

*Full Paper*

## **Potentiometric Sensor for Determination of Sulfate Ions based on 2-Amino-6-(tbutyl)-4-(pyridin-2-yl)pyrimidine (dichlorido)palladium(II)**

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**Abstract-** A novel PVC-based membrane sensor based on 2-Amino-6-(tbutyl)-4-(pyridin-2-yl)pyrimidine(dichlorido)palladium(II) (ATPP) for determination of trace amounts of sulfate ions is introduced. The electrode revealed Nernstian response towards sulfate over the wide concentration range from  $5.0 \times 10^{-1}$  to  $4.0 \times 10^{-7}$  M at the pH range of 2.9-9.5. The effect of solvent mediator, cationic additives and amount of ion-carrier on the behavior of the sensor was investigated. The sensor shows a short response time (<25s) in the whole concentration ranges. The detection limit of the electrode was  $1.8 \times 10^{-7}$  M and it could be used for 20 weeks without any measurable changes in the slope. The proposed electrode shows very good selectivity for sulfate ions over a wide variety of common inorganic and organic anions. 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.

**Keywords-** Sulfate ion-selective electrode, PVC membrane, 2-Amino-6-(tbutyl)-4-(pyridin-2-yl) pyrimidine(dichlorido)palladium(II), Potentiometry

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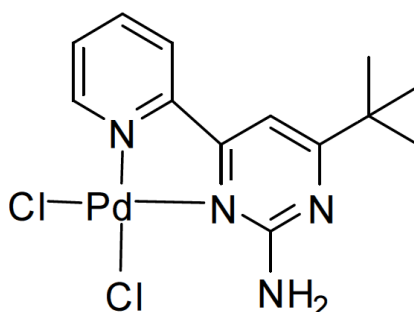
## 1. INTRODUCTION

Sulfate is a highly widespread anion, and its determination in environmental objects (such as sweet, mineral and sea water; atmospheric precipitation, in particular, acid rain), in various products and raw materials of chemical and pharmaceutical industry, in food, etc., has been an important task. Existing methods for sulfate determination have several drawbacks such as long duration and unacceptability for low concentrations (gravimetric methods); laboriousness, insufficient selectivity and reproducibility (optic methods including nephelometry and turbidimetry) [1]; complexity and high equipment cost (chromatographic and chromato-electrophoretic methods) [2,3]. Therefore, attention of researchers has long been focused on developing a sulfate-selective electrode suitable for sulfate determination in real objects.

Ion-selective electrodes based on solvent polymeric membrane with incorporating of ion carriers are shown to be very useful tools for many cations and some anions analyses. In addition to the cation-selective electrodes, recently the design and synthesis of sensory molecules for anion-selective electrodes has become a challenging subject. It is well known that the use of metal-ion containing ionophores as anion carriers in plasticized membrane electrodes may result in potentiometric anion selectivity pattern significantly different from the so-called Hofmeister selectivity sequence. Such anti-Hofmeister selectivity order is believed to originate from the selective axial ligation between the metal ion centers and certain anions [4]. Thus, the nature of the central metal is expected to play an important role in the realization of the selectivity patterns observed.

In recent years we have reported the successful use of some different ion carriers in constructions of PVC-based selective electrodes for Uranyl(II) [5,6], Cu(II) [7], Cr(III) [8], Co(II) [9], Th(IV) [10], Fe(III) [11], Ag(I) [12] and other Ions.

In this work, we report a novel sulfate electrode by using 2-Amino-6-(*t*butyl)-4-(pyridin-2-yl)pyrimidine)(dichlorido)palladium(II) (ATPP) (Fig. 1) as an excellent ionophore for potentiometric monitoring of trace amount of  $\text{SO}_4^{2-}$  ion in real samples.



**Fig. 1.** Structure of complex

## 2. EXPERIMENTAL

### 2.1. Reagents

Reagent grade o-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), benzyl acetate (BA), acetophenone (AP), hexadecyltrimethylammonium bromide (HTAB), hexadecylpyridinium bromide (HDPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Aldrich Chemical Company and used as received.

Potassium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Triply distilled de-ionized water was used throughout.

### 2.2. Synthesis of ligand

A solution of the corresponding ligands (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were added drop wise to a solution of 191 mg of bis(benzonitrile)palladium(II) chloride (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The mixture was stirred for 20 h at room temperature, the solution was concentrated and the product was precipitated by adding Et<sub>2</sub>O (10 mL). The product was filtered and washed with Et<sub>2</sub>O twice and dried under vacuum [13].

