Turk J Chem
31 (2007) , 449 – 456.
© TÜBİTAK

PVC-Membrane Electrodes Based on 18-Crown-6 and Dibenzo-18-Crown-6 Ethers for Determination of Silver

Mohsen Mousa ZAREH[1]*, Magda A. AKL[2], Ahmd Khlil GOHNEIM[1] and Mohmed Hussin ABD EL-AZIZ[3]
[1] *Department of Chemistry, Faculty of Science, Zagazig University, Zagazig-EGYPT*
e-mail: mohsenzareh@hotmail.com
[2] *Department of Chemistry, Faculty of Science, Mansura University, Mansura-EGYPT*
[3] *Central Laboratory, Egyptian Railway, Cairo-EGYPT*

Received 29.12.2006

PVC-membrane electrodes for Ag^+ based on either 18-crown-6 (I) or di-benzo-18-crown-6 ether (II) were applied for the first time. The effect of solvent mediator on the electrode performance was discussed. Nernstian slope values were 59 and 58.9 mV/decade for both I and II electrode types, respectively. The linear concentration range was 10^{-5}-10^{-1}M. The detection limit was 7.9×10^{-6} M. The working pH ranges were 5-9 or 4-9, depending on the concentration of Ag^+ ion. The electrodes showed good selectivity towards most of the common alkali, alkaline earths, and transition metal cations. The electrodes were applied successfully for the determination of silver in photographic wastewater and alloys that are part of railway engines. The recovery range was 96%-100%, and the relative standard deviation was (0.95-2.7) for n = 4. The obtained results were compared to those of an atomic absorption spectrophotometric method.

Key Words: Ag^+ determination, silver electrode, PVC-membrane electrode.

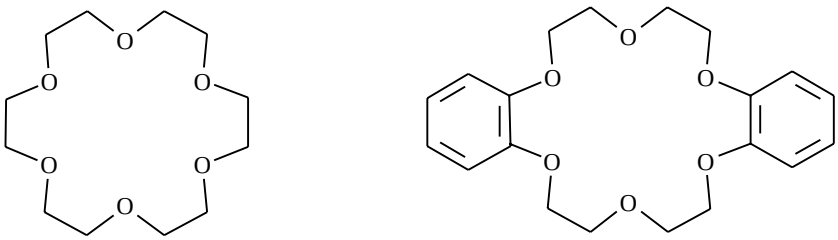
Introduction

Many ionophores and chelating agents were applied for preparing silver selective electrodes. Among them are calixarenes such as calix-4-arene[1,2] and calix-6-arene.[3] Some other chelating agents were also applied for the preparation of ion-selective electrodes like sulfanyl benzoic acid,[4] and 5,10,15-tris(pentaflourophenyl)corrole.[5]

It is well known that crown ethers work as chelating agents for many cations. The crown-ether complexes have been extensively applied to different metal cation-selective electrodes.[6,7] Several types of crown ether-metal were previously used to prepare Ag^+-selective electrodes. Of them are dibenzo-16-crown-5,[8] azathioethers crown containing 1,10-phenanthroline unit,[9] 14-membered thia-crown ether,[10] macrocyclic dithia-crown ether,[11] 16-crown-5,[12] 15-crown-5,[13] 15-crown-6,[14] 14-crown-4,[15] and hexathia-18-crown-6.[16]

*Corresponding author

In the present work, an extension of the studies about crown ethers as ionophores for Ag^+-selective electrodes will add some information about their behavior, especially selectivity and sensitivity. Accordingly, 18-crown-6 ether and its dibenzo-derivative were tried for Ag^+-selective electrodes. The present electrodes were advantageous, since Hg^{2+} did not show any interference with the measurements like that for 16-crown-5.[12] In addition, they are characterized by small selectivity coefficient values. They showed a wider linear range and working pH range (10^{-1}-10^{-5}M and 4-9 pH) than those for hexathia-18-crown-6 (3.2×10^{-3}-6×10^{-6}M and 2-7.5 pH).[16] Their response times were the same. They can be applied easily to actual samples containing silver.



