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Calix[4]arene Derivatives: Efficient Ionophores for Silver(I) Ion Sensors

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Calix[4]arene derivatives with four imine units at the upper rim and different spacers between two calixarenes were employed as highly promising lipophilic neutral carriers to prepare a series of silver-selective electrodes. These calix[4]-arenes possess a flexible conformation for rapid ion-exchange across the PVC membrane to provide good response for silver ions. The prepared silver ion-selective electrodes exhibited near-Nernstian responses for silver ions over a wide concentration range of 1.0×10^{-1}–1.0×10^{-5} M with a very low detection limit of $\sim 10^{-6}$ M. The potentiometric responses were independent of the pH of the test solution over wide acidic pH range. The effect of various plasticizers on the electrode characteristics was also examined, and bis(2-ethylhexyl) sebacate proved to be the most suitable, since it provided the best slope and other electrode characteristics. High selectivity for Ag^+ over Hg^{2+}, Na^+, and many other cations was found. The high selectivity for silver ions is mainly attributed to host–guest interactions that occur between the silver and appended groups of calix[4]arene derivatives. The electrodes were used as indicator electrodes in potentiometric titration involving silver ion, and provided a simple method for the determination of Ag^+ and Cl^- in water samples.

Today among the various techniques available for the determination of metal ions in clinical, industrial, agricultural, environmental, and laboratory analysis, neutral carrier-based potentiometric sensors represents an appropriate approach to chemical sensing, since their response rely on ion-extraction and complexation equilibria in the organic membrane phase. Ion-selective electrodes, which have become routine measuring tools, provide many advantages, such as accuracy, reproducibility, speed, and selective determination of analyte species of interest. They are relatively inexpensive and simple to use in the field as well as in the laboratory.

The versatile chemical selectivity of chemical sensors is made possible with lipophilic ionophores that exhibit widely different binding selectivities.[1,2] In last three decades, various macrocyclic compounds, like crown ethers, thioethers, cryptands, and podands, have been employed as sensing agents in chemical sensors for the determination of different metal ions due to their ability to form complexes with metal ions of compatible dimensions.[3–7] Recently, calixarene derivatives[8,9] have been shown to be valuable additions to the above chemical species for ionophores. Calixarenes are well known for their selective receptor properties and ease of structural modification, which makes them attractive electroactive materials for use in chemical sensors. A number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been incorporated as neutral carriers into ion-selective electrodes to determine sodium,[10,11] potassium,[12,13] and cesium.[14–16] It has been reported by Teixidor et al.[17] that any molecule with thioether group(s) is highly selective towards silver(I). O'Connor et al.[18] quantified the performance of calix-[4]arene derivatives having sulfur and nitrogen groups in ISEs sensitive to silver(I), and reported good sensitivity with some response to alkali metal ions. The best reported calix[4]arene for Ag^+ was thioalkyl ester derivative with an average selectivity against sodium ($\log K^{\mathrm{pot}}_{\mathrm{Ag,Na}} = -1.6$) with serious interference of Hg^{2+}; nothing was reported regarding the lifetime of the membranes. The present paper may provide an exception to the ideas of Teixidor and O'Connor.

Silver is of great commercial importance due to its widespread use in photography, dentistry, the electronic industry, and the field of medicine. Furthermore, it is well-known that silver inactivates sulfhydryl enzymes, and also combines with amine, imidazole, and carboxyl groups of various metabolites, such as high-molecular-weight proteins and metallothionein in tissue cytosol fractions.[19] Repeated exposure of animals to silver may produce anemia, cardiac enlargement, growth retardation, and degenerative changes in the liver. Therefore, the need for a highly sensitive and selective determination of silver ion arises from its economic value and its long-term toxicity for humans and the environment. Recently, we reported on carrier-based ion-selective electrodes for the determination of various metal ions, such as mercury(II), cesium(I), and silver(I) ions.[16,20,21a] In continuation to our efforts to prepare sensors for silver, we report here on a new series of calix[4]arene derivatives **I(a–e)** and **(II)** with four imine units at the upper rim and different spacers between two calixarenes as neutral carriers to prepare silver-selective sensors.

