Available online at www.sciencedirect.com

SCIENCE DIRECT

Talanta 69 (2006) 521–526

Talanta

www.elsevier.com/locate/talanta

Strontium(II)-selective electrode based on a macrocyclic tetraamide

A.K. Singh*, Puja Saxena, Sameena Mehtab, Barkha Gupta

Department of Chemistry, Indian Institute of Technology, Roorkee 247667, India

Received 29 August 2005; received in revised form 21 October 2005; accepted 21 October 2005

Abstract

A new PVC membrane electrode based on 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane (**I**) as an ion carrier, *o*-nitrophenyloctyl ether (*o*-NPOE) as solvent mediator and sodium tetraphenylborate (NaTPB) as lipophilic additive was fabricated and investigated as Sr^{2+}-selective electrode. The best performance was exhibited by the membrane having composition 8:200:4:120 (**I**:*o*-NPOE:NaTPB:PVC). The electrode exhibited a Nernstian response for strontium ion over a wide concentration range 3.98×10^{-6} to 1.0×10^{-1} M with a slope of 29.0 ± 0.1 mV/decade of concentration and a detection limit of 2.82×10^{-6} M. It showed a response time of less than 10 s and could be used for at least 3 months without any divergence in potential. The proposed electrode showed a good discriminating ability towards strontium(II) ion over a wide variety of other metal ions including alkali, alkaline earth, transition, and heavy metal ions. The electrode can be used in the pH range of 2.5–10.5 and in mixtures containing up to 35% (v/v) non-aqueous content. It was used as an indicator electrode in potentiometric titration of strontium ion against EDTA.

Keywords: Sr^{2+}-selective electrode; PVC membrane; Potentiometry; Tetraamide

1. Introduction

Carrier based PVC membrane sensors are well-established analytical tools used for the measurement of a wide variety of different ions selectively and directly in complex biological and environmental samples [1–4]. 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 and alkaline earth metal ions [5]. However, in comparison with other alkali and alkaline earth metal cations, only a few Sr^{2+}-selective sensors have been reported [6–16] which suffer from various limitations. This is despite the increasing interest as application of Sr^{2+} ion-selective electrodes in analysis of nuclear wastes [17–19] is important. Strontium is an important alkaline earth metal used in production of glasses for colored television sets and ferrite magnets [20], in refining of zinc and added to tin and lead alloys for increasing hardness and durability [21]. It has also been used as fireworks, signal flares, and as oxygen eliminator in electron tubes. A number of methods such as atomic absorption spectrometry [22], flame photometry [23], ICP-AES [24] have been reported for the determination of strontium. These methods are largely time consuming and require large infrastructure back up. Thus, a simple, cheaper and convenient method with fast response is required for analysis of large number of environmental and other samples. The analysis by ion-selective electrodes provides such procedures and for this purpose, a sufficiently selective and sensitive strontium sensor with low detection limit is yet to be developed.

The design and synthesis of new macrocyclic ligands for specific analytical applications is a subject of continuous interest. The inbuilt configurational rigidity induced by N-substituted amides present in the periphery of benzomacrocycles invokes preorganization leading to ionophoric selectivity [6]. The use of some lipophilic diamides as ion carrier in the preparation of ion-selective electrodes for Sr^{2+} [5,6] and other metal ions [25,26] has been reported. Recently, we have used macrocyclic ligands as suitable neutral carrier in PVC-based membrane electrode studies of different metal ions [27–31]. Due to lack of efficient commercial strontium ion-selective electrode and need for a strontium-selective sensor for potentiometric monitoring of Sr^{2+} in different samples, we were interested in preparation of PVC-based sensors for this cation. In this communication we report PVC membrane sensors based on a macrocyclic diamide

---

* Corresponding author. Tel.: +91 1332 285798.
E-mail address: akscyfcy@iitr.ernet.in (A.K. Singh).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.10.022

that exhibits significantly high selectivity to Sr^{2+} ion over other metal ions.