18-crown-6 (I) Dibenzo-18-crown-6 (II)

Figure 1. 18-Crown-6 (I) and dibenzo 18-crown-6 (II) ethers.

Experimental Section

Reagents and materials

18-Crown-6 (18CE6) (Fluka), and dibenzo 18-crown-6 (DB18CE6) were the main ionophores for preparing the membranes. The plasticizers were dioctylphenylphosphonate (DOPP) (Aldrich), dioctylphthalate (DOP) (Fluka), or nitrophenyl octylether (NPOE) (Fluka). Polyvinylchloride (PVC) (Fluka) was the membrane matrix. The membrane components were dissolved in tetrahydrofuran (THF) (Fluka). To perform the selectivity studies, analytical-reagent grade nitrates of Na^+, K^+, NH_4^+, Ag^+, Ni^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, and Al^{3+} were used.

To prepare silver 500 mg/L stock solution, 0.787 g of dried silver nitrate (Aldrich) was dissolved in bi-distilled water containing 1 mL of concentrated HNO_3. The solution was made up to the mark in a 1-L standard flask and stored in amber light bottles in a dark place. The solution was standardized amperometrically against 0.01 N standard KCl solution. Less concentrated solutions were obtained by careful dilution of the standard stock solution using 0.1 M $NaNO_3$. Double distilled water was used throughout.

Equipment

The potentiometric/pH-measurements were carried out (at 25 ± 1 °C) on a digital pH-meter (model 5986) Cole-Parmar (sensitivity ± 0.1 mV) coupled with a channel selector. The atomic absorption measurements were performed using a Perkin-Elmer spectrometer (model 2380).

Electrode preparation and potentiometric measurements

The electrode construction depends mainly on the membrane constituents. The membrane composition was 1% (w/w) ionophore [either 18CE6 (I), or DB18CE6 (II)], 33% (w/w) PVC, and 66% (w/w) solvent mediator (DOPP, DOP, DDP, or NPOE). These components were dissolved in distilled THF and poured into glass rings of 24 mm i.d. resting on a glass plate. After solvent evaporation, the obtained membrane was cut out into disks of 7 mm i.d. The membrane disks were mounted in electrode bodies (Type IS 561, Philips, Eindhoven, Netherlands) for potentiometric measurements. After electrode adjustments, it was soaked for 24 h in 10^{-2}M solution of $AgNO_3$. The electrode body was filled with the inner filling solution [$AgNO_3 10^{-3}$M + $NaNO_3$ 10^{-1}M].

The potentiometric measurements were carried out in the presence of 0.1 M $NaNO_3$ using the procedure described previously.[17] The cell potential was recorded corresponding to each Ag^+-concentration. A calibration graph has been constructed for the cell potential versus –log [Ag^+]. The following is a representation of the cell assembly:

Ag-AgCl Double Junction Reference || ***Sample solution*** || ***Membrane*** | ***Inner filling*** | ***Ag-AgCl***

The potentiometric selectivity coefficient ($K^{Pot}_{Ag+,X^{z+}}$) values for different common cations were obtained by the separate solution method[18] (10^{-3} M solutions for both silver and interferent). The pH adjustments of the tested solutions to the electrode optimum pH value were achieved with 0.1 M NaOH or 0.1 M HNO_3.

Preparation of silver samples

Samples (0.1 g) from the piston pin and carrier alloy from the turbocharger of EC, C, F, FB, and 710 General Motors-series engines (Egyptian Railway) were taken. Each sample was completely dissolved in 10 mL of hydrochloric acid (1:1) by heating on a water bath. Then it was added to a minimum volume of (1:1) HNO_3. The mixture was boiled to remove oxides of nitrogen.[19] The mixture was cooled, transferred to a 50-mL volumetric flask, and diluted with deionized water. Then the pH was adjusted to 5-8 with 0.1 N NaOH.

Photographic wastewater samples were collected from several local photographic studios. Then 5 mL of each water sample was treated with drops of nitric acid and diluted to 50 mL in a calibrated flask. Finally, it was adjusted to pH 5-9 using 0.1 N NaOH.

