Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.941307

56 (2015) 806–813
October

Taylor & Francis
Taylor & Francis Group

Ion-selective potentiometric determination of Pb(II) ions using PVC-based carboxymethyl cellulose Sn(IV) phosphate composite membrane electrode

Inamuddin[a,*], Mu. Naushad[b], Tauseef Ahmad Rangreez[a], Z.A. ALOthman[b]

[a]*Faculty of Engineering and Technology, Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202002, India, Tel. +91 571 2700920, Ext. 3008, Tel. +91 9557414508; email: inamuddin@rediffmail.com (Inamuddin), Tel. +91 9997605944; email: tauseefjh@gmail.com (T.A. Rangreez)*
[b]*Department of Chemistry, College of Science, Building #5, King Saud University Riyadh, Saudi Arabia, Tel. +966 1474198; email: shad81@rediffmail.com (Mu. Naushad)*

Received 9 February 2014; Accepted 20 June 2014

ABSTRACT

Pb(II) ion-selective electrode membranes were fabricated by using solution casting method using carboxymethyl cellulose Sn(IV) phosphate composite cation-exchange material. The membrane electrode showed response towards Pb(II) ions in the concentration range from 1×10^{-1} to 1×10^{-6} M with a Nernstian slope of 28.057 mV per decade change in Pb^{2+} ion concentration and can be used for five months without observing any deviation. The membrane electrode exhibited fast response time of 10 s studied for 1×10^{-2} and 1×10^{-3} M of Pb^{2+} ion concentrations. The membrane electrode was operated successfully at 1×10^{-2} M, 1×10^{-3} M and 1×10^{-4} M concentrations of lead ion over the pH range 2–4. The proposed electrode was found selective for Pb(II) in the presence of alkali and alkaline earth metal ions. It was also employed as an indicator electrode in the potentiometric titration of Pb(II) using ethylenediamine tetraacetic acid, disodium salt (EDTA). The sharp end-point corresponds to the stoichiometry of Pb(II)–EDTA complex.

Keywords: Composite cation exchanger; Potentiometric determination of Pb(II); Carboxymethyl cellulose Sn(IV) phosphate; Membrane electrode; Selectivity

1. Introduction

It is well known that among the list of toxic heavy metal species lead is on the priority of various environmental protection agencies [1–4]. It is ubiquitous in the environment and exists in various forms. All forms are toxic in nature above the permissible limit and adversely affect the central nervous, reproductive, immune and cardiovascular systems as well as kidney. It is also considered responsible for the decline of the developmental processes in children. Therefore, over the past decades, the determination of lead in natural and portable water bodies has generated increased interest in the development of novel sensors. Ion-selective membrane electrode (ISME) potentiometry has become a well-established electrochemical method for the determination of lead in environmental samples. It possesses a lot of advantages like simple instrumentation, low cost, fast response time and selectivity [5,6] over various analytical techniques used for this purpose [7].

During the last decade, various potentiometric sensors based on the crown ethers, calixarenes and other complex ionophores have been developed to detect

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*Corresponding author.

lead from environmental samples [8–17]. However, the complicated method of synthesis, high cost and low selectivity of these materials are major obstacles in the determination of lead ions from environmental samples. Recently, ion-selective electrodes (ISEs) based on ion-exchange membranes are considered cost effective, simple and economical alternatives to above-mentioned ionophores for the determination of several anions and cations, especially lead [18–25]. It is well known that the selectivity of ion-exchange membrane towards a particular metal ion enhances the preferential uptake by the fast replacement of counter ions through ion-exchange mechanism. In this study, a Pb(II)-selective membrane electrode based on carboxymethyl cellulose Sn(IV) phosphate composite cation exchanger is prepared and successfully used for the potentiometric determination of lead from environmental samples.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-Merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH/mV meter (744, Metrohm, Switzerland) with a saturated calomel electrode as a reference electrode was used for the potential measurement at room temperature (25 ± 2˚C).

