The Use of Ti/Ti-Oxide Electrode in Potentiometric Titrations of Acetic, Propanoic and Phosphoric Acids. Oxidation Reduction Titration of Ferrous Ions with $KMnO_4$.

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Abstract: *Titanium/titanium-oxide electrode has been prepared and used as indicator electrode in potentiometric acid-base and oxidation-reduction titration in aqueous solutions. The E-pH curve is linear with slope of 0.055V at 298.15K. This value is more or less closed to the theoretical value 2.303RT/2F (0.059 V at 298.15). The standard potential of this electrode,* E^o*, is computed as 242.1 mV with respect to the SCE as reference electrode. Three acids: acetic, propanoic and phosphoric acids were potentiometrically titrated with NaOH as titrants in aqueous medium at 298.15 K using the* Ti/TiO_2 *electrode. Also ammonium ferrous sulphate was potentiometrically titrated with KMnO4 as titrant in the same conditions.*

Keywords: titanium/titanium oxide electrode, potentiometric titration, acid-base titration, oxidation-reduction titration.

INTRODUCTION

The properties of oxide electrode systems and their application for measuring pH have been reviewed by Ives and Janz[1]. The basic requirements are rather difficult to fulfill, e.g. while the metal must be rather noble its oxide must be stable, strictly, stoichiometric, reasonably conducting, non-passivating and not unduly soluble. It should also be amphoteric so that it may equilibrate with H_3O^+ and OH^- ions in solution over a wide pH range. Most electrodes of this type, of which antimony-antimony oxide [2] is probably the best-known example, appear to be empirically attained compromises, which require frequent calibration and occasional reactivation. Deposite these disadvantages, the robustness and ease of preparation of metal-metal oxide micro-electrodes has led to continuing interest in their behavior, specially in the biological sciences [3].

The possible use of an iridium electrode as a pH-monitoring system has been mentioned by various authors [4-6]. The original work was carried out by Perley and Godshalk [5] who described both a technique for preparing the electrode and some applications. The use of reacting sputtered iridium oxide films as pH sensors has been reported by Katsube and co-workers [6] who observed a normal (2.303RT/F) open-circuit potential/pH shift for this system.

As an alternative for glass electrodes, metal-metal oxide electrodes are often suggested. Many metal-metal oxide electrodes have been studied on their pH response and a number of them have been used successfully [7].

Two types of metal-metal oxide electrodes can be distinguished. For type I the formation of the oxide of the metal is response to pH –dependence of the electrode potential.

$$Me + nH_2O = MeO_n + 2nH^+ + 2ne^-$$

Example of this type is the mercury-mercuric oxide, the antimony and the bismuth electrode. For the type II the response to pH is governed by the sensitivity of the oxide towards changes in hydrogen or hydroxyl ion concentration. The pH response mechanism of type II electrodes includes ion exchange and different kinds of redox reactions. Examples of this type are the IrO_2, the PtO_2 and the TiO_2 electrode [7].

The mercury-mercuric oxide [8] and the antimony electrode [2, 9, 10] are commonly used, but both are found to be applicable only over a limited pH range. Ti/TiO_2 electrode was prepared by electrochemical oxidation of Ti in fused KNO_3 at 350°C [11]. This electrode can be used as an indicator electrode in potentiometric acid-base titrations in molten nitrate. It behaves reversibly and responds theoretically to the oxide-ion concentration in melts [11].

This work aims to investigate the possibility of use Ti/TiO_2 electrode as an indicator electrode in different potentiometric titrations in aqueous solutions.

EXPERIMENTAL

The equipment used in this work was similar to that described previously [12, 13]. The titanium/titanium-oxide electrode was prepared from pure titanium sheet of thickness 2mm. The dimensions of electrodes were 5mm width and 250mm length. The electrode surface was mechanically polished and chemically pickled. The mechanical polishing was affected by 2/O and 3/O emery papers then rubbing the electrode surface against a soft cloth of cotton wool, after which bright surface was obtained. After a mechanical polishing the electrode was dipped for few seconds in a pickling bath. This consisted of concentrated H_2SO_4-HNO_3-HF mixture with volume ratio 10: 4: 3, respectively, similar to that used by Tegart [14] and Young [15]. The electrode then removed from the pickling mixture and thoroughly rinsed by distilled water and dried by paper tissues.

