Cu(II) Ion-Selective Electrodes Based on Cu(II) Complex with Cyclized Salophen

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Several versions of Cu(II) ion selective electrodes (ISE), based on cyclized N,N′-bis(salicylidene)-o-phenylenediamine (salophen) complexes with Cu(II), were fabricated for determination of Cu(II) in aqueous solutions. The response of the ISE was optimized by variation of membrane composition and evaluation of various experimental conditions. Near Nernstian slopes (~ 28–32 mV/decade) were obtained for some preparations. The linear range of the ISE ranged from 5×10^{-5} to 1×10^{-2} M Cu(II). Coated-wire and coated disc ISE resulted practically in a similar response as screen printed electrodes (SPE). The potentiometric selectivity coefficients (K_{ij}) for all electrodes were determined for Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+}, Hg^{2+}, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}, CH_3COO^-, Br^-, I^-, NO_3^-, and SCN^-. The selectivity coefficients were in the range from 10^{-2} to 10^{-3} for all ions tested except Hg^{2+}, I^-, and to less extent Fe^{3+}. Fabricated ISE using the Cu(II)-salophen complex are reliable and stable.

Key words: Coated-Wire , Coated-Disc, Cyclized Salophen

Introduction

Ion selective electrodes, especially solid state and screen printed electrodes (SPEs), are still attracting the interests of the scientific community [1–10]. The search for inexpensive reliable chemical sensors, in terms of better response and long-term stability, has been the focus of many research projects for decades. Coated-wire and ion selective SPEs satisfy many of the features anticipated in a chemical sensor. Those ISEs are well adapted to miniaturization, can be used for the detection and determination of analytes in a variety of samples, they are easily prepared and are cost effective, especially when working in hostile environments. Koncki *et al.* [6] described the preparation of a SPE for copper. Cu(II) and Ag(I) ion selective electrodes were also fabricated using aza and thia macrocycles [11–13]. However, the search for new ionophores that have better selectivities, extended stability, and better performance continues to be an active area of research.

Recently, a salophen-uranyl complex was evaluated as a sensor for nitrite, phosphate, and fluoride by a group of authors [14–16]. Other groups evaluated the catalytic behavior of the salophen complexes [17–19].

In the present work, we introduce a new version of the salophen-Cu(II) complex that was cyclized
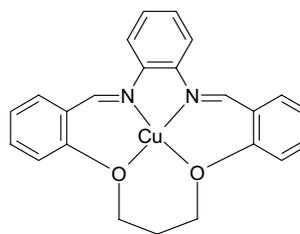
Structure of the Cu(II) ionophore

using 1,3-dibromopropane yielding a diaza dioxa macrocycle, the structure of which is shown above. This ionophore is studied for its electrochemical ion-selective characteristics and possibility for use as the ionophore in a Cu(II) ISE using different sensor versions.

Experimental Section

Apparatus

The emf measurements were done at 25 ± 2 °C and recorded using a Hanna mV/pH (HI 859) meter. A double junction saturated calomel electrode (SCE) from Orion Research, USA, was used to check the performance of the Ag/AgCl reference electrode. The silver/silver chloride electrode was constructed from a silver wire (0.2 mm, 99.99%) purchased from EMS, USA. A strip of three screen printed electrodes (graphite, platinum, and

Ag/AgCl) was a gift from the Institut für Chemo- und Biosensorik (ICB), Münster, Germany.

Reagents and solutions

All chemicals obtained were of analytical grade and were used without further purification, except for salicylaldehyde, o-phenylenediamine and 1,3-dibromopropane. All aqueous solutions were made using freshly distilled water. The interferent solutions of cations were prepared from the respective metal chloride or nitrate while the interferent solutions of anions were prepared from their sodium or potassium salts. The standard Cu(II) solution was prepared from $Cu(NO_3)_2$ as a 0.10 M solution and was freshly diluted when necessary.

Procedures

Synthesis of the ionophore

1.0 mmol of o-phenylenediamine was mixed with 2.0 mmol of salicylaldehyde in 20 ml of methanol. The solution was refluxed for 2 h followed by addition of 1.0 mmol $Cu(NO_3)_3$ in water and the solution was heated for 10 min. Cyclization was achieved by addition of 0.2 g of 1,3-dibromopropane and 0.08 g of solid NaOH with continuous stirring under reflux conditions for 1 h. The product was collected by suction filtration, washed with methanol and dried in air.

