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Direct Determination of Ultra-Trace Amounts of Cadmium with Use of a High-Sensitive and Selective Coated Graphite Electrode

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Novel PVC-based polymeric membrane (PME), coated graphite (CGE) and coated silver wire electrodes (CWE) for sensing Cd^{2+} ion based on (13E)-N-benzylidene-2-(3-((E)-2-(benzylideneamino)ethyl)-2-phenylimidazolidin-1-yl)ethanamine (L) are prepared. The electrodes exhibited linear Nernstian responses to Cd^{2+} ion in the concentration range of 1.0×10^{-6} to 1.0×10^{-1}M (for PME, LOD= 8.9×10^{-7} M), 1.7×10^{-7} to 2.3×10^{-1}M (for CWE, LOD= 1.0×10^{-7} M) and 1.2×10^{-8} to 1.7×10^{-1}M (for CGE, LOD= 9.8×10^{-9} M).The potentiometric responses are independent of the pH of the test solutions in the pH range 3.5-7.9. The proposed electrodes process very good selectivities over a wide variety of the cations including alkali, alkaline earth, transitions and heavy metal ions. The selectivity coefficients for the CGE and CWE being much improved over those for the PME. The electrodes could be used for at least 13 weeks without any divergence in potential.

Keywords: PVC membrane (PME); coated graphite (CGE); Ion-selective electrode; ultra-trace; Potentiometry; Cadmium

1. INTRODUCTION

The determination of heavy metals, especially some toxic metals which play important roles in biological metabolism, has received particular attention [1]. Cadmium is a toxic metal and its concentration in unpolluted environmental water is sometimes at the ng ml^{-1} level or below. Several techniques, including flame atomic absorption spectrometry (FAAS) [2–4], electrothermal atomic absorption spectrometry (ETAAS) [5–6], inductively coupled plasma mass spectrometry (ICP-MS) [7], atomic fluorescence spectrometry (AFS) [8] and instrumental neutron activation analysis [9] have been widely used for the determination of trace elements in different samples because the available data are highly precise and accurate; however, These methods involve expensive instrumentation and sample pretreatment, which is time consuming and inconvenient. In contrast, potentiometric detection based on ion-selective electrodes (ISEs), offers advantages of speed and ease of procedures, simple instrumentation, relatively fast response time, wide dynamic range, reasonable selectivity, and low cost [10-20].

Due to urgent need for Cd^{2+}-selective sensors for potentiometric monitoring of cadmium ions in chemical, industrial and environmental sample, in recent years, a number of ion-selective electrodes for cadmium assay have been reported in the literature [21–35]. However, most of these electrodes suffer from one or more of the following drawbacks: lack of stability and selectivity, limited concentration range and small range of working pH and considerable interferences from other cations such as Ag^+, Zn^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+}.

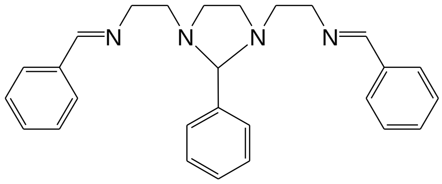

Figure 1. Structure of ligand (L)

In this work, we used a recently synthesized (7E)-N-benzylidene-2-(3-((E)-2-(benzylideneamino)ethyl)-2-phenylimidazolidin-1-yl)ethanamine (L, Fig. 1) for the preparation of novel polymeric membrane (PME), coated graphite (CGE) and coated silver wire electrodes (CWE) for highly selective and sensitive determination of Cd^{2+} ion, Which exhibit significantly high selectivity to Cd^{2+} ions over alkali, alkaline earth and several transition metal ions.

2. EXPERIMENTAL

2.1. Reagents and materials

Reagent grade nitrophenyl octyl ether (NPOE), dibutyl phetalate (DBP), Benzylacetate (BA), tetrahydrofuron (THF) and high relative molecular weight PVC call from Merck were used as received. Nitrate slats of all cations used call from Merck were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. (13E)-N-benzylidene-2-(3-((E)-2-(benzylideneamino) ethyl)-2-phenylimidazolidin-1-yl) ethanamine was gifted from the Inorganic chem. laboratories, (Faculty of Chemistry, University of Tehran, Tehran, Iran). Triply distilled deionized water was used throughout.

2.2 Preparation of electrodes

Membrane solution were prepared by thoroughly dissolving 5 mg of L, 30 mg of powdered PVC, 3 mg of additive and 62 mg of plasticizer in 5 ml of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained.

A Pyrex tube (3mm o.d. on top) was dipped into the mixture for about 10 S so that a nontransparent membrane of about 0.3mm thick was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1h. The tube was then filled with an internal filling solution (1.0×10^{-3}M Cd^{2+} ion). The electrode was finally conditioned for 20h by soaking in a 1.0×10^{-2} M Cd^{2+}. A Silver/Silver chloride electrode was used as the internal reference electrode.

