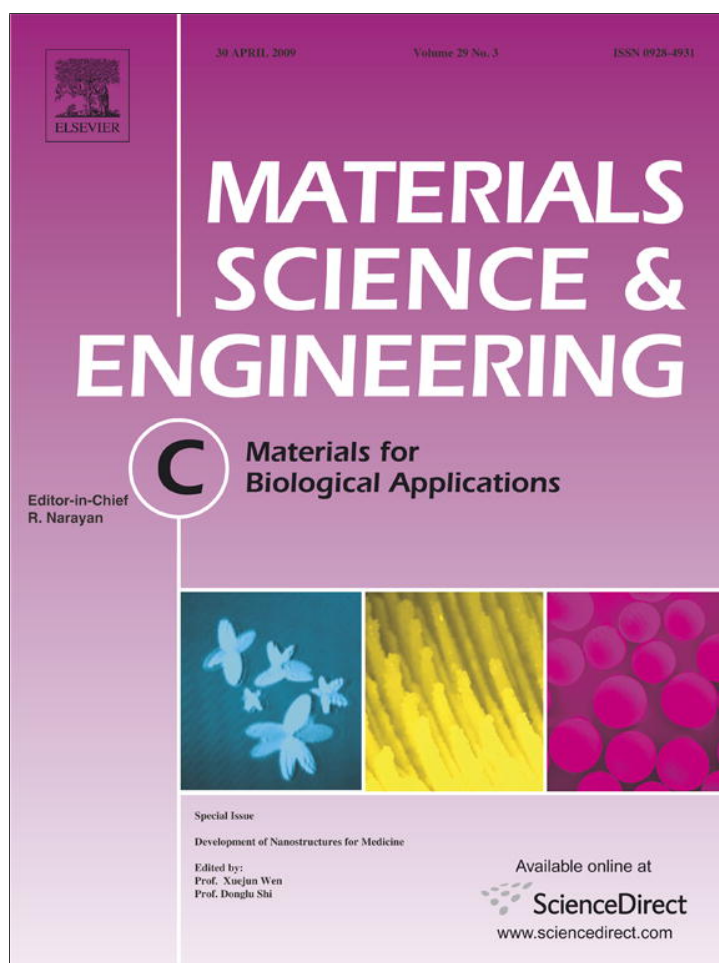


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2,3-Diphenylquinoxaline-4',4''-dioxytriethylene glycol as a sensing and selective material for construction of strontium-PVC membrane sensor

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ABSTRACT

The PVC membrane containing 2,3-diphenylquinoxaline-4',4''-dioxytriethylene glycol (PQTEG) as a suitable ionophore, presents a linear dynamic range of 1.0×10^{-6} – 1.0×10^{-2} M with a Nernstian slope of 29.9 mV per decade and a detection limit of 6.7×10^{-7} M. The response time is quick (smaller than 15 s), it can be used in the pH range of 4.1–8.9 and its duration is at least 55 days without noticing any considerable potential divergence. The proposed electrode has very good selectivity with respect to all common alkali, alkaline earth in the range of –3.28 to –4.00, and for transition metal ions in the range of –3.38 to –4.00. It was successfully applied as an indicator electrode in potentiometric titration of Sr(II) ions with EDTA.

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1. Introduction

Strontium is an important alkaline earth metal used in the production of glass for colored television sets and ferrite magnets. It is also particularly used in the refining of zinc, added to tin and lead alloys for increasing hardness and durability [1]. Therefore, the determination of strontium is important and several instrumental methods are used in order to determine strontium such as atomic absorption spectrometry [2,3], flame photometry [4], ICP-AES [5,6], ion-selective electrodes [7–11], etc. Among these techniques, the ion-selective electrode method is relatively simple, fast and inexpensive. Due to the critical importance of selective Sr(II) ion determination, especially, in biological, industrial and water samples, there are a number of recent reports on the preparation of Sr(II) selective membrane electrodes based on a variety of ionophores [7–11]. Consequently, in this study we have tried to prepare a selective sensor to determine the amount of strontium.

Recently, several very selective and sensitive polyvinyl chloride (PVC)-membrane ISEs for various metal ions have been reported [11–21]. The aim of this work is the fabrication of a highly selective and sensitive Sr²⁺ PVC membrane electrode based on 2,3-diphenylquinoxaline-4',4''-dioxytriethylene glycol (PQTEG) as a suitable ionophore

for the selective and sensitive potentiometric determination of Sr(II) ion over a wide concentration range (Fig. 1).

