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Sorption of Metal Ions on Acrylamidezirconium (IV) Arsenate and its Synthesis of PVC based Lead (II) Selective Electrode

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Abstract: The adsorption of different metal ions on acrylamidezirconium (IV) arsenate has been studied. The effect of surfactant concentration (Tween 80-R and Tritron X-100) on sorption of different metal ions acrylamidezirconium (IV) arsenate was explored. The effect of experimental parameters such as contact time, temperature, and pH on adsorption of Pb^{2+}ions was studied. The promising feature of the material is its specificity for Pb^{2+} ions. A new PVC based Pb^{2+} ion-selective electrode using *acrylamidezirconium (IV) arsenate* as electro-active material has been fabricated. The electrode works well over a wide range of concentration 1×10^{-1} M–1×10^{-7} M with a Nerstian slope of 30 ± 1 mV per decade. The sensor shows the short response time of 20 seconds and can operate in the pH range of 2–7. The sensor can be used for the period of over 4 months with out deviation in response characteristics. The electrode has been successfully used as an indicator electrode for potentiometric titration of Pb^{2+} ions in solution against EDTA solution.

Keywords: Hybrid exchanger, acrylamide, Pb^{2+} ions, ion selective electrode, surfactants

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INTRODUCTION

The presence of heavy metals in the environment is of great concern because of their toxicological and physiological effects. These metals, if present beyond certain concentration, can be a serious health hazard and can lead to many disorders in the normal functioning of the body. So it is imperative to device methods for qualitative and quantitative determination of such metal ions viz Cd^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+} etc. From past few years large numbers of the selective hybrid ion exchanger have been synthesized (1–3) which have been widely used in metal recovery process, water softening, removal of interfering ions, fabrication of ion-selective electrodes, and fuel cells. However, their use as ion selective electrodes had attracted much attention because of versatile analytical tools and recommended widely for quick, easy to use, and allowing accurate determination of chemical species at a relatively low level. Potentiometery with ion-selective electrodes is in principle particularly well-suited for its selective response to free ions in aqueous solution. There is a continuous work going on for the synthesis of ion selective electrodes for the determination of these heavy metal ions. Some of the heterogeneous ion-exchange membranes consisting of suitable colloidal ion-exchanger particles as ionophore embedded in the polymer binder have been extensively studied as potentiometric sensor (4–7). Recently organic-inorganic composite ion-exchangers were used as electro-active material for fabrication of ion-selective (8–13). The present paper reports the effect of surfactant concentration on distribution coefficients of metal ions on hybrid ion-exchanger *acrylamidezirconium (IV) arsenate* and fabrication of its ion selective electrode for the determination of Pb^{2+} ions. The sensor was compared with few other Pb^{2+} ion selective electrodes reported in the literature (14–17).

Lead in general is a metabolic poison, enzyme inhibitor, and causes damage to the nervous systems and kidneys and is a suspected carcinogen. Thus ion selective electrodes for detection of Pb^{2+} ion have received much attention because of health concerns. Though, there are a number of methods devised for the determination of Pb^{2+} ions such as spectrophotometery, polorography, atomic absorption spectrometry and HPLC. Such methods however, require a good infrastructure development, maintenance, and adequate expertise while as ion selective electrode provide simple, cheap, and easy to use device for analysis of Pb^{2+} ions.

EXPERIMENTAL

Reagents and Instruments

Zirconiumoxychloride and sodium arsenate were obtained from LOBA-CHEMIA. (India), Acrylamide from CDH. (India), PVC (polyvinyl chloride) and Tetrahydrofuran obtained from Merck. All other reagents used were of analytical reagent grade. Elico L 610 pH meter was used for pH measurements and digital Potentiometer EI 118 for the potential measurements.

