

Highly Selective Liquid Membrane Sensor Based on 1,3,5-Triphenylpyrylium Perchlorate for Quick Monitoring of Sulfate Ions

Mohammad Reza Ganjali,* Maryam Ghorbani, Azadeh Daftari, Parviz Norouzi, Hooshang Pirelahi, and Hossein Daryanavard Dargahani

Department of Chemistry, Tehran University, P.O. Box 14155-6455, Tehran, Iran

Received May 2, 2003

A highly selective membrane electrode based on 1,3,5-triphenylpyrylium perchlorate (TPPP) is presented. The proposed electrode shows very good selectivity for sulfate ions over a wide variety of common inorganic and organic anions. The sensor displays a nice Nernstian slope of -29.7 mV per decade. The working concentration ranges of the electrode is $1.0 \times 10^{-1} - 6.3 \times 10^{-6}$ M with a detection limit of 4.0×10^{-6} M (480 ng per mL). The response time of the sensor in whole concentration ranges is very short (< 6 s). The response of the sensor is independent on the pH range of 2.5-9.5. The best performance was obtained with a membrane composition of 32% PVC, 59% benzyl acetate, 5% TPPP and 4% hexadecyltrimethylammonium bromide. It was successfully used as an indicator electrode for titration of sulfate ions with barium ions. The electrode was also applied for determination of salbutamol sulfate and paramomycine sulfate.

Key Words : Pyrylium derivative, TPPP, Sulfate, Potentiometry, PVC

Introduction

Investigations about ion selective electrodes are steadily increasing. The rapid development of these electrodes, reflect the extent to which these devices meet the need for accurate, cheap and rapid analytical and control techniques. These electrodes are being used in clinical analysis and in routine control analysis of cations and anions.¹ It has been well documented that the selective complexation of anions by synthetic ionophores can be used to design anion selective electrodes that exhibit non-Hofmeister selectivity pattern, *i.e.*, selectivities that are not based solely on the analyte lipophilicity.² Most of these electrodes are based on vitamin B₁₂ derivatives,^{3,4} metalloporphyrines,⁵ organomercury compounds,⁶ Schiff's base complexes of metal ions,⁷ trialkyltin derivatives,⁸ phthalocyanines⁹ and metal complexes of organophosphines.¹⁰ In all these cases, ligation of the primary anion to the central metal ion is responsible for the observed selectivity.

Recently, new sulfate ion selective sensors based on a bis-thiourea ionophore,¹¹ a derivative of imidazole,¹² a zwitterionic bis (guanidinium) ion carrier¹³ a tris (2-aminoethylamine) derivative¹⁴ and hydrotalcites¹⁵ with a Nernstian behavior and relatively wide working concentration range have been reported. The interference effect of anions such as Cl⁻, HSO₃⁻, HCO₃⁻, CH₃COO⁻, and HPO₄²⁻ for these new sensors is significantly reduced, but they suffer serious interference from other anions such as NO₃⁻, Br⁻, F⁻, NO₂⁻, ClO₄⁻ and SCN⁻. In this work, we wish to introduce a highly selective membrane electrode for quick determination of sulfate ions in various samples based on TPPP.

Experimental Section

Reagents. Reagent grade *o*-nitrophenyloctyl ether (NPOE), dibutyl phthalate (DBP), benzyl acetate (BA), tetrahydrofuran (THF), hexadecyltrimethylammonium bromide (HTAB) and high relative molecular weight PVC were purchased from Merck chemical company and used as received. Reagent grade potassium salts of all anions used (all from Aldrich) were of highest purity available and used without any further purification except for vacuum drying over P₂O₅. All other reagents needed were purchased from Merck and used as received. 1,3,5-triphenylpyrylium perchlorate (TPPP) (Fig. 1) was synthesized and purified as described elsewhere.¹⁶ Triply distilled de-ionized water was used throughout.

Electrode preparation. The general procedure to prepare the PVC membrane was to mix thoroughly, 32 mg of PVC, 5 mg of TPPP, 4 mg of HTAB and 59 mg of BA. Then the mixture was dissolved in 3 mL of dry freshly distilled THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a nontransparent membrane of about 0.3 mm thickness is formed.¹⁷⁻²⁰ Then, the tube was pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with internal solution (1.0×10^{-3} M K₂SO₄). The electrode was finally conditioned for 24 h by soaking in a solution containing 1.0×10^{-2} M K₂SO₄.

