

N,N'-Bis(1'-hydroxy-2'- acetonaphthone)propylenediamine: Synthesis, Extractive Properties, and Use as an Ionophore in a Cu(II)-Selective Potentiometric Sensor

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The binding ability of *N, N'*-bis(1'-hydroxy-2'-acetonaphthone)propylenediimine (H₂L) towards metal ions was investigated by performing liquid-liquid extraction experiments to extract Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺ ions from nitrate solutions. Extraction takes place by a cation exchange mechanism and the ligand shows a pronounced selectivity towards Cu²⁺ ions. Conventional log-log analysis of the extraction data reveals that the Cu²⁺ ions are extracted by a 1:1 (metal to ligand) complex formation. The effect of parameters influencing the extraction process, such as type of diluent and concentration of electrolyte in the aqueous phase, has been studied. The selectivity of the ligand was evaluated by competitive extraction of copper ions from a synthetic sample.

The selective extraction of copper ions allows the use of H₂L as an ion-sensing material for fabricating a Cu(II)-ion-selective electrode. This sensor gave a good Nernstian response of 29.7 ± 0.3 mV/decade over a concentration range of 10⁻⁴-10⁻¹ M of copper ions, independent of pH in the range of 3.5-6.5, with a detection limit of 2 × 10⁻⁵ M and a response time of < 20 s. The electrode was used as a potentiometric indicator for the complexometric titration of a copper solution with a standard solution of EDTA.

Introduction

Schiff bases comprise a group of both cyclic and acyclic chemical compounds containing azomethene moieties (-C=N-R). They are made from the condensation of an amine and a molecule bearing an active carbonyl function. The presence of potentially donating atoms in their structure makes these molecules an important class of ionophore, which are widely used in metal ion complexation studies.¹⁻⁵

The ion receptor characteristics of *N, N'*-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane were evaluated by its application as the extractant in liquid-liquid extraction of copper ions.⁶ Solid phase extraction

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using an octadecyl-bonded silica membrane is also among the techniques frequently used to examine the efficiency of this group of ligands to bind metal ions.⁷ The application of Schiff bases as carriers in preparation of potentiometric sensors for determining cations and anions is the subject of some recent studies.^{8–17} Another approach to the ion-binding properties of these receptors has been investigated by using them for the synthesis of Schiff base-based metal complex catalysts.^{18,20}

In this paper the synthesis of a new Schiff base ligand, *N, N'*-bis(1'-hydroxy-2'-acetonaphthone)propylenediimine (Figure 1), is reported. The ion-binding properties of the synthesized ligand were examined by using it in solvent extraction for Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺ ions from aqueous nitrate solutions into the organic phase. The ionophore was used as an ion carrier for the preparation of a copper ion-selective electrode.

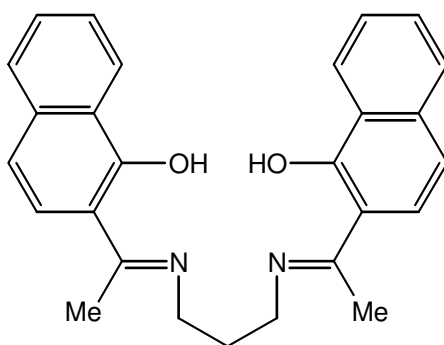


Figure 1. *N, N'*-Bis(1'-hydroxy-2'-acetonaphthone)propylenediimine (H₂L).

Experimental

Materials

All materials used in this work were obtained from Merck, except *ortho*-nitrophenyl octyl ether (NPOE), which came from Panreac. 1,3-Diaminopropane, 1'-hydroxy-2'-acetonaphthone, and ethanol were used without further purification. NPOE, benzyl acetate (BA), acetophenone (AP), sodium tetraphenylborate (NaTPB), and high molecular weight polyvinyl chloride (PVC) were used as received for preparation of the ion-selective electrode. Solvents used for the extraction experiments were washed 3 times with distilled water to remove the solvent stabilizers and to saturate them with other. Metal nitrates were laboratory-reagent grade.

