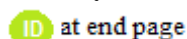




Development of calcium-selective potentiometric electrode using 10,19-Bis[(octadecylcarbamoil)methoxyacetyl]-1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane compound as ionophore

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ABSTRACT

This work deals with the development of micro-size potentiometric calcium-selective electrode. A simple and rapid potentiometric method of determining calcium concentration, based on 10,19-Bis[(octadecylcarbamoil) methoxyacetyl]-1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane, is described. For this aim, calcium-selective polyvinylchloride (PVC) membrane was prepared by coating on the surface of solid-contact. Calcium-selective PVC membrane electrode does not contain internal reference electrode and solution. The potentiometric performance of calcium-selective PVC membrane electrode (selectivity constant, liner working range, detection limit, response time, pH working range, repeatability, lifetime, and time dependent potential decay) was determined using computer controlled measurement system in static conditions. The results showed that the calcium-selective electrode exhibited good reproducibility in calcium determination.

Keywords: Potentiometric electrode, ionophore, calcium selective electrode.

İyonofor olarak 10,19-Bis [(oktadesilkarbamoil) metoksiasetil]-1,4,7,13,16-pentaoкса-10,19-diazasikloheniikosan bileşiğini kullanarak kalsiyum seçici potansiyometrik elektrotun geliştirilmesi

ÖZ

Bu çalışma mikro boyutta potansiyometrik kalsiyum-seçici elektrotun geliştirilmesi ile ilgilidir. 10,19-Bis [(oktadesilkarbamoil) metoksiasetil] - 1,4,7,13,16 - pentaoksa - 10,19-diazasikloheniikosan temelli kalsiyum konsantrasyonunu belirleyen basit ve hızlı potansiyometrik bir yöntem tarif edilmiştir. Bu amaçla, kalsiyum seçici polivinilklorid (PVC) membran katı hal kontak yüzeyi üzerine kaplanarak hazırlanmıştır. Kalsiyum-seçici PVC membran elektrot, iç referans elektrot veya çözelti içermemektedir. Kalsiyum-seçici PVC membran elektrotun (seçicilik sabiti, liner çalışma aralığı, tayin sınırı, cevap süresi, pH çalışma aralığı, tekrarlanabilirlik, ömür ve zamana bağlı potansiyeldeki değişim) potansiyometrik performansı, statik koşullarda bilgisayar kontrollü ölçüm sistemi kullanılarak belirlenmiştir. Sonuçlar, kalsiyum seçici elektrotun kalsiyum tayininde iyi tekrarlanabilirlik sergilediğini gösterdi.

Anahtar Kelimeler: Potansiyometrik elektrot, iyonofor, kalsiyum seçici elektrot.

1. INTRODUCTION

Calcium is the fifth element in the earth's crust and the third most abundant metal. This element is vital for the life of plants and animals because it is found in animal skeletons, dentistry, egg shells, corals and many

other soils. Calcium is the most common metal in the human body. It is an important component of a healthy diet and a mineral necessary for life. It is also very important for other physical functions, such as blood circulation and muscle control. Calcium deficiency is one of the main causes of osteoporosis.¹ Osteoporosis is a

disease that causes the bones to become excessively porous and to be exposed to the fracture. The calcium requirement of the human body varies with age. The recommended diet amount for calcium by the Food and Nutrition Committee is approximately 1100 mg per day for adults.^{2,3} Calcium is an important component of the diet, and its monitoring and analysis in biological fluid, food and environmental samples is important.

Several techniques have been used to determination of calcium in biologic liquids, foods and environment samples. These techniques consist essentially of flame atomic absorption spectrometry (FAAS),⁴ titrimetry,⁵ inductively couple plasma-optical emission spectrometry (ICP-OES)⁶ and inductively couple plasma mass spectrometry (ICP-MS).⁷ However, these developed methods are expensive, time-consuming and not sufficiently selective and sensitive and can be used with too many solvents.

This work deals with preparation of micro-size potentiometric PVC membrane calcium-selective electrode. For this aim, calcium-selective electrode membrane was prepared by coating of cocktail on the surface of solid-state-contact.⁸ The electrode does not contain an internal reference electrode or solution. The potentiometric performance of calcium-selective PVC membrane electrode (linear working range, response time, detection limit, selectivity, repeatability, and pH working range, lifetime, and time dependent potential decay) was determined using computer controlled measurement system in static conditions.

