



Single-Piece Solid-Contact Polymeric Membrane Ion-Selective Electrodes for Silver Ion

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Single-piece solid-contact polymeric membrane Ag⁺ ion-selective electrodes (ISEs) have been fabricated based on conducting polymer poly(3-octylthiophene) (POT) dissolved into the Ag⁺ ion-selective membrane. The effects of the amounts of POT on the potential responses of the single-piece solid-contact Ag⁺-ISEs were investigated in detail. Results indicate that the single-piece solid-contact Ag⁺-ISE with 10 wt% POT displays excellent reproducibility and stability of the potential response. The linear range of 3.0×10^{-8} – 3.0×10^{-5} M can be obtained in AgNO₃ solution with the slope 56.84 ± 0.92 mV/dec ($n = 3$, $R = 0.9984$) and the detection limit is 1.90×10^{-8} M. In addition, the single-piece solid-contact Ag⁺-ISE with 10 wt% POT shows excellent selectivity, stable potential response over a pH range of 3.5 to 6.0 and no significant redox sensitivity. The proposed electrode with 10 wt% POT has been successfully applied to potentiometric titration of chloride ion and determination of Ag⁺ ion concentrations in spiked waters with high accuracy and good reliability.

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Silver is well known for its excellent antimicrobial property. It has been widely used in medicine, photography and production of ornaments. However, its potential damage to the environment has been easily neglected, although it is not as toxic to humans as other heavy metals. It has been reported that silver salts or silver nanoparticles show unacceptable toxic effects to the environment and human health.¹ The U.S. Environmental Protection Agency reported that the amount of Ag⁺ ion higher than 1.6 nM in water is toxic to fish and microorganisms² and the maximum contaminant level of total silver in drinking water is limited to 0.9 μM.³ Therefore, it is necessary to detect Ag⁺ ion using efficient analytical methods.

Potentiometry with ion-selective electrodes (ISEs) is a promising method for directly determining various ions in clinical, environmental and industrial analysis, owing to their attractive features including simple design, small size, low energy consumption and low cost. Solid-contact ion-selective electrodes (ISEs) have recently attracted considerable attentions for simple fabrication, easy miniaturization and less maintenance, compared to the traditional polymeric membrane ISEs with inner filling solutions.⁴ Moreover, solid-contact ISEs can place in any position or configuration without the risk of leakage of the inner solution. However, the coated-wire electrodes (CWEs),⁵ as the initial solid-contact ISEs, suffer from the poor potential stability resulting from the blocked interface between the electronic conductor and the ion-selective membrane (ISM).⁶ Various materials have been used as solid-contact transducers to improve potential stability of solid-contact ISEs, including hydrogels,⁷ redox-active self-assembles monolayers,⁸ three-dimensionally ordered macroporous carbon,⁹ carbon nanotubes,¹⁰ fullerene,¹¹ graphene,¹² gold nanoparticles¹³ and conducting polymers.^{14–16} Among these materials, the conducting polymer poly(3-octylthiophene) (POT) is one of the most promising ion-to-transducers in solid-contact ISEs, because POT is less electroactive and may not take part in electrochemical side reactions to the same extent as the highly p-doped conducting polymers, such as poly(3,4-ethylenedioxythiophene).⁴ Moreover, POT is highly lipophilic, which may avoid the accumulation of water and salt between the electronic substrate and the ion-selective membrane. On the other side, single-piece solid-contact ISEs have been proposed by dispersing various electroactive materials into the ion-selective membranes.^{17–24} The fabrication procedures are much easier than that of the conventional solid-contact ISEs, which need the additional step to produce the intermediate layer.^{25,26}

Here, we proposed a single-piece solid-contact polymeric membrane Ag⁺ ion-selective electrode with conducting polymer poly(3-octylthiophene) (POT) dissolved into the ion-selective membrane. The effects of POT concentrations on potential stability and selectivity were investigated in detail.

Experimental

Chemicals.— The ionophore *o*-xylylene-bis(*N*, *N*-diisobutyl)dithiocarbamate), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), high molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE) and regioregular poly(3-octylthiophene-2,5-diyl) (POT) were purchased from Sigma-Aldrich.