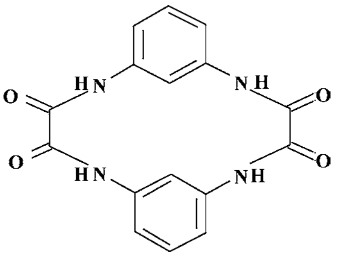
2. Experimental

2.1. Reagents

Diethyloxalate and 1,3-phenylenediamine were procured from E. Merck (Germany). MeOH was refluxed and distilled over lime before use. High molecular weight PVC and acetophenone (AP) was purchased from Ranbaxy (India). Sodium tetraphenylborate (NaTPB) and tris(2-ethylhexyl)phosphate (TEHP), BDH (England); dioctylphthalate (DOP), Acros organics (Belgium); and *ortho*-nitrophenyloctyl ether (*o*-NPOE), Sigma Aldrich, were used. Strontium(II) nitrate was obtained from Merck. Metal salt solutions were prepared in doubly distilled water. Solutions of different concentrations were prepared by diluting stock solution (0.1 M).

2.2. Synthesis of macrocycle (I)

A solution of diethyloxalate (2.92 g, 0.02 mol) was added to a solution of 1,3-phenylenediamine (2.16 g, 0.02 mol) in MeOH (20 cm^3). The solution was then refluxed with stirring for 8 h. The resulting product obtained on cooling was filtered off and washed with cold methanol. It was recrystallized from a 1:1 mixture of MeOH/$CHCl_3$ and dried invacuo. The product gave a yield of 65%, M.P. 220 °C. ^1H-NMR of the ligand gave a multiplet at δ 7.22–7.81 ppm attributed to aromatic ring protons (8H), a broad singlet at δ 8.14–8.20 ppm attributed to –NH (4H) protons. Found: C 59.22%, H 3.5%, N 17.25; calc. C 59.26%, H 3.7%, N 17.28. Mass (*m*/*z*): 324.



2.3. Preparation of membrane

Varying amount of the ion-active phase **I**, anion excluder NaTPB and an appropriate amount of PVC were dissolved in 10 ml of THF and solvent mediators AP, DOP, TEHP and *o*-NPOE were added to get membranes of different composition. The mixture was shaken vigorously with a glass rod and the solvent was allowed to evaporate. When the solution became viscous, it was poured in an acrylic rings resting on a smooth glass plate. After 24 h colorless membrane of about 0.1 mm thickness were obtained which were then cut to size and glued to one end of a pyrex glass tube with araldite. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membrane developed reproducible, noiseless and stable potentials. Membrane to membrane reproducibility was assured by carefully following the optimum conditions of fabrication.

2.4. Potential measurement

The prepared membranes were equilibrated for 3 days in 1.0×10^{-1} M Sr^{2+} solution. All potential studies were carried out at 25 ± 0.1 °C by using the following cell assembly:

SCE|test solution||PVC membrane||0.1 M $Sr(NO_3)_2$|SCE

Saturated Calomel Electrodes (SCE) were used as the reference electrodes and the cell potentials were measured by varying the concentration of $Sr(NO_3)_2$ in test solution in the range 1.0×10^{-7} to 1.0×10^{-1} M.

3. Results and discussion

A number of PVC-based membrane electrodes of macrocyclic diamide (**I**) of different composition along with different plasticizers were prepared and their potential response to strontium was determined. It is well known that the membrane composition and the nature of plasticizer influence the sensitivity and selectivity of an electrode [32–37]. The composition of membranes with different plasticizers, performing best is given along with their characteristics in Table 1. It is seen that the membrane with *o*-NPOE plasticizer performs best as it exhibits the widest working concentration range and near-Nernstian slope with low response time. The effect of macrocyclic diamide (**I**) amount (Fig. 1, Table 2) on the functioning of membrane was also investigated. It was found that the membrane having a composition as I:NaTPB:NPOE:PVC as 8:4:200:120 (w/w) exhibits the best results. Thus, sensor no. 4 responds to Sr^{2+} ions over a wide concentration range of 3.98×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 29.0 ± 0.1 mV/decade of Sr^{2+} activity and a limit of detection [38] as 2.82×10^{-6} M. It is seen from Table 2, that the optimum amount of **I** is 8 mg (Fig. 1). A further addition of ionophore shows no significant improvement in the characteristics of the sensor.

