Highly selective copper membrane electrode using *C*-*p*-nitrophenyl-*N*-phenylnitrone

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The construction, performance characteristics and applications of a polymeric membrane electrode for Cu(II) ion are reported. The electrode was prepared by incorporating *C*-*p*-nitrophenyl-*N*-phenylnitrone as the charge carrier into a plasticized poly(vinyl chloride) membrane. The influence of membrane composition, pH and concentration of the solution were investigated. The electrode exhibits a potentiometric response for Cu^{2+} ion over the concentration range 1×10^{-6}–1×10^{-1} M with a detection limit of 5×10^{-7} M Cu^{2+}. It shows a relatively fast response time of about 15 s and can be used for about two months without any considerable divergence in potential. The electrode can be used at a pH of between 4.0–8.0. The selectivity of proposed electrode for Cu^{2+} in the presence of several metal ions. It was used as an indicator electrode in the potentiometric titration of Cu^{2+} with EDTA.

Introduction

Ion-selective electrodes provide a convenient and fast method for determination of metal or nonmetal ions. Potentiometric detection based on ISEs offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the last few years.[1]

Organic molecules containing O, N, S, *etc.* are capable of forming electron-rich interior cavities and possessing the ability to complex with ions through dipole–dipole or ion–dipole interaction.

Copper is one of the most widely distributed elements in the environment of industrialized countries. It is present in all organisms, land and marine. It has been shown that copper is an essential element for many biological processes, *e.g.* blood formation and the function of many important enzymes.[2–6] The demand for trace analysis for Cu^{2+} arises primarily in environmental and biological sciences since copper, although essential to life, is toxic at higher concentrations.

The purpose of this work was the development of a copper(II)-selective electrode based on a plasticized poly(vinyl chloride) (PVC) membrane, containing *C*-*p*-nitrophenyl-*N*-phenylnitrone as the membrane active phase, coated on the surface of a platinum-wire electrode. The electrochemical selectivity for a variety of ions and the effect of membrane matrix, ionophore concentration, additives, and pH on the potentiometric response properties of the electrode were investigated. The electrode was also used as an indicator electrode for titration of Cu^{2+} ion with chloride and for the determination of copper in real samples.

Experimental

Reagents

Reagent grade tetrahydrofuran (THF), sodium hydroxide, nitric acid, sodium tetraphenylborate (NaTPB) and ethylenediaminetetraacetic acid (EDTA), all from Merck, were used as received, except THF, which was distilled before use. Poly(vinyl chloride) of high relative molecular-weight and dibutyl phthalate (DBP) of the highest purity available from Aldrich were used without further purification. All metal ion solutions were prepared in doubly distilled water and solutions of different concentration were prepared by diluting 0.1 M, stock solutions, pH adjustments were made with nitric acid or sodium hydroxide solution, as required.

Preparation of *C*-4-nitrophenyl-*N*-phenylnitrone

This compound was prepared as described elsewhere.[7,8] A solution of *N*-phenylhydroxylamine (4.96 g, 0.045 mol) and 4-nitrobenzaldehyde (6.84 g, 0.045 mol) in the minimum amount of ethanol was allowed to stand at room temperature overnight. The crystalline precipitates were filtered and recrystallized from a mixture of 3:2 benzene:petroleum ether (40–60) to afford the nitrone (10 g, 91.7%) as yellow crystals. M.P. 184–185 °C. ^1H NMR ($CDCl_3$): δ ppm 8.42–8.56 (m, 2H), 8.26–8.36 (m, 2H), 8.06 (s, 1H), 7.65–7.76 (m, 2H), 7.38–7.52 (m,3H).

The chemical structure of *C*-4-nitrophenyl-*N*-phenylnitrone is shown in Fig. 1.

Electrode preparation

The coated-wire electrodes were prepared according to a previously reported method.[9] A mixture of PVC, plasticizer (DBP), and the membrane additive, total mass 200 mg, was dissolved in approximately 8 ml freshly distilled THF. To this

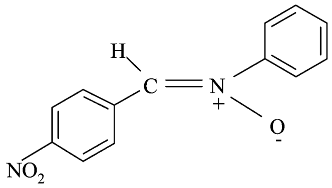

Fig. 1 Structure of *C*-4-nitrophenyl-*N*-phenylnitrone.

mixture was added the electroactive material (*C*-4-nitrophenyl-*N*-phenylnitrone), and then solution was mixed well. A platinum wire, approximately 1 mm in diameter and 10 mm long, sealed into the end of a glass tube and soldered on to a shielded cable, was cleaned with nitric acid. The clean wire was then coated by repeated dipping into the membrane solution in THF and left to dry overnight. The electrodes were rinsed with water and conditioned in 0.1 mol L^{-1} copper(II) nitrate solution. The first conditioning time was approximately 3 h and then 30–40 min for successive uses. The coating solutions are stable for several weeks if kept under refrigeration and can be used for the construction of new membranes.