All other chemicals were of analytical reagent grade. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

Preparation of single-piece solid-contact Ag⁺ ion-selective electrode.— The glassy carbon (GC, CH instruments, USA) electrodes with the diameter of 3 mm were used for fabrication of single-piece solid-contact Ag⁺ ion-selective electrodes. They were polished with 0.05 μm alumina slurries, rinsed with deionized water and then ultrasonically cleaned.

The membrane components for single-piece solid-contact Ag⁺ ion-selective electrodes contained 0.77 wt% ionophore (15 mmol/kg), 0.44 wt% NaTFPB (5 mmol/kg), 32.93 wt% PVC and 65.86 wt% *o*-NPOE. POT (3.6 mg/mL) was prepared with chloroform. The membrane cocktail was prepared by dissolving 180 mg of membrane components in 2 mL of tetrahydrofuran (THF) and stirred for 2 h. Then a certain amount of POT solution was added into the membrane cocktail, which was kept under stirring for 1 h to form homogeneous mixture. The mixture were poured into a glass ring (i.d. 20 mm) fixed on a glass plate. After overnight solvent evaporation, a disk of 5 mm diameter was punched from the membrane and then glued to the polished bare GC electrode with THF. Based on the different ratio between the weight of POT and that of the ionophore, the above prepared single-piece solid-contact electrodes are denoted as GC/Ag⁺–ISM (0% POT), GC/Ag⁺–ISM (1% POT), GC/Ag⁺–ISM (10% POT), GC/Ag⁺–ISM (50% POT) and GC/Ag⁺–ISM (100% POT) electrodes, respectively. For the traditional potential measurements, the electrodes were conditioned for 1 day in 1.0×10^{-4} M AgNO₃. For the lower detection limit measurements, the electrodes were conditioned in 1.0×10^{-4} M AgNO₃ overnight and then in 1.0×10^{-9} M AgNO₃ for 2 days. For the selectivity

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measurements using the separate solution method (SSM),²⁷ the electrodes were conditioned in 1.0×10^{-3} M NaNO₃ for 1 day.

Potentiometric measurements.— The potentiometric measurements were carried out using a CHI660C electrochemical workstation (Shanghai Chenhua Apparatus Co.) at room temperature in stirred solutions. The external reference electrode consisted of a double-junction Hg/Hg₂Cl₂ electrode with a 0.1 M LiOAc bridge electrolyte and saturated KCl solution as reference electrolyte. All potential values were corrected for liquid-junction potentials according to the Henderson equation and the ion activities were calculated by the Debye-Hückel approximation.

Redox sensitivity of the single-piece solid-contact Ag⁺ ISEs was carried out by measuring the potential response of the electrodes in 1 mM Fe(CN)₆^{3-/4-} redox couple with the ratio of Fe(III)/Fe(II) ranging from 1/10 to 10/1 at a constant ionic background of 0.1 M KCl solution.

Results and Discussion

Selectivity of single-piece solid-contact Ag⁺ ion-selective electrodes.— The selectivity of single-piece solid-contact ISEs are usually influenced by conducting polymers that are dissolved into the ion-selective membrane.⁴ Therefore, separate solution method (SSM) is used to estimate the selectivity coefficients of the single-piece solid-contact Ag⁺-ISEs in order to investigate the effect of POT.²⁷ Fig. 1 shows the results of the selectivity coefficients of single-piece solid-contact Ag⁺-ISEs with different amounts of POT. It can be seen that the selectivity coefficients of the GC/Ag⁺-ISM (1% POT) and GC/Ag⁺-ISM (10% POT) electrodes are slightly better than that of the GC/Ag⁺-ISM (0% POT), except for H⁺ and Cu²⁺ ions. The results may be due to the interaction between Ag⁺ and sulfur atoms and π -coordination present in POT backbone,²⁸ besides the interaction with the ionophore. However, the selectivity coefficients of the GC/Ag⁺-ISM (50% POT) and GC/Ag⁺-ISM (100% POT) electrodes become poorer than that of the GC/Ag⁺-ISM (1% POT) and GC/Ag⁺-ISM (10% POT) electrodes, which may be due to the fact that the excess of conducting polymer backbone influences the interaction between Ag⁺ ion and the ionophore. Therefore, the GC/Ag⁺-ISM (0% POT), GC/Ag⁺-ISM (1% POT) and GC/Ag⁺-ISM (10% POT) electrodes were employed for the subsequent experiments. In addition, it's found that the selectivity of the proposed single-piece solid-contact Ag⁺-ISEs are much better than that of the reported Ag⁺-ISEs based on the chemically synthesized POT and [2.2.2] *p, p, p*-cyclophane as silver ionophore,²⁸ which may be due to the fact that the proposed Ag⁺-ionophore with sulfur as coordinating sites shows much stronger interaction than that of cyclophane with π -coordination.²⁹

