APPLICATION OF CALIXARENE IONOPHORES IN PVC BASED ION SELECTIVE ELECTRODES FOR HEAVY METALS DETECTION

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ABSTRACT

A functionalized calixarenes molecules 26,28-dihydroxy-25,27-dimethoxycalix[4]arene-11,23-diphosphonic acid for Pb(II) and 25,26,27,28-tetra-(2-dimethydithiocarbamoly-ethoxy)calix[4]arene for Hg(II) were tested as a possible ionophore in ion selective electrodes (ISEs) and successfully applied for the detection of heavy metals ions from environmental and industrial waste waters. These electrodes gave more stable potential readings when used around neutral pH 5.5–8.5 in both cases. The sensors were found to work satisfactorily in partially non-aqueous media up to 25% (v/v) content of acetone, methanol or ethanol and could be used over a period of 5 months. Potentiometric selectivity coefficients as determined by match potential method (MPM) indicate excellent selectivity for Pb^{2+} and Hg^{2+} ions. The sensors could be used successfully in the estimation of lead and mercury in electrochemical battery wastes and also as indicator electrodes in potentiometric titration.

Keywords: Calixarene ionophores, PVC, Ion selective electrodes, Lead(II), Mercury(II), Potentiometry

1. INTRODUCTION

Determination of the heavy metals becomes one of the basic requirements in many chemical investigations nowadays. The information is particularly crucial in studies related to environmental, toxicological and physiological investigations. The common methods applied for the determination of heavy metals are separation of the species by chromatography, followed by detection and determination of the element with a specific detector such as atomic absorption spectrometry or mass spectrometry [1,2]. These methods are rather expensive and time-consuming. Thus, there are no doubts, electroanalytical methods have much more to offer in terms of species-selective detection than spectroscopic methods. Potentiometry with ion-selective electrodes in the principle particularly well suited to separation studies because of its selective response to free ions in aqueous solutions.

Based on the recent advance of host-guest chemistry, polymeric membrane ISEs for heavy metals ion have been extensively developed by the use of crown ether and related calixarenes hosts as well as acyclic ligands [3-7]. In this paper, two functionalized calixarene molecules *viz.*, 26,28-dihydroxy-25,27-dimethoxycalix[4]arene-11,23-diphosphonic acid (**I**) and 25,26,27,28-tetra-(2-dimethydithiocarbamoly-ethoxy)-calix[4]arene (**II**) have been used as an neutral ionophores in a PVC based ion selective electrodes (ISEs) for lead(II) and mercury(II) ions, respectively.

2. EⅩPERIMENTAL

All reagents were of the highest grade commercially available and used as received. Double distilled water was used for the preparation of solution of metal salts of different combination by diluting stock standard solutions (0.1 M). High molecular weight poly(vinyl chloride), tetrahydrofuran (THF) and dibutyl phthalate (DBP) were purchased from Aldrich. Alkali, alkaline earth and transition metal salts in the form of nitrate or chloride were obtained from Merck. The functionalized calixarene molecules (**I**) and (**II**), as an ionophore are prepared and purified as described previously [8,9].

2.1 Membranes preparation

Both membrane electrodes were prepared according to the method reported by Craggs *et al* [10]. Varying amounts of the ionophores (**I** and **II**), and PVC were dissolved in minimum amount of THF, separately. The solvent mediators DBP, DOP, DMS, DBBP and NaTBP were also added in different proportions to get membranes of different compositions. The solutions thus obtained, after complete dissolution of various components, were poured into a glass ring placed on a smooth and clean surface and allowed to evaporate at room temperature. After 48 h, non-transparent membranes were obtained with a thickness of 0.3 mm, then cut to size

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and attached to a glass tube with the help of PVC. The membranes were equilibrated with respective 0.01 M metal(II) nitrate solutions for 2-3 days and the potentials across the membranes were measured by setting up the following cell assembly.