Experimental

Ionophore. Calix[4]arene derivatives were prepared as reported elsewhere.[21] The structures of various calix[4]arene derivatives used as neutral carriers in the preparation of silver ion sensors are shown in Fig. 1.

Other Chemicals. Poly(vinyl chloride) (PVC) and bis(2-ethylhexyl) sebacate or dioctyl sebacate (DOS) were purchased from Fluka Chemicals (Switzerland). Dioctyl adipate (DOA), dioctyl phthalate (DOP), dibutyl phthalate (DBP), and 1-decanol (D-ol) were obtained from S.D. Fine Chemicals (India). Analytical-grade

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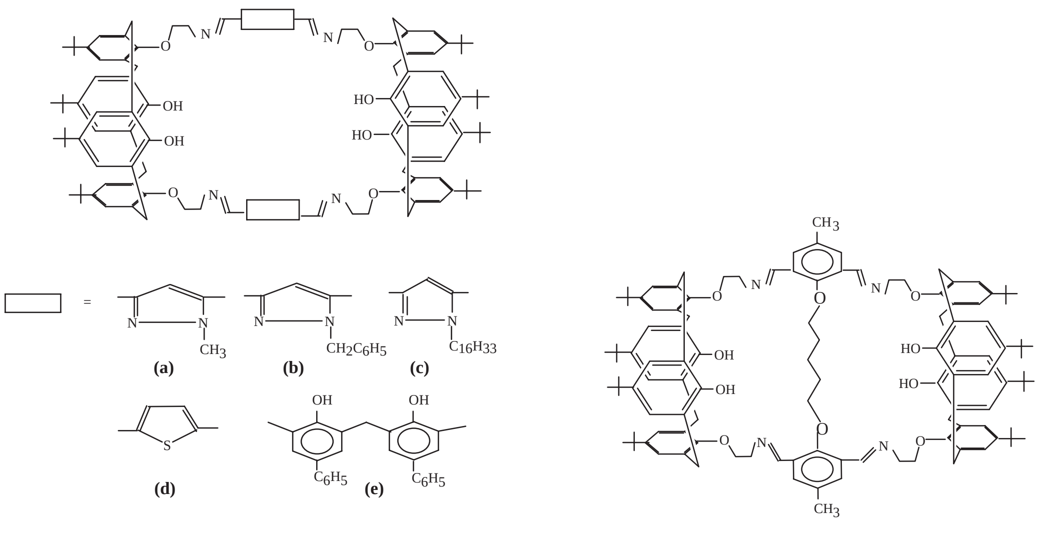

(I) **(II)**

Fig. 1. Structures of calix[4]arene derivatives.

Table 1. Composition and Electrode Characteristics of Ag^+-ISEs Based on Calix[4]arene Derivatives

Ag^+-ISEs	Composition (w/w%)			Linear range /M	Slope (mV/dec)	Detection limit/M	Response time/s (approx.)	pH Range
	PVC	DOS[a)]	Calix[4]arene					
EI(a)	33.6	64.8	1.6	1.0×10^{-1}–1.0×10^{-5}	56.17	9.33×10^{-6}	30	1.1–5.9
EI(b)	32.8	65.6	1.6	1.0×10^{-1}–5.0×10^{-6}	59.27	4.07×10^{-6}	30	1.3–6.5
EI(c)	34.5	63.8	1.7	1.0×10^{-1}–5.0×10^{-5}	56.02	28.20×10^{-6}	30	1.1–6.4
EI(d)	33.7	64.8	1.5	1.0×10^{-1}–1.0×10^{-5}	60.07	8.71×10^{-6}	30	1.1–6.2
EI(e)	32.2	66.3	1.5	1.0×10^{-1}–5.0×10^{-5}	58.75	17.40×10^{-6}	20	1.2–6.8
EII	32.5	65.5	1.7	1.0×10^{-1}–1.0×10^{-5}	57.90	9.30×10^{-6}	20	1.2–6.9

a) DOS: Dioctyl sebacate.

reagents, like tetrahydrofuran (THF) and nitrates of all cations, were used as received. All solutions were prepared using doubly distilled deionised water (DDW).