To prepare the coated graphite electrodes (CGE) and coated wire electrodes (CWE), spectroscopic grade graphite rod (10mm×3mm o.d.) and a clean silver wire (20mm×2mm o.d.) were used, respectively. In the case of CGE, a shielded copper wire was glued to the end of the graphite rod. The electrodes were then sealed into the end of PVC tubes of about the same diameter with epoxy resin. The working surface of the electrodes were polished with fine alumina slurries on a polishing close, washed with water and dried in air. The polished electrodes were dipped into the membrane solution mentioned above, and the solvent was evaporated. A membrane was formed on the electrode surfaces, and the electrodes were allowed to stabilize over night. The electrodes were finally conditioned by soaking in a 1.0×10^{-2} M Cd $(NO_3)_2$ solution for 36 h.

2.3. Conductometric procedure

The complexation of L with a number of cations was conductometricaly investigated in an acetonitrile solution, at 25±0.05 ◦C, in order to obtain a clue about the stability and selectivity of the resulting complexes. Cation solutions 20mL of were titrated with a 0.01M L solution in acetonitrile. The resulting molar conductance versus [L]/ [M^{n+}] molar ratio showed the formation of 1:1 complexes between L and metal ions tested. The complex formation constants, K_f, were evaluated by computer fitting of the molar conductance/molar ratio data with appropriate equations, and the results are summarized in Table 1 [37].

Table 1. The formation constants of L -M^{n+} complexes at 25.0 ± 0.1 ºC

Ion	Log K_f	Ion	Log K_f
Cd^{2+}	5.73±0.02	Zn^{2+}	2.76±0.02
Ni^{2+}	3.12±0.03	Al^{3+}	<2.0
Co^{2+}	2.81±0.01	Rb^{+}	2.11±0.04
Cu^{2+}	1.97±0.02	La^{3+}	2.22±0.03
Pb^{2+}	2.75±0.02	Be^{2+}	2.35±0.02
Mg^{2+}	2.42±0.03	Ni^{2+}	3.85±0.02
Hg^{2+}	2.17±0.01	Ag^{+}	2.51±0.01
Na^{+}	<2.0	Fe^{2+}	2.86±0.03
K^{+}	<2.0	Ca^{2+}	3.00±0.05

2.4. Emf measurements

All electromotive force (emf) measurements were carried out with the following cell assemblies:

Ag–AgCl|1.0×10^{-2} Cd $(NO_3)_2$M|PVC membrane|test solution |Hg–Hg_2Cl_2, KCl (sat) (PME)

Graphite or Ag|PVC-membrane|test solution|Hg–Hg_2Cl_2, KCl (sat) (CGE and CWE)

The emf observations ware made relative to a double – Junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solutions. A double-junctions Silver / Silver chloride electrode (Metrohm) containing a 3M solutions of KCl was used as the internal reference electrode. Activities were calculated according to the Debye – Hückel procedure.

3. RESULTS AND DISCUSSION

3.1. Preliminary study of L complexation with some metal ions

To examine ligand selectivity against various metal ions including Cd(II), Ni(II), Co(II), Cu(II), Pb(II), Mg(II), Hg(II), etc, the interaction of L with metal ions in an acetonitrile solution by conductometric method was investigated [36-42]. In all measurements, the cell should be thermo stated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In typical experiments, 20 mL of an ion solution (1.0×10^{-4} mol L^{-1}) is placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} mol L^{-1}) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved. The 1:1 binding of the cations with the ionophore and the complex formation constant in terms of the molar conductance can be expressed as [36]:

$$(1)\quad K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]}$$

Where:

$$(2)\quad K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})}$$

Where, Λ_M is the molar conductance of the cation before the addition of the ionophore; Λ_{ML} is the molar conductance of the complexes, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant (K_f) and the molar conductance of the complex, Λ_{ML}, were obtained by computer fitting Eqs. (1) and (2) to the molar conductance–mole ratio data, using the nonlinear least-squares program KINFIT [43]. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values of the resulting 1:1 complexes in Table 1 showed that log K_f is 5.73±0.02 for Cd^{2+} and 3.12±0.03 or less for other metal ions used. As can be seen from these results, L can be used as a sensing material in a Cd (II) sensor.

3.2. Potential response

In order to check the suitability of L as an ion carrier for Cd(II) and other metal ions, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including a number of metal ion such as Cd(II), Ni(II), Co(II), Cu(II). Pb(II), Mg(II), Hg(II), etc. At first experiment we used 30 mg PVC, 60 mg BA, 5 mg L and 5 mg OA for membrane fabrication. The potential responses different ion-selective electrodes based on L are depicted in Fig. 2.