### 2.3. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 32 mg of powdered PVC, 60 mg of plasticizer NPOE, 3 mg of additive HTAB, and 5 mg of ionophore L in 4 mL of fresh THF. 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. 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 an internal filling solution (1.0×10<sup>-3</sup> M of K<sub>2</sub>SO<sub>4</sub>). The electrode was finally conditioned by soaking in a 1.0×10<sup>-2</sup> M K<sub>2</sub>SO<sub>4</sub> solution for 24 h [14,15]. A silver/silver chloride wire was used as an internal reference electrode.

### 2.4. The emf measurements

The emf measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

Ag–AgCl| 3 M KCl| internal solution, 1.0×10<sup>-3</sup> M K<sub>2</sub>SO<sub>4</sub>| PVC membrane| test solution| Hg –Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Hückel procedure [16].

### 3. RESULT AND DISCUSSION

#### 3.1. Preliminary Studies

Preliminary Studies show that the ATPP has fluorescence property. Thus, at first we carried out some spectrofluorimetric measurements in acetonitrile solution in order to obtain quantitative information about the anion-ATPP interactions. The fluorescence intensity vs. anion/ATPP mole ratio plot for some anions was test. Result shown, addition of sulfate ion to an ATPP solution resulted in a distinct quenching of the fluorescence of ATPP, and the formation of a stable 1:1 sulfate-ATPP 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 ATPP and other anions. The formation constants ( $\log K_f$ ) [17] of the ATPP and some anions are summarized in Table 1. As it is seen, there is a strong interaction between sulfate and ATPP.

**Table 1.** Stability constants of anion-ATPP complexes

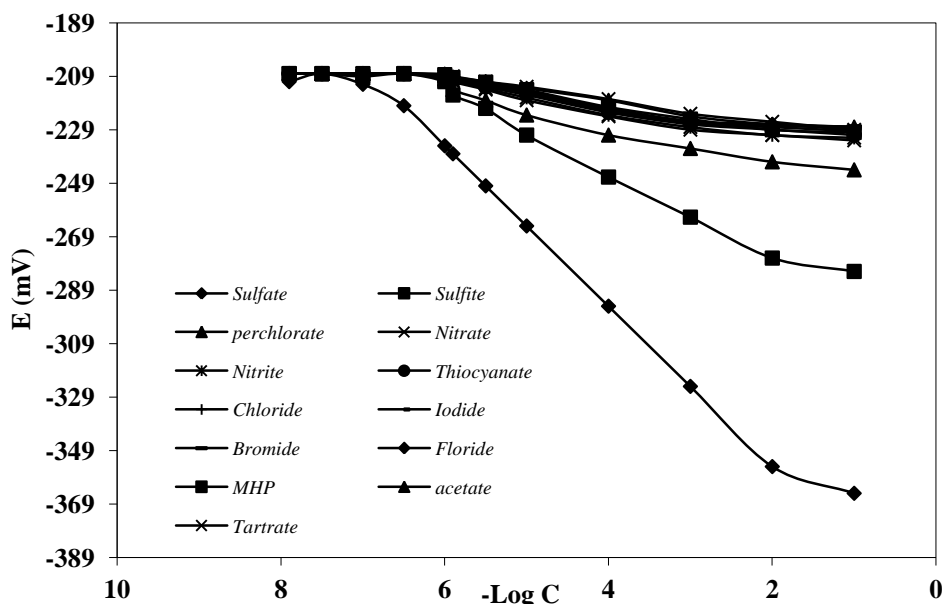
Anions	Log $K_f$	Anions	Log $K_f$
$SO_4^{2-}$	$5.02 \pm 0.05$	I <sup>-</sup>	$2.34 \pm 0.05$
$SO_3^{2-}$	$3.41 \pm 0.04$	Br <sup>-</sup>	$2.21 \pm 0.05$
$ClO_4^-$	$3.16 \pm 0.05$	F <sup>-</sup>	$2.16 \pm 0.05$
$NO_3^-$	$2.87 \pm 0.06$	$HPO_4^{2-}$	<2
$NO_2^-$	$2.75 \pm 0.05$	$CH_3COO^-$	<2
$SCN^-$	$2.61 \pm 0.05$	Tartrate <sup>2-</sup>	<2
Cl <sup>-</sup>	$2.55 \pm 0.05$		

In next experiments, the ATPP was used as an ionophore in construction of anion selective membrane electrodes for common organic and inorganic anions. The potential responses of these sensors in the concentration ranges of  $1.0 \times 10^{-7}$  -  $1.0 \times 10^{-1}$  M are shown in (Fig. 2). As can be seen from Fig. 2, the PVC-based membrane sensor shows very good selectivity towards sulfate ions over other anions.

