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Chelating ionophores based electrochemical sensor for Hg(II) ions

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Abstract

Poly(vinyl chloride) (PVC)-based membranes of pyrimidines, 1-(2′-aminoaryl)-4, 4, 6-trimethyl-1, 4, 5, 6-tetrahydro-6-hydroxypyrimidine-2-thiol (HPT) (R = –H, $–CH_3$, $–OCH_3$) with sodium tetraphenylborate (NaTPB) as an anion inhibitor and dibutylphthalate (DBP), dioctylphthalate (DOP), dibutyl (butyl) phosphonate (DBBP) and 1-chloro naphthalene (CN) as plasticizing solvent mediators were prepared and used as Hg^{2+} selective electrodes. Optimum performance was observed with the membrane having HPT($–OCH_3$)–PVC–NaTPB–DOP in the ratio 1:33:1:65 (w/w). The electrode works well over a wide concentration range 5.0×10^{-6}–1.0×10^{-1} M (detection limit 1.0 ppm) with Nernstian compliance (29.5 mV decade^{-1}) between pH 2.5 and 4.0 with a fast response time of about 20 s. The selectivity coefficient values of the order of 0.001 for mono-, bi- and trivalent cations, indicate high selectivity for Hg^{2+} ions over these cations. Further, anions such as Cl^- and SO_4^{2-} do not interfere in the functioning of Hg^{2+} sensor. The electrodes were used over a period of five months with good reproducibility (std. dev. ± 0.2 mV) and the performance of the electrodes was found satisfactory even up to 10% nonaqueous medium. The electrode assembly was also evaluated for potentiometric determination of Hg^{2+}.

1. Introduction

The need for fast and accurate quantification of heavy metals has long been realized. Amongst several heavy metals, determination of mercury is often required due to its high toxicity. Several analytical methods for the direct determination of mercury are available, of these spectrophotometry using dithizone, atomic absorption spectrophotometry and radioisotope methods are generally employed. These methods usually involve complicated methodology, for sample pretreatment, and are cost ineffective. A technique which permits rapid, accurate and low-cost analysis is the ideal choice and such a situation is met to a great extent by ion-sensors. These sensors offer several advantages over other analytical techniques particularly in regard to speed, simplicity and cost of operating systems.

Several mercury-selective sensors based on AgI–Ag_2S and dithiacrown ethers have been reported [1–6]. In addition to these, liquid membrane electrodes using Hg(II)-chelates have also been tried for Hg^{2+} determination [7–9]. Efforts made in this direction have been summarized by Radić [10]. However, these electrodes generally have slow response time, poor selectivity, and interference from Ag^+ ions. Therefore, the need of a mercury sensor with a fast response time, wide working concentration range, high selectivity and good reproducibility has been often realized.

Applications of cheating ionophores in the selective detection of metals is well established and a number of sensors based on these ionophores are documented in the periodical reviews published by Janata and coworkers [11]. We have earlier reported cerium(IV) selenite and antimony(III) arsenate, based inorganic ion-exchange membranes using polystyrene as binder [12, 13]. These electrodes exhibit linearity in the concentration range 1.0×10^{-5}–1.0×10^{-1} M in Nernstian manner with good reproducibility, moderate response time (30–40 s) and fairly good selectivity over a few cations. In the present communication, efforts have been made using 1-(2′-aminoaryl)-4,4,6-trimethyl-1,4,5,6-tetrahydro-6-hydroxypyrimidine-2 thiol (HPT) as a chelating ionophore. These pyrimidines exhibited excellent selectivity for Hg^{2+} ions in solvent extraction studies [14] and are thus likely to act as suitable sensor materials.

2. Experimental details

2.1. *Reagents*

All reagents used were of analytical grade. High molecular weight poly(vinyl chloride) (PVC), Aldrich; sodium tetraphenylborate (NaTPB), BDH, England; dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel India; dibuty(butyl) phosphonate (DBBP), Mobil, USA and 1-chloro naphthalene (CN), E. Merck, Germany were used without further purification. Metal (nitrates) solutions prepared were standardized according to appropriate and approved methods. Solutions of different concentrations were made by diluting 0.1 M stock solutions. Double distilled water was used throughout.