Synthesis of Acrylamidezirconium (IV) Arsenate

Acrylamidezirconium (IV) arsenate was prepared by adding a mixture of (1:2) aqueous solution of sodium arsenate (0.25 M) and acrylamide (0.25 M) into the aqueous solution of zirconiumoxychloride (0.25 M) slowly at a flow rate of 1 ml min^{-1}. The pH of the solution was adjusted to 1.0 by adding the dilute solution of ammonia or nitric acid. The resulting white precipitate so formed was stirred for half an hour at temperature $70 \pm 2°C$ and kept for 24 hours to let the precipitate settle down and finally filtered under suction. The excess of acid was removed by washing with dimineralized water and dried at 50°C in an oven. The dried material was converted into H^+ form by treating with 1.0 M nitric acid for 24 hours with occasional shaking. The material thus obtained was finally washed with demineralized water to remove excess of acid and dried at 50°C in an oven and stored for further use.

Effect of Time on Adsorption of Pb^{2+} Ions

300 mg portions of the *acrylamidezirconium (IV) arsenate* in H^+ form were taken in an Erlenmeyer flask and shacked with 30 ml of lead nitrate solutions. The amount of Pb^{2+} ions adsorbed at different intervals of time was determined.

Effect of Temperature on Adsorption of Pb^{2+} Ions

300 mg portions of the *acrylamidezirconium (IV) arsenate* in H^+ form were taken in Erlenmeyer flasks with 30 ml of lead nitrate solution. The contents were shacked for 4 hours at different temperature 25, 30, 35, 40, and 45°C.

Effect of pH on Adsorption of Pb^{2+} Ions

300 mg portion of the *acrylamidezirconium (IV) arsenate* in H^+ form were taken in Erlenmeyer flasks with 30 ml of different lead nitrate solution having pH ranging from 1–7 for 4 hours.

Distribution (Sorption) Studies

The distribution coefficient (K_d) of metal ions were determined by batch method in two different surfactant mediums Tritron X-100 and Tween-80R.

Various 400 mg portion of the *acrylamidezirconium (IV) arsenate* in H^+ form were taken in Erlenmeyer flasks and treated with 40 ml of different metal nitrate solution in desired medium and shacked for 4 hours in temperature controlled shaker at $25 \pm 2^\circ C$ to attain the equilibrium. The metal ion concentration before and after the equilibrium were determined by EDTA titration. The distribution coefficients were calculated using the equation

$$\mathrm{Kd} = \frac{\text{Amount of metal ion in the exchanger phase/g of exchanger}}{\text{Amount of metal ion in the solution phase/mL of solution}}$$

In our case

$$\mathrm{Kd} = \frac{\mathrm{I\text{-}F}/400\,\mathrm{mg}}{\mathrm{F}/40\,\mathrm{ml}}$$

where I is volume of EDTA solution used before treatment. F is the volume of EDTA consumed by metal ion left in the solution phase after treatment with the exchanger.

Quantitative Separations of Metal Ions in Synthetic Binary Mixtures

Important separation of metal ions were achieved on column of acrylamidezirconium (IV) arsenate (height 35 cm, i.d 0.6 cm, bed height 5.5 cm) containing 2.0 g of the exchanger in H^+ form. The column was washed thoroughly with demineralized water and then with the suitable solvent. The binary mixture of metal ions was loaded and eluted with suitable solvent. The effluent was collected in 10 mL fractions at a flow rate of 5 to 6 drops per minute. The metal ion in the effluent was determined by EDTA titration.

Preparation of Acrylamidezirconium (IV) Arsenate Membrane

The ion exchange material acrylamidezirconium (IV) arsenate (0.6 g) was grounded to fine powder and mixed thoroughly with PVC (2.0 g) dissolved in 15 mL of THF. The resulting solution was carefully poured on the glass plate and left for the complete evaporation of the solvent. A 12 mm disc was cut from the master membrane and glued to one end of the Pyrex glass tube. 0.1 M Pb $(NO_3)_2$ solution was used as internal solution. Detection limit, slope response curve, response time, and the working pH range of the electrode were evaluated to study the characteristics of the electrode. Three different membranes were prepared with varying the amount of ion exchanger and keeping the amount of PVC constant