#### 3.2. Membrane Composition

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 [5-12]. Thus, different aspects of membrane preparation based on the ATPP for sulfate ions were optimized and the results are given in Table 2. As expected, the

amount of ionophore was found to affect the PVC membrane sensitivity (nos. 1-4). The calibration slope increased with increasing ATPP content until a value of 6% was reached. However, further addition of the ionophore resulted in a diminished response slope of the electrode, most probably due to some in homogeneity and possible saturation of the membrane [18].



**Fig. 2.** Potential responses of different ion selective electrodes based on ATPP

The potentiometric response of the membrane ion-selective electrodes based on neutral ionophores is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components [18-20]. The influence of the nature of plasticizer on the  $\text{SO}_4^{2-}$  response was studied on electrodes containing three types of plasticizers having different dielectric constants, namely, DBP, BA and NPOE. As shown in Table 2, NPOE with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses.

It should be noted that the nature of the plasticizer affects not only the dielectric constant of membrane phase but also the mobility of ionophore molecules and the state of the ligands [19,21]. Also amount of plasticizer in membrane was tested. The calibration slope increased with increasing NPOE content until a value of 61% was reached. However, further addition of the NPOE resulted in a diminished response slope of the electrode.

It is well known that the incorporation of lipophilic additives can significantly influence the performance characteristics of a membrane sensor [22-25]. The presence of additives not only improves the response characteristics and selectivity [23] but also may catalyze the exchange kinetics at the sample-membrane interface [26]. In this work, we examined the influence of HTAB as suitable lipophilic additives, on the response characteristics of the

proposed PVC membrane, and the results are also included in Table 2. The data given in Table 2 indicate that, in the absence of a proper additive, the sensitivity of the PVC membrane based on L is quite low (nos. 1-6, with slopes of  $< -21.9$  mV decade<sup>-1</sup>). However, the presence of 4% HTAB (no. 8), as suitable lipophilic additive, will improve the sensitivity of the SO<sub>4</sub><sup>2-</sup> sensor considerably (with a slope  $30.1 \pm 0.3$  mV decade<sup>-1</sup>). It is interesting to note that, in membrane 8, the weight ratio of the ionophore to HTAB is 1.5, which implies that HTAB is not primarily a phase transfer catalyst but also contributes to the complexation mechanism, as described by Eugster et al [27]. Moreover, with a fraction of 4% wt, HTAB is expected to contribute significantly to the dielectric constant of the membrane in addition to the plasticizer.

As is obvious from Table 2, membrane 8 with a PVC/NPOE/HTAB/ATPP percent ratio of 29:61:4:6 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

### 3.3. Effect of Internal Solution

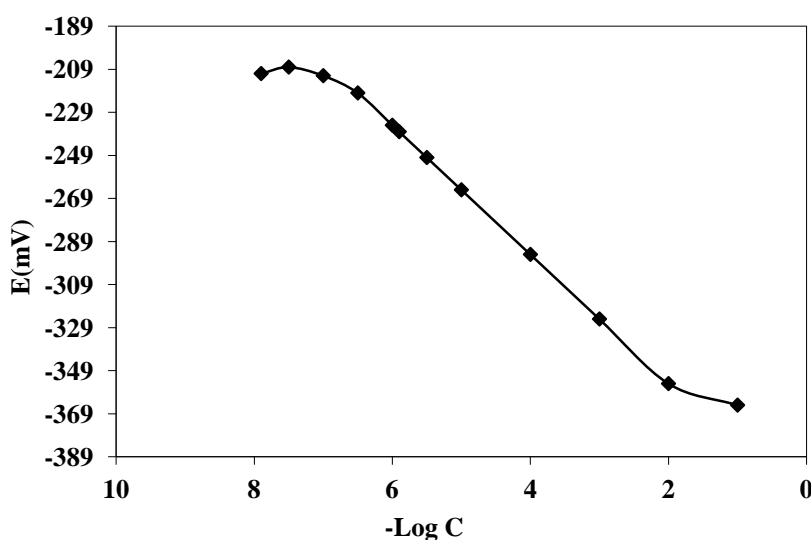
The concentration of the internal solution K<sub>2</sub>SO<sub>4</sub> in the electrode was changed from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-5}$  M and the potential response of the sulfate ion-selective electrode was measured. It was found that the variation of the concentration of the internal 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  $1.0 \times 10^{-3}$  M concentration of the reference solution is quite appropriate for the smooth functioning of electrode system.

