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A Comparative Study of Ag^+-Selective Electrodes Based on Two 21-Membered N_3S_4-Macrocycles as Neutral Ionophores

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The performances of two 21-membered N_3S_4-azathiacrown ethers as neutral carriers for Ag^+-selective electrodes (Ag^+-ISEs) were investigated. Potentiometric responses revealed that the flexibility of the crown ether has great effect on the selectivity and sensitivity of sensors to Ag^+. The addition of ion-exchanger and different plasticizers has also been found to substantially improve the performance of the Ag^+-ISEs. With the optimal conditions, the electrode based on ionophore derived from benzene-1, 2-dithiol gives a better response and reveals a Nernstian behavior over a wide concentration range of 3.0×10^{-7} - 3.0×10^{-3} M with a detection limit of 6.7×10^{-8} M Ag^+. The electrode possesses advantages of low resistance, very fast response time, long lifetime and, especially, good selectivity relative to a wide variety of other cations. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0–8.9. The electrode can be used as indicator electrode in the potentiometric titration of Cl^- in tap water and spiked water.

Keywords: Ion-selective electrode, Silver ion, Crown ether

1. INTRODUCTION

One promising fields within supermolecular chemistry is the preparation of sensors for target analytes. Macrocycles containing nitrogen and/or sulfur atoms as donor sites are of interest as they exhibit high sensitivity towards heavy metal ions, and their selectivity is readily tunable by altering the donor number, ring flexibility and ligand geometries [1-3]. Mixed-donor crown ethers, therefore, form a prospective class of compounds, and one of the successful applications of them is in analytical chemistry. In particular, the ion-selective electrode (ISE) is the most important target in analytical applications due to their good property such as high selectivity, good precision, low cost and simplicity [4].

Due to its germicidal properties, silver salts have been used to disinfect water used for drinking and recreational purposes, in dental and pharmaceutical antibacterial. However, it is also well known that silver inactivates sulfhydryl enzymes, combines with amine, imidazole and carboxyl groups of various metabolites. It has been found that an excess of silver is toxic to fish and microorganisms at a concentration as low as 0.17 μg/L [5]. Because of the increasing demand of silver compounds in industry and common life, severe contamination of the environment by Ag^+ is rising. Thus, the detection of Ag^+ concentration is of great importance.

Since dithiacrown ethers were employed in the first neutral carrier-type Ag^+-ISEs which showed very high Ag^+-selectivities against alkali metal ions [6], thiacrown ethers have been a very important class of ionophores for Ag^+-ISEs [7-9]. However, the application of crown ethers was limited by the synthesis difficulty, many different methods have been proposed, but few give a better yield than 50% [10]. In this work, two new azathiacrown ethers were designed and synthesized in a simple route with high yields (>90%). These ligands, which have different numbers of benzene group as sub-units, are expected to form selective complexes with transition metal ions and to give an improved selectivity for the silver ions. Potentiometric evaluation of the plasticized poly (vinyl chloride) (PVC) membrane electrodes using those two compounds as Ag^+-ionophores has been done in terms of their selectivity coefficients and detection limits for Ag^+. Comparison of the ISEs behavior based on these new ionophores will serve our further understanding of the structure-selectivity relationship in the Ag^+-ISEs.

