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REGULAR ARTICLE

Silver(I)-selective PVC membrane potentiometric sensor based on 5,10,15,20-tetra(4-pyridyl)-21*H*, 23*H*-porphine and potentiometric applications

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Abstract. In this study, all-solid-state contact PVC membrane silver(I)-selective sensor has been prepared and 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine used as ionophore. Optimum membrane composition; 3.5% ionophore, 59.6% Bis(2-ethylhexyl) sebacate (BEHS), 1.0% potassium tetrakis (p-chlorophenyl) borate (KTpClPB) and 35.9% polyvinyl chloride (PVC). The developed silver(I)-selective sensor exhibited a linear response ($E = -51{,}57\ (-\log[Ag^+]) + 1690{,}6$ and $R^2 = 0{,}9986$) in the varying concentration range of 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} silver ions. The limit of detection of the sensor was calculated as 1.9×10^{-6} mol L^{-1}. The silver(I)-selective sensor exhibited good selectivity towards some alkali, alkali earth and heavy metal ions. The sensor can be used in the pH range from 4.0 to 10.0. The sensor has been shown to have good reusability and response time less than 8 s. The sensor was used as an indicator electrode in titrations of silver nitrate with sodium chloride solution and was successfully applied for the determination of the different water samples.

Keywords. Sensors; silver; solid state; porphyrins; potentiometry.

1. Introduction

Potentiometric ion sensors or ion-selective electrodes (ISEs) are an important subgroup of electrochemical sensors. The ion-selective electrodes (ISEs) in the class of potentiometric sensors were first described in 1906,[1] after the 1960s, great advances have been made in this field and to date, ion-selective sensors have been identified for a large number of species. The studies in the field of ion-selective electrodes are progressing very rapidly in accordance with the requirements by using the knowledge in many fields of science together with the developments in technology. Nowadays ion-selective sensors are used to determine agricultural, environmental and medical fields,[2,3] some poly ions such as heparin and protamine,[4,5] some neutral species such as CO_2, O_2, SO_2,[6,7] ammonia, organic amines, alcohols and nonionic surfactants.[8] Potentiometric methods offer great advantages such as easy preparation and procedures, short response time, high selectivity, low-energy consumption, wide linear working range at low cost compared to the other analytical methods such as spectrophotometry, high-performance liquid chromatography (HPLC), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and neutron activation analysis.[9–17]

Silver is an important element that is usually loaded with +1 in its compounds. Silver is used in many areas including photographic industry, electronic parts, ornaments, electrical and electrical equipment, jewellery, alloys, dental and medical products as well as silver-zinc and silver-cadmium batteries.[18–23] Therefore, the determination of silver in different biological and environmental samples is highly important.

Porphyrin compounds have been the subject of intensive research due to their importance in biological systems and material chemistry. Initial studies on porphyrins started with the isolation of these compounds from natural compounds and then synthetically synthesized in laboratory conditions. The synthesis of porphyrin was first made by Rothemund in 1935.[24] Porphyrin is a molecule system consisting of four pyrrole rings connected by four methines (-CH=) bridges. Porphyrins and their structural derivatives are intensely reported as an

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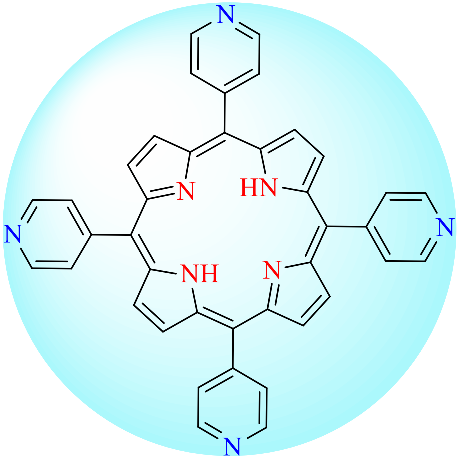

