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All-solid-state poly (vinyl chloride) membrane thiocyanate–selective potentiometric electrode

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Thiocyanate,
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Ion-selective electrode,
PVC membrane

Abstract — A novel all-solid-state contact poly (vinyl chloride) (PVC) membrane–containing thiocyanate-selective electrode has been prepared. The electrode exhibits the best performance with a membrane composition of PVC:BEHS:ionophore:KTpClPB of 33.0:64.0:2.0:1.0 (%, *w*/*w*). The thiocyanate–selective electrode displays a linear response in the concentration range of 1.0×10^{-4} – 1.0×10^{-1} M. The proposed electrode shows good reusability. The thiocyanate–selective electrode shows a better selective response towards thiocyanate compared to different anions. The electrode has a fast response time of the 20s and can be used in a pH range of 5.0–9.0.

Subject Classification (2020):

1. Introduction

Potentiometric ion-selective electrodes (ISEs) are considered useful analytical devices and offer significant advantages such as wide linear concentration range, high selectivity, ease of preparation, long lifetime, low detection limit, fast response time portability and low cost [1–5]. Based on these advantages, ion-selective electrodes are widely used in many areas, such as environmental, industrial, food, clinical, drug, and agricultural analysis [6–8].

Thiocyanate (SCN^-) is present as a normal constituent of mammalian tissues, and it is widely used in medicine, textile dyeing, photography, catalysis, hydrometallurgy, electroplating, also in the production of agricultural chemicals, in the prevention of erosion and photofinishing in industrial processes [9–11]. Thiocyanate is usually present at low concentrations in human serum, saliva and urine as a by-product from the digestion of some foods such as cabbage, turnip, kale, milk and cheese [12, 13]. In addition, thiocyanate is found in cigarette smoke and car exhaust. Thiocyanate in food and environmental samples can be transformed into highly toxic cyanides (CN^-) through radiation and chlorination [14]. Therefore, the determination of thiocyanate in food, environment and biological samples is crucial. Different analytical methods such as atomic absorption spectrometry (AAS) [15], gas chromatography (GC) [16], Raman spectroscopy [17], spectrophotometry [18] and voltammetry [19] have been reported

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to be used in the determination of thiocyanate concentration in different environmental and biological samples. Potentiometric methods, which have many advantages over these methods, are essential alternatives in determining various ions.

This work developed a novel electrode to detect thiocyanate concentration, and its potentiometric properties were investigated.

2. Material and Methods

2.1. Chemicals and Reagents

All the chemicals and reagents used in the current study were of analytical reagent grade. Bis(2–ethylhexyl) sebacate (BEHS), high molecular weight PVC, potassium tetrakis (*p*–chlorophenyl) borate (KTpClPB), nitric acid (HNO_3), sodium hydroxide (NaOH), sodium salts of the anions, graphite and tetrahydrofuran (THF) were purchased from Sigma and Merck companies. Epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were obtained from Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany), respectively; and they were used in the preparation of all–state–solid contact. Deionized water was obtained by using a DI 800 Model deionized water system.

2.2. Apparatus

The potential measurements were carried out on a computer-controlled multichannel potentiometric system (Medisen Medical Ltd. Sti., Turkey). The system has a lab-made software program. A micro-sized solid Ag/AgCl (Thermo–Orion) electrode was used as a reference electrode for the potential measurements.

2.3. Method

2.3.1. Preparation of thiocyanate-selective potentiometric electrodes

In this study, all-solid-state thiocyanate–selective electrodes were prepared based on protocols reported in previous studies (Figure 1) [20, 21]. PVC membrane electrodes were prepared by using ionophore (iron–azadipyromethene derivative molecule), PVC, plasticizer (BEHS) and conductivity enhancer (KT*p*ClPB) at different ratios (Table 1). As can be seen in Table 1, between 1.0×10^{-1} – 1.0×10^{-4} M concentration range, the optimum membrane composition with the highest R^2 (0.9812) value was determined to be the membrane mixture 2 with the content of 2.0% ionophore, 64.0% BEHS, 33.0% PVC and 1.0% KT*p*ClPB. Membrane mixture 2 was used in the subsequent steps of the study.

