N′, N″, N‴-tris(2-pyridyloxymethyl) ethane as ionophore in potentiometric sensor for Pb(II) ions

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Abstract. N′,N″,N‴ tris(2-pyridyloxymethyl) ethane (TPOME) has been used as an ionophore in a polyvinylchloride (PVC)-based membrane. Membrane electrode with a composition 30:5:62:3 (PVC:TPOME:o-NPOE:NaTPB) exhibits Nernstian response towards Pb(II) ions with a slope of 30 mV/decade, over a concentration range of 1×10^{-5} M to 1×10^{-1} M. Potential response remains almost unchanged over pH range of 3.7–6.4. The electrode shows fast response time of 15 ± 2 s and a lifetime of four months. It shows good selectivity for Pb(II) ions over other mono-, di- and trivalent cations. Electrode response is satisfactory in mixed solvent media up to 30% (v/v) non-aqueous contents. Selectivity of the ionophore for Pb(II) ions was determined by spectrophotometric method. The electrode can also be used as an indicator electrode in potentiometric titration of Pb(II) ions with standard chromate solution and its determination in real-life samples. Surface morphology of membrane electrode at different stages of its development and use is also discussed.

Keywords. PVC; neutral carrier; ionophore; liquid membrane; lead ions; selectivity coefficients; Nernstian response.

1. Introduction

Development of electroactive artificial ionophores for selective cation recognition has attained significant interest, as cations play a fundamental role in a wide range of chemical and biological processes.[1,2] Potentiometric sensors have attracted attention for their simple construction, low-cost, good selectivity, sensitivity and offer quantitative information using inexpensive and portable equipment.[3] Several analytical techniques such as atomic absorption spectrometry (AAS),[4] inductive coupled plasma atomic emission spectrometry (ICP-AES), inductive coupled plasma mass spectrometry (ICP-MS),[5] anodic striping voltametry,[6] chromatography,[7] spectrophotometry[8] and low detection limit ion selective electrode (ISE),[9,10] etc. are available for quantification of lead. Lead is one of the most toxic and hazardous species because of its non-biodegradability. Exposure to high concentration of lead can cause serious health problems, including nervous system dysfunction, haemotoxic effects, gastrointestinal tract alterations, interference in the metabolism of calcium and vitamin D and impaired haemoglobin formation, causing anaemia.[11] The World Health Organization (WHO) and US Environmental Protection Agency (EPA) have established an action level of 15 ppb for lead in drinking water.[12]

Tripodal ionophores are gaining increasing interest as tools for analysis and separation of metal ions as well as many biological and other applications. It is a unique class of complexing agents in which each of the three legs, containing at least one donor atom (X, Y and Z), is connected to a bridgehead atom. The first new tripodal compound was reported in 2000 by Berrocal *et al.* with sulphate recognition properties for anion-selective electrodes.[13] Yan *et al.* synthesized 1,1,1-tris(N-ethyl-N-phenylamino-carboxylmethoxymethyl) propane and used it as an ionophore in polyvinylchloride (PVC) membrane electrode for the analysis of alkali and alkaline earth metal cations.[14] Kim *et al.* published a paper on new C-3 symmetric, tripodal trifluoroacetophenone derivatives as anion ionophores.[15] Mittal *et al.* published a paper on 8-hydroxyquinoline-based neutral tripodal ionophore as a copper (II) selective electrode.[16] Several studies have shown that tripodal ligands can be categorized by two main groups: flexible tripodal ligands and rigid tripodal ligands.[17–23]

A number of lead-selective sensors have been developed, and many ligands have been investigated as lead-sensing agents as ionophores incorporated into the PVC membranes in ion-selective electrodes (ISE).[2] Crown
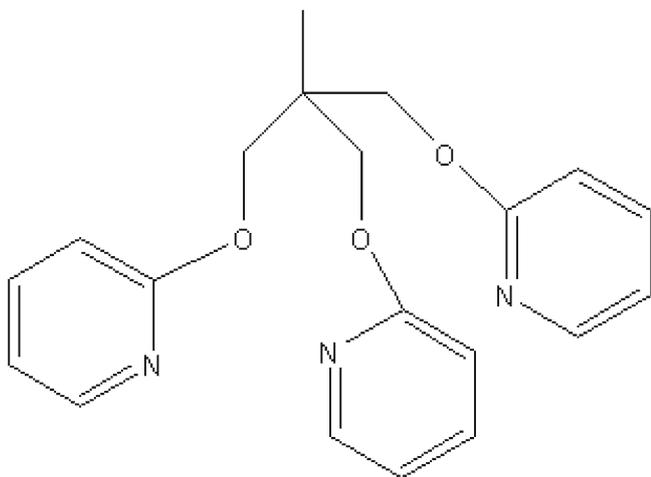
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Figure 1. Chemical structure of N′,N″,N‴-tris(2-pyridyloxymethyl) ethane (TPOME).

