JCRS

Journal of Chemical Reactivity and Synthesis 2020: 10(4) 175-185

Calcium measurement using ion selective electrode based on a benzo-18-crown-6 as an ionophore

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ARTICLE INFO:

Received:
19 September 2020

Accepted:
27 November 2020

Available online:
4 December 2020

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ABSTRACT

A new PVC based membrane using benzo-18-crown-6 as an ionophore has been developed as a calcium ion selective electrode. The electrode comprises of ionophore (4%), PVC (30%) and plasticizer (63%). The electrode shows a linear dynamic response in the concentration range of 1×10^{-5} M to 1×10^{-1} M with a Nernstian slope of 29.8 mV/decade and detection limit is 4.0×10^{-6} M. The proposed sensor shows reasonably good selectivity with respect to alkali, alkaline earth and transition metal ions. It can be used in the pH range of 5 to 12. The proposed electrode also was applied for the direct determination of Ca^{2+} cation in doubly distilled deionized water samples spiked with different concentrations of calcium. This electrode was also used for determination of Ca^{2+} in real samples with a very good recovery.

Keywords: Calcium (II) cation; Ion selective electrode; Potentiometry.

1. Introduction

Ion-selective electrodes (ISEs) possess many advantages over traditional methods of analysis and provide accurate, reproducible, fast, and regular selective determination of various ionic species. In addition, ion-selective electrodes allow non-destructive, on-line monitoring of particular ions in a small volume of sample without any pretreatment. Because of these merits, the use of ISEs is increasing day by day in medicinal, environmental, agricultural, and industrial fields [1,2]. Macrocyclic ligands have been widely used as suitable neutral carriers for the construction of membrane selective electrodes especially for alkali and alkaline earth metal cations [3,4]. In the present study, a novel PVC-membrane sensor based on benzo-18-crown-6 as a neutral carrier for the selective and sensitive determination of Ca (II) cations in aqueous media was developed. Very few studies are available in literature on the old crown ethers that were used as ion selective electrodes. Gahan and co-workers have investigated the interaction of monoazapolyoxacrown ethers with Pb^{2+}, Hg^{2+}, Cd^{2+} and Zn^{2+} by potentiometry [5,6]. In this study, a calcium selective electrode based on a benzo-18-crown-6 as an ionophore was fabricated.

2. Experimental

2.1. Materials and method

Potanciumeter (Zag chemi co, Iran, Model PTR-79) and glass electrode Ag/Agcl (azar electrode, Iran) were used for potential different and respectively. pH measurements were made with a digital pH meter (Horbia, Japon, Model pH F-11). Hot plate magnetic stirrer (Pars faraso, Iran, Model F-60) and dijital scale (Sartorius, Swiss, Model PB210D) was used.

2.2. PVC membrane-coated electrode

The electrodes were prepared from a graphite bars (3mm diameter and 50mm long). The graphite bars were polished and put in a concentrated HNO_3 solution overnight to clean the surface of the graphite bars. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A mixture of ionophore (benzo-18-crown-6) and PVC, plasticizer (DOP) and carbon powder (for increasing the electrical conduction and mechanical stability of coated membrane) to give a total mass 300 mg was dissolved in about 5 mL of THF and the solution was mixed well. The graphite bar was coated by dipping it into the membrane solution for a few seconds and allowed to dry overnight. The electrode was conditioned in 0.001 M Calcium nitrate for 24 h, and stored in mild concentration solutions of Calcium nitrate, when not in use. The coating solution was stable for several days and could be used for construction of new membranes.

2.3. Apparatus and potential measurements

All potential measurements were made with a potentiometer having ±0.01 mv accuracy with an Ag/AgCl reference electrode. All measurements were carried out at 25 °C with a cell type:

Ag/AgCl;KCl(satd.) ‖ Ca^{2+} sample solution | Ion selective membrane | graphite bar

The potential readings were made after the potential reached to a constant value. The performance of the electrode was investigated by measuring the potential of Ca^{2+} solutions over the range of 1.0×10^{-8} to 1.0×10^{-1} M. The data were plotted as observed potential vs the logarithm of Ca^{2+} cation concentration.

