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Strontium Ion-Selective Electrode Based on 18-Crown-6 in PVC Matrix

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A potentiometric strontium-selective electrode based on 18-crown-6 in PVC matrix for measurement of strontium ion is reported. The electrode was prepared by coating the surface of a graphite by a membrane containing dioctylphthalate (DOP), 18-crown-6 and carbon powder in poly(vinyl chloride) (PVC) in tetrahydrofuran (THF). The membrane composition consisting of 18-crown-6, PVC, DOP, carbon, the thickness of coated membrane, effect of pH and possible interfering cations and anions were investigated and optimized electrode were evaluated. The electrode exhibits significantly enhanced response toward strontium ions over the concentration range 1×10^{-7} to 1×10^{-2} M with slope of 27.35 mV per decade change. Fast and stable response, good reproducibility, long-term stability is demonstrated. The electrode has a response time of 20-25 s and can be used for at least 6 weeks without any considerable divergence in their potential response. The proposed electrode shows fairly good discrimination of strontium from several cations. The electrode was used for direct potentiometric measurements of strontium ions over the concentration range 1×10^{-7}–1×10^{-2} M. The practical utility of the electrode has been demonstrated by using it successfully as an indicator electrode in the potentiometric titration of Sr^{2+} with EDTA.

Key Words: Strontium ion-selective electrode, 18-Crown-6, Graphite electrode, PVC membrane, Potentiometry.

INTRODUCTION

Strontium is an important alkaline earth metal using in production of glasses for coloured television sets and ferrite magnets[1], in refining of zinc and added to tin and lead alloys for increasing hardness and durability[2]. It has also been used as fireworks, signal flares and nuclear wastes[3-5]. A number of methods such as atomic absorption spectrometry[6], flame photometry[7], ICP-AES[8] have been reported for the determination of strontium. These methods are largely time consuming and require infrastructure backup. Thus, a simple, cheaper and convenient method with fast response is required for analysis of large number of environmental and other samples.

The potentiometric method by using ion-selective electrodes provides such procedures and for this purpose, a sufficiently selective and sensitive strontium electrode with low detection limit is yet to be developed. The PVC membrane ion-selective electrodes were well-established as analytical tools for the measurement of a wide variety of different ions in complex biological and environmental samples[9-12]. Electrically neutral lipophilic ligands containing the appropriate number of binding sites of high dipole moment and high polarizability could be employed as ion-active phase for alkali earth metal ions[13]. However, in comparison with other alkali and alkaline earth metal cations, only a few Sr^{2+}-selective sensors have been reported[14-24].

Recently, various macrocyclic ligands have been used as suitable neutral carrier in PVC-based membrane electrode studies for different metal ions[25-29]. Crown ethers and related compounds[30] have widely been used as complexing agents for metal selective extractions, phase transfer catalysis, membrane transport and as ionophores for the fabrication of ion-selective electrode. Efforts have also been made by using these compounds to develop Sr^{2+}-selective electrodes. Due to lack of efficient commercial strontium ion-selective electrode and need for strontium selective sensors for potentiometric determination, poly(vinyl chloride) matrix ion selective electrodes were developed by using 18-crown-6 as ionophore.

EXPERIMENTAL

18-Crown-6 ($C_{12}H_{24}O_6$) was obtained from (Riedel-deHaen, India), nitrates of strontium(II), barium(II), lead(II), cadmium(II) and zinc(II) and tetrahydrofuran (THF), ethylenediamine tetraacetic acid (EDTA) and carbon powder were purchased (Merck, Germany). Poly(vinyl chloride) (PVC) powder and dioctylphthalate (DOP) were purchased from Mahshahr, Iran. Metal salts solutions were prepared in doubly distilled water and graphite electrode bars from dry battery.

Solutions of different concentrations were prepared by diluting the stock solutions of 0.1 M concentration with doubly distilled water. The pH adjustments were made by using dilute nitric acid and sodium hydroxide solutions as required.

Preparation of membrane and electrode construction: The electrode was prepared from a graphite bar (3 mm diameter and 50 mm long) from battery. The graphite bar was rinsed with distilled water and THF and allowed to dry. A mixture of PVC (as matrix), DOP (as plasticizer) and carbon powder (for increasing the electrical and mechanical conduction of coated membrane) to give a total mass of 225 mg, was dissolved in *ca.* 4 mL of THF. To this mixture was added the electroactive material, 18-crown-6 and the solution was mixed well. The graphite bar was then repeatedly dipped (three times, a few seconds between dips) into the membrane solution. A membrane was formed on the graphite surface as sensing layer with 0.025 mm thickness, which was allowed to set overnight at room temperature. The coated electrode was rinsed with water and before use, it was conditioned in a 1×10^{-1} M strontium nitrate solution for 24 h and stored in the same solution when not in use. The coating solutions were stable for several days and could be used for construction of new membranes. The best composition of coated membrane (w/w) was found: 4.247 % ionophore, 55.672 % PVC, 20.035 % plasticizer and 20.018 % carbon powder.

