CHARACTERIZATION OF A NEW Ag^+ -SELECTIVE ELECTRODE BASED ON N_3S_5 -THIAAZACROWN ETHER AS NEUTRAL IONOPHORE

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ABSTRACT

A N_3S_5 -azathiacrown ether has been newly synthesized in high yield. Electrode using this compound as ionophore shows high selectivity and sensitivity towards Ag^+ . The effect of plasticizers and ion-exchanger on the properties of electrode was also studied and detection limit of 3.8×10^{-8} M Ag^+ was obtained. This sensor has a fast response time of <12 s and performs satisfactorily over a wide pH range of 3.6–8.2. The electrode was also successfully used as indicator electrode in the titration of Cl^- in tap water.

Keywords: Silver; Ion-selective electrode; Azathiacrown ether.

1. INTRODUCTION

With the development of industry, many severe accidents were caused by heavy metals pollution. Selective and sensitive detection of heavy and transition metal ions is of great importance from the ecotoxicological point of view.¹ Silver has been widely used in the photographic film production industry, the electrical and electronic industries. Silver salts have been successfully applied to disinfect water for drinking and recreation purposes, dental and pharmaceutical antibacterial agents, owing to their unique germicidal properties. However, silver can inactivate sulfhydryl enzymes, and combine with amine, imidazole and carboxyl groups of various metabolites. An excess of silver is toxic to fish and microorganisms at a concentration as low as $0.17 \mu\text{g/L}$.² Because of the increasing demand of silver compounds in industry and common life, severe contamination of the environment by silver is rising. Therefore, the sensitive and selective determination of silver is very important.

Crown ethers are powerful tools for separation, enrichment and analysis of ionic species and have enjoyed widespread use in various areas of science and technology.³ One of the successful applications of them is in analytical chemistry. In particular, ion-selective electrodes (ISEs) is the most important target in analytical applications due to their good properties such as high selectivity, good precision, low cost and simplicity.⁴⁻⁸

Since dithiacrown ethers were employed in the first neutral carrier-type Ag^+ -ISEs, which showed high Ag^+ -selectivity against alkali metal ions,⁹ thiaethers have been a very important class of ionophores for Ag^+ -ISEs.^{6-8,10-12} However, the applications of crown ethers are often subject to the difficulties of synthesis technique. Taking this into consideration, we reported a simple method for the synthesis of azathiacrown ether with high yield in this work. This ligand is expected to form selective complexes with transition metal ions and to give an improved selectivity for silver ions. Potentiometric evaluation of the plasticized poly (vinyl chloride) (PVC) membrane electrodes using those compounds as Ag^+ -ionophore has been done in terms of its selectivity coefficients and detection limit for Ag^+ .

2. EXPERIMENTAL

2.1. Reagents and instrumentation

2, 2'-thiodiethanethiol, 2-nitrophenyl octyl ether (*o*-NPOE), bis (2-ethylhexyl) sebacate (DOS), dibutylphthalate (DBP), dioctyl phthalate (DOP), sodium tetrakis [3, 5-bis (trifluoromethyl)phenyl]borate (NaTFPB) and PVC were purchased from Sigma-Aldrich. All other reagents used were purchased from Sinopharm Chemical Reagent and of analytical grade purity or better. Deionized water with specific resistance of $18.2 \text{ M}\Omega \text{ cm}$ was obtained by a Pall Cascada laboratory water system.

Melting points were taken on a WRS-1B digital melting-point apparatus. Infrared (IR) spectra were recorded on KBr pellets using Perkin-Elmer 1430 spectrometer. Nuclear magnetic resonance (NMR) spectra were measured with a Bruker WM-300 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agilent 1100.

The synthesis route of thiaazacrown ether **L** was shown in Scheme 1.

Scheme 1. The synthesis route of azathiacrown ether **L**.

2.2. Synthesis of azathiacrown ether **L**

2.2.1 Synthesis of compound **1**

Compounds **1** was synthesized as described before.¹³ ¹H NMR (δ : ppm, d_6 -DMSO): 8.06-8.08 (d, 2H, Ar-H), 6.92-6.94 (d, 2H, Ar-H), 3.88-3.91 (t, 4H, ClCH₂-H), 3.79-3.82 (t, 4H, NC-H).

