A SILVER(I) PVC-MEMBRANE SENSOR BASED ON SYNTHESIZED DILAKTAM CROWN ETHER

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ABSTRACT

In this work, we introduce a highly selective and sensitive silver(I) PVC-membrane sensor. Dilaktam Crown ether (DLCE) was used as a membrane-active component to prepare a highly sensitive Ag(I)-selective polymeric membrane electrode. This sensor illustrated very good selectivity and sensitivity towards silver ions over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The sensor exhibited a Nernstian behavior (with a slope of 59.8 ± 0.2 mV per decade) for a concentration range (1.0×10^{-5} – 1.0×10^{-1} M) with a detection limit of 6.8×10^{-6} M. It displayed a response time in the whole concentration range (~ 20 s) and its usage exceeded a 75 days period in the pH range of 5.1–7.2. The proposed electrode application was found to be successful as an indicator electrode in the titration with NaCl.

Keywords: Dilaktam Crown ether, Silver, sensor, PVC Membrane, Ion-selective electrode, Potentiometry

INTRODUCTION

The quick determination of minute quantities of ionic species by simple methods is of special interest in analytical chemistry. During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and nondestructive analysis of different samples with small volume samples. Ion-selective sensors based on plasticized PVC membranes were successfully applied to the determination of many cations in various industrial, environmental and biochemical samples.¹⁻³ Construction and application of ion selective electrode as a potentiometric sensor offers interesting advantages such as simplicity, speed, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures. These characteristics have inevitably led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown substantially over the past years.⁴

Silver ions and silver compounds show a toxic effect on some bacteria, viruses, algae and fungi, typical for heavy metals like lead or mercury, but without the high toxicity to humans that are normally associated with them. Its germicidal effects kill many microbial organisms in vitro. The widespread use of silver went out of fashion with the development of modern antibiotics. However, recently there has been renewed interest in silver as a broad-spectrum antimicrobial. In particular, silver is being used with alginate, a naturally occurring biopolymer derived from seaweed, in a range of products designed to prevent infections as part of wound management procedures, particularly applicable to burn victims.^{5, 6, 7}

Some techniques such as atomic absorption spectroscopy,⁸ inductively coupled plasma,⁹ spectroscopy with complexation agents¹⁰ and Rayleigh light-scattering¹¹ have been used to determine amount of silver. Because of the increasing use of silver compounds in industry and medicine the quick determination of trace quantities of Ag⁺ ion by simple methods is important in chemical, clinical and environmental analysis. Literature survey revealed that there were some reports on silver-selective membrane sensor.¹²⁻¹⁸

Recently, several greatly selective and sensitive PVC-membrane ion-selective electrodes for various metal ions have been reported.¹⁹⁻³⁷ Nevertheless, this paper focuses on the introduction of a highly silver(I)-selective sensor based on Dilaktam Crown ether (DLCE) (Fig. 1), as a novel neutral ionophore for monitoring silver concentration.

Figure 1. The DLCE structure.

EXPERIMENTAL

Reagent

The ionophore Dilaktam Crown ether (DLCE) was prepared as formerly described.³⁸ Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and Aldrich, used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Triply distilled de-ionized water was used throughout.

EMF measurements

The assembly for the emf (electromotive force) measurements included, on the one hand, an Ag–AgCl | internal solution, 1.0×10^{-3} M AgNO₃ | PVC membrane | sample solution | Hg–Hg₂Cl₂, KCl (satd.) and, on the other hand, a Corning ion analyzer with a 250 pH/mV meter for the potential measurements at 25.0 °C.

The activities were calculated according to the Debye–Huckel procedure.³⁹

Electrode Preparation

The membrane was prepared by dissolving 33 mg of PVC, 63 mg of dioctyl phthalate (DOP), as plasticizer and 4 mg of DLCE as ionophore in 2 mL of tetrahydrofuran. The resulting mixture was transferred into a glass dish

of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed.^{40–50} The tube was then pulled out from the mixture and kept at the room temperature for about 24 h. The tube was then filled with internal filling solution (1.0×10^{-3} M of AgNO_3). The electrode was finally conditioned by soaking in a 1.0×10^{-3} M AgNO_3 solution for 24 h. A silver/silver chloride wire was used as an internal reference electrode.