Table 1. Composition ratios of the prepared electrodes with linear working concentration R^2 values

No	Composition (% w/w)						
	Ionophore	PVC	KT*p*ClPB	BEHS	R^2	Linear working concentration (M)	Calibration Equation
1	2.0	34.0	1.0	63.0	0.9794	10^{-3} – 10^{-5}	$E = -19{,}3\ [SCN^-] + 1060{,}5$
2	2.0	33.0	1.0	64.0	0.9812	10^{-1} – 10^{-4}	$E = -22{,}6\ [SCN^-] + 1215{,}4$
3	3.0	30.0	1.0	66.0	0.9677	10^{-3} – 10^{-5}	$E = -17{,}3\ [SCN^-] + 1016{,}1$
4	3.0	31.0	1.0	65.0	0.9763	10^{-1} – 10^{-4}	$E = -19{,}7\ [SCN^-] + 1033{,}7$

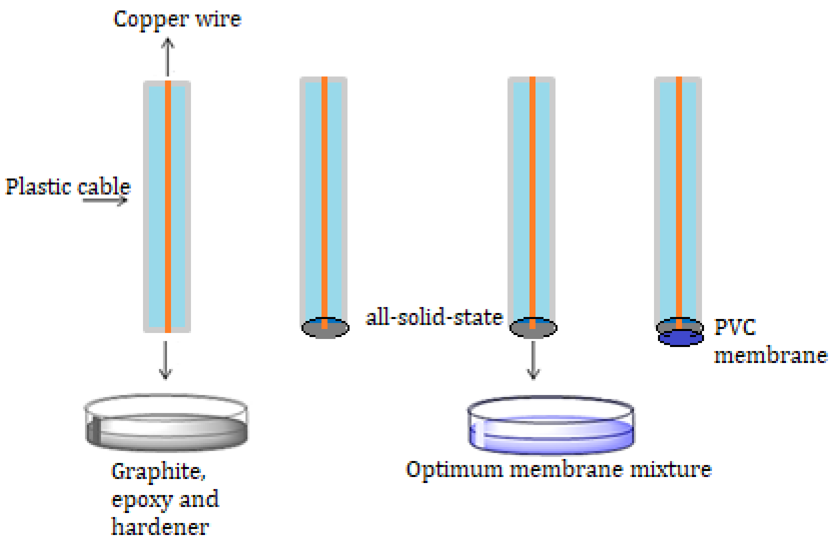

Figure 1. Preparation steps of PVC membrane thiocyanate–selective electrodes

3. Result and Discussion

The potentiometric properties of the thiocyanate–selective electrodes, namely calibration curve, reusability, selectivity, pH working range and response time, depend on the ratio of PVC membrane components. The potential response of all prepared PVC membranes as a function of thiocyanate activity was studied in the concentration range from 1.0×10^{-7} to 1.0×10^{-1} M of thiocyanate ion. The thiocyanate–selective electrode showed linear potential response over concentrations ranging from 1.0×10^{-4} to 1.0×10^{-1} M (Figure 2). In addition, the thiocyanate–selective electrode was found to display a relatively lower detection limit of 6.30×10^{-5} M.

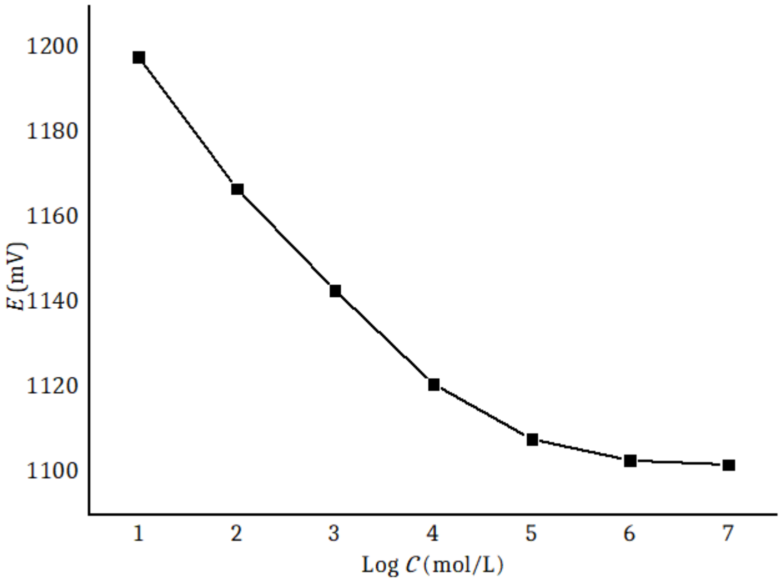

Figure 2. The calibration curve of thiocyanate–selective electrode

The response time of the thiocyanate–selective electrode was evaluated based on the recommendations of the IUPAC [22]. Thus, it was determined that the thiocyanate–selective electrode reached the equilibrium in 20 seconds for every 10–fold change in the concentration.

