

Coated wire lead(II) selective potentiometric sensor based on 4-*tert*-butylcalix[6]arene

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Abstract

A coated-wire lead ion-selective electrode (ISE) has been constructed using 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene as neutral carrier in a poly(vinyl chloride) matrix. The sensor exhibited a linear Nernstian response over the range 1×10^{-6} to 1×10^{-1} M with a slope of 30 ± 1 mV per decade change and a detection limit of 6×10^{-7} M. The working pH range of the sensor is 1.5–6.0 and it shows good selectivity for Pb(II) ions over other mono-, bi- and trivalent cations. The selectivity coefficients (K_{ij}) were determined for Na(I), K(I), Ag(I), Mg(II), Ca(II), Ba(II), Sr(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Cr(III), Fe(III) and Al(III); the values for these ions being in the range of 10^{-4} – 10^{-2} . The sensor was successfully used as an indicator electrode in potentiometric titration of lead ions with EDTA. The ISE was also used for determination of lead in electroplating bath solutions, alloy sample, battery waste samples and effluent waters.

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1. Introduction

The need for determination of lead(II) ions in monitoring the environment and in clinical analysis has led to substantial interest in carrier-based sensors for this analyte. Many ligands have been investigated as sensing agents for lead in electrodes based on ionophore doped poly(vinyl chloride) (PVC) membrane [1–15] the nature and characteristics of different types of lead ion membrane sensors having been reviewed [16]. The potentiometric selectivity coefficients of ion-selective electrodes for inorganic cations [17], inorganic anions [18] and organic ions [19] have been compiled by Umezawa et al. in a technical report. During the last two decades, calixarenes have attracted much attention as a kind of key receptors in supramolecular chemistry [20–22]. Calixarenes have been found suitable for this purpose [20] because of the ease in their large-scale synthesis and the different ways in which they can be selectively functionalized at the lower rim (polar)

or at the upper rim (non-polar). Because of these properties, calixarenes can form inclusion complexes with a wide range of guest species. Phosphine oxide derivatised calixarenes, amide, thiol and crown functionalised calixarenes have been incorporated as neutral carriers into ISEs or chemically modified electrodes sensitive to lead ions [23–26].

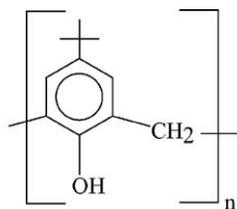
Among those calixarenes studied, most are devoted to calix[4]arene or its derivatives. There are relatively fewer reports about the hexamers and octamers [27–30] of this kind of macrocyclic ligands. Therefore, it was decided to develop coated-wire ISEs based on these calixarenes. Here, we report on the fabrication of the Pb(II) sensors based on calixarenes and their characteristics, which have been evaluated for usefulness in the determination of lead ions in solutions. The performance of the sensor based on calix[6]arene was comparable and in some respects superior to those of various Pb(II) selective electrodes reported previously [16,17].

One of the important aspects of using a coated-wire ISE is that it not only needs a very small volume of sample, but also has other advantages *viz.* simplicity of design, lower cost, mechanical flexibility, *i.e.* the electrode can be used at any angle, absence of internal solution, and the possibility of miniaturization and microfabrication. [31–34].

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where $n = 4$ for calix[4]arene (I), 6 for calix[6]arene (II), 8 for calix[8]arene (III).

Fig. 1. Structures of the macrocycles used in the present work.

2. Experimental

2.1. Chemicals

Nitrates of sodium(I), potassium(I), silver(I), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), chromium(III), iron(III), aluminium(III), and lead(II), tetrahydrofuran (THF), dibutyl phthalate (DBP), diethyl phthalate (DEP), dibutyl maleate (DBM), ethylenediaminetetraacetic acid (EDTA), sodium tetraphenyl borate (NaTPB), hydrochloric and nitric acids were of analytical grade and used as such. Magnesium, calcium, strontium and barium perchlorates were prepared by general methods described elsewhere [35]. High molecular weight poly(vinyl chloride) and manganese(II) nitrate were purchased from Fluka and used as such. 4-*tert*-butylcalix[4]arene, 4-*tert*-butylcalix[6]arene and 4-*tert*-butylcalix[8]arene were synthesized by Gutsche's method and characterized as described in the literature [36]. The structures of the calixarenes used in the present work are given in Fig. 1. Standard solutions of metal salts were prepared in double distilled deionized water and standardized by the recommended methods wherever necessary [37]. Working solutions of different concentrations were

prepared as required by suitable dilution with the same water. The pH of the solutions was adjusted with 0.1 M HNO₃.

