

PHYSICAL METHODS
OF INVESTIGATION

Highly Selective Lead(II) Coated Graphite Sensor Based on 4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane as a Neutral Ionophore¹

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Abstract—4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD) has been explored as a neutral ionophore for preparing polyvinyl chloride (PVC)-based membrane sensor selective to lead(II). The optimized membrane incorporating kryptofix22DD as the active material, nitrobenzene as plasticizer and sodium tetraphenylborate as an anion excluder and membrane modifier in PVC (in the weight ratio of 5.0 : 63.0 : 2.0 : 30.0, respectively) was directly coated on the surface of graphite rod. The sensor exhibits a Nernstian slope (29.4 mV/decade) in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M Pb^{2+} . The detection limit of the sensor is 6.5×10^{-6} M. The proposed sensor has a fast response time (~ 10 s), a satisfactory reproducibility and relatively long lifetime. The electrode shows high selectivity toward Pb^{2+} ion in comparison to other common cations. The proposed sensor is suitable for use in aqueous solutions in a wide pH range of 2.0–10.0. It was used as an indicator electrode for the end point detection in the potentiometric titration of Pb^{2+} ion with ethylenediaminetetraacetic acid (EDTA) and sodium iodide (NaI) solutions. The proposed sensor was successfully applied for the recovery of Pb^{2+} ions spiked in real water samples.

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1. INTRODUCTION

Electroanalytical chemistry can play a very important role in the protection of our environment, in particular, chemical sensors. A useful definition for a chemical sensor is “a small device that as the result of a chemical interaction or process between the analyte and the sensor device, transforms chemical information of a quantitative, or qualitative type into an analytically useful signal.” Chemical sensors have a chemical or molecular target to be measured. Most of these devices fall into two major categories (in accordance with the nature of the electrical signal): amperometric and potentiometric. In contrast to amperometric sensors, where current is monitored as a function of time, in potentiometric sensors, the analytical information is obtained by converting the recognition process into a potential signal, which is proportional to the concentration of species generated or consumed in the recognition event. Such devices rely on the use of ion selective electrodes (ISEs) for obtaining the potential signal.

The quick determination of trace quantities of ionic species, by simple methods, is of special interest in analytical chemistry. Ion selective electrodes based on

solvent polymeric membranes with incorporation of ion carriers are shown to be very useful tools for chemical, clinical and environmental analyses as well as in process monitoring [1, 2]. They have been the subject of interest for analytical chemists as they provide accurate, rapid and low cost method for analysis. This technique is also nondestructive and adaptable to very small sample volume; moreover, online monitoring is also possible by these devices. Some commercialized sensors for alkali and alkaline earth metals, halides, etc. are available [3–7]; however, more efforts are required to develop ion selective electrodes of commercial standard for heavy metal ions, which are toxic beyond a certain concentration level [8–10].

Lead is one of the most toxic and hazardous heavy metals because of its non-biodegradability. Common sources of lead exposure include industrial activities, production of pigments, anticorrosion coatings, car gases, soil, water, air and contaminated foods [11]. For humans, lead is a neurotoxic metallic element that can be absorbed by the body, primarily through the lungs and stomach. Lead poisoning occurs with repeated exposure to a lead-containing environment, allowing lead to accumulate slowly in bones and teeth. Exposure to high concentrations of lead can cause serious health problems, including nervous system dysfunc-

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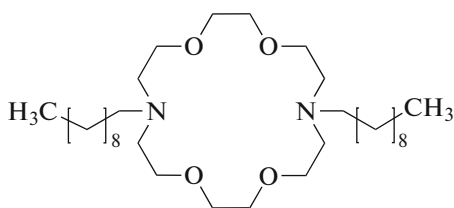


Fig. 1. Chemical structure of 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD).

tion, hemotoxic effects, gastrointestinal tract alterations, interferences in the metabolism of calcium and vitamin D and impaired hemoglobin formation, causing anemia [12, 13].

Potentiometer monitoring, based on the ion selective PVC-membrane sensor as a simple method, offers several advantages such as fast response time, wide dynamic range, reasonable selectivity and low detection limit. Therefore, the use of ISEs for the detection of lead has received much interest and many ligands have been investigated as sensing agents in electrode based ionophore-doped polyvinyl chloride membranes [14–19].