ether derivatives (18-crown-6,[24] monobenzo-15-crown-5,[25] 4′-vinylbenzo-15-crown-5,[26] nitrobenzo18-crown-6 (NB18C6),[27] dibenzopyridino-18-crown-6,[28] 1,10-dibenzyl-1,10-diaza-18-crown-6,[29] N,N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane,[30] cryptand (222),[31] calixarene derivatives (4-t-butylcalix[4]arene),[32] 4-t-butylcaix[6]arene,[33] 5,11,17,23-tetrakis[(p-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene,[34] 5,11-dibromo-25,27-dipropoxycalix[4]arene,[35] calixarene phosphine oxide derivatives,[36,37] double-armed calix[4]arene amide derivatives,[38] porphyrin ionophores (5,10,15,20-tetrakis(3,4-dimethoxyphenyl) porphyrin,[39] tetraphenylporpyrin,[40] amide-linked diporphyrin xanthenes[41] and Schiff base derivatives (N,N′-bis(5-methyl salicylidine)-2,6-pyridinediamine[42] have been used as ionophores in lead selective sensors. Other ionophores employed for fabrication of lead ISEs are acyclic amides,[43] macrocyclic oxamides,[44] dithiomides,[45] pyridine carboxamide derivatives[46] and 9,10-anthraquinone derivatives.[47] In this study, N′,N″,N‴ tris(2-pyridyloxymethyl) ethane (TPOME) ionophore is a flexible molecule containing the nitrogen donor groups. In this branch of tripodal ligands, N-containing motifs are usually soft donor groups. Presence of donor groups in the tripodal ligand leads to complexation of the ligand with metal with a good formation constant. Chemical structure of TPOME used in this study as an ionophore is shown in figure 1.

2. Experimental

2.1 *Reagents*

High molecular weight PVC, sodium tetraphenylborate (NaTPB), metal nitrates were received from Sigma Aldrich USA, Analytical reagent grade tetrahydrofuran (THF), nitric acid, sodium hydroxide were obtained from SD-fine India. Solutions of metal nitrates were prepared in doubly distilled deionized water and standardized by the reported method wherever necessary. Working solution of different metal concentrations was prepared by diluting 0.1 M stock solution.

2.2 *Preparation of PVC membranes*

PVC-based membranes[48] were prepared by dissolving different amounts of the ionophore (I), anion excluder NaTPB, and solvent mediator o-NPOE and PVC in THF. Different components were mixed in terms of weight percentages as per combinations given in table 1. After complete dissolution of all the components, the homogenous mixture was concentrated by evaporating THF and then poured in glass rings placed on smooth glass plates. To obtain membrane with reproducible characteristics, the solvent evaporation was carefully controlled; otherwise, morphology and thickness of membranes shows significant variations which may ultimately affect sensor response. Transparent membranes so obtained were removed carefully from the glass plate. A 6 mm diameter piece of the membrane was cut out and glued to one end of the 'Pyrex' glass tube. The membrane thus prepared was equilibrated for two days in Pb^{2+} (0.1 M) solution. It is known that sensitivity, linearity and selectivity for a given ionophore depend significantly on the membrane composition and nature of plasticizers used.[49] Hence, several membranes of varying composition were prepared and investigated. The membrane which gave reproducible results and best performance characteristics was selected for detailed studies. Optimum composition of the membrane with best performance is given in table 1.

2.3 *Potential measurements*

Potential measurements were carried out at 25 ± 0.1C with a digital Euip-Tronics potentiometer (EQ-602, accuracy, ±0.1 mV, Mumbai, India) and pH of the solution was monitored simultaneously using Equip-Tronics pH meter (EQ-614, Mumbai, India) and conventional glass pH electrode.

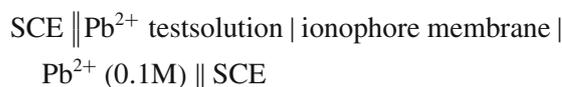All emf measurements were carried out with the following electrochemical cell assembly.