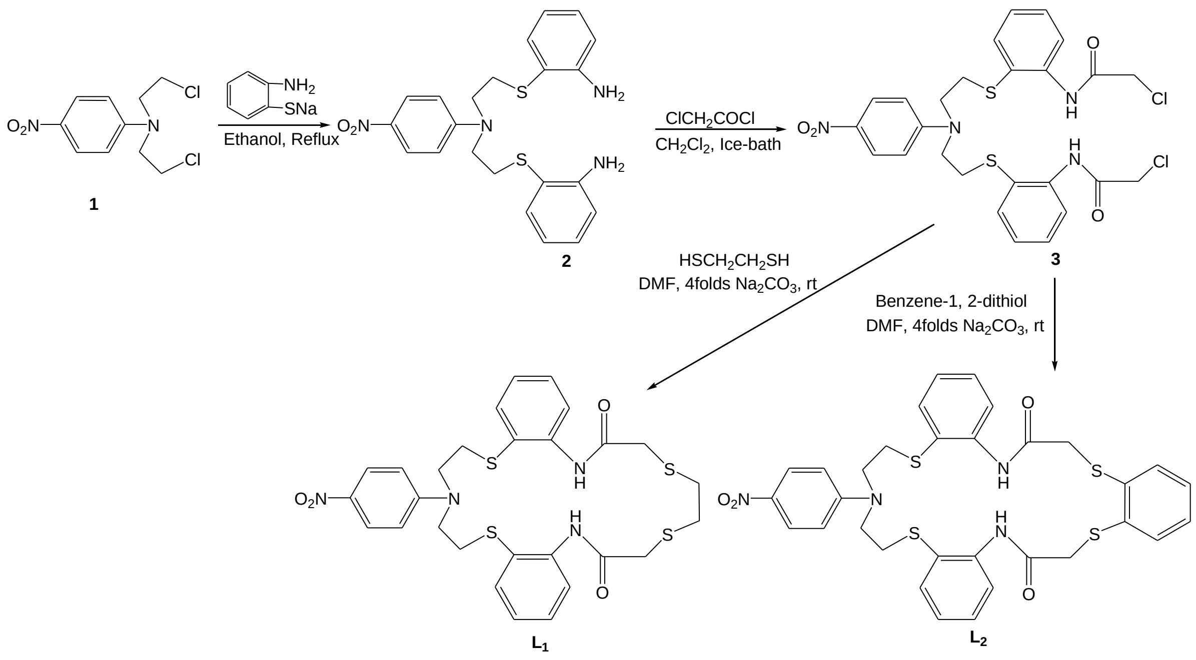
2. EXPERIMENTAL

2.1. Reagents and instrumentation

Ethane-1, 2-dithiol, benzene-1, 2-dithiol, 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 MΩ cm was obtained by a Pall Cascada laboratory water system.

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

The synthesis route was shown in Scheme 1.



Scheme 1. The synthesis route of azathiacrown ethers L_1-L_2.

2.2. Synthesis of azathiacrown ethers L_1-L_2

2.2.1. Synthesis of compound 1

Compound 1 was synthesized as reported method [11-12]. ^{1}H 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, ClC-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: 75.3%. ^{1}H 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). ^{13}C NMR (δ: ppm, d_6-DMSO): 152.21 (C-NO_2), 150.20, 136.41, 136.00, 130.29, 126.19, 116.97, 114.99, 114.69, 110.68 (Ar-C), 50.55 (N-CH_2), 30.30 (S-CH_2).

2.2.3. Synthesis of compounds 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 ^oC 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: 65.8%. ^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-CH_2Cl), 3.53-3.56 (t, 4H, NCH_2), 3.06-3.09 (t, 4H, S-CH_2). ^{13}C NMR (δ: ppm, d_6-DMSO): 165.43 (C=O), 152.21 (C-NO_2), 137.52, 136.73, 132.14, 128.56, 128.31, 126.67, 126.36, 125.02, 111.13, (Ar-C), 50.29 (N-CH_2), 43.61 (O=C-CH_2), 30.70 (S-CH_2).

2.2.4. Synthesis of macrocyclic compounds L_1-L_2

Compounds L_1-L_2 were synthesized with a similar method as reported. A solution of 3 (0.5 mmol) in DMF (50 mL) and that of Ethane-1, 2-dithiol or benzene-1, 2-dithiol (0.5 mmol) in DMF (50 mL) were added simultaneously to a solution of DMF (50 mL) containing 2 mmol anhydrous Na_2CO_3 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.

L_1: yellow crystal, yields: 92.6%. M.p.: 192.4–193.4 ^oC. IR (KBr tablet, cm^{-1}): 3283.2 (N-H), 1660.3 (C=O), 1579.4, 1528.3, 1433.8, 746.3. ^1H NMR (δ: ppm, d_6-DMSO): 9.69 (s, 2H, N-H), 7.83-7.85 (d, 2H, Ar-H), 7.79-7.80 (d, 2H, Ar-H), 7.53- 7.55 (d, 2H, Ar-H), 7.33-7.36 (t, 2H, Ar-H), 7.16-7.19 (t, 2H, Ar-H), 6.24-6.26 (d, 2H, Ar-H), 3.50-3.53 (t, 4H, NCH_2), 3.45 (s, 4H, O=CCH_2), 3.02-3.05 (t, 4H, SCH_2), 2.86 (m, 4H, SCH_2). ^{13}C NMR (δ: ppm, d_6-DMSO): 168.50 (C=O), 152.04 (C-NO_2), 138.59, 136.70, 133.34, 128.81, 127.00, 126.32, 125.93, 124.22, 110.90 (Ar-C), 50.50 (N-CH_2), 35.80 (O=C-C), 32.38, 31.33 (S-CH_2). MS: m/z 614.82 $[M]^+$, 636.81 $[M+Na]^+$.