Figure 1. Structure of 5,10,15,20-tetra(4-pyridyl)-21*H*, 23*H*-porphine.

ionophore for ion-sensitive electrodes. Porphyrins are one of the nitrogen-containing macrocyclic aromatic structures. Due to their rich redox chemistry, delocalized aromatic π-system and synthetic flexibility, they are frequently used in ionophore sensors.[25–27] Because of all these properties, porphyrin derivatives are preferred as ionophores and different ions sensitive sensors have been reported in the literature.[28–31]

In this study, 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (Figure 1) was used as ionophore and silver(I)-selective potentiometric PVC membrane sensor was developed. Potentiometric properties of the developed sensor were investigated.

2. Experimental

2.1 *Apparatus*

The potentiometric measurements were conducted by using a laboratory-made computer-controlled multi-channel potentiometric measurement system. The system has a home-made software program. The potential values as steady-state responses of the PVC membrane silver(I)-selective sensor were performed for different concentrations of standard solutions of silver(I) respectively. A micro-sized solid silver/silver chloride electrode (obtained from Isedo medical instruments, Turkey) was used as reference electrode with the silver(I)-selective PVC membrane sensor throughout the measurements.

2.2 *Materials*

All the chemicals were of analytical-reagent grade unless otherwise stated, and deionized water was used throughout. The 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (ionophore) were obtained from Sigma Aldrich. High molecular mass polyvinylchloride (PVC, high molecular weight), Bis(2-ethylhexyl)sebacate (BEHS, density 0.914 g/mL at 25 °C), o-nitrophenyl octyl ether (o-NPOE, density 1.04 g/mL at 25 °C), Dibutyl phthalate (DBF, density 1.043 g/mL at 25 °C) and Bis(2-ethylhexyl) adipate (DEHA, density 0.925 g/mL at 20 °C), Potassium tetrakis (4-chlorophenyl)borate (KTpClPB), tetrahydrofuran (THF, anhydrous, density, 0.889 g/mL at 25 °C) and graphite obtained Sigma Aldrich. Epoxy (Macroplast Su 2227) from Henkel (Istanbul, Turkey) and hardener (Desmodur RFE) from Bayer AG (Darmstadt, Germany), were obtained and used in the preparation of all state solid contact. Deionized water was obtained by using a DI 800 Model deionize water system. All reagent and nitrate salts of the cations used in selectivity studies were in analytical grade and obtained from Sigma Aldrich. Stock solutions were prepared by using distilled deionized water. The stock solution was diluted gradually from 1.0 × 10^{-1} to 1.0 × 10^{-6} mol L^{-1}.\

2.3 *Method*

2.3a *Preparation of silver(I)-selective sensors*: Sensors were prepared at two steps. At the first step, solid-state contact was prepared. A mixture of conductive material consisting of 50.0% (w/w) graphite, 35.0% (w/w) epoxy and 15.0% (w/w) hardener was prepared by solving in sufficient THF (5 mL).[32] At the second step, PVC membrane sensor was prepared. The optimum PVC membrane was prepared by thorough mixing of 59.60% plasticizer (BEHS), 35.90% PVC, 3.5% ionophore and 1.0% additive KTpClPB in 5 mL of THF. This mixture was placed on the sensors surface and allowed to dry for 24 h. Prior to first use, the prepared sensors were conditioned in a 1.0 × 10^{-2} mol L^{-1} $AgNO_3$ solution for 12 h. Preparation of other membranes and optimized of membrane ingredients are summarized Table 1.

The preparation of the sensors and the potentiometric measurement system are summarized in Figure 2.

