Copper ion selective electrode based on copper (II) complex of 4-Azocyanoacetamido-m-toludine antipyrine

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Abstract: The characterization performance and construction of copper (II) complex of 4-Azocyanoacetamido-m-toludine antipyrine {$[Cu_2L^2Cl_4].2H_2O$} (Cu-HL^2)-polyvinyl chloride (PVC) sensor is described. The sensor is based on the use (Cu-HL^2) ionophore as electro active material In PVC matrix in presence of DOP, DOS and NOPE as solvent mediator. (Cu-HL^2) membrane sensors show a stable, near Nernstian response at 25 ± 0.1 °C in pH in the range 4–8. the electrode has The low detection limit of 5.1×10^{-6} M and displays a linear EMF versus log [Cu^{2+}] response over the concentration range 1.0×10^{-6} to 1.0×10^{-2} M Cu^{2+} with cationic slope of 29 ± 0.1 mVdecade^{-1} have been attained. The sensor is stable for 8weeks. Selectivity coefficient data for some common ions show negligible interferences. The electrode has been used as an indicator electrode in potentiometric titration of Cu^{2+} with EDTA and direct determination of Cu^{2+} in wastewater of the electroplating industry.
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1. Introduction

Copper is one of the most widely spread heavy metals, hence its determination in environmental and industrial objects is of tremendous interest. Small quantities of copper are essential for living beings whereas it is highly toxic in a high concentration on the other hand, copper is an important material and extensively used for industrial, agricultural and domestic purposes due to its high electrical conductivity, chemical stability, plasticity, and capacity to form alloys with many metals. Therefore, the copper content in many industrial, biological, medical, geochemical, and environmental objects must be controlled on a daily basis and as a result, a development of novel methods for low-cost, simple, rapid, remote, and on-line detection and determination of copper in samples of different origin is of big interest [1]. Various analytical techniques have been proposed for determination of copper including spectrophotometric methods [2–7], atomic absorption spectrometry (AAS) [8, 9], cold vapour AAS or flame AAS with electrothermal atomization [10, 11], inductively coupled plasma emission spectrometry [12, 13], gravimetry [14, 15], chromatography [16, 17], and anodic stripping voltammetry [18, 19]. Most of the mentioned methods usually have sufficiently low detection limit and high selectivity, but also in many cases posses' drawbacks such as high cost of equipment and expensive materials, time-consuming and complicated operation. Thus, these methods are generally unsuitable for simple, low cost and remote determination of copper, especially in field and domestic conditions. The pressure on analytical chemists to develop new sensors for the increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is putting more and more fast, accurate, reproducible and selective determination of various species. Relatively fast response, wide dynamic range, reasonable selectivity and low cost of materials. During the past few decades, many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes have been reported. wide range of organic reagents has been used as ion carriers for construction of copper selective electrodes (Table 1) [1, 20-57];table1 but most of these sensors have one or more of the following disadvantages: high detection limits[27,28,32,45];low sensitivity[34,60]; Narrow working concentration range [22,24,26,52,53]; complicated procedure and high cost of the carrier synthesis [27,29,37,53]. Relatively low selectivity [20,32-28,31-36,38-42,48,51-57]; and large response time [20,27,36,38,43,45,48,49,51]; In fact, the described sensors although being prepared independently, have rather similar parameters (e.g. compare the slopes of potentiometric responses), however, none of them has all excellent analytical parameters (selectivity, sensitivity, response, low detection limits and long life time) and the cost is also important for such devices. Therefore, we decided to prepare a new inexpensive electrode with better parameters at least for some of the above

mentioned points. Newer materials synthesized are continuously being examined for such role. Continuing efforts in this direction, as in this paper we synthesized three membranes in PVC matrixes as Cu^{2+} selective sensors. The results of this investigation are presented in the following.

Table 1. Analytical parameters for some reported copper-selective PVC-membrane sensors [a].

