Design and construction of electrochemical selective sensors for copper(II) in water samples based on $C_{18}H_{18}N_6S_2$ and $C_4H_8O_4S_2$ Dithio ligands as neutral carriers

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A R T I C L E I N F O

A B S T R A C T

Dithio based chelating ionophores such as 1-anilino-6-(3, 4-xylyl)-2, 5-dithiobiurea (A) and Dithiodiglycolic acid (B) were used as active components of PVC membrane electrode and explored as Cu^{2+}-ion selective electrodes. The membranes having the composition (A): o-nitrophenyl octyl ether (o-NPOE): polyvinyl chloride (PVC): potassium tetrakis(4-chlorophenyl) borate (KTpClPB) in the ratio of 3: 78: 40: 2 (w/w; mg) and (B): (o-NPOE): (PVC): (KTpClPB) in the ration 3 :80 :40 :3 are found to be exhibiting the best sensor characteristics. The fabricated sensors exhibited Nernstain response (29.301 and 28.223 mV decade^{-1}) over concentration ranges of 1.0×10^{-8} to 1.0×10^{-1} mol/L and 1.0×10^{-7} to 1.0×10^{-1} mol/L and exhibit detection limit of 2.2×10^{-8} and 8.3×10^{-7} mol /L for sensor No. 9 and 6 for ionophores A and B, respectively. The best performances were observed with the sensor having the composition of (A): (o-NPOE): (PVC): (KTpClPB) in the ratio of 3: 78: 40: 2 (w/w; mg), and the electrodes have a response time of 9 - 12 s with a pH range of 3.0 - 7.0, and could be used over a period of 3 months without any significant deviation in its potentiometric characteristics. The analytical usefulness of the proposed sensor has been evaluated by its application in the determination of copper in water samples, the results obtained by the proposed ISEs are in good agreement with the results obtained by direct flame AAS method. The sensor No. 9 has been used also in the potentiometric titration of Cu^{2+} with EDTA.

1. Introduction

Determination of trace elements in food and water as some of them have nutritional significance is of great importance, although others are toxic (Mahajan et al., 2005). Copper is one of the essential trace elements (Shepard et al., 2002). It is also widely used in industries, agriculture and domestic purposes, and is therefore, most widely distributed element in the environment of industrialized countries (Gil et al., 1995; Shvedene et al., 1991). Consequently, determination of copper ion in a wide range of chemical and biological processes in various materials such as water, biological, environmental, medical and industrial samples play a significant role (Hundhammer and Wilke, 1989).

As Copper (II) is a highly toxic ion, the removal of Cu (II) from wastewater has been the subject of many researches. Copper ion is a common hazardous pollutant in wastewater and is often released by metallurgical, plating, printing circuit, fertilizer and refining industries (Ali et al., 2013; Lagos et al., 1999; Liu et al., 2007; Olivares et al., 1998) .The tolerance limit for Cu(II) for discharge into inland surface waters is 3.0 mg/L and in drinking water is 0.05 mg/L (Olivares and Uauy, 1996).

Although sophisticated analytical techniques, viz. atomic absorption spectrometry (AAS), UV–Vis spectrometry (Cobben et al., 1994), high performance liquid chromatography (Singh et al., 2007) ,inductively coupled plasma-optical emission spectrometry (ICP-OES) (Van Staden et al., 1997) and stripping Voltammetry (Katsu et al., 2002) are used for determination copper ion at low concentration level. Better to be like this: These available "or existing" methods provide accurate results, but are not very convenient for analysis of a large number of environmental samples as they generally require expertise and sample manipulation

as well as being relatively expensive and time consuming.

Ion-selective electrodes (ISEs) are useful tools for determination of an ion in the presence of other ions, offering interesting advantages such as fast response, simple instrumentation, low cost and wide concentration range (Gupta et al., 2007; Javanbakht et al., 2007; Singh et al., 2007; Zhang et al., 2008). Many efforts have been made for selective potentiometric monitoring of Cu^{2+} ions at lower concentration level. In this regard, several ion-selective electrodes have been reported for the determination of Cu^{2+} ion in various environmental samples (Ghanei-Motlagh et al., 2011; Gupta et al., 2012). However, many of these are suffering with some limitations such as narrow working concentration range, low pH range, substantial interference from a variety of cation and high response time. This led us to construct and design a new potentiometric (metal–nitrogen–sulfur ligand) for the determination of Cu^{2+} in aqueous solutions. In this work, two different ionophores 1-anilino-6-(3, 4-xylyl)-2, 5-dithiobiurea (A) and Dithiodiglycolic acid (B) have been synthesized and explored as an ion selective electrode for highly selective and sensitive determination of Cu^{2+} ion in water samples.

