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A novel sensor as indicator electrode in potentiometric and conductometric acid-base titrations in aqueous solution

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ABSTRACT

This work deals with the preparation of Ti/Co_3O_4/(SnO_2+Sb_2O_3) modified electrode by thermal deposition of alloy Sn and Sb in titanium substrate and its use as indicator electrode in potentiometric and conductometric acid-base titration in aqueous solution at 298.15 K. The E-pH curves are linear with slopes of (0.0503) at 298.15 K. This value is close to the theoretical value 2.303RT/2F (0.059 V at 298.15 K). The standard potential of these electrodes, E^0, are computed with respect to the SCE as reference electrode. The recovery percentage for potentiometric and conductometric acid-base titration is calculated. The cell constant for pair electrode was determined. The specific conductance for standard KCl was determined and compared with that of glass conductive electrode. The variation of molar conductance with dilution for some common electrolytes was tested. Also the molar conductance at infinite dilution of some common electrolytes is determined by each conductive cell and conductive glass electrode. Three acids: acetic, propanoic and phosphoric acids were potentiometrically titrated with NaOH as titrants where acetic, hydrochloric and a mixture of acetic and hydrochloric acids was conductometrically titrated with NaOH as titrants in aqueous medium at 298.15 K using the prepared electrode.

KEYWORDS

Potentiometric;
Conductometric;
Titration;
Modified electrodes;
Thermal deposition;
Indicator.

INTRODUCTION

Glass electrodes have been the most popular pH electrodes for the last seven decades because of their sensitivity, selectivity, stability, and long lifetime[1]. However, glass electrodes have 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. As a result, various kinds of potentiometric pH sensors have been developed[2-14]. In addition to glass electrodes, metal-metal oxide electrodes have been used as acid-base indicator electrodes. The most frequently used are the antimony[15], niobium[16], copper[17], tantalum[18], stainless steel[19], iridium[20], tungsten[21] and a platinum-20% rhodium alloy electrodes. The feasibility of electrodeposited metal-oxides in a matrix of graphite[22, 23], platinum[24, 25] and other materials[26, 27] was studied as potentiometric electrodes for H_3O^+.

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/2F (0.059V at

298.15)[28].

The possible use of an iridium electrode as a pH-monitoring system has been mentioned by various authors[29-31]. The original work was carried out by Perley and Godshalk[30] who described both a technique for preparing the electrode and some application. The use of reacting sputtered iridium oxide films as pH sensors has been reported by katsube and co-workers[31] who observed a normal (2.303RT/F) open-circuit potential/pH shift for this system.

Dry cell graphite (DCG) electrodes activated with potassium permanganate and Aluminum has been employed as potentiometric indicator electrodes for acid-base titrations[32, 33].

A simultaneous conductometric titration method for determination of mixtures of acetic acid, monochloroacetic acid, trichloroacetic acid and extremely diluted solutions (EDS) is proposed by Ghorbani *et. al.*[34] and K.Hiller[35]. Also conductometric titration of thiosulfate with silver ions using non-conventional conductivity cells with different cell constants and electrode constructions, equipped with silver amalgamated silver, stainless-steel and polished platinium electrodes were used[36].

Wu *et. al.* fabricated miniaturized polysilicon electrodes for conductometric sensors and compared them to Pt black and Pt electrode[37]. An automated conductometric titration system has been designed and investigated by Hail and Holler[38].

A new sensor for ammonium determination based on interdigitated conductometric thin-film planar electrodes was fabricated by including nonactin in a plasticised poly (vinyl chloride) membrane deposited on the sensitive area of the transducer. The effects of pH, buffer concentration, the interferences of Na^+, K^+ and Ca^{2+} ions, the effect of ionic strength and of temperature were investigated[39].

A new conductometric cell design, for precise conductance measurements has been developed and tested using aqueous lidocaine hydrochloride as a model system. The pK_a value obtained, 7.28, is close to the previously reported conductometrically determined average, 7.18[40].

EXPERIMENT

Treatment of titanium surface

Pretreatment of the titanium surface was carried out following the procedures suggested by Feng[41]. The sheet of titanium was polished on 320-grit paper strips, using water as lubricant, followed by 1Mm siliceous past blasting. The sheet was then degreased in 40% NaOH, cleaned in a hot 1:1 mixture of HNO_3 and H_2SO_4 and finally washed in water. The treated surface was immersed in a boiling aqueous solution of oxalic acid (15%) until the TiO_2 dissolved. Coating by active metal oxide was carried out immediately to minimize formation of TiO_2[42].

