

## A New Cone Shaped Asymmetrically Substituted Calix[4]arene as an Excellent Ionophore in Construction of Ag(I) ion-Selective Membrane Electrode

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A PVC membrane electrode for silver ion based on a new cone shaped calix[4]arene (CASCA) as membrane carrier was prepared. The electrode exhibits a Nernstian response for Ag<sup>+</sup> over a wide concentration range ( $1.0 \times 10^{-1}$ – $8.0 \times 10^{-6}$  M) with a slope of  $58.2 \pm 0.5$  mV per decade. The limit of detection of the sensor is  $5.0 \times 10^{-6}$  M. The sensor has a very fast response time (~5 s) in the concentration range of  $\leq 1.0 \times 10^{-3}$  M, and a useful working pH range of 4.0–9.5. The proposed sensor displays excellent discriminating ability toward Ag<sup>+</sup> ion with respect to common alkali, alkaline earth, transition and heavy metal ions. It was used as an indicator electrode in potentiometric titration of Ag<sup>+</sup> with EDTA and in direct determination of silver ion in wastewater of silver electroplating.

**Key Words :** Substituted calix[4]arene, Ag(I), Ion-selective membrane electrode

### Introduction

The most attractive potentiometric sensor is a neutral carrier based one, that realizes excellent ion selectivities. In these sensors, neutral carriers are dissolved and dispersed in ion-sensing membranes that are generally liquid or plasticized polymeric membranes. Synthetic ionophores, such as crown ether derivatives, polyether amides, and calix[4]-arenes are examples of ion-carriers that have been designed and used as neutral carriers. When some of its oxygen atoms are replaced with sulfur atoms, the synthesized ionophores, exhibit high affinity toward soft metal ions such as Ag<sup>+</sup>.<sup>1–3</sup> Thus, several macrocyclic and non-macrocylic ligands containing sulfur atoms, have been designed and used in construction of Ag<sup>+</sup> ion-selective electrodes.<sup>4,5</sup>

The interaction between sulfur atoms and Ag<sup>+</sup> ion is much stronger than that of ion-dipoles present between a metal ion and oxygen atoms. This often brings about slow metal-ion exchange equilibria in the membrane interface that is the cause of some of the disadvantage of the thia compound based ion sensors (such as slow response time and relatively poor sensitivity).

Ag<sup>+</sup> as a soft acid can interact with  $\pi$  coordinate group. This interaction is quite selective and relatively weak.<sup>6–8</sup> In this work we used a new calix[4]arene (Fig. 1) containing  $\pi$ -coordinate group in construction of a PVC membrane Ag<sup>+</sup> ion-selective electrode for sensitive and selective determination of silver ions in different samples.

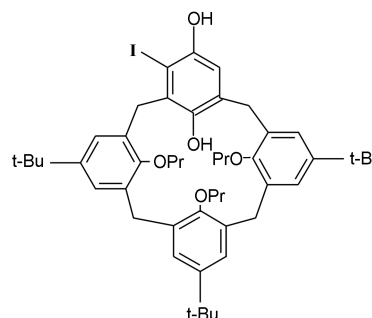


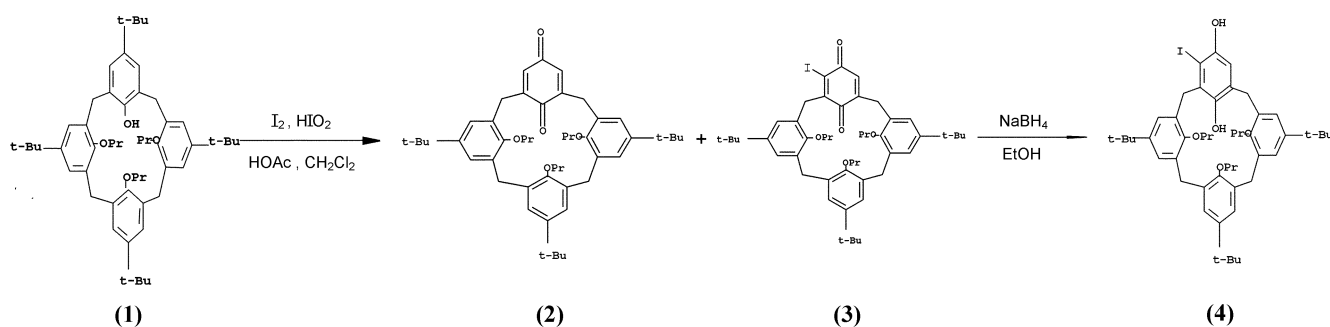
Figure 1. The structure of CASCA.

