

Copper(II) ion selective PVC membrane electrode based on *S,S'*-bis(2-aminophenyl)ethanebis(thioate)

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Abstract. *S,S'*-bis(2-aminophenyl)ethanebis(thioate) (APhET) was synthesized and used as ion carrier in the preparation of copper(II) ion selective PVC membrane electrodes. The best performances were obtained by a membrane electrode with the composition: PVC as matrix (66 mg), APhET as ionophore (4 mg), *o*-NPOE as plasticizer (132 mg) and NaTBP as anionic additive (1/2 mole ratio in respect to APhET). This electrode exhibited a linear potential response to copper(II) in the concentration range $6.0 \times 10^{-6} - 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, with Nernstian slope of 29.5 mV/decade and detection limit down to $4 \times 10^{-6} \text{ mol dm}^{-3}$. It is suitable for copper(II) determination within pH between 4 and 7, and performs well over a period of 3 months. The electrode is selective for copper over a large number of metal ions, except Hg^{2+} . No interference was noticed by chlorides and other examined anions. Described membrane electrode can be used in analytical measurements by direct potentiometry as well in potentiometric titration.

Keywords: copper(II), ISE, *S,S'*-bis(2-aminophenyl)ethanebis(thioate), polymer membrane electrodes, potentiometry

INTRODUCTION

Potentiometric measurements using ion-selective electrodes (ISE) for determination of the respective metal ions is advantageous due to speed, wide dynamic ranges, and no requirement for the sample pretreatment. The development of highly specific ion-selective electrodes for application in industrial, environmental, clinical, and laboratory analysis is an ongoing challenge.

Modern solvent polymer membrane electrodes (ISEs) represent a generic approach to chemical sensing compared to other types of ISEs (*e.g.* glass-, single crystal-, or precipitate- based electrode materials). The incorporated ion carrier (ionophore) is the key compound of the polymeric membrane that defines the membrane selectivity by interaction with primary ion (cavity size, geometry of the molecules and type of functional group which leads to a specific metal-ligand interaction).¹ Hence, the electrode with satisfying potentiometric and electrochemical properties can be achieved by synthesis of highly lipophilic and selective complexing agents that can be doped within the membrane. The potentiometric characteristics, obtained for a given ionophore, depend significantly on the membrane composition, nature of plasticizer and additive used, combined with optimum lipophilicity of the ionophore and plasticizer that ensure

stable potential and long life time.

Due to many applications of copper in industry, biological and medical systems, fast and accurate determination of copper is important with respect to its widespread occurrence in diverse samples. The ISEs for copper determination have received much interest, and many different organic compounds were prepared and investigated as sensing ionophores for copper(II) ion. Bühlmann *et al.* summarized the ionophores for Cu^{2+} sensors in 1998,² and recently Cu^{2+} ionophores have also been reported.^{3–24}

In this work we studied a novel copper(II) membrane electrodes based on *S,S'*-bis(2-aminophenyl)ethanebis(thioate) (APhET), which forms stable, in water insoluble complex with copper(II) ion.²⁵ Influence of different plasticizers and different components ratio were investigated for obtaining a sensor with optimal response characteristics for determination of copper(II) ion in water samples in wide pH range.

EXPERIMENTAL

Reagents

All reagents used in this research were of analytical grade. Metallic potassium, absolute ethanol, 2-amino

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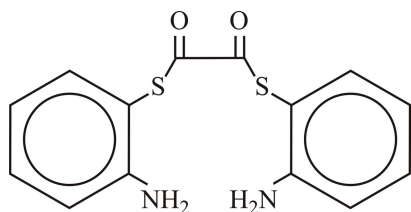


Figure 1. Structure of *S,S'*-bis(2-aminophenyl)ethanebis(thioate).

thiophenol, oxalyl chloride, sodium tetraphenylborate (NaTPB), poly(vinyl chloride) (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), dibutyl sebacate (DBS), diethyl sebacate (DES), dimethylformamide (DMF), tetrahydrofuran (THF) were purchased from Fluka (Buchs, Switzerland). Copper and potassium nitrates, sodium hydroxide and hydrochloric acid were from Kemika (Zagreb, Croatia). Working solutions were prepared by diluting 0.1 mol dm^{-3} stock solutions. All aqueous solutions were prepared in double distilled water.

