Novel PVC-membrane potentiometric sensors based on a recently synthesized sulfur-containing macrocyclic diamide for Cd^{2+} ion. Application to flow-injection potentiometry

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ABSTRACT

A new sulfur-containing macrocyclic diamide, 1,15-diaza-3,4,12,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido)cyclooctadecan-2,14-dione, **L**, was synthesized, characterized and used as an active component for fabrication of PVC-based polymeric membrane (PME), coated graphite (CGE) and coated silver wire electrodes (CWE) for sensing Cd^{2+} ion. The electrodes exhibited linear Nernstian responses to Cd^{2+} ion in the concentration range of 3.3×10^{-6} to 3.3×10^{-1} M (for PME, LOD = 1.2×10^{-6} M), 2.0×10^{-7} to 3.3×10^{-1} M (for CWE, LOD = 1.3×10^{-7} M) and 1.6×10^{-8} to 1.3×10^{-1} M (for CGE, LOD = 1.0×10^{-8} M). The CGE was used as a proper detection system in flow-injection potentiometry (FIP) with a linear Nernstian range of 3.2×10^{-8} to 1.4×10^{-1} M (LOD = 1.3×10^{-8} M). The optimum pH range was 3.5–7.6. The electrodes revealed fairly good discriminating ability towards Cd^{2+} in comparison with a large number of alkali, alkaline earth, transition and heavy metal ions. The electrodes found to be chemically inert, showing a fast response time of <5 s, and could be used practically over a period of about 2–3 months. The practical utility of the proposed system has also been reported.

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1. Introduction

During the past two decades, an extensive effort has been made in the synthesis and characterization of neutral ionophores possessing high selectivities for specific metal ions to develop new potentiometric and optical sensors for the determination of the respective metal ions in real samples [1–3]. The design and synthesis of new functionalized macrocyclic ligands for specific analytical applications has been the subject of continuous recent interest [3–5]. The in-built configuration rigidity induced by N-substituted amides present in periphery of benzomacrocycles invokes preorganization leading to ionophoric selectivity [6–8]. In past decade, we have synthesized and used several novel benzo-substituted macrocyclic diamide derivatives as suitable ionophores in the preparation of highly selective potentiometric sensors for Zn^{2+} [9], Sr^{2+} [10,11], Hg^{2+} [12], Cs$^+$ [13], Ca^{2+} [14], Ag$^+$ [15], Co^{2+} [16], Be^{2+} [17], UO$_2^{2+}$ [18], Cu^{2+} [19].

While there is no report that definitely indicate Cd^{2+} ion as an essential trace element in biological processes, it is well known that this element is highly toxic to a wide variety of living organisms, including man [20]. Thus, 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 [21–34]. 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, relatively long response time and considerable interferences from other cations such as Ag$^+$, Zn^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+}.

We have previously reported tow cadmium ion-selective electrodes based on a synthesized tetrol compound [21] and tetrathia-12-crown-4 [23]. Based on our previous experiences on the use of benzo-substituted macrocyclic diamides in the preparation of highly selective potentiometric sensors [9–19], in this work, we used a recently synthesized thia-containing dibenzopyridino macrocyclic diamide 1,15-diaza-3,4,12,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido)cyclooctadecan-2,14-dione (**L**, Scheme 1) with an 18-member ring cavity 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. The CGE was also used as a proper detection system in flow-injection potentiometry (FIP) of cadmium.

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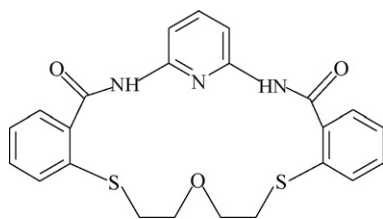
Scheme 1. Structure of ligand **L**.

It is worth mentioning that, due to the advantages of flow-injection potentiometry by ion selective electrodes, including low cost, simple instrumentation, rapid response, high sampling rate and wide linear response, it has been well recognized over the past two decades for the determination of a variety of metal ions [35–37] including Cd²⁺ [38,39]. Moreover, the transient nature of the signal in flow-injection analysis may help to overcome the effects of interfering ions if the electrode's response to these ions is slower than that to the target analyte.

2. Experimental

2.1. Reagents

Reagent grade o-nitrophenyl octyl ether (o-NPOE), dimethyl sebacate (DMS), diethyl sebacate (DES), dibutyl sebacate (DBS), dioctyl sebacate (DOS), dibutyl phthalate (DBP), oleic acid (OA), tetrahydrofuran (THF) and powdered PVC were purchased from Merck and used as received. Cadmium nitrate and the nitrate salts of other cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum-drying over P_2O_5. Triply distilled de-ionized water was used.

2.2. Synthesis of ionophore **L**

The benzo-substituted macrocyclic diamide 1,15-diaza-3,4;12,13-dibenzo-8-oxa-16,18-pyridine-5,1-dithiacyclooctadecane-2,14-dione, **L**, was synthesized (according to Scheme 2), purified and fully characterized according to a previously published paper from this research group [40].

