes based on *N,N'*-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine as an ion carrier were prepared and tested for the copper-ion selective electrode. The membrane has a linear dynamic range between 10^{-6} and 10^{-2} M with a Nernstian slope of 29.6 mV per decade, and its detection limit was $10^{-5.62}$ M. The potentiometric response is independent of the pH range of 3-5. The proposed electrode showed good selectivity and response for Cu^{2+} over a wide variety of other metal ions in pH 4.0 buffer solutions.

Key Words : Polymeric membrane electrode, *N,N'*-Bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine, Ionophore, Copper-selective electrode

Introduction

The narrow window of concentration between essentiality and toxicity warrants the determination of copper in water.[1,2] The environmental analysis of water samples has focused on known toxic forms, such as ionic copper.[3] Thus, the determination of trace amounts of copper becomes increasingly important because of an increased interest in environmental pollution. During the past two decades, an extensive effort has expanded in the synthesis and characterization of neutral ionophores with high selectivity for specific metal ions and developed new potentiometric sensors for the determination of the respective metal ions in different samples.[4-7] A variety of ion carriers have been used to construct copper(II) selective electrodes. These copper ion carriers include small-size thiacrown ethers,[8,9] non-cyclic neutral ionophores containing dithiocarbamate groups,[10,11] and nitrogen atom,[12] calix[4]arenes[13] and Schiff base.[14] However, all of the following problems: (1) high detection limit, (2) narrow working concentration range and (3) serious interfering effect of cations such as Na^+, Sr^{2+}, Co^{2+}, Ni^{2+}, Cs^+, Ag^+ and K^+.

In this study, we report on a highly selective copper electrode using a lipophilic Schiff base, *N,N'*-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine, as a novel neutral carrier for the potentiometric monitoring of ultra-trace amounts of Cu^{2+} ion, because this polymeric electrode gives negligible interference of Pb^{2+} and Ni^{2+} for the determination of Cu^{2+} ion.

Experimental Section

Reagents.

***N,N'*-Bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine:** (see Figure 1) tested as copper ionophore was prepared according to the procedure described previously.[15] High molecular weight PVC, dioctyl sebacate (DOS), dioctyl adipate (DOA), dioctyl phthalate (DOP), 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(4-chlorophenyl)borate
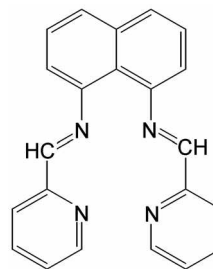

Figure 1. The structure of *N,N'*-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine.

(KT*p*ClPB) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. The nitrate salts of cations used (all from Merck) were used without any further purification except for vacuum drying over P_2O_5. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

Preparation of polymeric ion-selective electrodes. The compositions of PVC-based copper-selective electrodes were summarized in Table 1, and the typical one was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore and KT*p*ClPB (50 mol% of ionophore). The ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes. Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane measured by micrometer was about 0.3 mm.

Potentiometric measurements. The electrochemical properties of copper-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl solution was used as an internal filling solution. All electrodes were finally conditioned for 24 h by soaking in 1.0×10^{-2} M $Cu(NO_3)_2$ solution. A silver/silver chloride coated wire was

Table 1. The compositions of membranes and their potentiometric characteristics of the copper-selective electrodes in pH 4.0 buffer solutions

Membrane	Ionophore[a]	PVC[a]	*o*-NPOE[a]	DOS[a]	DOA[a]	DOP[a]	DBS[a]	KT*p*ClPB[b]	LOD (log a)	Slope (mV)
m-1	1	33	66					0	−4.25	−3.3
m-2	1	33	66					50	−5.00	15.0
m-3	1	33		66				0	−5.63	3.2
m-4	1	33		66				20	−5.51	18.9
m-5	1	33		66				50	−5.62	29.6
m-6	1	33		66				100	−5.43	16.8
m-7	1	33			66			50	−4.60	6.4
m-8	1	33				66		50	−5.46	5.4
m-9	1	33					66	50	−4.55	9.7

[a]in mg. [b]in mol% relative to the ionophore.