Synthesis of *S,S'*-bis(2-aminophenyl)ethanebis(thioate)

S,S'-bis(2-aminophenyl)ethanebis(thioate) (Figure 1) was synthesized according to the similar procedure described previously.²⁵ First, potassium ethoxide, produced by mixing 40 mmol (1.56 g) metallic potassium with 50 cm³ absolute ethanol under nitrogen atmosphere, reacted with 40 mmol (5.01 g) 2-amino thiophenol. In further, 20 mmol (2.6 g) oxalyl chloride was slowly added to this solution, and mixed for 2 hours at room temperature and thereafter the mixture was refluxed for 2 hours. The mixture was filtered while hot and than filtrate was evaporated and recrystallized in ethanol. The pale-yellow, air-stable, crystalline solid was insoluble in water, and soluble in methanol, ethanol, and chloroform. The purity of this reagent was checked by physical data: melting point range, 90–92°C; IR (cm⁻¹) 3377–3295 (NH₂), 1608 (C=O). ¹H NMR, δ (ppm:CD₃Cl): 4.20 (NH₂, 4H); 6.30–7.20 (Ar-H, 8H).

Electrode preparation

Typical membrane components, 32 % PVC, 66 % plasticizer and 2 % ionophore with NaTPB as anionic excluder, were dissolved in minimal amount of THF, mechanically mixed and poured into Teflon moulds. THF was allowed to evaporate 48 hours at room temperature. These membrane discs were cut and fixed to the PVC tubing using silicone. The tube was filled with internal filling solution ($1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cu}^{2+}$ in $0.1 \text{ mol dm}^{-3} \text{ KCl}$). The electrode was finally conditioned for 24 hours by soaking in $1 \times 10^{-3} \text{ mol dm}^{-3}$ copper(II) solution. Membranes with different compositions were prepared and investigated.

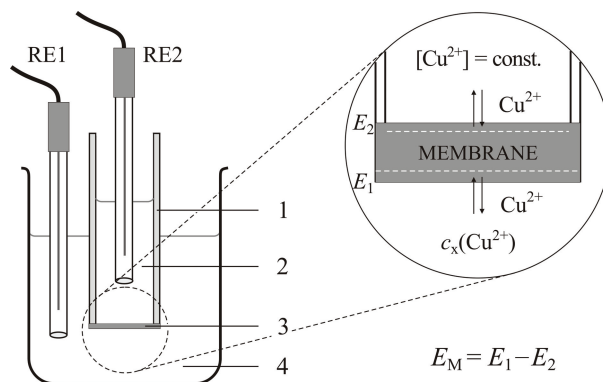


Figure 2. Cell assembly used in potentiometric measurements of copper(II) membrane electrode potential (E_M): 1 - PVC tube; 2 - internal reference solution; 3 - membrane; 4 - analyte solution.

Apparatus and potentiometric measurements

All potentiometric measurements were carried out by using the following cell assembly showed in Figure 2. A saturated calomel electrode (SCE) was used as an internal reference electrode. External reference electrode was double junction Ag/AgCl (KCl, 3 mol dm^{-3}). All potentiometric measurements were carried out with the following assembly: Hg/Hg₂Cl₂ (saturated) | internal solution ($1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cu}^{2+}$ in $0.1 \text{ mol dm}^{-3} \text{ KCl}$) | PVC membrane | test solution. The potentiometric measurements were Metler Toledo InLab 301 electrode. The potentiometric measurements were carried out with Mettler Toledo SevenEasy pH meter. Dynamic response was recorded with computer connected to the pH meter. The potential was recorded after addition of 0.01 mol dm^{-3} or 0.1 mol dm^{-3} standard copper(II) solution in magnetically stirred $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ (pH 6.4). The investigated concentration of copper(II) ion in sample solution was from $1 \times 10^{-6} \text{ mol dm}^{-3}$ to $5 \times 10^{-2} \text{ mol dm}^{-3}$. Detection limits were estimated according to IUPAC,²⁶ as the intersection of two linear lines, the one extrapolated from 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 plot of the potential change and the concentration of copper(II) ion.