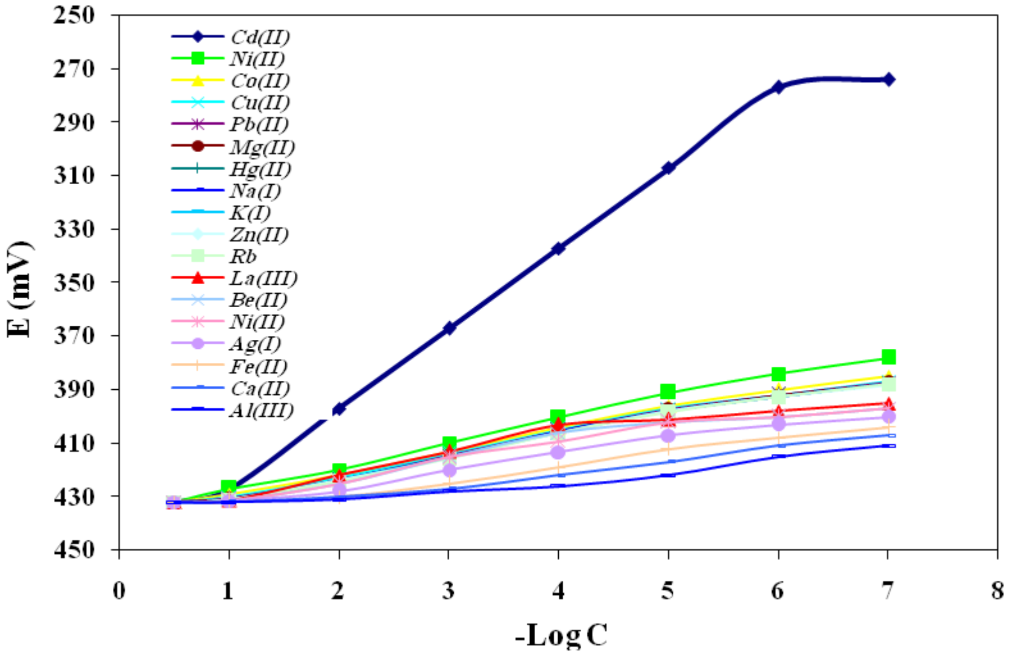

Figure 2. Potential response of various ion-selective electrodes based on L

With the exception of Cd(II) ions, all the tested cations showed relatively weak responses in the concentration range 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1}, due to their weak interactions with the ionophore.

3.3. Optimization of potentiometric response of the PME, CGE and CWE

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition [10-35]. Thus, different compositions of the membrane preparation based on ionophore L were examined in order to obtain the optimized membrane composition, and the results are summarized in Table 2.

Table 2. Optimization of membrane ingredients during design of Cd(II) selective membrane sensor.

No.	Composition (%)				Slope (mV decade^{-1})	Linear range (M) PME
	PVC	Plasticizer	Addetive	Ionophere		
1	30	BA,70	-	-	≈0	-
2	30	BA,66	-	4	16.3	4.7×10^{-5} to 5.6×10^{-2}
3	30	BA,65	-	5	19.9	2.1×10^{-5} to 1.0×10^{-1}
4	30	BA,64	-	6	18.6	7.5×10^{-5} to 3.3×10^{-1}
5	30	BA,60	OA,5	5	23.6	9.8×10^{-5} to 4.5×10^{-1}
6	30	BA,55	OA,10	5	22.8	1.0×10^{-4} to 5.0×10^{-1}
7	30	BA,63	NaTPB,2	5	26.9	5.0×10^{-4} to 1.0×10^{-1}
8	30	BA,62	NaTPB,3	5	28.0	5.0×10^{-4} to 1.0×10^{-1}
9	30	BA,61	NaTPB,4	5	27.1	5.0×10^{-6} to 1.0×10^{-1}
10	30	NPOE,62	NaTPB,3	5	29.1	1.0×10^{-6} to 1.0×10^{-1}
11	30	DMS,62	NaTPB,3	5	26.3	5.0×10^{-5} to 1.0×10^{-2}
12	30	AP,62	NaTPB,3	5	27.5	2.2×10^{-5} to 8.5×10^{-1}

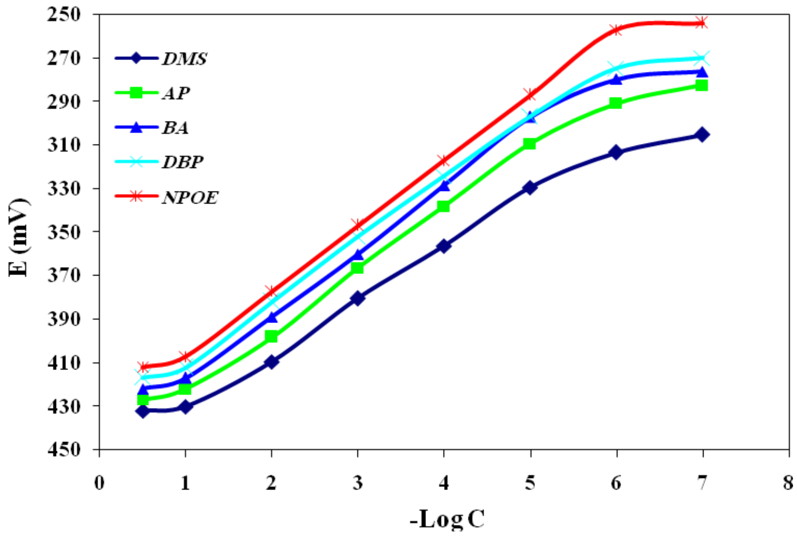

Figure 3. Effect of different plasticizers on the potential response of the Cd^{2+} on selective electrode based on L.