used as an internal reference electrode. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-20) with two chambers. This reference electrode has two different filling solution : inner chamber filling solution is green colored solution saturated with AgCl, outer chamber filling solution consists of 10% KNO$_3$. The potential measurements were carried out at 25 ± 1 °C with Kosentech 16-channel potentiometer (KST101-1) coupled to a computer by setting up the following cell assembly: Ag/AgCl/0.1 M KCl/PVC membrane/test solution/Ag/AgCl. The electrochemical measurements were conducted after within 1 mV variance of open circuit potential with 5 minutes. The dynamic response curves were produced by adding standard solutions of cations to magnetically stirred pH 6.0 buffer solution (0.05 M Tris-HCl). The selectivity coefficients (log $K^{pot}_{Cu^{2+}, j}$) were determined by the separate solution method (SSM) using nitrate salts of the cations involved. Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range and the other parallel to the X-axis drawn through the mean potential value of the lowest metal ion concentration used in the plot of the potential change and the concentration of Cu^{2+}.

Results and Discussion

Schiff bases as ligands seem to be a potential ionophore for soft heavy metal ions in the PVC membrane electrodes, because of its excellent metal-binding properties, rapid exchange kinetics, and water insoluble.[5,16,17] *N,N'*-Bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine was used as an ionophore for preparing PVC membrane ion-selective electrodes for a wide variety of metal ions. The pH dependence on the potentiometric response of the novel membrane electrode (m-5) is studied in a variety of pH solutions and shown in Figure 2. The results indicate that the potentiometric response for m-5 electrode depends on the solution pHs employed, but the potential obtained from m-5 electrode gives a similar value between pH 3 and pH 5. Therefore, the potentiometric response of PVC polymeric Cu^{2+}-ISEs based on *N,N'*-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine was examined for many metal ions in
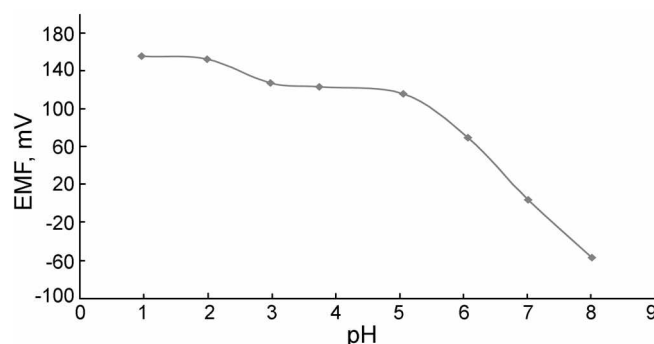

Figure 2. pH Effect of test solution on the potential response of the Cu^{2+}-ISE.

pH 4.0 buffer solutions in order to avoid the formation of metal-hydroxide complex at higher pH.

A potential-time plot for the electrode is shown in Figure 3. The static response time of the membrane electrode thus obtained was < 5 sec for the increased concentration from 1.0 × 10^{-5} M to 1.0 × 10^{-4} M copper ion solution, indicating that the equilibrium can reach very quickly in pH 4.0 buffer solutions.

The Cu^{2+}-ISE membrane compositions were optimized to produce the best sensitivity and selectivity towards copper ion, because the sensitivity of the ion-selective electrodes depends on the nature of ionophore used as well as significantly on the membrane compositions and selectivity of the electrodes depends on the nature of ionophore. The optimization was carried out with varying of the ratio in PVC membrane components such as plasticizer and additive (KT*p*ClPB). The polymeric membranes are investigated to measure the ability of the ionophore to act as an ion carrier in the absence and presence of the ion exchanger. The response of the membranes without additive ion-exchanger (KT*p*ClPB) gave the worse sensitivity and selectivity than those with KT*p*ClPB. Most of membrane electrodes were prepared with KT*p*ClPB in this work. The potentiometric response of the membranes was evaluated as to the slope and detection limit towards copper ion. The slope and detection limit for membranes were determined in accordance with IUPAC recommendations.[18] Figure 4 illustrates typical response curves for copper ion, measured in pH 4.0 (0.05 M
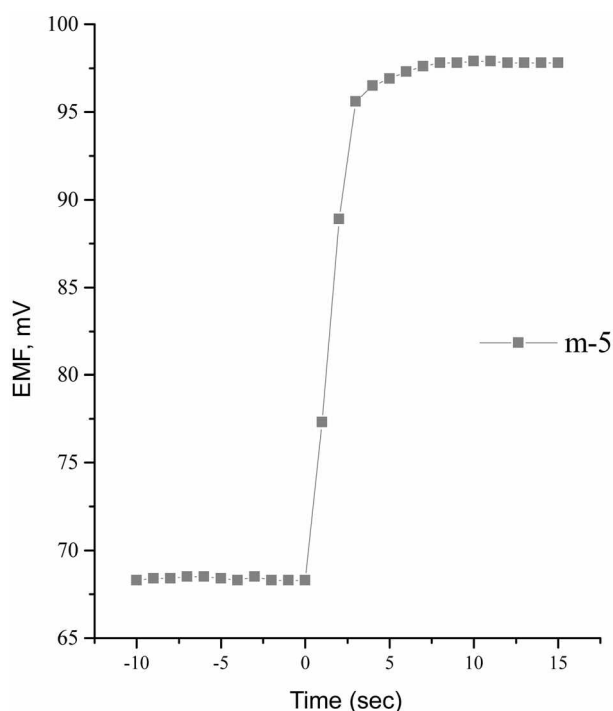
Figure 3. Response-time profile of the Cu^{2+} ion-selective electrodes based on ionophore (m-5).