Determination of silver by Flame AAS

The samples and the standard solutions should contain 5% (v/v) HNO_3 to keep Ag^+ in solution. The interferences from bromide, chromate iodate, iodide, permenganate, and chloride precipitation of silver could be eliminated using a 5% acetic acid solution. Standard atomic absorption conditions for silver measurement were applied at wavelength 328.1 nm and with an air-acetylene flame.

Determination of silver by ISE

Sample solutions (50 mL) were filtered and transferred to a 100-mL beaker. Then it was adjusted to the optimum electrode pH range 5-9. The electrode set comprising either Ia or IIb electrodes in conjunction

with the reference electrode was dipped into the sample solution. The potential reading of the resulting solution was referred to a previously prepared calibration graph for silver in the presence of 0.1 M $NaNO_3$ for ionic strength adjustment. The obtained results were compared to those given by air acetylene flame atomic absorption spectrometer detected at a wavelength of 328 nm.

Results and Discussion

Effect of membrane composition

Both 18-crown-6 ether (18CE6) and the dibenzo-18-crown-6 ether (DB18CE6) were tried as ionophore (ion-carrier) for preparing silver PVC membranes with different plasticizers. Three types of plasticizers were used, namely diester types (DOP, DOS, and DDP), ether type (2-NOPE), and phosphonate type (DOPP). The plasticizers constitute the major component, approaching 66.0% by weight of membrane composition, which ensures the mobility of the free and complexed ionophores, sets the dielectric constant, and provides suitable mechanical properties of the membrane.

Table 1 shows the characteristics of Ag^+-selective type-I electrodes incorporating different plasticizers. It can be observed that 18CE6 plasticized with DOPP (Ia electrode) gives a linear range of 5×10^{-5}-10^{-1} M together with a slope value of 52.98 mV/decade. The best Nernstian slope (59 mV/decade) was recorded when DDP-plasticizer (Id electrode) was used, although the linear range was short (10^{-3}-10^{-1} M). The lowest value of the Nernstian slope was found when DOP and NPOE (electrodes Ib and Ic) were used. This is because the solvent interaction affects the stability of the formed complexes.[20]

Table 1. Response characteristics of silver electrodes based on (18CE6) (I) and (DB18CE6) (II) incorporating different solvent mediators.

Electrode type	Solvent mediator	Slope, mV/decade (n = 3)	Linear range, M	Detection limit, M	Correlation coefficient, R^2
I-a	DOPP	52.98	5×10^{-5}-10^{-1}	1.5×10^{-5}	0.997
I-b	DOP	37.9	10^{-4}-10^{-1}	10^{-5}	0.998
I-c	2-NPOE	44.9	10^{-4}-10^{-1}	10^{-5}	0.9999
I-d	DDP	59	10^{-3}-10^{-1}	10^{-4}	0.9999
II-a	DOPP	57.98	5×10^{-5}-10^{-1}	1.5×10^{-5}	0.9994
II-b	DOP	58.9	10^{-5}-10^{-1}	7.9×10^{-6}	0.9997
II-c	2-NPOE	46	10^{-4}-10^{-1}	7.9×10^{-5}	0.9998
II-d	DDP	52.5	10^{-3}-10^{-1}	3.98×10^{-4}	0.9976

When DB18CE6 was used, the best value of the Nernstian slope (58.9 mV/decade) was observed for the IIb electrode. The linear range was wider (10^{-5}-10^{-1}M) than those for the Id and IIa electrodes, although they have suitable Nernstian slopes (59 and 57.98 mV/decade). In addition, the IIc electrode showed a non-Nernstian slope (46 mV/decade). Table 1 shows the obtained results.

The life span of the IIb electrode was checked practically in a comprehensive way using a procedure explained in an earlier work.[6] The obtained calibration graphs reveal that 1 day is enough for the electrode conditioning. The recorded slope value was 58.9 mV/decade within a linear range of 10^{-5}-10^{-1}M. After 1 week a small decrease in the slope was observed (55.1 mV/decade), and the linearity range was 3.98 ×

10^{-5}-10^{-2} M). However, they still have their practical Nernstian response and almost the same linearity range. The life span of electrodes extends up to 1 month. Table 2 shows the obtained results.