2.2.2 Synthesis of compound **2**

2-amino thiophenol (1.25 g, 10 mmol) was added to sodium ethoxide formed by addition of sodium (0.23 g, 10 mmol) to absolute ethanol (50 mL) under nitrogen atmosphere. A degassed solution of **1** (5 mmol) in absolute ethanol (20 mL) was added dropwise to the refluxing sodium thiophenolate solution with constant stirring. After the reaction was finished, the reaction mixture was cooled to room temperature and filter off. The solvent was removed under reduced pressure. The solid so obtained were recrystallized from ethanol as yellow crystal. Yields: 75%, m. p. 129.4-129.9 °C. IR (KBr tablet, cm^{-1}): 3336.25 (N-H), 2923.56 (C-H), 1592.91, 1511.92, 1473.35, 1403.92, 752.10. ¹H NMR (δ : ppm, d_6 -DMSO): 7.78-7.80 (d, 2H, Ar-H), 7.27-7.28 (d, 2H, Ar-H), 7.11-7.14 (t, 2H, Ar-H), 6.79-6.80 (d, 2H, Ar-H), 6.55-6.58 (t, 2H, Ar-H), 6.22-6.24 (d, 2H, Ar-H), 5.38 (s, 4H, N-H), 3.47-3.50 (t, 4H, C-H), 2.84-2.87 (t, 2H, C-H). ¹³C NMR (δ : ppm, d_6 -DMSO): 152.21 (C-NO₂), 150.20, 136.41, 136.00, 130.29, 126.19, 116.97, 114.99, 114.69, 110.68 (Ar-C), 50.55 (N-CH₂), 30.30 (S-CH₂).

2.2.3 Synthesis of compound **3**

A solution of chloroacetic anhydride (50 mmol) in CH_2Cl_2 (50 mL) was added through a dropping funnel to a stirred solution of **2** (16 mmol) in CH_2Cl_2 (250 mL) at 0-5 °C over a 1 h period. The mixture was stirred overnight under nitrogen atmosphere at room temperature. At the end of this period, the mixture was filtered off. Filtrate was washed with saturated aqueous NaHCO_3 , and solvent was removed under reduced pressure. The resulting mass was washed with ethanol and diethyl ether and then dried in vacuum. The crude products were purified by recrystallization from acetonitrile to give compounds **3** as dark yellow solids. Yields: 65%, m. p. 167.8- 168.2 °C. IR (KBr tablet, cm^{-1}): 3313.11 (N-H), 2954.41 (C-H), 1681.62 (C=O), 1585.20, 1515.78, 759.82. ¹H NMR (δ : ppm, d_6 -DMSO): 9.74 (s, 2H, NH), 7.92-7.94 (d, 2H, Ar-H), 7.68-

7.70 (d, 2H, Ar-H), 7.53-7.54 (d, 2H, Ar-H), 7.33-7.36 (t, 2H, Ar-H), 7.21-7.24 (t, 2H, Ar-H), 6.48 (t, 2H, Ar-H), 6.46-6.48 (d, 2H, Ar-H), 4.36 (s, 2H, O=C-CH₂Cl), 3.53-3.56 (t, 4H, NCH₂), 3.06-3.09 (t, 4H, S-CH₂). ¹³C NMR (δ: ppm, *d*₆-DMSO): 165.43 (C=O), 152.21 (C-NO₂), 137.52, 136.73, 132.14, 128.56, 128.31, 126.67, 126.36, 125.02, 111.13, (Ar-C), 50.29 (N-CH₂), 43.61 (O=C-CH₂), 30.70 (S-CH₂).