3. Results and discussion

3.1. Effect of membrane composition on the sensor response and calibration curve

It is well known that some important features of the PVC-based membranes, such as the nature and amount of the ionophore, the properties of the plasticizer, the plasticizer/ PVC ratio and especially the nature of the additives used, significantly influence the sensitivity and selectivity of the ion selective sensors [7,8]. Thus, different aspects of preparation of membranes based on benzo-18-crown-6 were investigated and the results are given in Table 1. The best response was observed with the membrane composed of the following ingredients: 30.0 mg PVC, 63.0 mg DOP, 4.0 mg benzo-18-crown-6 and 3.0 mg NaTPB (membrane No. 3). The characteristic properties of this optimized coated membrane were studied and the calibration curve for Ca^{2+} cation is shown in Figure 1. Over the concentration range from 1.0×10^{-5} to 1.0×10^{-1} M of the cation, the electrode potential response was linear with the logarithm of Calcium cation concentration. The slope of the calibration curve was found to be: 29.8±0.2 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.0×10^{-6} M.

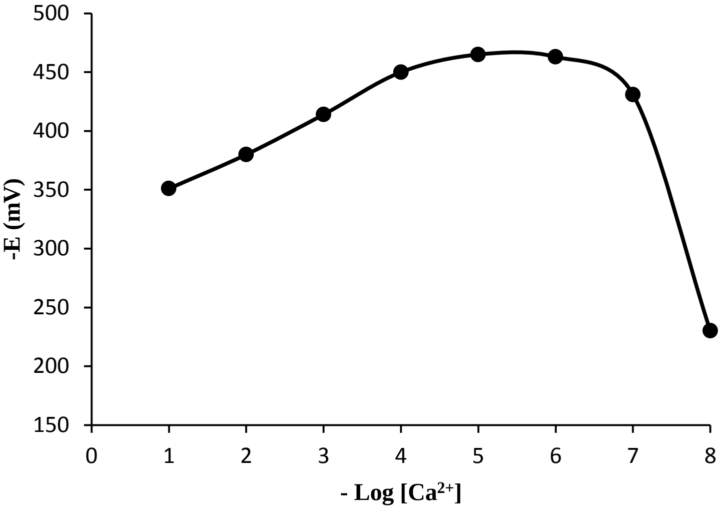

Fig. 1. Calibration curve of the Ca^{2+} selective sensor based on benzo-18-crown-6.

3.2. Analytical performance

The proposed Ca^{2+} sensor was found to work well under laboratory conditions. This electrode was used to determine the end-point in the potentiometric titration of Ca^{2+} with EDTA solutions. Two typical titration curves are shown in Fig. 2. In this process, 25 mL of 1.0×10^{-2} M and 25 mL of 1.0×10^{-3} M calcium nitrate solutions were titrated with 1.0×10^{-1} M and 1.0×10^{-2} M EDTA solutions, respectively. As can be seen, the end points of titration are sharp and this titration method can determine the amount of calcium ion accurately.

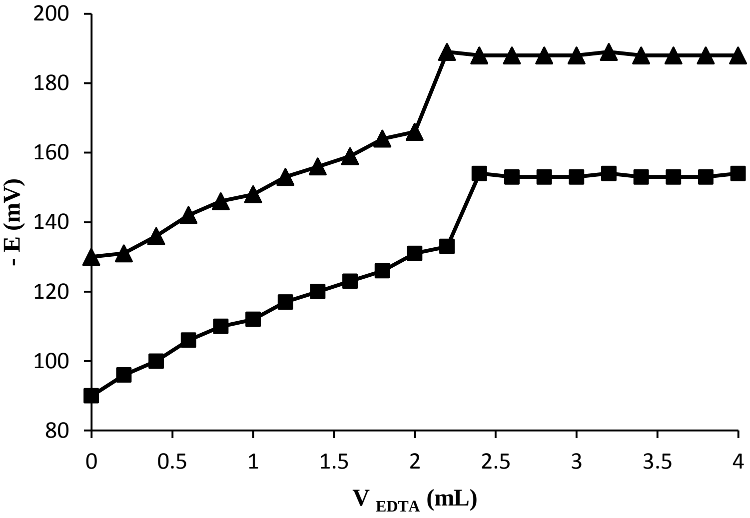

Fig. 2. Potentiometric titration curves of 25 ml of Ca^{2+} (■1.0×10^{-2} M and ▲1.0×10^{-3} M) with 1.0×10^{-1} M and 1.0×10^{-2} M of EDTA solutions.

3.3. Effect of pH

The pH dependence of the proposed electrode potential was investigated over the pH range of 1.0-14.0 for 1.0×10^{-3} and 1.0×10^{-2} M of Ca^{2+} ion solutions. The graphical results shown in Fig. 3 indicate that the potential was independent of pH in the range of 5.0-12.0 pH units.