2.3b *Potentiometric measurements*: Potentials were measured using Ag/AgCl reference electrodes. Potential measurements were carried out at 25 ± 0.1 °C by setting up the following cell assembly:

$$\mathrm{Ag/AgCl;\ KCl\ (saturated)}\|\mathrm{Ag^+\ sample\ solution}\ |\mathrm{Ag^+\ selective\ PVC\ membrane}$$

3. Results and Discussion

3.1 *Potentiometric performance of the PVC membrane silver(I)-selective membrane sensor*

The PVC membrane silver(I)-selective membrane sensor was evaluated by potentiometric performance for optimizing membrane composition. PVC membrane silver(I)-selective membrane sensor was

Table 1. Preparation of membranes and optimized of membrane ingredients.

Membrane	Composition (% w/w)							
	Ionophore	PVC	KTpClPB	DBF	o-NPOE	DEHA	BEHS	R^2
1	**3.5**	**35.9**	**1.0**	–	–	–	**59.6**	**0.9986**
2	3.5	36.4	1.0	–	59.1	–	–	0.9770
3	3.8	30.7	1.0	64.5	–	–	–	0.9664
4	3.8	32.0	1.0	–	–	63.2	–	0.9818
5	3.5	33.0	1.0	–	–	–	62.5	0.9776

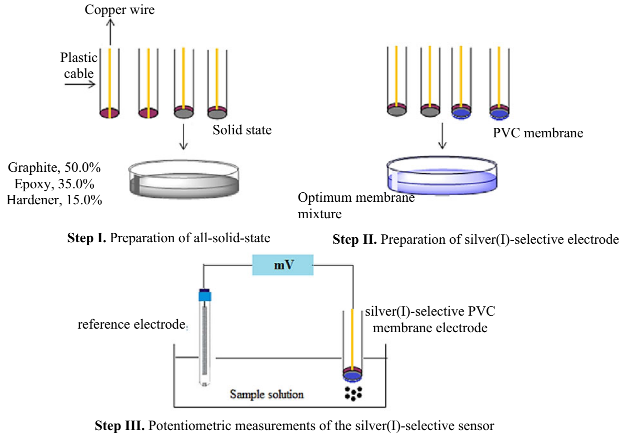

Figure 2. Schematic diagram for the step-wise preparation of silver(I)-selective sensors.

determined by the calibration curve of the over silver(I) concentration range from 1.0 × 10^{-1} to 1.0 × 10^{-6} mol L^{-1}. Figure 3 represents that PVC membrane silver(I)-selective membrane sensor have highly reproducible. PVC membrane silver(I)-selective sensor exhibited a linear response, the graph of the linear response was defined by the equation of $E = -51.57\ (-\log[Ag^+]) + 1690{,}6$ with a correlation coefficient $R^2 = 0.9986$.

3.2 *Calibration curve*

Figure 4 depicts the potentiometric response of silver(I)-selective sensor. The potential response of sensor exhibited a linear concentration range 1.0 × 10^{-5}–1.0 × 10^{-1} mol L^{-1} of silver ion in the calibration solution. The linear range of the graph and the tangent points from the deviation were plotted. The detection limit was calculated by substituting the potential value that is the projection of the cut-off point (1396.0 mV) in the correct equation. The developed sensor displays a low detection limit of 1.9 × 10^{-6} mol L^{-1}.

