Microchim. Acta 144, 177–181 (2004)
DOI 10.1007/s00604-003-0072-7

Microchimica Acta
Printed in Austria

Original Paper

All-Solid-State PVC Membrane Ag^+-Selective Electrodes Based on Diaza-18-Crown-6 Compounds

Ibrahim Isildak[1,*], **Murat Yolcu**[1], **Omer Isildak**[2], **Nadir Demirel**[3], **Giray Topal**[4], and **Halil Hosgoren**[3]

[1] Department of Chemistry, Faculty of Science, Ondokuzmayis University, 55139, Samsun, Turkey
[2] Department of Chemistry, Faculty of Science, Gaziosmanpasa University, 60200, Tokat, Turkey
[3] Department of Chemistry, Faculty of Science, Dicle University, 21280, Diyarbakır, Turkey
[4] Department of Chemistry, Faculty of Education, Dicle University, 21280, Diyarbakır, Turkey

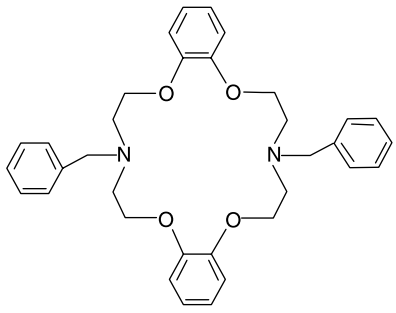
Received January 15, 2003; accepted June 9, 2003; published online November 20, 2003

Abstract. Two diaza-crown ether compounds were synthesized and evaluated as Ag^+-selective carriers in polyvinylchloride (PVC) membrane electrodes of solid-state type. The all-solid-state PVC membrane electrode based on N,N-Dibenzyl-dibenzo-diaza-18-crown-6 exhibited a super-Nernstian response (75 ± 10 mV per decade) over the concentration range of 1×10^{-1} to 7×10^{-6} M of Ag^+ ion and a detection limit of 3×10^{-6} M, at a wide range of pH (pH 4–7). The response time of the electrode was fast (less than ~10s), and it can be used for three months without any significant deviation in potential. The proposed all-solid-state PVC membrane electrodes revealed high selectivity toward Ag^+ ion with respect to alkali, alkaline earth, heavy and transition metal ions. A flow-through cell of all-solid-state PVC membrane Ag^+-selective electrode based on N,N-Dibenzyl-dibenzo-diaza-18-crown-6 has also been prepared and applied for flow-injection analysis of Ag^+ ion in solution.

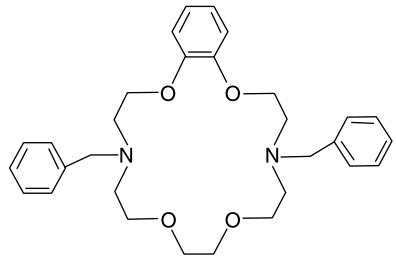
Key words: Diaza-crown ethers; all-solid-state; PVC membrane; silver-selective electrodes; FIA.

PVC-based membrane ion selective electrodes are well established analytical tools routinely used for chemical, biological and environmental analysis of a wide variety of different ions [1–5]. One of the important components of PVC membranes is the carrier that determines the selectivity of the electrodes. Due to their electrical neutrality, lipophilic character, and capability to selectively and reversibly bind metal ions [6], mycrocyclic compounds have attracted considerable attention for the development of carrier-based PVC membrane sensors sensitive toward cationic species [1–5, 7–9]. Crown ether classes of mycrocyclic compounds, containing only oxygen as the heteroatom in the mycrocyclic ring, exhibit ionophore properties, e.g. a strong affinity for alkali metal cations within the PVC membrane [10–13]. With the introduction of a different number of the mycrocyclic ring or replacing atoms by nitrogen atoms in the mycrocyclic ring, the affinity will be expected to be toward heavy or transition metal cations [14–16]. However, by using aza-crown ethers as neutral carriers in PVC membranes, highly selective electrodes for heavy [17] and transition metal [18] cations, and silver ions [19] have been developed. Recently, the use of 1,10-dibenzyl-1,10-diaza-18-crown-6 as neutral carrier in the preparation of a lead ion-sensitive electrode was reported by Mousavi et al. [20]. However, while monovalent cations gave significant responses, the authors did not consider Ag^+ as a potential interfering ion in detail.

