

New cesium ion-selective PVC membrane electrode based on a novel calix[6]arene derivative

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Cesium-selective polymeric membrane electrode, based on a recently synthesized calix[6]arene compound of 5,11,17,23,29,35-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tricyanomethoxy-calix[6]arene, is described. The electrode exhibits a near Nernstian response for Cs (I) ions over a wide concentration range of 1.0×10^{-1} to 1.0×10^{-5} M with a slope of 55.3 ± 1.2 mV/p[Cs]. The developed electrode has a very short response time (4-5 s) and it can be used for at least 30 days without any considerable divergence in potentials. The proposed electrode shows high selectivity towards cesium (I) ions with respect to alkali, alkaline earth, several transition and heavy metal ions. The potentiometric response is independent of pH of the test solution in the pH range of 3.0-10.0. The electrode can be used as an indicator electrode in the potentiometric titrations of cesium (I) ions with sodium tetraphenylborate and for direct determination of cesium in tap water samples.

Keywords: PVC membrane; cesium; ion-selective electrode; calix[6]arene.

1. INTRODUCTION

In recent years, the development of novel sensors for the detection of various metal ions has been motivated by the control of the levels of environmental pollutants in natural waterways and potable water. Under normal conditions, cesium is not considered as a major contaminant of natural and groundwaters. It preferentially adheres to soils, thereby showing relatively low mobility. However, in the case of a nuclear reactor accident large amounts of radioactive cesium isotopes could be released into aquatic environments, which will be very dangerous for human health. That is why, the use of ion-selective electrodes (ISEs) for the detection of cesium has received much interest, and many ligands used as sensing molecules in new cesium ion-selective poly(vinyl chloride) (PVC) membrane electrodes have been reported [1-3].

Calix[*n*]arenes and their derivatives act as strong ligands, by selectively binding cations and small organic molecules (such as chloroform, toluene and fullerene). The presence of a cavity and of specific electron donor sites results in their ability to form stable host-guest systems with

electron-acceptor molecules and that is why they are excellent complexing agents that are capable of binding alkali-metal cations [4]. In this respect, calixarenes have advantages over other classes of macrocyclic compounds as ionophores for poly(vinyl)chloride (PVC)-based ion-selective electrodes (ISEs) and ion-sensitive field effect transistors (ISFETs) [2-5]. Recently Cs-ISEs have seen increasing interest for clinical and environmental analysis. However, in comparison with sodium and potassium, only limited Cs-ISEs based on crown ethers and neutral ionophores have been reported [6-7]. In early studies about Cs-ISEs based on ion-exchangers, tetraphenylborate and its derivatives were reported [8]. Quadruply-bridged calix[6]arenes were first used as ionophores by Choi *et al.* Polymeric cesium ion-selective electrode exhibited high selectivity over alkali, alkaline earth and ammonium ions [9].

The purpose of this study was to develop a new cesium ion-selective electrode using the recently synthesized 5,11,17,23,29,35-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tricyano-methoxy-calix[6]arene as a neutral carrier and to use this electrode for *in situ* determination of cesium ions in waste water. The lifetime, response time, optimum working range, and other response characteristics of the electrode were determined.

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2. EXPERIMENTAL

Reagents and solutions

5,11,17,23,29,35-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tricyanomethoxy-calix [6] arene was synthesized at the Department of Organic Chemistry of Selçuk University by the procedures developed in ref. [10]. The structure of the ionophore studied in this work is shown in Fig.1. High-molecular-weight poly(vinylchloride) (PVC), 2-nitrophenyloctylether (2-NPOE), 2-nitrophenylpentylether (2-NPPE), tetrahydrofuran (THF) were obtained from Fluka as selectophores.

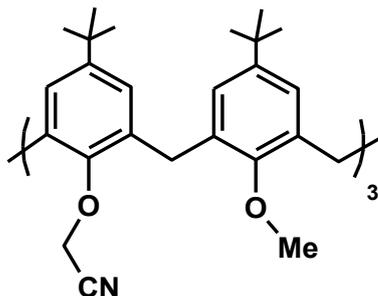


Fig. 1. 5,11,17,23,29,35-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tricyanomethoxy-calix[6]arene.

Potassium tetrakis(*p*-chlorophenyl)borate (KTPClPB) and sodium tetraphenyl borate (NaTPB) as lipophilic anionic additives were obtained from Aldrich. Britton-Robinson (BR) buffer solutions (pH 2-12) were used to investigate the performance of the prepared cesium ion-selective electrode. All chemical substances were of reagent grade and were used without further purification. Metal solutions of different concentrations were made by dilution of 0.5 M stock solutions of each metal ion. Deionized water obtained from Human power I⁺, Ultra Pure Water System was used throughout the experiments.