2.2. Preparation of the electrodes

Varying amounts of the ionophore (calix[4]arene, calix[6]arene and calix[8]arene), anion excluder NaTPB and PVC were dissolved in 3 cm³ of THF along with the solvent mediator (DBP/DEP/DBM) to get different compositions as given in Table 1. To prepare the electrodes, platinum wires were used as substrates to coat the slurries by dipping it several times in the respective slurries until the beads were formed. The beads thus prepared were allowed to dry in air for 24 h and thereafter used to check their performance as Pb(II) ISEs.

2.3. Conditioning and storage

The electrodes thus prepared were conditioned for 2–3 days in 1.0 M Pb(II) solution. The slurries prepared for the bead preparation were stored in an airtight chamber when not in use. A fresh electrode was prepared by adding THF into the slurry and repeating the above process.

Table 1

Compositions and characteristics of PVC based membranes having 4-*tert*-butylcalix[4]arene (I), 4-*tert*-butylcalix[6]arene (II) and 4-*tert*-butylcalix[8]arene (III) as ionophores

Sensor no.	Ionophore (%)	NaTPB (%)	DBP (%)	DEP (%)	DBM (%)	PVC (%)	Working range (M)	Slope (mV/decade)	Response time (s)
1	I-0.8	–	–	–	–	65.6	7×10^{-4} to 1×10^{-1}	39 ± 2	80
2	I-0.8	0.3	33.3	–	–	65.6	6×10^{-5} to 1×10^{-1}	27 ± 1	30
3	I-0.8	0.3	–	33.3	–	65.6	8×10^{-5} to 1×10^{-1}	24.5 ± 2	35
4	I-0.8	0.3	–	–	33.3	65.6	8×10^{-5} to 1×10^{-1}	26 ± 1	35
5	II-0.8	–	–	–	–	65.6	7×10^{-5} to 1×10^{-1}	36.6 ± 2	55
6	II-0.8	–	33.3	–	–	65.6	1×10^{-6} to 8×10^{-2}	18.6 ± 1	40
7	II-0.4	0.3	33.3	–	–	65.6	9×10^{-6} to 1×10^{-1}	30.1 ± 1	25
8	II-0.6	0.3	33.3	–	–	65.6	3×10^{-6} to 1×10^{-1}	30.2 ± 1	18
9	II-0.8	0.3	33.3	–	–	65.6	1×10^{-6} to 1×10^{-1}	30 ± 1	15
10	II-0.8	0.3	–	33.3	–	65.6	4×10^{-6} to 1×10^{-1}	28 ± 2	20
11	II-0.8	0.3	–	–	33.3	65.6	3×10^{-6} to 1×10^{-1}	29 ± 2	18
12	II-1.0	0.3	33.3	–	–	65.6	1×10^{-6} to 1×10^{-1}	30 ± 1	15
13	II-1.2	0.3	33.3	–	–	65.6	1×10^{-6} to 1×10^{-1}	30 ± 1	15
14	III-0.8	–	–	–	–	65.6	1×10^{-3} to 1×10^{-1}	41 ± 2	105
15	III-0.8	0.3	33.3	–	–	65.6	1×10^{-4} to 1×10^{-1}	25.5 ± 2	38
16	III-0.8	0.3	–	33.3	–	65.6	5×10^{-4} to 1×10^{-1}	24.9 ± 1	45
17	III-0.8	0.3	–	–	33.3	65.6	3×10^{-4} to 1×10^{-1}	25 ± 1	40

2.4. Apparatus and emf measurements

All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204, Switzerland). A Mettler Toledo DL53 (Switzerland) autotitrator with automatic temperature compensation (ATC) was used for the standardization of metal salt solutions. A CyberScan 2500 pH meter (Eutech Instruments, Singapore) having ± 0.1 mV accuracy with a SCE as reference electrode and KNO_3 salt bridge was used for potential measurements.