Table 2. Effect of soaking on the response of IIb electrode for silver.

Soaking time	Slope, (mV/decade)	Linear range, M	Detection limit, M	Correlation coefficient, R^2
1 h	52.8	5.6×10^{-5}-10^{-1}	3.98×10^{-5}	0.9996
1 day	58.9	10^{-5}-10^{-1}	7.9×10^{-6}	0.9997
7 days	55.1	4.98×10^{-5}-10^{-1}	3.8×10^{-5}	0.9993
30 days	50.98	3.98×10^{-5}-10^{-1}	2.5×10^{-5}	0.9984

The potential-time curves of the Ia and IIb electrodes are shown in Figure 2. The response time of the electrodes was calculated according to the IUPAC definitions of ion selective electrodes.[18] Twenty-four seconds are sufficient to reach to the steady state potential value (within 1 mV), whatever the Ag^+-concentration (10^{-1}-10^{-6} M).

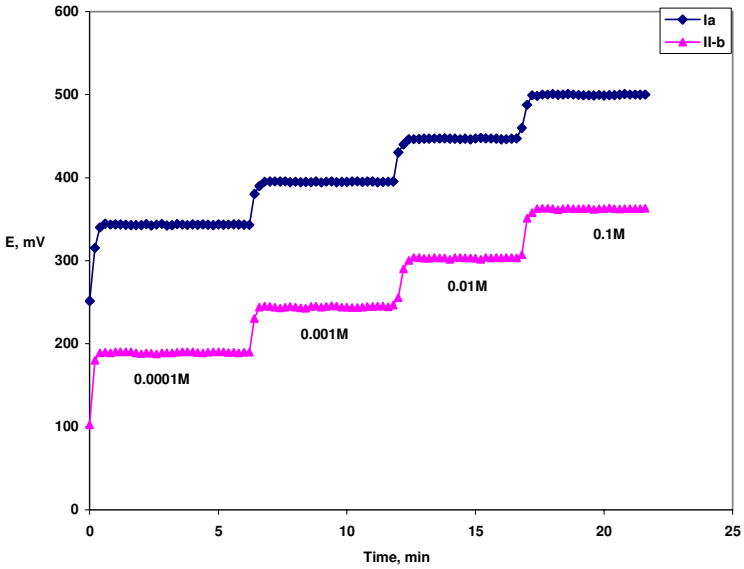


Figure 2. Dynamic response of silver-selective electrodes based on 18-crown-6 ether (Ia) and dibenzo 18-crown-16 ether (IIb).

The pH effect of the measured solution was also studied. Figure 3 shows the potential variations with the pH changes for the IIb electrode. The 2 types of membrane behave similarly toward the pH changes. The decrease in potential is markedly observed at pH 1-4 for 10^{-2}M and 10^{-3}M Ag^+ solutions. In the case of 10^{-4}M Ag^+, the large potential drops occur at pH 1-5. In other words, the plateau potential is observed at pH 4-9 for 10^{-2} M and 10^{-3}M Ag^+ and at pH 5-9 for 10^{-4}M Ag^+. This agrees with the precipitation pH of AgOH (pH 9).