SCE ‖ Pb^{2+} testsolution | ionophore membrane |
Pb^{2+} (0.1M) ‖ SCE

Table 1. Optimization of membrane ingredients and their response characteristics for Pb(II) selective electrode.

Sr. No.	Ionophore (% w/w)	PVC (% w/w)	NaTPB (% w/w)	o-NPOE (% w/w)	*Lower detection limit (M)	Slope (mV/decade)
1	–	33	–	–	–	–
2	–	33	–	67	–	–
3	1.5	33	–	65.5	5×10^{-5}	33
4	2.0	33	–	65.0	5×10^{-5}	35
5	3.0	33	–	64.0	6×10^{-5}	37
6	5.0	33	–	62.0	5×10^{-5}	32
7	6.0	33	–	61.0	1×10^{-5}	30
8	8.0	33	–	59.0	1×10^{-5}	25
9	10.0	33	–	57.0	6×10^{-5}	25
10	3.0	32	1.5	63.5	6×10^{-5}	29
11	**5.0**	**30**	**3.0**	**62.0**	**6×10^{-5}**	**30**
12	6.0	29	6.0	59.0	8×10^{-5}	35
13	6.0	30	3.0	61.0	1×10^{-4}	29

*Lower range of the calibration plot.
Electrode composition selected for further studies is given in bold

3. Results and discussion

3.1 *Spectrophotometric study of TPOME and metal ion interaction*

To explore the binding efficiency of TPOME towards various metal ions, UV-visible spectroscopic technique was applied.[50] The complexation ability of TPOME was examined in methanol (1×10^{-5} M) with the addition of 1×10^{-5} M of different metal ions such as Pb^{2+}, Cu^{2+}, Co^{2+} and Ca^{2+}. A UV-visible spectrum of TPOME after the addition of metal ions shows a shift in position of absorption peaks and absorbance values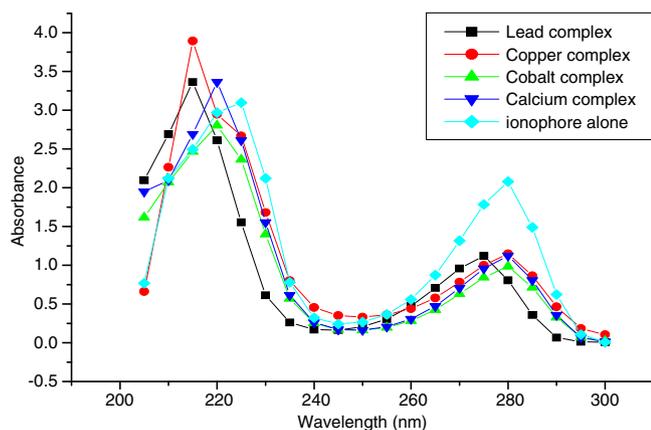 in figure 2. TPOME alone exhibits two absorption peaks at 280 nm and 227 nm. After the addition of required amounts of these ions separately, spectra were taken. When Pb(II) interacts with TPOME, pronounced changes in the absorption spectra are observed, absorbance peak at 227 nm shifted to 214 nm (blue shift) and intensity of the band increased while absorption peak at 280 nm shifted to 273 nm (blue shift) and intensity of the band decreased slightly. In case of the other metal ions, the peak at 280 nm remains same in the complexation state while peak positions at 227 nm shifted to 214 nm (blue shift). This observation confirms that the presence of Pb^{2+} results in remarkable change in position and intensity and shape at two spectral regions. Hence, this study confirmed selectivity of the ionophore for Pb(II) ions.

3.2 *Determination of binding constants of TPOME using sandwich membrane method*

The ionophore-complex formation constant was determined by potentiometric method. Sandwich membrane was prepared by mechanically pressing together, the two individual membranes; the membrane with ionophore to the membrane without ionophore after blotting them individually and drying with filter paper. The experimental set-up was same as described earlier. Experiments were carried out according to the sandwich membrane method.[51,52] In this method, the potential of sandwich membranes E_m was determined by subtracting the cell potential for a membrane without ionophore from that of sandwich membrane. The

Figure 2. UV-visible complexation study of different metals (Pb^{2+}, Cu^{2+}, Ca^{2+} and Co^{2+}) in MeOH; [TPOME] = 1×10^{-5} M; [metal ion] = 1×10^{-5} M.

formation constant is then calculated from the following equation:

$$\beta_{IL_n} = \frac{(L_T - nR_T)^{-n}}{Z_I} \exp\left(\frac{E_m Z_I F}{RT}\right),$$

where L_T is the total concentration of the ionophore in the membrane segment, R_T is the concentration of the lipophilic ionic site additives, n is the ion-ionophore complexes stoichiometry; R, T and F are the gas constant, absolute temperature and Faraday constant. The tested ion, I carries a charge of Z_I.