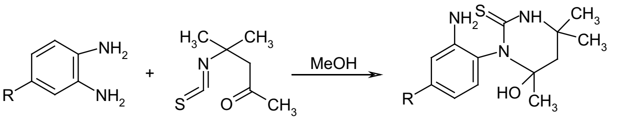
2.2. *Apparatus*

Potentiometric measurements were carried out at 25 ± 0.1 °C on a Mettler Toledo pH/ion analyser (model MA235). The membranes were equilibrated for 3–5 days in 0.5 M Hg^{2+} solution and the potentials were measured using PVC matrix membranes in conjunction with saturated calomel electrodes (SCE) by setting up the following cell assembly:

$$\text{SCE}\,|\,\text{internal solution }(0.1\,\text{M Hg}^{2+})$$
$$|\,\text{membrane}\,|\,\text{test solutions}\,|\,\text{SCE}$$

2.3. *Synthesis of pyrimidines (HPT)*

HPT was prepared by the reported method [15] by dissolving 4-substituted-*o*-phenylenediamine (2.16 g, 0.02 M) in methanol (20 ml) and adding to it 4-methyl-4-isocyanato-2-pentanone (3.50 g, 0.22 M). The reactants were heated under reflux for 4 h. Solvent was removed under reduced pressure and the solid so obtained was filtered, washed with cold methanol and air-dried. The product was then purified by recrystallization from THF. By changing the substituent R in 2′-aminoaryl group, three HPT (R = –H, (HPT_a), $-CH_3$ (HPT_b) and $-OCH_3$ (HPT_c) ionophores were prepared *via* Equation 1. These compounds were characterized by ^1H NMR and C,H,N analysis [15].



2.4. *Preparation of membranes*

The membranes were prepared by adding THF (5–10 ml) to various amounts of (1–10%) of HPT and anion excluder NaTPB (1%). Solvent mediators (DBP, DOP, DBBP and CN) and appropriate amounts of PVC (33%) were further added to obtain membranes of different compositions (Tables 1–3). The optimum composition of the membranes was obtained after a good deal of experimentation. After complete dissolution of all the components and thorough mixing, the homogeneous mixture was poured into polyacrylates rings placed on a smooth glass plate. THF was allowed to evaporate at room temperature, after 24 h, transparent membranes of 0.5 mm thickness were obtained. A 5 mm diameter piece was cut out and glued to one end of a Pyrex glass tube. The membranes were further used for potential measurement studies.

3. Results and discussion

3.1. *Working concentration range and slope*

The lowest detection limit and slope for all the membrane electrodes (no. 1–15) are recorded in Tables 1–3. They exhibit linearity in the concentration range as shown in Figures 1, 2 and 3 for the membranes consisting of HPT_a, HPT_b and HPT_c ionophores, respectively. The membrane of HPT_a (no. 1) shows linearity in the concentration range 3.0×10^{-4}–1.0×10^{-1} M with a slope of 25.5 mV decade^{-1}. The solvent mediators, namely, DBP, DOP, DBBP, CN etc. were added to improve the performance of the membranes. The lipophilicity, polarity, viscosity and dielectric constant of solvent mediator play a significant role in the optimization of the membrane ingredients and functioning of the sensor so as to ensure a long and stable response. The addition of solvent mediator DBP and DOP to the HPT_a membrane enhanced the working concentration range to 5.0×10^{-5}–1.0×10^{-1} and 1.0×10^{-5}–1.0×10^{-1} M with an improved slope of 28.5 and 29.0 mV decade^{-1}, respectively (Figure 1). Improvements in working concentration range and slope were also observed using HPT_b as membrane material and DBP and DOP as solvent mediators. Further, the membrane (no. 11) of HPT_c demonstrates a linear potential response in the concentration range 1.0×10^{-5}–1.0×10^{-1} M with a slope of 27.0 mV decade^{-1} of activity. On the addition of solvent mediator DOP, an improvement in the working concentration range (5.0×10^{-6}–1.0×10^{-1} M) and Nerns-

Table 1. Composition of PVC membranes of HPT_a and performance characteristics of Hg^{2+} selective electrodes based on them

