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Chinese Chemical Letters 21 (2010) 464-467

CHINESE Chemical Letters

www.elsevier.com/locate/cclet

# A comparative study of four 20-membered $N_2S_4$ -crown ethers as ionophores for polymeric membrane silver selective electrodes

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Received 17 August 2009

#### Abstract

Four 20-membered N<sub>2</sub>S<sub>4</sub>-monoazathiacrown ethers have been synthesized and explored as neutral ionophores for Ag<sup>+</sup>-selective electrodes. Potentiometric responses reveal that the flexibility of the ligands has great effect on the selectivity and sensitivity to Ag<sup>+</sup> ions. The electrode based on ionophore 9,10,20,25-tetrahydro-5*H*,12*H*-tribenzo[b,n,r][1,7,10,16,4,13]tetrathiadiaza cycloicosine 6,13-(7*H*,14*H*)-dione (**C**) with 2-nitrophenyl octyl ether (*o*-NPOE) as solvent in a poly(vinyl chloride) (PVC) membrane matrix shows a measuring range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-3}$  mol/L with a Nernstian slope of  $54.9 \pm 0.3$  mV/decade. This electrode has high selectivity for Ag<sup>+</sup> with negligible interference from many other cations and can be used in a wide pH range of 3.6-9.2. (**C**) 2009 Wei Qin. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Ion-selective electrodes; Silver; Ionophore; Azathiacrown ether

Crown ethers containing S and/or N as donor atoms are of interest as they exhibit high affinities towards transition metal ions [1]. Most of transition metal ionophores for use in ion-selective electrodes (ISEs), such as  $Ag^+$ -ionophores, possess S and/or N atoms. The selectivity of crown ethers towards  $Ag^+$  is tunable by altering the composition of donor atoms, ring size and ligand geometry [2]. Many crown ethers have been utilized as  $Ag^+$ -ionophores [3,4]. However, most of them suffer from problems of complicated synthesis procedures and poor selectivities. In this work, four 20-membered  $N_2S_4$ -crown ethers have been synthesized as  $Ag^+$ -ionophores by a simple route with high yields, and electrodes based on these ionophores show excellent affinities to  $Ag^+$ . The effects of flexibilities of these ligands on the response of polymeric membrane  $Ag^+$ -ISEs have been studied.

## 1. Experimental

The ionophores A-D were synthesized by a three-step reaction (Scheme 1). A solution of 4 or 5 [5] (0.5 mmol) in DMF (50 mL) and a solution of ethane-1,2-dithiol or benzene-1,2-dithiol in DMF (50 mL) were added simultaneously to 50 mL DMF containing 2 mmol anhydrous Na<sub>2</sub>CO<sub>3</sub> over 1.5 h at room temperature. At the end of this period, the

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Scheme 1. The synthesis route of crown ethers A-D.

solvent was removed under reduced pressure. The solid was washed with water and dried in vacuum. The products so obtained were recrystallized from DMF to give white crystals of A-D [6–9].

The membranes contained (totaling 134.6 mg) ionophore, 2-nitrophenyl octyl ether (*o*-NPOE), poly(vinyl chloride) (PVC) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) with a thickness of 180  $\mu$ m. All the electrodes were conditioned with 0.01 mol/L AgNO<sub>3</sub> overnight. Membrane potentials were measured in the galvanic cell: SCE//1 M LiOAc/sample solution/ISE membrane/inner solution/AgCl/Ag.