2.2.1. Thiosalicylic acid salt **2**
KOH (11.2 g, 20 mmol) in EtOH (200 mL) were placed in a 500 mL two necked flask fitted with stirrer and reflux condenser, and refluxed for 30 min. Then, thia salicylic acid (15.4 g, 10 mmol) was added dropwise and refluxed for 3–5 h. Then the mixture was cooled and the precipitate filtrated to give the yellowish-green salt of thia salicylic acid in 95% yield.

#### 2.2.2. S,S-(3-oxa-1,5-pentylene)-bis-thiosalicylic acid
A mixture of potassium thiosalicylate **1** (0.77 g, 5 mmol) and diethylene glycol dibromide (1.16 g, 2.5 mmol) in DMF (10 mL) was heated under reflux for 15 min (precipitation of KBr occurred). The solvent was then removed in vacuum and the remaining material was washed with water (20 mL) and recrystallized from dil. EtOH to give colorless crystals of diacid **3** in 90% yield; mp 182–184 °C. IR (KBr): 698, 732, 914, 1114, 1272, 1413, 1465, 1562, 1693, 2958 cm⁻¹. ¹H NMR (DMSO, 250 MHz): δ = 3.11 (m, 4H, CH₂S), 3.43 (m, 4H, CH₂O), 7.18–8.04 (m, 8H, ArH), 13.05 (s, 2H, COOH) ppm. ¹³C NMR (DMSO, 62.9 MHz): δ = 30.81, 68.27, 123.89, 125.56, 128.51, 130.78, 139.60, 167.44 ppm. MS: m/z (%) = 378 (M⁺, 0.1), 180, 153 (100), 137, 109, 97, 77, 69, 63, 45. UV (EtOH): ε_{max} (nm) = 230.3 (2460), 261.9 (2186), 316.7 (856).

2.2.3. Sulfur dicarboxylic acid dichloride **4**
Sulfur dicarboxylic acid **3**, (9.45 g, 0.025 mol) was heated in SOCl₂ (50 mL) for 8 h at 50–60 °C. The SOCl₂ was evaporated from the solution at low temperature and the residue was crystallized from petroleum ether to give **4** as a yellow cream solid in 85% yield; mp 82–87 °C. IR (neat): 648, 657, 860, 1189, 1195, 1431, 1554, 1585, 1575, 2370, 3420 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ = 3.26 (m, 4H, CH₂S) 3.75 (m, 4H, CH₂O), 7.23–8.31 (m, 8H) ppm. ¹³C NMR (CDCl₃, 62.9 MHz): δ = 32.22, 69.35, 124.88, 126.14, 130.72, 134.77, 135.57, 136.07 ppm.

2.2.4. Synthesis of macrocyclic diamide **L**
A solution of diamine (2 mmol) in anhyd solvent (10 mL) was added quickly to a vigorously stirred solution of dicarboxylic acid dichloride **4** (2 mmol) in anhydrous dichloromethane at r.t. The mixture was stirred for a further 5–20 min and then was washed with NaHCO₃ (2 × 10 mL) and water (2 × 10 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated to give a solid product. The crude product was purified by column chromatography (petroleum ether–EtOAc). IR (KBr): 695, 763, 1195, 1280, 1452, 1570, 1666, 2827, 3315 cm⁻¹. ¹H NMR (acetone–CH₂Cl₂, 250 MHz) δ = 3.22 (m, 8H, CH₂S), 3.68 (m, 8H, CH₂O), 6.66–8.32 (m, 22H, Ar), 10.56 (s, 4H, NH) ppm. ¹³C NMR (DMSO, 62.9 MHz): δ = 34.64, 38.87–40.88, 68.77, 77.51, 110.84, 126.94, 128.80, 130.95, 133.95, 138.25, 140.60, 150.27, 167.23. MS: m/z (%) = 451 (M⁺, 5.9), 406, 377, 288, 163, 151, 137, 121, 109, 96, 83, 68, 57, 43 (100). UV (CHCl₃): ε_{max} (nm) = 250.6 (2809), 300.7 (2769).
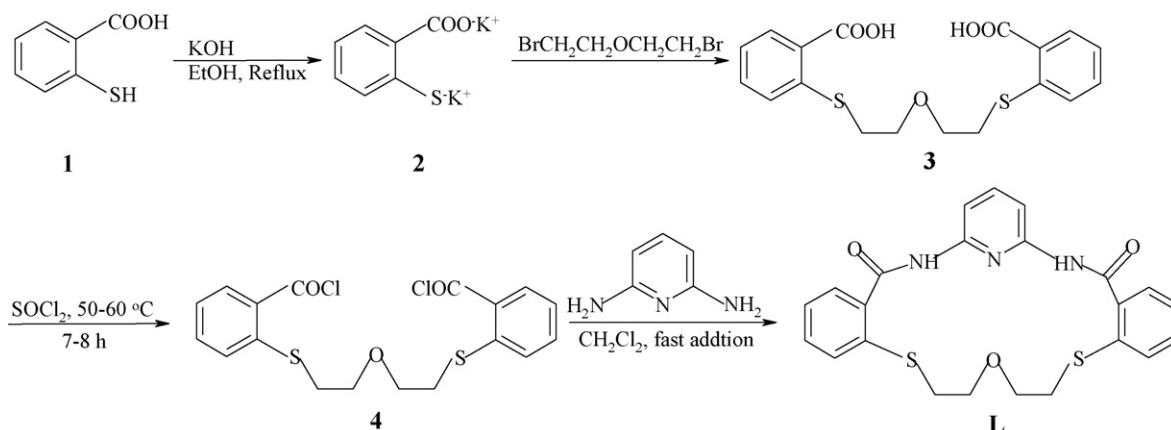
Scheme 2. Synthetic pathway for the preparation of ligand **L**.