### Experimental Section

**Reagents.** Reagent-grade dibutyl phthalate (DBP), benzyl acetate (BA), ortho-nitrophenyl octyl ether (NPOE), sodium tetraphenylborate (NaTPB), potassium tetrakis(4-chlorophenyl)-borate) (KTK), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Aldrich chemical company and used as received. Nitrate salts of all cations used (all from Merck) were of highest purity available and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Doubly distilled de-ionized water used throughout.

**Synthesis of calix[4]arenes.** The synthesis of the cone shaped asymmetrically substituted calix[4]arene, 5,11,17,tri-tert-butyl-24-iodo-23,25-dihydroxy-26,27,28-tris(propoxy)-calix[4]arene (CASCA) was done by oxido-iodination of rigidly cone conformation of calix[4]arene triether (1).<sup>9</sup> Oxidation of (1) by HIO<sub>3</sub>/I<sub>2</sub> affords a mixture of quinone (2) and its iodo substituted (3) in 3 : 1 ratio. Reduction of (3)

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produces (CASAC) in quantitative yield. H-NMR spectroscopy of (CASCA) shows the bridge methylene protons (Ar-CH<sub>2</sub>-Ar) as four doublets of doublet, also C-NMR exhibits a set of 24 peaks for aromatic region, indicating the asymmetric structure of the CASCA.

5,11,17, Tri-tert-butyl-24-iodo-23,25-dihydroxy-26,27,28-tris(propoxy)-calix[4]arene (**4**): mp 165 °C;  $\delta$ H (400 MHz; CDCl<sub>3</sub>) 0.81 [9H, s, C(CH<sub>3</sub>)<sub>3</sub>], 0.86 [9H, s, C(CH<sub>3</sub>)<sub>3</sub>], 0.94 [3H, t, CH<sub>3</sub>], 1.09 [3H, t, CH<sub>3</sub>], 1.26 [3H, t, CH<sub>3</sub>], 1.35 [9H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.82-1.94 [4H, m, CH<sub>2</sub>], 2.36 [2H, m, CH<sub>2</sub>], 3.18 and 4.29 [2H, d of d,  $J = 13.3$  Hz, ArCH<sub>2</sub>Ar], 3.21 and 4.35 [2H, d of d,  $J = 12.3$  Hz, ArCH<sub>2</sub>Ar], 3.21 and 4.38 [2H, d of d,  $J = 12.5$  Hz, ArCH<sub>2</sub>Ar], 3.81 and 4.53 [2H, d of d,  $J = 13.8$  Hz, ArCH<sub>2</sub>Ar], 3.67-3.76 [4H, m, OCH<sub>2</sub>], 3.84 [2H, m, OCH<sub>2</sub>], 5.05 [1H, s, OH], 5.09 [1H, s, OH], 6.51 [1H, d,  $J = 2.8$  Hz, ArH], 6.52 [1H, d,  $J = 2.8$  Hz, ArH], 6.58 [1H, d,  $J = 2.3$  Hz, ArH], 6.65 [1H, d,  $J = 2.3$  Hz, ArH], 6.84 [1H, s, ArH], 7.15 [2H, s, ArH];  $\delta$ C (100 MHz) 9.49, 10.66, 10.74, 22.34, 23.30, 23.36, 39.63, 31.02, 31.06, 31.08, 31.28, 31.63, 34.09, 34.50, 69.47, 76.31, 77.62, 77.91, 113.62, 123.31, 124.39, 125.07, 125.21, 125.60, 125.67, 130.37, 130.94, 132.07, 132.15, 132.43, 134.41, 135.84, 136.16, 145.11, 145.53, 145.61, 145.73, 146.77, 147.83, 151.51, 152.07, 153.78; M/Z (FD) 861 (M<sup>+</sup>, 100%), 819 (M<sup>+</sup>-Pr, 3.2%), 735 (M<sup>+</sup>-I, 5.3%). Anal. Calcd. for C<sub>49</sub>H<sub>65</sub>O<sub>5</sub>I: C, 68.36%; H, 7.61; found C, 68.3%; H, 7.8%.

