Full Research Paper

Design of a Selective and Sensitive PVC-Membrane Potentiometric Sensor for Strontium Ion Based on 1,10-Diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione as a Neutral Ionophore

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Abstract: A novel PVC membrane sensor for the Sr^{2+} ion based on 1,10-diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione has been prepared. The sensor possesses a Nernstian slope of 30.0 ± 0.6 mV decade^{-1} over a wide linear concentration range of 1.6×10^{-6}-3.0×10^{-3} M with a detection limit of 6.3×10^{-7} M. It has a fast response time of <15 s and can be used for at least two months without any considerable divergence in potential. The potentiometric response is independent of the pH of test solution in the pH range 4.3-9.4. The proposed electrode shows good selectivities over a variety of alkali, alkaline earth, and transition metal ions.

1. Introduction

Strontium is widely distributed in many biological systems and throughout the environment, at various concentration levels, and plays a fundamental role in ecological systems [1]. It is deposited is preferentially in the bones and teeth of the human body. Some strontium compound such as strontium oxide, strontium hydroxide and strontium carbonate have a strongly irritant effect on skin and mucous membranes especially eyes [2,3]. A radioactive half-life of 29 years makes strontium-90 one of the

most hazardous products of radioactive fallout [3]. The activity measurement of Sr^{2+} in aqueous systems is thus of vital importance from an important environmental point of view.

Ionophore-based PVC membrane electrodes are well-established analytical tools routinely used for the measurement of the activity of a wide variety of different ions selectively and directly in complex biological and environmental samples [4-6]. The key ingredient of such plasticized PVC membrane is an incorporated ionophore, which defines the selectivity of the electrodes via selective complex formation with the cation of interest.

Because macrocyclic ligands can form selective and stable complexes with metal ions of compatible dimensions [7], and can potentially be applied to their selective separation and determination [6,8,9], continuous interest has been focused on the design and synthesis of new functionalized macrocycles for specific applications [10]. Several macrocyclic diamides, prepared from salicylaldehade derivatives and appropriate diamino compounds [11], have been reported to have successful use as ion carriers in the construction of PVC-based ion-selective electrodes for Cu^{2+} [12], Zn^{2+} [13], Hg^{2+} [14], Sr^{2+} [15], Ca^{2+} [16], Cs^+ [17], Co^{2+} [18], Ag^+ [19], and Be^{2+} ions [20].

In this paper, the suitable cavity size of macrocyclic diamide derivative 1,10-diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione (L) as well as its water insolubility led us to examine its ability as a potential ion carrier in the preparation a new PVC-membrane electrode for Sr^{2+} ions. It should be noted that, despite urgent need for new potentionmetric sensors for the selective determination of low level amounts of strontium in different samples, there are only limited reports on the Sr^{2+} ion-selective electrodes in the literature [1,15,21-23].


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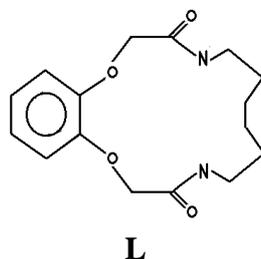
2. Results and Discussion

Ligands for use as ionophores in a strontium ion-selective electrode should fulfill certain conditions including (1) increased selectivity for Sr^{2+} over other metal ions, (2) rapid exchange kinetics of the resulting complex and (3) sufficient lipophilicity to prevent leaching of the ligand into the surrounding aqueous solution. The selectivity of ordinary crown ethers for alkaline earth metal ions is much lower than that for alkali cations [6]. However, the introduction of an amide linkage in the polyether ring has been clearly shown to modify the binding properties of the crown compounds in favor of an alkaline earth with respect to alkali metal ions [15,16,20]. Moreover, amide substitution in the cavity of benzocrown ethers may not only contribute to their cation selectivity but also allow the macrocycles to have properties more closely resembling those on the naturally occurring ionophores [26].

To investigate the potential response of the macrocyclic diamide L for different ions, it was used as a neutral ionophore to prepare PVC-membranes for a wide variety of cations. The potential responses of the most selective electrodes in the concentration range of 10^{-7}-10^{-1} M are shown in Figure 1. As seen, except for the Sr^{2+} ion-selective electrode, in all other cases the slope of the corresponding

