Full Paper

Cd(II) Ion-Selective Electrode Based on 2–Acetylthiophene Semicarbazone in Polymeric Membrane

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Abstract- A new polyvinylchloride membrane sensor for Cd^{2+} ions has been prepared using 2–acetylthiophene Semicarbazone (ATS) ligand as an electroactive ionophore and dibutylphthalate (DBP) as a plasticizing agent. The best performance was recorded with a membrane composition of PVC: DBP: Ionophore: NaTPB as 31: 64: 3.2: 1.8 (w/w %). The sensor exhibits a Nernstian response for Cd^{2+} ions over a wide concentration range (1.0×10^{-5} to 1.0×10^{-1} M) with a slope of 29.4 ± 0.2 mV decade^{-1}. It has a fast response time of <10 s and can be used for at least 5 weeks without any divergence in potential. The electrode can be used in the pH range from 3.4 to 7.6. The proposed sensor revealed relatively good selectivity and high sensitivity for Cd^{2+} ions in presence of a number of mono, di and trivalent interfering cations within the working range of the electrode. The electrode was successfully applied for the direct determination of Cd^{2+} in solution and, as an indicator electrode, in potentiometric titration of cadmium ions using ethylenediamine tetraacetic acid (EDTA) as titrant.

Keywords- Ion Selective Electrodes, Cadmium, PVC membrane, Semicarbazide

1. INTRODUCTION

In recent years there has been a growing need or desire for constructing chemical sensors for fast and economical monitoring of our environmental samples especially for heavy metal

ions in real time [1]. One of the chemical sensors that concerns researchers these days is ion selective electrode (ISE) which is a very wide electrochemical sensor usage. Polymeric membrane ion selective electrode (ISEs) provides one of the most powerful sensing methods because it is possible to select various sensory elements according to the charge and size of the target ion in clinical and environmental assays [2-5]. Ion selective electrodes (ISE) are appropriate for this purpose because they show good selectivity for inorganic ions and they are easy to build. They are relatively of low cost and used in the places of interest.

Recently, much attention has been paid to use of ionophore (ligands or complexes) as sensing materials for neutral carrier type ion selective electrodes due to the unique properties of the compounds. Schiff base with N and O donor atoms are well known to form strong complexes with transition metal ions. Some of the Schiff bases are reported to form strong complexes with a specific ion due to geometric factor [6,7]. Schiff's bases and their metal complexes have proved to be good ion carriers for the construction of ion selective sensors both for cations and anions.

The cadmium (II) ion shows no definite indication of being an essential trace element in biological processes; on the contrary, it is highly toxic to a wide variety of living organisms, including man [8]. However, despite the urgent need for cadmium-ion selective sensors for the potentiometric monitoring of Cd^{2+} ions, there have been only limited reports on Cd^{2+} ion selective electrodes in the literature [9–15]. Among them majority of the reported electrodes suffer from small working pH range, interfering effects of cations such as Zn^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Pb^{2+}, Ag^+ and lack of selectivity and sensitivity. V. K. Gupta and coworkers have also reported several crown molecules such as dibenzo-24-crown-8, monoaza-18 -crown-6, dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 [13-15] in PVC matrix for of Cd(II)-ion sensing electrodes. *Panggabean et. al.* (2011) has also developed ISE for Cd^{2+} ions from the PVC membrane of chitosan polymer. This chitosan based Cd^{2+} sensor also suffer from short linear concentration range, narrow pH range and interference from different cations such as Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, SO_4^{2-} [16].

We have recently reported some (PVC)-based membrane sensors for lead [17] and magnesium ions [18] developed by using semicarbazide based ligands. These electrodes were succussfully applied as an indicator electrode, for the potentiometric titrations and for the direct determination of ions in solution. Among the various ligands available for ion-selective electrodes, the Schiff's bases have many of the requirements of an efficient ionophore to satisfy for the use in ion-selective electrodes.

In the present study, we reported a PVC membrane sensor for Cd^{2+} ion, which is based on 2–acetylthiophene semicarbazone ligand as an ionophore and dibutyl pthalate (DBP) as a plasticizer. It shows better potentiometric response as compared to the previously reported Cd^{2+} sensors with low detection limits over a wide pH range of 3.4-7.6.