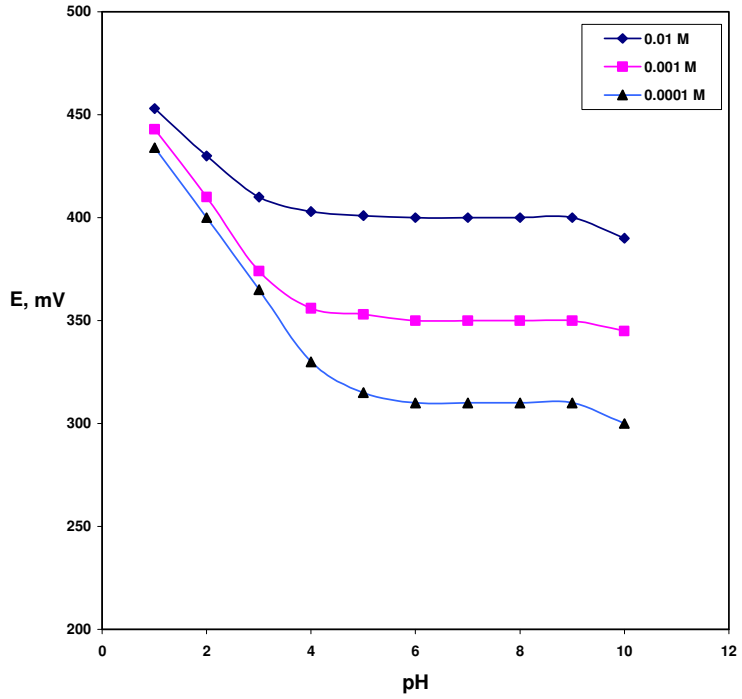


Figure 3. Effect of pH changes on the potential response of silver ion selective electrode (IIb) based on dibenzo 18-crown-6.

Electrode selectivity

Table 3 shows the selectivity coefficient values for both the Ia and IIb electrodes. For the IIb electrode the selectivity coefficient values are between -1.96 and -2.91 for all of the divalent cations. The transition metals of the same Ag-group ($Hg^{2+}$and Cu^{2+}) did not interfere (log $K^{pot}_{Ag+,jz+}$ values are -2.33 and -2.40). The non-interfering cations are observed to have ionic radii between 0.51 Å for Al^{3+} and 1.12 Å for Sr^{2+}. All of them are divalent or trivalent cations (different charge). Their smaller ionic radii result in a loose bonding with the crown ether. The stronger interfering cations are mostly monovalent (similar charge to Ag^{+}). They have larger ionic size (e.g., K^{+}= 1.33 Å and NH_4^{+} = 1.43 Å) than Ag^{+} = 1.26 Å. The same conclusion was observed for the Ia electrode, but with an improved selectivity coefficient values for all the tested monovalent cations. This is because the silver ion is more bonded to crown ether than its dibenzo derivative, due to the smaller polarity of the dibenzo18-crown-6.[21]

Determination of Ag^{+} in developed photographic plate wastewater and piston pin carrier alloy

Samples of alloys taken from parts of railway engines, piston pin turbochargers, and photographic wastewater were analyzed with both Ia and IIb electrodes. The mean recovery range was 97%-100% for the analyzed samples (5.3-12.0 ppm). The relative standard deviation values are in the range 0.95%-2.7% for 4 determinations. The same samples were analyzed by the method recommended by the AAS.[19] The obtained results agreed with those of the present ISE method, which ensures the validity of both electrodes for analysis. Table 4 shows the obtained results.

Table 3. Selectivity coefficient $K^{pot}_{Ag+,jz+}$ of silver selective electrodes with membrane (type Ia), (type IIb).

Interferent	log $K^{pot}_{Ag+,jz+}$	
	Type Ia	Type IIb
1. Na^+	-1.24	-0.48
2. K^+	-1.43	0.27
3. NH_4^+	-1.07	-0.63
4. Mg^{++}	-2.61	-2.46
5. Ca^{++}	-2.58	-2.96
6. Sr^{++}	-2.59	-2.91
7. Hg^{++}	-2.43	-2.33
8. Mn^{++}	-2.38	-1.96
9. Cd^{++}	-2.09	-2.21
10. Cu^{++}	-2.24	-2.40
11. Co^{++}	-2.53	-2.45
12. Ni^{++}	-2.05	-2.72
13. Fe^{+++}	-1.63	-2.45
14. Zn^{++}	-2.52	-2.70
15. Al^{+++}	-3.22	-2.79

Table 4. Determination of silver in various samples using silver electrodes with membrane types Ia and IIb.