Conditioning of Membrane and Potential Measurement

The membrane was equilibrated for 5 days in a 0.1 M Pb $(NO_3)_2$ solution and for 1 hour at least before use for the potential measurements. Potential measurements were performed at $25 \pm 2°C$ using the digital potentiometer (EI) 118. The electrochemical representation of the cell is given as Ag, AgCl|KCl (satd): Sample solution|ISE membrane|0.1 M KCl|Ag, AgCl. The potential measurements were done in the concentration range of 1×10^{-1}–1×10^{-8} mol L^{-1}. All the solution prepared by the serial dilution method and pH adjustments was done by dilute solution of ammonia or nitric acid.

Water Content

The conditioned membrane was put in the demineralized water (DMW) to elute out the diffusible salts and soaked with whattman paper to remove excess of the moisture on the surface of membrane. The membrane was then dried in the oven at $50 \pm 2°C$ for 24 hours. The water content was calculated by formula

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} 100$$

W_w weight of the wet membrane, W_w weight of dry membrane

Response Time

The response time of the electrode was measured by recording the potential at different intervals of time (after every 5 seconds) till the potential attains the constant value. Initial potential was measured at zero seconds when the electrode was dipped into (2×10^{-2} M) test solution of Pb $(NO_3)_2$.

Selectivity Coefficients

One of the most important characteristics of the ion-selective electrode is its response to foreign ions discussed in terms of selectivity coefficient. Different methods are employed such as *Mixed Solution Method and Separate Solution Method* for determination of selectivity coefficients. In the present work we used the fixed interference method was used, which is one of the mixed solution methods. The selectivity coefficient is calculated using the equation given below.

$$K^{\mathrm{pot}}_{\mathrm{A,B}} = \mathrm{a_A}/(\mathrm{a_B})^{\mathrm{z_A}/\mathrm{z_B}}$$

Where a_A and a_B activities of primary and interfering ion and z_A and z_B are charges on the ions.

RESULTS AND DISCUSSION

The ion exchange material *acrylamidezirconium (IV) arsenate* was synthesized at pH 1. The material shows a good ion-exchange capacity of 1.58 meq/g for Na^+ ions. In order to explore the separation potentiality of the material sorption behavior of 16 metal ions were studied in two different surfactant mediums Tween-80 R and Tritron X-100 (Tables 1 and 2). The results are given in terms of Fig. 1 and Fig. 2. Surfactants were chosen as they are the surface active agents which can play a lead role in modifying the absorption behavior of ion-exchangers. It has been found that the sorption of the metal ions by the exchanger increases with the increase in concentration of the surfactant (Tween-80R) upto 4% (Fig. 1). Further increase in the concentration decreases therefore the 4% concentration of Tween-80R is most adequate for the sorption of metal ions. In case of the Tritron X-100 the reverse trend was observed. It has been observed that the uptake of metal ions decreases as the concentration of Tritron X-100

Table 1. Effect of varying concentration of nonionic surfactant Tween 80-R on distribution coefficients of different metal ions

Metal ion	DMW	Tween 1%	Tween 2%	Tween 4%	Tween 6%	Tween 8%
Mg^{2+}	24.3	38.8	48.0	96.0	70.0	42.0
Ca^{2+}	24.3	61.2	70.5	82.2	42.0	42.0
Sr^{2+}	31.2	70.0	85.0	155.0	63.0	56.0
Ba^{2+}	87.0	95.60	125.0	350.0	110.0	100.0
Pb^{2+}	583.3	720.0	925.0	1540	1320.0	660.0
Hg^{2+}	102.0	333.3	441.0	450.0	380.0	212.0
Zn^{2+}	31.2	50.0	75.0	110.0	88.8	78.8
Cd^{2+}	24.3	74.5	78.2	145.0	100.0	78.8
Mn^{2+}	33.0	58.3	40.5	90.0	60.0	60.0
Cu^{2+}	40.0	109.0	107.2	175.0	120.0	110.0
Al^{3+}	42.5	104.4	220.0	260.0	225.0	212.0
Ni^{2+}	20.0	25.0	42.0	48.0	20.0	18.8
Fe^{3+}	64.0	77.7	156.0	173.0	64.0	65.5
Th^{4+}	28.0	131.3	185.0	360.0	130.0	120.0
Ce^{3+}	125.0	362.0	650	800.0	700.0	320.0
La^{3+}	80.0	350.0	500.0	800.0	400.0	225.2