* Author for correspondence. E-mail: iisildak@omu.edu.tr



1



2

Fig. 1. Structures of neutral ionophores 1 and 2 for Ag^+ ion

Because Ag^+ occurs in nature with other metallic cations, highly selective carriers are always needed; thus, the utility of such compounds can be exploited for the development of Ag^+-selective PVC membrane electrodes. On the other hand, in recent years, there has been an increasing interest in the field of ion-selective electrodes, mainly those based on the use of all-solid-state contact types [21, 22] similar to coated-wire electrodes. The all-solid-state contact prepared uses a mixture of graphite-epoxy resin in suitable ratios. In these types of electrodes, the sensing membrane adhered better to the surface of all-solid-state contact without an internal reference solution. An extended life-time and robusting can thus be obtained without any loss in its potentiometric response property. All-solid-state membrane electrodes are also cheap, easy to prepare, and allow miniaturizing construction. In this paper, we therefore describe the preparation of all-solid-state PVC membrane Ag^+-selective electrodes based on two different diaza-crown ethers (Fig. 1) previously synthesized in our laboratory and recorded in literature [23, 24]. The potentiometric behavior of all-solid-state PVC membrane silver-selective electrodes based on these neutral carriers and flow-injection analysis for the determination of Ag^+ ions were investigated.

Experimental

Equipment

Potential measurements were performed with an Olivetti-286 home computer equipped with a custom built (Molspin Instruments, Newcastle-upon-Type, UK) analog/output board and electrode interface module controlled by laboratory written software. All potential measurements were made with reference to a porous-plug double-junction saturated calomel electrode (Russel, Auchtermuchty, Fife, UK) in solutions with stirring by means of a magnetic stirring bar.

The compounds N,N′-Dibenzyl-7,16-diaza-1,4,10,13-tetraoxa-2,3,11,12-dibenzocycloocta deca-2,11-diene (1) and N,N′-Dibenzyl-7,16-diaza-1,4,10,13-tetraoxa-2,3-benzocyclooctadec-2-ene (2) were synthesized and purified according to the procedures of the literature [24].

For the preparation of the PVC membrane cocktails, high molecular mass poly(vinylchloride) (PVC), potassium tetrakis(4-chlorophenyl) borate (KTClPB), 2-nitrophenyl octyl ether (o-NPOE), Dioctyl sebacate (DOS), Dibutyl(phthalate) (DBP), tetrahydrofuran (THF), obtained from Fluka (Buchs, Switzerland) were used. The silver nitrate and reagent grade nitrates and chlorides of sodium, potassium, ammonium, calcium, magnesium, copper, nickel, lead, zinc, cadmium, mercury, cobalt, iron (II), and (III), chromium and aluminium were supplied by Merck (Darmstad, Germany). All other reagents were of analytical grade and were used to prepare buffers and standard solutions. Deionized water was used for all experiments.

Preparation of All-Solid-State PVC Membrane Ag^+-Selective Electrodes

The construction of all-solid-state PVC matrix membrane Ag^+-selective electrodes without an inner reference solution was carried out as described below. The epoxy resin mixture used to bind the graphite in preparing the internal conductivity support of the electrode was made from epoxy (Macroplast Su 2227, Henkel) and hardener (Desmodur RFE, Bayer) in THF solvent in the proportions 1.0:0.5 w/w. The powdered graphite was mixed with the epoxy resin mixture in the proportions 1.0:1.0 w/w. After mixing, the solution was allowed to stand for 20–30 min in air. When the appropriate viscosity was attained, a shielded copper wire (ca. 0.5–1 mm in diameter and 10 mm long) was polished and dipped in the solution several times to obtain a uniform coating, and allowed to stand overnight in an oven at 40 °C. The all-solid-states were dipped into the membrane solution at appropriate viscosity three times, and then the coated membranes were allowed to dry in air for at least 3 h [25]. The Ag^+-selective membrane solution comprised neutral carrier, plasticizer, KTpClB and PVC, dissolved in 5 mL of THF (Table 1). The prepared membrane electrodes were then soaked in a 10^{-2} M solution of $AgNO_3$ for at least 6 h before use. Performance characteristics of the prepared electrodes were subsequently examined by measuring the emfs of silver nitrate solutions with a concentration range of $0.1–10^{-7}$ M. The electrochemical cell was Cu/all-solid-state PVC membrane/measured solution/reference electrode.