**Electrode preparation.** The general procedure to prepare the PVC membrane was to mix thoroughly 33 mg of powdered PVC, 60 mg of plasticizer DBP and 2 mg of NaTPB in 3 mL of THF. To this mixture was added 5 mg of ionophore (CASCA) and the solution was mixed well. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A glass tube (5 mm on top) was dipped into the mixture for about 30 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. The tube was then filled with internal filling solution (1.0 × 10<sup>-3</sup> M AgNO<sub>3</sub>). The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10<sup>-2</sup> M solution of silver nitrate. A silver-silver chloride coated wire was used as an internal reference electrode. The ratio of various ingredients, concentrations of equilibrating solution, and time of contact were optimized to provide membranes that result in reproducible, noiseless and stable potentials.

**EMF measurements.** All emf measurements were carried

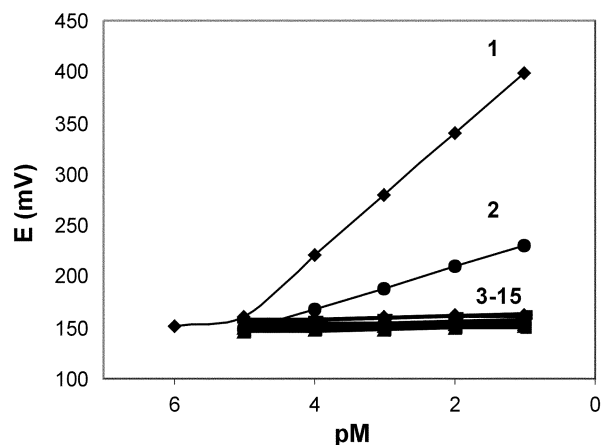
out with the following assembly: Ag-AgCl/KCl (3M)/internal solution (1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> AgNO<sub>3</sub>)/PVC membrane/test solution/HgHg<sub>2</sub>Cl<sub>2</sub>, KCl (satd).

A Corning ion analyzer 250 pH/mV meter was used for potential measurements at 25.0 ± 0.1 °C. Activities were calculated according to the Debye-Hückel procedure.<sup>10</sup>

## Results and Discussion

In primary experiments CASCA used as a neutral carrier to prepared PVC membrane ion-selective electrode for wide variety of metal ions. The potential responses of various ion-selective electrodes based on the CASCA used are shown in Figure 2. As seen, with the exception of Ag<sup>+</sup>, in all other cases, the slope of the corresponding potential-pM plots is much lower than the expected Nernstian slopes of 59 and 29.5 mV per decade for univalent and bivalent cations, respectively. The results thus obtained indicate that Ag<sup>+</sup> ions are more easily attracted to the PVC-CASCA membrane, resulting in a Nernstian potential-pM response in a wide range.

Since the sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane ingredients and the nature of solvent and additives used,<sup>11-15</sup> we investigated the influence of membrane composition on the potential response of the Ag<sup>+</sup> sensor. The effect of plasticizers (DBP, BA and NPOE), additives (NaTPB and KTK)



**Figure 2.** Potential responses of various ion-selective electrodes based on the ligand CASCA. 1: refers to Ag<sup>+</sup>, 2: refers to Hg<sup>2+</sup>, 3-15: refer to Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>.