potential-pM plots is much lower than the expected Nenstian slope of 29.5 mV decade^{-1} for bivalent cations, although over a limited concentration range. As is obvious from the results obtained, Sr^{2+} ion with the most sensitive response over a wider concentration range seems to be suitably determined with the membrane electrode based on the ligand L. This is due to the highly selective behavior of the ionophore for Sr^{2+} over other metal ions. The observed selectivity of ionophore L toward Sr^{2+} ion is most probably due to the rigid structure of the macrocycle as well as its convenient cavity size (16-membered cavity) for the bivalent strontium ion [7,15].
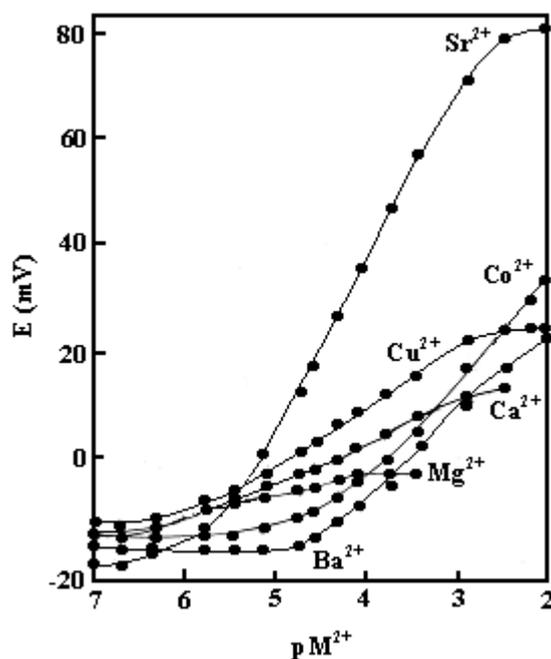
Figure 1. Potential response of various ion-selective membranes based on ionophore L. Conditions: membrane ingredients, 2% L, 30% PVC, 1.7% STP and 66.3% AP, internal solution, 1.0×10^{-3} M of the corresponding cations for each ion-selective sensor.

Some important features of the PVC membranes such as the nature and amount of ionophore, the properties of the plasticizer, the plasticizer/PVC ratio, and specially, the nature of additives used are reported to significantly influence the sensitivity and selectivity of the ion selective electrodes [12-20,27]. Thus, the effects of membrane composition, nature and amount of plasticizer, and amount of additive salt on the potential response of the Sr^{2+} sensor were investigated, and the results are summarized in Table 1.

As with many ionophore-based membrane electrodes, the potential response of the electrode depends on the concentration of lipophilic anionic salts incorporated in the membranes (Nos. 2-4). As seen, addition of STB will increase the sensitivity of the electrode response considerably. Use of 1.7% STB resulted in a Nernstian behavior (NO.4). The presence of such lipophilic anionic species as tetraphenylborate in cation-selective membrane electrodes is proved to have a beneficial influence on different sensor characteristics. It will not only reduce the ohmic resistance [33] and improve the response behavior and selectivity [27] but also, in cases where the extraction capability of the

ionophore is poor, enhance the sensitivity of the membrane electrode [28]. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface [2].

Table 1. Optimization of membrane ingredients.

No	Composition (%)				Slope	Linear range[a]
	PVC	Plasticizer	STB	L	(mV decade^{-1})	(M)
1	32.5	AP, 66.0	0.5	0.0	13.5	4.6×10^{-5}-1.3×10^{-3}
2	31.0	AP, 67.0	0.0	2.0	22.0	1.7×10^{-5}-6.3×10^{-3}
3	31.0	AP, 66.0	1.0	2.0	25.0	3.6×10^{-6}-6.3×10^{-3}
4	30.0	AP, 66.3	1.7	2.0	30.5	1.6×10^{-6}-3.0×10^{-3}
5	30.0	NPOE, 66.3	1.7	2.0	23.5	3.6×10^{-6}-1.2×10^{-3}
6	30.0	DBP, 66.3	1.7	2.0	16.8	3.6×10^{-6}-1.0×10^{-3}
7	30.0	DOP, 66.3	1.7	2.0	14.7	3.6×10^{-6}-6.3×10^{-3}
8	30.0	DMS, 66.3	1.7	2.0	12.8	3.6×10^{-6}-6.2×10^{-3}

[a] In all cases, the correlation coefficient of the linear calibration plot was at least 0.99.

Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [29], it is expected to play an important role in determining the ion-selective characteristics. Thus, five membrane of similar composition (i.e., 30% PVC, 66.3% plasticizer, 2% ionophore and 1.7% STB) but with five different plasticizers having dielectric constant over the range 4-24, namely DMS ($\varepsilon = 4.0$), DBP ($\varepsilon = 6.4$), DOP ($\varepsilon = 7.0$), NPOE ($\varepsilon = 24.0$) and AP ($\varepsilon = 17.3$) were prepared and tested (Table 1, Nos 4-8). It is apparent from the performance characteristics that the membrane plasticized with AP had the highest sensitivity with a nice Nernstian slope, widest linear range and lowest detection limit in this series. The slopes of the corresponding potential responses of membranes plasticized with DMS, DBP, DOP and NPOE were 12.8, 14.7, 16.8 and 23.5 mV decade^{-1}, respectively.