It is reported that the response characteristics of ion-selective electrodes are also largely affected by the nature and amount of plasticizer used [43-45]. This is due to the influence of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [46]. As it is seen from Table 2, among four different plasticizers used, NPOE results in the best sensitivity (Fig. 3). Moreover, 5% of the ionophore was chosen as the optimum amount of ionophore in the PVC-membrane. Meanwhile, the optimization of perm selectivity of the membrane sensors is known to be highly dependent on the incorporation of additional membrane components [10-35]. In fact, it has been clearly demonstrated that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance [47,48] and improving the response behavior and selectivity [49,50], but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [51]. Moreover, additives may catalyze the exchange kinetics at the sample-membrane interface [52]. From the data presented in Table 2, it is seen that the addition of NaTPB will increase the sensitivity of the electrode response considerably. The use of 3% NaTPB resulted in a Nernstian behavior of the electrode (no. 10). As is obvious from Table 2, membrane number 10 with PVC: NPOE: ionophore: NaTPB percent ratio of 30: 62: 5: 3 resulted in the Nernstian behavior of the membrane electrode over a wide concentration range.

3.4. Effect of internal solution concentration

The proposed electrode was also used at different concentrations of the internal reference solution. The Cd $(NO_3)_2$ concentrations were changed from 1.0×10^{-4} to 1.0×10^{-2}M and the emf–pCd^{2+} plot was obtained. It was found that the variation of the concentration of the internal Cd^{2+} solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. However, a 1.0×10^{-3}M concentration of the reference solution found to be quite appropriate for smooth functioning of the system. The optimum conditioning time for the membrane electrode in a 1.0×10^{-3}M Cd $(NO_3)_2$ was 24 h, after which it generates stable potentials in contact with Cd^{2+} solutions.

3.5. Linear concentration range and detection limit

Under the optimized composition, the linear responses to the activity of Cd^{2+} ion were investigated for the prepared PME, CGE and CWE and the resulting plots are shown in Fig. 4. As is obvious from Fig. 4, in the case of all three electrodes, Nernstian responses are obtained in very broad concentration ranges of 1.0×10^{-6} to 1.0×10^{-1}M (for PME), 1.7×10^{-7} to 2.3×10^{-1}M (for CWE) and 1.2×10^{-8} to 1.7×10^{-1}M (for CGE). The resulting limit of detection (LOD) for PME, CWE and CGE, obtained from the intersection of the two linear parts of the calibration plots, were found to be 8.9×10^{-7}, $1.0\times10^{-7}$and 9.8×10^{-9} M, respectively.

It is worth mentioning that, while all three electrodes (i.e., PME, CWE and CGE) possess a nice Nernstian response, the linear range and LOD of the CWE and CGE are greatly improved relative to those of the PME. This is presumably originated from the coated electrode technology, where an internal cadmium nitrate solution, in PME, has been replaced by a silver (in CWE) or copper wire (in CGE) of much higher electrical conductivity [53-55]. It should be emphasized that the fluxes existing in the PME when using an inner solution of relatively high concentration of cadmium ion (1.0×10^{-3}M in this case) result in significant bias and increases the LOD. However, in the case of solid contact CWE and CGE that do not contain inner solution, fluxes are significantly reduced and, in turn, result in improvement of LODs. The CWE and CGE are also advantageous in terms of simplicity, high mechanical durability and low cost, and they are capable of reliable response over a very wide concentration range of the analyte.

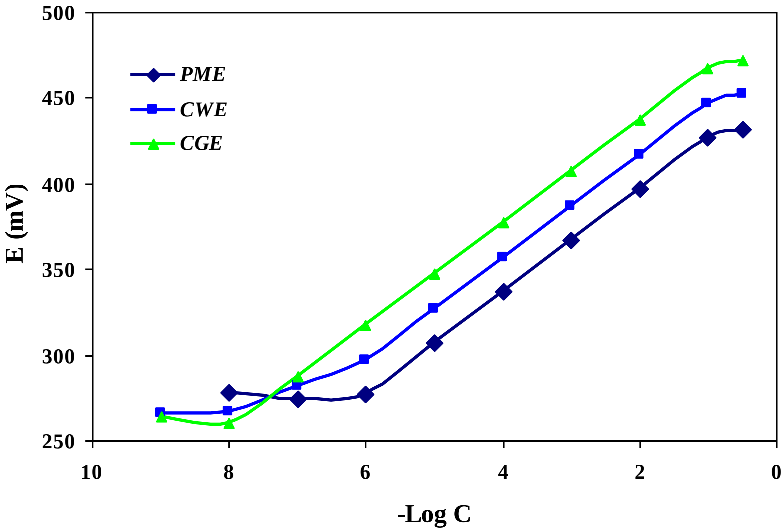

Figure 4. Calibration curves different Cd^{2+} ion-selective electrode based on L: PME, CWE and CGE,