Samples	AAS method			ISE method Membrane type Ia			ISE method Membrane type IIb		
	Silver found, ppm	Mean recovery, %	RSD* %	Silver found, ppm	Mean recovery, %	RSD* %	Silver found, ppm	Mean recovery, %	RSD* %
Piston carrier turbocharger (Railway engine)	11.0	98.9	0.9	10.6	96.0	1.3	10.7	97.0	2.1
Piston pin Turbocharger (Railway engine)	12.0	99.1	1.3	11.5	96.0	1.7	12	100.0	1.03
Photographic wastewater	5.3	99.5	0.97	5.1	96.2	2.7	5.2	98.0	1.00
	9.5	99.0	1.41	9.3	98.0	0.95	9.3	98.0	1.5

*Relative standard deviation (4 determinations)

Conclusion

In this work, 2 conclusions can be drawn. The first is that the neutral ionophores 18-crown-6 and the dibenzo-18-crown-6 like previously tried crowns[6−16] behave Nernstianly toward Ag^+. The presented electrodes showed wider linearity and pH ranges. The second conclusion is that the selectivity coefficient values toward the tested monovalent cations are better for the Ag^+-electrode based on 18-crown-6 ether (I) than for an electrode based on its dibenzo derivative (II). This represents an improvement for the electrode properties.

References

1. R.K. Mahajan, I. Kaur, V. Sharma and M. Kumar, **Sensors 2**, 417 (2002).
2. Q.L. Jian, W.P. Dai, S.Z. Xian and W.H. Xi, **Electroanal. Chem. 568**, 37 (2004).
3. J.Q. Lu, J.L. Lu, X. Zhou and X. He, **Fenxi Kexue Xuebao 19**, 30 (2003).
4. A. Abbaspour, A. Izadyar, and H. Sharghi, **Anal. Chim. Acta 525**, 91 (2004).
5. X.-B. Zhang, Z.-X. Han, Z.-H. Fang, G.-L. Shen and R.-Q. Yu, **Anal. Chim. Acta 562**, 210 (2006).
6. M.M. Zareh, A.K. Ghonaim and M.H. Abd El-Aziz, **Talanta 54**, 1049 (2001).
7. H. Aghaie, M. Giahi, M. Monajjemi, G.H. Nafissi and M. Aghaei, **Sensor. Actuat. B-Chem. 107**, 756 (2005).
8. C.C. Su, M.C. Chang and K. Liu, **Anal. Chim. Acta 432**, 261-267 (2001).
9. S. Mojtaba, J. Mehran, L. Vito, G. Alessandra, D. Greta, R.G. Mohammad and Y. Abdullah, **Anal. Chim. Acta 462**, 225 (2002).
10. D. Siswanta, Y.K. Nagatsuka, H. Yamada, K. Kumakur, H. Hisamoto, Y. Shichi, K. Toshima and K. Suzuki, **Anal. Chem. 23**, 4166 (1996).
11. D.R. Tsingarelli, G. Yu. Mamedova and K.L. Shpigun, **Zh. Anal. Khim. 3**, 286 (1995).
12. M. Oue, K. Kimura, K. Akama, M. Tanaka and T. Shono, **Chem. Lett. 3**, 409 (1988).
13. T.M. Lai and S.J. Shih, **Analyst 8**, 891 (1986).
14. J. Casabo, C. Perez-Jimerez, L. Escriche, S. Alegret, E. Martinez-Fabregas, and F. Teixidar, **Chem. Lett. 7**, 1107 (1990).
15. M. Oue, K. Akama, K. Kimura, M. Tanaka and T. Shono, **Anal. Sci. 2**, 162 (1989).
16. M.H. Mashhadizadeh and M. Shamsipur, **Anal. Chim. Acta 381**, 111 (1999).
17. M.M. Zareh and E. Malinowska, **J. AOAC International 90**, 147 (2007).
18. G.G. Guilbault, R.A. Durst, M.S. Frant, H. Freiser, H.E. Hansen, T.S. Light, E. Pungor, G. Rechnitz, N.M. Rice, T.J. Rohm, W. Simon and J.D.R. Thomas, **Pure Appl. Chem. 48**, 127 (1976).
19. L. Capacho-Delgado and D.C. Manning, **Atom. Absorps. Newslett. 5**, 1 (1966).
20. W.G. Gokel, D.M. Goli, C. Minganti, and L. Echegoyen, **J. Am. Chem. Soc. 105**, 6786 (1983).
21. H.-C. Sheu and J.-S. Shih, **Anal. Chim. Acta 324**, 125 (1996).