Membrane or electrode	Percentage (w/w) of various components in membranes							Detection limit /ppm	Slope mV decade^{-1}	Response time /s
	HPT_a	PVC	NaTPB	DBP	DOP	DBBP	CN			
1	1	99	–	–	–	–	–	60.1	25.5	90
2	1	33	1	65	–	–	–	10.0	28.5	25
3	1	33	1	–	65	–	–	200	29.0	30
4	1	33	1	–	–	65	–	100	26.0	40
5	1	33	1	–	–	–	65	160	25.0	45

Table 2. Composition of PVC membranes of HPT_b and performance characteristics of Hg^{2+} selective electrodes based on them

Membrane or electrode	Percentage (w/w) of various components in membranes							Detection limit /ppm	Slope /mV decade^{-1}	Response time /s
	HPT_b	PVC	NaTPB	DBP	DOP	DBBP	CN			
6	1	99	–	–	–	–	–	100	25.0	75
7	1	33	1	65	–	–	–	6.00	28.0	28
8	1	33	1	–	65	–	–	200	28.5	25
9	1	33	1	–	–	65	–	60.1	25.5	45
10	1	33	1	–	–	–	65	16.0	26.0	45

Table 3. Composition of PVC membranes of HPT_c and performance characteristics of Hg^{2+} selective electrodes based on them

Membrane or electrode	Percentage (w/w) of various components in membranes							Detection limit /ppm	Slope /mV decade^{-1}	Response time /s
	HPT_c	PVC	NaTPB	DBP	DOP	DBBP	CN			
11	1	99	–	–	–	–	–	20.1	27.0	80
12	1	33	1	65	–	–	–	4.00	28.0	30
13	1	33	1	–	65	–	–	1.00	29.5	15
14	1	33	1	–	–	65	–	10.0	33.2	40
15	1	33	1	–	–	–	65	16.0	35.0	30

tian slope (29.5 mV decade^{-1} of activity) was observed. It is reported that the addition of solvent mediators not only improves the workability of the membrane but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [16–20]. However, the selectivity is usually unaffected and mainly depends on the metal-ionophore interaction. Repeated monitoring of potentials (20 measurements) at the same concentration (1.0×10^{-3} M) gave a standard deviation of ±0.2 mV. Since HPT_c-based electrode (no. 13) exhibited the lowest detection limit (1.0 ppm) with Nernstian compliance (Table 3), only it was used for further studies, except for selectivity studies wherein the membrane of all the ionophores (HPT_a, HPT_b and HPT_c) were investigated.

3.2. *Response and lifetime*

The response time is the time taken by the electrode to achieve a stable potential. Electrodes without solvent mediator gave a steady response in 75–90 s while the electrodes with plasticizers (DBP and DOP) as

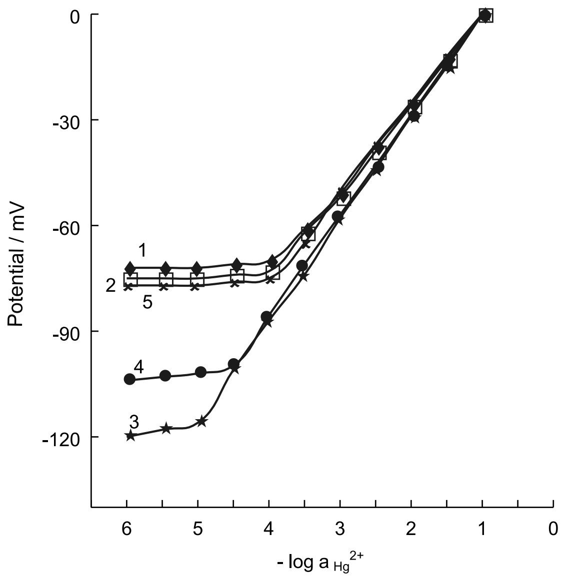


Fig. 1. Variation of cell potential with activity of Hg^{2+}; PVC based membrane of HPT_a without solvent mediator (1), with solvent mediators, DBP (2), DOP (3), DBBP (4) and CN (5).