2.2.4 Synthesis of macrocyclic compound **L**

A solution of **3** (0.5 mmol) in DMF (50 mL) and that of 2,2'-thiodiethanethiol (0.5 mmol) in DMF (50 mL) were added simultaneously to a solution of DMF (50 mL) containing 2 mmol anhydrous Na₂CO₃ over 1.5 h. The whole process was operated under nitrogen atmosphere with vigorously stir for overnight at room temperature. The resulting mixture was filtered off and the solvent was removed under reduced pressure. The remaining residue was washed in turn with water, ethanol and diethyl ether and then dried in vacuum. The solid products were collected and crystallized from DMF to obtain pure compounds **L** as yellow crystal. Yields: 85%, m. p. 201.3–202.7 °C. IR (KBr tablet, cm⁻¹): 3313.11 (N-H), 1681.62 (C=O), 1585.20, 1515.78, 1434.78, 759.82. ¹H NMR (δ: ppm, *d*₆-DMSO): 9.75 (s, 2H, N-H), 7.85-7.87 (d, 2H, Ar-H), 7.80-7.81 (d, 2H, Ar-H), 7.57- 7.58 (d, 2H, Ar-H), 7.35-7.39 (t, 2H, Ar-H), 7.19-7.22 (t, 2H, Ar-H), 6.24-6.25 (d, 2H, Ar-H), 3.51-3.54 (t, 4H, NCH₂), 3.46 (s, 4H, O=CCH₂), 3.02-3.05 (t, 4H, S-CH₂), 2.76-2.80 (m, 8H, S-CH₂). ¹³C NMR (δ: ppm, *d*₆-DMSO): 168.52 (C=O), 151.94 (C-NO₂), 138.74, 136.72, 133.60, 128.94, 127.05, 126.34, 126.03, 124.23, 110.77 (Ar-C), 50.60 (NCH₂), 35.74 (O=C-C), 32.74, 31.34, 31.20 (SCH₂). MS: *m/z* 676.12 [M+1]⁺.

2.3. Membrane preparation

The membrane components, containing appropriate amount of PVC, plasticizers (*o*-NPOE, DOS, DBP or DOP), NaTFPB and ionophore (Total 240 mg), were dissolved in 3.0 mL of THF and stirred vigorously for at least 2 h, and then poured into a glass ring (30 mm i.d.) fixed on a glass plate. The solvent was evaporated overnight at room temperature to give a transparent membrane of 180 μm thickness. For each ISE, a disk of 7 mm diameter was punched from the membranes and glued to a plasticized PVC tube (i.d. 6 mm, o.d. 9 mm) with THF/PVC slurry. The tube was then filled with inner filling solution (0.1 M AgNO₃) and conditioned for 1 day in 1.0×10⁻³ M AgNO₃. For long-term measurements, the electrodes were kept in dark to avoid the photolysis of AgNO₃.

2.4. Potential measurements

Membrane potentials were measured with a Model PXSJ-216 digital ion analyzer (Shanghai Instruments) in mechanically stirred solution with magnetic stirrer at room temperature (13 °C, and temperature were corrected) in the galvanic cell: Hg/Hg₂Cl₂|KCl (sat.)||1.0 M LiOAc||sample solution||ISE membrane|0.1 M Ag⁺|Ag/AgCl. Activity coefficients were calculated according to the Debye–Hückel approximation and EMF values were corrected for liquid-junction potentials with the Henderson equation. The reference electrode Hg/Hg₂Cl₂ with double junction was used with 1.0 M LiOAc as salt bridge electrolyte.

2.5. Selectivity measurements

For selectivity measurements, the electrodes with 10×10⁻³ M NaCl as inner filling solution were firstly conditioned in 1.0×10⁻² M NaNO₃ solution overnight. Then, potential measurements were made in the respective nitrate solutions. The sequence of the sample ions was: Li⁺, H⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Hg²⁺ and Ag⁺. For detection of Hg²⁺, solutions were adjusted to pH = 4 using 0.1 M HNO₃ to avoid precipitation. All the measurements were done in three times. The selectivity coefficients were calculated from the potential values according to the separate solution method assuming theoretical slopes.

3. Results and discussion

3.1 Influence of membrane composition

The sensitivity, selectivity, working range and stability of an ISE depend on many factors, such as the nature of the ionophore, the addition of ion-exchanger and the nature of various plasticizers.^{12,14} Therefore, membranes with different compositions have been prepared and their potentiometric response characteristics were evaluated. The effect of plasticizers on Ag⁺-selective electrodes based on different crown ethers is shown in Table 1. It is clear that *o*-NPOE is more effective plasticizer than others in preparing the Ag⁺-ISEs, which can be explained by the fact that *o*-NPOE plasticized PVC membranes have much higher dielectric constants than DOS, DBP and DOP based membranes.¹⁵ In addition, *o*-NPOE plasticized the membranes dissolve the ion association complexes and adjust both permittivity and ion exchanger sites mobility to give highest possible selectivity and sensitivity.