2. MATERIALS AND METHODS

2.1. Reagents

The solid-contact components and graphite was obtained from Sigma-Aldrich Company. Hardener (Desmodur RFE) and epoxy resins (Macroplast Su 2227) were supplied Henkel and Bayer Company, respectively. The polymer membrane components, the plasticizers and high molecular weight polyvinylchloride (PVC), bis(2-ethylhexyl) sebecate (DOS), bis-(2-ethylhexyl) phtalate (DOP), bis-(2-ethylhexyl) adipate (DOA), 2-nitrophenyloctyl ether (NPOE) and lipophilic anionic additive reagent potassium tetrakis-(p-chlorophenyl) borate (KTCIPB), were from Fluka company. Tetrahydrofuran (THF) was from Merck Company. Calcium-selective ionophore (10,19 - Bis[(octadecylcarbamoil) methoxyacetyl] - 1,4,7,13,16 - pentaoxa - 10,19 - diazacycloheneicosane) was from Sigma-Aldrich Company (Figure 1). Standard metal salts were of analytical grade (Merck). All solvents were used after purification. The other reagents used were of analytical reagent grade. All solutions were prepared with twice-distilled deionize water. All of the experiments were operated at room temperature, 25±1 °C.

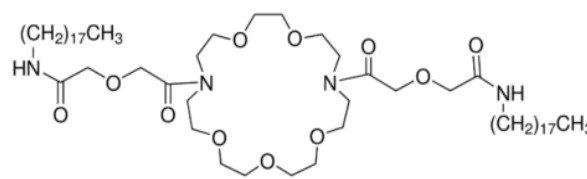


Figure 1. 10,19 - Bis[(octadecylcarbamoil) methoxyacetyl]-1,4,7,13,16 – pentaoxa - 10,19 – diazacycloheneicosane.

2.2. Preparation of solid state contact

Solid state contact mixture composed of 50.0 mg of graphite, 35.0 mg of epoxy and 15.0 mg of hardener was dissolved in THF and was stirred thoroughly until a suitable viscosity provided. The surface of the copper wire (about 0.5-1 mm thickness, 5-15 cm long) was coated by dipping into this mixture 4-5 times. It was allowed to stand overnight at room temperature.

2.3. Preparation of membrane cocktail

The membrane cocktail was prepared using a mixture of 3.0 mg of ionophore, 32.0 mg of PVC, 64.0 mg of plasticizer and 1.0 mg of KTpCIPB. The components were dissolved in dried THF and were stirred thoroughly until a suitable viscosity provided and the solid-state contact surface is coated in a specific thickness. Calcium-selective electrode, then allowed to dry for 3-4 hours and 10^{-2} M Ca^{2+} was conditioned for 24 hours at room temperature.

2.4. Preparation of solution

A stock Ca^{2+} solutions (1.0×10^{-1} mol l^{-1}) were prepared in deionize water. The diluted solutions (1.0×10^{-1} to 1.0×10^{-5} mol l^{-1}) of Ca^{2+} were prepared by dilution of the stock solution. The stock solutions of metals (1.0×10^{-1} mol l^{-1}) were obtained by dissolving salts of the corresponding metals.

2.5. Apparatus

Potentiometric measurements were performed at room temperature (25±1 °C) using a computer-controlled multichannel potentiometric system. All potential measurements were made with a micro-sized silver/silver chloride reference electrode and the calcium-selective membrane electrode. The potentiometric characteristics of the calcium-selective PVC membrane electrode were investigated with measurements of the potential differences between two points which is the cause of electrical currents. Measurements were taken in the following cell assembly:

Micro-sized solid silver/silver chloride reference electrode/test solution/calcium-selective electrode/solid-state contact/Cu wire.

3. RESULTS AND DISCUSSION

3.1. Optimization of membrane composition

The response characteristics of electrode such as working range and response time depend on optimum membrane composition.⁹ The electrode membrane while preparing cocktails, each of the different plasticizers (DOS, DOP, DOA, and NPOE) were used separately and the best potentiometric behavior was detected which exhibits the plasticizer. Of these plasticizers, DOP exhibited the best sensitivity in the linear working range. Good compatibility with ionophore-based PVC membrane electrodes is explained by the high polarity of DOP.¹⁰ 10,19-Bis [(octadecylcarbamoyl) methoxyacetyl]-1,4,7,13,16-pentaoxa-10,19-diazacikloheniikosan based PVC membrane electrodes were prepared in different amounts and potential measurements were performed. The results are summarized in Table 1.