RESULTS AND DISCUSSION

APhET tends to form a stable 1:1 complex with copper(II) cation by coordination with both nitrogen and sulfur atoms.²⁵ Because of its solubility in an organic solvent and insolubility in water, we used APhET as sensing ionophore for PVC membrane electrode.

In such a case the electrode response to copper(II) ion may be the consequence of the complexation reaction at the membrane surface:

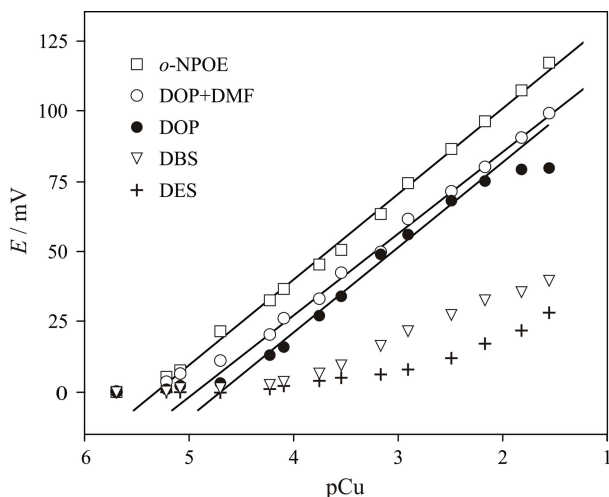
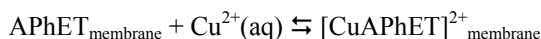


Figure 3. Potentiometric response of copper(II) membrane electrodes prepared by different plasticizers.



where AphET is neutral carrier. Neutral carrier based cation-selective electrodes require lipophilic ionic sites with charge opposite to that of the primary ion for obtaining a Nernstian response. Otherwise, charged carrier based ISEs need ionic sites with the same charge sign as the primary.¹ All the AphET membrane electrodes prepared without anionic sites (NaTPB) show significantly deterioration in slope (not shown) and it appears that *S,S'*-bis(2-aminophenyl)ethanebis(thioate) acts like neutral ionophore in the membrane. The lipophilicity, polarity, viscosity and dielectric constant of plasticizer play a significant role in efforts to ensure the long and stable response by the sensor assembly.²⁷ The influence of used plasticizer, namely: DES ($\epsilon = 5$), DBS ($\epsilon = 4$), DOP ($\epsilon = 7$) and *o*-NPOE ($\epsilon = 24$) is shown at Figure 3. The performance of membranes without the ionophores was also investigated and it was seen that they generate no potential.

Membrane electrode prepared with *o*-NPOE exhibited Nernstian response of 29.5 mV per decade, with linearity down to 6.0×10^{-6} . The change of plasticizer, toward higher dielectric constant, improved lower detection limit and also extended linear range to higher concentration. It has been attributed to the polarity of the plasticizer, which can be estimated from the interaction of charged species with a continuum of given dielectric constant. A plasticizer with high dielectric constant as *o*-NPOE ($\epsilon = 24$) permit divalent ion sensors and generation of free ions rather than ion-pairs,²⁸ although dielectric constant of membrane does not necessarily have to correspond exactly to the dielectric constant of the plasticizer.

According to the above, we intended to increase dielectric constant of DOP membrane by adding 40 mg