2.3. Preparation of electrodes

Membrane solution was prepared by thoroughly dissolving mg amounts of membrane ingredients under optimal conditions (i.e., 28.1 mg PVC, 56.1 mg NPOE, 12.0 mg OA and 3.8 mg **L**) in 4 mL of THF. The resulting solution was evaporated slowly until an oily mixture was obtained. Pyrex tubes (5 mm o.d. on top) were dipped into the mixture for about 10 s so that non-transparent membranes of about 0.3 mm thickness were formed. The tube were then pulled out from the mixture and kept at room temperature for 6 h. The tubes were then filled with an internal solution (1.0×10^{-2} Cd(NO$_3$)$_2$ M). The electrodes were finally conditioned for 24 h in a 1.0×10^{-2} Cd(NO$_3$)$_2$ M solution. A silver/silver chloride electrode was used as the internal reference.

To prepare the coated graphite and coated wire electrodes, a spectroscopic grade graphite rod (10 mm × 3 mm o.d.) and a clean silver wire (20 mm × 2 mm 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} Cd(NO$_3$)$_2$ M solution for 36 h.

2.4. Electromotive force 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$_2$Cl$_2$, KCl (sat) (PME)

Graphite or Ag|PVC-membrane|test solution|Hg–Hg$_2$Cl$_2$, KCl (sat) (CGE and CWE)

A Hioki multimeter was used for the potential measurements at 25.1 ± 0.1 °C. The emf observations were made relative to a saturated calomel electrode (Metrohm). Activities were calculated according to the Debye–Huckel procedure.

A schematic representation of manifold of the flow-injection potentiometric analysis system employed is shown in Fig. 1. A home-made polyacrylamide 70-μL flow cell was used. The cell contained a coated graphite cadmium ISE with effective surface area of 4.90 mm^2 and a commercial Ag/AgCl reference electrode (Metrohm) with a double junction having a terminal tube diameter of 2.5 mm. A 12-channel peristaltic pump (Desaga) was used to continuously draw solution through the cell. A low-pressure rotary injection valve (model 5020 Rheodyne four way rotary valve, USA) was used in the flow system.
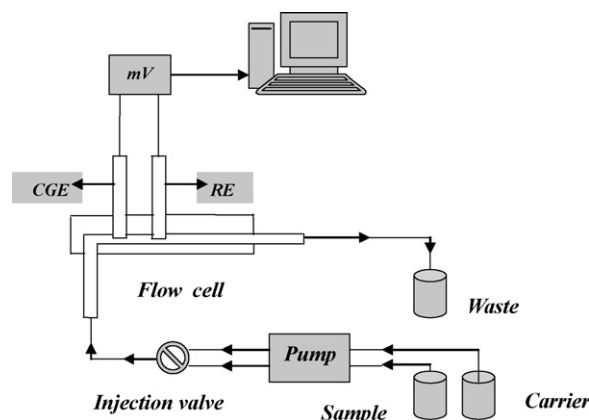

Fig. 1. Manifold of the flow-injection potentiometric system.

3. Results and discussion

3.1. Preliminary studies

In preliminary experiments, the complexation of **L** with some potential transition and heavy metal ions including Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions was investigated conductometrically [41] in acetonitrile solution at 25.00 ± 0.05 °C. It was observed that, in all cases, addition of the neutral ligand to the cation solution (1.0×10^{-4} M) caused a rather large and continuous increase in the conductivity of solution, indicating the higher mobility of the complexed cations compared to the solvated ones [41]. The increased conductivity of the metal nitrates in acetonitrile solution upon addition of the ligand can also be related to some extent to the dissociation of some ion-paired species usually present in acetonitrile as a solvent of intermediate dielectric constant and relatively low solvating ability, as a result of the metal on complexation with **L** [31]. It is interesting to note that, in the case of Cd^{2+} ion, the slope of the corresponding conductivity-[**L**]/[Cd^{2+}] mole ratio plot changed sharply at the point where the ligand-to-cation mole ratio was about 1, indicating the formation of a stable 1:1 complex in solution (with log K_f > 4). However, in the case of other metal ions tested, the relatively large increase in solution conductivity upon addition of L did not show a significant tendency of leveling off even at mole ratios greater than 3, emphasizing the formation of weaker complexes (with log K_f < 3).