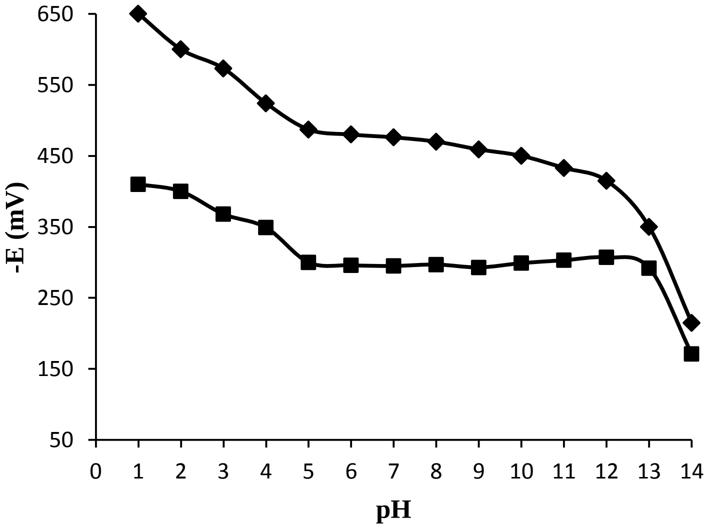

Fig. 3. Effect of pH on potential response of the Ca^{2+} selective sensor using (■) 1.0×10^{-2} M and (♦) 1.0×10^{-3}M of Ca^{2+} solutions.

Table 1. Optimization of the membrane ingredients.

No.	Composition (wt. %)					
	PVC	Ionophore	NaTPB	Plasticizer	Linear range (M)	Slope (mV/decade)
1	30	6	4	(NB) 60	10^{-8}-10^{-5}	19.9±1.8
2	30	4	2	(DOP) 64	10^{-6}-10^{-3}	23.3±0.4
3	30	4	3	(DOP) 63	10^{-5}-10^{-1}	29.8±0.2
4	30	4	3	(DOS) 63	10^{-7}-10^{-5}	31.0±1.0
5	30	5	4	(DBP) 61	10^{-8}-10^{-4}	30.0±1.4

3.4. Determination of Ca^{2+} ion in real samples

The proposed sensor was also successfully applied to the direct determination of calcium (II) in real samples using standard addition method and the results are shown in Table 2. As can be seen, the recoveries of calcium from different water samples are in the range of 85.0-92.0%. Results indicate that the composition of the real samples do not interfere significantly on the detection of Ca^{2+} ions. In fact, the accuracy of calcium recovery in different solution samples is almost quantitative.

Table 2. Potentiometric determination of Ca^{2+} ion in different real samples using the Ca^{2+} selective sensor.

Real samples	Added Ca^{2+} concentration (M)	Found Ca^{2+} concentration (M)	Recovery (%)
Dez river	3.0×10^{-4}	2.6×10^{-4}	86.6
Ahvaz city water	2.0×10^{-4}	1.7×10^{-4}	85.0
Karoon river	5.0×10^{-3}	4.6×10^{-3}	92.0

3.5. Response time characteristics of the proposed sensor

The response time is an important factor for ion selective sensors. The static response time of the sensor was studied by plotting the potential response vs. time, at 1.0×10^{-3} M and 1.0×10^{-2} M of Ca^{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 potentials stay constant for about ~150 s.

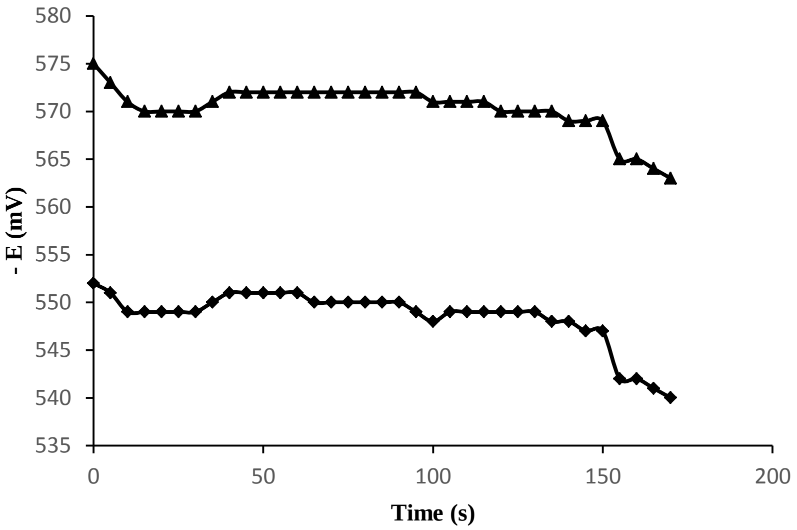

Fig. 4. The response time curves of the Ca^{2+} selective sensor (♦ 1.0×10^{-2} M, ▲ 1.0×10^{-3} M).