Apparatus

NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer. The ¹H-NMR data were referenced relative to residual protonated solvents (7.26 ppm for CDCl₃) and the ¹³C-NMR chemical shifts are reported relative to CDCl₃ (77.0 ppm). FT-IR spectra were recorded on a Unicam (Matson 1000) spectrometer. A digital melting point measuring device (Electrothermal 9100) was used for determination of the melting point of the prepared ligand. A Varian (AA220) flame atomic absorption spectrometer (air/acetylene) was used for metal ion identification. A Metrohm 780 pH-meter was used for pH and potential measurements.

Synthesis of N,N'-bis(1'-hydroxy-2'-acetonaphthone)propylenediimine (H₂L)

N, N'-Bis(1'-hydroxy-2'-acetonaphthone)propylenediimine is a new Schiff base, and was synthesized as follows: a 30-mL solution of 1,3-diaminopropane (2.000 g, 0.027 mol) in absolute ethanol was refluxed with 10.044 g (0.054 mol) of 1'-hydroxy-2'-acetonaphthone for 2 h. The yellow solid was filtered and recrystallized twice from chloroform. The purity of the product was checked by thin layer chromatography. Yield: 10.3 g (93%); decomposition point: 208-210 °C. IR (KBr): $\nu_{O-H} = 3232 \text{ cm}^{-1}$, $\nu_{C-H} = 2931 \text{ cm}^{-1}$, $\nu_{C=N} = 1538 \text{ cm}^{-1}$, $\nu_{C=C} = 1589 \text{ cm}^{-1}$, and $\nu_{C-O} = 1149 \text{ cm}^{-1}$. ¹H-NMR (CDCl₃): δ 2.33 (m, 2H, NCH₂CH₂CH₂N), 3.48 (s, 6H, CH₃), 3.82 (t, 4H, NCH₂CH₂CH₂), 6.81-8.50 (m, 12H, ArH), and 16.69 (s, 2H, OH). ¹³C-NMR (CDCl₃): δ 14.54 (CH₃), 29.19 (CH₂CH₂CH₂), 42.22 (CH₂CH₂CH₂), 171.6 (azomethine, C=N), and 108-137.23 (aromatic C).

Solvent extraction experiments

The solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath (25 ± 0.1 °C) using equal volumes (5 mL) of the organic and aqueous phases. The pH of the aqueous phases was controlled by the addition of nitric acid and sodium hydroxide solutions. The extraction equilibrium was reached after 20 min under continuous magnetic stirring. After separation of the 2 phases, the concentration of metal ions remaining in the aqueous phase was measured using flame atomic absorption spectrometry. The metal concentration in the organic phase was similarly measured by AAS, following back-extraction of the phase with a dilute solution of nitric acid (0.01 M).

Stability of the ligand

A solution of the ligand (0.02 M) in dichloromethane was mixed with an aqueous solution containing NaNO₃ (0.1 M) at different pHs (4-7) for 20 min. After separation of the phases, the organic solvent was evaporated, the residue was dissolved in CDCl₃, and the ¹H-NMR spectrum was recorded. The obtained spectrum was similar to that of the ligand before use in this experiment, revealing that the Schiff base is stable under extraction experiment conditions.

Preparation of copper potentiometric sensor

The procedure for the preparation of a coated graphite electrode is described elsewhere.^{21,22} The membrane solution was obtained by dissolving 30 mg of PVC, 1 mg of NaTPB, 67 mg of NPOE, and 2 mg of ionophore in 5 mL of THF. This solution was used to coat a graphite carbon electrode. A shielded copper wire was glued to one end of a graphite rod (10 mm × 3 mm). The end of the electrode was sealed into the end of a PVC tube with epoxy resin. This electrode was dipped into the membrane solution and the solvent was evaporated. A membrane was formed on the graphite and the electrode was allowed to stabilize overnight. The prepared coated graphite was finally conditioned for 48 h by soaking in a 0.1 M solution of Cu(NO₃)₂. A double junction silver/silver chloride reference electrode (Azar Electrode, Iran) was used for potential measurements. All potential measurements were performed using the following assembly:



Results and Discussion

Liquid-liquid extraction study

Extraction of Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+}

In order to evaluate the binding ability of the H_2L ligand towards metal ions, the liquid-liquid extractions of Cu^{2+} , Zn^{2+} , Co^{2+} , and Ni^{2+} from the sodium nitrate solution into a dichloromethane solution of the Schiff base, as a function of the aqueous phase pH, was studied (Figure 2). As is seen, the extraction percentage of the metal ions increased with an increase in pH. This confirms that the extraction process has taken place via a cation exchange mechanism. Evaluation of the results shows a pronounced extraction efficiency of the extractant towards copper ions. For all the studied ions, the extraction percentage decreases at higher pH values, revealing metal hydroxide formation.