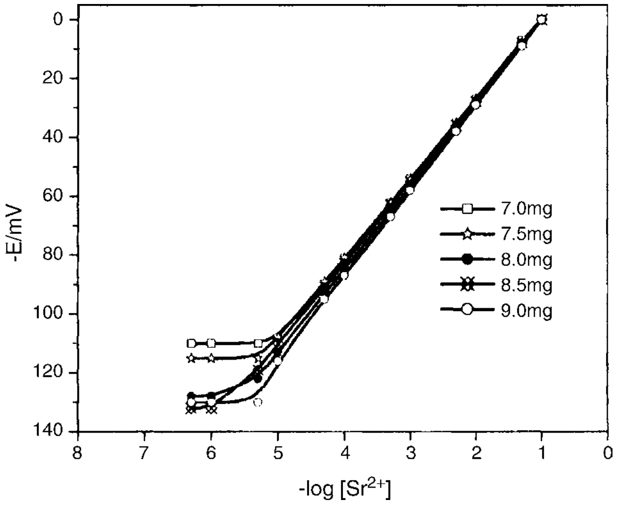


Fig. 1. Electrode response with varying amount of ionophore (**I**).

Table 1
Optimization of membrane ingredients

S. No.	Composition of membrane (w/w)							Working concentration range (M)	Slope (mV/decade)	Response time (s)	Detection limit (M)
	I	PVC	NaTPB	DOP	AP	*o*-NPOE	TEHP				
1	8.0	120	4.0	–	–	–	–	1.0×10^{-1} to 2.24×10^{-4}	41.0	45	1.78×10^{-4}
2	8.0	120	4.0	200	–	–	–	1.0×10^{-1} to 2.51×10^{-5}	32.5	20	1.58×10^{-5}
3	8.0	120	4.0	–	200	–	–	1.0×10^{-1} to 5.01×10^{-6}	26.5	14	3.98×10^{-6}
4	8.0	120	4.0	–	–	200	–	1.0×10^{-1} to 3.98×10^{-6}	29.0	<10	2.82×10^{-6}
5	8.0	120	4.0	–	–	–	200	1.0×10^{-1} to 2.24×10^{-5}	31.0	25	1.78×10^{-5}

Table 2
Effect of amount of **I** on the response of Sr^{2+}-selective electrode

S. No.	Composition of membrane (w/w)				Detection limit (M)	Slope (mV/decade)
	I	PVC	*o*-NPOE	NaTPB		
1	7.0	120	200	4.0	1.0×10^{-1} to 1.0×10^{-5}	27.0
2	7.5	120	200	4.0	1.0×10^{-1} to 7.08×10^{-6}	28.0
3	8.0	120	200	4.0	1.0×10^{-1} to 2.82×10^{-6}	29.0
4	8.5	120	200	4.0	1.0×10^{-1} to 3.16×10^{-6}	28.5
5	9.0	120	200	4.0	1.0×10^{-1} to 4.46×10^{-6}	28.0

The response of the membrane electrode to different kinds of plasticizers with varying dielectric constants was investigated (Table 1, Fig. 2). Membrane no. 1 without any solvent mediator exhibited a narrow working concentration range of 1.78×10^{-4} to 1.0×10^{-1} M with a super Nernstian slope of 41.0 mV/decade of concentration. Further it attains stable potential in 45 s at higher concentration and 65 s in lower concentration, i.e. below 1.0×10^{-4} M. With the addition of plasticizer significant improvement with regard to working concentration range, slope and response time, was observed (Table 1, Fig. 3). Thus, the addition of solvent mediators DOP (no. 1), AP (no. 2), *o*-NPOE (no. 4) and TEHP (no. 5) improved the response characteristics of the membrane which showed a relatively wider concentration range and the slope approached a Nernstian value. The addition of AP and *o*-NPOE improved the working concentration range and slope significantly giving a value of 5.01×10^{-6} to 1.0×10^{-1} M and 3.98×10^{-6} to 1.0×10^{-1} M with slopes 26.5 ± 0.2 and 29.0 ± 0.1 mV/decade of concentration, respectively. The addition of solvent mediator DOP (no. 2) and TEHP (no. 5) exhibited a working concentration range of 2.51×10^{-5} and 2.24×10^{-5} M with slopes 32.5 ± 0.2 and 31.0 ± 0.3 mV/decade of concentration, respectively. It is apparent from the Table 1, that the membrane no. 4 with *o*-NPOE as plasticizer performed the best. The result can be interpreted in terms of polarity of the plasticizer. *o*-NPOE which has a high dielectric constant ($\varepsilon \approx 21.0$) is more polar and favors the trans-