The structure of the ionophores and their geometric factors play important roles in determining the ion selectivities. There are basic factors, which can effectively change the selectivity of the ligand or the ionophore including: the ligand topology which can be sub-classified into the ligand dimensionality, its connectivities, shape, size, conformation, chirality and also its cavity or ring size. The degree of flexibility of the ligand holding of the donor atoms by the host backbone, which makes their positions suitable to match the shape of the coordination sphere of the target species, is another factor. Finally, the presence of lariats (functional groups, arms or chains added to the ionophores to change selectivity) has a great effect on binding. Another very important factor that affects the complexation properties of the ligand binding sites which depends on the nature and number of the binding sites is their shape, size, arrangement and reactivity [20]. The structure macrocyclic and cyclic organic molecules such as crown compounds and cryptands containing O, N, S are capable of forming electron rich interior cavities and can complex through dipole-dipole and ion–dipole interaction with metal ions of compatible dimensions [21–26].

In this paper, we employed 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (trade name kryptofix22DD) (Fig. 1) as an excellent ionophore to fabricate a highly selective sensor for potentiometric determination of Pb^{2+} cation.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD), tetrahydrofuran (THF), nitrobenzene (NB), dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctyl sebacate (DOS), sodium tetraphenylborate (NaTPB), ethylenediaminetetraacetic acid disodium salt, nitric acid, sodium hydroxide and all metal salts were obtained from Merck. High molecular weight polyvinyl chloride (PVC) powder was purchased from Fluka. All reagents were of the highest purity available and used without any further purification. Doubly distilled deionized water was used throughout.

2.2. Fabrication of Electrodes

The electrodes were prepared from graphite bars (3 mm diameter and 50 mm length). The graphite bars were polished and put in a concentrated HNO_3 solution overnight to clean the surface of the electrodes. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A shielded copper wire was glued to one end of the graphite bar and the bar was inserted into the end of a polyethylene tube. A mixture of PVC, plasticizer, ionophore (kryptofix22DD) and the membrane additive (NaTPB) to give a total mass of 100 mg was dissolved in about 2 ml of THF and the solution was mixed well. A homogeneous mixture was obtained after complete dissolution of all the components and the viscosity of the solution was carefully controlled to obtain membranes with reproducible characteristics and uniform morphology and thickness; otherwise, have shown a significant variation which ultimately affected the sensor response. Then, the graphite bar was coated by dipping into the membrane solution for a few seconds and a membrane was formed on the graphite surface of the electrode. The electrode was allowed to stabilize overnight to dry and evaporate the solvent and was finally conditioned by soaking in a 0.001 M solution of lead nitrate for 24 h. Thus, several membranes of varying compositions were prepared and investigated.

2.3. Apparatus and EMF Measurements

The response characteristics of the prepared coated graphite electrodes were determined by recording potential across the membrane as a function of Pb^{2+} concentration at a constant temperature of $25.0 \pm 0.1^\circ C$. All potential measurements were carried out with a digital pH/mV meter model PTR-79 (Zag Chimi, Iran) having ± 0.01 mV accuracy with an Ag/AgCl reference electrode. The potential build up across the electrode was measured using the galvanic cell of the following type:

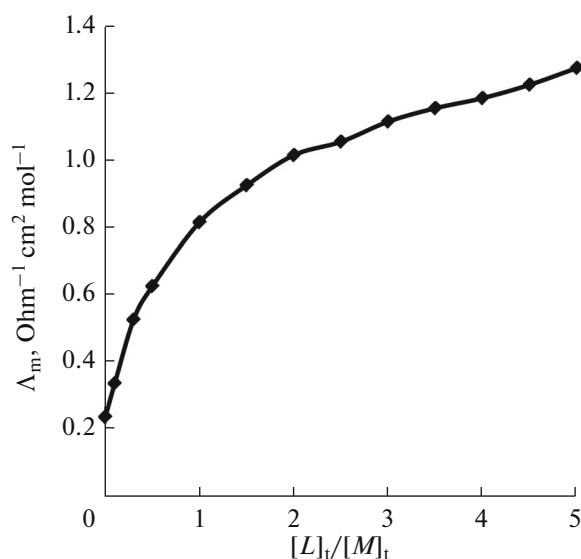


Fig. 2. Molar conductance-mole ratio plots for (kryptofix22DD.Pb)²⁺ complex in pure acetonitrile at 25°C.