Dynamic response time of the sensor has been recorded by changing solutions with different Ca^{2+} concentrations. The measurement sequence was from the lower (1.0×10^{-5} M) to the higher (1.0×10^{-1} M) concentrations and the results are shown in (Fig. 5). As it is seen, the sensor reached the equilibrium response in a very short time of about 10 s. This is most probably due to the fast exchange kinetics of complexation-decomplexation of Ca^{2+} cation with the ion carrier at the test solution-membrane interface. To evaluate the reversibility of the 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.

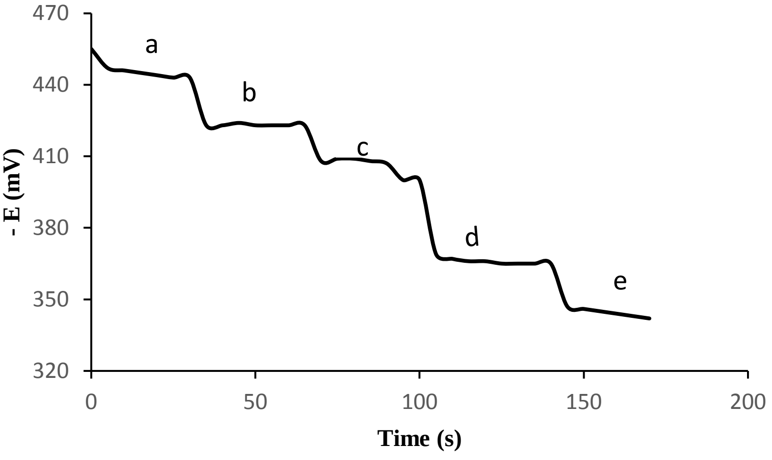

Fig. 5. Dynamic response of the Ca^{2+} selective sensor for step changes in concentration of Ca^{2+} cations: (a) 1.0×10^{-5} M, (b) 1.0×10^{-4} M, (c) 1.0×10^{-3} M, (d) 1.0×10^{-2} M, and (e) 1.0×10^{-1} M.

The results indicate that the potentiometric response of the sensor is reversible (Fig. 6). The sensing behavior of the electrode remained unchanged when the potentials were recorded either from low-to-high concentrations or vice versa.

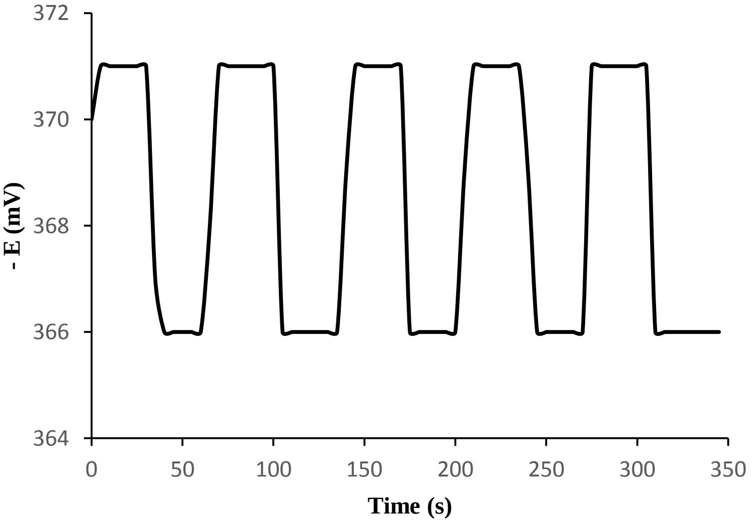

Fig. 6. Response characteristics of the Ca^{2+} selective sensor for several high-to-low (1.0×10^{-2} to 1.0×10^{-3} M) sample cycles.

3.6. Potentiometric selectivity

The most important characteristic of a sensor is the selectivity, as it reflects its utility for target sample. The potentiometric selectivity coefficients of the proposed coated graphite sensor were determined by the separate solution method (SSM) [9,10], using the respective nitrate salts at 0.001 M concentration according to the following equation:

$$LogK_{ij}^{pot} = \frac{(Ej - Ei)Z_i F}{2.303RT} + \left(1 - \frac{Z_i}{Z_j}\right) \log a_i$$

where E_i and E_j are the measured potentials of primary (Ca^{2+}) and interfering ions and z_i and z_j are their respective charges. The K_{Caj}^{pot} of mono-, di- and trivalent cations was measured and the results are shown in Table 3. It is obvious from the selectivity coefficient data that alkali, transition and heavy metal cations could not significantly disturb the Ca^{2+} ion selective sensor function. As it is evident from the data in Table 3, most of the selectivity coefficients of interfering ions are low, indicating no significant interference in the performance of the sensor (except for Ag^+ and Zn^{2+}) and the sensor can, therefore, be used for Ca^{2+} determination in the presence of several other ions.