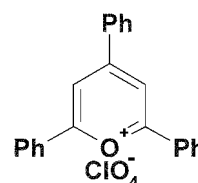


Figure 1. Structure of TPPP.

*Corresponding Author. Fax: +98-21-6495291, e-mail: Ganjali@khayam.ut.ac.ir

Potential measurements. All emf measurements were carried out with following assembly:

Ag–AgCl | internal solution (1.0×10^{-3} M K_2SO_4) | PVC membrane | test solution | Ag–AgCl | KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25 ± 0.1 °C.

Results and Discussion

Stability constants of different anion-TPPP complexes.

It is well known that the TPPP and other pyrylium derivatives have fluorescence property.²¹ Thus, at first we carried out some spectrofluorimetric measurements in acetonitrile solution in order to obtain quantitative information about the anion-TPPP interactions. The fluorescence intensity vs. anion/TPPP mole ratio plot for some anions is shown in (Fig. 2). As it is seen, addition of sulfate ion to a TPPP solution resulted in a distinct quenching of the fluorescence of TPPP, and the formation of a stable 1 : 1 sulfate-TPPP complex in solution. While, the presence of other anions displays a gradual decrease in fluorescence intensity, which does not tend to level off even at mole ratio > 2 , indicating that formation of weak complex between TPPP and other anions. The formation constants ($\log K_f$)²²

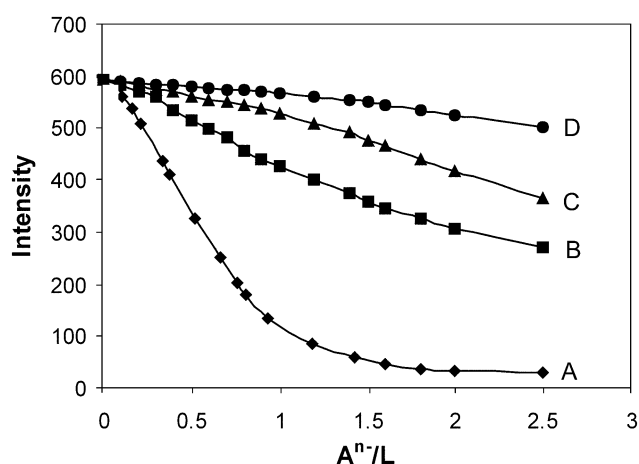


Figure 2. The fluorescence intensity vs. anion/TPPP mole ratio plot of (A) (\blacklozenge SO_4^{2-}), (B) (\blacksquare SO_3^{2-}), (C) (\blacktriangle CN^-), (D) (\bullet I^-).

Table 1. Stability constants of anion-TPPP complexes

Anions	$\log K_f$
SO_4^{2-}	> 6.0
SO_3^{2-}	3.29 ± 0.05
HPO_4^{2-}	2.17 ± 0.03
NO_2^-	2.91 ± 0.07
NO_3^-	2.63 ± 0.03
CH_3COO^-	2.31 ± 0.05
ClO_4^-	< 2.0
I^-	2.44 ± 0.07
Br^-	2.50 ± 0.03
Cl^-	2.39 ± 0.06
F^-	< 2.0

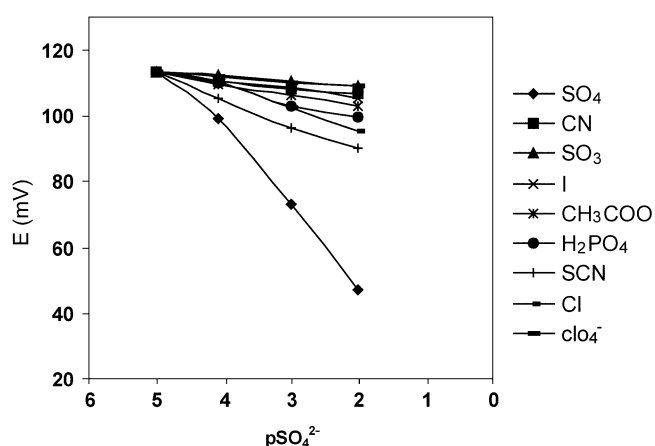


Figure 3. Potential responses of different ionselective electrodes based on TPPP (\blacklozenge SO_4^{2-}), (\cdots SCN^-), ($---$ Cl^-), (\bullet $H_2PO_4^-$), (\ast CH_3COO^-), (\times I^-), (\blacksquare CN^-), (\blacktriangle SO_3^{2-}).

of the TPPP and some anions are summarized in Table 1. As it is seen, there is a strong interaction between sulfate and TPPP.

