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Copper(II) Selective PVC Membrane Based on 3-Doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) as a Novel Ionophore

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In this research, membrane electrode was prepared base on ligand (ionophore) 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) for determination of transition elements. It has a fast response time (< 10 s), can be used for a period of 2 months with a good reproducibility. Dioctyl phthalate (DOP) plasticizer is used in polyvinyl chloride (PVC) matrix and tetrahydrofuran (THF) as a solvent. The result of calibration curve for fabricated electrode for copper cation over a concentration range of 1×10^{-2} to 4×10^{-7} M at pH = 5-6 have Nernst slope 29.7 ± 0.4 mV/decade with detection limit of 1×10^{-7} M. The practical utility of the proposed chemical sensor has been observed by using it as an indicator electrode in the titration of ions with EDTA. The electrode was also used to the copper ion detection in black tea.

Key Words: Copper(II) PVC membrane electrode, Potentiometry, 3-Doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone).

INTRODUCTION

The use of ion sensors in the field of environmental, agricultural, industrial and medical analysis is putting more and more pressure on analytical chemists to develop new sensors for the fast accurate, reproducible and selective determination of various species. Due to the vital importance of copper in industry[1,2] and many biological systems[3-5] and the urgent need for a copper-selective sensor for potentiometric monitoring of Cu^{2+} in different industrial, medical and environmental samples, a variety of potential ion carriers have been employed in the construction of Cu^{2+} ion-selective membrane electrodes. These copper ion carriers include thia- and aza-substituted crown ethers[6,7] and acyclic neutral ionophores with dithiocarbamate groups[6] and with nitrogen atoms[8], calixarenes[9], macrocyclic diamides[10] and Schiff bases[11-13]. Schiff base macrocyclic ligands based on thiosemicarbazones and their complexes have received considerable attention, because of their pharmacological properties. They have numerous application, such as antibacterial and anticancer agent[14-16]. They can yield mono-or polynuclear complex, some of which are biologically relevant[16-19], for example, some copper complexes can serve as model for enzyme such as galactose oxidize and may be used as effective oxidant and redox catalysts[20,21]. Furthermore, they allow selective complexation and extraction of metallic cations and anions of biochemical and environmental importance[22-25]. The number and relative position of donor atoms and the cavity size in the macrocyclic compound give these molecules special reactivity.

However, up to now some copper(II) ion-selective electrode based on macrocyclic and non-macrocyclic ionophores have been described[6,8,10,26-31]. Most of these copper sensors suffer from the interfering effect of cations such as Zn^{2+}, Cd^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+} and Ag^{+}, deviation from Nernstian behaviour and small linear range.

We have recently reported a number of highly selective membrane sensors for various metal ions[32-34]. In this work, we reported a novel Cu^{2+} membrane sensor base on a new selective ionophore 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) (I) (Fig. 1) as excellent ion carrier to prepare highly selective potentiometric sensors for the Cu^{2+} ion. The complexation of 3-doexy-D-erythro- hexos-2-ulose *bis*(thiosemicarbazone) with the Cu^{2+}, Pd^{2+} and Pt^{2+} cations was reported[35]. The ligand(I) was synthesized and purified as described elsewhere[35].

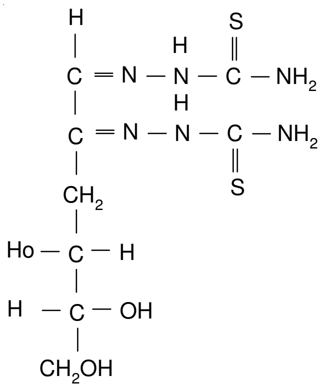

Fig. 1. The ionophore (I) structure

EXPERIMENTAL

Aldrich and the Merck Chemical Co., supplied the following reagents; nitrate and chloride salts of all the cations, reagent-grades of dibutyl phthalate (DBP). The dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC (MW 110,000 g). Moreover, ligand 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) was synthesized and purified as described elsewhere[35]. All the reagents were used without any modification. As far as the nitrate and chloride salts are concerned, they were of the highest purity available and were P_2O_5-vacuum dried. During the experiments, triply distilled de-ionized water was used.