Preparation of the Ag/AgCl reference electrode

A piece of a silver wire was coated with parafilm except for the bottom part (about 15 mm). The wire was cleaned by dipping in a 1:1 nitric acid solution for 10 s followed by immersion in a 1:1:1 solution of 65% nitric acid, 32% hydrochloric acid, and water for 10 min. The AgCl coated silver wire was then removed from the acidic solution, thoroughly washed with distilled water and placed in an electrode body containing 3.5 M KCl. The electrode was allowed to equilibrate and stand alone for 24 h and it was then tested against a SCE giving a potential of – 45 mV. The electrode was fairly stable where its potential was frequently checked against the SCE.
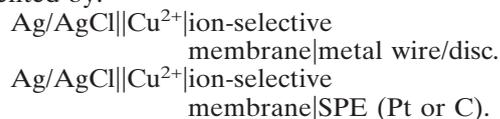
Construction of the ISE

Silver wires/discs and copper wires/discs (5 × 0.2 mm) were first soaked in a 1:1 nitric acid solution for few seconds, washed with distilled water and acetone and left to air dry for few minutes.

The discs were soldered to copper leads and sealed to one end of a glass tube using a commercial non-conductive epoxy resin. The ionophore polymeric solution was prepared by dissolving 25–35 mg of high molecular weight polyvinylchloride (PVC), 3–4 mg of ionophore, 2 mg of cetyltrimethylammonium bromide (CTAB), and 60–70 mg of diethylphthalate (plasticizer) in 3 ml of tetrahydrofuran (THF). The resulting solution was allowed to evaporate slowly for about 1 h followed by dipping of the electrodes for 20 s. The electrodes were then air-dried and/or oven-dried overnight at 60 °C. The fabricated electrodes were brought to room temperature, washed with distilled water, and conditioned for 30 min in an ionic strength adjustment solution containing 0.2 M KCl in a 0.01 M acetate/acetic acid buffer. The screen printed electrodes were constructed by transferring 5 μl of the freshly prepared ionophore solution, described above, to the platinum or graphite surface. The SPE was allowed to slowly air dry for 2 h and was then transferred to the conditioning solution as above.

Measurement of emf

The coated-wire or disc ISE was connected to the pH/mV meter as an indicator electrode and the Ag/AgCl reference electrode was connected to the reference terminal of the meter. A 20 ml portion of 0.01 M acetate buffer containing 0.2 M KCl was transferred to a 50 ml beaker and the two electrodes were immersed in this solution, and the solution was stirred using a small magnetic stirrer. The ISE was allowed to equilibrate till a steady-state response was achieved (about 15 min). An accurately measured volume of standard Cu(II) solution was added to the stirred solution and the potential was recorded after 40 s. Successive amounts of Cu(II) were added so that a final Cu(II) concentration in the range from 5×10^{-6} to 2×10^{-2} M was obtained. The potential of the electrode against the Ag/AgCl reference electrode was recorded after each Cu(II) addition. The reference electrode used in case of the platinum and graphite SPE was the screen printed Ag/AgCl reference electrode. All measurements were carried out at 25 ± 2 °C where the cells can be represented by:

Ag/AgCl||Cu^{2+}|ion-selective
       membrane|metal wire/disc.
Ag/AgCl||Cu^{2+}|ion-selective
       membrane|SPE (Pt or C).

Results and Discussion

Effect of coating composition and drying conditions

Several membranes of different coating compositions were prepared. The ratios of PVC, ionophore, and plasticizer were varied. Some of the results of this study are summarized in Table 1. It is clear from these results that the composition of the membrane very much affects the response and performance of the electrode. This is a well known and expected characteristic as reported in the literature. The ratios of all constituents should be optimized for best performance of the sensor. However, it is noteworthy that the drying conditions of the electrodes are also of extreme importance. It was evident in this study that drying the constructed ISE overnight at 60 °C always resulted in a much improved performance as compared to drying in air. Also, the physical shape of the membrane was improved where it seems that oven-drying, for prolonged periods, has an annealing effect on the membrane structure. In all cases of oven-dried ISEs, an improvement in shape and slope were clearly observed. Therefore, all ISEs prepared in this study were oven-dried at 60 °C for at least 18 h. Also, the membrane composition which was judged suitable with regard to slope contained 30% PVC, 4% ionophore, 2% CTAB, and 64% plasticizer. This composition was used to construct the Cu(II) ISE.