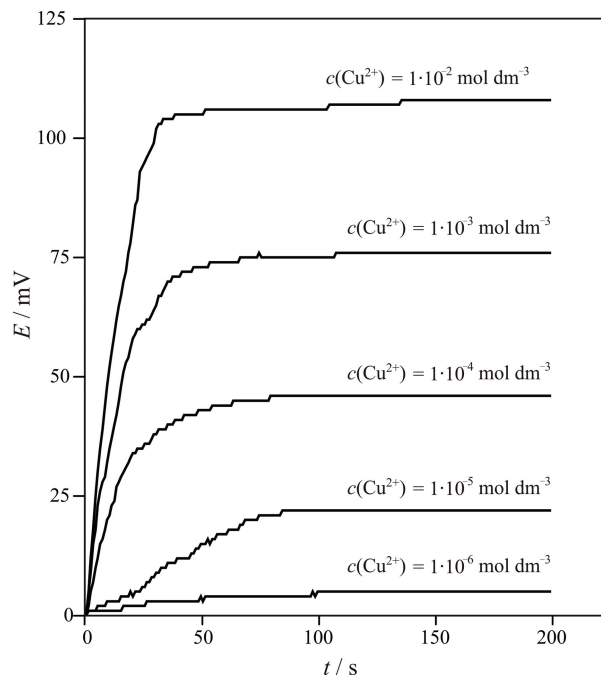


Figure 4. Dynamic response of copper(II) membrane electrode with *o*-NPOE as plasticizer on different concentration of copper(II).

of DMF ($\epsilon = 38$) into membrane cocktail. Significant improvement, concerning linearity, at high copper(II) concentrations was observed (Figure 3). However, as a consequence of DMF extraction into a sample solution during exploitation, deterioration in slope and detection limit was noticed.

Response time and reversibility

The response time of the prepared electrode has been determined by measuring the time required for the achievement of a stable potential after addition of a standard solution of copper(II) ion. A dynamic response at different concentration of copper(II) ion in solution was examined. On Figure 4 it can be seen that the increase of copper(II) ion concentration decreased time for reaching the equilibrium state. The response time was typically around 70 s for concentrations lower than $1 \times 10^{-4} \text{ mol dm}^{-3}$ and around 30 s for concentrations above $1 \times 10^{-3} \text{ mol dm}^{-3}$. Above mentioned indicates that a genesis of the potential was governed by the processes at the interface of the aqueous and organic membrane phases.

The reversibility of the electrode was evaluated by alternatively immersion of membrane electrode in two different concentrations (1×10^{-4} and $1 \times 10^{-3} \text{ mol dm}^{-3}$) of copper(II) ion. It can be seen from Figure 5 that the electrode exhibited satisfactory reversibility.

Potentiometric response characteristics of membrane electrode remained unchanged after 3 months, when membrane electrodes were kept in dry and dark

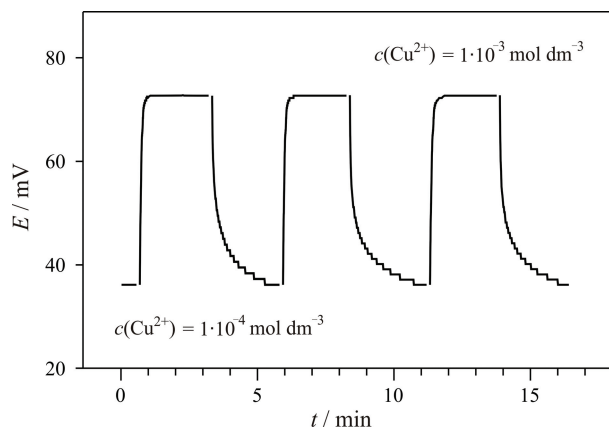


Figure 5. Reversibility of copper(II) membrane electrode with *o*-NPOE as plasticizer.

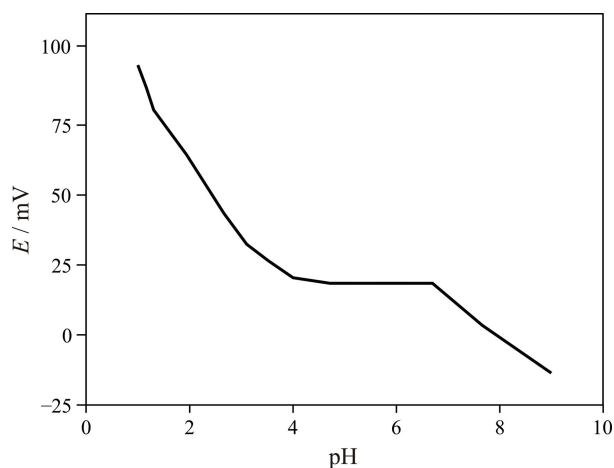


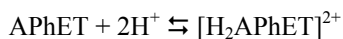
Figure 6. The effect of pH on the response of copper(II) membrane electrode with *o*-NPOE as plasticizer for 1×10^{-3} mol dm $^{-3}$ copper(II).

place. Before measurement the electrode had been conditioned for 3 hours in 1×10^{-3} mol dm $^{-3}$ copper(II) solution.