Electrode preparation: The required amounts of the membrane ingredients (30 mg powdered PVC and 66 mg of dioctyl phthalate as plasticizer) were mixed and dissolved in 3 mL of THF. To this mixture, 4 mg ionophore I was added and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm i.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm in thickness was formed[36-46]. Afterwards, the tube was removed from the solution kept at room temperature for 24 h and then filled with an internal solution (1×10^{-2} M $CuCl_2$). The electrode was finally conditioned for 24 h by soaking in a 1×10^{-2} M solution of $CuCl_2$. A silver/silver chloride electrod was used as an internal reference electrode.

EMF measurements: The EMF measurements were carried out with the cell assembly of: Ag-AgCl | internal solution, 1×10^{-2} M $CuCl_2$ | PVC membrane | sample solution | $Hg\text{-}Hg_2Cl_2$, KC1 (satd.). The pH of the solution is adjusted to 6 with acetic acid and ammonium acetate buffer.

A corning ion analyzer (250 pH/mV m) was used for the potential measurements at 25.0 ± 0.1 ºC. The activities were calculated in agreement with the Debye-Huckel procedure[47].

Procedure of conductance study: Conductivity measurements were carried on with a Metrohm 691 conductivity meter. A dip-type conductivity cell made of platinum black with a cell constant of 0.85 cm^{-1} was used. In all measurements the cell was thermstated at the desired temperature of 25.0 ± 0.05 ºC, using a circulator immersion thermostat. In typical experiment, 10 mL of a metal ion nitrate solution (1×10^{-4} M) was placed in water jacketed cell equipped with magnetic stirrer and connected to the thermostat circulating water at the desired temperature. The experimental procedure amount of ionophore I (1×10^{-3} M) solution was added in a stepwise manner using a micropipette. The conductance of the solution was measured after each addition. Addition of ionophore I was continued until the desired I-to-metal ion mole ratio was achieved. The variation of molar conductance, $\wedge_m$, *versus* the ligand to the cation ratio ($[l]_t/[M]_t$) where $[l]_t$ is the total concentration of the ligand, $[M]_t$ is the total concentration of the metal cations for complex of ionophore I with Pd^{2+}, Pt^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} cations in aqueous solution were studied at 25 ºC. It was shown that for Cu^{2+}, Pd^{2+}, Pt^{2+}, Ni^{2+}, Co^{2+} with ionophore I, molar conductance nearly constant in mole ration 1:1, the other cations were not change conductance during the titration and thus probability could not be complex formation stable. The ligand to cation mole ratio is 1. The formation constants (K_f) of the resulting 1:1 complexes at 25 ºC were evaluated by the computer fitting of the molar conductance-mole ratio data to appropriate equations[47]. The details of calculation of the stability constant of complexes by conductometric method have been described[48]. The resulting stability constant (log K_f) for $I\text{-}M^{2+}$ ($M^{2+} = Cu^{2+}$, Ni^{2+}, Pd^{2+}, Pt^{2+}, Co^{2+}) complexes are listed in Table-1. As it is immediately obvious Table-1, the interaction between I with these cations very stronger than other cations and it seems may be act as a selective ion carrier in construction of a Cu(II) membrane sensor.

TABLE-1
DETERMINATION OF log K_f BY CONDUCTOMETRY

Element ion	log K_f
Cu^{2+}	6.31 ± 0.43
Ni^{2+}	5.23 ± 0.77
Co^{2+}	4.62 ± 0.24
Pt^{2+}	4.17 ± 0.37
Pd^{2+}	2.89 ± 0.51

Procedure of spectrophotometric study: Absorbance measurements were made on a Biowave UV-visible single-beam spectrophotometer with a 1 cm glass cell at 25 °C.