3.6. Response time

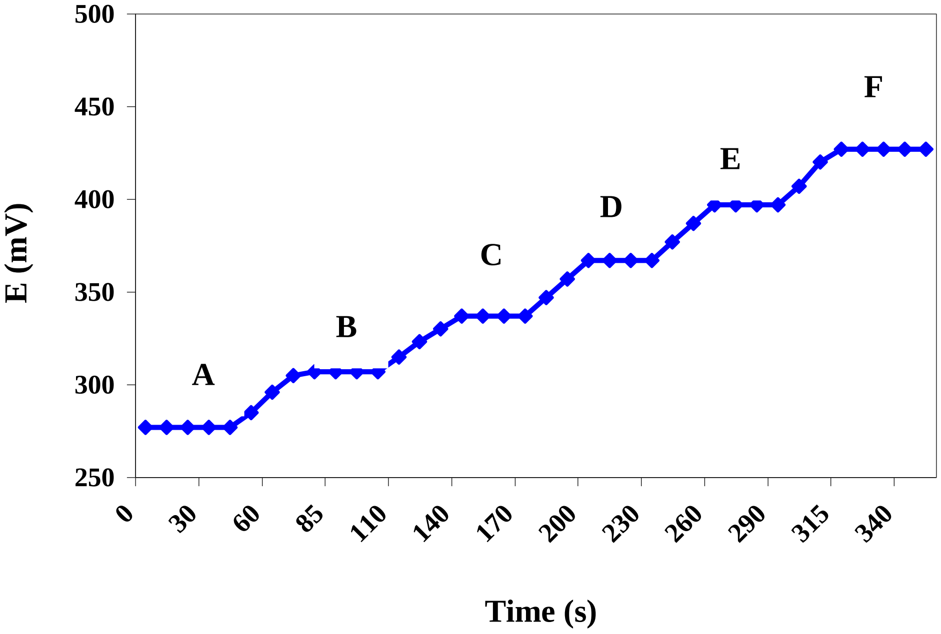

Figure 5. Dynamic response time of the proposed sensor for step changes in the concentration of C^{d2+} (M): A) 1.0×10^{-6}, B) 1.0×10^{-5}, C) 1.0×10^{-4}, D) 1.0×10^{-3}, E) 1.0×10^{-2} , F) 1.0×10^{-1}.

For analytical applications, the response time of a membrane sensor is on important factor. The static response time of the electrode tested by measuring the average time required to achieve a potential within ±1mV of the final steady state potential upon successive immersion of a series of Cd^{2+} ions, each having a tenfold difference in concentrations, was within < 35S for PME and < 25S for CGE and CWE for Cd^{2+} concentrations < 10×10^{-3}M. (Fig. 5)

3.7. pH effect on the electrode response

The influence of pH of the test solution on the potential response of the membrane electrode was tested in the pH range of 1-11, and the results are shown in Fig. 6. As seen, the potential remained constant from pH 3.5 to 7.9, beyond which the potential changed considerably.

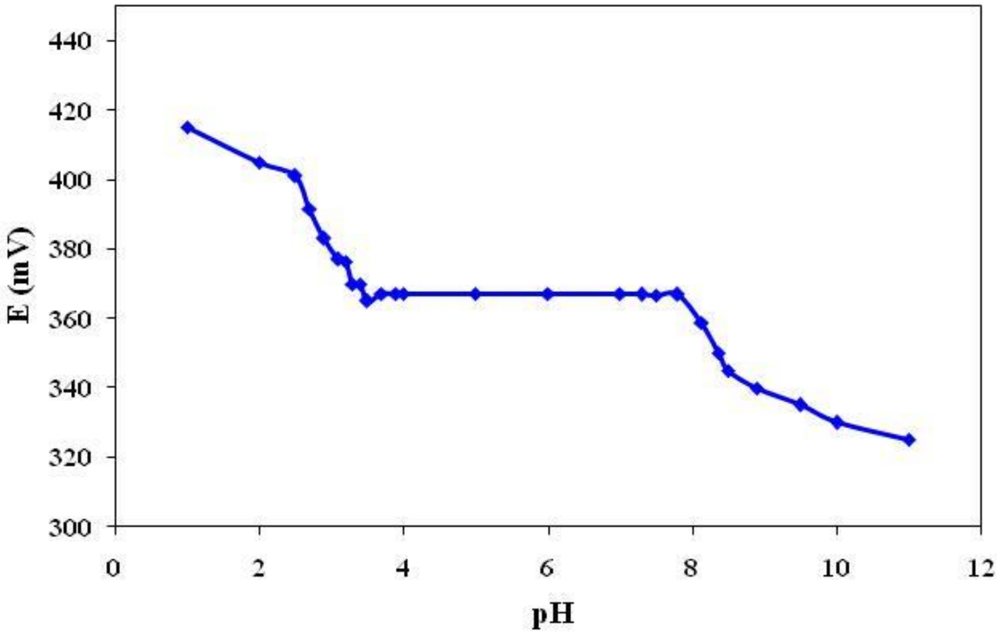

Figure 6. Influences of pH of the test solution on the potential response of electrode in the presence of 1.0×10^{-3} M Cd^{2+}.