2. Experimental

2.1. Reagents

Polyvinyl chloride (PVC) used as polymer, Potassium tetrakis (p-chlorophenyl) borate (KTpClPB) used as ionic exchange and THF as solvent were obtained from Sigma Aldridge. O-nitrophenyloctyl ether (o-NPOE) used as solvent mediators / plasticizer and Silver wire 0.5mm diameter 99.99% were obtained from Alfa Aesar. 1-anilino-6-(3,4-xylyl)-2,5-dithiobiurea (A) and Dithiodiglycolic acid (B) as ionophore were obtained from Fluka and Sigma Aldridge. All other chemicals were the best laboratory available reagents and all solutions were prepared from analytical reagent grade salts without any further purification using distilled de-ionized water (Fig. 1).
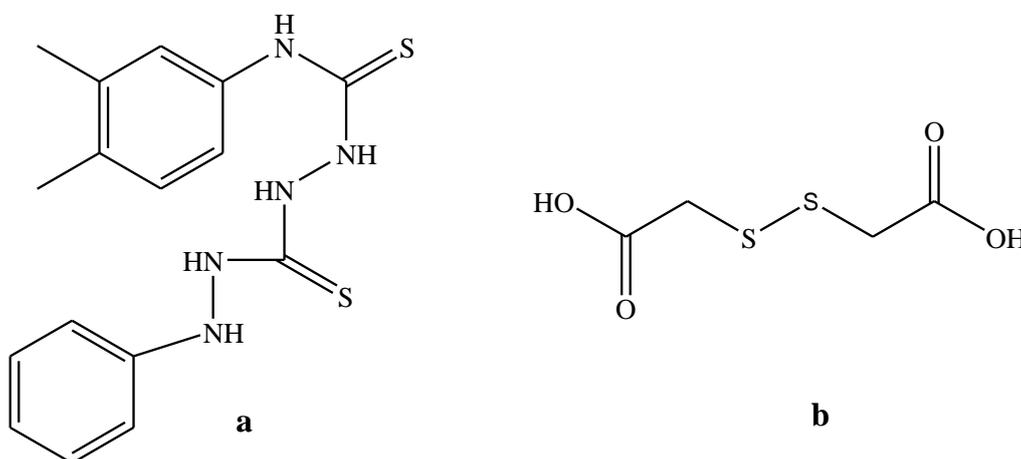
Fig. 1: The molecular structure of (a) 1-Anilino-6-(3,4-xylyl)-2,5-dithiobiurea as ionophore (A), and (b) Dithiodiglycolic acid as ionophore (B).

2.2. Apparatus and potential measurements

VC97 3/4 Digital Multimeter LCD Digital Multi Meter Tester Auto Range - AC DC Meter was used for potential measurements. The activities of the ions tested were calculated according to the Debye-Huckel procedure. The activities of metal ions were based on the activity coefficient γ, data calculated from the modified form of the Debye-Huckel equation No. 1, which is appropriate to any ions (Eq. 1):

$$\log \gamma = -0.511 Z^2 \left[\frac{\mu^{0.5}}{(1+1.5\mu^{0.5})} - 0.2\mu \right] \qquad (1)$$

All measurements were carried out at room temperature. All the metal chloride solutions were freshly prepared by an accurate dilution from their stock standard solution with deionized water where μ is the ionic strength and Z the charge (Katsu et al.,

2002). All electromotive force (emf) measurements were carried out with the following cell assembly: Ag-AgCl | internal solution, 1.0×10^{-3} mol L^{-1} CuCl$_2$ | PVC membrane |test solution |KC1 (satd.) | Ag-AgCl

2.3. General procedure for electrode preparation

The membranes have been fabricated by general procedure (Bakker et al., 2000). Polymeric membrane based on high molecular weight PVC was prepared by dissolving 40 mg of PVC, 2-3 mg ($C_{18}H_{18}N_6S_2$ or $C_4H_8O_4S_2$) of ionophore and 78-80 mg of o-NPOE as mediators / plasticizer in a minimum amount of tetrahydrofuran (THF) (~1.5 ml). The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm in top) was dipped into the oily mixture for about 15 s, so that a transparent film of about 0.3-0.4 mm thickness was formed, the tube was then removed from the mixture and kept at room temperature for about 6 h. The tube was filled with

an internal filling solution (1.0×10^{-3} M of Copper chloride). The electrode was finally conditioned for 24 h by soaking in 1.0×10^{-3} M solution of $CuCl_2$. A silver/ silver chloride coated wire was used as an internal reference electrode.