Response time of the electrode

The response times of all ISEs prepared were measured using 4.76 mM Cu(II) solution. The steady state response was reached in less than 30 s for all electrodes. This response time is reasonable for such sensors but can possibly be improved if a thinner coating is applied. However, no attempts to decrease the response time were carried out.
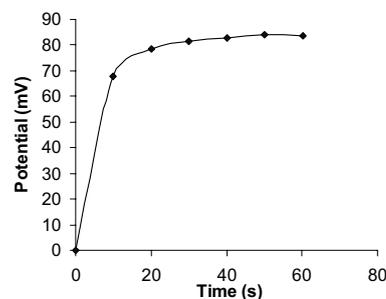

Fig. 1. Response time of the coated-copper Cu(II) electrode. Each point was recorded in presence of 4.76 mM Cu(II) solution.

All emf measurements were conducted at 40 s after Cu(II) addition. Fig. 1 shows the relationship between potential (mV) and time (s) where most of the signal intensity was reached in less than 15 s.

Effect of ionic strength

A 0.01 M acetate buffer, pH 3.7, containing different concentrations of KCl was tried. The variation in potential was very small (about ± 1 mV) in the KCl concentration range used (0.1–0.5 M). It was decided to use a 0.2 M KCl solution in 0.01 M acetate buffer as an ionic strength adjustment solution.

Effect of pH

The behavior of the fabricated ISEs was studied in 0.01 M acetate buffer solutions containing 0.2 M KCl at different pH. The pH was varied from 3.7–5.6 where it was observed that the pH, in the range used, did not affect the slope of the calibration curve. Buffers at higher pH's were not tried as Cu(II) starts to form the hydroxide which may complicate the explanation of the results. The independence of the performance of the Cu(II) ISE on pH is a merit of the proposed sensors where

Table 1. Membrane composition and its effects on the slope characteristics of the Cu(II) ion-selective electrode.

Membrane	PVC (mg)	DEP (mg)	Ionophore (mg)	CTAB (mg)	Slope (mV/decade)			SPE
					Ag Wire	Cu Wire	Pt	C
1 (air-dried)	30	65	3	2	16.5	30.7		
1 (oven-dried)	30	65	3	2	23.6	39.0		
2	30	64	4	2	28.1	48.5	28.7	50.9
3	35	60	3	2	31.5	40.5		
4	25	70	3	2	35.0	47.8		

exact control of the pH is unnecessary. In this study, it was decided to perform all measurements and experiments in an acetate buffer at pH 3.7.

Effect of light

A rather interesting effect of light on the performance of the fabricated ISEs was observed. The slope of the electrode was found to decrease in presence of light and increase as light is obscured. This behavior could be attributed to a ligand to metal charge transfer (LMCT) phenomenon observed for complexes of some transition metals with ligands containing oxygen and nitrogen chelating groups [20]. This unexpected effect can be clearly seen in Fig. 2. The slope of the calibration plot approaches Nernstian response in strong light and approaches the response for a monovalent Cu(I) in the dark. This phenomenon is currently being investigated in our laboratory where a set of related complexes are studied.