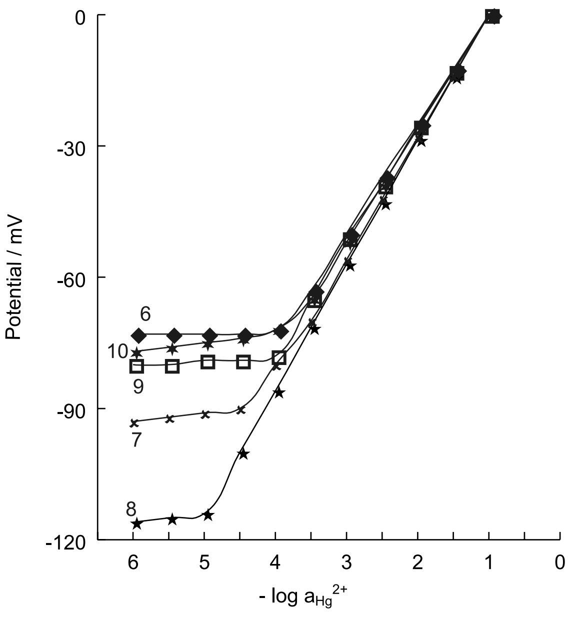


Fig. 2. Variation of cell potential with activity of Hg^{2+}; PVC based membrane of HPT_b without solvent mediator (6), with solvent mediators, DBP (7), DOP (8), DBBP (9) and CN (10).

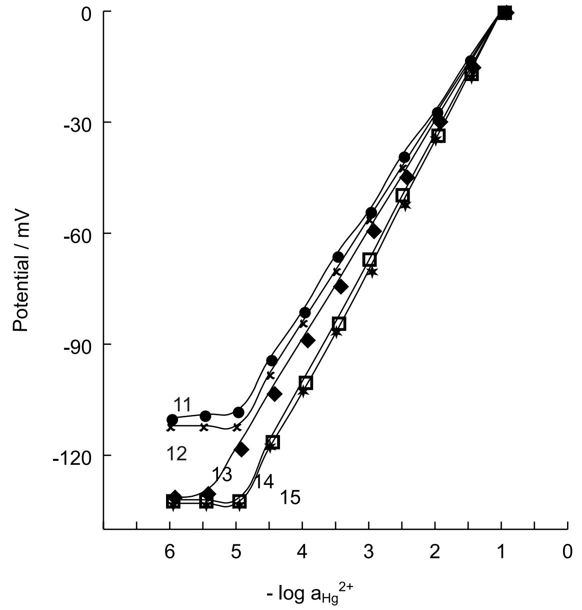


Fig. 3. Variation of cell potential with activity of Hg^{2+}; PVC based membrane of HPT_c without solvent mediator (11), with solvent mediators, DBP (12), DOP (13), DBBP (14) and CN (15).

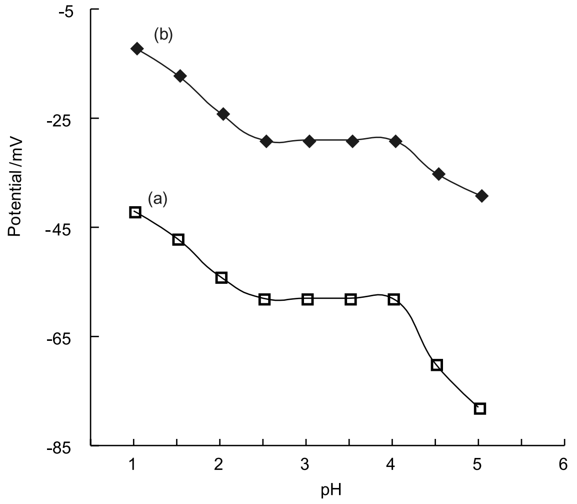


Fig. 4. Effect of pH on cell potential; $[Hg^{2+}] = 1.0 \times 10^{-3}$ (a) and 1.0×10^{-2} (b) for electrode 13.

membrane ingredients achieved equilibrium response within 15–30 s over the whole concentration range. The main factor for limited lifetime is the loss of ionophores from the membrane while contacting with aqueous solution. Sufficient lipophilicity of ionophore and plasticizer ensures stable potentials and long lifetimes [16–18]. The membranes were used over a period of five months without significant change in potentials. Whenever a drift in potential was observed, membranes were re-equilibrated with 0.5 M Hg^{2+} for 2–3 days. The membranes were stored in 0.1 M Hg^{2+} solution when not in use.