**Table 1.** Optimization of membrane ingredient

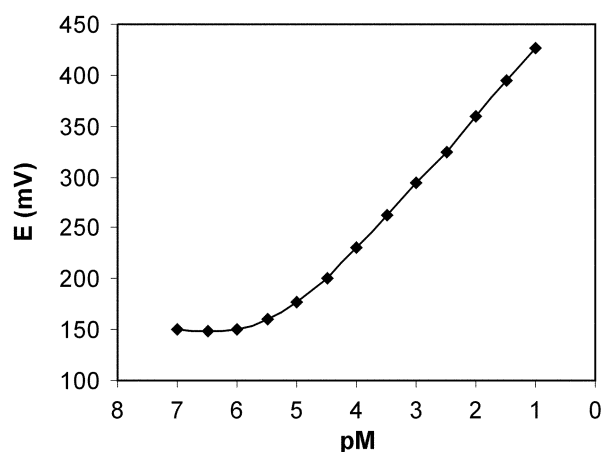
Membrane Number	Composition (%)								Slope (mV/decade) <sup>a</sup>
	PVC	CASCA	DBP	BA	NPOE	KTK	NaTPB		
1	33	–	66	–	–	–	–	~0 ± 0.3	
2	33	1	66	–	–	–	–	5.6 ± 0.1	
3	33	2	65	–	–	–	–	11.3 ± 0.2	
4	33	4	63	–	–	–	–	15.9 ± 0.1	
5	33	5	62	–	–	–	–	23.5 ± 0.3	
6	33	6	61	–	–	–	–	23.2 ± 0.1	
7	33	5	–	61	–	–	–	21.5 ± 0.2	
8	33	5	–	–	61	–	–	20.9 ± 0.3	
9	33	5	60	–	–	2	–	49.9 ± 0.1	
10	33	5	59	–	–	3	–	47.3 ± 0.2	
11	33	5	60	–	–	–	2	58.2 ± 0.3	
12	33	5	–	60	–	–	2	51.7 ± 0.1	
13	33	5	–	–	60	–	2	51.5 ± 0.2	
14	33	–	65	–	–	–	2	9.5 ± 0.3	

<sup>a</sup>Values in parenthesis are based on triplicate measurements.

and amount of ion-carrier on the performance of the membranes were studied and, the results are given in Table 1. As it is seen, among three solvent mediators used, the DBP displays the best sensitivity (No. 11).

The optimization of perm-selectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane component. In fact, it has been demonstrated that, the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance,<sup>16</sup> improving the response behavior and selectivity,<sup>17</sup> but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode.<sup>18</sup> Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface. Table 1 shows that in the presence of 2% NaTPB as a suitable additive, the slope of proposed sensor increases to 58.2 mV (No. 11).

However, the membrane (No. 11) with the composition 5.0: 2.0: 33.0: 60.0 of CASCA: NaTPB: PVC: DBP gave the



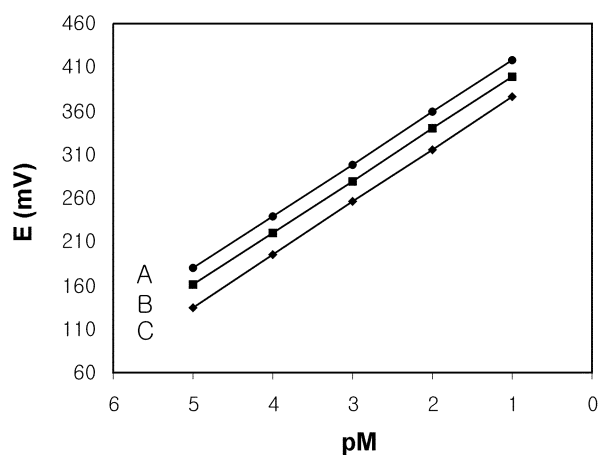
**Figure 3.** Calibration graph of silver ion-selective electrode based on CASCA with membrane no. 11.

best response characteristics (Table 1).

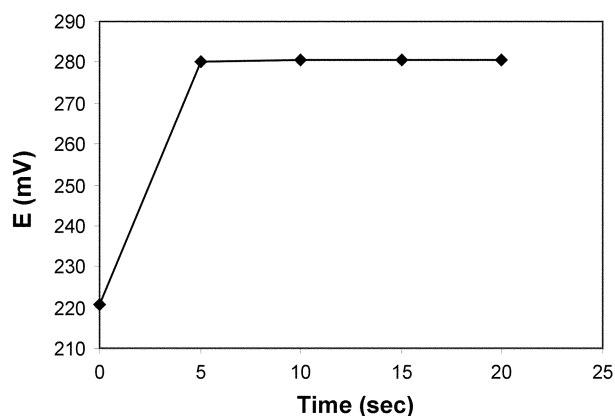
The electrode shows a linear response to the concentration of Ag<sup>+</sup> ion in the range of  $1.0 \times 10^{-1}$  to  $8.0 \times 10^{-6}$  M. The slope of calibration curve was  $58.2 \pm 0.5$  mV decade<sup>-1</sup> (Fig. 3). The limit of detection, as determined from the intersection of the two extrapolated segments (*i.e.*, the linear part of the graph and the curved part at low concentration levels) of the calibration graph, was  $5.0 \times 10^{-6}$  M ( $0.54 \mu\text{g mL}^{-1}$ ).

