



DEVELOPMENT OF $Ti/PbO_2/Sb_2O_3$ ELECTRODE AS INDICATOR ELECTRODE FOR PH MEASUREMENTS AND CONDUCTOMETRIC TITRATIONS IN AQUEOUS SOLUTIONS

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ABSTRACT

$Ti/PbO_2/Sb_2O_3$ electrode was used as indicator electrode in potentiometric and conductometric titration in aqueous solution at 298 K. The E-pH curve is linear with a slope of 0.0505 V/dec at 298 K which is close to the theoretical value $2.303RT/F$ (0.059 V at 298 K). The standard potential of this electrode, E^0 , is computed with respect to the SCE as reference electrode. The recovery percentages for potentiometric and conductometric titration are calculated. The cell constant for this conductometric cell was determined. The specific conductance for standard KCl was determined and compared with that of glass conductivity cell. The variation of molar conductance with dilution for some common electrolytes was tested as well as the molar conductance at infinite dilution of some common electrolytes is determined by the conductive cell and conductive glass cell. The prepared modified electrode was used in potentiometric and conductometric titrations for H_3PO_4 and HCl respectively against NaOH as titrant in aqueous medium at 298 K.

KEY WORDS: Potentiometric; conductometric titration; solid state pH electrode; Electrode.



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1. INTRODUCTION

The glass electrode is by far the most commonly used pH sensor due to its sensitivity, selectivity, stability, and long lifetime [1]. However, it has several disadvantages due to the intrinsic nature of the glass membrane. The drawbacks of glass electrodes have led to intensive research for alternative pH electrodes. One is the glass bulb is mechanical not so stable and it breaks very easily so that such electrodes cannot be used for food application. Another drawback is that glass electrodes cannot be designed in planar structures. As a result, various kinds of potentiometric pH sensors have been developed [2-7]. Metal oxide electrodes are becoming alternative to glass electrodes. They can be used as acid-base indicator electrodes. However in extreme acidic and basic conditions of the pH scale, great deviations of the Nernstian behavior are observed [8]. Recently, there are many potentiometric methods developed for measuring the acidity and basicity for aqueous solutions under different conditions [9]. Different metal/ metal oxide electrodes have been used as acid-base indicator electrodes. Of those, the most frequently used are the antimony, niobium, copper, tantalum, stainless steel, iridium and tungsten electrodes [10-12]. The applications of Ta₂O₅, ZrO₂, Al₂O₃ and Si₃N₄ films produced on SiO₂-Si substrates as pH-sensitive membranes for ion-selective field-effect transistors have also been described in the literature [13-15]. Titanium/ Titanium-oxide electrode has been prepared and used as indicator electrode in potentiometric acid-base and oxidation-reduction titration in aqueous solution. The E-pH curve is linear with slope closed to the theoretical value $2.303RT/F$ (0.059V at 298 K) [16].

Conductometric titrations have a more selective character when acid-base, complexometric or precipitation reactions are explored [17-19], thus widening the range of analytical applications. Pantel *et al* had developed conductometric and high-frequency conductometric methods for the determination of the endpoint of catalytic titrations [20]. A

simultaneous conductometric titration method for determination of mixtures of acetic acid, monochloroacetic acid and trichloroacetic acid based on the multivariate calibration partial least squares is proposed by Ghorbani *et. al* [21]. Fifteen metal acetates in aqueous medium have been conductometrically titrated with trichloro-acetic acid by Gaslini and Nahum [22]. Wu *et al* fabricated miniaturized polysilicon electrodes for conductometric sensors and compared them to Pt black and Pt electrode. This conductometric setup was used to detect urea concentration [23]. A new design of a dual, UV photometric-contactless conductometric detector is described by Novotny *et al* [24]. A conductometric biosensor for nitrite detection was developed and reported by Zhang *et al* [25]. A conductometric biosensor for phosphate [26] and ammonium detection [27] were developed based on interdigitated conductometric thin-film planar electrodes. In the present study a modified electrode, Ti/PbO₂/Sb₂O₃, is prepared and used for the first time as an indicator electrode against standard calomel electrode for potentiometric titration while a pair of the above modified electrode is used for conductometric acid-base and oxidation-reduction titrations in aqueous solutions.

2. EXPERIMENTAL

2.1. Preparation of electrodes: Ti/PbO₂/Sb₂O₃.

2.1.1. Treatment of titanium surface

The titanium surface was pretreated according to the procedures suggested by Yang *et al* [28] as follows: The titanium sheet was polished on 320-grit paper strips, using water as lubricant, followed by 1 μm siliceous past blasting. The sheet was then degreased in 40% NaOH, cleaned in a hot 1:1 mixture of HNO₃ and H₂SO₄ and finally washed in water. The treated surface was immersed in a boiling aqueous solution of oxalic acid (15%) until the TiO₂ dissolved. Coating by active metal oxide was

carried out immediately to minimize formation of TiO_2 [29].