Waste water sample treatment

For determination of silver in electroplating waste water, 20 mL of each sample were filtered using a millipore paper filter (0.45 μm). Then, 5 mL of filtered solution transfer into a 100 mL volumetric flask and diluted with distilled water. The pH of the solution adjusts to 5 by using 0.1 M solution of HNO_3 . In this condition, the silver is in the form of Ag^+ and the pH of the solution is in the working pH range of the sensor. Then, Ag^+ concentration in the samples was determined directly by using the calibration method.

RESULTS AND DISCUSSION

Potential electrode responses

In the DLCE structure, the existence of three donating nitrogen and sulphur atoms was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, more than other metal ions. Therefore, in the primary experiments, DLCE was used as a potentially suitable neutral carrier in the fabrication of a number of PVC Membrane ion-selective electrodes for $\text{Ag}(\text{I})$ ion and common metal ions. The potential responses for these metal ions are depicted in Figure 2. As it can be concluded from Fig. 2, among the examined metal ions, only the resulting $\text{Ag}(\text{I})$ -selective sensor possesses a Nernstian behaviour over a very wide concentration range.

Figure 2. Potential responses of various ion-selective electrodes based on DLCE.

Effect of membrane composition on the potential response of the Ag^+ sensor based on DLCE

The sensitivity and selectivity of the ion-selective sensors not only depend on the nature of the employed DLCE but also on the membrane composition and the used additives.^{51–58} Thus, the influences of membrane compositions sensor were studied, on the potential responses of the Ag^+ and the results are given in Table 1. In accordance with Table 1, using 4% of DLCE in the membrane electrode displays Nernstian slope towards silver ion (membrane No. 3). Since the plasticizer nature influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands,^{51–58} the plasticizer nature was expected to play a key role in the determination of the selectivity, in the definition of the working concentration range and the response time of the membrane electrode. Of the two tried solvent mediators (DOP and DBP), DOP was found to provide the best sensitivity for the construction of the Ag^+ membrane sensor. However, the membrane sensor with the composition of 33% PVC, 63% DOP and 4% DLCE displays a very nice Nernstian behavior.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition (wt %)			Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	DLCE		
1	54	DOP,43	3	48.5 ± 0.3	1.0×10^{-1} – 1.0×10^{-5}
2	38	DOP,57	5	46.1 ± 0.3	1.0×10^{-1} – 1.0×10^{-5}
3	33	DOP,63	4	59.8 ± 0.2	1.0×10^{-1} – 1.0×10^{-5}
4	54	DBP,43	3	43.2 ± 0.4	1.0×10^{-1} – 1.0×10^{-5}
5	38	DBP,57	5	51.0 ± 0.3	1.0×10^{-1} – 1.0×10^{-5}
6	33	DBP,63	4	32.4 ± 0.2	1.0×10^{-1} – 1.0×10^{-5}

Calibration graph and statistical data

The plot of EMF vs. pAg obtained under optimal membrane ingredients for the sensor (Figure 3), indicate that it has a Nernstian behavior over a very wide concentration ranges of Ag^+ ion (1.0×10^{-5} – 1.0×10^{-1} M). The slope and linear range of the resulting calibration graph was 59.8 ± 0.2 mV per decade and 1.0×10^{-5} – 1.0×10^{-1} M, respectively. The limit of detection, defined as the concentration of Ag ion obtained when the linear regions of the calibration graph extrapolated to the base line potential, is 6.8×10^{-6} M. The proposed PVC-based membrane sensor could be used for at least 75 days (usage of 1 h daily and, then, washed and dried). After this period, the electrode slope reduced (from 59.8 ± 0.2 to 53.7 ± 0.4 mV per decade) (Table 2).

Figure 3. Calibration curve of the DLCE based silver electrode (membrane no. 3).

Table 2. Life time of the Ag -sensor.

Life time (day)				Slope (mV/decade)
75	55	28	10	
$\pm 0.453.7$	$\pm 0.354.6$	58.1 ± 0.2	59.8 ± 0.2	
0.9801	0.9916	0.9978	0.9977	r

Effect of pH

The dependence of the membrane potential on pH was studied at 1.0×10^{-3} M silver ion concentration, and the results are shown in Figure 4. As can be seen, the potential remains constant in the pH range of 5.1–7.2, which may be taken as the functional pH range of the sensor.

Figure 4. The pH effect of the test solution (1.0×10^{-3} M) on the potential response of the silver sensor (membrane no. 3).