The concentration of the internal solution (AgNO<sub>3</sub>) of the electrode was changed from  $1.0 \times 10^{-3}$  M to  $1.0 \times 10^{-5}$  M and the potential response of the Ag<sup>+</sup> selective electrode was obtained (Fig. 4). It was found that the variation of concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plot. A  $1.0 \times 10^{-3}$  M concentration of the AgNO<sub>3</sub> solution is quite appropriate for smooth functioning of the electrode system.

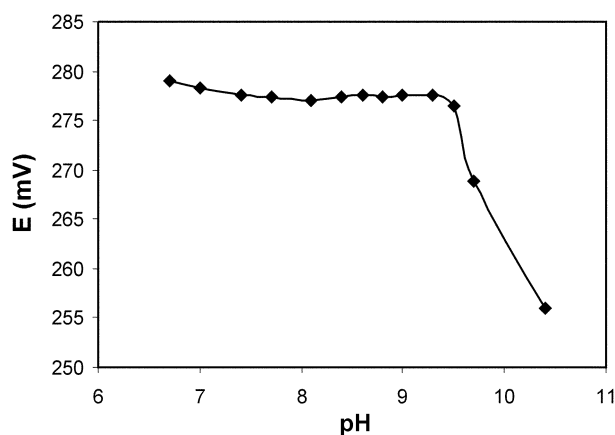
The static response time of the PVC membrane, according



**Figure 4.** The effect of concentration of the internal reference solution concentration on the electrode response; (A)  $1.0 \times 10^{-3}$  M, (B)  $1.0 \times 10^{-4}$  M, (C)  $1.0 \times 10^{-5}$  M of silver ion.



**Figure 5.** The static response time of silver sensor based on CASCA using a  $1.0 \times 10^{-4}$  M solution of  $\text{AgNO}_3$ .



**Figure 6.** The effect of the pH of the test solution ( $1.0 \times 10^{-3}$  M of  $\text{AgNO}_3$ ) on the potential response of the silver sensor.

to IUPAC recommendations,<sup>19</sup> was measured in the concentration range of  $\leq 1.0 \times 10^{-3}$  M and the results showed that the sensor reached its equilibrium in a very short time (5 s). It should be noted that the equilibrium potential essentially remains constant for more than 5 min, after which only a very slow divergence was recorded.

The influence of the pH of the test solution on the potential response of  $\text{Ag}^+$  sensor was tested at  $1.0 \times 10^{-4}$  M  $\text{Ag}^+$  concentration, over the pH range 4.5–10.5. The pH was adjusted by introducing small drops of nitric acid (0.1 M) or sodium hydroxide (0.1 M) and the results are shown in Figure 6. As it is seen, the potential remains constant from pH values 4.5–10.5, beyond which a drift in potential was observed. The observed drift at higher pH values could be due to the formation of some hydroxy complex of  $\text{Ag}^+$ .

**Table 2.** Selectivity coefficients of various interfering ions ( $M^{n+}$ )

Cation	K (MPM)
$\text{Na}^+$	$1.2 \times 10^{-4}$
$\text{K}^+$	$1.4 \times 10^{-4}$
$\text{Rb}^+$	$2.2 \times 10^{-4}$
$\text{Cs}^+$	$2.5 \times 10^{-4}$
$\text{Cu}^{2+}$	$3 \times 10^{-4}$
$\text{Co}^{2+}$	$4.5 \times 10^{-4}$
$\text{Ni}^{2+}$	$2.5 \times 10^{-4}$
$\text{Zn}^{2+}$	$3.2 \times 10^{-4}$
$\text{Cd}^{2+}$	$1.7 \times 10^{-4}$
$\text{Pb}^{2+}$	$1.8 \times 10^{-4}$
$\text{Hg}^{2+}$	$2.1 \times 10^{-4}$
$\text{Ca}^{2+}$	$6.1 \times 10^{-4}$
$\text{Mg}^{2+}$	$3.3 \times 10^{-4}$
$\text{Ba}^{2+}$	$7.3 \times 10^{-4}$