Potentiometric responses of the sensors based on TPPP.

In next experiments, the TPPP was used as an ionophore in construction of anionselective membrane electrodes for common organic and inorganic anions. The potential responses of these sensors in the concentration ranges of 1.0×10^{-5} – 1.0×10^{-1} M are shown in (Fig. 3). As can be seen from Figure 3, the PVC-based membrane sensor shows very good selectivity towards sulfate ions over other anions.

Besides the critical role of the nature of ion carrier in preparing membrane-selective electrodes, some other important features of the PVC membrane, such as the amount of ionophore, the nature of plasticizer, the plasticizer/PVC ratio, and especially, the nature of additives used, are known to significantly influence the sensitivity and selectivity of ion-selective electrodes.^{18–20} Thus, different aspects of membrane preparation based on the TPPP for sulfate ions were optimized and the results are given in Table 2. As can be seen, from Table 2, BA is a more effective solvent mediator than NPOE, DBP in preparing the sulfate ion-

Table 2. Optimization of membrane ingredients

Number of membrane	Composition %				Slope (mV per decade)
	PVC	Plasticizer	TPPP	HTAB	
1	32	68, BA	0	–	~ -2 mV
2	32	66, BA	2	–	-10.7 ± 0.2
3	32	64, BA	4	–	-12.8 ± 0.1
4	32	62, BA	6	–	-14.2 ± 0.2
5	32	63, BA	5	–	-14.7 ± 0.3
6	32	61, BA	5	2	-19.6 ± 0.3
7	32	60, BA	5	3	-24.8 ± 0.5
8	32	59, BA	5	4	-29.7 ± 0.2
9	32	59, NPOE	5	4	-18.6 ± 0.3
10	32	59, DBP	5	4	-15.7 ± 0.1
11	32	64, BA	–	4	-4.8 ± 0.4

selective electrode. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. The quantity of the ionophore TPPP was also found to affect the sensitivity of the membrane electrode (Nos. 2-5). The sensitivity of the electrode response increases with increasing ionophore content until a value of 5% is reached. The data given in Table 2 show that the presence of lipophilic additives has a beneficial influence on the performance characteristics of the membrane electrode. Table 2 shows that, addition of 4% HTAB will increase the slope of the potential response of the sensor from a poor value of -14.7 mV per decade (No. 5) to a Nernstian value of -29.7 mV/decade (No. 8). The presence of such cationic additives can reduce ohmic resistance²³ and improve the response behavior and selectivity of the membrane electrodes.²⁴ Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface.²⁵ As is obvious, the best response characteristics are obtained with a membrane composition of 32% PVC, 59% BA, 5% TPPP, and 4% HTAB (No. 8).

The concentration of the internal solution K_2SO_4 in the electrode was changed from 1.0×10^{-3} to 1.0×10^{-5} M and the potential response of the sulfate ion-selective electrode was measured. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for the smooth functioning of electrode system.

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-3} M K_2SO_4 was 24 h, after which it would generate stable potentials in contact with sulfate solutions. The electrode shows a linear response to the concentration of K_2SO_4 ions in the range of 6.3×10^{-6} – 1.0×10^{-1} M (Fig. 4). The slope of the calibration graph was -29.7 ± 0.2 mV per decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 4.0×10^{-6} M.

For analytical application, response time of sensor in

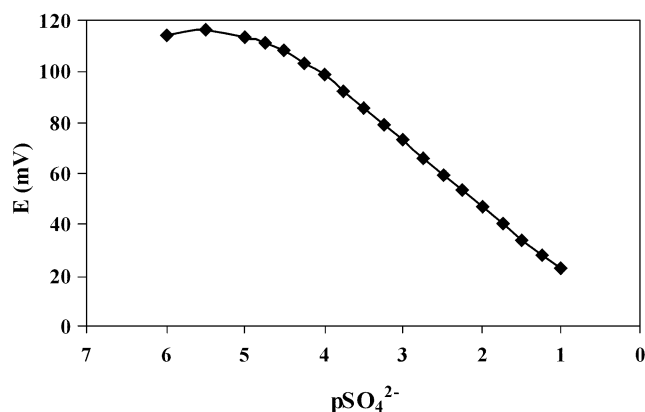


Figure 4. Calibration curves of sulfate electrode based on TPPP at pH 6.