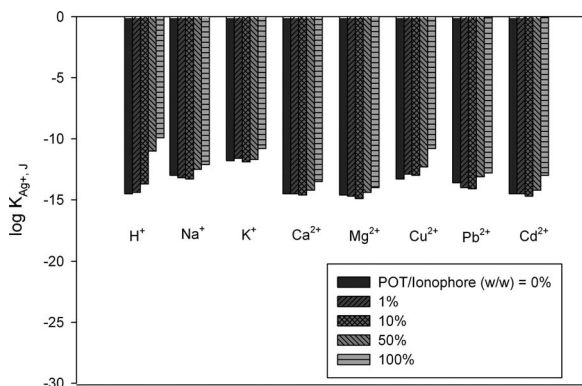


Figure 1. Potentiometric selectivity coefficients ($\log K_{Ag^+}^J, J^{POT}$) of single-piece solid-contact Ag⁺ ion-selective electrodes with the different ratio between the weight of POT and that of the ionophore using separate solution method (SSM).

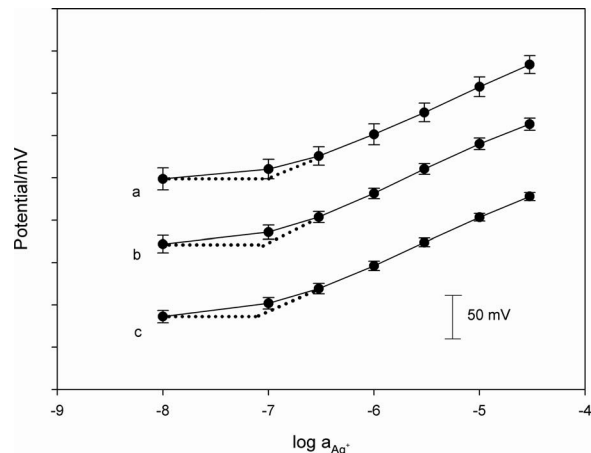


Figure 2. Calibration curves for (a) GC/Ag⁺-ISM (0% POT), (b) GC/Ag⁺-ISM (1% POT) and (c) GC/Ag⁺-ISM (10% POT) electrodes conditioned in 1.0×10^{-4} M AgNO₃ solution. Error bars represent the standard deviation for three identical electrodes.

Potentiometric response of single-piece solid-contact Ag⁺ ion-selective electrodes.— After conditioned in 1.0×10^{-4} M AgNO₃ solution overnight, the GC/Ag⁺-ISM (0% POT), GC/Ag⁺-ISM (1% POT) and GC/Ag⁺-ISM (10% POT) electrodes were measured in AgNO₃ solution, respectively. As can be seen in Fig. 2, all of the single-piece solid-contact Ag⁺-ISEs with different amounts of POT exhibit the linear potential responses in the activity range of 3.0×10^{-7} to 3.0×10^{-5} M AgNO₃. The slopes of the calibration curves are 54.53 ± 1.75 , 54.97 ± 0.74 and 55.72 ± 0.41 mV/dec and the detection limits calculated as the intersection of the two slope lines are $10^{-7.00}$, $10^{-7.08}$ and $10^{-7.11}$ M for the GC/Ag⁺-ISM (0% POT), GC/Ag⁺-ISM (1% POT) and GC/Ag⁺-ISM (10% POT) electrodes, respectively. In addition, it's found that the reproducibility of the GC/Ag⁺-ISM (10% POT) electrode is much better than that of the GC/Ag⁺-ISM (0% POT) and GC/Ag⁺-ISM (1% POT) electrodes (see the error bars in Fig. 2). Therefore, the GC/Ag⁺-ISM (10% POT) electrode would be used to detect Ag⁺ ion with a lower detection limit.