Ionophore	Detction limite (M)	Linear range(M)	Respons time(s)	Slope (mV\ decade)	Selectivity coefficient $\geq 10^{-3}$	Ref.
Tetraethylthiuram disulfide	1.0×10^{-8}	$1\times10^{-8} - 1\times10^{-1}$	27	30	Na^+,Mn^{2+},Pb^{2+}	[20]
13,14-Benzo-1,5-tetrathiacyclopentadecane		$1\times10^{-6} - 1\times10^{-1}$	10	29		[21]
Dithizone		$1\times10^{-5} - 1\times10^{-3}$				[22]
o-Xylelene-bis(methyloctadecyl-dithiocarbamate)		$1\times10^{-6} - 1\times10^{-1}$		29	$Na^+,K^+,Mg^{2+},Ca^{2+},Sr^{2+},Ba^{2+},$ $Mn^{2+},Co^{2+},Ni^{2+},Zn^{2+}$	[23]
Calixdithiocarbamoylarene		$1\times10^{-4} - 1\times10^{-2}$		30	$K^+,Ca^{2+},Pb^{2+},Cd^{2+}$	[24]
2,2' -[1,2-Ethanediyl-bis(nitriloethylidene)]-bis(1-naphthalene)	3.1×10^{-6}	$5\times10^{-6} - 5\times10^{-2}$	5	29.8	Na^+,Ni^{2+},Hg^{2+}	[25]
3,4,10,11-Tetraphenyl-1,2,5,8,9,12,13-octaaza-cyclotetra-deca-7,14-dithizone-2,4,9,11-tetraene	1.6×10^{-6}	$1\times10^{-5} - 1\times10^{-2}$	2	27	$Na^+, K^+, Mg^{2+},Ca^{2+} ,Al^{3+}, Fe^{3+},$ $Cd^{2+},Hg^{2+},Ba^{2+},Zn^{2+}, Pb^{2+}$	[26]
1,15-Diaza-3,4;12,13-dibenzo-5,8,11,18,21-pentaoxacyclotrieicosane-2,14-dione	1.2×10^{-5}	$1\times10^{-5} - 1\times10^{-1}$	20	30.0	Na^+,K^+,Cs^+,Sr^{2+}	[27]
Aza-thioether crown containing a 1,10-phenanthroline	8.0×10^{-6}	$1\times10^{-5} - 1\times10^{-1}$	15	29.4	Ag^+,La^{3+}	[28]
2' -Picolyl sym-dibenzo-16-crown-5 ether	1.0×10^{-6}	$1\times10^{-5} - 1\times10^{-1}$		42		[29]
Bis-thiophenalpropanediamine	2.0×10^{-8}	$6\times10^{-8} - 1\times10^{-2}$	5	29.3	Zn^{2+},Hg^{2+}	[30]
Bis-2-thiophenal propanediamine	3.0×10^{-8}	$1\times10^{-8} - 1\times10^{-1}$	5	29	$Ni^{2+}Pb^{2+},Co^{2+}$	[31]
2,2' -Dithiodianiline	6.0×10^{-6}	$7\times10^{-7} - 5\times10^{-2}$	10	30	$Pd^{2+},Cd^{2+},Hg^{2+},Ni^{2+},Pb^{2+} Fe^{3+}$	[32]
Copper(II)-salicylalaniline Schiff's base + cyanocopolymer matrice		$2.5\times10^{-7} - 1\times10^{-2}$	13	28	$Li^+,Na^+,K^+,Cs^+,Ag^+,Ca^{2+}, Co^{2+},$ $Ni^{2+},Zn^{2+},Cd^{2+}, Mn^{2+}$	[33]
1,3-Dithiane,2-(4-methoxyphenyl)	1.0×10^{-6}	$3\times10^{-6} - 5\times10^{-2}$	5	29	$K^+, Cs^+, Mg^{2+},Ca^{2+},Sr^{2+},Ag^+,$ $Co^{2+},Ni^{2+}, Mn^{2+}, Zn^{2+},Cd^{2+},Hg^{2+}$	[34]
Diphenylisocyanate- bis(acetylacetone)ethylenedi-imine	6.0×10^{-7}	$1\times10^{-6} - 1\times10^{-1}$	15	29.8	Ni^{2+},Zn^{2+},Cd^{2+}	[35]
1-H Hydroxy-2-(prop-2'-enyl)-4-(prop-2'-enyloxy)-9,10-antraquinone	5.0×10^{-8}	$1\times10^{-5} - 1\times10^{-1}$	20	29.1	$Tl^+,Ag^+,K^+,Co^{2+},Ni^{2+},Zn^{2+}, Pb^{2+},Cd^{2+}$	[36]
3,6,9,14-Tetrathiabicyclo[9.2.1]tetradeca-11,13-diene	3.2×10^{-7}	$8\times10^{-8} - 5\times10^{-2}$	10	28.0	Ag^+	[37]
2-Quinolyl-2-phenylglyoxal-2-oxime(phenylglyoxalalphamonoxime)	5.0×10^{-7}	$1\times10^{-6} - 1\times10^{-1}$	10-50	28.2	K^+,Al^{3+},Fe^{3+}	[38]
Hydrotris(3-isopropylpyrazolyl)methane	2.0×10^{-6}	$1\times10^{-6} - 1\times10^{-2}$	10	29	Co^{2+},Ni^{2+}	[39]
2-(1'-(4'-(1''-Hydroxy-2''- naphthyl)methyleneamino)	8.0×10^{-7}	$1\times10^{-6} - 1\times10^{-1}$	5	29.0	Tl^+	[40]
2,2'-[4,4'-Diphenyl-methane bis(nitrilomethylidyne)]–bisphenol	3.0×10^{-6}	$8\times10^{-6} - 1\times10^{-1}$	15	29.5	Pb^{2+}	[41]
1,3-Dithiane,2-(4-methoxy phenyl)	1.0×10^{-6}	$3\times10^{-6} - 5\times10^{-2}$	15	29.5	Na^+,Ag^+,Pb^{2+}	[42]
Schiff base(2,3-diaminopyridine + o-vanilin)	3.0×10^{-6}	$5\times10^{-6} - 1\times10^{-1}$	30	29.6	Ag^+,Hg^{2+}	[43]
N,N'-ethylene bis(p-tert- butylsalicylaldiminato)	1.5×10^{-6}	$4\times10^{-6} - 1\times10^{-1}$		29.5	Pb^{2+}	[44]
Thiosemicarbazone	6.0×10^{-6}	$6\times10^{-6} - 1\times10^{-1}$	10-50	29.2	Hg^{2+},Pb^{2+}	[45]
2,2-[1,2-Ethandiyl-bis(nitrilomethylidine)- bis]para-cresole	3.1×10^{-6}	$1\times10^{-5} - 1\times10^{-1}$	10	29.7	Ni^{2+},Co^{2+}	[46]
6-Methyl-4-(1-phenylmethylidene) amino-3-thioxo-1,2,4-triazin-5-one	4.8×10^{-7}	$1\times10^{-6} - 1\times10^{-1}$	10	29.2	Ca^{2+},Sr^{2+}	[47]
N,N,N',N'-tetracyclohexyl-3- thiaglutaric diamide	2.0×10^{-9}	$1\times10^{-7} - 1\times10^{-6}$	60	33.5	$Ag^+,Zn^{2+},Cd^{2+},Pb^{2+}$	[48]
4-Amino-6-methyl-1,2,4-triazin-5-one-3- thione	6.2×10^{-7}	$1\times10^{-6} - 1\times10^{-1}$	20	29.3	Hg^{2+},Fe^{3+}	[49]
2-Mercaptobenzoxazole	2.0×10^{-6}	$5\times10^{-6} - 1.6\times10^{-2}$		29.2	Ni^{2+},Pb^{2+}	[50]
1,8-Bis(2-hydroxynaphthaldiminato)3,6- dioxaoctane	1.0×10^{-6}	$3.3\times10^{-6} - 1.0$	10-15	29.0	$Na^+,K^+,Ag^+,Ca^{2+},Co^{2+},Fe^{3+}, Al^{3+}$	[52]
2-{1-(E)-2-((Z)-2-{(E)-2-[(Z)-1-(2-Hydroxyphenyl)ethylidene]hydrazono}-1-methyl propylidene)hydra zono ethyl} phenol	5.0×10^{-12}	$1\times10^{-11} - 1\times10^{-5}$	5	25.9	$Ni^{2+},Zn^{2+},Pb^{2+},Cd^{2+}$	[53]
2,2'-[1,9-Nonanediyl bis(nitriloethylidyne)]-bis-(I-naphthol)	8.0×10^{-7}	$1\times10^{-6} - 1\times10^{-3}$	10	29	Pb^{2+},Zn^{2+},Fe^{3+}	[54]
2-(2- Mercaptophenylnitrilomethylidyne)- phenol	5.0×10^{-6}	$7\times10^{-6} - 2.6\times10^{-2}$	10	28.3	$Li^+, Ca^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ce^{3+},$ $Hg^{2+}, Ag^+, Fe^{3+}, Al^{3+}, La^{3+}$	[55]
1,2,5,6,8,11-Hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene	8.1×10^{-8}	$2\times10^{-7} - 1\times10^{-1}$	5	29.5	$K^+,Tl^+,Zn^{2+},Sr^{2+},Mg^{2+},Co^{2+},$ Cd^{2+},Mn^{2+},Cr^{3+}	[56]
Schiff Base(phenylalanine + salicylaldehyde)		$1.9\times10^{-5} - 1\times10^{-1}$	12	30	$Mg^{2+}, Sr^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+},$ $Mn^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}$	[57]
1-Phenyl-2-(2- hydroxyphenylhydrazo)butane-1,3-dion	6.30×10^{-7}	$2\times10^{-6} - 5.0\times10^{-3}$	10	28.8	Fe^{3+}	[1]