3. Results and discussion

3.1. The response of the electrode based on ionophore (A) and (B) to Cu (II) ion

In preliminary experiments, the optimal modified Cu^{2+} ion sensors Fig. 2. (a and b) were tested for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. Except for the Cu^{2+} ion for all other cations where the slope of the corresponding potential plot is much lower than the expected Nernstian slopes. As is obvious from the obtained results, the proposed electrode based on ionophore (A) and (B) exhibited linear responses to the activity of Copper ions over a wide concentration range, with a Nernstian slope of 29.301 and 28.223 mV per decade and a correlation coefficient of 0.9974 and 0.9957 as shown in the Table 1 and 2 for ionophore (A) and (B) respectively, with low detection limit. The results might indicate that the selectivity towards this ion is masked by the low detection limit of the electrode, which is most probably due to the transport of Cu^{2+} ions from the measuring solution to the boundary between membrane and the solution as discussed by Bakker (Cobben et al., 1994).
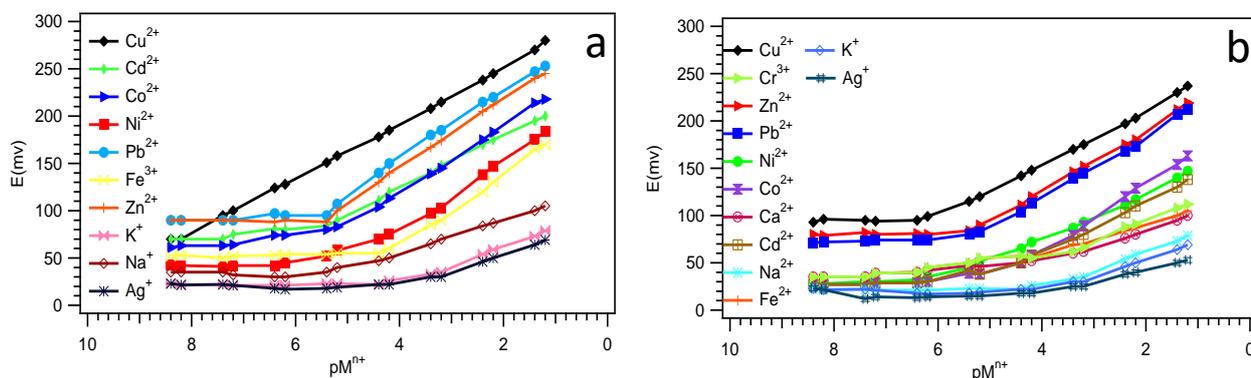

Fig. 2: The Potential response of various metal ion-selective electrodes based on (a) ionophore (A) and (b) ionophore (B)

Table 1: The potential response of various metal ion-selective electrodes based on ionophore (A)

Cations	Slope (mv.decade^{-1})	R^2	Response time(s)	Linear range (mol.L^{-1})
Cu^{2+}	29.301	0.9974	10	1.0×10^{-7}-1×10^{-1}
Cd^{2+}	30.807	0.9856	18	1.0×10^{-5}-1×10^{-1}
Co^{2+}	32.554	0.9963	23	1.0×10^{-5}-1×10^{-1}
Ni^{2+}	19.851	0.9914	15	1.0×10^{-5}-1×10^{-1}
Pb^{2+}	28.665	0.9860	20	1.0×10^{-6}-1×10^{-1}
Fe^{3+}	28.202	0.9945	22	1.0×10^{-6}-1×10^{-2}
Zn^{2+}	13.001	0.9375	31	1.0×10^{-4}-1×10^{-2}
K^+	10.145	0.9739	40	1.0×10^{-4}-1×10^{-1}
Na^+	13.557	0.9036	30	1.0×10^{-4}-1×10^{-1}
Ag^+	25.601	0.9824	20	1.0×10^{-5}-1×10^{-1}

Table 2: The potential response of various metal ion-selective electrodes based on ionophore (B)

Cations	Slope (mv.decade^{-1})	R^2	Response time (s)	Linear range (mol.L^{-1})
Cu^{2+}	28.223	0.9957	18	1.0×10^{-7}-1×10^{-1}
Zn^{2+}	30.807	0.9956	20	1.0×10^{-6}-1×10^{-1}
Co^{2+}	31.554	0.9963	23	1.0×10^{-6}-1×10^{-1}
Ni^{2+}	23.851	0.9914	20	1.0×10^{-6}-1×10^{-1}
Pb^{2+}	27.965	0.986	25	1.0×10^{-6}-1×10^{-1}
Na^+	16.088	0.9023	40	1.0×10^{-5}-1×10^{-1}
K^+	13.202	0.9345	43	1.0×10^{-3}-1×10^{-2}
A^+	13.001	0.9375	40	1.0×10^{-4}-1×10^{-2}
Fe^{3+}	10.145	0.9539	31	1.0×10^{-3}-1×10^{-1}
Cd^{2+}	13.557	0.9536	28	1.0×10^{-5}-1×10^{-1}
Ca^{2+}	25.601	0.9924	21	1.0×10^{-5}-1×10^{-1}
Cr^{3+}	10.192	0.8847	36	1.0×10^{-5}-1×10^{-1}

3.2. Optimization of membrane composition

The potential response of the ion-selective electrode (ISE), obtained for a given membrane depends significantly on the membrane ingredients and the nature of plasticizer and additives used. Therefore, several membranes based on ionophore (A) and (B) with different compositions have been prepared and the results are summarized in Table 3 and 4. A comparison of the performance features of

all the sensors clearly revealed that the sensors No.9 and 6 having membranes with ionophores (A) and (B) respectively, and o- NPOE as plasticizer are the best. It is reported that the response characteristics of ion-selective electrodes are also largely affected by the nature and amount of plasticizer used (Liu et al., 2007). This is because of the importance of the influence of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands.