3.3. *pH and nonaqueous effect*

The dependence of electrode potential response on pH was tested over the range 1.0–5.0 for 1.0×10^{-2} and 1.0×10^{-3}M Hg^{2+} ions (Figure 4). The operational range was studied by varying the pH of the test solutions with nitric acid or ammonia. Figure 4 shows that the potential is independent of pH in the range 2.5–4.0. The performance of these sensor systems was also investigated in nonaqueous media using water–methanol and water–ethanol mixtures. The membranes work satisfactorily up to a maximum 10% (v/v) content of methanol and ethanol. In these mixtures, the working concentration range and slope remained unaltered; however, above a 10% nonaqueous content the slope was appreciably decreased and the membranes were destroyed due to leaching of the ionophore from the PVC matrix.

3.4. *Potentiometric selectivity*

The potentiometric selectivity coefficients were determined by the 'fixed interference method' at 1.0×10^{-2} M concentration of interfering ions (Table 4). The selectivity coefficient values of the order of 0.001 are indicative that the sensor is selective for Hg^{2+} ions over a number of mono, bi and trivalent cations (except for Na^+ and Ag^+ ions). Therefore, the electrodes can be used for the determination of Hg^{2+} in the presence of these cations. A critical comparison of potentiometric selectivity data of Table 4 shows that the electrode based on HPT_c is more selective for Hg^{2+} ions as compared to the electrodes of HPT_a and HPT_b. Further, the selectivity of each type of electrode having different plasticizers such as DBP, DOP, DBBP, CN was found to be independent of the lipophilicity, polarity and dielectric constant of the solvent mediator [20].

Ag^+ is known to cause serious interference in the determination of Hg^{2+} ions. Results presented in Table 4 further corroborate these observations. However, little

Table 4. Selectivity coefficients of electrodes 3, 8 and 13 based on the membranes of HPT_a, HPT_b and HPT_c, respectively

Interfering ion (B)	Selectivity coefficients $[K^{Pot}_{Hg^{2+}}]_B$		
	HPT_a	HPT_b	HPT_c
Li^+	4.5×10^{-3}	4.0×10^{-3}	1.1×10^{-3}
Na^+	6.5×10^{-1}	6.3×10^{-1}	5.0×10^{-1}
K^+	6.0×10^{-3}	6.4×10^{-3}	1.2×10^{-3}
Tl^+	7.8×10^{-3}	7.2×10^{-3}	2.0×10^{-3}
Cs^+	6.0×10^{-3}	5.4×10^{-3}	2.1×10^{-3}
Ag^+	7.4×10^{-1}	7.2×10^{-1}	7.0×10^{-1}
Ca^{2+}	6.3×10^{-3}	6.5×10^{-3}	1.5×10^{-3}
Sr^{2+}	8.2×10^{-3}	8.5×10^{-3}	1.2×10^{-3}
Ba^{2+}	5.6×10^{-3}	5.0×10^{-3}	1.5×10^{-3}
Mg^{2+}	6.1×10^{-3}	6.0×10^{-3}	1.0×10^{-3}
Ni^{2+}	7.5×10^{-3}	7.0×10^{-3}	1.8×10^{-3}
Cd^{2+}	8.2×10^{-3}	7.0×10^{-3}	1.2×10^{-3}
Zn^{2+}	8.1×10^{-3}	8.5×10^{-3}	2.4×10^{-3}
Cu^{2+}	7.4×10^{-3}	7.5×10^{-3}	1.5×10^{-3}
Co^{2+}	8.0×10^{-3}	8.5×10^{-3}	1.2×10^{-3}
Fe^{3+}	7.2×10^{-3}	7.0×10^{-3}	1.0×10^{-3}
Ce^{3+}	8.4×10^{-3}	8.0×10^{-3}	1.8×10^{-3}