In primary experiments, we have studied complexation of I (ionophore) with Cu^{2+}, Ni^{2+}, Co^{2+} ions aqueous solution by spectrophometry. The absorption spectrum of the complex was recorded aginst of blank, similarly the absorption spectrum ligand (I) was recorded aginst of blank, the spectra of complex and ligand have the maximum absorbance and hence doesnot interfere with each other. Thus absorbance measurement of complex was made at wavelength maximum of complex with cations at 465, 400 and 400 nm for determination Cu^{2+}, Ni^{2+}, Co^{2+} cations, respectively. In Job's continuous variation method, plot of spectrophotometric data in λ_{max} complex at pH 6 showed that, in all cases, the ligand (I) can form fairly stable 1:1 (ligand-to-metal) complexes with M^{2+} (Cu^{2+}, Ni^{2+}, Co^{2+}) ions. The constant formation of the complexes were evaluated by computer fitting of the absorbance-mole ratio data. The result (Table-2) shows that Cu^{2+} ion complex has the most formation constant (log K_f) among complexes formed.

TABLE-2
DETERMINATION OF log K_f BY SPECTROPHOTOMETRY

Metal ion	log K_f
Cu^{2+}	6.53 ± 0.41
Ni^{2+}	5.75 ± 0.72
Co^{2+}	4.67 ± 0.51
Pt^{2+}	3.64 ± 0.51
Pd^{2+}	3.29 ± 0.36

RESULTS AND DISCUSSION

We have studied the complexation of 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) with several alkaline earth and transition metal ions in aqueous solution with conductometry and spectrophotometry UV-vis. It was found that, the complextion with Cu^{+2}, Ni^{2+}, Co^{2+} more stable than the other metal cations. Based on the experiments, in this work the ligand 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) was employed as potential ion carriers in the PVC membranes, in order to investigate their abilities in the preparaties of some new ion-selective electrodes. Thus, in preliminary experiments, ligand 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) were used to prepare PVC membrane ion-selective electrode for a Cu^{2+}, Ni^{2+}, Co^{2+} ions. In comparison with the other cations tested, only the Cu(II) ion shows a strong response (with a slope of 29.5 ± 0.5 mV/decade) to the ionophere (**I**) based membrane sensors. Therefore, the ionophore (I) was selected as a suitable sensing material for Cu^{2+} ions in the PVC matrix. It is well known that the sensitivity, selectivity, working concentration range and response time of ion-selective electrodes depend on membrane composition and the properties of the plasticizer employed. Thus, the influences of the membrane composition and the nature of plasticizer on the potential of the Cu(II) ion-selective electrodes based on ionophore I was investigated and the results are summarize in Table-3. The potential responses of all of the membrane sensors were studied in a wide range of concentrations of Cu(II) solution. Table-3 shows that the total potentiometric response of the electrode towards Cu(II) ions is dependent on the concentration of ionophore (I) that is incorporated within the membrane. As can be seen from Table-3, larger slopes are observed by increasing the amount of I up to 4 % in the membranes. A maximum slope of 29.7 mV/decade of copper concentration was observed for the membrane No. 3 with 4 % of ionophore (I). Among the different solvent mediators tested, it is found that DOP compared to DBP results in the best sensitivity in construction of the Cu(II) membrane sensor. The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane which is based on a neutral carrier decreases the ohmic resistance and improves the response behaviour and selectivity. Here, a NaTPB addition of 3 % as an additive led to the slope increase of the potential sensor response from the value of 29.3 ± 0.5 mV/decade (No. 9) to the Nernstian value of 29.7 ± 0.4 mV/decade (No.7). Table-3 displays that the optimum response characteristics were obtained with a membrane composition of 30 % PVC, 65 % DOP, 3 % NaTPB and 4 % I (No. 9).

