



Designing and synthesis of bis(2,4-dihydroxybenzylidene)-1,6-diaminohexane and its efficient application as neutral carrier for preparation of new copper selective electrode

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ABSTRACT

A new copper carbon paste electrode (CPE) based on incorporation bis(2, 4-dihydroxybenzylidene)-1,6-diaminohexane (DHBDAH) in graphite powder matrix has been described. The influence of variables including an amount of graphite, sodium tetrphenylborate (NaTPB), DHBDAH and nujol on the Cu^{2+} carbon paste electrode response was studied and optimized. The optimum carbon paste composition was set as follows, graphite powder: NaTPB: Nujol: DHBDAH with amount of 150:2.3:30:4 mg, respectively. At the optimum conditions, the potential response is linear over the concentration range of 5.0×10^{-8} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 29.5 ± 1.1 mV per decade of Cu^{2+} ion concentration. The good performance of electrode such as low detection limit of (LOD) (4×10^{-8} mol L^{-1}), wide applicable pH range (2.5–5.5), fast response time (10 s) and adequate shelf life (69 days) indicate the utility of the proposed electrode for evaluation of Cu^{2+} ion content in various analysis. Due to moderate potentiometric selectivity coefficients of proposed electrode obtained by fixed interference method (FIM) and separate solution method (SSM), the proposed electrode successfully can be applied for the determination of Cu^{2+} ions content in some real samples.

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1. Introduction

Copper is an essential element in human body and due to its important roles in various biological processes has widespread occurrence in environmental samples. Copper is an essential element at trace level while it is toxic element (fatal to organisms) at high concentration level. Although, large amount of copper ion (Cu^{2+}) can be tolerated by human beings, however, its excessive dosage and long term exposure may cause irritation of the nose, mouth and eyes and that lead to causes headache, stomach ache, dizziness, vomiting and diarrhea [1–3]. This element plays a vital importance in the performance of the human nervous and cardiovascular systems, skin, bone, immune and reproductive systems (gene transcription). Copper concentration in potable water is usually very low ($\leq 20 \mu\text{g L}^{-1}$), and its high concentration (more than $1 \mu\text{g mL}^{-1}$) impart a bitter taste to water [4], cause vomiting and may eventually cause liver damage. For these reasons a precise, accurate and rapid procedure for evaluation of Cu^{2+} ion content has been much interest for researches. Reactivity and biological uptake of copper are strongly affected by its free ion concentration.

A number of instrumental methods such as inductively coupled plasma/mass spectrometry, stripping voltammetry, flame atomic absorption spectrometry (FAAS) [5–11] and ion selective electrode (ISE) have been used for trace determination of Cu^{2+} ion content at low concentration levels [12,13]. Most of these methods are time consuming, has multiple sample manipulations and/or need expensive analytical laboratories. Among these methods, ISEs widely use for the direct determination of ionic species in complex systems and direct potentiometric measurement of various ionic species in environmental, industrial and clinical samples. ISEs based on solvent polymeric membranes or carbon paste incorporating specific ion carriers with unique advantages such as ease of preparation, fast response, non-destructive, low cost, wide linear range, relatively low detection limit and especially adequate selectivity, have been shown to be very useful tools for chemical, clinical and environmental analysis [12–15].

Potentiometric method based on ISE as indicator electrode is an alternative method for determination of analytes ions [16–18]. Potentiometric measurement with a copper selective electrode allows direct determination of free copper ion concentration in water samples. For this reason researchers attempted to develop sensors (ISE) for its determination with high selectivity and sensitivity [19–22]. The wide application of ISEs in different fields leads to pressure on analytical chemists to develop new sensors for fast, accurate,

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reproducible, and selective determination of various species [23–28]. The operation mechanism of the carbon paste electrodes (CPEs) depends to the properties of the modifier materials that control the electrode selectivity towards the target species. Schiff base ligands especially those derived from substituted salicylaldehyde derivatives and various amines have been found to play an important role in revealing the preferred co-ordination geometries of metal complexes. Schiff base ligands are one of the most important classes of chelating agents. Present Schiff base is a N_2O_2 donor Schiff base can be coordinated to metal ion as four dentate ligand via azomethine nitrogen and phenolic oxygen atoms form very stable complexes with transition metal ions. N_2O_2 Schiff base coordinate to copper ion as four dentate and form easily four coordinated complex. Therefore they can be used as modifier materials in ISEs. The unique nature of N-donor and hydroxyl Schiff bases is enhanced by the existence of a widely spread π -conjugation system. Based on these opinions, in this work, bis(2,4-dihydroxybenzylidene)-1,6-diaminohexane (DHBDAH) as a novel carrier was applied for determination of Cu^{2+} ion content in a wide concentration range. The selectivity for a variety of ions and the effect of the membrane matrix, ionophore, additive amount and pH on the potentiometric response properties of the proposed electrodes are investigated.