Apparatus

Potentials were measured with a Metrohm model 691 pH/mV meter. A saturated calomel electrode (SCE) with a fiber junction was used as the reference electrode. Atomic absorption spectrometer (Perkin-Elmer) model 2380 was used for determination of copper. Measurements were performed according to the manufacturer's directions using the manual book. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode.

Potential measurement and calibration

The coated-wire electrode containing *C*-4-nitrophenyl-*N*-phenylnitrone carrier was used as the measuring electrode in conjunction with a saturated calomel electrode. The electrochemical system for these electrodes can be represented as follows:

$$\text{Hg, } Hg_2Cl_2\text{, KCl(sat.)} \parallel \text{Sample solution} \mid \text{PVC membrane} \mid \text{Pt electrode}$$

The electrode performance was investigated by measuring its potential in copper solutions prepared in the concentration range 1×10^{-7}–1×10^{-1} mol L^{-1} by serial dilution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential against the logarithm of the Cu^{2+} concentration. All solutions were freshly prepared by dilution from stock standard solution, 0.1 mol L^{-1} with deionized, distilled water. Activities were calculated according to the Debye–Hückel procedure.[10] The potentiometric titration of Cu^{2+} solutions was carried out with EDTA solution using the copper coated wire electrode as the indicator electrode in conjunction with a fiber junction SCE. Potentiometric selectivity coefficients ($K_{Cu^{2+}, M}$) were determined by means of the fixed interference method (FIM).

Results and discussion

C-4-nitrophenyl-*N*-phenylnitrone as an ionophore was found to be highly responsive to Cu^{2+} ion relative to several other metal ions. We therefore studied in detail the performance of the plasticized PVC membrane containing this ionophore for copper ion.

Influence of membrane composition

Several coated wire ion selective electrodes were constructed by varying the proportions of PVC, DBP, NaTPB and membrane active material *C*-4-nitrophenyl-*N*-phenylnitrone and their responses were investigated. It is well known that the sensitivity and selectivity of the coated wire ion selective electrodes depend not only on the nature of the ionophore used, but also significantly on the membrane composition, and the properties of the additives employed. Table 1 shows membrane compositions percents with linearity sensors.

The best response was observed with the membrane composed of 32% PVC, 3.5% NaTPB and 5% *C*-4-nitrophenyl-*N*-phenylnitrone. It was also observed that the potentiometric response of the electrode toward copper(II) ion depended on the concentration of the ionophore incorporated within the membrane. Increasing the amount of *C*-4-nitrophenyl-*N*-phenylnitrone up to 5% resulted in membranes for which slopes were larger and the linear range wider.

The slope of calibration and selectivity of sensor were greatly improved by the presence of the lipophilic anionic additive, NaTPB. It is known that lipophilic salts not only reduce the membrane resistance but also enhance the response behavior and selectivity and reduce interference from sample anions.[10–13] The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion-selective electrodes.[14,15] For charged carrier-based ion-selective electrodes, however, the charge sign of the ionic sites that results in the highest potentiometric selectivity depends on the charge of the ionophore, charge of the primary (analyte ion) and interfering ions, and the stoichiometry of their complexes with the ionophore.[16] However, as will be also shown below for ISEs based on ionophore *C*-4-nitrophenyl-*N*-phenylnitrone, it is not required that the primary ion (copper ion) and the ionophore have the opposite signs. Indeed, electrodes have previously been reported as Ca^{2+} selective electrode.[17] Among the different compositions studied responses were best for the membrane incorporating 32% PVC, 59.5% DBP, 3.5% NaTPB, and 5% *C*-4-nitrophenyl-*N*-phenylnitrone. This composition was, therefore, used to study the performance of the electrode, *viz.*, working concentration range, selectivity, lifetime, response time, and effect of pH. The characteristic properties of the optimized membrane are summarized in Table 2.