Coating Co_3O_4 on Ti-Surface

Co_3O_4 electrode was prepared by thermal decomposition of nitrate precursor deposited onto a titanium plat. Ti plates were smoothly polished with emery paper, degreased in CH_2Cl_2, etched in concentrated nitric acid, rinsed with distilled water, and wiped with a filter paper. Immediately after pretreatment, a 0.5 M $Co(NO_3)_2.6H_2O$ isopropanol solution was layered onto the support. Then the support was dried at 60^0C to evaporate the solvent and heated in air at 300^0 C for 10 min. Oxide layers were deposited by repeating this procedure 10 times to achieve full coverage of the metallic surface. Final annealing was done by keeping the sample for one hour at 300^0 C to complete the thermal decomposition[43].

Coating of mixture of SnO_2 and Sb_2O_3 on Ti/Co_3O_4-surface

The thermal deposition of SnO_2 on titanium sheet was carried out according to the procedure of Lipp and Pletcher[43]. The pretreated titanium sheet was immersed for some minutes in a solution of 20% wt $SnCl_4$.5H2O and 2% wt $SbCl_3$ in 2-propanol. The excess of alcohol was allowed to evaporate by heating in air at 90^0C for 10 min. This stage was then repeated. After two applications, the oxide layer was formed thermally by heating at 500^0C for 20 min in a muffle furnace, with a low and continuous flow of oxygen. These stages were repeated until the SnO_2 coating reached a loading of about 0.8 mg cm^{-2}; it was normal to employ five applications. Finally, the coating was annealed at

500^{0}C for 60 minutes[42].

Chemicals

Chemical used in potentiometric titrations were, CH_3COOH, CH_3CH_2COOH, H_3PO_4 ferrous ammonium sulphate,HCl, CH_3COOH, NaOH, $KMnO_4$, HNO_3, H_2SO_4, NaF, 2-propanol, $SnCl_4.5H_2O$, $SbCL_3$,oxalic acid, $Co(NO_3)_2.6H_2O$, $Pb(NO_3)_2$, The chemicals are of analytical pure grades.

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 to ± 5mv. The potential of $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$, electrode was measured vs. 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[44].

Titration was carried out in a (50ml) Pyrex glass beaker in 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 electrode (indicator and reference) was 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 results were reproducible to satisfactory value of ± 5 mv for potential measurements. The process of addition of the titrant was repeated until the equivalence point was reached.

Sensor design of conductometric cell

Conductometric cells consist of two identical pairs of modified thin films 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 (1cm^2). Conductance of the two parallel electrodes was measured and compared with standard conductivity meter (CM-30V) (TOA electronic ltd 44 CT 121 W Japan). 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.

RESULTS AND DISCUSSION

The use of $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode as an indicator electrode in potentiometric acid-base titration in aqueous solution at 298 K.

The E-pH relation of $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode

Figure 1 shows the change of the open circuit potential (E) of the $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode with pH. The E-pH plot of the $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode fits straight line with slope of 0.0541 V at 298.15 K. This value is close to the magnitude of the term 2.303 RT/F at the corresponding temperature (0.059 V at 298 K) which indicates that the working electrode behaves reversibly and can be used as an indicator electrode for [H$^+$] ion determination.

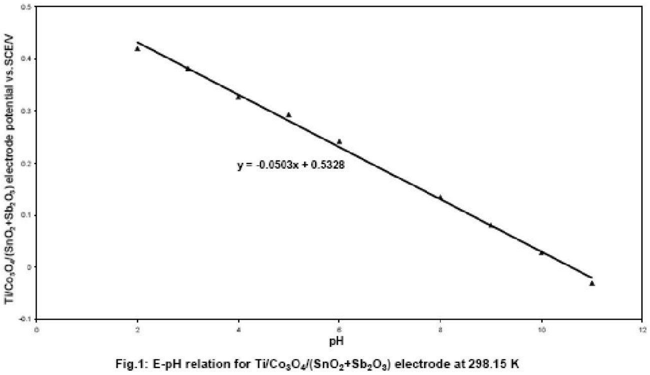

Figure 1 : E-pH relation for $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode at 298.15 K.

$$\mathbf{Sn + 2Sb + 5H_2O \rightarrow SnO_2 + Sb_2O_3 + 10H^+ + 10e^-} \quad (1)$$

Nernst equation of this reaction can be written as:

$$E_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} = E^0{}_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} + \frac{2.303RT}{10F}\log \frac{[SnO_2 + Sb_2O_3][H^+]^{10}}{[Sn + 2Sb][H_2O^+]^5} \quad (2)$$

Where Sn, Sb, SnO_2 and Sb_2O_3 are solids, and H_2O in excess, their activities = 1

$$E_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} = E^0{}_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} + \frac{2.303RT}{F}\log[H^+] \quad (3)$$

$$E_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} = E^0_{Ti/Co_3O_4/(SnO_2+Sb_2O_3)} - \frac{2.303RT}{F}pH \qquad (4)$$

This equation is applicable for the reversible behavior of working electrode. From the developed Nernst equation we indicate that working electrodes can be used as pH-indicator. From Figure 1 the E^0 value of the $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode, i.e. the potential at $[H^+] = 1$, is computed as 532.8 mV relative to the saturated calomel electrode.