In order to obtain further information about the conformational change of **L** upon complexation to the cadmium ion, the molecular structures of the uncomplexed ligand and its 1:1 Cd^{2+} complex were built with the Hyperchem program version 7 [42]. The structure of free ligand was optimized using the 6-31G* basis set at the restricted Hartree–Fock (RHF) level of theory. The optimized structure of the ligand was then used to find out the initial structure of its 1:1 cadmium complex. Finally, the structure of the resulting 1:1 complex was optimized using the Lan12mb basis set at the RHF level
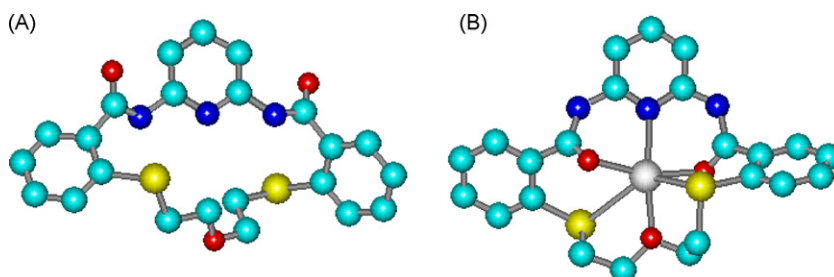

Fig. 2. Optimized structures of free **L** (A) and its 1:1 complex with Cd^{2+} ion (B).

of theory. No molecular symmetry constraint was applied; rather, full optimization and frequency option of all bond lengths, bond angles and torsion angles were carried out using the Gaussian 98 program [43].

The optimized structures of **L** and (Cd**L**)$^{2+}$ species are shown in Fig. 2. It should be noted that, only real frequency values were observed, indicating that the structural geometries shown in Fig. 2 are quite acceptable [44,45]. As it is obvious from Fig. 2A, the ligand forms a more or less planar cavity in which the amide oxygens are pointing out of the ring while the ethereal oxygen of the molecule is some how twisted out of the planar cavity. Meanwhile, the two donating sulfur atoms together with the three nitrogens of the ring (i.e., two amide nitrogens and the pyridine nitrogen) are located in a more or less planar situation. Interestingly, in the optimized structure of the 1:1 (Cd**L**)$^{2+}$ complex (Fig. 2B), the cadmium ion is well incorporated inside the twisted macrocyclic cavity and coordinated to six donating atoms of the ligand, including the two sulfur atoms, two C=O oxygens, the etherial oxygen and the pyridine ring nitrogen, in an distorted octahedral geometry, as previously reported for some cadmium(II) complexes in the corresponding crystal structures [46]. It is interesting to note that, unlike the optimized ligand structure, the two amide group oxygens in the optimized complex structure are pointed inside the cavity ring so that they have the opportunity to participate in bond formation with the central cadmium ion.

In preliminary experiments the macrocyclic diamide was used as a neutral carrier to prepare PVC-membrane ion-selective electrodes (PMEs) for a wide variety of transition and heavy metal ions. The potential responses obtained for the most sensitive ion-selective electrodes based on the ionophore are shown in Fig. 3. The metal ions of soft and intermediate acid character (i.e., Cd^{2+}, Cu^{2+}, Hg^{2+} and Ag$^+$) reveal the most sensitive response in the series, among which Cd^{2+} ion provides the most suitable ion-selective electrode. The results thus obtained indicated that the Cd^{2+} ions are more easily attracted to the PVC-macrocyclic diamide membrane, resulting in a Nernstian potential-concentration response in a wide concentration range.

3.2. 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 [9–19,21–28]. 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 1. It is reported that the response characteristics of ion-selective electrodes are also largely affected by the nature and amount of plasticizer used [47–49]. This is due to
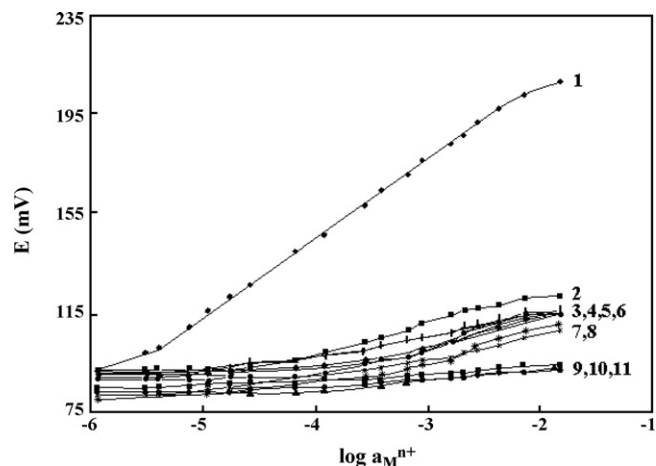