Response characteristics of the electrode

The pH response profile of the membrane electrode was examined using two Cu^{2+} concentrations. As illustrated in Fig. 2 for 1×10^{-3} mol L^{-1} Cu^{2+}, this remains constant within a pH range of approximately 4–8. Variation of the potential at pH < 4.0 could be related to protonation of the ligand in the membrane phase, which results in a loss of its ability to complex with Cu^{2+}, the potential drop may be because of hydrolysis of the Cu^{2+} ions, and also interaction OH^- with

Table 1 Optimization of membrane ingredients

No	%PVC	%DBP	%Ionophore	%NaTPB	Slope mV decade^{-1}	Linear range (mol L^{-1})
1	30	61	9	0	22.3	1×10^{-4}–1×10^{-1}
2	30.5	61	6.5	2	26.8	1×10^{-4}–1×10^{-1}
3	31	59	8	2	25.9	1×10^{-5}–1×10^{-1}
4	31	59	9	1	25.1	1×10^{-4}–1×10^{-1}
5	32	59.5	6.5	2	26.5	1×10^{-5}–1×10^{-1}
6	32	59.5	5	3.5	28.5	1×10^{-6}–1×10^{-1}

Table 2 Characteristics of optimized Cu^{2+}-ISE

Linear range	1×10^{-6}–1×10^{-1} M
Slope	28.5 mV decade^{-1}
pH range	4.0–8.0
Precision	At concentrations of 1×10^{-2} M and 1×10^{-3} M Cu^{2+} standard deviations were of ±0.5 and ±0.9 mV respectively.
Detection limit	5×10^{-7} M
Life time	2 months

Table 3 Stability and reproducibility of the copper electrode ($n = 5$)

Time (day)	Slope	Linear range
1	28.5 ± 0.4	1×10^{-6}–1×10^{-1} M
7	28.5 ± 0.4	1×10^{-6}–1×10^{-1} M
14	28.3 ± 0.5	1×10^{-6}–1×10^{-1} M
21	28.0 ± 0.5	5×10^{-6}–1×10^{-1} M
35	27.5 ± 0.6	8×10^{-6}–1×10^{-1} M
49	27.2 ± 0.6	5×10^{-5}–1×10^{-1} M
60	27.0 ± 0.6	1×10^{-5}–1×10^{-1} M
70	26.0 ± 0.8	1×10^{-5}–1×10^{-1} M

ligand. Therefore, all of the measurements were performed at pH 5.0.

The potentiometric response of the coated-wire electrode to different concentrations of Cu^{2+} was examined using the optimized membrane composition and conditions described above. The calibration graph is shown in Fig. 3, which shows the linear range to be from 1×10^{-6} to 1×10^{-1} mol·L^{-1}, the near-Nernstian slope is 28.7 mV decade^{-1} of Cu^{2+} concentration. The response time of the electrode was measured after successive immersion of the electrode in a series of Cu^{2+} solutions, in each of which the Cu^{2+} concentration increased tenfold, from 1×10^{-6} to 1×10^{-1} mol·L^{-1}. The static response time thus obtained was 15 s. Repeated monitoring of potentials (20 measurements) on the same portion of the sample at 1×10^{-2} mol·L^{-1} and 1×10^{-3} mol·L^{-1} Cu^{2+} resulted in standard deviations of ±0.5 and ±0.9 mV, respectively.

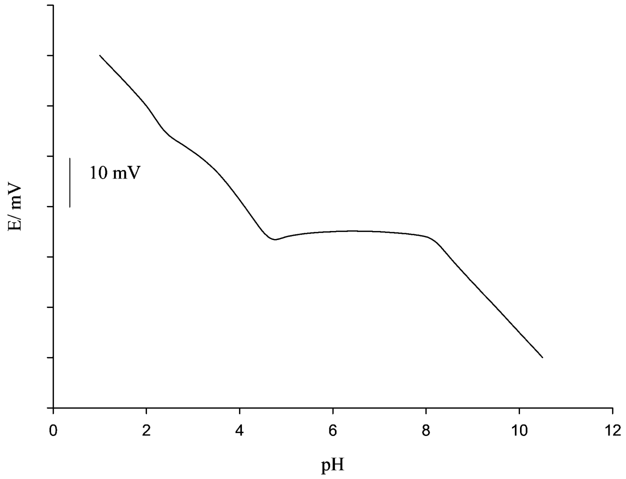

Fig. 2 Effect of pH of the test solution on the emf response of optimized Cu^{2+}-ISE, concentration of Cu^{2+} solution was 1×10^{-4} M.

