NEW SILVER ION-SELECTIVE PVC MEMBRANE AND COATED-GRAPHITE ELECTRODES BASED ON A NOVEL CALIX[4]ARENE DERIVATIVE

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ABSTRACT

A new PVC membrane and a coated graphite electrode (CGE) based on a recently synthesized calix[4]arene compound of 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene as a suitable carrier for silver (I) ion are described. The electrodes exhibit a Nernstian slope of 57.7 ±1.3 mV/p[Ag] for PVC membrane electrode and 54.7 ±2.1 mV/p[Ag] for CGE over a wide concentration range from 1.0×10^{-2} to 1.0×10^{-6} M and 1.0×10^{-2} to 1.0×10^{-5} M, respectively. They have a fast response time (~10 s) and can be used for at least 60 days for PVC membrane electrode and 30 days for CGE without any considerable divergence in potentials. The proposed electrodes show high selectivity towards silver (I) ions with respect to alkali, alkaline earth and several transition and heavy metal ions. Only interference of Hg^{2+} is found. The potentiometric responses are independent of the pH of test solution in the pH range of 2.0-6.0. Application of only PVC membrane electrode as an indicator electrode in potentiometric titrations of chloride, bromide and iodide ions was reported.

Key words: PVC membrane; coated-graphite electrode; silver ion-selective electrode; calix[4]arene

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INTRODUCTION

There has been a profound development in potentiometric methods on ion-selective electrodes over the past few decades due to their great advantages such as speed and ease of preparation and procedures, relatively fast response, reasonable selectivity, wide linear dynamic range and low cost /1, 2/ when compared to different analytical techniques used in many fields like agriculture, industry, environment and pharmacy. From a broad point of view, measuring and controlling the concentration of metal ions especially the heavy metal ions became an important goal during the last few decades due to the growing environmental problems. Thus, the need for fast and selective determination of precious metal ions such as silver (I) has increased immensely. Its presence in some part of the human body, such as human hair /3/, its role in electrical and electronic applications, photographic film production and manufacturing of fungicides are well known /4/. Hence, the determination of trace amounts of silver ion in various media is necessary and analysis by the use of silver (I) - selective electrodes has been initiated. It is still desirable to continue efforts to make a sufficiently selective silver electrode with a low detection limit.

Many intensive studies showed that the main problem in the area of ISEs is the non-availability of ionophores with high affinity for the silver ion. The design and function of synthesized macrocyclic carriers for cationic selective membrane sensors are usually based on such diverse parameters as the structure and suitable cavity size of ion carrier, the stability and selectivity of its metal ion complexes, its solubility and its ability to extract the target ion into membrane phase /5/. In recent decades, much effort has been made in the field of designing and subsequent syntheses of new ionophores for ion-selective electrodes. Specially designed several macrocyclic ligands have been used for preparing a variety of silver - selective electrodes /6- 63/. Among these, it is well known that ligands containing donor atoms such as sulfur, nitrogen and oxygen can selectively coordinate different transition and heavy metal ions. In general, according to the hard-soft acid-base theory, various ionophores with donor atoms have the ability to coordinate with silver ion as a soft acid. As a relatively new class of macrocyclic ligands, calixarene derivatives having donor atoms have been focused on during the last decades and numerous types of silver (I) - selective electrodes based on calixarenes have been prepared /6- 24/.

As a part of our interest to develop ion-selective electrodes /23, 64- 68/, in the present work, we investigated whether we could use 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene (Fig. 1) as a novel ionophore in construction of a new PVC membrane and coated-graphite silver - selective electrodes or not. The influences of the membrane composition, pH of sample solutions, and internal filling solution on the potential response of the PVC membrane silver (I) - ISE were assigned. Furthermore, the question whether these electrodes can be used for analytical purpose as an indicator electrode was studied.

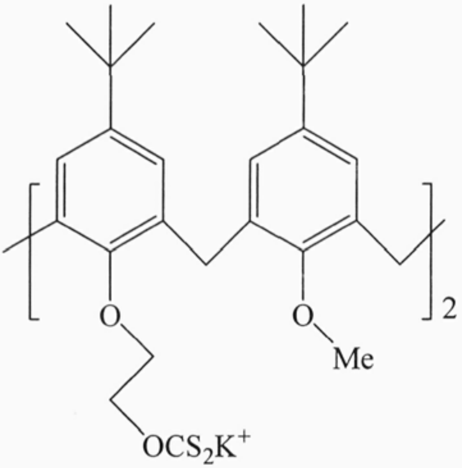

Fig. 1: The structure of 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene.