Anal. Calcd. for $C_{28}S_4N_4O_4H_{30}$ (614.82): C, 54.70; H, 4.92; N, 9.11. Found: C, 54.69; H, 4.93; N, 9.10.

L_2: yellow crystal, yields: 91.2%. M.p.: 191.5–191.4 ^oC. IR (KBr tablet, cm^{-1}): 3289.2 (N-H), 1675.1 (C=O), 1581.4, 1538.3, 1443.2, 748.2. ^1H NMR (δ: ppm, d_6-DMSO): 1.04 (s, 2H, N-H), 8.42-8.43 (d, 2H, Ar-H), 7.84-7.84 (d, 2H, Ar-H), 7.49- 7.51 (d, 2H, Ar-H), 7.38-7.41 (t, 2H, Ar-H), 7.19-7.21 (m, 2H, Ar-H), 7.07-7.10 (t, 2H, Ar-H), 6.98-7.00 (m, 2H, Ar-H), 5.96-5.97 (d, 2H, Ar-H), 3.38-3.41 (t, 4H, NCH_2), 2.86 (s, 4H, O=CCH_2), 3.02-3.05 (t, 4H, S-CH_2), 2.75-2.78 (t, 4H, S-CH_2). ^{13}C NMR (δ: ppm, d_6-DMSO): 166.01 (C=O), 150.95 (C-NO_2), 139.16, 137.83, 135.65, 134.23, 130.58, 127.71, 127.44, 126.12, 124.92, 121.94, 120.59, 110.15 (Ar-C), 50.87 (N-CH_2), 36.49 (O=C-C), 31.44 (S-CH_2). MS: m/z 663.10 $[M+1]^+$, 685.03 $[M+Na]^+$.

Anal. Calcd for $C_{32}S_4O_4N_4H_{30}$ (662.87): C, 57.98; H, 4.56; N, 8.45. Found: C, 57.95; H, 4.56; N, 8.44.

2.3. Membrane preparation

The membrane components 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 allowed to evaporate 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. Electrodes were conditioned for one day in 1.0×10^{-3} M $AgNO_3$ with 1.0 M $AgNO_3$ as inner solution. For long-term measurements, the electrodes were kept in dark to avoid the photolysis of $AgNO_3$.

2.4. Potential measurements

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/Hg_2Cl_2 with double junction was used with 1.0 M LiOAc as salt bridge electrolyte. Membrane potentials were measured with a Model PXSJ-216 digital ion analyzer (Shanghai Instruments) in magnetically stirred solution at room temperature (13°C, and temperature are corrected) in the galvanic cell: SCE|1.0 M LiOAc|sample solution|ISE membrane|inner solution (1.0 M Ag^+)|AgCl/Ag.

2.5. Selectivity measurements

The electrodes with 1.0×10^{-3} M NaCl as an inner filling solution were conditioned in 1.0×10^{-2} M $NaNO_3$ solution overnight. Measurements were made in the respective nitrate solutions. The sequence of the sample ions was: Li^+, H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and Ag^+. For detection of Hg^{2+}, solutions were adjusted to pH = 4 using 0.1 M HNO_3 to avoid precipitation. All the measurements were done in triplicate. The selectivity coefficients were calculated from the emf values according to the separate solution method assuming theoretical slopes.

3. RESULTS AND DISCUSSION

3.1. Influence of ligand geometries on the selectivity of Ag^+-ISEs

Newly synthesized ion-selective neutral carriers L_1-L_2 were evaluated with plasticized PVC membranes. The coordination properties of the ligands to Ag^+ were firstly studied, and the results show that electrode based on L_2 has better selectivity and sensitivity to Ag^+ than L_1. This is likely due to the fact that ligand geometries play important roles on the selectivity. Atoms link with benzene group in which the carbon atoms have *sp*^{2} hybrid orbitals exist in the same planar with the benzene group.