The method of preparation of Ti/TiO_2 electrode was as previously mentioned [16]. After these surface treatments the titanium electrode was simply immersed in molten $NaNO_3$ for few hours, at a temperatures of 400^oC, whereby thick layer of Ti-oxide formed on its surface. The titanium oxide layer can be obtained by heating the titanium electrode in an electric furnace, in presence of air, at a temperature of $500\text{-}600^oC$ for few hours. In these cases the most probable titanium oxide formed is TiO_2. For this reason the prepared electrode can be designated as Ti/TiO_2 electrode [17].

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/TiO_2 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 [18]

Titration was carried out in a Pyrex glass beaker in which the acid or the reductant put in it and the base or the oxidant placed in a 25ml micro burette. The solution in a beaker is stirred by means of a magnetic stirrer.

In the present study titanium/ titanium-oxide electrode is used as an indicator electrode in aqueous acid-base and oxidation-reduction titrations.

Chemicals used in potentiometric titrations were: H_3PO_4, CH_3COOH, CH_3CH_2COOH, ferrous ammonium sulphate, NaOH and $KMnO_4$. The chemicals are of analytical pure grades.

RESULTS AND DISCUSSION

The E-pH relation of titanium / titanium-oxide electrode:

Fig.1 shows the change of the open circuit potential (OCP) of the titanium/titanium-oxide electrode with pH. The E-pH plot of the titanium/titanium-oxide electrode fits straight line, with slope of 0.055 V at 298.15K. This value is more or less close to the magnitude of the term 2.303RT/2F at the corresponding temperature (0.059 V at 298.15K). As is clearly seen, there is a good agreement between theory and experiment, which indicates that the Ti/TiO_2 electrode behaves reversibly and can be used as an indicator electrode for $[H^+]$ ion determination. From Figs.1, the E^o value of the Ti/TiO_2 electrode, i.e. the potential at $[H^+] = 1$, is computed as 242.1 mV relative to the saturated calomel electrode.

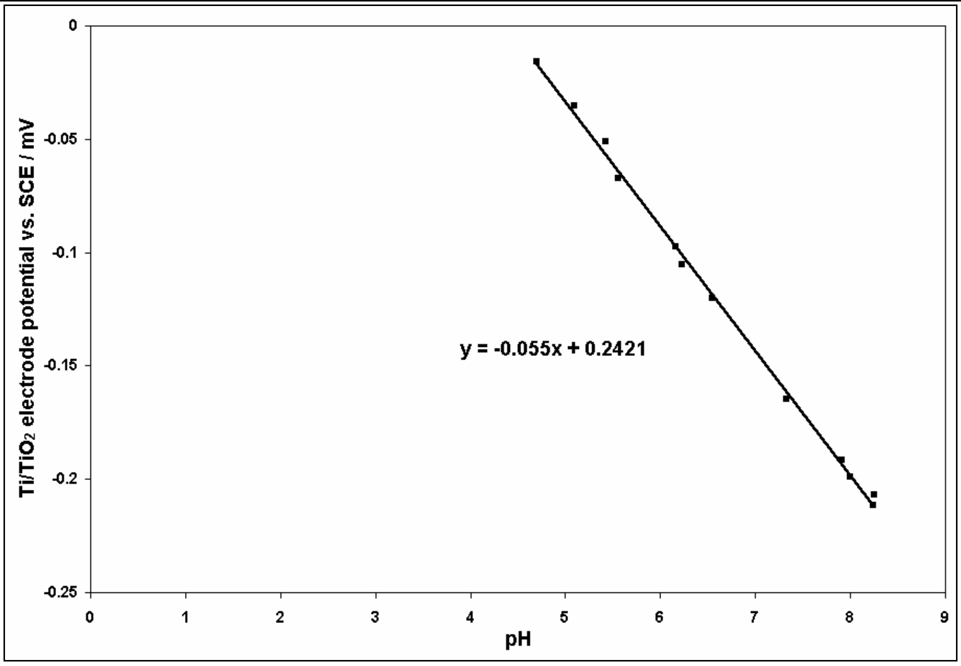

Fig. (1): E-pH relation for Ti/TiO_2 electrode in acetic acid at 298.15K

The formation of oxide can be represented by the following equation:

$$Ti + 2H_2O \leftrightarrow TiO_2 + 4H^+ + 4e \qquad (1)$$

Nernst equation of this reaction can be written as:

$$E_{Ti/TiO_2} = E^0_{Ti/TiO_2} + \frac{2.303RT}{4F}\log\frac{[TiO_2][H^+]^4}{[Ti][H_2O]^2} \qquad (2)$$

where Ti, TiO_2 are solids, and H_2O in excess, their activities =1

$$E_{Ti/TiO_2} = E^0_{Ti/TiO_2} + \frac{2.303RT}{F}\log[H^+] \qquad (3)$$

$$E_{Ti/TiO_2} = E^0_{Ti/TiO_2} - \frac{2.303RT}{F}pH \qquad (4)$$

This equation is applicable for the reversible behavior of Ti/TiO_2 electrode. This indicates that Ti/TiO_2 electrode can be used as pH-indicator electrode.

Potentiometric acid-base titration:

It was of interest to establish whether titanium/titanium-oxide electrode feasible for potentiometric acid-base titrations.

Figs.(2-4) represent the relation between the volume of 0.1 M NaOH with each potential shift in the titrations of acetic acid, propanoic acid and phosphoric acid, respectively. The variation of the titanium/ titanium-oxide electrode potential at 298.15K 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. The time needed for the metal/metal-oxide electrode to reach an equilibrium value after each addition were few seconds. At the equivalent points, distinct drops in the potential of the indicator electrode are recorded.