Conditions: Reference solution ( $1.0 \times 10^{-6}$  M of  $\text{Ag}^+$ ), primary ion ( $1.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$  M of  $\text{Ag}^+$ ), interfering ion ( $1.0 \times 10^{-3}$ – $1.0 \times 10^{-2}$  M).

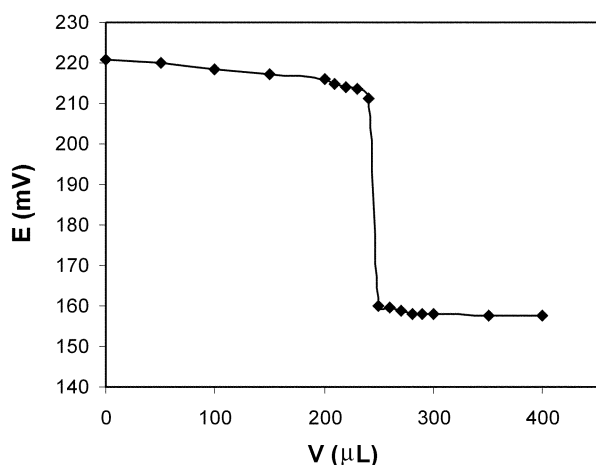
Potentiometric selectivity coefficients, describing the preference of the proposed electrode for an interfering ion, B, relative to silver ion, A, were determined by the matched potential method (MPM), which is proposed<sup>20</sup> to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation. According to this method, the specified activity (concentration) of the primary ion (A) is added to a reference solution ( $1.0 \times 10^{-6}$  M of  $\text{AgNO}_3$ , in this case), and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution until the measured potential matched that obtained before by adding the primary ions. The matched potential method selectivity coefficient,  $K_{A,B}^{\text{MPM}}$ , is then given by the resulting primary ion to interfering ion activity (concentration) ratio,  $K_{A,B}^{\text{MPM}} = a_A/a_B$ .

The resulting  $K_{Ni}^{\text{pot}}$  values thus obtained for proposed  $\text{Ag}^+$  ion-selective electrode are summarized in Table 2. As it is seen, the alkali, alkaline earth, and transition metal ions used as interfering ions can not disturb the functioning of the  $\text{Ag}^+$  ion-selective membrane electrode significantly.

In Table 3 the serious interfering ions, slope and detection limit of different  $\text{Ag}^+$  ion-selective electrodes based on derivatives of calix[4]arenes, are compared with those of this work. As it is seen, not only the detection limit of the proposed sensor, but also its slope and serious interfering ions are superior to those reported for other  $\text{Ag}^+$  ion-selective electrodes.<sup>21–23</sup>

**Table 3.** Comparison of serious interfering ions of different  $\text{Ag}^+$  ion-selective

Ionophore	Detection Limit	Serious interfering ions	Slope (mV decade <sup>-1</sup> )	Ref
Bis(3-Pyridinecarboxylate) Calix[4]arene	$1.0 \times 10^{-5}$	$\text{Hg}^{+2}$	57.0	21
Calixarene (containing nitrogen)	$8.0 \times 10^{-6}$	$\text{Hg}^{+2}$	47.0	22
Calixarenes derivatives (allyl, benzyl, propargyl)	$5.0 \times 10^{-5}$	$\text{Tl}^+$ , $\text{Na}^+$ , $\text{Li}^+$ , $\text{Hg}^{+2}$	57.0	23
CASCA	$6.0 \times 10^{-6}$	No interfering ion	58.2	This work



**Figure 7.** Potentiometric titration curves of 25 mL  $1.0 \times 10^{-4}$  M of  $\text{Ag}^+$  solution with EDTA  $1.0 \times 10^{-2}$  M, using the proposed sensor as an indicator electrode.