TABLE-3
OPTIMIZATION OF MEMBRANE INGREDIENTS

No.	Composition (Wt. %)				Linear range	Slope (mV/decade)
	PVC	Plasticizer	NaTPB	Ligand		
1	30	DBP, 68	–	2	1×10^{-2}-1×10^{-4}	13.2 ± 0.5
2	30	DBP, 67	–	3	1×10^{-2}-1×10^{-6}	19.5 ± 0.3
3	30	DBP, 66	–	4	1×10^{-2}-1×10^{-6}	23.2 ± 0.5
4	30	DBP, 65	–	5	1×10^{-2}-1×10^{-6}	18.6 ± 0.4
5	30	DOP, 67	–	3	1×10^{-2}-1×10^{-6}	25.8 ± 0.3
6	30	DOP, 66	–	4	1×10^{-2}-1×10^{-7}	28.5 ± 0.5
7	30	DOP, 65	–	5	1×10^{-2}-2×10^{-7}	31.2 ± 0.3
8	30	DOP, 65	2	4	1×10^{-2}-4×10^{-7}	29.3 ± 0.3
9	30	DOP, 65	3	4	1×10^{-2}-4×10^{-7}	29.7 ± 0.4

Effect of pH: The influence of pH of the test solution on the potential response of the Cu(II) sensor was tested at 1 × 10^{-4} M Cu(II) concentration over the pH 2-7 and the result are shown in Fig. 2. As seen, the potential remained constant from pH 5-6, the observed drift at higher pH values could be due to the formation of some hydroxyl of the Cu(II) ion in solution. The effect of pH of the test solution on the potential response of the copper sensor was investigated, the electrode below pH = 5 did not show a good Nernstian response, but the response of the electrode was stable in solution without addition of any buffer in pH of solution Cu(II) was stable with a good Nernstian slope.

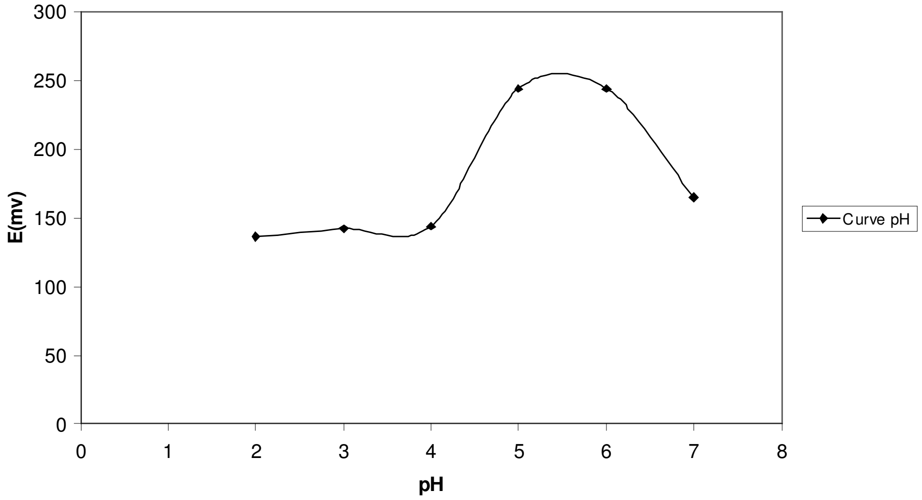

Fig. 2. The pH effect of the test solution (1 × 10^{-4} M) on the potential response of the cupper sensor (membrane No. 9)

Dynamic response time of the sensor Cu^{2+}: For analytical applications, dynamic response time is very important for any sensor. The dynamic response time of the membrane was measured at various concentrations (4 × 10^{-7} M to 1 × 10^{-2} M) of the test solutions and results are illustrated in Fig. 3. As can be seen, in the whole concentration range the electrode reaches its equilibrium response, very fast (< 10 s).

Potentiometric selectivity: Potentiometric selectivity coefficients of the sensor were determined by the matched potential method[32-36]. According to this method, a specified activity (concentration) and the potential are measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{MPM} = a_A/a_B$. The resulted potentiometric selectivity coefficients values are summarized in Table-4. The data given in Table-4, show the selectivity coefficients of the proposed Cu^{2+} membrane sensor were 3 × 10^{-4} or smaller and revealed that the proposed