Potentiometric acid-base titration

Figure 2 represents the relation between the volume of 0.1 M NaOH with each potential shift in the titrations of acetic, propanoic, and phosphoric acids, respectively. The variation of the $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode potential at 298 K with the different volumes of NaOH followed typical potentiometric titration curves. These curves show slight decrease in potential (to more negative values) with the addition of the titrant.

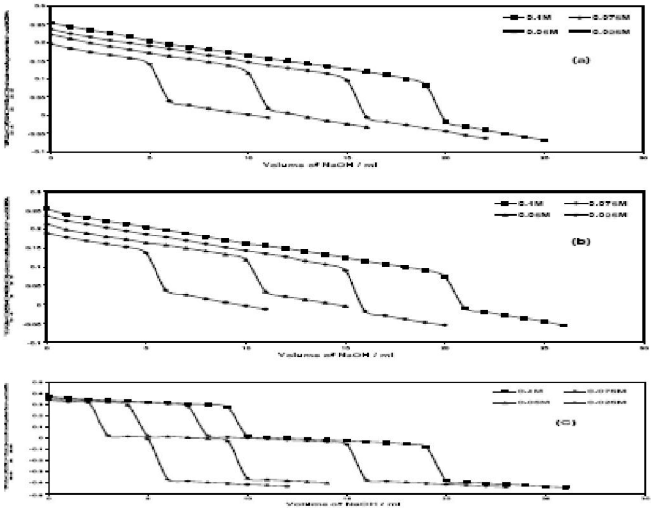

Figure 2 : Potentiometric titration of acetic acid (a), propanoic acid (b) and phosphoric acid (c) with 0.1 M NaOH at 298.15 K.

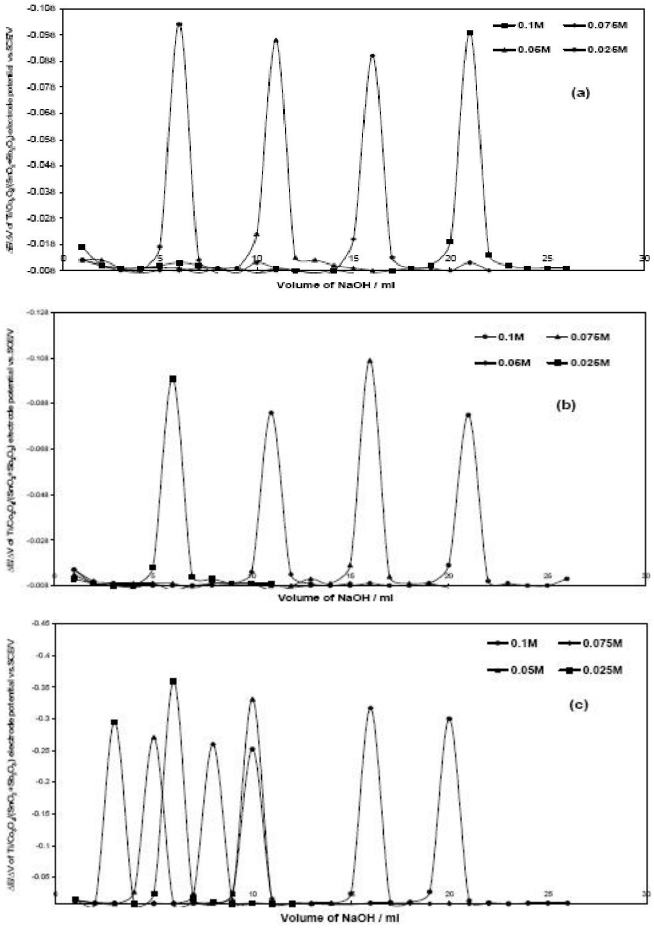

Figure 3 : Potentiometric titration of acetic acid (a), propanoic acid (b) and phosphoric acid (c) with 0.1 M NaOH at 298.15 K (for locating end points).