Electrode Preparation. The general procedure adopted to prepare PVC membranes was as follows. Appropriate amounts of calix[4]arene derivative, plasticizer, and PVC were mixed and dissolved in a minimum amount of tetrahydrofuran (THF). The resulting mixture was stirred vigorously, and after removing air bubbles, transferred into a 50 mm petridish. The solvent was allowed to evaporate off at room temperature overnight. A flexible, transparent membrane of thickness 0.4 mm was obtained. A membrane of suitable size was cut and fixed to a PVC tube with the help of PVC glue and conditioned in 1.0×10^{-2} M $AgNO_3$ for 2–4 days. The ratio of the membrane ingredients i.e. the calix[4]arene derivative, plasticizer, and PVC along with the conditioning or equilibration medium, were optimized first so that the membrane developed a reproducible potential that remained stable for a long time. Table 1 gives the composition of silver-selective membranes that gave the best performance. A silver/silver chloride-coated wire was used as an internal reference electrode.

EMF Measurements. All of the measurements of the electrode potentials were made with an Equip-tronics model EQ-602 potentiometer, and all of the pH measurements were made with an Elico LI-model-120 pH meter. The cell assembly used was shown in Chart 1.

Ag-AgCl	Internal reference solution ($1.0\text{x}10^{-2}$ M $AgNO_3$)	PVC membrane	Test solution	Ag-AgCl

Chart 1.

Results and Discussion

In preliminary experiments, calix[4]arene derivative **I(a)** was used as a potential neutral carrier for the preparation of PVC membrane ion-selective electrodes for different metal ions, including some alkali metal ions (Na^+ and K^+) and heavy metal ions (Hg^{2+}, Cu^{2+}, Pb^{2+}, and Ag^+). The potentiometric response curves so obtained for these ISEs based on calix[4]arene derivative **I(a)** are shown in Fig. 2. It is clear from the figure that among the metal ions examined, the calix[4]arene derivative **I(a)** provided the most sensitive and selective sensor for silver. The Ag^+-ISE based on calix[4]arene derivative **I(a)** exhibited a near-Nernstian slope of 56.17 mV/dec over a wide linear concentration range of 1.0×10^{-1}–1.0×10^{-5} M. Other metal ion-selective electrodes were found to display non-Nernstian slopes with a very narrow linear range of the concentration. From the results obtained in preliminary experiments, it was clear that the calix[4]arene derivative **I(a)** can

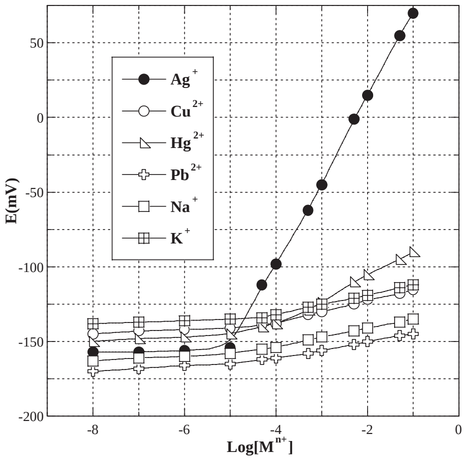

Fig. 2. Potentiometric response of ion-selective electrodes based on calix[4]arene derivative **I(a)** for various metal ions.

act as an efficient ionophore for preparing silver-selective PVC membrane electrodes. Based on preliminary investigations, it was decided to prepare and study the functional properties of a series of silver selective sensors based on calix[4]arene derivatives, **I(a–e)** and **(II)**.