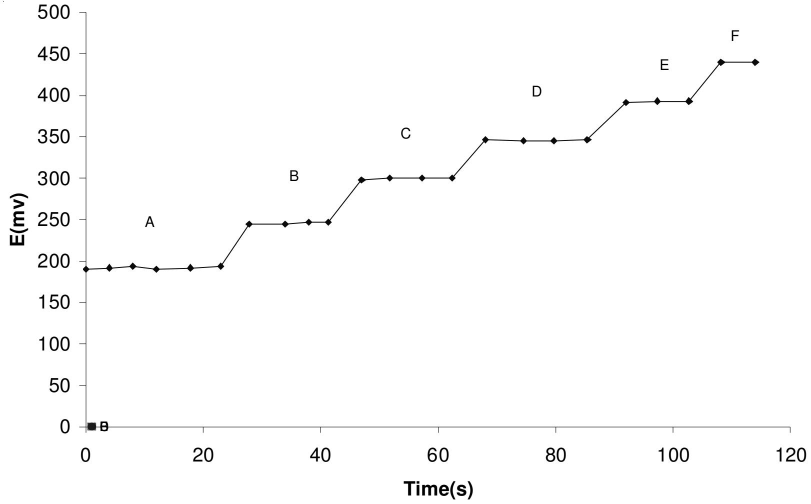

Fig. 3. The dynamic response time of the copper electrode (membrane No. 9) for step changes in the Cu^{2+} concentration: (A) 1×10^{-7} M, (B) 1×10^{-6} M, (C) 1×10^{-5} M, (D) 1×10^{-4} M, (E) 1×10^{-3} M, (F) 1×10^{-2} M

TABLE-4
SELECTIVITY COEFFICIENT VALUES ($K_{Cu, M}^{pot}$) OF VARIOUS INTERFERING IONS

Ion	$K_{Cu, M}^{pot}$	Ion	$K_{Cu, M}^{pot}$
Li^+	1.2×10^{-5}	Cd^{2+}	5.1×10^{-5}
Na^+	1.7×10^{-5}	Pd^{2+}	7.4×10^{-4}
Ag^+	4.0×10^{-5}	Pt^{2+}	3.7×10^{-4}
Hg^{2+}	1.8×10^{-5}	Co^{2+}	3.0×10^{-4}
Ca^{2+}	4.3×10^{-5}	Ni^{2+}	9.6×10^{-4}
Sr^{2+}	1.3×10^{-5}	Fe^{2+}	3.0×10^{-4}
Mg^{2+}	1.7×10^{-5}	UO_2^{2+}	2.7×10^{-5}
Pb^{2+}	4.1×10^{-5}	Zn^{2+}	8.1×10^{-5}
Al^{3+}	2.5×10^{-5}	SO_4^{2-}	2.5×10^{-5}
Cr^{3+}	5.8×10^{-5}	NO_3^-	1.5×10^{-6}

Cu^{2+} membrane sensor is highly selective with respect to most of the transition and heavy metal ions. The surprisingly high selectivity of the membrane electrode for copper ions over other cations used, most probably arises from the strong tendency of the carrier molecules for copper ions. Due to the charge density, size of the copper ion and the concept of HSAB-theory, an ionophore like I, with suitable intermediate or soft donor atoms in its structure, can form a complex with copper ion with the optimum free energies. This can be justified according to the intermediate nature of the ion due to its free *d*-orbital, which makes it suitable to complex with I having intermediate donor atoms (N and S atom). Thus, the high Cu^{2+} ion extraction into the liquid membrane was a result of the elevated ionophore tendency to form a selective complex with the Cu^{2+} ions.

Comparison with other Cu^{2+} electrodes: In Table-5, the major interfering ions, the dynamic linear range, the detection limit and response time of the developed electrode is compared with the best data of the previously reported Cu^{2+} selective membrane electrode[6,8,10,12,26-32]. Evidently, the suggested Cu^{2+} sensor in terms of selectivity coefficients, dynamic linear range and detection limit and response time is superior to the former Cu^{2+} ion-selective electrode.