#### 2. Results and discussion

The optimization of ISE membrane was performed by varying different plasticizers and amounts of ionophore and ion-exchanger. The membrane containing (in wt%) ionophore (1.0), *o*-NPOE (65.7), PVC (32.9) and NaTFPB (0.4) shows the best response to Ag<sup>+</sup>. The selectivity coefficients of Ag<sup>+</sup>-ISEs were measured according to Bakker's method [10] (Table 1). Using log  $K_{Ag,EI4N}^{pot} = 4.84$  for the ionophore-free membrane [11], formal complex formation constants, log  $\beta = 6.47, 7.32, 9.56$  and 4.63, were obtained for ionophores A–D, respectively. The data show that electrode based on ionophore C has better selectivity and sensitivity to Ag<sup>+</sup> compared to other three ionophores (Fig. 1). Since the number of donor atoms and the ring-member are the same, the hardness of the benzene group plays an important role in the selectivity of A–D to Ag<sup>+</sup> by affecting the flexibility of the crown ethers. The ISE using ionophore C shows Nernstian response over a concentration range of  $10^{-6}$  to  $10^{-3}$  mol/L with a response time of <15 s. The standard deviation of the Nernstain response slope for one electrode is 0.3 mV/decade (n = 3). The ISE can be used in a pH range of 3.6–9.2 with a lifetime of 2 months.

The fabricated ISE based on ionophore C was successfully used as an indicator electrode for potentiometric titration of chloride ions. Fig. 2 shows a typical titration curve of KCl solution with AgNO<sub>3</sub> as titration reagent, which indicates that the end-point can be accurately determined by the proposed ISE.

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Ion J	Iono. A	Iono. B	Iono. C	Iono. D
Li <sup>+</sup>	-5.68 (47.83)	-7.00 (48.75)	-9.39 (55.35)	-6.66 (56.0)
$H^+$	-5.35 (60.82)	-6.74 (63.56)	-8.96 (53.85)	-6.21 (63.3)
Na <sup>+</sup>	-5.12 (57.93)	-6.28 (52.40)	-8.64 (50.78)	-5.99 (53.90)
K <sup>+</sup>	-3.63 (53.64)	-5.06 (53.63)	-6.94 (52.68)	-4.84 (53.70)
Mg <sup>2+</sup>	-6.64 (29.60)	-7.76 (24.83)	-10.38(26.94)	-7.57 (25.9)
Ca <sup>2+</sup>	-10.83 (35.87)	-7.39 (29.32)	-9.95 (29.81)	-7.27 (33.9)
Cu <sup>2+</sup>	-6.27 (32.81)	-7.47 (25.12)	-9.36 (21.34)	-7.24 (34.8)
Cd <sup>2+</sup>	-6.47 (32.32)	-8.04 (27.35)	-9.74 (22.55)	-7.23 (26.8)
Pb <sup>2+</sup>	-5.85 (34.35)	-6.13 (27.39)	-8.55 (29.05)	-6.62 (35.0)
Hg <sup>2+</sup>	0.54 (56.94)	-0.58 (63.13)	-0.99 (60.30)	-1.55 (81.4)
$Et_4N^+$	0.65 (58.31)	-0.64 (55.02)	-3.08 (58.75)	1.41 (58.03)

Table 1 Potentiometric selectivity coefficients,  $\log K_{Avl}^{\text{pot}}$ , and response slopes obtained with membranes based on ionophores A–D.



Fig. 1. EMF responses of the ionophores (A-D)-based Ag<sup>+</sup>-ISEs. Inset shows the time-dependent EMF response of the C-based Ag<sup>+</sup>-ISE.



Fig. 2. Titration curve of 50 mL of 10<sup>-3</sup> mol/L KCl with 0.1 mol/L AgNO<sub>3</sub> obtained by using Ag<sup>+</sup>-ISE based on ionophore C.

#### Acknowledgments

This work was financially supported by the Chinese Academy of Sciences (No. KZCX2-YW-410), the National Natural Science Foundation of China (No. 40776058), the National 863 High Technology Project of the Ministry of Science and Technology of China (No. 2007AA09Z103), the Outstanding Youth Natural Science Foundation of Shandong Province (No. JQ200814) and the Taishan Scholar Program of Shandong Province.