All measurements were carried out at 25°C with a cell of the following type: $\text{Hg}, \text{Hg}_2\text{Cl}_2; \text{KCl (satd.)}/\text{Pb(II)}/\text{ion-selective membrane (bead)}/\text{Pt wire}$.

To check for Nernstian behavior, standard solutions of lead nitrate (1×10^{-1} to 1×10^{-8} M) in 0.05 M KNO_3 and 0.05 M NH_4NO_3 were prepared and the emfs were noted every 30 s over a period of 5 min or less until the emf's were stable to within ± 0.1 mV. The medium with 0.05 M KNO_3 was found to give the best response and was maintained for the rest of the studies.

A GBC 906AA atomic absorption spectrophotometer with air acetylene flame was used at 217.0 nm to analyze real samples.

2.5. Sample preparation

The concentration of lead was determined in some synthetic samples containing various cations in addition to lead by directly dipping the ISE in the sample solution after appropriate dilutions. Also, the concentration of lead in the samples from electroplating baths and effluent waters was determined by directly dipping the ISE in the sample solutions after appropriate dilution. The electroplating bath solutions contained tin, fluoboric acid, boric acid, and some organic additives and brighteners in addition to lead. The effluent waters contained copper and zinc in addition to lead. In the case of solder alloy, which also contained tin other than lead, the measurements were done after treatment with concentrated hydrochloric and nitric acids and appropriate dilution [37]. The Eveready battery waste sample was dissolved in distilled water by adding a few drops of concentrated nitric acid, filtered and used for further analysis. The scooter battery waste sample was used directly for measurements after filtration. In all the cases, appropriate quantity of potassium nitrate was added to give 0.05 M KNO_3 in the final solutions for measurements and wherever required, the pH was adjusted with 0.1 M HNO_3 before carrying out further analyses.

3. Results and discussions

Ionophores for use in sensors should have rapid exchange kinetics and adequate complexation formation constants in the membrane. In addition, they should be well soluble in the membrane matrix and have a sufficient lipophilicity to

prevent leaching from the membrane into the sample solution [38]. The selectivity of the neutral carrier-based ISEs is known to be governed by the stability constant of the neutral carrier-ion complex and its partition constant between the membrane and sample solution [38]. From a study of the complexation behavior of lead ions with **(I)**, **(II)** and **(III)** in DMF by conductivity measurements [39], it was found that **(II)** was the stronger complexing ligand for Pb(II) out of all the three calixarenes studied ($\log K = 4.52$).

Preliminary studies carried out with Pb(II) CWISEs based on **(I)**, **(II)** and **(III)** to evaluate the potential response in the concentration range of 1×10^{-8} – 1×10^{-1} M in 0.05 M KNO_3 media are summarized in Table 1. Membranes without any solvent mediator (sensors 1, 5 and 14) exhibited narrow working concentration ranges (10^{-3} – 10^{-1} M) and high response times. It is well known that the sensitivity and the selectivity of the ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizers and additives used [38]. Thus, the addition of the plasticizers DBP, DEP and DBM showed improved response characteristics for all the membranes, which now show a wide concentration range of approximately 10^{-6} – 10^{-1} M with enhancement in their respective slopes and response times. The membranes of typical P : PVC = 2 : 1 content were also examined, however, the optimized composition of P : PVC = 1 : 2 has been arrived at in the present work after checking the ratio of the membrane ingredients so that the membrane develops reproducible, noiseless and stable potentials.