Ag/AgCl; KCl(satd.)||Pb²⁺ sample solution|ion selective membrane|graphite bar

The performance of each electrode was investigated by measuring the potential of Pb²⁺ solutions with concentrations ranging from 1.0×10^{-8} to 1.0×10^{-1} M by serial dilution of the 0.1 M stock solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The observed potential versus the logarithm of the Pb²⁺ ion concentration was plotted. Flame atomic absorption spectrometric (FAAS) measurements were performed on a 990-PG instrument equipped with a lead-hollow cathode lamp. The pH of the solutions was measured by a conventional glass pH electrode.

The conductance measurements were performed on a Genway model 4510 conductometer in a thermostated water-bath with a constant temperature maintained within $\pm 0.03^\circ\text{C}$. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.98 cm^{-1} .

3. RESULTS AND DISCUSSION

The existence of two donating nitrogen atoms in the ionophore (kryptofix22DD) was expected to increase both the stability and selectivity of its complexes with transition and heavy metal cations, more than other metal ions [27–30]. Thus, in preliminary experiments, the complexation of kryptofix22DD with Pb²⁺ metal cation was investigated conductometrically. The changes of molar conductivity (Λ_m) versus the ligand to the cation mole ratio ($[L]_t/[M]_t$) for complexation of kryptofix22DD with Pb²⁺ cation were

measured in acetonitrile solution at 25°C (Fig. 2). $[L]_t$ is the total concentration of kryptofix22DD and $[M]_t$ is the total concentration of Pb²⁺ cation. As is obvious in this figure, the slope of the corresponding molar conductivity versus $[L]_t/[M]_t$ plots changes at the point where the ligand to cation mole ratio is about 1, which is an evidence for the formation of a relatively stable 1 : 1 [M : L] complex between Pb²⁺ cation and kryptofix22DD. The stability constant ($\log K_f$) of (kryptofix22DD.Pb)²⁺ complex at 25°C was calculated from the changes of the molar conductance as a function of ligand/cation mole ratios using a GENPLOT computer program [31]. The details of the calculation of the stability constants of complexes by conductometric method have been described elsewhere [32]. The results show that this ligand forms a stable 1 : 1 complex with Pb²⁺ cation in acetonitrile ($\log K_f = 4.23 \pm 0.09$). The obtained results clearly indicate that kryptofix22DD acts as a highly selective ionophore for preparation of lead(II) selective sensor.

Thus, by considering the high enough lipophilicity of the ligand and its suitable complexation with lead(II) cation, it was tested as a potential ionophore for fabrication of a new coated graphite sensor for this metal cation.

3.1. Optimization of Membrane Composition

Besides of the critical role of the nature of ion carrier in preparing ion selective electrodes, some other important features of the PVC membrane, such as the amount of ionophore, the nature of plasticizer, the

Table 1. Optimization of the membrane ingredients

Membrane no.	Membrane mass composition, %				Slope, mV/decade	Linear range, M
	PVC	ionophore (Kryptofix22DD)	additive (NaTPB)	plasticizer		
1	30	—	7.0	63.0 (NB)	14.0 ± 0.2	10 ⁻³ –10 ⁻¹
2	30	7.0	—	63.0 (NB)	21.4 ± 0.1	10 ⁻⁴ –10 ⁻¹
3	30	8.0	2.0	60.0 (NB)	31.1 ± 0.1	10 ⁻⁵ –10 ⁻¹
4	30	3.0	2.0	65.0 (NB)	26.3 ± 0.2	10 ⁻⁵ –10 ⁻²
5	30	5.0	2.0	63.0 (NB)	29.4 ± 0.2	10 ⁻⁵ –10 ⁻¹
6	30	6.0	3.0	61.0 (DOP)	27.0 ± 0.1	10 ⁻⁵ –10 ⁻¹
7	30	8.0	2.0	60.0 (DOP)	28.5 ± 0.2	10 ⁻³ –10 ⁻¹
8	30	5.0	2.0	63.0 (DOP)	32.5 ± 0.2	10 ⁻³ –10 ⁻¹
9	30	5.0	2.0	63.0 (DBP)	25.0 ± 0.1	10 ⁻³ –10 ⁻¹
10	30	6.0	3.0	61.0 (DBP)	18.1 ± 0.1	10 ⁻⁵ –10 ⁻²
11	30	3.0	2.0	65.0 (DBP)	27.2 ± 0.4	10 ⁻⁴ –10 ⁻¹
12	30	3.0	2.0	65.0 (DOS)	24.6 ± 0.1	10 ⁻⁵ –10 ⁻¹
13	30	3.0	3.0	64.0 (DOS)	24.1 ± 0.3	10 ⁻⁴ –10 ⁻¹
14	30	6.0	2.0	62.0 (DOS)	18.6 ± 0.1	10 ⁻⁴ –10 ⁻¹