Flow-Through Detector Cell and FIA System

A flow-through detector cell was prepared for FIA of Ag^+ ion. The construction of the tubular flow-through membrane electrode without inner reference solution was carried out as described in our recent study [26, 27]. The detector cell consisted of the flow-through

Table 1. Optimization of membrane composition

Composition (%)						Slope (mV per decade)*	Linear range (M)	Detection limit (M)
	PVC	NPOE	DOS	DBP	KTClPB			
Ionophore 1								
2.8	28.2	68	–	–	1.0	72 ± 14	$1\times10^{-5}-5\times10^{-2}$	5×10^{-6}
3.2	28.0	68	–	–	0.8	75 ± 10	$7\times10^{-6}-1\times10^{-1}$	3×10^{-6}
3.6	27.6	68	–	–	0.8	75 ± 12	$5\times10^{-6}-1\times10^{-1}$	3×10^{-6}
4.0	27.0	68	–	–	1.0	75 ± 12	$8\times10^{-6}-1\times10^{-1}$	3×10^{-6}
3.2	27.8	–	68		1.0	70 ± 12	$2\times10^{-5}-5\times10^{-2}$	1×10^{-5}
3.2	27.8	–	–	68	1.0	70 ± 14	$2\times10^{-5}-5\times10^{-2}$	1×10^{-5}
3.2	28.8	68	–	–	–	70 ± 30	$3\times10^{-5}-5\times10^{-2}$	1×10^{-5}
Ionophore 2								
3.2	28.0	68	–	–	0.8	90 ± 12	$1\times10^{-5}-1\times10^{-1}$	6×10^{-6}

* Values represent the average potentials and standard deviations ($\bar{x} \pm \lambda(\bar{x})$) for n = 10 with the confidence level of 95%, obtained with two electrodes.

tubular PVC membrane Ag^+-selective electrode and the double junction calomel reference electrode. The FIA system, which was similar to that proposed in our recent work [28] except for the detector cell which is potentiometric in the present case, consisted of the tubular flow-through detector cell, an HPLC pump (Perkin Elmer Series 3) with a Rheodyne injection valve and tubings. The carrier solution was 10^{-2} M sodium nitrate adjusted to pH 4.0 with nitric acid.

Results and Discussion

Performances of the All-Solid-State PVC Membrane Ag^+-Selective Electrodes

The selectivity of ordinary crown ethers for heavy and transition metal ions is much lower than that for alkali cations [29]. But the replacement of oxygen donor atoms by nitrogen atoms in the mycrocyclic ring, with sufficient rigidity and lipophilicity, was expected to increase the membrane selectivity toward heavy metal ions over alkali and alkaline earth cations [30]. Therefore, we prepared all-solid-state PVC membrane Ag^+-selective electrodes using two structurally different diaza-crown ether compounds as neutral carriers and initially measured the potential responses of both electrodes to a variety of metal ions including alkali and alkaline earth, heavy and transition metal ions, and some anions (Fig. 2a and b). In preliminary experiments, for the electrode based on ionophore 1 with NPOE as the plasticizer, a linear potential response with a slope of 75 ± 10 mV per decade is observed for the Ag^+ ion within a wide concentration range of $1\times10^{-1}-7\times10^{-6}$ M. For the electrode based on ionophore 2 consisting of NPOE as the plasticizer, the linear response was 90 ± 12 mV within the concentration range of $1\times10^{-1}-10^{-5}$ M. The limit of detection of the all-solid-state PVC membrane