[a] When the parameter was not indicated in the corresponding paper, a blank space is left in table.

2. Experimental
2.1 Reagents and chemicals

All chemicals were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Poly (vinyl chloride) powder (PVC) powder of molecular weight ca. 10000 was obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). Tetrahydrofuran (THF) with a purity of 99 %, inhibited by 0.025 % butylatedhydroxytoluene was obtained from Aldrich Chem. Co (Milwaukee, WI, USA). Dioctylsebacate (DOS) plasticizer with a purity of ca. 99 % was obtained from Aldrich Chem.

Co (Milwaukee, WI, USA). Dioctylphthalate (DOP) plasticizer with purity of ca. 99 % was obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). o-nitrophenyloctylether (o-NPOE) plasticizer with purity of ca. 99 % was obtained from Aldrich Chem. (NaTPB) as ion-exchanger (electro active material). The salts of all the cations used were of analytical grade and used without any further purification. Double distilled water was used for the preparation of metal salts solutions of different concentrations. $Cu(NO3)_2$ (1.0×10^{-7}–1.0×10^{-2} M) standard solutions were prepared. The following cations and compound solutions were prepared and standardized using the Standard methods dilute solutions (1.0×10^{-2} –1.0×10^{-7} M) of these cations and compounds were prepared by10-fold dilution of the stock solutions.

2.2 Apparatus

All Potentiometric measurements were made at $25 \pm 1°C$ with an Orion (Model 720) pH/mV meter. Double junction Ag/AgCl reference electrode was used. An Orion electrode (Model 90-02) filled with 10% (w/v) potassium chloride was used in the outer compartment. Combination glass (Ross pH) electrode (Orion Model 81-02) was used for all pH measurements. All EMF measurements were carried out using the following assembly:

Ag–AgCl| KCl (3M) | internal solution, 1.0×10^{-3} $Cu(NO3)_2$ sol. | PVC membrane| test solution | Hg–Hg_2Cl_2, KCl (saturated).

2.3. Synthesis of the ionophore
2.3.1 Synthesis of Cu-HL2

The ionophore $[Cu_2L^2Cl_4]2H_2O$ was synthesized as follow [59]: The ligand 4-azocyanoacetamido-m-toludine antipyrine scheme 1 was prepared by coupling the diazonium salt of m-toludine with cyanoactamido antipyrine in pyridine. The product was recrystallized several times from ethanol. The copper complex (Cu-HL^2) was prepared by heating under reflux on water bath for ca.24 hrs. 0.002 moles of copper salt ($CuCl_2$)

with 0.002, 0.004 or 0.001 moles of 4-Azocyanoacetamido-m-toludine antipyrine in ca.50 ml EtOH in presence of appropriate amount of AcONa. The resulting solid was filtered off, washed several times with EtOH and dried under vacuum over P_4O_{10}.