In order to obtain the trace level measurements of Ag⁺ ion, the GC/Ag⁺-ISM (10% POT) electrode was conditioned in 1.0×10^{-4} M AgNO₃ overnight and then in 1.0×10^{-9} M AgNO₃ for 2 days. Fig. 3 shows the calibration curve obtained by successively increasing Ag⁺

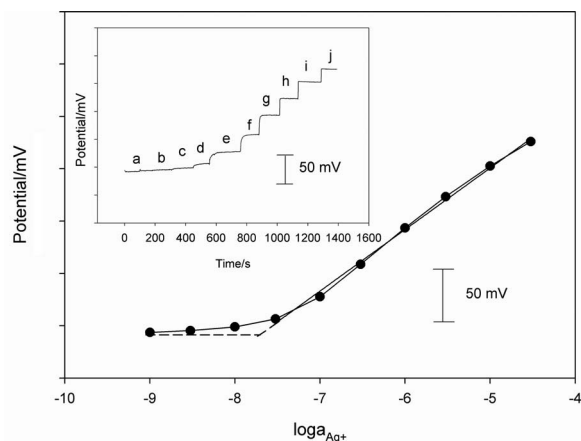


Figure 3. Calibration curve obtained with GC/Ag⁺-ISM (10% POT) electrode conditioned in 1.0×10^{-4} M AgNO₃ overnight and then in 1.0×10^{-9} M AgNO₃ for 2 days. Inset: Time traces of potential response of the single-piece solid-contact Ag⁺-ISE (10% POT). Concentrations of Ag⁺ ion (a-j): 1.0×10^{-9} , 3.0×10^{-9} , 1.0×10^{-8} , 3.0×10^{-8} , 1.0×10^{-7} , 3.0×10^{-7} , 1.0×10^{-6} , 3.0×10^{-6} , 1.0×10^{-5} and 3.0×10^{-5} M.

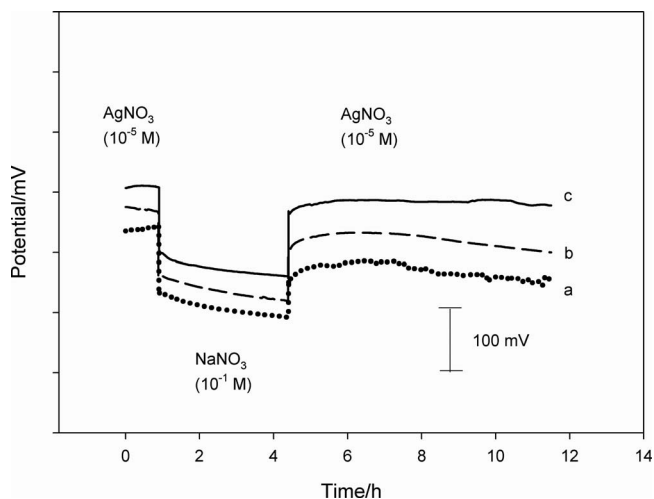


Figure 4. Water layer test for GC/Ag⁺–ISM (0% POT) (a), GC/Ag⁺–ISM (1% POT) (b) and GC/Ag⁺–ISM (10% POT) (c) electrodes.

activities using the GC/Ag⁺–ISM (10% POT) electrode. The linear range of 3.0×10^{-8} – 3.0×10^{-5} M was obtained with the slope 56.84 ± 0.92 mV/dec ($n = 3$, $R = 0.9984$). The detection limit is $(1.90 \pm 0.08) \times 10^{-8}$ M, which is much lower than that of the POT-based potentiometric Ag⁺ ion sensors.²⁸ In addition, the response time is less than 20 s (see inset of Fig. 3).

Water layer test.— For long-term measurements of solid-contact ISEs, the formation of a thin aqueous layer at the interface between the electronic substrate and ion-selective membrane would lead to the instability of potential. Therefore, the effect of water layer on potential was investigated by the potentiometric water layer test.⁶ After conditioned in 1.0×10^{-4} M AgNO₃ solution overnight, the GC/Ag⁺–ISM (0% POT), GC/Ag⁺–ISM (1% POT) and GC/Ag⁺–ISM (10% POT) electrodes were alternately measured in 1.0×10^{-5} M AgNO₃ for 1 h, 0.1 M NaNO₃ for 3.5 h and again 1.0×10^{-5} M AgNO₃ for 7 h. As seen in Fig. 4, the GC/Ag⁺–ISM (10% POT) electrode shows potential drift less than 1.1 ± 0.05 mV/h after the sample solution is changed from 0.1 M NaNO₃ to 1.0×10^{-5} M AgNO₃ solution, while the potential changes are equal to 4.88 ± 0.20 and 4.57 ± 0.14 mV/h for the GC/Ag⁺–ISM (0% POT) and GC/Ag⁺–ISM