For locating end points, better results are obtained by constructing a plot of ΔE/ΔV against V of titrant. Figure 3 represents ΔE/ΔV against V plot for the potentiometric titrations of CH_3COOH, CH_3CH_2COOH and H_3PO_4, with 0.1 M NaOH, respectively. From the plots the values of end points are determined. The ob-

TABLE 1 : The molar amounts A of CH_3COOH acid, CH_3CH_2COOH acid, H_3PO_4 acid, experimental and theoretical amounts of NaOH, Be, Bt and recovery percentage (R%) for acid-base titrations using $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ indicator electrode.

A cid	CH_3COOH acid			CH_3CH_2COOH acid			H_3PO_4 acid					
							First step			Second step		
A(M)	B_e(M) NaOH	B_t(M) NaOH	R%	Be(M) NaOH	Bt(M) NaOH	R%	Be(M) NaOH	Bt(M) NaOH	R%	Be(M) NaOH	Bt(M) NaOH	R%
0.100	0.095	0.100	95.00	0.094	0.100	94.00	0.046	0.050	92.00	0.930	0.100	93.00
0.075	0.073	0.075	97.30	0.073	0.075	97.30	0.036	0.037	97.20	0.074	0.075	98.60
0.050	0.047	0.050	94.00	0.046	0.050	92.00	0.023	0.025	92.00	0.046	0.050	92.00
0.025	0.024	0.025	96.00	0.027	0.025	108.00	0.013	0.012	108.30	0.026	0.025	104.00

tained results are listed in TABLE (1) for acetic, propanoic and phosphoric acids respectively.

The values of the recovery percentage (R%) for the all above titrations are calculated as equation (5). From the plots the values of end points and the values of the recovery percentage (R%) are determined as:

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

Where Be = experimental amount of base and Bt = theoretical amount of base calculated from the stiochiometric 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 92% in potentiometric titrations. These differences in the recovery percentage may attribute, to the impurities in the reagents.

TABLE 2 : The molar amounts A of CH_3COOH acid, CH_3CH_2COOH acid, H_3PO_4 acid and experimental pKa for acid-base titrations using Ti/Co_3O_4/(SnO_2+Sb_2O_3) indicator electrode.

Acid	CH_3COOH acid	CH_3CH_2COOH acid	H_3PO_4 acid	
			First step	Second step
A(M)	pK_a	pK_a	pK_{a1}	pK_{a2}
0.100	4.76	4.85	2.13	7.19
0.075	4.76	4.83	2.09	7.21
0.050	4.76	4.81	2.11	7.21
0.025	4.69	4.83	2.13	7.23

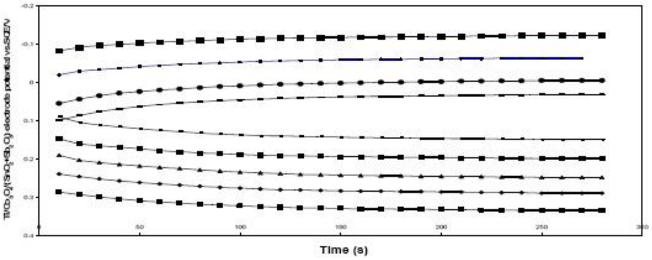

Figure 4 : Response time of the Ti/Co_3O_4/(SnO_2+Sb_2O_3) pH sensor at different pH values. Upper curve at pH =2 and lower one for pH=11

The values of pKa for different acids can be determined using the method of half neutralization[45]. They are close to the previously reported values as shown in TABLE (2) for the tested acids.

The response time of the sensor

Figure 4 shows the response time of the Ti/Co_3O_4/(SnO_2+Sb_2O_3) pH sensor at different pH values. Response time was achieved 50 seconds, which rendered the sensor highly practical.

Effect of temperature on the response characteristics

The Ti/Co_3O_4/(SnO_2+Sb_2O_3) pH sensor response was evaluated at different temperatureas shown in Figure 5. At lower temperatures, like 283 K, the slope of the sensor was about 35.8 mV/decade and the sensor would be used for pH measurements in the range from (2-11). However, when the temperature of the test solutions was adjusted to 333 K, the slope significantly increased to 54.8 mV/decade. By raising the temperature to 353 K, the slope increased to 59.1 mv/decade.

Figure 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 0.9956, 0.9979,0.9986, 0.9995, respectively. This indicates that better results could be obtained at higher temperature. Overall, it can be easily recognized that excellent correlation between the results obtained by the solid-state pH sensor and the conventional glass pH electrode could be achieved.