LH^2
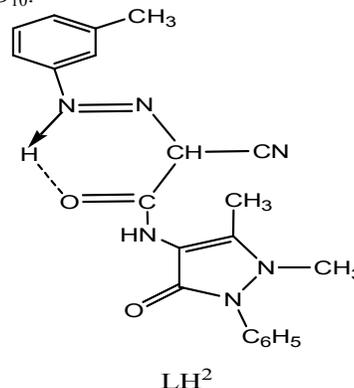
Scheme 1. The structure of LH^2

2.3.2 Characterization of prepared compounds

Elemental analyses (C, H, Cl) were preformed and copper analysis were carried out by standard method [59]. IR spectra were preformed as KBr discs, using aperkin-Elmer1430 recording spectrometer. H^{1}NMR spectrum was recorded in d^6-DMSO using a 300MHZ Varian NMR spectrometer. The electronic spectra were carried out in N,N-dimethylformamide (DMF) solution using a Perkin-Elmer lambda 4B spectrophotometer. The molar conductivity measurements were made in DMF solutions (10^{-3}M) using a Tacussel conductometer. Magnetic susceptibilities were measured at 27°C by the modified Gouy method, the magnetic moments were calculated, and ESR spectra were recorded with a Varian E104 spectrometer and calibrated with diphenyl picrylhydrazide. The characterization of HL^2 and Cu-HL^2 by elemental analysis, infrared,^{1}H NMR spectroscopy, molar conductivities and magnetic properties Presented in Table 2(a-c).

Table 2.a Infrared spectral bands for HL2and (Cu-HL2)

compound	V(H_2O)	V(OH)	V(N-H)	V(C≡N)	V(C=O)^a	V(C=O)^b	V(C=N)	V(N=N)	V(Cu-O)	V(Cu-N)	V(Cu-Cl)
(Cu-HL^2)	3400(br)	—	3440^d(s), 3340(m), 3230(m)	—	1660(s)	1640(s)	1630(s)	—	459(m)	445(W)	315(m)
HL^2	—	—	3380, 3180	2210(s), 2255(sh)		16655(s)	1610(s)	—	—	—	—

(note: 1680(s) appears in the V(C=O)^a column for HL^2)

Table 2.b Colors, molar conductivities and magnetic properties of HL2and (Cu-HL2)

No.	compound	color	A_M(ohm^{-1} cm^{2}mol^{-1})	μ_{eff}(B.M) per Cu^{2+}ion
1	HL^2	yellow	—	—
2	$[Cu_2L^2Cl_4].2H_2O$ (Cu-HL^2)	green	45.0	1.65

Table 2.c ESR spectral parameters of Cu-HL^2 complex.

complex	Temp.	g_{11}or g_1	g_2	$g_1$or g_3	g_{av} or g_{iso}
$[Cu_2L^2Cl_4].2H_2O$ (Cu-HL^2)	RT	2.221	2.093	2.022	2.122
	77K	2.232	2.079	2.026	2.119

2.4 Electrode preparation

(66–65.3) mg PVC powder,(132–133) mg plasticizer [Dioctylphthalate (DOP, Dioctylsebacate DOS or o-nitro phenyl octylether (o-NOPE)], (0.0–0.1) anionic additives sodium tetraphenylborate (NaTPB) and (1.0–2.1) mg ionophore (Cu-HL^2) were dissolved in 5mL tetrahydrofuran (THF), and stirred vigorously for 5min. The resulting mixture was transferred into glass dish of ca.5 cm diameter. After evaporation of solvent ca.24hrs, the formed transparent membrane of 0.2mm thickness was removed carefully from the glass plate, and then a 5mm diameter piece was cut out and glued with commercial liquid PVC to one end of a PVC tube with the same diameter. After 24hrs the electrode was filled with an internal filling solution [1.00×10^{-2} M Cu(NO$_3$)$_2$ solution ×3M KCl solution], Preconditioned for 24h in a1.00×10^{-2} M solution of Cu(NO$_3$)$_2$ before use and stored in the same solution when not in use.

2.5 Equilibration of membranes and potential

The electrodes preconditioned for 24 h in 1.0×10^{-3} solution of Cu(NO$_3$)$_2$ before use and stored in the same solution when not in use. The potentials measured by varying the concentration of Cu(NO$_3$)$_2$ in the test solution in the range (1.0×10^{-7}–1.0×10^{-2} M).Standard Cu(NO$_3$)$_2$.the solution prepared by 10-fold dilution of the stock solutions.

3. Results and Discussion

3.1. Optimization of electrode membrane composition

Since the membrane composition and the nature of the plasticizer influence the sensitivity, selectivity and the detection limit of the electrode, the effect of the membrane composition on the potential response of the Cu^{2+} electrode was investigated. For this purpose, the performance characteristics of several membranes having ingredients of different preparations are listed in Table3. Among the different plasticizers (o-NOPE, DOP, DOS) used o-NOPE is the more effective solvent mediator in preparing the copper membrane electrode. It should be noted that the nature of the plasticizer influence as well as the mobility of ionophore molecules and its complex, the potentiometric response of the membrane was greatly improved also in the presence of lipophilic anionic additives (NaTPE). It is known that lipophilic salts not only reduce the ohmic resistance of the membrane, but also enhance the response and selectivity, reduce the interference caused by other anions and also may accelerate the exchange on the sample-membrane interface[29-57-92]. Thus, the influence of NaTPB was studied, the presence of 0.1

mg NaTPB as an additive improved the sensitivity of copper membrane electrode. The amount of the ionophore was also found to affect the response of membrane electrode, the sensitivity of the electrode response increased with increase in the ionophore content till the value 2.0mg, considerably (no.1, 5and 9) (fig.1.). as can be seen from (Table 3) that the membrane having composition PVC: NOPE:Cu-HL^2: NaTPB as 65.9: 132.0: 2.0: 0.1 (W/W/W/W) exhibits the best performance with Nerenstian slope 29 ± 0.1 and limit of detection 5.1×10^{-6} M This sensor gave response to copper ion over wide concentration range (1.0×10^{-6}–1.0×10^{-2} M). The influence of concentration of the internal solution on the potential response of the membrane electrode was also studied, it was found that the variation of concentration of the internal solution corresponding to significant change in the intercept of the resulting Nernstian plots in range (1.0×10^{-5}–1.0×10^{-4} M). A1.0×10^{-2} M concentration of the reference solution is quite proper functioning of the electrode system.