Moreover, 3 mg of the ionophore was chosen as the optimum amount of ionophore in the PVC-membrane for sensor (No. 9) ionophore (A), and sensor (No. 6) ionophore (B) because the surface conditions of the PVC membrane worsened on decreasing and increasing the ionophore content. From the data presented in Table 3 and 4 for ionophores (A) and (B), it is seen that the addition of KTpClPB increases the sensitivity of the electrode response considerably. The use of 2-3 mg KTpClPB resulted in a Nernstian behavior of the electrode. Among all the membranes prepared so far, the membranes obtained with (A): (o-NPOE): (PVC): (KTpClPB) in the ratio of 3: 78: 40: 2 (sensor No.9) in Table 3 and (B): (o-NPOE): (PVC): (KTpClPB) ratio as 3: 80: 40: 3 (sensor No.6) in Table 4 show good Nernstian slope over wide Cu^{2+} concentration range. All the additional studies were carried out with the cells employing sensors (No. 9 and 6) for ionophores (A) and (B) respectively.

Table 3: Optimization of membrane composition based on ionophore (A)

Sensor No.	Composition (wt. %)				Slope (mVdecade^{-1})	Concentration range (mol L^{-1})
	PVC	Plasticizer (o-NPOE)	Additive (KTpClPB)	Ionophore A		
1	40	70	3	3	28.004	1.0×10^{-7}-1.0×10^{-1}
2	40	72	3	3	28.666	1.0×10^{-7}-1.0×10^{-1}
3	40	74	3	3	27.024	1.0×10^{-7}-1.0×10^{-1}
4	40	76	3	3	27.221	1.0×10^{-7}-1.0×10^{-1}
5	40	78	3	3	28.554	1.0×10^{-7}-1.0×10^{-1}
6	40	80	3	3	28.023	1.0×10^{-7}-1.0×10^{-1}
7	40	78	0	5	20.215	1.0×10^{-4}-1.0×10^{-1}
8	40	78	1	4	29.002	1.0×10^{-7}-1.0×10^{-1}
9	40	78	2	3	29.304	1.0×10^{-8}-1.0×10^{-1}
10	40	78	3	2	29.024	1.0×10^{-7}-1.0×10^{-1}
11	40	78	4	1	23.011	1.0×10^{-5}-1.0×10^{-1}
12	40	78	5	0	14.021	1.0×10^{-3}-1.0×10^{-1}
13	35	78	2	3	28.001	1.0×10^{-8}-1.0×10^{-1}
14	45	78	2	3	28.722	1.0×10^{-8}-1.0×10^{-1}

Table 4: Optimization of membrane composition based on ionophore (B)

Sensor No.	Composition (wt. %)				Slope (mVdecade^{-1})	Concentration range (mol L^{-1})
	PVC	Plasticizer (o-NPOE)	Additive (KTpClPB)	Ionophore B		
1	40	70	3	3	27.004	1.0×10^{-6}-1.0×10^{-1}
2	40	72	3	3	27.056	1.0×10^{-6}-1.0×10^{-1}
3	40	74	3	3	27.821	1.0×10^{-6}-1.0×10^{-1}
4	40	76	3	3	28.024	1.0×10^{-6}-1.0×10^{-1}
5	40	78	3	3	28.100	1.0×10^{-6}-1.0×10^{-1}
6	40	80	3	3	28.224	1.0×10^{-7}-1.0×10^{-1}
7	40	78	0	5	18.215	1.0×10^{-4}-1.0×10^{-1}
8	40	78	1	4	31.022	1.0×10^{-7}-1.0×10^{-1}
9	40	78	2	3	30.824	1.0×10^{-7}-1.0×10^{-1}
10	40	78	3	2	31.024	1.0×10^{-7}-1.0×10^{-1}
11	40	78	4	1	25.111	1.0×10^{-5}-1.0×10^{-1}
12	40	78	5	0	16.021	1.0×10^{-3}-1.0×10^{-1}
13	35	78	2	3	28.001	1.0×10^{-7}-1.0×10^{-1}
14	45	78	2	3	28.008	1.0×10^{-7}-1.0×10^{-1}

3.3. Selectivity coefficient for Cu (II) ion sensor

Selectivity behavior is one of the most significant characteristics of a sensor. It gives the response of ion-sensitive sensor for the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficients ($K^{pot}_{cu, B}$). As it is seen from Table 5, that the selectivity coefficients determined are much smaller than 1.0. Thus, both the electrodes are substantially selective to Cu^{2+} ions over all the interfering ions studied and listed in Table 5.