Fig. 3. Potential response of various ion-selective electrodes based on **L**: (1) Cd^{2+}, (2) Fe^{3+}, (3) Cu^{2+}, (4) Hg^{2+}, (5) Ni^{2+}, (6) Co^{2+}, (7) Al^{3+}, (8) Ag$^+$, (9) Pb^{2+}, (10) Na$^+$, (11) Mg^{2+}.
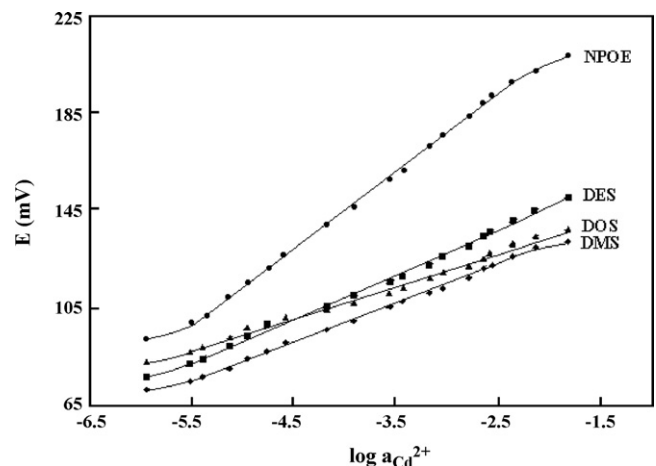

Fig. 4. Effect of different plasticizers on the potential response of the Cd^{2+} ion-selective electrode based on **L**.

the influence of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [50]. As it is seen from Table 1, among four different plasticizers used, NPOE results in the best sensitivity (Fig. 4). Moreover, 2.8% of the ionophore was chosen as the optimum amount of ionophore in the PVC-membrane.

Meanwhile, the optimization of permselectivity of the membrane sensors is known to be highly dependent on the incorporation

Table 1
Optimization of membrane components.

| Electrode number	Components (%)				Slope (mV/decade)	Linear range (M)
	Plasticizer	PVC	Ionophore	Additive		
1	64.1 (NPOE)	32.1	3.8	–	15.0	1.0×10^{-4} to 1.0×10^{-2}
2	58.8 (NPOE)	29.4	3.8	8 (OA)	17.1	3.3×10^{-6} to 3.0×10^{-2}
3	56.1 (NPOE)	28.1	3.8	12 (OA)	29.4	3.3×10^{-6} to 3.0×10^{-2}
4	63.5 (NPOE)	31.7	3.8	1 (NaTPB)	21.8	1.0×10^{-4} to 1.0×10^{-2}
5	53.5 (NPOE)	26.7	3.8	16 (OA)	21.3	3.3×10^{-6} to 3.0×10^{-2}
6	58.6 (NPOE)	29.4	–	12(OA)	1.8	2.7×10^{-3} to 3.0×10^{-2}
7	58.3 (NPOE)	29.2	0.5	12 (OA)	21.1	3.3×10^{-6} to 3.0×10^{-2}
8	57.5 (NPOE)	28.7	1.8	12 (OA)	25.0	2.7×10^{-5} to 7.0×10^{-3}
9	56.8 (NPOE)	28.4	2.8	12 (OA)	26.8	3.3×10^{-6} to 3.0×10^{-2}
10	56.1 (DOS)	28.1	3.8	12 (OA)	11.8	6.0×10^{-5} to 7.0×10^{-3}
11	56.1 (DMS)	28.1	3.8	12 (OA)	21.9	2.7×10^{-5} to 1.7×10^{-2}
12	56.1 (DES)	28.1	3.8	12 (OA)	22.4	1.0×10^{-5} to 3.0×10^{-2}
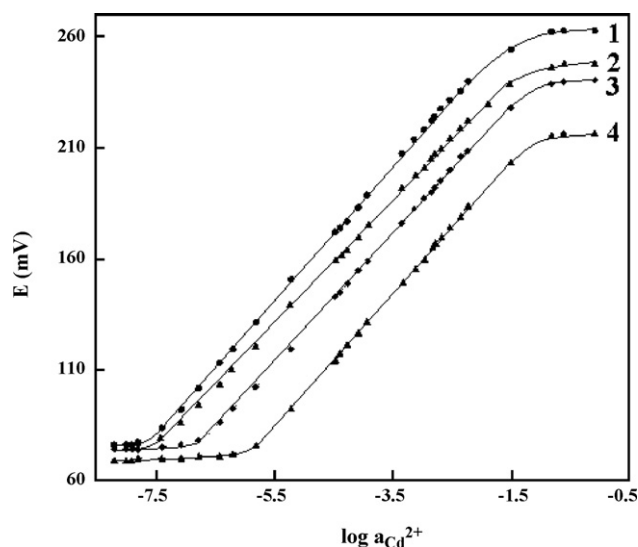
Fig. 5. Calibration curves different Cd^{2+} ion-selective electrode based on **L**: (1) CGE, (2) CGE-FIP, (3) CWE, (4) PME.

of additional membrane components [9–19,21–28]. 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 [51,52] and improving the response behavior and selectivity [53,54], but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [55]. Moreover, additives may catalyze the exchange kinetics at the sample-membrane interface [56]. From the data presented in Table 1, it is seen that the addition of OA will increase the sensitivity of the electrode response considerably. The use of 12% OA resulted in a Nernstian behavior of the electrode (no. 3). We have previously reported the first use of fatty acids such as palmitic acid and oleic acid as very suitable lipophilic additives in inducing permselectivity to several bulk liquid membrane [57,58] and PVC-membrane selective electrodes [9,12,16,17,22].