At low pH, the potential increased, indicating that the membrane sensor also responded to H^+ ions, by the protonation of the nitrogen atoms of the ionophore., while the observed large decrease in potential at higher pH values could be due to the formation of some hydroxyl complexes of Cd^{2+}in solution.

3.8. Potentiometric selectivity

The selectivity behavior is obviously one of the most important characteristics of a membrane sensor, determining whether a reliable measurement in the target sample is possible. In this work, the influence of several transition and heavy metal ions on the potential response of the cadmium-selective electrode was tested by determining the potentiometric selectivity coefficients of the electrodes by the separate solution method (SSM) [56,57]. In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with two separate solutions.

One contains the ion of interest i at the activity a_i (but no j) and the other containing the interfering ion j at the same activity $a_j = a_i$ (but no i). In this method the values are the selectivity coefficient can be derived from the following equation:

$$K_{ij}^{pot} = \frac{(E_2 - E_1)}{2.303RT/Z_iF} + \left(1 - \frac{Z_i}{Z_j}\right)\log a_i$$

Where E_1, E_2 and Z_i, Z_j are the respective measured potentials and charges on the ions i and j

The resulting $\log K_{Cd,M_i}^{pot}$ values obtained are summarized in Table 3. It is seen that, in all cases, the log selectivity coefficients are in the order of -2.5 and lower, indicating negligible interference in the performance of the membrane sensor assemblies. Meanwhile, Table 3 indicates that, in all cases, the selectivity coefficients obtained for the CWE and CGE are lower than those for the PME, emphasizing the superiority of the former electrodes in this respect as well [53–55, 58].

In Table 4, the linear range (LR) and selectivity coefficients of the proposed CGE are compared with the corresponding values for the best previously reported cadmium ion-selective electrodes based on different neutral ion carries [21-35].

Table 3. The selectivity coefficients of various interfering cations for the membrane sensor.

M^{n+}	Log $K^{pot}_{Cd,M}$		
	PME	*CWE*	*CGE*
Ni^{2+}	-2.5	-2.7	-2.9
Co^{2+}	-2.9	-3.1	-3.0
Cu^{2+}	-3.0	-3.3	-3.4
Pb^{2+}	-3.5	-3.7	-3.9
Mg^{2+}	-3.3	-3.8	-3.5
Hg^{2+}	-3.9	-4.1	-4.1
Na^{+}	<-5.0	<-5.0	<-5.0
K^{+}	<-5.0	<-5.0	<-5.0
Zn^{2+}	-4.1	-4.5	-4.3
Al^{3+}	<-5.0	<-5.0	<-5.0
Rb^{+}	-4.7	-4.9	<-5.0
La^{3+}	-4.9	<-5.0	<-5.0
Be^{2+}	-4.6	-4.8	-5.0
Ni^{2+}	-4.4	-4.8	-4.9
Ag^{+}	-4.5	-4.7	-4.7
Fe^{2+}	-3.9	-4.3	-4.5
Ca^{2+}	-3.6	-3.9	-3.7

Table 4. Comparison of selectivity coefficients, $\log K^{pot}_{Cd,M_i}$ and linear range, LR, of present work and previous studies .

LR(pCd)	$\log K^{pot}_{Cd,M}$									Ref.
	Na^+	Ag^+	Co^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Al^{3+}	La^{3+}	
1.0-5.0	-2.79	-3.10	-5.69	-0.37	-2.30	-3.23	-3.43	-	-	21
1.0-6.4	-1.92	+1.00	-3.00	-2.00	-3.39	-1.40	-	-	-	23
1.0-4.7	-0.37	-1.15	-1.07	-1.04	-1.21	-0.43	-0.02	-1.00	-	24
1.0-4.0	-1.70	-	-	-1.04	-1.40	-0.74	-1.15	-1.40	-	25
1.0-5.0	-2.8	-	-3.0	-2.6	-2.6	-2.1	-2.8	-	-	26
5.0-9.0	-8.37	-	-	-1.03	-5.97	-0.79	-	-	-	28
1.0-7.1	-3.32	-3.09	-3.76	-2.82	-3.41	-3.31	-3.58	-	-	30
1.0-6.0	-	-1.04	-2.57	-0.68	-1.8	-1.63	-	-3.14	-	33
1.0-8.3	-5.11	-	-2.2	-	-2.96	-3.14	-	-3.68	-	32
3.5-7.5	<-5	-	-2.1	-5.2	-4.7	-2.9	-	-3.6	-6.3	34
0.8-7.8	<-5	-3.4	-2.6	-2.4	-2.6	-3.4	-2.2	-3.3	-3.6	35
0.77-7.9	<-5	<-5	-2.9	-3.0	-4.1	-3.5	-3.9	-4.9	<-5	This work, CGE

From the data given in Table 4 it is immediately obvious that the linear range of the proposed sensor is superior to those reported before, except for the case of Ref. [28].While, the proposed CGE for Cd^{2+} ion shows somewhat similar (or sparsely worse), in some cases, or superior, in most cases, selectivity behavior relative to the PVC-membrane sensors reported previously.