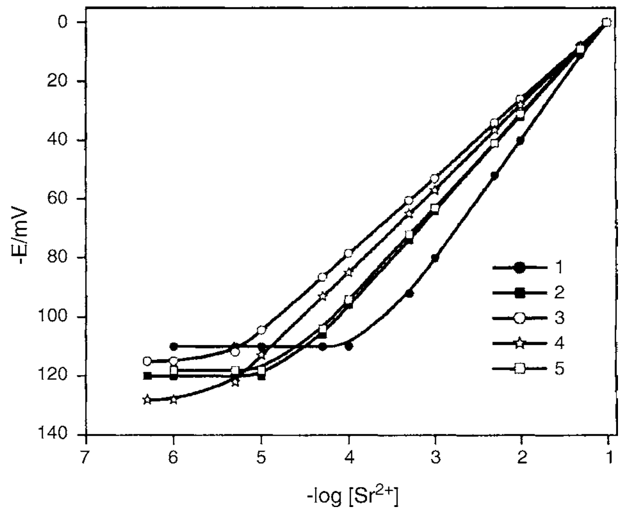


Fig. 2. Plots showing variation of membrane potentials with the concentration of Sr^{2+} ions based on (**I**) without plasticizer (no. 1) and with plasticizers (nos. 2–5).

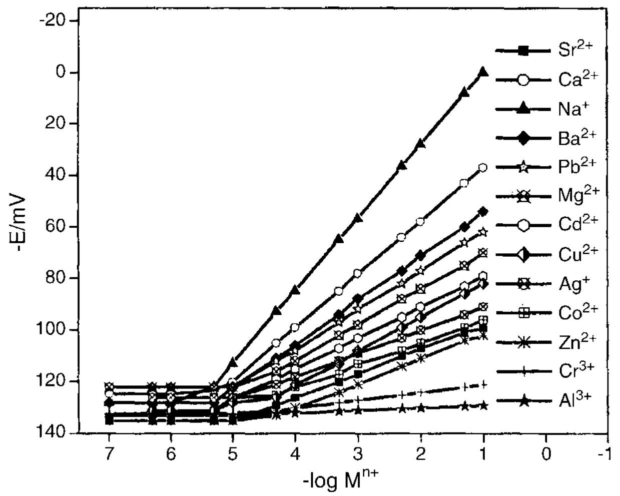


Fig. 3. Potential responses of ion-selective electrode based on (**I**) for various metal ions.

port of ions with higher charge density [39]. Thus, giving a better response to Sr^{2+} ions than the other less polar plasticizers viz AP ($\varepsilon \approx 17.1$), DOP ($\varepsilon \approx 5.1$) and TEHP ($\varepsilon \approx 4.8$).

The response time of the electrode was determined by measuring the time required to achieve a 90% of the steady potential. The results of response time are shown in Table 1. It is seen that the membrane without the solvent mediator gave the response time of 45 s. The response time improved significantly with the addition of plasticizer. The best results were shown by sensor no. 4 (<10 s) over the entire working concentration range. The potentials remained constant for more than 4 min after which a slow divergence was observed. Membrane nos. 2, 3 and 5 also performed satisfactorily as the response time for these membranes are 20, 14 and 25 s, respectively. The sensor could be used over a period of 3 months without any divergence in the potentials if stored in 0.1 M Sr^{2+} solution. After this period, a slight change was observed in response time and slope that could be corrected by re-equilibrating the membrane with 1.0 M Sr^{2+} solution for 2–3 days. During usage the membranes were stored in 0.1 M Sr^{2+} solution.