Effect of conditioning time of ISEs

The coated-wire and coated disc electrodes performance was evaluated for different soaking times, in the ionic strength adjustment buffer used. The slope was found to be generally independent of soaking times up to 18 h. Fig. 3 shows the effect of soaking on the coated-copper Cu(II) electrode where it is clearly seen that soaking did not practically affect the slope. However, since the soaking solution is the same as the test solution, it is recommended that the electrodes be stored in the buffer solution while not in use. The electrodes in
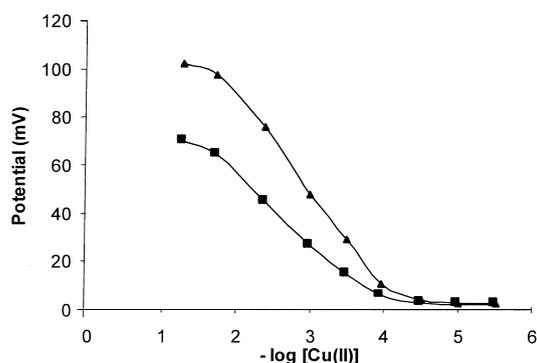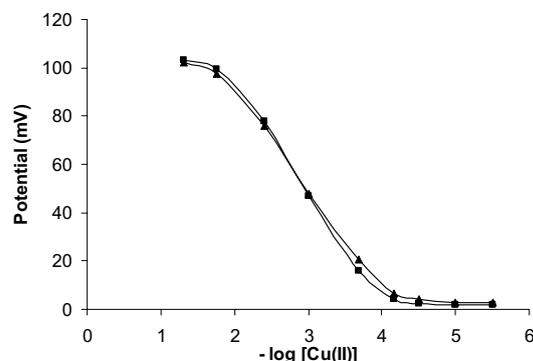

Fig. 3. Calibration plots for a Cu(II) coated-copper electrode after 1 h (▲) and 18 h (■) of soaking the ISE in the ionic strength adjusted buffer at pH 3.7.

this study were always stored in a 0.01 M acetate buffer, pH 3.7, containing 0.2 M KCl at room temperature (25 ± 2 °C).

Selectivity coefficients

The potentiometric selectivity coefficients (K_{ij}) for a variety of cations and anions was tested using the separate solution method (SSM) [21]. The Cu(II) concentration used was 3.00 mM and that of the interferent ions was 15.0 mM. Results of this study are summarized in Table 2 for the coated-silver Cu(II) ISE. Results are a characteristic of the membrane selectivity rather than the type of material coated. Results show a good selectivity of the prepared ISEs over most ions tested. However, Hg^{2+}, Fe^{3+}, and I^- were found to significantly interfere in all cases and should, therefore, be removed for successful determination of Cu(II). It was observed that the electrodes have a Nernstian response to I which may be due to coordination of I to Cu(II) and oxidation to give iodine, an observation under thorough investigation in our laboratory. Analysis of synthetic samples excluding Hg^{2+}, Fe^{3+}, and I at different concentrations of various ions resulted in essentially the same response for the specified Cu(II) concentration whether these ions were absent or present (at concentrations up to 0.5 M in some cases), suggesting a very high selectivity of the sensors.

Conclusion

Several versions of Cu(II) ion-selective electrodes were fabricated. These electrodes are sim-

Fig. 2. Effect of light on the potential of the coated-copper Cu(II) electrode. Response in the dark (▲) and in presence of light (■).

Interferent cation	K_{ij}	Interferent anion	K_{ij}
Na^+	3.01×10^{-2}	CO_3^{2-}	2.69×10^{-3}
NH_4^+	3.01×10^{-2}	$H_2PO_4^-$	2.91×10^{-3}
Ca^{2+}	8.87×10^{-3}	HPO_4^{2-}	2.49×10^{-3}
Mg^{2+}	6.01×10^{-3}	SO_4^{2-}	2.49×10^{-3}
Pb^{2+}	6.01×10^{-3}	Br^-	1.97×10^{-3}
Zn^{2+}	6.50×10^{-3}	I^-	0.510
Cd^{2+}	6.50×10^{-3}	NO_3^-	1.97×10^{-3}
Ni^{2+}	8.21×10^{-3}	SCN^-	5.42×10^{-3}
Co^{2+}	6.01×10^{-3}		
Fe^{3+}	0.211		
Hg^{2+}	1.01		

Table 2. Selectivity coefficients for Cu(II) ion-selective electrode.

ple, fast, and cheap for routine analysis. The electrodes should also be easily adapted to both miniaturization and mass production as their construction is extremely simple. The screen printed ISE results in essentially the same characteristic response as the coated-wire/disc electrodes. The selectivity of the described ISE is good over many possible interferents, which suggests a wide application for these devices. This work also revealed the possibility of a LMCT process in the Cu(II)-salophen ionophore which requires further investigation.

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