Internal saturated calomel electrode | internal 0.01 M Metal(NO$_3$)$_2$ soln. | membrane | test solution | external reference electrodes (SCE).

All potential measurements were made by using digital pH metal potentiometer (Elico LI-10, India) in conjunction with saturate calomel electrodes (SCE) as reference electrodes.

2.2 ANALYTICAL PROCEDURES

Determination of lead in the effluents of lead coating material factory: An amount of 1.0 mL of effluent containing lead mineral sample was dissolved in 5.0 mL of concentrated nitric acid by heating and the pH of solution was adjusted to the optimum electrode pH-range (3.0-6.0). The solution was filtered through a filter paper. The filtered solution was diluted to 100 mL with distilled water in a calibrated flask.

Determination of mercury from a developed radiological film: A 6 cm × 9 cm sheet of the film was left in a furnance of 2 h at 700 ºC. The residue was dissolved in hot 1:1 nitric acid-water and the pH of the resulting solution was adjusted to about 5 by NaOH solution. Finally, the solution was completely transferred into a 250 mL volumetric flask and diluted to the mark with water.

Determination of mercury from a solder sample: A 0.324 of a sample of the solder was dissolved in 5 mL of conc. nitric acid and the solution was heated until fumes were observed. 5 mL of water was added to the solution after it had been cooled to room temperature, and the solution was again heated until fumes were observed. The treatment was repeated three times to ensure complete dissolution of the sample. The resulting solution was completely transferred into a 100 mL volumetric flask and diluted to the mark with water. Finally, 2 mL of this solution was diluted to 500 mL in a volumetric flask with water.

3. RESULTS & DISCUSSION

Calix[4]arenas are widely used as building units for construction of preorganized molecules for supramolecular and coordination chemistry applications. The calix[4]arene moiety can be substituted on the upper or lower rim with a large variety of substituents. The coordination properties of such ligands are tuned by appropriate choice of substituents, differing in hydrophilicity-hydrophobicity, the number and type of donor atoms present, *etc.* and moreover displayed the selectivities for various metal ions in the complexation, extraction, transport and liquid membrane experiments [11-16].