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode. The potential response of the membranes was determined as a function of concentration not only of Sr^{2+} but many other ions and the results obtained are shown in Fig. 3. It is seen that the membrane responds to Sr^{2+} ions best in terms of wide concentration range, slope and response time. This type of response of sensor is a pointer to high sensitivity and better selectivity of the electrode to Sr^{2+}. The selectivity of sensor was quantified by determining the selectivity coefficient by fixed interference method (FIM) [40]. The selectivity coefficient $K^{\mathrm{Pot}}_{\mathrm{A,B}}$ is calculated from the following equation:

$$K^{\mathrm{Pot}}_{\mathrm{A,B}} = \frac{a_{\mathrm{A}}}{(a_{\mathrm{B}})^{Z_{\mathrm{A}}/Z_{\mathrm{B}}}}$$

where, a_{A} is the activity of primary ion; a_{B} the activity of interfering ion; Z_{A}, and Z_{B} are their respective charges.

In this method a fixed concentration of interfering ions (1.0×10^{-2} M) and a varying concentration of Sr^{2+} ion (1.0×10^{-1} to 1.0×10^{-7} M) was used at pH 6.0. The selectivity coefficients determined for different cations are given in Table 3. The selectivity coefficient data indicates that the ISE is selective towards Sr^{2+} over a variety of ions including the transition metal ions, alkali metal and other alkaline metal ions. However, Ca^{2+} may cause some interference as selectivity coefficient for Ca^{2+} slightly higher. To have an actual idea of the levels of interference caused by Ca^{2+} ions, some mixed run studies were performed [41–43]. Fig. 4 shows that in presence of 1.0×10^{-4} M Ca^{2+} ions, the sensor can be used to determine Sr^{2+} in the concentration range 1.78×10^{-5} to 1.0×10^{-1}M.

The performance of the electrode was also assessed at different pH values. For this purpose the potential of sensor no. 4 was determined at 1.0×10^{-3} and 1.0×10^{-2} M Sr^{2+} solution in the pH range 1.0–12.0. The pH was adjusted by using diluted HCl and NaOH solution. The results obtained are given in Fig. 5, which shows that the potential remains constant in the pH range 2.5–10.4. Therefore, the working pH range for the sen-

Table 3
Selectivity coefficient values ($K^{\mathrm{Pot}}_{\mathrm{Sr^{2+},B}}$) of various interfering ions for Sr^{2+}-selective membrane electrode no. 4 based on **I** at 1.0×10^{-2} M

Interfering ion	$K^{\mathrm{Pot}}_{\mathrm{Sr^{2+},B}}$
Li^{+}	5.4×10^{-3}
Na^{+}	2.5×10^{-2}
K^{+}	7.8×10^{-2}
Ag^{+}	7.1×10^{-2}
Mg^{2+}	5.2×10^{-2}
Ca^{2+}	3.8×10^{-1}
Ba^{2+}	3.4×10^{-2}
Hg^{2+}	4.8×10^{-2}
Pb^{2+}	4.1×10^{-2}
Cd^{2+}	5.8×10^{-2}
Cu^{2+}	6.9×10^{-2}
Mn^{2+}	7.4×10^{-2}
Co^{2+}	8.9×10^{-2}
Zn^{2+}	1.9×10^{-3}
Cr^{3+}	4.8×10^{-3}
Al^{3+}	6.7×10^{-3}

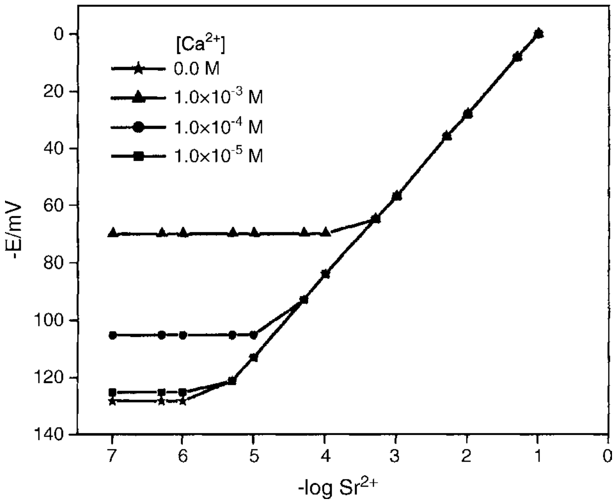


Fig. 4. Variation of membrane potential as a function of Sr^{2+} concentration in the presence of different concentrations of Ca^{2+} ions.