2. EXPERIMENTAL

2.1. Reagents and solutions

All the chemicals used were of analytical grade (AR) and of the highest purity. Reagent grade high molecular weight PVC (Sigma-Aldrich), tetrahydrofuran (THF), 2–acetylthiophene (CDH), Semicarbazide (CDH) was used as recieved. Dioctylphthalate (DOP), Tri n-butyl phosphate (TNBP), Dibutylphthalate (DBP), 2-nitrophenyloctyl ether (NPOE) and sodium tetraphenyl borate (NaTPB), all purchased from CDH and nitrate salts of all metal used (E. Merck) were of highest purity available and used without any further purification. Standard solutions were freshly prepared in deionized water.

2.2. Instrumentation

The C, H, N and S were analyzed on a Vario Micro Cube elemental analyzer, Model Vario-III. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker, Model DPX-300 NMR spectrophotometer using DMSO as solvent. Chemical shift are given in ppm relative to tetramethylsilane (TMS). The IR spectra were recorded as KBr pellets on a Perkin Elmer FT-IR spectrophotometer, Model No. BX-2. A Perkin-Elmer Model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace was used.

2.3. Syntheses of ionophore

Hot ethanolic solution (20 mL) of 2–acetylthiophene (1.26 g, 0.01 mmol) was mixed with equivalent amount of semicarbazide hydrochloride (1.12 g, 0.01 mmol) and sodium acetate (0.82 g, 0.01 mmol) with constant stirring .The mixture was refluxed for 2-3 hrs. And the solid white coloured product formed was separated out by filtration, washed several times with 50% cold EtOH and dried in vacuum over P_4O_{10}.
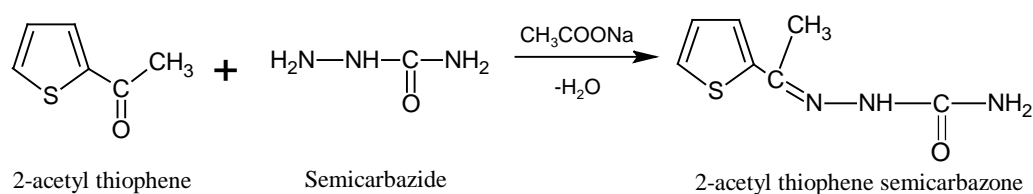

Fig. 1. Synthesis of ionophore

2.3.1. Acetylthiophene Semicarbazone

Yield (90.0%), M. P: 190 °C, Anal. calc. for (%)=$C_7H_9N_3OS$: C, 45.89%; H, 4.95%; N, 22.94%; O, 8.73%; Found: (%) : C, 45.68%; H, 5.08%; N, 22.82%; O, 8.54%; FT-IR (KBr):

$\upsilon(NH_2)$ 3471 (b), $\upsilon(NH)$ 3147 (b), $\upsilon(C=N)$ 1592 , $\upsilon(C=O)$ 1702 cm^{-1}; ^{1}HNMR (CDCl$_3$ 300 MHz): δ ppm= δ3.0 (s,>NH); δ9.13 (s, H$_2$N-CO); δ2.18 (s, H$_3$C-C); δ6.91-7.21 (m, Ar-H).

2.4. Electrode Preparation

The membranes were prepared by the method given by Craggs et.al. [19,20], with certain variations in composition of PVC, ionophore and plasticizers/ solvent mediators like DBP, NPOE, DOP, TNBP etc. For the membrane preparation, fixed mixture of PVC: Plasticizer: Ionophore: Excluder in 31: 64: 3.2: 1.8 (w/w %) was taken. The mixture was thoroughly dissolved in THF (10 mL). A 5 mm diameter Pyrex tube was dipped into this mixture for few seconds and then removed. To obtain a 0.3 mm thick non-transparent membrane fixed one end of the Pyrex tube with the help of Araldite. After getting dried for 5 hrs, this tube was filled with 1.0×10^{-2} M internal solution of cadmium and immersed in the 1.0×10^{-2} M cadmium nitrate solution, at least for 2 days prior to use. It is known [21-26] that the sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of the plasticizer used. Thus, the ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized after a good deal of experimentation. Membranes, which generate reproducibility and stable potentials, have been studied. The blank membrane having only PVC as membrane ingredients was also prepared and studied. While membrane having PVC with plasticizer were generate small potential with slope of ~9 mV/decade.