EXPERIMENTAL

Reagents

5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxy-calix[4]arene was synthesized at the Department of Organic Chemistry of Selçuk University by using the procedures developed in Ref. 69. High-molecular-weight poly(vinyl chloride) (PVC), *o*-nitrophenyl octylether (*o*-NPOE), *o*-nitrophenyl pentylether (*o*-NPPE), tetrahydrofuran (THF) were purchased from Fluka in selectophores and potassium tetrakis(4-chloro-phenyl)borate (KTpClPB) and sodium tetraphenyl borate (NaTPB) as lipophilic anionic additives were obtained from Aldrich.

All of the chemical substances were of reagent grade, and were used without further purification. Stock solution of silver nitrate (Fluka) was prepared using deionized water, and working solutions were obtained by serial dilution of the stock solution with deionized water. Nitrates of all metals were supplied by Fluka and metal solutions of different concentrations were made by dilution of 0.5 M stock solutions of each metal ion. The pH adjustments were made with appropriate amounts of dilute nitric acid and sodium hydroxide solutions. Deionized water was obtained from Human power I^+, Ultra Pure Water System and was used throughout the experiments.

Apparatus and potential measurements

All potential and pH measurements were carried out at 20 ± 1 °C, using an Orion 720A Model pH ion meter. Potentials were measured relative to an Ag/AgCl double junction reference electrode (Orion 9002), containing 17 % KNO_3 and 5 % KCl mixture saturated with AgCl (Cat. No: 900002) as the inner chamber filling solution and the outer chamber filling solution was consist of 10 % KNO_3 (Cat. No: 900003). The pH measurements were done with Ingold (10.402.3311) combined glass pH electrode. The combined glass electrode was kept in water when it was not in use.

The performance of the developed silver - selective electrodes was investigated by measuring the potential in Ag (I) solutions prepared in the concentration range of 1.0×10^{-2}-1.0×10^{-8} M containing 0.1 M KNO_3. The working solutions were stirred with a magnetic stirrer and the potentials were recorded after the equilibrium potentials had been reached.

Using the double-junction Ag/AgCl reference and the silver (I) ion-selective electrodes, the following electrochemical cells were prepared for potential measurements:

a) For PVC membrane electrode:

Reference electrode | | Analyte solution | Membrane | Inner filling solution | Ag,AgCl

b) For CGE:

Reference electrode | | Analyte solution | ion-selective coating membrane | graphite rod | Copper wire

Preparation of the PVC membrane electrode

The procedure to prepare the membrane of the silver ion-selective electrode was as follows: 4.3 mg of calix[4]arene, 285.0 mg of *o*-nitrophenyl octylether and 1.6 mg of potassium tetrakis(4-chloro-phenyl)borate were dissolved in 5 mL of tetrahydrofuran. 136.1 mg of PVC was slowly added to this mixture. The homogenous mixture formed was poured onto a glass disc with a diameter of 3.5 cm attached to a glass plate and was kept at room temperature for 24 h for the evaporation of tetrahydrofuran. The 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.

An internal filling solution containing 1.0×10^{-5} M silver nitrate was put into this glass tube and a AgCl-coated silver wire was placed into it. The prepared PVC membrane electrode was conditioned in 1.0×10^{-5} M silver nitrate solution for 12 h. The PVC membrane silver ion-selective electrode thus obtained was used as an indicator electrode.

Preparation of the PVC coated-graphite electrode

The same membrane ingredients used for the above mentioned PVC membrane electrode was dissolved in 5 mL of THF in a glass dish and was evaporated slowly until an oily concentrated mixture was obtained. This solution was used to coat graphite rods (3mm diameter and 6mm long) as described in literature /24, 57-63/: A shielded copper wire was attached to one end of the graphite rod, and the rod was inserted into the end of a glass tube. The emptiness between the glass tube and the graphite rod is filled with polyester. The working surface of the graphite rod was polished and the electrode was rinsed with water and then methanol and allowed to dry. The polished graphite electrodes were then coated by repeated dipping (five times, a few minutes between dips) into the concentrated membrane solution and the solvent was evaporated at room temperature between each dip. Then the selective membrane was formed on the graphite surface and it was allowed to set overnight and finally conditioned for 12 h in 1.0×10^{-5} M silver nitrate solution before use. The coating solutions are stable for several weeks if kept in an airproof glass dish and can be used for the construction of new electrodes by adding appropriate amounts of THF into the mixture and repeating the above process.