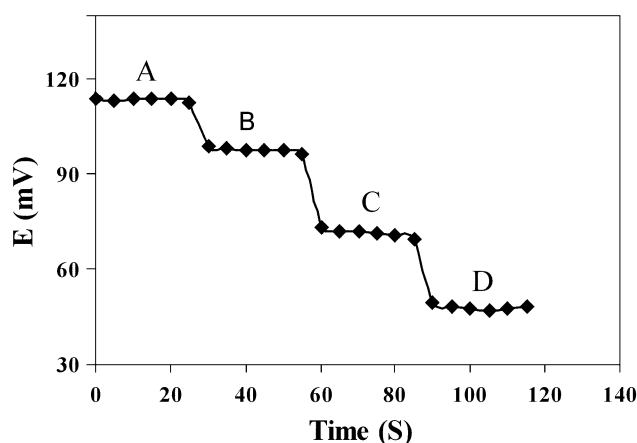


Figure 5. Dynamic response time of the sulfate electrode for step changes in concentration of SO_4^{2-} : (A) 1.0×10^{-5} M, (B) 1.0×10^{-4} M, (C) 1.0×10^{-3} M, (D) 1.0×10^{-2} M.

different concentrations is an important factor. In this study, the practical response time was recorded by immediate changing of sulfate concentration from 1.0×10^{-5} to 1.0×10^{-1} M and the results are shown in Figure 5. As it is seen, in whole concentration ranges, the sensor reaches to the equilibrium response in a very short time (6 s).

The influence of the pH of the test solution (1.0×10^{-3} M of K_2SO_4) on the potential responses of the sulfate PVC-based membrane electrode was tested in the pH range 2.0–12.0, and the results are depicted in Figure 6. As it is seen, the response of the sensor is independent of the pH in the range 2.5–9.5. At higher alkaline media, the potential changed sharply, due to the response of the sensor to both sulfate and hydroxide ions. At lower pH than 2.5, due to the protonation of sulfate ions (formation of HSO_4^-), the potential response of the sensor increases.

Potentiometric selectivity coefficients, describing the preference of the TPPP-based membrane sensor for an interfering ion, B, relative to sulfate ion, A, were determined by the matched potential method.²⁶ According to this method, the specified activity (concentration) of the primary ion ($A = 1.0 \times 10^{-5}$ – 1.0×10^{-1} M) is added to a reference solution (5.0×10^{-6} M), and the potential is measured. In a

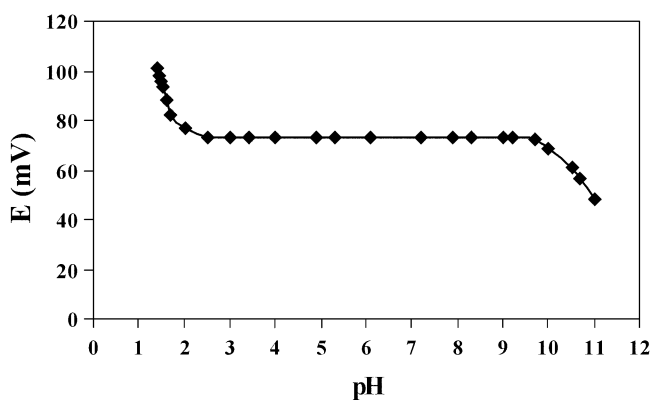


Figure 6. The effect of the pH of the test solution on the potential response of the sulfate sensor.

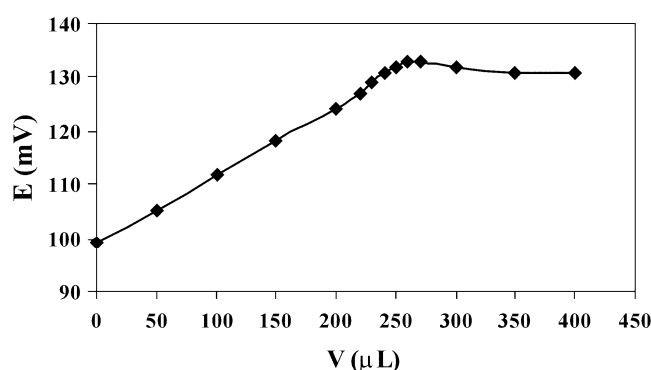
Table 3. Selectivity coefficients of various interfering anions