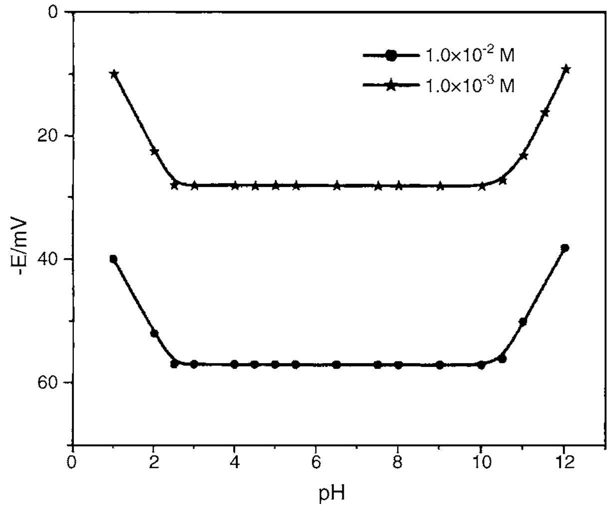


Fig. 5. Effect of pH at 1.0×10^{-2} and 1.0×10^{-3} M Sr^{2+} solutions on the potential response of membrane no. 4.

Table 4
Performance of membrane no. 4 in partially non-aqueous media

Non-aqueous content (%v/v)	Working concentration range (M)	Slope (mV/decade activity)
0	1.0×10^{-1} to 3.98×10^{-6}	29.0
Methanol		
10	1.0×10^{-1} to 3.98×10^{-6}	29.0
20	1.0×10^{-1} to 3.98×10^{-6}	29.0
30	1.0×10^{-1} to 4.14×10^{-6}	28.4
35	1.0×10^{-1} to 7.92×10^{-6}	20.2
Ethanol		
10	1.0×10^{-1} to 3.98×10^{-6}	29.0
20	1.0×10^{-1} to 3.98×10^{-6}	29.0
30	1.0×10^{-1} to 4.18×10^{-6}	28.8
35	1.0×10^{-1} to 7.97×10^{-6}	19.8
Acetone		
10	1.0×10^{-1} to 3.98×10^{-6}	29.0
20	1.0×10^{-1} to 3.98×10^{-6}	29.0
30	1.0×10^{-1} to 5.21×10^{-6}	28.2
35	1.0×10^{-1} to 1.76×10^{-5}	21.0

Table 5
Comparison of the proposed Sr^{2+}-selective electrode with the reported electrode

S. No.	Ionophore	Working concentration range (M)	Slope/mV (decade activity)$^{-1}$	pH range	Response time (s)	Reference
1	Diamide with pyridine ring	2.0×10^{-5} to 1.0×10^{-2}	29.0	3.0–11.5	NM	[4]
2	Dibenzo-18-crown-6	5.0×10^{-6} to 1.0×10^{-1}	28.0	2.0–6.0	25	[9]
3	4-*t*-Butyl calix[8]arene	2.0×10^{-5} to 10×10^{-1}	31.3	2.4–4.8	15	[11]
4	Benzosubstituted diamide	3.2×10^{-5} to 1.0×10^{-1}	28	2.0–6.0	10	[3]
5	Ester derivative of 4-*t*-butyl calix[8]arene	3.2×10^{-5} to 1.0×10^{-1}	30.0	3.0–10.0	10	[12]
6	Modified calix[6]arene	1.9×10^{-5} to 1.0×10^{-1}	30.0	3.0–10.0	10	[13]
7	Teraamide macrocycle	3.98×10^{-6} to 1.0×10^{-1}	29.0	2.5–10.4	<10	Proposed electrode

sor is 2.5–10.4. Below and above these pH values sharp change in potential was observed which may be due to co-transport of H^+ ions and the formation of $SrOH^+$ ions [44].