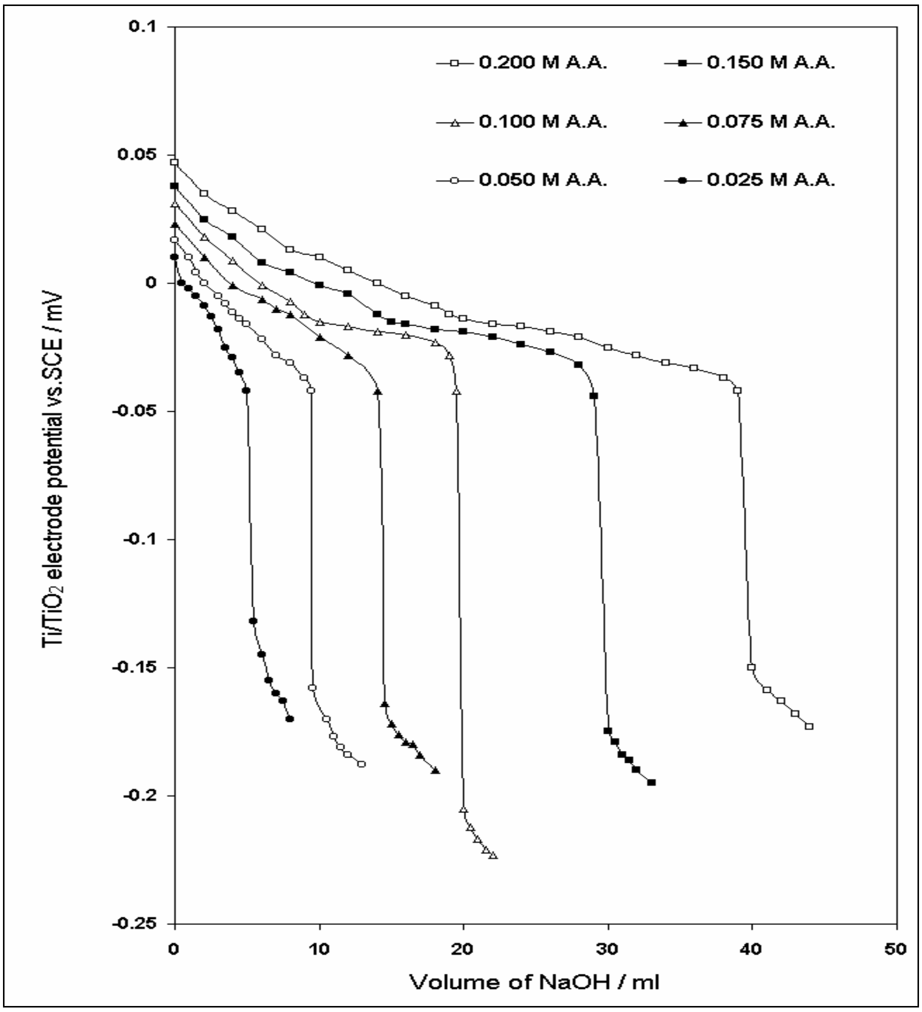

Fig.(2): Potentiometric titration of acetic acid with 0.1 M NaOH at 298.15K

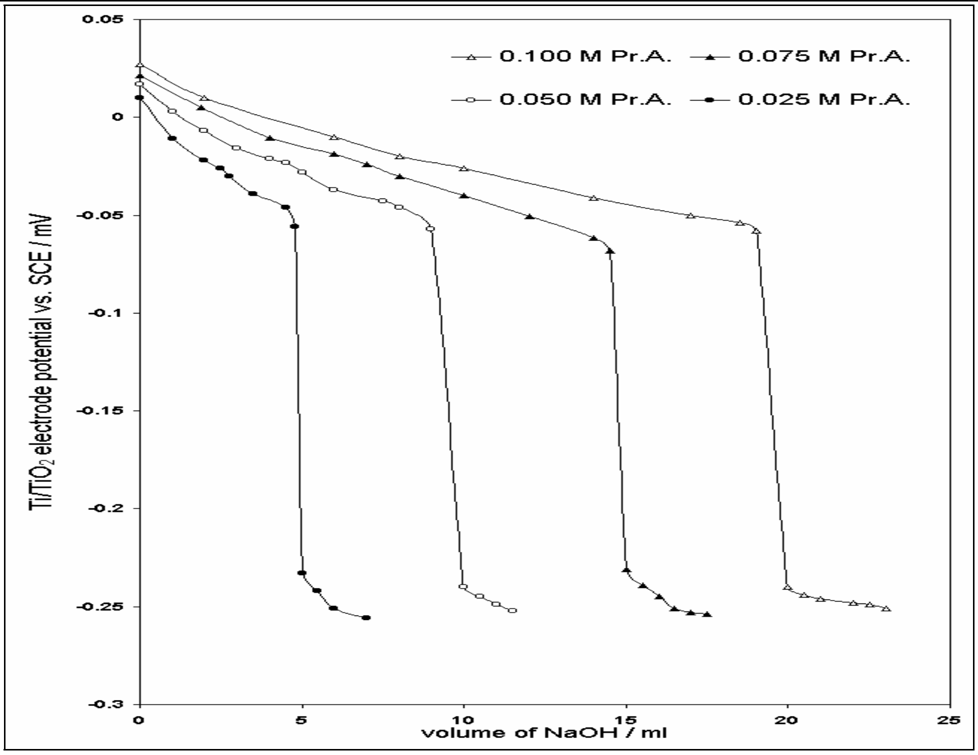

Fig. (3) Potentiometric titration of propanoic acid with 0.1 M NaOH at 298.15K

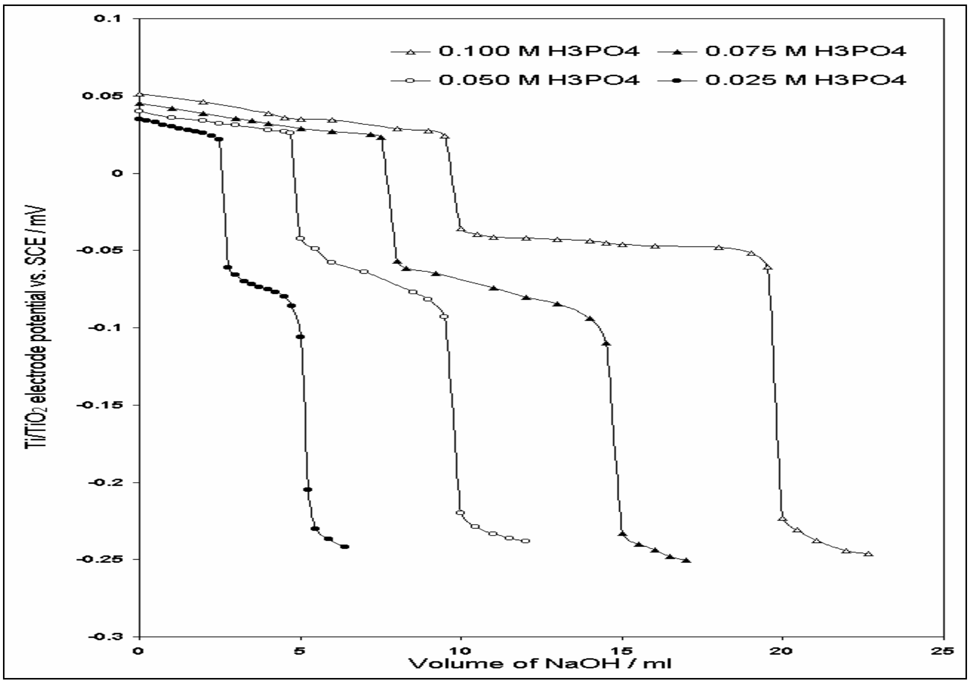

Fig. (4) Potentiometric titration of H_3PO_4 with 0.1 M NaOH at 298.15K

For locating end points, better results are obtained by constructing a plot of ΔE/ΔV against V of titrant. Figs.(5-7) represent ΔE/ΔV against V plots for the potentiometric titrations of CH_3COOH, CH_3CH_2COOH and H_3PO_4, with 0.1M NaOH, respectively. From the plots the values of end points are determined. The obtained results are listed in tables (1-3) for the acetic, propanoic, and phosphoric acid, respectively.