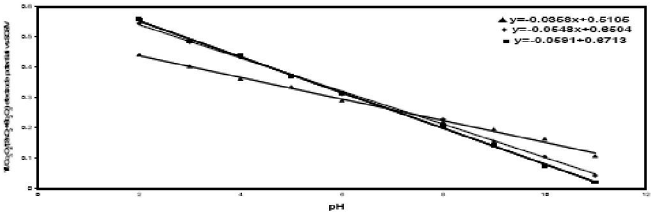

Figure 5 : Effect of temperature on slope of Ti/Co_3O_4/(SnO_2+Sb_2O_3) pH sensor at 283K(▲), 333K(♦), and 353K(■).

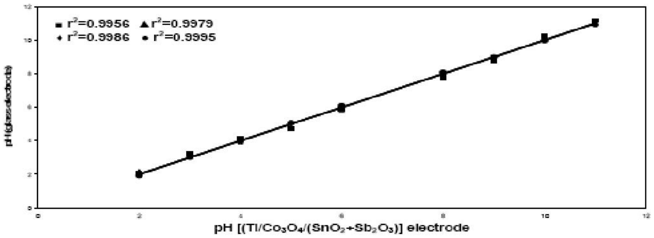

Figure 6 : Correlation between the conventional glass pH electrode and Ti/Co_3O_4/(SnO_2+Sb_2O_3) pH sensor at 283K(■), 298K(▲), 333K(♦) and 353K(●).

Potentiometric oxidation-reduction titration

Figure 7 represents the relation between the volumes of 0.1 N $KMnO_4$ with each potential shift in the titration of ferrous ammonium sulphate. The variation of the $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode potential at 298.15 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.

TABLE 3 : The molar amounts A of Fe (II) experimental and theoretical amounts of $KMnO_4$, Be, Bt and recovery percentage (R%) for oxidation-reduction titrations using $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ indicator electrode.

Fe(II) (N)	Be(N) $KMnO_4$	Bt(N) $KMnO_4$	R%
0.100	0.093	0.100	93.00
0.075	0.074	0.075	99.00
0.050	0.047	0.050	94.20
0.025	0.027	0.025	108.00

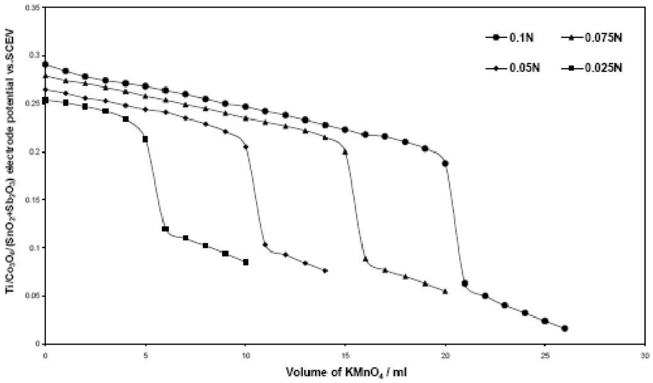

Figure 7 : Potentiometric titration of Fe (II) with 0.1 N $KMnO_4$ in aqueous solution at 298.15K.

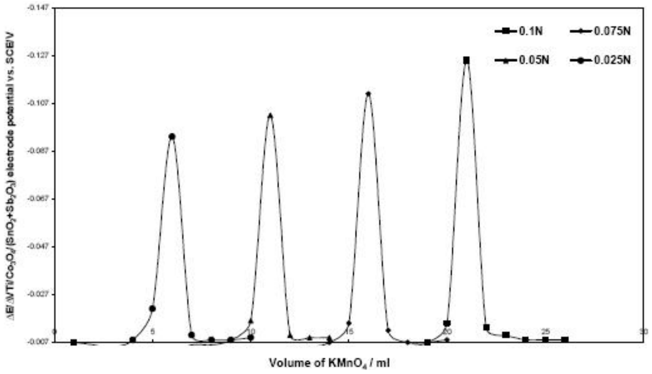

Figure 8 : Potentiometric titration of Fe (II) with 0.1 N $KMnO_4$ in aqueous solution at 298.15K (for locating end points).

Figure 8 represents $\Delta E/\Delta V$ against V plots for the potentiometric titration of ferrous ammonium sulphate with 0.1 N $KMnO_4$. The obtained results are listed in TABLE (3).

The use of $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode as an indicator electrode in conductometric acid-base titration in aqueous solution at 298K.

Conductometric acid-base titration

Figure 9 shows the relation between the conductance of the pair $Ti/Co_3O_4/(SnO_2+Sb_2O_3)$ electrode with 0.1 M NaOH in the titration of different concentration of acetic, hydrochloric and a mixture of acetic and hydrochloric acids at 298 K.