TABLE-5
COMPARISON OF THE SELECTIVITY COEFFICIENTS
OF DIFFERENT Cu(II) ELECTRODES

Interf. ions,B	References											This work
	[6]	[8]	[10]	[12]	[26]	[27]	[28]	[29]	[30]	[31]	[32]	
Li^+	–	–	–	–	–	–	–	-3.20	-2.34	–	-3.24	-4.90
Na^+	–	–	–	-1.34	–	–	–	-4.20	-1.07	–	-3.09	-4.98
K^+	–	–	–	-3.89	–	–	–	-3.40	-1.22	–	-3.40	-4.59
Mg^{2+}	–	–	–	-3.03	–	–	–	-3.90	-1.21	–	-3.00	-4.75
Ca^{2+}	–	–	–	-3.00	–	–	–	-3.30	-1.20	–	-2.43	-4.37
Sr^{2+}	-4.00	-3.62	-1.03	-3.09	–	-2.82	–	-4.30	-1.08	–	-2.50	-3.87
Ba^{2+}	–	–	–	-3.14	–	–	–	–	-1.25	–	-3.00	-4.10
Ag^{2+}	–	–	–	–	–	-2.31	–	2.90	-0.27	-4.00	-3.12	-4.40
Pb^{2+}	-1.79	-0.74	-2.20	-2.39	-1.22	-2.70	–	-2.70	–	-3.70	-3.23	-4.39
Hg^{2+}	–	–	-2.41	-1.19	–	-3.13	–	–	-0.34	–	-4.00	-4.75
Zn^{2+}	-3.96	-2.25	-2.35	-209	-3.00	-2.87	-2.00	-4.00	-1.09	-3.40	-3.05	-4.09
Ni^{2+}	-3.79	-3.20	-2.01	-1.52	-2.00	-3.18	-3.40	-4.00	-1.12	-3.70	-2.33	-3.02
Co^{2+}	–	–	–	-2.13	–	–	–	-3.60	-1.09	–	-2.12	-3.52
Cd^{2+}	-4.47	-4.37	-1.58	-2.08	-2.00	-3.40	-2.70	-3.70	-1.08	-3.52	-3.07	-4.29
Mn^{2+}	–	–	–	-2.29	–	–	–	–	–	–	-2.55	-3.74
Al^{3+}	–	–	–	–	–	–	–	–	–	–	-3.30	-4.61
Fe^{3+}	–	–	–	–	–	–	–	–	-1.14	–	-2.38	-3.52
Cr^{3+}	–	–	–	–	–	–	–	–	–	–	-3.17	-4.24
Ce^{3+}	–	–	–	–	–	–	–	–	–	–	-3.15	-4.12
Pd^{2+}	–	–	–	–	–	–	–	–	-1.07	–	–	-2.13
Pt^{2+}	–	–	–	–	–	–	–	–	–	–	–	-2.43
La^{3+}	–	–	–	–	–	–	–	–	–	–	-3.03	-4.40

Calibration curve: The optimum responses of the sensors based on ionophore I were evaluated after conditioning of the membranes with same composition, for different periods of time in 0.01 M $CuCl_2$ solution. The slope obtained using 24 h of conditioning was closer to the theoretically expected slopes, on the basis of the Nernst equation longer conditioning times produced no further improvements in the response. The optimum conditioning solution was determined to have a concentration of about 0.01 M. The potential response of the PVC-based membrane sensor at varying concentrations of $CuCl_2$ (Fig. 4) indicates a linear working concentration range from 1×10^{-2}-4×10^{-7} M ($r > 0.997$). The slope of the calibration graph was 29.7 ± 0.4 mV/decade of copper ions concentration. The detection limit of the electrode that determined from the intersection of the two extrapolated segments of the calibration graph was 1.0 × 10^{-7} M. The standard deviation for ten replicate measurements was ± 0.4 mV. Daily, the sensor was used for 1 h, washed and dried. Its usage was found to last for at least 60 days. In the end of this time period, the electrode slope reduced (from 29.7-27.7 mV/decade).