**Table 2.** Optimization of membrane ingredients

No.	Composition%				Slope mV decade <sup>-1</sup>
	PVC	Plasticizer	ATPP	HTAB	
1	30	BA, 70	0	--	~0
2	29	BA, 67	4	--	-15.2±0.5
3	29	BA, 65	6	--	-20.1±0.4
4	29	BA, 63	8	--	-19.5±0.5
5	29	DBP, 65	6	--	-18.6±0.6
6	29	NPOE, 65	6	--	-21.9±0.3
7	29	NPOE, 62	6	3	-27.1±0.3
8	29	NPOE, 61	6	4	<b>-30.1±0.3</b>
9	29	NPOE, 60	6	5	-28.5±0.5

### 3.4. Response Characteristics of $\text{SO}_4^{2-}$ -ISE

The optimum equilibration time for the membrane electrode in the presence of  $1.0 \times 10^{-3}$  M  $\text{K}_2\text{SO}_4$  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  $\text{K}_2\text{SO}_4$  ions in the range of  $5.0 \times 10^{-1}$  -  $4.0 \times 10^{-7}$  M (Fig. 3). The slope of the calibration graph was  $-30.1 \pm 0.3$  mV decade $^{-1}$ . The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was  $1.8 \times 10^{-7}$  M.



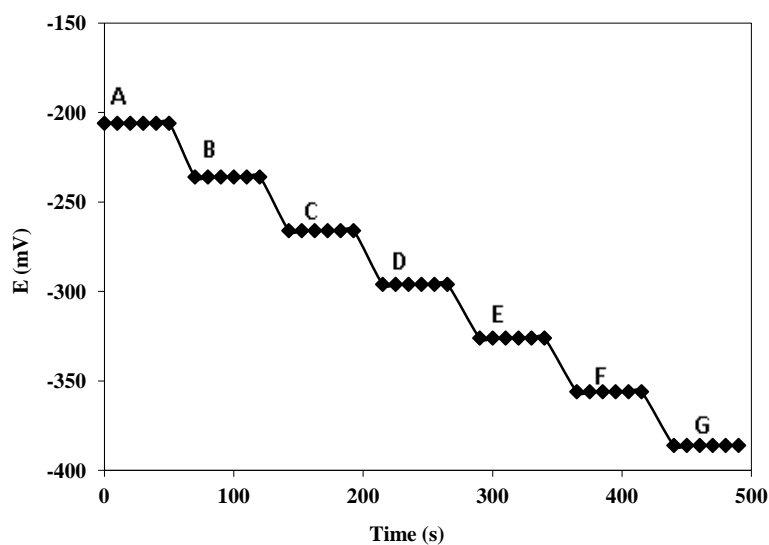
**Fig. 3.** Calibration curves of sulfate electrode based on ATPP at pH 6.5

### 3.5. Response time

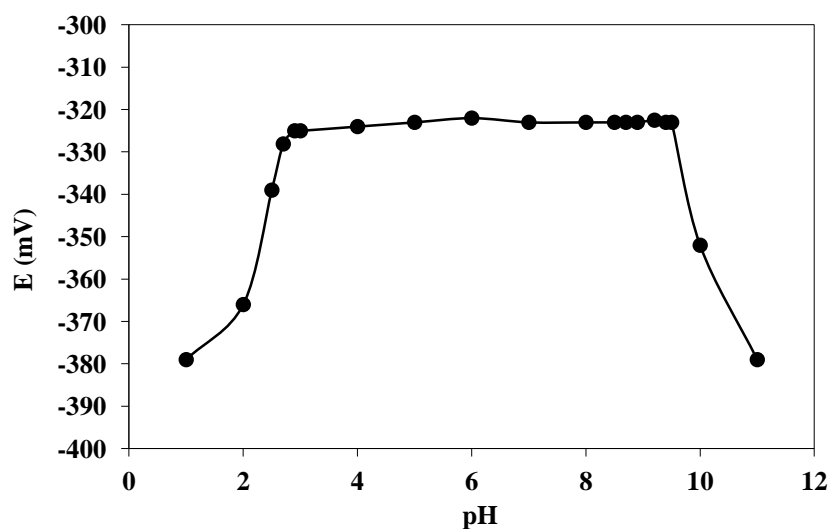
For analytical application, response time of sensor in different concentrations is an important factor. In this study, the practical response time was recorded by immediate changing of sulfate concentration from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M and the results are shown in Fig. 4. As it is seen, in whole concentration ranges, the sensor reaches to the equilibrium response in a short time (<25 s).