Table 1. Influence of the nature of plasticizers on the characteristics of Ag⁺-ISEs.

Electrode No.	Composition of membrane w%				Liner range, M	Detection limit, M	Slope, mV/dec.
	PVC	Plasticizer	Additive	L			
L_A	32.8	65.6 NPOE	0.65	0.99	1.0×10 ⁻⁷ –3.0×10 ⁻³	3.8×10 ⁻⁸	56.9
L_B	32.8	65.6, DBP	0.65	0.99	1.0×10 ⁻⁵ –3.0×10 ⁻³	3.5×10 ⁻⁶	56.1
L_C	32.8	65.6, DOP	0.65	0.99	3.0×10 ⁻⁶ –1.0×10 ⁻³	5.6×10 ⁻⁷	48.7
L_D	32.8	65.6, DOS	0.65	0.99	1.0×10 ⁻⁵ –3.0×10 ⁻⁴	3.5×10 ⁻⁶	53.1

As we all known, lipophilic anionic additives (NaTFPB) can act as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction. Accordingly, the effects of the amount of NaTFPB in Ag⁺-selective membranes on the electrode characteristics were also investigated. The amount of NaTFPB was altered while maintaining the same amounts of ionophore, PVC and plasticizer (*o*-NPOE) in the membranes (Table 2). The results show that the electrode based on ionophore **L** and NaTFPB in a mole ratio of 2:1 present the best potential responses, which indicates that compound **L** form complex with silver ion in a mole ratio of 1:1 in membrane phase. The time-dependent potentiometric response of Ag⁺-ISE based on **L** with optimal compositions are given in Fig.1, and we can see that the electrode reached the equilibrium response in a very short time (<12 s).

Table 2. Influence of NaTFPB concentrations on the characteristics of Ag⁺-ISEs.

Electrode No.	Composition of membrane w%				Liner range, M	Detection limit, M	Slope, mV/dec.
	PVC	Plasticizer	Additive	L			
L_A	32.8	65.6, NPOE	0.65	0.99	1.0×10 ⁻⁷ –3.0×10 ⁻³	3.8×10 ⁻⁸	56.9
L_E	32.8	65.8, NPOE	0.43	1.00	3.0×10 ⁻⁶ –1.0×10 ⁻³	5.6×10 ⁻⁷	57.0
L_F	32.9	65.8, NPOE	0.33	1.00	1.0×10 ⁻⁶ –1.0×10 ⁻³	3.0×10 ⁻⁷	55.4

Fig. 1: Time-dependent EMF responses of the Ag^+ -ISEs (Sensor No. L_A): a, 3.0×10^{-2} ; b, 3.0×10^{-3} ; c, 3.0×10^{-4} ; d, 3.0×10^{-5} ; e, 3.0×10^{-6} ; f, 3.0×10^{-7} ; g, 3.0×10^{-8} M.

3.2 Potentiometric selectivity of silver electrodes

The influence of interfering ions on the response behavior of the ISE is usually described in terms of selectivity coefficients. The selectivity coefficients, K_{AgJ}^{pot} , of Ag^+ -ISE were determined by using Bakker's method to eliminate the influence of the inherent sensitivity limit on the response toward discriminated ions.¹⁶ Table 3 shows the selectivity coefficients of Ag^+ -ISE based on the ionophore **L**. It can be seen that the electrode based on **L** as ionophore gives the best selectivity and sensitivity toward Ag^+ than other cations.

Moreover, the complex formation constants, $\lg \beta_{IL}$, of Ag^+ have been calculated for all ionophores, according to the proposed method.¹⁷ The $\lg \beta_{IL}$ values of sensors based on ionophores **L** was 9.46. The result also indicate that ligand **L** has good affinity and selectivity towards Ag^+ .