plasticizer/PVC ratio, and, especially, the nature and amount of additives used are known to significantly influence the sensitivity and selectivity of ion selective electrodes [33, 34]. Thus, different aspects of composition of membranes based on the kryptofix22DD for Pb²⁺ ions were optimized and the results are given in Table 1.

Since the nature of the plasticizer influences both the dielectric constant of the membrane phase and the mobility of the ionophore molecules, it was expected to play a key role in the sensitivity and selectivity of ion selective sensors. As it is seen from Table 1, several plasticizers including DBP, DOP, DOS and NB, were evaluated. Among these four different plasticizers examined, NB results in the best sensitivity. Different values for plasticizer/PVC ratios were examined. As is shown in Table 1, membranes prepared with plasticizer/PVC ratio of about 2 were found to have the best sensitivity and the widest linear concentration range.

The perm-selectivity optimization of membrane sensors is known to be highly dependent on the incorporation of additional membrane components. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improves the sensitivity of certain cation-selective electrodes by reducing the ohmic resistance and improving the

response behavior and selectivity and in some cases by catalyzing the exchange kinetics at the sample-membrane interface [35–37]. The data given in Table 1 reveals that, in the absence of a proper additive, the sensitivity of the lead(II) sensor based on kryptofix-22DD reduces from the Nernstian slope (membrane no. 2 with a slope of 21.4 ± 0.1 mV/decade). However, the presence of NaTPB as a suitable lipophilic additive will improve the sensitivity of the Pb²⁺ sensor considerably.

As a result, membrane composition of 30% PVC, 5% kryptofix22DD, 2% NaTPB and 63% NB (membrane no. 5) exhibits the best Nernstian slope (29.4 mV/decade) and linear concentration range (from 1.0 × 10⁻⁵ to 1.0 × 10⁻¹ M). The calibration curve for this sensor is shown in Fig. 3. The detection limit of this sensor, as determined from the intersection of the two extrapolated segments of the calibration graph is 6.5 × 10⁻⁶ M. The standard deviation of 3 replicate measurements is ±0.2 mV/decade.

3.2. Static and Dynamic Response Time

For analytical purposes, response time is one of the most important factors that are taken into account. Therefore, the static response time of the proposed

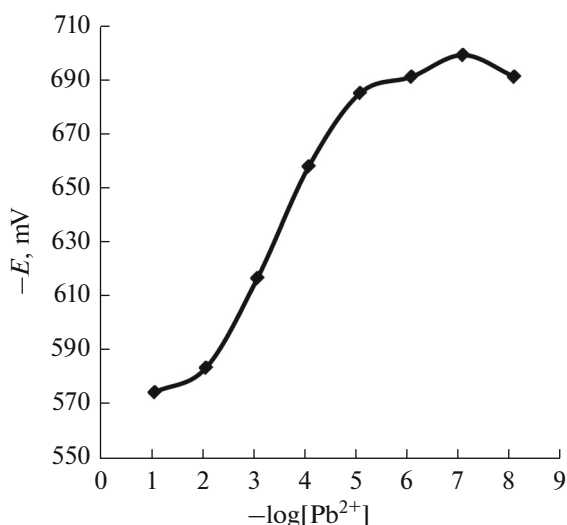


Fig. 3. Calibration curve of the Pb^{2+} selective sensor based on kryptofix22DD.

sensor (membrane no. 5) was studied by plotting the potential response vs. time, at 1.0×10^{-3} M and 1.0×10^{-2} M of Pb^{2+} ion solutions (Fig. 4). As is evident in this figure, in the whole concentration range, the sensor reaches its equilibrium response in a short time (~ 10 s) and no change is observed in about 2 min.