2. Experimental

2.1. Reagents

The Aldrich and the Merck Chemical Co. supplied the following reagents; nitrate and chloride salts of all the cations, reagent-grades of dibutyl phthalate (DBP), dioctyl phthalate (DOP), benzyl acetate (BA), tetrahydrofuran (THF) and relatively high molecular weight PVC (MW 110,000 g). Moreover, all reagents were used without any modification. As far as the nitrate and chloride salts are concerned, they were of the highest purity available and were P₂O₅-vacuum dried. During the experiments, triply distilled de-ionized water was used.

2.2. Electrode preparation

The required amounts of the membrane ingredients (40 mg powdered PVC and 57 mg DOP as plasticizer) were mixed and dissolved in 5 mL of THF. To this mixture, 3 mg ionophore PQTEG was added and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture

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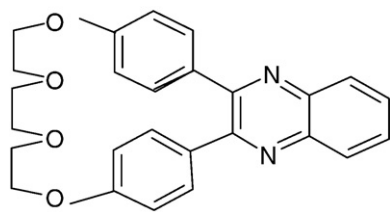


Fig. 1. The PQTEG structure.

was obtained. A Pyrex tube (3–5 mm i.d.) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm in thickness was formed [22–32]. Afterwards, the tube was removed from the solution kept at room temperature for 12 h, and then filled with an internal solution (1.0×10^{-3} M SrCl_2). The electrode was finally conditioned for 36 h by soaking in a 1.0×10^{-3} M solution of SrCl_2 . A silver/silver chloride coated wire was used as an internal reference electrode.

2.3. The emf measurements

All emf measurements were carried out with the following assembly:

Ag–AgCl|internal solution, 1.0×10^{-3} M SrCl_2 |PVC membrane|sample solution|Hg–Hg₂Cl₂, KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. Activities were calculated according to Debye–Huckel procedure.

2.4. Synthesis of PQTEG

2.4.1. Preparation of 4-[3-(4-hydroxyphenyl)-2-quinoxaliny] phenol (1)

A two-necked flask, equipped with a Dean–Stark trap and gas inlet tube, was charged with a mixture of acetic acid (60 mL), 1,2-di[4-hydroxyphenyl]-1,2-ethanedione (1.73 g, 7.14 mmol), 1,2-diaminobenzene (0.77 g, 7.1 mmol), and 11 mL of toluene was refluxed for 12 h under nitrogen, and then it was poured into cold water (145 mL) containing 7 mL HCl. The solid product was obtained by recrystallisation from ethanol/charcoal. The melting point was 329–330 °C, and the yield 63%.

¹H NMR: (acetone-*d*₆ – 100 MHz) δ : 6.8(d, 4H, *J* = 8.88 Hz), 7.34 (d, 4H, *J* = 8.88 Hz), 7.7 (q, 2H), 8.7 (s, H).

FT-IR (KBr): 609.5, 762.5, 735.1, 981.7, 1105.1, 1143.7, 1168.8, 1220.9, 1278.7, 1352, 1400.2, 1438.8, 1488.9, 1591.2, 1608.5, 1666.4, 1764.7, and 3200–3520 cm^{-1} .

2.4.2. Preparation of 2,3-diphenylquinoxaliny-4,4-dioxytriethyleneglycol (PQTEG)

To a solution of 4-[3-(4-hydroxyphenyl)-2-quinoxaliny] phenol (1) (0.5 g, 1.59 mmol) in dry acetonitril (60 mL), potassium carbonate (1 g, 1.59 mmol) was added. The resulting mixture was refluxed, and then solution of triethylene glycol ditosylate (0.72 g, 1.59 mmol) in dry acetonitril (40 mL) was added drop wise. The mixture was refluxed for 72 h. The reaction mixture was concentrated by distillation under

Table 1
Optimization of the membrane ingredients.