These results indicate that the polar ketone and ether type solvent mediators give a strontium ion sensor with more favorable potentiometric characteristics than nonpolar ester type solvents. This is in agreement with the previous reports showing that the response characteristics and selectivities of multivalent cations of high lipophilicities are favored by the use of high dielectric constant plasticizers [12-20]. As it is obvious from Table 1, the membrane obtained with the PVC/AP/L/STB ratio of 33.0%/66.3%/2.0%/1.7% (no. 4) shows the best response characteristics for selective determination of strontium ion.

Optimum conditioning time for the membrane sensor in a 1.0×10^{-3} M strontium nitrate solution was investigated from 5 to 24 h and found to be 20 h; it then generates stable potentials when placed in contact with Sr^{2+} solutions.

The average time required for the Sr^{2+} ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value was measured after successive immersion of a series of strontium ion solution, each 10-fold different in concentration. The static response time thus obtained was < 15 s for

strontium ion concentrations ≤10⁻³ M, and the potential stayed constant for more than 5 min, after which only a very slow divergence with in the resolution of the pH meter (±0.1 mV) was recorded.
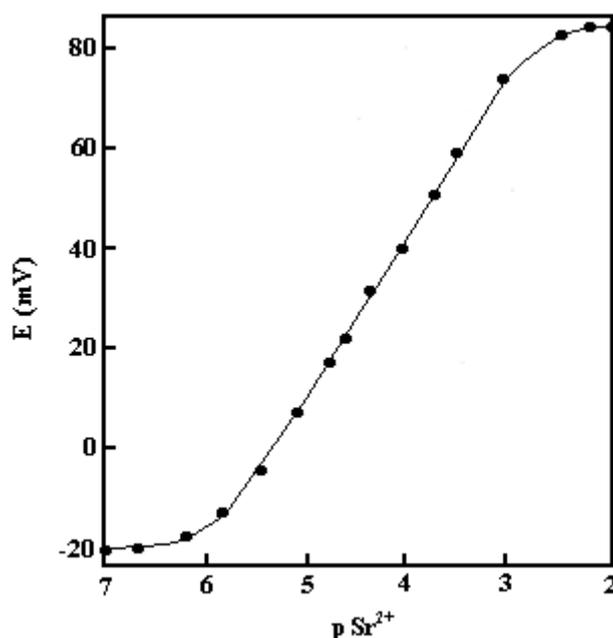

Figure 2. Calibration graph for the strontium ion-selective electrode.

The PVC-membrane electrode based on L prepared under optimized experimental conditions resulted in a potential-pM concentration response with a Nernstian slope of 30.5 ± 0.6 mV/decade (n = 7) over a wide linear concentration range of 1.6×10^{-6}-3.0×10^{-3} M (Figure 2). The detection limit, as evaluated from the intersection of the two extrapolated segments of the calibration graph, was 6.3×10^{-7} M.

The membrane sensor prepared could be used for at least two months without any measurable divergence. After two months, the slope of the calibration curve decreased to 27.0 mV decade⁻¹ without any measurable change in the linear range.

The effect of pH of test solution on the response of the membrane electrode for a 1.0×10^{-4} M solution of Sr^{2+} was studied over the pH range 3.5-11.5, the results are given in Figure 3. It is immediately obvious that the potential stays constant from pH 4.3 to 9.4, beyond which sharp increases in potential are observed. The observed sharp change in potential response below pH 4.3 might be due to the simultaneous response of the electrode to Sr^{2+} ion and H^{+} and at pH higher than 9.4, it could be because of relatively strong competition between Na^{+} (from NaOH) and Sr^{2+} ions.

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the electrode proposed can be obtained. Thus, its potential response was investigated in the presence of various interfering foreign cations using the matched potential method (MPM) [30]. The MPM is a recently recommended procedure which gets ride of the limitations of the corresponding methods based on the Nicolski-Eisenman equation for the determination of potentiometric selectivity coefficients. These limitations include non-Nernstian behaviors of interfering ions and inequality of charges of any primary interfering ion.
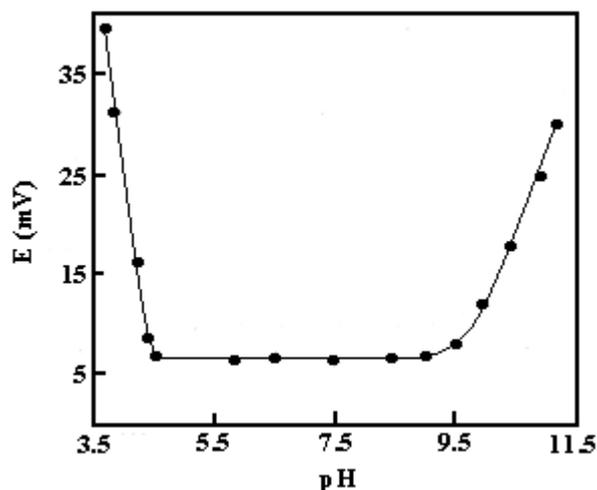
Figure 3. Effect of pH on the strontium test solution.