Such rigid structure makes it difficult for the ionophore to twist to form a stable complex with certain ions which either bigger or smaller than the ring cavity. L_1 has a more flexible structure and it can torture the structure to coordinate with different size cations, thus Ag^+-ISE based on L_1 as ionophore has worse selectivity than L_2. So far as these two ligands were considered, the rigid structure of L_2 just offers a suitable space which in coordination with the size of Ag^+ so that a more stable Ag^+-L_2 complex was formed. The selectivity coefficients of Ag^+-ISEs obtained by using Bakker's method gave a proof that Ag^+-ISE based on L_2 really has a better selectivity than that of L_1 (Table 1) [13].

In order to obtain a clue about the affinity of ligands L_1–L_2 towards Ag^+, their complex formation constants $\lg\beta_{IL}$ with Ag^+ were also calculated according to the proposed method [14]. The $\lg\beta_{IL}$ values of sensors based on ionophores L_1–L_2 were 3.65 and 7.23, respectively, which proves that ligands L_2 has better affinity to Ag^+ than L_1.

Table 1. Potentiometric selectivity coefficients and response slopes obtained with the separate solution method for Ag-ISEs based on ionophores $L_{1\text{-}2}$

Ion J	Iono. L_1	Iono. L_2
Ag^+	0 (59.0)	0 (58.3)
Li^+	-3.27 ± 0.03 (48.0)	-6.44 ± 0.02 (49.0)
H^+	-2.87 ± 0.02 (52.8)	-5.86 ± 0.01 (53.3)
Na^+	-2.49 ± 0.01 (46.4)	-5.46 ± 0.02 (57.2)
K^+	-0.87 ± 0.02 (51.0)	-4.43 ± 0.02 (50.4)
Mg^{2+}	-3.58 ± 0.01 (24.1)	-7.05 ± 0.03 (26.1)
Ca^{2+}	-3.38 ± 0.01 (28.7)	-6.53 ± 0.02 (28.7)
Cu^{2+}	-3.98 ± 0.02 (31.4)	-6.73 ± 0.04 (33.1)
Cd^{2+}	-3.98 ± 0.01 (22.8)	-6.77 ± 0.03 (25.3)
Pb^{2+}	-3.35 ± 0.03 (27.5)	-5.41 ± 0.02 (31.2)
Hg^{2+}	-0.72 ± 0.01 (59.6)	-1.64 ± 0.02 (60.9)
Et_4N^+	3.65 ± 0.01 (60.0)	0.48 ± 0.01 (57.7)

3.2. Influence of membrane composition

The sensitivity, selectivity, working range and stability of an ISE depend on many factors, such as the nature of the ionophores, the addition of ion-exchanger and the nature of various plasticizers [5, 15, 16]. Therefore, different 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 was shown in Table 2.

Table 2. Influence of the nature of plasticizers on the characteristics of Ag^+-ISEs.

Electrode No.	Composition of membrane w%				Liner range, M	Det. limit, M	Slope, mV/dec.
	PVC	Plasticizer	Additive	L			
L_{1a}	33.0	66.0, *o*-NPOE	0.27	0.73	1.0×10^{-6}–1.0×10^{-3}	3.0×10^{-7}	52.9
L_{1b}	33.0	66.0, DBP	0.27	0.73	1.0×10^{-5}–3.0×10^{-3}	3.5×10^{-6}	53.6
L_{1c}	33.0	66.0, DOP	0.27	0.73	3.0×10^{-6}–1.0×10^{-3}	5.6×10^{-7}	46.2
L_{1d}	33.0	66.0, DOS	0.27	0.73	1.0×10^{-5}–3.0×10^{-4}	3.5×10^{-6}	50.6
L_{2a}	33.0	66.0, *o*-NPOE	0.25	0.75	3.0×10^{-7}–3.0×10^{-3}	6.7×10^{-8}	56.2
L_{2b}	33.0	66.0, DBP	0.25	0.75	1.0×10^{-5}–3.0×10^{-3}	1.4×10^{-6}	48.7
L_{2c}	33.0	66.0, DOP	0.25	0.75	1.0×10^{-5}–1.0×10^{-3}	1.9×10^{-6}	51.6
L_{2d}	33.0	66.0, DOS	0.25	0.75	1.0×10^{-5}–1.0×10^{-3}	1.9×10^{-6}	42.7

Study shows that *o*-NPOE plasticized PVC membranes have much higher dielectric constants than DOS, DBP and DOP based membranes [17], and it is clear from Table 2 that *o*-NPOE is more effective plasticizer than others in preparing the Ag^+-ISEs. This indicates that *o*-NPOE plasticized the membrane, dissolve the ion association complexes and adjust both permittivity and ion exchanger sites mobility to give highest possible selectivity and sensitivity.