For any ion selective sensor, dynamic response time is an important factor. In this study, the practical response time of the proposed sensor was recorded by changing the Pb^{2+} concentration in solution in a concentration range of 1.0×10^{-5} to 1.0×10^{-1} M and the results are shown in Fig. 5. From this figure, it can be derived that the electrode reaches its equilibrium response rapidly, about 10 s, in the whole concentration range. This is most probably due to the fast exchange kinetics of the complexation-decomplexation of Pb^{2+} ions with the ionophore at the test solution-membrane interface.

3.3. Reversibility in Response

To evaluate the reversibility of the proposed sensor response, similar measurements were carried out in the sequence of high-to-low (1.0×10^{-2} to 1.0×10^{-3} M) sample concentrations and the results are shown in Fig. 6. It shows that the potentiometric response of the sensor is reversible and has no memory effect. The sensing behavior of the electrode remained unchanged when the potentials recorded either from low-to-high concentrations or vice versa.

3.4. Effect of pH

The pH dependence of the proposed sensor potential for 1.0×10^{-2} and 1.0×10^{-4} M Pb^{2+} was examined

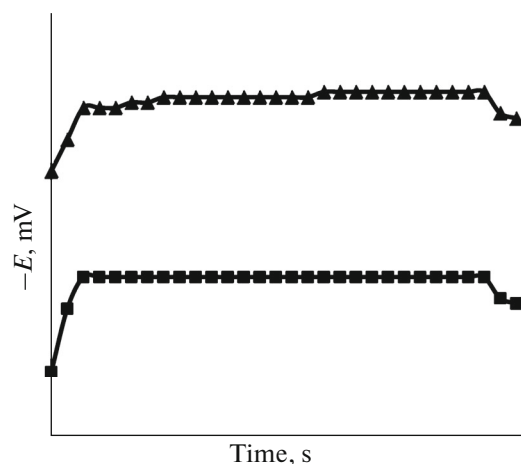


Fig. 4. Static response time curves of the Pb^{2+} selective sensor (\blacksquare 1.0×10^{-2} M, \blacktriangle 1.0×10^{-3} M).

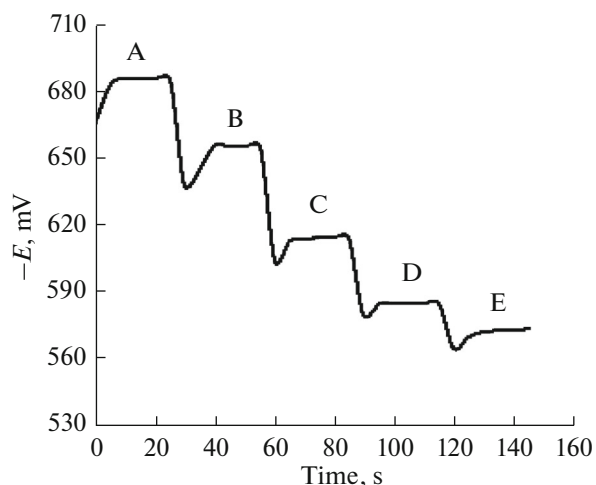


Fig. 5. Dynamic response time of the Pb^{2+} selective sensor for step changes in the concentration of Pb^{2+} : (A) 1.0×10^{-5} , (B) 1.0×10^{-4} , (C) 1.0×10^{-3} , (D) 1.0×10^{-2} , (E) 1.0×10^{-1} M.

over the pH range 1.0–12.0, where the pH was adjusted with HNO_3 or NaOH solutions as required. The results are shown in Fig. 7. It can be seen from this figure that the potentials are independent of pH in the range of 2.0–10.0 and the same can be taken as the working pH range of the sensor. The observed changes of potential at lower and higher pH values could be due to the protonation of the ion carrier and formation of some hydroxyl complexes of Pb^{2+} ion in solution, respectively.

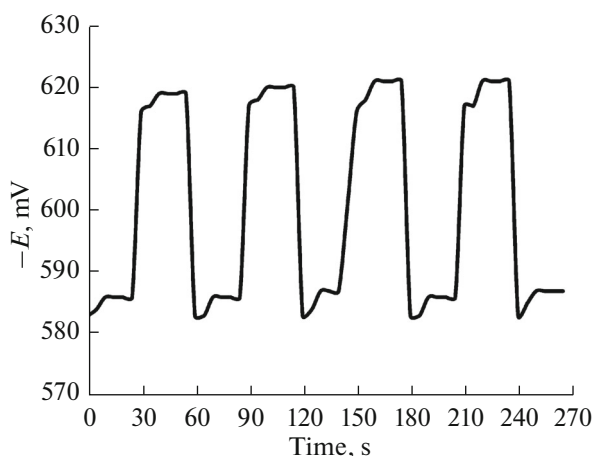


Fig. 6. Reversibility of the Pb^{2+} selective sensor for several high-to-low (1.0×10^{-2} to 1.0×10^{-3} M) sample cycles.