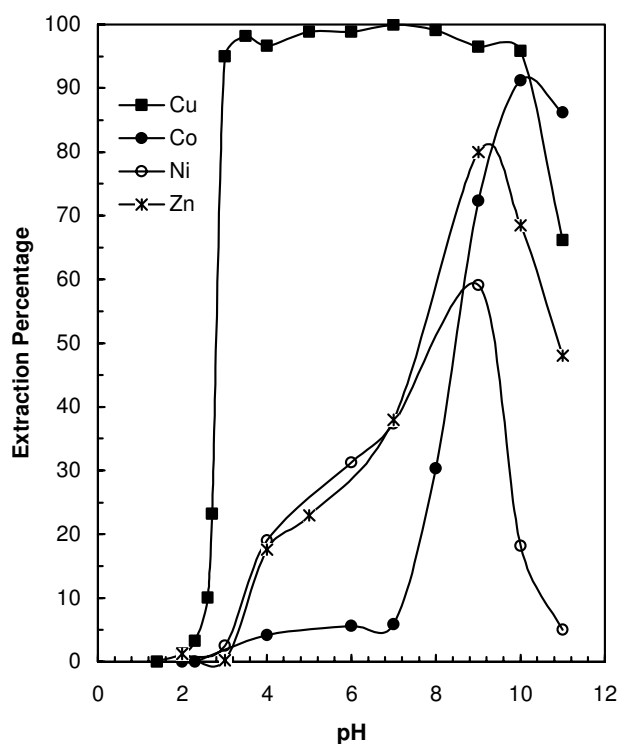


Figure 2. Extraction of Cu^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} (initial concentration 10^{-4} M) from aqueous sodium nitrate solutions (0.1 M) into a dichloromethane solution of H_2L (0.02 M), as a function of pH in the single extraction experiments at 25 °C.

Characterization of the extracted copper species

Characterization of the extracted copper complexes into the organic phase was performed using conventional log-log analysis of the extraction data. Considering the following equilibrium for description of the copper ions extraction,



(where $_{aq}$ and $_{org}$ denote the phase, aqueous or organic, in which the species is present), the definition of the corresponding equilibrium constant (K_{ex}) is

$$K_{ex} = \frac{[CuL]_{org}[H^+]_{aq}^2}{[Cu^{2+}]_{aq}[H_2L]_{org}} \quad (2)$$

Substitution of the distribution ratio

$$D = \frac{[Cu^{2+}]_{org}}{[Cu^{2+}]_{aq}} \quad (3)$$

and the arrangement of Eq. (2) give the logarithmic expression of this equation as

$$\log D = \log K_{ex} + \log [H_2L]_{org} + 2pH \quad (4)$$

A plot of $\log D$ versus $\log [H_2L]_{org}$ provides the metal/ligand ratio of the extracted species. This method was used for the extraction of copper ions from sodium nitrate solutions into a dichloromethane solution of the Schiff base at 25 °C (Figure 3). The slope (~ 1) is consistent with the formation of a 1:1 metal to ligand ratio for the extracted copper complexes.

A further confirmation for the proposed extraction equilibrium (Eq. (2)) was achieved by performing experiments to extract copper ions with the ligand, as a function of the aqueous phase pH (Figure 4). A plot of $\log D$ versus pH gave a slope close to 2. The obtained slope agrees with a cation exchange mechanism for the extraction experiment in which 2 hydrogen ions are released, as shown in Eq. (1).