RESULTS AND DISCUSSION

As seen from the structure 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene, the existence of donor atoms as well as its sufficiently high rigidity and lipophilicity was expected to increase both the selectivity and stability of its transition and heavy metal ion complexes over alkali and alkaline earth cations. In preliminary experiments, in order to determine the suitability of ligand as a neutral carrier for silver (I) ion, it was used to prepare several PVC membrane and coated-graphite ion-selective electrodes under identical conditions for cations, including ammonium ions, alkali (K^+, Na^+, Li^+), alkaline earth (Mg^{2+}, Ca^{2+}), some transition (eg, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) and heavy metal (Pb^{2+}) ions. The potential responses of various PVC membrane and coated-graphite ion-selective electrodes prepared by using 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene are shown in Fig. 2 and Fig. 3.

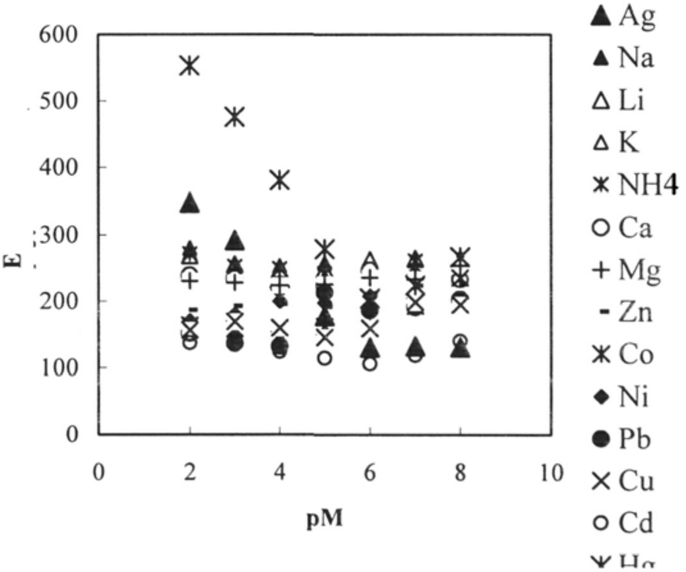

Fig. 2: Potential response of PVC membrane ion-selective electrode based on 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene to various metal ions at pH 3.0 (Electrode A4).

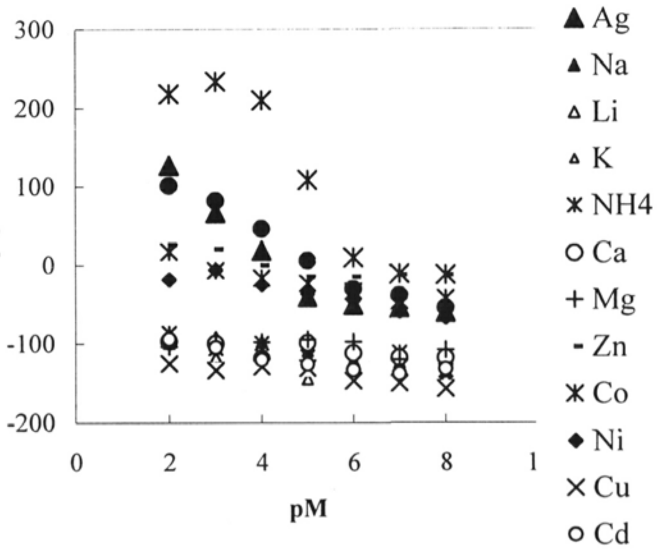

Fig. 3: Potential response of coated-graphite ion-selective electrode based on 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene to various metal ions at pH 3.0 (Electrode B6).