Tris-HCl) buffer solutions by membranes (m-3, m-4, m-5, m-6) containing different amount of additive (KTpClPB), respectively. They show that the ionophore gives membrane electrodes with best sensitivity towards copper ion containing in 50 mol% additive. The effects of the membrane composition, the nature of plasticizers, ionophores, and lipophilic additive on the potentiometric response of the Cu^{2+}-ISE were investigated and summarized in Table 1. A membrane (m-5) prepared by DOS as a plasticizers, 50 mol% of additive displays a good Nernstian response to Cu^{2+} over the wide range. The slope of the calibration curve was 29.6 mV/decade of Cu^{2+} concentration at room temperature, and the limit of detection (LOD) of $10^{-5.62}$ M. In Figure 4, the potential response for the electrodes prepared from the other amount of additive is also included for comparison. As seen, the m-4 prepared with 20 mol% additive resulted in a diminished slope (18.9 mV/decade). The m-6 prepared with 100 mol% additive were obtained a low slope (16.8 mV/decade) and a LOD ($10^{-5.43}$ M) also. The different slope can be attributed to the complexation factor and sensing rate according to the membrane formulation. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes provides the decrease of the ohmic resistance as well as the improvement of their sensitivity and selectivity.

The effect of plasticizer on Cu^{2+}-ISE membrane electrodes based on N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine is shown in Figure 5. According to Figure 5 and Table 1, it is clear that DOS is a more effective solvent mediator than others in preparing the Cu^{2+}-ISEs. It is noteworthy that the lipophilicity of plasticizer influences
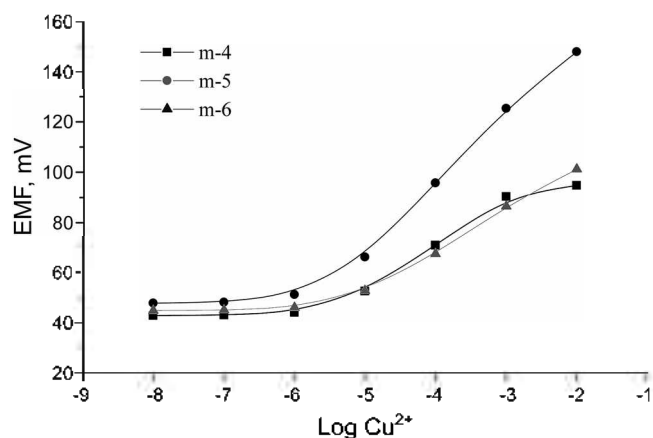

Figure 4. Potentiometric responses of the Cu^{2+} ion-selective electrodes based on different mol% of additive: m-4; 20 mol%, m-5; 50 mol%, and m-6; 100 mol%.

both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex, because the dielectric constant of the membranes controls the mobility of metal ions. The prepared electrodes were also examined on the effect of inner reference solution. It was found that the concentration and composition of the internal solution affected on the potentiometric response insignificantly. Thus, 0.1 M KCl as a reference solution are quite appropriate for smooth functioning of the electrode system. The optimum equilibration time for the membrane electrode is 48 h. It then generates stable potentials when placed in contact with Cu^{2+} solutions.