Composition of Silver-Selective Membranes. It is well known that the performance characteristics of membrane sensors, such as the sensitivity, working range, selectivity, and potential stability, depends not only on the nature of the ionophore used, but also significantly on the composition of the membrane. A large number of membranes containing varying amounts of calix[4]arene and an appropriate proportion of poly(vinyl chloride) (PVC) and plasticizer, dioctyl sebacate (DOS), were prepared and subjected to preliminary investigations. Only those membranes that produced reproducible Nernstian or near-Nernstian potential response over a wide concentration range with a short response time ($t_{95\%}$), were selected for further studies; the compositions of such membranes along with the electrode characteristics are summarized in Table 1.

Potentiometric Response of Silver-Ion Sensors. The prepared membrane electrodes based on calix[4]arene derivatives were equilibrated in 1.0×10^{-2} M $AgNO_3$ solutions for 2–4 days until they generated stable and reproducible potentials. After an equilibration period, the PVC-based membrane electrodes incorporating dioctyl sebacate (DOS) as a plasticizer and calix[4]arene derivatives as ionophores generated a stable potential when placed in contact with a silver nitrate solution. The EMF response curves of all the Ag^+-ISEs in the presence of a wide range of silver ion solutions are shown in Fig. 3. The electrode characteristics, such as slopes, linear concentration range, detection limit, and response time of all silver selective electrodes as evaluated from these plots, are given in Table 1. All silver sensors exhibited good near-Nernstian or Nernstian slopes (in the range from 56.02 to 60.07 mV/dec) over wide linear concentration ranges of $\sim 1.0 \times 10^{-1}$–5.0×10^{-6} M $AgNO_3$. The selective response towards silver ion is attributed to the size of the ionophore cavity fit to Ag^+ and cation-π interaction as suggested by Shinkai.[22–24] The detection limits of sensors, as determined from the intersection of two extrapolated segments of the calibration curve, are also tabulated in Table 1, and were found to be quite low.

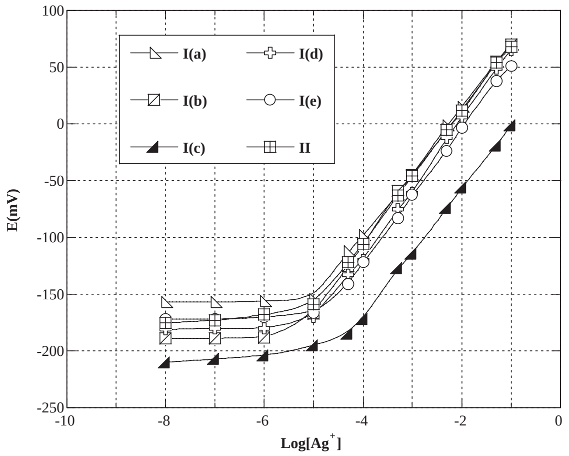

Fig. 3. Potentiometric response curves of various Ag^+-ISEs.

Response Time and Lifetime of Silver Sensors. The average time required for the Ag^+ sensor to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Ag^+ solutions, each having a 10-fold difference in concentration, was measured. The static response times, thus obtained for various silver ion-sensors based on calix[4]arenes derivatives, are also tabulated in Table 1. As can be seen from Table 1, the sensors yielded steady state potentials within 20–30 s, and the electrode potential remained constant for more than 5 min, after which a very slow divergence was observed. It can be seen that the response time ($t_{95\%}$) for all of the sensors was reasonably short, and the stability of the potentiometric signal was quite satisfactory. The sensing behavior of the membrane sensors remained unchanged when the potential was recorded either from low to high concentration, or vice versa.