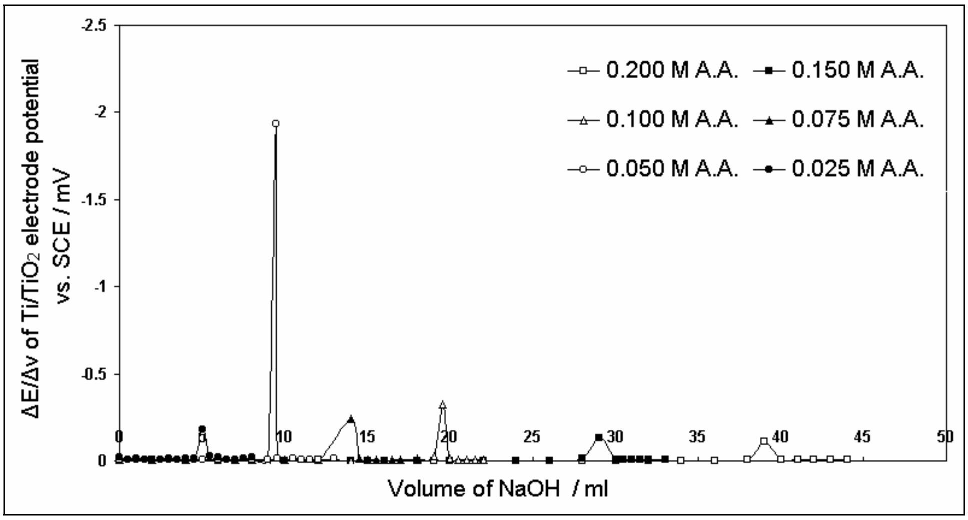

Fig. (5) Potentiometric titration of acetic acid with 0.1 M NaOH at 298.15K

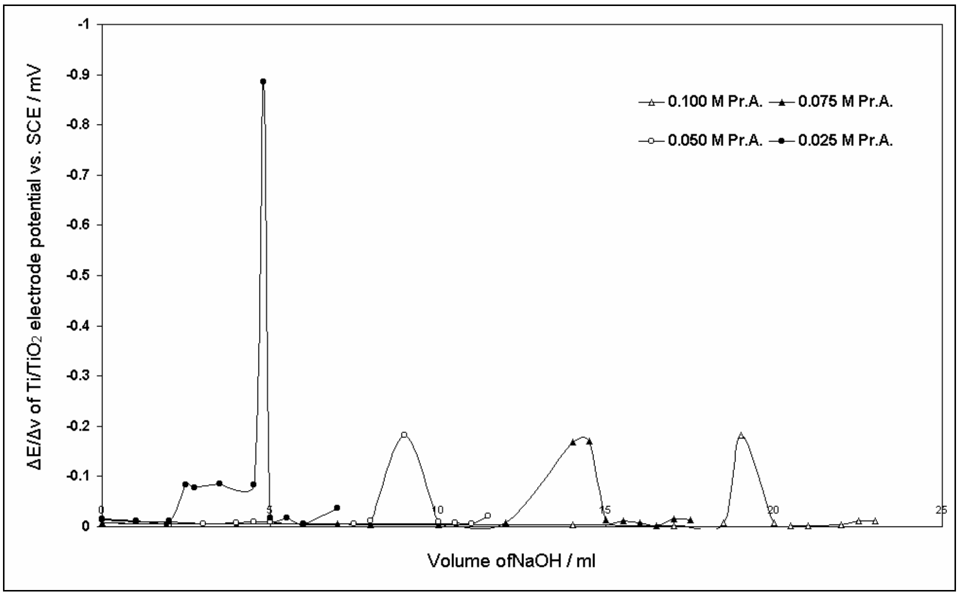

Fig. (6) Potentiometric titration of propanoic acid with 0.1 M NaOH at 298.15K

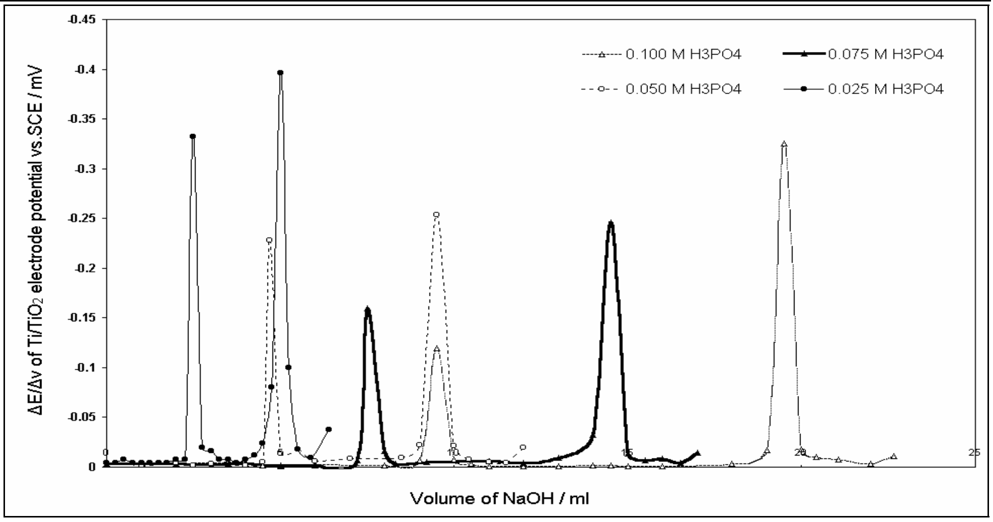

Fig. (7) Potentiometric titration of H_3PO_4 with 0.1 M NaOH at 298.15K

The values of the recovery percentage (R%) for the all above titrations are calculated as:

$$R\,\% = \frac{Be}{Bt} X\ 100 \tag{5}$$

where Be = experimental amount of a base

Bt = theoretical amount of a base calculated from the stiochiometric equations of neutralization reactions

The calculated values of (R%) are listed in Tables (1-3). It is clear from these data that the Ti/TiO_2 electrode can be used as an indicator electrode with the satisfactory recovery percentage not less than 90%. These differences in the recovery percentage may attributed, to the impurities in the reagents.

The values of pKa for different acids can be determined using the method of half neutralization [19]. The obtained values are listed in tables (4-6) for acetic, propanoic, phosphoric acids, respectively.