The conductance of the acetic acid will be low on account of its poor dissociation. On adding the alkali, highly ionized sodium acetate is formed and hence the conductance begins to increase.

$$CH_3COOH(aq)+\left[Na^+(aq)+OH^-(aq)\right] \rightarrow CH_3COOH(aq)+Na^+(aq)+H_2O(l) \qquad (6)$$

When the acid is completely neutralized, further addition of alkali introduces of fast moving hydroxyle ions. The conductance of the solution, therefore, begins to increase even more sharply than before. On plotting the conductance against the volume of the alkali added, the two lines obtained will be as shown in Figure (9a). The point of intersection gives the end point.

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 below:

$$H^+(aq)+Cl^-(aq)+\left[Na^+(aq)+OH^-(aq)\right] \rightarrow Na^+(aq)+Cl^-(aq)+H_2O(l) \qquad (7)$$

Hence, on continued addition of sodium hydroxide, the conductance will keep on decreasing until the acid has been completely neutralized. Any subsequent addition of alkali will result in introducing fast moving hydroxyle ions. The conductance, there, after reaching a certain minimum value, will begin to increase. On plotting the conductance against the volume of sodium hydroxide added as in Figure (9b) the point of intersection of these two lines gives the volume of sodium hydorxide required for the neutralization.

When a mixture of a strong and a weak acid is to be titrated against a strong alkali using a pair of studied electrode as indicator electrodes a combination of curves shown in Figure (9c) is obtained. Hydrochloric acid, a much stronger acid, will get titrated first. The

TABLE 4 : The molar amounts A of CH_3COOH acid, HCl, mixture of CH_3COOH and HCl, experimental and theoretical amounts of NaOH, Be, Bt and recovery percentage (R%) for acid-base titrations using Ti/Co_3O_4/(SnO_2+Sb_2O_3) indicator electrode.

Acid	CH_3COOH acid			HCl			Mixture of CH_3COOH and HCl			
A(M)	B_e(M) NaOH	B_t(M) NaOH	R%	Be(M) NaOH	Bt(M) NaOH	R%	A(M)	Be(M) NaOH	Bt(M) NaOH	R%
0.1000	0.0997	0.1000	99.75	0.0099	0.0100	99.20	0.006 CH_3COOH + 0.004 HCl	0.0027	0.0030	90.00
0.0 750	0.0700	0.0750	93.30	0.0075	0.0075	100.00		0.0019	0.0020	95.00
0.0500	0.0490	0.0500	98.80	0.0047	0.0050	93.20	0.005 CH_3COOH + 0.005 HCl	0.0026	0.0025	104.00
0.0250	0.0240	0.0250	96.00	0.0025	0.0025	100.00		0.0024	0.0025	96.00

TABLE 5 : The end points of different concentration of CH_3COOH acid, HCl, mixture of CH_3COOH and HCl for Ti/Co_3O_4/(SnO_2+Sb_2O_3) electrode and glass conductive electrode in aqueous solution at 298.15 K.

Acid (M)	End point of CH_3COOH		End point of HCl		A(mole)	End points of mixture CH_3COOH and HCl			
	glass electrode	studied electrode	glass electrode	studied electrode		glass electrode	studied electrode	glass electrode	studied electrode
0.1000	20.90	21.00	26.60	26.40	0.006 + 0.004	5.50	5.49	4.00	4.11
0.0750	14.80	14.80	20.10	20.20					
0.0500	10.30	10.40	12.70	12.40	0.005 + 0.005	5.10	5.90	3.70	3.60
0.0250	4.90	5.10	6.60	6.70					