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- [6] 9,10,12,13,15,17,23,24,25,26-Decahydrodibenzo[b,q][1,7,10,13,19,4,16]pentathiadiaza cyclotricosine 6,16-(5H,7H)-dione A: 91.2%, mp: 217.5–218.3 °C. MS: *m*/z 501.10 [M+Na]<sup>+</sup>. IR (KBr tablet, cm<sup>-1</sup>): 3290.9 (N–H), 1670.0 (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.78 (s, 2H, N–H), 8.36–8.38 (d, 2H, Ar–H), 7.44–7.50 (d, 2H, Ar–H), 7.26–7.35 (t, 2H, Ar–H), 7.06–7.10 (t, 2H, Ar–H), 3.45–3.49 (s, 4H, O=CCH<sub>2</sub>), 2.95–2.99 (t, 4H, ArSCH<sub>2</sub>), 2.79 (t, 4H, SCH<sub>2</sub>), 1.59–1.65 (m, 4H, CH<sub>2</sub>).

- [7] 14,16,22,23,24,25-Hexahydrotribenzo[b,h,n][1,7,10,16,4,13]tetrathiadiaza cycloicosine 6,15-(6H,11H)-dione B: 92%, mp: 201.2–203.0 °C. MS: *m*/z 549.04 [M+Na]<sup>+</sup>. IR (KBr tablet, cm<sup>-1</sup>): 3269.7 (N–H), 2920.7 (Ar–H), 1689.3 (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.93 (s, 2H, NH), 8.44–8.46 (d, 2H, Ar–H), 7.48–7.52 (d, 2H, Ar–H), 7.33–7.37 (t, 2H, Ar–H), 7.26–7.28 (d, 2H, Ar–H), 7.14–7.21 (t, 2H, Ar–H), 7.05–7.09 (t, 2H, Ar–H), 3.84–3.91 (s, 4H, O=CCH<sub>2</sub>), 2.66 (t, 4H, SCH<sub>2</sub>), 1.53–1.56 (m, 2H, SCH<sub>2</sub>CH<sub>3</sub>).
- [8] 9,10,20,25-Tetrahydro-5*H*,12*H*-tribenzo[b,n,r][1,7,10,16,4,13]tetrathiadiaza cycloicosine 6,13-(7*H*,14*H*)-dione C: 89%, mp: 240.5–241.1 °C (lit. 133–136 °C [5]). MS: *m/z* 527.09 [M+1]<sup>+</sup>. IR (KBr tablet, cm<sup>-1</sup>): 3269.7 (N–H), 1657.5 (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.70 (s, 2H, N–H), 8.35–8.37 (d, 2H, Ar–H), 7.33–7.37 (d, 2H, Ar–H), 7.12–7.16 (t, 2H, Ar–H), 7.01–7.05 (d, 2H, Ar–H), 6.98–7.00 (t, 2H, Ar–H), 4.00 (s, 4H, O=CCH<sub>2</sub>), 3.40 (t, 4H, ArSCH<sub>2</sub>), 2.96–2.97 (t, 4H, SCH<sub>2</sub>).
- [9] 17,19,26,28-Tetrahydrotetrabenzo[b,h,n,r][1,7,10,16,4,13]tetrathiadiaza cycloicosine 18,27-(6H,11H)-dione D: 93.5%, mp: 47.8–49.1 °C. MS: *m/z* 575.09 [M+1]<sup>+</sup>. IR (KBr tablet, cm<sup>-1</sup>): 3287.1 (N–H), 1678.7 (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): *δ* 9.56 (s, 2H, NH), 8.40–8.42 (d, 2H, Ar–H), 7.33–7.36 (t, 4H, Ar–H), 7.20–7.23 (t, 2H, Ar–H), 7.13–7.16 (t, 2H, Ar–H), 7.00–7.03 (t, 2H, Ar–H), 6.86–6.90 (t, 2H, Ar–H), 6.43–6.47 (t, 2H, Ar–H), 3.93 (s, 4H, O=CCH<sub>2</sub>), 3.85 (s, 4H, SCH<sub>2</sub>).
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