The selectivity coefficients of the new membranes are very important for determining their quality as ISEs. The selectivity coefficients represent their response to the species to be measured over other ions present in solution. They were evaluated by the separate solution method. The selectivity coefficients towards Cu^{2+} were determined against the interfering cations, Pb^{2+}, Ag^+, Rb^+, Cs^+, Na^+, K^+, Co^{2+}, Cd^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ni^{2+}, Ba^{2+}. The selectivity coefficients (log $K_{Cu,J}^{pot}$) with respect to the corresponding
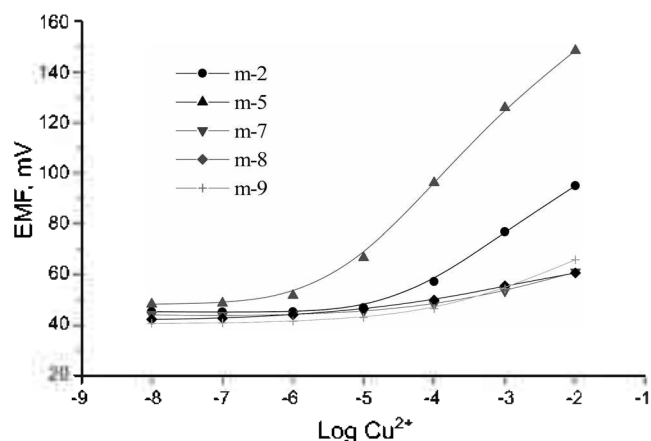

Figure 5. Potentiometric responses of the membrane prepared from different plasticizers with the ionophore towards Cu^{2+}.

Table 2. Selectivity coefficients ($K^{pot}_{Cu^{2+},j}$) for various interfering ions for membrane (m-5) electrodes obtained by SSM

Membrane No.	Ionophore (mg)	$\log K^{pot}_{Cu^{2+},j}$															
		Cu^{2+}	Pb^{2+}	Ag^+	Rb^+	Cs^+	Na^+	K^+	Co^{2+}	Cd^{2+}	Mn^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ni^{2+}	Ba^{2+}
m-5	1	0	−3.55	−4.37	−4.32	−4.24	−4.36	−4.39	−4.23	−4.23	−4.34	−4.28	−4.41	−4.39	−4.46	−3.55	−4.48

nitrate of the interfering ion tested are shown in Table 2. From these, it can be considered that N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine as an ionophore employed is selective towards copper ion against all interfering ions tested. Among membranes tested, the best results were gained from m-5 membrane. As can be seen, with the exception of Cu^{2+}, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating they would not significantly disturb the functioning of the Cu^{2+} selective electrode. It should be noted that Pb^{2+} and Ni^{2+} provides negligible interference with ($-\log K^{pot}_{Cu^{2+},j}$ = 3.55) for the determination of copper ion. Thus, it is clear that the membrane electrode has good selectivity over monovalent and divalent cations. Meanwhile, the effect of counter anions was investigated using the copper salts of chloride and nitrate, indicating that no significant changes in the working concentration range and slope were observed. Examination of the selectivity data for the electrodes employed in this study indicates that the extent of complex formation between ionophore and metal ion and the geometrical structure are the major factors determining the selectivity. The result indicates that the geometry and ligating cavity of the N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine should be significant factor for determining a selectivity toward others. Based on the data of m-5 in Table 1 and 2, the good sensitivity and highest selectivity towards copper ion are attributed to the strong complexation of copper ion to N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine which has geometrically the proper cavity to coordinate to the ligand, and its complexation with other cations should be weaker than the copper complexation. The electrode was applied to the direct measurement of Cu^{2+} in prepared solutions. The potential was measured by direct potentiometry in pH 4.0 buffer solutions. The prolonged stability of these membranes was measured as a function of time, it was evidenced in both the slopes of the calibration curve and the detection limits. The membranes are stored in pH 4.0 buffer solutions when not in use. After two weeks, the electrodes were responding at 96% of the initial response. By the end of one month, the response observed was still responding at 92% of the initial value.

Conclusion

The membrane electrode incorporating N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine as an ion carrier can be used in the development of a copper ion-selective electrode. Among membranes tested, polymeric membrane m-5 based on N,N'-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine with DOS and liphophilic additive of 50 mol% displays a good Nernstian response (29.6 mV/decade) to Cu^{2+} and the limit of detection of $10^{-5.62}$ M. Most of metal ions would not affect the selectivity of the copper electrode seriously. It can be concluded that the membrane electrode has a rapid potential response and excellent selectivity towards copper ion over other interfering metal ions.

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