2.1.2. Electrodeposition of PbO_2 layer on Ti - surface

The electrodeposition of PbO_2 was performed at constant anodic current (100mA, 30 min) from 0.1 M HNO_3 solution containing 0.5 M $\text{Pb}(\text{NO}_3)_2$ and 0.04 M NaF. During electrolysis the potential was ranged from 1.5 to 1.8 V. Electrodeposition was carried out for 30 min, achieving a PbO_2 loading of about 14 mg cm^{-2} . In order to verify the reproducibility of the electrode preparation, experimental runs were repeated with different electrodes prepared according to the procedure described above. Results showed a fair reproducibility: current efficiencies measured on the three electrodes (when the same operative conditions were adopted) differed by about 5%. Electrodes were also sufficiently stable to allow their use in consecutive runs: the analyses of solutions revealed that no metal dissolution occurred during electrolysis [29].

2.1.3. Coating of Sb_2O_3 by thermal decomposition on Ti/ PbO_2 -surface electrodes

The thermal deposition of Sb_2O_3 on titanium sheet was carried out according to the procedure of Lipp and Pletcher [30]. Ti/ PbO_2 -surface was immersed for some minutes in a solution of 2% wt SbCl_3 in 2-propanol. The excess of alcohol was allowed to evaporate by heating in air at 90°C for 10 min. This stage was then repeated twice. After that the oxide layer was formed thermally by heating at 500°C for 20 min in a muffle furnace, with a low and continuous flow of oxygen. These stages were repeated until the Sb_2O_3 coating reached a loading of about $0.8 (\pm 0.01) \text{ mg cm}^{-2}$: it was normal to employ five applications. Finally, the coating was annealed at 500°C for 60 minutes.[29]

2.2. Chemicals

Phosphoric acid, hydrochloric acid, ferrous ammonium sulphate, sodium hydroxide, potassium permanganate, nitric acid, sulphuric acid, sodium fluoride, 2-propanol, antimony

chloride, oxalic acid, lead nitrate, were of analytical grade and purchased from Merck.

2.3. Sensor design of potentiometric cell

The potential of the indicator electrode relative to that of the reference electrode was measured on a digital multimeter model 1008 (Kyoritsu, Japan). Potentials were measured with an accuracy of $\pm 5 \text{ mV}$. The potential of Ti/ PbO_2 / Sb_2O_3 electrode was measured against a saturated calomel electrode (SCE). The error in the measurement of the potential due to liquid- junction potentials in these electrolytes is estimated to be about 0.001 V [31]. Titration was carried out in a (50ml) Pyrex glass beaker which the acid or reductant put in it and the base or the oxidant placed in a 25 ml micro burette. The solution in a beaker is stirred by means of a magnetic stirrer. The electrodes (indicator and reference) were dipped slowly into aqueous solution (acid or reductant). After the steady-state potential was attained, the titration of the acid was carried out by addition of 1ml of the base to the acidic solution, waiting until the steady potential is established and then measured. The potential variation depends on the type of the base, the progress of neutralization process and on the initial concentration of the acid to be titrated. The results were reproducible to satisfactory value with an accuracy of $\pm 5 \text{ mV}$ for potential measurements. The process of addition of the titrant was repeated until the equivalence point was reached.

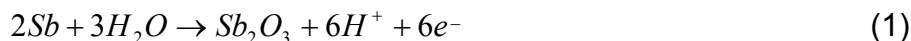
2.4. Sensor design of conductometric cell

Conductometric cells consist of two identical pairs of modified thin film electrodes. These modified electrodes serve as sensing elements and are placed at a fixed distance apart to make contact with solution, which conductivity is to be determined. The length between the sensing electrodes are 1cm and the surface area 1 cm^2 . Conductance of the two parallel electrodes was measured and compared with standard conductivity meter (CM-30V) (TOA electronic ltd 44 CT 121 W Jaban). Titration was carried out in a Pyrex glass beaker (100 ml) in which the acid put in it and the base placed in a (25) ml

microburette. The solution in a beaker is stirred by means of a magnetic stirrer.

3. RESULTS AND DISCUSSION

3.1. The use of Ti/PbO₂/Sb₂O₃ electrode as an indicator electrode in potentiometric acid-base titration in aqueous solution at 298K.



Nernst equation of this reaction can be written as:

$$E_{Ti/PbO_2/Sb_2O_3} = E^0_{Ti/PbO_2/Sb_2O_3} + \frac{2.303RT}{6F} \log \frac{[Sb_2O_3][H^+]^6}{[Sb]^2[H_2O]^3} \quad (2)$$

Where Sb and Sb₂O₃ are solids, and H₂O in excess, their activities = 1

$$E_{Ti/PbO_2/Sb_2O_3} = E^0_{Ti/PbO_2/Sb_2O_3} + \frac{2.303 RT}{F} \log [H^+] \quad (3)$$

$$E_{Ti/PbO_2/Sb_2O_3} = E^0_{Ti/PbO_2/Sb_2O_3} - \frac{2.303 RT}{F} pH \quad (4)$$

Equation(4) can be applied for the reversible behavior of working electrode. which indicates that the working electrode can be used as pH-indicator. From Fig.1 the E⁰ value of the Ti/PbO₂/Sb₂O₃ electrode, i.e. the potential at [H⁺] = 1, is computed as 428.4 mV relative to the saturated calomel electrode.