Table 2. Effect of varying concentration of nonionic surfactant Tritron X-100 on Distribution coefficients of different metal ions

Metal ion	DMW	Tritron 1%	Tritron 2%	Tritron 4%	Tritron 6%
Mg^{2+}	24.3	40.0	34.4	20.0	17.2
Ca^{2+}	24.3	34.0	23.2	20.1	18.2
Sr^{2+}	31.2	34.0	36.2	28.0	17.2
Ba^{2+}	87.0	206.0	104.2	88.0	78.5
Pb^{2+}	583.3	800.0	657.0	420.2	420.2
Hg^{2+}	102.0	87.0	86.5	50.4	44.2
Zn^{2+}	31.2	27.4	25.5	22.5	12.4
Cd^{2+}	24.3	78.3	58.0	45.3	38.3
Mn^{2+}	33.0	44.0	40.0	38.8	26.4
Cu^{2+}	40.0	100.0	71.6	160.5	120.0
Al^{3+}	42.5	127.0	103.2	70.2	68.4
Ni^{2+}	20.0	28.0	25.0	22.5	12.5
Fe^{3+}	64.0	225.0	170.0	125.3	120.0
Ce^{3+}	125.0	400.0	340.0	152.0	122.0
Th^{4+}	28.0	124.0	70.8	57.2	40.0
La^{3+}	80.0	110.2	110.2	102.2	80.0

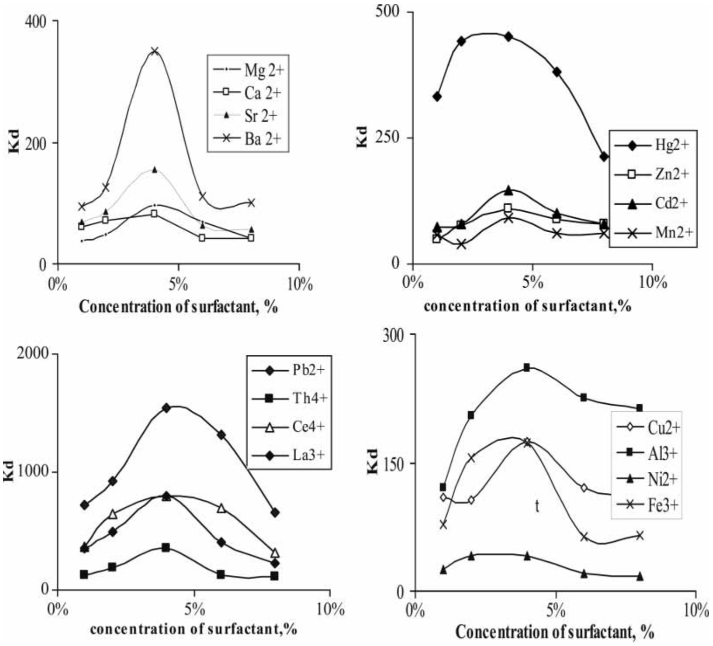

Figure 1. Effect of concentration of Tween-80R on sorption of different metal ions on acrylamidezirconium (IV) arsenate.