Effect of pH

Effect of pH on the potential response of membrane electrode was examined at concentration of 1.0×10^{-3} mol dm $^{-3}$ copper(II) ion. A pH range was 1–9 and it was controlled using HCl and NaOH solutions. As can be seen on Figure 6, a constant potential for the membrane electrode was obtained in the pH range between 4 and 7.

The variation of the potential at pH lower than 4 can be attributed to the protonation of ionophore $-\text{NH}_2$ group:



and the electrode response became preferable on H^+

Table 1. Selectivity coefficients for the copper electrodes determined by MPM*

Interferent species B	$K_{\text{Cu}^{2+},\text{B}}^{\text{pot}}$		
	DOP	<i>o</i> -NPOE	DOP+DMF
Zn $^{2+}$	3.2×10^{-5}	3.0×10^{-5}	2.9×10^{-5}
Cd $^{2+}$	2.5×10^{-4}	2.7×10^{-4}	2.7×10^{-4}
Pb $^{2+}$	1.3×10^{-3}	2.9×10^{-3}	2.0×10^{-3}
Fe $^{2+}$	4.8×10^{-3}	6.3×10^{-3}	5.9×10^{-3}
Ni $^{2+}$	6.7×10^{-5}	6.9×10^{-5}	6.3×10^{-5}

*MPM match potential method.

over copper(II) ion. On the other hand in alkaline media the potential drop was the consequence of $\text{Cu}(\text{OH})_2$ precipitation.

Selectivity of the electrode

Selectivity is clearly one of the most important characteristic of any ion-selective sensor as it determines the extent of sensor utility in real sample measurement. The selectivity coefficients represent electrode response to the species to be measured over other ions present in solution. As for IUPAC recommended match potential method (MPM)²⁹ selectivity coefficient is given by relation:

$$K_{\text{A},\text{B}}^{\text{pot}} = \frac{a_{\text{A}}' - a_{\text{A}}}{a_{\text{B}}}$$

where a_{A}' is a known activity of the copper(II) ion in solution added into a reference solution that contains a fixed activity a_{A} of copper(II) ion. The corresponding potential change is recorded. After that, a solution of an interfering ion (a_{B}) is added to the reference solution until the same potential change is recorded. A value of 1 for selectivity coefficient indicates equal response to both primary and interfering ions.

The selectivity coefficients toward copper(II) are presented in Table 1. No response was noticed on the Co^{2+} , Mn^{2+} , Ca^{2+} , Ag^+ , K^+ , Na^+ . Values of selectivity coefficient in the case of the Fe^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} indicated that these ions, in investigated concentration range of copper(II) ion, did not significantly affect the electrode response. It was found that Hg^{2+} causes a strong interference with $K_{\text{A},\text{B}}^{\text{pot}} > 10$, indicating that APhET makes stronger complex with Hg^{2+} than with Cu^{2+} . This evidence needs further investigating of APhET as sensing ionophore for Hg selective electrode.

The interference of anions was also investigated, as halides are known to cause interference in the determination of copper(II) ion. There was not any interference noticed on examined anions: SO_4^{2-} , CH_3COO^- , salicylate, Br^- , Cl^- , phosphate, NO_3^- and SCN^- .