Further, to get optimum composition of the ingredients, different compositions were tried by varying the amount of **II**. As is apparent from Table 1, among all the Pb(II) ISEs prepared, the membrane containing 33.3 wt.% plasticizer dibutyl phthalate and 0.8 wt.% ionophore **II** (sensor no. 9) gave the best response in 0.05 M KNO_3 over a long period of time. On further increase in the amount of **II**, there was no considerable improvement in any of the characteristics of the membrane. The presence of lipophilic additives in ISEs not only diminishes the ohmic resistance and enhances the response behavior and selectivity [38], but also, in some cases catalyzes the exchange kinetics at the sample-membrane interface [40]. The data given in Table 1 revealed that for the optimized membrane composition, in the absence of a proper additive, the sensitivity of the PVC membrane based on calix[6]arene is quite low (sensor no. 6 with a slope of 18.6 ± 1 mV per decade). However, the presence of 0.3 wt.% NaTPB as a suitable lipophilic additive exhibited an improvement in the sensitivity of the lead sensor considerably (sensor no. 9 with a slope of 30.0 ± 1 mV per decade) and therefore electrode no. 9 was used for all further studies.

3.1. Nernstian slope and response time

The plot of the difference of the potential between the working CWISE and the reference calomel electrode against

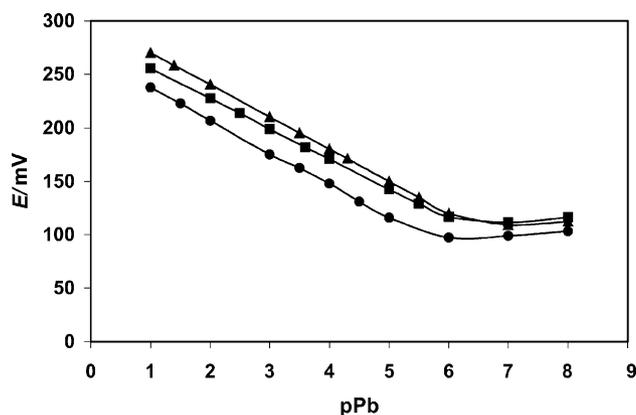


Fig. 2. Plot of potential vs. log Pb(II). Nernstian response using different plasticizers: (▲) dibutyl phthalate; (■) diethyl phthalate; (●) dibutyl maleate.

the logarithm of the concentration of Pb(II) in 0.05 M KNO_3 is given in Fig. 2. It is seen from the figure that electrode no. 9 gives a linear Nernstian response in the concentration range 1×10^{-6} to 1×10^{-1} M with a slope of 30 ± 1 mV per decade and a detection limit of 6×10^{-7} M. The response time of membrane sensors, i.e. the time in which stable and constant potentials are achieved was arrived by measuring the potentials in the entire concentration range. It is seen from Table 1 that the response time of sensor no. 5 (without solvent mediator) is approximately 55 s. The addition of plasticizers improved the response time significantly; especially for sensor no. 9 to 15 s over the whole working concentration range which was found to be better/comparable to those observed earlier [13,14,16,41,42].

3.2. Effect of pH

To study the effect of pH on the electrode response, the electrode potentials were measured over a pH range of 1.0–7.0 for 1×10^{-2} , 1×10^{-3} and 1×10^{-4} M Pb(II) solutions. The potential was found to be independent of change in pH in the range of 1.5–6.0 (Fig. 3). The electrode has a wide lower working range of pH as compared to those reported earlier [2,13,14,16,41,42].

3.3. Interferences by ions

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of foreign ions. This is measured in terms of potentiometric selectivity coefficient ($K_{\text{Pb}, \text{M}^{2+}}$) which was studied by the mixed solution method [43] in the present investigation by having a fixed concentration of interfering ion (1×10^{-3} M) and a varying concentration of Pb(II) ion (1×10^{-1} to 1×10^{-6} M). The selectivity coefficients determined for the different cations are given in Table 2. The selectivity coefficient data indicate that the ISE is selective towards lead over the transition metal ions, alkali and alkaline earth