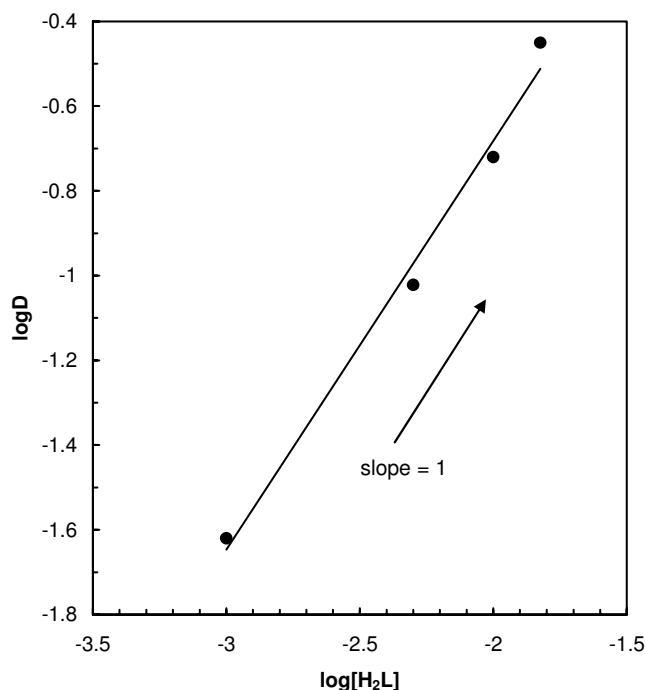


Figure 3. Plot of $\log D$ vs. $\log [H_2L]$ for the extraction of Cu^{2+} (initial concentration 10^{-4} M) from a sodium nitrate (0.1 M) aqueous phase (pH = 2.5) by H_2L in dichloromethane at 25 °C.

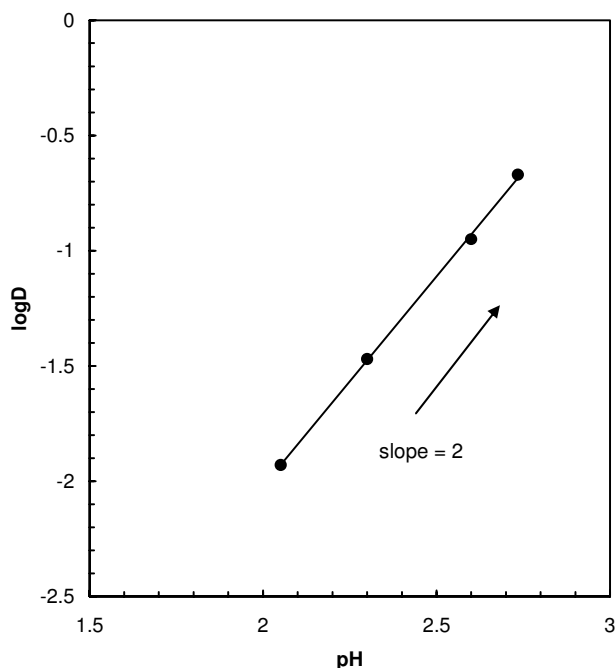


Figure 4. Plot of logD vs. pH for the extraction of Cu^{2+} (initial concentration 10^{-4} M) from a sodium nitrate (0.1 M) solution by H_2L (0.02 M) in dichloromethane at 25 °C.

Effect of solvent

In order to investigate the effect of the solvent on the extraction efficiency of the ligand, experiments to extract Cu^{2+} from the sodium nitrate solution (0.1 M) into chloroform, dichloromethane, and 1,2-dichloroethane solutions of the extractant were performed. The extraction efficiency of the ligand remains almost unchanged when changing the organic solvent.

Effect of NaNO_3 concentration

Sodium nitrate was used in this study for keeping the ionic strength of the aqueous phase constant. The extraction percentage increased as NaNO_3 concentration increased. This observation can be attributed to the salting out agent and effect lowering the degree of hydration of the copper ions.

Selectivity of the extraction

The ability of the method to separate transition metal ions was assessed by performing a competitive extraction of Cu^{2+} ions from a mixture containing Co^{2+} , Ni^{2+} , and Zn^{2+} ions. The results are shown in Table 1. The potential of the studied ligand to selectively extract the copper ions, with respect to the other metal ions, is calculated by the selectivity factor (SF). The logarithm of this factor is defined as

$$\log \text{SF} = \log \frac{D_{\text{Cu}}}{D_{\text{M}}} \quad (5)$$

It is seen that the ligand has a very good selectivity towards copper ions over cobalt, nickel, and zinc ions, at pH 3.