3.5. Selectivity

The potentiometric selectivity of an electrode as one of the most important characteristics is defined by its relative response for the primary ion over other ions present in the solution [38]. In this study, the potentiometric selectivity coefficients of the proposed sensor were determined by the Separate Solution Method (SSM). The K_{ij}^{pot} of mono-, di- and trivalent cations were measured and the results are summarized in Table 2. The selectivity coefficient pattern clearly indicates that the proposed sensor is highly selective to

Table 2. Selectivity coefficients ($K_{\text{Pb},j}^{\text{pot}}$) of various interfering ions for lead(II) selective sensor using Separate Solution Method (SSM)

Interfering ions	Selectivity coefficients ($K_{\text{Pb},j}^{\text{pot}}$)
Ag^+	$<10^{-6}$
K^+	$<10^{-6}$
Zn^{2+}	1.8×10^{-6}
Sr^{2+}	8.7×10^{-4}
Cu^{2+}	7.9×10^{-4}
Ni^{2+}	4.4×10^{-6}
Co^{2+}	1.5×10^{-5}
Cd^{2+}	4.8×10^{-6}
Cr^{3+}	$<10^{-6}$
Fe^{3+}	$<10^{-6}$
Ce^{3+}	1.8×10^{-4}

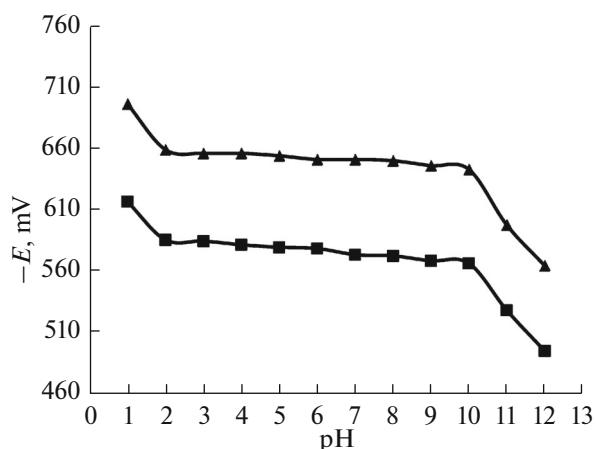


Fig. 7. Effect of the pH of test solutions on potential response of the Pb^{2+} selective sensor (■ 1.0×10^{-2} M, ▲ 1.0×10^{-4} M).

Pb^{2+} ion over alkali and several transition and heavy metal ions. From the data presented in this Table 2, it is obvious that kryptofix22DD interacts relatively strongly with Pb^{2+} ion and can be used successfully as a sensing agent for lead(II) selective sensor.

3.6. Effect of Non-Aqueous Media

The functioning of the electrode was investigated in partially nonaqueous media using acetone–water and ethanol–water mixtures and the results obtained are presented in Table 3. It is observed that the slope is acceptable in the presence of acetone and ethanol until about 25% (v/v) in the water and for the higher percentage, the slope decreases. Therefore, in acetone–water and ethanol–water mixtures (up to 25%), there is only a small decrease in slope and working concentration range and hence the electrode can be satisfactorily used.

3.7. Lifetime

The main factor limiting the lifetime of the ion selective sensor in potentiometric measurements is the leakage of ionophore into the aqueous solutions. For long usage of the electrode, ionophore should be sufficiently lipophilic to ensure a long and stable response of the ion selective electrode [39]. The lifetime of the proposed Pb^{2+} sensor was tested over a period of 9 weeks (Table 4). The proposed PVC-based sensor could be used for 7 weeks (use of 1 h daily). After its utilization, it was washed and kept dry. During this certain time period, the sensor could be used without any measurable divergence. After 7 weeks changes were observed in the slope and linear concentration range (from 29.4 to 16.7 mV/decade and from 1.0×10^{-5} to 1.0×10^{-4} M, respectively).