2.2. Preparation of standard solution

A solution of 0.1 M $Pb(NO_3)_2$ was prepared by dissolving $Pb(NO_3)_2$ salt in 100 ml demineralized water (DMW) while other standard $Pb(NO_3)_2$ solutions of $1 \times 10^{-1} - 1 \times 10^{-10}$ M concentrations were prepared by dilution step by step. Solutions of 0.1 M stannic chloride and 0.1 M tri-sodium orthophosphate dodecahydrate and *N*-cetyl-*N,N,N*-trimethyl ammonium bromide (CTAB) were prepared in 4 M HCl and DMW, respectively.

2.3. Preparation of carboxymethyl cellulose Sn(IV) phosphate composite cation exchanger

Composite cation exchanger carboxymethyl cellulose Sn(IV) phosphate was prepared as reported by Mohammad et al. [26]. The ion-exchange capacity of the composite cation exchanger was determined by the standard column process. For this purpose, one gram (1 g) of the dry cation exchanger in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M $NaNO_3$ as eluent was used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion-exchange capacity in meq dry g^{-1} of the exchanger is determined. The ion-exchange capacity of this composite cation exchanger was found to be 2.13 meq dry g^{-1} of exchanger.

2.4. Preparation of carboxymethyl cellulose Sn(IV) phosphate membrane

The method of preparation of carboxymethyl cellulose Sn(IV) phosphate composite ion-exchange membrane was very similar to that of Coetzee and Basson [27]. The electroactive material, i.e. carboxymethyl cellulose Sn(IV) phosphate cation exchanger was ground to fine powder and was mixed thoroughly with PVC, dissolved in 10 ml of tetrahydrofuran (THF) and finally, mixed with 10 drops of dioctylphthalate used as a plasticizer [28]. The mixing ratio of the ion exchanger was varied with a fixed content of PVC in order to obtain a composition, which gave the membrane showing the best performance, and the resulting solutions were carefully poured into a glass-casting ring (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way, four sheets of different thickness of master membranes were obtained.

2.5. Characterization of membrane

The pre-requisite performance of an ion-exchange membrane is its complete physicochemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were membrane water content, porosity, thickness, swelling, etc. and were determined as described elsewhere [29–32] after conditioning the membrane as given below.

2.5.1. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5–6.5 (to neutralize the acid present in the film).

2.5.2. Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture and immediately weighed. These were further dried to a constant weight in vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as:

$$\%\,\text{Total wet weight} = \frac{W_w - W_d}{W_w} \times 100 \qquad (1)$$

where W_w = weight of the soaked/wet membrane and W_d = weight of the dry membrane.

2.5.3. Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume of the water content data.

$$\varepsilon = \frac{W_w - W_d}{A\,L\,\rho_w} \qquad (2)$$

where A = area of the membrane, L = thickness of the membrane and ρ_w = density of water.

2.5.4. Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane using screw gauze.

The swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. The results of the membrane characterization are given in Table 1.

2.6. Fabrication of ISE

The membrane sheet (M-1) of 0.28 mm thickness as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with 0.1 M $Pb(NO_3)_2$ solution. A saturated calomel electrode was inserted in the tube for electrical contact and other saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)	Internal electrolyte 0.1 M Pb^{2+}	Membrane	Sample solution	External reference electrode (SCE)

2.7. EMF measurement

All response potentials of the ISME were measured by varying the concentration of $Pb(NO_3)_2$ in a range between 1×10^{-10} and 1×10^{-1} M obtained from the sequential dilution from stock solution of 1×10^{-1} M $Pb(NO_3)_2$. Essentially, the membrane electrode was conditioned by soaking in a 0.1 M $Pb(NO_3)_2$ solution for 5–7 d and for 1 h at least before use. The experiments were conducted in air thermostat maintained at 25 ± 1˚C. After performing the experiment, membrane electrode was removed from the test solution and kept in a 0.1 M $Pb(NO_3)_2$ solution to maintain the activity. Potential measurements of the membrane electrode were plotted against the logarithmic function of selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