Altered methods of the selectivity determination can be found in the literature. The IUPAC suggests two methods: separate solution method (SSM) and fixed interference method (FIM). There is also an alternative method of the selectivity determination called matched potential method (MPM). In the present work the selectivity coefficients of two ionophores have been measured for the two Copper sensors (No. 9 and 6) using fixed interference method (FIM) as suggested by Sa'ezde Viteri and Diamond (Sa'ez de Viteri, 1994; Viteri, 1994). The selectivity coefficient was estimated from the potential measured on solutions containing a fixed

concentration of interfering ion (1.0×10^{-2} mol L^{-1}) and varying amounts of Cu^{2+} ion solution ranging from 1.0×10^{-1}- 1.0×10^{-8} mol L^{-1} and 1.0×10^{-1}- 1.0×10^{-7} mol L^{-1} for ionophore (A) and (B) respectively, the potential values so obtained, plotted versus activity of Cu^{2+} and the resulting selectivity coefficient values are summarized in

Table 5. The selectivity of the sensor (No. 9) towards Cu^{2+} is high for most of the cations from other conventional Cu^{2+} ion-selective electrodes. As sensor (No. 9) for ionophore (A) is better than the sensor (No. 6) for ionophore (B) in terms of wider working concentration range, low response time, high selectivity and Nernstian compliance.

**Table 5:** Selectivity coefficient of various interfering ions

No.	Interfering (1.0×10^{-2} mol.L^{-1})	Selectivity coefficients log $K^{pot}_{cu, B}$	
		ISE (A)	ISE (B)
1	Na^+	2.3×10^{-5}	2.3×10^{-3}
2	Ag^+	1.0×10^{-4}	4.0×10^{-4}
3	K^+	3.2×10^{-2}	2.2×10^{-3}
4	Ca^{2+}	2.0×10^{-2}	1.0×10^{-3}
5	Ni^{2+}	7.8×10^{-2}	4.8×10^{-1}
6	Pb^{2+}	2.0×10^{-1}	-1.204
7	Zn^{2+}	3.1×10^{-1}	-0.224
8	Cr^{3+}	1.1×10^{-2}	7.0×10^{-3}
9	Fe^{3+}	5.3×10^{-2}	3.0×10^{-4}
10	Co^{2+}	2.3×10^{-4}	4.0×10^{-3}
11	Cl^-	3.1×10^{-6}	$3. \times 10^{-5}$
12	Mn^{2+}	5.5×10^{-3}	42×10^{-3}
13	Br^-	1.2×10^{-4}	8.2×10^{-5}

3.4. The calibration curve of Cu2+ ion sensor and detection limit

The potential response of the optimized sensors, to varying concentrations of Cu^{2+} ions, was studied. By using the condition mentioned above for the sensors (No.9 and 6) for ionophore (A) and (B) respectively. By soaking in conjunction with a reference electrode in a 50 mL beaker containing a 25 ml of copper solution of concentration ranging from 1.0×10^{-8} to 1.0×10^{-1} mol L^{-1} and adjusted the pH to 5, the potentials were recorded after stabilization to $\pm$ 0.3 mV. A calibration graph was then constructed by plotting the recorded potentials as a function of -log a_{cu}^{2+}. The resulting graph was used for subsequent determination of unknown

copper concentration, the calibration plots are shown in Fig. 3.

It is obvious from the obtained results, the potential response of the electrodes is determined and they found to have a linear response over wide concentration range from 1.0×10^{-8} to 1.0×10^{-1} mol/L and 1.0×10^{-7} to 1.0×10^{-1} mol/L of Cu (II) with a Nernstian slope of 29.301 and 28.223 mV decade^{-1} and exhibit detection limit of 2.2×10^{-8} and 8.3×10^{-7} mol L^{-1} for sensor (No. 9 and 6) for ionophores (A) and (B), respectively. As it is clear that the sensor (No. 9) is better than sensor (No. 6) for determination of copper in the water sample, and additional studies were carried out with sensor (No. 9) for ionophore (A) only.
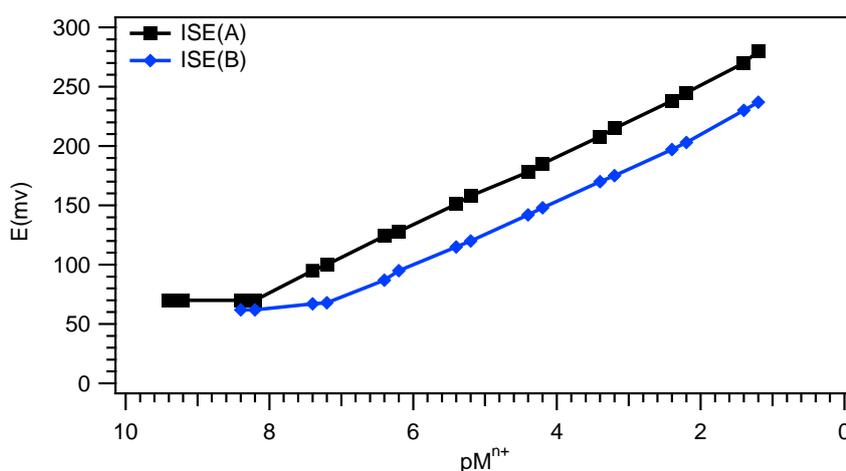
Fig. 3: Calibration curves of the Cu^{2+} based on Ionophores (A) and (B)