Anions	$K_{A,B}^{APPM}$
SCN	3.10×10^{-3}
Cl	1.78×10^{-3}
H ₂ PO ₄	1.12×10^{-3}
CH ₃ COO	5.62×10^{-4}
CN	3.16×10^{-4}
SO ₃ ²⁻	2.24×10^{-4}
NO ₃	5.41×10^{-4}
NO ₂	1.99×10^{-3}
I	4.47×10^{-4}
ClO ₄ ⁻	6.52×10^{-4}

separation experiment, the interfering ion ($B = 1.0 \times 10^{-1}$ - 1.0×10^{-3} M) is successively added to an identical reference solution until the measured potential matched that obtained before by adding the primary ions. The matched potential method selectivity coefficients, is then given by the resulting primary ion to interfering ion activity (concentration) ratio. The selectivity coefficients for various anions are summarized in Table 3. As it is seen, for all organic and inorganic anions used, the selectivity coefficients are smaller than 3.1×10^{-3} , indicating that, they would not significantly disturb the functioning of the sulfate ion-selective electrode.

Table 4 compared the selectivity coefficients of the proposed membrane sensor with those reported before.¹¹⁻¹⁵ Noteworthy, this is just a gross relative comparison, since the selectivity data have been reported using different experimental methods as indicated in Table 4. As it is seen, the proposed sensor in term of selectivity coefficients is superior to those previously reported by the other researchers.¹¹⁻¹⁵

The proposed membrane sensor was found to work well under laboratory conditions. The sensor was used as an indicator electrode in the titration of sulfate ion (1.0×10^{-1}

**Figure 7.** Potentiometric titration curve of 25.0 mL 1.0×10^{-4} M solution of SO₄²⁻ with 1.0×10^{-2} M of Ba²⁺.

M) with a standard barium solution (1.0×10^{-2} M). The results of titration are shown in Figure 7, indicating that the amount of sulfate ion can be accurately determined with the electrode.

The sensor was also used for direct determination of salbutamol sulfate and paromomycine sulfate. 0.1 g of powdered of each compound was dissolved in 100 mL of distilled water and the sulfate content of the resulting solutions were then determined by the proposed sensor using the calibration method. The results obtained by the sensor together with those obtained by gravimetric method and declared amounts are summarized in Table 5. As it is seen, there are satisfactory agreements between the results obtained by the proposed sulfate sensor and those by gravimetric method and declared amounts.

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Table 4. Comparison of selectivity coefficients ($K_{A,B}$) for different sulfate ion- selective electrodes

Anion	Ref. 11	Ref. 12	Ref. 13	Ref. 14	Ref. 15	This work
Bromide	12.6	7.9	2.5×10^2	1.0×10^{-3}	1.0×10^{-1}	1.93×10^{-3}
Carbonate	-	-	7.9	-	-	-
Chloride	7.9×10^{-1}	1.1×10^{-1}	6.3×10^{-1}	1.0×10^{-3}	3.0×10^{-1}	1.78×10^{-3}
Cyanide	-	-	-	-	-	3.16×10^{-4}
Iodide	-	-	2.5×10^7	1.0×10^{-3}	-	4.47×10^{-3}
Nitrate	4.0×10^1	1.2×10^2	2.0×10^4	1.0×10^{-3}	3.3	5.40×10^{-4}
Nitrite	4.0	2.0	-	-	-	1.99×10^{-3}
Perchlorate	-	-	2.5×10^1	1.0×10^{-3}	-	6.52×10^{-4}
Sulfite	5.0×10^{-1}	-	-	5.0×10^{-1}	-	2.24×10^{-2}
Thiocyanate	8.0×10^2	-	-	1.0×10^{-3}	1.0×10^2	3.10×10^{-3}
Acetate	-	-	-	-	-	5.62×10^{-4}
Dihydrogenphosphate	-	-	-	-	-	1.12×10^{-3}

Table 5. Determination of Salbutamol sulfate and Paromomycin sulfate by the proposed sensor

Drugs	ISE method	Gravimetric method	Declared amount
Salbutamol sulfate	65.4 ± 0.1 (%W/W)	66.2 ± 0.3 (%W/W)	67 ± 0.2 (%W/W)
Paromomycin sulfate	63.2 ± 0.4 (%W/W)	63.7 ± 0.3 (%W/W)	64 ± 0.3 (%W/W)

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