The lifetime of the **EI(a)** was studied by re-calibrating it after regular intervals of time using a series of standard solutions of $AgNO_3$ and calculating the slope over a linear concentration range. The results obtained from E (mV) vs log[Ag^+] plots are summarized in Table 2. It can be seen from this table that the slopes of the electrode were found to be near-Nernstian over a period of 5 months, during which the detection limit and linear concentration range changed by a small factor. Hence, it can be said that the sensor was stable and could be used over a period of 5 months without observing any significant change in the potentiometric response characteristics. Similarly, other Ag^+-selective membrane electrodes could be used over a period of 5 to 6 months without any significant change in the value of slope, working concentration range, and response time. The standard deviation for the slope was found to be ±1 mV/dec, which shows good reproducibility.

Effect of pH. The pH dependence of silver-selective membrane electrodes based on calix[4]arene derivatives was examined over a pH range of 1–12 at different concentrations of silver. Figure 4 demonstrates the variation of the electrode potentials of Ag^+-ISEs, with pH at a silver(I) ion concentration of 1.0×10^{-2} M. From the plots shown in Fig. 4, it is evident that for every sensor the electrode potential remained constant over a wide acidic pH range, which was taken as the functional pH

Table 2. Lifetime Behavior of Ag^+-ISE, **EI(a)**, Based on Calix[4]arene Derivative **I(a)**

Time	Linear range /M	Slope (mV/dec)	Detection limit /M
1 day	1.0×10^{-1}–1.0×10^{-5}	56.17	9.33×10^{-6}
7 days	1.0×10^{-1}–1.0×10^{-5}	56.17	9.33×10^{-6}
2 weeks	1.0×10^{-1}–1.0×10^{-5}	56.17	9.33×10^{-6}
1 month	1.0×10^{-1}–1.0×10^{-5}	56.17	9.33×10^{-6}
2 months	1.0×10^{-1}–1.0×10^{-5}	56.14	9.33×10^{-6}
3 months	1.0×10^{-1}–1.0×10^{-5}	55.75	10.71×10^{-6}
5 months	1.0×10^{-1}–5.0×10^{-5}	55.06	14.53×10^{-6}
6 months	1.0×10^{-1}–5.0×10^{-5}	50.32	47.92×10^{-6}
7 months	1.0×10^{-1}–1.0×10^{-4}	42.95	64.51×10^{-6}

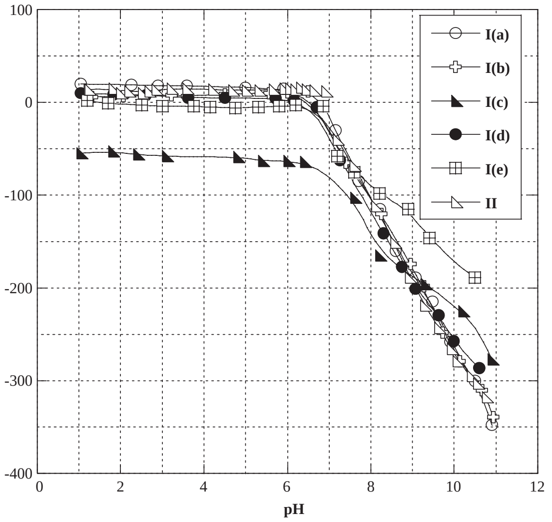

Fig. 4. Effect of pH of test solutions on the potentiometric response of silver sensors at silver ion concentration of 1.0×10^{-2} M.

range of the sensor. The functional pH ranges (1–6.9) of all the sensors are summarized in Table 1. The sharp decrease in the electrode potential above pH 7.0 can be related to the formation of AgOH. Beyond the functional pH range, a high variation of the potentiometric response corresponds to the pH limit, and points towards the applicability of the developed sensors in moderately acidic media. Pure solutions of silver nitrate do not need any pH adjustment, since their pH lies in the functional pH ranges of the sensors, and all of the measurements were carried out in a moderately acidic pH range.