Potential measurements: Potential measurements were made with a model PHM-632 (Metrohm, Swiss) having ± 0.01 mV accuracy with an Ag|AgCl (Metrohm AG.CH-9101 Herisav) as reference electrode. All measurements were carried out at room temperature with a cell of following type:

Ag|AgCl; KCl (satd.)||Sr^{2+} sample solution | Ion-selective electrode (coated graphite)

The performance of the electrodes was examined by measuring the emfs of $Sr(NO_3)_2$ solutions prepared with a concentration range of 10^{-2} to 10^{-7} M by successive dilution.

RESULTS AND DISCUSSION

Macrocyclic crown ethers are well known as selective carriers for various ions. These compounds react with some bulky ions and the produced species were successfully used as neutral electrical carriers for some ions[31-33]. 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 liphophilicity to prevent leaching from the membrane into the sample solution[34].

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. The plasticized PVC-based coated graphite electrode containing the 18-crown-6 carrier generated stable potential response in solutions containing Sr^{2+}. Therefore, the performance of membrane electrodes based on this carrier for strontium in aqueous solutions were performed in detail. In the presence of the proposed carrier, the optimized membranes demonstrated Nernstian responses and remarkable selectivity for Sr^{2+}.

Effect of coated membrane composition: It is well known that the sensitivity, linear dynamic range and selectivity of the ISEs depend not only on the nature of carrier used, but also significantly on the membrane composition and the properties of the additives employed[35,36]. Thus, the influence of the membrane composition, the nature and amount of the plasticizer and carbon powder on the potential response of the Sr^{2+} sensor was investigated. Several membranes were prepared with different compositions. The best response was observed with the membrane composed of the following ingredients: 4.274 % ionophore, 55.672 % PVC, 20.035 % DOP and 20.018 % carbon powder.

The electrodes containing DOP generally showed better potentiometric responses, *i.e.* better sensitivity and linearity of the calibration plots. It seems that DOP, as a low polarity compound among other plasticizers such as DBP, DOPP, NPPE provides more appropriate conditions for incorporation of the highly liphophilic Sr^{2+} into the membrane. Therefore, it was used DOP as a suitable plasticizer for further studies.

It was also observed that the potentiometric response of the electrode toward strontium ion depends on the concentration of the ionophore incorporated within the membrane. Increasing the amount of the ionophore up to 4 % resulted in membranes for which slopes were larger and the linear range wider. Further addition of the ionophore concentration worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane. The potential response of the electrode was worsened in the presence of cationic or anionic additives and thus no ionic additive was used in the membrane preparation.

Performance characteristics of the electrode: The characteristic properties of the optimized coated membrane are summarized in Table-1. Over the concentration range from 1×10^{-7} to 1×10^{-2} M (Fig. 1) of strontium, the electrode potential response was linear with the logarithm of strontium concentration. The calibration curve slope was 27.35 mV per decade of activity.

TABLE-1
SPECIFICATIONS OF THE Sr-ISE BASED ON THE 18-CROWN-6 AS CARRIER

Properties	Values / range
Optimized coated membrane composition	PVC (55.672 %), DOP (20.035 %), 18C6 (4.274 %), C (20.018 %)
Electrode type	Coated-graphite electrode
Thickness of coated membrane (mm)	0.025
pH	7
Linear range (Sr^{2+}, M)	1×10^{-7} to 1×10^{-2}
Slope (mV $decade^{-1}$)	27.35
S.D. of slope (mV $decade^{-1}$)	± 0.8
S.D. of 10 measurements	± 0.84 at 1×10^{-3} M Sr^{2+}
Response time (s)	20-25
Life time of the Sr-ISE	At least 6 weeks