The response time was measured by recording the e.m.f. of the electrode as a function of time when it was immersed in the solution to be studied. The electrodes were first dipped in 1×10^{-3} M and 1×10^{-4} M solutions of the ion concerned and immediately shifted to other solutions (pH 3.0) of 1×10^{-2} M and 1×10^{-3} M ion concentrations of the same ion (10-fold higher concentration), respectively. The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s. The potentials were then plotted against the time. The time during which the potentials attain a constant value represents the response time of the electrode. The lifetime of the membrane electrode was determined by periodically recalibrating the potentiometric response to Pb^{2+} ions in standard $Pb(NO_3)_2$ solutions. The influence of pH of the test solution on the potential response of ISME was tested at 1×10^{-2} M, 1×10^{-3} M and 1×10^{-4} M concentrations of lead over the pH range 1–6. The pH variations were brought out by the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded and was plotted against pH.

Table 1
Characterization of ion-exchanger membranes

	Membrane composition						
S. No.	Carboxymethyl cellulose Sn(IV) phosphate (mg)	PVC (mg)	Plasticizer (drops)	Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
M-1	100	200	10	0.28	12.00	0.064	0.2
M-2	150	200	10	0.37	15.00	0.121	0.2
M-3	200	200	10	0.44	20.00	0.221	0.2
M-4	250	200	10	0.60	21.13	0.432	0.2

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ISME were determined by the mixed solution method as discussed elsewhere [33]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1}–1×10^{-10} M) of the primary ion. Now the potential measurements were made using the membrane electrode assembly and plotted against the logarithm of the concentration of ions under study.

3. Results and discussion

An electroactive material carboxymethyl cellulose Sn(IV) phosphate having ion exchange capacity of 2.13 meq dry g^{-1} of exchanger was prepared as reported by Mohammad et al. [26]. To study the electrode properties, four samples of PVC-based carboxymethyl cellulose Sn(IV) phosphate cation-selective membranes were prepared using different mixing ratios of electroactive material carboxymethyl cellulose Sn(IV) phosphate and PVC dissolved in tetrahydrofuran (THF) with a fixed amount (10 drops) of plasticizer dioctylphthalate. The amount of the ion exchanger was varied to change the thicknesses of the membranes. These membranes were characterized to find out one membrane of good electrochemical performance for the purpose of preparation of an ISME and the results are given in Table 1. It is observed that as the amount of electroactive carboxymethyl cellulose Sn(IV) phosphate increased, the thickness, swelling, water content, and porosity increased. Thus, the lower orders of water content, swelling and porosity with less thickness of this membrane suggest that interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Hence, membrane sample M-1 (thickness 0.28 mm) was selected for the preparation of the ISE for further studies.

The measuring range of an ISE for the determination of a particular ion is considered the linear part of the calibration curve. Similarly, it is also defined as the activity range of an ion between the upper and lower detection limits of an ISME. Thus, the measurements of an ion using an ISE can be performed in this range only. In this study, the electrode prepared from membrane sample M-1, showed a linear Nernstian response to the concentration of Pb^{2+} in the range of 1×10^{-1}–1×10^{-6} M as shown in Fig. 1. The slope of calibration graph was 28.057 ($R^2 = 0.999$) mV/decade change in concentration of Pb^{2+}. Thus, the working concentration range was found to be 1×10^{-1} – 1×10^{-6} M for Pb^{2+} ions. The limit of detection for an ISE can be determined by extrapolating the linear part of the ISE calibration curve. The limit of detection of this electrode calculated by extrapolating of the two segments of the calibration curve was found to be 1×10^{-6} M as shown in Fig. 1.