The effect of the amount of lipophilic anionic additives (NaTFPB) on Ag^+-selective membranes on the electrode characteristics was also investigated.

The amount of NaTFPB was changed while maintaining the same amounts of ionophore, PVC and plasticizer (*o*-NPOE) in the membranes. Many studies have shown that the optimal number of anionic sites is usually 50 mol % relative to the ionophore [1]. This is due to fact that NaTFPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction.

So far as sensors based on L_1 and L_2 were concerned, the results in Table 3 show that ionophore and NaTFPB in a mole ratio of 4:1 present the best responses, this is proved that compounds L_1 and L_2 form sandwich complexes with Ag^+.

Table 3. Influence of NaTFPB concentrations on the characteristics of Ag^+-ISEs.

Electrode No.	Composition of membrane w%				Liner range, M	Det. limit, M	Slope, mV/dec.
	PVC	Plasticizer	Additive	L			
L_{1a}	33.0	66.0, *o*-NPOE	0.27	0.73	1.0×10^{-6}–1.0×10^{-3}	3.0×10^{-7}	52.9
L_{1e}	33.0	66.0, *o*-NPOE	0.32	0.68	3.0×10^{-6}–1.0×10^{-3}	5.6×10^{-7}	54.5
L_{1f}	33.0	66.0, *o*-NPOE	0.42	0.58	6.0×10^{-7}–3.0×10^{-3}	4.0×10^{-7}	51.8
L_{2a}	33.0	66.0, *o*-NPOE	0.25	0.75	3.0×10^{-7}–3.0×10^{-3}	6.7×10^{-8}	56.2
L_{2e}	33.0	66.0, *o*-NPOE	0.31	0.69	1.0×10^{-6}–3.0×10^{-3}	3.2×10^{-7}	55.2
L_{2f}	33.0	66.0, *o*-NPOE	0.40	0.60	3.0×10^{-6}–3.0×10^{-3}	9.3×10^{-7}	57.6

3.3. Dynamic response of Ag$^+$-ISE based on L_2

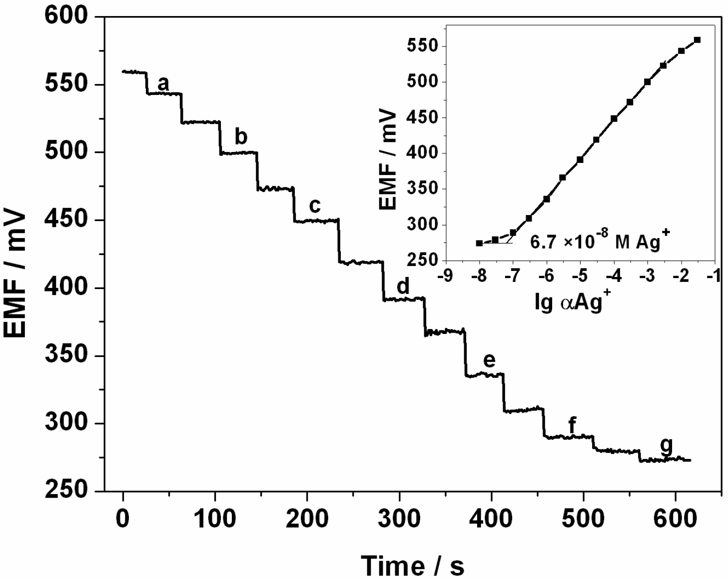


Figure 1. Time-dependent EMF responses of the Ag$^+$-ISE (Sensor No. L_{2a}): a. 1.0 × 10^{-2}, b. 1.0 × 10^{-3}, c. 1.0 × 10^{-4}, d. 1.0 × 10^{-5}, e. 1.0 × 10^{-6}, f. 1.0 × 10^{-7}, g. 1.0 × 10^{-8} M.

For analytical purposes, response time is one of the most important factors that are taken into account. In this work, the practical response time was recorded by immediate and successive changing of Ag$^+$ concentration from 1.0 × 10^{-8} - 3.0 × 10^{-2} M and the results are shown in Fig. 1. As it can be seen, in the whole concentration range, the Ag$^+$-ISE based on ionophore L_2 (sensor No. L_2a) need a very short time (< 20 s) to reach equilibrium response.