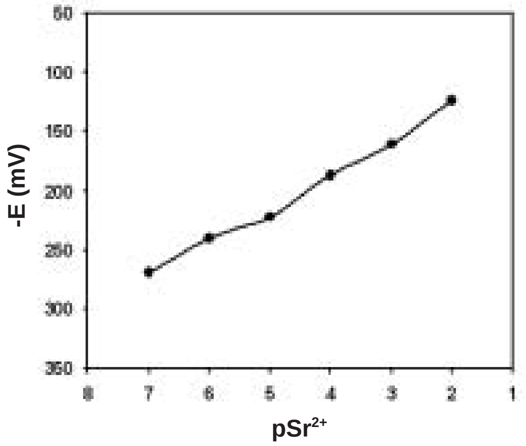

Fig. 1. Potentiometric response of the strontium selective electrode based on 18-crown-6

In practice, slopes between 55/2 and 59/2 mV decade^{-1} are referred to as Nernstian for analytical purposes[37]. The optimum equilibration time for the coated membrane electrode in the presence of 1 × 10^{-4} M $Sr(NO_3)_2$ was 24 h, after which it generated stable potentials in contact with strontium solutions. 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. The response time of optimized coated membrane composition was *ca.* 5 min.

The potential response of strontium selective electrode was studied at different pH. The slopes of the calibration curves for potential response of the optimized strontium selective electrode at different pH of Sr^{2+} solutions (1 × 10^{-7}–1 × 10^{-2} M) are given in Table-2.

TABLE-2
THE SLOPES OF THE CALIBRATION CURVES FOR POTENTIAL RESPONSE OF THE OPTIMIZED STRONTIUM SELECTIVE ELECTRODE AT DIFFERENT pH

pH	Slope	pH	Slope
2	6.178	9	17.928
4	10.857	11	11.714
7	27.357		

Reproducibility of the coated membrane electrode was determined for the 5 designed electrodes at the same conditions by drawing the calibration curve in the dynamic range of 1 × 10^{-7} to 1 × 10^{-2} M for Sr^{2+} with a standard deviation of slopes ± 0.8 mV decade^{-1}, as shown in Table-1. The electrode could be used for 6 weeks without any appreciable change in its sensitivity. After this time the linear range reduced to 10^{-5}-10^{-2} M.

Interferences by ions and electrode selectivity

Effect of interfering cations on ISE response: The most important characteristic of an ion-selective electrode is its selectivity and response for the primary ion in the presence of foreign ions such as Pb^{2+}, Ba^{2+}, Cd^{2+}, Ni^{2+}. The potential response of the membranes was determined as a function of concentration of Sr^{2+} ions and the results are shown in Fig. 2. It is seen that the electrode responds to Sr^{2+} ions best in terms of wide concentration range and Nernstian slope. This type of response of electrode is appointer to high sensitivity and better selectivity of the electrode to Sr^{2+}.

The selectivity of electrode was quantified by determining the selectivity coefficient by the modified Nernst equation according to the recommendations of IUPAC[38]. The selectivity coefficient $K_{sr,M}^{pot}$ is calculated from the following equation:

$$K_{sr,M}^{pot} = a_{sr} /(a_M)^{Z_{sr}/Z_M} \text{ (Fixed interfering method or FIM)}$$

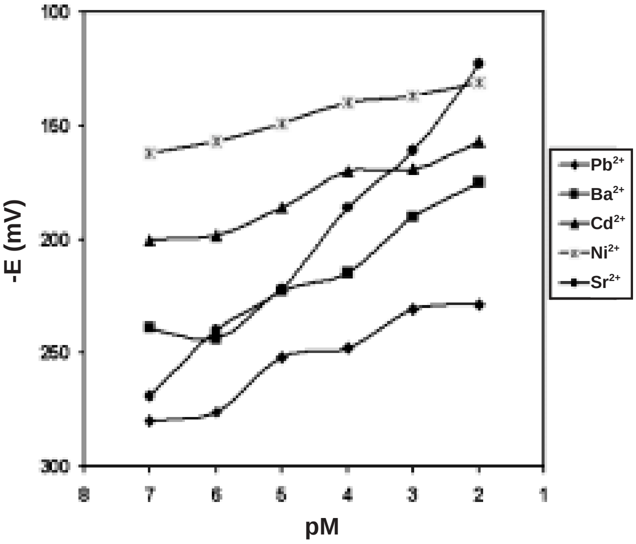

Fig. 2. Potential response of the optimized strontium selective electrode for various metal ions

where, a_{sr} is the activity of strontium ion; a_M the activity of interfering ion; Z_{sr} and Z_M are their respective charges. The activities of metal ions were based on activity coefficient data calculated by using the extended Debye-Huckel equation.

The selectivity coefficients of the electrodes for strontium towards different cationic species (Pb^{2+}, Ba^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Ca^{2+} and Mg^{2+}) are given in Table-3. In this experiment a fixed concentration of interfering ions (1×10^{-4} M) and a varying concentration of Sr^{2+} ion (1×10^{-7}–1×10^{-2} M) was used. The selectivity coefficient data indicates that the ISE is selective towards strontium over other divalent cations.