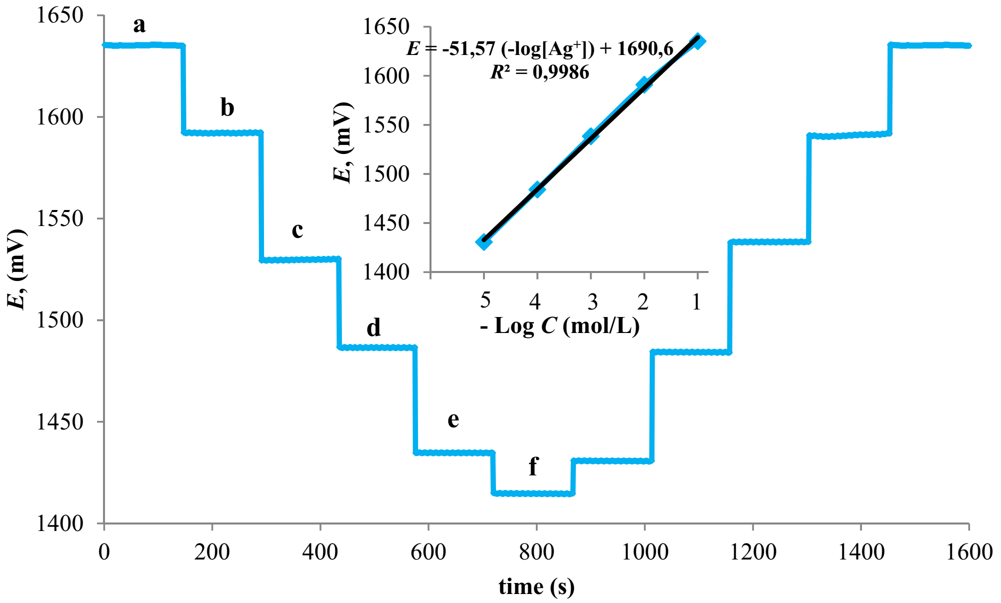

Figure 3. The potentiometric response to exhibits of silver(I)-selective membrane sensor (**a**: 10^{-1} mol L^{-1}, **b**: 10^{-2} mol L^{-1}, **c**: 10^{-3} mol L^{-1}, **d**: 10^{-4} mol L^{-1}, **e**: 10^{-5} mol L^{-1} and **f**: 10^{-6} mol L^{-1}) and the variation of average potential values (mV) with $\log[Ag^+]$ for silver(I) solutions in the range 10^{-1}–10^{-5} mol L^{-1}.

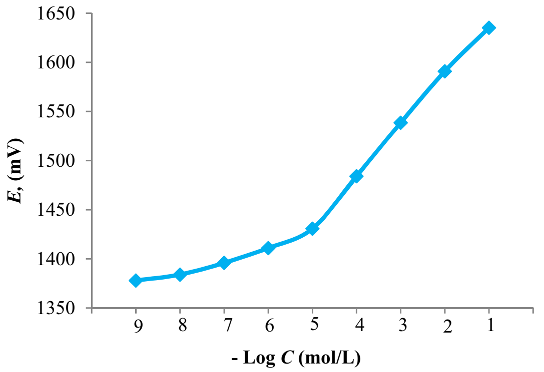

Figure 4. Calibration curve of silver(I)-selective sensor.

$$E = -51{,}57(-\log[Ag^+]) + 1690{,}6$$

3.3 *The selectivity of silver(I)-selective PVC membrane sensor*

The potentiometric selectivity coefficients are one of the most important characteristic parameters of an ion-selective electrode and measure its relative response for the primary ion in the presence of other ions present in the solution. The nitrate salts of different cations were measured at varying concentrations by the developed sensor. In this study, the selectivity coefficients of silver ion and other cations were calculated according to the following equation at a concentration of 1.0 × 10^{-2} mol L^{-1} by using the fixed interference method by IUPAC.[33]

$$\log k^{\mathrm{pot}}_{\mathrm{A,B}} = \frac{(E_{\mathrm{B}} - E_{\mathrm{A}})Z_{\mathrm{A}}F}{RT\ln 10} + \left(1 - \frac{Z_{\mathrm{A}}}{Z_{\mathrm{B}}}\right)\log a_{\mathrm{A}}$$

The obtained logarithmic values are reported for NH_4^+, K^+, Na^+, Li^+, Cd^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Sr^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+}, Cr^{3+}. The calculated selectivity coefficients are summarized in Table 2. In Table 2, we observed that the prepared silver(I)-selective sensor is highly selective with respect to a variety of other cations.

The developed sensor as a result of selectivity studies showed the highest potential value and linear operating range compared to other metals. The ionophore has a great effect at this point.