The membrane potential E_m was determined by subtracting the cell potential for a membrane without ionophore, from that for the sandwich membrane. This method allows convenient determination of the ion–ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs. The calculated binding constants for Ag^+, Sr^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+} and Pb^{2+} are 4.9, 5.5, 5.6, 5.1, 5.4, 6.0, 4.9, 5.4 and 6.1, respectively. The results show highest stability for lead ions as compared to other ions.

3.3 *Optimization of membrane ingredients and effect of ionophore concentration*

In preliminary experiments, the membranes with and without carrier were prepared. The blank membrane showed insignificant selectivity towards Pb^{2+} ions and their responses were unreliable whereas, in presence of the proposed ionophore, the optimized membrane gave Nernstian response and remarkable selectivity for Pb^{2+} ions over several other metal cations. Preferential response towards Pb^{2+} ions is believed to be associated with selective coordination of the ionophore to the Pb^{2+} ions. Pb^{2+} selective electrodes prepared with different amounts of the ionophore are shown in table 1. Since the sensitivity and selectivity of a given membrane electrode is significantly related to the composition of the membrane, particularly, the amount of the ionophore,[53,54] PVC and additive were varied to study their effect on the potential response of the proposed electrode. The data clearly indicates that the composition of the electrode having composition less than or greater than 5% leads to non-Nernstian responses. This deviation in the electrode response at high or lower concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier-based ISEs.[1]

3.4 *Calibration curve, response time, lifetime of the electrode*

The polymeric membrane electrode for Pb^{2+} ions based on ionophore TPOME has been examined according to IUPAC recommendations[55] at various concentration of inner filling solution of $Pb(NO_3)_2$ in the range of 1×10^{-3} to 1×10^{-1} M and the potential response of the electrode have been observed. Best results in terms of slope and working concentration have been obtained with inner filling solution of concentration 1×10^{-1} M. Emf of the membrane electrode at varying Pb(II) concentration shows a linear range from 1×10^{-5} M to 1×10^{-1} M with a Nernstian slope of $30\,mV/decade$. Detection limit (lower range of the calibration plot) is 6×10^{-6} M as determined from the intersection of the extrapolated segments of the calibration plots shown in figure 3. Below concentration 1×10^{-5} M, emf of the cell increases due to leaching of the primary ion (from the internal electrolyte solution), which leads to its higher activity at outer surface in contact with the outer solution (relative to the bulk sample). These fluxes maintain a micro molar activity in the proximity of the membrane–solution interface, even if the sample contains virtually no primary ions. Such a localized accumulation of ions makes it impossible to measure dilute samples and restricts the detection limits to the micromolar range. Hence, it shows parabolic fit.

3.5 *Surface characterization of the membrane electrode*

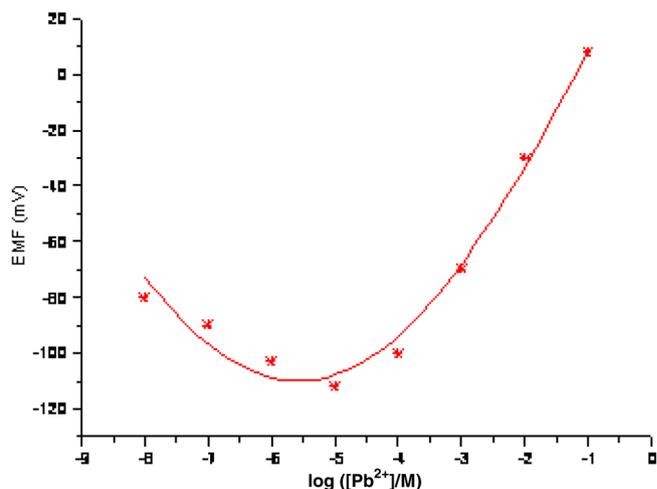Surface morphology of Pb^{2+} selective membranes is shown in figure 4a. A remarkable change is noticed