Table 3. Performance of the lead(II) selective sensor in partially non-aqueous media

Non aqueous content %(v/v)	Slope, mV/decade	Linear range, M
Acetone		
10	28.6	1.0×10^{-4} – 1.0×10^{-1}
20	29.5	1.0×10^{-4} – 1.0×10^{-1}
25	30.2	1.0×10^{-4} – 1.0×10^{-1}
30	22.1	1.0×10^{-3} – 1.0×10^{-1}
Ethanol		
10	29.5	1.0×10^{-5} – 1.0×10^{-1}
20	30.3	1.0×10^{-4} – 1.0×10^{-1}
25	28.9	1.0×10^{-4} – 1.0×10^{-1}
30	19.0	1.0×10^{-3} – 1.0×10^{-1}

Table 4. Lifetime study for lead(II) selective sensor

Period (weeks)	Slope, mV/decade	Linear concentration range, M
1	29.4	10^{-5} – 10^{-1}
2	29.3	10^{-5} – 10^{-1}
3	29.4	10^{-5} – 10^{-1}
4	29.1	10^{-5} – 10^{-1}
5	30.8	10^{-5} – 10^{-1}
6	29.6	10^{-5} – 10^{-1}
7	28.1	10^{-5} – 10^{-1}
8	16.7	10^{-4} – 10^{-1}
9	14.5	10^{-4} – 10^{-1}

Table 5. Determination of Pb^{2+} concentration in doubly distilled deionized water samples spiked with 4 and 8 ppm lead(II) using the proposed sensor and comparison with AAS

Sample no.	AAS, ppm ($n = 3$)	Proposed sensor, ppm ($n = 3$)
1	4.1 ± 0.2	3.9 ± 0.3
2	7.8 ± 0.1	7.9 ± 0.2

Table 6. Determination of Pb^{2+} ion in real water samples using the lead(II) selective sensor

Real water samples	Added Pb^{2+} concentration, mol/L	Found Pb^{2+} concentration, mol/L	Recovery, %
Tap water (Ahvaz city, Iran)	3.0×10^{-4}	2.9×10^{-4}	96.6
River water (Karoon river, Ahvaz, Iran)	3.0×10^{-4}	2.7×10^{-4}	90.0
River water (Dez river, Dezful, Iran)	3.0×10^{-4}	2.8×10^{-4}	93.3
Persian Gulf water	3.0×10^{-4}	2.8×10^{-4}	93.3

3.8. Analytical Applications

The practical utility of the proposed sensor was tested by using it as an indicator electrode for the titration of 25 ml 1.0×10^{-3} M of Pb^{2+} ions with 1.0×10^{-2} M of EDTA and NaI solutions, and the resulting titration curves are shown in Figs. 8 and 9, respectively. As can be seen, the amount of lead(II) ions in solution can be accurately determined with the sensor. Very good inflection points, showing a perfect stoichiometry and efficiency of the sensor in the potentiometric determination of Pb^{2+} cation in solutions.

The proposed sensor was also successfully applied to the direct determination of Pb^{2+} in doubly distilled deionized water (DDW) spiked with 4 and 8 ppm lead(II). The results were compared with the data obtained from atomic absorption spectrometry (AAS) (Table 5). As can be seen from Table 5, the obtained results show satisfactory agreement with those obtained by AAS. Therefore, the designed lead(II) selective sensor is preferable to AAS as an alternative method, because it is simple, rapid and relatively inexpensive.

3.9. Determination of Pb^{2+} Ion in Real Samples

The proposed sensor was successfully applied to the determination of lead(II) ions in real water samples using standard addition method and the results are shown in Table 6. The recoveries of the method were in the range of 90.0–96.6%. Results indicate that the composition of the real samples do not interfere significantly the detection of Pb^{2+} ions. In fact, lead(II) selective sensor seems to provide an alternative device for the quantitative determination of Pb^{2+} ions in real water samples.