Silver sensitivity of the macrocyclic ring could be driven by both pyridine group attached the *meso* carbon and pyrrolic nitrogen in the structure. When the molecular structure of 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine is considered, nitrogen groups attract to silver ions which increases the sensitivity of electrodes toward to silver ions.

3.4 *The reusability of silver(I)-selective membrane sensor*

The all-solid-state PVC membrane silver(I)-selective sensor investigated reusability. In this study, silver(I)-selective sensor was determined by taking repeated measurements at 10^{-2}, 10^{-3}, and 10^{-4} mol L^{-1}

Table 2. The selectivity coefficient of various interference ions.

Interfering ions	Selectivity coefficient, $\log k^{pot}_{Ag^+,M^{n+}}$	Interfering ions	Selectivity coefficient, $\log k^{pot}_{Ag^+,M^{n+}}$	Interfering ions	Selectivity coefficient, $\log k^{pot}_{Ag^+,M^{n+}}$
Cd^{2+}	−2.94	Al^{3+}	−3.29	Co^{2+}	−3.43
K^+	−3.16	Na^+	−3.35	Ca^{2+}	−3.44
Zn^{2+}	−3.17	Mg^{2+}	−3.42	Pb^{2+}	−3.46
NH_4^+	−3.23	Cu^{2+}	−3.43	Li^+	−3.47
Cr^{3+}	−3.24	Sr^{2+}	−3.43	Ni^{2+}	−3.55

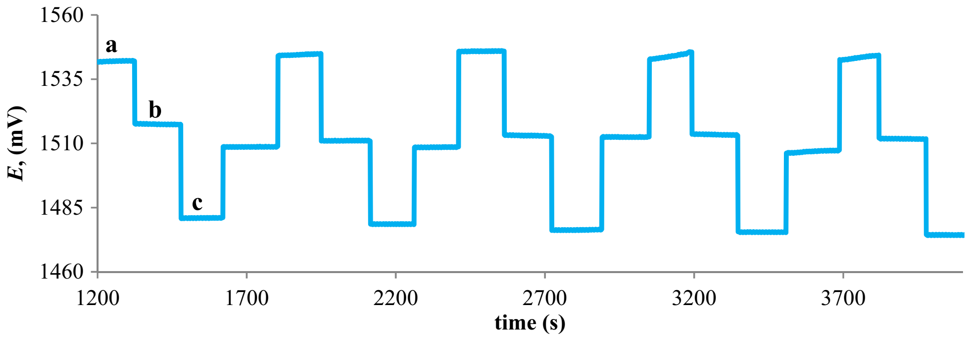

Figure 5. The reusability of silver(I)-selective membrane sensor (**a**: 10^{-2} mol L^{-1}, **b**: 10^{-3} mol L^{-1} and **c**: 10^{-4} mol L^{-1}).

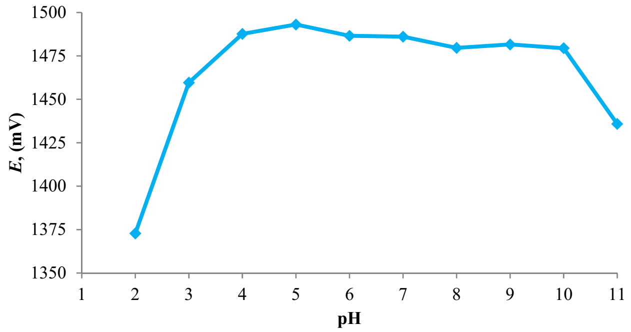

Figure 6. pH dependence of silver(I)-selective membrane sensor.