3.1.2. Potentiometric acid-base titration:

Fig.2 represents the relation between the volume of 0.1 M NaOH with each potential shift in the titrations of phosphoric acid. The variation of the Ti/PbO₂/Sb₂O₃ electrode potential at 298 K with the different volumes of NaOH followed typical potentiometric titration curves. These

3.1.1. The E-pH relation of Ti/PbO₂/Sb₂O₃ electrode:

Fig.1 shows the change of the open circuit potential (E) of the Ti/PbO₂/Sb₂O₃ electrode with pH. The E-pH plot of the Ti/PbO₂/Sb₂O₃ electrode fits straight line with slope of 0.0505 V/decade at 298 K. This value is nearly close to the term 2.303 RT/F at 0.059V and temperature of 298 K This indicates that the tested electrode behaves reversibly and can be applied as an indicator for [H⁺] ion determination.

curves show slight decrease in potential (to more negative values) with the addition of the titrant. For locating end points, better results are obtained by constructing a plot of ΔE/ΔV against V of titrant. Fig.3 represents ΔE/ΔV against V for the potentiometric titrations of H₃PO₄ against 0.1 M NaOH. From the plots the values of end points are determined. The obtained results are listed in tables (1) for phosphoric acid. The values of the recovery percentage (R%) for all above titrations are calculated from equation (5). From the plots the values of end points and the values of the recovery percentage (R%) are determined as

$$R\% = \frac{Be}{Bt} \times 100 \quad (5)$$

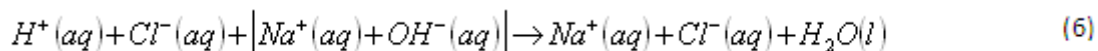
where Be = experimental amount of base and Bt = theoretical amount of base calculated from the stichiometric equations of neutralization reactions. It is clear from these data that the working electrode can be used as indicator electrode with the satisfactory recovery percentage not less than 95 % in potentiometric titrations. These differences in the recovery percentage may be attributed to the impurities in the reagents. The values of pK_a for phosphoric acid can be determined using the method of half neutralization [32].

3.1.3. The response time of the sensor

Fig.4 shows the response time of the $Ti/PbO_2/Sb_2O_3$ pH sensor at different pH values. Response time, in the range of (50-80) seconds was achieved, which rendered the sensor highly practical.

3.1.4. Effect of temperature on the response characteristics

The $Ti/PbO_2/Sb_2O_3$ pH sensor response was evaluated at different temperature, Fig.5. At lower temperatures, like 283 K, the slope of the sensor was about 39.5 mV/decade and the sensor would be used for pH measurements in the range from (2-11). However, when the temperature of test solutions was adjusted to 333 K, the slope significantly increased to 54.4 mV/decade and the slope reached the value of 59.3 mV/decade at 353K. Fig.6 shows the square of the correlation coefficient (r^2) for pH measurements using the solid-state sensor, at different temperatures, as compared to pH values obtained by a conventional pH electrode (Hanna Instruments HI 1131 pH combination electrode) was found to increase as the temperature increases where as r^2 values for measurements at 283 K, 298 K, 333 K, and 353 K were 0.9963, 0.9965, 0.9983, 0.9990, respectively. This indicates that better results below:



Hence, on continued addition of sodium hydroxide, the conductance will keep on decreasing until the acid has been completely

could be obtained at higher temperature. Overall, it can be easily recognized that there is an excellent correlation between the results obtained by the solid-state pH sensor and that of the conventional glass pH electrode.

3.1.5. Potentiometric oxidation-reduction titration

Fig.7 represents the relation between the volume of 0.1 N $KMnO_4$ against the potential shift in the titration of ferrous ammonium sulphate. The variation of the $Ti/PbO_2/Sb_2O_3$ electrode potential at 298 K with the different volumes of $KMnO_4$ followed typical potentiometric titration curves. For locating end points, better results are obtained by constructing a plot of $\Delta E/\Delta V$ against V of titrant. Fig.8 represents $\Delta E/\Delta V$ against V plots for the potentiometric titration of ferrous ammonium sulphate with 0.1 N $KMnO_4$. From the plots the values of end points and the values of the recovery percentage (R%) are determined as previously illustrated in the abovementioned equation (5). The obtained results are listed in table (3).

3.2. The use of $Ti/PbO_2/Sb_2O_3$ electrode as an indicator electrode in conductometric acid-base titration in aqueous solution at 298 K.

3.2.1. Conductometric acid-base titration:

Fig.9 shows the relation between the conductance of the pair $Ti/PbO_2/Sb_2O_3$ electrode with 0.1 M NaOH in the titration of different concentration of hydrochloric acid at 298 K. The conductance of hydrochloric acid using working electrodes is due to the presence of hydrogen and chloride ions. As alkali is added gradually, the hydrogen ions are replaced by slow moving sodium ions, as represented

neutralized. On plotting the conductance against the volume of sodium hydroxide added as in Fig.9. the point of intersection of these two

lines gives the volume of sodium hydroxide required for the neutralization. The values of the recovery percentage (R%) for all above titration are calculated from the equation (5). The calculated values of (R%) are listed in table (4). It is clear from these data that the Ti/PbO₂/Sb₂O₃ electrode can be used as an indicator electrode with the satisfactory recovery percentage not less than 95%. These differences in the recovery percentage may be attributed to the impurities in the reagents. Table (5) represents the relation between the end points of HCl for Ti/ PbO₂/Sb₂O₃ and glass conductive electrode at 298 K.