It is quite obvious from both of the figures that, among these ions, those of hard acid character (alkali and alkaline earth ions) showed negligible responses, due to their very weak interactions with sulfur atoms as soft bases. Furthermore, most of the transition metal ions of intermediate acid character and lead (II) ion do not indicate noticeable potential responses. However, the metal ions of soft acid character i.e Hg (II) and Ag (I) revealed the most sensitive response in these cations. In particular, linear responses and Nernstian slopes for the corresponding potential-pAg plots in both cases were obtained and only the interference of Hg(II) ions were found. Before deciding to the target ion, the potential response of both electrodes to Hg(II) ions were examined in the range of 1.0×10^{-2}-1.0×10^{-8} M but calibration curves were not linear and the responses slowly got down while the range got narrower. Thus, it is decided to prepare PVC membrane and coated-graphite silver (I) - selective electrodes based on this novel calix[4]arene to compare with each other.

Since 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 nature of the ionophore but also significantly on the membrane ingredients as plasticizers, lipophilic additives and ratios of these ingredients in the membrane /70- 74/, their influence on the potential response characteristics was investigated.

Effect of membrane composition on the response of the electrodes

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 /75/. Since in preparation of many PVC membrane electrodes a plasticizer/PVC ratio (m/m) of nearly 2 has resulted in very suitable performance characteristics /76/, this ratio was kept at about 2 in optimization of the ingredients of the silver (I) ion-selective electrodes proposed. Thus, in order to improve the characteristics of the electrodes, various optimization studies were made and the influence of nature of plasticizer, KTpClPB as a lipophilic additive and amount of calix[4]arene as neutral carrier on the potential response of the PVC membrane and coated-graphite silver (I) ion-selective electrodes were investigated. The results are summarized in Table 1.

Concerning the effect of the amount of the ionophore, first of all we prepared blank membranes including 285.0 mg *o*-NPOE, 136.1 mg PVC and 1.6 mg KTpClPB without ionophore and then the membranes in the same composition with 4.3 mg ionophore to construct the silver (I) - selective PVC membrane and coated-graphite electrodes. When the related electrodes A1, A4 for silver (I) - selective PVC membrane and B1, B4 for silver (I) - selective coated-graphite electrodes given in Table 1 are compared, adding ionophore provided good response to Ag^+ with the linear range of 1.0×10^{-2}-1.0×10^{-6} M for silver (I) -selective PVC membrane and 1.0×10^{-2}-1.0×10^{-4} M for silver (I) - selective coated-graphite electrodes. The corresponding slopes of the electrodes were 57.7±1.3 and 48.6±1.0, respectively. In order to obtain the right composition of ionophore, we also tried to increase the amount of ionophore from 4.3 to 8.6 mg. According to the electrodes A5 and B5 with *o*-NPOE, one can say that the linear working ranges became narrower and their slopes got down. However, when *o*-NPPE was employed to construct silver (I) - selective coated-graphite electrode including 8.6 mg of ionophore (B6), Nernstian response was obtained. This phenomenon showed that in our study the effect of the ionophore ratio on the potential response of the proposed PVC membrane and coated-graphite silver (I) – selective electrodes was not the same. The reason for this situation was not clearly understood.

It is known that the addition of a lipophilic excluder to the media changes the specific features of the electrodes with neutral carrier membrane /77, 78/. They contain ionic sites with a charge sign opposite to that of the primary ion and thus not only improve the Nernstian response of the sensor but also help in reducing the membrane resistance, improving the selectivity and reducing the interference from sample anions. In our study, the data listed in Table 1(Electrodes A3, B3 and A4, B4) reveal that the sensitivities of the membranes against silver (I) ions prepared by the use of KTpClPB as lipophilic anionic additive improved the sensitivity of the electrodes in accordance with the literature /77/.