In order to obtain a clue about the stoichiometry and stability of the ionophore **I**-Pb^{2+} and ionophore **I**-Hg^{2+} ion complexes, in preliminary studies, we investigated the complexation of these functionalized calixarene molecules with Pb^{2+} and Hg^{2+} ion in acetonitrile solution spectrophotometrically. In both cases, the functionalized calixarene molecules concentrations in acetonitrile were kept constant at 5.0×10^{-5} M and a concentrated M^{2+} (M = Pb^{2+} and Hg^{2+}) solution in the same solvent was added while the absorbance intensity of the resulting solution at various M^{2+}/ functionalized calixarene molecules mole ratios were measured, until a desired mole ratio is reached. The corresponding spectra and the resulting mole ratio plots are shown in Fig. 1. As is obvious from Fig. 1, both the absorption spectra of functionalized calixarene molecules show distinct changes upon complexation with the respective metal ions in solution. In both cases, the resulting mole ratio plots are indicative of the formation of a stable 2:1 (functionalized calixarene molecules:M^{2+}) complex in acetonitrile solution. Based on the above observations, we decided to examine the capability of functionalized calixarene molecules (ionophores **I** and **II**) as a very suitable complexing agent for the construction of a heavy metals ion-selective electrodes. Thus, in preliminary experiments, functionalized calixarene molecules were used as a potential neutral ionophore for the preparation of PVC membrane ion-selective electrodes for a variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions.
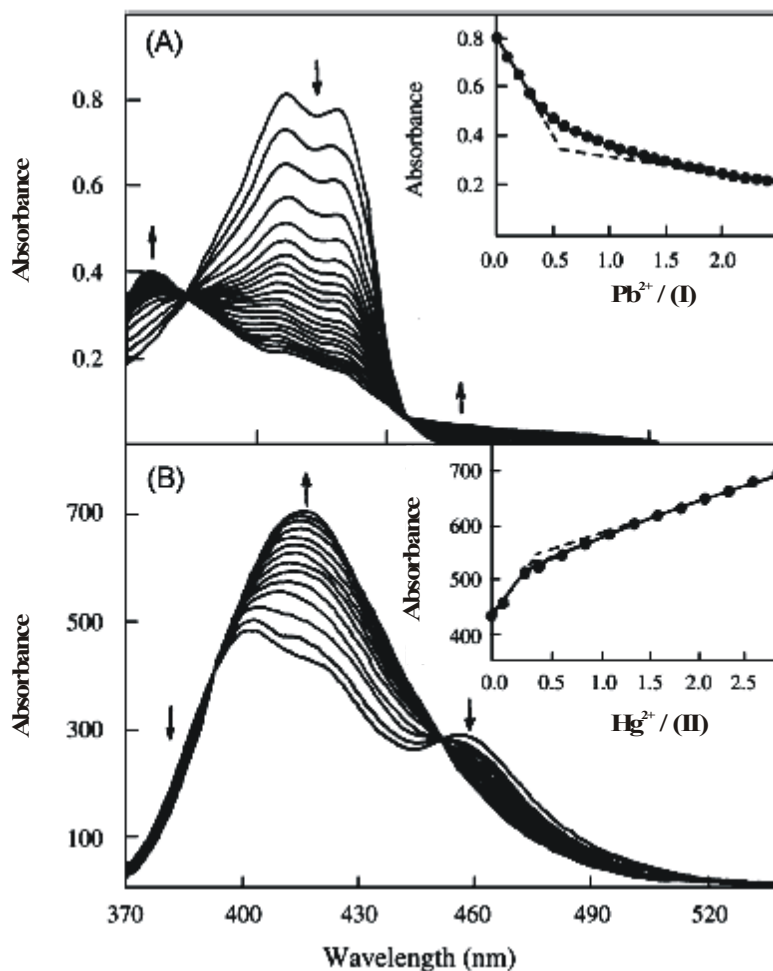
Fig. 1. Absorption spectra of a 5.0×10^{-5} M solution of Ionophores (**I** and **II**) in acetonitrile upon addition of increasing amount of Pb(II)/Hg(II) ion. The corresponding mole ratio plots are also shown in the insets.

Optimum membrane ingredients were tested by changing the plasticizer/PVC ratio from 0.5 to 4.0, while keeping the amount of ionophores constant (i.e., 3.5 %). The most sensitive, reproducible and stable results were obtained at a plasticizer/PVC ratio of about 2. It is reported that the response characteristics of ion-selective electrodes are largely affected by the nature of plasticizer used [17-20]. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [20,21]. Thus in the present work, we examined DOP, DBP, NB and TEP as plasticizer while keeping the membrane composition and nature of other ingredients constant. The slopes of the resulting potential responses for Pb^{2+} concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and for Hg^{2+} concentration range of 1.0×10^{-8} to 1.0×10^{-1} M, for the electrodes based on DBP, DOP, NB and TEP were found to be 29.45, 22.6, 18.2 and 20.9 mV/decade, respectively. Thus, DBP was selected as the best plasticizer in both cased for the preparation of Pb^{2+} and Hg^{2+}-selective PVC-membranes.

The average time required for the cations ion sensors to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of respective metal(II) ion solutions, each having a 10-fold difference in concentration, was measured. The static response time of the membrane sensor thus obtained was 10 s for Pb^{2+} concentrations and 15 s for Hg^{2+} concentration solutions (Fig. 2). It should be noted that the equilibrium potential