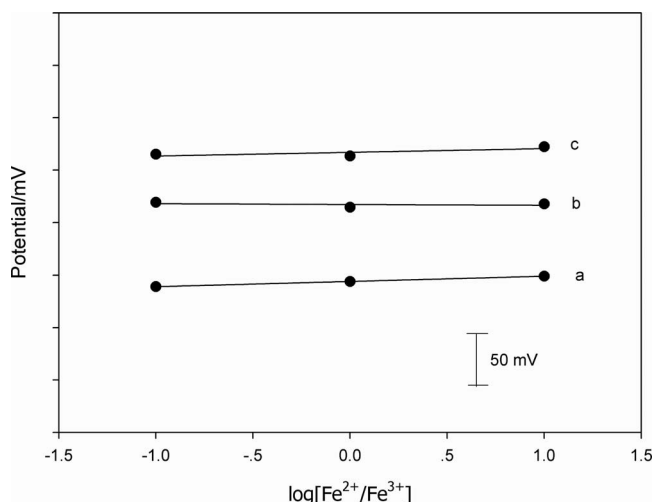


Figure 5. Redox sensitivity of GC/Ag⁺–ISM (0% POT) (a), GC/Ag⁺–ISM (1% POT) (b) and GC/Ag⁺–ISM (10% POT) (c) electrodes.

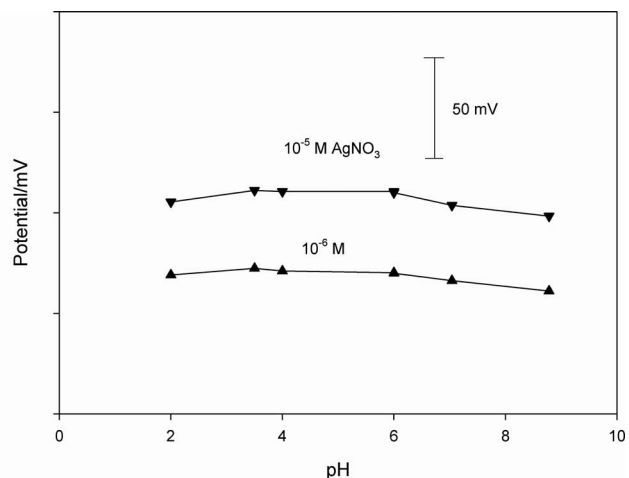


Figure 6. Effect of pH on the potential responses of the GC/Ag⁺–ISM (10% POT) electrode in 1.0×10^{-6} and 1.0×10^{-5} M AgNO₃ with 0.1 M NaNO₃ as a constant ionic background.

(1% POT) electrodes, respectively. Therefore, the GC/Ag⁺–ISM (10% POT) electrode shows more stable potential response.

Redox sensitivity.— The redox sensitivity measurements were investigated for the GC/Ag⁺–ISM (0% POT), GC/Ag⁺–ISM (1% POT) and GC/Ag⁺–ISM (10% POT) electrodes, respectively. As shown in Fig. 5, all of the single-piece solid-contact Ag⁺–ISEs with different amounts of POT show no significant redox sensitivity, which may be due to the fact that PVC-based ion-selective membrane is an electronic insulator and undoped POT is an electronic semiconductor with relatively low conductivity.³⁰

pH effect.— The effect of pH on the potential response of the GC/Ag⁺–ISM (10% POT) electrode was estimated in 1.0×10^{-6} and 1.0×10^{-5} M AgNO₃ at a constant ionic background of 0.1 M NaNO₃ solution. The pH of the solutions was adjusted using HNO₃ or NaOH. As shown in Fig. 6, the potential of the GC/Ag⁺–ISM (10% POT) electrode remains almost constant over a pH range of 3.5 to 6.0. The potential change at lower (<3.5) and higher (>6.0) pH values could be due to the protonation of the ionophore and the formation of silver hydroxide,³¹ respectively.