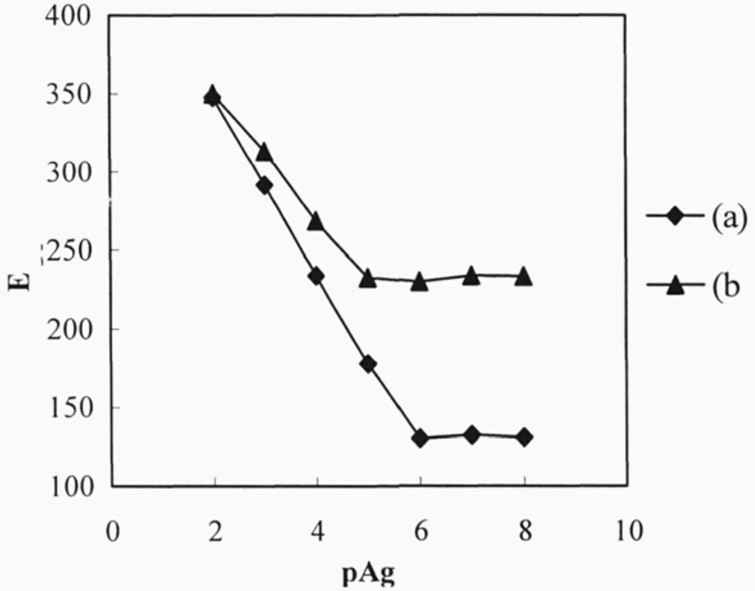

Fig. 4: The effect of the plasticizer on the response of PVC membrane Ag(I) - selective electrodes with membranes (a) 4.3 mg calix[4]arene, 136.1 mg PVC, 1.6 mg KTpClPB 285.0 mg *o*-NPOE, (b) 4.3 mg calix[4]arene, 136.1 mg PVC, 1.6 mg KTpClPB 285.0 mg *o*-NPPE.

Table 1

Optimization of membrane ingredients of some PVC membrane and coated-graphite Ag^+ - selective electrodes based on 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene

				Plasticizer, mg			
Electrode	Ionophore, mg	PVC,mg	KTpClPB, mg	*o*-NPOE	*o*-NPPE	Slope, mV/pAg	Linear Working Range, M
A1	-	136.1	1.6	285.0	-	-	-
A2	4.3	136.1	1.6	-	285.0	43.5±1.1	1.0×10^{-3}-1.0×10^{-5}
A3	4.3	136.1	-	285.0	-	38.2±2.5	1.0×10^{-2}-1.0×10^{-4}
A4	4.3	136.1	1.6	285.0	-	57.7±1.3	1.0×10^{-2}-1.0×10^{-6}
A5	8.6	136.1	3.2	285.0	-	54.5±1.5	1.0×10^{-2}-1.0×10^{-5}
B1	-	136.1	1.6	285.0	-	-	-
B2	4.3	136.1	1.6	-	285.0	48.2±1.7	1.0×10^{-2}-1.0×10^{-5}
B3	4.3	136.1	-	285.0	-	-	-
B4	4.3	136.1	1.6	285.0	-	48.6±1.0	1.0×10^{-2}-1.0×10^{-4}
B5	8.6	136.1	1.6	285.0	-	27.2±1.0	1.0×10^{-2}-1.0×10^{-4}
B6	8.6	136.1	3.2	-	285.0	54.7 ±2.1	1.0×10^{-2}-1.0×10^{-5}

* at 95% confidence level

The nature of plasticizer, the dielectric constant of membrane phase, the mobility of the neutral carrier and the state of ligand largely affect the response characteristics of ion-selective electrodes /77/. As can be seen from Table 1, Fig. 4 and Fig. 5, among the two different plasticizers studied (*o*-NPOE, *o*-NPPE), *o*-NPOE resulted in the best sensitivity for PVC membrane silver (I) - selective electrode and *o*-NPPE for the coated-graphite silver (I) - selective electrode. This divergence of the electrodes was not clearly understood. But it can be explained from the point of view that this variation could be a result of the better attachment of membrane with *o*-NPPE to the graphite surface than membrane with *o*-NPOE.