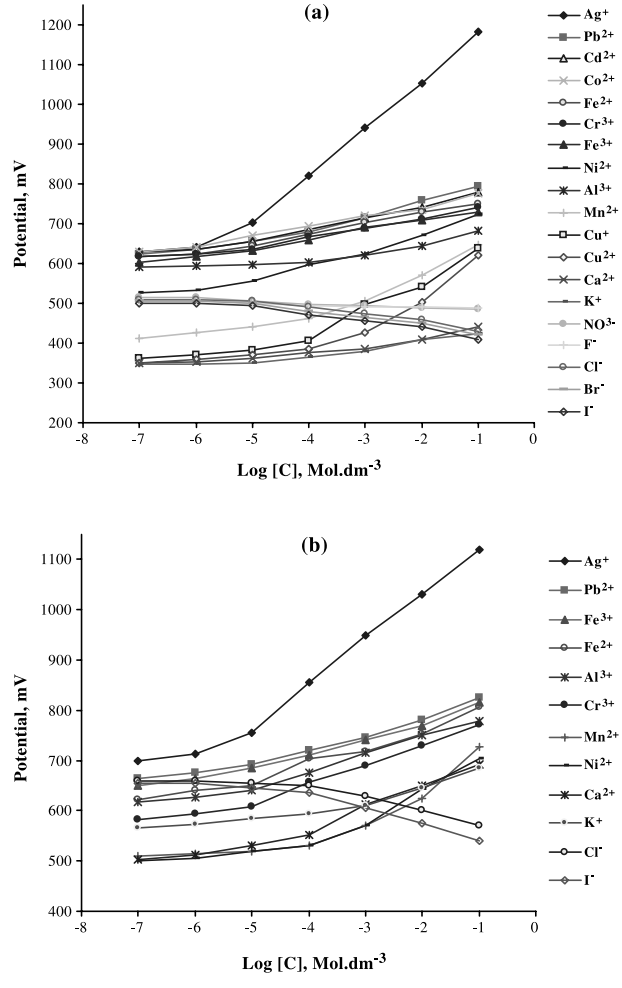


Fig. 2. Potentiometric response of all-solid-state PVC membrane Ag^+-selective electrode based on ionophore 1 (a) and ionophore 2 (b) to several cations

Ag^+-selective electrodes based on ionophore 1 and 2 was 3×10^{-6} M and 6×10^{-6} M, respectively, as evaluated from the intersections of the two extrapolated

segments of the calibration graphs. Both electrodes exhibited a negligible response to univalent, bivalent and polyvalent cations in the solution. However, it should be noted here that both electrodes exhibited some degree of response toward halide anions, in opposite direction to that of silver, while no response was observed to the other anions tested. The decrease in the measured potential confirms the release of Ag^+ from the membrane to form insoluble Ag^+-halide compounds in the surface of the membrane or in solution [31].

Since it was concluded that diaza-18-crown-6 compounds are excellent neutral carriers in Ag^+-selective PVC membranes, all-solid-state PVC membrane Ag^+-selective electrodes based on ionophore 1 were evaluated over the membrane composition which significantly influences the sensitivity and selectivity of a given electrode [29]. The results are summarized in Table 1. As can be seen from the Table, variations in amounts of ingredients, among the compositions used, do not cause a significant difference in the electrode performance. However, the presence of KTClPB in the membrane is needed to increase the selectivity [32] and also the conductivity of the membrane [33]. The electrode did not exhibit a stable response to Ag^+ ion when the lipophilic salt was not incorporated in the membrane. Several plasticizers including NPOE, DOS and DBP, which are common PVC membrane solvents, were also examined. Among the plasticizers, NPOE gave a better sensitivity and linear range. The reason can be the high polarity of NPOE which works better at PVC membrane electrodes based on neutral ionophores [34]. Overall, the membrane composition consisting of 3.2% neutral ionophore, 28% PVC, 68% o-NPOE and 0.8% KTClPB, resulted in the best sensitivity and widest linear range and selectivity among the cations of all groups.

Potentiometric selectivities of all-solid-state PVC membrane Ag^+-selective electrodes toward Ag^+ cation relative to alkali, alkaline earth, heavy and transition metal cations were determined by the fixed interference method [35]. The selectivity coefficients expressed as $-\log k^{pot}_{Ag,M^{n+}}$ are presented in Fig. 3. All-solid-state PVC membrane electrodes based on both ionophores exhibit high selectivity for Ag^+ over all cations tested. Ionophore 1, which has two phenylene groups incorporated into the mycrocyclic ring, exhibited quite a high Ag^+ selectivity relative to the metal cations tested. Ionophore 2, which has one phenylene