As is obvious from Table 1, membrane number 3 with a PVC:NPOE:ionophore:OA percent ratio of 28.1:56.1:3.8:12.0 resulted in the Nernstian behavior of the membrane electrode over a wide concentration range.

The proposed electrode was also used at different concentrations of the internal reference solution. The $Cd(NO_3)_2$ concentration was 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, and some increase in LOD at higher concentrations of the internal solution (i.e., by a factor of 1.3–1.5), due to a significant potential bias. However, a 1.0×10^{-2} M concentration of the reference solution found to be quite appropriate for smooth functioning of the system, resulting in some improved linear range and shorter response time. The optimum conditioning time for the membrane electrode in a 1.0×10^{-2} M $Cd(NO_3)_2$ was 24 h, after which it generates stable potentials in contact with Cd^{2+} solutions.

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. 5. As is obvious from Fig. 5, in the case of all three electrodes, Nernstian responses are obtained in very broad concentration ranges of 3.3×10^{-6} to 3.3×10^{-1} M (for PME), 2.0×10^{-7} to 3.3×10^{-1} M (for CWE), 1.6×10^{-8} to 1.4×10^{-1} M (for CGE). The resulting limit of detec-

tion (LOD) for PME, CWE, CGE and CGE-FIP systems, obtained from the intersection of the two linear parts of the calibration plots, were found to be 1.2×10^{-6}, 1.3×10^{-7}, 1.0×10^{-8}, 1.3×10^{-8} 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 [59–61]. 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^{-2} 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.

The average time required for the for the proposed Cd^{2+} ion-selective electrodes to reach a potential within ± 1 mV of the final equilibrium value was measured after successive immersion of a series of cadmium ion solution, each having a 10-fold difference in concentration. The static response time thus obtained was < 5 s in all cases, and the potential stayed constant for more than 5 min, after which a very slow divergence within the resolution of the pH meter (± 0.1 mV) was recorded. The membrane electrodes PME, CGE and CWE were used practically for about 2, 2.5 and 3 months, respectively, at a stretch, without any change in response time, slope, or detection limit.

The influence of pH on the potential response of the Cd^{2+} ion-selective electrode was tested at 1.0×10^{-3} M Cd^{2+} concentration over the pH range 2–10. The results revealed that, in case of all three electrodes, the potential remained constant from pH 3.5–7.6 and the membrane electrodes can be suitably used in this range of pH. However, the potential found to decrease significantly at higher pH values, most possibly due to the formation of some hydroxyl complexes of Cd^{2+} ion in solution. On the other hand, at pH values lower the 3.5, the electrode potentials raised sharply. This is probably due to simultaneous response of the electrode to H_3O^+ and Cd^{2+} ions.

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 [1,2]. 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) [62,63]. 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:

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

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 $\log K_{Cd,M}^{pot}$ values obtained are summarized in Table 2. It is seen that, in all cases, the selectivity coefficients are in the order of 10^{-2} and lower, indicating negligible interference in the performance of the membrane sensor assemblies. Meanwhile, Table 2 indicates that, in all cases, the selectivity coefficients obtained for the CWE and CGE are lower than those for the PME,

Table 2
Selectivity coefficients of different membrane electrodes based on **L**.

M^{n+}	$\log K_{Cd,M}^{pot}$		
	PME	CWE	CGE
Na^+	>−5	>−5	>−5
NH_4^+	−4.0	>−5	>−5
Ag^+	−3.1	−3.4	−3.3
Mn^{2+}	−3.5	−3.5	−3.8
Co^{2+}	−2.4	−2.5	−2.6
Cu^{2+}	−2.1	−2.3	−2.4
Zn^{2+}	−2.4	−2.5	−2.6
Pb^{2+}	−3.4	−3.5	−3.4
Hg^{2+}	−2.1	−2.3	−2.2
Fe^{3+}	−2.3	−2.5	−2.7
Al^{3+}	−2.1	−3.1	−3.3
Cr^{3+}	−3.3	−3.5	−3.5
La^{3+}	−2.6	−3.7	−3.6
Ce^{3+}	−2.1	−3.1	−3.1

Fig. 6. Reproducibility of the flow-injection signals for six repetitive injections of a 1.0×10^{-3} M solution of Cd^{2+} ion.

emphasizing the superiority of the former electrodes in this respect as well [59–61,64]

In Table 3, the linear range (LR), response time (RT) 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 [21,23–28,32–34]. From the data given in Table 3 it is immediately obvious that the linear range and response time of the proposed sensor is superior to those reported before, except for the case of Refs. [26,35]. 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 [21–28].