### 3.6. Effect of pH of the Test Solution

The influence of the pH of the test solution ( $1.0 \times 10^{-3}$  M of  $\text{K}_2\text{SO}_4$ ) 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 Fig. 5. As it is seen, the response of the sensor is independent of the pH in the range 2.9-9.5. 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  $\text{HSO}_4^-$ ), the potential response of the sensor increases.



**Fig. 4.** Dynamic response time of the sulfate electrode for step changes in concentration of  $\text{SO}_4^{2-}$ : (A)  $1.0 \times 10^{-7}$  M, (B)  $1.0 \times 10^{-6}$  M, (C)  $1.0 \times 10^{-5}$  M, (D)  $1.0 \times 10^{-4}$  M, (E)  $1.0 \times 10^{-3}$  M, (F)  $1.0 \times 10^{-2}$  M, (G)  $1.0 \times 10^{-1}$  M



**Fig. 5.** The effect of the pH of the test solution on the potential response of the sulfate sensor

### 3.7. Selectivity Coefficients

Potentiometric selectivity coefficients, describing the preference of the ATPP-based membrane sensor for an interfering ion, B, relative to sulfate ion, A, were determined by the matched potential method [17]. According to this method, the specified activity (concentration) of the primary ion ( $A = 1.0 \times 10^{-5}$ - $1.0 \times 10^{-4}$  M) is added to a reference solution ( $5.0 \times 10^{-6}$  M), and the potential is measured. In a separation experiment, the interfering ion ( $B = 1.0 \times 10^{-1}$ - $1.0 \times 10^{-3}$  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 (except  $\text{SO}_3^{2-}$ ) are smaller than  $1.0 \times 10^{-3}$ , indicating that they would not significantly disturb the functioning of the sulfate ion-selective electrode.

**Table 3.** Selectivity coefficients of various interfering anions

Anions	$K_{A,B}^{MPM}$	Anions	$K_{A,B}^{MPM}$
$\text{SO}_3^{2-}$	$3.5 \times 10^{-3}$	I <sup>-</sup>	$2.3 \times 10^{-4}$
$\text{ClO}_4^-$	$9.1 \times 10^{-4}$	Br <sup>-</sup>	$1.9 \times 10^{-4}$
$\text{NO}_3^-$	$8.4 \times 10^{-4}$	F <sup>-</sup>	$1.1 \times 10^{-4}$
$\text{NO}_2^-$	$8.2 \times 10^{-4}$	$\text{HPO}_4^{2-}$	$< 10^{-5}$
$\text{SCN}^-$	$7.5 \times 10^{-4}$	$\text{CH}_3\text{COO}^-$	$< 10^{-5}$
Cl <sup>-</sup>	$3.6 \times 10^{-4}$	Tartrate <sup>2-</sup>	$< 10^{-5}$

Table 4 compared the selectivity coefficients of the proposed membrane sensor with those reported before. [28-34] 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. [28-34]