The performance of the membrane sensor was also investigated in partially non-aqueous media using methanol–water, ethanol–water and acetone–water mixtures (Table 4). It was observed that the sensor could tolerate up to 35% (v/v) (methanol, ethanol, acetone) non-aqueous content as working concentration range and slope remain unaltered. However, above 35% non-aqueous content, the potentials showed a drift with time.

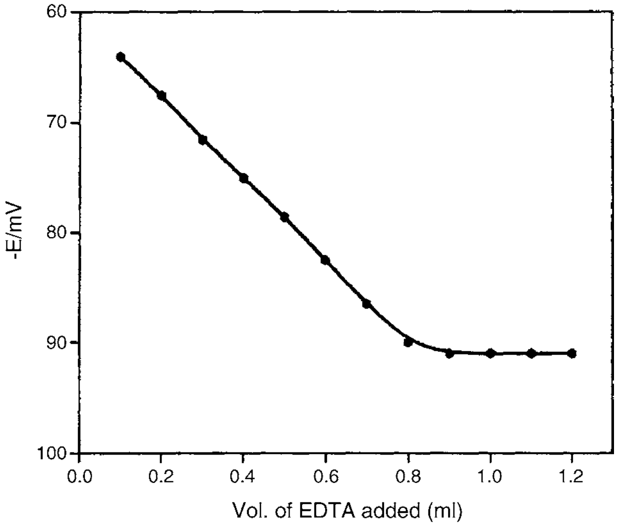


Fig. 6. Titration curve of 8 ml of 1.0×10^{-3} M Sr^{2+} solution with 1.0×10^{-2} M EDTA solution using membrane no. 4.

The analytical utility of the proposed membrane sensor was further evaluated as an indicator electrode by carrying out potentiometric titration of 8 ml of 1.0×10^{-3} M Sr^{2+}solution with a 1.0×10^{-2} M EDTA solution. The titration plot is shown in Fig. 6. As it can be seen, the amount of Sr^{2+} ions in solution can be accurately determined with the proposed electrode.

4. Conclusion

Among the various PVC-based membranes prepared using the tetraamide macrocycle 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane (**I**) as ionophore and different plasticizers, it is found that the membrane with *o*-NPOE plasticizer having a composition 8:4:200:120 (I:NaTPB:*o*-NPOE:PVC) gives the best performance. Its performance is compared with reported electrodes (Table 5) where it is seen that it is comparable to reported electrodes in many respects and shows significant superiority over them in terms of wide concentration range. Thus, the sensor prepared is an advancement over the reported systems and can be used for strontium determination both by direct potentiometry and potentiometric titration.

Acknowledgement

The financial support provided by the Ministry of Human Resource and Development, New Delhi, India, is greatly acknowledged.