According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion and the interfering ion that gives the same potential change in a reference solution. Thus, one should measure the change potential upon changing the primary ion activity, and then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient is determined as: $K_{A,B}^{MPM} = \Delta a'_A/a_B$, where $\Delta a_A = a_A' - a_A$, a_A is the initial primary ion activity and a_A' is the activity of A in the presence of interfering ion, B, and a_B is the interfering ion activity. Thus, according to this method, a specific activity (concentration) of the primary ion A (1.0×10^{-6}-1.0×10^{-5} M Sr^{2+}) is added to a reference solution (5.0×10^{-7} M Sr^{2+}) and the potential is measured. In a separate experiment, the interfering ions B are successively added to an identical reference solution (from 1.0×10^{-5} to 1.0×10^{-3} M of M^{n+}) until the measured potential matched that obtained before by adding the primary ions. The $K_{A,B}^{MPM}$ value is then calculated as $\Delta a'_A/a_B$. The resulting values are listed in Table 2. As it is evident from Table 2, most of the interfering ions show low values of selectivity coefficient, indicating negligible interference in the performance of the membrane sensor assembly.

Table 2. Selectivity coefficients of various interfering ions.

Interfering ion	$K_{A,B}^{MPM}$	Interfering ion	$K_{A,B}^{MPM}$
Na^+	1.3×10^{-2}	Ba^{2+}	9.2×10^{-2}
K^+	3.3×10^{-2}	Co^{2+}	8×10^{-2}
Cs^+	3.3×10^{-2}	Ni^{2+}	5.4×10^{-2}
Rb^+	3.1×10^{-2}	Cu^{2+}	9.2×10^{-2}
Mg^{2+}	6.3×10^{-2}	Pb^{2+}	7.2×10^{-2}
Ca^{2+}	8.9×10^{-3}		

In Table 3, the response characteristics of the proposed strontium-sensor are compared with those of the best Sr^{2+} ion-selective electrodes reported before [2,20,26,27,29]. From the data given in Table 3 it is immediately obvious that the limit of detection of the proposed sensor is superior to those reported

before, while the other response characteristics and selectivity coefficients obtained in this work are within the same ranges in comparison with those previously reported for the case of the best strontium ion-selective electrodes.

Table 3. Response characteristics and selectivity coefficients for different PVC-membrane Sr^{2+} ion-selective electrodes.

Figure 4. Potentiometric titration curve of 40 ml of 0.001 M $Sr(NO_3)_2$ with 0.1 M EDTA at pH 6.5, using the proposed sensor as indicator electrode.

The proposed membrane sensor can not only be used for the direct determination of Sr^{2+} ions in real samples (e.g., quantitative recovery of traces of Sr^{2+} ion from tap water), but was also found useful as an electrode in potentiometric titration procedures involved strontium ion. As an example, it was successfully applied as an indicator electrode for the titration of 40 ml of 1.0×10^{-3} M concentration of Sr^{2+} ions, at pH 5.5, with 0.100 M EDTA solution and results are shown in Figure 4. As seen, the amount of Sr^{2+} ions in solution can be accurately determined from the resulting titration curve providing a sharp end point.

3. Experimental Section

3.1. Reagents

Reagent-grade 2-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), dioctyl phthalate (DOP), acetophenone (AP), dimethylsebacate (DMS), tetrahydrofuran (THF), sodium tetraphenylborate (STB) and high relative molecular weight PVC were purchased from Fluka Chemical Company and used as received. Reagent-grade nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. The macrocyclic diamide L was synthesized and purified in as described elsewhere [24]. Triply distilled and deionized water was used throughout.

3.2. Electrode Preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 66.3 mg of plasticizer AP, 30 mg of powdered PVC and 2 mg of ionophore and 1.7 mg of STB in 0.5 ml of methanol and 3.5 ml of THF. The resulting mixture was transferred into a glass dish of 2-cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (4-5 mm diameter on the top) was dipped into the oily mixture for about 10 s so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and at room temperature for about 1 h. The tube was then filled with internal filling solution (1.0×10^{-3} M strontium nitrate). The electrode was finally conditioned for 20 h by soaking in a 1.0×10^{-3} M solution of $Sr(NO_3)_2$. A silver/silver chloride electrode was used as an internal reference electrode.

3.3. EMF Measurements

All emf measurements were carried out the following assembly:
Ag-AgCl (satd) | 3 M KCl | internal solution, 1.0×10^{-3} M $Sr(NO_3)_2$ | PVC membrane | test solution | Ag-AgCl, 0.1 M KCl |
A Metrohm ion analyzer pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. Activities were calculated according to Debye-Hückel procedure [25].

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