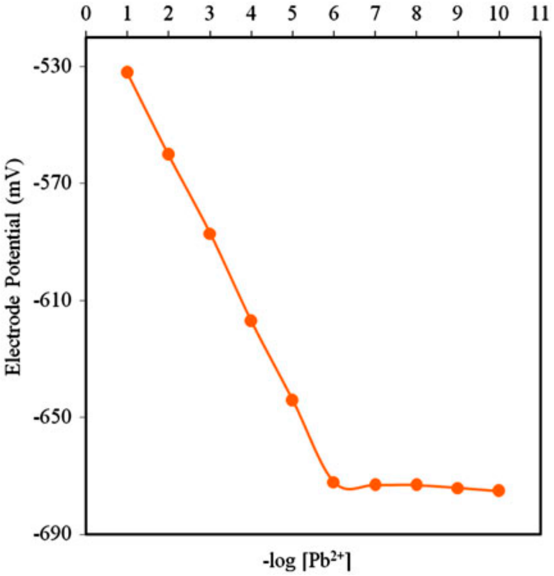

Fig. 1. Calibration curve for Pb^{2+} ion-selective carboxymethyl cellulose Sn(IV) phosphate membrane electrode.

The dynamic response time is also considered an important factor to access the analytical applicability of an ISE. Essentially, dynamic response time of an ISE is the time to reach a cell potential of 90% of the final equilibrium potential, after successive addition in a series of solutions each having a 10-fold higher difference. The dynamic potential-time response of the electrode obtained upon successive addition of 10-fold higher Pb(II) concentrations from 1×10^{-3} M and 1×10^{-4} M to 1×10^{-2} M and 1×10^{-3} M, respectively, were obtained as shown in Fig. 2. It was observed that the electrode potential of carboxymethyl cellulose Sn(IV) phosphate membrane electrode was found to be 10 s and was remained unchanged for varying concentrations of 1×10^{-2} M and 1×10^{-3} M Pb^{2+} ions (Fig. 2). This may be due to the fast exchange of Pb^{2+} ions with the test solution–membrane interface. In this study, a Pb^{2+} ion-selective organic–inorganic composite material of type X–H (where X is the polymer backbone and H is the counter ions) as electroactive material was used. The ion-exchange materials will selectively bind the Pb^{2+} leading to the generation of electrochemical signals proportional to the concentration of Pb^{2+}. Thus, the selectivity of this composite cation exchanger towards the Pb^{2+} ions was found responsible for the fast response time. It is very important that the performance of any ISE should be checked sooner every time before using it for any analytical purpose. For the present carboxymethyl cellulose Sn(IV) phosphate membrane electrode, it was observed that the measured potential of Pb^{2+} ions in a given concentration range of 10^{-1}–10^{-6} M was reproducible within ±2 mV and there was no significant change in the slope of the Nernst plot during the experiment over a time period of five months. This shows a longer electrode life and a stable electrode performance.

The response of this membrane electrode was also significantly affected by pH at the metal ion concentrations of 1×10^{-2} M, 1×10^{-3} M and 1×10^{-4} M as shown in Fig. 3. It was observed that the electrode potential of this electrode remained unchanged from pH 2 to 4. The drift in the potential above the pH value 4 may be due to the formation of soluble and insoluble Pb(II) ion hydroxyl complexes in the solution while the drift in the potential lower than the pH 2 is accounted for the re-protonation of the composite cation-exchange material. This behaviour of the proposed electrode was found comparable with previously reported electrodes [17]. Therefore, the working pH range for this electrode was assumed to be in the range of pH 2–4. In Table 2, the response characteristics of the proposed Pb^{2+} ISME based on composite cation-exchange material are compared with those of already reported and randomly selected ISME based on various types of materials. It is evident from the table that the performance of the proposed Pb(II) ISME based on the organic–inorganic composite cation exchanger is comparable and better in many respects, such as the slope, response time, linear concentration range, life time, pH range and selectivity. The interference of other ions on the selectivity of this ISME was determined at pH 3 by the mixed solution method. The response potentials in the presence of interfering ions were observed and were plotted against the logarithms of the Pb^{2+} ion concentration as shown in Fig. 4. It is evident from Fig. 4 that alkali and alkaline earth metal ions do not interfere with the