Table 3. Potentiometric selectivity coefficients and response slopes obtained with the separate solution method for *o*-NPOE/PVC membranes based on ionophore **L**

Ions	$\log K_{AgJ}^{pot}$	Ions	$\log K_{AgJ}^{pot}$
Ag^+	0 (57.82)	Ca^{2+}	-7.83 ± 0.02 (33.67)
Li^+	-7.62 ± 0.01 (46.34)	Cu^{2+}	-8.19 ± 0.01 (32.66)
H^+	-7.25 ± 0.02 (53.29)	Cd^{2+}	-8.25 ± 0.03 (22.84)
Na^+	-6.21 ± 0.02 (46.73)	Pb^{2+}	-7.41 ± 0.02 (30.89)
K^+	-5.33 ± 0.01 (58.47)	Hg^{2+}	-1.02 ± 0.01 (54.44)
Mg^{2+}	-8.00 ± 0.01 (19.54)	Et_4N^+	-0.51 ± 0.01 (61.46)

3.3 Effect of pH

The influence of pH on the response of Ag^+ -ISE based on ionophores **L** (for sensor No. L_A) in 1.0×10^{-3} M and 1.0×10^{-4} M AgNO_3 was studied by adjusting the pH of the test solutions with 0.1 M HNO_3 and 0.1 M NaOH (Fig. 2). It is clear that the best performance for the Ag^+ -ISE based on ionophore **L** can be obtained in the pH range of 3.6-8.2.

Fig. 2: pH effect on the performance of sensor based on **L** (Sensor No. L_A) for $\bullet$: 1.0×10^{-3} M Ag^+ , $\blacktriangle$: 1.0×10^{-4} M Ag^+ .

3.4 Life time study of the proposed electrode

The degradation of the sensitivity in the polymeric membrane, resulting from ionophores leaching from the membrane, is dependent upon the lipophilicity and chemical stability of the ionophore. The proposed electrodes based on ionophore **L** can be used over a period of 3 months without significant drift in potentials, because of the high lipophilicity of crown ether. However, it is necessary to point out that the electrode should be stored in dark to avoid the photolysis of AgNO_3 when not in use.

3.5 Analytical applications

The fabricated electrode based on ionophore **L** was successfully used as the indicator electrode for the titration of chloride ion in lab tap water. Titration curves of Cl^- with 0.1 M AgNO_3 solution are illustrated in Fig. 3. From the end-point, the concentration of Cl^- 1.52×10^{-3} M was got, which is lower than the standard value (GB5749-85: 4.63×10^{-3} M).

Fig. 3 Titration curve of 50 mL tap water with 0.1 M Ag^+ as titration reagent obtained by using Ag^+ -ISE based on ionophore **L** (Sensor No. L_A).

In addition, the response characteristic of the proposed PVC membrane electrode is compared with those of the best Ag^+ -ISEs reported earlier (Table 4). It is apparent that the proposed electrode is superior to the existing electrodes with regard to working concentration range and low detection limit.

Table 4 Comparative analysis of proposed electrode with the reported electrodes.

Reference no.	Ionophore	Detection limit, M	Working concentration Range, M
15	bis (dialkyldithiocarbamates)	2.7×10^{-7}	1.0×10^{-6} to 1.0×10^{-3}
18	Calix[2]furano[2]pyrrole	2.6×10^{-7}	1.0×10^{-6} to 1.0×10^{-2}
19	Calixarene derivative	5.0×10^{-6}	5.0×10^{-6} to 1.0×10^{-2}
20	Benzothiazole calix[4] arene	5.0×10^{-7}	1.0×10^{-6} to 1.0×10^{-2}
21	lariat crown ethers	1.0×10^{-6}	5.0×10^{-5} to 5.0×10^{-1}
22	Calix[4]Arene derivative	3.0×10^{-6}	4.2×10^{-6} to 1.0×10^{-1}
This work	Azathiacrown ether	3.8×10^{-8}	3.0×10^{-7} to 3.0×10^{-3}

4. CONCLUSIONS

In summary, we present here the synthesis and characterization of a new azathiacrown ether **L** with good yields and employed as PVC-based membrane electrode for potentiometric determination of Ag^+ . The sensor **L** shows good selectivity, wide working concentration (3.0×10^{-7} – 3.0×10^{-3} M) range, minimum detection limit (3.8×10^{-8} M) and fast response time (<12 s) with a slope of 56.9 mV/decade of activity between pH range 3.6–9.0. The sensor based on **L** has also been used as indicator electrode in the titration of Cl^- concentration of lab tap water.

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