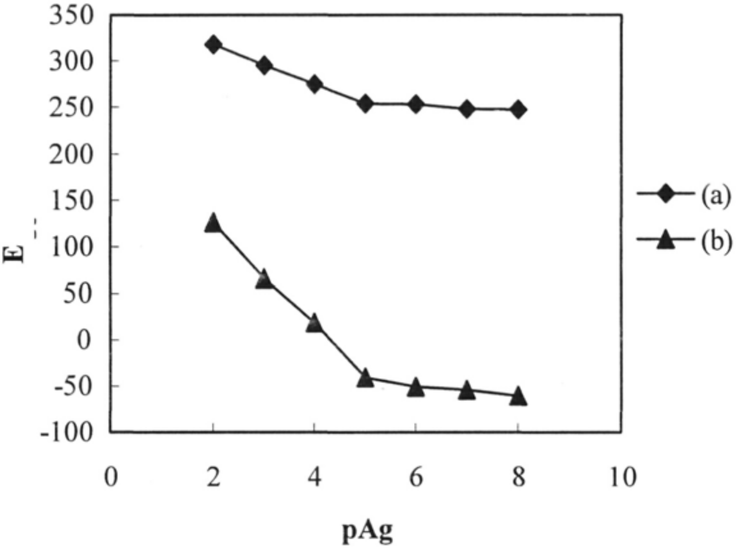

Fig. 5: The effect of the plasticizer on the response of coated-graphite Ag(I) - selective electrodes with membranes (a) 4.3 mg calix[4]arene, 136.1 mg PVC, 1.6 mg KTpClPB 285.0 mg *o*-NPOE, (b) 4.3 mg calix[4]arene, 136.1 mg PVC, 1.6 mg KTpClPB 285.0 mg *o*-NPPE.

Effect of internal filling solution on the potential response of the PVC membrane silver (I) - selective electrode

The effect of internal solution concentration on the potential response of the PVC membrane silver (I) - selective electrode was investigated. For this purpose, silver nitrate solution of 1.0×10^{-3}, 1.0×10^{-5} M and hydrochloric acid solution of 1.0 × 10^{-2} M were used and the calibration curves were drawn. It was found that the concentration of internal solution has an important effect on the slope and the working range of the electrode. The silver nitrate solution of 1.0 × 10^{-5} M was found quite appropriate for a smooth Nernstian function and a wider working range of this electrode.

Effect of pH on the potential response of the electrodes

The influence of pH on the response of Ag (I)-ion selective electrodes with the optimum membrane compositions was studied over the pH range of 1-10 at 1.0 × 10^{-2}, 1.0 × 10^{-3} and 1.0 × 10^{-4} M Ag (I) containing solutions. We found that the response characteristics (response slope and linear working range) of the electrodes could not be changed by changing the pH values of the solution in the range of 2-6 (as illustrated in Fig. 6 and Fig. 7). Outside this range, the responses of the electrodes changed drastically. The obtained changes of potential at lower (< pH 2) and higher (> pH 6) pH values could be due to the protonation of the ionophore and formation of some hydroxy complexes of Ag^+ ion in solution, respectively /20, 23, 54, 59, 73/. In this study, all measurements were made at pH 3.0.

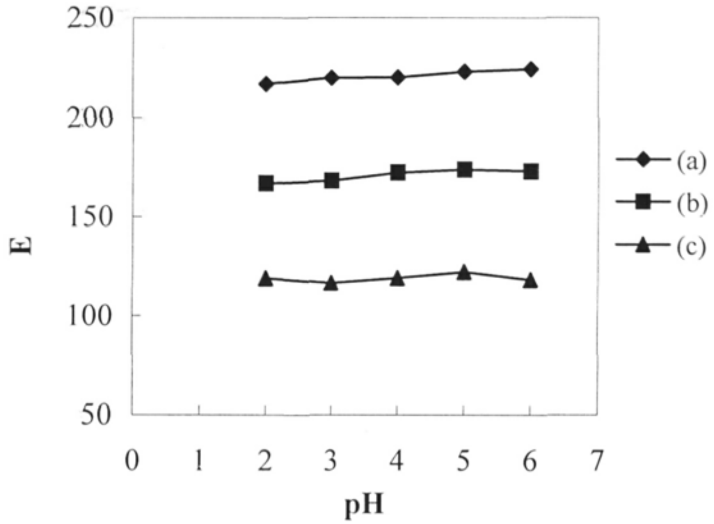

Fig. 6. The effect of pH of test solutions containing (a) 1.0 × 10^{-2} M, (b) 1.0 × 10^{-3} M and (c) 1.0 × 10^{-4} M $AgNO_3$ on the response of the PVC membrane Ag (I) – selective electrode (Electrode A4).