TABLE-3
SELECTIVITY COEFFICIENTS OF VARIOUS INTERFERING CATIONS (M^{n+}) FOR THE Sr-ISE

M^{n+}	K_{sr}^{pot}	M^{n+}	K_{sr}^{pot}
Pb^{2+}	4.44×10^{-2}	Zn^{2+}	2.20×10^{-2}
Ba^{2+}	2.38×10^{-2}	Ca^{2+}	8.64×10^{-3}
Cd^{2+}	1.28×10^{-2}	Mg^{2+}	4.10×10^{-2}
Ni^{2+}	7.65×10^{-2}	–	–

Effect of interfering anions on ISE response: In this method, a fixed concentration of Sr^{2+} ion (1×10^{-3} M) and a varying concentration of interfering anions (1×10^{-4}–1×10^{-1} M) from sodium salts of SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, NO_3^-, NO_2^-, Cl^-, Br^-, OH^- was used at pH 7 (Fig. 3). At anion concentration higher than 1×10^{-4} M for CO_3^{2-} and OH^- there was serious interfering to ISE response.

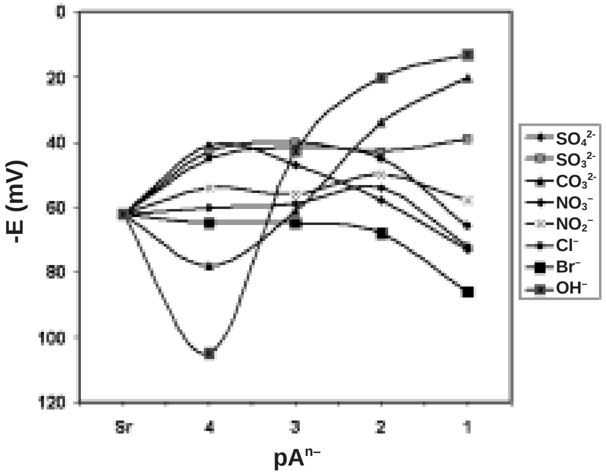

Fig. 3. Effect of various interference anions (1×10^{-4}–1×10^{-1} M) in 1×10^{-3} M Sr^{2+} solution on potential response of Sr-ISE

Potentiometric titration: The analytical utility of the proposed coated membrane electrode was further evaluated as an indicator electrode by carrying out potentiometric titration of 80 mL of 1×10^{-2} M Sr^{2+} solution with a 1×10^{-1} M EDTA solution. The titration plot is shown in Fig. 4. As it can be seen, the amount of Sr^{2+} ions in solution can be accurately determined with the proposed electrode. However, the sharp break point corresponds to the stoichiometry of Sr^{2+}-EDTA complex for the determination of Sr^{2+} potentiometrically.

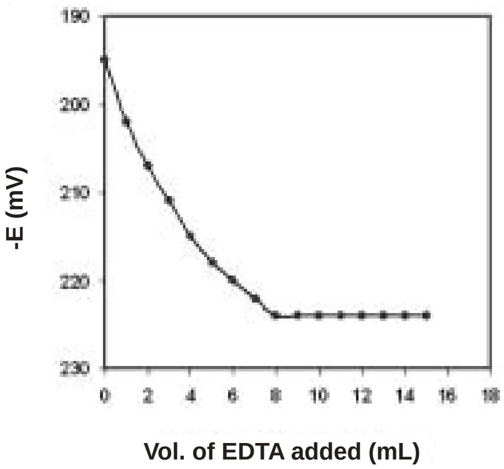

Fig. 4. Titration curve of 80 mL of 1×10^{-2} M Sr^{2+} solution with 1×10^{-1} M EDTA solution using Sr-ISE

Conclusion

The ionophore is selective for strontium ion, due to the good fit condition of Sr^{2+} to 18-crown-6 cavity. The main advantage of the potentiometric strontium-selective coated-membrane electrode is its simple of preparation, short conditioning time, fast response time, Nernstian behaviour and improved good selectivity. The coated-membrane is long lived and chemically stable.

The fabricated electrode based on 18-crown-6 as ionophore displays a near-Nernstian response (27.35 mV/decade of activity), offers a wide linear response range (1×10^{-7} to 1×10^{-2} M). The Sr^{2+}-selective electrode was successfully applied to direct determination of Sr^{2+} in solution and as an indicator electrode in potentiometric titration with EDTA.

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