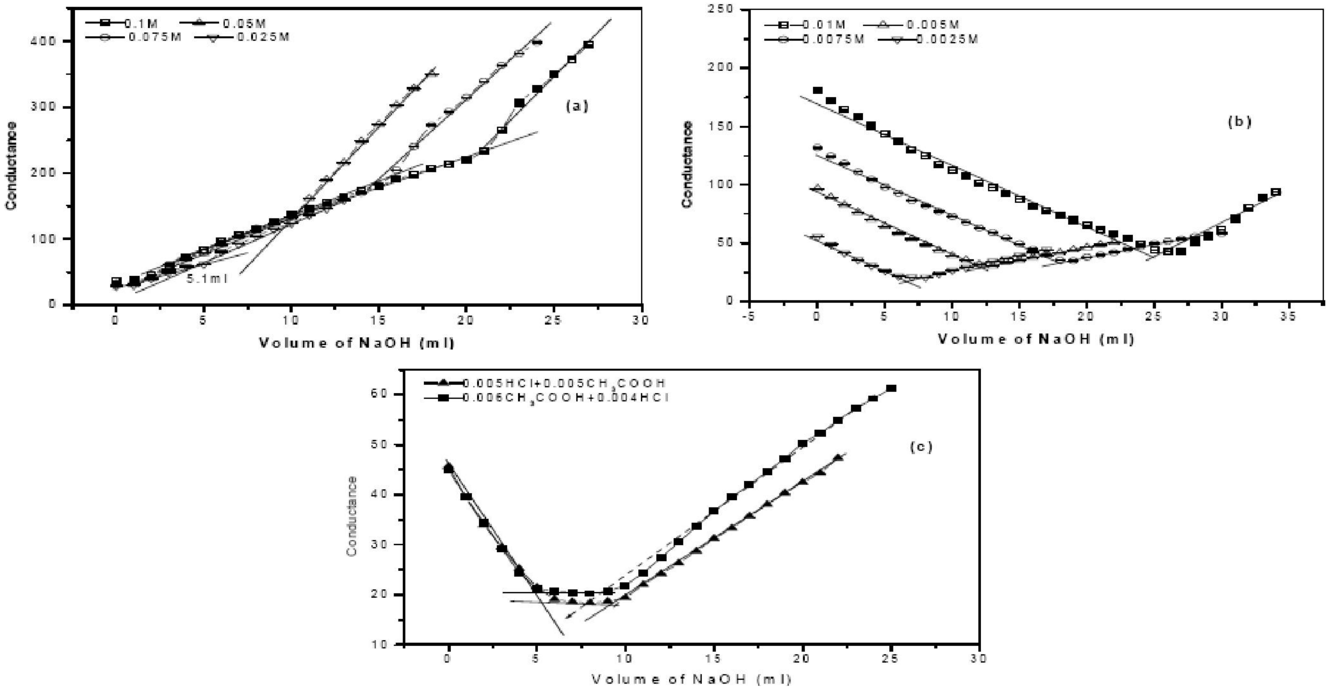

Figure 9 : The relation between the conductance of a pair Ti/ Co_3O_4 / (SnO_2 +Sb_2O_3) electrode with 0.1M NaOH in the titration of different concentration of CH_3COOH
(a) HCl (b) and a mixture of CH_3COOH and HCl (c) at 298.15K

titration of acetic acid will commence only after hydrochloric acid has been completely neutralized. Hence a combination of curves as mentioned above is obtained. The points of the intersection give the end point of hydrochloric acid has been completely neutralized. Hence a combination of curves as mentioned above is obtained. The points of the intersection give the end point of hydrochloric acid, acetic acid and sodium hydroxide respectively. As clear the values of the end points using the working electrodes are more or less close to the magnitude of the values given using glass conductive electrode. There is a good agreement between the modified electrodes and the glass electrode which indicate that the working electrodes behave reversibly and can be used as indicator electrode for conductive titration in aqueous solution.

The values of the recovery percentage (R%) for all above titration are calculated from equation (5). The calculated values of (R%) are listed in TABLE (4). It is clear from these data that the Ti/Co_3O_4/(SnO_2+Sb_2O_3) electrode can be used as an indicator electrode with the satisfactory recovery percentage not less than 90%. 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 CH_3COOH, HCl and a mixture of CH_3COOH and HCl for Ti/Co_3O_4/(SnO_2+Sb_2O_3) and glass conductive electrode at 298 K.

Cell constant

The conductance obtained will, therefore have to be multiplied by a certain factor in order to get the specific conductance. This factor is called the cell constant which is determined from the dimensions of the cell.

The value of cell constant for Ti/Co_3O_4/(SnO_2+Sb_2O_3) electrodes in aqueous solutions at 298 K equal 148.7. Specific conductance of normal, decinormal and centinormal solutions of potassium chloride at different temperatures are given in TABLE (6).

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

TABLE 6 : The relation between the specific conductance of KCl solutions for Ti/Co_3O_4/(SnO_2+Sb_2O_3) 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	
	glass electrode	studied electrode	glass electrode	studied electrode	glass electrode	studied electrode
1.00	6.543	6.539	9.817	9.799	11.169	11.167
0.10	0.715	0.715	1.119	1.119	1.288	1.288
0.01	0.077	0.077	0.122	0.122	0.141	0.141

TABLE 7 : The relation between the molar conductance, $\wedge_m$, in units of 10^{-4} Sm^2mol^{-1}, at some common electrolytes and the glass conductive electrode in aqueous solution at 298.15 K.