References

[1] D. Ammann, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch, W. Simon, Ion Sel. Electrode Rev. 5 (1983) 3.
[2] M.E. Mayerhoff, M.N. Opdyche, Adv. Clin. Chem. 25 (1986) 1.
[3] G.J. Moody, B.B. Saad, J.D.R. Thomas, Sel. Electrode Rev. 10 (1988) 71.
[4] K. Kimura, T. Shono, in: Y. Inoue, G.W. Gokel (Eds.), Cation Binding by Macrocycles, Marcel Dekker, New York, 1998.
[5] G. Qian, H.B. Wu, G. Wu, S. Huang, Y. Yan, B. Tian, Talanta 47 (1998) 1149.
[6] M. Shamsipur, S. Rouhani, H. Sharghi, M.R. Ganjali, H. Eshghi, Anal. Chem. 71 (1999) 4938.
[7] E.W. Baumann, Anal. Chem. 47 (1975) 959.
[8] N. Faizan, M.C. Chattopadhyaya, J. Inst. Chem. 62 (1990) 95.
[9] A.K. Jain, S.K. Srivastava, R.P. Singh, S. Agarwala, J. Appl. Chem. Biotechnol. 27 (1977) 680.
[10] S.K. Srivastava, C.K. Jain, Bunseki Kagaku 33 (1984) E525.
[11] N. Akmal, H. Zimmer, H.B. Mark, Anal. Lett. 24 (1991) 1431.
[12] A.K. Singh, G. Bhattacharjee, S. Baniwal, M. Singh, J. Ind. Chem. Soc. 76 (1999) 53.
[13] M.R. Ganjali, R. Kiani, M. Yousefi, M. Faal-Rastegar, Anal. Lett. 36 (2003) 2134.
[14] V.K. Gupta, A.K. Jain, U. Khurana, L.P. Singh, Sens. Actuators B 55 (1999) 201.
[15] A.K. Jain, V.K. Gupta, J.R. Raisoni, Sensors 4 (2004) 115.
[16] V.K. Gupta, R. Ludwig, S. Agarwal, Anal. Sci. 21 (2005) 293.
[17] G.J. Moody, J.D.R. Thomas, Ion-Sel. Electrode Rev. 1 (1979) 3.
[18] R.M. Izzat, J.S. Bradshaw, R.L. Bruening, B.J. Tarbet, M.L. Bruening, Pure Appl. Chem. 67 (1995) 1069.
[19] P.K. Mohapatra, P.N. Pathak, A. Kelkar, V.K. Manchanda, New J. Chem. 28 (2004) 1004.
[20] Bureau of Mines, Mineral Commodity Summaries, 1986, p. 152.
[21] E. Browning, Appleton Century Crofts, Toxicity of Industrial Metals, second ed., New York, 1969, p. 302.
[22] M. Shamsipur, R. Mojtaba, F. Raufi, Mikrochim. Acta 137 (2001) 163.
[23] N.V. Bondareva, E.S. Zolotoritskaya, Zhavod. Lab. 57 (1991) 36.
[24] D.K. Tarun, M. Sarin, Geostd. Newslett. 26 (2002) 301.
[25] A.S. Attiyat, Y.A. Abrahim, A.M. Kadry, R.Y. Ryxie, G.D. Christian, Fresenius J. Anal. Chem. 12 (1987) 239.
[26] E. Malinowska, J. Jurczak, T. Stankiewicz, Electroanalysis 5 (1993) 489.
[27] A.K. Singh, R. Singh, P. Saxena, Sensors 4 (2004) 187.
[28] A.K. Singh, P. Saxena, R. Singh, Anal. Sci. 21 (2005) 179.
[29] A.K. Singh, P. Saxena, R. Singh, Anal. Lett. 38 (2005) 589.
[30] A.K. Singh, R. Singh, R.P. Singh, P. Saxena, Sens. Actuators B 106 (2005) 779.
[31] A.K. Singh, P. Saxena, Talanta 66 (2005) 993.
[32] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083.
[33] X. Yang, N. Kumar, H. Chi, D.B. Hibbert, P.N.W. Alexander, Electroanalysis 9 (1997) 549.
[34] U. Schaller, E. Bakker, U.E. Spischiger, E. Pretsch, Anal. Chem. 41 (1994) 379.
[35] W. Kim, D.D. Sung, G.S. Cha, S.B. Park, Analyst 123 (1998) 379.
[36] E. Bakker, E. Malinowska, R.D. Schaller, M.E. Mayerhoff, Talanta 41 (1994) 881.
[37] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083.
[38] R.P. Buck, E. Lindner, Pure Appl. Chem. 66 (1994) 2527.
[39] Z. Yan, Y. Fan, Q. Gao, H. Lu, H. Hou, Talanta 57 (2002) 81.
[40] IUPAC, Pure Appl. Chem. 48 (1976) 127.
[41] A.K. Jain, V.K. Gupta, U. Khurana, L.P. Singh, Electroanalysis 9 (1997) 857.
[42] V.K. Gupta, R. Prasad, P. Kumar, R. Mangla, Anal. Chim. Acta 420 (2000) 19.
[43] V.K. Gupta, R. Prasad, A. Kumar, J. Appl. Electrochem. 33 (2003) 381.
[44] A.K. Jain, V.K. Gupta, L.P. Singh, Anal. Proc. 32 (1995) 263.