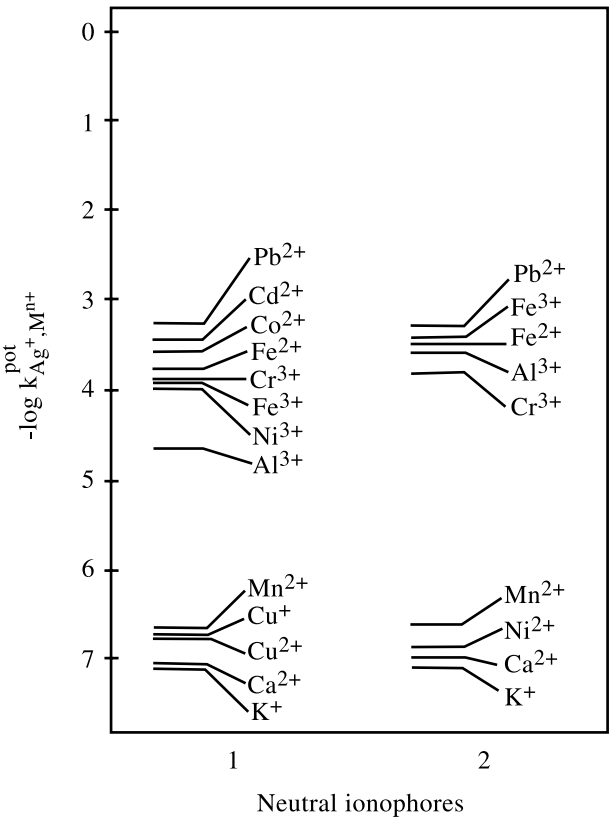


Fig. 3. Selectivity coefficients of the all-solid-state PVC membrane Ag^+-selective electrodes based on ionophores 1 and 2. The ionophore is indicated at the bottom of the Fig.

group in the ring, gave a selectivity diminished almost by a factor of two or more when compared to ionophore 1. A distinguished decrease in the selectivity for Ag^+ relative to Cu^{2+}, Mn^{2+}, Ca^{2+} and K^+ also occurred with ionophore 2, although these selectivities are superior to those for a crown ether [36] and hexathia-crown ether [37] ionophores. Incorporation of nitrogen atoms and phenylene groups into the mycrocyclic ring of a crown ether compound enhances the Ag^+ selectivity over all cations tested.

The response time (t_{95}%) of the electrode was measured as the time required to reach 95% of the steady potential value for a 10^{-4} M solution, the Ag^+ concentration was rapidly increased from 10^{-5} to 10^{-4} M or from 10^{-4} to 10^{-3} M, and the t_{95}% values was measured with the all-solid-state electrodes based on both ionophores. The response time obtained was always less than 10 s for both electrodes.

The pH dependence of the electrode response was examined using 10^{-4} M $AgNO_3$ solution adjusted with nitric acid and sodium hydroxide. The

all-solid-state PVC membrane Ag^+-selective electrode based on ionophore 1 showed a potential unchanged between pH 4–7. With ionophore 2, the electrode response was slightly pH-dependent. An increase in potential was observed at levels lower than pH 5.0, which may be due to easy protonation of the ionophore 2. The pH dependence of the electrode was not tested over pH 7.0 due to basicity of the solution in which silver can obviously react with hydroxide to give insoluble silver hydroxide precipitate.

FIA Application

A tubular flow-through detector cell, as described previously [26, 27], prepared with Ag^+-selective membrane based on ionophore 1 was successfully applied for the determination of Ag^+. The pump was used to propel the samples and carrier solution. Ag^+ ion solutions were injected into the carrier stream by a Rheodyne injection valve provided with a 100 µL loop. In the system, the potential of Ag^+ ions was measured with the tubular flow-through detector which was connected to a computer with incorporated data acquisition software. A calibration graph was obtained under the working conditions: flow rate $0.8\,mL \cdot min^{-1}$, volume injected 20 µL, and sodium nitrate carrier solution at pH 4.0. The calibration graph was linear over the range of $1 \times 10^{-2} - 1 \times 10^{-5}$ M standard solution of Ag^+ ion. The relative standard deviation for 10 injections of standard sample containing 1×10^{-4} M Ag^+ ion was less than 1%. The short response time and sensitivity of the all-solid-state PVC membrane Ag^+-selective electrode cell allowed a detection limit (signal-to noise ratio of 3) of 2×10^{-6} M for a 20 µL injection volume under the working conditions.