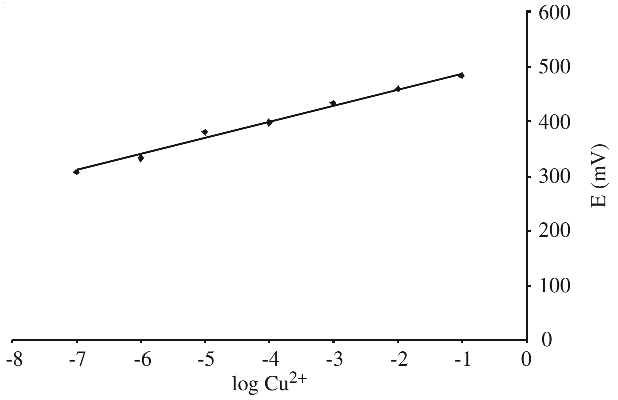

Fig. 4. Calibration curve of the copper electrode (membrane No. 9) based on the ionophore (I)

Analytical applications: Potentiometric copper-selective membrane sensor based on ionophore can estimate Cu^{2+} ions in the concentration range from 1 × 10^{-2}-4 × 10^{-7} M with the slope of 29.7 ± 0.4 mV/decade of activity. The sensors were found to work well in the pH range of 5-6 with response time of less than 10 s and showed reproducible and stable potentiometric signals. The Cu^{2+} sensor was successfully used as an indicator electrode in the titration of 40 mL of a 1 × 10^{-4} M Cu^{2+} solution with a 1 × 10^{-2} M EDTA (at pH = 6). The resulting titration curve is given in Fig. 5. The amount of Cu^{2+} ions in the solution can be effectively determined with the electrode. The sensor of copper(II) in different ions solution successfully used to determine copper(II) ions in samples of Iranian black tea. The results (Table-6), obtained with the sensor and those of atomic absorption spectrometric (AAS) analysis, were close enough to reach the conclusion that the recommended sensor could be used in the monitoring of copper ions in real sample. The procedure used for the extraction of copper was similar to that reported in the literature[49].

Conclusion

The PVC-based membrane electrode of 3-doexy-D-erythro-hexos-2-ulose *bis*(thiosemicarbazone) the with the composition 4 % ionophore, 30 % PVC, 3 % NaTPB and 63 % DOP exhibited the best performance characteristics with Nernstian behaviour across the concentration range of 4 × 10^{-7}-1 × 10^{-2} M Cu^{2+} and a fast response time of 10 s. These sensor works well in a pH range of 5-6 and also, it was successfully used as an indicator electrode in the copper ion titration with EDTA and direct determination of copper in black tea.

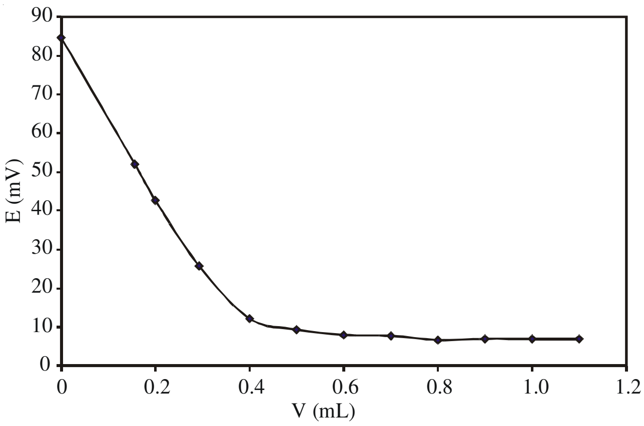

Fig. 5. Potentiometric titration curve of 40 mL from the Cu^{2+} solution 1×10^{-4} M with 1×10^{-2} M of EDTA

TABLE-6
DETERMINATION OF COPPER IN BLACK TEA

Sample No	Copper (ppm)	
	ISE	AAS
1	4.6 (± 0.3)	4.7 (± 0.2)
2	5.9 (± 0.2)	6.0 (± 0.2)
3	6.1 (± 0.2)	6.0 (± 0.2)
4	6.5 (± 0.3)	6.3 (± 0.2)
5	5.7 (± 0.2)	5.8 (± 0.1)

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