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remained constant for more than 6 min in both cases, after which only a slow divergence within the resolution of the potentiometer (± 1 mV) was reported. The both membrane electrodes prepared could be used for at least 8 months (while keeping dry) without any measurable divergence. It should also be noted that the reuse of the dried electrodes required further conditioning. The standard deviation of 10 replicate measurements is ± 0.4 mV for Pb^{2+} and ± 0.3 mV for Hg^{2+} electrodes.
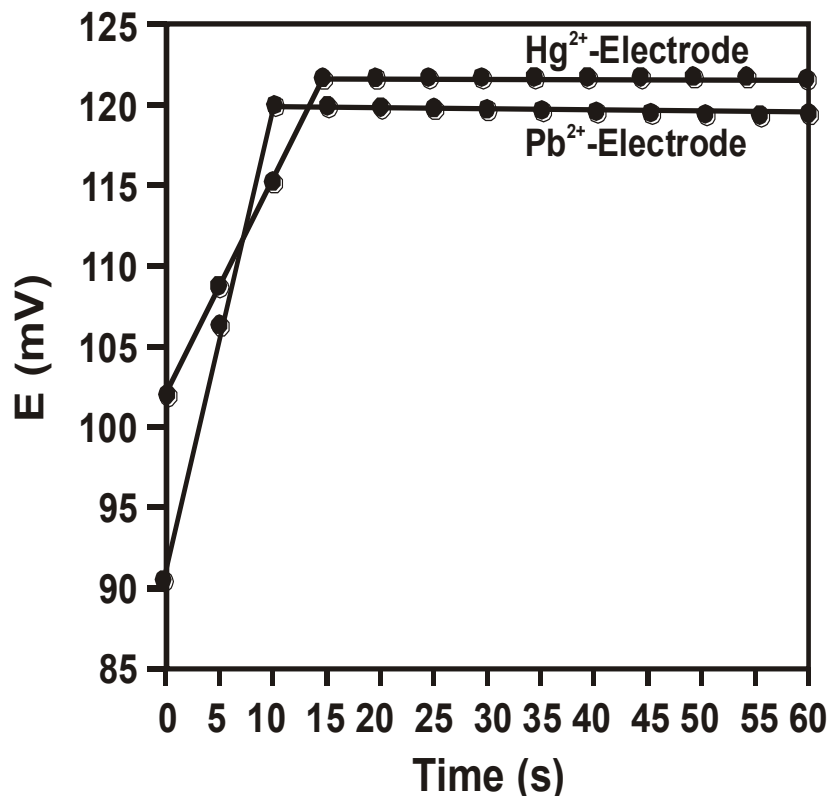

Fig. 2. Response time curves of the Proposed Pb(II)/Hg(II) ion selective electrodes

The influences of the pH of the test solution on the potential response of the sensors were tested in the pH range 2.0-11.0 and the results are shown in Fig. 3. As seen, both membrane electrodes can be suitably used in the pH range 3.5-8.0. However, the observed changes below and above this pH range may be due to protonation of the L and formation of some hydroxy complexes of respective bivalent metal ions in solution, respectively. The performances of the sensors were also investigated in partially non-aqueous medium using water-ethanol and water-acetone mixture up to 25% (v/v). In these mixtures, the working concentration range and slope remains almost the same (Table 1). However, above the 25% non-aqueous contents, the slope decreased appreciably, which indicates that the sensor has become less sensitive to both Pb^{2+} or Hg^{2+} ions in non-aqueous media. In addition to this, the response times of the membrane electrodes have also been investigated in non-aqueous systems and found that the response time are steady for few hours, after that the potential deviates drastically (Table 2).
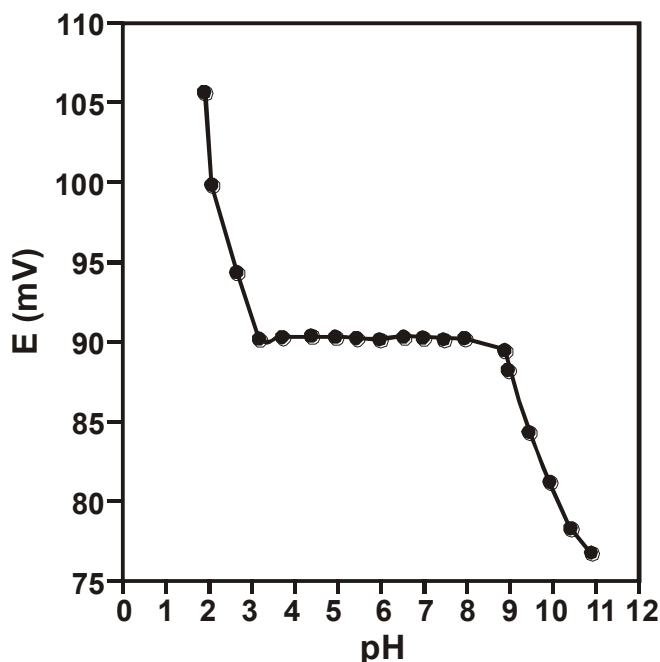
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Fig. 3. Effect of pH on potentiometeric response of the proposed Pb(II)/Hg(II) ion selective electrodes