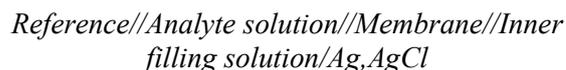
Membrane composition and electrode preparation

The Cs⁺-selective electrode was constructed using a PVC-based membrane as reported previously [11-12]. The membrane was prepared by dissolving optimized amounts of PVC, plasticizer, lipophilic additives and ionophore in a ratio of 33.32: 64.86: 0.75: 1.06, respectively, in 5 mL of tetrahydrofuran. The mixture was shaken vigorously and the clear solution was poured onto a glass disc 3.5 cm in diameter. The solvent was allowed to evaporate at room temperature, until polymeric membrane was obtained. For preparation of the electrodes, 0.7 cm diameter disc of the polymer membrane was cut and fixed to the end of

a glass tube with a diameter of 0.5 cm and a length of 10 cm. The tube was then filled with internal filling solution (1.0×10^{-3} M CaCl₂). The prepared PVC membrane electrode was conditioned for 24 h by soaking in 1.0×10^{-4} M CsCl solution. A silver/silver chloride electrode was used as an internal reference electrode.

Apparatus and potential measurements

Using the double-junction Ag/AgCl reference and the cesium-selective electrode the following electrochemical cells were prepared.



The potential measurements were made by the use of Orion 720A Model pH ion meter. The reference electrode was a double-junction Ag/AgCl electrode (Orion 9002) and the pH measurements were done with an Ingold (10.402.3311) combined glass pH electrode. The performance of the proposed cesium-selective electrode was investigated by measuring the potential in Cs (I) solutions prepared in the concentration range of $1.0 \times 10^{-1} - 1.0 \times 10^{-6}$ M. The working solutions were stirred with a magnetic stirrer and the potentials were recorded after the equilibrium potentials had been reached.

3. RESULTS AND DISCUSSION

Ion selectivity

It is well known that the sensitivity and the selectivity of the ion-selective electrodes obtained for a given ionophore not only depend on the ion-binding properties of the ionophore but also significantly on the membrane ingredients as plasticizers, lipophilic additives and ratios of these ingredients in the membrane [13-14]. The former is an intrinsic property of the ionophore, while the membrane composition can be optimised experimentally. The literature survey showed that the usual range of composition in the preparation of PVC matrix membrane electrodes was 1–7% ionophore, 28–33% PVC (internal matrix), 60–69% plasticiser (solvent) and 0.03–2% lipophilic anion [15]. Since in preparation of many PVC membrane electrodes a plasticizer/PVC ratio (m/m) of nearly 2 has resulted in very suitable performance characteristics [16], this ratio was kept at about 2 in optimization of the ingredients of the cesium (I) ion-selective electrode proposed.

Effect of the anionic sites

The presence of lipophilic anionic sites in the cation-selective membrane electrode not only lowers ohmic resistance and significantly reduces response times and selectivity, but also enhances the sensitivity of the membrane electrode especially in case where the extraction capability of the ionophore is poor [15, 17]. Moreover, lipophilic additives may catalyze the exchange kinetics at the membrane interface [18]. We prepared the electrode by using potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) and sodium tetraphenylborate (NaTPB) as a lipophilic anion. The membrane containing sodium tetraphenylborate (NaTPB) did not show any response for cesium ions. This may be attributed to the fact that sodium ions form ion pairs with the tetraphenylborate that settle in the cavity of the calix[6]arene and decrease the number of active sites in the membrane.

Effect of the plasticizer

The influence of the plasticizer on the characteristics of the cesium ion-selective electrode was investigated. It is known that the nature of the solvent mediator influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands. So, it plays an important role in determining the ISE characteristics [19]. In our study, in order to investigate the effect of the plasticizer on the characteristics of the proposed electrode, two sets of membranes of similar composition, but with different plasticizers (2-NPOE or 2-NPPE) were prepared and tested. We observed only minor differences in the performance of the electrodes, however slightly better selectivity was obtained with 2-NPOE. That is why 2-NPOE was chosen for the further experiments.

Working range and slope of the electrode

Over the concentration range $10^{-1} - 10^{-5}$ M of cesium in the calibration solutions, the electrode potential response was linear (Fig. 2). The slope of the calibration curve was 55.3 ± 1.2 mV/pCs and the detection limit, calculated as recommended by IUPAC [20], was 4.36×10^{-6} M. The slope of the electrode was found to be close to the Nernstian value. Although the electrode does not give a full Nernstian response, it is stated in the literature that the electrodes with slopes in this vicinity range could be used for analytical applications [21, 22].

This range was found to be compatible with many PVC membrane electrodes mentioned in the literature [23 - 25].