Table 3. Selectivity coefficient values observed for Ca^{2+} selective sensor no. 5 for various interfering ions using separate solution method

Interfering ions	Selectivity coefficients (K_{Caj}^{pot})
K^+	2/4 × 10^{-5}
Cd^{2+}	4/2 × 10^{-6}
Sr^{2+}	1/7 × 10^{-3}
Cu^{2+}	5/1 × 10^{-5}
Fe^{3+}	4/0 × 10^{-8}
Zn^{2+}	1/2 × 10^{-1}
La^{3+}	2/6 × 10^{-4}
Ag^+	8/9 × 10^{-2}
Cr^{3+}	3/4 × 10^{-3}

4. Conclusions

A PVC membrane electrochemical sensor incorporating benzo-18-crown-6 as an ionophore was successfully used to determine calcium (II) cations over a concentration range of 1.0×10^{-5}- 1.0×10^{-1} M. The sensor displayed a Nernstian slope of 29.8±0.2 mV/decade. The Ca (II) selective membrane sensor can be used for the direct determination of Ca (II) cations in real samples. The investigations demonstrate the utility of the coated graphite sensor incorporating benzo-18-crown-6 as electroactive phase in determining Ca^{2+} cation in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M. This sensor exhibits either comparable or better performance to the existing electrodes, already reported by many researchers for the determination of Ca^{2+} ions, regarding linear concentration range, pH range; response time and detection limit (Table 4). Therefore, the proposed sensor is a good addition to the existing list of the Calcium (II) ion selective sensors reported till date.

Table 4. General performance characteristics of some calcium (II) ion selective sensors

Ref. no.	Response time (s)	Linear range (M)	pH range	Slope (mV/decade)	Detection limit (M)
[11]	4	10^{-7}-10^{-1}	---	28.0	2.0×10^{-8}
[12]	15	10^{-6}-10^{-1}	8-11	---	---
[13]	30	10^{-5}-10^{-1}	3-11	28.0±0.2	4.0×10^{-6}
[14]	10	10^{-7}-10^{-1}	3.5-9	29.5±0.5	---
[This work]	10	10^{-5}-10^{-1}	5-12	29.8±0.2	4.0×10^{-6}

References:

[1] M. Mazloum, M. Salavati Niassary, M. K. Amini, *Sens. Actuators B* 82 (2002) 259-268.

[2] M. Shamsipur, M. R. Ganjali, A. Rouhollahi, A. Moghimi, *Anal. Chim. Acta* 434 (2001) 23-31.

[3] E. Bakker, P. Bühlmann, E. Pretsch, *Chem. Rev.* 97 (1997) 3083-3094.

[4] V. Alexander, *Chem. Rev.* 95 (1995) 273-287.

[5] K. Byriel, K. R. Dunster, L. R. Gahan, C. H. L. Kennard, J. L. Latten, I. L. Seann, P. A. Duckworth, *Inorg. Chim. Acta* 205 (1993) 191-198.

[6] K. Byriel, K. R. Dunster, L. R. Gahan, C. H. L. Kennard, J. L. Latten, I. L. Seann, P. A. Duckworth, *Polyhedron* 11 (1992) 1205-1212.

[7] V. K. Gupta, A. K. Singh, S. Mehtab, B. Gupta, *Anal. Chim. Acta* 566 (2006) 5-12.

[8] M. R. Ganjali, T. Poursaberi, M. khoobi, A. Shafiee, M. Adibi, M. Pirali-Hamedani, P. Norouzi, *Int. J. Electrochem. Sci*. 6 (2011) 717-724.

[9] Y. Umezawa, K. Umezawa, H. Sato, *Pure Appl. Chem*. 67 (1995) 507-512.

[10] R. P. Buck, E. Lindner, *Pure Appl. Chem.* 66 (1994) 2527-2531.

[11] E. L. Jammal A. Bouklouze A. A. Patriarche, *Talanta*, 38 (1991) 929-935.

[12] M. Yi-long, R. Xiao-hong, Z. Shi-ming, *J. Tongji Medical Uni.* 12 (1992) 98-102.

[13] A. Kumar, S. K. Mittal, *Sens. Actuators B* 99 (2004) 340-343.

[14] A. Kumar, M. Sameena, *Sens. Actuators B* 123 (2007) 429-436.