3.2 Response and lifetime

Response time is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the instant at which the potential has reached 90% of the final value [61]. The response time was around10 s and was remained unchanged by varying concentration. In this study, the practical response time was recorded by fast stepwise changing of the Cu^{2+} concentration from 1.0×10^{-7} to 1.0×10^{-2} M. The actual potential versus time (Fig. 2) shows that the dynamic response time was <10 s (thus mainly limited by diffusion, i.e. the rate of stirring) and then the potential remained unchanged at all studied concentrations. This short response time is most probably due to the fast exchange kinetics of complexation–decomplexation of Cu^{2+} ion with the Cu-HL^2 ionophore on the tested solution–membrane interface. A similar procedure in the opposite direction demonstrated the independence of the response time from the order of dilution. The durability tests show that the membrane electrode with the best characteristics (run 10 from number1 from (Table 3) can be used for at least 8 weeks without any measurable response decay. After this time the Nenstian slope (the sensitivity) and detection limit of the sensor decrease and increase, respectively. It was established that the leaching of plasticizer, carrier, or ionic site from the polymeric film is the primary reason for the limit in the sensors' lifetime; analogously, we suppose that these factors also influence the decay of our electrode.

Table 3 Composition of PVC based membranes of (Cu-HL^2) and performance characteristics of Cu^{2+} selective electrode based on them

| No.	Composition of the membrane (mg)				Slope mV\decade	Linear range(M)
	Ionophore	PVC	Additive NaTPB	plasticizer		
	2.0	65.9	0.1	132.0(o-NOPE)	29 ± 0.1	1.0×10^{-2}—1.0×10^{-6}
	2.0	66.0	0.0	132.0(o-NOPE)	27.1±0.1	1.0×10^{-2}—1.0×10^{-6}
	2.0	65.3	0.0	132.7(o-NOPE)	24.0 ± 0.1	1.0×10^{-2}—1.0×10^{-5}
	1.0	66.0	0.0	133.0(o-NOPE)	9.5 ± 0.1	1.0×10^{-2}—1.0×10^{-4}
	2.0	65.9	0.1	132.0(DOP)	33 ± 0.1	1.0×10^{-2}—1.0×10^{-6}
	2.0	66.0	0.0	132.0(DOP)	22.5 ± 0.1	1.0×10^{-2}—1.0×10^{-6}
	2.0	65.3	0.0	132.7 (DOP)	21.0 ± 0.1	1.0×10^{-2}—1.0×10^{-5}
	1.0	66	0.0	133.0(DOP)	7.0 ± 0.1	1.0×10^{-2}—1.0×10^{-4}
	2.0	65.9	0.1	132.0(DOS)	27 ± 0.1	1.0×10^{-2}—1.0×10^{-6}
	2.0	66.0	0.0	132.0(DOS)	21.5 ± 0.1	1.0×10^{-2}—1.0×10^{-5}
	2.0	65.3	0.0	132.7 (DOS)	14.5 ± 0.1	1.0×10^{-2}—1.0×10^{-5}
	1.0	66.0	0.0	133.0 (DOS)	5.5 ± 0.1	1.0×10^{-2}—1.0×10^{-4}
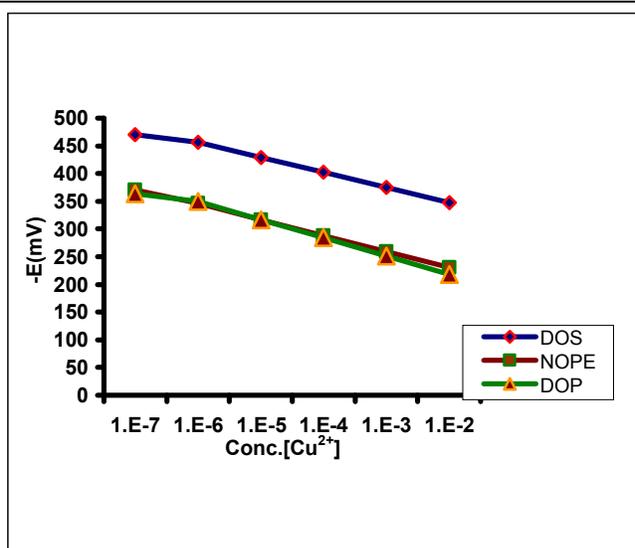
Fig.1. Calibration curves and the optimum responses of Cu^{2+} based on Cu-HL^2 with different plasticizers (DOS, DOP and NOPE).
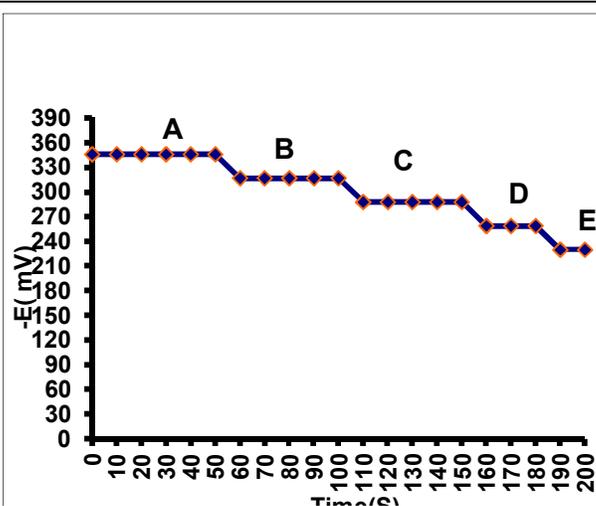