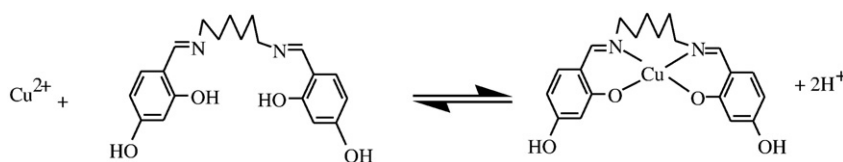
2. Experimental

2.1. Apparatus, reagents and materials

All the potential and pH measurements were carried out with a pH/ion meters model 691 Metrohm (Switzerland). Absorbance measurements were carried out with a Jasco model V-570 spectrophotometer using 1 cm quartz cells (Jasco Co., Hachioji, Tokiyo, Japan). The evaluation of Cu^{2+} ion content was carried out on a Shimadzu 680 AA atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector, at wavelengths 324.8 nm using an air-acetylene flame. Analytical-reagent grade and Graphite powder and high-purity Nujol oil, Sodium tetraphenylborate (NaTPB) supplied from Fluka Co. (Buchs, Switzerland) were used for the construction of unmodified and modified CPE. All solutions were prepared from analytical reagents and distilled water.

2.2. Synthesis of carrier (DHBDAH)

An ethanolic solution of hexane-1, 6-diamine (0.581 g, 5 mmol) was added to a solution of 2, 4-dihydroxybenzaldehyde (1.38 g, 10 mmol) in absolute ethanol (20 mL) and refluxed for 4 h. After several hours and gradual evaporation of solvent, the product was obtained AS yellow precipitate. The powder was filtrated and washed twice with cooled ethanol and dried under air (74% yields). Elemental analysis: $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86; found: C, 68.9; H, 6.7; N, 7.9. IR(KBr, cm^{-1}): 3433(w, OH(H_2O)) 3300–3500(bs, ν OH(phenolic)), 3051(w, CH- Aromatic), 2951(w, Aliphatic), 2932(w, CH-Aliphatic), 2861(w, CH-iminic), 1640(vs, ($-C=N$)asym), 1603(s, ($-C=N$) sym), 1534(m, C=C), 1481(s, C=C), 1443(m, C=C), 1352(m, CH_2), 1271(s, C-N), 1237(s), 1171(s), 1112(m, C-O), 1011(m, C-O), 974(m), 932(w), 853(m), 792(s), 756(m). Structure of this ligand and its probable complexation with copper(II) ion has been illustrated in scheme 1.



Scheme 1. Structure of ligand and its probable complexation with copper(II) ion.

2.3. Electrode preparation and potential measurements

Unmodified CPE was prepared by mixing of 150 mg of reagent-grade graphite powder and 30 mg of Nujol oil with a mortar and pestle. Modified CPE (MCPE) with various compositions was prepared by mixing 150 mg of graphite powder, 30 mg of Nujol with different weight of the carrier and additive to get different compositions. Both unmodified and modified CPEs were packed into 5.0 mL polyethylene syringes with diameter of 2.5 mm, while its tip had been cut off and its electrical contact to the paste was established via inserting a thin copper wire through flank.

2.4. Measurements of electromotive force (emf)

The electromotive force (emf) measurements were carried out at 25 °C with the following cell assembly:

MCPE | Sample solution | Reference electrode.

All emf observations were made relative to a double junction of Ag/AgCl reference electrode with the chamber filled with a KCl solution. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. The performance of the electrodes was investigated by measuring the emfs of Cu^{2+} nitrate solutions with concentration in the range of 1×10^{-9} to 1×10^{-1} mol L^{-1} by serial dilution 0.5 mol L^{-1} . In each solution after stirring and reaching the equilibrium the potential was measured and plotted versus logarithmic function of Cu^{2+} ion concentration.

2.5. Spectrophotometric titrations

Standard stock solutions of DHBDAH (1.0×10^{-2} mol L^{-1}) and Cu^{2+} ions (1.0×10^{-2} mol L^{-1}) were prepared by dissolving required amount of compounds in dimethylsulfoxide (DMSO) solvent to investigate the stoichiometry and stability constant of respective complexes by spectrophotometric method. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution (5×10^{-5} mol L^{-1} , 2.5 mL) was carried out by the addition of microliter amounts of a concentrated standard solution of the Cu^{2+} ion in DMSO (1.57×10^{-3} mol L^{-1}) using a pre-calibrated micro syringe [29–31].

3. Result and discussion

The titled Schiff base ligand was synthesized by condensation reaction between 1,6-diaminohexane and 2,4-dihydroxy benzaldehyde in molar ration of 1:2 in ethanol. Analytical data are well in agreement with proposed structure. In IR spectrum, absence of characteristic vibrations of diamine and aldehyde attributed to NH_2 and carbonyl groups respectively and appearance of new characteristic asymmetric and symmetric stretching vibrations assigned to azomethine groups($C=N$) at 1640 and 1603 cm^{-1} as well as other stretching or bending vibrations as in experimental section confirm the synthesis of ligand. Because of existence donor group in structure of DHBDAH Schiff base (two nitrogen atoms and four hydroxyl groups), this ligand (as ionophore) is coordinated to copper ion as fourdentate via N_2O_2 and form easily very stable square planner four coordinated complex [32] and therefore

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