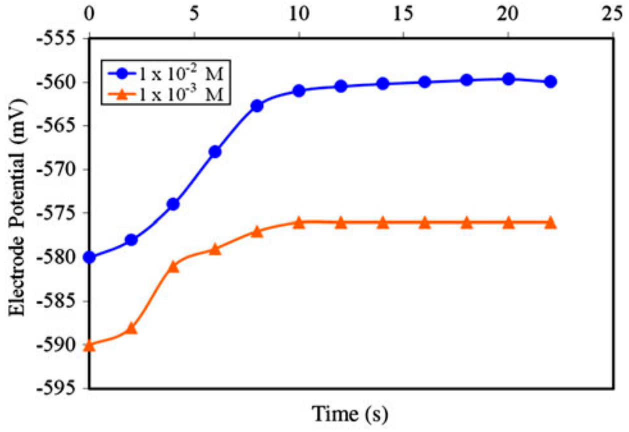

Fig. 2. Response time characteristics of Pb^{2+} ion-selective carboxymethyl cellulose Sn(IV) phosphate membrane electrode at different time interval for 1×10^{-2} and 1×10^{-3} M concentrations of lead.

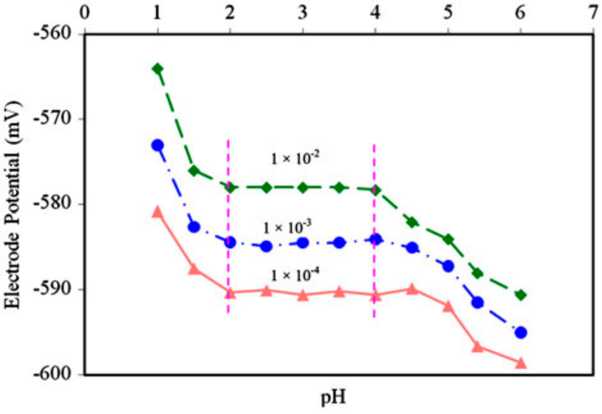

Fig. 3. Effect of pH of the test solution on the potential response of the carboxymethyl cellulose Sn(IV) phosphate ISME at 1×10^{-2} M, 1×10^{-3} M and 1×10^{-4} M concentrations of lead.

Table 2
A comparison of previously reported ISMEs with the proposed study

Working concentration range (*M*)	Life time (months)	pH range	Response time (s)	Slope (mV)/decade change in concentration	References
5×10^{-5}–1×10^{-1}	10	N.A.	10	29.3 ± 0.7	[8]
1×10^{-6}–1×10^{-1}	2	3.5–6.5	<15	~29.6	[9]
1×10^{-6}–1×10^{-2}	1	4–7	<20	29.4	[11]
3.1×10^{-6}–3.1×10^{-2}	5	3–5	14	29.8	[17]
5×10^{-6}–1×10^{-1}	Not mentioned	3.0–8.5	35	29.17	[23]
1×10^{-8}–1×10^{-1}	5	2.5–6.5	10	29.48	[34]
4×10^{-6}–1×10^{-2}	3	2–7	70	29.0 ± 0.3	[35]
2×10^{-6}–2×10^{-3}	4	N.A.	30	29.0 ± 0.3	[36]
2.5×10^{-6}–1×10^{-1}	4	2.8–5.2	12	28.9	[37]
1×10^{-6}–1×10^{-1}	5	2–4	10	28.057	Proposed assembly

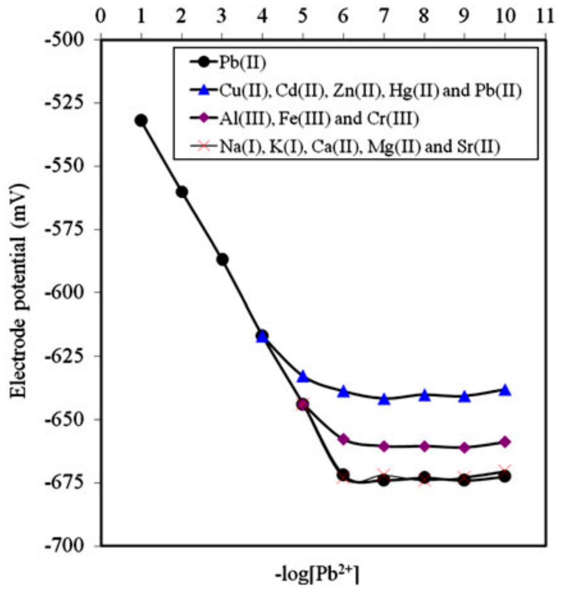

Fig. 4. Response curve of the Pb(II)-selective membrane electrode for the interference of other metal ions.