References

[1] Ammann D, Morf W E, Anker P C, Pretsch E, Simon W (1983) Ion Sel Electrode Rev 5: 3
[2] Ohki A, Lu J P, Bartsch R A (1994) Anal Chem 66: 651
[3] Daunert S, Bachas L G (1990) Anal Chem 62: 1428
[4] Moody G J, Saad B B, Thomas J D R (1988) Sel Electrode Rev 10: 71
[5] Ito T (1998) Anal Sci 14: 89
[6] Janata J, Josowics M, Vanysek P, Devaney D M (1988) Anal Chem 70(R): 179
[7] Mashhadizadeh M H, Shamsipur M (1999) Anal Chim Acta 381: 111
[8] Mahajan R K, Kumar M, Sharma V, Kaur T (2001) Analyst 126: 505
[9] Perez-Marin L, Lopez-Valdivia H, Avila-Perez P, Otazo-Sanchez E, Macedo-Miranda G, Gutierrez-Lozano O, Alonso J, De Torres-Orazco J, Carapia-Morales L (2001) Analyst 126: 501
[10] Umezawa Y (1990) CRC handbook of ion selective electrodes. CRC Press, Boca Raton, FL
[11] Rieckemann B, Umland F, Frezeniuss Z (1986) Anal Chem 326: 241
[12] Visser H C, Reinhoudt D N, De Jong F (1994) Chem Soc Rev, p 75
[13] Faulkner S, Kataky R, Parker D, Teasdale A (1995) J Chem Soc, Perkin Trans 2: 1761
[14] Fakhari A, Ganjali M R, Shamsipur M (1997) Anal Chem 69: 3693
[15] Shamsipur M, Rouhani S, Sharghi H, Ganjali M R, Eshgi H (1999) Anal Chem 71: 4839
[16] Ganjali M R, Moghimi A, Shamsipur M (1998) Anal Chem 70: 5259
[17] Tavakkoli N, Shamsipur M (1996) Anal Lett 29: 2269
[18] Shamsipur M, Poursaberi T, Rouhani S, Nicham K, Sharghi H, Ganjali M R (2000) Anal Sci 17: 1049
[19] Buhlmann P, Pretsch E, Bakker E (1998) Chem Rev 98: 1593, and references therein
[20] Mousavi M F, Sahari S, Alizadeh N, Shamsipur M (2000) Anal Chim Acta 414: 189
[21] Magalhaes J M C S, Cespedes F, Alegret S, Machado A A S C (1997) Anal Chim Acta 355: 241
[22] Alegret S, Florido A (1991) Analyst 116: 473
[23] Demirel N (1999) M.Sc. Thesis, Diyarbakır, Turkey
[24] Topal G, Demirel N, Togrul M, Turgut Y, Hosgoren H (2001) J Hetereocyclic Chem 38: 281
[25] Isildak I (2000) Turkish J Chem 24(4): 389–394
[26] Isildak I (1999) Chromatographia 49(5–6): 338
[27] Isildak I, Cavington A K (1993) Electroanalysis 5: 815
[28] Asan A, Andac M, Isildak I (2001) Anal Sci 17(9): 1125
[29] Bakker E, Buhlmann P, Pretsch E (1997) Chem Rev 97: 3083, and references therein
[30] Izatt R M, Pawlak K, Bradshaw J S, Bruening R L (1991) Chem Rev 91: 1721
[31] Bakker E (1996) Sensor Actuator B 35(1–3): 20
[32] Ammann D, Pretsch E, Somin W, Simon W, Lindner E, Bezegh A, Pungor E (1985) Anal Chim Acta 171: 119
[33] Eugster R, Gehrig P M, Morp W E, Spichiger U, Simon W (1991) Anal Chem 63: 2285
[34] Ohki A, Maeda S, Lu J P, Bartsch R A (1994) Anal Chem 66: 1743
[35] Recommendation for Nomenclature of Ion Selective Electrodes (1976) Pure Appl Chem 48: 127
[36] Su C C, Chang M C, Liu L K (2001) Anal Chim Acta 432: 261
[37] Mashhadizadeh M H, Shamsipur M (1999) Anal Chim Acta 381: 111