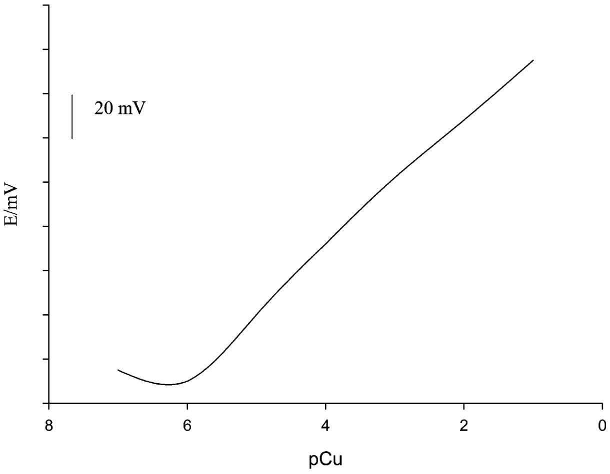

Fig. 3 Calibration graph for the optimized Cu^{2+}-ISE.

The electrode was tested over a period of two months to investigate stability. Life time studies were based on monitoring the change in electrode slope and linear response range with time (Table 3).

Potentiometric selectivity coefficients ($K_{Cu^{2+},M}$) describing the preference of the membrane for an interfering ion M relative to Cu^{2+} were determined by the fixed interference method (FIM).[18] The selectivity coefficients ($K_{Cu^{2+},M}$) for various cations were evaluated with a fixed concentration of interference (0.1 M), and varying Cu^{2+} concentrations. Table 4 lists the potentiometric selectivity coefficient data of the sensor for several cations to Cu^{2+}. The selectivity coefficients clearly indicate that the electrode selective to Cu^{2+} over a number of other cations. The ionophore of *C*-4-nitrophenyl-*N*-phenyl nitrone, seems to fit the coordination tendencies of Cu^{2+} ion better than any of the remainder cations tested.

Analytical applications

The optimized coated-wire electrodes were successfully applied as an indicator electrode in the direct potentiometric method for determination of Cu^{2+} in real samples. A suitable amount of the rock sample was dissolved by addition of concentrated nitric acid and hydrochloric acid. Then the resulting mixture was heated until it had completely dissolved. Then, the solution was neutralized with NaOH solution. Finally, 10 mL of a sodium acetate/acetic acid buffer solution of pH 5.0 was added. The solution was diluted with water in a 25 mL volumetric flask.

The copper content was measured by use of the coated-wire electrode and the standard addition method, and also by atomic absorption spectrometry (AAS). The results are presented in Table 5. In addition, the sensor was used for potentiometric titration determination of Cu^{2+} with EDTA. Typical titration results for 25 mL of 0.004 M Cu^{2+} with 0.01 M EDTA have a very good inflection point, showing perfect stoichiometry is observed in the titration plot. Therefore, the amount of Cu^{2+} ion in solution can be accurately determined with the electrode.

Table 4 Potentiometric selectivity coefficients for a optimized Cu^{2+}-selective electrode

Interference species	$K_{Cu,M}$	Interference species	$K_{Cu,M}$
Li^{+}	9×10^{-4}	Hg^{2+}	1×10^{-4}
Na^{+}	3×10^{-3}	Ba^{2+}	1×10^{-3}
K^{+}	3×10^{-4}	Zn^{2+}	5×10^{-4}
Ag^{+}	9×10^{-3}	Cd^{2+}	6×10^{-4}
Mg^{2+}	5×10^{-4}	Ce^{4+}	9×10^{-4}
Ca^{2+}	1×10^{-3}	Sr^{2+}	1×10^{-5}
Ni^{2+}	2×10^{-4}	Al^{3+}	3×10^{-3}
Pb^{2+}	9×10^{-3}	Mn^{2+}	4×10^{-4}
Co^{2+}	1×10^{-3}	Fe^{2+}	3×10^{-3}

Table 5 Determination of copper in different samples

Sample	Atomic absorption spectrometry(mmole/l)[a]	Copper selective electrode(mmole/l)
Synthesis sample	0.22 ± 0.02	0.23 ± 0.03
Rock sample	0.48 ± 0.03	0.47 ± 0.03

[a] Mean value ± standard deviation

Conclusions

Taking all these discussed results into account, the high degree of copper selectivity by the electrode makes it potentially useful for monitoring concentration levels of copper in real samples. The proposed sensor has been shown to have a good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range).

Acknowledgements

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