| Sensor no. | Composition (wt.%) | | | Slope (mV/decade) | Concentration range (M) |
|------------|--------------------|-------------|-------|-------------------|---|
| | PVC | Plasticizer | PQTEG | | |
| 1 | 40 | DOP,59 | 1 | 20.2 | 1.0×10^{-1} – 1.0×10^{-6} |
| 2 | 40 | DOP,57 | 3 | 29.9 | 1.0×10^{-1} – 1.0×10^{-6} |
| 3 | 40 | DOP,56 | 4 | 34.2 | 1.0×10^{-1} – 1.0×10^{-6} |
| 4 | 40 | DBP,56 | 3 | 35.4 | 1.0×10^{-1} – 1.0×10^{-6} |
| 5 | 40 | DBP,57 | 4 | 46.1 | 1.0×10^{-1} – 1.0×10^{-6} |
| 6 | 40 | BA,60 | 3 | 19.5 | 1.0×10^{-1} – 1.0×10^{-4} |
| 7 | 40 | DOP,60 | – | 8.3 | 1.0×10^{-2} – 1.0×10^{-4} |

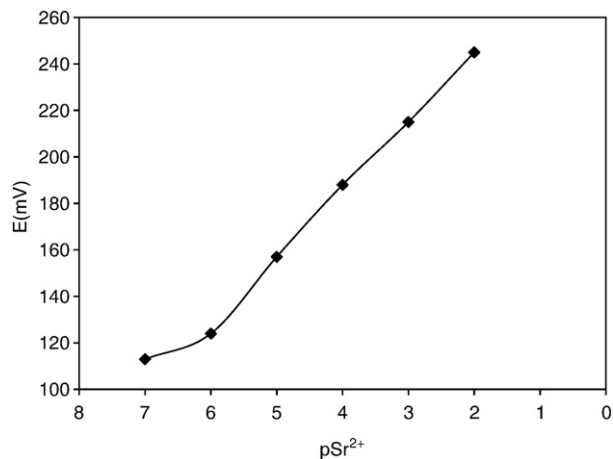


Fig. 2. The calibration curve of the strontium electrode (membrane no. 2) based on the PQTEG.

reduced pressure. The residue was dissolved in chloroform (60 mL) and washed with de-ionized water. The organic layer was condensed after drying over anhydrous sodium sulfate, to produce (PQTEG) in a 60% yield. The melting point was 187–190 °C.

¹H NMR: (acetone-*d*₆ – 100 MHz) δ : 3.6 (s, 4H), 3.7 (t, 4H), 6.65–6.75 (m, 4H), 7.45 (m, 4H), 7.6 (dd, 2H), 7 (dd, 2H).

FT-IR (KBr): 675, 761.8, 737, 781.4, 927.7, 974, 1051.1, 1134.1, 1172.6, 1249.8, 1296.1, 1344.3, 1390.6, 1440.7, 1506.3, 1604.7, 1666.4, 1699.2, 1715.5, 1764.7, 2335.6, and 2869.9 cm^{-1} .

3. Results and discussions

3.1. Influence of the membrane compositions on the potential response

Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligands [33–37], it was expected to play a key role in determining the selectivity, working concentration range and response time of the membrane electrode. The PVC-based membrane sensor based on PQTEG generated stable potential response in aqueous solutions containing strontium ions after conditioning for about 36 h in a 1.0×10^{-2} M strontium nitrate solution. The potential responses of all of the membrane sensors were studied in a wide range of concentrations of strontium nitrate solution. Table 1 shows that the total potentiometric response of the electrode towards Sr(II) ions is dependent on the concentration of the PQTEG that is incorporated within the membrane. As can be seen from Table 1, larger slopes are observed by increasing the amount of PQTEG up to 3% in the

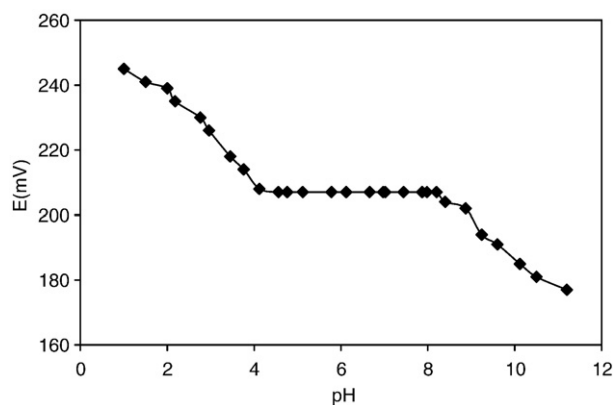


Fig. 3. The pH effect of the test solution (1.0×10^{-3} M) on the potential response of the strontium sensor (membrane no. 2).