3.4. Effect of pH

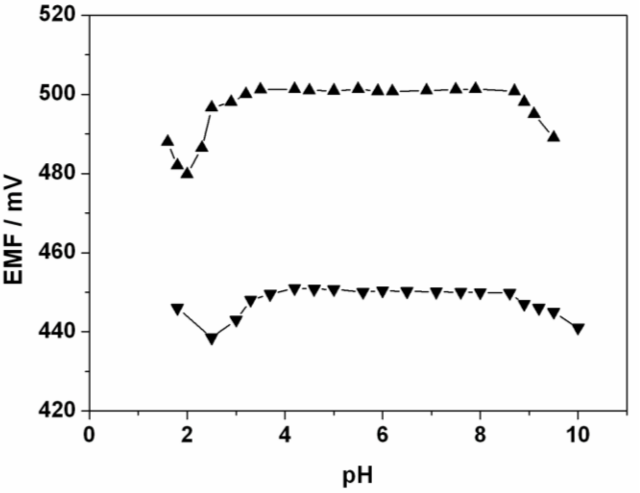


Figure 2. pH effect on the performance of sensor based on L_2 (Sensor No. L_{2a}) for ▲: 1.0 × 10^{-3} M Ag$^+$, ▼: 1.0 × 10^{-4} M Ag$^+$.

The influence of the pH on the response of ion-selective electrodes based on ionophore L_2 (sensor No. L_{2a}) was studied by varying the pH test solutions with 0.1 M HNO_3 and 0.1 M NaOH for 1.0×10^{-3} M and 1.0×10^{-4} M $AgNO_3$, respectively.

The results are illustrated in Fig.2. It is clear from Fig.2 that the operational pH range was 3.0-8.9 for the electrode based on ionophore L_2 (sensor No.L_{2a}). At the pH value below 3.0, high concentration of H^+ can go into the membrane to replace Na^+ and cause the drop of membrane potentiometry. At higher pH values, the Ag^+ will form precipitate with OH^- and also cause the drop of potentiometry. Thus, appropriate potential measurement of Ag^+ was performed within pH 3.0- 8.9.

3.5. Analytical application

The suggested Ag^+-ISE (sensor No. L_{2a}) was found to work well under the laboratory conditions. It was effectively applied to the titration of tap water (50.0 mL) and a spiked 5.0×10^{-3} M NaCl solution, respectively. The titration curve in Fig. 3 demonstrates that the Cl^- amount in these two solutions can be determined with good accuracy, and the Cl^- concentration in tap water (1.5×10^{-3} M) is not over the standard of drink water (GB5749-85: 4.6×10^{-3} M).

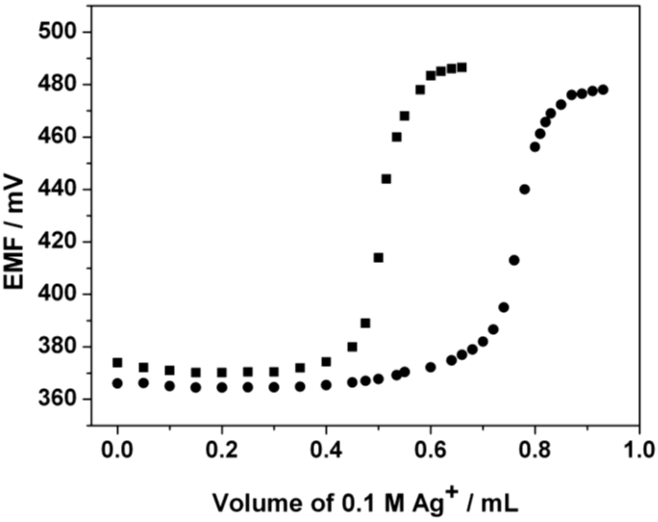


Figure 3. Titration curve of 50 mL 1.0×10^{-3} M Cl^--spiked water (■) and 50 mL tap water (●) with 0.1 M Ag^+ as titration reagent obtained by using Ag^+-ISE based on ionophore L_2 (Sensor No. L_{2a}).

4. CONCLUSION

Two new thiaazacrown ethers were synthesized with high yields. The number of benzene as subunit in the thiaazacrown ethers has great effect on the selectivity and sensitivity of ISEs to cations. With the better ones as Ag^+-ionophore, the constructed Ag^+-ISE has a wide working range of $3.0 \times 10^{-7} – 3.0 \times 10^{-3}$ M and low detection limit of 6.7×10^{-8} M Ag^+.

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