Fig.2. Dynamic response of the optimized [PVC: NOPE: Ionophore: NaTPB as 66.0: 132.0: 1.9: 0.1 (W\W\W\W)] membrane electrode of run 10(table 2) for step changes in concentration of Cu^{2+} ;(A) 0×10^{-6} M; (B) 0×10^{-5} M; (C) 0×10^{-4} M; (D) 0×10^{-3} M; (E) 0×10^{-6} M.

3.3. Effect of pH

The effect of pH of the copper nitrate test solutions (1.0×10^{-3} and 1.0×10^{-4} M) on the sensor potential was investigated by following the potential variation over the pH range 2.0 – 9.0. The potential remains constant over the 4.0–8.0 pH range, beyond which the potential changes considerably Fig. 3(a–c). The observed drift at higher pH values could be due to the formation in solution of some hydroxo complexes of Cu^{2+} or even to Cu (OH)$_2$ Precipitate [20–57]. The observed change in potential at low pH values could be due to protonation ionophore or lipophilic additives, which results in an increased potential of the system by increasing concentration of proton in solution, Since the potential remains constant over pH 4.0–8.0, this can be taken as the working pH range for the proposed electrode system; in particular, pH 5.0 was used for all the experiments.
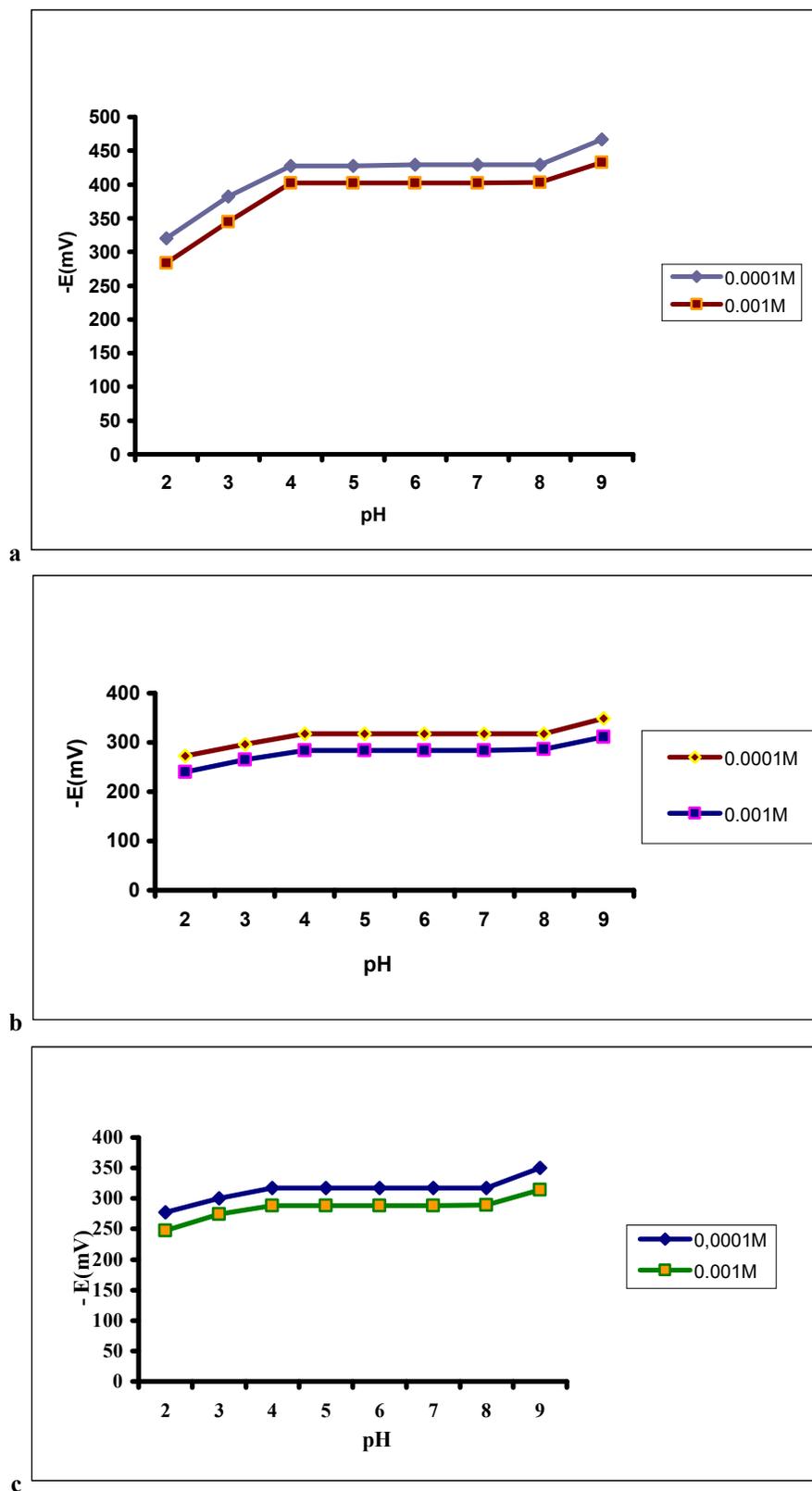
Fig.3a,b,c. Effect of pH of the test solution on the potential reading: 1.0×10^{-4} mol L^{-1} and 1.0×10^{-3} mol L^{-1} Cu^{2+} solution at 25 C using electrode which contain DOS,DOP and NOPE electrode