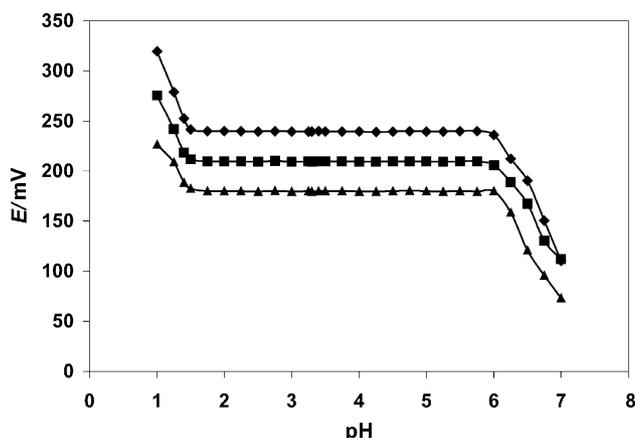


Fig. 3. Effect of pH on electrode potential at (●) 1.0×10^{-2} M; (■) 1.0×10^{-3} M; (▲) 1.0×10^{-4} M.

metals and other polyvalent ions. From the data given in Table 2, it is obvious that, except with Hg^{2+} ion, the selectivity coefficients of the cations tested are in the order of 1.3×10^{-3} or smaller, which seem to indicate negligible interference in the performance of the electrode assembly. The selectivity coefficient for mercury ion is somewhat larger (i.e. 2.9×10^{-2}). Even so, it should be noted that an even more serious interference effect from Hg^{2+} and some other cations on the functioning of other Pb^{2+} selective electrodes has been reported in the literature [1,2,4,6,14,41,42], which can be seen from the compilation given in Table 2. In addition, in comparison to conventional PbS-based lead(II) electrodes, the calix[6]arene-lead(II) ISE demonstrates the advantage of virtually no interference from some common metal ions such as Ag(I), Cu(II), Cd(II), Zn(II) and Hg(II).

3.4. Lifetime

The electrode was used over a period of five months without any significant effect on the membrane potential. The lifetime of the electrode was determined by reading the potential values of the calibration solutions and plotting the calibration curves for the five month period. The slope of the electrode (30 mV per decade change) was observed to show a gradual decrease after 140 days. After 150 days, the slope reached approximately 28 mV per decade change. We can therefore conclude that the lifetime of the proposed electrode prepared by use of calix[6]arene is at least 5 months which is much better than previously reported ISEs [13,14,41]. After this period, the slight change in the observed slope could be corrected by conditioning the membrane with 1.0 M Pb(II) solution for 1–2 days. With this treatment, the assembly could be used over a period of two more months and then replaced by a fresh membrane. The lifetime of ion selective electrodes mainly depends on the type of ionophores and plasticizers used, and also on the number of times it is used [44]. After five months, the electrode response deteriorated;

Table 2
Selectivity coefficient values and analytical properties for Pb(II) selective sensor