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 25.0 mL of  $1.0 \times 10^{-4}$  M of  $\text{Ag}^+$  solution with EDTA  $1.0 \times 10^{-2}$  M and the resulting titration curve is shown in Figure 7. As it is seen, the amount of  $\text{Ag}^+$  ( $1.0 \times 10^{-4}$ ) can be determined with the electrode.

The electrode was also successfully applied to the direct determination of silver in wastewater sample from Tehran electroplating factory. The silver content obtained from three replicate measurements ( $2.3 \pm 0.1$  ppm) was found to be in satisfactory agreement with that obtain by atomic absorption spectrometry ( $2.4 \pm 0.1$  ppm).

### References

- Casabo, J.; Mestres, L.; Escriche, L.; Texidor, F.; Pevez-Jimenez, C. *J. Chem. Soc. Dalton Trans.* **1991**, 1961.

- Chung, S.; Kim, W.; Park, B.; Yoon, I.; Lee, S. S.; Sung, D. *Chem. Commun.* **1997**, 965.
- Malinowska, E.; Brozka, Z.; Kasiura, K.; Egberink, R. J. M.; Reinhoudt, D. N. *Anal. Chim. Acta* **1994**, 298, 245.
- Siswanta, D.; Nagatsuka, K.; Yamada, H.; Kumakura, K.; Hisamoto, H.; Shichi, Y.; Toshima, K.; Suzuki, K. *Anal. Chem.* **1996**, 68, 4166.
- Chung, S.; Kim, W.; Park, S. B.; Kim, D. Y.; Lee, S. S. *Talanta* **1997**, 44, 1291.
- Ikeda, A.; Tsuzuki, H.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 2* **1994**, 2073.
- Fulterer, T.; Merz, A.; Lex, J. *Angew. Chem. Int. Ed. Engl.* **1997**, 6, 611.
- Choi, H. S.; Suh, S. B.; Cho, S. J.; Kim, K. S. *Proc. Nati. Acad. Sci. U. S. A.* **1998**, 95, 12094.
- Iwamoto, K.; Araki, K.; Shinkai, S. *Tetrahedron* **1991**, 47, 4325.
- Kamata, S.; Bhale, A.; Fukunaga, Y.; Murata, A. *Anal. Chem.* **1998**, 60, 2464.
- Ganjali, M. R.; Moghimi, M.; Shamsipur, M. *Anal. Chem.* **1998**, 70, 5259.
- Ganjali, M. R.; Hosseini, M.; Javanbakht, M.; Hashemi, O. R. *Anal. Lett.* **2000**, 33, 3139.
- Ganjali, M. R.; Moghimi, A.; Buchanan, G. W.; Shamsipur, M. *J. Inclusion Phenom.* **1998**, 30, 29.
- Koryta, J. *J. Anal. Chim. Acta* **1990**, 233, 1.
- Wolfbeis, O. S. *Anal. Chim. Acta* **1991**, 250, 181.
- Ammann, D.; Pretsch, E.; Simon, W.; Lindner, E.; Bezegh, A.; Pungor, E. *Anal. Chem.* **1991**, 171, 1380.
- Huster, M.; Gehring, W. E.; Morf, E.; Simon, W.; Lindner, E.; Jeney, J.; Toth, K.; Pungor, E. *Anal. Chem.* **1991**, 63, 1380.
- Ammann, D.; Morf, W. E.; Meier, P. C.; Pretsch, E.; Simon, W. *IonSel, Electrode Rev.* **1983**, 5, 3.
- IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature, *Pure Appl. Chem.* **1976**, 48, 127.
- Umezawa, Y.; Umezawa, K.; Sato, H. *Pure Appl. Chem.* **1995**, 67, 507.
- Chen, L.; He, X. W.; Zhao, B.; Liu, Y. *Anal. Chim. Acta* **2000**, 417, 51.
- Liu, Y.; Zhao, B. T.; Chen, L. X.; He, X. W. *Microchem. J.* **2000**, 65, 75.
- Kimura, K.; Yajima, S.; Tatsumi, K.; Yokoyama, M.; Masatoshi, O. *Anal. Chem.* **2000**, 72, 5290.