Table-1 Effect of Non-Aqueous Solvents on Calibration Curve of Proposed Functionalized Calixarene Molecules Based I- And Ii-Pvc Membrane Electrodes

Solvent	Composition (v/v) %	Slope (mV/decade concentration change)	
		Pb^{2+}-electrode	Hg^{2+}-electrode
Water	----	29.45	29.35
Ethanol	2	29.45	29.35
Ethanol	5	29.45	29.40
Ethanol	10	29.40	29.45
Ethanol	15	29.45	29.45
Ethanol	25	29.45	29.45
Acetone	2	29.45	29.15
Acetone	5	29.45	29.42
Acetone	10	29.40	29.45
Acetone	15	29.45	29.45
Acetone	25	29.40	29.40

Table-2 Response Time for Non-Aqueous Solvents of Proposed Functionalized Calixarene Molecules Based I- And Ii-Pvc Membrane Electrodes

S.No.	Time (Sec)	Potential(-mV) 10% Ethanol		Potential(-mV) 25% Ethanol		Potential(-mV) 10% Acetone		Potential(-mV) 25% Acetone	
		Pb^{2+}-electrode	Hg^{2+}-electrode	Pb^{2+}-electrode	Hg^{2+}-electrode	Pb^{2+}-electrode	Hg^{2+}-electrode	Pb^{2+}-electrode	Hg^{2+}-electrode
1	0	02	03	01	03	05	03	09	02
2	5	09	12	04	06	08	09	11	06

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3	10	17	15	09	08	11	10	14	09
4	15	23	27	09	08	14	14	15	15
5	20	24	30	11	10	19	17	18	15
6	25	27	35	11	10	22	18	20	16
7	30	28	38	12	13	22	18	20	16
8	35	28	38	14	28	22	18	20	16
9	40	28	38	15	20	22	18	20	16
10	45	28	38	15	20	22	18	20	16
11	50	28	38	15	20	22	18	20	16
12	55	28	38	15	20	22	18	20	16
13	60	28	38	15	20	22	18	20	16

The selectivity behaviour is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the target sample is possible. To investigate the selectivity of the membrane electrode proposed, its potential response was investigated in the presence of various interfering foreign cations using the matched potential method (MPM) [22]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution [23]. Thus one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The concentration of metal(II) used, as primary ion in this study was 5.0×10^{-5} M. The resulting selectivity coefficients are summarized in Table-3. As seen, the most, hard, soft and borderline metal ions used did not disturb the function of the both Pb^{2+} and Hg^{2+} ion-selective membrane electrodes significantly.