3.10. Comparison with Other Pb^{2+} Sensors

Finally, a comparison with other Pb^{2+} selective sensors based on various ionophores reported in the literatures was made. Table 7 presents the main analytical characters of some lead(II) selective electrodes. The proposed sensor based on kryptofix22DD ionophore exhibits superior in many respects than those reported ionophores, such as sensitivity, pH range and

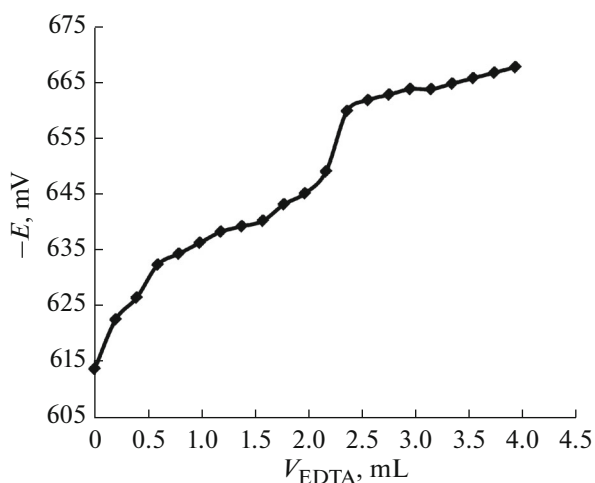


Fig. 8. Potentiometric titration curve for 25 ml 1.0×10^{-3} M of Pb^{2+} solution with 1.0×10^{-2} M of EDTA.

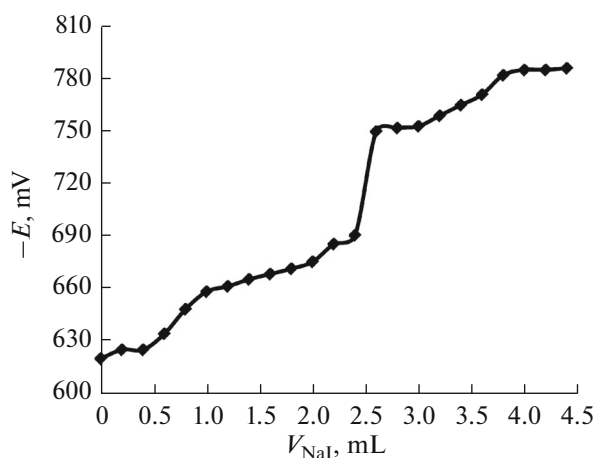


Fig. 9. Potentiometric titration curve for 25 ml 1.0×10^{-3} M of Pb^{2+} solution with 1.0×10^{-2} M of NaI.

response time. Therefore, this sensor can be used widely in the future.

4. CONCLUSION

On the basis of the results discussed in this paper, 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD) can be considered as a neutral carrier for construction of a PVC-based membrane coated graphite ion-selective electrode for

determination of Pb^{2+} ion in solution. The proposed sensor has good characteristics such as; wide concentration range from 1.0×10^{-5} to 1.0×10^{-1} M Pb^{2+} , fast response time (~ 10 s) and good selectivity coefficient for many cations. The potentiometric response of this sensor is independent of the pH of the test solution in the pH range 2.0–10.0. The sensor was successfully used as an indicator electrode in potentiometric titrations and in direct potentiometry for determination of lead(II) in real samples.

Table 7. Comparison of the characteristics of the proposed sensor with those of the previously reported Pb^{2+} sensors

Ref. no.	Ionophore	Detection limit, M	Slope, mV/decade	pH range	Linear range, M	Response time, s
[14]	2'-Methoxyethoxyl sym-dibenzo-16-crown-5 ether	1.0×10^{-6}	28.9	—	5.0×10^{-5} – 5.0×10^{-1}	30
[15]	Piroxicam	4.0×10^{-6}	30.0	4.0–8.0	1.0×10^{-5} – 1.0×10^{-1}	45
[16]	3,15,21-Triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione	2.0×10^{-6}	—	3.7–6.5	3.6×10^{-6} – 1.3×10^{-2}	16
[17]	3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene	—	28.5	5.0–8.0	1.0×10^{-6} – 1.0×10^{-1}	20
[18]	1,3-Bis(<i>N'</i> -benzoylthioureido)benzene	—	31.5	2.2–6.0	4.0×10^{-6} – 1.0×10^{-2}	14
[19]	Schiff base complex: [Co(L) ₂](ClO ₄)(C ₃ H ₆ O)(H ₂ O) L = 2-((E)-(3-aminopyridin-4-ylimino)methyl)-phenol	4.6×10^{-6}	23.9	4.0–13.0	1.0×10^{-5} – 1.0×10^{-2}	10
[This work]	4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix22DD)	6.5×10^{-6}	29.4	2.0–10.0	1.0×10^{-5} – 1.0×10^{-1}	10

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