Table (1): The molar amounts of CH_3COOH acid A, experimental and theoretical amounts of NaOH, B_e, B_t and recovery percentage (R%) for acid-base titrations using Ti/TiO_2 indicator electrode

A (mole)	**B_e (mole)**	**B_t (mole)**	**R%**
0.200	0.195	0.200	98
0.150	0.145	0.150	97
0.100	0.097	0.100	98
0.075	0.070	0.075	93
0.050	0.047	0.050	95
0.025	0.025	0.025	100

Table (2): The molar amounts of CH_3CH_2COOH acid A, experimental and theoretical amounts of NaOH, B_e, B_t and recovery percentage (R%) for acid-base titrations using Ti/TiO_2 indicator electrode

A (M)	**B_e (mol)**	**B_t (mol)**	**R%**
0.100	0.095	0.100	95
0.075	0.072	0.100	97
0.050	0.045	0.050	90
0.025	0.024	0.025	96

Table (3): The molar amounts of H_3PO_4 acid A, experimental and theoretical amounts of NaOH, B_e, B_t and recovery percentage (R%) for acid-base titrations using Ti/TiO_2 indicator electrode

First step				**Second step**		
A (mole)	**B_e (mole)**	**B_t (mole)**	**R%**	**B_e (mole)**	**B_t (mole)**	**R%**
0.100	0.047	0.050	95	0.097	0.100	98
0.075	0.037	0.037	100	0.072	0.075	97
0.050	0.023	0.025	94	0.047	0.050	95
0.025	0.012	0.012	100	0.025	0.025	100

Table (4): The molar amounts of CH_3COOH acid A and experimental pKa for acid-base titrations using Ti/TiO_2 indicator electrode

A (mole)	**pka**
0.200	4.77
0.150	4.76
0.100	4.75
0.075	4.76
0.050	4.77
0.025	4.76

Table (5): The molar amounts of CH_3CH_2COOH acid A and experimental pKa for acid-base titrations using Ti/TiO_2 indicator electrode

A (M)	**pKa**
0.100	4.812
0.075	4.797
0.050	4.870
0.025	4.827

Table (6): The molar amounts of H_3PO_4 acid A and experimental pKa_1 and pKa_2 for acid-base titrations using Ti/TiO_2 indicator electrode

First step		Second step
A (mole)	pK_{a1}	pK_{a2}
0.100	2.150	7.21
0.075	2.150	7.22
0.050	2.095	7.19
0.025	2.150	7.21

The obtained values of pKa for the investigated acids are more or less close to the previously reported values in literature [19].

Potentiometric oxidation-reduction titration:

Fig.(8) represents the relation between the volume of 0.1 N $KMnO_4$ with each potential shift in the titrations of ferrous ammonium sulphate. The variation of the titanium/titanium-oxide electrode potential at 298.15K with the different volumes of $KMnO_4$ followed typical potentiometric titration curves. These curves show slight decrease in potential (to more negative values) with the addition of the titrant. The time needed for the metal/metal-oxide electrode to reach an equilibrium value after each addition were few seconds. At the equivalence points, distinct drops in the potential of the indicator electrode are recorded.