Dynamic response time

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^{-5} – 1.0×10^{-1} M and the results are shown in Figure 5. As it can be seen, in the whole concentration range, the electrode reaches to its equilibrium response in a very short time (20 s).

Figure 5. Dynamic response time of the silver electrode (membrane no. 3) for step changes in the Ag^+ concentration: A) 1.0×10^{-5} M, B) 1.0×10^{-4} M, C) 1.0×10^{-3} M, D) 1.0×10^{-2} M, E) 1.0×10^{-1} M.

The sensor selectivity

The influence of the interfering ions on the response behavior of any ion-selective sensor is usually described in terms of selectivity coefficients, K_{sel} . In this work, the selectivity coefficients were determined with the aid of the matched potential method (MPM).⁵⁹⁻⁶⁷ According to this method, the specified activity (concentration) of the primary ions ($A = 5 \times 10^{-5}$ M) is added to a reference solution (1.0×10^{-5} M of AgNO_3), and the potential is measured. In a separate experiment, the interfering ions ($B = 1 \times 10^{-5}$ to 1.0×10^{-1} M) are successively added to an identical reference solution, until the measured potential matches that obtained before the addition of the primary ions. The MPM selectivity coefficients are then given by the resulting primary ion activity to the interfering ion activity ratio, $K^{\text{MPM}} = a_A/a_B$.

The resulting values are listed in Table 3. As it is immediately obvious, the selectivity coefficients of the electrode for all the diverse ions are in the order of 7.2×10^{-3} or smaller, indicating they would not significantly disturb the function of the Ag(I) selective membrane sensor.

Table 3. Selectivity coefficients of the electrode.

Ions	Selectivity coefficients (MPM)	Ions	Selectivity coefficients (MPM)
Ni^{2+}	4.8×10^{-3}	Mg^{2+}	2.3×10^{-3}
Cd^{2+}	4.9×10^{-3}	Pb^{2+}	7.2×10^{-3}
Zn^{2+}	2.7×10^{-3}	Co^{2+}	5.6×10^{-3}
K^+	2.2×10^{-3}	Sr^{2+}	5.8×10^{-3}
Na^+	5.2×10^{-3}	Ca^{2+}	4.5×10^{-3}

Analytical application

The suggested silver cation-selective electrode was found to work well under the laboratory conditions. It was effectively applied to the titration of 50.0 mL of a 1.0×10^{-2} M silver solution with a 1.0×10^{-1} M NaCl solution. The titration curve in Figure 6 demonstrates that the Ag^+ amount in the solution can be determined with good accuracy.

Figure 6. Potentiometric titration curve of 50.0 mL from a 1.0×10^{-2} M Ag^+ solution with 1.0×10^{-1} M of NaCl.

In this study, as an application of the present electrode in real sample, the determination of silver in waste water samples were carried out. The waste water is produced from electroplating factory in Tehran, indicating that the matrix of the waste water sample do not interfere significantly with the detection of silver. For determination of silver, the calibration curve of silver in the range of 1.0×10^{-5} – 1.0×10^{-1} M silver solution was used. The silver content of three waste water samples was determined also by the inductively coupled plasma (ICP-OES). The results obtained by the proposed silver (I) electrode together with those obtained by ICP-OES (with detection limit of 10 ppb) are summarized in Table 4. As is shown in Table 4, the determined concentration of silver in these samples by the present method using simple aqueous standards for calibration was in good agreement with the certified method of ICP-OES.

Table 4. Determination of silver ion in different waste water samples

Samples	Ag ⁺ amount (M)	
	The proposed electrode*	ICP-OES
1	$6.2 \pm 0.3 \times 10^{-4}$	6.1×10^{-4}
2	$4.3 \pm 0.2 \times 10^{-4}$	4.2×10^{-4}
3	$8.5 \pm 0.3 \times 10^{-4}$	8.3×10^{-4}

* The results are based on triplicate measurements

CONCLUSION

The silver PVC membrane electrode based on the Di-laktam Crown ether (DLCE) ligand with the composition 4 % ionophore, 33 % PVC and 63 % DOP exhibited the best performance characteristics. This electrode illustrated a Nernstian response, a detection limit of 6.8×10^{-6} M, a fast response time of 20 s in the presence of barium with the pH range 4.7-7.2 and very low interference from common alkali, alkaline earth, transition and heavy metal ions. This sensor was successfully applied as indicator electrode in titration of silver ion with NaCl and waste water samples.

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