Figure 3. Calibration curve for Pb(II)-selective electrode based on TPOME.
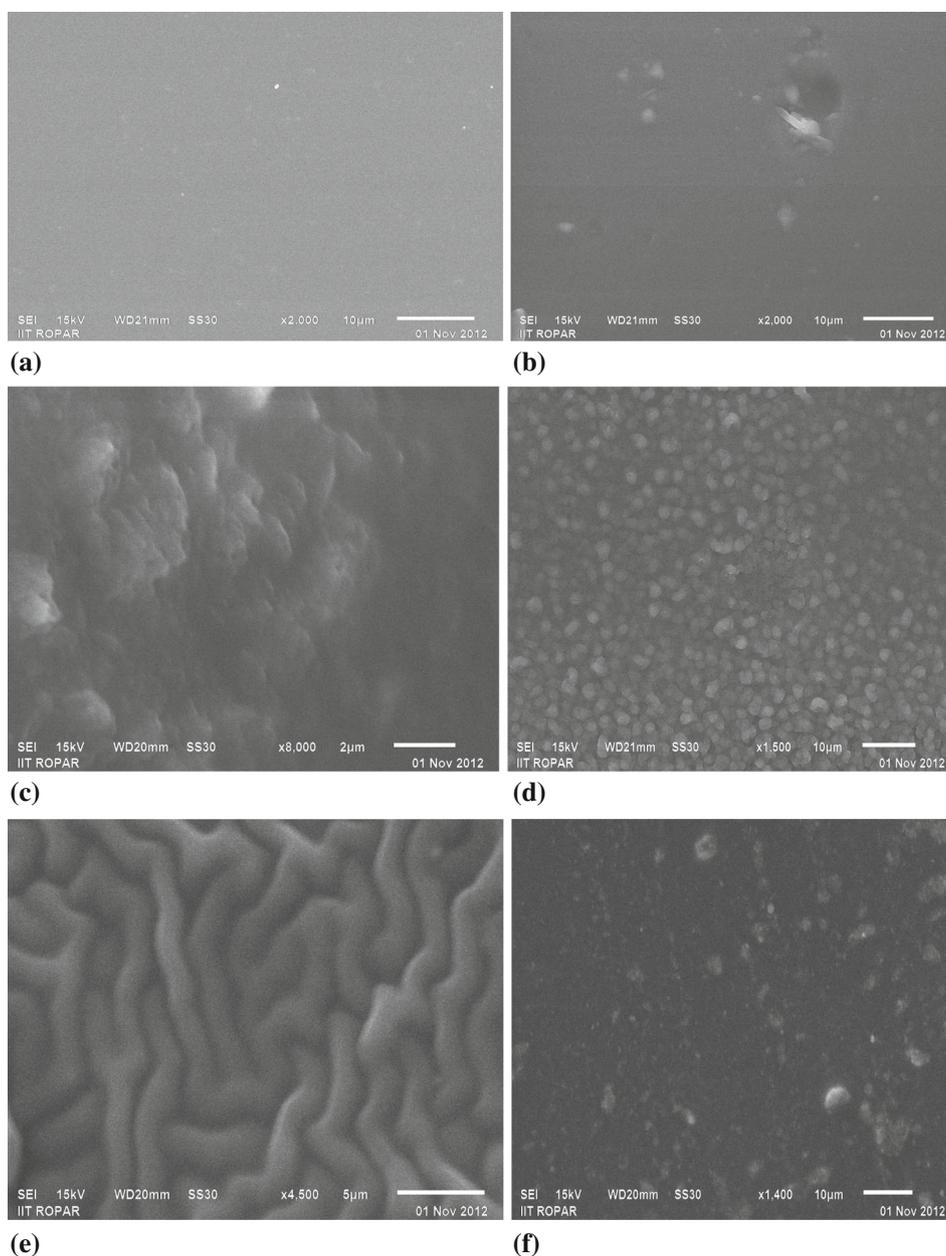
Figure 4. SEM images of liquid membrane based on TPOME. (**a**) PVC. (**b**) PVC + o-NPOE. (**c**) PVC + o-NPOE + NaTPB. (**d**) PVC + o-NPOE + NaTPB + TPOME. (**e**) Equilibration of (**d**) with Pb(NO$_3$)$_2$ solution. (**f**) After 4 months use of (**d**) membrane.