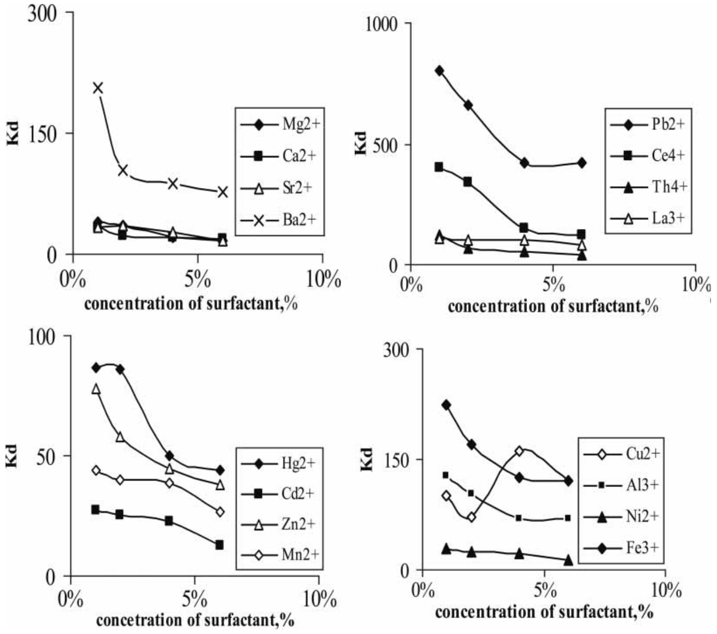

Figure 2. Effect of concentration of Tritron X-100 on sorption of different metal ions on acrylamidezirconium (IV) arsenate.

increases in almost all the metal ions except copper while in the case of La^{3+} the Tritron X-100 concentration has no effect on the extent of the sorption. The effect of the time, the pH, and the temperature on the sorption of Pb^{2+} ions on acrylamidezirconium (IV) arsenate was studied. Fig. 3a shows that the sorption becomes optimum and constant after 4 hours of shaking period. The maximum absorption of Pb^{2+} ions occurs at pH 3 as indicated by Fig. 3b. At higher pH Pb^{2+} ions are hydrolyzed and at lower pH the higher concentration of H^+ ions in solution suppress the exchange of ions. Fig. 3c shows that the adequate temperature for the sorption of Pb^{2+} ions is 30 ± 2°C. It is evident from the K_d values that the Pb^{2+} ions are highly sorbed by the material than any other metal ions studies. The promising feature of acrylamidezirconium (IV) arsenate is its specificity for Pb^{2+} ions which makes the material most useful for determination of lead in a complex mixture containing several other metal ions. The elution curves of binary separation (Fig. 4) shows that the elution of metal ions is quite sharp and recovery is quantitative and reproducible. The practical utility was explored by quantitative separation of lead ions (Table 3) from the binary mixtures on acrylamidezirconium (IV) arsenate columns. On the basis of the specificity for lead ions, an ion-selective electrode for the determination of microqauntities of lead ions was fabricated. Three different membranes