Table-3 Selectivity Coefficients Calculated By Mi×Ed Potential Method for Proposed Functionalized Calixarene Molecules Based I- And Ii-Pvc Membrane Electrodes

Interfering ions	$K_{Pb^{2+},B}^{Pot}$	$K_{Hg^{2+},B}^{Pot}$	Interfering ions	$K_{Pb^{2+},B}^{Pot}$	$K_{Hg^{2+},B}^{Pot}$
NH_4^+	2.1×10^{-4}	1.7×10^{-4}	**Mg^{2+}**	2.5×10^{-4}	*5.6×10^{-3}*
Na^+	6.6×10^{-4}	3.9×10^{-4}	*Hg^{2+}*	1.1×10^{-4}	**-**
K^+	2.4×10^{-4}	4.7×10^{-4}	*Sn^{2+}*	5.7×10^{-4}	4.6×10^{-4}
Li^+	6.2×10^{-4}	2.3×10^{-4}	**Sr^{2+}**	5.6×10^{-4}	2.5×10^{-4}
Co^{2+}	1.7×10^{-3}	3.4×10^{-4}	**Cr^{3+}**	5.0×10^{-4}	2.4×10^{-4}
Cd^{2+}	3.5×10^{-3}	2.3×10^{-4}	Al^{3+}	5.7×10^{-4}	7.2×10^{-4}
Pb^{2+}	-	3.4×10^{-4}	Fe^{3+}	4.7×10^{-4}	6.8×10^{-4}
Zn^{2+}	3.0×10^{-3}	1.8×10^{-3}	Bi^{3+}	3.9×10^{-4}	1.3×10^{-4}
Ni^{2+}	3.2×10^{-3}	1.0×10^{-3}	La^{3+}	5.0×10^{-4}	1.5×10^{-4}
Cu^{2+}	3.2×10^{-3}	3.9×10^{-3}	Th^{4+}	6.0×10^{-4}	2.4×10^{-4}
Ba^{2+}	6.5×10^{-3}	1.5×10^{-3}	Cr^{6+}	2.0×10^{-4}	1.1×10^{-4}

The lead-selective membrane electrode introduced not only be used for direct determination of Pb^{2+} ions, but also it can be useful as an indicator electrode in titration of Pb^{2+} with CrO_4^{2-}. The results of the titration 50.0 mL of 1.0×10^{-3} M solution of Pb^{2+} ion with a 1.0×10^{-2} M potassium chromate solution are shown in Fig. 4. The potential of the electrode was decreased upon addition of the chromate precipitation agent. It is clear that the concentration of lead ion in solution can be accurately determined from the resulting neat titration curve providing a sharp end point. The proposed electrode was also successfully applied to the determination of lead in the residue of lead coating material factory situated in Avadh Industrial Area, Lucknow. The lead content in sample was determined by direct potentiometric (by using the standard addition method). The results obtained from three replicate measurements $(3.38 \pm 0.20) \times 10^{-4}$ M were found to be in satisfactory agreement with that obtained atomic

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absorption spectrometry, AAS, $(3.56 \pm 0.06) \times 10^{-4}$ M. Thus, it can be concluded that, the membrane electrode may have applications in the environmental monitoring of Pb^{2+} ions.
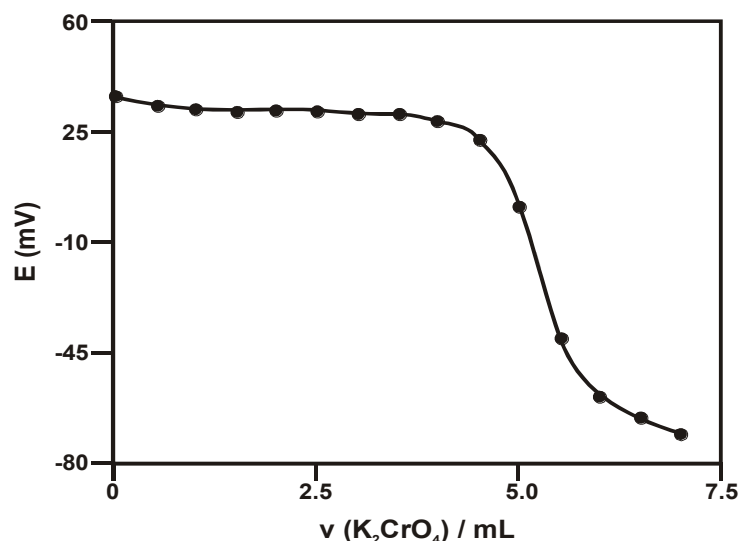