after addition of each membrane ingredient. PVC membrane surface without any other ingredient shows uniform homogeneity (figure 4a), while figure 4b shows a uniform dense packing due to the presence of plasticizer on the PVC membrane. Further, on addition of lipophilic salt, there is a huge change in morphology with non-preferential orientation, no observable cracks and appeared to be composed of dense and loose aggregation of small particles as shown in figure 4c. However, on addition of TPOME ionophore 5%, a uniform distribution of TPOME can be seen in figure 4d. A

different morphology was noticed in figure 4e; when membrane was equilibrated for 24 h with Pb^{2+} ions, then membrane surface looks like a swollen, clear non-uniform layer due to presence of Pb^{2+}-ionophore complexes distributed in plasticizer solvent and this makes a movable and permeable structure that included channels to diffuse the Pb^{2+} metal ions. In figure 4f, big change was observed in surface morphology with appearance of a bare type PVC membrane; this may be due to leaching of membrane ingredients, after its lifetime of 4 months.
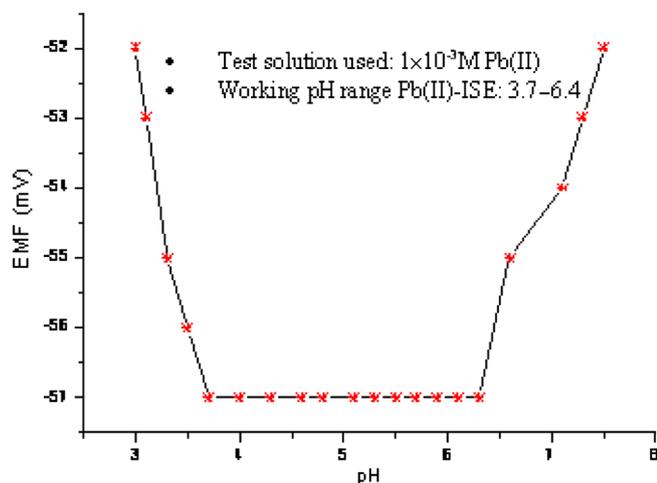
Figure 5. Effect of pH on the potential response of Pb(II)-selective electrode.

3.6 *Effect of pH on the response of Pb(II) selective electrode*

Influence of pH on the response of the electrode was studied for Pb(II) solution of concentration 1×10^{-3} M (figure 5) in the pH range of 3–9.7. The potentials were found to remain unaffected by the change in pH in the pH range of 3.7–6.4. Sudden decrease of potential below pH 3.5 may be attributed to the partial protonation of the ionophore, while the decrease in potential above pH 6.5 could be due to the formation of some soluble and insoluble complexes of Pb^{2+} such as $Pb(OH)^+$ and $Pb(OH)_2$,[56] which might have resulted in a loss of ability of the ionophore to sense Pb^{2+} ions (figure 5).

3.7 *Effect of interfering ions on electrode performance and selectivity*

Selectivity is the term which is used to describe the utility of the sensor. It gives the magnitude of selectivity of a sensor towards primary ion A in presence of secondary ions B present in the solution. It is expressed in terms of potentiometric selectivity coefficient ($K_{A,B}^{Pot}$). Potentiometric selectivity coefficients in the present case have been determined by fixed interference method (FIM) as per IUPAC recommendations.[2,57] Concentration of the interfering ion was kept fixed at 1×10^{-2} M. Values of selectivity coefficient so determined for Na^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, La^{3+}, Fe^{3+} and Ag^+ are -0.33, -1.77, -2.02, -2.02 -1.80, -0.22, -0.80, -0.74, -2.04, -2.62, -2.76 and -0.33, respectively. Selectivity coefficient data indicate that $\log K$ values are in the order 10^{-2} for divalent and trivalent metal ions (except K^+, Cu^{2+}, Hg^{2+} and Ag^+). Therefore, the electrode can be used for the determination of Pb^{2+} ions in the presence of certain interfering ions. Electrodes already reported in literature generally suffer from strong interference by mercury ions, but the proposed electrode system shows good selectivity for copper ion even in presence of these ions. $\log K$ values for Pb^{2+} selective electrode are compared with those reported for other Pb(II) selective electrodes reported in literature in table 2.