Effect of pH on the response characteristics of the electrode

The influence of pH on the response of the Cs (I)-ion selective electrode with o-NPPE as the

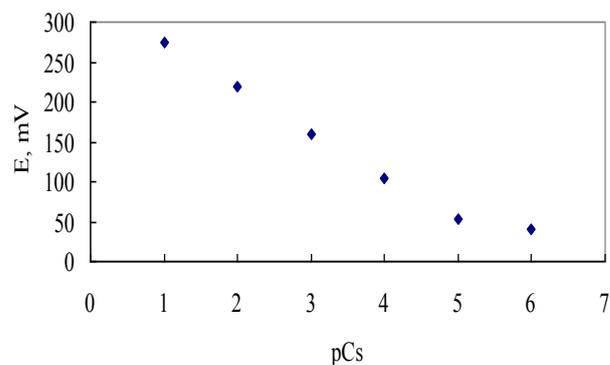


Fig.2. Calibration curve of the cesium ion-selective electrode based on 5,11,17,23,29,35-*tert*-butyl-37,39,41-trimethoxy-38,40,42-tricyanomethoxy-calix[6]arene

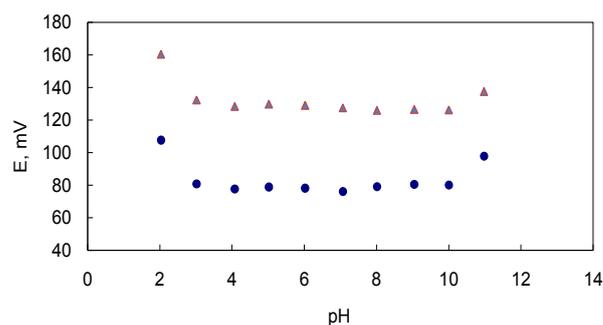


Fig.3. The effect of pH of test solutions containing a) 1.0×10^{-2} M (\blacktriangle) and b) 1.0×10^{-3} M (\bullet) cesium ions on the response of the Cs-selective electrode.

plasticizer was studied over the pH range 2 – 11 at 1.0×10^{-2} and 1.0×10^{-3} M Cs (I) containing solutions. We found that the response characteristics (response slope and linear working range) of the electrode did not change by changing the pH values of the solution in the range 3 – 10 (as illustrated in Fig. 3). This can be taken as the useful pH range over which the electrode can be used. All further measurements were made at pH 6.0.

The lifetime and the response time of the electrode

The lifetime of the electrode was determined by recording its potential at an optimum pH value and plotting its calibration curve for each day. No

significant change in the slope of the electrode was observed within one month, after which, a gradual decrease in the working concentration range, slope and response time of the electrode was registered. The response time and the lifetime of the proposed PVC membrane electrode is compatible with those of most similar electrodes reported in the literature [7, 21, 26]. The static response time was 4-5 s over the working ranges of the electrodes and no change was observed in 10 minutes.

Selectivity coefficients of the electrode

The selectivity coefficients for Cs (I) over a variety of interfering ions were determined by the fixed interference method, which is based on the Nicolsky-Eisenman equation recommended by IUPAC. In this work, the concentration of the cesium ion was varied in the concentration range $1.0 \times 10^{-1} - 1.0 \times 10^{-6}$ M, while that of the interfering ion was 1.0×10^{-3} M. It was observed that the proposed Cs (I)-selective electrode is highly selective with respect to a variety of other common cations (K^+ , NH_4^+ , Na^+ , Li^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+}). The values of the selectivity coefficients are listed in Table 1.

Table 1. Selectivity coefficients ($k_{Cs, X}^{pot}$) of the cesium(I) ion-selective electrode using fixed interference method

Interfering ions	Selectivity coefficients ($k_{Cs, X}$)	Interfering ions	Selectivity coefficients ($k_{Cs, X}$)
K^+	1.66×10^{-2}	Co^{2+}	3.16×10^{-4}
Li^+	1.00×10^{-2}	Cu^{2+}	3.16×10^{-4}
Na^+	1.58×10^{-2}	Cd^{2+}	1.66×10^{-2}
NH_4^+	7.38×10^{-3}	Ni^{2+}	3.16×10^{-4}
Mg^{2+}	3.16×10^{-4}	Pb^{2+}	4.91×10^{-4}
Ca^{2+}	4.46×10^{-4}	Sr^{2+}	4.37×10^{-4}
Zn^{2+}	3.16×10^{-4}		

The selectivity coefficients for some common interfering ions of the proposed calix[6]arene-based electrode are compatible with the corresponding values previously reported for PVC-membrane Cs (I)-selective electrodes based on different neutral ion carriers [4, 7, 10, 13, 23].