Table 1. Results of the competitive extraction of Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺.^a

Cations	[M ²⁺] ₀	[M ²⁺] _{org}	E%	logSF ^b
Cu ²⁺	10 ⁻⁴ M	8.10 × 10 ⁻⁵ M	81.0	-
Ni ²⁺	10 ⁻⁴ M	3.20 × 10 ⁻⁶ M	3.2	2.13
Co ²⁺	10 ⁻⁴ M	8.00 × 10 ⁻⁷ M	0.8	2.75
Zn ²⁺	10 ⁻⁴ M	7.00 × 10 ⁻⁷ M	0.7	2.78

^aAqueous phase: initial cations concentration, [M]₀; [NaNO₃], 0.1 M; pH 3. Organic phase: [H₂L], 0.02 M in dichloromethane. ^blogSF = log(D_{Cu}/D_M).

Preparation of Cu²⁺-selective electrode

Selection of the membrane composition

The apparent selectivity of the studied Schiff base for copper ions led us to study the efficiency of this receptor as an ionophore in a potentiometric sensor for copper ions. In the first step of this study, 11 compositions containing various amounts of PVC, plasticizer (NPOE, BA, and AP), ionophore (H₂L), and additive (NaTPB) were prepared and used as membranes for preparing the Cu²⁺-selective electrode. The potential variation as a function of the logarithm of the copper concentration (activity) from 10⁻⁷ up to 0.1 M was verified. The studied compositions with the values of the slopes found for the linear parts of the curves and the corresponding detection limits are given in Table 2.

Table 2. Examined ingredients composition of the membrane.^a

No.	H ₂ L	NaTPB	Plasticizer	PVC	LR ^b	DL ^b	Slope ^c
1	1	0	69 (NOPE)	30	10 ⁻³ -10 ⁻¹	6.1 × 10 ⁻⁴	16.4
2	2	0	68 (NOPE)	30	10 ⁻⁴ -10 ⁻²	3.0 × 10 ⁻⁵	25.2
3	3	0	67 (NOPE)	30	10 ⁻³ -10 ⁻¹	5.2 × 10 ⁻⁴	20.2
4	2	1	67 (NOPE)	30	10 ⁻⁴ -10 ⁻¹	2.0 × 10 ⁻⁵	29.7
5	3	2	65 (NOPE)	30	10 ⁻⁴ -10 ⁻¹	3.3 × 10 ⁻⁵	27.6
6	4	2	64 (NOPE)	30	10 ⁻⁴ -10 ⁻²	5.4 × 10 ⁻⁵	23.3
7	5	2	63 (NOPE)	30	10 ⁻³ -10 ⁻¹	3.2 × 10 ⁻⁴	18.7
8	6	3	61 (NOPE)	30	10 ⁻³ -10 ⁻¹	2.6 × 10 ⁻⁴	16.9
9	2	1	67 (AP)	30	10 ⁻⁴ -10 ⁻²	6.3 × 10 ⁻⁵	20.3
10	2	1	67 (BA)	30	10 ⁻⁴ -10 ⁻²	4.2 × 10 ⁻⁵	20.8
11	0	1	69 (NOPE)	30	10 ⁻³ -10 ⁻²	2.1 × 10 ⁻⁴	7.2

^aValues in percent (%). The slopes are calculated from 3 independent electrodes. $\sigma_{N-1} \leq 0.4$ mV/decade. ^bLR: linear range, DL: detection limit. ^cIn mV/decade.

Characteristics of the electrode prepared by compositions 1 and 11 show that the presence of the ionophore affects the response of the electrode. The examination of the results obtained by the electrodes based on compositions 4, 9, and 10, reveals that the application of NPOE as a plasticizer gives better results in comparison to benzyl acetate and acetophenone. A comparison of the characteristics of electrodes prepared by compositions 2-5 demonstrates the enhancement of the membrane response in the presence of an anion excluder in the membrane. Finally, an optimum concentration for the ionophore was determined to be 2% of the membrane composition.

Based on the results presented in Table 2, composition 4 was selected for further study. As an example, Figure 5 shows the variation of the cell potential versus the logarithm of the concentration of copper ions for the electrode prepared with composition 4. This membrane, composed of 30% PVC, 67% NPOE, 2% Schiff base, and 1% NaTPB, gives the best characteristics, with a slope of 29.7 ± 0.3 mV/decade (for 3 electrodes) in the concentration range of 10^{-4} - 10^{-1} M, and a detection limit of 2.0×10^{-5} M. Therefore, composition 4 was used throughout the work.