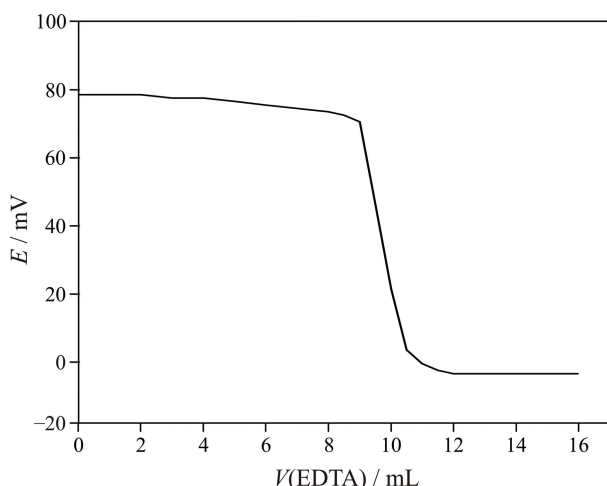


Figure 7. The potentiometric titration plot for artificial sea water (30 cm^3) containing $3 \times 10^{-3} \text{ mol dm}^{-3}$ copper(II) against EDTA (0.01 mol dm^{-3}) using copper(II) membrane electrode with *o*-NPOE as plasticizer.

Analytical application

The membrane electrode with *o*-NPOE was used as an indicator electrode in the potentiometric titration of copper(II) ion with EDTA in artificial sea water prepared according to Kester et al.³⁰ Typical results for titration of a 30 cm^3 $3 \times 10^{-3} \text{ mol dm}^{-3}$ copper(II) solution with 0.01 mol dm^{-3} EDTA are shown in Figure 7. The obtained titration plot shown on Figure 6 is a standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Cu-EDTA complex. This indicates that the amount of copper(II) ion can be accurately determined from the resulting neat titration curve providing a good end point.

CONCLUSIONS

Copper(II) PVC membrane electrodes based on APhET as ion carrier, with different plasticizer were prepared

Table 2. Properties of copper(II) membrane electrode with *o*-NPOE as plasticizer*

Parameter	
Slope per decade	29.5 mV
Response time	70–30 s depending on concentration (see text)
pH range	4–7
Detection limit	$4.0 \times 10^{-6} \text{ mol dm}^{-3}$
Linear range	$6.0 \times 10^{-6} - 5.0 \times 10^{-2} \text{ mol dm}^{-3}$
Life time	3 months

*membrane composition: PVC (66 mg), APhET (4 mg), *o*-NPOE (132 mg) and NaTBP (1/2 mole ratio in respect to APhET).

and characterized. Obtained results revealed that membrane electrode with *o*-NPOE as plasticizer exhibited the best response characteristics (Table 2).

It was found interference from Hg^{2+} , while other investigated ions had no influence on electrode selectivity toward copper(II) ion.

Membrane electrode based on APhET as ionophore can be recommended for determination of copper(II), especially in presence of chloride ions. It can be used in analytical measurements by direct potentiometry as well as potentiometric titration.

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SAŽETAK

Bakrova(II) ion selektivna elektroda na bazi *S,S'*-bis(2-aminofenil)etanbis(tioate)

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Opisana je priprava PVC membranske elektrode za potenciometrijsko određivanje bakrova(II) iona sa *S,S'*-bis(2-aminofenil)etanbis(tioate) (APhET) kao aktivnom vrstom. Od pripremljenih i ispitanih elektroda najbolja se pokazala ona sastava: PVC (66 mg), APhET (4 mg), *o*-NPOE kao plastifikatora (132 mg) i NaTBP (1/2 molnog omjera u odnosu na APhET). Linearna ovisnost potencijala o koncentraciji bakrovih(II) iona između 6.0×10^{-6} i 5.0×10^{-2} mol dm⁻³, odgovara Nernstovom odzivu za divalentne katione (29.5 mV po dekadi). Uz vijek trajanja od 3 mjeseca ovom elektrodom moguće je određivanje bakrova(II) iona u području pH između 4 i 7, do donje granice detekcije od 4×10^{-6} mol dm⁻³. Od ispitanih metalnih iona jedino su živini(II) ioni pokazali značajniji utjecaj na selektivnost elektrode, a analitička primjena ovog senzora osim u direktnoj potenciometrijskoj analizi moguća je i pri potenciometrijskoj titraciji u kloridnom mediju.