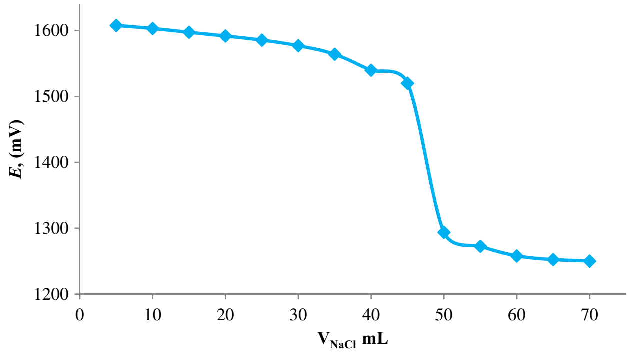

Figure 7. Potentiometric titration of 1.0 × 10^{-2} mol L^{-1} $AgNO_3$ solution with 1.0 × 10^{-2} mol L^{-1} solution NaCl.

silver(I) concentrations. Figure 5 shows that exhibit to results can be good repeatedly.

3.5 *The pH dependence of silver(I)-selective membrane sensor*

The prepared sensor dependence of pH-potential profiles, and adjusted to various pH values in the range of 2 to11 by using NaOH and HNO_3. The silver(I)-selective membrane sensor showed a potential change against the silver concentration of 10^{-3} mol L^{-1} in acidic and basic mediums. In Figure 6, it is clear that there is no potential remained unaffected over a pH range of 4–10.

3.6 *The response time of silver(I)-selective membrane sensor*

The response time is known as the time period for the presented potential of the sensor to reach equilibrium with the sensible part of the membrane.[34] In this work, the response time was measured from 1.0 × 10^{-1} mol L^{-1} to 1.0 × 10^{-6} mol L^{-1} for sensor. The sensor response time obtained was always less than 8 s.

3.7 *Analytical applications*

3.7a *The potentiometric titration of silver(I)-selective membrane sensor*: The analytical application of the sensor was investigated by using it as an indicator sensor in the potentiometric titration of 1.0 × 10^{-2} mol L^{-1} silver nitrate solution with 1.0 × 10^{-2} mol L^{-1} sodium chloride solution. In this work, 1.0 × 10^{-2} mol L^{-1} silver nitrate solution was taken and 1.0 × 10^{-2} mol L^{-1} sodium chloride solution were added continuously and the results are shown in Figure 7. As seen, prepared silver(I)-selective PVC membrane sensor was used successfully as an indicator electrode in potentiometric titration of $AgNO_3$ with NaCl.

3.7b *Analysis of real samples*: To prove that the silver(I)-selective sensor can be applied to real samples was carried out by adding a standard silver(I) ion to the water samples including tap water precipitated rainwater and some commercially available bottled waters. By using the silver(I)-selective sensor, the concentration was adjusted with standard silver(I) ion solutions ranging from 1.0 × 10^{-5} to 1.0 × 10^{-1} mol L^{-1} and the correct equation was obtained. Then, the potential values of each sample prepared by standard addition method were measured. Measured values were written in the correct equation created by using the calibration graph and the silver(I) quantities of each sample were calculated. Table 3 shows potentiometric determination of silver(I) ions in water samples which have been

Table 3. Real water sample analyzes with silver(I)-selective PVC membrane sensor.

	Ag^+ quantity (mol/L)		
Real Sample	Added Ag^+	Mean (± SD) found with sensor*	% Regain
Precipitated rain water	1.00 × 10^{-3}	8.99 (±1.53) × 10^{-4}	89.99
Commercial water 1	1.20 × 10^{-3}	1.14 (±0.66) × 10^{-3}	95.00
Commercial water 2	1.40 × 10^{-3}	1.29 (±0.80) × 10^{-3}	92.14

*Mean and standard deviation values are given for three different experimental measurements (n = 3).

Table 4. Comparison with other reported silver(I)-selective sensors.