3.4. Potentiometric selectivity

The selectivity is the most important characteristics, as it determines the extent of utility of any sensor in real sample measurement. As per Nicolskii–Eisenman formalism, the electrode response is given by the following simplified Nernst equation

$$E = E^0 + \frac{RT}{Z_I F} \ln(a_i)$$

Where a_i is the primary ion activity in pure solution, however, in presence of interfering ion Nernst equation is modified as follows

$$E = E^0 + \frac{RT}{Z_I F} \ln\left(a_i + K_{i,j}^{pot} \left(a_j\right)^{Z_i/Z_j} \right)$$

Where a_j is the activity of interfering and Z_i and Z_j are the charges on the primary and interfering ion. As per IUPAC recommended match potential method (MPM) [62-65] selectivity is given by

$$K_{i,j}^{pot} = \frac{a'_A - a_A}{a_B}$$

In this method, at first a known activity (a'_A) of the primary ion solution is added to a reference solution that contains fixed activity (a_A) of primary ion and the potential change is recorded. Secondly, a solution of interfering ions is added to the primary ion solution until the same potential change is observed. In the present studies a_A (1.0×10^{-3} MCu^{2+}), (a'_A) (1.0×10^{-2}M Cu^{2+}) and a_B (1.0×10^{-2} M interfering ion) were taken to measure the selectivity coefficients. The results can be observed from Fig. 4(a–c) No significant interference is caused by the examined ions.
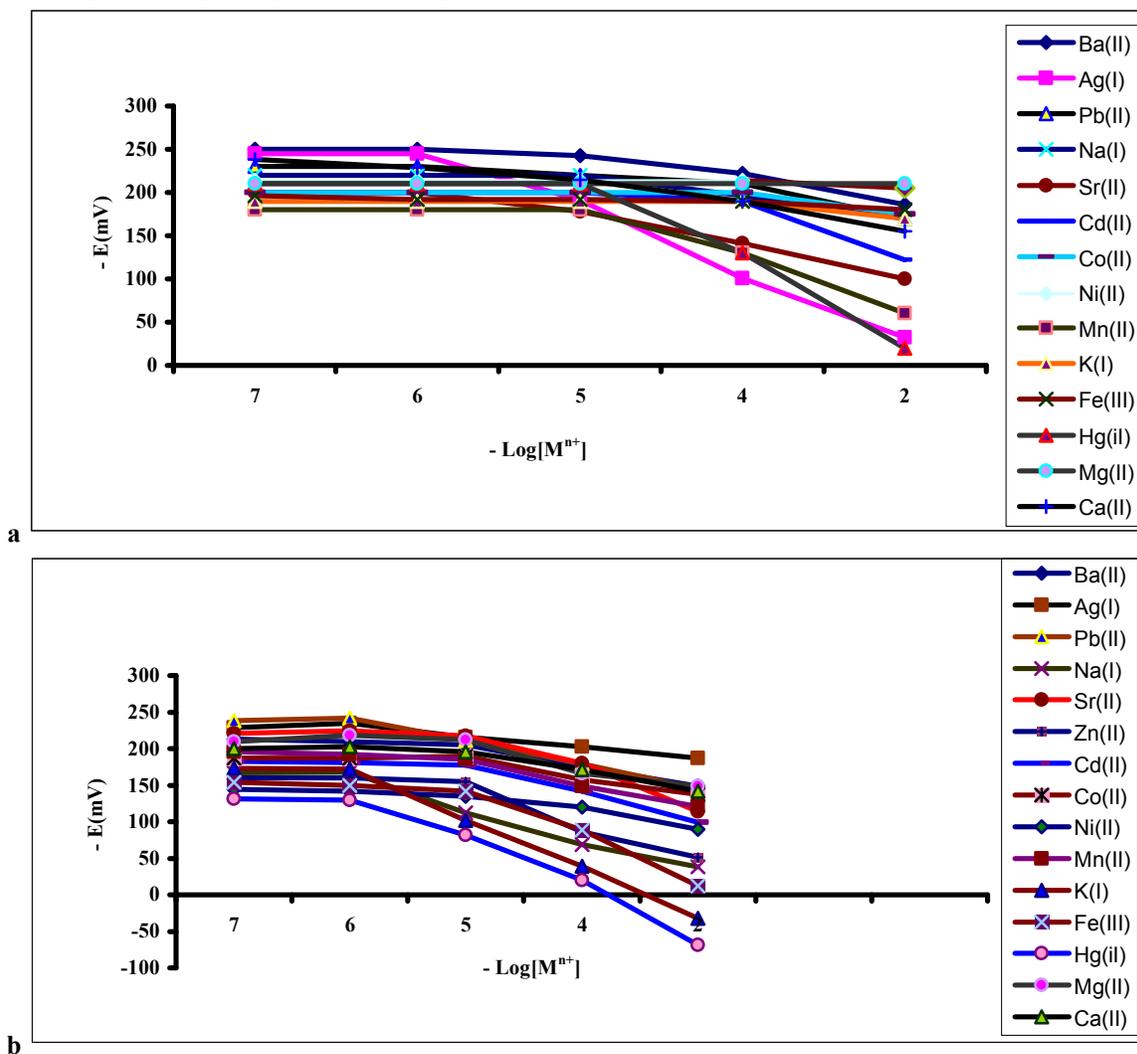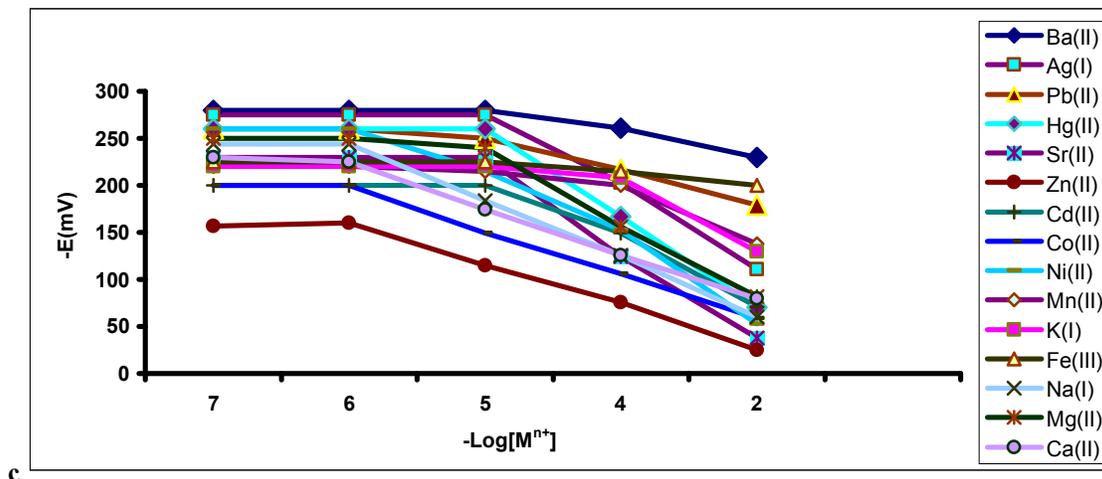
Fig.4a,b,c. Potential response of (DOP,NOPE and DOS) electrode to various metal ions.