A(M)	HCl		NaCl		KCl		H_2SO_4		CH_3COOH		NH_4OH	
	glass electrode	studied electrode	glass electrode	studied electrode	glass electrode	studied electrode	glass electrode	studied electrode	glass electrode	studied electrode	glass electrode	studied electrode
0.1000	391.10	390.98	106.61	105.93	128.88	128.88	250.78	250.72	5.19	5.18	3.60	3.50
0.0100	411.93	411.86	118. 47	117.98	141.23	141.19	336.39	336.28	16.27	16.18	16.29	16.23
0.0010	421.40	420.78	123.62	123.39	146.88	146.93	399.48	399.35	49.16	49.00	49.18	49.10
0.0005M	422.20	421.95	124.47	124.39	147.88	147.76	412.88	412.76	67.07	67.06	67.17	67.16

ammonium hydroxide. The electrolytes of the first category (KCl, HCl, etc.) are known as strong electrolytes while those of second category (CH_3COOH, NH_4OH, etc.) are known as weak electrolytes.

The variation of molar conductance with dilution for some common electrolytes is shown in TABLE (7) and the variation of molar conductance of infinite dilution in the case of some common electrolytes is shown in TABLE (8).

TABLE 8 : The relation between the molar conductance, $\wedge_m$, in units of 10^{-4} Sm^2mol^{-1}, at infinite dilution for some common electrolytes and that of glass conductive electrode in aqueous solution at 298.15 K.

	^{0} $(10^{-4}Sm^{2}\ mol^{-1})\wedge_m$	
electrolyte	**glass electrode**	**studied electrode**
HCl	426.14	426.11
NaCl	126.22	126.98
KCl	149.90	149.62
CH_3COOH	390.61	390.58

The response time of the sensor

Figure 10 represents the relation between the conductance and response time at 298 K for a pair Ti/Co_3O_4/(SnO_2+Sb_2O_3) electrode at different concentrations of CH_3COOH, HCl and a mixture of CH_3COOH and HCl respectively. It is clear from Figure (10) that the response times for the studied electrodes are in the range of (50-100) second, which rendered the sensor highly practical.

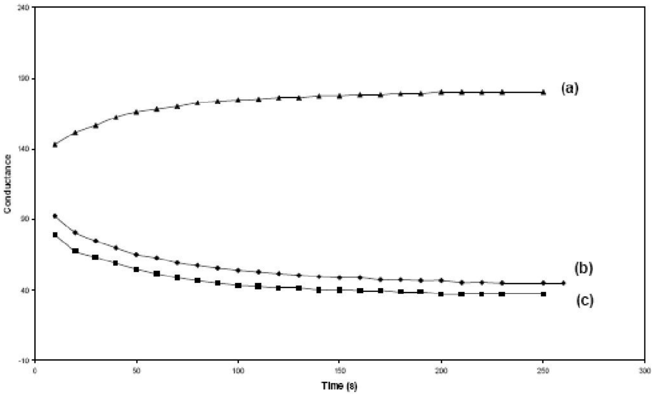

Figure 10 : The relation between the conductance and response time at 298.15 K for a pair Ti/Co_3O_4/(SnO_2+Sb_2O_3) electrode at different concentrations of CH_3COOH (a), HCl (b) and a mixture of CH_3COOH and HCl (c) respectively.

CONCLUSION

A modified sensor, Ti/Co_3O_4/(SnO_2+Sb_2O_3), was developed and used as indicator electrode in the potentiometric and conductometric acid-base titrations in aqueous solution at 298.15 K. This electrode was prepared by thermal deposition of some metal and alloys from their baths on the titanium substrate. The recovery percentage for potentiometric and conductometric acid-base titration was calculated. The E-pH curve is linear with slope of (0.0503) for the Ti/Co_3O_4/(SnO_2+Sb_2O_3) 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^0, is computed as (532.8) mV with respect to SCE as reference electrode.

To prove the capability of the above mentioned electrode, three acids: acetic, propanoic and phosphoric acids were successfully potentiometric titrated with NaOH as titrants in aqueous medium at 298 K while in conductometric hydrochloric, acetic and a mixture of both acids were also titrated against the same titrant. The cell constant for the pair electrode was determined from the dimensions of the cell. The relation between the specific conductances of standard KCl solutions for the cell against the glass conductive electrode at different temperature was studied. The variation of molar conductance with dilution for some common electrolytes was tested using the modified electrode. Also the variation of molar conductance of infinite dilution in case of some common electrolytes is determined by each conductive cell and the conductive glass electrode.

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