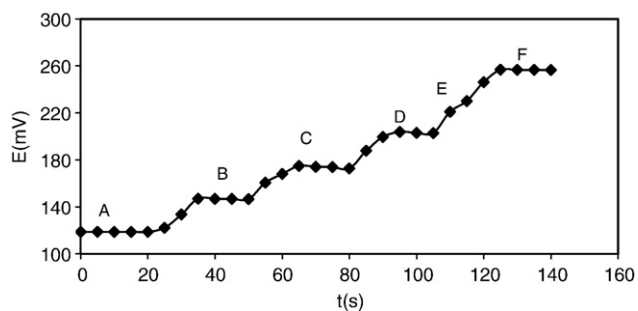


Fig. 4. The dynamic response time of the strontium electrode (membrane no. 2) for step changes in the Sr^{2+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M, F) 1.0×10^{-1} M.

membranes. A maximum slope of 29.9 mV per decade of strontium concentration was observed for the membrane No. 2 with 3% of PQTEG. Among the two different solvent mediators tested, we found that DOP compared to DBP results in the best sensitivity in construction of the Sr(II) membrane sensor.

3.2. Calibration graph and statistical data

The optimum responses of the sensors based on PQTEG were evaluated after conditioning of the membranes with same composition, for different periods of time in 0.01 M strontium nitrate solution. The potential response of the Sr(II) PVC-based membrane sensor at varying concentrations of strontium nitrate (Fig. 2) indicates a linear working concentration range from 1.0×10^{-6} to 1.0×10^{-1} M. During the experiments pH of the solutions were kept 5.5 by using sodium acetate buffer.

The slope of the calibration graph was 29.9 mV per decade of strontium ions concentration. The detection limit of the electrode determined from the intersection of the two extrapolated segments of the calibration graph was 6.7×10^{-7} M. The proposed PVC-based membrane sensor could be used for at least 55 days (use of 1 h daily). After its use, it was washed and kept dry for use in next day. During this certain time period, the membrane sensor could be used without any measurable divergence.

3.3. Effect of pH

The pH dependence of the membrane electrode was tested for the pH values (concentrated NaOH or HCl was used for the pH adjustment) from 1.0 up to 11.0 at certain Sr^{2+} ion concentration (1.0×10^{-3} M) and the result is depicted in Fig. 3. As can be seen, the potential remains constant in the pH range of 4.1–8.9. Beyond this range, a gradual change in the potential was detected. The observed potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Sr(II) and

Table 2 Comparison of selectivity coefficients, detection limit and linearity range of proposed Sr^{2+} sensor and the previously reported Sr^{2+} ion-selective electrodes.

| | [8] | [9] | [10] | [11] | This work |
|--------------------------|--|--|--|--|--|
| Linearity rang (M) | 3.2×10^{-5} 1.0×10^{-1} | 9.0×10^{-6} 1.0×10^{-1} | 3.2×10^{-5} 1.0×10^{-1} | 1.9×10^{-5} 1.0×10^{-1} | 1.0×10^{-6} 1.0×10^{-1} |
| Detection limit (M) | 8.0×10^{-6} | 5.0×10^{-6} | – | – | 6.7×10^{-7} |
| Selectivity coefficients | Log K_{MPM} | Log K_{MPM} | Log K_{FIM} | Log K_{FIM} | Log K_{MPM} |
| Na^+ | –1.40 | –1.30 | –1.70 | –1.60 | –3.28 |
| K^+ | –1.00 | –2.30 | –1.60 | –1.70 | –3.43 |
| Mg^{2+} | –1.68 | –3.00 | –1.30 | –1.51 | –3.38 |
| Ca^{2+} | –1.00 | –2.60 | –1.50 | –1.45 | –3.13 |
| Ba^{2+} | –1.31 | –2.20 | –1.41 | –1.47 | –4.00 |
| Cd^{2+} | –2.52 | – | –1.20 | –1.10 | –4.00 |
| Ni^{2+} | –1.70 | – | –1.70 | –1.36 | –3.38 |
| Pb^{2+} | –1.30 | –2.50 | –1.20 | –1.36 | –4.00 |