The reusability of the thiocyanate-selective electrode was performed by measuring 10^{-1}, 10^{-2} and 10^{-3} M thiocyanate solutions. The potential–time graph in Figure 3 indicated that the developed thiocyanate–selective electrode has good reusability in the given concentration range.

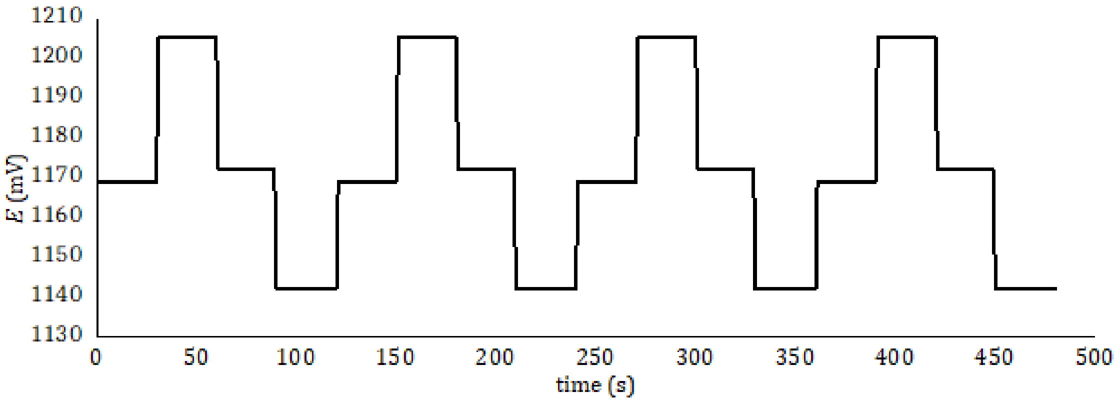

Figure 3. Reusability of thiocyanate–selective electrode

The selectivity of an ion-selective electrode is one of the most important parameters that determines the utility of the electrode. For this purpose, the thiocyanate–selective electrode was investigated for its selectivity in the presence of different interfering anions, and selectivity coefficients were determined with the equation given below, using the separation solution method (SSM) [23, 24]:

$$\log K_{\mathrm{A,B}}^{\mathrm{pot}} = \frac{(E_{\mathrm{B}} - E_{\mathrm{A}})Z_{\mathrm{A}}F}{RTln10} + (1 - \frac{Z_{\mathrm{A}}}{Z_{\mathrm{B}}})\log a_{\mathrm{A}}$$

The selectivity study of the thiocyanate–selective electrode is summarized in Figure 4 and Table 2. Based on these data, it can be stated that the electrode exhibited a higher potential response compared to toward other anions.