One of the other parameters of the PVC membrane composition to be investigated is the ionophore concentration. For this purpose, PVC membrane electrodes were prepared and tested using the different ratio of 10,19-Bis[(octadecylcarbamoyl)methoxyacetyl]-1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane.

Optimum ionophore ratio was determined as 3.0%. From the data shown in Table 1, the membrane composition with optimized PVC: DOP: ionophore: KTpCIPB weight percentage ratio of 32:64:3.0:1.0 was selected for further studies.

3.2. Working concentration range and slope

The potential behavior of calcium-selective PVC membrane electrode was determined in calcium nitrate solutions of the concentration 1×10^{-1} to 1×10^{-5} mol l⁻¹. The potential changes of the electrode are shown in Figure 2 and the calibration curve is shown in Figure 3.

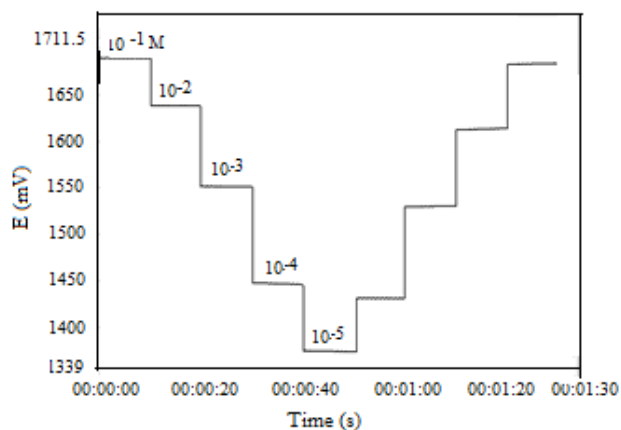


Figure 2. Potentiometric response of all-solid-state PVC membrane Ca²⁺-selective electrode.

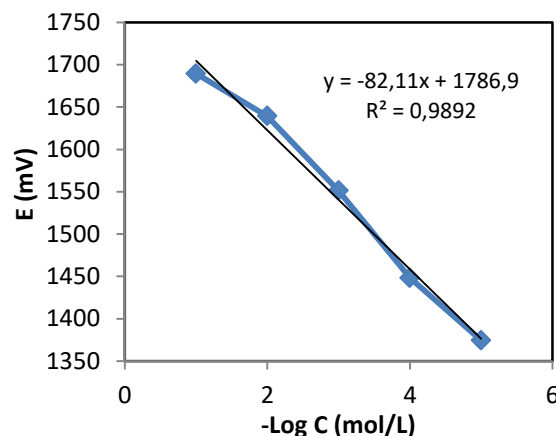


Figure 3. Calibration curve of all-solid-state PVC membrane Ca²⁺-selective membrane electrode obtained over Ca²⁺ concentration range of 1×10^{-1} to 1×10^{-5} mol l⁻¹.

As shown in Figure 1, the calcium-selective PVC membrane electrode showed a good potential change against the concentration change of the calcium ions. The calcium-selective electrode has a good concentration of working range and appears to exhibit Nernst behavior. It was also observed that the response time of the electrode was shorter than 15 s. The response time is defined as the time when the potential is balanced and unchanged after the ion is added to the sample. Electrodes were held in Ca²⁺ solution before measurement, and then measurements were taken.

3.3. pH effect

The pH working range of the electrode was determined by measuring the potential values of 0.01 M Ca solutions ranging between pH 2 and 7. The pH of the solutions used in the measurements was adjusted with HNO₃. We did not take measurements after pH 7 because Ca(OH)₂ precipitated in basic medium. As shown in Figure 4, the electrode was able to operate between pH 2 and 7 without being affected by the pH.