3.8 *Effect of electrode response in mixed solvent media*

Effect of partially non-aqueous medium was also investigated by using the sensor in methanol–water, acetone–water, dimethylsulphoxide–water mixtures using 10%, 20% and 30% non-aqueous content. However, beyond these non-aqueous contents, both working concentration range and slope decreased drastically and results were slightly irreproducible.

3.9 *Potentiometric titration*

To further determine analytical utility of the proposed sensor, quantification of the Pb^{2+} ions has been carried out by potentiometric titration (figure 6) using potassium chromate as a titrant. 50 mL of 1×10^{-4} M $Pb(NO_3)_2$ was titrated against 1×10^{-3} M K_2CrO_4. The plot obtained is a semi-sigmoid shape, which indicates that sensor is highly selective for Pb^{2+} and the end point corresponds to 1:1 stoichiometry of the lead chromate complex. The sensor was also used for testing municipal waste water and the results obtained are in agreement with those obtained by AAS.
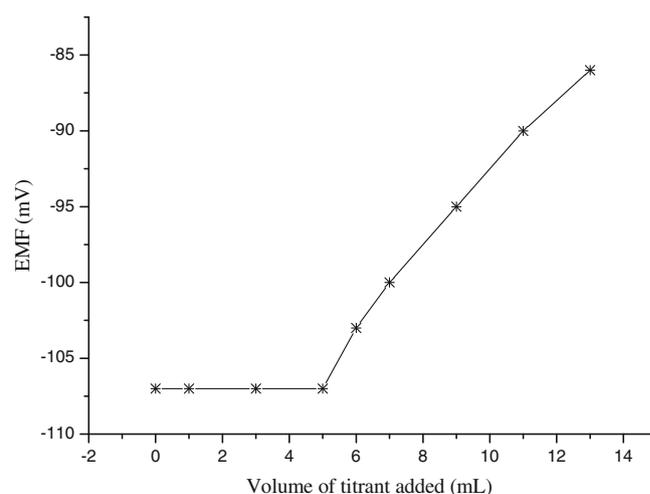

Figure 6. Potentiometric titration of 50 mL of 1×10^{-3} M $Pb(NO_3)_2$ titrated against 1×10^{-2} M K_2CrO_4.

Table 2. Comparison of proposed Pb(II)-selective electrode with the reported electrodes.

Ionophore	Working conc. Range (M)	pH range	Slope (mV/decade)	Detection limit
Dibenzo 18-crown-6 [58]	10^{-2}–10^{-6}	3.6–7.0	28	0.0435 mg/L
9,10-Anthraquinone derivatives [59]	10^{-3}–10^{-6}	NR	29	NR
Crown ethers [60]	10^{-1}–10^{-5}	3–6	28 ± 1 mV	10^{-6} M
Bis(1′-hydroxy-2′-acetonaphthone)-2,2-diiminodiethylamine [61]	10^{-2}–10^{-6}	4.0–7.0	27.8	4.0×10^{-7} M
3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene [62]	10^{-1}–10^{-6}	5.0–8.0	28.5	8×10^{-7} M
N, N′-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD) [63]	10^{-1}–10^{-6}	3.5–7.5	29	3.2×10^{-6} M
Piroxicam [64]	10^{-1}–10^{-5}	4.0–8.0	30	1.0×10^{-6} M
Polyaminoanthraquinone (PAAQ) microparticles [65]	10^{-1}–10^{-6}	1.0–6.0	29	776 nM
Calixarene carboxyphenyl azo derivative [66]	10^{-2}–10^{-6}	4.0–7.0	29.4	$1 \times 10^{-6.1}$ M
Benzo-substituted diamides [67]	10^{-2}–10^{-6}	3.7–6.5	30	2.0×10^{-6} M
N,N′-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine [68]	10^{-1}–5×10^{-5}	NR	30	$1 \times 10^{-5.74}$ M
TPOME (this study)	10^{-1}–10^{-5}	2.6–6.3	30	1×10^{-5} M

NR: Not reported in literature

4. Conclusion

Results obtained from this study revealed that the potentiometric PVC-based membrane on N′,N″,N‴ tris(2-pyridyloxymethyl) ethane (TPOME) works as an excellent Pb^{2+} selective membrane electrode. The sensor developed using this ionophore exhibits wide operational concentration range, high selectivity, long-term stability and fast response time with a long lifetime period of 4 months. Selectivity of membrane sensor towards Pb^{2+} ion is quite good and response characteristics of the proposed electrode are better than the earlier sensors in presence of Hg^{2+} and other ions.

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