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

Ref.	Br <sup>-</sup>	Cl <sup>-</sup>	I <sup>-</sup>	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{ClO}_4^-$	$\text{SO}_3^{2-}$	$\text{SCN}^-$	$\text{CH}_3\text{COO}^-$
28	12.6	$7.9 \times 10^{-1}$	-	$4.0 \times 10^1$	4	-	$5.0 \times 10^{-1}$	$8.0 \times 10^2$	-
29	7.9	$1.1 \times 10^{-1}$	-	$1.2 \times 10^2$	2	-	-	-	-
30	$2.5 \times 10^2$	$6.3 \times 10^{-1}$	$2.5 \times 10^7$	$2.0 \times 10^4$	-	$2.5 \times 10^{-1}$	-	-	-
31	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	-	$1.0 \times 10^{-1}$	$5.0 \times 10^{-1}$	$1.0 \times 10^{-3}$	-
32	$1.0 \times 10^{-1}$	$3.0 \times 10^{-1}$	-	3.3	-	-	-	$1.0 \times 10^2$	-
33	$1.9 \times 10^{-3}$	$1.8 \times 10^{-3}$	$4.5 \times 10^{-3}$	$5.4 \times 10^{-4}$	$2.0 \times 10^{-3}$	$6.5 \times 10^{-4}$	$2.2 \times 10^{-2}$	$3.1 \times 10^{-3}$	-
34	$5.0 \times 10^{-1}$	$1.9 \times 10^{-1}$	-	7.9	-	$1.0 \times 10^3$	-	$4.0 \times 10^2$	$1.0 \times 10^{-1}$
<b>This work</b>	$1.9 \times 10^{-4}$	$3.6 \times 10^{-4}$	$2.3 \times 10^{-4}$	$8.4 \times 10^{-4}$	$8.2 \times 10^{-4}$	$9.1 \times 10^{-4}$	$3.5 \times 10^{-3}$	$7.5 \times 10^{-4}$	$< 10^{-5}$

### 3.8. Stability and lifetime

For the investigation of the stability and lifetime of the sulfate membrane sensor, two electrodes were tested over a period of 25 weeks. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 20 weeks (use of 1 hour daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 20 weeks changes were observed in the slope and detection limit (from 30.1 to 28.5 mV decade<sup>-1</sup> and  $1.8 \times 10^{-7}$  to  $1.0 \times 10^{-6}$  M or less, respectively).

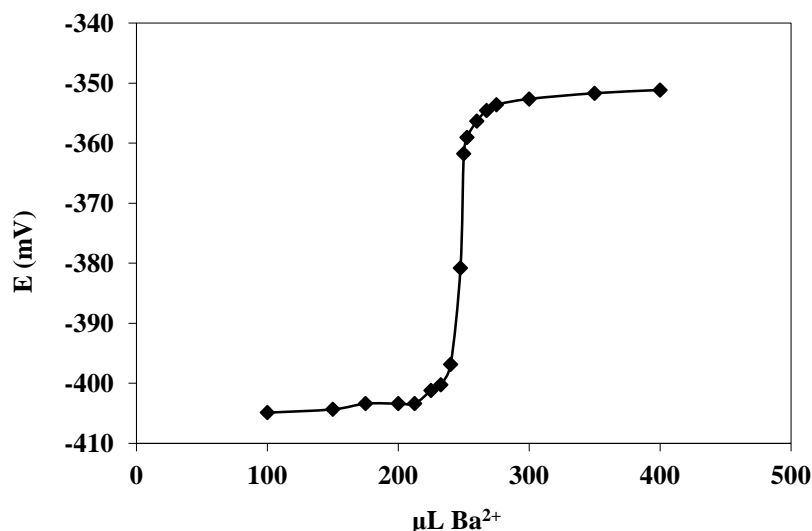
### 3.9. Analytical application

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 ( $1.0 \times 10^{-4}$  M) with a standard barium solution ( $1.0 \times 10^{-2}$  M). The results of titration are shown in Fig. 6, 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.

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

Drugs	Sulfate selective electrode (%w/w)	Gravimetric method (%w/w)	Declared amount (%w/w)
Salbutamol sulfate	67.0±0.5	68.7±0.3	69.3±0.4
Paromomycin sulfate	64.8±0.4	66.6±0.5	65.1±0.2



**Fig. 6.** Potentiometric titration curve of 25.0 mL  $1.0 \times 10^{-4}$  M solution of  $\text{SO}_4^{2-}$  with  $1.0 \times 10^{-2}$  M of  $\text{Ba}^{2+}$

#### 4. CONCLUSION

The membrane assembly prepared using 2-Amino-6-(tbutyl)-4-(pyridin-2-yl)pyrimidine (dichlorido)palladium(II) (ATPP) as membrane ingredient with plasticizers (NPOE) and cation excluder (HTAB) exhibited linearity over a wide concentration range ( $5.0 \times 10^{-1}$ - $4.0 \times 10^{-7}$  M) with Nernstian slope ( $-30.1 \pm 0.3$  mV decade<sup>-1</sup> of activity), fast response time (<25s), long lifetime (25 weeks) and selectivity (of the order of  $10^{-4}$  and  $10^{-5}$  except for  $\text{SO}_3^{2-}$ ) over a number of anions. The Sulfate ion-selective electrode can be employed 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.

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