3.3. Flow-injection potentiometry with CGE

In the next step, the proposed Cd^{2+}-selective CGE was successfully used as a suitable indicator electrode in the flow-injection system shown in Fig. 1. In order to achieve the best FIP response several flow-injection parameters including tubing length, flow rate sample volume, composition of carrier solution and sampling rate were thoroughly investigated.
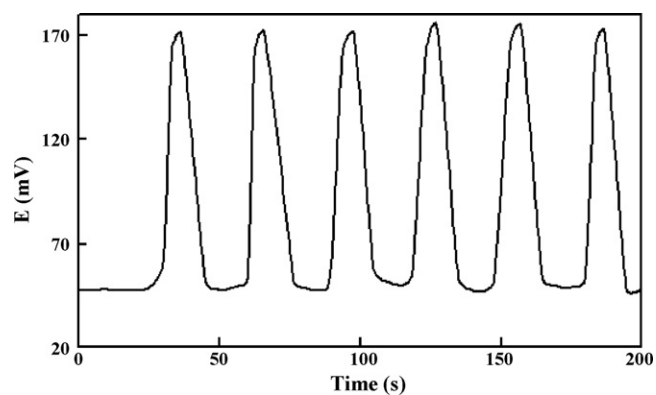
The length of tubing from the injection valve port to the flow cell was kept as small as practically possible to minimize dispersion and dilution. For the proposed electrode, a 10 cm length was selected for tubing.

The dependency of the peak heights and peak width (and time to recover the base line) with flow rate was studied using the electrode response to a 1.0×10^{-3} M solution of cadmium ion. As the flow rate increased, the peaks became narrower and increased in height up to a nearly plateau at a flow rate of $36\,mL\,min^{-1}$. However, the peak width increased considerably at flow rates

higher than $36\,mL\,min^{-1}$. Thus, this flow rate was selected as an optimum value for further studies. It is interesting to note that this flow rate is higher than those previously reported in the literature [65–67].

In general, the peak heights increased with the increasing sample volume, although the effect was less marked at higher concentrations [6,50]. For the proposed sensor, different sample volumes from 100 to 500 μL were studied; the peak height reached nearly 100% of steady state at 200 μL injected. Thus, this sample volume was selected as an optimum amount.

It is well-known that, in FIP, the composition of the carrier solution also affects the response behavior of ion-selective electrode in terms of the base line stability [66]. In the proposed flow system, a 0.01 M KNO_3 solution was used as carrier, which resulted in good stable base lines, when samples were injected in the concentration range of 3.2×10^{-8} to 1.4×10^{-1} M.

In the analytical flow systems, the sampling rate (sample throughput) is an important factor representing the capability of system in online analysis. The proposed potentiometric FIA system revealed sampling rates higher than 120 injections per hour.

Repeatability of the proposed CGE in the flow-injection system under the optimized conditions was checked by six repetitive injection of a 1.0×10^{-3} M solution of Cd^{2+} ion and the results are shown in Fig. 6. The peak height relative standard deviation (%RSD) for six replicate injections of 1.0×10^{-2} M solutions of Cd^{2+} was found to be 1.0%.

In Fig. 7 are also shown the peaks from the proposed FIP system obtained under optimal experimental conditions for varying concentrations of Cd^{2+} solutions in the range of 1.0×10^{-8} to 1.0×10^{-1} M concentrations. The corresponding emf–pCd^{2+} plot is also included in Fig. 5. As it is seen from Fig. 5, the calibration curve is quite linear over a wide concentration range of 1.6×10^{-8}

Table 3
Comparison of present work and previous studies in respect to the different ion selective electrode characteristics (i.e., selectivity coefficients, $\log K_{Cd,M}^{pot}$, linear range, LR, and response time, RT).

LR (pCd)	RT(s)	$\log K_{Cd,M}^{pot}$													Ref.
		Na^+	NH_4^+	Ag^+	Mn^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Fe^{3+}	Al^{3+}	Cr^{3+}	La^{3+}	Ce^{3+}	
1.0–5.0	<15	−2.79	–	−3.10	–	−5.69	−0.37	−2.30	−3.23	−3.43	−4.20	–	–	–	–	[21]
1.0–6.4	<10	−1.92	−1.92	+1.00	−3.94	−3.00	−2.00	−3.39	−1.40	–	−2.29	–	−1.95	–	−3.60	[23]
1.0–4.7	17	−0.37	−1.17	−1.15	–	−1.07	−1.04	−1.21	−0.43	−0.02	−1.66	−1.00	−1.26	–	−1.15	[24]
1.0–4.0	25	−1.70	–	–	−1.52	–	−1.04	−1.40	−0.74	−1.15	−1.30	−1.40		–	–	[25]
1.0–5.0	10	−2.8	–	–	–	−3.0	−2.6	−2.6	−2.1	−2.8	–	–	–	–	–	[26]
5.0–9.0	–	−8.37	–	–	–	–	−1.0.3	−0.79	–	–	–	–	–	–	–	[28]
1.0–7.1	10	−3.32	−1.95	−3.09	−3.97	−3.76	−2.82	−3.41	−3.31	−3.58	−3.89	–	−2.27	–	−4.10	[30]
1.0–6.0	<8	–	–	−1.04	−2.78	−2.57	−0.68	−1.8	−1.63	–	−1.15	−3.14	−3.40	–	–	[33]
1.0–8.3	11	−5.11	−5.34	–	−3.11	−2.2	–	−2.96	−3.14	–	−3.36	−3.68	−3.31	–	–	[32]
3.5–7.5	6	>−5	>−5	–	−4.2	−2.1	−5.2	−4.7	−2.9	–	–	−3.6	–	−6.3	−6.3	[34]
0.8–7.8	<5	>−5	>−5	−3.4	−3.8	−2.6	−2.4	−2.6	−3.4	−2.2	−2.7	−3.3	−3.5	−3.6	−3.1	This work, CGE