3.2.2. Cell constant

The conductance obtained will, therefore have to get the specific conductance can be calculated by multiplying the obtained conductance by a certain factor. This factor is called the cell constant which can be determined from the dimensions of the cell. The value of cell constant for Ti/ PbO₂/Sb₂O₃ electrode in aqueous solutions at 298 K equals 161.9 m⁻¹. Specific conductance of normal, decinormal and centinormal solutions of potassium chloride at different temperatures are given in table (6).

3.2.3. Variation of molar conductance with dilution

Molar conductance of an electrolyte increases with increase in dilution. This was attributed to increase in the degree of dissociation of the electrolyte. We define degree of dissociation as the fraction of the total electrolyte in solution

which exists in the form of its ion. In other words, on dilution, the same amount of electrolyte is capable of furnishing a large number of ions. It may be pointed out; however, that increase in the number of ions by dilution is much less than increases in the volume of the solution. Therefore, the number of ions per unit volume (eg; per c.c.) actually decreases. Hence, the specific conductance decreases although the molar conductance increases on progressive dilution. It is seen that in each case, molar conductance increases with dilution. The increase in the case of electrolytes like hydrochloric acid, potassium chloride and copper sulphate is not as large as in the case of acetic acid or ammonium hydroxide. The electrolytes of the first category (KCl, HCl, etc.) are known as strong electrolytes while those of second category (CH₃COOH, NH₄OH, etc.) are known as weak electrolytes. The variation of molar conductance with dilution for some common electrolytes is shown in table (7). The variation of molar conductance at infinite dilution for some common electrolytes is shown in table (8).

3.2.4. The response time of the sensor

Fig.10 represents the relation between the conductance and response time at 298 K for a pair Ti/PbO₂/Sb₂O₃ electrode at different concentrations of HCl. It is clear from Figure 10 that the response times for the studied electrode is nearly 70 second, which rendered the sensor highly practical.

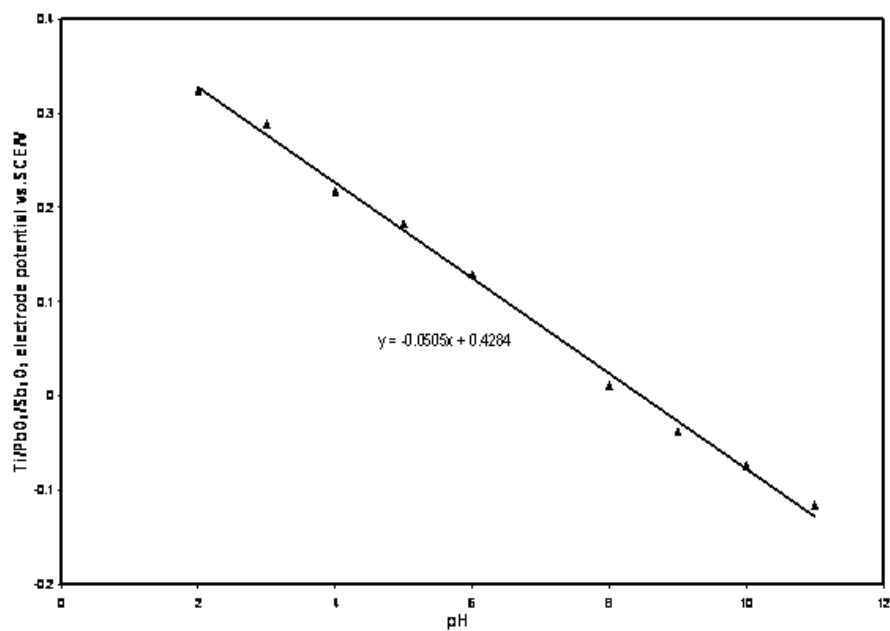


Fig 1

Figure 1
E-pH relation for Ti/PbO₂/Sb₂O₃ electrode at 298 K.

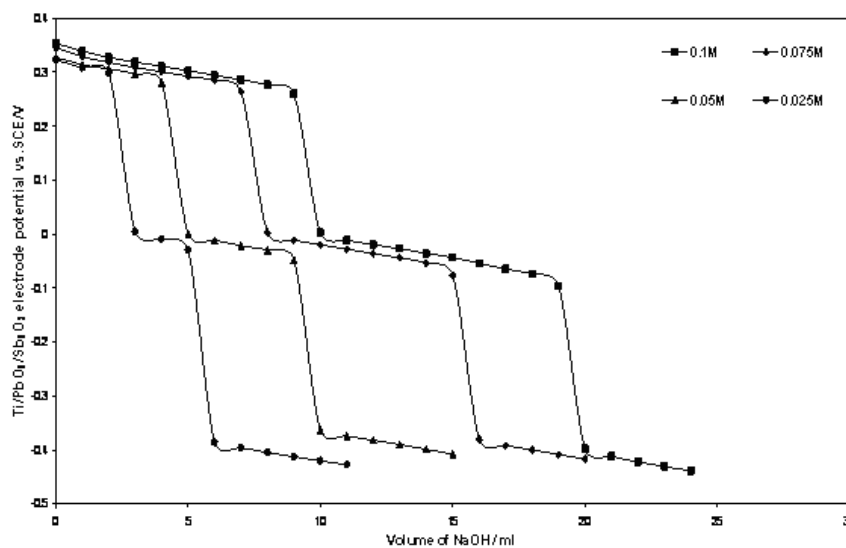


Fig 2

Figure 2
Potentiometric titration of H₃PO₄ acid with 0.1 M NaOH at 298 K.