3.9. Stability and lifetime

Table 5. Lifetime of Cd(II) selective membrane sensor.

Week	Slope (mV $decade^{-1}$)	Detection Limit (M)
1	29.1±0.1	1.1×10^{-8}
2	29.1±0.1	1.1×10^{-8}
3	29.0±0.1	1.9×10^{-8}
4	28.9±0.1	2.1×10^{-8}
5	29.0±0.1	2.5×10^{-8}
6	29.1±0.1	2.3×10^{-8}
7	28.9±0.1	3.0×10^{-8}
8	29.0±0.1	3.6×10^{-8}
9	28.9±0.1	3.3×10^{-8}
10	28.8±0.1	4.9×10^{-8}
11	28.7±0.1	5.1×10^{-8}
12	28.9±0.1	7.9×10^{-8}
13	28.5±0.1	9.3×10^{-8}
14	27.6±0.1	2.5×10^{-7}
15	23.9±0.1	7.3×10^{-7}

For the investigation of the stability and lifetime of the Cd(II) membrane sensor, two electrodes were tested over a period of 15 weeks and the results are in Table 5. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 13 weeks (use of 1 hour daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 13 weeks changes were observed in the slope and detection limit (from 29.1 to 28.5 mV decade^{-1} and 1.0×10^{-8} from 9.3×10^{-8} mol L^{-1}, respectively) [59-61].

3.9. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from 1.0×10^{-2} to 1.0×10^{-3} mol L^{-1}) sample concentrations and the results showed that, the potentiometric responses of the electrode was reversible; although the time needed to reach equilibrium values (35 s) were longer than that of low-to-high sample concentrations [16] (Fig.7).

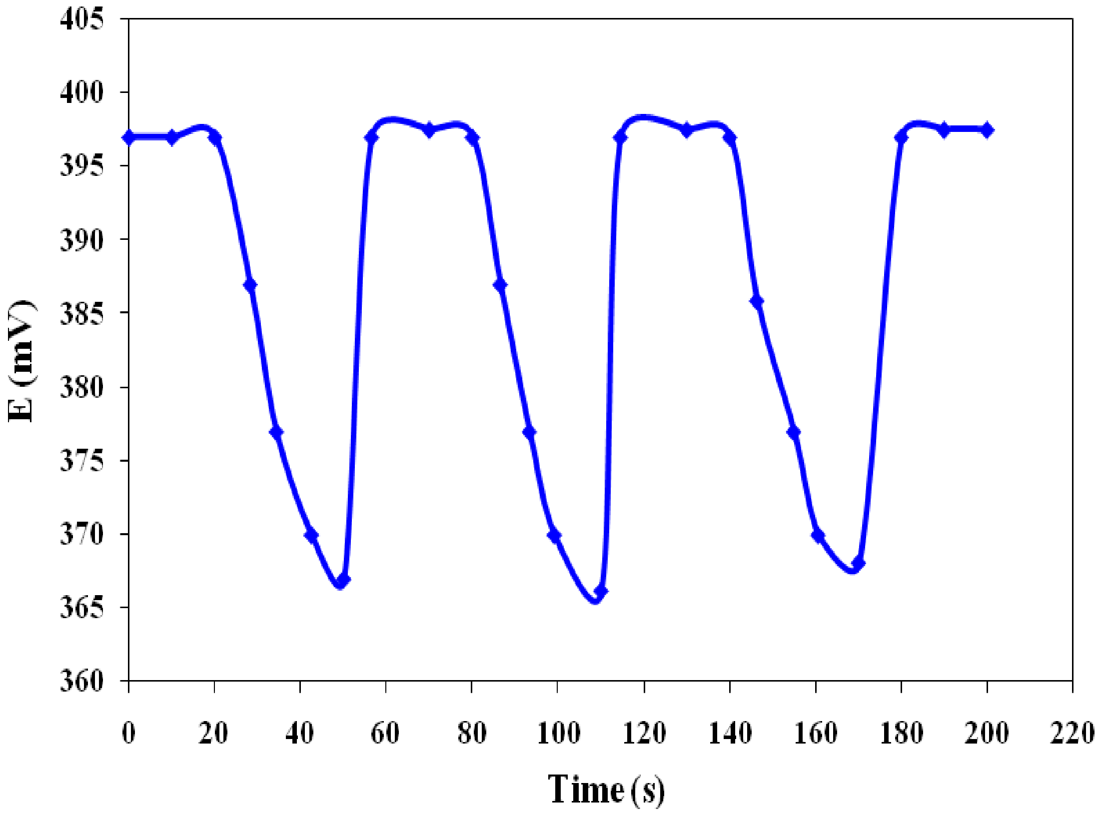

Figure 7. Dynamic response characteristics of the Cd^{2+} membrane sensor for several high-to-low sample cycles.