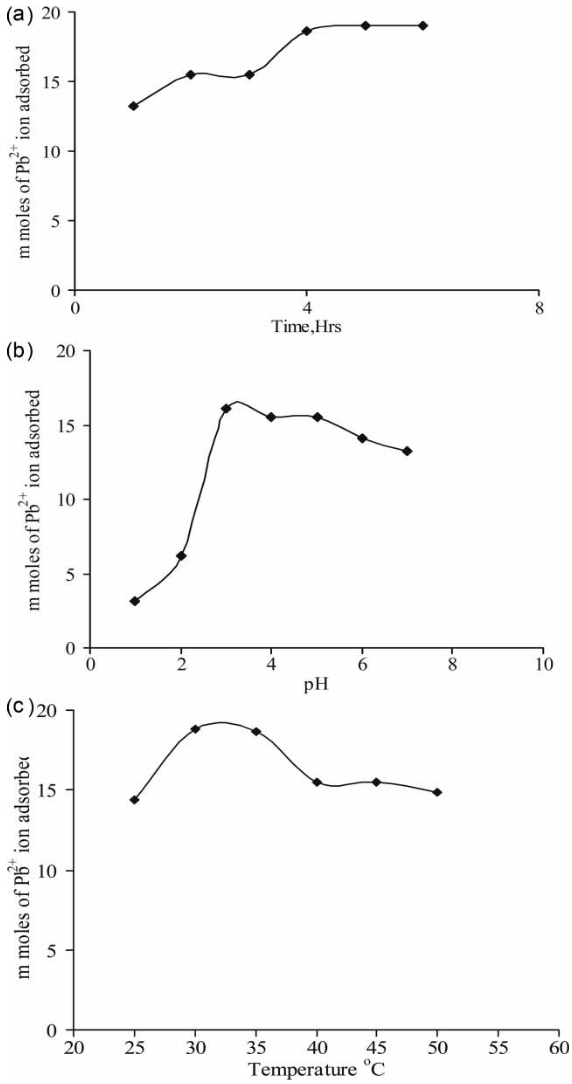

Figure 3. Effect of time, pH and temperature on sorption of Pb^{2+} ions on acrylamidezirconium (IV) arsenate.

were prepared by varying the amount of ion-exchanger in exchanger-PVC mixture (Table 4). It was observed that increasing the amount of ion-exchanger in the mixture the thickness of the membrane increases; however, it decreases the response time and the slope of the membrane. On the basis of quick response time and slope membrane M-2 was selected for further studies. The potential response of the electrode measure for different Pb^{2+} ion concentration is given in the Fig. 5. It reveals that the working

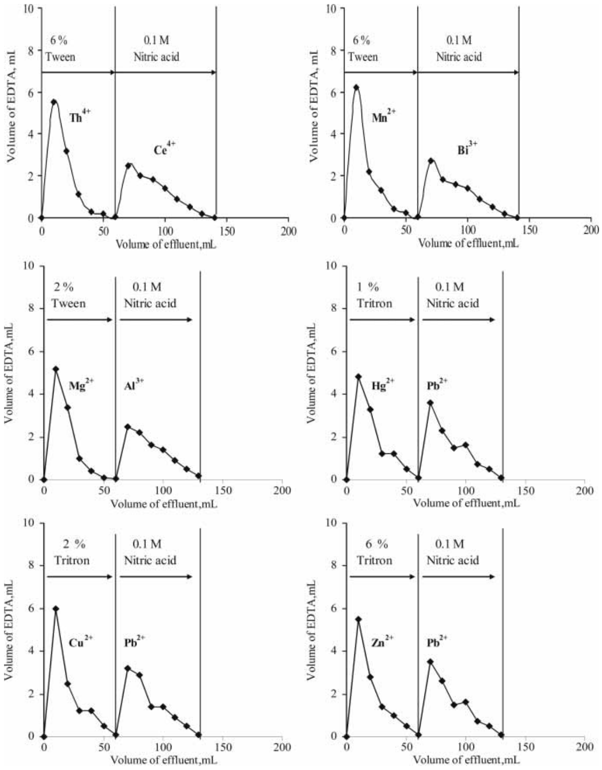

Figure 4. Binary separations of metal ions acrylamidezirconium (IV) arsenate columns.

Table 3. Binary separation of metal ions on acrylamide zirconium arsenate columns

Metal ions	Amount loaded, mg	Amount recovered, mg	% Recovery	Eluent used	Eluent volume, mL
Mn^{2+}	5.21	5.20	99.8	6% Tween	40
Bi^{3+}	18.60	18.42	99.0	0.1 M nitric acid	70
Mg^{2+}	2.40	2.28	95.0	2% Tween	50
Al^{3+}	2.98	2.70	90.0	0.1 M nitric acid	90
Th^{4+}	20.80	20.65	99.2	6%Tween	60
Ce^{4+}	12.95	12.80	98.9	0.1 M nitric acid	90
Hg^{2+}	20.59	20.32	98.62	1% Tritron	50
Pb^{2+}	19.68	19.38	98.40	0.1 M nitric acid	70
Zn^{2+}	5.88	5.52	93.87	6% Tritron	50
Pb^{2+}	19.68	19.32	98.10	0.1 M nitric acid	70
Cu^{2+}	6.20	6.02	97.09	2% Tritron	60
Pb^{2+}	19.68	19.42	99.06	0.1 M nitric acid	80