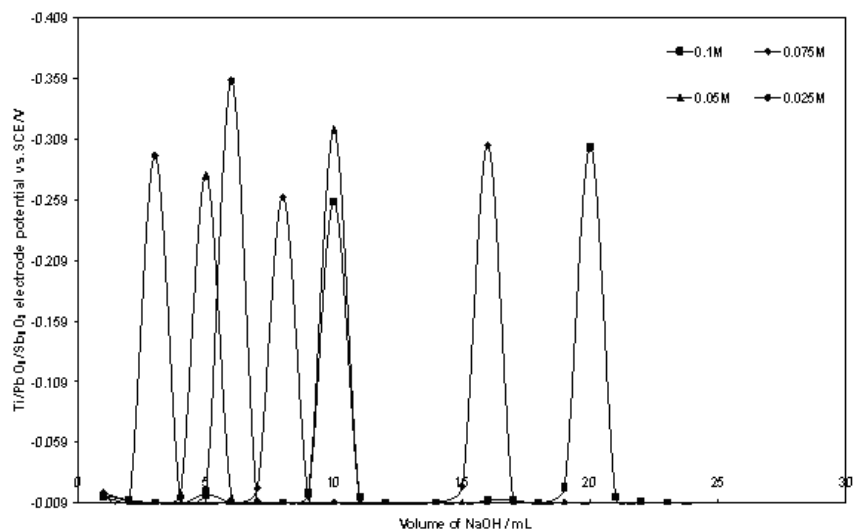


Fig.3

Figure 3
Locating the end points for potentiometric titration of H_3PO_4 acid with 0.1 M NaOH at 298 K.

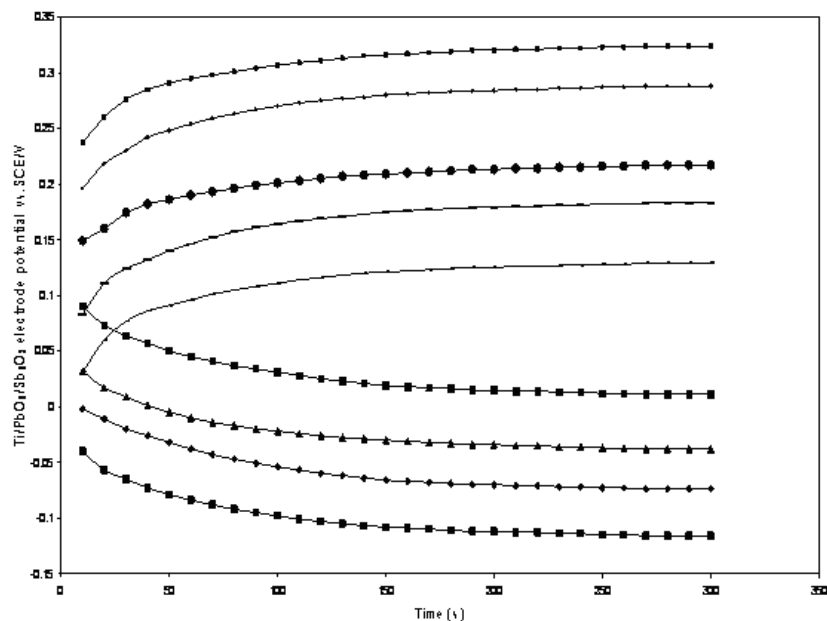


Fig.4

Figure 4
Response time of the $Ti/PbO_2/Sb_2O_3$ pH sensor at different pH values. Upper curve at pH =2 and lower one for pH=11.

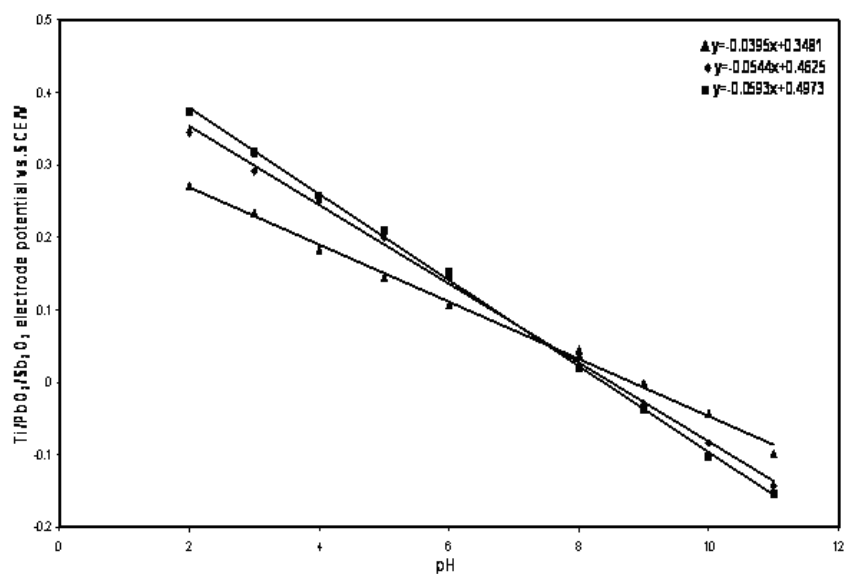


Fig5

Figure 5
Effect of temperature on slope of $Ti/PbO_2/Sb_2O_3$ pH sensor at 283K(\blacktriangle), 333K(\blacklozenge) and 353K(\blacksquare).