Analytical applications

The electrode was used in the titration of 25.0 mL 1.0×10^{-2} M cesium ions with 0.1000 M sodium tetraphenylborate. The titration curve was plotted and the concentration of cesium ions was determined in order to elucidate whether the

prepared cesium ion-selective electrode can be employed as an indicator electrode. The titration curve is given in Fig. 4.

The proposed electrode was also applied to the determination of cesium ions in tap water. The water sample was analyzed without pH adjustment and filtering. The sample was divided into two equal parts and each part was spiked with an aliquot of a standard (1000 ppm) CsCl solution to give 5 and 10 ppm Cs^+ , respectively. The cesium content in the sample was determined by direct potentiometric measurement. The tested samples

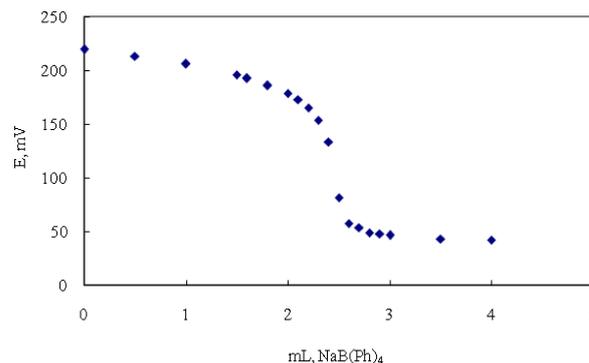


Fig.4. Potentiometric titration curve for 25 mL of 1.0×10^{-2} M Cs^+ solution with 0.1000 M $NaB(C_6H_5)_4$, using the proposed Cs(I)-ISE as an indicator electrode.

Table 2. Analysis of water samples spiked with cesium(I)

Sample No	[Cs] AES ^a , ppm	[Cs] ISE ^b , ppm	Recovery (%)
1	5.19 ± 0.02	5.03 ± 0.02	100.6
2	11.26 ± 0.12	11.43 ± 0.03	114.3

^aAtomic emission spectrometric method

^bThe developed Cs^+ ion-selective electrode

were also analyzed by atomic emission spectrometry to determine the reliability of the proposed electrode. As can be seen from Table 2, the results were found to be reliable at the 95% confidence level. Hence, the electrode prepared could be successfully employed in potentiometric titrations and direct potentiometric measurement of cesium ions.

4. CONCLUSIONS

Calix[6]arene can be successfully used as an ionophore in the cesium (I) ion-selective electrode. The prepared Cs^+ ion-selective electrode can be used to determine cesium ion concentrations in the range $1.0 \times 10^{-1} - 4.36 \times 10^{-6}$ M with a slope of 55.3 ± 1.2 mV/pCs. This electrode is very easy to prepare, shows high selectivity and sensitivity, wide dynamic range, and low detection limit. The

wide pH range (3-10), in which the electrode can be employed, is suitable for application in natural water samples without pH adjustment. It has a relatively fast response time (less than 4-5 seconds) and can be used for at least one month without any considerable divergence in potentials. Unlike most previously developed electrodes, for which there is no reported analytical application, e.g., [14,15], the electrode proposed in the present work is applied as a sensor for the determination of cesium ions concentration in tap water and the results show a good correlation with those obtained by atomic emission spectrometry. The electrode was also used as an indicator electrode in the potentiometric titration of cesium ions with sodium tetraphenylborate.

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НОВ СЕЛЕКТИВЕН КЪМ ЦЕЗИЕВ ЙОН МЕМБРАНЕН ЕЛЕКТРОД ОТ PVC НА ОСНОВАТА НА НОВПОЛУЧЕНО КАЛИКС[6]АРЕНОВО ПРОИЗВОДНО

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(Резюме)

Описан е цезий-селективен полимерен мембранен електрод, на основата на наскоро синтезирано каликс[6]ареново съединение 5,11,17,23,29,35-*терт*-бутил-37,39,41-триметокси-38,40,42-трицианометокси-каликс[6]арен. Електродът показва почти Нернстов отклик на йони Cs (I) при широк диапазон на концентрации от 1.0×10^{-1} до 1.0×10^{-5} М с ъглов коефициент 55.3 ± 1.2 mV/p[Cs]. Разработения електрод има много кратко време на отклик (4-5 s) и може да се използва поне 30 дни без някакво значимо отклонение на потенциалите. Предложеният електрод показва висока селективност към цезиевите (I) йони по отношение на йони на алкални, алкалоземни, някои преходни и тежки метали. Потенциометричният отклик не зависи от рН на опитния разтвор при изменение на рН от 3.0-10.0. Електродът може да се използва като индикаторен електрод при потенциометрично титруване на цезиеви (I) йони с натриев тетрафенилборат и за определяне на цезий в проби на водопроводна вода.