3.5. The influence of pH

In order to check the effect of pH on the proposed sensor (No. 9), the potential of sensor was tested at 1.0×10^{-3} M and 1.0×10^{-2} M of Cu^{2+} ion concentration over the pH range of 1.0 – 9.0. The pH

has been adjusted by using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M), and the results are shown in Fig. 4. As can be seen, the potential remains constant in the pH range 3.0 - 7.0 and the membrane electrodes can be suitably used in this range of pH. However, the change in potential at higher pH may

be attributed to the formation of metal hydroxide species in the matrix. It should be noted that the formation of these species is slow kinetic interactions. And the drop of potential of response is also dependent on the resistance of membrane with ionophore in alkali media (Singh et al., 2014), On the other hand, at pH values lower than 3.0, the sensor observed increase in potential which indicates that the protonated ionophore possesses a poor response to the copper ions in solution. The electrodes start responding to H_3O^+ ions along with Cu^{2+} ions leading to an increase in the potentials.
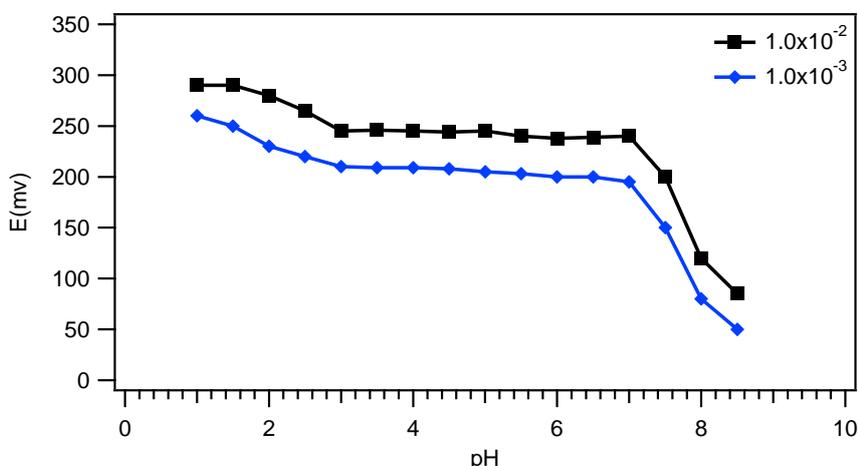

Fig. 4: Influence of pH on the potential response of electrode No.9 based on ionophore (A)

3.6. Dynamic response time of sensor

For analytical applications, the response time of an electrode is of critical importance. According to IUPAC recommendations, the response time of an ion selective electrode is defined as the length of time between the instant at which the ion selective electrode and reference electrode are immersed in the solution and the moment at which the potential of the cell reaches its steady-state value within ±1 mV (Tutulea-Anastasiu et al., 2013; Vlascici et al., 2013a). To measure the response time of the proposed sensor, the concentration of the test solution successively changed from 10^{-8} to 10^{-1} mol L^{-1} solution by a rapid 10-fold increase in the Cu (II) ion concentration measured. The response time of the sensor (No. 9) yielded a steady potential within 9 s as shown in the Fig. 5. Moreover, the measurements were performed in the sequence of high-to-low from (1.0×10^{-1} to 1.0×10^{-8} mol L^{-1}) sample concentrations and the results showed that the potentiometric responses of the electrode were reversible; although the time needed to reach equilibrium values (38 s) were longer than that of low-to-high sample concentrations. The best response of the sensor (No. 9) as compared other membrane may be due to the higher conductivity of ionophore in the membrane with copper (II) ion, and how the fast transfer of Cu^{2+} ions between sample solution and membrane.
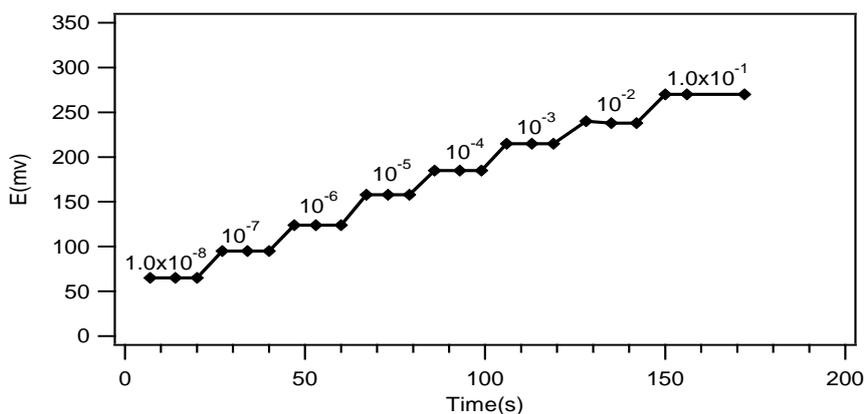