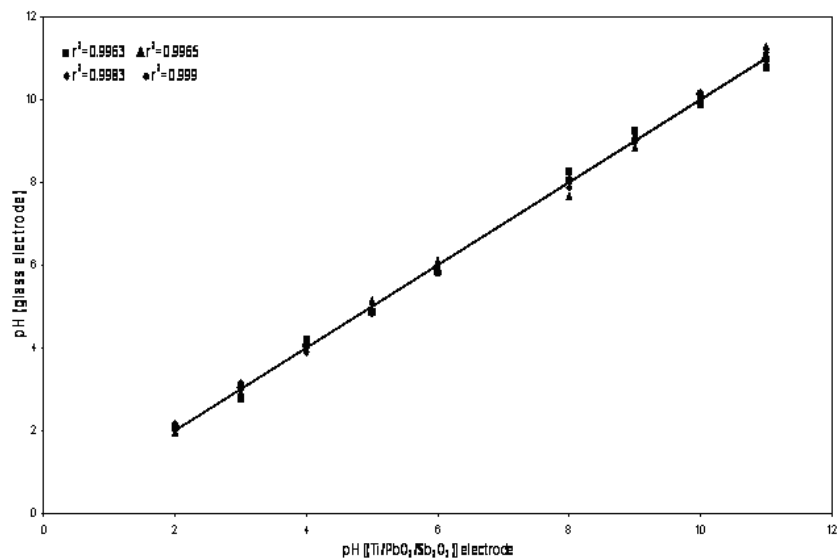


Fig6

Figure 6
Correlation between the conventional glass electrode and $Ti/PbO_2/Sb_2O_3$ pH sensor at 283 K(\blacksquare), 298 K(\blacktriangle), 333 K(\blacklozenge) and 353 K(\bullet).

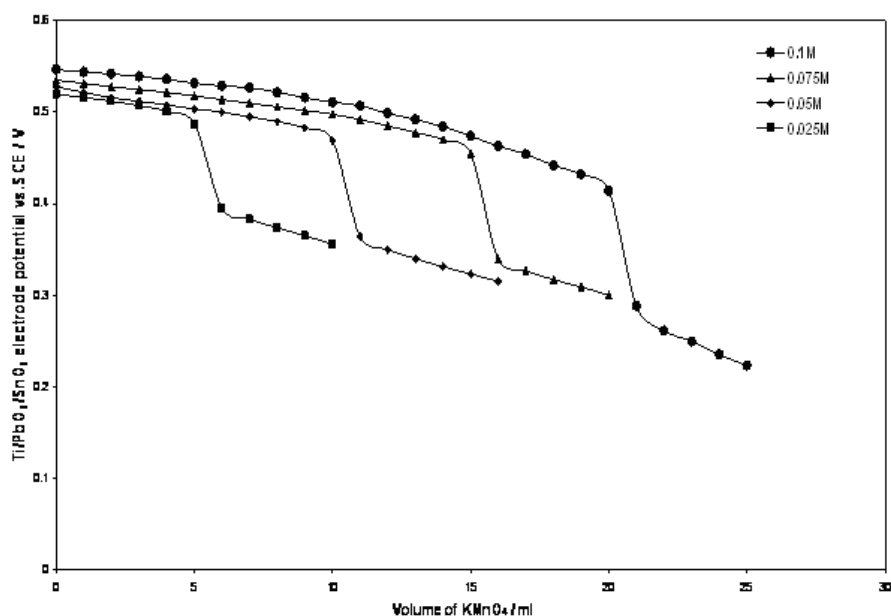


Fig.7

Figure 7
Potentiometric titration of Fe (II) with 0.1 N $KMnO_4$ in aqueous solution at 298 K.

