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Theoretical and practical investigations of copper ion selective electrode with polymeric membrane based on N,N′-(2,2-dimethylpropane-1,3-diyl)-bis(dihydroxyacetophenone)

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ABSTRACT

A novel ion-selective poly(vinyl chloride) (PVC) membrane sensor for Cu^{2+} ions based on N,N′-(2,2-dimethylpropane-1,3-diyl)-bis(dihydroxyacetophenone) (NDHA) as a new ionophore was prepared and studied. The best performance was observed for the membrane composition, including 30:65:1:4 (wt%) = PVC:DBP:KT*p*ClPB:NDHA. The electrode showed a good Nernstian slope of 30.0 ± 0.5 mV/decade in a wide linear range activity of 3.0×10^{-7} to 1.0×10^{-2} mol dm^{-3} $Cu(NO_3)_2$ with limit of detection 2.5×10^{-7}. Sensor exhibited a fast response time ($t_{95\%} < 10$ s) and could be used for about 4 months in the pH range of 3.0–7.4. The proposed potentiometric sensor was found to work satisfactorily in partially non-aqueous media up to 30 (vol%) content of methanol, ethanol and acetone. Applications of this electrode for the determination of copper in real samples, and as an indicator electrode for potentiometric titration of Cu^{2+} ion using EDTA, were reported. In order to predict the extraction ability of NDHA for different metallic ions, the complexes [M(NDHA)] and $[M(H_2O)_6]$ (where M = Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, K^{+} and Al^{3+}) were investigated using ab initio theoretical calculations. The metal binding capability was evaluated using the binding energy. Results of our study could be useful for prediction of the extraction power of this Schiff base and could play a guiding role in planning experiments.

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1. Introduction

Copper is an essential trace element in biological systems [1] and in living organisms where it serves as a cofactor in at least 30 important enzymes [2]. However, above a healthy limit it accumulates in the liver, causing diarrhea, vomiting, transpiration and depending on its concentration, death from bleeding [3,4]. In view of widespread use of Cu and consequently, its occurrence in environments and its poisonous nature, it is important to monitor it. There are several techniques, which have been used for determination of copper in solution including flame atomic absorption spectroscopy (FAAS) [5–8], stripping voltammetry [9,10], inductively coupled plasma-optical emission spectrometry (ICP-OES) [11,12], electrothermal atomic absorption spectrometry (ET-AAS) [13–15], spectrophotometry [16,17] and inductively coupled plasma-mass spectrometry (ICP-MS) [18]. In spite of the fact that these methods provide accurate results, they are not very convenient for analysis of the large number of environmental samples because of the requirement of sample pre-treatment and sufficient infrastructure backup. Ion-selective electrodes (ISEs), especially those with neutral carrier-based solvent polymeric membranes, have been studied for more than three decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples [19,20]. Potentiometric detection based on ISEs is a simplest method, offers several advantages such as fast and easy preparation procedures, simple instrumentation, relatively fast response time, wide concentration range, reasonable selectivity, low cost and may also be suitable for online analysis. Recently, copper selective electrodes, especially those based on crown ethers [21], aza [22] and thia [23] compounds, different noncyclic ionophores containing nitrogen atoms [24–26], calixarenes [27,28] and Schiff base derivatives [29–32] have been reported as possessing improved selectivity characteristics. Schiff bases (SBs) or imines, $R_2C{=}NR$– are the condensation products of aldehydes and ketones reacting with primary amines and these ligands are well known to form stable complexes with metal ions. The geometric and cavity control of the host-guest complexation and modulation of lipophilicity in SBs provide remarkable selectivity, sensitivity and stability for specific ion [33]. In the present study a Schiff base, N,N′-(2,2-dimethylpropane-1,3-diyl)-

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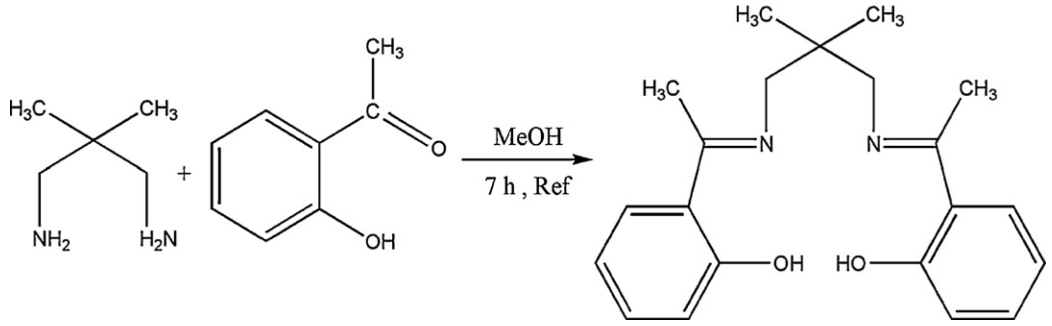

Scheme 1. Synthesis procedure of the ionophore.

bis(dihydroxyacetophenone) (NDHA) as an ionophore with N and O donor atoms was used for construction of Cu(II) ion-selective sensor.