2.5. Potential Measurements

All the membrane electrode potential measurements were performed at constant temperature (25±0.05 $^{\circ}$C) using digital pH meter, potentiometer (ELICO L1-10, India) in conjugation with saturated calomel electrodes as reference electrodes. The representation of electrochemical cell for the EMF measurements is as follows:

Ag-AgCl, KCl (saturated) | internal solution (1.0×10^{-2} M) Cd(NO$_3$)$_2$ | PVC membrane | test solution | Hg-Hg$_2$Cl$_2$, KCl (saturated)

3. RESULTS AND DISCUSSION

3.1. Response of the cation

The response of different metal ions and rare earth ions were plotted as the negative log of concentration and the potential values obtained for different metal ions (Fig. 2). It has been observed that the membrane performs best with Cd^{2+} as the response is linear over a wide concentration (1.0×10^{-5} to 1.0×10^{-1} M). Thus, membranes used as Cd^{2+} sensor.
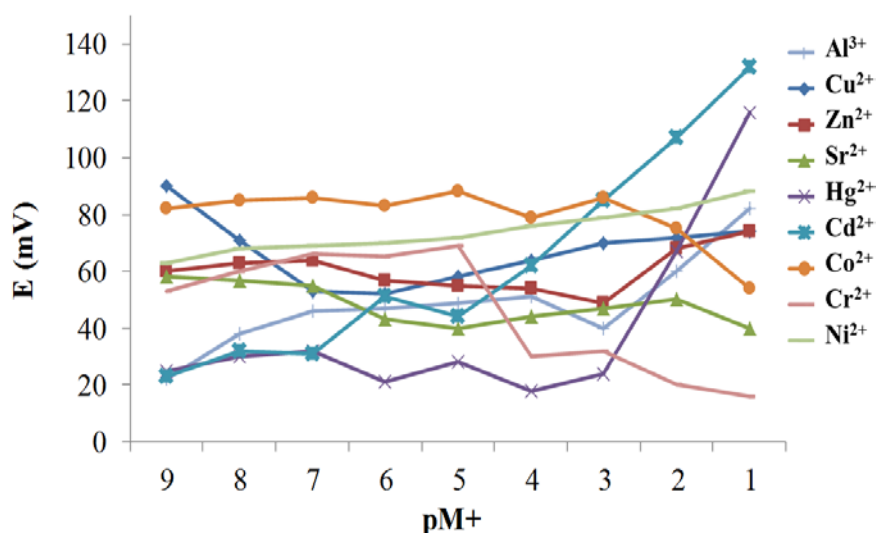
Fig. 2. Potential response of various ion selective electrodes based on 2–acetylthiophene semicarbazone ligand

3.2. Working concentration range and slope of Cd²⁺ sensor

The membranes were first equilibrated with 1.0×10^{-2} M Cd^{2+} solution. The experiments have shown that 2 days equilibration time is required for generating reproducible and stable potential. Further result of changes in the membrane composition on the electrode response was studied. It is well known that sensitivity and selectivity obtained for a given ionophore, is significantly affected by the membrane composition of an ion sensor membrane.

Table 1. Composition of PVC membrane of (ZATSC) and performance characteristics of Cd^{2+} selective sensors

S. No.	Composition of membranes (*w/w %*)				Working conc. range (M)	Slope (± mV/decade)
	Ionophore	PVC	Excluder NaTBP	Plasticizer		
1	3.8	33	4.5	-	1.0×10^{-7} to 1.0×10^{-1}	25.2
2	**3.2**	**31**	**1.8**	**DBP, 64**	**1.0×10^{-5} to 1.0×10^{-1}**	**29.4**
3	3.3	30	4.7	DOP, 62	1.0×10^{-5} to 1.0×10^{-3}	22.6
4	4.2	27	3.8	TNBP, 65	1.0×10^{-5} to 1.0×10^{-1}	23.0
5	3.2	31	4.8	DBP, 61	1.0×10^{-6} to 1.0×10^{-2}	26.4
6	4.0	32	2.0	NPOE, 62	1.0×10^{-7} to 1.0×10^{-1}	20.2

The different membrane ingredients, such as amount of ionophore, amount and nature of the plasticizer and additives influence the potentiometric response behaviour of the sensor [22,27-28]. Best optimized studies membrane for Cd^{2+} selective electrode is reported in

Table 1. The results given in the Table 1, shows that the electrode worked well in Plasticizer/ PVC ratio of nearly 2, which ensures enough mobility of the membrane constituents. The best sensitivity and selectivity was recorded for DBP as plasticizer. Further the amount of ionophore also affected the Nernstian slope value. Hence, a very small amount of ionophore is required for the study. The best performance is obtained with DBP plasticizer with membrane (sensor no. 2) having composition: 31: 64: 3.2: 1.8 (PVC: DBP: ionophore: NaTPB) (w/w; %). This sensor exhibits wide working concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a linear-Nernstian slope of 29.4 ± 0.2 mV/decade of activity.