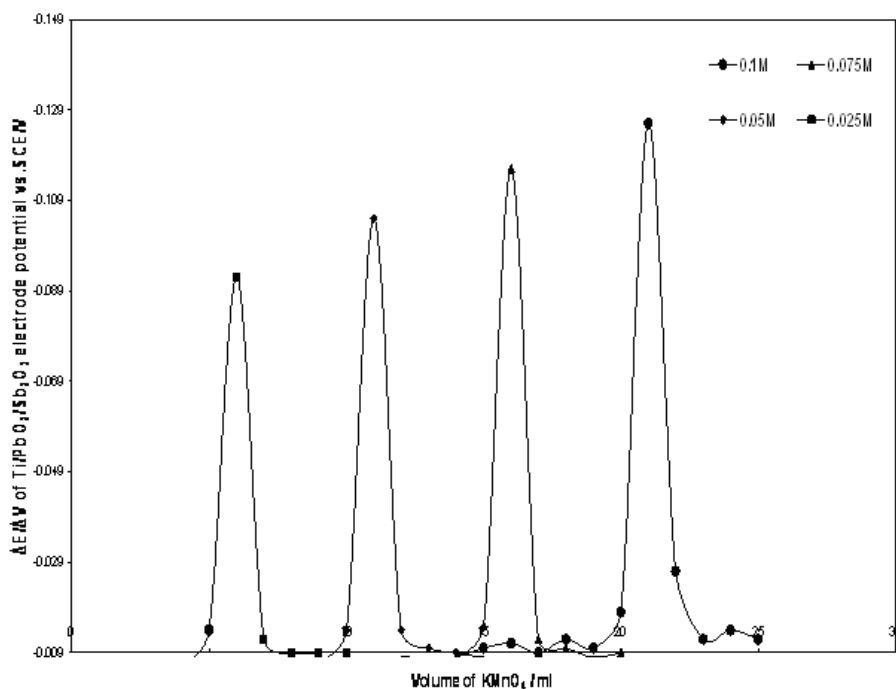


Fig.8

Figure 8
Locating the end points for the potentiometric titration of Fe (II) with 0.1 N $KMnO_4$ in aqueous solution at 298 K.

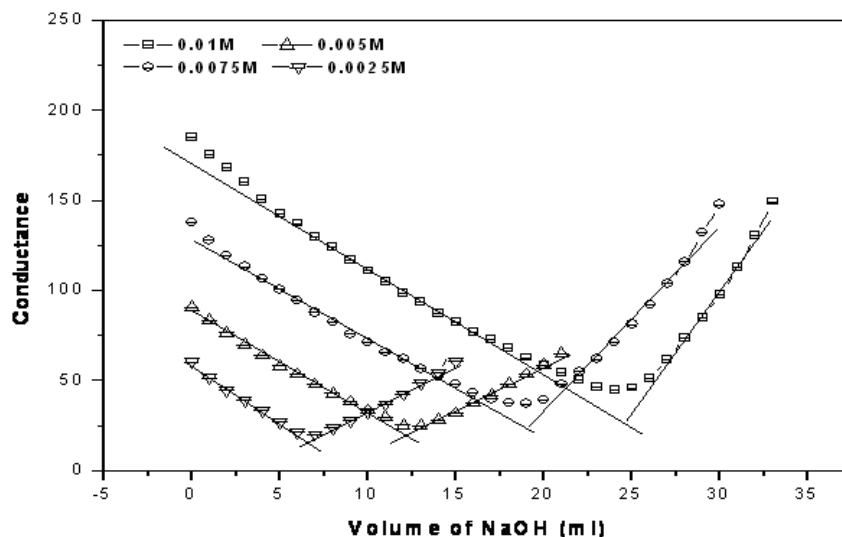


Fig.9

Figure 9

The relation between the conductance of a pair Ti/PbO₂/Sb₂O₃ electrode with 0.1M NaOH in the titration of different concentration of HCl at 298 K

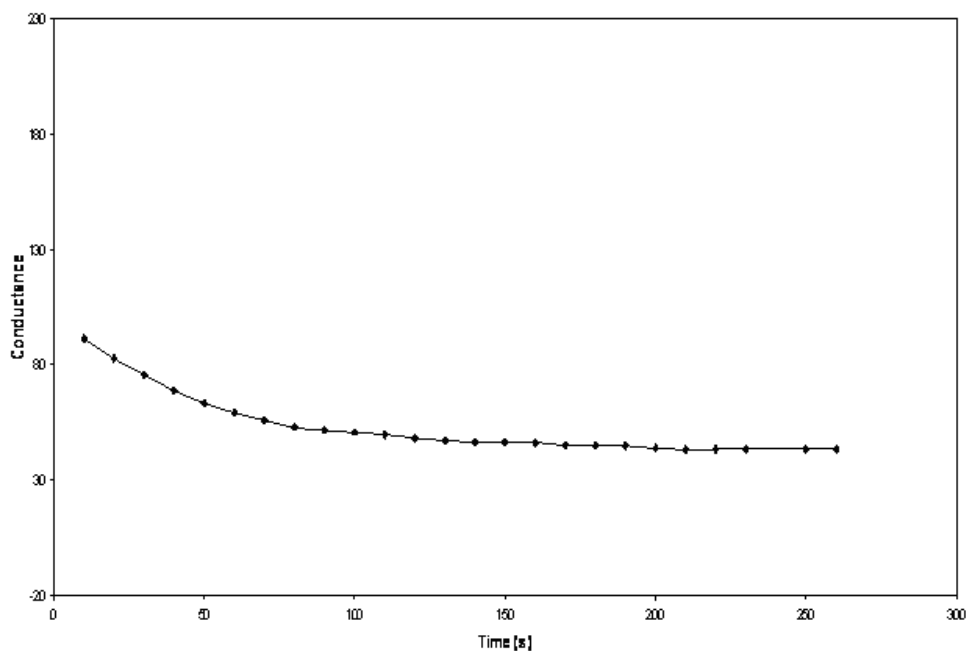


Fig.10

Figure 10

The relation between the conductance and response time at 298 K for a pair Ti/PbO₂/Sb₂O₃ electrode at different concentrations of HCl.

Table 1

The molar amounts A of H_3PO_4 acid, experimental and theoretical amounts of NaOH, Be, Bt and recovery percentage (R%) for acid-base titrations using $Ti/PbO_2/Sb_2O_3$ indicator electrode.

