Characterization of a Ag+-Selective Electrode Based on Naphthalimide Derivative as Ionophore

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Abstract

A naphthalimide derivative has been explored as neutral ionophore for Ag^+-selective electrode. Potentiometric response revealed that electrode based on the proposed ionophore with 2-nitrophenyl octyl ether as solvent in a poly (vinyl chloride) membrane matrix shows a measuring range of 1.0×10^{-6}-1.0×10^{-2} M with a slope of 50.4 ± 0.3 mV/decade. This electrode has high selectivity to Ag^+ with respect to alkaline, alkaline earth and other heavy metal ions.

Keywords: Naphthalimide derivative; Ion-selective electrode; Ionophore; Ag^+

Introduction

The favorite donor binding site atom based on the hard-soft acid base (HSAB) concept is still the primary factor,[1] so the most of the reported heavy metal ionophores for use in ion selective electrodes (ISEs) possess sulfur and/or nitrogen atoms.[2] Among the heavy metal ions, Ag^+ has attracted the interest of researchers, and many compounds have been used to construct Ag^+-ISEs.[2-4] Among these compounds, crown ethers show strong ability to form remarkably stable and selective complexes with heavy metal ions and have been found to exhibit interesting host-guest complexation characteristics.[3] Especially, crown ethers containing nitrogen and sulfur donor atoms are of interest as they exhibit high affinities towards Ag^+.[5] During the last decade, considerable attention has been devoted to the construction of Ag^+-selective electrodes with mixed-donor crown ethers as ionophores.[2-4] In this work, a thiaazacrown ether has been characterized as Ag^+-ISE ionophore and the response of polymeric membrane Ag^+-ISE has been studied.

Materials and Methods

Reagents and Instruments

Ionophore was synthesized as reported method.[5] Poly (vinyl chloride) (PVC), bis (2-ethylhexyl) sebacate (DOS), dibutylphthalate (DBP), dioctyl phthalate (DOP), 2-nitrophenyl octyl ether (o-NPOE) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) were purchased from Sigma-Aldrich. All other reagents used were purchased from Sinopharm Chemical Reagent and of analytical grade purity. Deionized water with specific resistance of 18.2 MΩ cm was obtained by a Pall Cascada laboratory water system and was used throughout.

Membrane preparation

The membranes were prepared as reported method.[6] The membrane components were dissolved in 3.0 mL of THF and shaken vigorously for at least 2 h, and then poured into a glass ring (30 mm i.d.) fixed on a glass plate and covered with a big beaker. The solvent was allowed to evaporate overnight at room temperature to give a transparent membrane (thickness of 0.18 mm), and the resulting membrane was cut to size (6 mm i.d.) and glued with a PVC/THF slurry on the top of PVC tube mechanically fixed onto a pipette tip.

Conditioning of membranes and potential measurements

The membranes were conditioned in 0.01 M $AgNO_3$ solution with 0.1 M $AgNO_3$ as inner solution for at least one day. 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 in the galvanic cell:

SCE//1.0 M LiOAc/Sample solution/ISE membrane/Inner solution/AgCl/Ag

Selectivity measurements

For selectivity measurements, the electrodes were conditioned in 0.01 M $NaNO_3$ solution overnight with 0.001 M NaCl as an inner filling solution, and the electrode was firstly measured against the interfering metal ions and then used to measure the response of silver nitrate solutions. The measurement was done in triplicate (using new membrane for one replicate). The interfering ions studied here were H^+, Li^+, Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}.

Results and Discussion

Optimization of membrane compositions

The composition of PVC membrane affects the selectivity, linearity and sensitivity of the electrode and optimization was done by varying the ratio of ionophore and ion-exchanger (NaTFPB).[7] Ag^+-ISEs were prepared with different mole ratio of ionophore to NaTFPB (4:1, 2:1, 1:1).

Table 1 Potentiometric responses of electrodes based on the proposed ionophore with different amounts of ion-exchangers.

| Electrode No.	Composition of membrane w%				Liner range, M	Detection limit, M	Slope, mV/dec.
	PVC	Plasticizers	Additive	Ionophore			
a	32.80	65.70, *o*-NPOE	0.38	1.12	1.0×10^{-6}–3.0×10^{-2}	3.4×10^{-7}	48.7
b	32.80	65.50, *o*-NPOE	0.59	1.10	1.0×10^{-6}–1.0×10^{-2}	3.3×10^{-7}	50.4
c	32.70	65.39, *o*-NPOE	0.98	0.93	3.0×10^{-6}–3.0×10^{-4}	1.0×10^{-6}	56.4

It was observed from **Table 1** that the membranes composed of the ingredients: Ionophore : Plasticizer : PVC as (mg, w/w) of 1.34:88.22:4.22 and NaTFPB in a mole ratio of 1:2 with ionophore displayed the best performance for Ag^+.

Table 2 Potentiometric responses of electrodes based on ionophore with different plasticizers.