Fig. 4. Potentiometric titration curve of 50 ml of 1×10^{-3} M Pb^{2+} solution with 1×10^{-2} M of CrO_4^{2-} using the proposed membrane electrode as an indicator electrode

The practical utility of the proposed Hg^{2+}-membrane electrode was also tested successfully by its use as an indicator electrode for the titration of 50.0 mL of 4.9×10^{-4} M mercuric nitrate with a 5.0×10^{-2} M potassium iodide solution, and the resulting titration curve is shown in Fig. 5. As seen, the amount of mercuric ions can be accurately determined with the electrode. The electrode was also successfully applied to the direct determination of mercury content of a solder sample, a developed radiological film and a photographic developing solution, and the results, together with those obtained by AAS, are summarized in Table 4. As observed from Table 4, the results obtained by the proposed Hg^{2+}-selective electrode are in satisfactory agreement with those obtained by AAS.
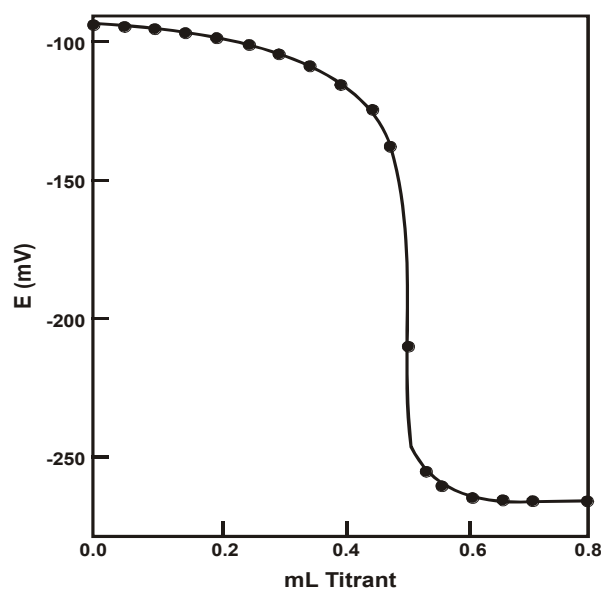

Fig. 5. Potentiometric titration curve of 50 mL of 4.9×10^{-4} M Hg^{2+} solution with 5.0×10^{-2} M of KI using the proposed membrane electrode as an indicator electrode

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Table-4 Mercury Content of the Final Solutions of Different Samples[a]

Sample	Proposed	ISE AAS
Solder	$(7.23 \pm 0.2) \times 10^{-5}$ M	$(7.21 \pm 0.1) \times 10^{-5}$ M
Radiological film Photographic	$(8.10 \pm 0.3) \times 10^{-5}$ M	$(8.05 \pm 0.05) \times 10^{-5}$ M
Developing solution	$(9.3 \pm 0.3)\ 10^{-5}$ M	$(8.99 \pm 0.45) \times 10^{-5}$ M

[a]The results of three replicate measurements.

4. CONCLUSION

The incorporation of two functionalized calixarenes molecules 26,28-dihydroxy-25,27-dimethoxycalix-[4]arene-11,23-diphosphonic acid for Pb(II) and 25,26,27,28-tetra(2-dimethydithiocarbamoly-ethoxy)calix[4]-arene for Hg(II) as an ionophore incorporating into the PVC matrix along with NPOE as a plasticizer and NATPB as a solvent mediator developed a specific ISEs. Fabricated ISEs composition shows quick response time (15 s), long shelf-life and selectivity (on the order of 10^{-4} and 10^{-5} M) over a number of interfering cations. The developed electrodes successfully detects Pb(II) and Hg(II), from the real samples and the result is compared with the conventional AAS technique.

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