determination of Pb(II) ions, while Cu(II), Cd(II), Zn (II), Hg(II) and Pb(II) and Mn(II) interfere to a large extent and they start interfering from 10^{-4} M of Pb(II) concentration, and Al(III), Fe(III) and Cr(III) interfere to a very small extent starting from 10^{-5} M of Pb(II) ion concentration. Thus, it is evident that the proposed electrode worked selectively for the determination of Pb(II) in the presence of alkali and alkaline metal ions while the heavy metals interference cannot be ignored.

It is proposed that the Pb^{2+} ISE based on carboxymethyl cellulose Sn(IV) phosphate can not only be used for the determination of Pb^{2+} ions using calibration method, but the analytical utility of this membrane electrode can also be considered as an indicator electrode in the potentiometric titration of various concentrations of lead solutions against an EDTA solution as a titrant. In this study, 15 ml $Pb(NO_3)_2$ solutions at 1×10^{-2} and 1×10^{-3} M concentrations were titrated against 1×10^{-2} M EDTA solution and the electrode potential was measured after each successive addition of 1 and 0.3 ml of EDTA, respectively. The necessary adjustment of pH (3) was made before adding the titrant. The addition of EDTA causes a decrease in potential as a result of the decrease in free, Pb(II) ion concentration due to the formation of a complex with EDTA (Fig. 5). The amount of Pb(II) ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp endpoint. It is also clear from the figure that the sharp

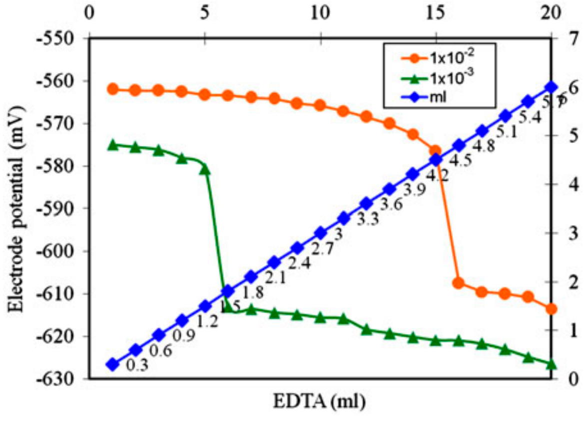

Fig. 5. Precipitation titration curves of 15 ml $Pb(NO_3)_2$ solutions at 1×10^{-2} and 1×10^{-3} M concentrations against 1×10^{-2} M EDTA solution.

end-point at 15 and 1.5 ml of EDTA corresponds to the stoichiometry of Pb(II)–EDTA complex. It is also clear from this study that the maintained stoichiometry of the titration may be due to no interference caused by Na(I) released from the titrant EDTA, which also supports the selectivity of this Pb^{2+} ISME in the presence of alkali metal ions.

4. Conclusions

A carboxymethyl cellulose Sn(IV) phosphate composite membrane electrode selective for Pb(II) ions was fabricated. The electrode exhibited fast response time for Pb(II) and permissible working pH range for the determination of Pb(II) ions. The membrane electrode could be used to determine Pb^{2+} ions in the concentration range of 1×10^{-1}–1×10^{-6} M. It also showed good selectivity in the presence of alkali and alkaline metal ions. However, heavy metal ions interfere to some extent. It showed good reproducibility, detection limit and lifetime of five months. The membrane electrode can also be used as indicator electrode in the potentiometric titration of various concentrations of Pb^{2+} solutions with EDTA. Potentiometric titration indicated that titration maintained the stoichiometry of Pb(II)–EDTA complex.

Acknowledgements

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center. The authors are also thankful to Department of Applied Chemistry, Z.H. College of Engineering and Technology, AMU (Aligarh) for providing research facilities.

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