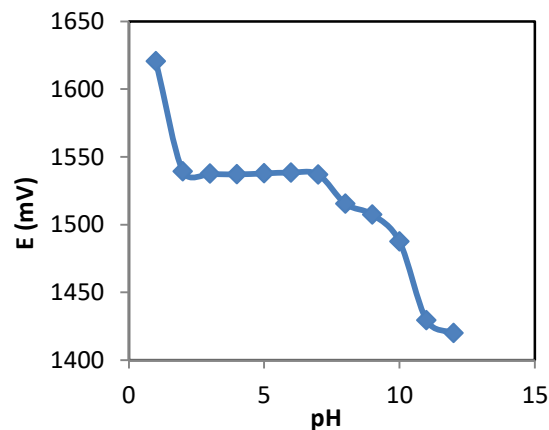


Figure 4. The dependence of the all-solid-state contact Ca²⁺-selective membrane electrode response in pH.

Table 1. The membrane compositions of all-solid-state PVC membrane Ca²⁺-selective electrode

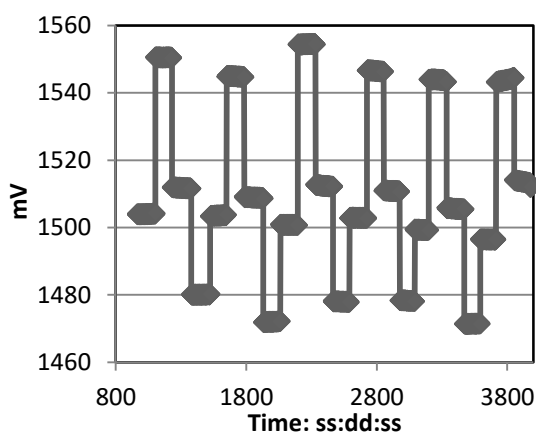
(Active ingredient) Ionophore	Composition (%) (w/w)					
	PVC	Plasticizer				(Conductivity enhancer) KTCIPB
		NPOE	DOS	DOP	DOA	
2.0	30	-	67	67	-	1.0
2.5	31	65	-	65	65	0.5
3.0	32	64	64	64	64	1.0
3.5	33	62	62	62	-	1.5
4.0	34	61	-	-	61	1.0
5.0	34	65	-	65	-	1.0

3.4. Selectivity

Selectivity is one of the most important parameters of PVC membrane electrode and determines whether reliable measurement is possible. Selectivity of calcium selective PVC membrane electrode was determined according to the separate solution method proposed by IUPAC. The selectivity coefficient values of the calcium-selective PVC membrane electrode are shown in Table 2. According to the values in Table 2, the existence of interfering ions seems to be selective against the Ca²⁺ ions of the PVC membrane electrode.

3.5. Repeatability

Measurements made with calcium-selective PVC membrane electrode have shown that the electrode gives reproducible results. Figure 5 shows repeat measurements of the sensor against calcium concentrations of 10⁻², 10⁻³, and 10⁻⁴ mol l⁻¹.

**Figure 5.** Potentiometric repeatability of all-solid-state PVC membrane Ca²⁺-selective electrode.

4. CONCLUSIONS

The proposed calcium-selective PVC membrane electrode is a sensitive, low cost, precise and highly selective method for determination of Ca²⁺ ion, based on the 10,19 – Bis [(octadecylcarbamoyl) methoxyacetyl] –

1,4,7,13,16 – pentaoxa – 10,19 – diazacycloheneicosane entrapped in PVC matrix. The electrode produced a linear response for calcium concentration range of 1.0x10⁻¹ – 1.0x10⁻⁵ M. As a result of this study, we will provide a contribution to the existing methods in the literature as an alternative method for the determination of calcium ion.

Table 2. Selectivity coefficient values of all-solid-state PVC membrane Ca²⁺-selective electrode.

Interfering ion	k _{Ca²⁺} ^{pot} , M	Log k
Na ⁺	5.88x10 ⁻³	-2.23
K ⁺	3.38x10 ⁻⁴	-3.47
Cu ²⁺	5.24x10 ⁻³	-2.28
Cd ²⁺	1.51x10 ⁻⁴	-3.82
Co ²⁺	3.71x10 ⁻⁴	-3.43
Mg ²⁺	7.24x10 ⁻²	-1.14
Pb ²⁺	7.07x10 ⁻³	-2.15
Mn ²⁺	3.01x10 ⁻³	-2.52
Ba ²⁺	6.76x10 ⁻⁵	-4.17
Ni ²⁺	4.57x10 ⁻⁶	-5.34
Al ³⁺	1.44x10 ⁻⁴	-3.84
Cr ³⁺	1.86x10 ⁻³	-2.73

Conflict of interest

Author declares that there is no a conflict of interest with any person, institute, company, etc.

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