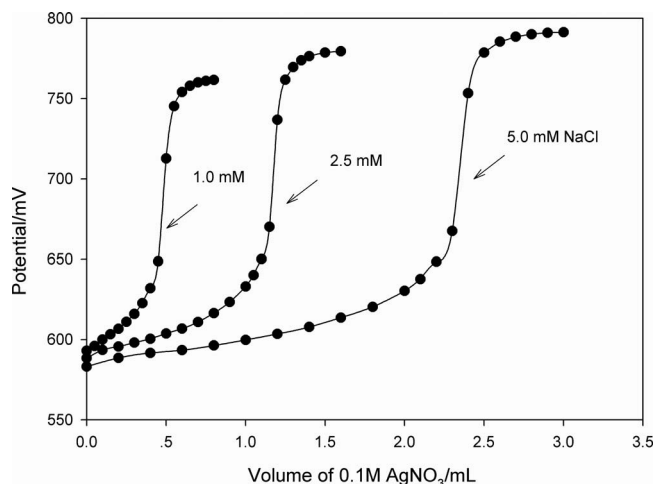


Figure 7. Titration curves of 50.0 mL of 1.0, 2.5, 5.0 mM NaCl solutions with 0.1 M AgNO₃ as titration reagent obtained by using GC/Ag⁺–ISM (10% POT) electrode as indicator electrode.

Table I. Application of the proposed GC/Ag⁺–ISE (10% POT) to detect Ag⁺ ion in spiked waters.

Sample	Added (μM)	Found ^a (μM)	Recovery (%)
Tap water 1	0	ND ^b	–
	0.100	0.103 ± 0.008	103.0
	0.300	0.285 ± 0.015	95.0
Tap water 2	0	ND ^b	–
	0.050	0.048 ± 0.005	96.0
	0.100	0.094 ± 0.006	94.0
Lake water 1	0	ND ^b	–
	0.100	0.109 ± 0.010	109.0
	0.300	0.299 ± 0.008	99.7

^aMean of three determinations ± S.D.^bNot detected.

Analytical applications.— The GC/Ag⁺–ISM (10% POT) electrode was successfully applied as an indicator electrode in the potentiometric titration of NaCl solution with AgNO₃. Fig. 7 shows the typical titration curves of 1.0, 2.5, 5.0 mM NaCl solutions with 0.1 M AgNO₃ as titration reagent. It can be seen that obvious inflection points are observed in the titration curves, which indicates that the amount of Cl[–] ion in the solution can be accurately determined with the perfect stoichiometry by using GC/Ag⁺–ISM (10% POT) electrode.

The application of the GC/Ag⁺–ISM (10% POT) electrode was further tested by measuring Ag⁺ ion concentrations in spiked waters using standard addition potentiometric method. Table I shows that recoveries vary from 94.0 to 109.0%, which indicate that the proposed GC/Ag⁺–ISM (10% POT) electrode can be successfully applied to detect Ag⁺ ion in real samples with high accuracy and good reliability.

Conclusions

Single-piece solid-contact polymeric membrane Ag⁺ ion-selective electrodes have been successfully developed using conducting polymer poly(3-octylthiophene) (POT) dissolved into the ion-selective membrane. The potential responses of the electrodes are significantly influenced by the amounts of POT in the ion-selective membrane. Results indicate that the single-piece solid-contact Ag⁺ ion-selective electrode with 10 wt% POT displays excellent potential reproducibility, stability and selectivity. The calibration curve can be obtained in AgNO₃ solution using the proposed electrode with 10 wt% POT in the linear range of 3.0×10^{-8} – 3.0×10^{-5} M with the slope 56.84 ± 0.92 mV/dec ($n = 3$, $R = 0.9984$) and the detection limit is 1.9×10^{-8} M. Moreover, the electrode exhibits no significant redox sensitivity, which is attributed to the electronic insulated PVC-based ion-selective membrane and undoped POT with low conductivity. The proposed electrode with 10 wt% POT has been successfully applied to potentiometric titration of chloride ion and determination of Ag⁺ ion concentrations in spiked waters with high accuracy and good reliability.

The proposed sensor provides a promising method for fabrication of a simple, robust and reliable Ag⁺–ISE that can be miniaturized and applied in many fields to detect Ag⁺ ion.

Acknowledgments

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