First step				Second step			
A(M)	Be(M) NaOH	Bt(M) NaOH	R%	Be(M) NaOH	Bt(M) NaOH	R%	
0.100	0.0490	0.050	98.00	0.0950	0.100	95.00	
0.075	0.0362	0.037	97.80	0.0745	0.075	99.30	
0.050	0.0253	0.025	101.20	0.0490	0.050	98.00	
0.025	0.0120	0.012	100.00	0.0244	0.025	97.60	

Table 2

The molar amounts A of H_3PO_4 acid and experimental pKa for acid-base titrations using $Ti/PbO_2/Sb_2O_3$ indicator electrode

A(M)	First step	Second step
	pK _{a1}	pK _{a2}
0.100	2.123	7.208
0.075	2.150	7.191
0.050	2.166	7.225
0.025	2.130	7.190

Table 3

The normal amounts A of Fe (II) experimental and theoretical amounts of $KMnO_4$, Be, Bt and recovery percentage (R%) for oxidation-reduction titrations using $Ti/PbO_2/Sb_2O_3$ indicator electrode

Fe(II) (N)	Be(N) $KMnO_4$	Bt(N) $KMnO_4$	R%
0.100	0.0993	0.100	99.30
0.075	0.0723	0.075	96.40
0.050	0.0485	0.050	97.00
0.025	0.0241	0.025	96.40

Table 4

The molar amounts A of HCl acid, experimental and theoretical amounts of NaOH, Be, Bt and recovery percentage (R%) for acid-base titrations using Ti/PbO₂/Sb₂O₃ as indicator electrode

A(M)	Be(M) NaOH	Bt(M) NaOH	R%
0.1000	0.0095	0.0100	95.00
0.0750	0.0074	0.0075	98.90
0.0500	0.0049	0.0050	98.00
0.0250	0.0025	0.0025	100.00

Table 5

The end points of different concentration of HCl acid for Ti/PbO₂/Sb₂O₃ electrode and glass conductive electrode in aqueous solution at 298 K.

	G.E*	S.E**
0.1000	24.90	24.89
0.0750	17.80	17.90
0.0500	12.14	12.15
0.0250	06.57	06.55

- * glass electrode
- ** studied electrode

Table 6

The relation between the specific conductance of KCl solutions for Ti/PbO₂/Sb₂O₃ electrode against the glass conductive electrode at 273K, 291K and 298K.

A(M)	Specific conductance (Sm ⁻¹) at 273 K		Specific conductance (Sm ⁻¹) at 291 K		Specific conductance (Sm ⁻¹) at 298 K	
	G.E*	S.E**	G.E*	S.E**	G.E*	S.E**
1.00	6.5330	6.5290	9.8150	9.8140	11.1720	11.1720
0.10	0.7152	0.7150	1.1230	1.1220	1.2882	1.2880
0.01	0.0775	0.0775	0.1222	0.1222	0.1412	0.1412

- * glass electrode
- ** studied electrode

Tables 7

The relation between the molar conductance, \wedge_m , in units of $10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$, of some common electrolytes and the glass conductive electrode in aqueous solution at 298 K.

A(M)	HCl		NaCl		KCl		H ₂ SO ₄		CH ₃ COOH		NH ₄ OH	
	G.E*	S.E**	G.E*	S.E**	G.E*	S.E**	G.E*	S.E**	G.E*	S.E**	G.E*	S.E**
0.1000	392.23	392.15	107.42	107.36	128.82	128.80	250.60	250.55	5.16	5.16	3.59	3.54
0.0100	412.26	412.18	118.11	118.05	141.23	141.19	336.38	336.27	16.11	16.08	16.26	16.25
0.0010	421.77	421.69	123.49	123.45	146.89	146.84	399.44	339.43	48.24	48.25	49.18	49.17
0.0005	422.18	422.09	124.41	124.37	148.56	148.51	413.07	412.97	67.27	67.23	67.70	67.67

Table 8

The relation between the molar conductance, \wedge_m , in units of $10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$, at infinite dilution for some common electrolytes and that of glass conductive electrode in aqueous solution at 298 K.

electrolyte	$^{\circ} (10^{-4} \text{ Sm}^2 \text{ mol}^{-1}) \wedge_m$	
	G.E*	S.E**
HCl	426.27	426.70
NaCl	125.87	125.84
KCl	149.89	149.85
CH ₃ COOH	390.11	390.11

- * glass electrode
- ** studied electrode

4. CONCLUSION

Ti/PbO₂/Sb₂O₃ electrode was developed and used as indicator electrode in the potentiometric and conductometric acid-base titrations in aqueous solution at 298 K. The recovery percentage for potentiometric and conductometric acid-base titration was calculated. The E-pH curve is linear with slope of 0.0505 V/decade for the Ti/PbO₂/Sb₂O₃ electrode at 298 K. This value is close to the

theoretical value 2.303 RT/F (0.059 V at 298 K). The standard potential of the tested electrode, E° , is computed as 428.4 mV with respect to SCE as reference electrode. Successful potentiometric and conductometric titrations with NaOH were conducted. The cell constant and different variations of molar constant for some electrolytes were studied.

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