Fig. 5: Dynamic response time of Cu^{2+} sensor for changes in concentration range

3.7. Shift life time of sensor

One of the most important characteristics of a sensor is its lifetime. The criterion to assess the lifetime is the extent of leaching of the ionophore from the membrane. The lifetime of the proposed modified Cu (II) sensors was evaluated by periodically recalibrating the potentiometric response to Cu (II) ion in a series of standard copper solutions for the interval ranging from 1 to 12 weeks till the electrode lost its Nernstian behavior. (Gholivand and Nozari, 2001). The results are shown

in Table 6. The electrode was gently washed with distilled water, dried and stored at room temperature when not in use. As it can be seen from the Table 6, before 2 and 3 months for sensor No 9, no significant change in the performance of the sensor was observed (slope, detection limit and working concentration range). After 3 months, the slop start gradual decrease and detection limit increase due to loss of plasticizer, ionophore, or ionic site from the PVC polymeric membrane into the sample solution, which is a primary reason for the limited lifetimes of the sensors.

3.8. Comparison of previously reported Cu2+ sensor with the new proposed sensor

A comparison of the performance characteristics with previously reported sensors, as shown in Table 7. In the present work, it becomes apparent that the newly developed sensor is greater to the formerly reported Cu^{2+} sensors in terms of selectivity, response time, detection limit and dynamic concentration range. From the data listed therein, it

can be noticed that not only the concentration range and detection limits of the proposed sensor but, also the pH range are in the good agreement or better than some other previous report. It is evident from this table that in many cases, the performances of the proposed electrode show superior behavior if compared with the best previously reported Cu (II) sensors.

Table 6: Lifetime of proposed sensor Cu^{2+}- ISE

Weeks	Slope(mv decade^{-1})	Detection limit (M)
1	29.301	2.2×10^{-8}
2	29.022	4.3×10^{-8}
3	29.012	8.2×10^{-8}
4	28.896	8.2×10^{-8}
5	28.859	5.2×10^{-8}
6	28.775	8.7×10^{-7}
7	28.551	7.2×10^{-8}
8	27.324	2.3×10^{-7}
9	27.209	4.8×10^{-7}
10	27.112	4.4×10^{-7}
11	27.102	3.7×10^{-6}
12	27.00	5.2×10^{-6}

Table 7: Comparison of the proposed Cu^{2+} sensor with previously reported sensors

Sensor No.	Slope (mvdecade^{-1})	detection limit	Response Time (s)	pH range	Working range (mole L^{-1})	Reference
1	30	9.2×10^{-7}	15	3-5	5.0×10^{-7} to 7×10^{-2}	(Gholivand and Nozari, 2001)
2	28.2	5.1×10^{-7}	18	3-6.5	1.0×10^{-6} to 1×10^{-1}	(Katsu et al., 2002)
3	29.2	2.0×10^{-6}	10	4-6	5.1×10^{-6} to 1×10^{-2}	(Dhara et al., 2004)
4	29.3	8.2×10^{-6}	13	8.2-9	4.4×10^{-6} to 1×10^{-1}	(De-Oliveira et al., 2006)
5	29.5	9.1×10^{-6}	15	4-7	6.0×10^{-6} to 5×10^{-1}	(Wolcott et al.,2009)
6	28.6	5.4×10^{-6}	25	3-7	1.0×10^{-5} to 1×10^{-1}	(Vlascici et al., 2013b; Zou et al., 2012)
7	29.5	4.8×10^{-6}	25	2-6	1.0×10^{-5} to 7×10^{-1}	(Vlascici et al., 2013)
8	28.4	9.0×10^{-8}	10	2-8	1.0×10^{-7} to 7×10^{-1}	(Tutulea-Anastasiu et al., 2013)
9 Nano	29.2	6.3×10^{-9}	9.0	2-8.5	1.0×10^{-8} to 7×10^{-1}	(Singh et al., 2014)
10	29.301	2.2×10^{-8}	9-12	3-7.5	1.0×10^{-8} to 7×10^{-1}	Present work

4. Analytical applications

4.1. Potentiometric titration of copper (II) ions with EDTA

It should be noted that the copper-selective membrane electrode introduced not only be used for direct determination of Cu^{2+} ions in water samples, but also it can be used as an indicator electrode in the titrimetric determination of copper ions with EDTA, as the results shown in Fig. 6. A very good inflection point, showing perfect stoichiometry, is observed in the titration plot. As seen, the amount of copper ion in solution can be accurately determined with the sensor No.9.