Effect of pH on the electrode response

The effect of pH on the test solutions, regarding the potential response of the sensor, was investigated (Figure 6). The potential was independent of pH and remained constant in the pH range of 3.2-6.5. The potential diminishes when the pH is > 6.5 . This observation can be attributed to the formation of copper hydroxide in solution; however, an increase in the response of the electrode when the pH is < 3.2 is a consequence of the protonation of the ligand and a possible response of the electrode to the anions. Such variation of the potential of ion selectivity as a function of pH has been observed elsewhere.²³

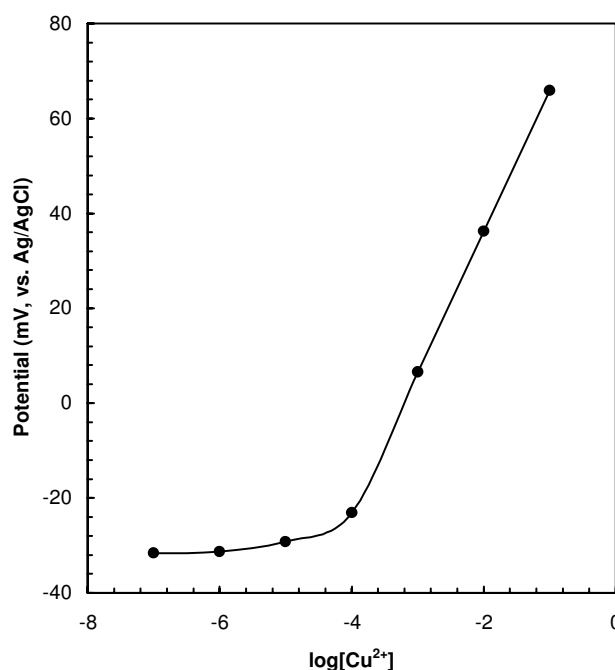


Figure 5. Plot of the variation of electrode potential vs. $\log[\text{Cu}^{2+}]$.

Dynamic response time

One important factor that demonstrates the performance of an ion selective electrode is its dynamic response time. In order to determine the response time of the prepared electrode, the potential of a stirred solution (initial copper concentration 10^{-4} M) was recorded as a function of time by a 10-fold stepwise increase of the metal ion concentration up to 10^{-1} M. The response time was < 20 s.

Selectivity of the electrode

Selectivity of the prepared PVC membrane electrode towards copper ions over some mono-, di-, and trivalent ions (Ag^+ , NH_4^+ , Na^+ , K^+ , Sr^{2+} , Ba^{2+} , Pb^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+} , La^{3+} , and Sm^{3+}) was tested using the match potential method (MPM).²⁴ In this method, a specified amount of the analyte (here Cu^{2+}) is added to a reference solution and the potential is measured. Then, the interfering ion (M^{n+}) is gradually added to a separate sample of the same reference solution until the same potential is attained. The evaluated selectivity coefficients are given in Table 3.

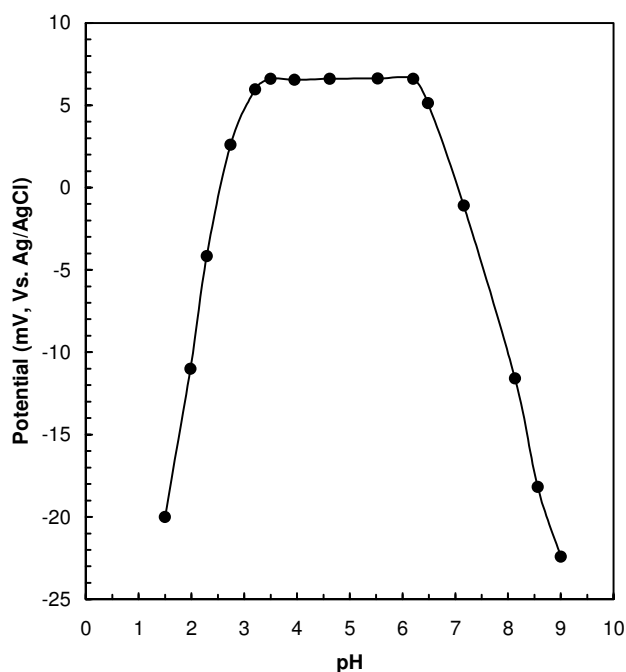


Figure 6. Electrode response of the electrode as a function of pH of the sample solutions at 10^{-3} M of Cu^{2+} .