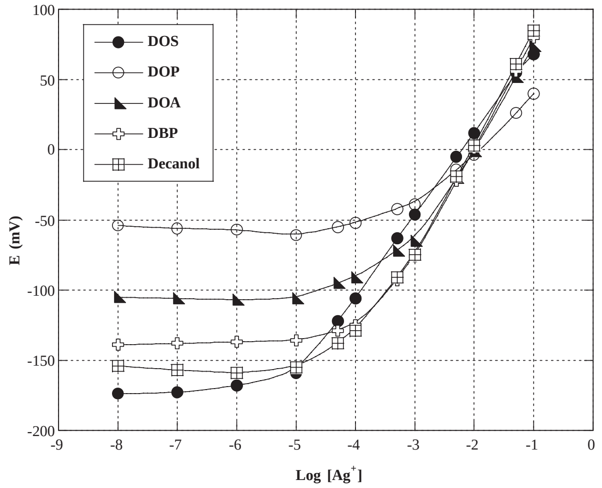

Fig. 5. Effect of plasticizer on the potentiometric response of silver ion sensors based on calix[4]arene derivative (**II**).

Effect of Plasticizers. The plasticizer, an important component of an ion-selective membrane, influences the dielectric constant of the membrane phase, the mobility and state of the ionophore molecules in the PVC matrix. It is expected to play an important role in determining various characteristics, such as the sensitivity and selectivity of an ion-selective membrane electrode. In the present study, the effect of five plasticizers of different polarities, such as dioctyl sebacate (DOS), dioctyl adipate (DOA), dioctyl phthalate (DOP), dibutyl phthalate (DBP), and 1-decanol (D-ol), was investigated on silver ion-selective electrodes based on the calix[4]arene derivative (**II**). The potentiometric response curves of silver sensors employing different plasticizers are shown in Fig. 5. As expected, it was found that the response characteristics of membrane electrodes, such as the slope, linear concentration range, and detection limits of the PVC membrane, were greatly influenced by the type of plasticizer employed. It is clear that DOS proved to be the most suitable plasticizer because it provided the best sensitivity among six plasticizers used with a slope of 57.90 mV/dec and a lower detection limit of 9.30×10^{-6} M. With other plasticizers, the electrode characteristics were found to be inferior to that containing DOS.

Potentiometric Selectivity of Calix[4]arenes. Selectivity is an important characteristic of a sensor, which measures its suitability for primary ion determination in the presence of various secondary ions. This is expressed in terms of the potentiometric selectivity coefficients ($K^{\mathrm{Pot}}_{\mathrm{Ag,B}}$), which have been evaluated using the fixed interference method (FIM) at a constant concentration of interfering ions in the background. In this method, the concentration of silver ions is varied while that of the interfering ions is kept constant, i.e. 1.0×10^{-2} M. Table 3 shows the values of $\log K^{\mathrm{pot}}_{\mathrm{Ag,B}}$, as computed from potential data of Ag^+-ISEs for the interfering cations relative to Ag^+. It is obvious from the data that all of the Ag^+-ISEs show high selectivity towards Ag^+ ions with respect to many of the common ions. The proposed sensors show better selectivity towards silver ions against most of the alkali and alkaline metal ions, since the $\log K^{\mathrm{pot}}_{\mathrm{Ag,B}}$ values are lying in the range of −2.53 to −4.55. Similarly, for heavy metal ions like Pb^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+}, etc. the values are very low (−3.05 >

Table 3. Selectivity Data ($\log K^{\mathrm{pot}}_{\mathrm{Ag,B}}$) of Ag^+-ISEs Based on the Calix[4]arene Derivatives

Ag^+-ISEs	K^+	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Pb^{2+}	Hg^{2+}	Cd^{2+}	Zn^{2+}
EI(a)	−3.45	−3.60	−2.20	−3.65	−3.30	−3.70	−3.57	−3.05	−3.45	−4.57	−2.45	−3.75	−3.82
EI(b)	−3.75	−3.25	−2.55	−3.62	−3.90	−4.27	−3.60	−3.95	−3.67	−4.30	−2.00	−4.10	−3.98
EI(c)	−2.53	−2.70	−2.88	−3.73	−3.55	−3.85	−3.75	−3.30	−4.05	−3.60	−1.55	−3.75	−3.60
EI(d)	−3.20	−3.10	−2.62	−3.87	−3.55	−3.62	−3.62	−4.05	−3.77	−3.40	−2.55	−3.77	−3.99
EI(e)	−3.55	−3.45	−2.87	−3.70	−4.55	−4.25	−4.45	−4.67	−4.20	−4.80	−2.25	−4.72	−4.50
EII	−3.00	−3.01	−2.94	−3.95	−3.94	−4.00	−4.11	−4.01	−3.76	−4.27	−2.40	−3.63	−3.77