Ionophore	Concentration range (mol L^{-1})	Limit of detection (mol L^{-1})	pH working range	Response time (s)	Real samples applications	Refs.
N,N'-ethylenebis-(3-methoxy salicylaldimine	1.0×10^{-6}–1.0×10^{-1}	8.3×10^{-7}	3.0–8.0	15	Waste water and photographic film	35
Schiff-base-p-tertbutylcalix[4]arene	1.0×10^{-5}–1.0×10^{-1}	6.3×10^{-6}	1.0–6.0	30	Natural water	36
Hexathia-18-crown-6	6.0×10^{-6}–3.2×10^{-3}	4.0×10^{-6}	2.0–7.5	< 10	Not worked	37
Resorc[4]arene	1.0×10^{-5}–1.0×10^{-1}	3.0×10^{-6}	1.5–6.0	< 20	Tap water samples	38
p-tert-butylthiacalixarene	7.0×10^{-6}–8.0×10^{-3}	3.9×10^{-6}	3.0–5.0	10–20	Pharmaceutical samples	39
Bis-pyridine tetramide macrocycle	4.0×10^{-5}–1.0×10^{-1}	–	–	5	Water samples	2
Benzothiazolyl calix[4]arene	5.0×10^{-6}–1.0×10^{-1}	3.2×10^{-6}	2.5–7.0	< 10	Not worked	18
1,3-bis(2- benzothiazolyl) thioalkoxy-*p*-*tert*-butylcalix[4]arenes	1.0×10^{-5}–1.0×10^{-1}	1.6×10^{-6}	2.5–6.5	–	Not worked	40
Meso-tetraphenylporphyrin	1.0×10^{-7}–1.0×10^{-1}	1.0×10^{-7}	3.0–9.0	< 10	Different real samples	41
N,N-Dibenzyl-dibenzo-diaza18-crown-6	7.0×10^{-6}–1.0×10^{-1}	3.0×10^{-6}	4.0–7.0	< 10	Not worked	42
5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine	1.0×10^{-6}–1.0×10^{-1}	1.9×10^{-6}	4.0–10.0	< 8	Water samples	This work

successfully performed with developed silver(I)-selective PVC membrane sensor.

3.8 *Comparison with other reported sensors*

A comparative study of the response characteristics of the developed sensor with some of the reported sensors for silver(I) is shown in Table 4. The achieved results provide enough proof that the developed silver(I) ion-selective sensor is superior to the previously reported silver(I) sensors in terms of concentration range, the limit of detection, pH working range, response time and real samples applications.

In this study, the potentiometric properties of silver(I)-selective PVC membrane sensor are generally better than other membrane sensors in the literature (Table 4). The pH of the silver(I)-selective PVC membrane sensor we developed is wider than the working range of pH of others. In this study, the response time of the sensor was obtained for 8 s, while in other studies the response times ranged from 10 to 30 s. The concentration range of the silver(I)-selective PVC membrane sensor we developed was between 1.0×10^{-1}–1.0×10^{-6} mol L^{-1} and the limit of detection was determined as 1.9×10^{-6} mol L^{-1}. The potentiometric results of the silver(I)-selective PVC membrane sensor obtained are consistent with the literature results given in Table 4.

4. Conclusions

In this study, a novel potentiometric PVC membrane sensor that is sensitive and selective for the determination of silver ion in aqueous solutions was developed. The silver(I)-selective sensor showed a short response time and high sensitivity. The detection limit of the silver(I)-selective PVC membrane sensor was measured as 1.9×10^{-6} mol L^{-1} and the response time was shorter than 8 seconds. The linear operating range of the sensor was found to be between 1.0×10^{-1} and 1.0×10^{-6} mol L^{-1}. The sensor exhibited good potentiometric behavior and its stability remained unchanged at 4–6 °C and dry atmosphere for one month. The potential change of the silver(I)-selective sensor in the concentration range from 1.0×10^{-1} to 1.0×10^{-6} mol L^{-1} was found to be compatible with the Nernst equation. In addition, it was determined that silver(I)-selective membrane sensor could be used as an indicator electrode as a result of potentiometric titration studies. The sensor developed will make a significant contribution to the work to be done in this area.

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