Table 3. The selectivity coefficient of the electrode measured by the match potential method.

M^{n+}	$K_{\text{Cu},\text{M}}^{\text{MPM}}$
Na^+	1.1×10^{-2}
K^+	0.9×10^{-2}
NH_4^+	0.7×10^{-2}
Ag^+	1.2×10^{-2}
Sr^{2+}	2.1×10^{-2}
Ba^{2+}	1.9×10^{-2}
Pb^{2+}	2.7×10^{-2}
Mn^{2+}	1.3×10^{-2}
Co^{2+}	1.1×10^{-2}
Zn^{2+}	1.6×10^{-2}
Ni^{2+}	1.8×10^{-2}
Fe^{3+}	2.0×10^{-2}
Cr^{3+}	1.4×10^{-2}
La^{3+}	2.8×10^{-2}
Sm^{3+}	3.2×10^{-2}

Application of the sensor

The prepared sensor was used as an indicator electrode for the potentiometric titration of a copper solution (25 mL and 10^{-3} M) with a solution of EDTA (10^{-1} M), using a micropipette. The pH of the solution was adjusted to 5 using HCl/NaOH solutions. The potentiometric curve is presented in Figure 7. The curve shows the electrode can be used successfully for determination of copper ions in such experiments. The analysis of this curve reveals that 245 μ L of EDTA solution is required for achieving the end point of titration; therefore, a 2% error accompanies the titration experiment.

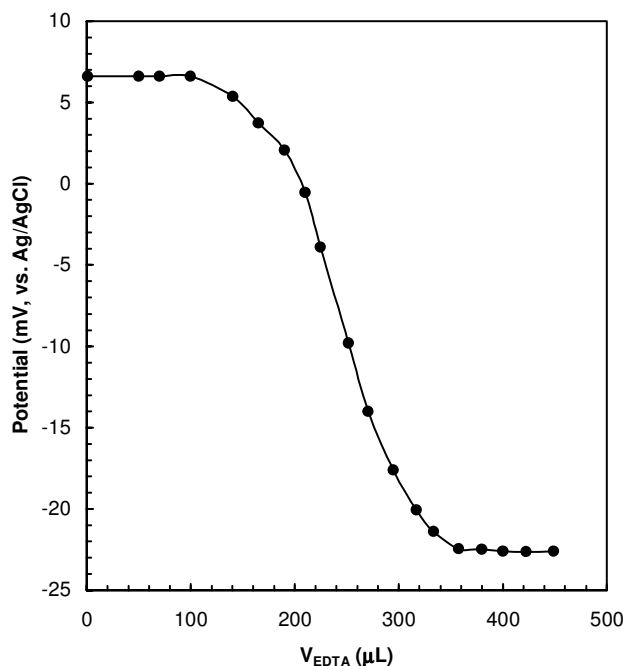


Figure 7. Potentiometric titration curve of 25 mL solution of Cu^{2+} (10^{-3} M) with a standard solution of EDTA (10^{-1} M) at pH 5, using the proposed electrode as an indicator.

Conclusions

N, N'-Bis(1'-hydroxy-2'-acetonaphthone)propylenediimine was synthesized from the reaction between 1,3-diaminopropane and 1'-hydroxy-2'-acetonaphthone in a one-step procedure. The prepared Schiff base is able to extract Cu^{2+} , Ni^{2+} , Zn^{2+} , and Co^{2+} from nitrate solutions into a dichloromethane solution by a cation exchange mechanism. At lower pH values, the ligand has significant selectivity towards copper ions. The analysis of the extraction data shows that the copper ions are transferred into the organic phase by 1:1 (metal to ligand) complex formation. The ionophore was used as a carrier for fabrication of a Cu^{2+} -ion-selective electrode. This electrode can be successfully used as a potentiometric indicator for complexometric titration of copper ion solutions by EDTA.

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