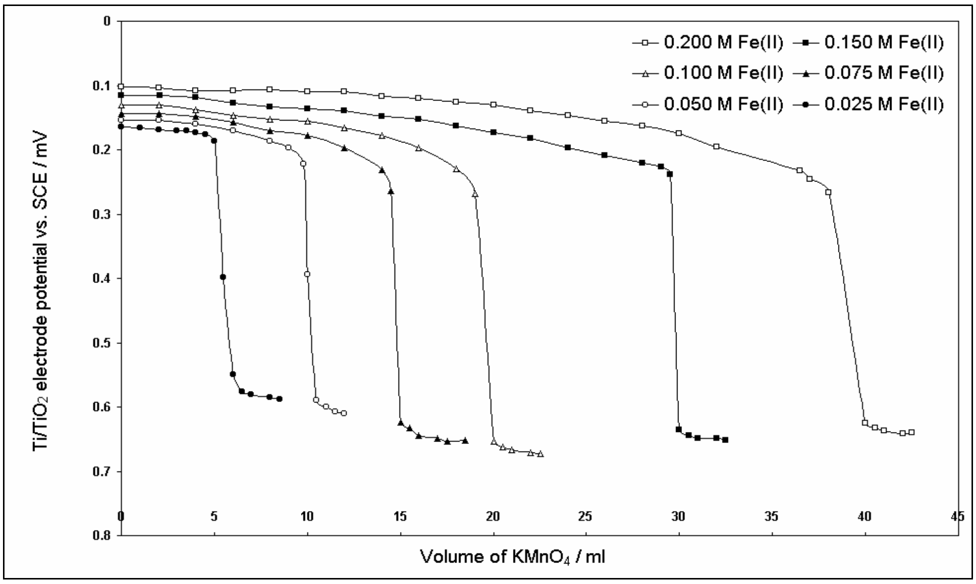

Fig. (8) Potentiometric titration of Fe(II) with 0.1N $KMnO_4$ in aqueous solution at 298.15K

For locating end points, better results are obtained by constructing a plot of ΔE/ΔV against V of titrant. Fig.(9) represent ΔE/ΔV against V plots for the potentiometric titrations 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 in the above-mentioned equation (5). The obtained results are listed in tables (7).

Table (7): The molar amounts of Fe (II) A, experimental and theoretical amounts of $KMnO_4$, B_e, B_t and recovery percentage (R%) for oxidation-reduction titrations using Ti/TiO_2 indicator electrode

A (mole)	B_e (mole)	B_t (mole)	R%
0.200	0.19000	0.200	95
0.150	0.14750	0.150	98
0.100	0.09500	0.100	95
0.075	0.07000	0.075	93
0.050	0.04900	0.050	98
0.025	0.02500	0.025	100.

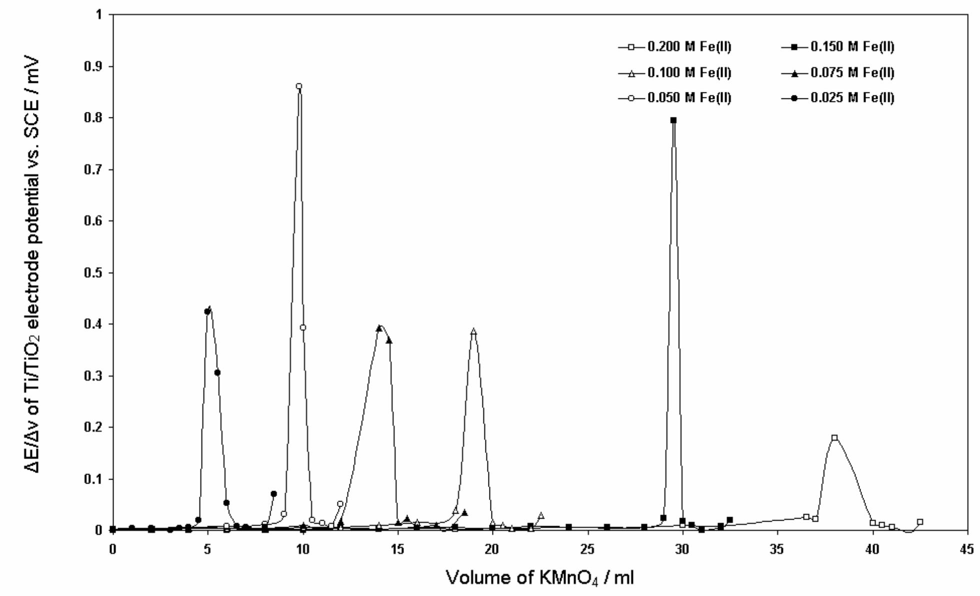

Fig. (9) Potentiometric titration of Fe(II) with 0.1N $KMnO_4$ in aqueous solution at 298.15K

CONCLUSION

In the present paper trials were made for the preparation of titanium/titanium-oxide electrode and its use as indicator electrode in the potentiometric titrations in aqueous medium at 298.15 K. This electrode is very sensitive indicator for hydrogen ions in potentiometric titration in aqueous solutions. It can be used effectively in titration of oxidation-reduction also.

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