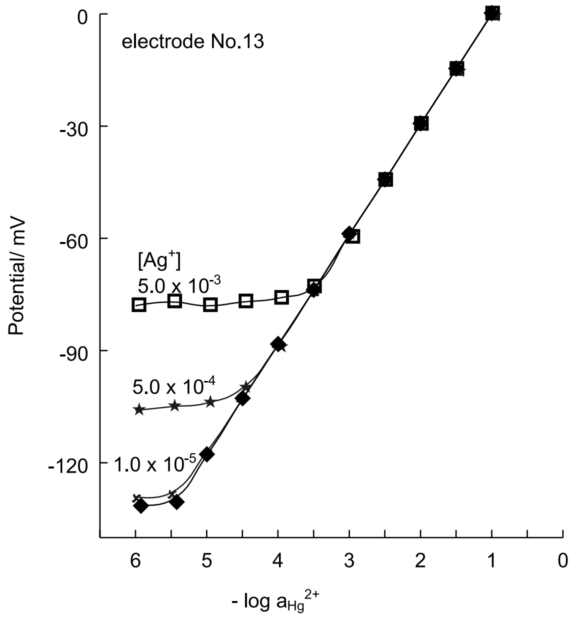


Fig. 5. Variation of cell potential with activity of Hg^{2+} (electrode 13) at different concentration levels of Ag^+ ions.

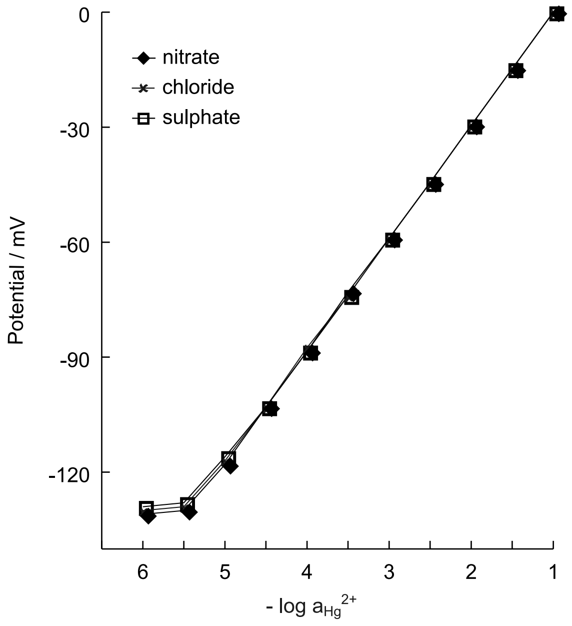


Fig. 7. Effect of anions; variation of cell potential with activity of Hg^{2+}.

interference is expected if they are present in lesser amounts as the selectivity is concentration dependent and varies with the concentration ratio of primary and interfering ions. In order to know the exact concentration of Ag^+ and Na^+ that can be tolerated in the determination of Hg^{2+}, some mixed run studies [21–26] were carried out. It is seen from Figure 5 that the presence of Ag^+ at a concentration of 1.0×10^{-5} M caused no divergence in the potential against concentration plot as obtained in pure Hg^{2+} solution (no. 13). Thus, the electrode can tolerate Ag^+ ions at the concentration $\leqslant 1.0 \times 10^{-5}$ M over the whole working concentration range. However, Ag^+ ions present in higher concentration caused divergence from the original potential againts Hg^{2+} concentration plot and thus, cannot be tolerated over the whole concentration range. It is seen from Figure 5 that Hg^{2+} can be determined in the reduced concentration range, 5.0×10^{-5}–1.0×10^{-1} M and 5.0×10^{-4}–1.0×10^{-1} M in the presence of 5.0×10^{-4} and 5.0×10^{-3} M Ag^+ ions, respectively. Similar studies for Na^+ ions revealed that the presence of Na^+ reduced the lower detection limit of Hg^{2+} ions to 1.0×10^{-5} and 5.0×10^{-5} M in the presence of 1.0×10^{-4} and 1.0×10^{-3} M Na^+ while $\leqslant 5.0 \times 10^{-5}$ M