Table 4(a). Determination of Silver(I) Ion Concentration in Synthetic Water Samples Using Silver-Selective Electrodes Based on Calix[4]arenes **I(a)** and **II**

Known concentration of Ag^+ in the sample /mM	Ag^+-ISE **I(a)**		Ag^+-ISE **II**	
	Amount of Ag^+ recovered from the sample/mM	% Recovery	Amount of Ag^+ recovered from the sample/mM	% Recovery
70	69.0	98.6	69.2	98.9
50	49.1	98.2	48.4	96.8
30	28.5	95	28.9	96.3
10	8.9	89	9.7	97.0

Table 4(b). Determination of Chloride Anion Concentration in Synthetic Samples Using Silver Sensor **EI(a)**

Amount of Cl^- added /mM	Amount of Cl^- recovered /mM	% Recovery
80	79.1	98.9
50	48.2	96.4
25	24.2	96.8
5	4.7	94.0

$\log K^{\mathrm{pot}}_{\mathrm{Ag,B}} > -4.80$). This silver-ion selectivity may be due to electrostatic interactions between the metal ion and four highly preorganized soft binding sites (imine units) surrounded by ethereal oxygen atoms, which provide a better fit of silver ions.

Many research groups have reported mercury(II) as being a major interfering ion in the determination of silver using carrier-based silver-selective electrodes. It can be seen from the selectivity data reported in the present paper that the $\log K^{\mathrm{pot}}_{\mathrm{Ag,Hg}}$ values are very low compared to those reported in many reports in the literature. It can be concluded that in these sensors, the interference from Hg^{2+} was found to be less prominent, since the $\log K^{\mathrm{pot}}_{\mathrm{Ag,Hg}}$ values range from −2.0 to −3.30. These results show that the present silver selective electrodes are better in this respect than the commercially available Ag_2S-based electrode.

Finally, a comparison with already reported PVC based Ag^+ ion sensors incorporating calix[4]arenes and other ionophores, has been made.[25–39] It was found that the present sensors showed comparable, or even better, selectivity vis-à-vis similar to PVC based ion-selective electrodes reported in the literature.

Application. The sensors were also used to determine the end-point in the potentiometric titration of Ag^+ with a standard solution of sodium chloride, and to determine the chloride anion concentration in tap water. The proposed sensors were examined to determine silver potentiometrically in synthetic water samples containing a known concentration of silver ions. The results obtained using sensors **I(a)** and **II** are summarized in Table 4a. Further, in order to access the application of the sensors in chloride anion determination, experiments were conducted to measure the Cl^- anion concentration of the water samples containing a known concentration of Cl^- anion (Table 4b). Although the amount of Cl^- anion recovered was somewhat less than the added amount, the sensor electrode **EI(a)** was confirmed to detect the Cl^- anion very efficiently with 99% recovery.

Conclusion

Based on the discussed results, it can be concluded that these calix[4]arene derivatives with imine units at the upper rim and different spacers can act as efficient ionophores for silver ion. The proposed sensors exhibited good operating characteristics, such as sensitivity, reproducibility, detection limits, better lifetimes, and excellent selectivity, against a wide range of common ions. In particular, heavy metals, such as Cu^{2+}, Pb^{2+}, and Cd^{2+}, which can destroy a Ag_2S electrode, were not at all interfering in the present sensors. The electrodes can be successfully used as indicator electrodes in potentiometric titrations of silver ion.

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