Interfering ion	$K_{Pb,M}^{2+}$					
	A	B	C	D	E	F
Na(I)	1.54×10^{-2}	1.03×10^{-2}	2.3×10^{-3}	4.20×10^{-2}	1.6×10^{-3}	3.0×10^{-3}
K(I)	2.44×10^{-1}	1.27×10^{-1}	2.8×10^{-3}	6.00×10^{-3}	2.6×10^{-3}	5.5×10^{-3}
Ag(I)	4.89×10^{-2}	–	8.0×10^{-3}	3.20×10^{-1}	8.6×10^{-2}	9.3×10^{-3}
Mg(II)	3.10×10^{-5}	2.65×10^{-5}	5.3×10^{-4}	3.96×10^{-3}	1.1×10^{-3}	4.8×10^{-4}
Ca(II)	1.28×10^{-5}	2.02×10^{-5}	6.7×10^{-4}	$< 1.0 \times 10^{-4}$	–	8.0×10^{-4}
Ba(II)	7.40×10^{-5}	–	8.2×10^{-4}	6.20×10^{-3}	1.9×10^{-4}	1.3×10^{-4}
Sr(II)	2.74×10^{-5}	–	–	5.16×10^{-3}	2.7×10^{-4}	2.0×10^{-4}
Mn(II)	–	–	–	–	3.1×10^{-3}	7.9×10^{-4}
Co(II)	2.00×10^{-5}	1.56×10^{-5}	1.3×10^{-3}	2.70×10^{-3}	3.8×10^{-3}	1.6×10^{-3}
Ni(II)	1.18×10^{-4}	2.07×10^{-4}	1.4×10^{-3}	5.58×10^{-3}	1.1×10^{-3}	6.3×10^{-3}
Cu(II)	8.13×10^{-5}	5.13×10^{-5}	1.6×10^{-3}	1.29×10^{-2}	2.5×10^{-3}	4.8×10^{-3}
Zn(II)	1.29×10^{-5}	2.08×10^{-5}	2.3×10^{-3}	1.20×10^{-3}	1.2×10^{-3}	1.3×10^{-3}
Cd(II)	7.77×10^{-6}	5.54×10^{-6}	7.5×10^{-3}	4.70×10^{-3}	1.8×10^{-3}	7.6×10^{-3}
Hg(II)	1.47×10^{-1}	–	1.5×10^{-2}	–	–	2.9×10^{-2}
Cr(III)	–	–	–	–	–	5.1×10^{-3}
Fe(III)	5.66×10^{-5}	–	–	–	–	3.5×10^{-3}
Al(III)	–	–	–	5.61×10^{-2}	–	2.4×10^{-3}
Slope (mV/decade)	30.0 ± 1.0	28.0 ± 1.0	29.0 ± 1.0	30.0 ± 0.2	29.3 ± 0.7	30.0 ± 1.0
Linear range/M	1.0×10^{-5} to 1.0×10^{-1}	1.0×10^{-5} to 1.0×10^{-1}	1.0×10^{-6} to 8.0×10^{-3}	1.0×10^{-5} to 1.0×10^{-1}	2.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-1}
Detection limit/M	1.0×10^{-5}	1.0×10^{-6}	8.0×10^{-7}	4.0×10^{-6}	1.2×10^{-6}	6.0×10^{-7}
pH range	3.0–9.0	3.0–6.0	3.0–6.0	4.0–8.0	3.5–6.3	1.5–6.0
Response time/s	<60	300	~40	45	45	15
Lifetime	–	–	2 months	12 weeks	50 days	5 months
Additive	–	–	Oleic acid	Oleic acid	–	NaTPB

A: [1]; B: [42]; C: [13]; D: [14]; E: [41]; F: (present work).

Table 3
Results obtained by direct potentiometry of synthetic samples (For $n = 5$)

Serial no.	Composition	Observed Pb^{2+} conc. (M)
1	0.0010 M $Pb(NO_3)_2$ + 0.01 M $NaNO_3$ + 0.01 M $Co(NO_3)_2$ + 0.01 M $Cu(NO_3)_2$	0.00097 \pm 0.00002
2	0.0010 M $Pb(NO_3)_2$ + 0.01 M $Ni(NO_3)_2$ + 0.01 M $Mn(NO_3)_2$ + 0.01 M $Mg(ClO_4)_2$	0.00099 \pm 0.00004
3	0.0010 M $Pb(NO_3)_2$ + 0.01 M $Ca(ClO_4)_2$ + 0.01 M $Cd(NO_3)_2$ + 0.01 M $Hg(NO_3)_2$	0.00102 \pm 0.00005
4	0.0010 M $Pb(NO_3)_2$ + 0.01 M $Zn(NO_3)_2$ + 0.01 M $NaNO_3$ + 0.01 M NH_4NO_3	0.00097 \pm 0.00003
5	0.0010 M $Pb(NO_3)_2$ + 0.01 M $AgNO_3$ + 0.01 M $Sr(ClO_4)_2$ + 0.01 M $Ba(ClO_4)_2$	0.00102 \pm 0.00004
6	0.0010 M $Pb(NO_3)_2$ + 0.01 M $Fe(NO_3)_3$ + 0.01 M $Cr(NO_3)_3$ + 0.01 M $Al(NO_3)_3$	0.00104 \pm 0.00002

Table 4
Comparison of the present ISE method, AAS and titrimetric methods in real samples