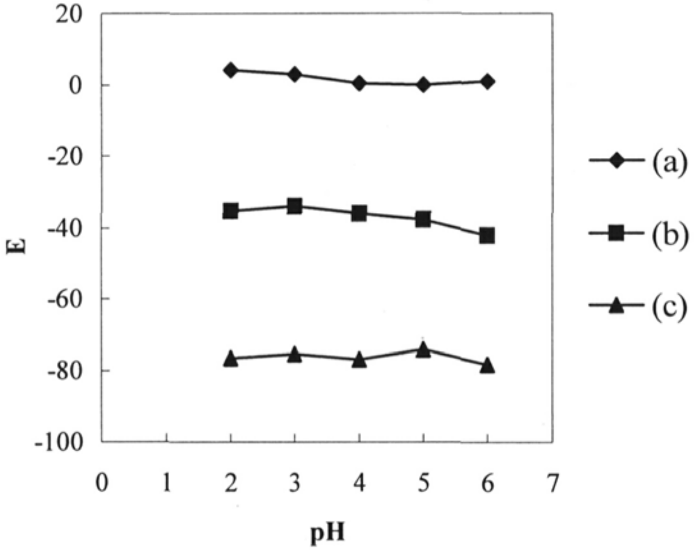

Fig. 7. The effect of pH of test solutions containing (a) 1.0 × 10^{-2} M, (b) 1.0 × 10^{-3} M and (c) 1.0 × 10^{-4} M $AgNO_3$ on the response of the coated-graphite Ag (I)–selective electrode (Electrode B6).

The response times and lifetimes

One of the important factors revealing the performance of the ion-selective electrodes is its response time. Therefore, the response time required for the electrode to reach 95 % of equilibrium mV values after successive immersion in a series of solution each having a 10-fold difference in concentration was measured. The static response time thus obtained was 10 s over the working ranges of the electrodes and no change was observed in 10 minutes. Potentials were monitored periodically at fixed concentration, and standard deviation of 15 identical measurement was ± 3 mV.

The lifetime of the electrodes were studied by periodically recalibrating the Ag (I) response in standard silver nitrate solutions. After the electrodes based on 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassium-ksantato)etoxycalix[4]arene had been repeatedly calibrated ten times during a period of one month, no significant change in the performance of the electrodes was observed. PVC membrane silver (I) – selective electrode can be used for at least two months while the silver (I) – selective coated-graphite electrode could be used no longer than 30 days. In conclusion, the response time and the lifetime of the proposed PVC membrane electrode is compatible with most similar electrodes reported in the literature /8- 11, 14, 18, 20, 22, 23/.

Table 2

Selectivity coefficients ($k^{pot}_{Ag, M}$) of the silver(I) ion-selective electrodes using fixed interference method

Interfering ions	PVC membrane Ag^+-selective electrode Log $k^{pot}_{Ag, M}$	Coated-graphite Ag^+-selective electrode Log $k^{pot}_{Ag, M}$
K^+	-2.2	-2.5
Li^+	-3.2	-2.7
Na^+	-3.0	-2.4
NH_4^+	-2.0	-2.6
Mg^{2+}	-4.3	-4.4
Ca^{2+}	-5.0	-4.7
Zn^{2+}	-2.6	-2.5
Co^{2+}	-2.9	-2.4
Cu^{2+}	-3.0	-3.1
Cd^{2+}	-2.0	-2.2
Ni^{2+}	-2.6	-2.6
Pb^{2+}	-2.2	-2.5
Hg^{2+}	-0.3	-0.2

Selectivity of the silver (I) electrodes

The most important characteristic of a membrane electrode is its response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficient. The selectivity coefficients of the electrodes for Ag (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 silver ion is varied in the concentration range of 1.0×10^{-2} - 1.0×10^{-6} M while that of the interfering ion is 1.0×10^{-3} M. It was observed that the proposed Ag (I)-selective electrodes revealed very good selectivity to silver ion with respect to a variety of other common cations (NH_4^+, Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}).

In most cases, the selectivity coefficients of the proposed electrodes are on the order of 10^{-3}. It seems to indicate that these cations have negligible impact on the functionality of Ag (I) - selective electrodes presented in this paper (Table 2). Although the Hg (II) ions act as the strongest interfere with log $k^{pot}_{Ag, Hg} > -1.0$, in comparison with solid-state membranes and previously reported similar electrodes based on different neutral carriers /6, 7, 10, 15-18, 23, 30, 31, 33-37, 39, 45-47, 49, 51/, the developed electrodes in this work demonstrate the advantage of virtually no interference from some alkali, alkaline earth, transition and heavy metal ions.