The reported ion selective electrode based on ionophores which have four to six donor atoms of (N, S and O) tend to form a 1:1 Cu^{2+}/ionophore complex (Katsu et al., 2002). This indicates that the amount of copper (II) ion can be accurately determined from the resulting neat titration curve providing a good end point. In the present work titration plot shown a standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Cu-EDTA complex. This indicates that the sensor can be used

to determine Cu^{2+} ion accurately under laboratory condition.

4.2. Determination of copper (II) ions in water samples.

The proposed sensor (based on ionophore (A), sensor No.9) were used successfully for monitoring of Cu (II) ions in water samples, and water samples of very low concentration of Cu (II) (below the detection limit of the electrodes) were spiked by adding aliquots of standard solution (standard addition method) of Cu (II) ion to the samples. The samples were acidified with some drops of 1.0 mol L^{-1} HNO$_3$ and heated for 1h until dissociate the metal-complexes, and then the pH of the water samples was adjusted at pH 5.5.

The assay method for Cu (II) ions over the concentration range of 1.0×10^{-8} - 1.0×10^{-1} mol L^{-1} was achieved, and the results obtained from the triplicate measurement of the proposed copper sensor (for water samples) are compared with that determined by atomic absorption spectroscopy (AAS) and are summarized in Table 8, the sensor

provides a good alternative for the determination of Cu^{2+} in real samples.
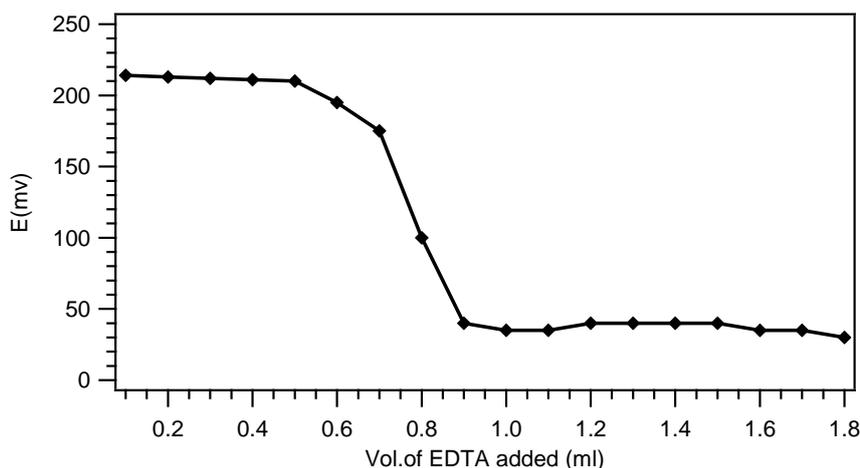
Fig. 6: The potentiometric titration plot for 20 ml of (1.0×10^{-3} mol L^{-1}) Cu^{2+} against EDTA (1.0×10^{-2} mol L^{-1}) using Copper (II) membrane sensor based on the ionophore (A) as an indicator electrode in pH = 5.5

Table 8: Determination of Cu^{2+} ion concentration (mgL^{-1}) in water samples

S. No.	Sample source	Cu (II) added (mg.L^{-1})	Found (mg.L^{-1})	AAS (mg.L^{-1})
1.	Tap water	8.0	7.23	8.21
		10	9.4	10.03
		12	11.10	12.50
2.	Sea water	8.0	7.82	8.0
		10	9.52	10.0
		12	11.30	12.51
3.	Well water	8.0	8.32	9.22
		10	9.0	10.65
		12	11.3	12.74

5. Conclusion

The investigations on PVC-based membranes of two ionophores, (A) and (B), have shown that they act as Cu^{2+} selective sensors. However, of the two chelates, the sensor No.9 based on ionophore (A) having a composition (A): (o-NPOE): (PVC): (KTpCIPB) in the ratio of 3: 78: 40: 2 (w/w; mg) exhibit excellent potentiometric performance. The potentiometric characteristics based on ionophore (A) for sensor No.9 exhibit the widest working concentration range 1. 0×10^{-8} to 1.0×10^{-1} mol/L, minimum response time 9-12 s, reasonable long-term stability about 3 months, Nernstian response (29.301 mV decade^{-1}) and responsive potential stability. Most of metal ions do not affect the selectivity of the copper sensor. The proposed sensors compared to some of those previously suggested as shown in the Table 7, implies that the proposed sensor is superior to those recorded in Table 7 in terms of sensitivity and detection limit. Therefore, we wish that present communication is an enhanced addition to the existing set of copper selective electrode ISE.

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