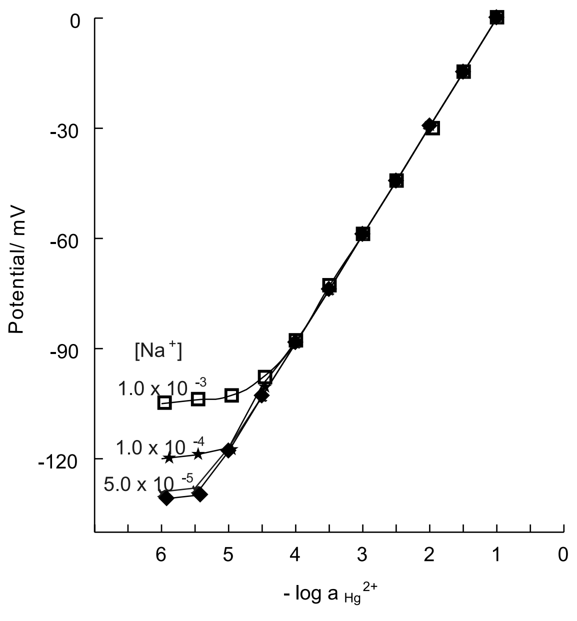


Fig. 6. Variation of cell potential with activity of Hg^{2+} (electrode 13) at different concentration levels of Na^+ ions.

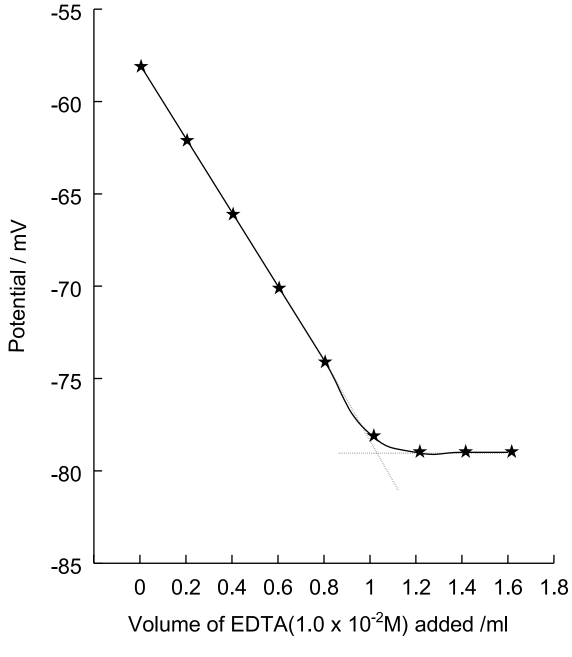


Fig. 8. Potentiometric titration plot of Hg^{2+} ions (1.0×10^{-3} M) with EDTA (1.0×10^{-2} M).

Na^+ can be tolerated over the whole concentration range (Figure 6).

Further, to investigate the effect of anions, cell potentials were obtained using chloride and sulfate salts of mercury. The plots in Figure 7 are all of a similar nature indicating no significant change in the working concentration range and slope. Therefore, anions such as Cl^- and SO_4^{2-} do not cause interference in the determination of Hg^{2+} ions. This may be attributed to the addition of NaTPB as membrane ingredient, which replaces NO_3^- in the membrane and inhibits the interference of anions.

3.5. *Potentiometric titration*

The electrode was also used to determine the end-point in the potentiometric titration of Hg^{2+} with EDTA. A 10 ml (1.0×10^{-3} M) solution of Hg^{2+} was titrated with 1.0×10^{-2} M EDTA solution at pH 6.0 using hexamine buffer. The addition of EDTA caused the formation of Hg–EDTA complex, and a decrease in Hg^{2+} concentration caused a decrease in potential. The plot given in Figure 8 is not of standard shape because of the response of the electrode to Na^+ ions and the fact that of the assembly is functioning above the working pH range. However, the end point corresponds to the stoichiometric formation of Hg–EDTA complex. Therefore, the membrane can be successfully used as an indicator electrode for determining Hg^{2+} by potentiometric titration.

4. Conclusion

Among the electrodes prepared (nos. 1–15) the membrane having HPT_c, NaTPB, DOP and PVC as ingredients (no. 13) exhibited the optimum performance with a detection limit of 1.0 ppm. The electrode is superior to existing electrodes in terms of fast response (15 s) time and selectivity over a number of cations while comparable with regard to other parameters such as working concentration range, Nernstian slope, pH range, shelflife and reproducibility. The electrodes are mechanically and chemically stable with a useful lifetime of five months. Further, the electrode can be used to determine Hg^{2+} ions both by direct potentiometry and titration.

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