Table 3

The response characteristics of the proposed Ag^+-ISEs

	PVC membrane Ag^+-ISE	PVC coated graphite Ag^+-ISE
Slope(mV/pAg)	57.7 ± 1.3	54.7 ± 2.1
Working Range(M)	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$	$1.0 \times 10^{-2} - 1.0 \times 10^{-5}$
Limit of detection	1.0×10^{-6}	1.26×10^{-5}
Response time	5- 10 s	10- 15 s
Lifetime	> 2 months	30 days
pH range	2-6	2-6

On the bases of the results discussed in this article and as it can be seen from Table 1, the electrodes A4 and B6 related to PVC membrane and coated-graphite electrodes, respectively have shown the best response characteristics among others. The comparison of the characteristics of the proposed electrodes is given in Table 3.

Analytical application

Obviously, the response characteristics of the proposed Ag(I) – selective PVC membrane electrode, including working range, detection limit, response slope, lifetime and selectivity are better than the Ag(I) – selective coated-graphite electrode. Nevertheless, both of the proposed silver (I) – selective electrodes were applied as an indicator electrode in potentiometric titrations of 50.0 mL 2.0×10^{-3} M of chloride, bromide and iodide ions with 1.0×10^{-1} M $AgNO_3$ solution at pH 3.0. The optimized PVC membrane and coated-graphite electrodes (Electrode A4, B6 in Table 1) were found to work well under laboratory conditions. The resulting titration curves for PVC membrane Ag(I)- selective electrode are shown in Fig. 8a, 8b and 8c. As can be seen, very good inflection points are observed in the titration curves for each halogen ion. Therefore, the end-point and the amount of three halogen ions can be accurately potentiometrically determined by using these electrodes.

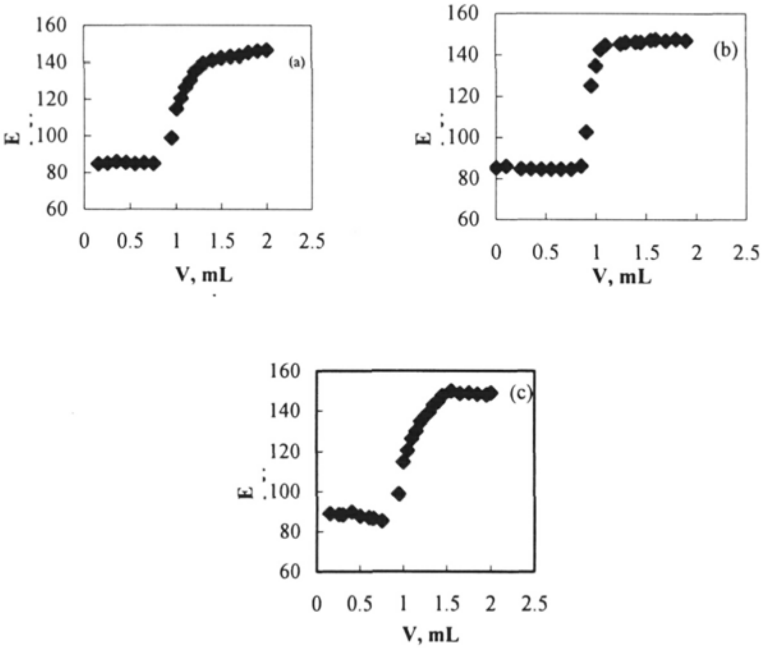

Fig. 8: Titration curves of the 50.0 mL of a) chloride, b) bromide and c) iodide ions (concentration of each ion was equal and 2.0×10^{-3} M) with 1.0×10^{-1} M silver nitrate obtained by using the PVC membrane Ag (I)-selective electrode at pH 3.0 (Electrode A4).

CONCLUSION

This work demonstrates that 5,11,17,23-tetra-*tert*-butyl-25,27-metoxy-26,28-bis(potassiumksantato)etoxycalix[4]arene may be considered as a neutral carrier for the construction of PVC membrane and coated-graphite silver (I) - selective electrodes. The proposed electrodes have been shown to have good operating characteristics such as sensitivity, detection limit, wide working range, response time, lifetime, stability, and reproducibility. It can be concluded that these electrodes could be an alternative for the conventional silver - selective electrodes based on Ag_2S and they are comparable in many respects with those reported in literature especially as indicator electrodes.

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