3.10. Analytical applications

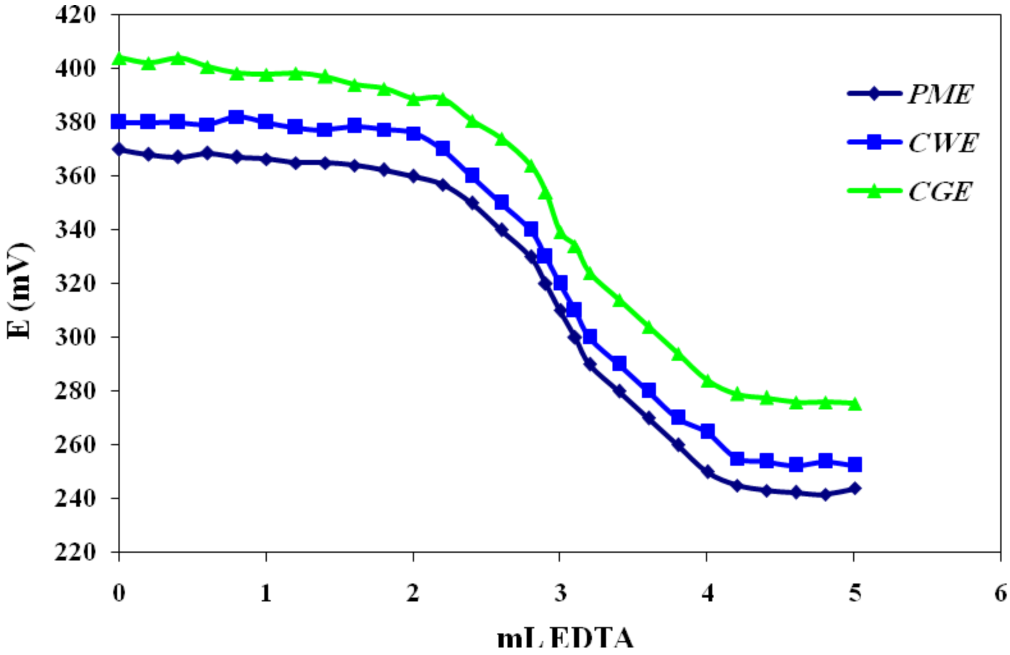

Figure 8. Titration curves of 30mL of 1.0×10^{-3}M Cd^{2+} with 0.01M EDTA solution at pH 6.0, using the proposed CGE, CWE and PME electrodes as indicator electrodes.

Table 6 Recovery data for cadmium ion spiked tap water samples containing diverse metal ions.

Sample no.	Diverse ion added (mgdm^{-3})	Cd^{2+} ion added (mgdm^{-3})	Cd^{2+} ion determined with ICP (mg dm^{-3})	Cd^{2+} ion determined with PME (mg dm^{-3})	Cd^{2+} ion determined with CGE (mg dm^{-3})
1	10.0 (Ni^{2+})	12.0	12.1	12.3	12.1
2	10.0 (Co^{2+})	12.0	12.3	12.2	12.2
3	10.0 (Cu^{2+})	12.0	12.4	12.1	11.9
4	10.0 (Pb^{2+})	13.0	13.3	13.0	12.8
5	10.0 (Mg^{2+})	14.0	14.1	14.1	13.9
6	10.0 (Hg^{2+})	9.0	9.3	9.2	9.1

The practical utility of the proposed membrane sensors were tested by their use as indicator electrodes for titration of 30mL of Cd^{2+} 1.0×10^{-3}M with a 0.01M standard solution of ethylenediaminetetraacetic acid (EDTA) solution at pH 6, and results are shown in Fig. 8. As seen, the amount of cadmium ions in solution can be accurately determined with these electrodes. The proposed PME and CGE system were also successfully applied to the direct determination of cadmium in different binary mixtures and results are presented in Table 6. As it is obvious from Table 6, there is a satisfactory agreement between the cadmium contents evaluated by the PME and CGE systems and those determined with ICP.

4. CONCLUSIONS

The results obtained from the above mentioned study revealed that a potentiometric PVC-based membrane sensor based on (13E)-N-benzylidene-2-(3-((E)-2-(benzylideneamino)ethyl)-2-phenylimidazolidin-1-yl)ethanamine (L) functions as a excellent Cd(II) selective membrane sensor and can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. Applicable pH range, lower detection limit, and potentiometric selectivity coefficients of the proposed sensor make it a very good device used for the determinations of Cd(II) ion.

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