3.3. PH and solvent effect

The influence of pH on the potential response was examined by use of Cd^{2+} solution in concentration 1.0×10^{-3} over the pH range 0.5–14 as shown in Fig. 3. The pH of the solutions was adjusted by the addition of dilute hydrochloric acid or sodium hydroxide solutions. It is clear from Fig. 3 that the useful pH range is 3.4–7.6, as the potentials remain constant in this range. At higher pH and below pH 3, a sharp change in potential may be due to the hydrolysis of Cd^{2+} and disruption of H^+ ions from the test solution, respectively. The working pH range is 3.4–7.6.
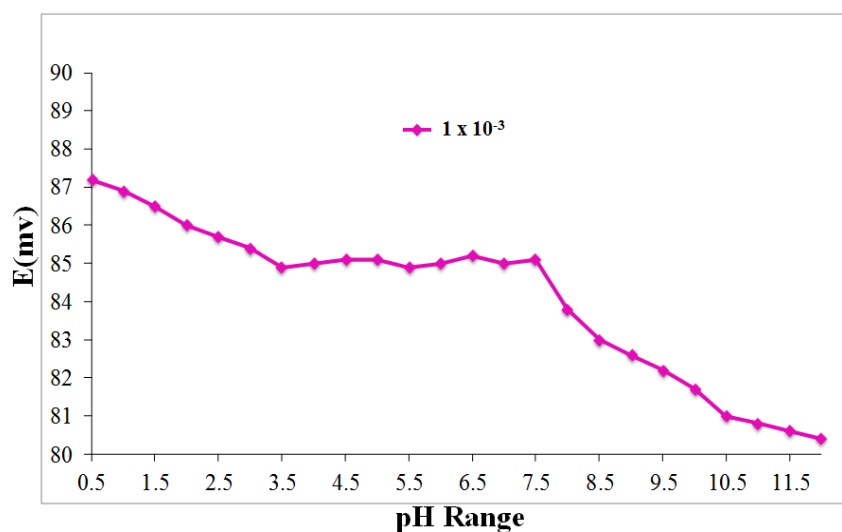

Fig. 3. Effect of pH variation on the Cd^{2+} selective electrode

The real sample may contain non-aqueous content, so the performance of the sensor no. 2 was also investigated in partially non-aqueous medium using methanol-water, ethanol-water, and acetone-water mixtures. The membrane worked satisfactorily in non-aqueous medium up to 20% (v/v) non-aqueous content as in these mixtures the working concentration range and slope remained unaffected as shown in Table 2. However, above 20% (v/v) non-aqueous content, slope, and working concentration range was reduced and potentials show drift with

time. The drift in potentials in the organic phase may be probably due to leaching of ionophore at higher organic content.

Table 2. Effect of partially non-aqueous medium on the working of Cd^{2+} selective sensor (sensor no. 2)

Non-aqueous content % (v/v)	Working concentration range (M)	Slope ($\pm$0.1 mV/decade of activity)
Methanol		
10	1.0×10^{-5} to 1.0×10^{-1}	29.4
20	1.0×10^{-5} to 1.0×10^{-1}	29.3
30	1.0×10^{-5} to 1.0×10^{-1}	29.1
Ethanol		
10	1.0×10^{-5} to 1.0×10^{-1}	29.5
20	1.0×10^{-5} to 1.0×10^{-1}	29.2
30	1.0×10^{-5} to 1.0×10^{-1}	29.4
Acetone		
10	1.0×10^{-5} to 1.0×10^{-1}	29.1
20	1.0×10^{-5} to 1.0×10^{-1}	29.3
30	1.0×10^{-5} to 1.0×10^{-1}	29.4

3.4. Potentiometric selectivity of ion sensing membranes

The Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions and extent of utility of any sensor in real sample measurement. The selectivity coefficient values were determined by fixed interference method (FIM) [29-31]. The selectivity coefficient values indicate that the electrode is moderately selective to Cd^{2+} over a number of other cations (Table 3). The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, a_B, and varying activity of the primary ion, a_A. The potential values obtained are plotted against the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will give the value of a_A which is to be used to calculate $K_{A,B}^{Pot}$ from the equation:

$$K_{A,B}^{pot} = (a_A/a_B)Z_A/Z_B$$

Where z_A and z_B are charge numbers of the primary ion, A, and of the interfering ion, B; a_A and a_B are the activities of the primary ion, A, and the interfering ion, B; and $K_{A,B}^{Pot}$ is the potentiometric selectivity coefficient for the primary ion A against the interfering ion, B. Here both z_A and z_B have the same signs, either positive or negative. Value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to primary as well as

interfering ions. However, values smaller then 1.0 indicate that membrane sensor is responding more to primary ion than to interfering ions and in such a cases the sensor is said to be selective to primary ion over interfering ion. Further, smaller is the selectivity coefficient, higher is the selectivity order. The values of selectivity coefficient so determined are compiled in Table 3. It is seen from the Table 3, that the selectivity coefficients determined are sufficiently smaller than 1.0 indicating that the present sensor are significantly selective to Cd^{2+} over all the interfering ions and it can be used to estimate Cadmium in the presence of these ions by direct potentiometry.

Table 3. Selectivity coefficient values $K_{A,B}^{Pot}$ for Cd^{2+} ion selective sensor by fixed interference method

S. No.	Interfering ion (B)	Selectivity coefficients
1	K^+	1.28×10^{-3}
2	NH_4	3.59×10^{-2}
3	Pb^{2+}	5.74×10^{-2}
4	Cl^-	6.38×10^{-3}
5	Ni^{2+}	2.71×10^{-2}
6	Fe^{3+}	2.82×10^{-2}
7	Co^{2+}	3.01×10^{-3}
8	Cu^{2+}	1.64×10^{-2}
9	Sr^{2+}	3.05×10^{-3}
10	SO_4^{2-}	3.65×10^{-2}
11	Zn^{2+}	4.94×10^{-2}
12	Al^{3+}	5.12×10^{-4}

3.5. Response and lifetime

Response time is critically reviewed when it comes to analytical application of the sensor [32].

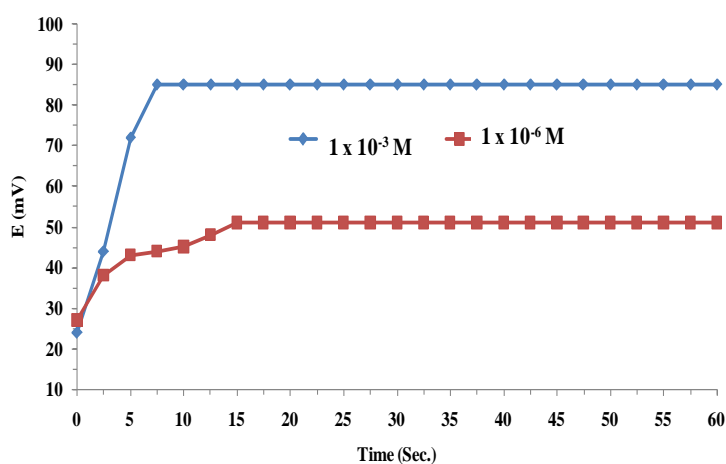**Fig. 4.** Static potential-time plots for Cd^{2+} concentrations: (a) 1.0×10^{-3} M; (b) 1.0×10^{-6} M

It is governed by the transport diffusion processes in the aqueous diffusion layer. Response time is defined as the time required to reach a potential within ± 1 mV of final equilibrium value after a sudden change in the primary ion activity [33]. The static response time of the membrane sensor thus obtained was <10 s, for concentration $\geq 1.0 \times 10^{-3}$ and <15 s for concentration of $\geq 10^{-6}$ (Fig. 4). The lifetime of the sensor (no. 2), which is a measure of sensor durability, was studied over a 4 months period. It was found that an equilibrating solution of 1.0×10^{-2} M and contact time of 2 days was appropriate for smooth functioning of the electrode. Membranes were stored in 1.0×10^{-2} M Cd(NO$_3$)$_2$ solution when not in used.

Table 4. Comparison of the potentiometric parameters of the proposed Cd^{2+} sensor with the literature reported

S. No.	Ionophore Name	Woking concentration Range (M)	Slope (mV/decade of activity)	pH range	Response time	Ref.
1.	tetrathia-12-crown-4	$4.0 \times 10^{-7} - 1.0 \times 10^{-1}$	29±1	2.5-8.5	<10	[34]
2.	Poly (styrene-*co*-acrylonitrile) copolymer	$4.46 \times 10^{-4} - 1.0 \times 10^{-1}$	29	3.2-6.8	12	[35]
3.	1,3-Bis(2-cyanobenzene) triazene	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	29.5	6-9	2	[36]
4.	(13E)-N-benzylidene-2- (3-((E)-2-(benzylideneamino) ethyl)-2-phenylimidazolidin -1-yl) ethanamine	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.1±1	3.5-7.9	<35	[37]
5.	N,N'(4 methyl 1,2 phenylene) diquinoline-2 carboxamide	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.9±0.5	4-9	3-8	[38]
6.	4-hydroxy salophen	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	30.1±1	2.8–8.1	20	[39]
7.	2-acetylthiophene Semicarbazone	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	29.4±0.2	3.4-7.6	<10	This research