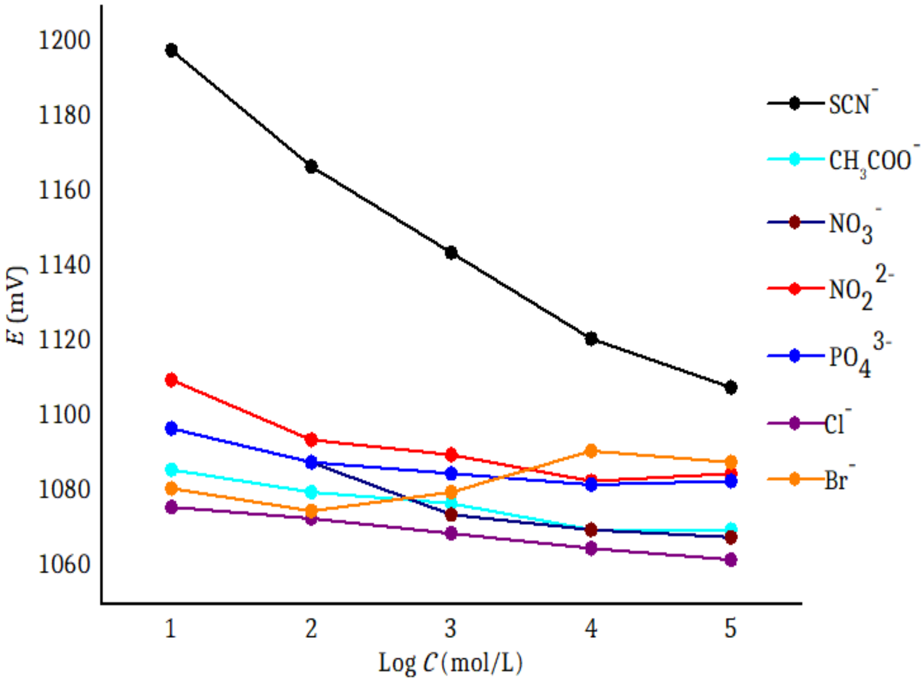

Figure 4. The potentiometric selectivity of the thiocyanate–selective electrode against interfering anions

Table 2. The selectivity coefficients of various interfering anions

Interfering anions	Selectivity coefficient, $logK_{SCN^{-},\ j}$	Interfering anions	Selectivity coefficient, $logK_{SCN^{-},\ j}$	Interfering anions	Selectivity coefficient, $logK_{SCN^{-},\ j}$
NO_2^{2-}	-1.24	NO_3^{-}	-1.34	Br^{-}	-1.56
PO_4^{3-}	-1.33	CH_3COO^{-}	-1.47	Cl^{-}	-1.59

The effect of pH on the electrode potential at 1.0 × 10^{-2} M thiocyanate ion concentration was studied with HNO_3 or NaOH solutions in the pH range of 2.0–12.0. The results were shown in Figure 5. It is clear that the pH change does not significantly affect the electrode potential in the pH range from 5.0 to 9.0.

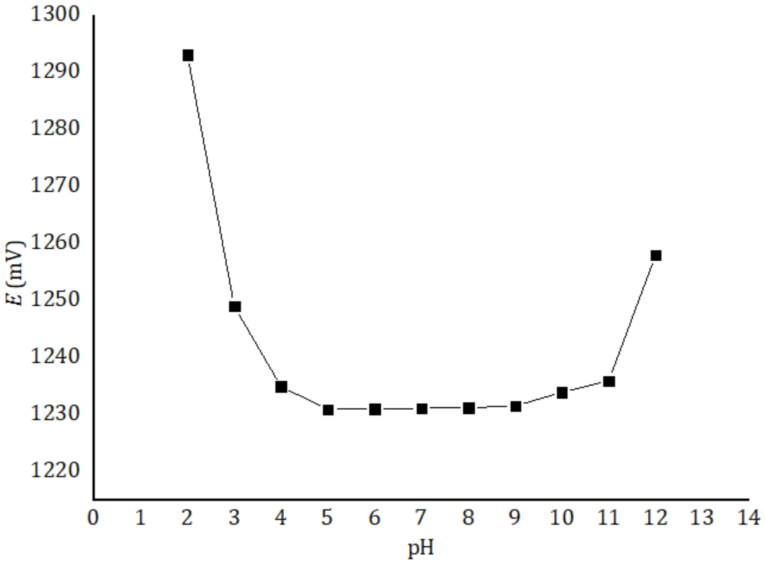

Figure 5. pH working range of the thiocyanate–selective electrode

4. Conclusion

This study used iron–azadipyromethene derivative molecule as an ionophore, and a thiocyanate–selective potentiometric electrode was developed. Potentiometric properties of the prepared electrode were investigated. The developed thiocyanate–selective electrode exhibited a linear response in the concentration range of 1.0 × 10^{-1} – 1.0 × 10^{-4} M of thiocyanate ions. The thiocyanate–selective electrode has a wide working pH range of 5.0–9.0. The proposed electrode exhibited good reusability, selectivity and fast response time.

Author Contributions

All authors contributed equally to this work. They all read and approved the last version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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