Theoretical calculations have become a powerful tool for clarifying the mechanism of selective capture and transportation of metal ions by ligands [34–38]. However, no theoretical investigation has been reported on the selective extraction of metal ions by Schiff base. In this research quantum chemical calculations were performed to investigate how the metal's properties can be used to predict the selective transport and separation of metal ions. The results of our study may provide contributions towards the prediction of the applicability of an extractant for different metal ions, the material design of metal ion recognition, and other related fields.

2. Experimental

2.1. Reagents

2-Hydroxyacetophenone and 2,2-dimethyl-1,3-propanediamine were purchased from Merck. For membrane preparation, high molecular weight poly(vinyl chloride) (PVC), dibutyl phthalate (DBP), dioctyl phthalate (DOP), dimethyl sebacate (DMS), o-nitrophenyl octyl ether (o-NPOE), chloronapthalene (CN), potassium tetrakis (p-chlorophenyl) borate (KT*p*ClPB), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), acetonitrile (MECN) and methanol were used as received from Merck or Fluka. The sample solutions used for potentiometric measurements were prepared using the nitrate salts of the given cations, of highest available purity obtained (all from Merck) without further purification except for vacuum drying over P_2O_5. All other reagents used were of analytical reagent grade, and doubly distilled water was used throughout.

2.2. Synthesis of ionophore

The Schiff's base NDHA was synthesized in the inorganic laboratory according to the following procedure [39]. The stirred solution of 2,2-dimethylpropane-1,3-diamine (0.005 mol dm^{-3} in absolute methanol) was added a solution of 2-hydroxy acetophenone (0.01 mol dm^{-3} in absolute methanol) (Scheme 1). Then the reaction mixture was refluxed for 7 h and a bright yellow precipitate of symmetrical Schiff-base ligand was obtained. The yellow precipitate was extracted and recrystallized from methanol and dried in vacuo. The compound was stable at room temperature. Anal. Calc. for [$C_{21}H_{26}N_2O_2$]: C, 74.41, H, 7.65, N, 8.36%. Found: C, 74.52, H, 7.74, N, 8.28%. The ^{1}H-NMR (DMSO-d_6) exhibited signals at: δ 11.88 (s, 2H, OH), 2.32 (s, 6H, –C(CH_3)=N–), 6.61–7.80 (m, 8H, aromatic), 3.52 ppm (s, 4H, CH_2) and 1.15 (s, 6H, CH_3–C–).

2.3. Apparatus and EMF measurements

Atomic absorption spectrophotometric measurements were made on AA220 spectrometer (Varian, Australia) under the recommended conditions based on the manufacturer's instructions. Conductivity measurements were carried out with a 9100 conductometer (Metrohm, Switzerland) in a water-bath ultrathermostat at the desired temperature 298±0.05 K. A dip-type conductivity cell made of platinum black with a cell constant of 0.79891 cm^{-1} was used. Potentials were measured using a 713 pH-mV meter (Metrohm, Switzerland) at the laboratory ambient temperature. All of the EMF observations were made relative to an Ag/AgCl double junction reference electrode (Azar electrode, Iran) under magnetic stirring. A silver/silver chloride electrode containing a 3 mol dm^{-3} solution of KCl was used as the internal reference electrode. The EMF measurement with the polymeric membrane electrode was carried out with the following cell assembly:

Ag–AgCl, KCl (3 mol dm^{-3})|inner filling solution (10^{-3} mol dm^{-3} Cu(NO_3)$_2$)|PVC membrane|test solution|Ag–AgCl, KCl (saturated).

Activity coefficients of ions in aqueous solutions were calculated according to the Debye–Huckel procedure, using following equation [40]:

$$\log f = -0.511Z^2 \left[\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} - 0.2\mu \right] \quad (1)$$

2.4. Fabrication of PVC membranes and sandwich PVC membranes

The PVC-based membranes were prepared by dissolving appropriate amounts of ionophore to different anionic additives NaTPB and KT*p*ClPB with plasticizers (DBP, DOP, DMS, o-NPOE or CN) and PVC in freshly distilled 5 cm^3 of THF by stirring for 10 min with a magnetic stirrer. The clear solution was poured into glass rings (20 mm i.d.) placed on a smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Disks of 6 mm in diameter were punched out from the parent membrane with a cork borer. The end of the blue pipette tip was cut with a razor blade to an approximate diameter of 5 mm then a disc (about 0.3 mm thickness) was positioned over this opening and sealed with PVC-THF slurry. Then the pipette tip was filled with an internal solution of in different concentration range (1.0 × 10^{-5} to 1.0 × 10^{-1} mol dm^{-3}) copper(II) nitrate solution. The electrode was finally conditioned for 24 h in 0.1 mol dm^{-3} copper nitrate solution [41,42] till it gave reproducible and stable potential. Soaking for longer than 24 h is not recommended to avoid leaching of active constituents (ionophore, anionic additive) into the bathing solution [43].

The sandwich membrane was prepared by pressing two individual membranes (ordinarily one without ionophore and one with the same components and an additional ionophore) together immedi-

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