This Sensor no. 2 was compared with some reported Cd^{2+} ion selective sensors (Table 4). It is seen that the selectivity, working concentration range and pH range of the proposed sensor toward Cd^{2+} ion is better as compared to reported sensors. At the same time, easy synthesis of a highly lipophilic macrocyclic and open chain ionophore in bulk, using easily and economically available starting materials, makes the proposed ISE a better membrane electrode.

3.6. Analytical applications

3.6.1. Potentiometric titration of Cd^{2+} *solution with a standard EDTA solution*

The proposed membrane sensor was found to work well under laboratory conditions. It was applied successfully as an indicator electrode in the potentiometric titration of 20 mL of 1.0×10^{-3} M solution of Cd^{2+} with 0.01 M EDTA solution and the resulting titration curve is shown in Fig. 5. Thus the amount of cadmium ion can be determined with the proposed sensor by potentiometric titration.
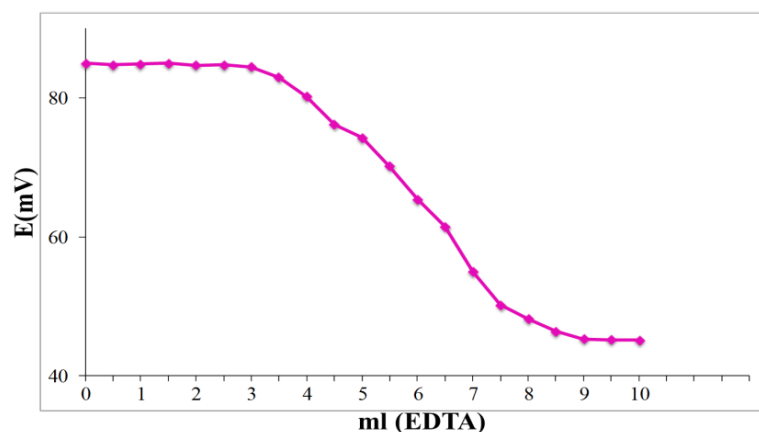

Fig. 5. Potentiometric titration curve of 20 ml solution of 1.0×10^{-3} M Cd^{2+} with 0.01 M EDTA by using the proposed sensor no.2

Table 5. Determination of Cd^{2+} in water sample using proposed sensor

Sample No.	Cd^{2+} by proposed sensor (mgL^{-1})	Found by AAS (mgL^{-1})	Std. Deviation	t-stat. value
S-1	0.564	0.544	0.014142	
S-2	0.470	0.485	0.010607	0.2497
S-3	0.452	0.431	0.014849	
S-4	0.428	0.412	0.011314	

3.6.2. Determination of Cd^{2+} *in water samples*

It was successfully applied to determine the Cd^{2+} ion in the water samples collected from the various sites in Delhi-NCR region. The results obtained were also compared with the atomic absorption spectrometry (AAS) analysed sample. It is found from the values in Table 5, that these were in a good agreement with the results obtained by the AAS method.

4. CONCLUSIONS

In this study, 2–acetylthiophene Semicarbazone (ATS) based polymeric membrane sensor electrode for Cd^{2+} ion has been developed. The proposed electrochemical sensor exhibit a membrane composition of 31% PVC, 64% DBP as solvent mediator, 1.8% NaTPB as cation excluder and 3.2% ATS ligand as an ionophore. The electrode can be used to determine Cd^{2+} ions in the concentration range 1.0×10^{-5} to 1.0×10^{-1} M with a Nernstian slope of 29.4 ± 0.2 mV decade^{-1} of activity. The electrode works in a relatively wide, independent pH range 3.4 to 7.6, and exhibits a fast response time, high sensitivity and selectivity for Cd^{2+} ions. The life time of the electrode was 5 weeks. The proposed electrode was successfully applied to the determination of cadmium in water samples by indirect potentiometry. The results obtained show a satisfactory agreement with those obtained using AAS method.

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