Table 4
Recovery data for cadmium ion spiked tap water samples containing diverse metal ions.

Sample no.	Diverse ion added (mg dm^{-3})	Cd^{2+} ion added (mg dm^{-3})	Cd^{2+} ion determined with ICP (mg dm^{-3})	Cd^{2+} ion determined with FIP (mg dm^{-3})
1	10.0 (Hg^{2+})	11.0	11.3	11.4
2	10.0 (Cu^{2+})	10.0	10.2	10.6
3	10.0 (Co^{2+})	13.0	13.3	13.1
4	10.0 (Ag^{+})	9.0	9.1	9.3
5	10.0 (Pb^{2+})	7.0	7.1	7.2
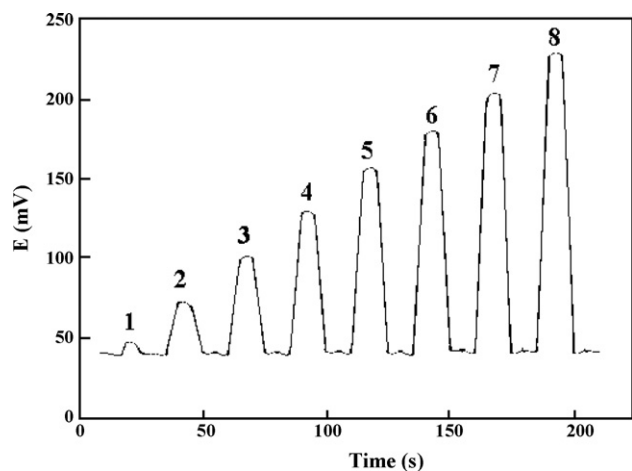
Fig. 7. Potentiometric peaks for measurement of different Cd^{2+} ion concentrations: (1) 1.0×10^{-8} M, (2) 1.0×10^{-7} M, (3) 1.0×10^{-6} M, (4) 1.0×10^{-5} M, (5) 1.0×10^{-4} M, (6) 1.0×10^{-3} M, (7) 1.0×10^{-2} M, (8) 1.0×10^{-1} M.
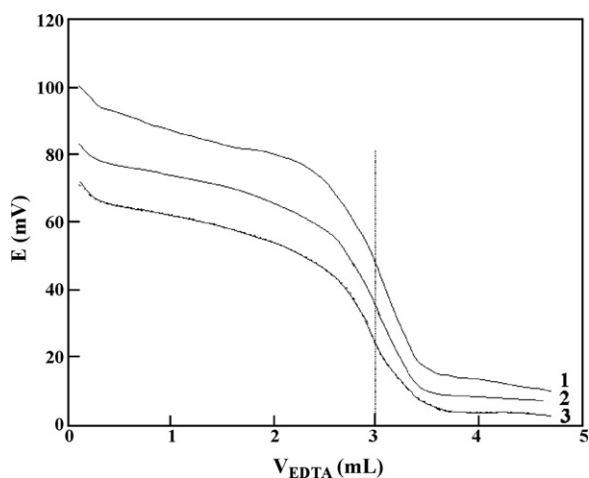

Fig. 8. Titration curves of 30 mL of 1.0×10^{-3} M Cd^{2+} with 0.01 M EDTA solution at pH 6.0, using the proposed CGE (1), CWE (2) and PME (3) electrodes as indicator electrodes.

to 1.3×10^{-1} M with a slope of 29.4 mV decade^{-1} and very low LOD of 1.3×10^{-8} M.

3.4. Applications

The practical utility of the proposed membrane sensors were tested by their use as indicator electrodes for titration of 30 mL of Cd^{2+} 1.0×10^{-3} M with a 0.01 M standard solution of ethylenediamine tetraacetic 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 FIP system was also successfully applied to the direct determination of cadmium in different binary mixtures and results are presented in Table 4. As it is obvious from Table 4, there is a satisfactory agreement between the cadmium contents evaluated by the FIP system and those determined with ICP.

Acknowledgements

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