Polymeric membrane ion-selective electrode for copper(II) ions based on Cu^II-cyclohexaneone thiosemicarbazone complex

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Abstract : A PVC-based membrane of copper(II)-cyclohexaneone thiosemicarbazone complex shows a Nernstain potentiometric response (with slope of 29.2 mV/decade) for copper(II) ions over a wide concentration range (1×10^{-1} to 1×10^{-9} *M*). The potential of the electrode is independent of pH in the range 2.0-7.0. It has a fast response of about 15 s and was used for a period of 2 months with good reproducibility.

Keywords : PVC-membrane electrode, copper(II), cyclohexaneone.

The determination of trace amounts of copper using ion-selective electrodes (ISE) has become increasingly important because of an increase interest in biological and environmental pollution. Cyclic ionophores[1] have been widely successful in developing highly selective sensors for cations, because of their geometry takes the form of a bowl- or ring-shape, i.e. pre-organized to accommodate predominantly spherical cations (the macrocyclic effect). A number of successful acyclic ionophores have also been employed for ISEs development and ion transport[2]. As the sulphur ligands coordinate well with the transition metal cations, such as copper or mercury, so thiohydrazone and thiosemicarbazone ligands form stable complexes with the transition metals, which makes these ligands suitable candidates for ion selective electrodes[3]. In the present paper we reported PVC-based membrane electrode based on Cu^II-cyclohexaneone thiosemicarbazone complex (1) as neutral ionophore for the determination of Cu^II is reported.

(1)
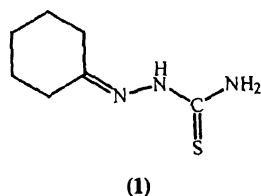
Results and discussion

After conditioning the PVC based membrane electrode for 3 days in 0.01 *M* solution of $Cu(NO_3)_2$, the electrode

potentials for a series of standard solutions were measured. Stable potentials were obtained within every 15 s. For the first five months the sensor showed a linear response with a slope of 29.2 mV per decade in the concentration range of 1×10^{-1} to 1×10^{-9} *M* $Cu(NO_3)_2$. With passage of time the slope deteriorated to 27.6 mV per decade, but the response remained linear.

The pH dependence of the electrode potentials for 1.0×10^{-3} and 1.0×10^{-4} *M* Cu^{2+} ions was tested over the pH range 1.0-8.0. It was found that the potentials are independent of pH in the range 2.0 to 7.0 and the same can be taken as the working pH range of the electrodes.

The potentiometric selectivity coefficients of the ISEs towards several cations were determined by the separate solution method (SSM) (Table 1). Despite its known limitations[4] it is a very convenient method when the selectivity for a large number of cations has to be determined. From Table 1, it is seen that except Co^{2+} all the other ions have selectivity coefficients of the order of 10^{-2} or lower and, therefore are not expected to interfere the functioning of the proposed Cu^{2+}-selective sensor even at high concentration levels. This may be attributed to the high selectivity of the ionophore for copper ion over other metal ions as well as the rapid exchange kinetics of the resulting complex. The presence of sulfur atoms as the soft coordination sites with a more or less convenient cavity size seems to generate great affinity of the ionophore towards Cu^{2+} ion, a d^9 low-valent transition metal ion[5].

The practical utility of the proposed membrane sensor

Table 1

Interfering ion (B)	Selectivity coefficients $\left(K_{Cu,M}^{pot}\right)$
Na^+	2.6×10^{-3}
K^+	1.4×10^{-3}
Tl^+	2.5×10^{-3}
Ag^+	2.7×10^{-3}
NH_4^+	4.6×10^{-3}
Mg^{2+}	2.2×10^{-3}
Ca^{2+}	5.1×10^{-3}
Co^{2+}	4.8×10^{-1}
Ni^{2+}	3.8×10^{-2}
Zn^{2+}	1.2×10^{-2}
Hg^{2+}	1.8×10^{-2}
Ce^{3+}	2.7×10^{-2}
Sm^{3+}	3.5×10^{-2}
Fe^{3+}	1.0×10^{-2}
Cr^{3+}	4.1×10^{-2}
Th^{3+}	1.3×10^{-2}

was tested by its use as an indicator electrode for the titration of $1.0 \times 10^{-2}\, M$ solution of Cu^{2+} with $1 \times 10^{-2}\, M$ EDTA solution. However, necessary adjustment of pH was required before adding the titrant. A sharp inflection point and perfect stoichiometry were obtained.

Experimental

Reagents : All reagents used were of analytical reagent grade. Doubly distilled deionized water was used throughout. Cu^{II}-cyclohexaneone thiosemicarbazone was synthesized as reported earlier[6]. The plasticizer dioctyl phthalate (DOP) and high molecular weight poly(vinylchloride) (PVC) were used as received from Fluka.

Electrode preparation : The general procedure to prepare the PVC membrane was to thoroughly mix 33 mg of powdered PVC, 6 mg of ionophores and 30 mg of plasticizer DOP. The mixture was then dissolved in 15

mL of dry THF. The resulting mixture was poured into a 50 mm petridish and the solvent was allowed to evaporate slowly at room temperature for 24 h. An opaque membrane of 0.4 mm thickness was obtained. The above mentioned composition is a very suitable one to avoid formation of cracks in the membrane using minimum amount of plasticizer. The membrane was cut to the size, attached to the glass-tube with the help of PVC glue, dried for 48 h and then conditioned with $1.0 \times 10^{-2}\, M\ Cu(NO_3)_2$ solution for 3 days.

Saturated calomel electrodes (SCE) were employed as reference electrodes and all potential measurements were made by using an Equiptronic-India Digital Potentiometer [EQ 602] at 25 ± 1 °C. The electrochemical system was as follows :

External saturated calomel electrode (SCE)	Internal 0.01 M Cu(NO₃)₂ solution	Membrane	Test solution	Internal saturated calomel electrode (SCE)

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