Table 4. Synthesis and properties of acrylamidezirconium (IV) arsenate membrane

	Composition of membrane					
Membrane sample	Ionophore (mg)	PVC (mg)	Thickness (mm)	Concentration range	Response time (sec)	Slope (mV)
M-1	200	250	0.36	1×10^{-1}–1×10^{-6}	25	25
M-2	250	250	0.40	1×10^{-1}–1×10^{-7}	20	30
M-3	300	250	0.52	1×10^{-1}–1×10^{-7}	29	27

concentration range of the membrane is $1 \times 10^{-1} - 1 \times 10^{-7}$ M of Pb $(NO_3)_2$ with a slope of 30 ± 1 mV decade^{-1}. The limit of detection determined by intersection of two extrapolated segments of the calibration graph was 5.0×10^{-6}. The response of the electrode is measured as time required reaching the steady potential of ±1 mV of the final equilibrium potential. Fig. 6 shows that the average response time for the electrode is 20 seconds. The sensor was tested over the period of 4 months to investigate its stability, during which time the calibration graph was plotted from time to

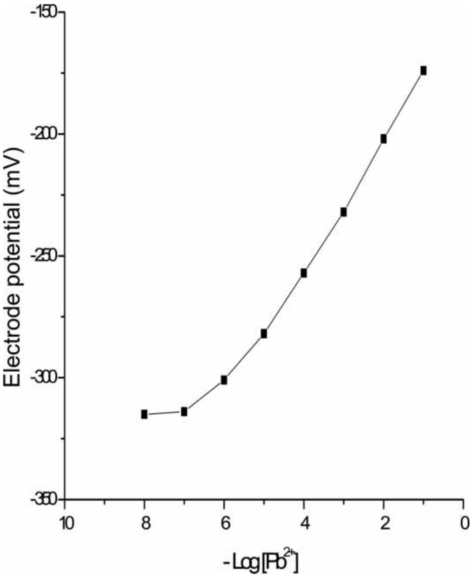

Figure 5. Calibration curve of Pb^{2+} ions using acrylamide zirconium (IV) arsenate membrane electrode.

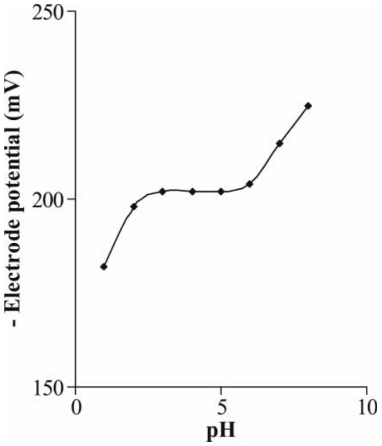

Figure 6. Effect of pH on electrode response.

time and no change was observed in the working concentration range, the slope, and the response time. However, it is necessary to keep the membrane dipped in 0.1 M Pb $(NO_3)_2$ when not in use. The effect of pH on the electrode response was studied (Fig. 7) in the range of 1–7 by using 1×10^{-2} M Pb $(NO_3)_2$ solutions, adjustment of the pH was done with dilute hydrochloric acid or ammonia. The response of the sensor was significantly affected by pH as sharp changes in the electrode potential below pH 2 as well as above pH 7 were observed. The reason for this behavior may be due to

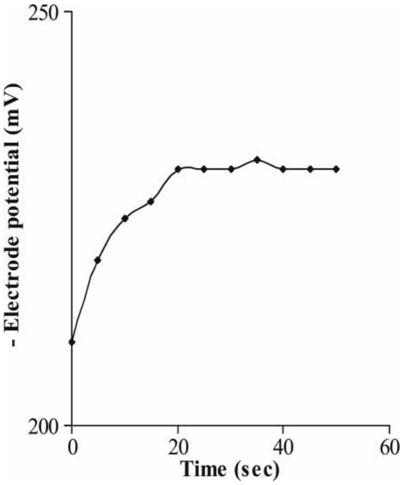

Figure 7. Response of the acrylamide zirconium (IV) arsenate membrane electrode at different time intervals.