3.5. Analytical Application

The selective copper membrane sensor was used as an indicator electrode in the titration of 1.0 $\times 10^{-4}$ M solution of copper ions with a standard 1.0×10^{-2} M EDTA. The resulting titration curve is shown in (Fig. 5). As can be seen, the amount of Cu^{2+} ions in the solution can be accurately determined with the electrode. The electrode was also successfully applied to the direct determination of copper in wastewater samples. The results of the copper determination in copper electroplating samples using both the proposed electrode (calibration curve method) and AAS are given in Table 4. As can be seen from the Table, the results obtained by the sensor show a satisfactory agreement with those obtained by AAS.

Table 4. Determination of copper in wastewater of copper electroplating

Sample no.	ISE, M*	AAS, M*
1	1.2×10^{-3}	1.3×10^{-3}
2	6.4×10^{-3}	6.5×10^{-3}
3	2.5×10^{-4}	2.6×10^{-4}
4	1.7×10^{-4}	1.6×10^{-4}
5	2.9×10^{-4}	2.8×10^{-4}

*Results are based on three measurements.
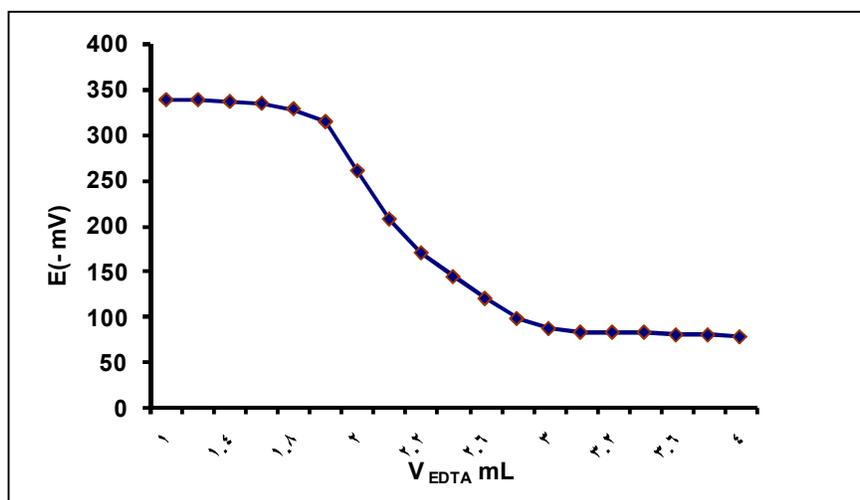
Fig.5. Potentiometric titration curve for 25.0 mL 1.0×10^{-4} M solution of Cu^{2+} with 1.0×10^{-2} M of EDTA.

Conclusion

A copper-selective PVC membrane electrode was prepared with copper (II) complex of 4-azocyanoacetamido-m-toludine antipyrine (Cu-HL^2) as a carrier and its composition (different plasticizers -NPOE, DOS-DOP; and alipophilic

additives- NaTBP) was optimized. From (table 3) that the membrane having composition PVC: NOPE:Cu-HL^2:NaTBP as 65.9: 132.0: 2.0: 0.1 (W/W/W/W) exhibits the best results with Nerenstian slope and limit of detection 5.1×10^{-6} This sensor gave response to copper ion over awide concentration range, fast response time and good selectivity over a large number of metal ions. A comparison between all the characteristics of the proposed potentiometric sensor and those of the previously known copper ion-selective electrodes (Table 1) [20–57] indicates that the current sensor shows better characteristics than several reported electrodes, i.e. being superior in terms of the detection limits, the response time and selectivity over other metal ions. This electrode has been used as an indicator electrode in potentiometric titration of Cu^{2+} with EDTA and direct determination of Cu^{2+} in wastewater of the electroplating industry.

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