Samples	ISE method ($g\ dm^{-3}$)	Titrimetric method ($g\ dm^{-3}$)	
(a) Electroplating bath solutions (For $n = 5$)			
Electroplating bath A	9.95 \pm 0.35	10.10 \pm 0.20	
Electroplating bath B	2.01 \pm 0.10	1.95 \pm 0.15	
Sample	ISE method (%)	Titrimetric method (%)	
(b) Alloy sample (For $n = 5$)			
Solder	39.8 \pm 0.20	39.5 \pm 0.40	
Samples	ISE method ($mg\ dm^{-3}$)	Titrimetric method ($mg\ dm^{-3}$)	AAS method ($mg\ dm^{-3}$)
(c) Battery waste and effluent water samples (For $n = 5$)			
Eveready battery waste	20.1 \pm 0.08	19.8 \pm 0.30	19.9 \pm 0.05
Scooter battery waste	14.6 \pm 0.08	14.3 \pm 0.40	14.5 \pm 0.03
Electroplating effluent A	6.5 \pm 0.15	–	6.2 \pm 0.07
Electroplating effluent B	5.8 \pm 0.10	–	5.8 \pm 0.05
Industrial effluent A	8.5 \pm 0.15	–	8.6 \pm 0.07
Industrial effluent B	5.0 \pm 0.10	–	5.2 \pm 0.08

which may be attributed to the aging of the PVC matrices, ionophore as well as plasticizer [44].

4. Analytical application

Table 3 shows the results obtained by direct potentiometry of synthetic samples containing various ions. As the analysis results show that these metal ions do not interfere seriously, which is also reflected from the selectivity coefficient study (Table 2; electrode no. F), the electrode was used to determine the concentration of lead in the electroplating bath solutions (Table 4). Effluent samples collected from plating shops and industrial units, solder alloy and battery waste samples were analyzed by the CWISE fabricated in the present work. The results, obtained by the proposed sensor are in good agreement with titrimetric method [37] (Table 4) and by AAS. The sensor was successfully used as an indicator electrode in the potentiometric titration of $Pb(II)$ with EDTA. $10.0\ cm^3$ of $1.0 \times 10^{-3}\ M\ Pb(NO_3)_2$ was titrated against $1.0 \times 10^{-2}\ M$ EDTA solution. The plot in Fig. 4 does not have a standard sigmoid shape. However, the sharp break point observed corresponds to the stoichiometry of Pb^{2+} –EDTA complex. The deviation in shape may be due to the interference caused by sodium ions of the EDTA salt and has been observed earlier also [45–47].

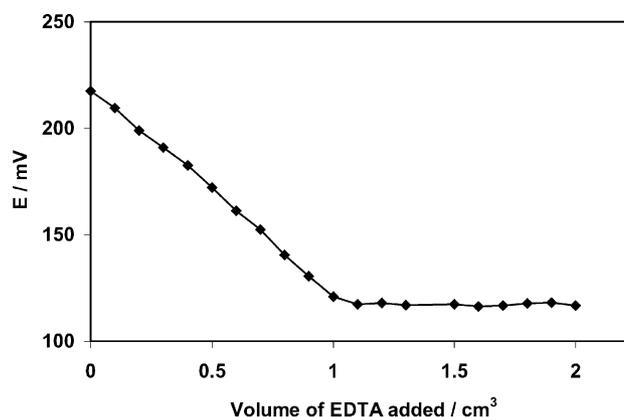


Fig. 4. Potentiometric titration of Pb^{2+} ($10.0\ cm^3$ of $1.0 \times 10^{-3}\ M$) with EDTA ($1.0 \times 10^{-2}\ M$).

5. Conclusion

The CWISE developed in the present work exhibited good reproducibility over a period of about 5 months in the concentration range 1×10^{-6} to $1 \times 10^{-1}\ M$. The functional pH range of the proposed sensor is 1.5–6.0 and most of the ions commonly found to be interfering with lead ion sensors do not cause any disturbance. Analytical applications of the

sensor proves that it holds promise for regular and routine analyses in the determination of Pb(II) ions.

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