Table 5. Selectivity coefficients for Pb^{2+} selective electrode for various interfering ions using fixed interference method

Interfering ions	Selectivity coefficients
Mg^{2+}	2.0×10^{-3}
Ca^{2+}	1.3×10^{-3}
Sr^{2+}	1.6×10^{-3}
Ba^{2+}	2.4×10^{-2}
Cu^{2+}	3.5×10^{-3}
Zn^{2+}	1.5×10^{-2}
Cd^{2+}	1.0×10^{-3}
Mn^{2+}	2.4×10^{-3}
Ni^{2+}	3.2×10^{-3}
Hg^{2+}	3.6×10^{-3}

the formation of lead hydroxide at high pH which decreases the response and at low pH the electrode responded to H^+ ions results in higher response. Hence the most suitable pH range for the sensor is between pH 2 and pH 7. The thickness of the membrane (M-2) was found to be 0.40 mm and the % water content of the wet membrane (M-2) was found to be 0.0226. The most important feature of the sensor is its selectivity towards the primary ion against the foreign ions. The selectivity coefficients for different divalent metal ions towards the Pb^{2+} sensor were determined. It is apparent from Table 5 that the values determined in range of 10^{-3} are less than unity hence the sensor prepared is selective towards Pb^{2+} ions in the presence of other interfering ions listed in Table 5. Table 6 shows the characteristic

Table 6. Characteristic properties of different lead selective electrodes

S. no	Ionophore	Concentration range (M)	Slope (eV)	Detection limit	Response time (sec)
1	Acrylamide zirconium (IV) arsenate	1×10^{-7}–1×10^{-1}	30.0	5×10^{-5}	20
2	Benzyl disulphide (14)	2×10^{-5}–5×10^{-2}	29.2	1×10^{-5}	240
3	Polypyrrole thorium(IV)-phosphate (3)	1×10^{-6}–1×10^{-1}	29.1	—	35
4	Piroxime (15)	1×10^{-5}–1×10^{-1}	30.0	4×10^{-6}	45
5	5,5′-dithiobis-(2-nitrobenzoic acid) (16)	4×10^{-6}–1×10^{-2}	29.0	1.5×10^{-6}	70
6	Capric acid (17)	1×10^{-5}–1×10^{-1}	29.0	6×10^{-6}	15

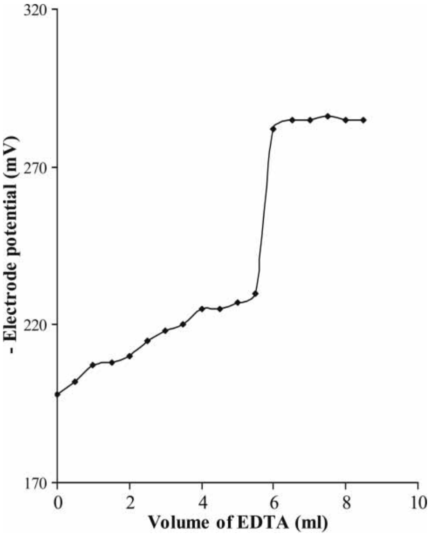

Figure 8. Precipitation titration of Pb^{2+} against EDTA solution.

properties of few lead selective electrodes. It can be inferred from the results that the present sensor is better than other electrodes in one or all aspects. The practical utility was explored by carrying the potentiometric titrations of the 0.01 M $Pb(NO_3)_2$ against 0.01 M EDTA solution as titrant using the sensor as indicator electrode. The potential was recorded after addition of every 0.5 mL of EDTA solution to 5 mL of 0.01 M $Pb(NO_3)_2$ diluted to 20 mL with demineralized water. The addition of EDTA decreases the potential as a result of decrease in free Pb^{2+} ions due to formation of complex with EDTA. The amount of Pb^{2+} ions can be accurately determined by the titration curve (Fig. 8) providing a sharp end point.

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