Electrode No.	Composition of membranes w%				Liner range, M	Detection limit, M	Slope, mV/dec.
	PVC	Plasticizers	Additive	Ionophore			
b	32.80	65.50, *o*-NPOE	0.59	1.10	1.0×10^{-6}–1.0×10^{-2}	3.3×10^{-7}	50.4
d	32.80	65.50, DBP	0.59	1.10	3.0×10^{-6}–3.0×10^{-2}	1.0×10^{-6}	45.4
e	32.80	65.50, DOP	0.59	1.10	1.0×10^{-5}–3.0×10^{-3}	3.3×10^{-6}	42.2
f	32.80	65.50, DOS	0.59	1.10	3.0×10^{-5}–1.0×10^{-3}	1.0×10^{-5}	47.6

Effect of plasticizers and working concentration range and slopes

The nature of plasticizers such as lipophilicity, high molecular weight, low vapor pressure and high capacity to dissolve the substrate and other additives present in the polymeric membrane has large effect on the sensitivity and stability of sensors.[8] We have tested several membranes of different plasticizers DOP, DBP, DOS and *o*-NPOE in PVC matrix and the results obtained are shown in **Table 2**. It can be seen from **Table 2** that the best results were obtained with the ISEs prepared by using *o*-NPOE as plasticizer, this indicates the solvent medium of *o*-NPOE can probably provide the best complexation environment between Ag^+ and their respective carriers. Electrode based on ionophore with optimal compositions show the best responses over a wide concentration range of 1.0×10^{-6}-1.0×10^{-2} M with a detection limit 3.3×10^{-7} M, the measurement sequence of high-to-low was from 1.0×10^{-2} to 3.0×10^{-8} M, and the dynamic response time is less than 10 s (**Fig. 1**).
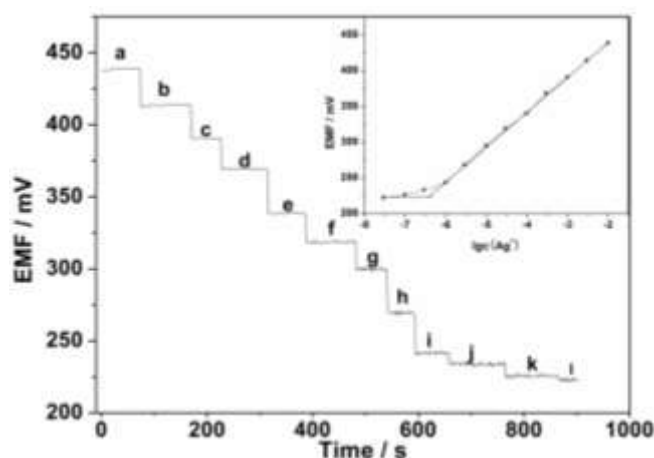
Figure 1 Dynamic response curves of the Ag^+-ISE. a. 1.0×10^{-2} M, b. 3.0×10^{-3} M, c. 1.0×10^{-3} M, d. 3.0×10^{-4} M, e. 1.0×10^{-4} M, f. 3.0×10^{-5} M, g. 1.0×10^{-5} M, h. 3.0×10^{-6} M, i. 1.0×10^{-6} M, j. 3.0×10^{-7} M, k. 1.0×10^{-7} M, l. 3.0×10^{-8} M Ag^+. (Inset: Liner range of the proposed Ag^+-ISE)

Lifetime of proposed Ag⁺-ISE

The high lipophilicity of ionophore and plasticizer ensure stable potentials and longer lifetime for the membranes.[9] The sensor based on *o*-NPOE and proposed ionophore can be used for two months. During this period, changes in potential were within the standard deviation (± 5 mV). It is important to emphasize that the membrane was kept in dark when not in use in order to avoid the silver nitrate photolysis.

Table 3 Potentiometric selectivity coefficients, $\log K_{AgL}^{pot}$, obtained with membrane based on ionophore (ISE No. **b**).

Ion J	$\log K_{AgL}^{pot}$	Ion J	$\log K_{AgL}^{pot}$
Ag⁺	0 (56.57)	Ca²⁺	-8.62±0.02 (23.94)
Li⁺	-7.67±0.03 (36.87)	Cu²⁺	-7.80±0.01 (23.17)
H⁺	-7.32±0.02 (51.10)	Cd²⁺	-8.45±0.02 (16.11)
Na⁺	-7.50±0.02 (47.78)	Pb²⁺	-7.28±0.02 (19.08)
K⁺	-6.59±0.02 (51.13)	Hg²⁺	-3.17±0.02 (56.57)
Mg²⁺	-9.28±0.01 (18.26)	Zn²⁺	-7.01±0.11 (22.05)

Potentiometric selectivity of Ag⁺-ISE

Potentiometric responses suggested that electrode based on the proposed ionophore has high selectivity toward Ag⁺. The selectivity coefficients of Ag⁺-ISE were explored based on the so-called "unbiased selectivity coefficient" proposed by Bakker and co-workers.[10] The characteristics of membranes examined based on the proposed ionophore are summarized in **Table 3**.

Conclusions

In this study, an azathiacrown ether has been characterized as Ag⁺-ionophore. The potentiometric properties reveal that the proposed compound has good selectivity to Ag⁺.

Conflicts of Interest

The authors declare no conflict of interest.

Funding Statement

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