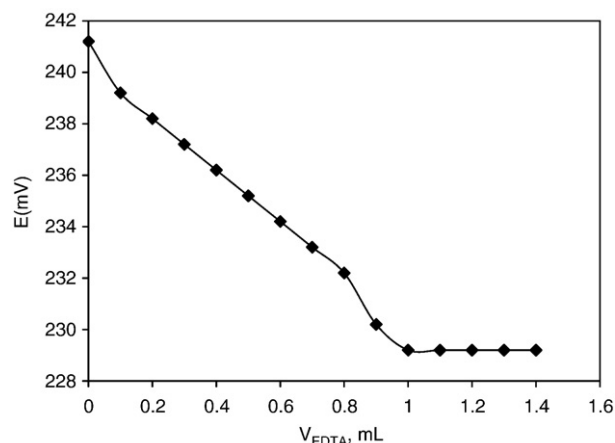


Fig. 5. The potentiometric titration curve of 10.0 mL from the Sr^{2+} solution 1.0×10^{-2} M with 1.0×10^{-1} M of EDTA.

insoluble strontium hydroxide, that in both cases, the concentration of free Sr(II) reduces in the solution. At pH values lower than 4.1, the potentials increase, indicating that the membrane sensor responds to hydrogen ions.

3.4. Dynamic response time

For any ion-selective electrode, response time is one of the most important factors. Here, we define response times as the average time required for the Sr(II) sensor to reach a potential within ± 1 mV of the final equilibrium value, after successive immersions of a series of Sr(II) ion solutions, each having a 10-fold concentration difference. In this study, this parameter was measured and the related results were plotted against the potential (Fig. 4). As observed, the plasticized membrane electrode reaches its equilibrium response in a very short time (~ 15 s) over the entire concentration range.

3.5. Selectivity of the sensor

Potentiometric selectivity coefficients of the sensor were determined by the matched potential method [38–40]. According to this method, a specified activity (concentration) of primary ions ($A: 10^{-2}$ M) is added to a reference solution (10^{-6} M) and the potential measured. In a separate experiment, interfering ions ($B: 10^{-2}$ – 10^{-3} M) are successively added to an identical reference solution, until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\text{MPM}} = a_A/a_B$.

A comparison is exhibited in Table 2 between the selectivity coefficients of the developed Sr(II) sensor with those of the best previously reported Sr(II) electrodes [8–11]. As it is immediately obvious, the selectivity coefficients of the electrode for all the diverse

Table 3 Results from the analysis of White cabbage (BCR-679).

| Element | Certified values (mg/kg) |
|---------|--------------------------|
| Cd | 1.66 ± 0.07 |
| Cu | 2.89 ± 0.12 |
| Fe | 55.0 ± 2.5 |
| Mn | 13.3 ± 0.5 |
| Mo | 14.8 ± 0.5 |
| Ni | 27.0 ± 0.8 |
| Sr | 11.8 ± 0.4 |
| Zn | 79.7 ± 2.7 |
| Hg | 6.3 ± 1.4 |
| Sb | 20.6 ± 2.6 |
| Tl | 3.0 ± 0.3 |

ions are in the order of 5.3×10^{-3} or smaller, indicating they would not significantly disturb the function of the Sr(II) selective membrane sensor. Furthermore, it is instantly clear that the concentration range, the detection limit of the recommended electrode and the selectivity coefficients are superior to those stated by other researchers.

3.6. Analytical application

The suggested strontium cation-selective electrode was found to work well under the laboratory conditions. The selective strontium membrane sensor was used as an indicator electrode in the titration of a 1.0×10^{-4} M strontium ion solution with a standard solution of 1.0×10^{-2} M EDTA (pH = 10). The resulting titration curve is shown in Fig. 5. According to this figure, the sensor is capable of monitoring the amount of strontium ions effectively.

3.6.1. Validation with CRM

The performance of the introduced sensor was estimated by its use in the Sr(II) ion determination of the White cabbage (BCR-679), as certified reference material (CRM). In Table 3, the respective CRM analysis is reported. It was noticed that the Sr(II) concentration was equivalent to 11.8 ± 0.4 mg/kg. After the employment of the calibration method, the Sr(II) concentration value was found to be 12.0 ± 0.2 mg/kg. After taking into consideration these two concentration values, it became evident that the Sr(II) sensor was an efficient device for the sensitive Sr(II) ions determination, despite the presence of other elements.

4. Conclusion

The PVC-based membrane electrode of the 2, 3-diphenylquinoxaline-4',4''-dioxytriethylene glycol ligand (PQTEG) with the composition 3% ionophore, 40% PVC and 57% DOP exhibited the best performance characteristics with Nernstian behavior across the concentration range of 1.0×10^{-6} – 1.0×10^{-2} M Sr^{2+} , and a fast response time of 15 s. The sensor works well in a pH range of 4.1–8.9, and also, it was successfully used as an indicator electrode in the strontium ion titration with EDTA.

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